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

[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.

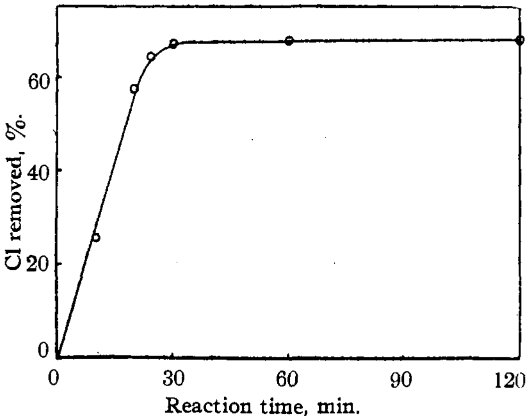

Fig. 1.

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).

tions of the hydroxyl group are shown. The compound usually becomes colored within a day after being distilled, but some samples have been kept for several months without discoloration. It is of possible interest as a slow-evaporating solvent for cellulose acetate.

Experimental

Hydrolysis of 1,2,3-Trichloro-2-methylpropane with Sodium Hydroxide at Atmospheric Pressure.—A quantity of 3-chloro-2-methylallyl alcohol was prepared by refluxing 1,2,3-trichloro-2-methylpropane with 5% aqueous sodium hydroxide. The reaction was carried out in a series of fifteen runs, using a 50% excess sodium hydroxide for each, refluxing the mixture for four hours, and finally recovering the excess base and any unchanged trichloride for use in the next run. The product was separated from the aqueous solutions by distilling off the azeotropic mixture, and was dried in a similar manner. The yield of the crude product was 84% on the basis of the trichloride used, and 87% on the basis of the sodium hydroxide.

Hydrolysis of 1,2,3-Trichloro-2-methylpropane at Pressures Greater than Atmospheric.—In the following experiments the effects of various factors were studied at elevated temperatures. The materials for each run were sealed in a Pyrex tube enclosed in an iron pipe, and heated in an oil-bath fitted with a motor-driven rocker and gas thermoregulator; the extent of reaction was determined in each case by titrating the chloride ion liberated.

In studying the effect of reaction time (Fig. 1), 1 cc. of the trichloride was treated in each run with 1.2 g. of calcium hydroxide and 10 cc. of water at 175–178°. To determine the effect of varying degrees of alkalinity, runs were made under comparable conditions, using (a) water only (acid from the reaction), (b) calcium carbonate (neutral) and (c) 10% sodium hydroxide; chlorine was removed to the extent of (a) 17.4% (thirty minutes), (b) 42.7% (thirty minutes) and (c) 54.5% (ten minutes), respectively. A comparison of these results with Fig. 1 shows clearly the accelerating effect of hydroxyl ion.

By increasing the water present from 10 to 25 cc., the extent of reaction in a given time was increased by about 10%; a corresponding decrease from 10 to 5 cc. diminished the hydrolysis by about 45%.

In a similar manner, 3.23 g. (0.02 mole) of the trichloride was heated with 2 g. (0.035 mole) of calcium hydroxide and 25 cc. of water for thirty minutes at 178°; 66.1% of the chlorine present was removed, and 1.5 cc. (80%) of 3-chloro-2-methylallyl alcohol was recovered.

Reactions of 3-Chloro-2-methylallyl Alcohol.—The alcohol (mixture of *cis* and *trans*) was converted to the corresponding acetate by boiling for fifty minutes with a slight excess of glacial acetic acid in the presence of concentrated hydrochloric acid, using an apparatus which permitted the continuous removal of the water formed in the reaction. A 60% yield of ester, boiling at 167–174° (748 mm.), was obtained. Pogorshelski[4] reported this ester as boiling at 176–178° (784 mm.).

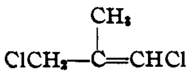
Dry hydrogen chloride reacted readily with the alcohol in the presence of zinc chloride; the product had in general the expected properties, but its analysis (found 54.8% Cl; $C_4H_6Cl_2$ requires 56.8%) leaves doubt as to its purity.

TABLE I

Cis- AND *Trans* 3-CHLORO-2-METHYLALLYL ALCOHOLS

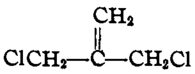
Isomer	Low-boiling	High-boiling
d^{25}_4	1.1290	1.1262
$n^{20}D$	1.4737	1.4730
B. p., °C., corr.	160–162	166–168
M. p. of 3,5-dinitrobenzoate, °C.	94.4–95.8	63.8–64.5
Cl, % (calcd. 33.3)	33.1	33.5

The Pyrolysis of 1,2,3-Trichloro-2-methylpropane.—The thermal decomposition of 1,2,3-trichloro-2-methylpropane results in the formation of three isomeric dichloroisobutenes, namely, *cis* and *trans*-1,3-dichloro-2-methylpropene (formula I), and 3-chloro-2-chloromethylpropene (formula II). Compound I is of interest as an intermediate in the formation of 3-chloro-2-methylallyl alcohol and in other reactions based on the difference in activity between the two chlorine atoms. Although the isomers were not separated directly, their presence was shown by the chlorination and hydrolysis experiments described below. Compound I has been described previously by Pogorshelski,[4] and compound II by Kleinfeller.[5]



$ClCH_2-\overset{CH_3}{\overset{|}{C}}=CHCl$

I



$ClCH_2-\overset{CH_2}{\overset{\|}{C}}-CH_2Cl$

II

The pyrolysis was carried out conveniently in an empty glass tube at 450–550° with a 60–70% conversion; attempts to increase the yield by higher temperature or exposure longer than two to three minutes resulted in the tube clogging with carbonaceous material. A number of gaseous and volatile substances were tried in the hope of finding an effective homogeneous catalyst for the reaction, but without success.

Experimental

Apparatus.—When a considerable quantity of material was being pyrolyzed, the apparatus shown in Fig. 2 was used. The flow of liquid from the feeder A is regulated and held constant by the influx of air through the capillaries B, the decrease in liquid pressure as the feeder empties being compensated by the corresponding increase in air pressure above the liquid. After being vaporized in the oil-bath C, the material passes through the reaction tube F, which is held at the required temperature by the salt-bath E. The liquid product is collected in H, while the hydrogen chloride is absorbed in water in the scrubber J. Any water-insoluble gases may be collected in the graduated cylinder K or allowed to escape at L.

In small-scale experiments, a 25-cc. buret was used as feeder and a 20-cm. test-tube as receiver; most of the hydrogen chloride was dissolved in cold water contained in the receiver itself. When gases formed part of the reaction mixture they were introduced through a T-joint immediately above C.

Description of Results.—The quantity of hydrogen chloride split out was used as a basis of comparison between different sets of conditions;

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(5) Kleihfeller, *Ber.*, **62**, 1590 *et seq.* (1929).

it did not, however, give a true measure of the extent of conversion, since the products themselves decomposed fairly rapidly under the conditions used. The time of exposure was estimated roughly from the temperature, capacity of the reaction tube and extent of decomposition.

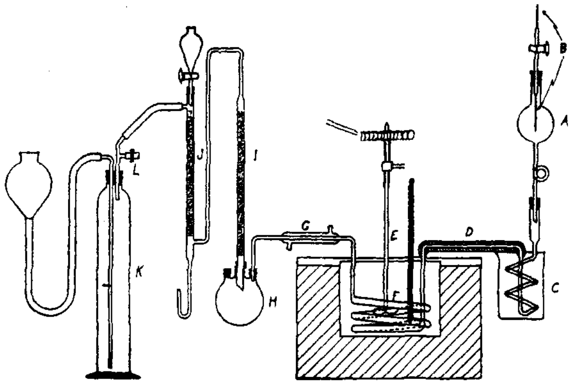

Fig. 2.

Table II shows the effect of temperature on the decomposition of the pure trichloride. Figure 3 shows the results obtained when foreign substances were introduced into the reaction; in general, none of these had any appreciable effect. In agreement with the observation of Weston and Hass[6] the reaction was not affected by the presence of carbonaceous deposits from previous runs.

From 434 cc. of 1,2,3-trichloro-2-methylpropane pyrolyzed at 460° with a reaction time of about forty-two seconds, a mixture containing about 240 cc. of dichloroisobutenes and 80 cc. of unchanged trichloride was obtained; this represents a yield of 80% from the trichloride consumed.

TABLE II

EFFECT OF TEMPERATURE ON THE PYROLYSIS

Run	Reaction time, min.	Temp., °C.	Chlorine removed, %
1	2.8	300	0
2	2.6	400	6.7
3	2.3	430	21.5
4	2.1	460	33.3

Chlorination of the Pyrolysis Product.—Sixty-two and one-half grams (0.5 mole) of the mixture of dichloroisobutenes from the above pyrolysis was chlorinated in the dark at 0° until the weight reached 101 g. (about thirty-seven hours). The product consisted of 1,1,2,3-tetrachloro-2-methylpropane and 1,2,3-trichloro-2-chloromethylpropane (the expected addition products from 1,3-dichloro-2-methylpropene and 3-chloro-2-chloromethylpropene, respectively) together with some pentachlorides.

Hydrolysis of the Pyrolysis Product.—A mixture of 12.5 g. (0.1 mole) of the dichloroisobutenes with 250 cc. of water and 4 g. of magnesium oxide was boiled under an efficient reflux condenser with stirring for thirteen hours. The chloride ion formed represented 60.5% of the chlorine originally present, which is intermediate between the results expected for 1,3-dichloro-2-methylpropene and for 3-chloro-2-chloromethylpropene. The reaction yielded 4.3 cc. (0.046 mole, 46%) of 3-chloro-2-methylallyl alcohol.

3-Chloro-2-methylallyl alcohol was produced similarly by the use of other alkaline and neutral reagents, such as calcium hydroxide and calcium carbonate. Under acid conditions, the reaction was different, yielding an aldehyde as one of the principal products.

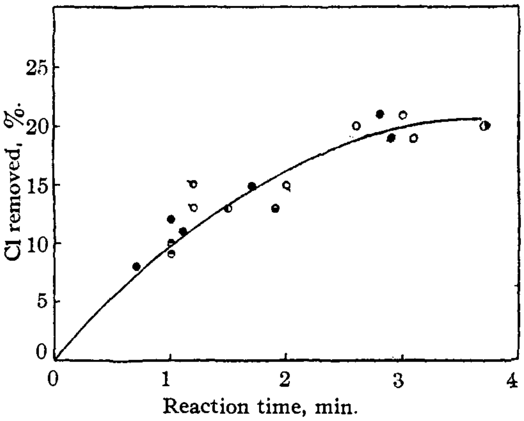

Fig. 3.—○, Blank; ●, nitrogen; ◐, nitrogen + water; ◑, pyridine; ⊖, mercuric chloride; ◓, carbon dioxide; ♀, water gas; ♂, nitric oxide.

Action of the Pyrolysis Products with Grignard Reagents.—It was hoped that the difference in activity between the two chlorine atoms of 1,3-dichloro-2-methylpropene might permit the synthesis of certain higher aldehydes through the reactions

$$ClCH_2C(CH_3){=}CHCl \xrightarrow{RMgX}$$

$$RCH_2C(CH_3){=}CHCl \xrightarrow{HOH} RCH_2C(CH_3)CHO$$

The action of normal- and isoamylmagnesium bromides yielded a complex mixture of products with no worthwhile yield of any one substance. Phenylmagnesium bromide gave a 40% yield of 1-chloro-2-methyl-3-phenylpropene, a liquid with a mild aromatic odor, density 1.042 g. per cc., b. p. 125° (36 mm.). Found: 21.55% Cl; $C_{10}H_{11}Cl$ requires 21.3%.

The difference between the action of the aliphatic and cyclic Grignard compounds agrees with the results of Bert[7] in his study of 1,3-dichloropropene.

Summary

1. The alkaline hydrolysis of 1,2,3-trichloro-2-methylpropane yields a mixture of *cis*- and *trans*-3-chloro-2-methylallyl alcohols; its pyrolysis yields *cis*- and *trans*-1,3-dichloro-2-methylpropene and 3-chloro-2-chloromethylpropene. The conditions suitable for these reactions have been studied.

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[6] Weston and Hass, THIS JOURNAL, **54**, 3340 (1932).

[7] Bert, *Compt. rend.*, **180**, 1504 (1925).

2. Some reactions of the hydrolysis and pyrolysis products are described, and the constants of the isomeric forms of 3-chloro-2-methylallyl alcohol and of 1-chloro-2-methyl-3-phenylpropene are reported.

Oak Park, Illinois Received March 7, 1936

[Contribution from the Chemical Laboratory of the University of California]

The Production of Temperatures below 1° A. The Heat Capacities of Water, Gadolinium Nitrobenzene Sulfonate Heptahydrate and Gadolinium Anthraquinone Sulfonate

By D. P. MacDougall and W. F. Giauque

Following our work on the production of temperatures below 1°K. by adiabatic demagnetization of gadolinium sulfate octahydrate[1] we investigated the effect of diluting the gadolinium atoms.

Numerous low temperature investigations of magnetic susceptibility, principally at the Kamerlingh Onnes Laboratory of the University of Leiden, indicate that ideal paramagnetic situations are more nearly approximated by compounds in which the distances between the magnetic atoms are large.

Gadolinium nitrobenzenesulfonate heptahydrate and anthraquinone sulfonate hydrate were selected because these substances, like most sulfonates, crystallize readily. The number of molecules of water of crystallization on the anthraquinone sulfonate was unknown but was presumably six or seven.

A brief summary of the results presented here has been given previously.[2]

Apparatus.—The magnetic and principal features of the apparatus were the same as in our previous work on gadolinium sulfate.[1] However, several parts of the apparatus were improved considerably. In a few measurements on gadolinium sulfate at a frequency of 1000 cycles/sec. the inductance changed by about 5% from the value at 60 cycles/sec. This effect was due to eddy currents set up in the surrounding metal apparatus by the alternating current used for measuring inductance. The eddy currents were almost entirely located in a brass container which surrounded the Dewar vessel used for maintaining a liquid helium bath around the sample and inductance coil. This brass container, which is shown as C in Fig. 2 of our previous paper,[1c] was immersed in liquid air and served as a vacuum tight enclosure for the helium gas. The brass container was discarded and the apparatus modified to the form shown in Fig. 1. Since the Dewar for liquid helium had to be enclosed to avoid the entry of air, and especially to permit the use of reduced pressure on the liquid helium bath, the inner tube of the solenoid case was used for this purpose. It is necessary to protect the exterior of the Dewar containing liquid helium by liquid air. This was done by passing liquid air through a non-inductively wound helical coil, E, of brass tubing 0.4 cm. o. d. which was firmly and closely attached to the exterior of the Dewar, by means of fiber separators and adhesive tape. The top of the apparatus was protected by liquid air in a cup, C, which also acted as a supply for the brass coil system. Such a system works well by gravity if the tubing is of sufficiently large diameter. However, for reasons of space economy we used small tubing and applied a vacuum at the exit end, B, of the tube. The level of the liquid air in the cup, C, was maintained constant by a float valve (not shown) attached to the end of a transfer tube connected with a 50-liter supply Dewar. The necessary flow, about 1.5 liter/hr., was maintained by means of a gas thermometer controlled magnetic valve on the vacuum line. The arrangement was very satisfactory and it was somewhat easier to solder only the inlet and outlet tubes than, as previously was necessary, to make the rather large solder joint on the brass Dewar case during assembly. The inner tube of the solenoid case was extended to the flange, D, where the joint was easily made tight by means of a gasket and stopcock grease.

We have previously[1c] commented on the difficulty of maintaining a vacuum in sealed Pyrex Dewars in contact with helium and since the large outer Dewar, I, was of Pyrex a pumping line was left permanently attached at J. It was not necessary to pump the Dewar during a forty or fifty hour run. The inner Dewar was made of Jena glass and this can be used for several months without reëvacuation.

In early experiments the upper portion of the Dewar for liquid helium contained a liquid hydrogen chamber, which is shown as D of Fig. 2 in our previous paper.[1c] The purpose of the liquid hydrogen was to cool the apparatus to a sufficiently low temperature before the addition of liquid helium and also to block off heat leak from above. Although the apparatus remained at liquid helium temperatures for about ten or twelve hours with one filling of liquid helium we soon reached the conclusion that the arrangement would be improved by the removal of the liquid hydrogen chamber. Actual removal of the chamber

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[1] Giauque and MacDougall, (a) *Phys. Rev.*, **43**, 768 (1933); (b) **44**, 235 (1933); (c) This Journal, **57**, 1175 (1935).

[2] (a) Meeting of the American Chemical Society in affiliation with the American Association for the Advancement of Science, Berkeley, California, June 18–23, 1934. (b) *Phys. Rev.*, **47**, 885 (1935).