[Contribution from the Hercules Experiment Station, Hercules Powder Company]

The Polymerization of 3-Chloro-2-chloromethyl-1-propene

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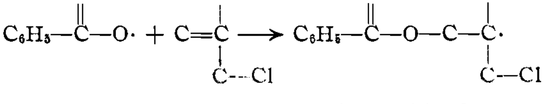
The polymerization of 3-chloro-2-chloromethyl-1-propene has been carried out to determine the identity of the products and the mechanism by which they are formed. The products from a benzoyl peroxide catalyzed polymerization and typical conversions are: 2,4,4-tris-(chloromethyl)-5-chloro-1-pentene (dimer), 33.6%; 2,2,6,6-tetrakis-(chloromethyl)-1,7-dichloro-4-methyleneheptane (trimer), 42.6%; mixture of compounds some of which contain initiator fragments 6.2% and higher polymers 5.1%. The dimer is analogous to the dimer from methallyl chloride and is readily explained by the mechanism of Wilzbach, Mayo and Van Meter.[1] The crystalline trimer is a reaction product of a monomer free radical and a dimer molecule rather than a dimer free radical and a monomer molecule. This trimer like *unsym*-dineopentylethylene, an acid-catalyzed trimer of isobutylene, forms an acid, by dichromate–sulfuric acid oxidation, without loss of a carbon atom.

The polymerization of 3-chloro-2-chloromethyl-1-propene has been carried out at moderate temperatures with benzoyl peroxide and with ultraviolet light. A conversion of about 90% was obtained by heating this vinylidene monomer with 5% benzoyl peroxide at 65° for six days. The use of high-temperature initiators such as di-*t*-butyl peroxide or acidic initiators such as boron fluoride gave low conversions to dark products.

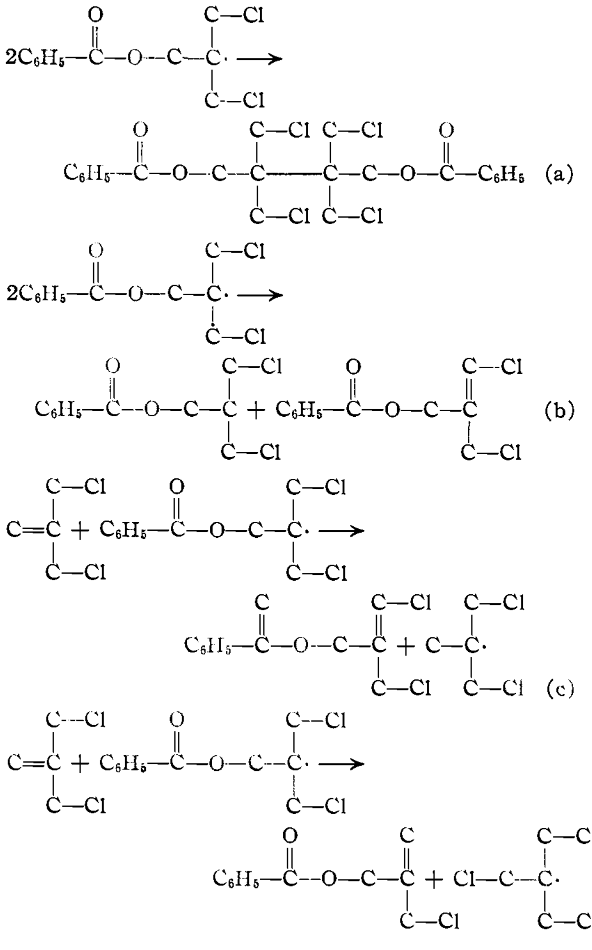
The polymer consists chiefly of a mixture of dimer and trimer. This low degree of polymerization may be attributed to steric hindrance and the ease of chain transfer. The mechanism proposed by Wilzbach, Mayo and Van Meter[1] for the polymerization of methallyl chloride is consistent with the polymer structures obtained from 3-chloro-2-chloromethyl-1-propene. The dimer, 2,4,4-tris-(chloromethyl)-5-chloro-1-pentene, is a water-white liquid as is the monomer. The principal trimer, 2,2,6,6 - tetrakis - (chloromethyl) - 1,7 - dichloro - 4-methyleneheptane, is a white crystalline solid melting at 117.0–117.5°. A fraction is obtained boiling above the trimer which is a very viscous yellow liquid. This has been shown by elementary analysis, infrared spectrum and molecular weight determination to be a mixture. Its components appear to be trimer, dimer in which phenyl and benzoate radicals were the initiating species, and some tetramer. There is a distillation residue of resinous character which is presumably higher polymers. The amounts of these materials from a typical polymerization are as follows: monomer, 7.5%; dimer, 33.6%; crystalline trimer, 42.6%; trimer, benzoate ester, etc., 6.2%, and higher polymers, 5.1%. This amounts to 95% of the weight of monomer charged for polymerization.

Structure of the Benzoate Ester.—The presence of a benzoate ester in the polymer is readily explained. The normal addition of a benzoate free radical to the monomeric species would yield a monomeric free radical (1). There is probably also initiation by phenyl radicals, but spectra data



$$C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\cdot + C{=}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}} \longrightarrow C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot \quad (1)$$

do not prove or disprove it. This free radical could conceivably (a) dimerize, (b) disproportionate or (c) lose an atom of hydrogen or chlorine to a monomer molecule.



$$2C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot \longrightarrow$$

$$C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\text{———}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\text{—}C\text{—}O\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}C_6H_5 \quad (a)$$

$$2C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot \longrightarrow$$

$$C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}} + C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{\overset{\|}{C}}} \quad (b)$$

$$C{=}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}} + C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot \longrightarrow$$

$$C_6H_5\text{—}\overset{\displaystyle C}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}} + C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot \quad (c)$$

$$C{=}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}} + C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot \longrightarrow$$

$$C_6H_5\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—}O\text{—}C\text{—}\underset{\displaystyle C\text{—}Cl}{\overset{\displaystyle C}{\overset{\|}{C}}} + Cl\text{—}C\text{—}\underset{\displaystyle C\text{—}C_l}{\overset{\displaystyle C\text{—}Cl}{C}}\cdot$$

Since 7.7 and 8.1 molecules of polymer were formed per equivalent of catalyst in two typical experiments, chain transfer must be the principal reaction.

Of course the benzoate ester free radicals may add monomer molecules to form dimeric or trimeric free radicals before the loss of the atom of halogen or hydrogen.

The benzoate ester was found in a fraction boiling above the trimeric 3-chloro-2-chloromethyl-1-propene. The infrared absorption spectra showed bands at 6.2 and 6.65 microns in common for ethyl benzoate and the high-boiling fraction. These are characteristic of the phenyl group. There was also a band at 5.70–5.75 microns which is common to ethyl benzoate and the unknown fraction which is not found in the monomer, dimer or trimer. This band is characteristic of the carbonyl group.

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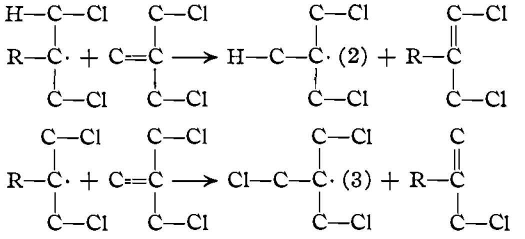
(1) Wilzbach, Mayo and Van Meter, This Journal, **70**, 4069 (1948).

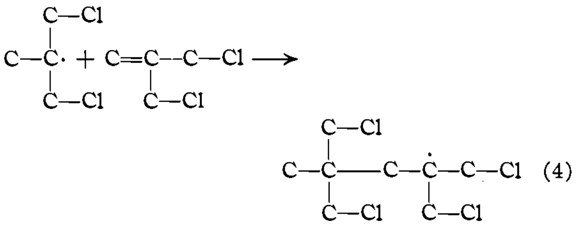
Confirmation is obtained from the ultraviolet spectrum which indicates 10–15% benzoate present (as methyl benzoate).

Structure of the Dimer.—Since there are approximately 8 polymer molecules formed per initiator fragment, the majority of the polymer molecules are initiated by the transfer of a hydrogen or chlorine atom from a polymeric radical (reaction (c) above) to a monomer molecule. Assuming that the initiating free radical will add to the end of the unsaturated linkage in the normal manner, two free radicals related to the monomer can be formed. These will correspond to the transfer of a chlorine or hydrogen atom to the 3-chloro-2-chloromethyl-1-propene. These monomeric free radicals, (2) and (3), may revert to the parent olefins with the loss of an atom or they may alternately add to a second olefin molecule in the same manner as the initiating atoms. The dimeric free radicals, (4) and (5), will lose a hydrogen atom and a chlorine atom, respectively, from carbon atoms adjacent to the free radical to form olefins. The chlorine and hydrogen atoms probably have no finite existence but are immediately accepted by a monomer molecule.

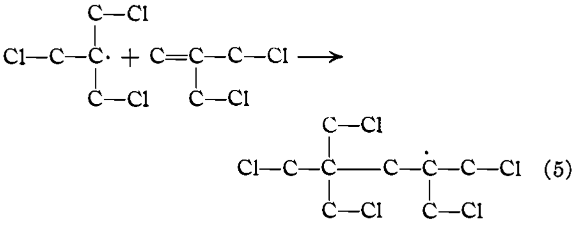


$$\mathrm{R-\overset{H-C-Cl}{\underset{C-Cl}{C}}\cdot + C{=}\overset{C-Cl}{\underset{C-Cl}{C}} \longrightarrow H-C-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot\ (2) + R-\underset{C-Cl}{\overset{\overset{C-Cl}{\|}}{C}}}$$

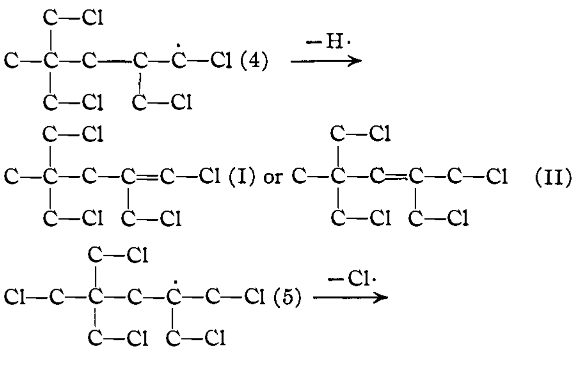
$$\mathrm{R-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot + C{=}\overset{C-Cl}{\underset{C-Cl}{C}} \longrightarrow Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot\ (3) + R-\underset{C-Cl}{\overset{\overset{C}{\|}}{C}}}$$



$$\mathrm{C-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot + C{=}\underset{C-Cl}{C}-C-Cl \longrightarrow C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{\dot{C}}-C-Cl\ (4)}$$



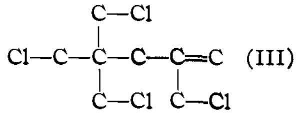
$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot + C{=}\underset{C-Cl}{C}-C-Cl \longrightarrow Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{\dot{C}}-C-Cl\ (5)}$$



$$\mathrm{C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{C}-\dot{C}-Cl\ (4) \xrightarrow{-H\cdot}}$$

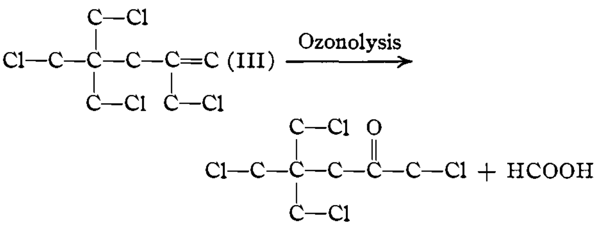
$$\mathrm{C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{C}{=}C-Cl\ (I)\ \text{or}\ C-\overset{C-Cl}{\underset{C-Cl}{C}}-C{=}\underset{C-Cl}{C}-C-Cl\ \ (II)}$$

$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{\dot{C}}-C-Cl\ (5) \xrightarrow{-Cl\cdot}}$$



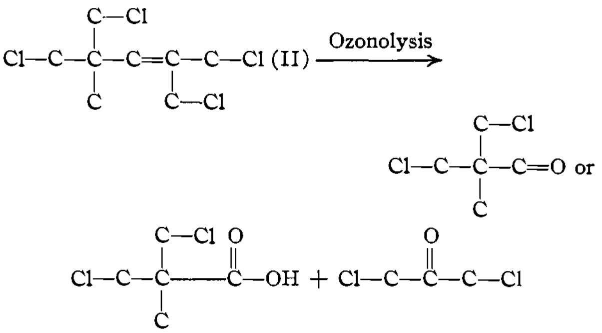
$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{C}{=}C\ \ (III)}$$

The dimer formed from 3-chloro-2-chloromethyl-1-propene was found to have only one active chlorine atom. This excludes Formula (II) as a possible structure for the dimer. Ozonolysis of the dimer yields formic acid[2] and a seven carbon tetrachloroketone. Thus ozonolysis excludes Formulas (I) and (II). Dimer (II) would yield *sym*-dichloroacetone and α,α-bis-(chloromethyl)-propionaldehyde or the corresponding substituted trimethylacetic acid. Dimer (I) would yield a trichloroheptanone.



$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{C}{=}C\ (III) \xrightarrow{Ozonolysis}}$$

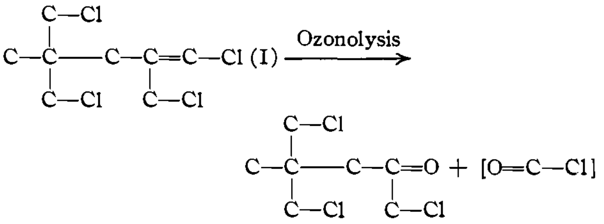
$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\overset{O}{\overset{\|}{C}}-C-Cl + HCOOH}$$



$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C}{C}}-C{=}\underset{C-Cl}{C}-C-Cl\ (II) \xrightarrow{Ozonolysis}}$$

$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C}{C}}-C{=}O\ \text{or}}$$

$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C}{C}}-\overset{O}{\overset{\|}{C}}-OH + Cl-C-\overset{O}{\overset{\|}{C}}-C-Cl}$$

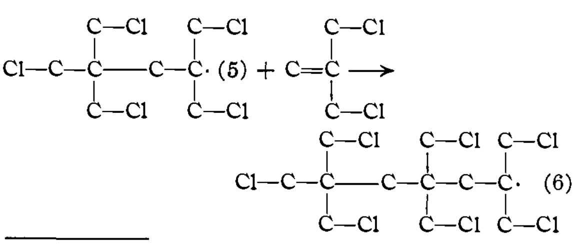


$$\mathrm{C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{C}{=}C-Cl\ (I) \xrightarrow{Ozonolysis}}$$

$$\mathrm{C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\underset{C-Cl}{C}{=}O + [O{=}C-Cl]}$$

Oxidation of 2,4,4-tris-(chloromethyl)-5-chloro-1-pentene with nitric acid apparently yielded nitration products instead of the expected tris-(chloromethyl)-acetic acid.

Structure of the Trimer.—If instead of splitting out a chlorine atom the dimeric free radical (5) added a monomer molecule, a trimeric free radical (6) would be formed. This free radical (6) could,



$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot\ (5) + C{=}\overset{C-Cl}{\underset{C-Cl}{C}} \longrightarrow}$$

$$\mathrm{Cl-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\overset{C-Cl}{\underset{C-Cl}{C}}-C-\overset{C-Cl}{\underset{C-Cl}{C}}\cdot\ \ (6)}$$

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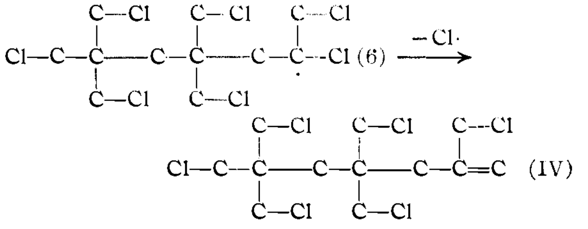
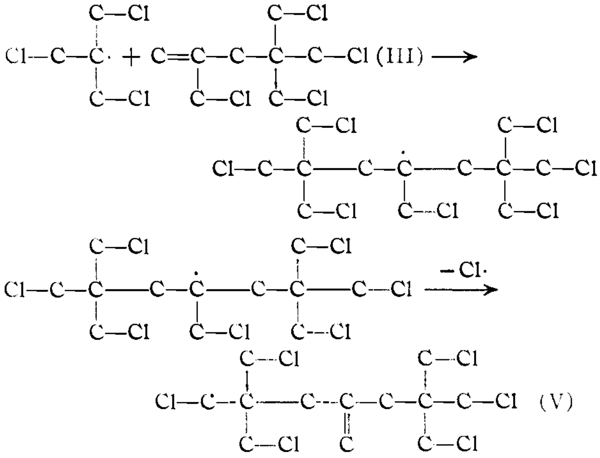
[2] No reducing agent was used during the ozonide decomposition which probably accounts for the formation of formic acid rather than formaldehyde. The analysis of the ketone was obtained from a purified sample of its 2,4-dinitrophenylhydrazone.

like the dimeric free radical (5), lose a chlorine atom to yield a trimer (IV). In contrast to this possible structure, the isolated trimer is a crystalline



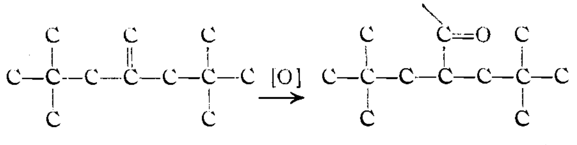
solid having no active (allylic) chlorines. It is, in addition, resistant to ozonolysis.

A second trimer structure (V) may be proposed which fits these properties. It would be formed by the addition of a monomeric free radical to the dimer (III) with subsequent loss of a chlorine atom from the adjacent carbon in the usual manner. This carbon skeleton like those of the other dimers and trimers (I through IV) is found in the di-

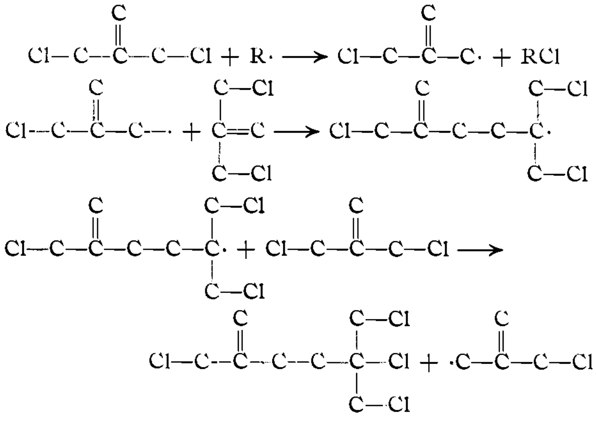


and tri-isobutylenes.[3] *unsym*-Dineopentylethylene has been shown to be resistant to ozonization and oxidation.[4] It would be expected then that this substituted *unsym*-dineopentylethylene (V) would be at least as unreactive.

Oxidation of the trimer with sodium dichromate and sulfuric acid produced an acid with the same number of carbon atoms as the original olefin. This has been shown to occur with *unsym*-dineopentylethylene.[5]



Refluxing of trimer with alcoholic potassium hydroxide for 24 hours produced no change in the compound. The compound would be expected to lose the elements of HCl if it contained a 1,2,3-trichloro-2-alkylpropane structure.[6] This structure would be present if the dimer and trimer were formed by a Bartlett-type mechanism.[7]



Experimental

The data given below are selected from several experiments. This is necessary since there was insufficient polymer from the first reaction to obtain all the desired data.

Preparation of 3-Chloro-2-chloromethyl-1-propene.—The mixture of 3-chloro-2-chloromethyl-1-propene and 1,3-dichloro-2-methyl-1-propene resulting from the chlorination of methallyl chloride was separated by fractional distillation. The former had an $n^{20}D$ of 1.4760, a boiling point of 58.8 to 59.8° at 50 mm. and a chlorine content of 56.5%. This chlorination has been carried out previously,[8] but the isomers were not isolated. The pure isomer, 3-chloro-2-chloromethyl-1-propene was prepared from tris-(chloromethyl)-acetic acid[9] and a value of 1.4758 obtained for the $n^{20}D$.

Polymerization of 3-Chloro-2-chloromethyl-1-propene.—A quantity of 120 g. of 3-chloro-2-chloromethyl-1-propene was heated with 6 g. (5%) of benzoyl peroxide in sealed Pyrex tubes for six days at 65°. The polymer was dissolved in benzene and washed neutral with sodium bicarbonate. The polymer solution was dried over potassium carbonate and distilled. The benzene was distilled at atmospheric pressure and the monomer, dimer, trimer and higher boiling fractions at progressively lower pressures. Data are given below on the original monomer and on monomer and polymer fractions from the above distillation.

Identity	Monomer charged, %	Description	$n^{25}D$	Active chlorine A[a]	B	C
Monomer[b]		Colorless fluid		16.2	39.9	56.3
Monomer[c]	7.5	Colorless fluid	1.4944			
Dimer	33.6	Colorless fluid	1.5216–1.5227		15.0	15.5
Trimer	42.6	White crystalline		nil		1.5
Trimer, benzoate ester, etc.	6.2	Viscous yellow				
Higher polymers	5.1	Brown resin				
	95.0					

[a] The value A for the active chlorine was obtained with alcoholic silver nitrate, B was obtained with sodium iodide and acetone by heating to reflux and C was obtained by refluxing for 10 minutes with sodium iodide and acetone. The theoretical value for two chlorines in the monomer is 56.8, for one chlorine in the dimer is 14.2, and for one chlorine in the trimer 9.4. [b] Monomer charged for polymerization $n^{20}D$ 1.4760. [c] The $n^{25}D$ is high because of the presence of benzene and dimer.

A dimer fraction was redistilled and the middle cut, boiling 107–108° (1.5 mm.) was analyzed for chlorine and the molecular weight determined. A fraction of solid crystalline trimer was recrystallized three times from petroleum

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[3] Whitmore and Church, This Journal, **54**, 3710 (1932); McCubbin, *ibid.*, **53**, 357 (1931).

[4] Wheeler, Ph.D. Thesis, The Pennsylvania State College, 1941; Bartlett, Fraser and Woodward, This Journal, **63**, 495 (1941); Whitmore and Surmatis, *ibid.*, **63**, 2200 (1941).

[5] Whitmore and Wilson, *ibid.*, **56**, 1397 (1934).

[6] Rogers and Nelson, *ibid.*, **58**, 1029 (1936).

[7] Bartlett and Altschul, *ibid.*, **67**, 816 (1945).

[8] Burgin, Hearne and Rust, *Ind. Eng. Chem.*, **33**, 385 1941); Suter and Bordwell, This Journal, **65**, 507 (1943).

[9] Mooradian and Cloke, *ibid.*, **67**, 942 (1945).

ether. The white needles melted at 117.0–117.5° (capillary). A fraction boiling above the trimer was treated twice with activated charcoal. The clear brown viscous liquid was then analyzed. The results of the analysis of the three samples are in the table.

ANALYSIS OF POLYMER FRACTIONS

Fraction	Cl, %	C, %	H, %	Mol. wt.
		$(C_4H_6Cl_2)_2$		
Dimer	56.4	38.88	5.05	229
	56.6	39.04	5.28	243
Calcd.	56.7	38.4	4.84	250
		$(C_4H_6Cl_2)_3$		
Trimer	56.2	38.36	4.94	347
	56.2	38.61	5.12	364
Calcd.	56.7	38.4	4.84	375
Viscous liquid	49.6	42.86	5.16	378
	49.8	43.24	5.21	404

Ozonolysis of Dimer.—A quantity of 9.28 g. of dimeric 3-chloro-2-chloromethyl-1-propene (b.p. 107–108° at 1.5 mm.) was ozonized at 0° in 40 ml. of olefin-free pentane. The aqueous residue and distillate from decomposition of the ozonide were acid but gave only a faint test for chloride ion. A positive test for formic acid was obtained with sodium acetate and mercuric chloride. A 2,4-dinitrophenylhydrazone of formaldehyde was not obtained. The organic layer from steam distillation of the ozonide decomposition products yielded a 2,4-dinitrophenylhydrazone melting at 143–144°. The analysis of this derivative is given below together with calculated values for a trichloroheptanone and a tetrachloroheptanone.

	Trichloro-heptanone	Tetrachloro-heptanone	Found
Cl, %	26.77	32.82	32.83
N, %	14.09	12.97	12.66
O, %	16.09	14.81	14.60
C, %	39.26	36.13	36.86
H, %	3.80	3.27	3.15
	100.00	100.00	100.10

Ozonolysis of Trimer.—A quantity of 1 g. of trimeric 3-chloro-2-chloromethyl-1-propene was ozonized in 50 ml. of redistilled methylene chloride at −78°. Attempts to prepare 2,4-dinitrophenylhydrazones from the various organic and aqueous fractions obtained by decomposition of the ozonide were unsuccessful. Organic solid remaining in the decomposition flask was dissolved in ether and treated with Darco. It melted at 75–82°. Two recrystallizations from hexane yielded unchanged trimer.

Oxidation of Dimeric 3-Chloro-2-chloromethyl-1-propene.—A quantity of 32.86 g. of 2,4,4-tris-(chloromethyl)-5-chloro-1-pentene was oxidized with 150 ml. of 98% nitric acid. The procedure was that used by Wilzbach, Mayo and Van Meter[1] for the oxidation of 4,4-bis-(chloromethyl)-2-methyl-1-pentene. The product was red in basic solution and was incompletely extracted from either basic or acidic solutions by ether.

Oxidation of Trimeric 3-Chloro-2-chloromethyl-1-propene.—A quantity of 37.8 g. of trimeric 3-chloro-2-chloromethyl-1-propene was oxidized in acetic acid with sulfuric acid and sodium dichromate according to the method of Whitmore and Laughlin.[10] The product consisted of an alkali-soluble fraction and an alkali-insoluble fraction. The acid fraction was dissolved in methanol and filtered hot. The methanol was replaced by hexane which failed to dissolve the solid but removed color bodies. It weighed 7.84 g. and had an m.p. of 150–154°. It was recrystallized from a 3:1 mixture of hexane and benzene. The m.p. was 151–154°. The analyses on this material are given below where the calculated values are for $C_{12}H_{18}O_2Cl_6$.

	% C	% H	% O	% Cl	A.N.	Mol. wt.
Calcd.	35.41	4.45	7.86	52.27	137.8	407
Found	36.07	4.75	7.64		145	384
	36.14	4.62	7.87	51.49	145	391

The neutral fraction of the oxidation product after two recrystallizations from hexane weighed 5.04 g. and melted from 109–112°. The crystals were mixed with 100 ml. of methanol, 150 ml. of hexane and enough water to effect layer separation. The two phases were separated and evaporated to 25 ml. The needles from hexane melted from 112–114° while those from methanol–water melted at 113–114°. Neither sample depressed the melting point of pure trimeric 3-chloro-2-chloromethyl-1-propene. They were combined for analysis. The calculated values are for $(C_4H_6Cl_2)_3$.

	% C	% H	% O	% Cl	A.N.	Mol. wt.
Calcd.	38.43	4.84	0.0	56.73	0	375
Found	38.47	5.17	.2	56.31	nil	367
	38.66	5.00				

Reaction of Trimer with Alcoholic KOH.—A quantity of 1.5 g. of trimeric 3-chloro-2-chloromethyl-1-propene was refluxed for 48 hours with 2 g. of C.P. potassium hydroxide dissolved in 30 ml. of 95% ethanol. The solution was cooled in a refrigerator and the crystals filtered. The crystals were washed with 50 ml. of distilled water. The crystals after drying weighed 1.4 g. and melted at 114–115°. They yielded a mixed melting point of 114–115° with the starting material.

WILMINGTON, DEL.

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(10) Whitmore and Laughlin, THIS JOURNAL, **56**, 1128 (1934).