recrystallized from dilute ethanol, m. p. 142–144°, undepressed when mixed with a sample prepared by the other procedure.

Ethyl Allylthenylmalonate.—The alkylation was carried out in the usual way.[17] From 131 g. of ethyl allylmalonate and 85 g. of chloromethylthiophene there was obtained 130 g. (68%) of the dialkylated ester, b. p. 122–124° at 0.6 mm.

Anal. Calcd. for $C_{15}H_{20}O_4S$: S, 10.82. Found: S, 11.11.

Allylthenylmalonic Acid.—The method given below was used for all the dialkylmalonic acids. To a stirred boiling solution of 101 g. of potassium hydroxide in 101 ml. of water there was added dropwise 127 g. of the ester. If the addition was rapid, after an induction period an exothermic reaction resulted. After six hours the mixture was poured into cold water. The solution was extracted with ether, cooled to 5° and carefully acidified with hydrochloric acid. The acid separated as an oil which was gathered in ether and dried over *white* Drierite. After removal of the ether, the acid solidified. It was recrystallized from benzene–ligroin; 86 g. (84%), m. p. 125–127°.

Anal. Calcd. for $C_{11}H_{12}O_4S$: neutral equivalent, 120. Found: neutral equivalent, 122.

The acid chloride prepared from this acid was 95% pure on the basis of the chlorine analysis.

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[17] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 250.

Allylbenzylmalonyl Chloride.—The following is a typical preparation of a dialkylmalonyl chloride. A mixture of 78 g. of allylbenzylmalonic acid and 150 ml. of thionyl chloride was gently refluxed for four hours. The chloride was then distilled to give 56.3 g. of the acid chloride. Since the chloride was reddish-yellow it was redistilled, b. p. 106–108° (0.75 mm.); 44.6 g. (50%).

Anal. Calcd. for $C_{13}H_{12}Cl_2O_2$: Cl, 26.15. Found: Cl, 26.16.

In the other cases the chlorides were not redistilled.

Preparation of the Diamides (VI).—To a solution of 17.7 g. (0.102 mole) of 4,6-diaminoquinaldine in 100 ml. of glacial acetic acid there was added slowly 0.051 mole of the acid chloride. The temperature generally rose about 20–30°. After cooling to room temperature, the acetic acid was decanted from either the resultant gum or solid. Trituration with ether converted the gummy hydrochlorides to more tractable solids. The yields at this point were quantitative. In most cases it was possible to recrystallize the salts. Otherwise the procedures indicated in Table I were followed.

Summary

Eighteen amides prepared from 4,6-diaminoquinaldine and dibasic acid chlorides are described. Preliminary data on their effectiveness against six species of trypanosomes was given.

RENSSELAER, N. Y.

RECEIVED MAY 4, 1948

[CONTRIBUTION NO. 82 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

The Preparation, Structure and Properties of the Dimer of Methallyl Chloride

BY K. E. WILZBACH,[1a] F. R. MAYO AND R. VAN METER[1b]

By refluxing methallyl chloride with 1% benzoyl peroxide for eight days, Bauer and Götz[2] polymerized the chloride in 33% yield to a dimer of unspecified structure. In this Laboratory the dimer has been obtained in yields as high as 79% by irradiating a solution of 0.5% tetraethyllead in methallyl chloride at 80° for five days. Since the action of light alone under the same conditions produces only 7.5% polymerization, the high yield of dimer per molecule of tetraethyllead indicates that the dimerization proceeds by a chain transfer reaction.[3a,b]

The dimer has been identified as 2-methyl-4,4-bis-(chloromethyl)-1-pentene. Its reactions, shown in Fig. 1, have been studied and found to include the easy formation of cyclopropane derivatives. The structure of the dimer shows that the transfer mechanism is unique, so far, in that it apparently involves transfer of an atom from a polymeric radical to a monomer, instead of in the reverse direction.

Structure of the Dimer.—In the formation of the dimer a chlorine or a hydrogen atom can be transferred either to the dimer radical or to the monomer. With the additional assumption that a radical would add to the terminal carbon atom of a double bond, several structures for the dimer can be proposed. These structures, in which the four carbon atom group on the left side of each formula is presumed to add to the group on the right, are shown in Fig. 2.

The absence of any chloride ion after heating the dimer with piperidine, alcoholic silver nitrate or alcoholic sodium hydroxide at 100° indicated that the halogens were attached by vinyl or neopentyl linkages. This result left for consideration only structures IV and VI, Fig. 2, which could be distinguished by oxidation at the double bond.

Oxidation by aqueous permanganate at room temperature produced one chloride ion per dimer molecule, a misleading result which suggested that one halogen was attached by a vinyl linkage, as in structure VI, Fig. 2. The organic residue polymerized upon distillation, even at reduced pressure, and attempts to prepare carbonyl derivatives were unsuccessful. However, when the dimer was ozonized in formic acid at 0° no chloride ion was found, in contrast to permanganate oxidation, and a nearly quantitative yield of a compound analyzing for $C_7H_{12}Cl_2O$ was obtained. The formation of carbonyl derivatives and a positive iodoform

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[1] Present addresses: (a) Argonne National Laboratory, Chicago, Ill.; (b) Bureau of Mines, Oil Shale Laboratories, Laramie, Wyoming.

[2] Bauer and Götz, U. S. Patent 2,338,893.

[3] (a) Flory, THIS JOURNAL, **59**, 241 (1937); (b) Mayo, *ibid.*, **65**, 2324 (1943).

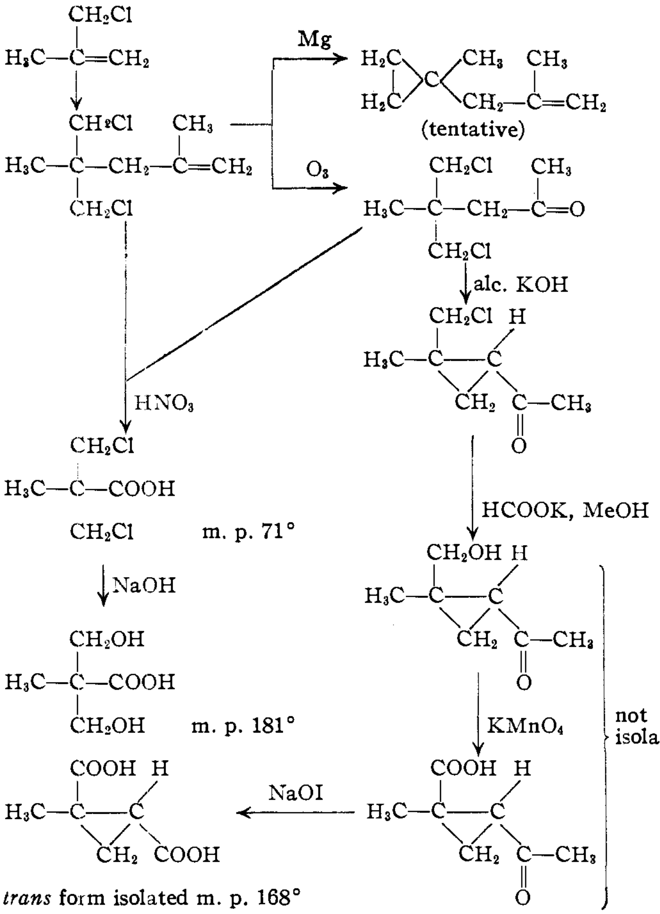
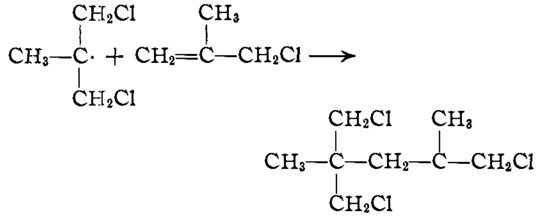


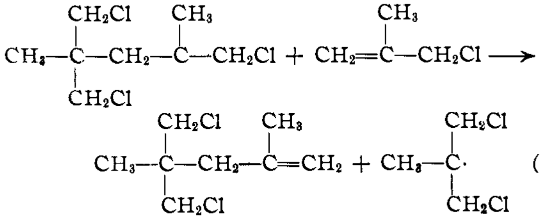
Fig. 1.—Reactions of the methallyl chloride dimer.

test indicated that the compound was a methyl ketone. The isopropenyl group $\left(\mathrm{CH_3\overset{|}{C}{=}CH_2}\right)$ was thus established as a structural unit of the dimer, and the inertness of the chlorine atoms was explainable only on the basis that they were attached by neopentyl linkages.

The only structure of those proposed which met these requirements was IV, Fig. 2, but to make identification complete the dimer was further degraded. Oxidation of the dimer, or the ketone obtained from it by ozonolysis, with fuming nitric acid at 80° yielded a crystalline acid (m.p. 70–71°) having a neutral equivalent of 171. When this acid was warmed with excess sodium hydroxide, two additional equivalents of base were neutralized and two chloride ions were produced. The melting point and neutral equivalent of the hydrolysis product were in agreement with the constants for dihydroxypivalic acid reported by Kolin and Mendelewitsch.[4]

(1) 

$$\mathrm{CH_3-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}\cdot + CH_2{=}\overset{CH_3}{C}-CH_2Cl \longrightarrow CH_3-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}-CH_2-\overset{CH_3}{C}-CH_2Cl}\tag{1}$$

 (2)

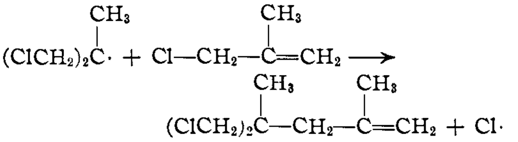
$$\mathrm{CH_3-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}-CH_2-\overset{CH_3}{C}-CH_2Cl + CH_2{=}\overset{CH_3}{C}-CH_2Cl \longrightarrow CH_3-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}-CH_2-\overset{CH_3}{C}{=}CH_2 + CH_3-\underset{CH_2Cl}{\overset{CH_2Cl}{C}}\cdot}\tag{2}$$

The dichloroneopentyl group was thus identified as a structural unit and 2-methyl-4,4-bis-(chloromethyl)-1-pentene was established as the only possible structure for the dimer of methallyl chloride.

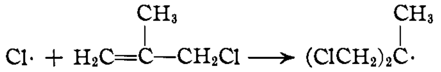
This structure indicates that the dimer is formed by transfer of a chlorine atom from the dimer radical to the monomer, as shown in reactions (1) and (2).

The fact that the dimer radical, unlike that derived from allyl chloride[2] or the tertiary radical in (1), does not add to another monomer unit is attributed to increased steric hindrance to further growth and the ease with which the alternative transfer reaction can occur. Dimerization by a similar chain transfer mechanism should be expected in other cases where there is appreciable steric hindrance to chain growth as, for example, in the dimerization of trichloroethylene.[5]

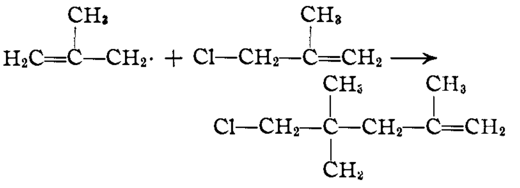
The only alternatives to this "reverse" transfer mechanism are chain reactions involving the steps (3–4) or (5–6)

 (3)

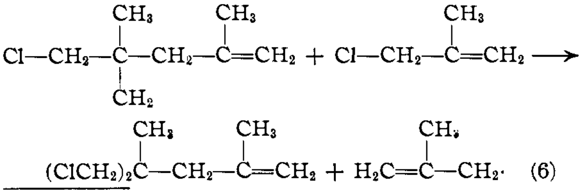
$$\mathrm{(ClCH_2)_2\overset{CH_3}{C}\cdot + Cl-CH_2-\overset{CH_3}{C}{=}CH_2 \longrightarrow (ClCH_2)_2\overset{CH_3}{C}-CH_2-\overset{CH_3}{C}{=}CH_2 + Cl\cdot}\tag{3}$$

 (4)

$$\mathrm{Cl\cdot + H_2C{=}\overset{CH_3}{C}-CH_2Cl \longrightarrow (ClCH_2)_2\overset{CH_3}{C}\cdot}\tag{4}$$

 (5)

$$\mathrm{H_2C{=}\overset{CH_3}{C}-CH_2\cdot + Cl-CH_2-\overset{CH_3}{C}{=}CH_2 \longrightarrow Cl-CH_2-\underset{CH_2}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}{=}CH_2}\tag{5}$$



$$\mathrm{Cl-CH_2-\underset{CH_2}{\overset{CH_3}{C}}-CH_2-\overset{CH_3}{C}{=}CH_2 + Cl-CH_2-\overset{CH_3}{C}{=}CH_2 \longrightarrow (ClCH_2)_2\overset{CH_3}{C}-CH_2-\overset{CH_3}{C}{=}CH_2 + H_2C{=}\overset{CH_3}{C}-CH_2\cdot}\tag{6}$$

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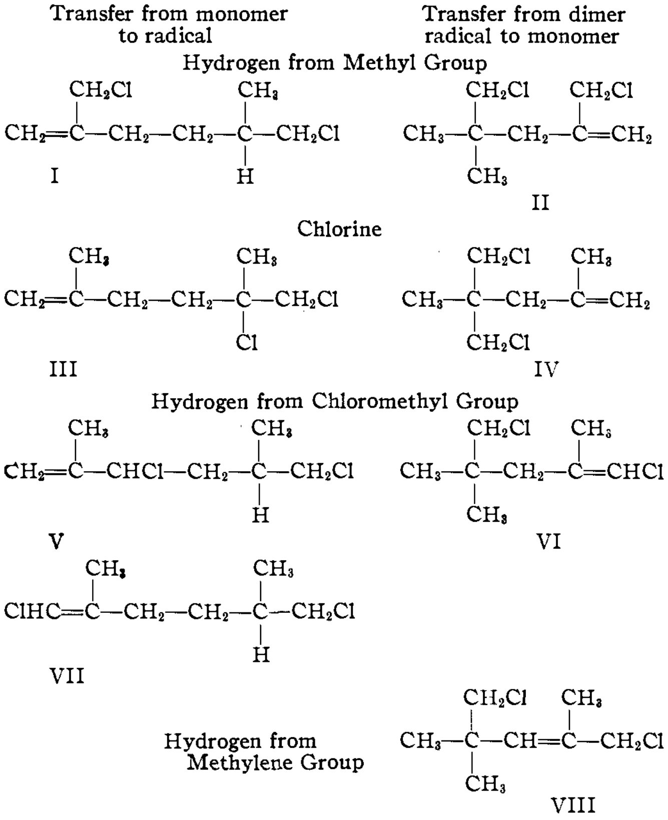
(4) Kolin and Mendelewitsch, *Monatsh.*, **42**, 233 (1921).

(5) Mugdan and Wimmer, Ger. Patent 718,057, Feb. 12, 1942.



I $CH_2{=}\overset{CH_2Cl}{C}{-}CH_2{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}CH_2Cl$

II $CH_3{-}\underset{CH_3}{\overset{CH_2Cl}{C}}{-}CH_2{-}\overset{CH_2Cl}{C}{=}CH_2$

III $CH_2{=}\overset{CH_3}{C}{-}CH_2{-}CH_2{-}\underset{Cl}{\overset{CH_3}{C}}{-}CH_2Cl$

IV $CH_3{-}\underset{CH_2Cl}{\overset{CH_2Cl}{C}}{-}CH_2{-}\overset{CH_3}{C}{=}CH_2$

V $CH_2{=}\overset{CH_3}{C}{-}CHCl{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}CH_2Cl$

VI $CH_3{-}\underset{CH_3}{\overset{CH_2Cl}{C}}{-}CH_2{-}\overset{CH_3}{C}{=}CHCl$

VII $ClHC{=}\overset{CH_3}{C}{-}CH_2{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}CH_2Cl$

VIII $CH_3{-}\underset{CH_3}{\overset{CH_2Cl}{C}}{-}CH{=}\overset{CH_3}{C}{-}CH_2Cl$

Fig. 2.—Possible structures for the methallyl chloride dimer.

In (3), contrary to the course of almost all other radical reactions, a tertiary radical must penetrate past the surrounding atoms and groups to become attached to a shielded interior atom. This reaction is also less exothermic than the alternative reaction (1) by the heat of addition of a chlorine atom to a double bond. In (5) a methallyl radical adds to a double bond not only to yield a primary instead of the expected tertiary radical, but in a direction which is sterically more difficult. Reactions (1–2) are therefore considered more probable but the others have not been definitely excluded.

Cyclization Reactions of the Dimer and its Derivatives.—During the course of this investigation some interesting cyclization reactions of the dimer and its derivatives were encountered.

In an early attempt to determine the carbon skeleton, it was noted that the reaction of the dimer with magnesium was unusual. The presence of a reactive halide was required to initiate reaction, and a precipitate formed during the reaction. The theoretical amount of chloride ion was never obtained, even in the presence of excess magnesium, but in some experiments more than one chloride ion per dimer molecule was found. Distillation of these reaction mixtures yielded, in addition to recovered dimer and a high boiling residue, an 8-carbon atom fraction containing no chlorine. This fraction had, by iodine titration, only one double bond and produced a seven carbon atom methyl ketone upon ozonolysis. The melting points of its semicarbazone and 2,4-dinitrophenylhydrazone excluded the possibility that this ketone was acyclic. Considering the structure of the dimer, and the fact that cyclopropane compounds have been obtained[6] by the reaction of magnesium with 1,3-dichloro compounds, the product of the Grignard reaction is almost certainly 1-methyl-1-methallylcyclopropane but identification has not yet been attempted.

When the ketone, 4,4-bis-(chloromethyl)-2-pentanone, obtained by ozonolysis of the dimer was treated with alcoholic potassium hydroxide vigorous reaction occurred producing one chloride ion per ketone molecule. The product was a methyl ketone, and analysis indicated that the chlorine atom had been removed as hydrogen chloride rather than replaced by an hydroxyl or an ethoxyl group. The product, however, did not reduce cold permanganate solution nor take up ozone, leaving the formation of a cyclic compound as the only possibility.

Identification of this compound seemed desirable to confirm the unexpectedly ready cyclization, which would most probably occur via formation of an anion on a carbon atom adjacent to the carbonyl group, with subsequent internal nucleophilic attack eliminating the chloride ion. Depending upon where the carbanion was formed either a three- or a five-membered ring could be produced. The formation of acetylcyclopropane by heating 5-bromo-2-pentanone with potassium hydroxide[7] suggests formation of a three-membered ring in the present case also. The product of such a cyclization would be 1-acetyl-2-methyl-2-chloromethylcyclopropane. That the ketone actually had this structure was proved by converting it, *via* hydrolysis, permanganate oxidation, and hypoiodite oxidation, to 1-methyl-1,2-dicarboxycyclopropane. The *trans* form of this acid, described by Ingold,[8] was isolated and identified by melting point and neutral equivalent.

The formation of a three-membered ring from 4,4-bis-(chloromethyl)-2-pentanone involves nucleophilic attack on a neopentyl halogen, notoriously slow.[9] In this case the reaction is intramolecular, however, and construction of an Hirschfelder model shows that there is relatively little steric hindrance to attack on the halogen from the rear.[10]

It appears probable that the primary product of

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(6) Haas and Hinds, U. S. Patent 2,098,239, Nov. 9, 1938.

(7) Lipp, *Ber.*, **22**, 1207 (1889).

(8) Ingold, *J. Chem. Soc.*, 387 (1925).

(9) Dostrovsky, Hughes and Ingold, *ibid.*, 173 (1946).

(10) The possibility of an easy intramolecular reaction of neopentyl halogen in the ketone was suggested by Dr. Saul Winstein.

the previously mentioned permanganate oxidation of the dimer was 4,4-bis-(chloromethyl)-2-pentanone which cyclized, with formation of a chlorine ion, in the slightly basic solution. In an acidic permanganate oxidation no chloride ion was produced and the dichloro ketone was isolated in good yield.

Experimental

Polymerization of Methallyl Chloride by Light and Tetraethyl Lead.—An unfrosted 150-watt incandescent lamp was mounted vertically in a bright tin can 11 inches in diameter and 12 inches high. Sealed Pyrex glass reaction tubes were placed in wire supports around the container, at the level of the filament, about 4 inches from its center. The temperature was maintained at 80 ± 5° by regulating ventilators at the top and bottom of the can. A solution of 3.85 g. (0.0119 mole) of tetraethyllead in 21.5 g. (0.238 mole) of freshly distilled methallyl chloride irradiated in this apparatus for one hundred twenty hours yielded upon distillation at atmospheric pressure 3.45 g. (16%) methallyl chloride, 17 g. (79%) dimer, and 1.05 g. (5%) of higher polymers.

Properties of the Dimer.—Methallyl chloride dimer is a colorless liquid with a pungent odor which boils with slight decomposition at 196° under normal pressure, but distills unchanged at reduced pressure, b. p. 75.5° at 10 mm. Physical constants are n^{20}_{D} 1.4774, d^{20}_{20} 1.0622 (Bauer and Götz[2] reported *d* 0.9328), *MR*D 48.41 (calcd. *MR*D 48.23).

Anal. Calcd. for $C_8H_{14}Cl_2$: Wijs number, 140.1; Cl, 39.16. Found: Wijs number, 140.7; Cl, 38.95.

Preparation of 4,4-bis-(Chloromethyl)-2-pentanone: (a) **By Ozonolysis of the Dimer.**—A suspension of 9.05 g. (0.05 mole) of dimer in 100 ml. of 90% formic acid was cooled to 0° in a fritted disk gas washing bottle. Oxygen containing 6% ozone was passed in at a rate of 125 ml./min. until the exit gases colored an acidic solution of potassium iodide. After addition of 50 ml. of water the solution was neutralized at 25° with 10 molal sodium hydroxide and extracted with ether. The ether extract was dried over sodium sulfate and fractionated. The product boiled at 74–75° at 3 mm. and weighed 8.6 g., a 95% yield. The ketone formed a semicarbazone melting at 132° and a 2,4-dinitrophenylhydrazone melting at 88°. Physical constants were n^{20}_{D} 1.4705, d^{20}_{20} 1.159, *MR*D 44.20 (calcd. *MR*D 44.43).

Anal. Calcd. for $C_7H_{12}Cl_2O$: C, 45.88; H, 6.61; Cl, 38.70. Found: C, 45.80; H, 6.73; Cl, 38.88.

(b) By **Permanganate Oxidation of the Dimer.**—A solution of 25 g. of potassium permanganate and 17 g. of sulfuric acid in 250 ml. of water was gradually (twenty-four hours) added to a suspension of 8.5 g. (0.047 mole) of dimer and 50 ml. of water in a flask mounted on a shaker. After the permanganate had been decolorized the slight amount of manganese dioxide was removed by filtration and the solution was extracted with ether. The ether solution was extracted with a carbonate solution, dried over sodium sulfate, and distilled to give 6.0 g. (70%) of ketone. From the carbonate extract was obtained 2.0 g. of acids, chiefly dichloropivalic acid and bis-(β-chloromethyl)-butyric acid.

Preparation of Dichloropivalic Acid.—To 200 ml. of fuming nitric acid (d. 1.49), stirred and cooled in ice, 44.5 g. of dimer was added at such a rate as to keep the solution at 30–35°. The temperature was then gradually raised to 80° and maintained there overnight. The cooled solution was diluted with 150 ml. of water and made basic with solid sodium carbonate. After removal of neutral material by extraction, the solution was acidified and again extracted with ether. Distillation of the acidic extract yielded 19.3 g. (46%) of dichloropivalic acid, collected at 108–113° at 1 mm. The acid crystallized upon standing at 5°, and after three recrystallizations from pentane melted at 71°. The neutral equivalent of a cooled solution was 170.8, compared with 171.0 calculated for $C_5H_8Cl_2O_2$. Upon warming with excess base two additional equivalents of base were neutralized and two chloride ions were produced.

Preparation of Dihydroxypivalic Acid.—A 0.5-g. sample of dichloropivalic acid (above) was heated one hour on a steam-bath with 17.5 ml. of 0.5 *N* sodium hydroxide. The solution was acidified with 10 ml. of 0.5 *N* hydrochloric acid and continuously extracted with ether for twelve hours. The white solid in the extraction flask melted at 181° after recrystallization from water and weighed 0.30 g., a 77% yield. Calcd. for $C_5H_{10}O_4$: neut. equiv., 134.1. Found: neut. equiv., 134.5.

Preparation of 1-Acetyl-2-methyl-2-chloromethylcyclopropane.—9.15 g. (50 m. e.) of bis-(4-chloromethyl)-2-pentanone, obtained from methallyl chloride dimer by ozonolysis, was heated with a solution of 3.10 g. of potassium hydroxide in 70 ml. of 95% ethanol. The precipitate, which formed immediately, was separated by filtration, diluted with water and titrated for chloride ion. The chloride ion found totaled 50.0 m. e., corresponding exactly to the removal of one chlorine. The excess base in the filtrate was neutralized with hydrochloric acid, and the potassium chloride was removed by filtration. Fractional distillation of the solution gave 7.0 g. (95%) of a liquid boiling 71–72° (14 mm.), and having n^{20}_{D} 1.4625.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.31; H, 7.56; Cl, 24.16. Found: C, 57.23; H, 7.50; Cl, 23.71.

Reaction of Dimer with Magnesium.—After initiating reaction with 0.5 g. of butyl bromide, a solution of 20.0 g. of dimer in 200 ml. ether was added to 3.5 g. of magnesium. The reaction mixture was stirred and refluxed for three days, then hydrolyzed with dilute acetic acid. Titration of the aqueous layer showed the presence of 5.75 g. of chloride ion, 73% of that available in the dimer. Fractionation of the ether layer gave 5.3 g. (43.5 mole per cent.) of hydrocarbon boiling 64° (230 mm.), 3.2 g. of dimer, and 5.5 g. of higher boiling material. The low boiling material contained no chlorine and had the physical constants: n^{20}_{D} 1.4205, d^{20}_{20} 0.7641; *MR*D 36.65 (calcd. *MR*D 37.18).

Anal. Calcd. for C_8H_{14}: Wijs number, 231. Found: Wijs number, 261.

Ozonized in 90% formic acid at 0°, this hydrocarbon formed a methyl ketone boiling at 83° (105 mm.). A 2,4-dinitrophenylhydrazone melting from 135–136° and a semicarbazone melting at 151° eliminated the possibility that the ketone was acyclic. Considering its source, this ketone is almost certainly 1-acetyl-1-methylcyclopropane but identification has not been attempted.

Summary

The yield of dimer from methallyl chloride has been increased to 79% by the use of tetraethyllead as catalyst in the light at 80°. The structure of the dimer has been established as 2-methyl-4,4-bis-(chloromethyl)-1-pentene. The yield and structure of the dimer and consideration of other possibilities indicate that the dimer is formed by a chain transfer reaction in which a chlorine atom is transferred *from* the dimer radical *to* the monomer, contrary to the course of other known transfer reactions.

The dimer and its oxidation products are easily converted to cyclopropane derivatives.

PASSAIC, N. J. RECEIVED MAY 10, 1948