THE STRUCTURE OF BUTADIENE DIMERS

PRODUCED BY A FREE-RADICAL CHAIN-TRANSFER MECHANISM

A Thesis

by

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GENERAL INTRODUCTION

Many investigations have been carried out to elucidate the structures of polybutadienes. The first ones established the occurrence of two kinds of structural units: one originating from a 1,4-addition of butadiene, the other resulting from a 1,2-addition; later, the percentages of each unit were determined quantitatively. Units originating from a 1,4-addition were found to appear either in a cis form or in a trans form; the amounts of each form were evaluated. Degradative methods provided other interesting fragments such as succinic acid, 1,2,4-butanetricarboxylic acid and resinous acids. From these findings, structures of polybutadienes were sketched but many details have yet to be revealed before a complete picture can be drawn. Thus, varieties of polymer chains as well as arrangements of units along the chains are unknown.

The aim of the present work is to gain more information about these details. The techniques previously used are not able to resolve completely these structural problems when they are applied to polybutadienes of high molecular weight. However, it was thought that the simplest polybutadienes, the dimers, would offer some interesting structural resemblances to their higher homologs and would be more readily dealt with.

The dimers were produced by a free-radical mecha-
nism in order to compare their structures with those of poly-
mers obtained by the same mechanism, since polymers of this
class are of outstanding commercial importance. A chain trans-
fer agent, chloroform, was used to stop the growing polymer
chain at the dimer stage. The structures of the dimers were
investigated by means of infrared spectroscopy and ozonolysis.

HISTORICAL INTRODUCTION

Structure Investigations of Polybutadienes

The structures of polybutadienes have been investigated by both chemical and physical techniques: ozonolysis, perbenzoic acid addition, and infrared spectroscopy. The three methods have their respective merits for the determination of the percentages of 1,2-and 1,4-addition. Ozonolysis gives more details about the intimate structure whereas the infrared spectroscopy distinguishes between cis-and trans-1,4-additions.

Ozonolysis

Harries introduced the ozonolysis technique to elucidate the structure of natural rubber (1). The rubber ozonide was decomposed by boiling with water and in the resulting solution were found large amounts of levulinic aldehyde and levulinic acid, indicating that the fundamental unit was isoprene. This was confirmed by Pummerer who cleaved the rubber ozonide through reduction by hydrogen (2). Later he applied the technique to sodium-catalysed polybutadiene and found large amounts of fragments corresponding to 1,2-and 1,4-addition (3).

Hill, Lewis and Simonsen were the first to employ ozonolysis to study the structure of butadiene polymers and copolymers obtained by a free-radical mechanism (4). Poly-

butadiene gave succinic acid, 1,2,4-butanetricarboxylic acid
and resinous acids which resulted from structural units I,
II and III, respectively.

$$-CH_2CH\dotplus CHCH_2CH_2CH\dotplus CHCH_2-$$

<div style="text-align:right">I</div>

1   4, 1   4

$$-CH_2CH\dotplus CHCH_2CH_2CHCH_2CH\dotplus CHCH_2-$$
$$CH$$
$$---\|---$$
$$CH_2$$

<div style="text-align:right">II</div>

1   4, 1 2,1   4

$$-CH_2CHCH_2CHCH_2CH-$$
$$CH\quad CH\quad CH$$
$$----\|----\|---- -\|----$$
$$CH_2\quad CH_2\quad CH_2$$

<div style="text-align:right">III</div>

1 2,1 2,1   2
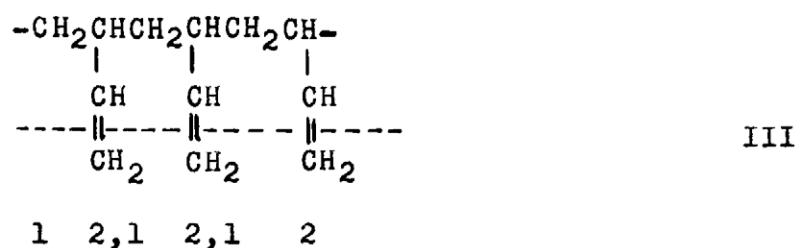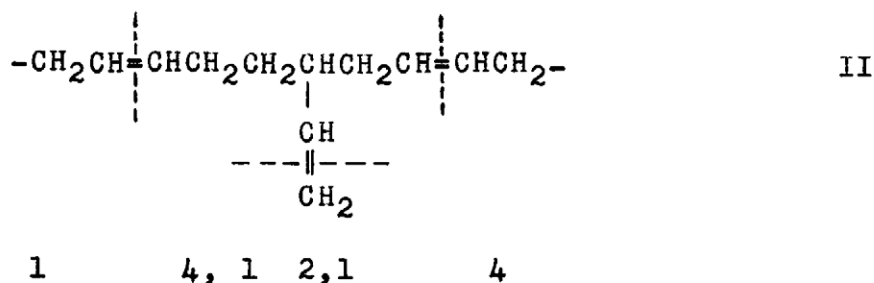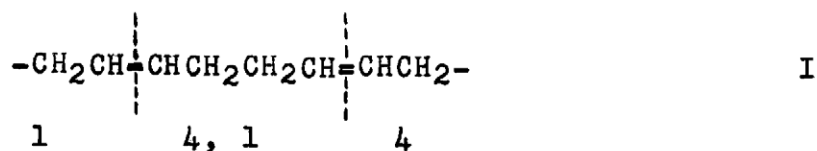
It was realised that butadiene might polymerize by three ad-
ditive mechanisms: 1,4-addition (I), conjunctive 1,2-and 1,4-
addition (II), and 1,2-addition (III); but a quantitative dis-
crimination between the various mechanisms was not possible.

They also established a copolymer structure for the
product of butadiene-methyl methacrylate copolymerization and
it was determined that butadiene had mainly polymerized ac-

cording to a 1,4-addition. Alekseeva arrived at a similar
conclusion with butadiene-acrylonitrile (5) and butadiene-
methacrylonitride copolymers (6).

A butadiene - styrene copolymer, whose molar ratio
was two to one, was submitted by Alekseeva and Belitzkaya to
ozonolysis and then to oxidative hydrolysis with hydrogen per-
oxide (7). Formic, succinic, phenyladipic and diphenylsuberic
acids were isolated and determined through the medium of their
methyl esters. Structural units IV, V and VI were believed
responsible for the last two acids.

$$-CH_2CH \doteq CHCH_2CH_2 \underset{C_6H_5}{CHCH_2CH} \doteq CHCH_2- \qquad IV$$

$$1 \qquad 4, \qquad S,1 \qquad 4$$

$$-CH_2CH \doteq CHCH_2CH_2 \underset{C_6H_5}{CHCH_2} \underset{C_6H_5}{CHCH_2}CH \doteq CHCH_2- \qquad V$$

$$1 \qquad 4, \qquad S, \qquad S, \; 1 \qquad 4$$

$$-CH_2CH \doteq CHCH_2CH_2 \underset{H_5C_6}{CHCH} \underset{C_6H_5}{CH_2CH_2CH} \doteq CHCH_2- \qquad VI$$

$$1 \qquad 4, \qquad S, \qquad S, \; 1 \qquad 4$$
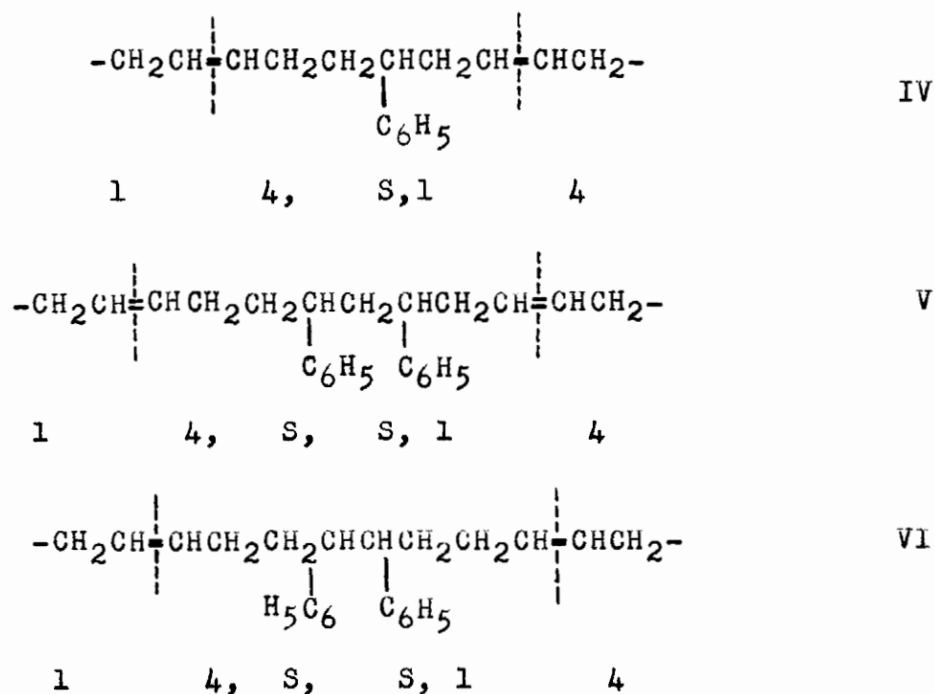
The quantity of the products obtained corresponded to 88 per
cent of the butadiene and 71 per cent of the styrene. Structur-
al unit IV accounted for 31.2 per cent of the styrene, units V

and VI for 40 per cent. The remaining 21 per cent was assumed
to have entered into indefinite structural units, such as VII,
which gave rise to acids of high molecular weight.

$$-\left[\begin{array}{c} CH_2\text{-}CH \\ | \\ CH \\ \| \\ CH_2 \end{array}\right]_m -\left[\begin{array}{c} CH_2CH \\ | \\ C_6H_5 \end{array}\right]_n - \qquad VII$$

$$1 \quad 2 \qquad\qquad S$$
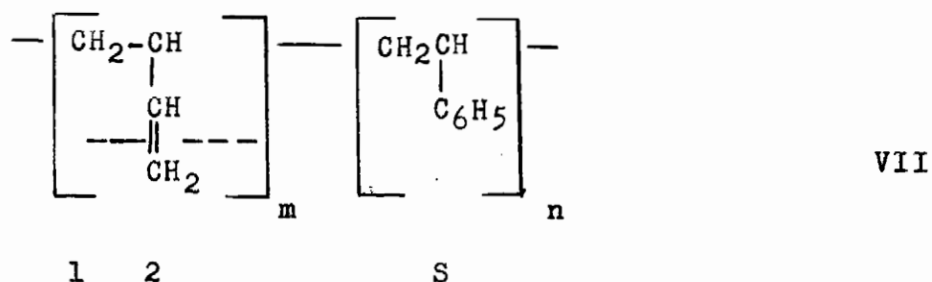
As formic acid resulted from vinyl side chains (units II, III,
VII), it was concluded that 23 per cent of the butadiene poly-
merized according to a 1,2-addition. Yakubchik, Vasil'iev and
Zhabina obtained 31.6 per cent of vinyl groups for a butadiene-
styrene copolymer (8) but Marvel, Bailey and Inskeep found 19.2
per cent (9).

Rabjohn and coworkers (10) repeated the work of Alek-
seeva and Belitskaya (7); the butadiene-styrene molar ratio of
three to one was assumed responsible for the small changes in
the proportions and in the nature of the products resulting
from ozonolysis. They also ozonized a series of butadiene co-
polymers in an attempt to determine the extent to which the
butadiene had polymerized by a 1,2-addition. Since they did
not consider their results strictly accurate, although repro-
ducible, they defined the apparent percentage of 1,2-addition
as an "ozonization number". However, they concluded that the
manner, in which the butadiene molecule had entered into the

growing copolymer chain, had not been greatly influenced by the experimental conditions. The "ozonization numbers" were 20 and 12 for emulsion polybutadienes prepared at 50° and $110^{\circ}C.$, respectively.

A butadiene -(o- chlorostyrene) copolymer was studied by Marvel and Light (11). The acids, resulting from oxidative hydrolysis of the copolymer ozonide, were seperated by partition chromatography on a silica gel column. Succinic acid was isolated in more than the expected amount and 1,2,4-butanetricarboxylic acid in less than the expected amount.

Marvel and coworkers found that the ozonolysis of polybutadienes of different conversions gave (succinic acid) / (1,2,4-butanetricarboxylic acid) ratios which seemed to indicate that more 1,4-addition than 1,2-addition had taken place in the early stage of polymerization (12). Polybutadienes formed at low temperature gave a higher percentage of 1,4-addition than those produced at $50^{\circ}C.$

Perbenzoic Acid Addition

This technique was used mostly for the determination of 1,2-addition and therefore was used less extensively. The first study of perbenzoic acid addition to carbon-carbon double bonds was made by Prileschajew (13). This reaction was introduced to rubber chemistry by Pummerer and coworkers to determine the degree of unsaturation (14, 15). Later, as reported by

Weidlein, the German synthetic industry adopted the reaction
to distinguish external and internal double bonds, the former
resulting from a 1,2-addition and the latter from a 1,4-ad-
dition (16). The method was based on the greater reactivity
of the internal double bonds.

Kolthoff, Lee and Mairs applied the reaction to a
study of various butadiene polymers and butadiene-styrene
copolymers (17). Polymerization temperature, type of cata-
lyst, percentage conversion and varying styrene content did
not greatly affect the percentage of external double bonds.
The percentages of external double bonds were found to be 20
and 58 per cent respectively, for the emulsion and sodium-
catalysed polybutadienes.

Saffer and Johnson (18), working on a series of
different natural and synthetic rubbers, obtained results
in good agreement with those of Kolthoff. Similar findings
were obtained by Marvel and Williams on butadiene polymers
and butadiene-2,3-dimethylbutadiene copolymers (19).

Infrared Spectroscopy

The application of infrared spectroscopy to the
study of the structure of natural and synthetic rubbers is
rather recent. Meyer (20), and Treumann and Wall (21) have
reported that the technique was applied in 1943 by White and
Flory to evaluate the percentage of 1,2-addition in copolymers
of butadiene, and by Swaney and White to examine the influence

of modifiers. Qualitative results were also obtained by Thompson and Torkington on different rubbers (22, 23).

The technique was made quantitative by Field, Woodford and Gehman (24). The percentages of 1,2-addition were 21 for an emulsion polybutadiene and 19 for an industrial butadiene-styrene copolymer. Hampton was the first to determine directly the percentages of 1,2-addition, trans-1,4-addition and cis-1,4-addition; these were 19.8, 59.2 and 18.5, respectively, for an emulsion polybutadiene (25).

Infrared spectroscopy was used by Hart and Meyer to investigate the effects of various styrene contents (26). Increasing the styrene content from 0 to 29 per cent caused a samll increase in the trans-1,4-addition and a corresponding decrease in the 1,2-addition. Foster and Binder arrived at the same conclusion (27). Johnson and Wolfangel found that the percentage of conversion and the amount of modifier had only a slight effect on the mode of addition of butadiene (28).

Hart and Meyer investigated also the effects of polymerization temperature (26). The percentage of trans-1,4-addition was found to increase and that of 1,2-addition to decrease with decreasing temperature. They stated that the heat and entropy of activation favored only slightly 1,4-addition over 1,2-addition. Condon calculated the variation in the percentages of the three modes of butadiene addition as a function of the polymerization temperature (29). His results were not in agreement with those of Medalia and Freedman who

found, by infrared spectroscopy, a small and irregular variation for various polybutadienes prepared at temperatures between 125° and 250°C. (30). Recently, the configuration of butadiene-styrene copolymers, produced at different temperatures with diazo compounds as initiators, was studied by Willis, Alliger, Johnson and Otto (31). They obtained results similar to those of Hart and Meyer (26).

From the investigations carried out by ozonolysis, perbenzoic addition and infrared spectroscopy, it is inferred that butadiene polymerizes simultaneously according to three modes of addition. The percentages of 1,2-addition, trans-1,4-addition and cis-1,4-addition are 20, 60 and 20 per cent, respectively, when the temperature of polymerization is 50°C.

Peroxide-Catalysed Additions to Butadiene

Since the first aim of our experimental work is to prepare the dimers of butadiene by a peroxide-catalysed process, it is of interest to review how inorganic and organic reagents generally add to butadiene. However, addition reactions of the Diels-Alder type, or, of ionic character, will not be included in this review; only those which are induced by atoms or free radicals will be considered.

Kharasch and his coworkers have studied the addition of many compounds, both inorganic and organic, to butadiene. Hydrogen bromide was allowed to react with butadiene at - 78° and - 15°C; the yield of 3-bromobutene-1, a 1,2-addition

product, was 60 and 25 per cent, respectively, whereas the yield of 2-bromobutene-2, indicating a 1,4-addition, was 40 and 75 per cent (32). The reaction between hydrogen chloride and butadiene gave 75 per cent of 3-chlorobutene-1, a 1,2-addition, and 25 per cent of 1-chlorobutene-2, a 1,4-addition; the percentages were not affected by an increase of the reaction temperature from -80° to $25^{\circ}C$; the results were the same with or without solvent (33). When butadiene was dissolved in bromotrichloromethane at $68^{\circ}C$, 1-bromo-5,5,5-trichloropentene-2, proof of 1,4-addition, was obtained in the proportion of 75 per cent (34).

The addition of free radicals, resulting from direct decomposition of hydroperoxides, were also studied. Thus, hydroperoxides, when decomposed at $0^{\circ}C$ in the presence of agueous ferrous salts, gave free alkoxy radicals (35).

$$ROOH + Fe^{++} \longrightarrow RO^{\bullet} + FeOH^{++} \qquad I$$
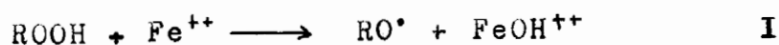
These free radicals formed the free 4-alkoxy-2-butenyl and 4-alkoxy-1-butenyl radicals by reacting with butadiene.

$$RO^{\bullet} + CH_2=CHCH=CH_2 \longrightarrow ROCH_2CH-CHCH_2^{\bullet}$$

$$1 \quad\updownarrow\quad 4 \qquad\qquad II$$

$$ROCH_2\underset{\bullet}{C}HCH=CH_2$$

$$1 \quad 2$$
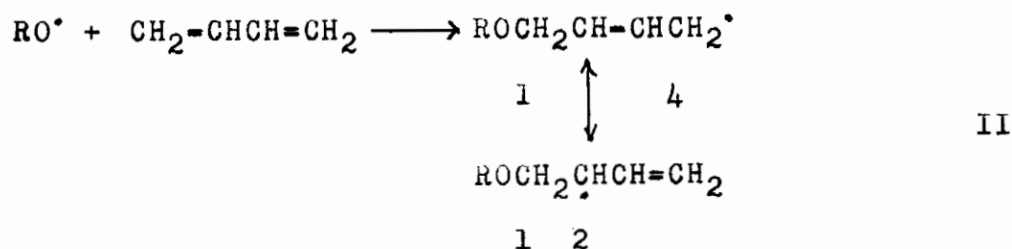
These, in turn, were assumed to demerize either separately
or jointly.

$$2 \ ROCH_2CH{=}CHCH_2{\cdot} \longrightarrow ROCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OR$$

    1   4   1   4, 4   1   III

$$2 \ ROCH_2\underset{\underset{\overset{\|}{CH_2}}{CH}}{CH}{\cdot} \longrightarrow ROCH_2CHCHCH_2OR \qquad IV$$

CH   CHCH
‖   ‖ ‖
CH₂   H₂C CH₂

        1   2   1 2,2 1

$$ROCH_2CH{=}CHCH_2{\cdot} + ROCH_2CH{\cdot} \longrightarrow ROCH_2CH{=}CHCH_2CHCH_2OR \qquad V$$

CH   CH
‖   ‖
CH₂   CH₂

1   4   1 2   1   4, 2 1
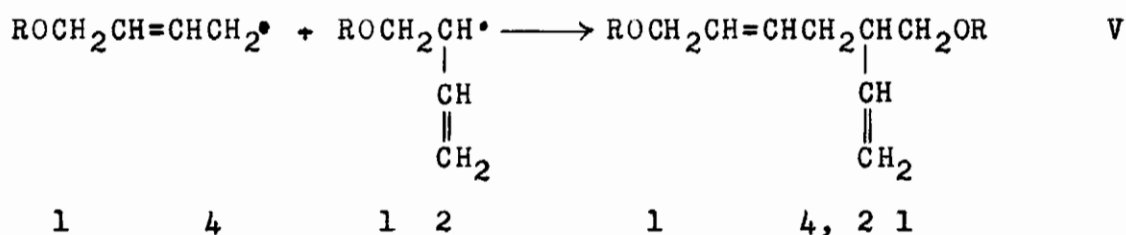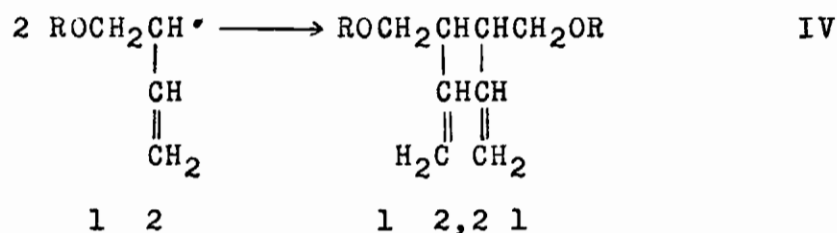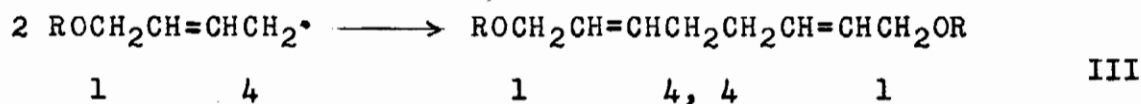
When tert-butyl hydroperoxide was used, 1,8-bis-tert-butoxy-
2,6-octadiene formed 80 per cent of the reaction products
(III). α-Cumyl hydroperoxide and hydrogen peroxide gave
similar products but the yields were smaller.

However, tert-butyl hydroperoxide, when decomposed
at $-7^{\circ}C$ by traces of cobalt salts, gave free tert-butyl peroxy
radicals which added to butadiene (36) in the following manner:
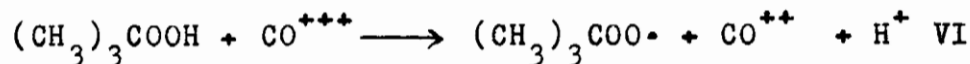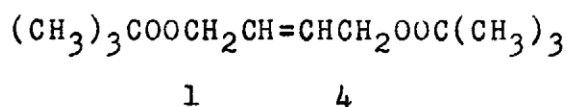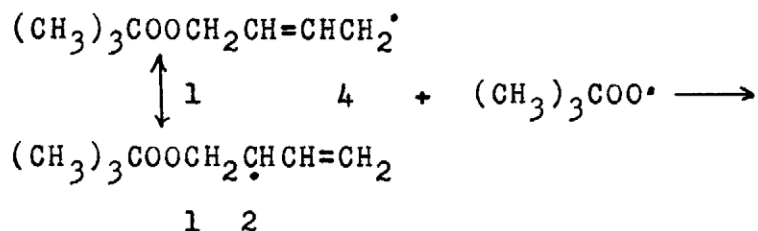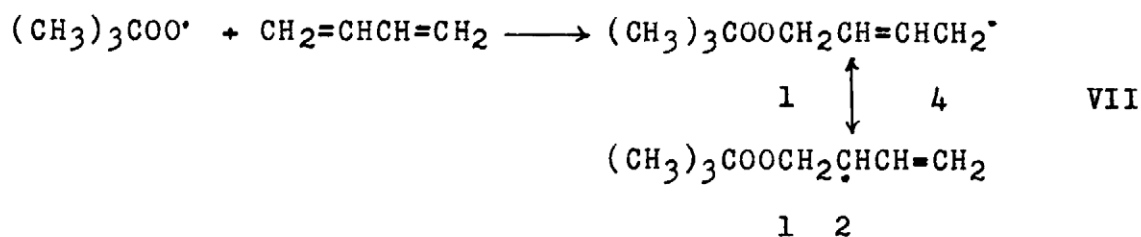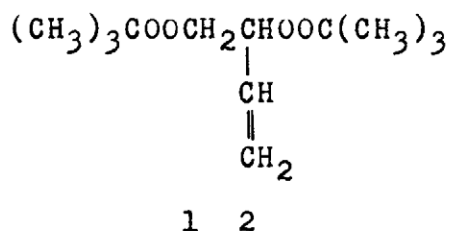
$$(CH_3)_3COOH + Co^{+++} \longrightarrow (CH_3)_3COO{\cdot} + Co^{++} + H^+ \qquad VI$$

$$C_4H_9SC_4H_6^{\bullet} + C_4H_9SH \longrightarrow C_4H_9SCH_2CH=CHCH_3 + C_4H_9S^{\bullet} \qquad XI$$
$$\phantom{C_4H_9SC_4H_6^{\bullet} + C_4H_9SH \longrightarrow C_4H_9S}1 4$$

$$C_4H_9SC_4H_6^{\bullet} + C_4H_9SH \longrightarrow C_4H_9SCH_2CH_2CH=CH_2 + C_4H_9S^{\bullet} \qquad XII$$
$$\phantom{C_4H_9SC_4H_6^{\bullet} + C_4H_9SH \longrightarrow C_4H_9S}1 2$$

$$C_4H_9SC_4H_6^{\bullet} + C_4H_9SH \longrightarrow CH_2=CHCHCH_3 + C_4H_9S^{\bullet} \qquad XIII$$

$$\begin{array}{c} | \\ S \\ | \\ C_4H_9 \\ 3 \ 4 \end{array}$$
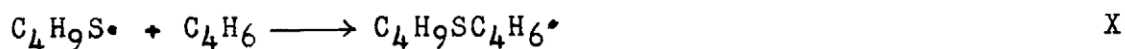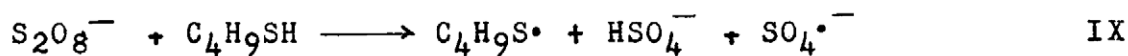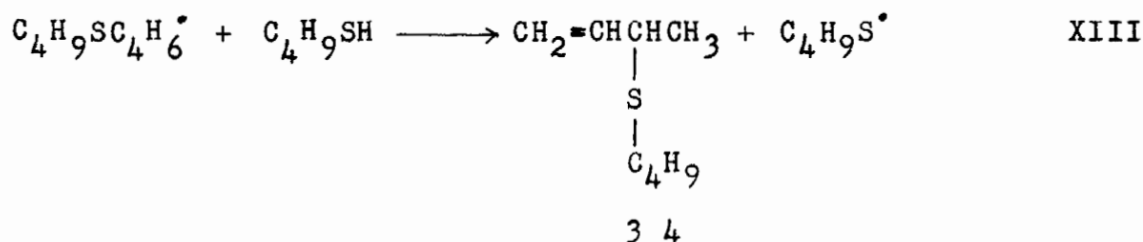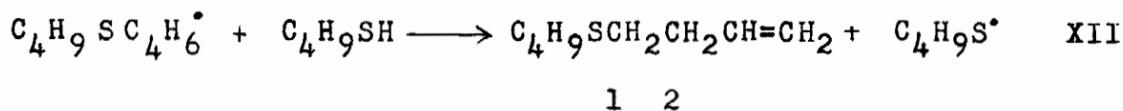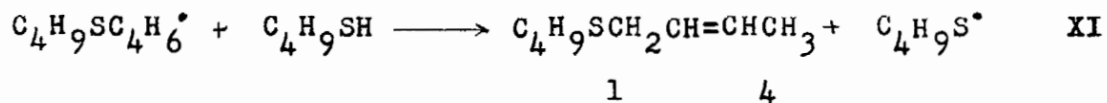
When equimolar amounts of n-butyl mercaptan and butadiene were allowed to react, the 1,4-addition product, crotyl n-butyl thioether, was formed (XI) exclusively.

The reaction between hexamethylenedithiol and butadiene was examined by Marvel and Cripps (38). This reaction did not yield polymers and the only product obtained was the dicrotyl ether of hexamethylenedithiol.

$$HS(CH_2)_6SH + 2C_4H_6 \longrightarrow CH_3CH=CHCH_2S(CH_2)_6SCH_2CH=CHCH_3 \quad XIV$$
$$1 4 1 4$$
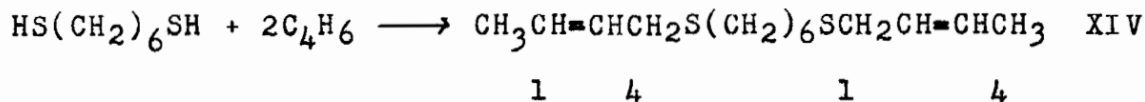
It is obvious from the preceeding works that the free-radical addition of inorganic and organic reagents to butadiene occurs preferentially at the terminal carbon atoms.

RESULTS AND DISCUSSION

Synthesis of Dimers

The facility with which butadiene polymerizes, is so great (39) that the preparation of dimers by a free-radical mechanism may not be realised unless a chain-transfer agent is used.

Solvent as chain-transfer agent

Flory (40) introduced the concept of chain transfer when Suess (41,42), Schulz (43), and Breitenbach (44) demonstrated implicitly that solvents might act as chain-transfer agents. Mayo developed a mathematical formula expressing the decrease of molecular weight of polystyrenes as a function of the concentrations of solvent and monomer (45). The formula was valid for various degrees of polymerization, except for the lower ones, as demonstrated by Gregg and Mayo (46, 47). Thus, the conditions for the preparation of dimers had to be determined experimentally.

Solvent chain-transfer was applied by Kharasch to obtain addition products between polyhalogenated methanes and various olefins (48, 49, 34). It was determined at that time that free radicals gave free trichloromethyl radicals by reacting with chloroform (48).

$$R^{\bullet} + CHCl_3 \longrightarrow RH + CCl_3^{\bullet}$$
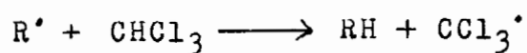
The latter free radical proved to be very reactive toward butadiene (34, 50).

Polyethylenes, with a degree of polymerization from one to five, were obtained by Joyce (51) and Harmon (52) when ethylene was dissolved in chloroform or in other halogenated methanes. Again, the solvent was incorporated in the polymer chain and the formation of free trichloromethyl radicals from chloroform was confirmed.

Dimerization mechanism

A dimerization mechanism may be proposed when chloroform is used as solvent and acetyl peroxide as a source of free radicals. The peroxide breaks down into free methyl and acetyl radicals which in turn liberate trichloromethyl radicals by reacting with chloroform.

$$(CH_3COO)_2 \longrightarrow CH_3^{\bullet} + CH_3COO^{\bullet} + CO_2 \qquad\qquad I$$

$$\begin{matrix} CH_3^{\bullet} \\ or\ CH_3COO^{\bullet} \end{matrix} + CHCl_3 \longrightarrow \begin{matrix} CH_4 \\ or\ CH_3COOH \end{matrix} + CCl_3^{\bullet} \qquad II$$
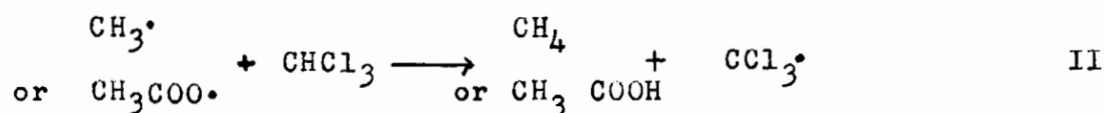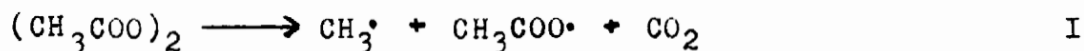
These, by attacking butadiene molecules at the terminal carbonatoms, form free trichloropentenyl radicals which are resonance hybrids:

$$CCl_3^{\bullet} + CH_2{=}CHCH{=}CH_2 \longrightarrow CCl_3CH_2CH{=}CHCH_2^{\bullet} \qquad III$$

$$1 \updownarrow 4$$

$$CCl_3CH_2\overset{\bullet}{C}HCH{=}CH_2$$

$$1\quad 2$$

Each trichloropentenyl radical gives rise to trichloronona-
dienyl radicals by reacting with butadiene molecules:

$$CCl_3CH_2CH=CHCH_2\cdot + CH_2=CHCH=CH_2 \longrightarrow CCl_3CH_2CH=CHCH_2CH_2CH=CHCH_2\cdot$$

$$\underset{1}{\quad} \underset{4}{\quad} \qquad \underset{1}{\quad} \underset{4,1}{\quad} \updownarrow \underset{4}{\quad}$$

$$CCl_3CH_2CH=CHCH_2CH_2\ \underset{\cdot}{C}HCH=CH_2$$

$$\underset{1}{\quad} \underset{4,1}{\quad} \underset{2}{\quad}$$

IV

$$CCl_3CH_2\underset{|}{CH}\cdot + CH_2=CHCH=CH_2 \longrightarrow CCl_3CH_2\overset{*}{\underset{|}{C}}HCH_2CH=CHCH_2\cdot$$

with side chain:

$$\underset{CH}{\underset{\parallel}{\quad}}$$
$$CH_2$$

$$\underset{1}{\quad} \underset{2}{\quad} \qquad \underset{1}{\quad} \underset{2,1}{\quad} \updownarrow \underset{4}{\quad}$$

V

$$\overset{*}{CCl_3CH_2\underset{|}{C}HCH_2\underset{\cdot}{C}HCH=CH_2}$$

$$\underset{CH}{\underset{\parallel}{\quad}}$$
$$CH_2$$

$$\underset{1}{\quad} \underset{2,1}{\quad} \underset{2}{\quad}$$

Each free trichlorononadienyl radical then becomes a stable
dimer by extracting a hydrogen atom from a chloroform mole-
cule, thus producing a new free trichloromethyl radical which
may repeat the same process (Equation III).

Four dimers, isomers of trichlorononadiene, may be
obtained according to the mode of addition of butadiene. The
first two are straight-chain molecules (Equation IV). Since
the last two isomers (Equation V) have an asymmetric (*) carbon
atom, two other optical isomers are possible.

Experimental procedure

After many lengthy trials, appropriate experimental conditions were determined and the following procedure was adopted. A solution, containing 18.5 gm. of butadiene (0.34 mole) and 20 gm. of acetyl peroxide (0.17 mole) per 4000 gm. of chloroform (33.5 moles), was maintained at $50^{\circ}C$. during seven days. At the end of this period, the chloroform was expelled by distillation in vacuo at room temperature until the volume of the solution had been reduced to 200 ml. It was then treated with an aqueous solution of ferrous sulfate to destroy any residual peroxide, washed with water and dried with anhydrous sodium sulfate. The remaining chloroform was removed under vacuo leaving a residue of 19.9 gm. (yield: 51 per cent).

This residue was a yellow liquid with a fishy odour (several people identified the odour as that of cod liver or whale oil). When a freshly prepared sample was heated above $50^{\circ}C$, it evolved hydrogen chloride. No distillation occurred when it was submitted to a vacuum of 10μ at room temperature.

Identification of dimers

The identification of the residue as butadiene dimer or dimers is based on the results shown in Table I.

Findings from elemental analysis and molecular weight determination agree with the calculated values. The molar refraction is lower than that calculated by 1.9 unit; this lower value is not unreasonable if one considers that the additivity of

TABLE I

IDENTIFICATION OF DIMERS

	Calculated or expected	Found
% Cl	46.5	46.7
% C	47.5	47.5
% H	5.75	5.59
Molecular weight	227.6	227.
Specific gravity at 25°C	---	1.214
Refractive index n_D^{25}	---	1.5061
Molar refraction	57.3	55.4
Ultraviolet spectrogram	no conjugated C = C bonds	no conjugated C = C bonds
Infrared spectrogram	$RCH = CHR^1$ cis	yes
	$RCH = CHR^1$ trans	yes
	$RCH = CH_2$	yes
	$- CH_3$ groups	yes
	C - Cl bonds	yes
	no C = O groups	traces
Iodine number (Wijs method)	223	152
(modified method)	223	168
(modified method)	223	208
Optical activity	---	none
Urea complex formation	---	none

constant increments for each typical bond is not strictly valid and that diferences have been observed between isomers (53).

The ultraviolet spectrogram revealed the absence of conjugated carbon-carbon double bonds as it was expected. The structural configuration RCH-CHR', which indicates a 1,4-addition, and the $RCH=CH_2$ configuration which denoted a 1,2-addition, were identified by infrared spectroscopy. Methyl groups, indicating a terminal 1,4-addition, and carbon-chlorine bonds were also identified. However, the revealed traces of carbonyl group were not expected. Carbonyl groups may have resulted from a reaction between free acetyl radicals and butadiene molecules, the reaction products not being eliminated completely during the purification of the dimers.

The iodine number, determined by the Wijs method (54) was low, 152. A value of 168 was found when the reaction time was increased from thirty to sixty minutes and a value of 208 was obtained when the concentration of chlorine was increased to five times the concentration of iodine, the reaction time being thirty minutes. Faragher, Gruse and Garner (55), von Mikusch and Frazier(56), and Rehner (57) established that the addition of iodine monochloride to ethylenic compounds gave unpredictable results. The experimental conditions of iodine monochloride addition were modified often in order to obtain the expected degree of unsaturation in natural and synthetic rubbers (57,58,59,60).

No optical activity was found although optical isomers were possible. However, their formation is not excluded because optical isomers would be produced in equal amounts.

Urea is known to form insoluble complexes with normal alkanes and alkenes (61, 62) but, when the dimer was treated by this reagent, no precipitate was obtained. This negative result is not a proof that straight-chain dimers were not formed; it is probable that the three chlorine atoms, even though they are on carbon one, prohibit a urea complex formation (62).

Structure of the Dimers

The infrared spectrogram revealed the presence of groupings which had been formed necessarily from 1,2-and 1,4- additions but other means had to be used to determine which of the four isomers were produced. Reduction, hydroxylation and ozonolysis were applied to elucidate the structures of dimers.

Reduction

A complete hydrogenation of the dimers or a selective hydrogenation of carbon-carbon double bonds is not suitable to distinguish each dimer since two of the possible isomers give the same nonane or trichlorononane (I);

A) $CCl_3CH_2CH=CHCH_2CH_2CH=CHCH_3$

    1   4, 1   4

B) $CCl_3CH_2CH=CHCH_2CH_2CH_2CH=CH_2$

    1   4, 1   2

$CH_3(CH_2)_7CH_3$

or   I

$CCl_3(CH_2)_7CH_3$
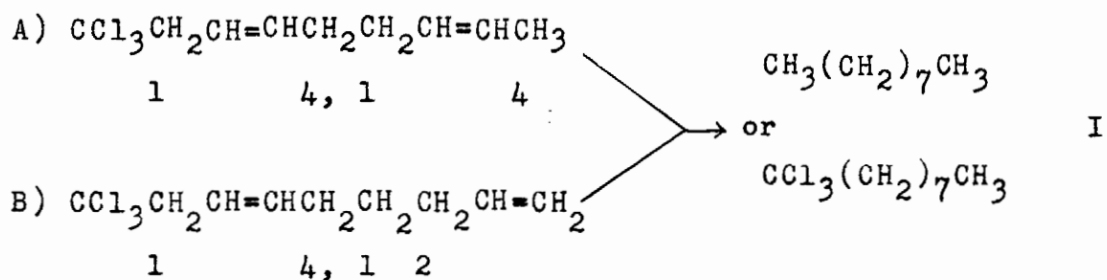
the other two produce the same ethylheptane or trichloroe-
thylheptane (II).

C) $CCl_3CH_2\underset{|}{C}HCH_2CH=CHCH_3$
              $\underset{\|}{CH}$
              CH_2

    1   2,1   4

$CH_3CH_2\underset{|}{C}H(CH_2)_3CH_3$
           $\underset{\|}{CH_2}$
           CH_3

or   II

D) $CCl_3CH_2\underset{|}{C}HCH_2CH_2CH=CH_2$
              $\underset{\|}{CH}$
              CH_2

    1   2,1   2

$CCl_3CH_2\underset{|}{C}H(CH_2)_3CH_3$
           $\underset{\|}{CH_2}$
           CH_3
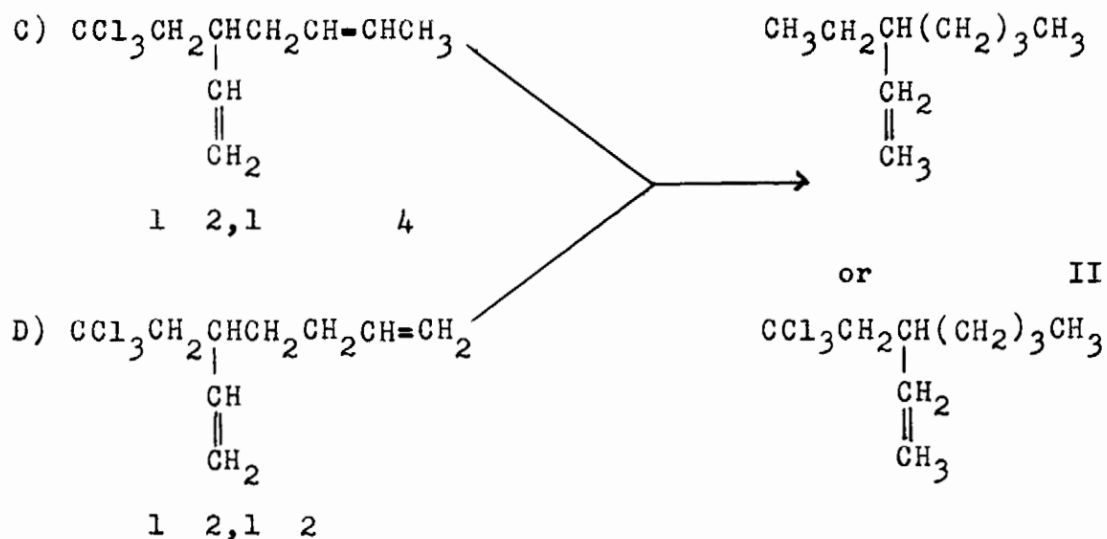
However, substitution of the chlorine by hydrogen
atoms leaves a mixture of nonadienes corresponding to the
original dimers. The mixture could afterwards be resolved
by fractional distillation. Johnson, Blizzard and Carhart
(63), Nystrom and Brown (64) and Dibeler (65) have established
that lithium aluminum hydride in anhydrous ether solution is
an efficient reagent to replace halogen by hydrogen atoms
without hydrogenation of carbon-carbon double bonds.

The dimers were treated by this reagent and nona-
dienes were obtained in good yield (93.5 per cent). Unfortu-
nately, the ultraviolet spectra of the nonadienes revealed
the presence of conjugated carbon-carbon double bonds, indica-
ting that the reduction reaction caused a displacement of the
double bonds. It was therefore impossible to distinguish the
original dimers by this method.

Hydroxylation

Hydroxylation of carbon-carbon double bonds yields
glycols which could be split by lead tetraacetate or periodic
acid (66); examination of the fragments would permit the re-
constitution of the original dimers. Hydroxylation may be
accomplished by peracetic acid as demonstrated by Swern, Billen,
Findley and Scanlan (67), or by N-bromosuccinimide as shown
by Raphael (68).

The reaction product obtained was a white sticky
paste when the dimers were treated by peracetic acid. No
distillation occurred when it was submitted to a vacuum of
10 μ but a darkening and an evolution of hydrogen chloride
were observed as the temperature was increased from 20 to
260°C. The following determinations were carried out on the
paste, considered to be $C_9H_{17}O_4Cl_3$.

	Calculated	Found
Iodine number - Wijs (54)	0.0	5.6 - 7.1
Hydroxyl group - acetylation (69)	23.0%	8.1%
Active hydrogen - Zerewitinoff (70)	1.35%	0.50%
Chlorine content - Stepanow (71)	36.1%	34.1%

These results indicated that hydroxylation with per-acetic acid gave poor yields since only one third of the hydroxyl groups and one third of the active hydrogen were found. Moreover, polymerization of the dimers was suspected to have proceeded along with the hydroxylation since the carbon-carbon double bonds were reduced to a greater extent than the hydroxyl groups were formed; theoretically, each carbon-carbon double bond should produce two hydroxyl groups. For these reasons, the hydroxylated product was not considered adequately representative of the original dimers.

When the dimers were treated by aqueous N-bromosuccinimide (68), a brown viscous liquid was obtained. The hydroxyl-group content (69) was found to be 3.0 per cent instead of 23 per cent, as calculated for $C_9H_{17}O_4Cl_3$. Since the yield in hydroxylated product was lower than by the peracetic acid technique, it was decided to abandon any hydroxylation scheme.

Ozonolysis

Ozonolysis followed by oxidative hydrolysis, was found to be more efficient than the preceeding techniques, even though it has not been considered strictly accurate by Rabjohn (10)

and Marvel (12).

If the dimers are submitted to that treatment, they produce the acids shown in Figure I. Each mole of dimer produces acids corresponding to four equivalents of neutralization. However, the nature and amount of each acid depend on the structure of each dimer. Succinic acid is formed only from dimer A. Acetic acid is obtained from dimer A and dimer C; one mole is obtained from one mole of each dimer. Formic acid is formed from dimer B and dimer D; dimer B gives one mole, whereas dimer D gives two moles of formic acid. By determining the amounts of succinic, acetic and formic acids produced by ozonolysis and oxidative hydrolysis of the dimers, a quantitative discrimination of each dimer is possible.

Experimental results

The dimers were treated with ozone and the resulting ozonides decomposed with hydrogen peroxide. The yield in organic acids was between 70 and 80 per cent, depending on the experimental conditions, such as temperature of ozonolysis and excess of ozone. This yield agrees well with those obtained by Alekseeva (7), Rabjohn (10) and Marvel (11).

The organic acids were separated by partition chromatography on a silica gel column according to the technique developed by Marvel and Rands (72), and improved by Bulen, Varner and Burrell (73). The chromatogram of the total acids is shown in Figure II. Two other chromatograms were obtained when the total acids were separated into volatile and non volatile fractions.

ACIDS OBTAINABLE FROM DIMERS

A) $CCl_3CH_2CH=CHCH_2CH_2CH=CHCH_3$ $\longrightarrow$ CCl_3CH_2COOH

    1   4, 1   4

+ $\boxed{HOOCCH_2CH_2COOH}$

+ $\boxed{CH_3COOH}$

B) $CCl_3CH_2CH=CHCH_2CH_2CH_2CH=CH_2$ $\longrightarrow$ CCl_3CH_2COOH

    1   4, 1   2

+ $HOOCCH_2CH_2CH_2COOH$

+ $\boxed{HCOOH}$

C) $CCl_3CH_2CHCH_2CH=CHCH_3$ $\longrightarrow$ $CCl_3CH_2CHCH_2COOH$

           | |

           CH   COOH

   −−||−−

           CH_2

+ $\boxed{CH_3COOH}$

    1   2,1   4

+ $\boxed{HCOOH}$

D) $CCl_3CH_2CHCH_2CH_2CH=CH_2$ $\longrightarrow$ $CCl_3CH_2CHCH_2CH_2COOH$

           | |

           CH   COOH

   −−||−−

           CH

+ 2 $\boxed{HCOOH}$
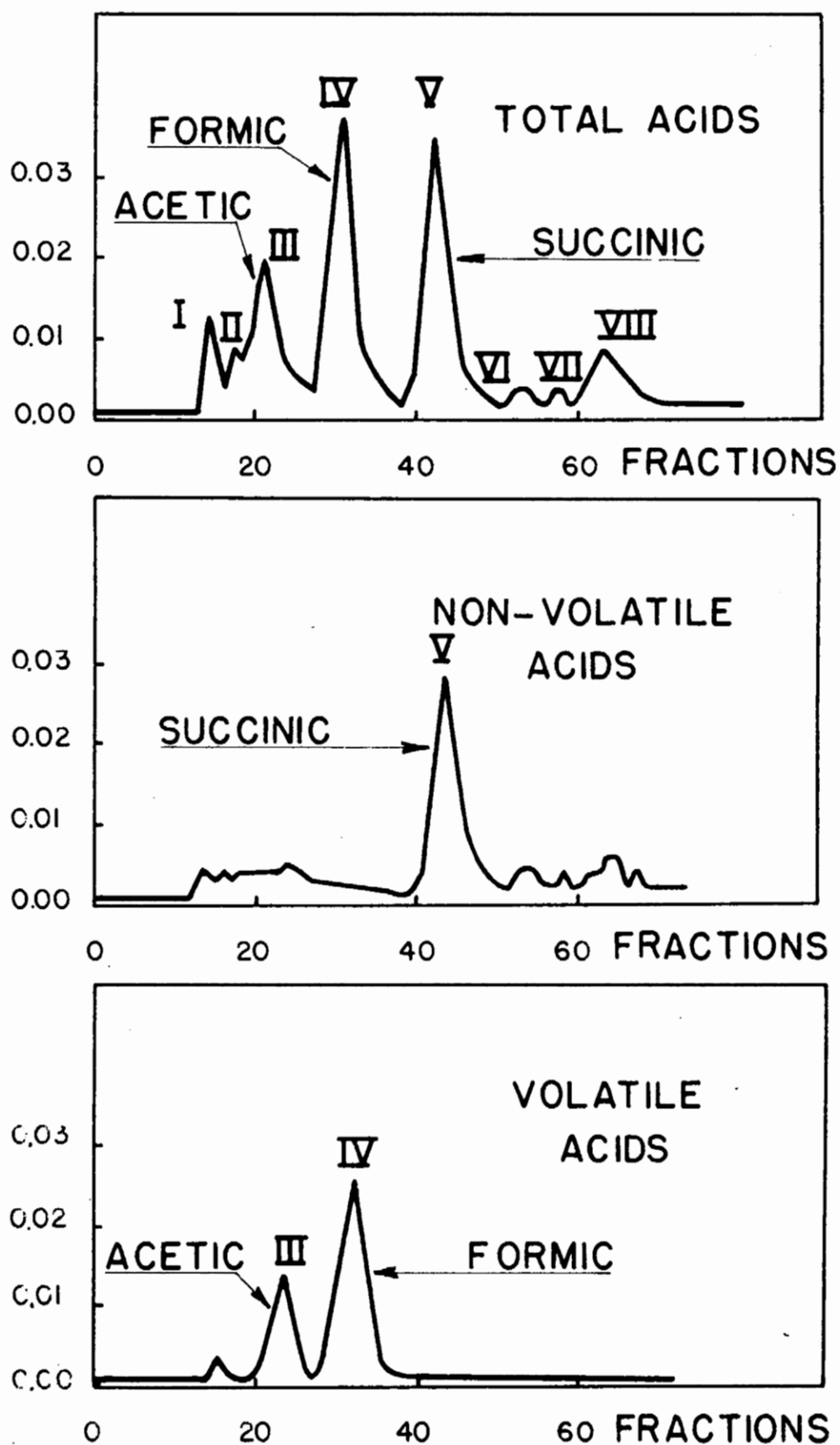
    1   2,1   2

Figure I

Figure II. . Chromatograms of the Acids Obtained
by Hydrolysis of the Dimers Ozonides.

Peak V in the total acids chromatogram was repro-
duced at the same eluant fraction in the non-volatile acids
chromatogram; the acid corresponding to this peak was identi-
fied as succinic acid. Peaks III and IV in the total acids
chromatogram occurred at the same eluant fractions in the vo-
latile acids chromatogram; the acids corresponding to these
peaks were identified as acetic and formic acids, respectively.

The acids corresponding to peaks I and II contained
chlorine. For reasons more apparent in the conclusion, they
were assumed to be mainly 3,3,3-trichloropropionic acid and
(2,2,2-trichloroethyl)-2-glutaric acid or fragments of these.
The 3,3,3-trichloropropionic acid hydrolyses very easily ac-
cording to Brown and Musgrave (74) and the (2,2,2-trichloroe-
thyl)-2-glutaric acid seems to be unknown. The acids corres-
ponding to peaks VI, VII and VIII did not contain chlorine;
they were assumed to be other hydrolysis products of the chlo-
rinated acids.

Conclusion

On a basis of one mole of dimer, 0.45 mole of succinic
acid, 0.44 mole of acetic acid and 1.0 mole of formic acid
were obtained.

Since only dimer A gives succinic acid and since one
mole of dimer A gives one mole of succinic acid, it is conclu-
ded that the mole fraction of dimer A is 0.45. Since the for-
mation of acetic acid is equal to the formation of succinic
acid, all of the acetic acid comes from dimer A. Thus, dimer C

is not produced; otherwise the experimental value for acetic
acid should be higher than that of succinic acid. If the re-
maining mole fraction, 0.55 mole, is the dimer D, it should
yield 2 x 0.55 mole of formic acid; experimentally 1.0 mole
of formic acid was determined. Thus the remaining mole frac-
tion is mostly dimer D, and if dimer B is produced, it is only
in small quantities.

Dimers A and D are obtained in approximately equal
amounts, 45 and 55 per cent. Consequently, when butadiene
is dimerized by a free-radical chain-transfer mechanism, if
the initial step is a 1,4-addition, the second step is also
a 1,4-addition as in the case of dimer A; if, on the other
hand, the initial step is a 1,2-addition, the second step is
also a 1,2-addition as in the case of dimer D.

Discussion

These results are in agreement with those obtained
by Kharasch (36); when tert-butyl hydroperoxide was decomposed
by traces of cobalt salts in presence of butadiene, nearly
equal amounts of 1,2-and 1,4-addition products were produced.
These results also confirm the work of Hart and Meyer (26)
who found that the heat and entropy of activation favor only
slightly 1,4-addition over 1,2-addition.

However, in polybutadienes the percentage of 1,2-
addition is not 50 per cent as it was found in our dimers,
but only 20 per cent. This discrepancy could be explained
by the fact that, in dimers, the predominating steps are the

initiation and termination of the chains, whereas, in polymers, the predominating step is the propagation of the chains. Alfrey, Bohrer and Mark state that a greater propagation rate for 1,4-addition over 1,2-addition can be ascribed to a steric effect (75).

The most striking fact is that the second step of the dimerization is like the initial step: a 1,4-addition when the initial step is a 1,4-addition, a 1,2-addition when the initial step is a 1,2-addition. If these results are extrapolated to polybutadienes, two other varieties of polybutadienes should be found along with the conjunctive 1,2-and 1,4-variety: one variety produced exclusively by 1,2-additions, another variety produced exclusively by 1,4-additions. This assumption, enuntiated by Hill, Lewis and Simonsen (4), has not as yet received direct experimental support. However, our calculations, based on the results obtained by several investigators, show that independent varieties of polybutadienes might be found.

Marvel found that polybutadienes of different conversions gave large amounts of succinic acid and small amounts of 1,2,4-butanetricarboxylic acid (12). Succinic acid may result only from adjacent 1,4-additions (I).
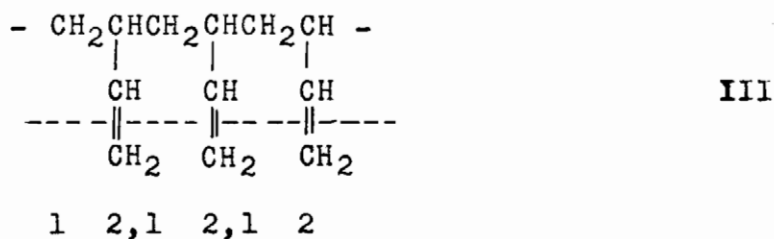
$$- CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2- \qquad I$$

1   4, 1   4, 1   4
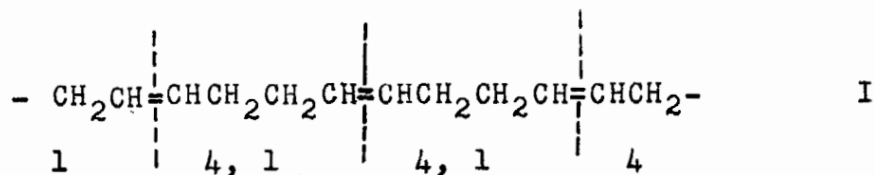
On the other hand, 1,2,4-butanetricarboxylic acid may be formed
only from a structural unit in which the 1,2-addition is in-
corporated between two 1,4-additions (II).

$$- CH_2CH\text{-}CHCH_2CH_2CHCH_2CH\text{-}CHCH_2- \qquad II$$
$$CH$$
$$---\|---$$
$$CH_2$$

1   4, 1   2,1   4
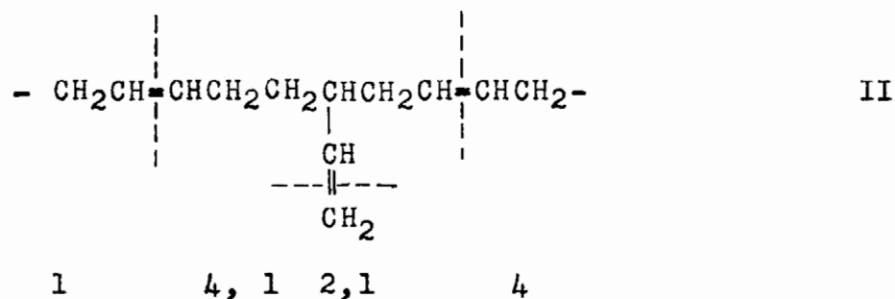
Taking into account that 20 per cent of the butadiene poly-
merizes according to a 1,2-addition, and, if each of these
1,2-additions occurs between two 1,4-additions (Il), the re-
sulting polybutadiene will give, under ozonolysis, a (succinic
acid) / (1,2,4-butanetricarboxylic acid) ratio equal to three
on a mole basis. From the results of Marvel (12) we calculated
this ratio to be about fourteen for many polybutadienes. For
butadiene - (o-chlorostyrene) (11) and butadiene-styrene (12)
copolymers, the ratios were eight and five, respectively.

A ratio higher than three may be explained only by
the formation of adjacent 1,2-additions in the polymers (III).

$$- CH_2CHCH_2CHCH_2CH -$$
$$CH \quad CH \quad CH \qquad III$$
$$--- -\|---- \|-- --\|----$$
$$CH_2 \quad CH_2 \quad CH_2$$

1   2,1   2,1   2

When adjacent 1,2-additions take place, less 1,2-units are available to form the structural unit II and more 1,4-units are available to become adjacent (I). A ratio of fourteen implies that most of the 1,4-additions are grouped together and consequently most of the 1,2-additions are also grouped together.

This implication is not a proof that independent varieties of polybutadienes are really produced during polymerization because long sequences of 1,4-additions and 1,2-additions may be distributed along the same chain. For instance, structural unit IV, where the sixteen 1,4-addition units are represented by A and the four 1,2 addition units by B, gives a ratio of fourteen under ozonolysis.

-A--A--A--A--A--A--B--A--A--A--A--A--A--A--A--B--B--B--A--A   IV

Structural unit IV resembles a copolymer chain where A and B are different monomers. The butadiene, before reaction, is a single species but, at the instant of its reaction or activation, it behaves like two monomers. Well, Powers, Sands and Stent have already set forth a somewhat similar opinion (76). On the other hand, Alfrey, Bohrer and Mark established that long sequences of the same units along the copolymer chain are remotely probable from a mathematical standpoint (77). Short sequences of each unit along the copolymer chain are obtained if the free-radical growing chain, whatever be the nature of the ending unit, has the aptitude to react nearly as well with one monomer as with the other. It seems that butadiene has not this aptitude since nearly all the dimers

are formed only by adjacent 1,4-additions or adjacent 1,2-additions, even though the overall percentage of 1,2-additions is 50 per cent instead of 20 per cent as in polymers. It follows that the probability of finding independent varieties of polybutadienes is relatively high.

Suggestions for further work

A direct experimental proof that independent varieties of polybutadienes are produced could be attempted by using a new technique, urea complex formation, which is efficient in seperating normal from branched alkenes (62). However, some difficulties, which will be encountered by using urea, may be mentioned. One is to find a mutual solvent for urea and polybutadienes. The urea complex formation with n-alkenes of high molecular weight is unknown. Chain branching seems to occur preferentially with 1,4-addition units, as determined by Marvel (12).

If the urea complex formation fails to give positive results with high molecular weight polymers, the reaction could be tried with polybutadienes of low molecular weight, using a straight-chain compound as chain-transfer agent. Gregg and Mayo have determined the efficiency of many straight-chain compounds as chain-transfer agents (78). The advantage of a butadiene trimer or tetramer is to reduce the difficulties previously mentioned but the approach of the problem becomes less direct.

EXPERIMENTAL PART

Experimental conditions leading to the preparation of butadiene dimers by a free-radical chain-transfer mechanism were studied. When produced, the dimers were identified by classical methods and their structures were examined by means of ultraviolet and infrared spectroscopy. Further investigations of their structures were attempted by reduction, hydroxylation, and ozonolysis but only ozonolysis was successful.

Determination of the Experimental Conditions

Purification of the reagents

Butadiene, supplied by Polymer Corporation Limited, was purified by passage through the following train: a trap for solids, two wash bottles half-filled with a 10 per cent aqueous solution of sodium hydroxide, a drying tube filled with anhydrous calcium chloride and a trap cooled at $-10^{\circ}C$; the butadiene was received in a flask cooled with a dry ice - acetone mixture. Chloroform was washed with water, dried with calcium chloride and distilled through a nine-plate column. At first a 30 per cent solution of acetyl peroxide in dimethyl phthalate was used as supplied by the Buffalo Electro-Chemical Company. Later, the acetyl peroxide was prepared specially.

Qualitative experiments

The initial experiments were qualitative only. Various amounts of butadiene and acetyl peroxide were dissolved in chloroform. The solutions (about 100 ml.) were maintained at 50°C. during seven, sixteen or twenty four hours. Hydroquinone was added to stop the polymerization. The chloroform was removed by distillation at atmospheric or reduced pressure. The residues, when there was a residue, were dark brown liquids or solids. When heated above 60°C. they started to decompose.

It was concluded that polybutadienes of low molecular weight could be produced in good yields by lengthening the polymerization time and increasing the quantities of reagents. The nature of these polymers did not permit their purification by a heating process. Thus, high-boiling compounds such as dimethyl phthalate and hydroquinone should be avoided in the polymerization solution.

Preparation of acetyl peroxide in chloroform solution

The acetyl peroxide in chloroform solution was prepared according to the procedure of Shawinigan Chemicals Company (79). In a flask equiped with a stirrer, 105 gm. of acetic anhydride, 91 gm. of chloroform and 0.75 gm. of calcium hydroxide were added in that order. The stirrer was started and run at least fifteen minutes while the reagents were cooled to 15°C. Then, 61 gm. of a 30 per cent solution of hydrogen peroxide were added in six portions. After each addition, the

temperature rose to 25°C. and was reduced to 15°C. before the next addition. At the end, the solution was stirred during thirty minutes until the temperature rose to 25°C. The solution was washed, in a separatory funnel, successively with 80, 120 and 150 ml. of distilled water. The acetyl peroxide in chloroform solution was dried with anhydrous calcium chloride and filtered through a fine cloth.

Analysis of acetyl peroxide

The acetyl peroxide in chloroform solution was analysed by the iodometric method of Nozaki (80). The peroxide sample (1.00 ml.) was placed in a glass-stoppered Erlenmeyer flask and 10 ml. of acetic anhydride and 1.5 gm. of powdered sodium iodide were added. After swirling to dissolve the iodide, the solution was allowed to stand from five to twenty minutes. Water (75 ml.) was added and the mixture was shaken vigorously for half a minute. The iodine was titrated with a 0.1 N. thiosulfate solution, using starch as indicator.

Quantitative experiments

The aim of these experiments was to determine which concentrations of butadiene and acetyl peroxide would give dimers. Different quantities of these reagents were dissolved in 4000 gm. of chloroform. The solutions were maintained at 50°C. during ninety or one hundred and sixty hours. At the end of this period, the chloroform was removed by distillation in vacuo at room temperature until the volume of the solution had been reduced to 200 ml. This operation required from six

to nine hours. The residual acetyl peroxide was destroyed by adding 30 ml. of acetic acid, 100 ml. of water and 30 gm. of ferrous ammonium sulfate. Vigorous stirring was necessary to mix the aqueous and chloroform phases. The aqueous solution was decanted and the operation was repeated with fresh solutions of ferrous sulfate until the green color of this solution did not change after a stirring of forty minutes. Usually four treatments were required. Then the chloroform solution was washed four times with 100 ml. of water and dried with anhydrous calcium chloride and magnesium sulfate. After filtration, the chloroform was expelled under vacuo, leaving a liquid polymer.

The degree of polymerization, n, was evaluated for each polybutadiene, $CCl_3(C_4H_6)_nH$, by determining its chlorine content. The theoretical variation of chlorine content with the degree of polymerization is given below.

Degree of Polymerization n	Chlorine Content (weight per cent)
1	61.0
2	46.5
3	37.6
4	31.6
5	25.6
10	16.1

The influence of butadiene and acetyl peroxide concentrations and the influence of polymerization time are shown in Table II. This may be summarized as follows; when the concentration of acetyl peroxide is increased and when the concentration of butadiene is decreased, the degree of polymerization is lower. When the polymerization time is increased, the degree of polymerization is higher except in the cases of low butadiene concentrations. Greater amounts of polymer were produced when the reaction time was longer. These results are in good agreement with those obtained by Mayo on styrene (47).

Determination of chlorine content

The chlorine content of each polybutadiene was determined by the method of Stepanow, improved by Drogin and Rosanoff (81) and further modified by Feldman and Powell (71). Each sample (0.1 to 0.3 gm.) was weighed in a small vial and placed in a 250 ml. Erlenmeyer flask fitted with a reflux condenser. Absolute alcohol (40 ml.), previously distilled over metallic sodium, was added and the flask was heated over a low Bunsen flame until the sample had dissolved. Then, the burner was removed and 5.5 gm. of sodium (reagent grade) were introduced through the top of the condenser. The sodium was cut into rods about 2.5 cm. long and forty minutes were allowed for the dissolution of sodium; at no time there were more than three pieces of sodium in the flask. At the end of the sodium addition, the solution was gently refluxed for ninety minutes, after which it was allowed to cool. Water (25 ml.) was added,

TABLE II

DEGREE OF POLYMERIZATION OF POLYBUTADIENES

Butadiene (mole fraction)	Acetyl Peroxide (mole fraction)	Degree of Polymerization for a Polymerization Time of 90h. and of 160h.	
0.16	0.08	11.	11.
0.16	0.008	7.6	13.
0.04	0.02	4.7	5.0
0.04	0.002	9.5	12.
0.02	0.01	3.6	4.0
0.02	0.001	4.9	8.5
0.01	0.005	2.3	2.1
0.01	0.0005	5.0	3.4
0.005	0.0025	2.3	2.2

at first drop by drop because the reaction was violent. The flask was held under running water and the solution was neutralized with a 6N. nitric acid solution. The adsorption indicator, dichlorofluorescein, was added and the solution was titrated with a 0.1N. silver nitrate solution.

Identification of the Dimers

The liquid product, having a degree of polymerization of 2.1 (Table 11), was submitted to vacuum distillation at temperatures between 20° and 45°C. When the vacuum was of 0.01 mm., only a few drops of distillate were collected from 5 ml. batches. Thus, this liquid product was considered as a mixture of dimers and not as a mixture of trichloropentenes, dimers, trimers, tetramers, etc. Trichloropentenes would have distilled under such conditions. The boiling temperatures of one trichloropentene and two trichloropentanes are between 70° and 84°C. when the absolute pressure is 15 mm. (82); if the absolute pressure is reduced to 0.01 mm., these compounds should boil theoretically at temperatures below 0°C. (83).

Elemental analysis

The chlorine content of the dimers was determined by the method of Stepanow (71); the average of five determinations was 45.6 per cent. By a complete analysis (I), chlorine,

---

(I) The complete analysis of the dimers was carried out by the "Laboratory of Microchemistry", Dr. Carl Tiedcke, Teaneck, N.J., U.S.A.

carbon and hydrogen percentages were found to be 46.68, 47.51 and 5.59, respectively, whereas the calculated values for $Cl_3C_9H_{13}$ are 46.5, 47.5 and 5.75.

Molecular weight

The molecular weight of the dimers was determined by cryoscopy in benzene.

Dimers (grams)	Benzene (grams)	$\dfrac{\text{Dimers x 100}}{\text{Benzene}}$	$\triangle t$	Molecular weight
0.140	27.005	0.52	0.113	235
0.270	26.895	1.00	0.201	256
0.440	26.775	1.64	0.321	262

These results were plotted and, by extrapolation to a zero concentration, the molecular weight of the dimers was found to be 227 as shown in Figure III. This is to be compared with a theoretical value of 227.6.

Specific gravity at $25^{\circ}C$

The specific gravity of the dimers was obtained by using a 10 ml. pycnometer. A specific gravity of 1.214 was found.

Refractive index, n_D^{25}

An Abbé-Spencer refractometer was used to determine the refractive index of dimers. A value of 1.5061 was obtained.
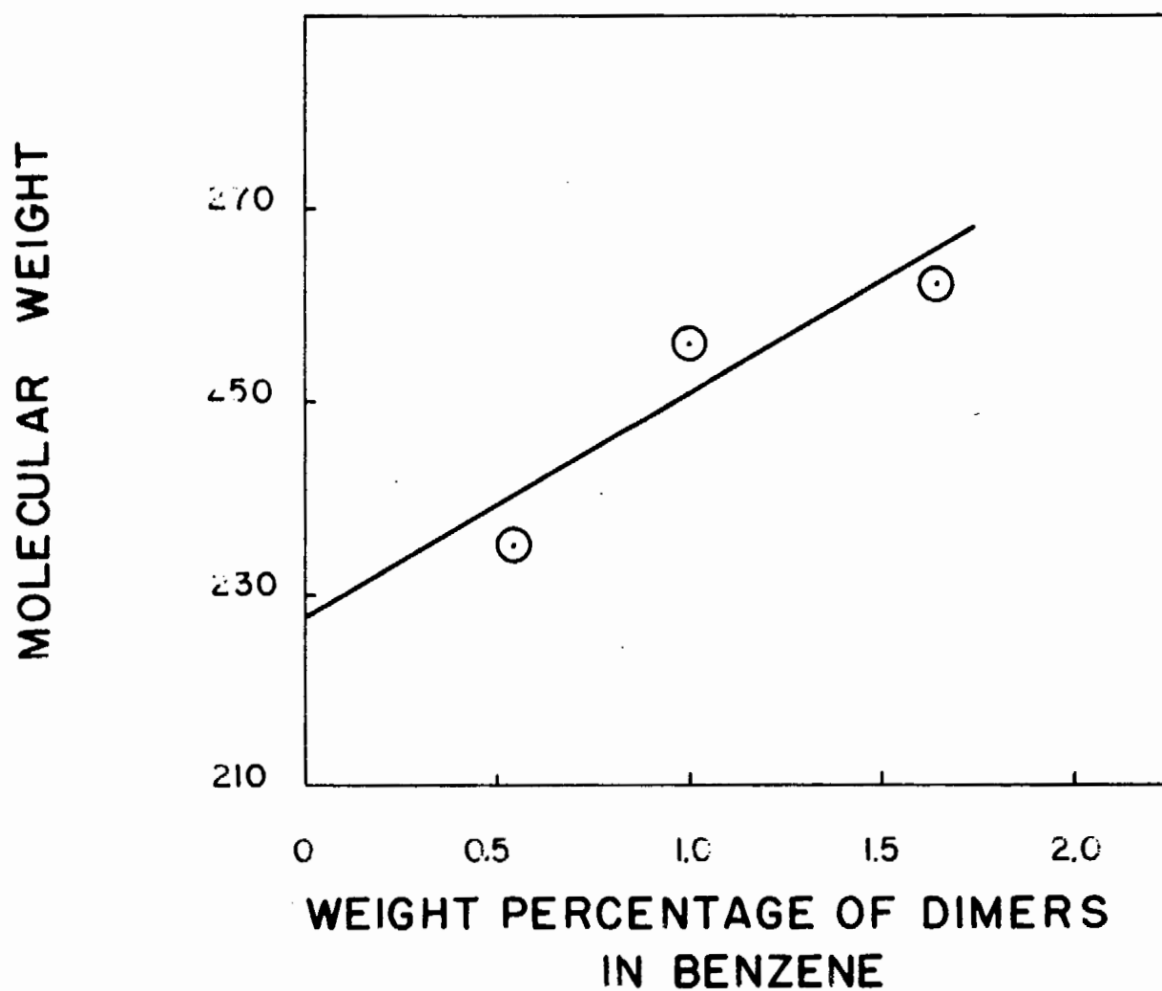
Figure III. Molecular Weight of the Butadiene Dimers

Ultraviolet spectrogram

A Beckman spectrophotometer, model DU, provided with the ultraviolet accessory set, was used. Optical density readings were taken at each 25Å from 2175 to 3500 Å. The slit was adjusted, before each reading below 3150Å, to obtain a 10 Å band. The dimers (0.0918 grams) were dissolved in purified cyclohexane (8.3506 grams) and this solution was diluted to one tenth with cyclohexane. The ultraviolet spectrogram of the dimers is shown in Figure IV. It was concluded that no conjugated carbon-carbon double bonds was present.

Infrared spectrogram

The infrared spectrogram of the dimers is shown in Figure V (I). The predominant peaks were identified as followed.

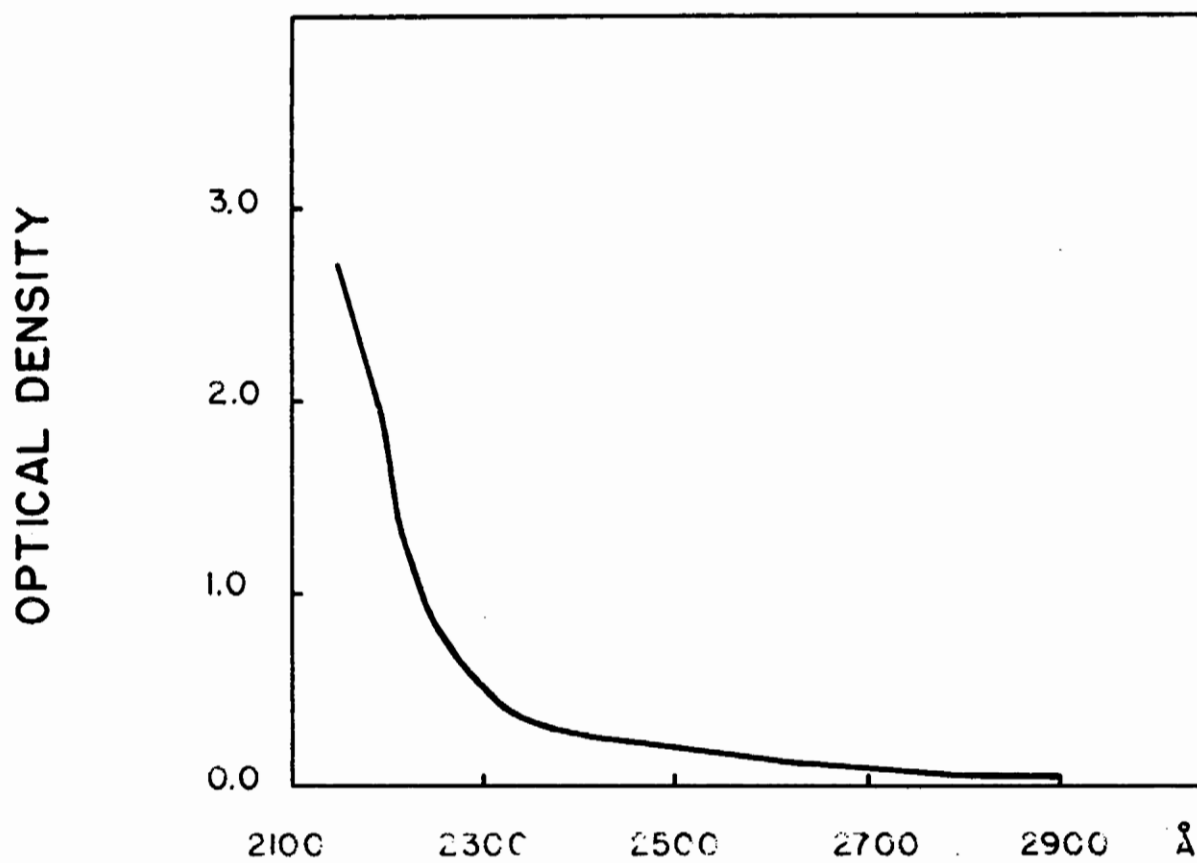| Peak I			was caused by $RCH=CHR'$, cis form
II	"	"	" C-Cl bond
III	"	"	" $R-CH=CH_2$
IV	"	"	" $RCH=CHR'$, trans form
V and VI were		"	" C-C and C-O bonds
VII	was	"	" CH_3COO- group
VIII	"	"	" $-CH_3$ group
IX	"	"	" $RCH=CH_2$
X	"	"	" $-CH_2-$ group

Figure IV.   Ultraviolet Spectrogram of the Dimers
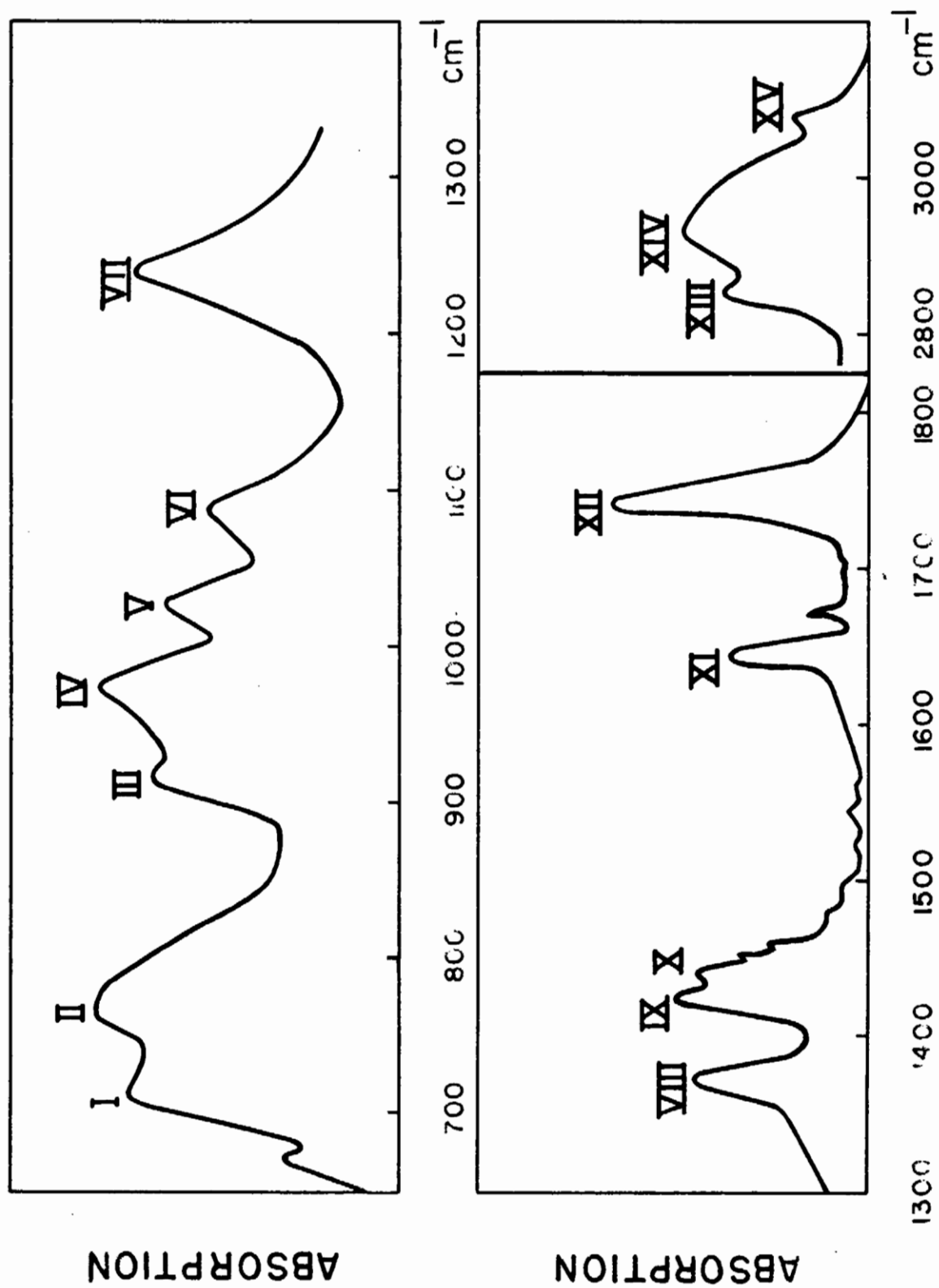
Figure V. Infrared Spectrogram of the Dimers

Peak XI   was caused by $- C = C -$ unconjugated group

      XII   "   "   " $- C = O$ ester group

      XIII and XIV were   "   " $- CH_2 -$ group

      XV   was   "   " $- C - CH_2$ group

Iodine number

The iodine number of the dimers was determined by the Wijs method (54). A weighed sample (approximately 0.15 gm.) of the dimers was dissolved in 20 ml. of chloroform, contained in an iodine flask. Then, a standardized acetic acid solution of iodine monochloride (25 ml.) was added and the flask was kept in a dark place for thirty minutes. A 15 per cent solution of potassium iodide (20 ml.) was poured into the flask followed by 100 ml. of water. The iodine was titrated with a 0.1N.thiosulfate solution, using starch as indicator.

The iodine number of the dimers was found to be 152. However, when the iodine flask was kept in a dark place for sixty minutes instead of thirty minutes, the iodine number was 168 and, when the chlorine concentration of the standardized acetic acid solution was five times the iodine concentration, the iodine number was 208 for a reaction time of thirty minutes. The theoretical iodine number is 223.

Optical activity

A saccharimeter, half-shadow, Lippich Polarizer, Bausch and Lomb, was used to determine the optical activity of the dimers. When a 200 mm. observation tube, filled with

the dimers, was placed in the saccharimeter, no optical activity was observed.

Urea complex formation

A few drops of the dimers were added to a saturated methanol solution (15 ml.) of urea (62); no insoluble urea complex was formed.

Structure of the Dimers

Reduction by lithium aluminum hydride (63, 64, 65)

Lithium aluminum hydride (15 gm.) was dissolved in 300 ml. of anhydrous ether and the dimers (5.11 gm) were added to 50 ml. of the same solvent. The two solutions were mixed and heated under reflux for fifteen hours. Water (52 ml.) was added to the ether solution, followed by 105 ml. of concentrated nitric acid diluted with 300 ml. of water. The aqueous phase was separated and washed with three portions (25 ml.) of ether. Washings were added to the main ether solution and dried with anhydrous sodium carbonate. The ether was evaporated at room temperature and there remained a yellow liquid, the dechlorinated dimers, or nonadienes.

From chlorine analysis on aliquots of the aqueous phase, it was concluded that 93.5 per cent of the chlorine was substituted. The ultraviolet spectrogram of the reduced dimers is shown in Figure VI and indicates that a conjugation of the carbon-carbon double bonds occurred during the reduction.
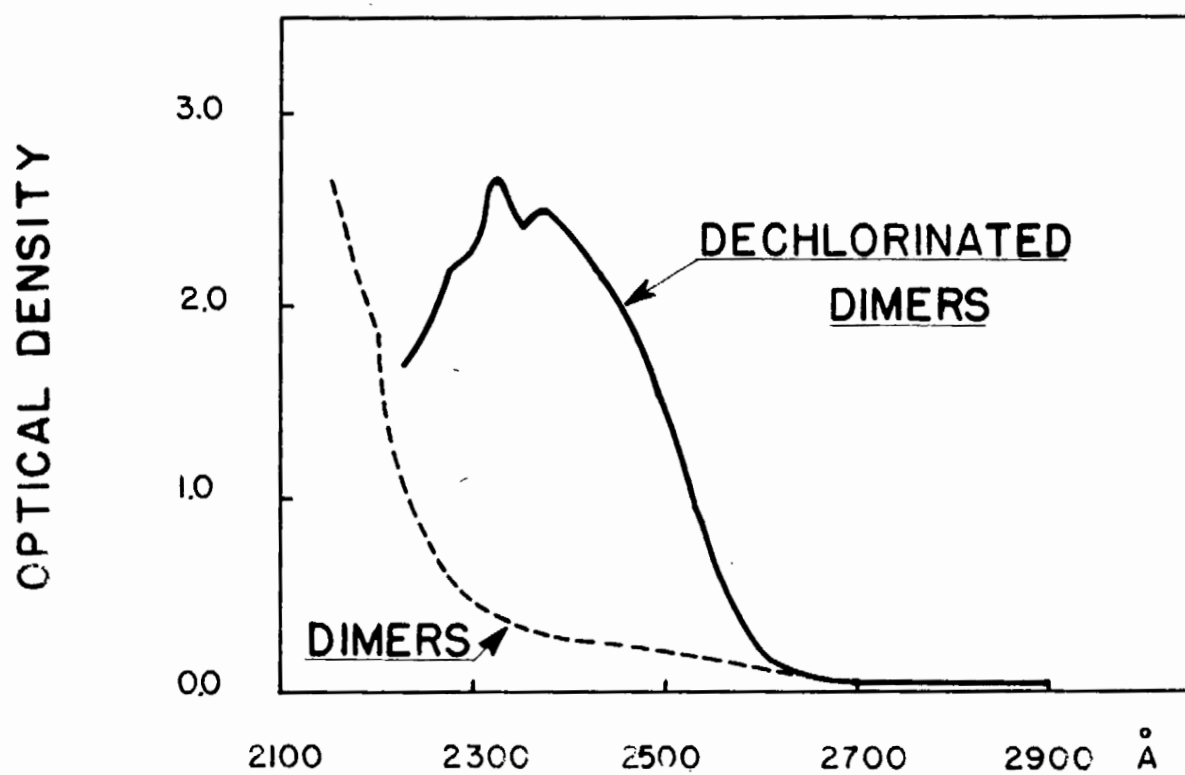
Figure VI.   Ultraviolet Spectrogram of the
              Dechlorinated Dimers.

Hydroxylation with peracetic acid (67)

The dimers (10 ml.) were dissolved in 150 ml. of glacial acetic acid containing concentrated sulfuric acid (2.0 ml.) and hydrogen peroxide (15 ml. of a 30 per cent solution) was added. The solution was maintained at 40°C. during twenty-four hours and the acetic acid was distilled under reduced pressure at a temperature near 40°C. The residue was dissolved in ether and washed with water. The ether was evaporated and the product was redissolved in 150 ml. of methanol containing hydrogen chloride (3 per cent) and heated under reflux for five hours. The methanol was removed by distillation and the residue was washed with water, methanol, and ether. After drying in a vacuum desiccator, the residue, a white sticky paste, was assumed to be the hydroxylated dimers.

The iodine number of the hydroxylated dimers was found to be 5.6 - 7.1 instead of 0.0 theoretically. The chlorine percentage was 34.1 when the calculated value is 36.1 per cent for $C_9H_{13}Cl_3(OH)_4$.

Hydroxyl group content

The hydroxyl group content of the hydroxylated dimers was determined by acetylation (69). A weighed sample (about 0.5 gm.) was introduced into a glass-stoppered iodine flask together with 5.00 ml. of acetic anhydride-pyridine reagent (one volume of acetic anhydride and three volumes of pyridine). The flask was placed on a steam bath for forty-five minutes.

Then, water (10 ml.) was added and the flask cooled. The sides of the flask and the stopper were rinsed with 10 ml. of n-butanol and the contents were titrated with a 0.5 N. alcoholic solution of sodium hydroxide. The hydroxyl group content was found to be 8.1 per cent, when the theoretical percentage for $C_9H_{13}Cl_3(OH)_4$ is 23.0 per cent.

Active hydrogen content

The active hydrogen content of the hydroxylated dimers was determined by the method of Zerewitinoff (70). A weighed sample (approximately 0.007 gm.) was introduced into the reaction vessel and 1.0 ml. of anhydrous n-amyl ether was added. The methylmagnesium iodide in n-amyl ether solution (1.0 ml.) was injected into the reaction vessel by means of an hypodermic syringe and the volume of methane formed was measured. The active hydrogen content was found to be 0.50 per cent whereas the theoretical content is 1.35 per cent for $C_9H_{13}Cl_3(OH)_4$.

Hydroxylation with N-bromosuccinimide (68)

The dimers (2.2 gm.), N-bromosuccinimide (2.9 gm.) and water (50 ml.) containing a few drops of glacial acetic acid were shaken at room temperature for fifteen hours. The products were extracted by ether and the ether solution was washed with solutions of sodium metabisulphite and sodium hydrogen carbonate and finally with water. After drying with anhydrous magnesium sulfate, the ether was evaporated and there remained a brown liquid. This liquid was dissolved in glacial

acetic acid (25 ml.) and acetic anhydride (5 ml.), and anhydrous potassium acetate (3 gm.) were added. The solution was heated under reflux for nineteen hours and the acetic acid and excess of anhydride were removed under reduced pressure. Then, the residue was dissolved in 15 ml. of methanol containing hydrogen chloride (3 per cent) and the solution was heated under reflux for six hours. The methanol was distilled and the residue, a brown viscous liquid, was regarded as the hydroxylated dimers.

The hydroxyl group content of this residue, determined by acetylation (69), was found to be 3.0 per cent. This is to be compared with a calculated value of 23.0 per cent for $C_9H_{13}Cl_3(OH)_4$.

Ozonizer construction and operation

An ozonizer, similar to that of Jacquemain and Baloué (84), was built as shown in Figure VII, with Pyrex tubing and was operated by means of an induction coil (spark length: 75 mm.). The temperature of the ozonizer was controlled by circulating a cooled mixture of methanol and water (one volume of each). For an oxygen flow rate of 10 liters per hour, the ozonizer produced 6.1, 7.8 or 12.2 millimoles of ozone per hour when its temperature was maintained at $18°$, $6°$ or $-20°C$.

Ozonolysis and oxidative hydrolysis

A weighed sample of the dimers (1.5 gm.) was dissolved in 250 ml. of chloroform and cooled to $-40°C$. A stream of oxygen containing 2.5 per cent of ozone was passed through
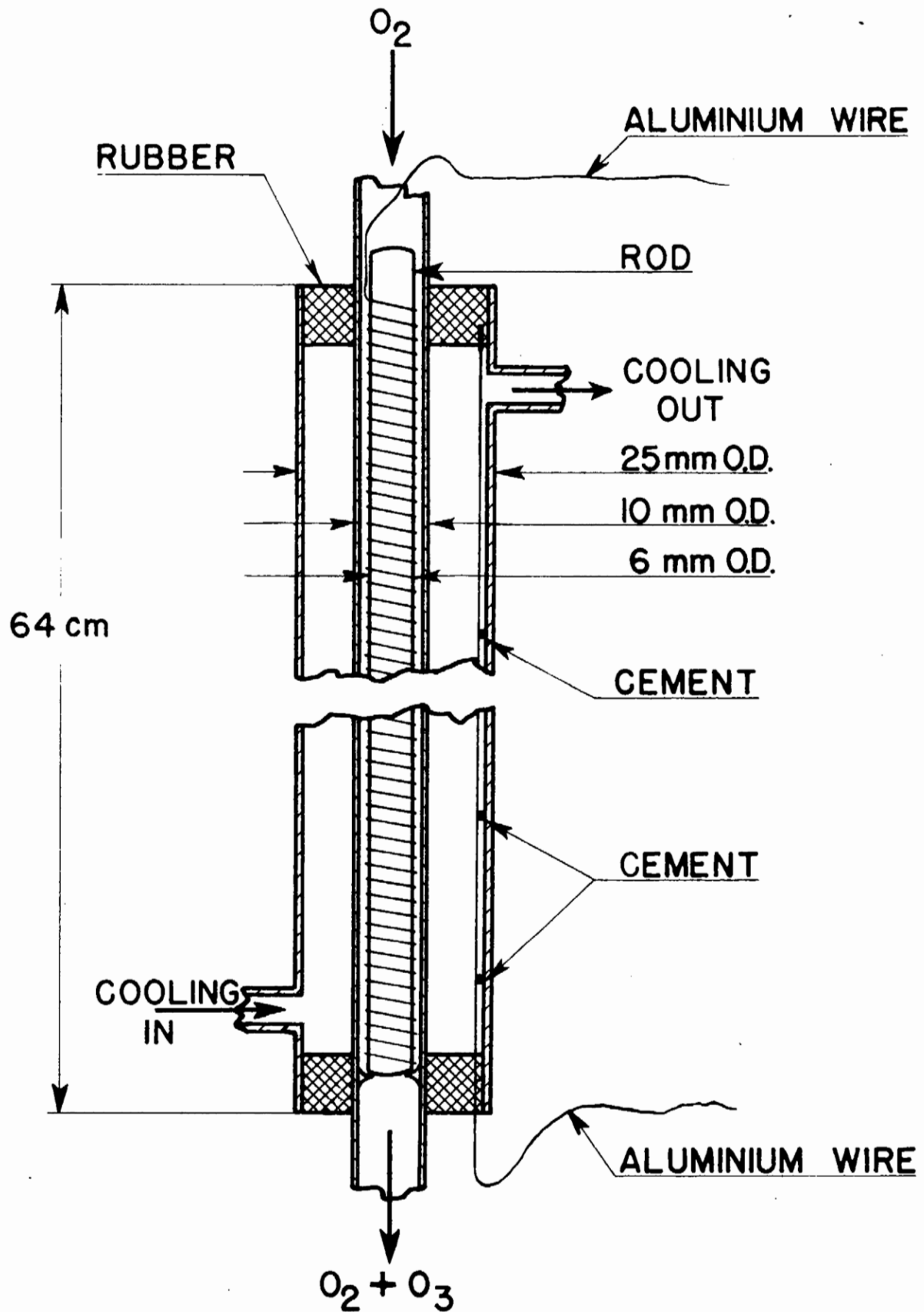
Figure VII.   Ozonizer

the solution until the exit gas turned to a yellow colour a 5 per cent solution of potassium iodide; the average ozonolysis time was forty minutes. The chloroform was distilled under vacuo at room temperature and the dry ozonides were treated with 40.0 ml. of a 0.9N. sodium hydroxide solution and 3 ml. of a 30 per cent solution of hydrogen peroxide. After leaving over-night at room temperature, it was not possible to detect any aldehyde or peroxide in the solution, which was transferred to a 100 ml. volumetric flask. The amount of total acids formed was determined by titrating the excess of sodium hydroxide in aliquots with a 0.1N solution of nitric acid. A 0.1N silver nitrate solution was used to determine the amount of hydrochloric acid produced.

The yield of organic acids was 77 per cent but, when the ozonolysis time was doubled (100 per cent excess of ozone), the yield was 80 per cent. When carbon tetrachloride was used as solvent instead of chloroform, the temperature of ozonolysis was - 20°C. instead of - 40°C. and the yield decreased to 71 per cent.

In a second method, the ozonides were decomposed by adding successive portions of a 6 per cent solution of hydrogen peroxide and by heating under reflux for several hours until disappearance of aldehydes and peroxides. The yield of organic acids was found to be between 60 and 70 per cent.

Chromatographic separation of organic acids (72, 73)

The chromatographic column was made from Pyrex tubing (inside diameter; 1.8 cm.: length; 48 cm.) constricted at the bottom and sealed to a stopcock. At the constriction a plug of glass wool and a disk of filter paper acted as support for the silica gel.

Silica gel was prepared from Mallinckrodt's silicic acid (chromatographic grade) by removal of the fine particles through repeated suspension in distilled water and decantation of the slower settling particules until one third of the original material was removed. The remaining fraction was dried in an oven at 100°C. for a day. Dry silicic acid (20 gm.) and 0.5N. sulfuric acid solution (12 ml.) were mixed thoroughly, and 100 ml. of chloroform were added to prepare a fine slurry. The slurry was transferred to the column and an air pressure of 60 cm. was applied to pack the column and to drain the chloroform until a thin coating only remained over the silica gel.

Samples corresponding to 0.6 milliequivalent of organic acids were prepared with aliquots of the aqueous solutions resulting from oxidative hydrolysis. The water was evaporated under vacuo and the remaining organic salts of sodium were dissolved in 1.0 ml. of a 0.5 N. sulfuric acid solution. The solution was mixed thoroughly with 2 gm. of dry silicic acid and the resulting free-flowing powder was transferred quantitatively to the top of the column. With

the aid of a glass rod, the silica gel containing the sample
was slurried in the chromatographic tube with 2 or 3 ml. of
chloroform. The excess of chloroform was drained through the
column and a glass wool plug was pressed down firmly on the
surface of the sample.

The development of the column was accomplished by
addition of a series of n-butanol - chloroform solutions.

Solution No	Amounts (ml.)	n-Butanol (volume per cent)	Chloroform (volume per cent)
1	100	0	100
2	100	5	95
3	100	10	90
4	100	15	85
5	100	20	80
6	100	25	75
7	100	30	70
8	100	35	65

Each solution of eluant, before addition to the column, was
shaken with an excess of a 0.5N. sulfuric acid solution and
the excess was removed. Small hydrostatic pressure was re-
quired to force the eluant through the column at a rate of
100 ml. per thirty or forty minutes. The effluent was col-
lected in 10 ml. fractions and each fraction was titrated with
a 0.02 N. aqueous sodium hydroxide solution, using phenol red
as indicator.

Chromatography of a known mixture

A known mixture of formic acid (0.865 milliequivalent), acetic acid (0.578 milliequivalent) and succinic acid (0.487 milliequivalent) was prepared and chromatographed according to the preceeding technique. The recovery of each acid was 95, 99 and 97 per cent for formic, acetic, and succinic acids, respectively. Marvel and Rands obtained, with smaller amounts of acids, recoveries between 99 and 102 per cent (72). The chromatogram of this known mixture is shown in Figure VIII.

Chromatography of oxidative hydrolysis products

The chromatogram of total acids resulting from cleavage of dimers ozonides is shown in Figure II (Page 27). Aliquots corresponding to 0.6 milliequivalent in total acids gave 0.062, 0.146, and 0.128 milliequivalent of acetic, formic, and succinic acids, respectively.

Other aliquots were acidified with a 1.0N. hydrochloric acid solution and distilled at reduced pressure, the distillate being received in a flask cooled at - 60°C. The residues (non-volatile acids) and the distillates (volatile acids) were chromatographed and their chromatograms are shown in Figure II (Page 27).

Identification of organic acids

Acetic, formic and succinic acids found among the hydrolysis products of the dimers ozonides were identified
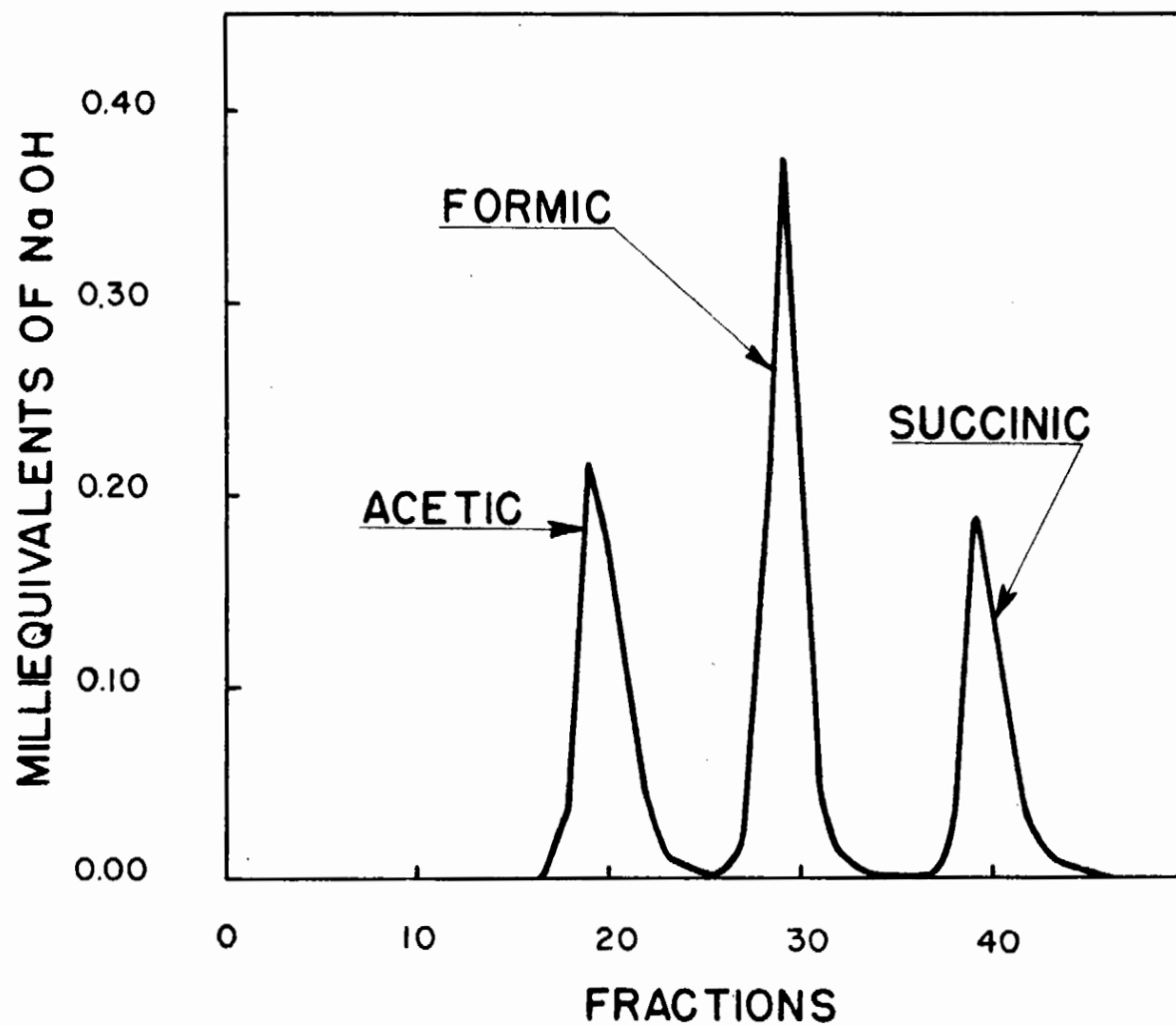
Figure VIII.   Chromatogram of a Known Mixture of
Acetic, Formic and Succinic Acids.

by chromatography. The fraction corresponding to the peak
of these acids was mixed with an authentic sample of the
assumed acid and the mixture was chromatographed (this is
like a mixed melting point). The eluants were n-butanol-
chloroform solutions but their concentration and addition
procedure were modified. Acetic acid was eluted only with
a 3.2 per cent solution of n-butanol, formic acid only with
a 7 per cent solution and succinic acid only with a 15 per
cent solution.

Isherwood (85), Marvel (72) and Bulen (73) demons-
trated that modifications of a standard procedure permit a
separation of acids which, otherwise, occur together. Never-
theless, only one peak was obtained in each mixed acids chro-
matogram, as shown in Figure IX, indicating that these acids
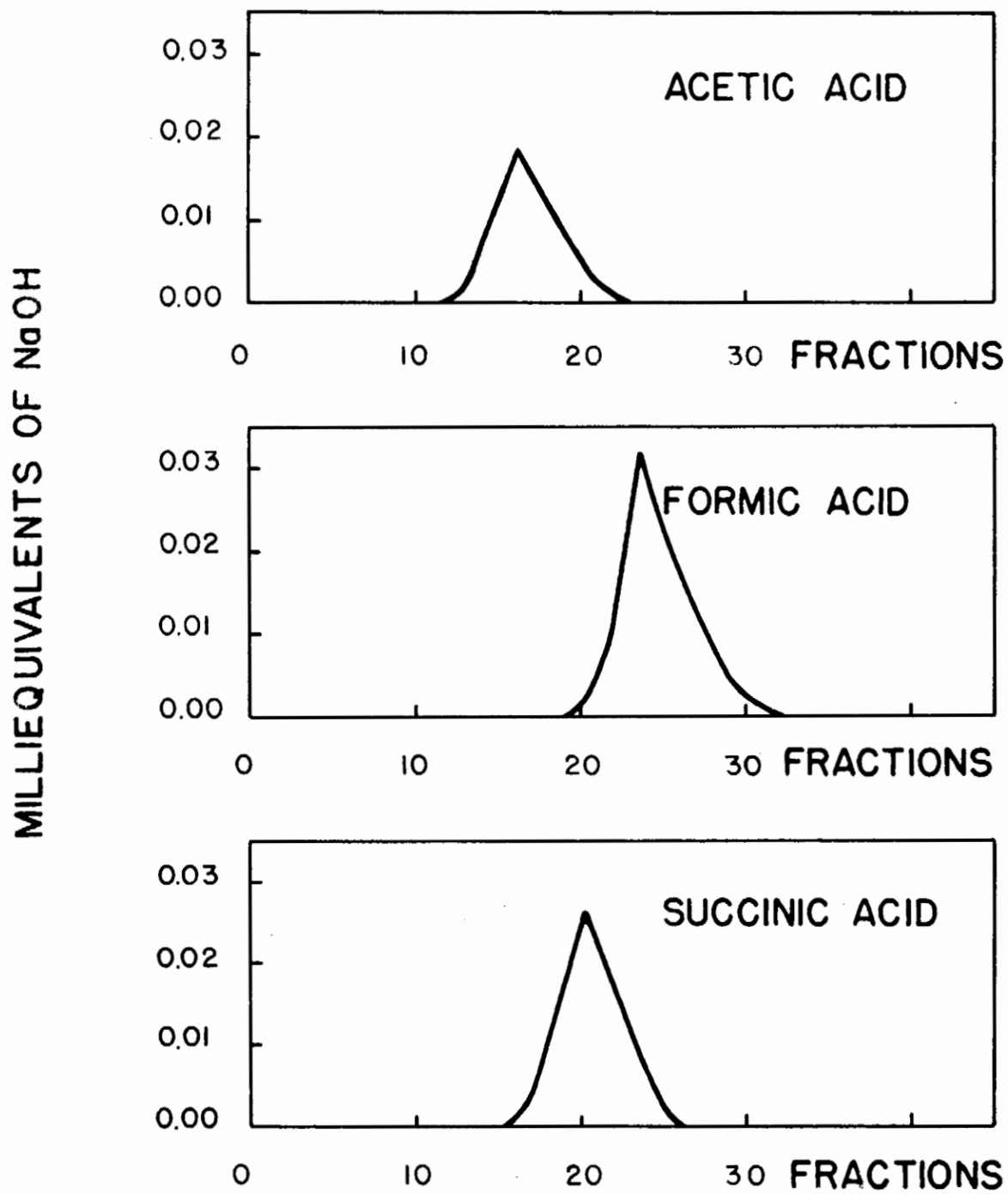were really acetic, formic and succinic.

Figure IX.   Chromatograms Obtained for the Identification
of Acetic, Formic and Succinic Acids.

SUMMARY

1.   Experimental conditions for the production of linear butadiene dimers by a free-radical chain-transfer mechanism were studied. The optimum yield of dimers was obtained when the concentrations of butadiene and acetyl peroxide in chloroform were 1.0 and 0.5 per cent on a mole basis.

2.   The dimers, trichlorononadienes, were identified by quantitative analysis of their elements and determination of their molecular weight.

3.   The dimers became unstable when they were heated above 50°C. and they did not distil under a reduced pressure of 0.01 mm. Their specific gravity was found to be 1.214 and their refractive index 1.5061. The dimers showed no optical activity and formed no insoluble complex with urea. A low value, 152 instead of 223, was found for their iodine number by the Wijs method; higher values were obtained with modified methods.

4.   The ultraviolet and infrared spectrograms revealed that the dimers had no conjugated carbon-carbon double bonds. Absorption maxima, indicating 1,2-additions, cis-1,4-additions and trans-1,4-additions, were recognized in the infrared spectrogram.

5.   Substitution of the chlorine atoms of the dimers by hydrogen atoms was accomplished by using lithium aluminum hydride. The yield was good (93.5 per cent) but the substitution reaction caused a displacement of the double bonds into conjugation. Therefore, this reaction could not be used as a means to structural determination.

6.   Hydroxylation of the dimers was attempted with peracetic acid and N-bromosuccinimide. The yields in hydroxylated dimers were poor, 33 and 8 per cent, respectively, of the theoretical.

7.   The structure of the dimers was established by means of ozonolysis. Two isomers were found and their amounts were nearly equal. One dimer was produced exclusively by 1,4-additions whereas the other was produced exclusively by 1,2-additions.

8.   These results were compared with results of other workers on high molecular weight polybutadienes. The overall percentages of 1,2-and 1,4-additions are 50 and 50 per cent for dimers whereas they are 20 and 80 per cent for polymers.

9.   The possibility that commercial polybutadienes are mixtures of different varieties of polybutadienes has been considered. One variety may be constituted of 1,2-addition units, another of 1,4-addition units and a third of conjunctive 1,2-and 1,4-addition units.

CLAIMS TO ORIGINAL RESEARCH

It is claimed that the following constitute original contributions to knowledge:

1. A study of experimental conditions for the production of low polymers of butadiene, such as dimers, by a free-radical chain-transfer mechanism.

2. The determination of some physical and chemical properties of linear butadiene dimers, trichlorononadienes.

3. An examination and elucidation of the structure of these dimers, and of the mechanism of their formations.

4. The acquisition of experimental support for the proposition that commercial polybutadienes are mixtures of different varieties of polybutadienes rather than copolymers formed from 1,2- and 1,4-structural units.

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