for the length of time given in Column 4, Table II, before carbonation. It was usually necessary to warm the mixture at the start in order to initiate the reaction. Conditions and yields are summarized in Table II.

## Conclusions

When diamyl mercury was treated with sodium and the product of the reaction carbonated, yields as high as 40–50% of butylmalonic acid were obtained. Diethyl mercury by the same series of reactions yielded methylmalonic acid.

An improvement in Frankland and Duppa's method for the preparation of diethyl mercury was realized. Diamyl mercury was prepared from amyl chloride by this same method.

Benzene and toluene were shown to participate in the reaction when they are used as solvents. Di- as well as monocarboxylic acids were obtained in each case. Substitution in the last solvent took place in the methyl group resulting in the formation of the corresponding malonic acid. Such participations of the solvent in the reaction have been designated as "solvent exchange reactions."

CAMBRIDGE, MASS.

RECEIVED APRIL 2, 1936

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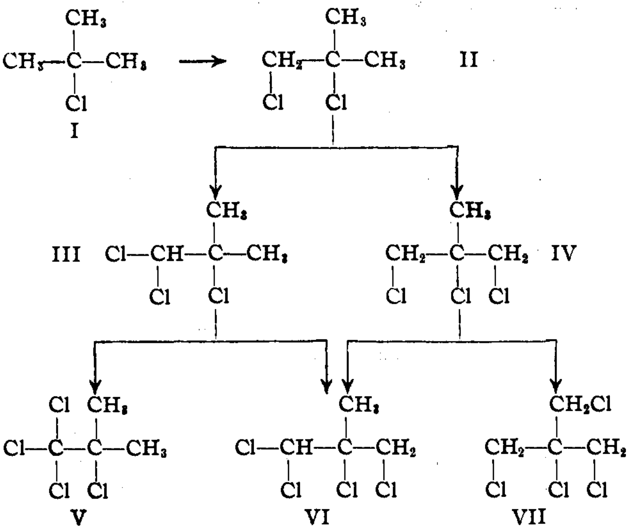
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# The Liquid-Phase Photochemical Chlorination of 2-Chloro-2-methylpropane and Some Related Compounds[1]

BY A. O. ROGERS AND R. E. NELSON

The chlorination of 2-chloro-2-methylpropane proceeds in a series of steps



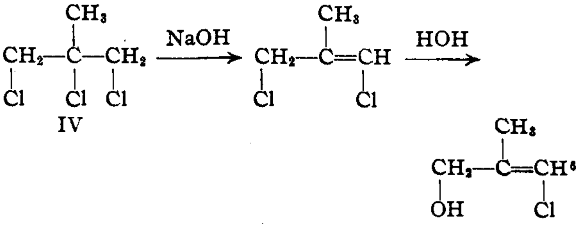
Although the literature contains a number of references to 1,2-dichloro-2-methylpropane (II), the higher polychlorides have received very little attention. Pogorshelski[2] identified 1,2,3-trichloro-2-methylpropane (IV) among the products from the chlorination of 2-methylpropene. The properties of 1,1,2-trichloro-2-methylpropane (III), 1,1,1,2-tetrachloro-2-methylpropane (V) and 1,2,3-trichloro-2-chloromethylpropane (VII) are not accurately described in the literature;[3,4,5] no mention of 1,1,2,3-tetrachloro-2-methylpropane (VI) has been found.

The identities of the various isomeric tri- and tetrachlorides may be deduced from the order of their boiling points, and are confirmed by the following facts.

(a) Compound IV agrees in physical properties with the compound to which Pogorshelski[2] assigned the same structure.

(b) The alkaline hydrolysis of compound IV yields an unsaturated chlorohydrin with a percentage of chlorine agreeing with the formula $C_4H_7OCl$ (equation below).

(c) The pyrolysis of compound IV yields a mixture of unsaturated compounds whose composition agrees with the formula $C_4H_6Cl_2$. This mixture, on chlorination, yields compounds VI and VII; on hydrolysis, about 60% of the chlorine present is removed, with the



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[1] Based upon a thesis submitted by A. O. Rogers to the Faculty of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

[2] Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36**, 1129–1184 (1904); *Chem. Zentr.*, **76**, I, 668 (1905).

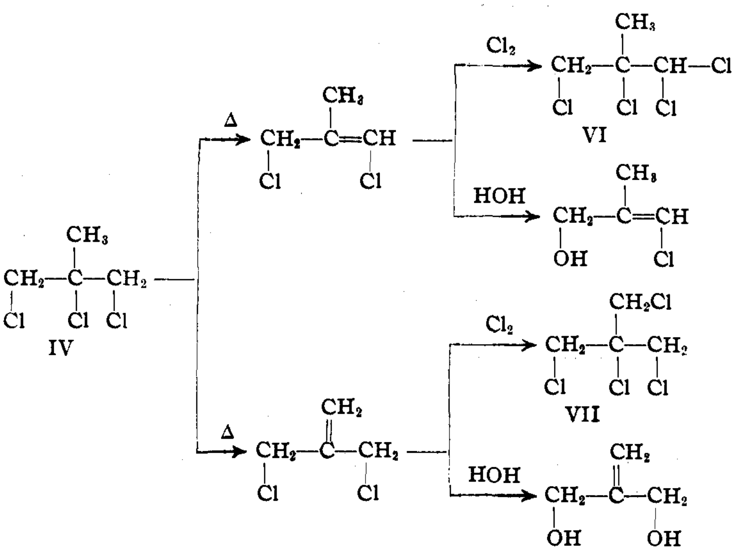
[3] Mouneyrat, *Ann. chim. phys.*, [7] **20**, 534 (1900); *Chem. Zentr.*, **71**, II, 721 (1900).

[4] Willgerodt and Dürr, *Ber.*, **20**, 540 (1887).

[5] Kleinfeller, *ibid.*, **62**, 1595 (1929).

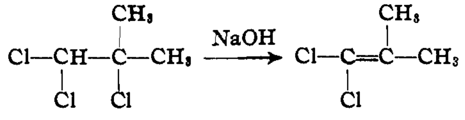
[6] Rogers and Nelson, THIS JOURNAL, **58**, 1029 (1936).

formation of the same unsaturated chlorohydrin obtained by the hydrolysis of compound IV.[6]



(d) The chlorination of 1,3-dichloro-2-methylpropane yields a product with boiling point corresponding to compound IV, but none corresponding to III.

(e) Compound III on chlorination yields compound V; on prolonged refluxing with dilute sodium hydroxide it loses approximately one-third of its chlorine.



$$\mathrm{Cl{-}\underset{Cl}{CH}{-}\overset{CH_3}{\underset{Cl}{C}}{-}CH_3 \xrightarrow{NaOH} Cl{-}\underset{Cl}{C}{=}\overset{CH_3}{C}{-}CH_3}$$

III

(f) The physical constants of compound V agree with those reported by Willgerodt and Dürr[4] for the product of the reaction between phosphorus pentachloride and chloretone, assuming that the material which they prepared was somewhat impure.

TABLE I

CHLORINATION PRODUCTS OF 2-CHLORO-2-METHYLPROPANE

| Formula | $d^{25}_4$ | $n^{20}_D$ | B. p. (corr.), °C. | M. p., °C. | Chlorine, % Calcd. | Chlorine, % Found |
|---|---|---|---|---|---|---|
| $(CH_3)_2C(Cl)CHCl_2$ | 1.2712 | 1.4666 | 144.5–145.4 | −6.5 to −6.0 | 65.9 | 65.9 |
| $CH_3C(Cl)(CH_2Cl)_2$ | 1.3020 | 1.4765 | 162.0–163.1 | | 65.9 | 66.0 |
| $(CH_3)_2C(Cl)CCl_3$ | | | 192 (1175 mm.) | 178.6–179.6 | 72.4 | 72.4 |
| $CH_3\underset{CH_2Cl}{C}(Cl)CHCl_2$ | 1.4393 | 1.4963 | 190.6–191.3 | −46 | 72.4 | 72.4 |
| $(CH_2Cl)_3CCl$ | 1.481 | 1.508 | 206–210 | | 72.4 | 73.2 |

The yields of the various isomers, as estimated from the distillation data, indicate that a chlorine atom already attached to a carbon promotes further substitution of chlorine for hydrogen on the same carbon atom under the conditions used; this effect is increased when two chlorine atoms are attached to the same carbon.

Due to the difficulty of separating 1,1,1,2-tetrachloro-2-methylpropane (sublimes *ca.* 174°) from 1,2,3-trichloro-2-methylpropane (b. p. 162–3.1°), the former compound was prepared in a separate experiment by the chlorination of 1,1,2-trichloro-2-methylpropane.

## Experimental

**Chlorination of 2-Chloro-2-methylpropane.**—2-Chloro-2-methylpropane was prepared from *t*-butyl alcohol in the usual manner.[7] It was chlorinated in the liquid phase under an efficient reflux condenser, using ordinary incandescent lamps for activation; the hydrogen chloride formed in the process was absorbed in ice water to prevent loss of the volatile chlorides. When the specific gravity of the product reached 1.29, the latter was washed, dried and fractionated under reduced pressure through a 110-cm. rectifying column packed with glass rings. From 3400 cc. of 2-chloro-2-methylpropane, the following yields (estimated from the distillation curve) were obtained:

| | Cc. | G. |
|---|---|---|
| 1,2-Dichloro-2-methylpropane | 305 | 330 |
| 1,1,2-Trichloro-2-methylpropane | 600 | 770 |
| 1,2,3-Trichloro-2-methylpropane | 875 | 1140 |
| 1,1,2,3-Tetrachloro-2-methylpropane | 460 | 660 |
| 1,2,3-Trichloro-2-chloromethylpropane | 130 | 190 |

1,1,1,2-Tetrachloro-2-methylpropane was present, but its quantity was small and could not be estimated accurately.

**Chlorination of 1,1,2-Trichloro-2-methylpropane.**—Four hundred cubic centimeters of 1,1,2-trichloro-2-methylpropane from the above experiment was chlorinated in the same manner until the specific gravity reached 1.37. The product was fractionated systematically, using an air condenser and filtering off the solid 1,1,1,2-tetrachloro-2-methylpropane which separated with each treatment; the yield of the latter was 140 g.

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[7] "Organic Syntheses," Coll. Vol. 1, 1932, p. 138.

**Chlorination of 1,2-Dichloro-2-methylpropane and 1,3-Dichloro-2-methylpropane.**—One kilogram of each of the above compounds (Eastman Kodak Co. "practical") was purified by prolonged treatment with concentrated sulfuric acid and distillation under reduced pressure. As expected, the distillation curves indicated the formation of 1,2,3-trichloro- and 1,1,2,3-tetrachloro-2-methylpropane from the 1,3-dichloride, and of 1,1,2-trichloro- and 1,2,3-trichloro-2-methylpropane from the 1,2-dichloride. It is probable that 1,1,3-trichloro-2-methylpropane was also formed from the 1,3-dichloride, but could not be separated from the 1,2,3-isomer.

**Characterization of Products.**—The liquid products from the chlorination of 2-chloro-2-methylpropane were purified by vacuum rectification; 1,1,1,2-tetrachloro-2-methylpropane was recrystallized from alcohol and sublimed. The constants of the products are listed in Table I.

## Summary

1. The production of tri- and tetrachloro-derivatives of isobutane by the liquid-phase photochemical chlorination of 2-chloro-2-methylpropane has been studied. Under the conditions used, all the possible products are formed, and their relative quantities indicate that chlorine attached to a carbon atom promotes the further substitution of chlorine for hydrogen on that atom.

2. The evidence for the structures assigned to the various isomers is discussed.

3. Physical constants are given for the two trichloro- and three tetrachloro- derivatives formed in the chlorination process.

OAK PARK, ILLINOIS RECEIVED MARCH 7, 1936

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# Some Reactions and Derivatives of 1,2,3-Trichloro-2-methylpropane[1]

BY A. O. ROGERS AND R. E. NELSON

## Introduction

In the thermal or photochemical chlorination of isobutane as studied in these Laboratories[2] 1,2,3-trichloro-2-methylpropane is one of the principal products; its synthesis from 2-chloro-2-methylpropane is described by us in another paper.[3] The research described below was undertaken as an attempt to find practical means of utilizing the compound in the event of its becoming available in large quantities.

**The Alkaline Hydrolysis of 1,2,3-Trichloro-2-methylpropane.**—Pogorshelski[4] reported the formation of 3-chloro-2-methylallyl alcohol from 1,2,3-trichloro-2-methylpropane through acetylation and hydrolysis of the resulting ester. The same product is formed directly when the trichloride is heated in an alkaline medium such as dilute sodium hydroxide solution or calcium hydroxide suspension.

In general, the rate of conversion is greater the more strongly alkaline the reagent used. When the quantity of water is limited it controls to a large extent the rate of the reaction; this effect diminishes when a larger volume of water is used, probably because under such conditions the product dissolves in the water layer, so that the activity of the trichloride remains constant. Under alkaline conditions, the reaction virtually stops when the theoretical two-thirds of the chlorine present has been removed (Fig. 1); when no base is used, all three chlorine atoms are removed, and the final product is a tar.

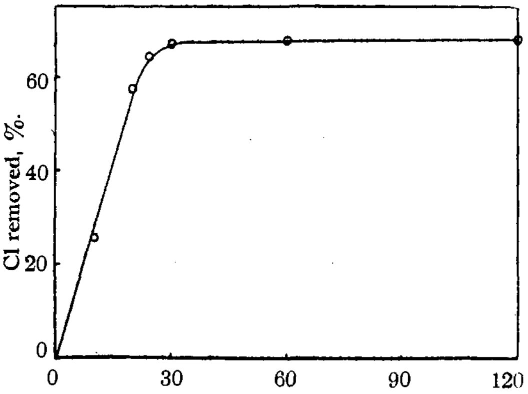

Fig. 1.

3-Chloro-2-methylallyl alcohol exists in *cis* and *trans* forms, which may be separated by careful rectification. The double bond is rather inert; it adds bromine very slowly and is not reduced by sodium amalgam, but is readily oxidized by dilute alkaline permanganate. The usual reac-

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(1) Based upon a thesis submitted by A. O. Rogers to the Faculty of Purdue University in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, June, 1935.

(2) Hass and McBee, private communication.

(3) Rogers and Nelson, THIS JOURNAL, **58**, 1027 (1936).

(4) Pogorshelski, *J. Russ. Phys.-Chem. Soc.*, **36**, 1129–1184 (1904); *Chem. Zentr.*, **76**, I, 668 (1905).