CHEMISTRY
OF DIOLEFINES.

THESIS

Work on

The Chemistry of Diolefines

by

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THE CHEMISTRY OF DIOLEFINES

GENERAL PART

Diolefines

Most of the work on the preparation of diolefines has been done since 1910, to which point the literature is covered in Beilstein's Handbook. Ditmar's booklet, "Synthese des Kautschuks", (Leipsic), gives an exact, if abbreviated, summary of the literature to 1912. Harries's book, "Untersuchungen über Kautschukarten", (Berlin, 1919), deals mainly with his own work, while Dubosc and Luttringer ("Rubber", London, 1918), although profuse, review only a part of the literature to that date[1]. For that reason, the following more or less complete reference tables on the preparation of isoprene and dimethylbutadiene have been included below (tables I to III).

I

Synthetic Preparation of Isoprene

Intermediates	Formulae	References
Isopropyl-Acetylene	$Me_2CH_2C{:}CH$	DRP 268102 (alumina at 400°)
Methyl-butenine	$CH_2{:}CMeC{:}CH$	290558 (see 288271, platinum and hydrogen)

[1] A recent work on the subject by Fonrobert, Harries and others ("Kautschuk und Flechtenstoffe", Abderhalden's Hand. d. Biol. Arb. XX, Berlin and Vienna, 1921) has not been obtainable.

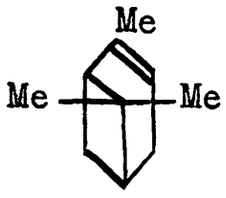
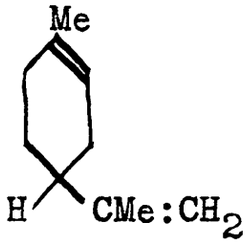
Intermediates	Formulae	References
Dimethyl-allene	$Me_2C:C:CH_2$	DRP 251216 (alumina at 300°)
Propylene and acetylene	$MeCH:CH_2$ + $CH:CH$	338030 (compression at 350-450°)
Acetone and acetylene	Me_2CO + $CH:CH$	Fr.P 427,286 (catalytic)
Acetone and alcohol (or ethylene)	Me_2CO + $MeCH_2OH$ (or $CH_2:CH_2$)	U.S.P. 1218332 (C. Abs. 1917, 1574.- fuming sulphuric acid).
Isopentenols	$Me_2COHCH:CH_2$	DRP 222623, 285770, 286920, 287933, 288217, 289497, 291185.
	$MeCHOHCMe:CH_2$	233519, 246241, 223207 (heating with acids, acid salts, alums, etc.)
Isopentane glycols	$Me_2CHOHCH_2CH_2OH$	246572, 262642, (see 250086, heating with acids, alums, etc.)
	$Me_2CHOHCHOHMe$	
Vinyl bromide and brom-propene	CH_2CHBr + $MeCBr:CH_2$	245180 (magnesium at 35°)
Vinyl bromide and acetone	CH_2CHBr + Me_2CO	346700 (zinc, aluminium or magnesium at 100 - 150°)
Isopentane and Isopentene halides and their ester and ether derivatives		243075, 243076, 246241, 251100, 255519, 257600, 258555, 261677, 263017, 264007, 264008, 267553, 268100, 268101, 275199, 279955, 280596 (heating with alcoholic potash, organic bases, soda lime, red phosphorus, barium chloride or alumina. See also Ipatiew, J. pr. (2) 55, 1 (1897).

Intermediates	Formulae	References
Brom-dimethyl-butyro-lactone	$CH_2CHBrCMe_2$ | | O——CO	Blaise & Courtot (Bull. 35, 993 (1906), (heating with quinoline).
Dibrom-trimethyl-acrylate	$Me_2CBrCMeBrCO_2Et$	E.P.5931 (alcoholic potash)
Quaternary basic derivatives of methyl-butenol, methyl-tetra-methylene, methyl-pyrrolidine, etc.		DRP 231806, 245713, 247144, 247145, 247271, 254713, 254714, 261876 (distillation of the free bases, or with alkalies or earth alkalies or from the salts in vacuum at 230-40°). See also Gustavson, B.25, Ref. 912 (1892); Euler, B.28, 2952, (1895); J.pr.57, 131 (1898); B.30, 1989 (1897).

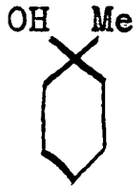
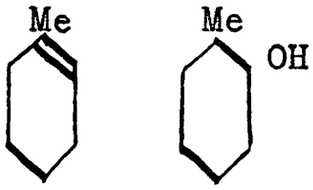
Of the less practicable pyrogenic methods for preparing isoprene, mention need only be made of the distillation of rubber, (Williams, Wallach, Buchardat, Weber, Fischer and Harries), of mineral oils (Norton and Andrews), petrol residues (Aschan), and vegetable oils like linseed, colza and castor (Tilden), resins (colophony, borneo or acaroid), resin oil (Matthews and Strange) or kauri gum (Anquetil). The more significant methods comprise the following (table II) :-

II

Pyrogenic Preparation of Isoprene

Intermediates	Formulae	References
Pinene		DRP 240074 (450-750° or red glow under reduced pressure (Silberrad)) 249947 (red hot filament in liquid or vapour phases under reduced pressure, also by silent discharge or ultra-violet light (Gottlob)) 269240 (improvement of yield to 30-40% by autoclaving 4 hours at 250° before depolymerising (Gottlob)) 270485 (with steam at 750°, 20% yield (Heinemann)) 278104 (silver at 450° or copper at 480°, 40-50% yield (Heinemann)#
Nopinene		260934 (iron at 500-520°, 10% yield (Schering))
Dipentene		257640 (glowing metal spiral in nitrogen at 20 mm., 60% yield (Staudinger)) 266402 (with benzol, etc., at 500-600° in presence of iron (Ostromisslensky)) 266403 (copper oxide at 305°, 34.5% yield (Gross)) 274348 (isoprene lamp, 60% yield(Gottlob)), also 254665 (dipentene from terpineol)#

EP 156122 ((C. Abs. 1921, 1728) ferromanganese, copper-silicon, silicates, etc.(Plauson))

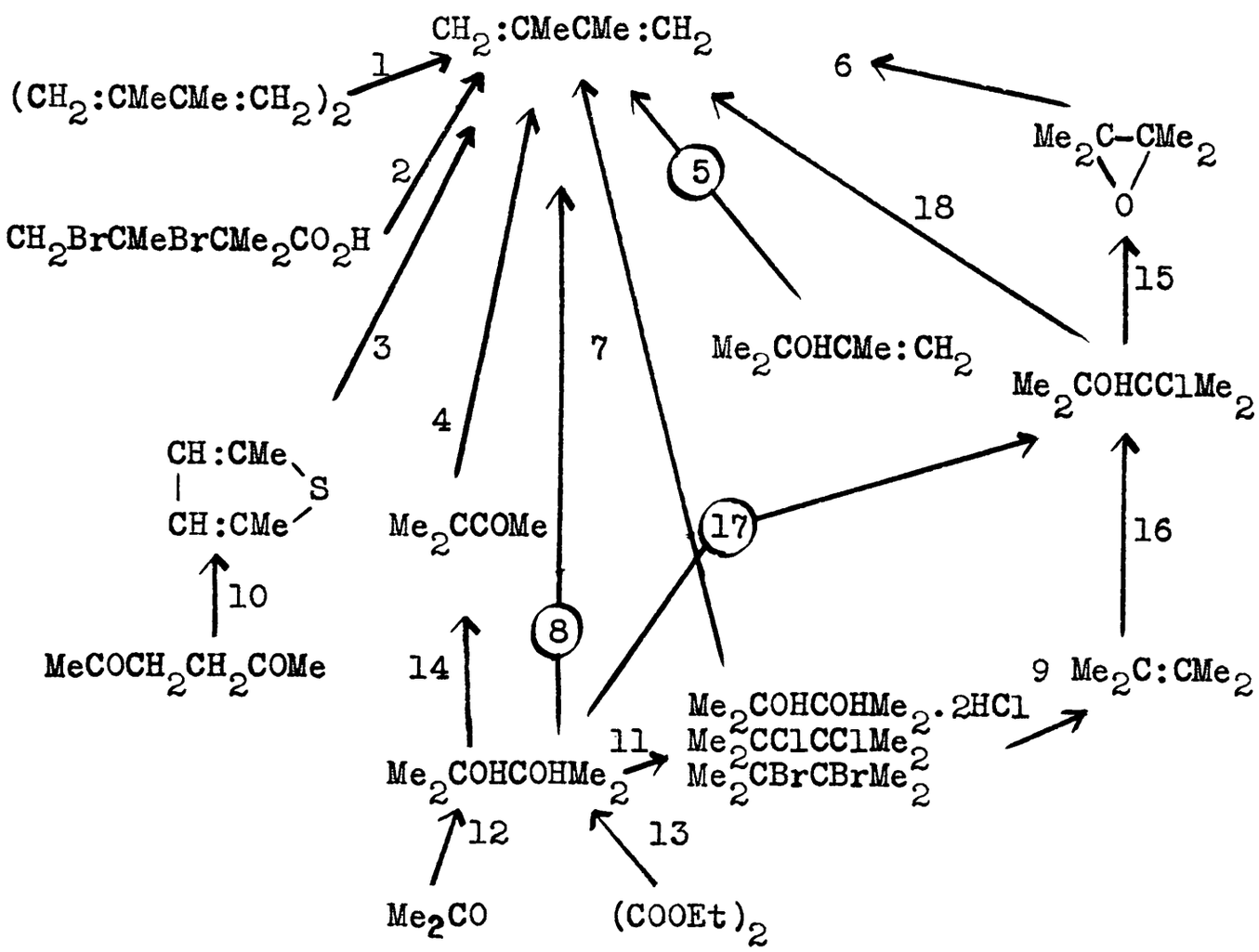
Intermediates	Formulae	References
Pinene and limonene hydrohalides		DRP 268722 (soda-lime or calcium oxide with iron in carbon dioxide at 500-600° or dull red glow, yield 40-50% (Gerlach & Koetschau))
Petrol		265172 (alumina and iron at 700° (Engler))
Methyl-cyclohexenol		241895 (alumina at 500-600° (Bayer)), also 254473.
Tetrahydro-toluene or hexahydro-o-cresol		252499 (alumina and carbon dioxide at 500°-or with nitrogen at red glow (Badische)).
Dimolecular a-methyl-butadiene		282817 (isoprene lamp (Bayer))
Camphor Oil		Nishizawa (C. Abs. 1921, 1277) asbestos-lampblack, copper-silver, silver-pumice, silver-asbestos, pumice; last two gave 8-10% yields.

Other references to the isoprene lamp include :-

Harries & Gottlob, A. 383, 228 (1911)
Staudinger & Klever, B. 44, 2212 (1911)
Andrejew (C. Zent. 1914, II, 325)
Ostromisslensky (J. Russ. 47, 1947 (1915))

III

Synthesis of Dimethyl-butadiene



Intermediates		References
1	Di-diisopropenyl	DRP 282817 (isoprene lamp, or 500-600°)
2	Trimethyl-dibrom-butyric acid	Courtot (Bull. (3) 35, 972 (1906); C.r. 140, 371 (1905) using quinoline)
3	Dimethyl-Thiophene	Heinemann (Dubosc)
4	Pinacoline	DRP 235311 (alumina at 400° under reduced pressure, 70% yield)
5	Dimethyl-isopropenylcarbinol	Marinza (J. Russ. 21,435(1889), zinc chloride or hydrochloric acid at 50-100°)
6	Tetramethyl-ethylene oxide	U.S.P.1033228 (aluminium silicate at 500-600° under pressure)
7	Tetramethyl-ethylene chloride or pinacone hydrochloride	Kondakow (J. pr.(2) 62, 169 (1900), alcoholic potash at 130-140°) Harries (A. 383, 183 (1911) soda-lime and carbon dioxide at 600°)
8	Pinacone	DRP 235311 (alumina at 400°, 70% yield) 246660 (organic or inorganic acid sulphates at 140-50°, 70% yield) 249030 (di- or polynaphthalene sulphonic acids at 120-60°) 250086 (ferrous or aluminium sulphates or alums at 140°, 70% yield) 253081 (small quantities of dilute sulphuric acid, aliphatic or aromatic sulphonic acids, at 130-40°, 70% yield) 253082 (aniline or naphthalene sulphonic acids at 130-40°) 256717 (alumina at 450°, 20 mm., 80% yield) Couturier (B.33, 454 (1880); Ann. Ch.Ph. (6) 26, 485 (1892), sulphuric acid or acetic anhydride) Kondakow (J.pr.62, 170 (1900), same) Delacre (Bull.(4) 23, 229 (1918) same)

Intermediates		References
9	Tetramethyl-ethylenedibromide	Thiele (B.27, 455 (1894), zinc dust and acetic acid at 15-20°)
10	Acetonyl-acetone	Heinemann (Dubosc)
11	Pinacone	Friedel & Silva (B.6, 35 (1873) phosphorus oxychloride) Couturier (Ann.Ch.Ph.(6),26,443 (1892), phosphorus trichloride) Kondakow (J. pr.(2) 62,166 (1900) hydrogen chloride at 10°) Harries (A.383, 183 (1911), hydrogen chloride and chloroform at 0°)
12	Acetone	Hollemann (C. Zent. 1906, II,748, magnesium and mercuric chloride) Couturier & Meunier (B.33,454 (1905), magnesium amalgam) Richard & Langlais (Bull.(4) 7, 455 (1910), magnesium amalgam, 60% yield) Thiele (B.27, 455 (1894), sodium and ether, 12% yield) DRP 233894 (magnesium with mercuric chloride & iodine with diluents) 241896 (aluminium and mercuric chloride, etc., 60% yield) 248252 (sodium & sodium hydroxide solution with ether, more than 12% yield) 306304 (electrolytic reduction in presence of Bi, Hg., Mn, Ni, Sb, Ag and Fe salts) 306523 (same, with Pb-Cu electrodes, pinacone 30 : isopropyl alcohol 1) 324919 (same, with Pb-Sn (or -brass, -bronze, 70% yield)
13	Ethyl oxalate	Valeur (C. r. 132,833 (1901), magnesium methyl iodide)
14	Magnesium pinacone	Couturier & Meunier (above, 21% yield at 300°)

Intermediates		References
15	Pinacone-chlorhydrine	Eltekow (B.16,339 (1883) solid potash)
16	Tetramethyl-ethylene	Eltekow (hypochlorous acid)
17	Pinacone	DRP 317635 (hydrogen chloride at 35-45° and subsequent distillation under reduced pressure; yield quantitative)
18	Pinacone-chlorhydrine	319505 (distillation with dimethylaniline)

The purest dienes are said to be obtained by distilling the quaternary ammonium bases (Harries, A.383,157 (1911)), since the halides, halo-hydrines and terpenes lead to appreciable amounts of related compounds like amylene and dimethyl-allene along with isoprene, tetramethyl-ethylene and butene with dimethyl-butadiene and erythrene respectively, although where the contact procedure is conducted under diminished pressure the products are claimed to be very pure (DRP 255519; Staudinger & Klever, B.44,2212 (1911)). These byproducts may be readily removed by selective oxidising agents like manganates, peroxides, perborates, persulphates and percarbonates, especially in the presence of alkali or earth-alkali metals (Ostromisslensky, DRP 276185, 314364). The symmetrical glycols also give pure dienes.

As the dienes readily isomerise or form condensation products, even when prepared by low temperature methods such as by the action of metals on unsaturated halides as described in DRP 245180 (Austerweil), their structure has to be determined by destructive methods, either by direct oxidation (Couturier, Ann. Chim. Ph. (6) 26, 485 (1892)), or through the halides or hydrohalides either by oxidation (Staudinger, H.C.Act. 5, 756 (1922)) or ozonation (Bergmann, J. Russ. 52, 24 (1920)) or by catalytic reduction of substitution products of the latter (such as ethers, formanilides, etc.) to the saturated hydrocarbons (Claisen, J. pr. 105, 65 (1922)).

The aliphatic diolefines, with the exception of butadiene itself which is a gas at ordinary temperature, are easily volatile, perfumed oils having a low specific gravity (about 0.7) and a medium refractive index (1.4-1.45). They solidify at very low temperatures only, isoprene at -120°, dimethylbutadiene at -65° (Enklaar, Recueil, 36, 247 (1916)). Owing to the inclusion of conjugated double linkages in their structure, the dienes show the phenomenon of optical exaltation to a greater or less extent (Anwers & Asinlohr, J. pr. (2) 82, 65 (1910)). They generally form two sets of halogen addition products, dihalides and tetrahalides. The dihalides are usually 1,4-compounds, known in two geometric forms (Griner, C. r. 117, 553(1893)).

The tetrabromides are known in either one or two forms (for review see Kondakow, J. pr. (2) 62, 117 (1900)). The halogen hydrides give two types of compound, the dihydrohalides being unsymmetrical; thus isoprene hydrobromide has been shown to have the formula $Me_2CBrCH:CH_2$ (Claisen, J. pr.(2) 105,65 (1922)) and the dihydrobromide $Me_2CBrCH_2CH_2Br$ (Ipatiew, J. pr. (2) 55, 1 (1897)). Dimethyl-butadiene has been shown to form a nitrosate of the formula $C_6H_{10}N_2O_4$ (Couturier, Ann.Ph.Chim.(6) 26,485 (1892)); isoprene and dimethyl-butadiene also form indefinite addition compounds with sulphur dioxide (DRP 236386), butadiene, however, does not (DRP 286640)#. By autoxidation, Greville Williams obtained from isoprene a solid peroxide of the empirical formula $C_{10}H_{16}O$ (Phil. Trans. 150, 241 (1861)). Herschmann got an oil, $C_8H_{14}O_2$ from the hydrocarbon C_8H_{14} (C.Zent.1893,II,196). But the dimethyl-hexadiene described in the experimental part has given a guminaceous oxidation polymer of the formula $C_{40}H_{70}O_{10}$.

The dienes also condense or couple with various organic substances including quinones (Euler, B. 53 (3), 822 (1920)) and diazo compounds (Meyer, B. 52 (3), 1468 (1919)).

Polymerisation of Diolefines

The most characteristic property of conjugated diolefines is their tendency to polymerise at ordinary or higher temperatures to form terpenes and rubbers. The latter are formed from 20 - 200° along with amounts of the terpenes which are the exclusive products at higher temperatures (DRP 250690).

A number of isomeric terpenes are formed simultaneously and there is some doubt about their nature. Harries (B. 35, 3265 (1902)) thought some of these were aliphatic compounds related to myrcene because of their lower boiling-points, refractive indices and characteristic odour. Their molecular refractions, however, indicated two rather than the three double bonds required by the open-chain structure; and as a matter of fact one cyclic terpene, dependene, has been recognised among the byproducts of isoprene polymerisation as well as in the pyrogenic decomposition products of rubber (Williams, Quart.J.C.S. 12,495 (1860)). Lebedew has more recently examined a number of these products by the ozonation method and found them to be cyclic terpenes (J.Russ. 45,1249 (1913)).

The diolefines differ considerably in their tendency to polymerise. A number of examples of this are cited in Houben-Weyl III, 1017 (1923), but no rule has been devised yet for predicting about new dienes, except that the β-substituted

compounds generally polymerise more easily than their α-isomers.

As may be seen from the following table (IV), polymerisation of diolefines may be effected by light, compression and a considerable number of catalysts, as well as by heat.

IV

Polymerisation of Dienes

Catalyst	References
Heat	DRP 235423, 235686, 250335, 250690, 255679.
Light	254371, Harries (Gummi Z. 35, 898 (1921)).
Pressure	329593.
Metals	248178, 249868 (sodium in liquid), 280959 (in vapour), 287787 (with carbon dioxide), 281966 (with alkalies), 264959 (colloidal metals), 255786 (metal alkyls), U.S.P. 1248888 (C.Abs.1918,440; sodium methylate, hydroxide or carbonate), Harries, (A. 383,157 (1911); 395,211 (1913)).
Bases	256413 (aniline, dimethyl-aniline); Heide, (B. 37,2103 (1904), pyridine).
Organic matter	254548 (solids), 254672, 255129 (viscous liquids or solutions).
Rubbers	248399, 254371, 254868, 329676.
Sulphur	251370; Ostromisslensky (J.Russ.,47,1910(1915))
Sulphur dioxide	E.P. 17253 (C. Abs. 1916, 296).
Bisulphates	U.S.P. 1161904 (C. Abs. 1916, 295).

IV (continued)

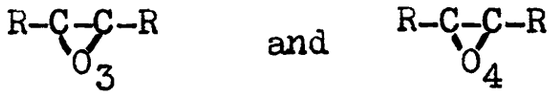
Catalyst	References
Acetic anhydride	DRP 257813; U.S.P. 1161904 (C.Abs.1916,295).
Amyl nitrate	301088.
Metal chlorides	Ann.K 64118 (zinc or aluminium chlorides with drying oils), Aschan (C.Abs.1919,309; 1920, 3823 - aluminium chloride)
Hydrogen fluoride	U.S.P. 1185654 (C.Abs.1916,2162).
Boron fluoride	DRP 264925
Ozonides and peroxides	Holt (Z. ang. 27, 156 (1914)).

The rubbers obtained by the above methods may be either simple or mixed, for instance from mixed dienes (DRP 255679) or from dienes and simple olefines (Ostromisslensky, J.Russ. 48, 1071 (1916)) or by mixture with heterogeneous dienes, like methyl-amine-acroline (CH_2:CHCH:NMe, E.P.156118 (J.S.C.I. 1922, 383 A)).

Ozonation of Rubber

The ozonation method worked out by Harries (see "Untersuchungen über das Ozon", Berlin, 1916), which has been instrumental in determining the molecular configuration of rubber hydrocarbons and other unsaturated compounds, consists in treating a substance, generally in an indifferent solvent

(methyl or ethyl chlorides, chloroform, carbon tetrachloride, acetone, acetic acid or ethyl acetate), with ozonised oxygen under cooling. The addition products so obtained are not homogeneous (Harries, A.390, 235 (1912)) but consist of monomolecular and polymeric ozonides and oxozonides of the general formulae



Similarly aldehydes and ketones (excepting acetone) give peroxides, the ketones also giving ozonide-peroxides, and unsaturated acids, ozonide- and oxozonide-peroxides. The method is not of much use with conjugated diolefines as complete saturation can only be obtained with very strong ozone (Harries, A.374, 288 (1910)).

The usefulness of the ozonides depends on the fact that on decomposition they do not usually regenerate the original substance but lead to fission at the point of entry of the ozone group, exceptions being mesityl-oxide- and fumaric-ozonides, which partly re-form the parent substance on heating or standing (Harries, ibid). The decomposition of the ozonides is catalysed by water at ordinary or higher temperatures, boiling acetic acid and alcohols. The alcohols lead to acetals, acetic acid to peroxides (avoided by addition of formic acid),

and water to aldehydes, ketones, acids, peroxides and hydrogen peroxide. Dilute alkalies give the acids. The decomposition has been effected by oxidation also (chrom-acetic acid), and reduction has been used with ozonides tending to form resins (formic acid, zinc and acetic acid, aluminium amalgam and Grignard reagents).

No definite conclusions about the molecular size of a hydrocarbon can be drawn from the nature of the ozonide, since this may be either a mixture (above) or a polymer or depolymerisation product. Koetschau has recently found that petrol is polymerised by ozone (Z. ang. 35, 509 (1922)). Ozonides and peroxides have been used as polymerisation catalysts (above); and, as mentioned later, the rubber ozonides appear to be depolymerisation products, derivatives of cyclo-octadiene homologues.

However, the decomposition of rubber ozonides and oxozonides has enabled Harries to determine the position of the double bond in the polymerisation unit. For instance, butadiene rubber (the heat polymer) led to succin-dialdehyde (CHO CH_2CH_2CHO) (Harries, B. 41,671 (1908)). Natural Hevea and normal isoprene rubber (obtained by heat) were found to give levulic aldehyde and acid ($MeCOCH_2CH_2CHO$ and $MeCOCH_2CH_2COOH$)(Harries, A. 383, 157 (1911)) as the chief products. The unit must, therefore,

have been -

$-CH=CMeCH_2CH_2-$ or $-CH_2CMe=CHCH_2-$

that is to say, either a condensation- or a true polymer (Staudinger, B. 53, 1073 (1920)), the skeleton being unchanged in the latter case as only the double bond would move as in 1,4- addition. The latter structure was shown to hold, for normal dimethyl-butadiene rubber gave only acetonyl acetone (Harries, A. 395, 264 (1913)) and normal piperylene rubber, methyl-succin-dialdehyde ($CHOCHMeCH_2CHO$)(Harries, A.395,211, (1913)). The units of the normal rubbers are consequently :-

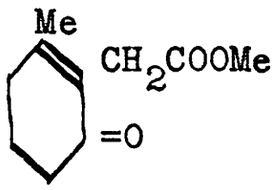
$-CH_2CH=CHCH_2-$	butadiene rubber
$-CH_2CMe=CHCH2-$	isoprene "
$-CH_2CMe=CMeCH_2-$	dimethyl-butadiene rubber
$-CH_2CH=CHCHMe-$	piperylene "

It appears from the ozonation of a rubber regenerated from the dihydrochloride by the use of pyridine (Harries, B.46,2590 (1913)), that the hydrochloride is analogous to the isoprene hydrobromide mentioned above in that the halogen reacts with the substituted member, the hydrochloride having the unit formula-

$$-CH_2CMeClCH_2CH_2-$$

But the variety of products obtained from the ozonide (formic and acetic acids, levulic aldehyde and acid, diacetyl-propane

$MeCO(CH_2)_3COMe$, hydrochelidonic acid $CO(CH_2CH_2COOH)_2$, methyl-cyclohexenone-acetic ester

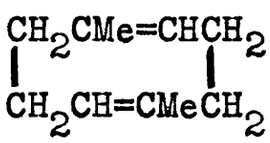


and a number of higher ketones mentioned later) indicate that the acid is not removed in a uniform way, the new rubber comprising a number of different unit types.

As yet no definite results have been got by the ozonation of sodium-rubbers (Harries, A.383,157 (1911); 395,211 (1913)), and the constitution of rubbers made in most other ways remains to be determined. Sodium-carbon dioxide rubber, however, is similar to the normal product, except in more readily yielding acetonyl acetone on ozonation (Harries, Gummi Z. 33,222 (1919)).

The constitution of Rubber

Attempts so far made to give a definite structure to rubber have not been very successful. At first Harries (B. 38,1195(1905)) and later Steimig (B. 47,350 (1914); 47,852 (1914)) favoured a cyclo-octadiene structure, as shown in the following figure -



mainly because of the apparent identity (in molecular weight, chemical properties, rates of decomposition and oxidation products) of the ozonides of butadiene rubber and cyclo-octadiene

itself (Harries, B.41,671 (1908)). It was apparent, however, that the structural unit could contain more than ten carbon atoms, since a tetra-ketone, pentadekatetrone ($C_{15}H_{24}O_4$, or $MeCO(CH_2)_3CO(CH_2)_3CO(CH_2)_3COMe$) was obtained from the regenerated rubber mentioned before. The ozonide also, although correspond- to a dimethyl-cyclo-octadiene ozonide in acetic acid was found to give molecular weights of 526-36 in benzol, $C_{25}H_{40}O_{15}$ being 580 (Harries, A.395,232 (1913)); so that Harries later gave the normal rubber an unsaturate ring structure of 24 members or $C_{30}H_{48}$ Latterly, however, Harries has abandoned his earlier views ("Kautschukarten", p.232; C. Zent.,1921,III,1358) and reverted to an indefinite structure of the type -

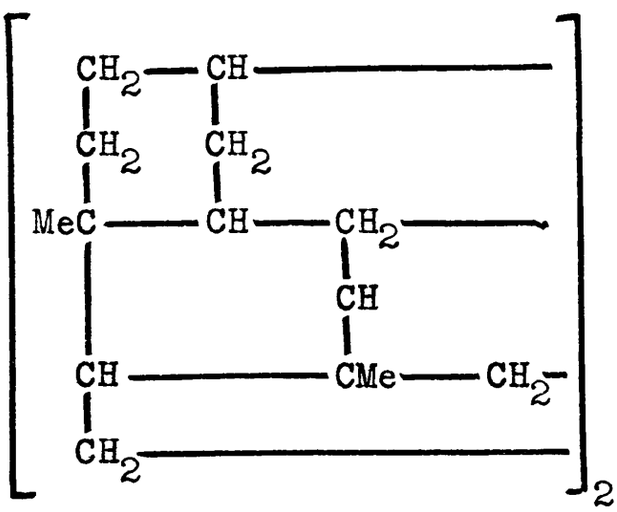
$$\left[\begin{array}{l} CH_2CMe{=}CHCH_2 \\ \vdots\quad\quad\quad\vdots \\ CH_2CH{=}CMeCH_2 \end{array}\right]_n$$

since the data on the molecular size appeared insufficient. It is not clear from his articles whether this structure is supposed to be a "labile polymer" or a qualified acceptance of the Pickles formula $(-CH_2CMe{=}CHCH_2-)_n$ (J.C.S.97,1085 (1910)).

It may be mentioned that Weber (Gum.Zeit.16,561 (1902)) arrived at the formula $C_{100}H_{160}$ or $(C_5H_8)_{20}$ from the limit of sulphur required for complete vulcanisation. Hinrichsen and Kindscher (B.42,4329 (1909)) have obtained 3173 by the

cryoscopic method as the molecular weight of rubber freshly extracted from latex. This corresponds to $C_{275}H_{440}$ or $(C_5H_8)_{55}$. The vapour pressure of the benzene solutions at normal temperatures has indicated a minimum molecular weight of 10,966 (Pohle, Koll. Bei. 13, 53 (1920)). By finding the extent to which the hydrochloride could be dissociated at 100°, Harries gave the minimum size as $C_{20}H_{32}$ (Lichtenberg, A.406,227 (1914)). Finally Plummerer (B.55,3458 (1922)) has concluded from the figures obtained in hydrogenating that the molecule includes more than 20 C_5H_8 units or is larger than $C_{100}H_{160}$.

Boswell and others (Ind.Rub.J. 64, 981 (1922)) have put forward a still more complex structure for rubber, namely $C_{28}H_{44}$ or -



based on the elementary analysis of a number of apparent derivatives of $C_{25}H_{40}$, $C_{20}H_{30}$, etc., which they obtained from rubber by the action of mild oxidising agents (oxygen, hydrogen peroxide,

and permanganate). They make the assumption that rubber is completely saturated (in spite of its forming definite addition products with halogens, hydrohalides, nitrous anhydride, ozone and chromyl chloride,all pointing to its unsaturated nature), and this has been more recently disproved by hydrogenation of the hydrocarbon effected catalytically by Staudinger (H.Ch.Act. 5,755 (1922)), Plummerer (B.55,3458(1922)) and Harries (B.56 (3), 1048 (1923)). The hydrocautchouc was found to be high molecular also, forming colloidal solutions and not distilling without decomposition. Besides this, the presence of the double bond has been demonstrated by optical examination of the solid gum (below).

Staudinger (B.53,1073(1920)) believes that high molecular polymers generally are best represented by chains of indefinite length, and is against the use of "latent valencies" in formulating even the more easily dissociated "labile polymers". He therefore favours Pickles's formula for rubber (above).

Ditmar ("Synth. des Kautschuks", p.12) has adapted an idea of Wechsler (C. News, 100,279 (1909)) in arriving at a spiral modification of the Pickles formula. A somewhat similar one is that of Kirschof (Koll Z.30,176 (1922)) and Barrows (Koll.Z. 15,43 (1914)). In the latter, the alternate double bonds come into approximation, forming successive spiral 8-membered rings.

These structures possess a good feature in inferring the possible existence of partial valences between the periodically recurring double bonds which may partly mask the unsaturated nature of the compound without necessarily altering its ultimate chemical behaviour.

SPECIAL PART

By the reduction of methyl-ethyl-ketone with magnesium to dimethyl-hexanediole following DRP 251330, 251331 and heating this with sulphuric acid after a procedure cited in DRP 253081 for the preparation of dimethyl-butadiene, a diolefine giving an analysis and molecular weight corresponding to C_8H_{14} was prepared which boiled at 67-79°/100 mm. or 123-34°/ordinary pressure. It therefore did not appear to be identical with that mentioned by Herschmann (C.Zent.1893,II,196) boiling at 117-121° which he obtained as a byproduct of the formation of a pinacoline $C_8H_{16}O$. Herschmann does not appear to have determined the nature of his hydrocarbon, but the above was found to be a more or less inseparable mixture comprising principally a new dimethyl-hexadiene (MeCH=CMeCMe=CHMe) as shown by permanganate oxidation to acetic acid. The preferential formation here of a dimethyl derivative rather than the two other possible structural isomers, the diethyl (CH_2=CEtCEt=CH_2) and the unsymmetrical methyl-ethyl (CH_2=CEtCMe=CHMe) compounds would indicate that the first was the most stable form. Two similar cases have been found in the literature, thus dimethyl-diethyl-butindiole (MeEtCOHC:CCOHEtMe) has given dimethyl-octidiene (MeCH:CMeC:CCMe:CHMe) (DRP 241424) and ethyl-butinol (MeC(Et)OHC:CH), methyl-pentinene (MeCH:CMeC:CH) (DRP 290558).

When brominated under dilution at 0°, the hydrocarbon gave an oily dibromide gradually decomposing at 20° with the formation of coloured products like the bromides obtained from dimethyl-hexane-diole itself (Norris and Green, Am.C.J.26, 315 (1901)). It absorbed 4 atoms of bromine on standing at 20°, but hydrogen bromide was evolved at the same time, so that the product could not have been a true addition product.

Although this substance formed a dibromide only, the presence of two conjugated double bonds could be demonstrated optically, as the various fractions exhibited the usual exaltation found for other diolefines substituted by methyl groups between the conjugated linkages.

As the different fractions were observed to show differences in refractive index without corresponding differences in chemical composition, it seemed a question whether the mixture did not contain geometrical isomers of the same hydrocarbon. Harries has discussed the question in his "Kautschukarten", pp. 62-3, in connection with differences of refraction and rotation between two samples of isoprene from different sources. He was able to come to no conclusion, however. Otherwise, no mention of the occurrence of stereo-isomerism among dienes has been found in the literature.

No attempt has yet been made to isomerise the diene by the use of dilute acids, but it has so far resisted any tendency

to undergo refractometric change at 100°, or to polymerise under this condition as judged by its unaltered molecular weight. Concentrated sulphuric acid gave a hydrocarbon boiling at 170 - 190°.

On standing in the air, the diene was transformed into a guminaceous oxidation polymer corresponding to the formula $C_{40}H_{70}O_{10}$, whereas Herschmann's hydrocarbon gave a sticky oil boiling at 200-230° to which he gave the formula $C_8H_{14}O_2$.

In an attempt to get the hydrocarbon another way, brom-butene (MeCH:CBrMe) was made eventually from butyl alcohol through butylene-dibromide by the potash method of Wislicenus (A.250, 231 (1889)). On treating this with magnesium as described by Austerweil (DRP 245180) for the preparation of erythrene or isoprene, a dimolecular product $C_{16}H_{34}O$, boiling at about 160°, was obtained as the chief product. A somewhat similar anomaly was found later in the action of methyl-magnesium-iodide on the dibromide of dimethyl-butadiene, the initial addition product hydrolysing with water to form two dimolecular compounds of the formula $C_{12}H_{20}$, one of which, boiling at 50°/20 mm., may have been the same as that mentioned in DRP 250335, but was evidently different from the dimethyl-menthadiene, boiling at 85°/13 mm. obtained by Lebedew (J.Russ.45, 1249 (1913)) as a byproduct of the polymerisation of dimethyl-butadiene. This is rather

interesting as Lebedew claims that symmetrical dienes will give only one terpene as against the two to be obtained from unsymmetrical compounds.

In order to get a synthetic rubber for comparison with the natural product, dimethyl-butadiene was prepared from pinacone by a number of methods, particularly following DRP 250086 using potash alum as catalyst. The dibromides of this, first prepared by Kondakow (J. pr.(2) 62,166 (1900)) were found to be interesting substances, the halogen atoms being particularly reactive. The constitution of these as 1,4-compounds had been formulated by Kondakow on basis of analogy with the butadiene bromides previously made by Griner (C. r.117,353(1893)), and from the detection of traces of bromacetone and acetylcarbinol among the permanganate decomposition products. The writer has confirmed this personally in the case of the solid dibromide in obtaining an 84% yield of the bromacetone by the use of ozone as recently applied by Bergmann (J.Russ.52,24 (1920)) to isoprene bromide.

Griner had shown that the liquid and solid dibromides of butadiene were apparently the cis- and trans- forms respectively, since the former was convertible by permanganate into the bromhydrine of erythritol, and eventually by potash and water into erythritol itself. This method is not applicable to the above

dibromide, however, as the corresponding tetrol is still unknown. But the liquid bromide was found to give a lower refractive index than the solid like the cis-form of butadiene-dibromide (v.Braun, B.55 (B) 3536 (1922)) although the molecular refraction turned out to be rather higher than that of the solid, possibly owing to the error at the temperature necessary for the observation (50°). The higher melting-point of the solid, and its lower solubility (in organic solvents) would, of course, be some indication of its being the trans- form were it not for the fact that the liquid compound had the greater molecular volume (at 50°). Again the liquid showed little tendency to isomerise into the solid form when heated to 100° although it is true that on distilling under reduced pressure the distillate was observed to crystallise more readily than the original sample (N# 84, 85). On the other hand, when the solid was heated for a time with some of the diene, partial isomerisation to the liquid compound occurred. A similar reaction took place on treating the solid with magnesium and ether.

It occurred to the writer that it might be possible to distinguish between the two by the fact that the cis- form should show the greater tendency to form ring compounds with ammonia, potassium sulphide and so on. As it turned out, v. Braun (ibid) had previously made one such compound by heating dimethylamine

with the solid erythrene-dibromide and his technique left little to be desired since the cyclic quaternary salts so formed were readily separable from the ditertiary derivatives obtained as byproducts. The solid and liquid bromides of the dimethyl compound were therefore allowed to stand for equal intervals of time with ethereal solutions containing the calculated amounts of diethylamine, when the bases were separated as their gold bromide salts as described below; and it was found that the liquid bromide did give more quaternary and less ditertiary salt than the solid isomer. The two ditertiary salts, melting at 177 - 9° were found to be identical as shown by mixed melting-points. The quaternary salts, however, though similar in composition, had widely different melting-points, that from the solid melting at 52 - 8°, from the liquid bromide 101 - 3°. Perhaps the difficulty here was that in the liquid bromide one has to deal with a mixture rather than a chemical individual. This is probably the reason why Kondakow was able to get the same tetrabromide from both liquid and solid dibromides; he has made no mention of the yields in either case.

A number of other basic derivatives of the solid dibromide were prepared, such as the dipyridonium compound, separated as the bromide, m.p. 124° and the platinichloride, m.p. 229°; a ditertiary-dimethylamine derivative separated as a di-aurichloride,

m.p. 188-9° and the corresponding quaternary compound separated as a platinichloride, m.p. 199°. Methylaniline gave only a di-tertiary base, m.p. 76-7°. As the latter derivatives were made at 100°, it appears that the failure here to form a cyclic structure was due to steric difficulties (see Fischer, B.33,345,1967 (1900)).

In addition to the above, the solid dibromide gave with sodium ethylate a diethyl-ether boiling at 90-95°/20 mm. (N#70), and the diene itself gave an addition compound with sulphur chloride separated by chlorination as a sulphoxide boiling at 139-141°/29 mm. (N#74 etc.). No compounds of the diene were got, however, with antimony chloride at 20° and with sulphur at 100°. This is in agreement with the failure of Steinkopf to get a thiophene derivative from isoprene and sulphur at the same temperature (A.403,11 (1914)).

The dimethyl-butadiene was converted into the normal rubber by prolonged heating at 100° following DRP 250335. For the purpose of observing its optical behaviour, it was deposited from solution in the form of a transparent sheet suitable for use in the Abbe refractometer by a special procedure described below. By the use of these sheets, reasonably exact refraction figures were got for both this and purified natural rubber. The molecular refractions so obtained indicated precisely one

double bond for each polymerisation unit, although Gladstone and Hibbert (J.C.S. 53, 679 (1888)) had been unable to get uniform results using rubber solutions. The figures showed the disappearance of one double bond in the polymerisation of the diene and the absence of conjugation between the units of the polymer. A slight degree of optical depression observed in both rubbers might or might not have been attributable to a certain amount of "mutual saturation" between the double bonds of the polymer as would be expected with a structure like that of Ditmar's (above).

A number of preliminary runs of isoprene have been carried out with amylene bromide following DRP 255519 using a barium chloride catalyst and from dipentene with a modification of the isoprene lamp, but this is as far as the preparation of the normal isoprene rubber has been taken at present.

Besides the above, an amount of additional experimental work has been done on antimony compounds in order to get the master's thesis in a form suitable for publication.

Experimental

Dimethyl-hexane-diole. The glycol, first made by Lawrmowitsch (A.185,124 (1877)), was obtained by Norris and Greene (Am.C.J. 26,315 (1901)) in 11-14% yield by the reduction of methyl-ethyl-ketone with sodium and moist ether. These writers did not observe its formation with aluminium amalgam, but the use of magnesium and aluminium with mercuric chloride has been outlined in DRP 251330, 251331, which note also the use of inert diluents like benzene or halogen-hydrocarbons, with or without antimony chloride, cuprous chloride and iodine. Practically, the magnesium reduction takes at most 2-3 hours, aluminium, however, up to 10 hours at 80°.

This compound is not as readily made as pinacone itself; at any rate the technique is more exacting. Thus, reducing in presence of excess ketone after the style of Richard and Langlais (see table III) (K#61), the yield was nil; so that the use of a diluting agent other than this was necessary. On the other hand, when too much benzene was used (K#81) the yield was reduced because the mercuric salt was precipitated unchanged and amalgamation was consequently slower. A good mean between the above has been found in K#96, the crude yield being as high as 41%. Sodium (K##75,77) was observed to give low yields, zinc and iron none at all (K##43,103). Aluminium appeared capable of giving

good yields under the best conditions, but magnesium has been preferred because of its convenience, though it has a drawback in forming a gelatinous addition compound with the pinacone.

The metal was used preferably in the form of clippings or shavings since the powdered metal, even under vigorous agitation, tended to form a lump (K#98). Where previously made amalgams were used (K#64) or where iodine was used as amalgamation catalyst (L#14) no external heat was needed and any amount of diluent could be used, without, however, improving the yield.

After the reduction was complete, the procedure was to decompose the magnesium compound with water, salt the pinacone out with caustic alkali following Norris and Greene (above), dry the benzene solution and distil in a vacuum.

The pinacone was purified by refractionation, when it came over between 124-7° at 55 mm., this being 55% or even more of the crude sample. One such sample analysed as follows (K#55b).

Calc. for $C_8H_{18}O_2$	C 65.8	H 12.33
Found	66.4	11.94
	66.2	12.52

It boiled at 200-202° and had $n_D^{25.25°}$ 1.4505 (K#65). It was not completely water-soluble owing to the presence of a small amount of oily impurity. It therefore melted at 22.5° only. According to N. and G. small amounts of impurity are sufficient to prevent crystallisation. The constants in the literature are :

b.p.200-205°(L.)205-205.7°/752mm.(N.&G.);m.p.28°(L.)49°(N.&G.) sp.g.0.9529 at 25°/4°;n_D25.25° 1.4521(N.&G.).

V

Preparation of the Glycol

Control	M red.agent	M ketone	M amalg.ag.	M dil.	B.p.	Yield
K 41	.75 Mg	1.67	.037 $HgCl_2$	2 C_6H_6	105-35°	25.35%
42	.5 Al	1.25	.033	1	100-40	37.85
43	1.224 Zn	1.25	.037	1	100 up	0
47	1 Al	2.5	.066	2	120-35	21.88
47b	2	5	.122	4	"	8.58
48	1	2.5	.066	1.1C_7H_8	"	12.56
49	1	3.35	.066	0	"	9.88
53	1	3	.074	0	"	12.88
58	1	3	.074	200ccEt_2O 120ccC_7H_8	100 up	0
61	.5 Mg	3.35	150g.Hg	0	125-35	0
64	.5	1.11	"	1.27 C_6H_6	120-35	33.8
65	1.5	4.86	.074 $HgCl_2$	6.66	120-35	28.4
75	1.35 Na	1.69	.037	4	"	9.46
77	1	1.33	.037	100ccC_6H_6 75ccC_8H_{10}	"	12.17
79	2 Al	5	.1293	3.5 C_6H_6	"	6.89
81	1 Mg	2.333	usual	5.11	"	14.88
96	1	2.22	.0747	2.13	"	41.2
98	1	2.22	.112	2.13	"	30.73
103	1 Fe	2.22	.0747	2.13	100 up	0
L 14	1 Mg	2.22	same, lg.I_2	2.13	120-35	38.6
21	1	2.22	same, lg.Cu_2Cl_2	2.13	"	36.2

The hydrocarbons C_8H_{14}. By following procedure such as in DRP 253081 and heating say 10-30 g. of the above glycol with a single drop of dilute sulphuric acid (20% by weight), at bath

140-50° in this case rather than 130-40° since the hydrocarbons here are of rather high boiling point, considerable oil and water collects in the receiver. For examination this has been mechanically separated, shaken in a small funnel successively with small quantities of $CaCl_2$ till no further partition occurred and the oil became transparent. As, however, it was observed to oxidise to a gum after exposure for a day or two, the drying has been completed most satisfactorily by sealing up with the $CaCl_2$ for a number of days in a largely evacuated ampule (28 mm.). The oil was then dry enough for fractionation, which was effected preferably under partly reduced pressure as a certain amount of charring etc. was to be observed under the ordinary conditions. Completely drying the oil by repeated distillation over small amounts of Na as mentioned by Couturier for dimethyl-butadiene was not applicable here since it appeared to cause a polymerisation with the loss of the oil. The crude yield in one case (K#67) amounted to about 84% of the theoretical, but this was unusual. The dried crude product naturally varied somewhat in composition, but one sample gave the following analysis (K#63)

Calculated for C_8H_{14}	C	87.26	H	12.73
Found		86		13.13
		86.3		13.17

It also gave the following molecular weights in benzol :-

VI

g. C_8H_{14} in 100g. soln.	M. Wt. found	Supercooling °C.
1.125	108.2 (Calc.110)	.233
.568	99.8	.0975
.568	110.4	.555
.3833	108	.295
.23825	113.6	.2325
.159	109.7	.16

A larger sample was fractionated (K#69) with the result that here impurities containing oxygen were detected as well as the hydrocarbon C_8H_{14}, boiling at 64-76°/100 mm. The complete examination of these has been tabulated below (VII). The hydrocarbons did not freeze at -30°.

VII

Fract. No.	b.p. 100mm.	b.p. n.	M.wt.	n_D^{25}	Atoms Br		Analysis	Found	Wt
1	64-71°	123-8°	108.8 108.6	1.4529	2.21	C_8H_{14}:	C87.25 H12.73 O 0	86.75 12.62 .63	1.4 g.
2	71-3	abt.131	104.2 108.8	1.4598	1.377#	C_8H_{14}	C H O	86.5 12.77 .075	3.5
3	73-5	132-4	95.2 99.2 111.8	1.4629	2.085	C_8H_{14}	C H O	86.8 12.95 .25	2.3
4	75-6	133-4	108.85	1.4637	2.025	C_8H_{14}	C H O	87.7 12.49 .19	4.3
5	up to 100° at 44.5mm.	141-3	115.2 113.3	1.4570	1.665#	$(C_8H_{14})_2O$	C81.3 H12.33 O 6.78	##	4.8
6 (residue)	indef -inite		126.3 137.4	-	-	$C_8H_{18}O_2$	C65.8 H12.33 O21.87	68.7 10.28 21.02	1

; ## - See next page

Error due to small quantity used when tit. with Br_2 direct in CS_2 at 0°.

Found C 82.6 81.25 82 avge. 81.95)
H 11.94 12.25 11.48 11.89) probably a mixture of
O 5.46 5.5 6.52 5.83) diene & pinacoline.

Identification as Dimethyl-hexadiene. - Ozonation of the fraction boiling above 70° at 100 mm. with moist ozone in carbon tetrachloride solution gave formaldehyde as the only recognised product. (K#82). In ethyl chloride solution the dry gas led to an oily ozonide, gradually dissolving on warming to boiling with water; the solution contained some formaldehyde and a higher aldehyde as well as some unrecognised acids (K#108). Diketones have not been recognised among the products, probably owing to the formation here of a monozonide giving rise rather to other products than to the diketones.

A more definite result was got with permanganate. The oxidation of a water suspension of the oil has been at such a concentration (3%) as to split the compound at the double bonds and completely oxidise the various residues to simple acids. Some difficulty was experienced at first in attempting to separate the acids by means of their basic lead salts after the method of Linnemann (A.160,233 (1871); also Haberland, Z.An.38,217(1899)) owing to the fact that the propionate, for instance, readily forms greatly supersaturated solutions. By the use of sufficient

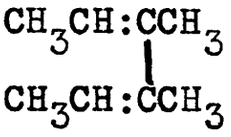
permanganate, however, the formate was completely destroyed and the acid was recognised by separation in the form of its readily crystallised and definite silver salt. The salts of acetic and propionic acids have about the same solubilities, so that if a mixture were obtained, the various crops should consist of mixed crystals. When the oxidation filtrate was neutralized with nitric acid and evaporated at 100° with excess silver nitrate (L#2), the first crop after drying analysed 64.6% Ag. The second crop turned out somewhat higher (65.3%), owing to contamination with metallic silver. The silver content of successive crops is given in the following table: (K#115) -

VIII

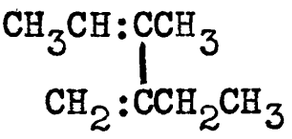
Silver salt from permanganate oxidation

Crop	Weight	Ag found	Calc. for CH_3COOAg
1	1.5005 g.	63.4 %	64.7
2	.0548	63.83	
3	.3003	63.85	
4	.1225	64.15	
5	.2080	64.2	
total	2.1861	or 25.55% of the theoretical maximum.	

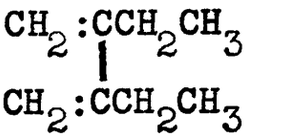
Of the three possible formulae for this compound, the first below, the hexadiene, is the only one that would give pure silver acetate free from at least an equivalent of propionate -



3,4-dimethyl-hexa 2,4-diene



3-methyl-4-ethyl penta-2,4-diene



2,3-diethyl-buta-1,3-diene

It did not appear to make any difference in the result whether the permanganate solution was added portionwise or at once; generally not more than about 80% of the calculated amount was added owing to the fact that the oxidation became very slow beyond this. Of course, the filtrate was further oxidised till permanently pink at room temperature. A considerable excess of silver nitrate was preferred as this helped in the crystallisation. The more recent oxidations have been concentrated under reduced pressure in order to prevent the auto-reduction of the silver salts which occurs at 100°. In this way it was found that the 2nd fraction of diene from K#90, boiling at 71-3°/100 mm., gave practically pure silver acetate.

IX

Calc. for CH_3COOAg		Found	Remark
Ag	64.7	64.6	Normal pressure (L#3)
		65.3	
		64.2	
		64.3	In vacuo (L#30)
		64.3	
		64.25	

A subsequent run, however, did not give a product of the same purity, as may be seen from an examination of the following table.

X

Fractionation and analysis of crude C_8H_{14} (L#11 et seq.)

No.	b.p./100	Wt.	n_D^{25}	Ag in Ag salt		Analysis		
1	62-7	1.9	1.4505	63.2		C	H	
2	67-8	3.8	1.4556	63.3	63.25	87.25	12.75	(calc. for C_8H_{14}
3	68-9	3.6	1.4565	62.9	62.75	-	-	
4	69-70	4.6	1.4584	63.4		-	-	
5	70-72	2	-	-		-	-	
6	72-3	4.3	1.4637	64.6	64.8			
				62.7		86.7	13.06	(found)
7	73-4	4.5	1.4660	63.7		-	-	
8	74-5	1.7	1.4669	63.15		-	-	
9	75-6	2.7	1.4680	63.65	63.7			
				62.95#		-	-	
10	76-83	4.8	1.4660	64.25	64.0			
				64.4		86.7	12.31	
11	above 83	5.7	-	-		##		

38.6(67.2%) # $Ba(MnO_4)_2$ gave salts of 63-25 - 64.2% Ag.

Probably contaminated with the pinacoline compound, b.p. 145-50° (Lawrinowitsch) as in the 5th fraction, table VII.

The refractive indices here rose steadily to a point at the 9th fraction. As the differences between the first and last were rather wide, these were taken to indicate the presence of isomers, either structural or geometric. The oxidation would indicate something of the former. With regard to the possibility of the latter, no mention has been yet noticed in the literature of the occurrence of geometric isomers among diolefines excepting Harries's speculations mentioned above.

Several preliminary experiments seemed to indicate that the various fractions could be isomerised to a pure hexadiene by heating, the analysis of the silver salt being materially improved.

XI

Behaviour of C_8H_{14} samples on heating (L##107,113,117,122)

Controls	Time at 100°	n_D^{25} Before	n_D^{25} After	M Before	M After	Ag in salt Before	Ag in salt After
L#11(3)	1-2 hrs.	1.4565	1.4568	-	-	62.75 62.9	63.7 63.4 63.4
L#11(4)	"	1.4584	-	-	-	63.4	63.7 63.7
L#11(7)	"	1.4660	1.4661	-	111.3	63.7	64.4 64.05
L#11(8)	2 days	1.4669	-	-	109.3	63.15	64.4

In the above no change in index or molecular weight took place. On repeating the above on a mixed sample, the same was noted, but in addition no appreciable change in the composition of the silver salt occurred; so that in the above the differences must have been accidental. The error in the oxidation analysis then appears appreciable.

XII

Effect of heating amixed sample of C_8H_{14} at 100° (M#10)

Time	n_D^{25}	Ag in salt	M	D
0	1.4625	63.85,64.15	-	-
3 hrs	-	63.9 ,63.4	-	-
4 days intermittent	1.4631	63.45,63.82	109.3 (M#40)	.7782627 at $\frac{27}{4}$ (M#39)

The samples were heated in sealed tubes at about 28 mm. Under these conditions it is apparent that there is no tendency to polymerise.

Molecular Refractivity of C_8H_{14} Mixture. The specific gravity compared to water at 27° (balance temp.) was found by the procedure of Ostwald (H.Meyer, "Konstitutionsermittlung", p.151) using a 0.5 cc. pipette, and this changed into the comparison figure for water at 4° after the formula (ibid, p.150). In order to avoid error the index was read on the Abbe instrument with the same thermometer at 27°. From these figures the M_D was calculated by the Lorentz and Lorenz formula. To get the exaltation, from this was subtracted the M_D calculated by the constants obtained by Conrady, which are those that Eisenlohr appears to use in his calculations (Auwers & Eisenlohr, J. pr. 82,65 (1910). The assembled data were: d27/4, 0.7782627; n_D^{27}, 1.4622; M_D found 38.68 (calc., 38.1; Eisenlohr gives 38.14 for C_8H_{14}/2). The EM_D was therefore 0.58# . Now for isoprene, di-isopropenyl, etc., the EM_D runs plus 0.51-0.82, while for pentadiene, hexadiene, etc., this varies from plus 1.02-1.71; so that the above product resembles the other diolefines substituted by methyl groups between the conjugated linkages.

The corresponding monosubstituted compound MeCH:CMeCH:CHMe prepared from methyl-hexenol (MeCH:CMeCHOHEt) by the action of potassium bisulphate gave according to Abelmann (B.43, 1574(1910)) no exaltation, but Eisenlohr (above) found the EM_D 1.08

The different fractions of dimethyl-hexadiene were found to have the same molar refraction: (M##82,93)

XIII

Fract.	b.p./100mm.	n_D	d_4^t	M_D	M_D calc./$\bar{2}$	EM_D
1	below 67°	$1.4544_{20.1}$	0.7667	38.88	38.1	0.78
2	67-70°					
3	70-73°	$1.4647_{19.2}$	0.7832	38.78	"	0.68
4	73-76°					
5	76-79°	1.4688_{20}	0.7895	38.75	"	0.65

On allowing a sample of the diene to stand for several months over metallic sodium, the latter was found to dissolve without evolution of hydrogen, a gelatinous substance being formed which was changed by alcohol into a resin (W#1). The diene on washing and drying, however, was found to be unchanged; found n_D^{25}= 1.4636, originally = 1.4631.

Change Effected by Sulphuric Acid. - When the diene was dissolved in 4 volumes of concentrated sulphuric acid and precipitated out again by water, it was found to have changed from a thin oil to a viscous liquid (L#13), the boiling-point rising from about 130° to 170-200°. The substance was found to contain some oxygen as indicated by the analysis (C=85.4, H=12.69). The index also had risen from 1.4650/25° to 1.4915/25°. By neutralising with barium carbonate and evaporating the filtrate a slight quantity of salt was obtained but this was found to be largely inorganic

(from the carbonate) as it gave very little insoluble residue on combustion and conversion into barium sulphate. Couturier (Ann.Chim.Ph.(6) 26,485(1892)) had mentioned a disulpho-derivative of di-isopropenyl obtained the same way by the action of sulphuric acid, without, however, mentioning his method of separation. The oil described above, of course, was probably an impure dimeric compound.

Autoxidation - A sample of diene allowed to stand in limited access of air for a week or more gave a colourless gum, which was extracted with methyl alcohol to remove byproducts. The residue, after drying in the oven, was brought into a boat by dissolving in ether and evaporating this off again. Analysis:

(M#9)	Calc. for $C_{40}H_{70}O_{10}$	Found
C	67.65	67.1
H	9.85	10.01

The substance was evidently a peroxide, since, although negative to potassium iodide, it gave a stronger brown peroxide reaction with titanic oxide than did ordinary hydrogen peroxide. The molecular weight found for the benzol solution was 640 (calculated 710).

Butyl Bromide - By treating butyl alcohol with hydrobromic acid after the method described by Adams (Organic Synthesis,I,p.5) the highest yield obtained was 73.1% (K#110).

2,3-Dibrombutane - Attempts to get the 1,2-dibrombutane from butyl bromide by the catalytic method of Reboul (Bull.(3) 7,125, (1892)) were without success (K#59), the dibromide formed after several weeks being negligible. The method of Linneman (A.161, 199(1872)) gave 15.5% of a dibromide boiling at 170-80 (K#97), probably the 1,3- compound. As Herzfelder had used iron as a catalyst (B.26,1260 (1893)), this was tried in conjunction with the method of Reboul, 32.8% of dibromide being obtained (K#99), boiling, however, at 158-161°; that is, the 2,3- compound. Meyer and Müller (J.pr.(2) 46,181 (1892)) had previously noticed this isomerisation of the 1,2- compound to the 2,3- compound on heating with iron. A recent example of a similar reaction (v. Braun, B. 55(B),3526 (1922)) is the conversion of 1,4-dibrombutane to the 1,2,3-tribromide with iron and bromine. Sulphur, iodine and aluminium were found to have no effect as catalysts (L#56). Yields of 22.6% were later obtained quickly by brominating at 100° in the presence of iron powder (L#53). A 53.4% yield was obtained also from butene obtained from butyl alcohol and thorium oxide at 450° (L#77). Analysis :

	Calculated for $C_4H_8Br_2$	Found
Br (lime)	74.1	73.8, 76.5 (L#26,32).

3-Brombutene(2) - It was found best to use an excess of potassium hydroxide in the hydrolysis of the dibromide by the

method of Wislicenus (A.253,231 (1889)), since where this was not done some of the latter remained unchanged, owing to the formation of an amount of butine as a byproduct (L#33,etc.). 263 g. of dibromide (1M), 82 g. of KOH (1.2 M) and 400 cc. of methyl alcohol gave 124.7 g. of brombutene, b.p. 89-93°, or 75.8% (L#71). An analysis of two earlier samples :

	Calculated for C_4H_7Br	Found	
Br (lime)	59.3	55.7,55.7	(L#31)
		57.3	(L#35)
M (benzol)	135	133.7	(M#44)

This bromide is known in two forms (Wislicenus), the above being described as the "high-boiling" modification.

Condensation of 3-Brombutene(2) with Magnesium - There appears to be an error in the Austerweil patent previously referred to (DRP 245180) in making reference to a magnesium compound of vinyl bromide, although Grignard reagents of acetylene compounds are known. For instance, Grignard himself was able to get allyl iodide to react with only one-half atom of magnesium, the resulting mixture not showing the usual reactivity of the reagents (C.r.132,561 (1901)). The matter has been cleared up by Meisen heimer & Casper (B.,54,1655 (1921)), who found that the compounds got were nothing other than two-phase ether solutions of diallyl and the compounds MgI_2 (or $MgBr_2$) plus $2Et_2O$. The reagent of the olefine is so unstable that it immediately reacts

with any unchanged halide.

The high-boiling brombutene above was able to dissolve only one-half atom of magnesium, iodine being added as catalyst. On carrying out the reaction in air and decomposing with ice and dilute acetic acid (L#39), the following fractions were separated:

XIV

Fract.	b.p.	Composition
1	38-41°	ether, n_D^{20} 1.3538 (found, n_D^{20} 1.3540
2	70-90	brombutene
3	100-150	oil with irritating, onion-like odour
4	abt. 185	dark oily residue

The third fraction included an oxidation product:

Calc. for $C_4H_8O_2$	$C_4H_9O_2$	Found (average of 3)
C 54.6	53.85	53.275
H 9.085	10.125	9.3725

A second experiment (M#7) gave the following fractions, showing no trace of the desired diene, but giving an impure dimolecular compound as the main product :

XV

Fract.	b.p.	Composition
1	abt. 34°	ether
2	" 86	brombutene, n_D^{25} 1.4562 (found 1.4510)
3	" 160	oil with character like above, n_D^{25} 1.4735.

The last fraction analysed:

Calculated for $C_{16}H_{34}O$		Found
C	79.3	80.2
H	14.05	13.82
M (benzol)	242	208.2

Pinacone Hydrate - The method of Richard and Langlais (Bull.(4),455 (1910)) gave a yield of only 31% (L#90), possibly owing to poor amalgamation. By the procedure described in DRP 233894, however, the product was obtained in 42.3% yield (L#111), iodine being added as a catalyst.

Dimethyl Butadiene - The hydrate on treatment with sulphuric acid or potassium bisulphate led mainly to pinacoline (N#94), the same being true of the action of the bisulphate on the water-free glycol (L#110) following DRP 246600. In an attempt to follow DRP 235311 by leading pinacoline and carbon dioxide over alumina at 420-40°, the yield was only 20%, high-boiling oils being formed (L#114). However, the product got from the water-free pinacone by sulphuric acid (DRP 235081) was found to be mainly diene (L#131).

The pinacone was not easily dehydrated by distillation methods, but the water was to be separated by melting the hydrate over various dehydrating agents like caustic alkalies or potassium carbonate, the yield in the last case being best (L#109). With potassium hydroxide a 62.5% yield of glycol,

boiling at 79.5°/21 mm., was obtained, (M#121). The glycol usually came over entirely at 172-4° at ordinary pressure. Following DRP 235081 as mentioned the pure diene gave a sharp fraction at 69-70° using a bead column; n_D^{20} 1.4376 (1.4377/20°, Kondakow). The molecular weights in benzol were 85.2, 85.9 (L#131), calculated, 82. Analysis :

Calculated for C_6H_{10}		Found
C	87.8	88.1, 88.2
H	12.2	11.72, 12.84

This method gave yields of from 35.5 to 42.75% of diene (M#85, N#4) and 20.4% of pinacoline (M#85). By using 2% of sulphanilic acid a 55% yield of diene was obtained (N#49). Using 10% of potash alum (following DRP 250086) and separating from the pinacone hydrate with an Anschutz attachment, the diene fraction amounted to 59.7% (N#58). Its formation was accompanied by 22.05% of pinacoline and 4.93% of hydrate. To avoid mechanical losses in the above it was necessary to fractionate once only, using, however, an effective column.

Dimethyl-butadiene Dibromides - Kondakow's solid and liquid dibromide (above) were prepared by brominating at 0° in carbon tetrachloride, ether (L#131) or ethyl chloride solution (N#81). The solid was obtained free from the liquid isomer by washing with methyl alcohol, when it melted at 45-6° (Kondakow gives the figure 47°). Analysis:

	Calculated for $C_6H_{10}Br_2$	Found	
Br (Boubigny & Chavanne)	66.1	65.2	(M##45,49)
M (benzol)	242	239	(M#45)

This solid was found to boil at 105-110°/18.5 mm. (N#84), the liquid modification obtained as a residue of successive crystallisations boiling also at 105-110°/18.5 mm.

The optical data on the solid: n_D^{50} 1.5470, D_4^{50} 1.6912, M_D 45.3 (45.04 calculated for $C_6H_{10}Br_2$ (N#10)), V_m^{50} 143.1.

Data on the liquid: n_D^{50} 1.5390, d_4^{50} 1.6502, M_D 45.85 (N#10), V_m^{50} 146.6.

In the bromination of an old sample of diene a certain amount of a polymeric bromide of indefinite melting-point was obtained. This was insoluble in the usual cryoscopic solvents excepting phenol, in which it dissolved with a purple colour (phenoxy- compound, Weber, B. 33,779(1900)). Found 46.7% Br ($C_{12}H_{20}Br_2$ requires 49.35% Br (M#87)). The substance dissolved in carbon disulphide but came out again as a gum.

Ozonation of Solid Dibrom-dimethyl-butadiene - On oxidation of the bromide with 3% permanganate in ether solution an unrecognised oil was obtained giving the following figures $n_D^{24.8}$ 1.4740, $d_4^{24.8}$ 1.4232, Br 48.85% (N#8). Oxidation with various amounts of chrom-acetic acid at temperatures from 50-90° gave traces of brom-acetone (N##66,69).

The ozonation of the bromide was effected in acetic acid as well as in ethyl chloride, but the acid complicated the sub-

sequent separation of the decomposition products (N##79,80,81).

The procedure finally adopted (N#83) was as follows :

3 g. of solid bromide dissolved in about 20 cc. of ethyl chloride was treated in a freezing-mixture with a stream of ozonised oxygen and carbon dioxide until the ozone was no longer absorbed (which was indicated by the smell of the emitted gas, the liberation of iodine from potassium iodide solution and the formation of a cloud above the latter). The solution was poured into a distilling flask and distilled with 30 cc. of water. The ethyl chloride came over first and escaped, later the brom-acetone came over with the first 10 cc. of water. This measured 1.75 cc. or 84.15% of the calculated amount. The distillate was positive to Congo Red (mineral acid) but negative to Fehling's solution (no aldehydes). For analysis the oil was taken up in ether, dried and distilled. All came over at 44-6°/20 mm. Colourless, intensely lachrymatory oil. Analysis:

	Calculated for C_3H_5OBr	Found
Br (Bacon)	58.4	58.1
M (benzol)	137	132.2

Isomerisation - It might be supposed that a simple method of arriving at a normal rubber would be through the 1,4-halides by the action of metals, but such has not been the experience so far.

Thus when the solid bromide of di-methyl-butadiene was refluxed with the calculated amount of zinc dust and 90% alcohol until the smell of the bromide had disappeared, the ether extract on brominating was found to give crystals melting at 42-3°, indicating that the product of the reaction was dimethyl-butadiene itself (N#62).

Similarly when the bromide was treated with less than the

calculated amount of magnesium in dry ether, no trace of a rubber or the compound $C_{12}H_{20}Br_2$ was obtained. The sole product separated here was an oil boiling at about 100°/20 mm., which was recognised by its molecular weight (229.4) as the liquid modification of dimethyl-butadiene-dibromide (N#19).

The same isomerisation was effected by heating the solid bromide to 100° for 12 hours with a molecular part of diene (N#18); here the products were unchanged diene (b.p. 70°), solid bromide (m.p. 43-4°) and liquid bromide (M 220.2, 219.8).

Formation of Terpenes - In an attempt to arrive at dimethyl-hexene, the bromide was added gradually to an ethereal solution containing an excess of magnesium methyl-iodide. Self-warming indicated the occurrence of a reaction. The solution was then treated with ice and any unchanged halides eliminated from the ether extract by the use of an excess of diethylamine. After extracting finally with dilute mineral acid and drying, the extract was fractionated, when the diene (recognised as its bromide, m.p. 45-6°) came over at 70°; at 50°/20 mm. an oil smelling like a terpene was obtained. The still residue contained an oil with a powerful smell. Both these oils were dimolecular products, as shown by their molecular weights (benzol (a) 163.2,166.4; (b) 168.8 168.2; as against 164 calculated for $C_{12}H_{20}$) (N#16).

Dimethylamine Derivatives - The procedure for making a cyclic

quaternary pyrrolinium compound by the action of dimethylamine on erythrene dibromide has been described by v. Braun (B.55 (B), 3536 (1922)). The corresponding derivative of dimethyl-butadiene was prepared by heating the solid dibromide with 2 molecules of dimethylamine (prepared by Menschutkin's method (C. Zent. 1898, II,478) in about 15 parts of benzol. After about 4 hours at 100°, the salts were extracted with dilute hydrochloric acid and the acid extract, after shaking with ether, was made alkaline and extracted again several times with ether to remove the tertiary base. On making acid again to Congo Red the solution gave a copious precipitate of a red gold bromide salt with gold chloride solution. For analysis the quaternary compound was separated less quantitatively as a sparingly soluble yellow platinichloride, melting at 199° with decomposition. Analysis: (N#68)

Calculated for $C_{16}H_{32}N_2Cl_6Pt$		Found
Pt (combustion)	29.55	29.9

The combined ether extracts, after washing with water, were extracted with dilute hydrochloric acid, made just acid to Congo Red, and the ditertiary salt separated as an insoluble yellow gold chloride salt melting at 188-9°. Analysis :

Calculated for $C_{10}H_{20}N_2Cl_8Au$		Found
Au	46.35	47.2.

As the yield of this salt amounted to 23.45% of the calculated maximum, it seems that the tendency towards ring formation at 100° is not as great here as with v. Braun's compound.

Action of Diethylamine on the Solid and Liquid Bromides -

Equal weights of the solid and liquid bromides dissolved in about 50 parts of ether were treated dropwise with 2 molecular proportions of diethylamine in an equivalent part of solvent. After a day and a half the two mixtures were evaporated and the products separated as insoluble gold bromide salts (N##38,39).

The solid bromide gave an 11.55% yield of a quaternary salt, melting at 52-8° (from ethyl acetate), Au found 28.78%; 27.2% yield of a tertiary salt melting at 177-9°.

The liquid bromide yielded 26.75% of a quaternary salt melting at 101-3° (ethyl acetate), Au 29.75%, and a 21.22% yield of a tertiary salt melting at 179-81°, Au 31.1%.

The mixed melting-point of the ditertiary salts was 177-9°, indicating identity. That the liquid bromide is capable of yielding two salts similar to or different from those of the solid individual is taken as an indication of its comprising a mixture. (See introduction).

These gold bromide salts, however, were not pure, as shown by the following analyses. The quaternary salt melting at 101-3° was recrystallised from ethyl acetate: dark red needles,

m.p. 106.7°. Analysis : (M#87)

Calculated for $C_{10}H_{20}NBr_4Au$		Found
C (Lead chromate)	19.35	18.35, 18.33
H	3.2	3.19, 3.18
Au	31.6	28.34, 29.15

The tertiary salt was purified by dissolving in methyl alcohol and precipitating with ether: orange powder, m.p. 177-8°. Analysis : (M#87)

Calculated for $C_{14}H_{32}N_2Br_8Au_2$		Found
C	13.32	14.825, 14.55
H	2.536	3.006, 3.288
N (Kjeldahl)	2.22	2.268
Au	31.3	32.68, 32.6

Diquaternary Pyridonium Salt - When the solid bromide was dissolved in about 20 parts of pyridine, the solution crystallized shortly in white needles, melting at 124° (from ether. Analysis : (N#6)

Calculated for $C_{16}H_{20}N_2Br_2$		Found
C (Lead chromate)	48	48.4
H	5	4.4
Br (Baubigny & Chavanne)	40	37.78, 38.36

A better analysis was obtained of the insoluble yellow platinichloride, melting with decomposition at 229° -

Calculated for $C_{16}H_{20}N_2PtCl_6$		Found
Pt	30.08	29.93

Ditertiary Methylaniline Base - Methylaniline (1.25 cc.), dibromide (1.377 g.) and 10 cc. of benzol were heated to 100°

for 3 hours. After separating the secondary and tertiary bases, the water solution was colourless and gave no precipitates with picric acid, gold or platinum chlorides (no quaternary salt formed; see introduction). The di-tertiary base was separated from unchanged methyl-aniline by recrystallisation from 90% alcohol: colourless leaves, m.p. 76-7°. The analysis, however, has not been very satisfactory (N#61).

Calculated for $C_{20}H_{26}N_2$		Found
C	81.7	80.7
H	8.84	7.325
N (Kjeldahl)	9.52	7.69
(titration)		7.37

Sulphur and Antimony Chloride and the Diene - When heated several hours at 100° with a benzene solution of dimethyl-butadiene, sulphur gave no thiophene derivative. The solid residue from the fractionation melted at 110-15° and analysed 101.3% S (Kratz) (N#52). Similarly when antimony trichloride was allowed to stand several days with a methyl alcohol solution of the diene, the colourless product isolated by precipitation with cold water and centrifuging was found to be antimony trioxide. Total Sb found, 81.25% (Sb_2O_3 requires 83.3%) (N#50).

Polymerisation of Dimethyl-butadiene - In the heat polymerisation following DRP 250335, the addition of various supposed catalysts (such as sulphur, natural rubber, acetic acid, piperidene, solid caustic soda, and zinc phenyl-methyl-dithiocarbamate)

was found to have no advantage (L#130, M#30), piperidine even keeping the substance liquid. One sample heated alone in a sealed tube for about two weeks at 100° was observed to have changed in molecular weight from 85.5-85.9 to 125.9 (M#35). For analysis, the rubber was separated by evaporation and precipitation from ether solution by alcohol. The alcohol was driven off in vacuo at 100°, and the rubber dried several days in a vacuum over sulphuric acid (M#70).

Calculated for $(C_6H_{10})_n$		Found
C	87.8	88.8
H	12.2	12.38

Optical Examination of Rubbers - By the use of benzene and toluene solutions of natural rubber, Gladstone and Hibbert (J.C.S. 53,679(1888)) had been unable to get uniform molecular refractions for natural rubber. The same procedure gave widely varying figures in the experience of the writer also (N#34). Constant results, however, have been got with rubber sheets (M#91) prepared by dropping ether solutions of rubber on to metal foil coated with a layer of sugar. When a film of sufficient thickness has been obtained, the whole is folded over a heavy wire frame and the sugar dissolved away. The rubber sheet, supported on the wire stretcher is dried a few hours in the air and finally in vacuo over sulphuric acid. When dry, the sheet is clipped into a strip suitable for the Abbe refractometer. The specific gravity has

been determined by the sinker method, the figures given representing the average of several determinations on pieces selected for their smoothness and freedom from bubbles.

Dimethyl-butadiene rubber: n_D^{20} 1.525, d_4^{20} 0.9292, M_D 27.03 (C_6H_{10} requires 27.2) (M#95), V_m^{20} 88.23.

Smoked sheet (Hevea): n_D^{20} 1.5208, d_4^{20} 0.9217, M_D 22.44 (C_5H_8 requires 22.6) (M##91,94), V_m^{20} 73.8.

As a check on the last, a/thoroughly extracted rubber with acetone was purified through precipitation by alcohol from benzene solution. It gave the following analysis: (N#35)

Calculated for $(C_5H_8)_n$		Found
C	88.23	88.7, 87.8
H	11.77	11.54,12.2

This rubber furnished the following data: (N#37) n_D^{20} 1.5219, d_4^{20} 0.9232, M_D 22.46. Twiss (Ind. Rub. J. 1923, 609) gives n_D^{15} 1.525 for a freshly rolled sheet and Gladstone (above) the d as "about .92". There can be little doubt, therefore, that only one double bond was lost in the polymerisation of the diene; and the absence of any exaltation indicates the disappearance of conjugation between the remaining double bonds of the polymer. In fact, a slight optical depression is to be observed, which might be considered as due to internal compensation. This depression, however, is just outside the margin of error (see introduction).

An interesting point in connection with the last rubber above was that the maximum index (n_D^{20} 1.5236) obtained by compression was not greatly higher than the normal figure quoted.

Amylene Bromide - Brominating in acetic acid following Harries (Mon.Scient.26,295(1912)), trimethyl-ethylene gave a 65.3% yield, b.p. 56-9°/19 mm.; ordinary amylene 60.9%, b.p. 57-9°/20 mm. (N##59,75).

Isoprene - By heating the amylene bromide with dimethyl aniline, as described in DRP 264007, only a negligible distillate was obtained (N#60). With a barium chloride-porous plate catalyst at 305-10°/22 mm., the procedure mentioned in DRP 255519, the yield of low-boiling distillate amounted to 59.5% (N#72). Two runs with a modified isoprene lamp at red glow (N#77) have indicated that the evolution of isoprene from dipentene by this method is very slow, not more than one cc. per hour.

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ADDITION TO THESIS

Sulphur Chloride Compound of Dimethyl-butadiene.-

An excess of freshly distilled diene diluted with carbon bisulphide was treated drop-wise with a solution of sulphur monochloride in the same solvent. After several days in the dark the smell of sulphur chloride had disappeared and the solution was evaporated in vacuo at a maximum temperature of 50°. The residue was a brown oil with a slight odour. It formed solid products on distillation. Analysis: (N° # 41)

Calculated for $C_{12} H_{20} S_2 Cl_2$		Found
S (Kratz)	21.4	21.2, 21.95
M (benzol)	299	262

$d\ ^{26}_{4} = 1.1172$, $n\ ^{26}_{D} = 1.5400$, $M_D = 83.8$ as against 82.32 for $C_{12} H_{20} S_2 Cl_2 F_2$.

Old samples of diene gave at the same time a solid polymer which could be separated by precipitation with acetone.

Chlorination and subsequent hydrolysis of the oil above gave a distillable sulphoxide which was purified by precipitation from acetic acid by water. It boiled at 139-41°/29 mm. The single analysis of this compound by the Kratz method gave a low figure owing to its stability to oxidation. Found: S 10.02; Calc. for $C_{12} H_{20} O_2 S_2 Cl_6$: S 13.55 .

Double Ethers of Dimethyl-butadiene.- The solid dibromide was heated under pressure with the calculated amount of alcoholate, diluted with water after cooling and the ethers

salted out with potassium hydroxide, dried and distilled. The dimethyl-ether was an oil with a slight smell resembling peppermint. It boiled at 81-4° /33.5 mm. Analysis: (N # 87)

Calculated for $C_8 H_{16} O_2$		Found
C	66.7	66.6
H	11.12	10.98
M (benzol)	144	133.3

The corresponding ethyl ether was an oil with a faint rose-like odour and boiled at 90-95°/25 Mm. (N#70)

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EXAMINATION OF NEOARSPHENAMINE.

BY A. DOUGLAS MACALLUM.

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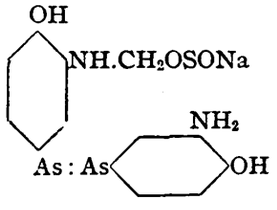
During the last few years many articles have appeared on the chemistry of arsphenamine, but practically nothing on that of neoarsphenamine. This is doubtless owing to the generally admitted obscure nature of the product, which in point of instability and difficulty of preparation stands midway between arsphenamine and sodium arsphenamine. The only references to the preparation of neoarsphenamine are confined to patent literature,[1] and these claim the manufacture of sulfoxylic acid derivatives of arsphenamine by the action of formaldehyde sulfoxylate salts on arsphenamine compounds or their intermediates. Atomic compounds may so be formed, the reaction, in distinction from that of formaldehyde bisulfite, taking place in the presence of either acids or alkalies, the degree of substitution depending on which condition occurs and such factors as temperature, time, concentration and proportion of the reacting substances. The primary products[2] are N-mono- and NN′-dimethylene-sulfoxylate derivatives of dihydroxy-diamino-arsenobenzene, and where technique is not good, mixtures are produced of one or the other, or both, and decomposition products.

Arsphenamine compounds, of course, owing to their amorphous character, cannot be made absolutely pure, this difficulty being increased in the neutral and alkaline derivatives by their lesser stability, so that neo- and sodium arsphenamines, for instance, as usually prepared, are diluted by greater or less amounts of by-products. Account should be taken of this, consequently, in the recognition of neoarsphenamine; *c. g.*, it is not sufficient that a powder should have a definite sulfur : arsenic ratio and be soluble in neutral solution, since it may be shown that preparations nearly always contain mechanically mixed free sulfur salts, and in some cases consist to a great extent of reaction by-products.

Considering the degradation products of neoarsphenamine, one course of decomposition may be represented thus,

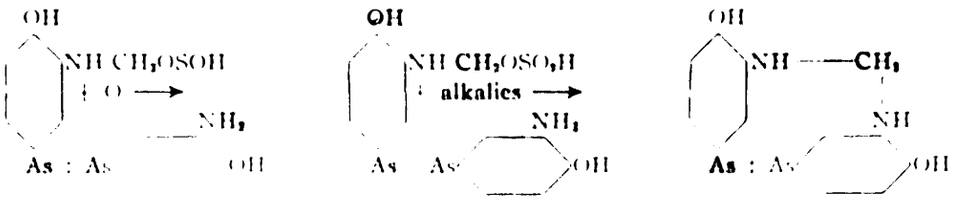
[1] *D. R. P.*, 245,756.

[2] Neoarsphenamine is defined as a compound prepared from arsphenamine by means of formaldehyde sulfoxylate. A monomethylenesulfoxylate formula is claimed for foreign preparations, including Ehrlich's, thus (Fig. 1).



Dihydroxy-diamino-arsenobenzene-*N*-monomethylene-sodium sulfoxylate.

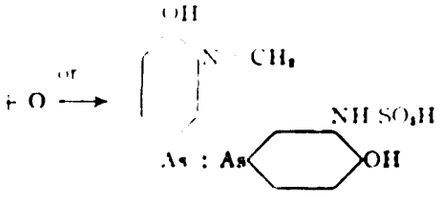
Fig. 1.



Dihydroxy diamino arseno benzene *N*-monomethylene sulfoxylic acid.

-methylene sulfurous acid

-methylene compound.



Corresponding sulfamic acid.

Fig. 2.

besides more involved side group and possible nuclear substitution derivatives.[1]

Disintegration of the arseno radical would lead to oxidation and hydrolytic fractures such as appear to occur in the catabolism of arsphenamine.[2] In neoarsphenamine such cleavages are to be detected by biological rather than chemical tests since the introduction of a side chain into the molecule creates colorimetric and reducing properties which would otherwise obscure their occurrence. This is not the case, however, with the above-mentioned sulfur by-products, which it would be a mistake to assume differ greatly in toxicity from the original sulfoxylate derivatives. But therapeutic interest centers on the latter as having the structure attributed to Ehrlich's compound. Considerable importance attaches, therefore, to the identity of the side group in commercial preparation.

Attempts to distinguish the monosulfoxylate derivative by the physical properties of the free acid led to nothing definite: the melting point, though distinct, was not very constant or much removed from those of other arseno compounds. Estimation of its sulfur : arsenic ratio gave better but not uniform results. A method was finally devised by the writer which served to distinguish the sulfoxylate derivative from the more immediate sulfur and non-sulfur by-products and depended on portionwise oxidation of neoarsphenamine solutions by iodine. This method, though having certain limitations, has given consistent analytical figures and possesses an advantage also in that it is effective with relatively small samples of the drug. The error is about 2% and this largely in the arsenic determination. The method is applicable in the toxicological

[1] Binz, *Ber.*, **50**, 1274 (1917).

[2] Sieburg, *Z. physiol. Chem.*, **97**, 53 (1916).

study of the progressive decomposition of neoarsphenamine solutions.[1] Under the conditions described below, oxidation of neoarsphenamine by iodine proceeds quantitatively according to the equation,[2]

$$OH(NH_2)C_6H_3As : AsC_6H_3(OH)NH.CH_2OSOH + 9H_2O + 12I \longrightarrow 2OH(NH_2)C_6H_3AsO(OH)_2 + HCHO + H_2SO_4 + 12HI.$$

Procedure.

Two g. of neoarsphenamine is dissolved in 100 cc. distilled water.

Total Reducing Power.—Ten cc. of this solution is pipetted into a 500-cc. wide-necked glass-stoppered bottle, acidified with 25 cc. of 1–20 hydrochloric acid, immediately treated with 50 cc. of 0.1 *N* iodine from a buret and titrated back with thiosulfate after 3 minutes' shaking. The cc. of iodine required multiplied by 5 is the total reducing power per g. of powder.

Free Reducing Substances.—Simultaneously with the above, 20 cc. of solution is removed to a 100-cc. volumetric flask with well-ground glass stopper, the flask filled with carbon dioxide or nitrogen, 50 cc. of 1–20 hydrochloric acid added, diluted with water to the mark, stoppered and inverted about 120 times in 3 minutes to dissolve the soluble constituents from the precipitate. The suspension is brought onto a dry folded filter, the first few cc. of filtrate discarded, then 25 cc. collected in a dried 50-cc. volumetric flask containing 25 cc. of 0.1 *N* iodine solution. The contents of this flask are poured into a 500-cc. bottle and the residue rinsed twice with water. Titrating back after 3 minutes, the cc. of iodine required multiplied by 10 is that required by the free reducing substances per g. of powder.

Arsenic.—Ten or 20 cc. of solution is oxidized and the arsenic determined by Lehmann's[3] or Rogers'[4] method. The per cent. of As times 5.333 is equivalent to the cc. of iodine required to oxidize the arsenic in 1 g. of powder.

Combined Sulfoxylate.—The iodine required to oxidize the combined sulfoxylate in 1 g. of powder is found by subtracting that required by the arsenic and free reducing substances from the total reducing power. This divided by 3.9553 gives the per cent. of sulfoxylate (as CH_2OSONa).

Calculation.—The ratio of sulfoxylate to arsenic, *e. g.*, M.S.: 2M.As is given by the equation M.S. = 150/% As. × % S./101.13, the theory for neoarsphenamine being unity.

Comment.

Analysis of best preparations has indicated that it is not possible to form products of sulfoxylate : arsenic ratio exactly 1:2, but that products closely approximating to this are quite practicable.

TORONTO, CANADA.

[1] Kolle, *Deut. Med. Wochschr.*, 1918, p. 1180.
[2] Reinking, *Ber.*, 38, 1069 (1905).
[3] Fargher, *J. Chem. Soc.*, 115, 992 (1919).
[4] Rogers, *Can. Chem. J.*, 3, 398 (1919).

[Reprinted from the Journal of the American Chemical Society,
Vol. XLIV, No. 11, November, 1922.]

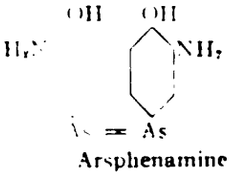
[Contribution from the Laboratory of the Synthetic Drug Company, Ltd.]

EXAMINATION OF NEOARSPHENAMINE. II. THE CONSTITUTION OF THE FRENCH DRUGS

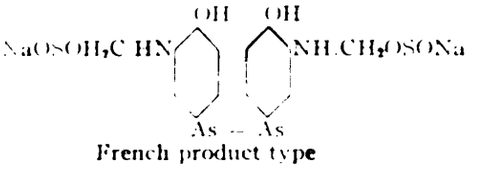
By A. Douglas Macallum

In a previous paper[1] the nature of American neoarsphenamines, but not of the European preparations, was indicated. The composition of some of the latter compounds is dealt with briefly below.

Some of these products, it is true, are similar to the American ones, but others, notably those of French origin, consist entirely of doubly substituted arsphenamines, the formation of which may be illustrated as follows:



Arsphenamine base



French product type

The most noticeable physical characteristic of the French compounds is that, unlike the neoarsphenamines, which are soluble in neutral and alkaline solution alone, they dissolve unchanged in weakly acid media as well.[2] The former darken and decompose at relatively higher temperatures, are less affected by atmospheric oxygen, and are of lower toxicity, but also of lower trypanocidal activity, than the neoarsphenamines. Otherwise the two kinds of drug much resemble each other, for example, in their ion reactions, solubilities and behavior on any sort of drastic treatment. The separation of the individual compounds in a pure state is rendered somewhat difficult by a tendency towards decomposition, so that up to the present, the identification of these has depended on analysis of samples as they stood.

In connection with the recognition of such compounds, the iodometric

[1] Macallum, This Journal, 43, 643 (1921).

[2] Including sulfuric acid,—sparing solubility in this reagent being the usual test for arseno compounds [Ehrlich, *Ber.*, 44, 1263 (1911)]. Consequently, it seemed a question whether such products were not substituted at the arseno as well as the amino groups. However, as soluble derivatives like these could not be made from arsenobenzene, or its intermediates, the writer concluded that the preparations were, after all, merely N,N'-di-substituted derivatives of arsphenamine.

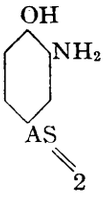
The series includes also less definite neutral complexes which are more readily decomposed than the above by mineral acids with the almost complete regeneration of arsphenamine salts. The latter are taken to be molecular compounds, but the distinction between these and the others is not very well marked.

method described in the first communication has been extended for analysis of the methylene-bisulfite group, which appears to rank in importance with the sulfoxylate in these preparations. The development consists essentially in making use of the oxidation figures obtained when a preparation is treated with iodine successively in acid and alkaline solution, and from these deriving the group configuration by the aid of the elementary analysis.

In the following table are shown the iodine requirements found to hold for the principal reducing groups in such compounds.

TABLE I

IODINE REQUIREMENTS FOR PRINCIPAL GROUPS

Group formula	Group name	Molecular iodine acid solution *M*	Requirements in alkaline solution *M*
—CH_2OSONa	-methylene-sulfoxylate	4[a]	6
—CH_2OSO_2Na	-methylene-bisulfite	0[a]	4
	arsphenamine base	7.755[b] (e. g. $K \times 8M$)	15.02[b] ($k' \times 16\ M$)

[a] Reinking, *Ber.*, **39**, 1069 (1905).

[b] The oxidation and substitution of "606" by iodine under the conditions described in this paper are not quite quantitative. Thus a sample of the pure drug gave the following titration figures.

	Cc. of 0.1 *N* iodine required by 1 g. of powder in	
	Acid solution	Alkaline solution
Found	165	310
	160.5	315
	160.5	316.5
Av.	162	313.8
Calc. for As:31.3%	167.1 (8 *M*)	334.2 (16 *M*)

Sulfoxylate and formaldehyde bisulfite are more completely oxidized, however.

Formaldehyde sulfoxylate (m. p. 64–5°, uncorr.)

	Cc. of 0.1 *N* iodine required by 1 g. of substance in	
	Acid solution	Alkaline solution
Found:	257.5	390
Calc. for $HOCH_2OSONa.2H_2O$:	259.5 (4 *M*)	394.5 (6 *M*)

Formaldehyde bisulfite (m. p. 78–9°, uncorr.)

Found:	2.5	259
Calc. for $HOCH_2OSO_2Na.H_2O$:	0	263 (4 *M*)

Analytical Procedure

The complete oxidation analysis may be carried out in the following steps in order to conform to the technique indicated in the original paper.

Partial Reducing Power.—Two-tenths g. of powder is dissolved in 10 cc. of distilled water in a 500cc. flask, acidified with 25 cc. of 0.5 *N* sulfuric acid, immediately treated with 50 cc. of 0.1 *N* iodine, and titrated back with thiosulfate and starch after 3 minutes' shaking. The cc. of iodine required multiplied by 5 gives the partial reducing power of 1 g. of powder.

Total Reducing Power.—One-tenth g. of powder is dissolved in 50 cc. of water and immediately treated with 100 cc. of 0.1 *N* iodine solution. After 3 minutes' shaking, 10 cc. of 2 *N* sodium hydroxide solution is added and the mixture shaken again for 3 minutes, when it is diluted with 50 cc. of water, acidified with 10.5 cc. of 2 *N* sulfuric acid and titrated back with thiosulfate solution, using, finally, starch. The cc. of iodine required multiplied by 10 is the total reducing power per gram of powder.

Arsenic.—The percentage of arsenic determined by Lehmann's method is multiplied by 5.172 (or 775.5/149.9) to give the cc. of iodine reduced by the arseno or arsenide radical in 1 g. of powder. When this amount would exceed the partial reducing power found, the presence of oxygenated arsenic groups is indicated.

Arsphenamine.—The percentage of arsenic times 10.02 (or 1502/149.9) equals the total cc. required by the group.

Sulfoxylate.—The iodine used by any sulfoxylate present is found by subtracting that required by the arsenic from the partial reducing power. This divided by 3.960 (or 400/101) gives the percentage of sulfoxylate (as $-CH_2OSONa$). The total iodine requirement of the sulfoxylate is 1.5 times the preceding number.

Bisulfite.—The iodine absorbed in the oxidation of any methylene-bisulfite in the preparation is found by subtracting from the total reducing power the added total iodine requirements from the arsphenamine and sulfoxylate groups, according to the following example, which shows the titer of a well-known drug.[3]

Calculation of Sulfoxylate.—		
Cc. of 0.1 *N* iodine per g. of powder		
Partial reducing power, (1) 125.4 (2) 116,	av.	120.7
Iodine required by arsenide radical, calc. (20.22 × 5.172)		104.5
Partial iodine requirement of sulfoxylate		16.2
whence sulfoxylate (16.2/3.96) = 4.09% and the total requirement of the sulfoxylate		24.3
Calculation of Bisulfite.—		
Total reducing power (1) 331; (2) 341.5; (3) 317;	av.	329.8
Total iodine required by arsphenamine group (20.22 × 10.2) or	206.2	
Total iodine requirement of sulfoxylate	24.3	
		230.5
Difference		99.3

This iodine requirement divided by 3.41 (or 400/117) gives the percentage of methylene-bisulfite (as $-CH_2OSO_2Na$). Thus in the above, this group was found to be present to the extent of 29.12%.

Determination of the Sulfur Groups.—The computation of results obtained by oxidation and elementary analysis is illustrated by tabulating the figures obtained with the same preparation.

[3] It should be mentioned that the errors here are greater than have been noticed in subsequent titrations. The most nearly uniform results are obtained when solution is effected in an indifferent atmosphere.

TABLE II

ANALYSIS

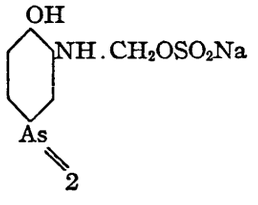
Element or Group	Av. % found		Molecular proportions		
As	20.22	2[a]			
N	4.3	2.274			
Cl	0	0			
S	11.43		2.64		
Na	7.52		2.422		2.422
Sulfone (presumably)			0.218		
Sulfoxylate (—CH_2OSONa)	4.09[b]			0.30	
Bisulfite (—CH_2OSO_2Na)	30.17			1.9108	
Total					2.210
Sulfonate (—SO_3Na)					0.212

[a] The cryoscopic depression of 0.26° found for the 2.95% water solution corresponds to a molecular weight of 209.9 g. Calc. for pure $C_{14}H_{14}O_8N_2As_2Na_2$: 598.2 g. Ionization is naturally a factor here. Arsphenamine itself under similar conditions gives low molecular weights.

[b] Free sodium sulfite (Na_2SO_3 or $NaHSO_3$) if present in small amounts would not readily be distinguishable from sulfoxylate.

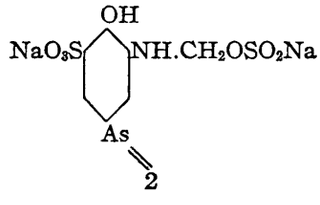
The Commercial Products

Rather more variation has been observed in European than in American products, no two makes of the former being alike; variation has been found, too, in different lots of the same make of drug. The makers' claims as to the constitution of a number of these preparations have not been substantiated by analysis. Graphic structures that are ascribed by the writer to several French compounds are shown below:



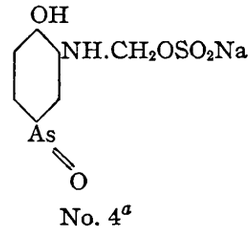
Nos. 1 and 2

Dihydroxy-diamino-arsenobenzene-N,N'-dimethylene-bisulfite



No. 3

Sulfo-bisulfite bisulfite compound



No. 4[a]

Formaldehyde bisulfite derivative of hydroxy-amino-phenylarsenoxide

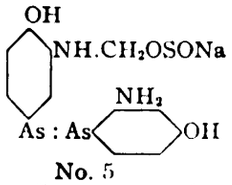
[a] This was found to differ entirely from lot to lot.

In confirming the composition of products like the above by synthetic methods, it has been found that not more than 2 sulfur groups could be introduced into their structures except where one was non-reducing, such as the sulfonic group, and this was assumed to have migrated to the nucleus after a manner already known.[4] Of the sulfur groups, the substituting activity of the sulfoxylate was seen to be the most marked, the

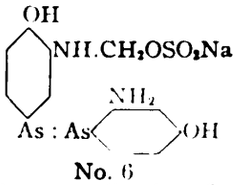
[4] King, *J. Chem. Soc.*, **119**, 1415 (1921).

formation of bisulfite derivatives often being of a secondary nature.

The following are examples of true neoarsphenamines.



No. 5
Dihydroxy-diamino-arsenobenzene-N-monomethylene-sulfoxylate



No. 6
Corresponding bisulfite derivative

The toxicological and therapeutic actions of the French drugs are compared with those of other arsphenamine preparations in the appended table. The figures show the results obtained in this laboratory with representative commercial samples, using mice infected with trypanosoma equiperdum.

TABLE III

RELATIVE DOSES

Preparations	As %	Curative dose G. per k.	Tolerated dose G. per k.
Arsphenamines	30	0.0075–0.0125	0.15–0.19
Sodium arsphenamines	20	0.015 –0.025	0.25–0.3
Neoarsphenamines	20	0.0225–0.04	0.3 –0.4
French neo mixtures	20	0.04 –0.06	0.4 –0.5

TORONTO, CANADA

Examination of Neoarsphenamine. II. The Constitution of the French Drugs, by A. Douglas Macallum.

P. 2581. Table II, the last three lines should read:

Element or group	Av. % found	Molecular proportions
Bisulfite (—CH_2OSO_2Na)	29 12	1.844
Total		2.144
Sulfonate (—SO_3Na)		0 278

P 2582. Note added by author (December 18, 1922).

The general sparing solubility of these compounds in alcohols is in agreement with an arseno structure, this property having been used at one time by Bart (Ger. pat. 270,-568) to distinguish certain arseno compounds from the arsenoxides and arsines.

Reprinted from the Journal of the Society of Chemical Industry, Dec. 7, 1923, Vol. XLII., No. 49, pp. 468 T–471 T.

o-AMINOAND *o*-ACETAMINOPHENYLSTIBINIC ACIDS.

BY A. DOUGLAS MACALLUM, M.SC.

As *p*-acetaminophenylstibinic acid has been used in the treatment of trypanosomiasis (Manson-Bahr, Lancet, 1920, **11**, 178; Uhlenhuth and Hügel, Deuts. Med. Woch., 1913, 2455; Hügel, Arch. Derm. Syph., 1913–4, **118**, 1) some interest will be attached to the preparation of the corresponding ortho-compound described in this paper.

Aromatic antimony compounds have been made by the Fittig reaction (Michaelis and Reese, Annalen, 1886, **233**, 39), the Grignard reaction (Pfeiffer, Ber., 1904, **37**, 4620), and the diazo reaction (Schmidt, Annalen, 1920, **421**, 174). A number of methods for making arsenic compounds, such as the Béchamp reaction (Ehrlich and Benda, Ber., 1907, **40**, 3292), the substitution of tertiary amines (Michaelis, Ber., 1908, **41**, 1514) or mercury derivatives (Michaelis, Ber., 1875, **8**, 1316; Roeder and Blasi, Ber., 1914, **47**, 2748) have not yet been successfully applied to the preparation of antimony compounds.

As the diazo reaction is generally preferred for the synthesis of the primary acids, this method was naturally attempted for the direct preparation of the acetamino acid from monoacetyl-*o*-phenylenediamine, but without success. However, the synthesis of the acid has been effected through the amino compound, which was made from the nitro acid by reduction with ferrous hydroxide or titanous chloride.

Curiously enough, while primary aromatic antimonic acids behave towards alkalis as if existing in a polymeric form, molecular weight determinations by the cryoscopic method have indicated a unimolecular structure in the acids so far examined by the author.

Experimental.

Oxanilide.—The following procedure has been found preferable to that of Perkins (J. Chem. Soc., 1892, **61**, 459) in the matter of yield. One part of crystalline oxalic acid and about three of aniline were heated on an oil bath until the still-head temperature reached 180° C. and the contents of the flask became molten. By decanting and extracting with cold alcohol, the oxanilide was obtained in the form of plates, m.p. 247°–248°, yield 72–73%.

o-Nitroaniline.—The oxanilide was nitrated by a slight modification of Wülfing's process (G.P. 65,212, 66,060). The nitroaniline, thoroughly washed and dried, was cautiously distilled *in vacuo* (b.p. 165°–166° at 28 mm.) to remove coloured by-products. The yield did not exceed 60% and the product usually melted at 69°–70° It was purified by saponifying the acetyl compound according to Witt and Utermann (Ber., 1906, **39**, 3901).

o-Phenylenediamine.—The pure diamine, m.p. 102°–103°, was made in 87% yield following Hinsberg (Ber., 1895, **28**, 2947). It was separated by distilling in a vacuum (b.p. 142°–143° at 28 mm.), and freed from unstable by-products by treatment with ether.

Monacetyl o phenylenediamine.—Manuelli and Valloni (Gazz., 1901, **31**, I., 22) obtained this compound, m.p. 145°, among the products of the decomposition of the diacetyl derivative

by oxalic acid. A less pure form has been prepared by treating a well-diluted solution of the diamine in ethyl acetate with an equivalent of acetic anhydride. The cooled solution was neutralised with potassium carbonate and the dried solution allowed to evaporate. The crystals formed, after extracting with ether, and drying at 100° C., melted at about 131°. The hydrochloride was also separated by passing dry hydrogen chloride through the cooled solution. It was dried *in vacuo* over sulphuric acid and caustic soda. Found: Cl (modified Volhard) 18·44% ($C_8H_{11}ON_2Cl$ requires Cl 19·05%).

o-Nitrophenylstibinic acid ($NO_2C_6H_4SbO_3H_2$).—The crude acid was obtained in a yield of 45% by a slight modification of the diazo method described by Schmidt (*loc. cit.*). After purifying (through the chloride) the yield had dropped to about 30%. For analysis, the acid was dried to constant weight over boiling toluene in the Viktor Meyer apparatus: N (Dumas) 5·19%, Sb (total) 40·8%; (2) N (modified Kjeldahl) 4·45%, Sb 40·5% (calc. for $C_6H_6O_5NSb$: N 4·79%, Sb 41·09%).

According to Schmidt, the alkaline solutions of the acid are too dark to titrate using phenolphthalein. No difficulty is experienced in getting end-points, however, providing the solutions are sufficiently dilute. Thus 0·1 g. dissolved in 100 c.c. of water and 20 c.c. of $N/10$ alkali, on titrating with sulphuric acid was found to require 3·63 and 3·71 c.c. of sodium hydroxide or 3·79 c.c. of lithium hydroxide (average 3·71 c.c.). The amount of chlorine still present in the product was 1·04% (Baubigny and Chavanne) or the equivalent here of 0·28 c.c. of alkali. The actual requirement was therefore 3·43 c.c. as against the calculated 3·37 c.c. for the unimolecular acid.

Molecular weight determinations on the acid in phenol solution, taking the usual precautions against access of moisture, gave the following figures: for a 3·15% solution 300·4, 280·6, 282·5. Another preparation used as a check gave 275·4, 273·8, 273·8 for a 3·75%, and 267·2, 266·8 for a 2·94% solution (calc. for $C_6H_6O_5NSb$, 292).

Similarly, *p*-aminophenylstibinic acid gave depressions corresponding to a unimolecular structure. The acid was made from the chloride of the acetyl derivative by saponifying with dilute sodium hydroxide. Analysis: found N 4·36%, Sb 42% (calc. for $C_6H_8O_3NSb$, H_2O: N 5%, Sb 42·85%). This gave depressions of 0·225°, 0·25° for a 1·1225% formic acid solution (calc. for $C_6H_8O_3NSb + H_2O$, 0·2245°).

It is difficult to reconcile these figures with such type formulæ as $3(C_6H_5SbO_2)H_2O$ or $3(NH_2C_6H_4SbO_2)3H_2O$, worked out by Schmidt (*loc. cit.*, see also Ber., 1922, **55**, 697) on the basis of the chemical analysis and behaviour of such acids on progressive titration with alkalis.

Tartrate of o-nitrophenylstibinic acid ($NO_2C_6H_4SbO(OH)C_4H_4O_6Na$).—Although the nitro acid dissolves in excess of tartaric acid, the resulting product was found to be no definite compound, since it could be separated by the use of organic solvents into various soluble and insoluble fractions. By boiling an excess of the acid with sodium bitartrate, however, the solution on evaporating and drying over toluene was found to contain a fairly definite complex. Analysis: Sb^v 24·3%, Sb (total) 24%, Na (Na_2SO_4) 5·9, 5·82%, N/10NaOH required per g. 46·45 c.c. (calc. for $C_{10}H_9O_{10}NNaSb$: Sb 26·93%, Na 5·17%, NaOH 44·8 c.c.). Molecular weights in 3·49% aqueous solution: 312·9, 286·3, 297·5 (calc. 446).

o-Aminophenylstibinic acid ($NH_2C_6H_4SbO_3H_2$). —The reduction of nitro derivatives of aromatic arsenic acids by ferrous hydroxide has been described by Benda (Ber., 1914, **47**, 1316); in dealing with antimonic acids a modification of procedure is necessary in order to prevent loss by precipitation. No such difficulty is experienced where the reduction mixture is very dilute, however, and Benda's technique has been followed for the reduction of the *o*-nitro acid under such conditions, only substituting ferrous sulphate for the chloride. In this case the alkaline filtrate from the reduction by-products was neutralised with acetic acid, the sulphate removed with barium acetate, and the amino compound precipitated as a neutral lead salt by addition of lead nitrate. Found: Sb (total) 27·5% ($C_{12}H_{14}O_6N_2Sb_2Pb,8H_2O$ requires 27·5%).

More concentrated solutions were obtained by reducing alkaline solutions of the nitro acid with ferrous hydroxide made from ferrous sulphate and hot barium hydroxide solution. By this means the alkali salt could be separated by the use of mixtures of acetone and ether, or by converting into an alkaline barium salt. One such salt gave the analysis: N (Kjeldahl) 3·25%, Sb (total) 25·05% ($C_6H_8O_3NBaSb,4H_2O$ requires N 2·97%, Sb 25·49%).

An alternative procedure was to separate by centrifuging an excess of ferrous hydroxide, this being stirred for 10–15 minutes with a solution of 5 g. of nitro acid in 150 c.c. of water and 15 c.c. of 5*N* sodium hydroxide. The suspension was centrifuged again, and the liquid treated with charcoal, salted, and acidified with acetic acid. The acid was dried on a porous plate *in vacuo* before extracting the salt with ice water in the centrifuge tube. As the acid usually contained enough iron to impart a brown colour to the sulphide, the proof of it

individuality depended on the constancy of the antimony-nitrogen figures. Found: N (Kjeldahl) 5·25%, (Van Slyke) 5·57%, Sb (total) 42·3%, loss (90°) 3·82% (calc. for $C_6H_8O_3NSb$, H_2O: N 5·0%, Sb 42·85%, loss 6·42%). The low loss was partly accounted for by the presence of 1·53% of salt.

By the action of potassium iodide and dilute sulphuric acid on solutions of the amino acid, *o*-iodoaniline was obtained, m.p. 56°–56·5°. Found: 57·4% I (Baubigny and Chavanne); C_6H_4NI requires 57·95%.

The acid darkened at indefinite temperatures above 150°. It formed a brownish powder soluble in about 200 parts of water. The more concentrated solutions in alkali gave precipitates with excess of concentrated alkali, potassium carbonate, and alcohols. Its solution in sodium hydroxide gave precipitates with most alkaline-earth and heavy metal salts excepting those of magnesium and zinc. The acid is soluble in methyl alcohol, warm glycerin, and dilute acetic acid. The aqueous solutions of the acid and its salts decompose on standing.

A product substantially the same as the above was obtained by the action of titanous chloride on suspensions of the acid in methyl alcohol In this case, the amino acid was precipitated by the addition of hydrochloric acid, washed with salt solution, and the mineral acid eliminated with sodium acetate.

o-Acetaminophenylstibinic acid ($CH_3CONH C_6H_4SbO_3H_2$).—This acid was prepared from moderately concentrated neutral solutions of the amino acid by the action of an excess of acetic anhydride at 0° C. It was separated by centrifuging and dried in the same way as the amino acid. Found: N 4·74%, Sb (total) 39·5% ($C_6H_{10}O_4NSb.H_2O$ requires N 4·7%, Sb 40·25%).

Saponification of the acetyl compound indicated that it usually contained slightly less than the single molecule of acetic acid shown in the formula.

The acid did not melt below 250° C. It was sparingly soluble in water, but readily soluble in formic acid, warm glycerin, and dilute acetic acid. It formed the usual soluble alkali and ammonium salts.

Di-o-chlorophenylstibinic- acid, $(ClC_6H_4)_2$ SbOOH.—This acid was the main product fo the action of antimony oxide on *o*-chlorodiazobenzene chloride. It was purified by converting into the chloride, m.p. 105°–110°, and precipitating this from alcoholic solution by water. With potassium iodide and dilute sulphuric acid it gave an oil, b.p. (capillary) 230°–235°, probably *o*-iodochlorobenzene. Found: Sb (Kjeldahl) 27·9%, C (lead chromate) 32·28%, H 2·31% (calc. for $C_{12}H_9O_2Cl_2Sb,3H_2O$: Sb 27·93%, C 33·5%, H 3·49%). The acid was sparingly soluble in alkalis.

Determination of antimony.—The author prefers the following modification of the Lehmann arsenic determination to the Kjeldahl method (Schmidt, *ibid.*) mainly because it requires only a short time to complete: 0·2 g. of substance, dissolved if possible in 10 c.c. of water by the addition of alkali, is treated with 1 g. of potassium permanganate and 10 c.c. of concentrated sulphuric acid. After heating for a time, the mixture is decolorised by boiling with 10–15 c.c. of hydrochloric acid, and diluted with 50 c.c. of water and 75 c.c. of hydrochloric acid. The antimony is reduced in the cooled solution by shaking for 3 minutes with 5 g. of potassium iodide. After diluting with a further 125 c.c. of water, the solution is titrated with $N/10$ thiosulphate, using starch as indicator. If a

blank be subtracted, each c.c. of thiosulphate then equals 0·006 g. of Sb or 3%.

The quinquevalent antimony in a preparation may usually be titrated directly under the above conditions, omitting, of course, the permanganate and sulphuric acid.

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