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XANTHATE METHYL ESTERS OF SIMPLE ALCOHOLS AND OF CELLULOSE - VINCENT XANTHATE METHYL ESTERS

OF SIMPLE ALCOHOLS

AND OF CELLULOSE

A Thesis

by

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GENERAL INTRODUCTION

The ultimate aim of the present research was to clarify the structure of cellulose xanthates, $\geq C-O-C-SNa$, with particular reference to the positions of the xanthate groups within the glucose units. Some attempts have been made in recent years to solve this problem by substituting the unstable xanthate groups by the much more stable methyl groups, using diazomethane, and by studying the structure of the resulting methylcelluloses. Although the effect of diazomethane on cellulose xanthate has not been examined in the present research, similar reactions with two simple xanthates have been shown to lead to the formation of the xanthate methyl esters, \geq C-O-C-SCH₃, rather than to substitution of the xanthate by the methyl ether group. Since the reaction of diazomethane with cellulose xanthate has to be discarded in structural studies, it becomes necessary to find some more reliable method of investigation. Unsuccessful attempts have also been made to bring about this same substitution by the action of Raney nickel on the simple xanthate methyl esters.

The major part of the present work was to collect data concerning the suitability of cellulose xanthate methyl ester for structural studies. The original plan was to methylate the remaining hydroxyl groups in the xanthate methyl ester, then to de-xanthate to a methylcellulose with free hydroxyl groups in the positions originally occupied by xanthate groups. The methylcellulose could then be examined, both directly and after degradation, and the original xanthate

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distribution inferred from the results. To test the feasibility of this plan, and to learn more of the properties of the xanthate methyl ester group in general, a series of preliminary experiments was carried out on the simple xanthate esters, chiefly on the new crystalline O-octadecyl S-methyl xanthate and O-hexadecyl S-methyl xanthate. The instability of xanthate esters to alkali, to silver salts, and to thallous ethylate showed that the original plan was not feasible, as methylation of the hydroxyl groups in cellulose xanthate methyl ester would be impossible by any of the usual methods without dexanthation occurring. A subsequent de-xanthation step, by the same token, could probably be accomplished easily.

Attempts were then made to degrade the cellulose xanthate methyl ester itself, in view of the somewhat surprising stability of the xanthate ester group to acid, which was briefly reported in the literature and was confirmed by a variety of experiments on the methyl esters of simple xanthates. Although the drastic conditions of degradation of the cellulose to a mixture of glucose methylxanthates always caused a considerable loss of sulfur, some of the hydrolysates were examined by paper chromatography and by other means. The interesting paper chromatograms can not be interpreted fully until the glucose analogues are known.

It seemed probable that a more stable xanthate derivative would have to be used if fully satisfactory degradations to glucose derivatives were to be attained. The search for a

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suitable new derivative was beyond the scope of the present research, which was limited to the methyl ester, but some exploratory work was carried out with the simple xanthates. Of the oxidants tried, bromine, periodate, and hydrogen peroxide, the last named produced crystalline derivatives from hexadecyl and octadecyl methyl xanthates. These new derivatives proved stable to mineral acid although their structures were not elucidated.

HISTORICAL INTRODUCTION

Xanthate Methyl Esters of Simple Alcohols

Standard textbooks explain that there are theoretically two dithiocarbonic acids, a dithiol (I) and a thionthiol (II) acid:

These structures, which are tautomeric, represent acids which are not known free, probably because of great instability. Simple dithic acids of the type RCSSH are known, but are extremely unstable.

Salts, esters, and other derivatives of both dithiocarbonic acids are well known. For example, esters of these acids may be prepared by the reaction of phosgene or thiophosgene with an alcohol or mercaptan.

$$\begin{array}{c} 0 \\ \parallel \\ \text{Cl-C-Cl} \end{array} \xrightarrow{\text{RSH}} \\ \end{array} \begin{array}{c} 0 \\ \parallel \\ \text{RS-C-SR} \end{array}$$
(1)

Compounds of the type RO.CS.SM, which are salts of the O-alkyl derivatives of (II), are commonly known as xanthates, or xanthogenates, and are most frequently prepared by the action of carbon disulfide on alkoxides.

$$RONa + CS_2 \longrightarrow RO.CS.SNa$$
(3)

The name xanthate is derived from the Greek (xanthos, yellow) and refers to the color of the yellow cuprous salts. Sodium and potassium xanthates are nearly colorless when pure, although they often have a yellow color owing to the presence of sodium trithiocarbonate. Because of the 0-alkyl group, a xanthate is an ester as well as a salt. However, the term "xanthate ester", as herein used, refers to a xanthate in which the metal has been replaced by an additional alkyl group, and hence is really a double ester, i.e., RO.CS.SR'. In the present work, the prefixes 0- and S- are frequently used, in order to avoid ambiguity. Although by no means universal, this was the practice of Bulmer and Mann (1) in their series of papers on xanthates and dithiocarbonates. The more formal International Union of Chemistry nomenclature is not used in this work, as its general unwieldiness in the case of xanthates is unsuited to a report where names are frequently repeated. For example, the ester C2H50.CS.SC2H5 is herein named 0-ethyl S-ethyl xanthate rather than ethyl ethoxymethanethionothiolate.

Although esters of both acids (I) and (II) may properly be termed dithiocarbonates, this designation is probably better restricted to derivatives of (I), thus distinguishing them from the xanthates, which are derivatives of (II). The dithiocarbonates, in this restricted sense, are quite

distinct from the xanthate esters, but can sometimes be made by heating the corresponding xanthate ester, as described later. Usually quite different methods of preparation are used for the two types of compounds; whereas xanthate esters are almost always made by methylation of the corresponding xanthate salts, the dithiocarbonates result from the action of phosgene on sodium alkyl sulfides (2) or from the hydrolysis of alkyl thiocyanates (3).

$$\begin{array}{c} S \\ \parallel \\ RO-C-SNa + CH_3I \longrightarrow RO-C-SCH_3 + NaI \qquad (4) \end{array}$$

$$0=C < C1 + 2NaSR \longrightarrow 0=C < SR + 2NaCl$$
(5)

$$2RSCN + 3HOH \longrightarrow 0=C < SR + CO_2 + 2NH_3 \qquad (6)$$

They are readily distinguished from the xanthate esters by phenylhydrazine (1, 4) which gives substituted thiourethanes with the latter but does not affect dithiocarbonates under the conditions used.

Several of the simple xanthate salts are used commercially as flotation and wetting agents, but the xanthate

esters have no commercial importance. They are sometimes of value as intermediates in organic synthetic work, for example in the Chugaev dehydration of an alcohol, to be mentioned later.

The xanthates were discovered by Zeise (5) in 1822 and are frequently encountered in the early literature. The esters are more stable than the salts, and are therefore usually chosen for experimental work. Many references to the esters (eg. 6, 7, 8) are contained in the early literature. For example, in 1850 Debus (6) showed that 0-ethyl S-ethyl xanthate is readily prepared from potassium ethyl xanthate and ethyl chloride. The simple xanthate esters are usually high-boiling liquids, insoluble in water, and possess a garliclike odor. Only a few such compounds have been reported as crystalline. Table I is a list of those which are methyl esters.

In nearly all cases, xanthate methyl esters are prepared by methylation of the corresponding sodium or potassium salts, usually with methyl iodide. Often, however, the salt is not isolated prior to methylation. A less common method of preparation is indicated by equation (2) (page 1).

The xanthate salt may be prepared by any one of at least three distinct methods, of which there are many modifications. A common method, used, for example, by Chugaev (19) in his classic researches on the xanthates involves the prior formation of the sodium or potassium alcoholate from

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Crysta	lline	S-Me	thvl	Xanth	ates
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S-Methyl Xanthate	Melting Point	Reference
0-Benzyl	29° C.	(9)
0-1-Menthyl	39° C.	(10)
0-1-Bornyl	56-57° C.	(11)
0-d-Bornyl	56-57° C.	(12)
0-Pivalyl	40 -41° C.	(13)
0-2,2,6,6-Tetramethyl- cyclohexyl	60 -6 5° C.	(13)
0-Hexahydrobenzyl	16.5° C.(a) (14)
O-cis-2-Phenylcyclohexyl	49 - 50° C.	(18)

(a) Both Chemical Abstracts (15) and British Chemical Abstracts (16) Incorrectly record the melting point as 165° C., omitting the decimal point. It is correctly given in Chemisches Zentralblatt (17) as 16.5° C. The original paper was not readily available. the corresponding alcohol by use of metallic sodium or potassium, followed by treatment with carbon disulfide, usually in the presence of a solvent, which is often merely an excess of the alcohol. This method is inconvenient, and slightly hazardous.

A second method of preparing xanthate salts is a onestep process using the appropriate alcohol, solid sodium hydroxide or potassium hydroxide, carbon disulfide, and often an additional solvent. The isolation of the intermediate alcoholate is thus avoided. It is assumed that the alcoholate is formed, nevertheless, in a reversible reaction:

 $ROH + NaOH \implies RONa + H_2O \qquad (8)$

The alcoholate reacts at once with carbon disulfide, and thus the equilibrium is shifted until the alcohol is all consumed. This method is not only more convenient, but is reported to give better yields (20). Moreover, it was the earliest method, since caustic soda or caustic potash was used in the xanthate preparations of Zeise (5) and other early workers. Dubsky (21) used this method to prepare the xanthates of several alcohols. The one-step process, long neglected, has been used in several more recent researches, including those of Whitmore (20), Vogel (22), and Bulmer and Mann (1).

In xanthations, trithiocarbonates are also formed in considerable amounts, giving the crude xanthates a yellow or orange color.

 $6NaOH + 3CS_2 \longrightarrow 2Na_2CS_3 + Na_2CO_3 + 3H_2O$ (9) It is often a matter of considerable difficulty to prepare a xanthate in a pure state, both because of the trithiocarbonate impurity and because of the inherent instability of the xanthate group. The best method of purification seems to be that of DeWitt and Roper (23), who employed repeated precipitation from acetone solution by large amounts of benzene and petroleum ether. Another way of getting rid of trithiocarbonate is to decompose it with a weak acid, such as carbonic acid, which does not affect the xanthate salt.

A method of preparing xanthates in which decomposition of trithiocarbonate by carbon dioxide plays an integral part is that devised by Lieser (24) for the preparation of xanthates of sugars and water-soluble alcohols in general. Its distinctive features are the use of aqueous barium hydroxide solution, and the subsequent use of carbon dioxide to serve the double purpose of destroying trithiocarbonate and of precipitating excess barium hydroxide as the carbonate.

 $BaCS_{3} + CO_{2} + H_{2}O \longrightarrow BaCO_{3} \downarrow + CS_{2} + H_{2}S$ (10) $Ba(OH)_{2} + CO_{2} \longrightarrow BaCO_{3} \downarrow + H_{2}O$ (11)

It was impossible to prepare sugar xanthates by the older methods.

The mechanism of simple xanthation was shown by Makolkin (25) to be:

$$ROH + HONa + CS_2 \longrightarrow RO-C-SNa + H_2O$$
 (12)

This mechanism, the expected one, was proved by following the reaction with O^{18} -enriched sodium hydroxide.

It is surprising that the methyl xanthates of a large number of relatively simple alcohols have never been reported in the literature. For example, those of hexadecyl (cetyl) alcohol and octadecyl (stearyl) alcohol, which have been prepared by the present worker, apparently have never been previously reported. The corresponding xanthate salts, however, have been mentioned. Potassium cetyl xanthate was made many years ago by de la Provostaye and Desains (26), using powdered potassium hydroxide and a solution of cetyl alcohol in carbon disulfide, and again by Hermans (27) who dissolved potassium hydroxide in molten cetyl alcohol and treated the solid obtained on cooling with carbon disulfide. Cetyl xanthate is interesting in that its concentrated aqueous solution at higher temperatures is an anisotropic liquid (27, 28). The sole reference to an octadecyl xanthate salt appears to be in a patent of Graves (29) where it is mentioned together with several others as being of possible use as a rubber vulcanization accelerator, or as a flotation or wetting agent. A procedure is given for the preparation of such salts.

The behavior of xanthate esters on heating depends somewhat on the nature of the particular ester. Those derived from primary alcohols are usually considered to be relatively stable to distillation (e.g., 20), but those from other alcohols often decompose to unsaturated hydrocarbons when

heated alone or with solvents. This, the Chugaev method (10, 19) for preparing such hydrocarbons, has been used extensively in the terpene series, for example in the preparation of menthene from menthol:

Many studies of this reaction have been made, among the more recent and interesting of which are those of McAlpine (30), Whitmore (20), Bulmer and Mann (1), and Alexander and Mudrak (18). Evidence now suggests that there is a preferential elimination of cis- β -hydrogen atoms, and that quasi sixmembered rings are involved, owing to hydrogen bonding of the sulfur (18).

Sometimes even the xanthates of primary alcohols behave in a similar manner; Namentkin and Kursanov (9), for example, showed that 0-benzyl S-methyl xanthate gave stilbene:



In this case, a Chugaev decomposition is not possible. Bulmer and Mann (1) studied the stilbene formation from

substituted benzyl xanthates in considerable detail. It is obvious, then, that distillation or extensive heating of these esters should in general be avoided, although vacuum distillation can often be used with caution.

A second reaction caused by heating xanthate esters is transformation to an isomeric dithiocarbonate:

$$\begin{array}{c} S & 0 \\ \parallel \\ RO-C-SR' \longrightarrow RS-C-SR' \end{array}$$
(15)

Apparently this reaction occurs only in certain cases, which are not yet clearly defined in the literature. An informative paper is that of Laakso (13), who observed such transformations of the methyl, ethyl, propyl, and isopropyl xanthate esters of 2,2,6,6-tetramethylcyclohexanol, of methyl fenchyl xanthate (III), and of methyl pivalyl xanthate (IV), but found little evidence of transformation in the case of methyl 1-methylcyclohexyl xanthate.



These are all xanthate esters of secondary alcohols. The thorough studies of Bulmer and Mann (1) show that certain substituted dibenzyl xanthates are incapable of transformation to dithiocarbonates, while others change quite readily. Although the reason is not clear, isomerization readily occurs when the para substituents of the two benzyl groups are identical, but in other cases substituted stilbenes result.

It is obvious that in cases where the isomerization occurs, the alcohol can be transformed to its corresponding thiol by xanthate ester formation, isomerization, and hydrolysis. Indeed, hydrolysis to the thiol has sometimes been used as a chemical proof that isomerization has occurred, as in the work of Laakso (13). This isomerization was used by Freudenberg and Wolf (31) to prepare 3-thioglucose, starting from diacetone glucose.

The course of these reactions is often somewhat complicated by the fact that both xanthates and dithiocarbonates often exist in "parent" and "stable" forms, whose nature is as yet undecided. The only difference seems to be that of thermal stability, and there appears to be sufficient evidence that it is not merely a matter of a trace impurity catalyzing the decomposition of the "parent" form, but that a more fundamental factor is involved. This question is discussed in the papers of McAlpine (30), and Bulmer and Mann (1). Some writers, notably Laakso (13), have confused the matter by referring to "parent" and "stable" forms when they mean xanthate and dithiocarbonate, but Bulmer and Mann

have clearly shown that these changes are distinct from the isomerization of xanthate to dithiocarbonate.

There are several early references to the hydrolysis of these esters, most of which do not clearly state experimental conditions. O-Ethyl S-ethyl xanthate was shown by Schmitt and Glutz (3) to be decomposed on heating with water to 160° C. in a sealed tube, giving carbon dioxide, hydrogen sulfide, ethanol, and ethanethiol. The action of alcoholic alkali was shown by Schmitt and Glutz (3) (cf. also 32) to give a thiol and a salt of an alkyl monothiocarbonic acid.



Alcoholates give thiols, alcohols, and salts of alkyl monothiocarbonic acids (e.g., 32, 33).

$$S = 0 = 0 = 0$$

 $RO-C-SR' + KOR'' + H_2O \longrightarrow ROH + R'SH + R'O-C-SK (17)$

The mechanism of such reactions was said by Salomon (32) to be:

$$s=C < SR' + H_2 O \longrightarrow COS + ROH + RSH$$
(18)

$$\cos * KOR'' \longrightarrow O = C \begin{cases} OR'' \\ SK \end{cases}$$
(19)

Thus, the salt of the alkyl thiocarbonic acid originated in the addition of alcoholate to the carbon oxysulfide produced in the first reaction. Wallach (33), however, gave quite a different explanation:





Quantitative experimental results appear to be lacking to confirm or deny this view.

In more recent years, several workers have mentioned hydrolysis of these esters. In some cases, there seems to be surprising stability to aqueous alkali. McAlpine (30) has mentioned that prolonged boiling with 40% aqueous potassium hydroxide had no effect on O-menthyl S-methyl xanthate, but concentrated alcoholic potassium hydroxide caused complete hydrolysis in 12 to 18 hours, giving pure menthol. Similar treatment of O-menthyl S-benzyl xanthate gave complete hydrolysis in six hours. With both compounds, alcoholic barium hydroxide gave only partial hydrolysis, some of the ester changing to the "more stable" form. Bornyl methyl xanthate was also unaffected by aqueous potassium hydroxide, in contrast to isobornyl methyl xanthate which Chugaev (19) had shown to be easily hydrolyzed. Lieser (34) reported the ready decomposition of a methyl xanthate of a-methylglucoside on treatment with dilute alkali, but surprising stability on heating with dilute hydrochloric acid and on heating alone to 140° C.

Very early references reported no reaction of xanthate esters with aqueous ammonia at ordinary temperatures (e.g., 35), but Debus (35), Schmitt (3), and others mentioned decomposition with alcoholic ammonia (conditions unstated) to mercaptans and thiourethanes:

$$s=C \underbrace{\stackrel{SC_2H_5}{\stackrel{}_{OC_2H_5}} + NH_3 \longrightarrow s=C \underbrace{\stackrel{NH_2}{\stackrel{}_{OC_2H_5}} + C_2H_5SH} (22)$$

Salomon (36) obtained ethanol, ethanethiol, and ammonium thiocyanate by heating the ester with aqueous ammonia to 120-140° C. in a sealed tube:

$$s = C < C_{2H_5}^{SC_2H_5} + 2NH_3 \longrightarrow NH_4SCN + C_2H_5OH + C_2H_5SH$$
 (23)

Recent workers, e.g. Laakso (13), have also prepared xanthamides (thiourethanes) by the reaction of alcoholic ammonia with xanthate esters.

The fact is well known that salts of silver, mercury, cadmium, and other metals can often be used to remove sulfur from certain organic compounds. Particularly in the field of sugar chemistry there are many interesting references to such reactions (e.g., 37, 38, 39, 40) which have been used to prepare aldehydo derivatives, glycofuranosides, and thioglucofuranosides. Lieser (34) used silver carbonate or mercuric acetate to decompose a methyl xanthate of a-methylglucoside and similar compounds. The xanthate residue is easily split off, leaving a 50% yield of a-methylglucoside. In some of these reactions the sulfur atoms may be removed progressively and intermediate compounds may be isolated. This appears to be a reasonable method of removing a xanthate residue without disturbing other groups attached to the sugar residue, and is the basis for some similar reactions to be described in a later section.

In recent years, Raney nickel has been used extensively for desulfurization of many types of compounds, the sulfur atom being replaced by hydrogen atoms. Such a reaction was first carried out by Bougault, Cattelain, and Chabrier (41) and later the method was developed extensively by Mozingo (42), Wolfrom (43), and others. Recent reviews of this method are available (44, 45). Apparently the only reference to its use with xanthate esters is in the sugar field, where Fletcher (46) prepared sugar alcohol anhydrides from S-glycosyl xanthates. There is no mention of what happened to the xanthate residue in this reaction. It has recently been reported by Baddiley (47) that certain dithioesters are desulfurized in this way to give hydrocarbons. For example:

$$\underbrace{ \begin{array}{c} \\ \\ \\ \end{array} \end{array}^{-CH_2-C-SCH_3} \xrightarrow{Raney Ni} \\ \underbrace{ \end{array} \end{array}^{-CH_2CH_3 + CH_4} (24)$$

An analagous reaction of a xanthate ester might be expected to give a methyl ether, but such a reaction has not been reported:

$$RO.CSSR' \longrightarrow ROCH_3 + RH$$
 (25)

There seems to have been no deliberate attempt to oxidize a xanthate ester and to isolate the product. However, Delépine (48) observed that simple xanthate esters are often spontaneously oxidized in the air at ordinary temperatures with the evolution of light and fumes, but the nature of the oxidation products was not mentioned. Low molecular weight xanthate esters are well known to be chemiluminescent in air (49). It has been reported (50) that 0-methyl S-methyl xanthate absorbs oxygen quickly in aqueous ammonia, the sulfur appearing as a mixture of several inorganic acids, including sulfuric, sulfurous, and thiosulfuric. 0-Ethyl S-ethyl xanthate also absorbs oxygen in aqueous ammonia solution to give 0-ethyl S-ethyl thiocarbonate.

The oxidation of xanthate salts, in contrast to the esters, is well known, and is not reviewed here.

Cellulose Xanthate and its Methyl Ester

The formation of cellulose xanthate from alkali cellulose and carbon disulfide was discovered by Cross, Bevan, and Beadle (51) in 1892, and is considered to be analogous to the formation of the simpler xanthates known much earlier.

Cell.-OH.NaOH + CS₂
$$\longrightarrow$$
 Cell.-O-C-SNa + H₂O (26)

There may not be a strict analogy, however, since alkali cellulose may not have the simple alcoholate structure. It is generally accepted that the sodium hydroxide in alkali cellulose is bound to the hydroxyl groups in some way, possibly in the form of a definite compound, but a review of the structure of alkali cellulose is beyond the scope of the present work.

A vast literature on cellulose xanthate has grown up, much of which is concerned with the technical aspects of its industrial manufacture. This subject is thoroughly discussed in the common text books of cellulose chemistry (e.g., 52, 53, 54) and is not reviewed here. As often pointed out, interest in cellulose xanthate itself has been subordinate to interest in the properties of viscose, the alkali solution of the crude xanthate, from which cellulose is regenerated in the manufacture of rayon and cellophane. Recent work on the more academic aspects of the reaction will be briefly reviewed insofar as they are related to the present research. These problems, still somewhat unsettled, include the extent of the heterogeneity of the reaction under the usual conditions, and related questions regarding the distribution of the xanthate groups. The distribution of the groups within the individual glucose units has attracted much attention recently and was a more particular interest of the present research.

Industrially, the process of preparing cellulose xanthate involves the treatment of pressed and shredded alkali cellulose with carbon disulfide in revolving vessels, after which the crude orange-colored xanthate crumbs are dissolved in dilute caustic soda to give the viscous solution known as viscose. Details may be found in several textbooks, of which those by Heuser (52) and Ott (53) are particularly valuable. Examination of the viscose reveals a degree of substitution of the order of 0.5, i.e. one xanthate for about two glucose units. After an "aging" or "ripening" of the viscose, an essential step, it has desirable characteristics for spinning. Ripening appears to be a rather complicated process involving considerable de-xanthation (55, 56) together with change in colloidal properties. A review of the fairly extensive work on the ripening process is beyond the scope of this work. The spun filaments are led into an acid bath, in which cellulose is regenerated. The viscose solution is also a raw material for the manufacture of cellophane.

Laboratory methods of preparing cellulose xanthate are found in the usual text books (e.g., 52, 53, 57, 58), and in many papers (e.g., 55, 59, 60, 61). They are essentially small-scale modifications of the industrial procedure. The different methods vary to some extent in the proportion of carbon disulfide used, the temperature and the strictness of

its control, and the time of reaction. The extent of pressing of the alkali cellulose prior to xanthation also varies, the "pressed weight ratios" varying from three to four. The concentration of the sodium hydroxide solution used for solution of the xanthate crumbs also varies somewhat, but is usually such that the sodium hydroxide content of the resulting solution is between 4% and 9% and the cellulose content is about 7%. From one-quarter to one-third of the carbon disulfide used is consumed in side reactions (62, 63) which lead to sodium trithiocarbonate, sodium carbonate, and sodium sulfide. In laboratory preparations, the ripening step may or may not be included, depending on the purpose of the particular research. When information regarding the chemical structure of the original xanthate is desired, ripening must be omitted or made very brief, because of the fundamental changes which De-xanthation, probably preferentially from particuoccur. lar positions, and ester interchange may change the pattern of group distribution completely. A ripened xanthate would be expected to show a much more uniform structure, both with regard to xanthate group distribution among the chains and glucose units, and also within the glucose units. In the first respect at least, this expectation is realized, as shown by Chen, Montonna, and Grove (55), and discussed in detail below. One simple piece of evidence that ester interchange must occur is the fact that cellulose can be dispersed in viscose under conditions where it cannot be dispersed in

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sodium hydroxide alone (64). The effect of ripening on group distribution is stressed here because it seems to have been disregarded in some researches reported in the literature. Conclusions regarding the structure of any cellulose xanthate depend on the history of preparation, particularly the extent of ripening.

In many academic researches, a pure cellulose xanthate in solid form is required. The phenomena observed during the ripening of viscose and the fact that solid cellulose xanthates lose their water solubility on standing for some time (61, 62) show that these xanthates are not stable, and the problem of isolating and purifying them is therefore difficult. Most methods of purification involve precipitation from viscose solution by methanol, ethanol, or acetone, although salting out with sodium or ammonium chloride has also been used (52, p. 312). Washing with methanol, ethanol, or acetone removes the orange-colored sodium trithiocarbonate and other impurities, although some excess sodium hydroxide always remains in the product (see p. 21), and may be largely removed by a weak acid.

Another method of obtaining a relatively pure cellulose xanthate was first used by Lieser (62). The xanthate is kept fibrous throughout the entire procedure, and the preparation of a viscose solution is avoided. The crude xanthate crumbs are repeatedly washed with alcohol - Lieser himself used methanol - to remove all trithiocarbonate, sulfide, and most alkali, leaving a nearly colorless product, but one which

contains a little excess alkali.

Although the present research is concerned with only the usual heterogeneous xanthation of cellulose, homogeneous conditions are obtained when a quaternary ammonium base is used as a solvent for the cellulose, in which case the trixanthate is readily prepared. This method apparently originated with Lieser (65).

After washing cellulose xanthate with alcohol, the sodium content is invariably higher (60, 62, 66, 67) than that required by the formula Cell.-O-CSSNa, and the excess is probably present as sodium hydroxide. Cross and Bevan (51) ascribe to the xanthate, isolated by precipitation by alcohol, formula (V). Others (e.g., 68) assume the extra sodium to be present as a cellulosate, formula (VI), and still others, e.g., Rassow and Aehnelt (67), have considered the extra sodium hydroxide to be attached to the C=S group, which is unlikely.

$$\frac{S}{II}$$
NaS-C-OC₆H₉O₅.NaOH
NaS-C-OC₆H₈O₃ONa
$$\frac{V}{VI}$$

Fink, Stahn, and Matthes (66) have subjected viscose to ultrafiltration, and found that the greater part of the sodium hydroxide passed into the filtrate. The retained part amounted to only one-fifth mole per glucose unit, in contrast to the one mole as formulated by Cross and Bevan.

It has often been stated that the excess caustic soda may be merely adsorbed on the cellulose or xanthate group, and that stoichiometric relationships are incidental. There is evidence both to support and to deny this view. Heuser and Schuster (60) present figures to show that, with increasing alkali content of the viscose, the xanthates obtained by precipitation with alcohol show an increasing sodium hydroxide content. In more recent years, Staudinger and Zapf (61) claimed that the sodium hydroxide must be bound chemically as it cannot be removed by several washings. Moreover, they found that for a large number of cellulose xanthates of widely varying degrees of substitution, the excess sodium hydroxide amounted to about one-half mole per xanthate group. These experiments were done on xanthates prepared essentially by Lieser's method, in which the xanthate crumbs are washed with alcohol until free of trithiocarbonate. However, they further purified these xanthates by solution to viscose, and precipitation with alcohol, and found that the approximate ratio of about one-half mole excess sodium hydroxide per xanthate group still held, even though the degree of substitution had dropped considerably.

In what appears to be the most recent work in this connection, Lauer and Pauer (69) found that with methanolwashed xanthates of degree of substitution 0.5 to 0.75, the relative excess of sodium hydroxide was fairly constant, the sodium content averaging 142% of theory. However, with

ethanol-washed xanthates, the sodium content dropped from 169% to 113% of theory as the degree of substitution increased from 0.5 to 0.75. Lauer concluded that the excess alkali is chemically bound, the equilibrium being determined by the solvent used for washing. The sum of the substitutions (per glucose unit) of xanthate and alkali was 0.71 for methanolwashed products, and 0.80 to 0.84 for ethanol-washed ones.

The removal of excess alkali by treatment with a weak acid is said not to affect the xanthate group to any appreciable extent. Heuser (60) acidified the viscose with dilute acetic acid and immediately precipitated an alkalifree xanthate with sodium chloride solution. Other workers steeped their alcohol-precipitated xanthates in acidic solutions, Chen and his collaborators (55), for example, using a 5% or 10% solution of acetic acid in absolute methanol at 0° C. for a short time. These treatments, if brief and at low temperatures, appear to decompose the xanthate group only slightly. The alkali-containing and alkali-free cellulose xanthates have been called "alkali cellulose xanthate" and "neutral cellulose xanthate" (e.g., 55), but this nomenclature seems confusing. An alkali-free cellulose xanthate in aqueous solution still reacts slightly alkaline, indicating a slight dissociation (52).

Staudinger (61) was apparently less successful than others in removing excess caustic soda. For this purpose, he precipitated the xanthate with a mixture of alcohol and a

weak acid, such as acetic acid, phenol, or acetoacetic ester. He lost about three-quarters of the xanthate groups and still had an excess of sodium hydroxide corresponding to about onehalf mole per xanthate group. However, he did not mention the earlier and divergent result of Heuser, but stated that "the excess of sodium hydroxide cannot be removed by weak acids, a sign of the firm binding of sodium hydroxide in cellulose xanthate". The possibility of excess caustic soda is the chief reason why the degree of substitution of a cellulose xanthate is determined from the sulfur-cellulose ratio and not from the sulfur content alone.

Lieser (62) claimed methanol to be more efficient than ethanol in washing the crude cellulose xanthate, reporting that the latter would not remove all impurities even after an hour's washing. He recognized the slow hydrolysis caused by methanol, however, but managed to wash his products fast enough to presume that this effect was negligible. As Lieser used cotton thread to prepare his xanthates, this washing was apparently not too difficult. However, when cotton linters are used, or when a higher level of xanthation is obtained, the product may be so gelatinous or the lumps so large that washing with methanol may be so time-consuming as to be impractical. It is now recognized (see below) that methanolwashing may result in a considerable loss of xanthate groups.

Staudinger (61, 70) used Lieser's method in much of his work on xanthates, but preferred ethanol for washing. He
pointed out that ethanol leads less easily to ester interchange, and that highly xanthated, degraded products are more difficultly soluble in ethanol than in cold methanol. His ethanol-washed products contained a higher percentage of sulfur than those washed with methanol. Lauer (69, 71) also used ethanol in his recent work, although otherwise his method of xanthate preparation resembled Lieser's. He stated (69) that the xanthate residues of more highly xanthated products are partly decomposed by methanol. The degree of substitution of his xanthates, originally as high as 0.77, was reduced to 0.5 to 0.6 by washing with methanol, but not with ethanol. This observation may explain why Lieser's xanthates always had a degree of substitution of about 0.5.

The same disadvantages are probably operative when xanthates are precipitated from viscose solution by means of methanol. However, methanol precipitations and purifications are undeniably far more convenient than those with ethanol. Methanol precipitates are very light colored gelatinous lumps which filter very easily after the gelation stage has passed (see later), while ethanol precipitates are often yellow, sticky, gummy masses, cf. Staudinger (61), which are extremely difficult to wash, and which soon harden to brittle lumps. Methanol is still often used for precipitation, for example by Chen and his collaborators (55).

The heterogeneous nature of the xanthation reaction has been well reviewed by Timell (72). Lieser (73), Lauer (69, 71)

and others (e.g., 74, 75) regard heterogeneous xanthation under the usual conditions to be a micellar-heterogeneous reaction, i.e. one affecting only the amorphous regions and micellar surfaces of cellulose. Many others, including Staudinger (70), Hermans (54, p. 328 ff.), and Heuser (52, p. 307 ff.), consider the reaction to become more or less permutoid as it proceeds, the micelles being penetrated quite early. As early as 1940, Staudinger (61) considered the entering groups to be distributed according to the laws of probability, not only in xanthates but in all cellulose derivatives. There is evidence supporting both points of view, and agreement has not been reached.

Lieser (73) believed that the production of a degree of substitution always of the order of 0.5 indicated the micellarheterogeneous type of reaction, since about half the glucose units were considered to be in the amorphous region or micellar surfaces (cf. 76). It has been shown, however, that much higher degrees of substitution can be obtained, even under heterogeneous conditions. Lauer (69) sets the limit at 0.75 to 0.8, but 1.1 (77) and even 1.5 (63) have been reported when a great excess of carbon disulfide was used. Hence the value 0.5 can have little significance in deciding this question. The fact that Lieser and others consistently obtained values of this order was said by Bredée (78), a strong critic of Lieser, to be simply because nearly all the alkali provided had been consumed by this time. Another explanation is implied in Lauer's recent work (69), which apparently shows

that washing with methanol removes more highly xanthated products to a great extent (see p. 25). Lauer's researches also appear to show, however, that this value may indeed be significant (see later), as it appears to correspond to the maximum number of mono-xanthated glucose units.

Another argument which Lieser (73, 79) considered to support his view may be briefly summarized. As discussed in detail later, he presumably substituted methoxyl groups for xanthate groups by means of diazomethane, and subjected the resulting methylcellulose to acetolysis. The yield of cellobiose octaacetate, 21-24%, was about half that obtained in a model acetolysis on cellulose itself. He considered that this relatively large yield indicated that large numbers of adjacent glucose units had not been xanthated, and that these units were in the interior of the micelles. It is now clear that even if the material had been uniformly attacked, and group distribution had followed the laws of chance, up to 32% of cellobiose octaacetate could have been obtained (80). Moreover, Lieser detected no monomethylcellobiose acetate or dimethylcellobiose acetate, and no conclusions can be drawn from this experiment. Lauer (71), nevertheless, recently reached the same conclusion from similar experiments. He pointed out that a loss of methoxyl groups during acetolysis under Lieser's conditions, perhaps accounted for the high yield of cellobiose octaacetate, but even when he used a method which avoids this loss he still obtained high yields. He came to the cautious conclusion that the crystalline

regions of the fibre are untouched by carbon disulfide. This conclusion may not be justified from his experiments. Also, the total hydrolysis of methylcelluloses obtained from xanthates by diazomethane produced about a 50% yield of unmethylated glucose, even when the degree of substitution of the xanthate was as high as 0.8. Additional xanthate groups must have entered glucose units which were already xanthated. As mentioned in a later section, the only other products isolated in such hydrolyses were 2-methylglucose and 2,3-dimethylglucose, which, together with glucose, accounted for practically all of the material hydrolyzed. He considered these results afforded clear evidence that the crystalline domains are not xanthated. This argument, as well as that of the acetolysis experiment, depends on the validity of the assumption that xanthate groups were precisely replaced by methoxyl groups in the diazomethane reaction, about which there may be some doubt.

Fink, Stahn, and Matthes (66) fractionally precipitated the diethylacetamide of cellulose xanthate of degree of substitution (D. S.) 0.5 and found that fractions of varying degrees of polymerization (D. P.) had about the same D. S. More recently, however, Scherer and Phillips (59) fractionally precipitated the same derivative, D. S. 0.6 to 0.7, from a chlorohydrin solvent by means of water, and showed the D. S. of the fractions to vary from 0.576 to 1.12. This definite heterogeneity was assumed to be caused by the slow penetration of carbon disulfide into the alkali cellulose,

probably because of the relative insolubility of carbon disulfide in sodium hydroxide solution. Similar results were recently found by Chen, Montonna, and Grove (55) who fractionated both freshly prepared and ripened viscose solutions by means of sodium chloride solution. A freshly prepared viscose of average D. S. 0.57 gave three fractions with D. S. 0.494, 0.525, and 0.636. Another freshly prepared viscose, D. S. 0.427, gave four fractions varying from D. S. 0.379 to 0.474. They stated that the most reasonable explanation was that "the cellulose chains are xanthated to widely different degrees of substitution. The cellulose chains on the outside of the fibre may be xanthated to a higher degree of substitution and the inner part of the fibre may have a lower sulfur content. The results of fractionation show that xanthation has the characteristics of a topochemical-macroheterogeneous reaction". Their fractionations of ripened viscoses showed, as expected, that ripening had made the distribution much more uniform (cf. p. 19). For example, a viscose ripened for four days, of an average D. S. 0.563 before ripening, gave six fractions varying only over the narrow range of D. S. 0.301 to 0.333. The drop in degree of substitution seems to indicate that uniformity is obtained at the expense of de-xanthation, with little re-xanthation of free hydroxyl groups.

The question of heterogeneity of xanthation under the usual conditions has also been considered in the light of many X-ray studies, which have recently been reviewed by

Timell (72, p. 194). Although the results of different workers are somewhat contradictory, it appears that in the case of the relatively short reaction times of the large scale process, the crystallites are not completely changed (56). With long reaction times, or on viscose ripening, X-ray interference of the original crystallites is no longer seen, thus supporting other evidence that under these conditions distribution becomes more uniform.

The distribution of the xanthate groups within the glucose units is of more particular interest to the present review. There have been three important researches which have examined this problem by direct experimental means, those of Lieser (73, 79), Lauer (71), and Chen, Montonna, and Grove (55).In addition to these, there is a less valuable earlier paper by Lauer and his collaborators (81), in which it is stated that the 2-position is first xanthated, followed by the 6-position in the same glucose unit. His evidence for this was indirect and doubtful, being based on the analogous reaction with ethylene oxide instead of carbon disulfide. Much earlier, Rassow (82) had suggested that the 6-position was preferred, but gave no experimental evidence for this assumption.

The first three of these researches depend on the validity of Lieser's (79) claim that methylation with diazomethane quantitatively and selectively replaces the xanthate groups of a cellulose xanthate by methoxyl groups. In most cases where diazomethane is used, it is produced by the action of alkali on nitrosomethylurea or nitrosomethylurethane, being subsequently led into the reaction mixture.



In the present case, however, the nitrosomethylurethane is used as such, being added in huge excess to a stirred suspension of xanthate in absolute methanol or ethanol at a low temperature. The slow hydrolysis of the xanthate was said by Lieser (79) to provide the necessary alkali. For the substitution to be of any value, it is necessary that all xanthate groups be replaced in precisely the same positions by methoxyl groups, and that no free hydroxyl groups be methylated. Ιt has been shown by Reeves and Thompson (83) that moist cellulose is itself methylated considerably by diazomethane, but that bone-dry samples react only very slightly. Lieser, Lauer, and Chen and his collaborators all claim to have examined the validity of the xanthate substitution, at least as far as this could be determined by simple experiments. Lieser (79) obtained a methoxyl content of less than 1% in cotton cellulose allowed to react with nitrosomethylurethane under conditions identical with the de-xanthation, except that small amounts of methanolic potassium hydroxide were added to the reaction mixture. With cellulose xanthate, he was able to obtain the theoretical methoxyl content in the product only by

using rather strict conditions, for instance an excess of the urethane in the order of 65 times the theoretical amount, and a reaction time of at least five hours. Smaller amounts, shorter reaction times, or higher temperatures gave unsatisfactory results. Moreover, it is clear that Lieser used xanthates containing excess sodium hydroxide. Chen, Montonna, and Grove (55) later showed that with these "alkali xanthates", the resulting methoxyl content was much higher than theoretical when the temperature of reaction was 20° C. rather than 2-4° C., and even at the lower temperature was not particularly satisfactory. This observation contrasted somewhat with the claim for the "neutral xanthate".

Chen, Montonna, and Grove (55) apparently made the most elaborate tests of the validity of the reaction, but they do not appear to be extensive enough to justify a definite conclusion. They did show, however, that the reaction was not valid with "alkali xanthates", i.e. those containing excess caustic soda. Under the conditions used in the de-xanthation with diazomethane, alkali cellulose, even when washed to apparent neutrality by means of methanol, gave methoxyl contents of the order of 4% to 5%, and cellulose itself 0.3% to 0.4%. It is obvious, then, why xanthates with excess caustic soda yield products with more methoxyl groups than those corresponding to the original xanthate groups. On the other hand, in the case of the "neutral xanthates", in which excess caustic soda had been removed by steeping in acidic solutions, Chen and his collaborators claimed that the substitution was valid. Their evidence is presented in its entirety in Table II.

TABLE II

Methylations of Cellulose Xanthate with Diazomethane Reported by Chen, Montonna, and Grove (55)			
D.S. of Cellulose	Maximum Reaction Temperature	Per Cen	t Methoxyl
Xanthate	(°C.)	Found	Calculated
0.543	2-4	3.26	9.94
0.566	5	7.43	10.33
0.499	20	10.30	9.16
0.591	5-8	10.96	10.77

In addition, Chen showed that acid-washed alkali cellulose was not attacked by nitrosomethylurethane, hence "the methoxyl groups can only be introduced through the replacement of the xanthate groups". Only the results of the fourth experiment in Table II could be considered as at all satisfactory, however, and the only other satisfactory result reported was that of the sample of methylcellulose which he used for structural analysis. On this evidence, he claimed the validity of the substitution, and stated that "this result confirms those of Lieser", who clearly used only xanthates with an excess of sodium hydroxide. Apparently neither Lieser nor Chen examined the sulfur contents of their products as an indication of complete substitution. Lauer (71) also recently claimed to have confirmed the view that free hydroxyl groups in cellulose are not attacked by diazomethane under the experimental conditions, although his own data are not given. It is also not apparent from his report whether he used "alkali xanthates" or "neutral xanthates", but it seems probable that he used the former, as Lieser did.

The results of these workers will now be considered separately. In each case, the methylcellulose resulting from the nitrosomethylurethane reaction was structurally examined, and the results used to infer the group distribution in the original xanthate. Chen found a nearly uniform distribution, and Lieser and Lauer both decided that xanthation was confined to the 2-position in the first stage of the reaction. То infer that this marked disagreement might be entirely due to the invalidity of the diazomethane substitution would be unjust, however, as Chen began with "an equilibrated viscose solution" (although his xanthate seems to have been precipitated soon after the formation of the viscose), while Lauer apparently began with a xanthate prepared by Lieser's method, in which the formation of viscose is avoided. As Lauer's experimental details are very meagre, this point is not entirely clear.

Lieser (79) hydrolyzed the methylcellulose with sulfuric acid, obtaining a mixture of glucose and 2-methylglucose, and drew the conclusion that the xanthate groups were in the

2-position. The methylglucose was not crystalline, but was established as the 2-derivative by means of a crystalline phenylhydrazone which was identical with that of a supposedly authentic sample of 2-methylglucose. He could not obtain an osazone from his methylglucose, and none would be expected from the 2-derivative. The yields of methylglucose and of hydrazone were not stated, but are presumed to be small, and there seems to be no reason why derivatives other than the 2-derivative could not have been present also.

Lieser, together with various collaborators (24, 34, 84-87), did a considerable amount of work on sugar xanthates which correlates rather closely with his researches on cellulose xanthate (62, 65, 73, 79, 88). Although this work will not be reviewed here, the monoxanthate which is readily prepared from a-methylglucoside by the barium hydroxide method (see p. 7) was considered by him to be the 2-derivative, largely by analogy with his results for cellulose xanthate, as his additional evidence was not conclusive. It might be expected that a sugar would xanthate most readily in the 6-position, i.e. on the primary hydroxyl group. However, Lieser (24, 85, 86) pointed out the exceptional behavior of the 2-position in many reactions, and also showed that secondary hydroxyl groups in sugars are capable of xanthation by preparing a xanthate of 1,6-anhydroglucose. Furthermore, he was unable to introduce more than one xanthate group into a sugar molecule by the usual methods (24, 84). Lieser (88)

later abandoned his view that cellulose xanthate is substituted entirely in the 2-position, and now favors a more random distribution.

Lauer's (71) recent work will now be summarized. He completely hydrolyzed the methylcellulose and fractionated the resulting glucosides by distillation at 0.01 mm. When the degree of substitution of the original xanthate was not over 0.55, he obtained glucose and 2-methylglucose exclusively, accounting for 92-94% of the original material, although he searched for the 3- and 6-derivatives. When the degree of substitution was in the range 0.55 to 0.8, the upper limit obtained by ordinary heterogeneous xanthation, the only additional product was 2,3-dimethylglucose, as shown by a large number of experiments. His conclusion supported Lieser's early view that, up to D. S. 0.5, only the 2-position is xanthated. Xanthation beyond this, according to Lauer, leads to substitution in the 3-position of glucose residues which are already xanthated, even though about half the glucose units remain unxanthated. Lauer implied that Lieser did not obtain any of the 2,3-derivative because methanol-washing destroyed this unit readily, whereas he used ethanol for washing (cf. p. 25). Lauer's research on the acetolytic decomposition of the methylcellulose has already been reviewed, and also supports Lieser's conclusions. Thus, according to Lauer, even up to D. S. 0.8, about half the glucose units remain unxanthated, presumably those in the interior of the micelles.

The results obtained by Chen, Montonna, and Grove (55)

indicate a nearly random distribution which would be impossible if Lauer's work were correct, assuming that each started with similar materials, although this point is not completely clear from the literature. Chen's somewhat elaborate scheme of analyzing the methylcellulose will not be considered in great detail, as it is a combination of methods which are now well known and accepted as valid. In brief, he determined glycol groups by periodate oxidation, free glucose in the hydrolysate by fermentation, and the relative amounts of mono-, di-, and trisubstituted products by an attempted fractional distillation of the methylglucosides formed from the hydrolysate after removal of glucose. Free hydroxyl groups in position 6 were determined by the tosylation-iodination method carried out on the methylcellulose; those in position 2 by an oxidation of the hydrolysate with lead tetraacetate; since the cis-1,2 glycol groups react much faster than the trans-2,3 or 3,4 groups, the rate curve was extrapolated to obtain the desired value. To determine free hydroxyl groups in position 3 he subjected the methylglucosides obtained by methanolysis of the methylcellulose to a periodate oxidation; the resulting number of glycol groups determined in this way is greater than the number in the original methylcellulose by an amount corresponding to 3,4 glycol groups, and a simple subtraction gives the number of hydroxyl groups in the 3-position. In a xanthate of D. S. 0.721, Chen found the proportions of xanthate groups at positions 2, 3, and 6 to be 0.270, 0.208, and 0.243 respectively, per glucose unit. The amount of free glucose was 0.279. In

agreement with Lauer, on the other hand, he found no dixanthate or trixanthate, unless a slight trace of dixanthate could be assumed from the results of the fractional distillation.

It may be noted that the initial group distribution in the cellulose xanthate may well depend on the distribution of sodium hydroxide among the hydroxyl groups in the alkali cellulose used, provided, of course, that alkali cellulose can be considered a definite compound with the sodium hydroxide associated with particular hydroxyl groups. Although not universally accepted, Lauer clearly supports this view, and has done much recent work (89) on alkali cellulose which is of relevance to cellulose xanthate. A detailed discussion of the nature of alkali cellulose, however, is beyond the scope of the present review.

The methyl ester of cellulose xanthate has received little attention in the literature. Lieser (62) attempted to prepare it in connection with his effort to find a reasonably stable derivative. He had little success, as there appeared to be considerable de-xanthation under the conditions which he used. The "most favorable" result was obtained by treating an ethanolic suspension of the sodium xanthate with a solution of methyl iodide in 80% alcohol, but the product had only about two-thirds of the theoretical amount of sulfur, and only about one-quarter of the theoretical amount of methylthio groups. His method of estimating this group was probably at fault, as discussed later.

The only other original reference to the methyl ester

appears to be that in Lilienfeld's patent (90) on the alkylation of cellulose xanthate. He prepared such esters by adding dimethyl sulfate or methyl iodide directly to the viscose solution. The products were said to be suitable for the manufacture of films, threads, coatings, etc., but the analytical data were not sufficient to show whether or not they were the esters desired.

RESULTS AND DISCUSSION

Xanthate Methyl Esters of Simple Alcohols

1. Preparation of the Esters

Only a few xanthate methyl esters are both known and crystalline (see p. 5), and of these the benzyl, hexahydrobenzyl, and menthyl esters were prepared for study. In addition, the octadecyl (stearyl) and hexadecyl (cetyl) esters were prepared, both of which are new compounds.

Originally it was thought that O-hexahydrobenzyl S-methyl xanthate would be an ideal model compound, but its melting point was discovered to be far lower than that incorrectly reported in the abstract literature (see p. 5). Aleksandrovich (14) prepared sodium hexahydrobenzyl xanthate from cyclohexylcarbinol, carbon disulfide, and sodium in ether, and then methylated the salt to obtain the methyl ester. Chiefly because the original paper was unavailable, but also as a matter of interest, the salt was prepared in the present research starting with sodium hydroxide instead of free sodium, apparently for the first time, and then methylated with methyl iodide. The procedure was a modification of that used by Whitmore (20) for similar compounds. In all, five small runs were carried out, with slightly varying procedures, but yields of the pure methyl ester were only about 30%, probably because of the difficulties encountered in the isolation and purification of the solid, which melted below room temperature (16.5° C.). It was quite probable, as with other preparations

reported here, that additional research would produce better yields, but this attempt was not thought to be justified on the present occasion.

O-Benzyl S-methyl xanthate, first made by Namentkin and Kursanov (9), was originally prepared merely as a model for the hexahydrobenzyl analogue, but proved more useful for subsequent studies, although its aromaticity made it unsuitable in some cases. As with all xanthate preparations in the present research, the sodium hydroxide method was used, thus avoiding the use of sodium or potassium metal. Of five small runs, the third probably represented the closest approach to optimum conditions, as a yield of 70% was obtained. In this run, the intermediate xanthate salt was not isolated prior to methylation. The greatest difficulty with such low-melting esters was experienced in producing well-formed crystals while at the same time avoiding large losses of product. To avoid the formation of oils which solidified to amorphous solids, a large excess of ethanol-water was usually needed for crystallization. Often two or three successive crops of relatively pure crystals were obtained by step-wise concentrating the solution and cooling very slowly. The benzyl ester (m.p. 29° C.) was obtained as a pure solid much more easily than the hexahydrobenzyl ester (m.p. 16.5° C.) as might be expected from the higher melting point.

The menthyl analogue was also prepared by the one-step process using sodium hydroxide, apparently for the first time

by this method, as Chugaev (10) and, still earlier, Bamberger (91) had used elementary sodium or potassium to prepare the corresponding xanthate salt. However, yields of the purified methyl ester were not over 30%, although the low recovery was doubtless partly because of less than optimum reaction conditions. A greater factor seemed to be the relatively large loss during purification. This ester was an example of one derived from a secondary alcohol.

The syntheses of the new octadecyl and hexadecyl esters were carried out to determine how large a simple straight chain alcohol had to be in order to form a solid xanthate methyl ester. It was found that the hexadecyl ester melted at 28-28.5° C. and the octadecyl ester at 38-39° C. The preparation of the octadecyl compound was first attempted after considerable experience had been gained in analogous cases, yet new problems were encountered, partly owing to solution difficulties and partly because of a somewhat sluggish reaction. In ten experiments, all by the sodium hydroxide method, the yields varied considerably, the best being 90% crude and 60% when relatively pure. In one case the crude intermediate xanthate salt was isolated prior to methylation in an attempt to eliminate traces of octadecanol from the final ester, observed in several experiments. Little success was achieved in this respect, and it was possible that the octadecanol resulted from partial hydrolysis of the ester rather than from incomplete reaction. In the first eight runs ether was

used as the reaction medium, but in the two final ones an excess of carbon disulfide was the sole solvent. The latter method gave better yields, and also partially avoided the solution difficulties encountered in the earlier runs. Sometimes there was a tendency to gel formation, possibly because of traces of water. It was rather difficult, as in the case of the other esters, to recrystallize the low-melting product without considerable loss. The octadecyl ester was used for most of the subsequent studies on the xanthate ester group, since it was prepared quite easily from a relatively inexpensive alcohol. The intermediate sodium octadecyl xanthate, incidentally, appeared to be a good emulsifying agent and detergent, its aqueous solution having a soapy feel. This property, which might be expected from the chemical structure, probably had little commercial application because of the instability of the salt and its slightly unpleasant odor after standing for some time. Its use as a wetting agent has been suggested in the patent literature (see p. 8).

The first four preparations of the new O-hexadecyl S-methyl xanthate used ether as the reaction medium, and of these only the fourth was successful. In this run, the intermediate xanthate salt was isolated prior to methylation. Two additional runs, however, in which an excess of carbon disulfide was the sole solvent, were successful, and in neither was the intermediate salt isolated. Many years ago, de la Provostaye and Desains (26) used essentially the same method for the preparation of potassium cetyl xanthate. The relatively low melting point of the xanthate ester (28-28.5° C.) made recrystallization somewhat difficult, but no real trouble was encountered. In the final run, the yield was practically 100% crude, and 80% when relatively pure.

Two other new xanthate methyl esters were perhaps prepared in a crude condition, the O-octyl and O-cyclohexylpropyl compounds. Purification difficulties were encountered and this work was not followed up, since by this time the octadecyl ester had been recognized as satisfactory for the subsequent studies. The first of the above two compounds was clearly a liquid at room temperature, while the second might be expected to be a very low-melting solid, as it was the second higher homologue of O-hexahydrobenzyl S-methyl xanthate of melting point 16.5° C.

2. The Reaction of Xanthate Salts with Diazomethane

As pointed out earlier, the action of diazomethane (actually nitrosomethylurethane and alkali) on cellulose xanthate was assumed by Lieser (79) and later by Lauer (71) and by Chen, Montonna, and Grove (55) to substitute methyl groups for entire xanthate groups. The effect of nitrosomethylurethane on two simple xanthate salts was therefore examined briefly. Sodium octadecyl xanthate was treated under conditions similar to those used by the earlier workers in the case of cellulose xanthate, except that a five-fold instead of a

65-fold excess of the urethane was used. Apparently no de-xanthation occurred, and a good yield of octadecyl methyl xanthate was obtained. In spite of attempts at purification, the starting xanthate salt was possibly no better than 85% pure, yet a crude yield of 89.3% (calculated on the assumption of a pure starting material) of xanthate methyl ester was obtained. This was apparently the first time that diazomethane had been allowed to react with a simple xanthate, and there seemed to be no previous report of a simple sodium salt being methylated by this means. A similar substitution of sodium by methyl groups must, however, have occurred when Chen and his collaborators (55) treated alkali cellulose with nitrosomethylurethane and obtained a product containing 4-5% of methoxyl groups. Diazomethane was probably the actual methylating agent because the solution became yellow as the nitrosomethylurethane was added.

Potassium benzyl xanthate also gave benzyl methyl xanthate with nitrosomethylurethane, although the yield was small, probably because of a poor method of isolating the product and because the starting material was somewhat impure. Additional experiments would in all probability make it possible to obtain a better yield.

The present results seem to destroy the assumptions underlying previous attempts to locate the xanthate groups in cellulose xanthate. During the action of nitrosomethylurethane and alkali, some xanthate groups were probably removed and some converted to methyl ester and a random methylation of the

cellulose occurred. None of the published data on this reaction included sulfur analyses of the products, which might have indicated whether or not the de-xanthation was complete. The methylation of the simple xanthates strongly suggests that the use of nitrosomethylurethane can lead to no valid conclusion about the distribution of xanthate groups in cellulose xanthate.

3. Some Reactions of Simple Xanthate Esters

Attempts were made to determine the saponification equivalents of the methyl esters by the usual method, assuming that both the O-alkyl and S-methyl groups would be cleaved when the reaction was complete. If this assumption were valid, the value of the "saponification number" after various less drastic conditions of alkalinity would be an indication of the stability of the compound to alkali.

Experiments were carried out with all five of the xanthate methyl esters prepared, although the most extensive work was done with the octadecyl ester. As shown in the Experimental Section, saponification, if continued long enough, gave numbers reasonably close to the expected values in all cases, although the phenolphthalein end points were not always distinct. In some cases, however, the results were surprisingly good and corresponded closely to the following reaction:

$$S=C < OR \\ SR' + 2NaOH \longrightarrow S=C < ONa \\ ONa + ROH + RSH$$
(28)

However, the reaction might not have been as simple as this, as the literature contained references (3, 6, 32, 33) to the formation of alkyl thiocarbonates when alcoholic alkali was used. This occurrence was unlikely here, as thiocarbonates too would be hydrolyzed if saponification went to completion. If sodium thiocarbonate was formed, as indicated in the equation, its extensive hydrolysis might be connected with the somewhat indistinct end points. Regardless of these questions, the fact was established that a reasonably good "saponification equivalent" could be determined, and that its value provided an index of stability toward various alkaline treatments.

The most careful saponifications of octadecyl methyl xanthate with approximately 1N alcoholic sodium hydroxide solution containing 10% of water indicated that an hour of heating under reflux was needed for complete reaction. Thirty minutes produced about 90% cleavage, and 15 minutes about 75%. Two days at room temperature also gave about 75% cleavage. Approximately the same figures were obtained when only 0.1N caustic soda was used. Mixtures of ester and alcoholic alkali kept for a week at room temperature gave anomalous results, indicating that some other reaction had also occurred. Experiments with esters other than the octadecyl were not so extensive, but, in general, heating for one hour under reflux appeared to cause complete hydrolysis.

Although methyl mercaptan reacts readily with sodium hydroxide, there seemed to be no interference from this cause.

Apparently all the mercaptan was expelled from the boiling solution, as its odor could be detected at the top of the condenser throughout these reactions, which were therefore conducted in a fume hood.

In another experiment, boiling 25% aqueous, as opposed to alcoholic, sodium hydroxide did not appreciably hydrolyze the octadecyl ester, even after two hours; the ester remained insoluble, and was recovered in over 95% yield. The insolubility in water was clearly the cause of the relative stability in this case.

The general behavior of the xanthate methyl ester group in alkali, however, clearly indicated that any projected methylation of cellulose xanthate methyl ester would not be successful if alkaline solutions were used, as in the usual Haworth (92) method with dimethyl sulfate. It is well known, of course, that alkali solutions of cellulose xanthate itself (viscose) undergo extensive changes on standing, chiefly owing to de-xanthation (see p. 18).

On the other hand, the octadecyl ester was stable to aqueous-alcoholic ammonia when the solution was allowed to stand for several days at room temperature, and in pyridine solution was only very slightly affected under the same conditions. Heating with pyridine, however, caused extensive decomposition.

The octadecyl ester showed surprising stability to hydrochloric acid, although Lieser (34) and McAlpine (30) had earlier observed this behavior with other xanthate esters

(see p. 13). Aqueous 6N acid had no measurable effect on the ester, even on heating under reflux for three hours. Heating for an hour under reflux with lN aqueous-alcoholic hydro-chloric acid was also ineffective, although the ester was soluble in this reagent. The effect of 43% hydrochloric acid at 0° C. for 24 hours was also examined, but again the unchanged ester was recovered in high yield. Neither heating under reflux with 3% hydrochloric acid in absolute methanol nor in a sealed tube at 120° C. with the same reagent for three days caused any appreciable decomposition. However, six days with this reagent in a sealed tube at a temperature eventually reaching 160° C. decomposed the ester extensively.

This stability toward acid suggested that the cellulose analogue might be degraded by 43% hydrochloric acid, for example, to glucose derivatives without de-xanthation occurring. This expectation was only partially fulfilled, as the analogy with cellulose was not as close as had been hoped.

A few experiments on the action of heavy metal salts were carried out, although all were on a small scale and were intended to be merely preliminary in nature. A test with silver nitrate at room temperature led to inconclusive results, perhaps because nitric acid was produced in the reaction. Lieser (34), however, used silver nitrate to decompose at least one xanthate ester. When the ester was heated in alcoholic solution under reflux with silver oxide for at least an hour, a rather drastic treatment, de-xanthation

to octadecanol occurred, although a considerable amount of lower melting material was also produced. Silver carbonate gave a similar result, producing octadecanol when heated under reflux with an alcoholic solution of the ester. On the other hand, an ether solution of the ester stood in contact with silver carbonate for a day at room temperature, with only a slight suggestion of decomposition. A small qualitative test with mercuric acetate was inconclusive, and a test with cadmium carbonate appeared to show that the ester was unchanged on standing with the salt at room temperature for two weeks.

Although these experiments were not extensive, it appeared that the silver salts at least (except those of strong acids) were good de-xanthating agents. The chief disadvantage, perhaps due to the somewhat drastic conditions used, seemed to be the difficult separation of the octadecanol in pure form from the crude reaction product.

If the xanthate ester group were stable to thallous ethylate, it might be possible to methylate the hydroxyl groups in a cellulose xanthate methyl ester by a thallation followed by treatment with methyl halide or sulfate (93). Even with rigorous exclusion of water, however, a thallous ethylate solution in benzene reacted readily with octadecyl methyl xanthate at room temperature, giving octadecanol and a black precipitate of a sulfide, or sulfides, of thallium. A few hours, however, seemed to be necessary for complete reaction.

It had been thought that the covalent nature of thallous ethylate might prevent the de-xanthation which occurred with other heavy metal salts, but such was not the case.

By analogy with the reaction of Raney nickel on dithioesters, octadecyl methyl xanthate might be expected to produce octadecyl methyl ether (see p. 16), a known compound of melting point 30-31° C. This expectation was not realized, although seven experiments were carried out under varying In all cases a considerable yield of octadecanol conditions. was obtained in addition to generally smaller amounts of a low melting material (28-33° C.) which was not the desired ether, and also some of the starting ester when very mild reaction conditions were used. The first three experiments, in which an ethanolic solution of the ester was heated under reflux with the nickel for four hours, gave a product which was about two-thirds octadecanol and one-third lower melting material. Standing for four hours at room temperature gave roughly 40% octadecanol and 60% low melting material. indicating that milder conditions gave a larger amount of the lower melting fraction, which might be an intermediate compound. However, about the same proportions were obtained when the reaction mixture stood for 1.5 hours at 9° C. Still milder conditions were used in a final experiment when a solution of the ester in dioxane (used to avoid the solubility difficulties experienced with ethanol at the lower temperature) stood for 10 minutes at 9° C. In this case, however, about

three-fifths of the recovered product was the original ester, and the remainder consisted of roughly equal amounts of octadecanol and the lower melting material. It was hoped that very mild reaction conditions might eliminate octadecanol from the product, but this was not the case.

Although the fractional recrystallization of the product from pentane was not completely satisfactory, and no better method of separation was found, there was no trouble in obtaining pure octadecanol, which was identified as the phenylurethane. In several cases, the low-melting fraction was repeatedly "crystallized" from methanol or from pentane, always giving a white waxy solid of melting points such as 29.5-30° C., 29-31° C., 28-30° C., and 29.5-31.5° C. Several experiments suggested that this was not a chemical individual, but perhaps a mixture of by-products. Analyses showed only about 2.2% of sulfur and 3.5% methoxyl groups, and the latter value decreased to 2.6% after additional "crystallization" of the product. The methoxyl values suggested that a small amount of octadecyl methyl ether might indeed have been present, but additional work would be necessary to confirm this supposition. In any case, a simple transformation to the methyl ether did not occur. If it had occurred, and if the reaction could have been extended to cellulose, a valid alternative to Lieser's diazomethane substitution might have been developed. On the other hand, with the simple esters at least, this reaction provided another method of de-xanthation

and one which occurred under neutral conditions.

A sample of the octadecyl ester was recovered nearly quantitatively from an acetylating mixture of acetic anhydride and zinc chloride, after standing at room temperature for 24 hours. This simple test confirmed the results of Lieser (34) who acetylated a xanthate methyl ester of *Q*-methylglucoside without disturbing the xanthate group, and then de-xanthated the product with silver salts. In the case of cellulose, the resulting acetate could not be used for degradation studies because the acetyl groups would not be stable, but might be examined in other ways.

In order to study the action of heat on the octadecyl ester, a five gram sample was gradually heated to 180-190° C., whereupon the temperature suddenly increased to about 290° C. An isomeric change possibly occurred, such as Laakso (13) observed with other xanthate esters (see p. 10), which behaved similarly when heated. An examination of the product for the unknown S-octadecyl S-methyl dithiocarbonate was not undertaken, however, as it could have no application to the cellulose xanthate problem. Such an isomerization might be of value in work on sugar xanthates, where known thio sugars might be prepared from xanthate esters of unknown structure. Freudenberg (31) showed that a sugar xanthate could behave in this way.

4. Oxidation and Reduction of Xanthate Methyl Esters

A solution of octadecyl methyl xanthate in glacial acetic acid, when allowed to stand for three days with 30% hydrogen peroxide in excess, produced a new compound of the formula $C_{20}H_{40}O_4S_2$ in a crude yield of 77%. This oxidation was suggested by the fact that sulfones are readily prepared from thioethers by similar means, as described in standard textbooks (e.g., 94). Crystallization from ethanol gave relatively pure white flakes in about 48% yield, although at least two further crystallizations from pentane or petroleum ether were necessary to obtain a strictly pure product. The formula $C_{20}H_{40}O_4S_2$ differed from that of the original ester $(C_{20}H_{40}OS_2)$ only in that three more oxygen atoms were present. Saponification in hot aqueous alkali led to octadecanol, and therefore the 0-octadecyl group was still present, and the compound was probably still an ester. When the saponification mixture was first heated, the solution turned yellow, and the material floating on the surface remained solid throughout most of the reaction time of several hours, and therefore could not be either the C₂₀H₄₀O₄S₂ compound (m.p. 66.2-67° C.) or octadecanol (m.p. 60°). It is known that the \geq C=S group in thioketones may readily change to \supset C=O with liberation of hydrogen sulfide by heating with alkaline solutions (95), and it was possible that some similar intermediate compound formed here prior to complete saponification in the present case. Hydrogen sulfide was certainly liberated, as a strong test for sulfide

ion was obtained from the resulting yellow solution. It appeared that at least one sulfur atom of the xanthate ester had remained in the reduced state in spite of the treatment with hydrogen peroxide, although a complete elucidation of structure was not attempted. An analogous oxidation of hexadecyl methyl xanthate gave the compound $C_{18}H_{36}O_{4}S_{2}$ of melting point 56-57° C.

Although this oxidation might be expected to be general for the xanthate esters, unsatisfactory results were obtained in the case of benzyl methyl xanthate in a preliminary experiment. A considerable portion of the product was benzyl alcohol, and white, sulfur-containing needles of m.p. 125° C., plus a yellow liquid distilling at 275-300° C. were also obtained. If applied to cellulose xanthate esters, it seemed possible that the hydrogen peroxide would cause other oxidations in the cellulose chains, thus interfering with the results. The stability toward acid hydrolysis, however, might be reasonably good, as a sample of the new octadecyl derivative was boiled in a test tube with concentrated hydrochloric acid for ten minutes, and was recovered unchanged.

Some unsuccessful attempts were made to determine methylthio groups quantitatively by titrating acidified solutions of octadecyl methyl xanthate with a bromide-bromate solution. These attempts were modifications of a method used by Siggia and Edsberg (96) for thioethers, in which the thioether was oxidized to a sulfoxide. With the xanthate esters, however, both sulfur atoms were clearly oxidized well beyond the sulfoxide stage, apparently to an indefinite extent depending on conditions, and the end point was not distinct.

In another experiment, an aqueous-alcoholic solution of the octadecyl ester was readily oxidized by liquid bromine, and the crude solid mixture obtained by dilution with water consisted largely of a white waxy compound of m.p. 61.6-62.6° C. which did not contain sulfur or halogen and therefore differed from the product obtained in the oxidations with hydrogen peroxide. The new compound was not stearaldehyde, whose melting point was given as 63.5° C. (97) or, more probably, as 38° C. (98). Neither was it stearic acid, since it failed to dissolve in warm 5% sodium hydroxide, although it became yellow.

As in many of the other experiments, oxidation of octadecyl methyl xanthate with periodate was attempted not so much to prepare a new compound as to determine whether the xanthate ester group was stable to the reagent. If so, then a periodate oxidation of the cellulose analogue might provide a measure of the unsubstituted glycol groups and hence some indication of the xanthate group distribution. Sodium metaperiodate or trisodium paraperiodate could not be conveniently used in this experiment, as they were not appreciably soluble in the nonaqueous media required for solution of the ester. Treatment of an ethanolic solution of the ester with paraperiodic acid, H_5IO_6 , produced free iodine and a small yield of a white waxy solid of m.p. 33-34° C., which was unidentified. It would be

expected, therefore, that the xanthate ester group would be similarly attacked in the cellulose derivative, and later experiments showed this to be the case.

Several attempts were made to devise a method of analysis for the methylthic group (-SCH3) in xanthate methyl esters by cleavage with hydriodic acid. Both the Vieböck (99, 100) and the Kirpal-Bühn (101, 102, 103, 104) methods and their modifications for methoxyl determination were found to be unsuitable. The former involved the absorption of the methyl iodide in a bromine solution, destruction of excess bromine with formic acid, reaction with potassium iodide, and titration of the resulting iodine with standard sodium thiosulfate. Many modifications of this method have appeared in the literature, and the Tappi Standard Method T-209 M-34 (105) is also essentially the Vieböck method. As shown in the Experimental Section, the lack of success was probably caused by the difficulty of cleaving the methylthic group rather than to any loss of methyl mercaptan. Although it is often stated that the Vieböck method is suitable for sulfur-containing compounds, this presumably does not refer to the case where sulfur replaces the oxygen in the methoxyl group itself. The only essential difference in the Kirpal-Bühn method and its several modifications is that the methyl iodide is absorbed in pyridine, which is subsequently evaporated to dryness, and the pyridine methiodide dissolved in water and titrated with silver nitrate. Gravimetric procedures are used in some modifications of this method. The claim

is made that this method is also suitable for sulfur-containing compounds, since mercaptan and hydrogen sulfide are not absorbed in pyridine.

There was some indication from the present experiments that a very long time of reaction with boiling hydriodic acid, perhaps three days or longer, might effect complete cleavage, but the reaction was not exhaustively examined. It was possible that Lacourt's method (106) might be made to work. This method involved cleavage at a somewhat higher temperature (180-190° C.) and was stated to have been practically quantitative for several thioethers and for two dithioesters.

Lieser apparently used the Kirpal-Bühn method in all his researches on xanthates, although details were not given, for both methoxyl and methylthic determinations. The only definite reference to methylthic analyses in his papers, however, was in connection with his supposed cellulose xanthate methyl ester (62), where he stated that he used the Kirpal-Bühn method, and where the methylthic content turned out to be only about onequarter of the expected value. He blamed this low result on side reactions during the methylation, and seemingly did not question the suitability of the analytical method. Strangely enough, in a later paper (34), he determined methoxyl groups in a xanthate methyl ester of α -methylglucoside and in other similar compounds by the Kirpal-Bühn method, and apparently the methylthic ether content of the compound did not interfere at all. This result in itself would indicate that methylthic groups could not be determined in this way, in spite of his own earlier attempts with cellulose xanthate methyl ester.

Difficulties in devising a suitable analytical method for the methylthic group are probably not insurmountable, although an exhaustive investigation was considered to be outside the scope of the present project. It might be possible to liberate methanethicl from the xanthate ester nearly quantitatively by alkaline hydrolysis, and to absorb the mercaptan in a suitable reagent, perhaps silver nitrate or cadmium chloride solution (cf. 107).

Cellulose Xanthate Methyl Ester

Sixteen preparations of cellulose xanthate were carried out, and of these, five followed Lieser's method (62) (see p. 20) in which the xanthate is kept fibrous throughout the entire procedure and the preparation of a viscose solution is avoided. The other runs were by the more common procedure of preparing a viscose solution and precipitating the xanthate with methanol. The method was similar to that of Chen, Montonna, and Grove (55), although it also resembled other reported procedures. Details were varied somewhat from run to run in the hope of obtaining a better product. In the Experimental Section, these variations are tabulated, although no new results of a general nature were forthcoming.

It was realized, of course, that the use of methanol to precipitate the xanthate was attended by certain disadvantages

(cf. p. 24) which included the possibility that the more highly xanthated material might stay in solution and that the xanthate group might decompose in methanol more rapidly than in some Indeed, some incidental experiments confirmed other liquids. these possibilities. Solutions from which methanol could produce no further precipitate gave slight additional precipitates when ethanol was added. Furthermore, a low degree of substitution in some products was doubtless partly due to excessive contact with methanol during precipitation, filtration, and washing. A pure product precipitated by methanol was far more convenient to prepare than one precipitated by ethanol, products from which were often gummy and difficult to handle. In the present research, whose primary purpose was to investigate possible methods of determining the distribution of xanthate groups, the exact nature of the cellulose xanthate was not very important, and a loss of a few of the more labile groups could be tolerated. The disadvantage of precipitating cellulose xanthate from methanol should be kept in mind, however, when quantitative data are to be interpreted in terms of the original group distribution. This might be considered another objection to some of Chen's work (55) in which methanol was used.

Only in the last two runs were degrees of substitution obtained (0.43 and 0.42) in pure products which approached that expected (about 0.5) for a heterogeneous xanthation, in spite of the use of a somewhat higher proportion of carbon disulfide than customary. In these runs, lower temperatures were used
during precipitation and purification, and the time of contact with methanol was reduced as much as possible. Moreover, the primary xanthate was dissolved in a 6% caustic soda solution instead of a 4%, as the concentration giving maximum stability was reported to be about 7% by Lieser (62) and 8-9% by Heuser (60). In addition, the time of xanthation and the amount of carbon disulfide were increased somewhat, and in one case the alkali cellulose was not pressed as free as usual of excess alkali. This factor had no effect in this case, although Lauer (69) showed that greater degrees of pressing produced lower degrees of xanthation.

Steeping the sodium cellulose xanthate for a short time in dilute solutions of acetic acid in absolute methanol did not appear to be completely effective in removing all excess caustic soda, to judge by sodium analyses, and the degree of substitution was also decreased to some extent by this treatment. The slightly excessive sodium to sulfur ratio in the products might have been due to traces of sodium acetate not completely removed by washing, rather than to incomplete neutralization.

In all cases, the degree of substitution (D. S.) was calculated by the usual method, depending on the sulfur to cellulose ratio. With one xanthate group per glucose residue, this ratio was 0.395.

$$\frac{\% \text{ Sulfur}}{\% \text{ Cellulose}} = \frac{2S}{C_6 H_{10} O_5} = \frac{64.12}{162.14} = 0.395$$

Therefore the D. S. could be calculated by dividing the determined sulfur to cellulose ratio by the factor 0.395. The

sulfur analysis alone did not give a reliable result, as varying amounts of excess caustic soda might be present.

Another method of determining the D. S. was developed by Fink, Stahn, and Matthes (66). Primarily for use with viscose solutions, it was not used in the present work. In this method, the viscose was treated with diethylchloroacetamide, and the resulting diethylacetamide derivative was analyzed for nitrogen, the D. S. being calculated directly from this analysis. They expressed their results in terms of the number of xanthate groups per 100 glucose units, the so-called "gamma number", which is often encountered in the literature. Some writers clearly restricted this term to the results of this particular method, but others used it more generally to express the degree of xanthation regardless of how it was determined.

In the present work, the total sulfur was sometimes determined by the Carius procedure (108), and sometimes by a hypobromite oxidation of viscose, followed by addition of barium chloride and the usual gravimetric estimation of sulfate ion. This method was credited to Delachanal and Mermet (109) in a paper by Barthélemy and Williams (110), but to Lindemann and Motten (111) by Heuser (60), and was briefly described in Dorée's textbook (112). Another method for the determination of sulfur in viscose was described by Barthélemy and Williams (110) and converted all sulfur to zinc sulfide by a treatment with sodium zincate solution, then titrated the sulfide iodometrically. This method was also tried, but gave results which were usually much too high. Both the zincate and hypobromite methods are usually applied to crude viscose solutions, and not to pure dry xanthates, which must first be re-dissolved in alkali. In the present work, the hypobromite method was nearly as satisfactory as the Carius, except for some products of very low D. S. which did not completely dissolve in the sodium hydroxide solution. When purified products were examined by any of these methods, the figure for total sulfur might be taken as representing xanthate sulfur. Various other sulfur methods are available, and are mentioned in the books of Heuser (52), Ott (53), and others, but are not discussed here.

As pointed out earlier, there is no decisive evidence that either Lieser or Lilienfeld really prepared the methyl ester of cellulose xanthate in a pure condition. It presented no difficulties, however, and presumably pure products were obtained. Undried samples of cellulose xanthate were methylated immediately after preparation, while in a swollen condition, the xanthate being allowed to stand in ether suspension with an excess of methyl iodide for several days. The resulting white powders were washed with methanol, then ether, and dried. The methvl ester was insoluble in water, but slowly soluble in dilute aqueous alkali with some decomposition, giving a clear viscous solution. Although it could not be satisfactorily analyzed for the methylthic group, its sulfur analyses agreed closely with the expected value and sodium analyses showed only trace The D. S. was calculated directly from the sulfur amounts.

analysis and agreed quite well with that of the original sodium xanthate. For example, two xanthates of D. S. 0.43 and 0.42 gave esters of D. S. 0.45 and 0.37 respectively.

As expected from the parallel experiment with octadecyl methyl xanthate, the xanthate ester group was not stable to the periodate ion in aqueous solution, over two moles per glucose residue being consumed within four days. The theoretical amount was less than one mole. This result made it impossible to determine the distribution of unsubstituted glycol groups by selective oxidation with periodate, as described for other cellulose derivatives on several occasions (e.g., 113, 114, 115, 72).

When the cellulose xanthate methyl ester was degraded with 43% hydrochloric acid at 0° C., as described for cellulose by Willstätter (116), it soon became apparent that de-xanthation was occurring, in spite of the stability of the simple xanthate methyl esters under similar conditions. A deep coloration, gradually increasing to nearly black, accompanied de-xanthation, as the color was not observed in control runs with cellulose itself. After isolation and drying of the products, varying proportions of the original sulfur content had been lost, about 37% in the best experiment and 90% in the worst.

A series of 13 runs under somewhat varying conditions is described in detail in the Experimental Section. It was found that concentrated hydrochloric acid (37%) at room temperature for a few hours was as satisfactory as the 43% acid

at 0° C. for longer periods. As de-xanthation was presumably not as extensive in more dilute acidic solutions, the general principle was to dilute to some extent as soon as this could be done without precipitation occurring, and again later, at intervals. Of course, degradation was also slowed down in the more dilute solutions, but it was necessary to compromise in this respect. In the best run, the ester stood in 37% acid at room temperature for five hours, then in approximately 18.5% acid for six days, and finally in approximately 9.2% acid for about four days. When the degradation was apparently complete, the solution was neutralized and the product separated. In some of the earlier runs, attempts were made to test for completeness of degradation in the diluted solutions by measuring the optical rotation at intervals until constant. This method proved unsatisfactory because the observed value was very small in the diluted solutions (less than a degree), and because of the turbidity which developed and was probably caused by free sulfur. In later runs, attempts were made to judge the end of the reaction by the constancy of the copper reducing value, as determined by the Shaffer-Hartmann-Somogyi method. Although not very satisfactory, probably because of interference of the xanthate group with the copper reagent, this method provided a guide to the completeness of reaction. It seemed probable that in most, if not all, of these hydrolyses the ester was not completely degraded to glucose xanthate methyl esters.

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It was also necessary to avoid de-xanthation during the isolation of the product. In two early runs, barium carbonate was used for neutralization, followed by evaporation to dryness, extraction with ethanol, and evaporation of the extract to obtain a solid residue, which was taken up in water and passed through ion-exchange columns to remove traces of inorganic material, and again evaporated to dryness. A neutralization with silver carbonate was not employed, as de-xanthation would occur with this reagent. This behavior, which would be expected from the results of tests on the simple xanthate esters, was confirmed by treating a small sample of a solution of the hydrolysate (obtained by the barium carbonate method) with silver carbonate, which turned black almost immediately. A more convenient method, used in later runs, was to neutralize with basic lead carbonate and remove most of the lead chloride by filtration, then to remove the remaining lead by treatment with hydrogen sulfide, and the last traces by ion-exchange. A test on a small sample had shown the xanthate ester groups to be stable to basic lead carbonate at room temperature. A disadvantage of both methods, however, was the probable loss of a considerable amount of product by adsorption on the inorganic precipitates. Examples of these procedures are given in the Experimental Section, and the results of all the runs are tabulated.

Another degradation was carried out with methanolic hydrochloric acid under pressure. About 87.5% of the original

sulfur content was lost after the xanthate ester had been heated in a sealed tube with a 3% solution of hydrochloric acid in absolute methanol for three days at 120° C., then for two days at 140° C. and for about 33 hours at 160° C. Although three days at 120° C. was sufficient for similar degradations of many cellulose derivatives (57), not all of the xanthate ester dissolved under these conditions.

It thus appeared unlikely that the ester could be degraded to the glucose stage without substantial de-xanthation occurring. Several known xanthate derivatives, including the diethylacetamide derivative, would probably survive the conditions of degradation no better than the methyl ester. The search for a suitable new derivative was beyond the scope of the present work, although some exploratory work was done with the simple xanthates as reported earlier. Recourse might have to be made to methods of examination not involving acid degradation. For example, considerable information might be obtained from a study of the structure of the cellulose acetate formed by the acetylation of cellulose xanthate methyl ester, followed by de-xanthation. Lieser (34) was able to acetylate glucose xanthate esters without de-xanthation occurring, and octadecyl methyl xanthate is also stable to acetylating conditions, as reported earlier.

Although much sulfur had been lost, three of the most promising products of acid degradation of cellulose xanthate methyl ester were examined by paper chromatography. In all

cases there were heavy glucose spots, in accord with the fact that degradation, if complete, would yield over 50% of glucose. In addition, there were always spots which had moved only very slightly from the starting line, and were clearly those of unhydrolyzed material, therefore degradation had not been complete. Most interesting, however, were the spots which might have been due to xanthate methyl esters of glucose. With two of the products examined, there were four such spots, of average $R_{\rm F}$ values 0.196, 0.390, 0.574, and 0.752, the first pair being very faint and the last two somewhat stronger. The third product gave similar results, except that the faint spot at Rp 0.390 had apparently resolved into two close spots in the The three possible monoxanthate esters of glucose same area. which could result from a degradation are the 2, 3 and 6 derivatives and could account for only three of the four or more spots obtained. Perhaps the first faint spot was due to a dixanthate ester of glucose, or, more likely, to a monoxanthate ester of cellobiose. Mr. A. Sanyal of these laboratories provided a solution for examination which was thought to contain glucose-3-methylxanthate, prepared by synthesis. The only reducing spot obtained from this solution did not correspond to any of the spots from the hydrolysates. A possible conclusion was that the hydrolysate did not contain any of the 3derivative, which would support Lauer's recent work (71). A future extension of this chromatographic investigation would involve separations of larger amounts of the hydrolysates

on a powdered cellulose column, from which the individual constituents could be separately eluted and examined.

In the meantime, an attempt to estimate glucose in the products of three hydrolyses was made by determining the copper reducing value before and after fermentation. The results showed 13%, 7%, and 9% of glucose, whereas the value should be at least 55% in all cases, if degradation had been complete. The fermentations appeared to proceed satisfactorily, but the xanthate ester group obviously interfered with the determination of reducing value. An alternative conclusion was that degradation had been very much less than assumed, but this was unlikely, or at least not an important enough factor to cause the observed result. A somewhat more satisfactory determination was made on one hydrolytic product by a different method. The glucose was separated from the other constituents by paper chromatography, and was extracted from the paper with water. Copper reducing values on the resulting solutions showed an average of 21.6% glucose, much greater than the 7% obtained for this product by the first method, but still much less than would have been obtained if degradation had been complete.

EXPERIMENTAL SECTION

Reagent grade chemicals were used in all cases.

Absolute ethanol, methanol, and ether were prepared by standard methods described by Fieser (117).

Melting points were uncorrected.

References to analytical procedures are given in the appropriate places in the text.

Xanthate Methyl Esters of Simple Alcohols

1. Preparation

O-Benzyl S-Methyl Xanthate

The two methods used in the five preparations of this ester are illustrated by Runs No. 1 and No. 3, which are reported below.

<u>Run No. 1</u>:- In this run, the xanthate salt was isolated and purified, then methylated in an ethanolic medium. Benzyl alcohol, 0.36 mole (39.0 g., 37.1 ml.), and potassium hydroxide pellets, 0.30 mole (16.8 g.), were mixed in a 500 ml. flask fitted with condenser and mercury-sealed stirrer. Heating under reflux caused all the potassium hydroxide to go into solution, but after cooling to room temperature the greater part came out again as a white flaky suspension. Then 0.45 mole (34.2 g., 27 ml.) of carbon disulfide was added in portions over a 20-minute period, giving an immediate reaction. Next day the voluminous precipitate was recovered on a filter, washed by thorough agitation with ether, and again recovered.

A small amount of orange-colored oil, immiscible in ether, was The crude salt was dissolved in hot ethanol, the not examined. solution filtered (a green-gray residue was discarded), cooled in an ice bath, and treated with dry ether to complete the precipitation. This method of purification was frequently reported in the literature (e.g., 118). After recovery and drying in a vacuum desiccator, the yield was 46.7 g. (67.5%) of pale yellow xanthate, which was positively identified as such by the molybdate method (119). This test was made by adding 5 mg. of the sample to two drops of a solution containing about 1 mg. of ammonium molybdate. When four drops of 2N hydrochloric acid were added, the red-blue color of the complex (ROCSSH)2.Mo03 developed. The xanthate salt was purified by solution in hot acetone, followed by filtration and reprecipitation in a voluminous white form by dilution with dry ether. This product appeared reasonably stable, although a sample became slightly yellow after standing for a long time. During the purification by acetone, complete solution was not effected even by a large excess of the boiling solvent. DeWitt and Roper (23) made the same observation with another xanthate, but discarded the acetone-insoluble portion without examination. In the present case, the pale yellow residue partly turned red when heated strongly, and was largely inorganic.

A 0.03 mole sample (5.76 g.) of the purified salt was warmed under gentle reflux with 6 ml. of absolute ethanol and 0.03 mole (4.26 g., 1.87 ml.) of methyl iodide for three hours.

Reaction was immediate, with liberation of heat and of an unpleasant odor from the top of the condenser, perhaps because a slight saponification of the newly formed ester was liberating traces of methanethicl. Two volumes of water were added to dissolve the precipitated potassium iodide. The lower layer of crude xanthate ester, a yellow oil, was removed, dried with anhydrous calcium sulfate, filtered, and subjected to diminished pressure for some time. Cooling with solid carbon dioxide caused solidification, and trituration with cold ethanol made it possible to recover the solid on a small filter cooled by solid carbon dioxide. After drying in a desiccator kept in a cold room, 0.5 g. (25%) of crystals remained, of m.p. 27-28° C.

Another sample of the purified xanthate salt was further purified by the method of DeWitt and Roper (23), which included solution in hot acetone, filtration, slow dilution with a large excess of benzene, filtration, solution in warm acetone, dilution with petroleum ether, filtration, washing with petroleum ether, and drying. Even after the final filtration, the precipitate became slightly yellow, particularly at the edges, on standing, but became nearly white again after two or three days in a vacuum desiccator containing sulfuric acid and activated charcoal. The salt was saved for later experiments.

Run No. 3:- In this run, which was more satisfactory, the intermediate salt was not isolated, and ether was the reaction medium for both steps. The method was adapted from that used by Whitmore (20) for the preparation of isoamyl methyl xanthate.

Benzyl alcohol, 0.25 mole (27 g., 25.7 ml.), and 0.25 mole (10.1 g.) of sodium hydroxide pellets were mixed in a 500 ml. round-bottomed flask fitted with a condenser and mercury-The hydroxide was completely dissolved by sealed stirrer. heating and stirring, and although much separated again on cooling, a reasonably good dispersion resulted. Then 150 ml. of ether and 12.5 ml. of carbon tetrachloride were added, followed by 0.25 mole (19.0 g., 15.0 ml.) of carbon disulfide over a 15-minute period, with continued stirring. Nearly 25 ml. of additional carbon disulfide was later gradually added in an attempt to cause complete reaction of the alkali, which otherwise might have caused partial saponification of the ester, as evidenced by the mercaptan odor. However, the solution was still blue to litmus, a reaction which might be expected of a crude xanthate solution, although a pure sample of xanthate salt was neutral.

Methyl iodide, 0.27 mole (38.4 g., 16.84 ml.), was added in three portions over 15 minutes and the mixture was gently heated under reflux for six hours with intermittent stirring. The reaction occurred readily, and at the beginning liberated enough heat to cause refluxing. There was no odor of mercaptan from the condenser. The ester was isolated as in Run No. 1. After being seeded, and kept overnight in the refrigerator, the product solidified and appeared purer than in earlier runs. Recrystallization from 30 ml. of ethanol, with filtering in the cold room and washing with ice-cold ethanol, produced white

crystals which were dried over calcium chloride in a desiccator kept in a cold room. Weight 41.5 g. (70%); m.p. 28.5-29.5° C. (recorded 29°) (9). Two additional crystallizations from ethanol-water gave better formed needles of m.p. 29-29.5° C. It was found that the best crystals were obtained by using a rather large excess of ethanol-water and very slow cooling, taking two or three successive crops to avoid large losses of material. In this way, the intermediate formation of an oil was avoided. Another technique, although not as satisfactory, was to use a smaller amount of solvent and to cool very quickly in a bath containing solid carbon dioxide, a procedure which gave very small white crystals with no intermediate oil formation.

O-Hexahydrobenzyl S-Methyl Xanthate

For early preparations, the necessary hexahydrobenzyl alcohol was obtained by the method given in "Organic Syntheses" (120), using a Grignard reagent of cyclohexyl chloride and formaldehyde. The cyclohexyl chloride was prepared by heating cyclohexanol with concentrated hydrochloric acid under reflux (121). The hexahydrobenzyl alcohol for later runs was obtained from the Eastman Kodak Company.

As essentially the same method was used in the five runs of the xanthate ester, Run No. 3 alone is presented in detail. It was largely modelled on Run No. 3 of the corresponding benzyl ester, in which the intermediate xanthate salt was not isolated. In one run, however, the salt was isolated (58% yield) and purified, although this procedure had no advantage over the other method.

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Run No. 3:- Pulverized sodium hydroxide, 0.1 mole (4.0 g.), hexahydrobenzyl alcohol, 0.1 mole (11.4 g.), 60 ml. of ether, and 5 ml. of carbon tetrachloride were stirred together in a 250 ml. flask fitted with a mercury-sealed stirrer and reflux condenser. After 0.5 hour, 0.1 mole (7.61 g., 6.02 ml.) of carbon disulfide was added dropwise over 10 minutes, with continuous stirring. Although the solution became yellow, a precipitate did not form immediately, and the reaction appeared more sluggish than with benzyl alcohol. After standing overnight, a small precipitate had formed. The mixture was stirred for two hours longer, and 6 ml. of additional carbon disulfide was added in portions over that time. The amount of precipitate increased considerably. Then 0.11 mole (15.85 g., 6.87 ml.) of methyl iodide was added over a five-minute period. The heat of reaction was noticeable after a minute or two, and although in 10 minutes reaction appeared to be largely complete, the mixture was warmed and stirred for some time longer. After about one hour, the precipitate (presumably sodium iodide) was adhering together in one large piece, a phenomenon not observed in the corresponding benzyl preparation. After another hour, an additional 1 ml. of methyl iodide was added, and stirring and warming continued for a total of four hours.

After the mixture had stood for two hours, the sodium iodide was dissolved by the addition of 50 ml. of water, the

layers were separated, and the washed ether layer was dried over anhydrous calcium sulfate for two days, filtered, and concentrated under reduced pressure. The residue was a yelloworange liquid, obviously impure, which did not solidify on standing in the refrigerator for several days. Distillation at 20 mm. pressure, possibly an inadvisable procedure because of possible decomposition or isomerization, gave a considerable fore-run, but most came over as a pale yellow liquid at 158-165° C. It was easily solidified in a bath containing solid carbon dioxide, and was kept in the refrigerator overnight. A few ml. of ethanol was added, and the crystals were recovered on a bed of solid carbon dioxide in a small Büchner funnel kept in the cold room (8° C.). After being washed with very cold ethanol, the white crystals were dried over anhydrous calcium chloride in a desiccator in the cold room. Weight 5.5 g. (27%).

This yield could probably have been increased slightly by taking an additional crop of crystals. The product was again crystallized from ethanol-water, using cold room techniques. M.p. 16-16.5° C. Sulfur analyses by the semimicro Carius procedure gave slightly low results, probably indicating that the sample was not yet completely free of solvent. Calculated for $C_{9H_{16}OS_{2}}$: S 31.38%. Found: S 30.90, 30.52, 30.94%.

O-Menthyl S-Methyl Xanthate

The method of preparing this ester was essentially the same as with the primary alcohols, although xarthation occurred

somewhat less readily. The following procedure was typical of the three preparations carried out.

Menthol, 0.2 mole (31.2 g.), and pulverized sodium hydroxide, 0.2 mole (8.1 g.), were stirred in 120 ml. of dry ether contained in a 250 ml. flask fitted with a mercury-sealed stirrer and reflux condenser; then 0.4 mole (30.4 g., 24 ml.) of carbon disulfide was added with rapid stirring, which was continued for two hours at a gentle reflux temperature. The yellow precipitate still seemed to be increasing in amount after this time, and the mixture was allowed to stand overnight, then was warmed again and stirred intermittently for five hours. The following day, the addition of 0.2 mole (28.39 g., 12.44 ml.) of methyl iodide gave an immediate although rather slow reaction. The mixture was warmed under reflux for a total of 10 hours, and allowed to stand for several days, during which time, at intervals, an additional 0.4 mole of methyl iodide was added. After removal of the potassium iodide by filtration, and evaporation of the filtrate under reduced pressure, the crude liquid product weighed 41.4 g. or 84%, if considered to be entirely the ester. Crystals were obtained by the addition of 50 ml. of absolute ethanol, cooling drastically, seeding, recovery in the cold room, and washing with cold ethanol. Three additional crops of crystals resulted from alternate concentration and cooling, with seeding, to give a total of 15.6 g. (31.7%) of not entirely pure ester. As usual, the chief difficulty was the recrystallization of the low-melting solid without a large loss. Another recrystallization from ethanol, using absorbent carbon, slow

cooling, cold room filtration, and drying, gave three successive crops of well-formed white needles of m.p. 38.5-39° C., in agreement with the recorded value (10) of 39° C.

O-Octadecyl S-Methyl Xanthate

Of the ten runs carried out, Run No. 7 was typical of the early runs in which ether was the reaction medium, and Run No. 9 was one of the two in which excess carbon disulfide was used instead of ether. Some details of Run No. 8 are also presented below, as it was one of two runs in which the intermediate xanthate salt was isolated and examined. Run No. 6 had shown that isolation of the intermediate salt did not prevent the final crude ester from containing octadecanol as an impurity.

<u>Run No. 7</u>:- Fulverized sodium hydroxide, 0.2 mole (8.0 g.), was added to 400 ml. of dry ether in a l litre three-necked flask, fitted with mercury-sealed stirrer and reflux condenser, and stirred to get a good suspension. Then 0.2 mole (54.1 g.) of octadecanol, which had been recrystallized from petroleum ether, was added in portions, with warming, to give a suspension, complete solution of the octadecanol not taking place even with the large amount of ether present. After standing for about 20 hours, in the vain hope of effecting further solution, the entire mixture had formed a solid cake, which was broken up by adding 300 ml. of additional ether and stirring for some time. Then 0.4 mole (24.08 ml.) (twice the theoretical quantity) of reagent grade carbon disulfide was added, with continuous stirring. Immediately the thick suspension largely disappeared, the solution became increasingly yellow, and a yellow precipitate of xanthate salt gradually formed. Intermittent stirring and gentle warming were continued for six hours, and the mixture was allowed to stand overnight after the addition of a further 0.4 mole of carbon disulfide. Then 0.22 mole (13.74 ml.) of methyl iodide was added, and warming and intermittent stirring were continued for eight hours. After standing for a day and a half, the white precipitate of sodium iodide was removed by filtration, the ether was distilled, and the final trace of solvent was evaporated under reduced pressure to leave 58.6 g. (81.7%) of an oily semi-solid yellow residue.

This product was crystallized from about 75 ml. of ethanol, which was cooled slowly to get 14.2 g. of good crystals melting at 38-39° C. By concentration of the liquors, a second crop of 21.5 g. was obtained (m.p. 38-39° C.) and similarly a third crop of 4.2 g. (m.p. 37-38° C.). An attempt to produce a fourth crop in the same way yielded 3.5 g. of a material melting at 54-55° C., probably largely octadecanol. However, much later, the mother liquor slowly deposited another 0.7 g. of m.p. 38-38.5° C. The total yield of quite pure ester was 40.6 g. (56.5%). Analytical data are given under Run No. 9.

Run No. 9:- In a 500 ml. three-necked flask, fitted with a mercury-sealed Hershberg stirrer and condenser with a calcium chloride tube, 0.15 mole (40.5 g.) of octadecanol was dissolved in 250 ml. of carbon disulfide with stirring. Several hours

were needed for complete solution at room temperature. Then O.15 mole (6.0 g.) of pulverized sodium hydroxide was added with stirring. Slight yellowing and the formation of a precipitate occurred almost immediately, and the heat of reaction was considerable. The mixture was allowed to stand for a day, after which time a heavy pale yellow precipitate of xanthate salt had formed. With stirring, 0.30 mole (18.68 ml.) of methyl iodide was added, with no apparent immediate effect. An hour later, a further 18.68 ml. of methyl iodide was added, and the mixture warmed very gently for a short time, then allowed to stand for two days. Reaction was apparently complete, resulting in a yellow solution over a white precipitate of sodium iodide.

Addition of an equal volume of ether promoted a far better settling of the precipitate, which was then removed by filtration and washed with ether. The filtrate and washings were concentrated nearly to dryness under reduced pressure at room temperature, and the residue dried in a vacuum desiccator. Weight 48.1 g. (89.1% crude yield) of pale yellow solid of m.p. 37.5-38° C., although a portion did not melt until 52° C., apparently because of contamination with octadecanol. The product was crystallized from 300 ml. of ethanol, taking four successive crops. The first, 22.1 g. of white flakes, melted at 37.5-38.5° C. A second crop, 10.0 g. of finer flakes, melted at 36-37° C., although it did not completely clear until 52-53° C. The third and fourth crops of 5.6 g. and 3.0 g. respectively were largely the starting octadecanol. The first

and second crops represented a 59.5% yield.

A sample of the purest material was recrystallized three more times from ethanol, finally melting at $38-39^{\circ}$ C. It was dried in a vacuum desiccator, and analyzed for carbon, hydrogen (122), and sulfur (Carius) (108). Calculated for $C_{20}H_{40}OS_2$: C 66.60; H 11.18; S 17.77%; mol. wt. 360. Found: C 66.49, 66.44, 66.54; H 11.00, 10.89, 11.00; S 17.91, 17.70, 17.65, 17.48%; mol. wt. (Rast) (122): 388, 352, 340, 378, 378, 342. Close estimates of molecular weight were also obtained from the saponification numbers, reported in a later section, which were multiplied by two.

Run No. 8:- Following a procedure nearly identical with that of Run No. 7, the xanthate salt was prepared from 0.08 mole (21.64 g.) of octadecanol. The salt was removed from its ether suspension by filtration, and dried in the open air overnight to give a crude yield of 27.3 g. (92.6%) of pale yellow crystals. The product was purified by the DeWitt and Roper method (23) (see pp. 7, 72), but about 2 g. did not dissolve in the acetone. The final white salt was dried in a vacuum desiccator over phosphorus pentoxide, activated charcoal, and paraffin wax. After three days, the white product weighed 19.1 g. (64.75% yield). Calculated for C19H370S2Na: S 17.40%. Found: S 15.42% (Bromine method), 15.04% (Carius method). In the bromine method, frequently used for the analysis of viscose (cf. p. 62), the salt was dissolved in 4% sodium hydroxide (although it gave a very turbid solution), treated with excess

bromine and warmed, acidified with hydrochloric acid, warmed to remove excess bromine, and finally treated with barium chloride according to the usual gravimetric procedure.

Since the xanthate salt, although white, was still obviously impure, it was crystallized from ethanol, although this solvent had given unsatisfactory results in Run No. 6. Warming to effect solution caused continual decomposition, as the clear solution rapidly became turbid. After a final filtration, the solution was rapidly cooled in the refrigerator and the resulting crystals removed by suction. These crystals were recrystallized at once by dissolving in excess acetone, filtering, and precipitating by adding about 10 volumes of pentane. After standing overnight, the white crystals were removed and dried in a vacuum desiccator. Calculated for C19H37OS2Na: S 17.40; Na 6.24%. Found: S 14.8, 14.9, 15.1% (Carius method); Na 4.74, 5.15%. The amount of sodium was determined by ashing samples with sulfuric acid and weighing as sodium sulfate (60). The analyses indicated a purity of 80 to 87%, assuming the impurity to contain neither sodium nor sulfur.

The xanthate groups were estimated by titration with iodine. The method of Whitmore and Lieber (118) was modified in several trial experiments, because the present salt was not completely soluble in water as the simpler xanthates were. Heating to aid solution caused some decomposition, as evidenced by the odor of mercaptan. The most satisfactory method was to dissolve the salt in a mixture of acetone and water at room

temperature, and to titrate with standard iodine solution, using a small layer of ether or carbon tetrachloride to reveal the iodine at the end point, as the blue color of starchiodine did not appear in the presence of acetone. In one titration, for example, 0.2426 g. of xanthate salt required 5.41 ml. of 0.104N iodine solution. Therefore the "iodine equivalent", according to Whitmore and Lieber (118), or mg. of iodine per g. of xanthate, was

5.41 $\times \frac{\text{mg. iodine per ml}}{\text{wt. of sample}} = \frac{5.41 \times 13.20}{0.2426} = 294.3$ Since the theoretical figure was 344.3, the purity was 85%. Another titration showed 88%. These values agreed with the 80-87% purity found by analyses for sulfur and sodium. It could be safely concluded that a considerable amount of impurity, perhaps octadecanol, was present in the salt. However, a sample was readily methylated with methyl iodide to give the xanthate ester, and similar material was used for the experiments with diazomethane reported later.

O-Hexadecyl S-Methyl Xanthate

This ester was prepared by the same methods used for the octadecyl analogue. Either ether or carbon disulfide could be used for the reaction medium, and the following procedure is an example of the latter method. In a 500 ml. three-necked flask, fitted with mercury-sealed stirrer and condenser, 0.15 mole (36.3 g.) of hexadecanol, previously recrystallized from petroleum ether, was dissolved in 200 ml. of reagent grade

carbon disulfide. The hexadecanol dissolved readily, in contrast to octadecanol. Then 0.15 mole (6.0 g.) of pulverized sodium hydroxide was quickly added, and washed down with 50 ml. of additional carbon disulfide. There appeared to be some reaction almost immediately and a considerable heat of reaction. In about 10 minutes, a heavy pale yellow gel had formed, in spite of continuous stirring. After standing overnight, 0.30 mole (42.58 g., 18.68 ml.) of methyl iodide was added in portions, with stirring. There was no apparent change after an Two hours later, an additional 0.30 mole of methyl hour. iodide was added. Continuous stirring did not completely break up the gel. After another day, however, the gel had disappeared and the mixture consisted of a pale yellow liquid over a white precipitate of sodium iodide, which was easily made to settle by the addition of an equal volume of ether. After filtration, the solution was evaporated under reduced pressure, and the resulting yellow liquid dried in a vacuum desiccator. Weight 50.2 g. (100.5% crude yield). After standing in the cold room for some time, this liquid solidified to a pale yellow solid of m.p. 24-25° C.

The product was twice crystallized from a large excess of ethanol, each time taking three or four successive crops. The yield of relatively pure white crystals was 40.0 g. (80%). A third crystallization from a great excess of ethanol gave 27.2 g. as a first crop, of m.p. 28-28.5° C. A small sample of this crop was again crystallized from ethanol, and dried

over phosphorus pentoxide in a vacuum desiccator in the cold room. Calculated for C₁₈H₃₆OS₂: C 64.82; H 10.91; S 19.28%. Found: C 64.70, 64.60, 64.94; H 10.59, 10.86, 11.02; S 19.97, 19.11%.

Attempted Preparation of O-Octyl S-Methyl Xanthate

This preparation followed the same procedure as Run No. 3 of the benzyl analogue, starting with 0.1 mole (13.02 g., 15.8 ml.) of octyl alcohol. There was difficulty with emulsions when separating the final ether layer. The ether was dried overnight with calcium sulfate and, after filtration, was evaporated under reduced pressure, to leave a yellow liquid which could not be induced to solidify, even after cooling with solid carbon dioxide. The later preparation of the hexadecyl ester as a very low-melting solid indicated that the octyl compound would be expected to be a liquid. The oil was purified by distillation at 20 mm. pressure, possibly an inadvisable procedure. A fairly large fore-run of colorless liquid was obtained at 55-70° C., but most came over as a pale yellow oil at 175-190° C. There was a considerable red-brown residue. The yellow oil could be solidified in a bath containing solid carbon dioxide, but liquefied on warming to the temperature of the refrigerator. There was no change on standing for two years. The oil was not definitely characterized, but was probably the desired ester.

Attempted Preparation of O-(3-Cyclohexylpropyl) S-Methyl Xanthate

A small run, starting with 0.01 mole (1.42 g.) of 3-cyclohexylpropanol-1 was carried out by a procedure similar to that used with hexahydrobenzyl alcohol. Reaction occurred readily, and the final liquid product was separated exactly as the octyl analogue, except that the distillation was omitted. The yellow oil could be solidified by drastic cooling, but liquefied in the refrigerator. An equal volume of ethanol was added, and from the solution crystals could be obtained by drastic cooling. These crystals dissolved, however, when warmed up to 0° C. in the refrigerator. Although this work was discontinued, the crystalline product could probably be obtained rather easily and would probably melt near room temperature.

Miscellaneous Experiments on Hexadecyl Alcohol

A peculiar behavior noted in the preparations of both the hexadecyl and octadecyl esters was that even very large amounts of ether would not dissolve the hexadecyl or octadecyl alcohol in the presence of powdered sodium hydroxide. Several test tube experiments were made on this phenomenon, but it remained unexplained.

Hexadecanol, 0.5 g., completely dissolved in a few seconds in 1.5 ml. of dry ether. These proportions did not result in complete solution in a xanthate run. Another 0.5 ml. of dry ether was added, and a very small amount of pulverized sodium hydroxide. After a minute or two, with occasional shaking, the amount of precipitate was much greater than could be accounted for by the sodium hydroxide alone, and was light and voluminous, probably hexadecanol.

When the procedure was reversed, and a small amount of pulverized sodium hydroxide was added to 2.5 ml. of dry ether, the precipitate remained unchanged and settled well, even after several minutes' shaking. Then 0.5 g. of hexadecanol was added, and about two minutes later the white voluminous precipitate appeared as before, and soon the tube contents had completely gelled.

When 0.5 ml. of carbon disulfide was added to each of these tubes, the contents thinned almost immediately, and the precipitate largely dissolved. Powdered potassium hydroxide had the same effect as sodium hydroxide in similar experiments.

In another experiment, 0.5 g. of hexadecanol was dissolved in 2.5 ml. of carbon disulfide, and a little powdered sodium hydroxide was added. After about two minutes, yellowing of the solution began and a heavy gelatinous precipitate, probably xanthate, began to appear. A few minutes later, the tube contents had completely gelled. Dilution with about three volumes of ether gave an easily filterable precipitate.

2. The Reaction of Xanthate Salts with Diazomethane The Reaction of Nitrosomethylurethane with Sodium Octadecyl Xanthate

For this and the succeeding experiment, the yellow-red nitrosomethylurethane was prepared by the action of nitrous

acid on ethyl N-methyl carbamate, following the method given in "Organic Syntheses" (123). The ethyl N-methyl carbamate originated from methylamine and ethyl chloroformate, as described in "Organic Syntheses" (124).

A clear solution of 1.0 g. (0.0027 mole) of sodium octadecyl xanthate in 100 ml. of absolute methanol was placed in a 500 ml. three-necked flask, fitted with mechanical stirrer, thermometer, and dropping funnel. The xanthate salt was that prepared in Run No. 8 (see p. 81) and was not completely pure, although the best available after several attempted purifications. A solution of 1.58 ml. (1.79 g., 0.0135 mole) of nitrosomethylurethane in about 20 ml. of absolute methanol was added dropwise over about 20 minutes to the stirred xanthate solution, which was kept at 3-5° C. by means of an ice-water bath. After about five minutes a white foamy precipitate had begun to appear on the surface of the solution, and increased in amount until the nitrosomethylurethane was all added. The mixture was stirred for 20 minutes longer, then allowed to stand for about two hours, after which time the temperature had risen to 15° C. The white solid was recovered by filtration on a Büchner funnel, washed with absolute methanol, and dried over phosphorus pentoxide in a vacuum desiccator. A second crop was obtained by evaporation of the filtrate at room temperature and reduced pressure to about 20 ml., filtration, washing with cold methanol, and drying. The filtrate from this operation was diluted with water to 250 ml., and filtered to remove a very small amount of yellow solid, which

was also dried. Fraction 1 weighed 0.5025 g., m.p. 36-38.5° C., and fraction 2, 0.3650 g., m.p. 36-38° C., although a trace did not melt below 100° C. Fraction 3, 0.0075 g., was yellow, and did not melt below 200° C., although there was a slight softening from 50° C. to about 100° C. Considering only the first two crops, the crude yield of octadecyl methyl xanthate (as it was later shown to be) was 0.8675 g. (89.3%), calculated on the assumption of a pure starting material.

The product was twice recrystallized from an excess of ethanol, after removing traces of a non-filterable turbidity by two treatments with absorbent carbon, and the resulting fine needles were dried in a desiccator. A second crop was obtained by evaporation to a smaller volume, and cooling. The first fraction, 0.30 g., melted at 37-38° C., the second, 0.15 g., at 36.5-37° C. The yield of relatively pure ester was 0.45 g. (46%, calculated on a pure starting material), and a mixed m.p. with an authentic sample of pure octadecyl methyl xanthate was not depressed. Analysis for sulfur (Carius) confirmed the identity of the product as octadecyl methyl xanthate. Calculated for $C_{20}H_{40}OS_2$: S 17.8%. Found: S 17.6, 17.9%.

The Reaction of Nitrosomethylurethane with Potassium Benzyl Xanthate

The potassium benzyl xanthate had been stored for about a year in a desiccator, but was purified before use by the DeWitt and Roper method (23), and dried in a vacuum desiccator over phosphorus pentoxide, activated charcoal, and paraffin wax.

Calculated for C₈H₇OS₂K: S 28.84%; "iodine equivalent" (according to Whitmore and Lieber, see p. 82) 570.8. Found: S 37.31, 37.40% (bromine method, cf. p. 81); "iodine equivalent" 722.5, 726.2, 735.9. Sulfur and iodine values of 26.6 to 29.5% over the calculated values indicated a large amount of decomposition. The nature of the impurity was unknown, although it could not have been the corresponding dixanthide, which did not react with iodine.

Following the same procedure as with sodium octadecyl xanthate, 2.31 ml. (2.61 g., 0.0225 mole) of nitrosomethylurethane in about 25 ml. of absolute methanol was allowed to react with 1.0 g. (0.0045 mole) of the above potassium benzyl xanthate dissolved in 100 ml. of absolute methanol. No solid product appeared at the surface, as in the case of the octadecyl compound. This difference might reasonably be expected, since benzyl methyl xanthate appeared to be more soluble in methanol than did the octadecyl ester. About 400 ml. of water was gradually added to the 125 ml. of solution in an attempt to precipitate the xanthate ester. A fine emulsion appeared, and the droplets resisted several attempts at crystallization. Resort was made to extractions with ether, and after evaporation of the ether (and methanol) in the extract, under reduced pressure, a small amount of yellow oil was This oil was dissolved in warm ethanol, the soluobtained. tion filtered, and cooled in the refrigerator. When seeded with a crystal of benzyl methyl xanthate, white crystals

were obtained in small amount, and were removed by filtration and dried over calcium chloride in a desiccator at a low temperature. A small second crop was obtained by concentration, cooling, and seeding of the mother liquor. Total yield: 0.077 g. (8.65%). M.p. 28-28.5° C. (recorded 29° C.) (9). The low yield might have been caused by a poor method of isolation, as well as by the impurity of the original salt.

3. Some Reactions of Xanthate Methyl Esters

Saponification of O-Benzyl S-Methyl Xanthate

Most of the saponifications were by a method adapted from a standard determination described by Shriner and Fuson (125). In a typical experiment (Table III, Run 1), a 0.2877 g. sample of the ester was heated with 10 ml. of 1.191N sodium hydroxide solution in 90% ethanol for one hour under reflux, and required 38.85 ml. of 0.225N hydrochloric acid for titration. The titrations had indistinct end points, as the red color of phenolphthalein developed again gradually, yet some of the saponification numbers approached the theoretical value of 99 quite closely. In all cases, a white precipitate or at least a turbidity was observed soon after the beginning of reaction and persisted throughout the titration.

The following saponification on a larger scale was for the purpose of recovering the benzyl alcohol. A sample of 5.963 g. of the ester was heated under reflux for 1.5 hr. with 75 ml. of 1.191N sodium hydroxide in 90% ethanol, after which the solid

(possibly sodium thiocarbonate) was removed, and the filtrate distilled to leave a yellow oil, which was extracted with ether, the extract dried over potassium carbonate, filtered, the ether evaporated, and the residue distilled. Most came over at 198-199° C. (uncorr.) (recorded b.p. for benzyl alcohol, 205° C.). Wt. of product 2.1627 g. (67%). The phenylurethane, m.p. 77° C., was prepared from a small sample of the product. (Recorded m.p. for the phenylurethane, 78° C.) (126).

TABLE III

Saponification of O-Benzyl S-Methyl Xanthate (a)

Reagent	Conditions	Saponification Number
10 ml. of 1.191N NaOH in 90% EtOH		
(1)	l hr. at reflux	91
(2)	11	100
(3)	u	84
15 ml. of 0.800N KOH in EtOH		
(4)	1.5 hr. at room temp., then 15 min. at reflux	101
(5)	· • • • • •	102
(6)	2 days at room temp.	102
(7)	6 hrs. at reflux	73

(a) Sample weights 0.2 to 0.3 g.

Saponification of O-Hexahydrobenzyl S-Methyl Xanthate

Two approximately 0.5 g. samples of the ester were heated under reflux with 15 ml. of 0.800N potassium hydroxide in ethanol, giving saponification equivalents of 95 and 116, whereas the calculated value was 102. Two samples, 0.3008 g. and 0.4703 g. were heated under reflux for one hour with 5 ml. and 10 ml. respectively of 1.191N sodium hydroxide in 90% ethanol, giving values of 104 and 93. The second of these mixtures, after standing for several months after the titration, required a large amount of additional acid to neutralize the solution, indicating a "saponification number", under these unusual circumstances, of 206. In these cases also, end points were indistinct because of the redevelopment of color.

Saponification of O-Menthyl S-Methyl Xanthate

A 0.2065 g. sample of ester was heated under reflux for one hour, perhaps not long enough, with 5 ml. of 1.173N sodium hydroxide in 90% ethanol, giving a "saponification equivalent" of 96, whereas the calculated value was 123. The end point was indistinct, and, after standing for two weeks after the titration, additional acid brought the value to 124. This correct result was probably merely coincidental, as longer standing would probably have made it still higher. In two additional saponifications, 76% and 63% of somewhat crude menthol were recovered from the reaction mixtures by a method similar to that used for benzyl alcohol.

Saponification of O-Hexadecyl S-Methyl Xanthate

A 0.1144 g. sample was heated under reflux for 0.75 hours, and allowed to stand for 1.5 hours, with 5 ml. of 0.800 N potassium hydroxide in ethanol, giving a "saponification equivalent" of 195, whereas the calculated value was 166. The great disparity was perhaps caused chiefly by the use of too small a sample of the high molecular weight ester, as only a small quantity was available when this early experiment was done. Moreover, this early sample was probably not completely pure.

Saponification of O-Octadecyl S-Methyl Xanthate

Table IV gives the results of a series of saponifications carried out on 0.19-0.32 g. samples of the ester, using freshly prepared alkali solutions and restandardized hydrochloric acid for the titrations. In experiment (1) for example, a 0.1920 g. sample of the ester was heated for an hour under reflux with 5 ml. of 1.191N sodium hydroxide in 90% ethanol, and required 21.64 ml. of 0.225N hydrochloric acid for titration. The expected value of 180 was reached quite closely with one hour's heating, but only partial hydrolysis occurred in 30 minutes. The end points with phenolphthalein were reasonably distinct.

It was not definitely known why so much sodium hydroxide appeared to be consumed in Runs No. 10 and No. 17. Perhaps there was reaction with liberated methanethiol, which might not have been driven off as thoroughly as in runs carried out

TABLE IV

Saponification:	of Octadecyl Methyl	Xanthate(a)	
Reagent(b)	"Sa	ponification	Per Cent
	Conditions	Number"	Cleavage
5 ml. of 1N NaOH			
(1)	hr. at reflux	177.	101.8
(2)	hr. "	182.	99.0
(3) 15	min. "	262.	68.8
10 ml. of 1N NaOH			
$ \begin{array}{cccc} (4) & & & \\ (5) & & 30 \\ (6) & & 30 \\ (7) & & 15 \\ (8) & & & \\ (9) & & 48 \\ (10) & & & & \\ \end{array} $	hr. at reflux	180.5	99.7
	min. "	194.7	92.5
	min. "	201.6	89.3
	min. "	244.3	73.7
	hr. at room temp.	903.	19.9
	hrs. "	228.1	78.9
	week "	111.4	161.
50 ml. of O.lN NaOH			
	hr. at reflux	181.5	99.2
	hr. "	182.7	98.5
	min. "	195.4	92.1
	imin. "	261.9	68.7
	hr. at room temp.	4417.	4.1
	hrs. "	240.1	75.0
	week "	102.7	175.

(a) Sample weights 0.19-0.32 g.

(b) The precise normalities of the sodium hydroxide solutions in 90% ethanol were 1.191 in Runs 1-3, 1.163 in Runs 4-10, 0.0871 in Runs 11 and 13, 0.0952 in Runs 12 and 14, 0.1076 in Runs 15 and 17, and 0.1012 in Run 16. In all cases the effective normality during saponification was slightly less, as a little ethanol was used to rinse the neck of the flask. at reflux temperature.

The white precipitate which persisted throughout the titration was recovered from Runs No. 1 and No. 2, recrystallized, and shown by its m.p. to be octadecanol. In an additional saponification to check the recovery of octadecanol, a sample was heated under reflux for one hour, the mixture was evaporated to dryness, extracted with boiling absolute ether for 30 minutes, and finally evaporated to a white solid. Weight 0.1678 g. (97%), m.p. 55-57° C. The phenylurethane of octadecanol was prepared from the product, and melted at 79.5-80° C. (recorded m.p. 79.5°) (127). In still another saponification, a 96.48% recovery of octadecanol was obtained by the same method. In this case, the product was recrystallized from petroleum ether, using absorbent carbon, to give 0.169 g. (72.1%) of pure white flakes.

Stability of the Octadecyl Ester in Aqueous 25% Sodium Hydroxide

A sample of the ester was heated under reflux for two hours with 30 ml. of 25% aqueous sodium hydroxide. The ester was insoluble in the aqueous solution and hydrolysis was very slight. Towards the end, the mixture became slightly yellow and there was a slight odor of mercaptan from the condenser. The ester was recovered, with correct m.p., in about 99% yield by extraction three times with ether and evaporation of the extract to dryness. The stability in aqueous alkali agreed with the work of McAlpine (30) on the menthyl analogue.
Stability of the Octadecyl Ester to Aqueous-Alcoholic Ammonia

A solution approximately 1N in ammonia was prepared by diluting 10 ml. of approximately 15 N aqueous ammonia to 150 ml. with ethanol. A 0.289 g. sample of the octadecyl ester was mixed with 15 ml. of this solution, and allowed to stand open to the air at room temperature, with occasional stirring, for nearly a week, when the liquid had completely evaporated. The ester did not go into solution appreciably at any time, and over 99% recovery was effected in the usual manner.

Stability of the Octadecyl Ester to Pyridine

A sample, 0.3085 g., of the ester was heated under reflux with 10 ml. of analytical reagent pyridine for one hour, then 30 ml. of dry ether was added after cooling, and the next day a small amount of a dark gum (soluble in benzene) was removed. The very dark filtrate was completely decolorized by two treatments with absorbent carbon. After evaporation at room temperature, the small amount of residual amorphous white solid melted at 43-48° C. after crystallization from ethanol. This substance was probably not octadecanol, of m.p. 60° C., and was not examined further. It was obvious that the ester was decomposed in boiling pyridine.

In another experiment, 0.2937 g. of the ester was dissolved in 15 ml. of pyridine and allowed to stand at room temperature for a week. After the first day, a slight yellowing of the solution was observed, but never any extensive

darkening. The pyridine was removed by evaporation under reduced pressure at room temperature, the product taken up in ether, filtered to get rid of a considerable turbidity, and slowly evaporated. Weight of crude product, 0.2712 g., recrystallized from ethanol to give 0.221 g. of m.p. 36.5-37.5° C. (M.p. of authentic ester, 38-39° C.) Under these conditions, the ester was, for the most part, unchanged.

Stability of the Octadecyl Ester in Aqueous 6N Hydrochloric Acid

A small sample of the ester was heated under reflux with 25 ml. of 0.225N aqueous hydrochloric acid for 20 minutes. As no obvious change occurred, sufficient strong hydrochloric acid was added to bring the concentration to approximately 6N. After three hours under reflux the ester still floated on the surface as an oil, and was recovered nearly quantitatively, with the correct m.p. Hydrolysis was therefore inappreciable.

Stability of the Octadecyl Ester in 1N Aqueous-Alcoholic Hydrochloric Acid

With cooling, 2 ml. of 12N aqueous hydrochloric acid was diluted to 24 ml. with ethanol, and a small sample of the ester was heated under reflux for one hour with 15 ml. of this solution, in which it became soluble. No odor of mercaptan was observed. The mixture was evaporated under reduced pressure, the residue taken up in ether, filtered, and evaporated. The weight of dried product showed a 97% recovery of slightly impure ester. Fart of this yield was recrystallized to give a purer ester of m.p. 37-38° C.

Stability of Octadecyl Methyl Xanthate in 43% Hydrochloric Acid at 0° C.

Concentrated hydrochloric acid was saturated at 0° C. with hydrochloric acid gas, and titration of a weighed sample, using special techniques to avoid loss of acid, showed 43.27% of hydrogen chloride.

A sample of the xanthate ester, 0.3007 g., was added to 25 ml. of the 43% acid at 0° in a 100 ml. glass-stoppered flask, and kept for 24 hours in the refrigerator at 0° C. The ester remained undissolved, in spite of vigorous shaking on several occasions. The mixture was finally diluted with an equal volume of water, was extracted three times with ether, and the extract allowed to evaporate at room temperature. After drying in a desiccator, the solid residue weighed 0.3082 g. (102% recovery, crude). Recrystallization from ethanol gave three crops whose total weight was 0.2353 g. (78.5%). Each melted at 37-37.5° C., and was the reasonably pure ester.

In an earlier less satisfactory similar experiment, the mixture was diluted as before and most of the water and acid were removed by simple distillation. The solid residue in the flask weighed 0.0984 g. and the solid which distilled with the steam, 0.0879 g., after drying. Each fraction was separately crystallized from ethanol, each time taking two crops. Melting points showed all these to be nearly pure octadecyl methyl xanthate, recovered in a total crude yield of 61%. It was later confirmed in separate experiments that both octadecanol

and octadecyl methyl xanthate were slightly volatile in steam, the ester apparently more so than the alcohol.

Stability of Octadecyl Methyl Xanthate when Heated in a Sealed Tube with 3% Methanolic Hydrogen Chloride

Hydrogen chloride gas was passed into absolute methanol until the gain in weight indicated that the desired concentration had been reached. Analysis showed 3.22% hydrogen chloride.

(a) In a preliminary experiment, a sample of 0.3061 g. of the ester was warmed under gentle reflux with 50 ml. of the reagent, this amount being necessary to dissolve the ester. The top of the condenser was fitted with a calcium chloride tube. After 30 minutes, with the calcium chloride tube momentarily removed, a trace of mercaptan could be detected, both by odor and by the yellow coloration imparted to lead acetate paper. After heating for 72 hours, the odor was still present. The mixture was then cooled, the crystals which separated were removed by filtration, washed with absolute methanol, and dried in a vacuum desiccator. A second crop was obtained from the filtrate by concentration and cooling. Both crops melted at 38-38.5° C. and represented a recovery of over 90% of the original ester. In a duplicate experiment the recovery was 93.5%.

(b) In a sealed tube experiment, 0.1 g. of the ester and 10 ml. of 3.2% hydrogen chloride in methanol were heated in a tube of approximately 20 ml. capacity in the small furnace

used for Carius tubes. After three days at 120° C., the tube was cooled and opened. A slight gas pressure and odor of mercaptan indicated that some decomposition had occurred. Most of the solid product had crystallized. When being transferred to a flask, the supersaturated solution suddenly evolved a considerable amount of gas, causing some loss of solid material at the same time. The mixture was cooled and filtered, and the resulting crystals dried in a vacuum desiccator. Weight 0.0335 g., m.p. 36-36.6° C. A second crop of 0.0050 g. was obtained by dilution with water. The total yield of 0.0385 g. was only a 38.5% recovery, but the melting point showed that no considerable amount of octadecanol was present.

(c) In another sealed tube experiment, 0.2 g. of ester and 10 ml. of the acid reagent were heated at 125° C. for three days as before, then the still colorless solution was heated at 140° C. for two days, and finally at 160° C. for 33 hours. These times corresponded to those used with a cellulose xanthate methyl ester run carried out at the same time. On cooling and opening, much of the contents was again lost because of vigorous gas evolution. The remainder was diluted with water, cooled, filtered, and the resulting solid dried and crystallized from pentane, to melt at 59-60° C. (recorded for octadecanol, 60° C.). It was clear that the ester had decomposed under these conditions. Action of Silver Nitrate on Octadecyl Methyl Xanthate

A solution of 0.00125 mole (0.4518 g.) of the ester in 10 ml. of ether was added to a mixture of about 2.0 g. of powdered silver nitrate and ether. A white precipitate appeared at once, which slowly darkened after about two hours, gradually becoming black. After standing for a week, the precipitate was removed and the ether evaporated. The weight of the crude product, 0.3989 g. of yellow oil, was more than could be accounted for by octadecanol alone. An odor of nitric acid was also noticeable. The crude oil was warmed with a little water, which then turned litmus paper red. Addition of 1 ml. of 5% sodium hydroxide, followed by ether extractions and evaporation of the ether, again gave a yellow liquid which largely solidified on cooling, and weighed 0.2966 g. after drying in a vacuum desiccator. After repeated crystallizations from ethanol, the product remained a white gum, melting at 29-32° C. The product was neither octadecanol nor the starting ester, but was not examined further.

Action of Silver Oxide on Octadecyl Methyl Xanthate

A 0.002 mole (0.7207 g.) sample of the ester in 20 ml. of absolute ethanol, in a 100 ml. flask, was treated with 0.02 mole (4.64 g., a large excess) of silver oxide, in portions, at room temperature. The mixture was then heated under gentle reflux for two hours, during which time a slight mirror formed on the walls of the flask, probably indicating

that a certain amount of oxidation had occurred. The product was filtered through sintered glass, and the residue on the filter washed with ethanol. The residue liberated hydrogen sulfide when treated with hydrochloric acid. The colorless filtrate was concentrated under reduced pressure to a nearly white solid, which was dissolved in ether and the solution filtered to remove a small amount of brown solid, again evaporated to dryness, and dried in a vacuum desiccator. The weight of 0.6278 g. was slightly more than could be accounted for by octadecanol alone. After recrystallization from ethanol, the m.p. was 37-42°, and a second recrystallization, followed by drying, gave a m.p. of 47-51° C. The obviously impure product gave no test for sulfur when the product of sodium fusion was tested with sodium nitroprusside solution. Moreover, a small sample gave no mercaptan odor when boiled with alcoholic sodium hydroxide, as did an authentic sample of the xanthate ester. A recrystallization from petroleum ether gave waxy leaflets of m.p. 52-55° C. From a sample of this, the phenylure thane of octade canol was prepared, m.p. 78-79° C. (recorded 79.5° C.) (127), although the amount was too small to calculate a satisfactory yield. Octadecanol was at least a major constituent of the product.

In a second experiment, a 0.01 mole (3.60 g.) sample of octadecyl methyl xanthate was dissolved in 125 ml. of absolute ethanol in a three-necked 250 ml. flask, fitted with a reflux condenser and glycerol-sealed stirrer. In portions,

0.05 mole (11.59 g.) of silver oxide was added to the mixture at just over room temperature, to keep the ester in solution. An hour under gentle reflux caused the formation of a slight mirror. The product was isolated as before, and again the weight of 3.1 g. was slightly more than could be accounted for by octadecanol alone. Recrystallization from low-boiling petroleum ether, 20 ml., gave well-formed leaflets, 0.92 g. (34% yield, if considered all octadecanol) of m.p. 57-58° C. after washing with petroleum ether and drying. A small second crop was obtained by concentration and cooling. The first crop was again crystallized from petroleum ether, to give a 0.7475 g. fraction of m.p. 57.5-60° C., and the filtrate was used to dissolve crop 2 for a further crystallization, which gave a 0.1080 g. fraction of m.p. 54.5-56.5° C. From the filtrate there was obtained a third crop of 0.1146 g., m.p. 48-52.5° C., and a fourth crop, very waxy, of 0.3602 g. and m.p. 35-38° C. Evaporation of the final filtrate gave a very low-melting solid residue of 0.2357 g. The total weight of product was 1.5660 g.

From 0.7 g. (about 0.0026 mole) of crop No. 1, 0.797 g. (79% yield) of the phenylurethane of octadecanol was prepared, melting at 78.5-79° C. (recorded 79.5° C.) (127), proving that crop No. 1, at least, was predominantly octadecanol.

Crops No. 2 and No. 3 were again recrystallized from petroleum ether, giving 0.0762 g. of m.p. 56.5-58° C. and 0.0382 g. of m.p. 55.5-57° respectively. Therefore at least 0.8619 g. (31.9%) of octadecanol was obtained. Probably more

satisfactory purification would show a higher yield.

The yellow waxy residue (0.2357 g.) was "crystallized" from methanol-ether to give a soft waxy white solid of m.p. 33-34° C., with some preliminary softening. This solid was similar in appearance and melting point to the low-melting material from the Raney nickel experiments (see below), but was not examined further.

Action of Silver Carbonate on Octadecyl Methyl Xanthate

The procedure was nearly identical with the second silver oxide run, and slight mirror formation was similarly observed. From 0.01 mole (3.60 g.) of the xanthate ester there were finally obtained, by recrystallization from petroleum ether, a first fraction of 0.3450 g., m.p. 56-59.5° C., a second of 0.2888 g., m.p. 35-40° C., a low-melting waxy pale yellow third fraction of 0.2790 g., and a similar residue of 0.1521 g. The yield of pure octadecanol was lower than in the silver oxide run, possibly owing to losses during treatment with absorbent carbon. The yellow residue was "crystallized" from methanol-ether to give a white waxy solid of m.p. 33-35° C., as in the silver oxide run.

In another test tube experiment, a solution of a small sample of the ester in ether was treated with a little silver carbonate. There was no darkening after standing for several hours at room temperature, and after a day there was only a very slight darkening. The salt obviously caused only very slight de-xanthation at room temperature.

Stability of the Octadecyl Ester to Mercuric Acetate

Two grams of mercuric acetate was dissolved in 50 ml. of ethanol by heating, and the filtered solution was added to a solution of 0.3969 g. (0.0011 mole) of the octadecyl ester in 15 ml. of ethanol. The mixture was shaken and allowed to stand. At once a heavy white precipitate formed. After nine days, this precipitate was recovered on a filter, and the filtrate was evaporated to a small volume at room temperature. Some more solid separated, and the remaining liquid was acid to litmus (probably acetic acid). The evaporation was continued over a steam bath, but this treatment was apparently too drastic, as a yellow solid began to separate (unidentified, but not elementary sulfur). After cooling the flask, the entire mixture solidified and was taken up in ether. The clear, filtered ether solution was then evaporated, but this procedure had hardly begun when yellow solid again began to separate on the sides of the tube. The evaporation was halted, and next day the liquid was decanted, and finally evaporated to give a nearly white solid, 0.3 g., after drying, m.p. 32.5-37° C., with a trace not melting even at 60° C. Crystallization from ethanol, with a treatment with absorbent carbon, left the m.p. at 34-35° C., with slight softening beginning at 32° C. The substance was not identified, but it might have been largely the original ester.

Stability of the Octadecyl Ester to Cadmium Carbonate

In a small qualitative test, an ether solution of the ester was treated with cadmium carbonate at room temperature. The white solid in the tube was probably only cadmium carbonate, as no yellow cadmium sulfide was observed, even after two weeks. After filtration, the filtrate was evaporated to a white solid of m.p. 38-38.5° C. The ester was therefore recovered unchanged.

Action of Thallous Ethylate on Octadecyl Methyl Xanthate

The normality of a solution of thallous ethylate in benzene, kindly provided by Dr. D. F. Manchester, was determined as 0.096, 0.094N by pipetting a known volume into a mixture of methanol and standard hydrochloric acid, the excess of which was titrated with standard sodium hydroxide (cf. 93).

In a preliminary test tube experiment, a little ester was added to a few ml. of the thallous ethylate solution. Within a few minutes, there was a heavy black precipitate, probably of the blue-black thallous sulfide, Tl₂S, or the black thallic sulfide, Tl₂S₃.

In the first quantitative experiment, 0.000848 mole (0.3054 g.) of the ester was added to 25 ml. of the cold (5-10° C.) thallous ethylate solution. Within a few seconds, the solution became yellow and turbid, and after a few minutes was deep brown. After 70 minutes, when the mixture was black, 50 ml. of 0.0987N hydrochloric acid, followed by about 20 ml. of methanol, was added to react with any remaining thallous ethylate. The excess acid was then titrated with 0.1119N sodium hydroxide, using phenolphthalein as indicator. It was calculated that 0.000629 moles of thallous ethylate had reacted with the 0.000848 moles of ester. As at least two, and perhaps four, moles of thallous ethylate would be expected to react with each mole of ester, the reaction was far from complete.

In a second experiment, 0.000831 mole (0.2993 g.) of the xanthate ester was dissolved in 25 ml. of the thallous ethylate solution and allowed to stand for 12 hours in the dark. The black mixture was then treated as in the first experiment. Titration was difficult and somewhat inaccurate, because of turbidity and some liberation of hydrogen sulfide. It appeared that 0.001625 mole of thallous ethylate had reacted with the 0.000831 mole of ester. If two moles of the ethylate were equivalent to one of ester, then the reaction was nearly quantitative (97.8%). A control experiment, similar in all respects to this one, but without the ester, showed that no thallous ethylate was used up.

A third experiment was done for the purpose of isolating the reaction product. This time 0.00169 mole (0.6076 g.) of ester was allowed to stand for 12 hours, in the dark, in 50 ml. of the thallous ethylate solution. The mixture was filtered on coarse sintered glass, and the precipitate was washed with ether. When treated with a drop of dilute hydrochloric acid, the precipitate gave a vigorous evolution of hydrogen sulfide, and was probably a sulfide of thallium. The filtrate was clear and nearly colorless, but acquired a white turbidity on standing a few minutes. Evaporation under reduced pressure gave a dirty yellow solid, which was taken up in ether and filtered to give a clear solution. After evaporation of the ether, the resulting solid was dried in a desiccator. The crude product, 0.6404 g. (106%), dirty-white and with an unpleasant odor, was recrystallized from an excess of pentane to give white leaflets having the appearance of octadecanol and melting at 56-57.5° C. (recorded for octadecanol, 60° C.). The phenylurethane melted at 78-78.5° (recorded for the phenylurethane of octadecanol, 79.5° C.) (127).

Experiments with Raney Nickel

The Raney nickel was prepared according to a standard method (128) which gave the "W-2" catalyst. The product was carefully washed free of alkali, and was kept under absolute ethanol, as it was strongly pyrophoric.

As a preliminary experiment to gain practice in handling the reagent, its action on diphenylthiourea was examined. The formation of N,N-diphenylformamidine by this method is mentioned in the literature (129), although the procedure was somewhat less drastic than used here.



In the present case, 5 g. (0.0218 mole) of diphenylthiourea

in 20 ml. of ethyl acetate and about 20 g. of Raney nickel, wet with ethanol, were heated together under gentle reflux for four hours. Evolution of hydrogen gas began immediately on mixing the reagents. No hydrogen sulfide was detected, but a little later an odor resembling that of formaldehyde was observed. The still pyrophoric nickel was removed by filtration on coarse sintered glass, and a small sample of it liberated hydrogen sulfide when treated with dilute hydrochloric acid. The filtrate was evaporated under reduced pressure to a slightly yellow solid, which was recrystallized from ethanolwater, using a treatment with absorbent carbon. When dry, the product (white needles) weighed 0.5 g. (about 12%), of m.p. 138-138.5° C. (recorded for N,N-diphenylformamidine, 136° C). The low yield was probably caused by the drastic reaction conditions, perhaps also to adsorption on the nickel or carbon.

Action of Raney Nickel on Octadecyl Methyl Xanthate

In connection with the following experiments it became necessary to find a good solvent for the crystallization and recovery of octadecanol. As shown in Table V, low-boiling petroleum ether appeared to be most satisfactory, in spite of the fairly large solubility of octadecanol in this solvent, and therefore subsequent crystallizations of octadecanol were done from petroleum ether or pentane.

TABLE V

Solvent	Approximate Solubility in mg. per ml.	Nature of Crystals Obtained on Slow Cooling		
Petroleum ether 30-50°	C. 12.5	Well-formed leaflets		
Benzene	38.5	Good		
Acetone	22	Good		
Ethanol	17	Small, poorly formed		
Me than ol	7	Small, poorly formed		
Ethanol-water, 3:1	2	Small, good only from concentrated solution		

Crystallization of Octadecanol(a)

(a) Procedure according to Cheronis and Entrikin (130).

Of the seven experiments carried out with Raney nickel under slightly varying conditions, three are reported below in some detail as representative.

<u>Run No. 3:- A 0.02 mole (7.2 g.) sample of the ester was</u> mixed with about 40-50 g. of Raney nickel, wet with ethanol, in a 250 ml. flask, together with enough absolute ethanol to bring the volume to 150 ml. The mixture was heated for four hours under reflux. For at least an hour an unidentified unpleasant odor was observed at the top of the condenser. This odor was not that of hydrogen sulfide, but lead acetate paper was turned a bright yellow, probably owing to mercaptan. The separation of a white solid during filtration through sintered glass, and as the alcohol cooled, was prevented by the addition of a small amount of ether. The residual nickel, still pyrophoric, was kept wet with solvent at all times, and was twice washed with slightly warm ethanol to prevent excessive adsorption of product. Nevertheless, a considerable amount probably remained adsorbed. The nickel residue was finally destroyed by nitric acid.

The filtrate, from which a white solid was beginning to separate, was distilled from a steam bath to remove ether and ethanol. The crude residue was dried, dissolved in ether and the solution filtered to remove a trace of nickel; the solution was again evaporated to dryness, and the residue dried in a vacuum desiccator, to a weight of 5.4 g. (98.7%, if this amount were entirely octadecanol). Recrystallization from petroleum ether, including a decolorizing treatment with absorbent carbon, yielded a first crop of 2.096 g., m.p. 53-55.5° C., a second crop of 0.133 g., m.p. 37-45° C., a third crop of 0.118 g., m.p. 33-37° C., and a fourth crop of 0.010 g., m.p. 33-35° C. Evaporation of the final filtrate gave a solid residue of 1.968 g., m.p. 28.5-30° C. The total recovery of 4.325 g. was only an 80% recovery of the crude product, although manipulative losses were seemingly not large. If crop No. 1 were considered octadecanol, it would be a 39% yield. This fraction was again crystallized to give two crops of material. The first of these, 1.5916 g., m.p. 57.5-59° C., was reasonably pure octadecanol and represented a 29.5% yield from the ester. The second crop of 0.1847 g. melted at 53-54° C.

The 1.968 g. of low-melting residue (m.p. 28.5-30° C.) was "crystallized" from methanol-ether to give a first fraction of 0.7423 g., m.p. 28-30° C., a second of 0.3328 g., m.p. 28-30.5° C., and a third of 0.1139 g., m.p. 28-30.5° C. The three crops were all white and had crystalline structures, although not well formed. A sample of the first fraction was tested qualitatively for the methoxyl group by the Tobie (131) technique, which was essentially a test tube modification of the Zeisel reaction, the liberated methyl iodide finally forming the colored mercuric iodide. This sensitive test was definitely positive whereas blanks were negative. Quantitative methoxyl estimations were then carried out by the usual method. Calculated for octadecyl methyl ether, C18H37OCH3: -OCH3 10.91%. Found: 3.46, 4.04%. It was clear that only a fraction of the material was the ether. The remainder of the first fraction was again "crystallized" from methanol-ether, and dried in a desiccator for a week, after which it melted at 29.5-31.5° C. Found: -OCH3 2.63, 2.60%. Similar low-melting material from later runs contained a small amount of sulfur (see below).

Run No. 5:- A 0.01 mole (3.6 g.) sample of the octadecyl ester and 20 to 30 g. of Raney nickel, wet with ethanol, were mixed in a 500 ml. flask, and enough ethanol was added to give a total volume of about 300 ml. This amount of ethanol was necessary to dissolve the ester without heating. After standing for four hours, the nickel was removed as before, and the filtrate and washings were concentrated at a low temperature and reduced pressure to near dryness, and the residue dried in a vacuum desiccator, to give 1.8358 g. of a white waxy solid melting at 42-47° C. Recrystallization from 40 ml. of pentane gave a first crop of 0.3807 g. of white flakes, m.p. 58-59° C., a second crop of 0.1513 g. of white flakes, m.p. 57.5-59° C., a third crop, 0.0743 g., of small white flakes, m.p. 48.5-52° C., and a residue on evaporation of 0.9370 g., m.p. 29-31.5° C. About 60% of the total of 1.5433 g. was lowmelting material, while nearly all the remainder was octadecanol.

Run No. 7:- A 0.01 mole (3.6 g.) sample of the ester was mixed at 9° to 10° C. with 20 to 30 g. of Raney nickel, wet with dioxane, and dioxane added to give a total volume of about 250 ml. The mixture stood in a flask, with frequent shaking, for 10 minutes, the stopper being loosened frequently, as a slight pressure was built up. After the nickel was removed by filtration and washed with dioxane, most of the solvent was removed by vacuum distillation and the residue was dried in a desiccator. The dioxane clung tenaciously, and several days of continuous evacuation were necessary to remove it. The semi-solid residue of about 2 g. was recrystallized from pentane, with cooling in the cold room, to give a first crop of 0.200 g., m.p. 49-57° C., and a negligible second crop of 0.007 g. The residue after evaporation and drying weighed 1.3530 g., and was semi-solid at room temperature (27-28° C.). Recrystallization of the first crop from pentane gave 0.0900 g. of flakes melting at 57.5-58.5° C., obviously octadecanol, as a first crop. The low-melting

residue was recrystallized from ethanol to give a first crop of 0.6140 g., m.p. 34-36° C., and a second crop of 0.1730 g., m.p. 29-29.8° C. This first crop was again crystallized from ethanol to give 0.4865 g. of m.p. 36-37.5° C., probably the original ester, as heating a sample with alcoholic sodium hydroxide liberated a mercaptan, detected by its odor and by the yellow color it gave to lead acetate paper. Of the recovered material, then, approximately one-fifth was octadecanol, one-fifth was low-melting material, and three-fifths was the original ester.

The low-melting material from runs 4, 5, 6, and 7 was combined and twice "crystallized" from methanol, giving a white waxy solid of m.p. 29.5-30° C., which gave a heavy test for sulfur, using the sodium fusion technique followed by sodium nitroprusside solution. A sample was again "crystallized" from methanol, giving a m.p. of 29.5-29.8° C. This product gave a negative isatin test for a mercaptan (132) and did not dissolve in 5% sodium hydroxide, even on heating. A sodium hydroxide fusion test for oxidized sulfur (133) was doubtful, probably negative. Analysis for sulfur (Carius) on another sample of the same material showed 2.1, 2.4, 2.3%. The product was probably a mixture.

Stability of Octadecyl Methyl Xanthate under Acetylating Conditions

In a small test tube, 0.5 g. of the ester was mixed with 2.5 g. of acetic anhydride and 0.025 g. of anhydrous zinc

chloride. The mixture was shaken thoroughly, stoppered, and allowed to stand for 24 hours. The ester had not dissolved. The mixture was poured onto ice, but no solid appeared other than the original ester, which was removed by filtration, washed with water, and dried in a vacuum desiccator. Weight 0.4836 g. (96.7% recovery), m.p. 37.5-38.5° C.

Action of Heat on Octadecyl Methyl Xanthate

Five grams of the ester was heated in a small pearshaped Claisen flask, using a sand bath and a small free flame. A thermometer inserted directly into the ester showed that the latter melted to a pale yellow liquid at 38° C. The temperature was slowly increased to 180-190° C., when a vigorous reaction occurred and the temperature went up to about 290° C. Although heating up to 315° C. was continued for a short time, only a few drops of distillate were obtained, but the odor of mercaptan was pronounced. After cooling to room temperature, the product in the distilling flask consisted of a white solid and a pale yellow liquid, in about equal amounts. Both dissolved in ether, but a detailed examination was not carried out.

4. Oxidation and Reduction of Xanthate Methyl Esters

Oxidation of Octadecyl Methyl Xanthate with Hydrogen Peroxide

The procedure given below (Run No. 3) was representative of the four experiments carried out.

Seven grams (0.01944 mole) of the xanthate ester was dissolved in 900 ml. of glacial acetic acid, an amount necessary to prevent precipitation of the ester when the hydrogen peroxide was added. Then 11.34 ml. of 30% hydrogen peroxide (12.46 g., containing approximately 3.76 g. of H202, 0.1167 mole) was added all at once, and mixed well with the solution. There was no immediate apparent effect, but after 1.5 hours the clear solution had begun to precipitate a white solid. After three days at room temperature, the mixture was diluted with an equal volume of water, which increased the volume of precipitate. After standing for a few hours in the cold room, the solid was removed by filtration under suction. Filtration was slow, as the somewhat waxy solid partially clogged the paper, which had to be replaced two or three The white solid was dried in a vacuum desiccator. times. Crude yield, 6.0996 g., calculated as 76.9%. M.p. 49-52.5° C.

This product was recrystallized from ethanol to give 3.7746 g. (47.5%) of relatively pure product, in two crops. The first crop (3.1803 g.) was then recrystallized twice from pentane to give a pure product of m.p. 66-66.2° C. (2.2395 g., 33.5%) and four times more to give a m.p. of $66.2-67^{\circ}$ C. which could not be increased. The white flakes gave a copious test for sulfur, using the sodium fusion technique and both lead acetate and sodium nitroprusside solutions. The sodium hydroxide fusion test for oxidized sulfur (133), which depended on the color change of nickelous hydroxide caused by liberated sulfur dioxide, appeared to be positive, although somewhat doubtful as even a blank gave a slight positive result. Found: C 58.62, 58.59; H 10.11, 9.80, 9.71; S 15.51, 15.69, 15.55, 15.53%; Mol. wt. (Rast) 395, 420, 420, 426. Calculated for $C_{20}H_{40}O_4S_2$: C 58.78; H 9.87; S 15.69%; Mol. wt. 408.

Examination of the Oxidation Product $C_{20}H_{40}O_4S_2$

In an attempt to saponify the compound, 1.0 g. was heated with 30 ml. of 25% sodium hydroxide under reflux for about seven hours, when there appeared to be no further change. The solid first melted, then partly solidified again and turned yellow. Finally the solution was yellow, and the substance floating on the surface had again liquefied. There was a slight unpleasant odor from the top of the condenser. The oily liquid was then steam-distilled although it was only slightly volatile. The distillate was filtered, and the white waxy solid was dried and identified as octadecanol by its m.p., 59.5-61.5° C., and that of its phenylurethane, m.p. 78.5-80° C. (recorded 79.5° C.) (127). The residue in the distilling flask was filtered, and a small sample of the resulting clear yellow solution gave a heavy black precipitate with lead acetate solution. Therefore there was liberation of hydrogen

sulfide during the saponification, and at least one sulfur atom of the compound $C_{20}H_{40}O_4S_2$ was still in the reduced state. Acidification of another sample produced a strong odor of hydrogen sulfide. Testing for sulfate with barium chloride, after acidification, gave a negative result.

A sample of the compound $C_{20}H_{40}O_4S_2$, when boiled for 10 minutes with concentrated hydrochloric acid, melted but did not dissolve. There was no apparent decomposition. The compound was recovered by cooling and filtration, to melt at 66-67° C., with slight softening at 63° C.

Another small sample, when warmed briefly with 5% sodium hydroxide, melted but did not turn yellow, as with the more concentrated alkali. On cooling, the sample solidified to a white waxy solid.

Oxidation of Hexadecyl Methyl Xanthate with Hydrogen Peroxide

Following the procedure used with the octadecyl ester, 0.04 mole (13.28 g.) of hexadecyl methyl xanthate in 1800 ml. of glacial acetic acid was treated with 24.5 ml. of 30% hydrogen peroxide (27.2 g. of solution, containing approximately 8.16 g. H_2O_2 , 0.24 mole) and allowed to stand for three days. It was nearly a day before a precipitate began to form, in contrast to the octadecyl reaction. An equal volume of water was added, and the mixture allowed to stand in the cold room. The solid was removed by filtration and dried in a vacuum desiccator over sodium hydroxide and phosphorus pentoxide. Weight 8.5 g. (55.8% as $C_{18}H_{36}O_4S_2$); m.p. 42-44° C. This product was recrystallized once from ethanol, and four times from pentane to raise the m.p. to 56-57° C. Found: C 56.99, 56.89; H 9.57, 9.65; S 16.96, 16.73%. Calculated for $C_{18}H_{36}O_4S_2$: C 56.80; H 9.54; S 16.85%. The sulfur analyses were by Waters' method (134) which involved oxidation to sulfuric acid by nitric acid and bromine.

Oxidation of Benzyl Methyl Xanthate with Hydrogen Peroxide

Guided by the results of a preliminary experiment, which showed that the heat of oxidation was considerable, the reaction was carried out in much more dilute solution than first used, in order to correspond more closely to the octadecyl and hexadecyl oxidations. In a 1 1. Erlenmeyer flask, 12 g. (0.0606 mole) of the benzyl ester, freshly recrystallized from ethanol, was dissolved in 500 ml. of glacial acetic acid and 75 ml. of water, and 37.2 ml. of 30% hydrogen peroxide (containing 0.3636 mole H202) was added, with precautionary (but unnecessary) cooling in an ice bath. A day later, there was a heavy turbidity in the solution and a small sediment which had the appearance of sulfur. After three days at room temperature, the mixture was filtered to give a clear solution. Dilution of a small sample with two volumes of water produced a slight turbidity but no precipitate, and this projected method of isolation was avoided. Neutralization of the acetic acid with 50% sodium hydroxide gave a great mass of crystals (needles) which dissolved on addition

of water. The mixture contained a considerable turbidity caused by oil droplets, and had a pleasant odor resembling that of benzaldehyde. The mixture was extracted three times with ether, the extract was dried with Drierite, and the ether was removed by distillation.

The residue of a few ml. was distilled at atmospheric pressure, and five fractions were collected. The third and largest boiled at 200-210° C., a small fourth fraction at 210-230° C., and a fifth (230-300° C.) solidified on cooling. About half did not distil below 300°, and solidified in the distilling flask on cooling. This half had an odor resembling that of benzaldehyde, in spite of its high boiling point (benzaldehyde b.p. 179° C.). Fraction No. 5 and the residue were combined, extracted with low-boiling petroleum ether, which took out the color and the odor, and left a white solid (0.4 g.). The solid was recrystallized from water to give colorless needles of m.p. 125° C., which did not dissolve in 5% sodium hydroxide, did not form an anilide, and was therefore not benzoic acid (m.p. 121° C.). The needles gave a definite but faint test for sulfur, using the sodium fusion technique and sodium nitroprusside solution.

The liquid fractions were combined and redistilled, giving 0.5 ml. boiling below 200° C., 2.5 ml. at 200-212° C. (recorded 205° C. for benzyl alcohol), and a dark still-residue of about 0.5 ml. The phenylurethane of benzyl alcohol was prepared from the main fraction, and melted at 77-77.5° C.

(recorded 78° C.). Evaporation of the petroleum ether extract gave a residue of about 1 ml. of yellow liquid, having an odor similar to that of benzaldehyde. The residue distilled at 275-300° C., but the yellow liquid distillate did not give a bisulfite test, and was not examined further.

Oxidation of Octadecyl Methyl Xanthate with Bromine

As mentioned earlier, the first experiments of this nature were attempts to determine the methylthic group by a titration with potassium bromate-potassium bromide solution (96). Weighed samples of the ester were dissolved with difficulty in glacial acetic acid, a little water was added, and the mixtures were titrated with standard bromate-bromide solution to a yellow end point. The end points were very indistinct, and high values indicated that both sulfur atoms were probably involved in the reaction. Moreover, the xanthate ester continually precipitated from the solutions during titration, thus making it less available for rapid reaction. Experiments using warm acetic acid only partially overcame the difficulty, and titration values were still higher. Attempts using ethanol as the solvent, both hot and at room temperature, also gave unreasonably high values and very vague end points, and the reaction was abandoned as a method of determining the methylthio group.

With the purpose of isolating the product, 1 g. of the ester was dissolved in 80 ml. of glacial acetic acid, and the warm solution was treated with 20 ml. of concentrated

hydrochloric acid and 50 ml. of approximately 0.1N potassium bromate-potassium bromide solution. Another 50 ml. of acetic acid was added to help prevent the reprecipitation of the The yellow color of liberated bromine was slow to ester. disappear at room temperature, but faded rapidly on warming. Finally 300 ml. of the bromate-bromide solution had been added before the yellow color was permanent. The oil floating on the surface solidified on cooling the solution, and was removed by filtration. A very small second crop was obtained by more drastic cooling, but remained liquid at room temperature. After drying, the first crop weighed 0.5903 g. and was a waxy solid melting only slightly above room temperature. Recrystallization from an excess of ethanol gave 0.2070 g. of a white solid of m.p. 58-60° C., which was then twice crystallized from petroleum ether to give a m.p. of 62-63° C.

Two similar experiments used liquid bromine as the oxidizing agent. Eight grams (0.02224 mole) of the octadecyl ester was dissolved in 600 ml. of ethanol and 50 ml. of water; the solution was warmed, and bromine was added in small portions. After 7 ml. had been readily taken up, the reaction slowed down. A total of 10 ml. was added, and the red solution allowed to stand. An hour later, an additional 2 ml. was added, as the solution was slowly decolorizing and a precipitate was beginning to form. Sixteen hours later the orange solution was warmed to drive off the excess bromine and to dissolve the precipitate. After being cautiously diluted with 1.5 volumes of warm water, and allowed to cool very slowly to about 10° C., a white waxy solid, most of which had solidified from an oil, was removed by filtration and crystallized from ethanol to give 6.3 g. Three crystallizations from pentane and two more from ethanol gave a m.p. of 61.6-62.6° C., unchanged by two further crystallizations from pentane. This product gave negative tests for sulfur and halogens, did not dissolve in 5% sodium hydroxide, but turned bright yellow on warming and the color remained after cooling. Warming with 25% sodium hydroxide also caused yellowing. An aldehyde test with dinitrophenylhydrazine solution was negative. The product was not examined further.

Oxidation of Octadecyl Methyl Xanthate with Periodate

Several preliminary test tube experiments showed that solubility difficulties would be the biggest problem in this oxidation. In one experiment, 0.5 g. of the ester did not react with 0.89 g. of sodium metaperiodate in about 9 ml. of water, on standing overnight, but merely floated on the surface. Although the xanthate ester dissolved readily in dioxane, 70 ml. of this solvent was insufficient to keep the above quantities dissolved in 12 ml. of water, and after three days 83% of the xanthate ester was recovered, m.p. 35-37.5° C.

Solubility difficulties were overcome by using ethanolic solutions of the ester and of paraperiodic acid (H_5IO_6) instead of sodium metaperiodate $(NaIO_4)$. A solution of 1.9015 g. of paraperiodic acid (0.00834 mole) in 40 ml. of ethanol was

mixed in a stoppered flagk with a solution of 1 g. (0.0028 mole) of the ester in 100 ml. of ethanol. A deep red color soon developed in the solution, which after a week was diluted with 750 ml. of water. A silky precipitate mixed with what appeared to be crystals of iodine formed. The precipitated mixture was removed by filtration and allowed to dry in the open air. After two days, practically all of the iodine had sublimed, leaving 0.3385 g. of dirty-white material which was crystallized from ethanol-water. The product melted at 33-33.6° C. and was still not pure white. Another recrystallization from ethanol-water gave a white waxy solid of m.p. 33-34° C., which was not examined further.

The Stability of Xanthate Methyl Esters with Hydriodic Acid

These experiments were attempts to determine the methylthio (-SCH₃) group by slight modifications of the standard methoxyl methods, which were mentioned earlier.

(1) Check of the usual Vieböck method on vanillin.
 Calcd. for C8H803: -OCH3 20.39%. Found: -OCH3 19.93, 20.11%.

(2) Check of the Kirpal-Bühn methoxyl method, with silver nitrate titration, on vanillin. Calcd. for C₈H₈O₃:
-OCH₃ 20.39%. Found: -OCH₃ 20.40, 21.30%.

(3) Attempted methylthio determination, by the Vieböck method, on octadecyl methyl xanthate, heating for 1.5 hours. Calcd. for $C_{20}H_{40}OS_2$: -SCH₃ 13.08%. Found: -SCH₃ 0.13, 1.15%.

(4) Repetition of (3), heating for 2.5 hours.
Calcd. for C₂₀H₄₀OS₂: -SCH₃ 13.08%. Found: -SCH₃ 0.512,
0.628%.

(5) Attempted methylthio determination, by the Vieböck method, on benzyl methyl xanthate, heating for one hour. Calcd. for $C_9H_{10}OS_2$: -SCH₃ 23.7%. Found: -SCH₃ 1.35, 2.34%.

(6) Attempted methylthio determination, by the Kirpal-Bühn method, on benzyl methyl xanthate, heating for four hours. Calcd. for $C_9H_{10}OS_2$: -SCH₃ 23.7%. Found: -SCH₃ 2.7, 1.94%.

(7) Attempted methylthio determination, by the Kirpal-Bühn method, on octadecyl methyl xanthate, heating for five hours. Calcd. for $C_{20}H_{40}OS_2$: -SCH₃ 13.08%. Found: -SCH₃ 2.14, 2.42%.

Cellulose Xanthate Methyl Ester

1. Preparation of Cellulose Xanthate

The cotton linters used were from a lot obtained from the Hercules Powder Co. in 1948, and were identified as Cook No. 05708, reported to have viscosity 440 sec. in 2.5 g. concentration, a soda soluble content of less than 2%, an ash content of 0.03, and a color of 0.2. These linters were extracted for 24 hours in a Soxhlet extractor with 2:1 benzene-ethanol, air-dried for a day, then dried in a vacuum desiccator over phosphorus pentoxide for over a week, until a sample had reached a constant weight. There was no essential reason why thoroughly dry cellulose needed to be used in xanthate preparations, and it was dried only in the first three runs, where attempts were made to duplicate Lieser's procedure exactly.

The 18% solution of sodium hydroxide for mercerization was made by dilution with freshly distilled water of 50% solution from which the settled carbonate impurity had been removed by filtration through sintered glass. Dilutions were carried out until hydrometer readings indicated a density corresponding to an 18% solution. Both 50% and 18% solutions were stored in paraffin-lined bottles.

Two representative procedures for the preparation of cellulose xanthate are given below.

<u>Run No. 3</u>:- A 0.7660 g. sample of dry cellulose was placed in a small weighing bottle of about 30 ml. capacity with a ground glass stopper. This weight was chosen, following Lieser (62), as the resulting xanthate should weigh 1.00 g. according to his assumptions, which were not necessarily correct. The sample was steeped in 25 ml. of 18% sodium hydroxide for two hours at room temperature (19° C.), then recovered on sintered glass, pressed as dry as possible, and finally pressed between clean sheets of filter paper. The mercerized sample was picked apart with tweezers into very small pieces over a period of 45 minutes and transferred to another small weighing bottle of the same size. Carbon disulfide, 0.56 ml., was added all at once, and the stoppered bottle was allowed to stand for 14.75 hours at 15° C. (Lieser usually kept his samples for 15 hours at 11-13° C., although he often varied

these conditions.) The slightly shrivelled mass, uniformly orange in color, was shaken in the same bottle with successive 25-30 ml. volumes of absolute methanol to dissolve impurities, chiefly sodium trithiocarbonate, each time filtering on coarse sintered glass. Eight washings over a 45-minute period were needed before a completely colorless filtrate was obtained, leaving a very pale yellow cellulose xanthate. Filtration was slow after three or four such washings, a phenomenon also observed by Lieser. In the present work the xanthate consisted of small somewhat gelatinous pieces, whose centres were only slowly penetrated by methanol, and remained orange until nearly the last washing.

The product was then exchanged into absolute ether several times, finally transferred to a small cylindrical weighing glass; and air, dried over sulfuric acid and then phosphorus pentoxide, was passed over the sample for 9.5 hours until it reached a practically constant weight of 1.0073 g. By this time, the loss over an hour was less than a milligram. (Lieser usually dried his products for about three hours to a weight "constant" to the nearest centigram.) The dried product had a slightly unpleasant odor when first removed from the container. Sulfur and sodium were determined by the bromine method (see p. 62) and by ashing with sulfuric acid as described by Heuser (60), respectively. Found: S 11.7%: Na 8.47% (Mole ratio 1:1.005, by coincidence almost exactly half the theoretical ratio for an alkali-free xanthate). Lieser reported 14.8% as the average sulfur content of ten

preparations which were washed with methanol for 20-30 minutes, and 12.2% for a preparation washed for one hour. He reported a sodium content of 7.42%, on the average.

Run No. 16:- Mercerization of 16.0 g. of air-dried dewaxed cotton linters was carried out in a beaker with 400 ml. of 18% carbonate-free sodium hydroxide. After two hours at room temperature, the linters were recovered on a coarse The alkali cellulose was pressed on sintered glass filter. the filter, then between filter papers, in about four portions, until its weight was reduced to 68.5 g., representing a "pressed weight ratio" of 4.25 (deliberately kept higher than in other runs). After being carefully picked apart into small pieces, the material was "aged" in a stoppered bottle for 65 hours. Then 16 ml. of reagent grade carbon disulfide was added, and the stoppered bottle was placed on rollers for five hours, at the end of which time the material was colored orange and adhered completely to the sides of the bottle. The xanthate was then dissolved in 216 ml. of 6% sodium hydroxide, which was precooled to 0° C., and added to the bottle. About 2.25 hours on the rollers, with frequent shaking, were necessary to effect complete solution. The viscose was poured into a 4 1. beaker, and 3 1. of methanol, precooled to 0° C., was added fairly rapidly, in portions, with continuous stirring. The temperature rose to 14° C. during the first five minutes of mixing, but only very slowly after that. About 30 minutes later, the viscosity began to increase, and 45 minutes after mixing the solution was

extremely viscous, but stirring was continued. The temperature was now 16° C. After about 20 minutes, the mixture had again thinned and a precipitate was beginning to settle. This precipitate was allowed to form for another 30 minutes before filtration, in order to prevent excessive clogging of the filter, and was recovered on two large, coarse sintered glass filters used simultaneously to shorten the time of filtration (about 40 minutes). Some clogging did occur, and the filters were removed and cleaned with water, then with methanol, half-way through the filtration. The product was washed once on the filter, with a total of 400 ml. of absolute methanol which had been cooled to 0° C., and was then steeped at 0° C. in 1 1. of 5% acetic acid in absolute methanol for 20 minutes, with occasional stirring and breaking up of any lumps with a glass rod. During this treatment the product turned very pale yellow, and hydrogen sulfide was liberated by the decomposi-The cellulose xanthate was then recovered tion of by-products. on a coarse glass filter and was washed several times with cold absolute methanol, until the washings showed no acid reaction to moist litmus paper. After thorough solvent-exchange into dry ether, the weight of the ether-wet product was 116 g. Seven grams was dried for analysis in a vacuum desiccator over phosphorus pentoxide, paraffin wax, and charcoal, and the remainder was methylated immediately. The dried portion finally weighed 1.4075 g., and, on a proportionate basis, the total dry yield would be 23.32 g.

Of the 16 preparations noted in Tables VI and VII, Runs No. 1 to No. 3 followed Lieser's method (62) (see p. 20) almost exactly, Runs Nos. 8, 11, and 13 were essentially by Lieser's method, and the remainder of the runs followed the more usual procedure of precipitating the xanthate from a viscose solution.

The dried products were analyzed for sulfur by the Carius and bromine methods already mentioned (see p. 62), for sodium by ashing with sulfuric acid and weighing as sodium sulfate as described by Heuser (60), and for cellulose by precipitation from viscose with dilute hydrochloric acid and drying at 105° C., as described by Heuser (60).

The excess caustic soda in the product from Run No. 14 was also estimated by dissolving weighed samples (0.4726 g. and 0.4742 g.) in 100 ml. of water, allowing to stand for about 12 hours, and titrating with 0.0979N acetic acid, using phenolphthalein as indicator (cf. a procedure in Heuser's book, ref. 52). Duplicate titrations of 1.15 ml. showed that there was 0.002587 g. of sodium as sodium hydroxide in each sample, i.e., 0.55% of the weight of the sample. From Table VII the difference between percentages of sodium calculated and found was 0.54. Attempts to determine total sodium by titration with hydrochloric acid, using methyl red as indicator, were not very satisfactory owing to indistinct color changes and a slow reaction at room temperature. Other attempts using a measured excess of standard hydrochloric acid, and backtitrating with standard sodium hydroxide, gave somewhat more

TABLE VI

Procedural Details of

Run No.	Wt. of lin- ters used (g.)	"Pressed weight ratio" of alkali cellu- lose	Aging time of alkali cellu- lose (hours)	Vol. of CS2 used (ml.)	Time of xantha- tion (hours)	Temp. of xantha- tion (°C.)	Vol. of NaOH solution for vis- cose for- mation (ml.)	Concen- tration of NaOH used (%)
1	0.766	-	0.25	0.56	15.25	15.5	_(a)	-
2	0.766	-	0.25	0.56	18.75	15.5	_(a)	-
3	0.766	-	0.75	0.56	14.75	15	_(a)	-
4	16	3.62	92	12(b)	4	23.5	173	4
5	8	3.75	72	6	4	22.5	₈₇ (a)	4
6	16	3.56	43	12	4	23	175(d)	4
7	· 8	3.52	69	6	4	22-23	87(d)	4
8	8	3.52	58	6	5	23 - 24	_(a,g)	-
9	8	3.58	65	6	4	24-25	8 7	4
10	8	3.75	63	6	3.75	26	90(d)	4
11	8	3.50	65	6	2	26	_(a)	-
12	8	3.70	59	6	4	25	100	4
13	8	3.60	61	6	4	25	_(a)	-
14	8	3.57	67	6	4	26	120	4
15	8	3.65	60	8	5	25	108(d)	6
16	16	4.25	65	16	5	25	216(k)	6

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For footnotes, see p. 134.
Cellulose Xanthate Preparations

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Run No.	Time from addition of NaOH to pptn. of xanthate (hours)	Vol. of Methanol for pptn. (ml.)	Complete or incomplete washing be- fore acid treatment	Time of steeping in 5% HOAc in methanol (min.)	Volume of 5% HOAc used (ml.)
1	-		-	-	
2	-	-	-	-	-
3	-	-	-	-	-
4	ca. 5	1200 ^(c)	Complete	330	190
5	ca. 5	1200	Complete	30	150
6	5	2000(e)	Complete	30	300
7	2.25	1000(f)	-	-	-
8	-	-	-	-	-
9	1.5	1200	Complete	20	100
10	2	1200	Complete	20	150
11	-	-	Complete	20-25	100
12	1.5	1250(h)	Incomplete	20	300
13	-	-	Incomplete	150(1)	500(1)
14	1.5	1500	Incomplete	20(1)	500(1)
15	1.75	1500 at 10°	Incomplete	20	500
16	2.25	3000 at 10°	Incomplete	20	1000

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TABLE VI (Continued)

Footnotes:

- (a) Runs Nos. 1, 2, 3, 8, 11, and 13 were by Lieser's method in which a viscose solution was not prepared.
- (b) This proportion was used by Chen (55) in much of his work.
- (c) Run 4 was the only one in which the product was centrifuged instead of filtered. Considering the volumes involved, filtration was more convenient.
- (d) In Runs Nos. 5, 6, 7, 10, and 15, about 20 to 40 ml. of water was also needed in order to prevent the viscose from becoming inconveniently thick.
- (e) Run No. 6 gelled during precipitation. In spite of a somewhat lumpy product, the run was continued, but washing was difficult and the final product was too dark in color.
- (f) In Run No. 7, ethanol was used for precipitation instead of methanol. The xanthate came down immediately in nearly unmanageable gummy masses, which could not be washed satisfactorily, even after extensive trituration with ethanol in a mortar. After some time, the product hardened to brittle lumps.
- (g) In Run No. 8, the somewhat gelatinous crude xanthate crumbs were washed with ethanol instead of methanol. The product consisted of gummy hard lumps, too yellow in color. Two reprecipitations from viscose solutions, again with ethanol, gave a nearly white product, but the D. S. was then probably too low.
- (h) In Run No. 12, an attempt was made to carry out the precipitation at -5° C. with methanol. No precipitate appeared, however, until the temperature had slowly risen to ca. 15° C.
- (i) In Runs Nos. 13 and 14, a 10% instead of 5% acid solution was used.
- (j) Chen (55) used an amount as high as this in some of his fractionation work.
- (k) The sodium hydroxide solution was cooled to 0° C. before addition to the xanthate crumbs. There was probably no great advantage in this procedure.

TABLE VII

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Run No.	Before or after acid treatment	% Cellulose	ダ Sulfur (Carius method)	% Sulfur (bromine method)	D.S.	% Sodium found	% Sodium calcd. (from % S)
15 After 72.1 $12.23 - 0.43 5.08 4.39$	2 3 4 5 6 9 9 10 11 12 13 14 15	- After Before After Before After After After After After After	- 89.1 9.08(b) 14.52(b) 73.1 80.4 86.3 81.6 89.7 84.6 72.8 78.3 76.3 72.1	- - - - - - - - - - - - - - - - - - -	8.80 11.7 3.56 0.885 1.17(c) 10.39 5.71 5.05 6.08 4.27 7.15 11.09 8.11 10.99	- 0.10 0.30 0.20 0.36 0.18 0.15 0.19 0.12 0.22 0.39 0.25 0.34 0.43	8.79 8.47 2.03 1.02 0.58 3.67 6.16 3.86 3.58 2.08 3.98 4.93 3.41 4.20 5.08	3.16 4.20 1.28 0.32 0.42 3.73 2.05 1.81 2.18 1.53 2.58 4.02 2.80 3.66 4.39

Analyses of Cellulose Xanthates (a)

- (a) Most figures are averages of two or more concordant analyses.
- (b) The analyses of product No. 5 were done on ether-wet samples, as merely the relative amounts of cellulose and sulfur were desired. This was not a very satisfactory procedure, however.
- (c) In this case the sulfur was determined by the zincate method (see p. 62), which in several other cases gave values much too high.

satisfactory results, but still not good.

In order to discover how completely methanol precipitated the xanthate and the best conditions for rapid filtration, a series of experiments were carried out on the methanolic mother liquors from runs 9 and 10. These experiments were in agreement with one another, and are typified by the following tests done on the filtrate from run 10. A 50 ml. sample was mixed with 50 ml. of ethanol, a second 50 ml. sample with 50 ml. of additional methanol, and a third sample, 100 ml., remained untreated. After the three mixtures had stood for 24 hours, a noticeable amount of white filterable precipitate had settled from the first sample, a very slight trace of brown precipitate from the second, and a very slight trace of light colored precipitate had appeared in the third. Thus the original precipitation of xanthate with methanol had been practically as complete as it would be with this liquid, but ethanol would produce a noticeable further precipitate.

2. Preparation of Cellulose Xanthate Methyl Ester

The procedure given below is typical of the five experiments carried out. Since dried cellulose xanthates could not be readily methylated, a fact confirmed in a small-scale experiment, they were methylated in the ether-wet state soon after preparation. The weight of xanthate used was estimated from the dry weight of a small sample.

A suspension of cellulose xanthate in absolute ether, enough to give a total volume of 10-15 ml. for each gram of

xanthate used, was treated with an approximately 20-fold excess of methyl iodide (e.g., 21 ml. for 7 g. of xanthate in Run No. 4) and allowed to stand in a glass-stoppered flask for several days in a dark place, with occasional swirling. In the first run, gentle heating under reflux was carried out for 48 hours, but the other runs were entirely at room temperature. About three or four days after mixing, the suspended material had become pure white in color, but was allowed to stand for at least two days longer. The mixture was filtered on coarse sintered glass, and the white solid washed with absolute methanol several times, both on the filter and by soaking it in a beaker, until a sample of the washings showed no test for iodide ion when diluted with water and tested with silver nitrate solution. After two or three additional washings, the product was exchanged into absolute ether, and finally dried to constant weight in a vacuum desiccator, to give a weight about equal to that estimated for the original xanthate salt. The resulting white powder was analyzed for sulfur by the Carius method, as the bromine method was unsatisfactory for the ester. Sodium analyses showed only trace amounts. The degree of substitution was calculated on the assumption that the product was free of sodium hydroxide and other impurities, using the relationship given below, which was developed by a method largely adapted from that used for other cellulose esters by Fordyce, Genung, and Pile (135).

Let S = Wt. % of sulfur,

M = Wt. % of xanthate methyl ester group,

and N = degree of substitution.

The formula for a cellulose xanthate methyl ester may be represented as

$$(c_6H_7O_5) - H (3-N)$$

The unit molecular weight for a xanthate methyl ester is therefore $C_6H_7O_5 + CS_2CH_3(N) + (3-N)H$

= 159.12 + 91.16 N + 3.02 - 1.01 N= 162.14 + 90.15 N

Then $M = \frac{9116 \text{ N}}{\text{Unit mol. wt.}} = \frac{9116 \text{ N}}{162.14 + 90.15 \text{ N}}$

Solving for N,
$$N = \frac{162.14 \text{ M}}{9116 - 90.15 \text{ M}} = \frac{1.799 \text{ M}}{101.12 - \text{ M}}$$

The wt. % of xanthate methyl ester group = wt. % sulfur $\times \frac{CS_2CH_3}{S_2}$

1.e.
$$M = \frac{91.16 \text{ S}}{64.12} = 1.422 \text{ S}$$

Therefore, $N = \frac{1.799 (1.422 \text{ s})}{101.12 - 1.422 \text{ s}} = \frac{1.799 \text{ s}}{71.11 - \text{s}}$

The white xanthate ester did not dissolve in water, but dissolved slowly in 4% sodium hydroxide, with some decomposition as evidenced by odor and slight yellowing, to give a clear viscous solution. Table VIII shows some of the details of the five preparations, and the analyses of the products.

TABLE VIII

Run No. of	D.S.	Approx. wt. of	Time	Analy	sis of	Product
cellulose xanthate used	or xanthate	xanthate used (g.)	or standing (days)	Na %	S %	D.S.
9	0.15	4	7(a)	0.5	4.51	0.12
10	0.12	2	5(b)	0.3	3.83	0.10
11	0.22	4	9.5	_(c)	-	-
15	0.43	7	6	0.2	14.25	0.45
16	0.42	22	10	-	12.21	0.37
	of cellulose xanthate used 9 10 11 15 16	of D.S. cellulose of xanthate xanthate used 9 0.15 10 0.12 11 0.22 15 0.43 16 0.42	of D.S. wt. of cellulose of xanthate xanthate xanthate used (g.) 9 0.15 4 10 0.12 2 11 0.22 4 15 0.43 7 16 0.42 22	of D.S. wt. of Time cellulose of xanthate of xanthate xanthate used standing (g.) (days) 9 0.15 4 $\gamma(a)$ 10 0.12 2 $5^{(b)}$ 11 0.22 4 9.5 15 0.43 7 6 16 0.42 22 10	ofD.S.wt. ofTime Time $xanthateAnalysMa(g.)Analys90.154\gamma(a)0.5100.1225^{(b)}0.3110.2249.5-(c)150.43760.2160.422210-$	ofD.S. cellulosewt. of xanthateTime of $xanthateAnalysis ofNa%90.154\gamma(a)0.54.51100.1225^{(b)}0.33.83110.2249.5-(c)-150.43760.214.25160.422210-12.21$

Preparation of Cellulose Xanthate Methyl Ester

- (a) Including two days of gentle heating under reflux.
- (b) In Run No. 2, no additional ether was used for suspension of the ether-wet xanthate. Instead, about an 80-fold excess of methyl iodide was used.
- (c) In Run No. 4, the product was not analyzed as the D. S. would obviously be lower than that desired.

3. Oxidation of Cellulose Xanthate Methyl Ester with Periodate

The method was adapted from one used by Timell (72) on cellulose itself. The trisodium paraperiodate was 0.06425M, and was buffered to pH 4.0 with acetic acid. Ten 100 mg. samples of the ester (product of Run No. 4) were kept in Erlenmeyer flasks in a dark place with 50.00 ml. of periodate solution in each. A blank was also prepared. The sides of the flasks were washed down well with a little water, and the flasks were swirled occasionally. At various times after mixing, a sample was filtered on sintered glass, and the solid washed well with water. The combined filtrate and washings were neutralized with sodium bicarbonate, treated with 6 ml. of 10% potassium iodide, and titrated with 0.0715M sodium arsenite. The results are shown in Table IX.

TABLE IX

Oxidations of Cellulose Xanthate Methyl Ester with Periodate

Time of testing (days after mixing)	Titration (ml. of arsenite)	consumed per glucose unit (average)
1	33.07, 33.40	1.70
2	32.30, 32.25	1.83
3	31.02, 31.38	1.99
4	30.30	2.12
8	29.10	2.29

As an example of the calculations, a titration after 24 hours was 33.07 ml. of standard arsenite solution, which contained 0.0715 X 0.03307 = 0.002365 moles of arsenite; therefore 0.002365 moles of periodate must have remained in the solution after reaction with the xanthate ester. Since the 50 ml. of periodate solution originally used contained 0.05 × 0.06425 = 0.003212 moles, 0.003212 - 0.002365 = 0.000847 moles were consumed by the 100 mg. sample of xanthate ester. The ester from Run No. 4 had a D. S. of 0.45, and using the relationship developed earlier (see p. 138) its unit average molecular weight was $162.14 + (90.15 \times 0.45) = 202.71$, and the number of glucose units in 100 mg. was $\frac{0.1}{202.71} = 0.000493$. Therefore the number of moles of periodate consumed per glucose unit was $\frac{0.000847}{0.000493} = 1.72$.

The results showed that the xanthate group was not stable to the periodate ion.

4. Degradations of Cellulose Xanthate Methyl Ester

To illustrate the different procedures used, detailed reports of four representative degradations are given below.

Run No. 1:- A 0.5 g. sample of the methyl ester (product of Run No. 1) and 50 ml. of 43% hydrochloric acid contained in a 100 ml. stoppered flask, were kept in the refrigerator at 0° C. The ester first changed to a pink gum, but within eight hours, with occasional stirring with a glass rod, yielded a clear orange solution. The flask was left at 0° C. for a total of 24 hours and then, unstoppered, at room temperature for about four hours, during which time the contents turned deep red but still remained clear. Two more days in the cold room (about 10° C.) gave a black solution, probably indicating extensive de-xanthation since a control run on cellulose itself was only pale yellow by this time. Dilution with two volumes of water made the solution red. After being kept at room temperature for a week, the solution was treated with absorbent carbon and on the next day was filtered. The clear colorless filtrate was neutralized with barium carbonate. Most of the water was removed by distillation at ca. 60 mm. pressure and the resulting solid was dried in a vacuum desiccator.

The crude product was extracted with 300 ml. of boiling absolute ethanol for an hour. The extract was evaporated at room temperature and reduced pressure to near dryness, and the solid residue was taken up in 200 ml. of distilled water. Filtration removed a slight turbidity, and the filtrate was passed through separate columns of Amberlite IR-120 cation exchange resin and Amberlite IR-4B anion exchange resin at approximately 8-10 ml. per minute. The final effluent and rinse water were distilled at 5-10 mm. and a temperature not over 50° C. to a volume of about 20 ml., at which point the evaporation was interrupted by another treatment with absorbent carbon. After the syrup had been dried to constant weight in a vacuum desiccator, the resulting slightly sticky yellow solid was found to contain only 0.7% of sulfur (Carius), therefore about 85% of the original sulfur content of the ester had been lost.

Run No. 8:- A 1 g. sample of the ester (product of Run No. 4) was allowed to stand with 50 ml. of concentrated hydrochloric acid (37%) for five hours at room temperature. The solution had become red at the end of two hours and purple after three hours, but remained clear. At the end of three hours, a 1 ml. sample was diluted with 1 ml. of water, but a precipitate was obtained. After five hours, a similar dilution of a 1 ml. sample gave a clear solution. The entire solution was then diluted with an equal volume of water. After six days, a little absorbent carbon was added to the slightly turbid, orange solution, and filtration left a clear filtrate of a very faint pink color. This solution was diluted with an equal volume of water (total dilution now 3:1) and a slight turbidity was removed on the seventh day with absorbent carbon.

The optical rotation of the clear colorless liquid, in a 4 dm. tube, at 20° C., was 0.40°, and 30 hours later was 0.36°. This rotation was considered to be constant within the limits of observation, but the values were too low to provide a sure indication of the completeness of the degradation. Between the two readings, a slight turbidity developed, perhaps caused by free sulfur, and a slight unpleasant odor was present. The solution was freed of hydrochloric acid with basic lead carbonate followed by hydrogen sulfide, and after being neutralized with sodium bicarbonate was passed through columns of Amberlite IR-120 and IR-4B resins as in the former runs.

The residual brittle yellow solid weighed 0.6189 g., or

64.5%, considering that samples had been removed. The sulfur content of 8.8, 8.8, 9.0% (average 8.9%) showed that 37.8% of the original sulfur content of the ester (14.3%) had been lost.

Run No. 12:- A 0.75 g. sample of the ester (product of Run No. 5) was allowed to stand in 38 ml. of concentrated hydrochloric acid (37%) at room temperature for four hours. Solution was complete in about 30 minutes, with the help of stirring, but at the end of four hours the colorless clear solution had become purple. The depth of color in these experiments might be a measure of the extent of de-xanthation. The solution was then diluted with an equal volume of water; no precipitate was formed, and five hours later the solution seemed to be no more deeply colored than when first diluted. The copper reducing value was then determined by the Shaffer-Hartman-Somogyi method, a 1 ml. sample being diluted with 25 ml. of water, and 5 ml. of this taken for the test. The reagent and method were as described by Browne and Zerban (136), who referred to the original paper of Shaffer and Somogyi (137), except that the heating time was increased from 15 to 30 minutes, as the mixture was still changing in appearance at the end of the first mentioned time. The thiosulfate titration values averaged 8.0 ml., 8.7 ml., and 7.8 ml. after 0, 12, and 24 hours, respectively. After isolation as in Run No. 8, the brittle yellow solid had a sulfur content of 6.77, 6.78%, therefore 44.5% of the original sulfur of the ester had been lost.

Run No. 13:- The purpose of this experiment was to examine the constancy of the Shaffer-Hartman-Somogyi copper reducing value over an extended time, using a solution which was undiluted, except for the dilution of each sample immediately before the determination.

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A 0.75 g. sample of the ester was allowed to stand in 38 ml. of 37% hydrochloric acid, and copper reducing values were taken at various times after mixing. In each case, a 1 ml. sample was diluted with 50 ml. of water, and 5 ml. of this was taken for the determination. The results (Table X) could not be transformed into absolute weights of glucose because an entirely valid calibration was not possible in this case. The xanthate ester groups had an unknown effect, and glucose xanthate esters were not available for comparison.

These values showed a slow increase over a longer period of time than used in the other runs, and hence the assumption that they were constant in these runs might not have been the case. The last few readings in particular were rather erratic, and perhaps not reliable. Over the first three or four hours the value seemed nearly constant, yet a considerable change must have taken place in the solution over this period, judging by the appearance of the solution on dilution for each test. It was difficult from these results to judge just when the hydrolysis should be considered complete, and of course this decision was somewhat arbitrary in most experiments. It was necessary to compromise to some extent, as long hydrolyses

TABLE X

Determination of Copper Reducing Value during Degradation of Cellulose Xanthate Methyl Ester with 37% Hydrochloric Acid

Deter- mination	Time of sampling (hrs. after mixing)	Appearance of solution after dilution with 50 ml. of water	Thiosulfate titration (ml. difference from blank)
1	1	considerable ppt.	6.52
2	1.5	considerable ppt.	6.48
3	2	slight ppt.	6.07
4	2.5	very slight ppt.	6.90
5	3	turbidity	6.90
6	3.5	very slight turbidity	6.95
7	7	clear	7.30
8	24	clear	9.83
9	44	very slight turbidity	9.30
10	72 (3 days)	slight ppt., and very dark solution	10.20
11	120 (5 days)	ppt. even before dilu- tion, solution very dark	8.13
12	168 (7 days)	ppt. even before dilu- tion, solution very dark	9.42

were accompanied by an excessive loss of sulfur. Certainly at least four or five hours in the undiluted 37% acid would appear to be necessary.

Table XI summarized all the experiments carried out; no conditions could be found that avoided a loss of about 40% at least of the xanthate groups during the degradations.

Degradation of Cellulose Xanthate Methyl Ester with Methanolic Hydrogen Chloride

A 0.4 g. sample of the ester was heated in a sealed tube of about 20 ml. capacity with 10 ml. of 3.2% hydrochloric acid in absolute methanol, or with proportions nearly identical to those reported for similar experiments on other cellulose derivatives (57). After being kept in a Carius furnace for three days at 125° C., there was still undissolved material present and the solution was pale brown in color. After two more days at 140°, the solid had still not completely dissolved, and the solution had a deeper color. Finally, after 33 hours at 160° C. there was no more undissolved material, but the solution was nearly black in color. The tube was allowed to cool, and opened. Soon after, a sudden liberation of gas ejected about half the contents, and a yield could not be calculated. The remainder was decolorized with absorbent carbon, filtered to give a pale yellow solution from which hydrochloric acid was removed with basic lead carbonate and hydrogen sulfide. The solution, now including much wash water, was passed through columns of

TABLE XI

Degradations	of	Cellulose	Xanthate	Me thyl	Ester

	Xant	hate es used	ster	нсі	used	Time and temperature
Run No.	Pro- duct No.	% S	(g .)	43% or 37%	Vol. (ml.)	before dilution
1	l	4.51	0.5	43	50	24 hrs. at 0°, 4 hrs. at 20°, 24 hrs. at 10°
2	1	4.51	1.0	43	50	17.5 hrs. at 0°
3	1	4.51	1.0	37	50	17.75 hrs. at 20°
4	2	3.83	1.0	37	50	14.5 hrs. at 0°
5	4	14.25	1.0	37	50	14.5 hrs. at 0°
6	4	14.25	1.0	43	50	14.5 hrs. at 0°
7	4	14.25	1.0	37	50	72 hrs. at 0°
8	4	14.25	1.0	37	50	5 hrs. at 20°
9	4	14.25	1.0	43	50	33 hrs. at 0°
10	5	12.21	0.75	37	38	5 hrs. at 20°
11	5	12.21	0.75	37	38	5 hrs. at 20°
12	5	12.21	0.75	37	3 8	4 hrs. at 20°
13	5	12.21	0.75	37	3 8	_(a)

For footnotes, see p. 150.

Further conditions of hydrolysis	Method of judging complete- ness of degrada- tion	- Reagent for neutral- ization	% S in dried pro- duct	% of orig- inal S con- tent lost
2:1 dilution for 8 days at ca. 20°	none	barium carbonate	0.7	85
10:1 dilution for 5 hrs. at ca. 20°, then heated under reflux 30 min.	none	11	0.5	8 9
9:1 dilution for 5.5 days at ca. 20°	rotation	b asic lead carbonate	0.7	85
9:1 dilution at 0° for a few hrs.(a)	-	-	-	-
4 ml. water added, 3.5 days at 0°(b)	-	-	-	-
25 ml. water added, 3.5 days at 0°, 5 ml. water added, 2 days at 0°, 1.5 days at ca. 20°, 20 ml. water added, 2 days at ca. 20°, then total 3:1 dilution for 4 days at ca. 20°	rotation	basic lead carbonate	7.75	45.5
7 ml. water added, 2 days at 0°, 1 day at ca. 20°, 1:1 dilution for 4 days at ca. 20°, 3:1 dilution for 3 days at ca. 20°	rotation	11	6.82	52.5
1:1 dilution for 6 days, 3:1 for 4 days, all at ca. 20	rotation	tt	8.85	37.8
40 ml. water added, 12 hr. at 20° 10 ml. water added (total 1:1), 4.5 days at ca. 20°, 3:1 dilution for 4 days at ca. 20°	rotation	12	6.94	51.5
1:1 dilution for 3 days, 3:1 for 30 hrs. all at ca. 20°	copper red. No.	łł	4.36	64.3
1:1 dilution for 3 days, 3:1 for ca. 8 days, all at ca. 20 (c)	22	-	-	-
1:1 dilution for 30 hrs. at ca. 20°	11	basic lead carbonate	6.78	45
-	11	-	-	-

with 43% or 37% Hydrochloric Acid

TABLE XI (Continued)

Footnotes:

- (a) Precipitate soon formed, and run was abandoned.
- (b) Run abandoned because of a slight precipitate.
- (c) Product not worked up as it would obviously have a still lower sulfur content than Run No. 10.
- (d) This run was described in detail in the accompanying text, and was carried out solely to examine the copper reducing value at various times.

ion-exchange resins as before, then concentrated, decolorized, and taken to dryness as in the other runs. Drying to constant weight in a vacuum desiccator gave a small amount of a yellow sticky semi-solid syrup of 1.53% sulfur content (Carius). Therefore 87.5% of the original sulfur content of the ester had been lost.

5. Examination of the Products of Degradation by Paper Chromatography

Aqueous solutions of the solid products obtained by the degradation of the cellulose xanthate methyl esters with concentrated hydrochloric acid were spotted on strips of Whatman #1 filter paper (about 18" x 3") and were examined by the methods of descending paper chromatography, which have been well described and discussed in the literature (e.g., 138, 139, 140, 141). In each case, the upper end of the strip was supported by a glass rod in a small rectangular metal tray containing the butanol-rich phase from an equilibrated butanolwater mixture, the whole being enclosed in a large cylindrical glass tank which was kept in a place well protected from drafts and temperature changes. The water-rich phase of the butanolwater mixture was placed in a shallow vessel at the bottom of the tank. The spotted strip of paper was put in place and equilibrated for some time (often several hours) before the butanol was introduced into the upper tray. Initial spotting was with a 0.1 ml. pipette calibrated to the nearest 0.001 ml., and in each case enough solution was put on each spot to

contain 0.5 to 1.0 mg. of solid in the qualitative work, or the amount indicated later for the quantitative work. Each drop was dried by an electric dryer before another was added. From 12 to 23 hours were required for the butanol to descend nearly to the bottom of the paper, the time depending partly on the particular tank used for the experiment.

The paper was removed, the solvent front marked with pencil, the paper dried, sprayed with an aqueous solution of aniline phthalate, and dried in an oven at 105° C. for at least 15 minutes. The brown spots developed soon after drying began, and the RF values were calculated (R_{F} = the distance of the centre of the spot from the starting line divided by the distance of the solvent front from the starting line). Several qualitative experiments, some in duplicate, were carried out on the products from degradations Nos. 7, 8, and 12 (Table XII). In all cases, there was a very faint spot not far advanced from the starting line, probably representing incompletely degraded material, and also a very faint spot on the starting line itself. In all cases, a heavy glucose spot, identified by running a parallel chromatogram of pure glucose, showed that hydrolysis had been at least fairly complete. In addition, products Nos. 7 and 8 showed four spots with well-separated R_F values, as indicated in the table, averaging 0.196, 0.390, 0.574, and 0.752 in different chromato-The first two of these were faint and the last two grams. somewhat heavier. With product No. 12 the second of these

TABLE XII

RF Values of Spots Obtained from Products of Degradation(a)

<u>un de la despoy de la Co</u>	Sheet 1		Sheet 2		Sheet 3	Sheet 4		Sheet 5			
Strength of spot	Pro- ducts 7 & 8	Glu- cose	Pro- duct 8	Pro- duct 12	Glu- cose	Pro- ducts 7 & 8 after fer- menta- tion	Pro-* duct 8	.3- deriva- tive (?)	Pro- duct 8	3- deriva- tive (?)	Mixture of product 8 and 3- deriva- tive
Very faint	. 034		.035	.035		?	.025		.023		.023
Strong	.125	.125	.135	.135	.135		.108		.078		.078
Faint	.193		.238	.238		.196	.191		.163		.163
Faint	.375		.422	.400 .445		.410	•370		.375		.375
Stronger	•550		.630	.630		.615	.548		.526		•526
	-							.683		.657	.657
Stronger	.722		.780	.780		.795	.730		.734		.734

(a) Solvent system butanol-water.

spots appeared to be split into two distinct spots of similar RF values, 0.40 and 0.45, while the other spots had the same relative positions as in products Nos. 7 and 8. Although RF values for the individual spots varied slightly from paper to paper, this behavior is considered normal.

A solution was provided by Mr. A. Sanyal of these laboratoraties, which was thought to contain glucose-3-methylxanthate, prepared by synthesis. This solution was chromatographed in a parallel experiment with product No. 8, as shown in the table, but gave a spot not identical with any of the others. The nonidentity was confirmed by chromatographing a mixture of product No. 8 and the presumed 3-derivative, and again the spots showed up separately.

6. Estimation of Glucose in the Products of Hydrolysis

(a) As only small amounts of the degradation products Nos. 7, 8, and 12 were available, 40 mg. samples were dissolved in water, made up to 100 ml. in volumetric flasks, and 5 ml. samples were taken for the Shaffer-Hartman-Somogyi determinations. The method was modified as mentioned earlier (p. 144), and gave titration values shown in Table XIII, Column 2. After fermentation of duplicate samples (see below), these determinations were repeated, using amounts for each test that would correspond to 2 mg. of the original solid, as before (Column 3). Differences from the former values were therefore 2.08, 1.00, and 1.36 ml. of the standard thiosulfate, respectively, and

TABLE XIII

Attempted Estimation of Glucose in the Hydrolysates

Hydro- lysate(a)	Before fermentation, ml. thiosulfate(b)	After fermentation, ml. thiosulfate(c)	Glucose %(d)
7	6.75, 5.85 - av. 6.30	4.22, 4.22 - av. 4.22	13
8	5.15, 6.27 - av. 5.71	4.82, 4.60 - av. 4.71	7
12	4.55, 6.57 - av. 5.56	3.90, 4.49 - av. 4.20	9

- (a) Hydrolyzed cellulose methyl xanthate.
- (b) Volume of standard sodium thiosulfate required for 5 ml. aliquots.
- (c) Volume required for 5 ml. aliquots after adjustment to original concentration of 0.04%.
- (d) Column 3 minus Column 2, reduction as glucose % of original hydrolysate.

reference to the Shaffer-Hartman-Somogyi calibration plot showed that these differences corresponded to 0.26, 0.14, and 0.18 mg. of glucose respectively, i.e., to 13, 7, and 9% of glucose in the original samples. As the Shaffer-Hartman-Somogyi reagent could only be calibrated in terms of pure glucose, the results might be expected to be unreliable, as xanthate ester groups appeared to exert an influence upon the estimation.

The fermentations were carried out by dissolving a 100 mg. sample in 25 ml. of water, adjusting the solution to about pH 4.5 with 0.1N acetic acid, and adding a few drops of a yeast suspension made up from 2 g. of Fleischmann's dry yeast, 0.2 g. of ammonium acetate, 0.2 g. of potassium dihydrogen phosphate, and 15 ml. of water (142). The samples stood at 35° C. for 72 hours. Similar mixtures were examined by paper chromatography after 48 hours, and fermentation was then complete, as shown by the disappearance of the glucose spot. The solutions for analysis were filtered through Super-Cel on a Büchner funnel, and the filtrate and washings made up to 250 ml., and 5 ml. aliquots taken for the Shaffer-Hartman-Somogyi estimations.

(b) A somewhat more satisfactory glucose analysis was carried out by extracting the glucose spots from quantitative paper chromatograms (e.g., 143).

Three strips of paper were each spotted with two 1.0 mg. quantities of product No. 8 and with a third spot for

indicator purposes, not so carefully measured. After removal from the tank and drying, the three indicator strips were cut off and developed as usual. Since the location of the spots was now accurately known, these areas were cut out of the unsprayed strips, giving three pieces of paper each having the glucose from 2 mg. of the original solid. Each piece of paper was separately extracted with 10 ml. of water in a micro-Soxhlet extractor for one hour, which was a sufficient time, as a dried extracted paper showed no glucose after spraying and developing. In each case the extraction was interrupted when the extract had a volume of 2-3 ml. After adding 1-2 ml. of water used for rinsing, the volume was made up to 5 ml., if necessary, and the reducing value determined on the entire solution. Two "blanks" were carried out by the same procedure, including the extraction of blank pieces of paper of the same area. The two "blanks" had titration values (differences between titration and the usual blank) of 0.17. and 0.13 ml. of the standard thiosulfate solution. Taking 0.15 ml. as the average value, this "blank" was subtracted from each of the three reducing values determined, giving 3.69, 3.51, and 3.64 ml. for the corrected titrations. These values corresponded to 0.440, 0.420, and 0.435 mg. of glucose respectively. An average of 0.432 mg. of glucose in 2 mg. of the original solid corresponded to 21.6% glucose in product No. 8, in contrast to 7% determined for the same product in the first method attempted.

SUMMARY

Two new crystalline xanthate methyl esters were prepared, those of octadecyl (stearyl) and hexadecyl (cetyl) alcohols, by a one-step xanthation involving reaction of carbon disulfide, sodium hydroxide, and the alcohol, followed by methylation with methyl iodide. Three previously known xanthate methyl esters were also prepared, those of benzyl and hexahydrobenzyl alcohols and of menthol, by the same general method. This was apparently the first time that the last two of these, at least, have been prepared by the sodium hydroxide method.

The stability of the xanthate methyl ester group in various reactions was examined in a variety of experiments on the five esters available, but chiefly on the new octadecyl methyl xanthate. These esters were saponified by one hour's boiling in 1N or 0.1N aqueous-alcoholic alkali and reasonably good saponification numbers were obtained. Boiling 25% aqueous sodium hydroxide did not appreciably saponify the octadecyl ester, however. On the other hand, the octadecyl ester was quite stable to hydrochloric acid under several drastic treatments, including three hours' heating under reflux with 6N acid, an hour's heating under reflux with 1N aqueous-alcoholic acid, 24 hours' standing with 43% acid at 0° C., and even heating with 3% methanolic hydrochloric acid at 120° C. in a sealed tube for three days. The last mentioned reagent decomposed it extensively during several days' heating

in a sealed tube at a temperature finally reaching 160° C.

The octadecyl ester was stable to aqueous-alcoholic ammonia at room temperature, and reasonably stable to pyridine at room temperature but not to pyridine at elevated tempera-Silver carbonate and silver oxide, when heated under tures. reflux with an alcoholic solution of octadecyl methyl xanthate, caused ready de-xanthation to octadecanol, although an ether solution of the octadecyl ester was not de-xanthated by silver carbonate at room temperature. Tests with silver nitrate and mercuric acetate were somewhat inconclusive, and a test with cadmium carbonate showed no de-xanthation at room temperature. Thallous ethylate dissolved in benzene easily de-xanthated octadecyl methyl xanthate to octadecanol, even at room temperature. Raney nickel, even at temperatures as low as 10° C., also readily decomposed it, giving octadecanol and low-melting material which was not identified. The octadecyl ester was stable under acetylating conditions but decomposed exothermally when heated to 180-190° C. The methylthic group in these esters was only very slowly cleaved by boiling hydriodic acid solution, in contrast to the methoxyl group, and could not be estimated in this way.

Oxidation of octadecyl and hexadecyl methyl xanthates with hydrogen peroxide gave the crystalline compounds $C_{20}H_{40}O_4S_2$ and $C_{18}H_{36}O_4S_2$ respectively. The structures of these compounds were not investigated in detail, although the O-alkyl groups still remained, and at least one sulfur atom in the molecule appeared to be still unoxidized. An analogous compound was not obtained from the corresponding benzyl ester, but two unidentified products resulted in small amounts from the oxidation. Oxidation of the octadecyl ester with bromine and with periodate did not give the compound obtained with peroxide, but different unidentified waxy solids, sulfur-free in the first case.

On treatment with nitrosomethylurethane at a low temperature, xanthate salts of octadecyl and benzyl alcohols gave the xanthate methyl esters, with no de-xanthation as occurred in a similar reaction of cellulose xanthate.

Cellulose xanthate was prepared by the usual procedures, and methylated with methyl iodide to give the xanthate methyl ester. This ester was degraded by 43% hydrochloric acid at 0° C. and by 37% acid at room temperature. In all cases, an excessive amount of de-xanthation occurred simultaneously, making the product unsatisfactory for any subsequent quantitative work which would lead to information regarding group distribution in the original xanthate. Methanolic hydrochloric acid also gave much undesirable desulfurization in a sealed tube reaction with the ester.

Glucose estimations on a representative product of degradation with 37% hydrochloric acid indicated that the scission of the glycosidic bonds might not have been complete. Attempts to measure the completeness of the degradation by optical rotation and by the copper reducing value were not satisfactory.

Examination of three representative products of degradation by means of paper chromatography showed at least four unidentified spots for each product, in addition to those caused by glucose and by incompletely degraded material. There was an indication, but no definite proof, that none of these spots was that of glucose-3-methylxanthate.

CLAIMS TO ORIGINAL RESEARCH

1. Two new crystalline xanthate methyl esters were prepared, those of octadecyl and hexadecyl alcohols. Their melting points were 38-39° C. and 28-28.5° C. respectively.

2. The xanthate methyl esters of hexahydrobenzyl alcohol and menthol were prepared apparently for the first time by the method in which sodium hydroxide was used instead of elementary sodium.

3. A series of experiments on the xanthate methyl esters, chiefly the new octadecyl methyl xanthate, provided much information regarding the stability and reactions of these compounds. Their behavior with Raney nickel, thallous ethylate, and oxidizing agents was entirely new work, while the experiments with acid, alkali, ammonia, pyridine, acetic anhydride, heavy metal salts, and simple heating, generally confirm and extend the fragmentary reports concerning the behavior of compounds of this type. All these reactions were tried for the first time with the new, crystalline octadecyl ester.

4. Octadecyl methyl xanthate and hexadecyl methyl xanthate were oxidized by hydrogen peroxide to the crystalline compounds $C_{20}H_{40}O_4S_2$ and $C_{18}H_{36}O_4S_2$ respectively, the structures of which were not investigated in detail.

5. The action of nitrosomethylurethane on two xanthate salts

gave the corresponding methyl esters. This was apparently the first time this reagent had been used on a simple xanthate salt, although with cellulose xanthate de-xanthation occurred. This observation demolished the theoretical basis hitherto used to locate the xanthate groups in the macromolecules of cellulose.

6. Cellulose xanthate methyl ester was prepared without reasonable doubt for the first time, in a pure condition.

7. Periodate oxidations of cellulose xanthate methyl ester showed this method to be unsatisfactory for structural studies, owing to interference by the xanthate ester group.

8. Degradations of the cellulose ester with 43% hydrochloric acid at 0° C., with 37% acid at room temperature, and with 3% methanolic hydrochloric acid, all were accompanied by de-xanthation to the extent of 37% or more.

9. Paper chromatography of the products of acid degradation showed a number of interesting spots, which could not be identified because the possible xanthate methyl esters of glucose have not been prepared for chromatography in parallel experiments.

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