[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

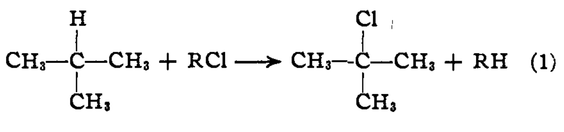
Condensation of Saturated Hydrocarbons with Haloöefins. II. The Reaction of Isobutane with *cis*- and *trans*-Dichloroethylene

BY LOUIS SCHMERLING

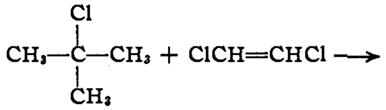
It was shown previously[1] that the condensation of isobutane with allyl chloride and vinyl chloride in the presence of aluminum chloride at −10° apparently proceeds via the conversion of the isoparaffin to *t*-butyl chloride which then adds to the chloroölefin to yield, respectively, 1,2-dichloro-4,4-dimethylpentane and 1,1-dichloro-3,3-dimethylbutane. The greater part of the former reacts with isobutane, producing 1-chloro-3,4-dimethylpentane as the major product. On the other hand, the 1,1-dichloro-3,3-dimethylbutane undergoes little conversion to monochloride and is, therefore, isolated as the principal chlorine-containing product.

The condensation of isobutane with a dichloroolefin, namely, 1,2-dichloroethylene, has now been investigated. It was found that the chief product is 1,1,2-trichloro-3,3-dimethylbutane, the same trichlorohexane which is obtained by the addition of *t*-butyl chloride to the dichloroethylene.[2] The intermediate conversion of the isobutane to *t*-butyl chloride is again indicated. Furthermore, since no dichlorohexane was isolated, it may be concluded that the trichloride is quite stable toward further reaction with the isobutane; that portion which does react is eventually reduced to paraffin (*i. e.*, all three chlorine atoms are successively replaced by hydrogen) by means of the hydrogen–chlorine exchange reaction with isobutane.[3] The trichloride is relatively unreactive because two of the chlorine atoms are attached to a primary carbon atom and the third to a secondary carbon atom which is in a neopentyl group. The intermediate di- and mono-chlorohexanes are comparatively unstable because tertiary carbon atoms are formed during the hydrogen–chlorine exchange; for example, the trichloride is probably converted to 1,1-dichloro-2,3-dimethylbutane which then isomerizes to reactive 1,2-dichloro-2,3-dimethylbutane.

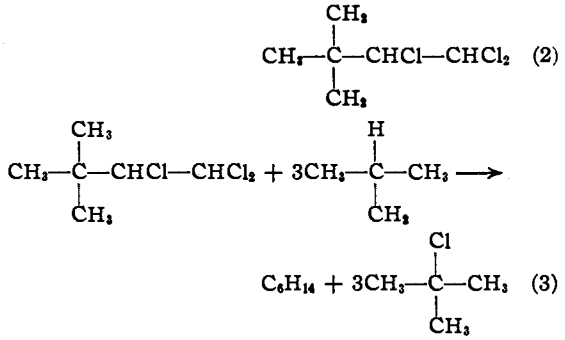
The mechanism of the condensation may be written as



$$CH_3-\overset{H}{\underset{CH_3}{C}}-CH_3 + RCl \longrightarrow CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3 + RH \quad (1)$$



$$CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3 + ClCH{=}CHCl \longrightarrow$$



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHCl-CHCl_2 \quad (2)$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CHCl-CHCl_2 + 3CH_3-\overset{H}{\underset{CH_3}{C}}-CH_3 \longrightarrow C_6H_{14} + 3CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3 \quad (3)$$

t-Butyl chloride formed as in equation 3 (actually the sum of three successive reactions) reacts with dichloroethylene as in equation 2. Since the reaction of equation 1 is a chain initiating step only, the nature of RCl (which might be dichloroethylene, trichloroethane, complex of catalyst with dichloroethylene, etc.) is unimportant. It is apparent that the highest possible yield of trichlorohexane is two-thirds of a mole per mole of dichloroethylene.

There is a very marked difference in reactivity between the *cis* and *trans* isomers of 1,2-dichloroethylene. The trichloride was obtained in 35% yield[4] by the reaction of isobutane with the *cis* compound at room temperature and in less than 5% yield by reaction with the *trans* isomer under the same conditions. A similar difference was found[2] for the condensation of the two isomers with isopropyl chloride or *t*-butyl chloride. Steric effects are presumably involved.

The structure of the trichloride was proved by converting it to a chlorohexene by reaction with zinc and alcohol; that the chlorohexene was 1-chloro-3,3-dimethyl-1-butene was shown by the facts that it yielded trimethylacetic acid on oxidation and that it was identical with the product obtained by the dehydrochlorination of 1,1-dichloro-3,3-dimethylbutane (obtained by the condensation of *t*-butyl chloride with vinyl chloride[5]).

It seems worth while at this time to discuss further[6] the significance which the reaction of isobutane with chloroölefins bears on the mechanism of the alkylation of isoparaffins with olefins. Gorin, Kuhn and Miles[7] have recently proposed an alkylation mechanism which is similar to those of Caesar and Francis[8] and of McAllister, Anderson,

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[1] L. Schmerling, THIS JOURNAL, **67**, 1438 (1945).

[2] L. Schmerling, *ibid.*, **68**, 1655 (1946).

[3] P. D. Bartlett, F. E. Condon and A. Schneider, *ibid.*, **66**, 1531 (1944).

[4] Based on the dichloroethylene charge, assuming that the limiting, over-all reaction may be represented by $3C_4H_{10} + 3C_2H_2Cl_2 \rightarrow C_6H_{14} + 2C_6H_{11}Cl_3$.

[5] L. Schmerling, THIS JOURNAL, **68**, 1650 (1946).

[6] *Cf.* L. Schmerling, *ibid.*, **67**, 1778 (1945).

[7] M. H. Gorin, C. S. Kuhn, Jr., and C. B. Miles, *Ind. Eng. Chem.*, **38**, 795 (1946).

[8] P. D. Caesar and A. W. Francis, *ibid.*, **33**, 1426 (1941).

Ballard and Ross[9] in that all three postulate that the isoparaffin undergoes carbon to carbon cleavage to yield two alkyl fragments (isopropyl and methyl in the case of isobutane). By assuming that the fragments (behaving as if positively and negatively charged) add to a complex formed between catalyst and olefin and by setting up rules governing the structure of the complex, Gorin, *et al.*, make it possible for this type of mechanism to explain why some isomers are formed and others are not. They state "The assumption that carbon–carbon fission occurs in the isobutane molecule . . . was recently rejected by Schmerling[6] in a criticism of the alkylation mechanisms proposed by these investigators [Caesar and Francis,[8] and McAllister, *et al.*[9]]. In the opinion of the writers, however, such a rupture of the isobutane molecule is scarcely less likely, *a priori*, than the similar α–β shift of a methyl group embodied in the mechanism of Schmerling or required, for that matter, to account for isomerization of alkanes. There seems to be little to choose between the two proposals on the basis of information now available."

Even without entering into a discussion of the vast literature on intramolecular rearrangements which involve *shifting* of methyl groups,[10] it is possible to furnish information which permits making a choice between the two proposals. This information consists in the results obtained in the condensation of isobutane with chloroölefins (*i. e.*, with olefins which have been "tagged"). The Gorin, *et al.*, mechanism can explain the formation of 1-chloro-3,4-dimethylbutane by the reaction of isobutane with allyl chloride; on the other hand, it cannot explain the formation of 1,2-dichloro-4,4-dimethylpentane as by-product of this reaction. Furthermore, it does not account for the principal chlorinated product of the reaction of isobutane with vinyl chloride (namely, 1,1-dichloro-3,3-dimethylbutane) or with 1,2-dichloroethylene (namely, 1,1,2-trichloro-3,5-dimethylbutane). In contrast to this, the mechanism proposed by the present writer for the alkylation of isoparaffins with olefins readily explains the formation of these polychloroalkanes; indeed, they are the inherent products of the second step of the mechanism (*cf.* equation 2). As has already been indicated, these compounds are comparatively unreactive and more or less of each will therefore be isolated as such. The analogous product of the alkylation of an isoparaffin with an olefin is an alkyl chloride (or other alkyl ester if catalyst other than aluminum chloride is used) which is usually not isolated because it readily undergoes the third step of the mechanism (*cf.* equation 3).

Experimental[11]

Procedure.—The dichloroethylene, isobutane and aluminum chloride were weighed into a glass liner (cooled in a bath at −78°) for an Ipatieff-type rotating autoclave of 850-cc. capacity. The liner was sealed into the autoclave which was then rotated at room temperature for four hours, after which it was allowed to stand overnight. The gaseous products were discharged through a soda lime tower to absorb hydrogen chloride and thence into a trap immersed in Dry Ice–acetone. The liquid product in the liner was decanted from the catalyst layer, washed, dried and distilled.

Reaction of *cis*-Dichloroethylene with Isobutane.—The reaction of 50 g. (0.52 mole) of *cis*-dichloroethylene (prepared by the isomerization[12] of *trans*-dichloroethylene) and 122 g. (2.1 mole) of isobutane in the presence of 10 g. of aluminum chloride yielded 11 g. (0.30 mole) of hydrogen chloride, 28 g. of red-brown, fluid catalyst layer, and a liquid product, distillation of which yielded 13 g. of product, b. p. 39–100°, n^{20}_D 1.3680–1.3842; 9 g., b. p. 100–106°, n^{20}_D 1.4056–1.4508; 23.5 g. (0.12 mole, 35% yield) of trichlorohexane, b. p. 196–200°, m. p. −16 to −17°, n^{20}_D 1.4755; and residue, 2.5 g.

Similar results were obtained in the presence of added hydrogen chloride. The reaction of 60 g. (0.62 mole) of *cis*-dichloroethylene and 125 g. (2.2 mole) of isobutane in the presence of 10 g. of aluminum chloride and 12 g. of anhydrous hydrogen chloride yielded 18 g. of liquid product, b. p. 45–190°; 28 g. (0.15 mole, 36% yield) of the trichlorohexane, b. p. 68–70° (6 mm.) or 198–200°

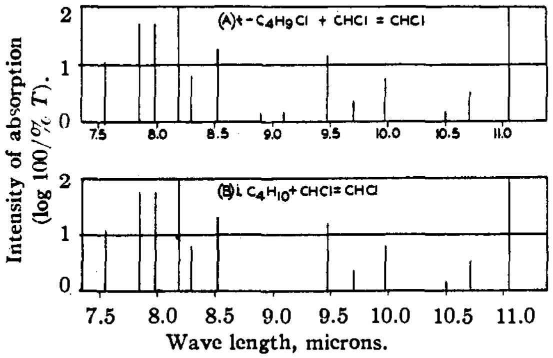

Fig. 1.—The infrared absorption spectra of the trichlorohexane formed by the reaction of *cis*-dichloroethylene with (A) *t*-butyl chloride and (B) isobutane.

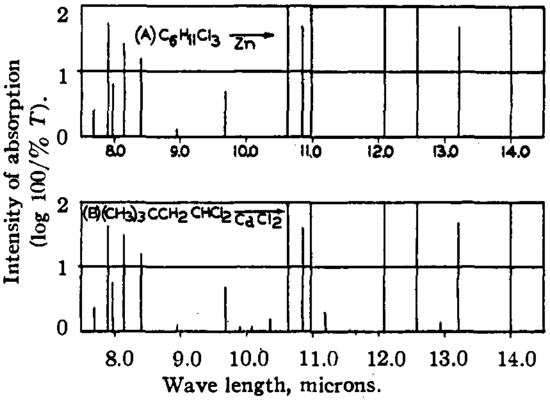

Fig. 2.—The infrared absorption spectra of the chlorohexene obtained by the reaction of (A) the trichlorohexane with zinc and (B) 1,1-dichloro-3,3-dimethylbutane over calcium chloride.

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(9) S. H. McAllister, J. Anderson, S. A. Ballard and W. E. Ross, *J. Org. Chem.*, **6**, 647 (1941).

(10) That the postulated migrations of methyl groups do occur when the particular alkylation intermediates are converted to paraffins was proved experimentally.[6]

(11) Microanalyses by Dr. T. S. Ma, University of Chicago.

(12) G. Chavanne, *C. A.*, **7**, 1180 (1913); **9**, 2898 (1915).

(760 mm.), m. p. −13 to −12°, n^{20}_D 1.4760; d^{20}_4 1.2078; and residue, 2.5 g. The catalyst was converted to 30 g. of red-brown viscous liquid; 14 g. of hydrogen chloride was recovered.

Anal. Calcd. for $C_6H_{11}Cl_3$: C, 38.00; H, 5.85; Cl, 56.15. Found: C, 38.10; H, 5.71; Cl, 56.42.

The presence of *t*-butyl chloride in the lower-boiling liquid (b. p. 45–60°) was proved by adding about 0.1 g. of aluminum chloride to a solution of 1 cc. of the liquid in 1 cc. of benzene. Hydrogen chloride was evolved and the catalyst was converted to a clear yellow liquid. The upper layer was decanted and the excess benzene was permitted to evaporate spontaneously (overnight). Crystals of *p*-di-*t*-butylbenzene (m. p. 76°) were deposited.

The trichlorohexane (m. p. −13 to −12°) was shown to be substantially the same as the product (m. p. −14 to −13°) obtained by the addition of *t*-butyl chloride to *cis*-dichloroethylene[2] in the presence of aluminum chloride. A mixture of the two products melted at −13.5 to −13°. Comparison of the infrared spectra[13] (see Fig. 1) confirmed their identity.

Reaction of *trans*-Dichloroethylene with Isobutane.—Comparatively little reaction occurred when a mixture of 30 g. of *trans*-dichloroethylene (purchased from Eimer and Amend), 55 g. of isobutane and 6 g. of aluminum chloride was rotated in the autoclave at room temperature. The liquid product consisted chiefly of unreacted dichloroethylene; about 6 g. of intermediate material and 2 g. of trichlorohexane fraction (b. p. 190–200°) were obtained.

Reaction of 1,1,2-Trichloro-3,3-dimethylbutane with Zinc.—A solution of 30 g. of the trichlorohexane in 100 g. of *n*-propyl alcohol was refluxed over 10 g. of zinc dust for sixteen hours. The product was distilled until addition of water to the distillate no longer yielded an appreciable amount of water-insoluble material. There was obtained 15.5 g. of reaction product, n^{20}_D 1.4272. Redistillation yielded 14 g. (75% yield) of chlorohexene (b. p. 102–103°; n^{20}_D 1.4260; d^{20}_4 0.8815; *MR* calcd., 34.26; *MR* obs. 34.42) and 1.5 g. of residue (n^{20}_D 1.4320).

Anal. Calcd. for $C_6H_{11}Cl$: C, 60.74; H, 9.35; Cl, 29.91. Found: C, 60.54; H, 8.85; Cl, 30.34.

The infrared spectrum[13] of the chlorohexene was compared with that of product (b. p. 102–104°, n^{20}_D 1.4262) obtained by the dehydrochlorination of 1,1-dichloro-3,3-dimethylbutane[5] over calcium chloride at 450°. The materials were found to be substantially the same (see Fig. 2).

Oxidation of 1-Chloro-3,3-dimethyl-1-butene.—A mixture of 6.5 g. of the chlorohexene and a solution of 16 g. of potassium permanganate in 500 cc. of water was stirred at ice-bath temperature for eight hours and then at 2–10° for an additional eight hours. All of the permanganate reacted. The product was filtered and the filtrate was evaporated to 30 cc. and acidified with dilute sulfuric acid. Steam distillation of the acidified solution yielded 3 cc. of organic material which was taken up in ether. Removal of the ether yielded 2.5 g. of trimethylacetic acid, b. p. 161–162°, m. p. 30–31°, characterized as the *p*-bromophenacyl ester, m. p. 76°.

Acknowledgment.—The continued interest of Professor V. N. Ipatieff is gratefully acknowledged.

Summary

A trichloride, 1,1,2-trichloro-3,3-dimethylbutane, is the principal product of the reaction of isobutane with 1,2-dichloroethylene in the presence of aluminum chloride at room temperature. It is obtained in 35% yield when *cis*-dichloroethylene is used, and in less than 5% yield when *trans*-dichloroethylene is used.

The probable mechanism of the reaction is presented.

It is shown that the reaction serves as a means of evaluating recently proposed mechanisms for the alkylation of isoparaffins with olefins.

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[13] The writer is indebted to Dr. W. S. Gallaway of the Physics Division, Universal Oil Products Co. for the infrared analyses and the figures; for a description of the procedure used, see THIS JOURNAL, 69, 1124 (1947).

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Sulfur as a Promoter for a Nickel Catalyst in Dehydrogenation

BY HOMER ADKINS, DOROTHY S. RAE,[1] JAMES W. DAVIS,[2] GLENN F. HAGER[3] AND KATHRYN HOYLE[1]

The method of aromatizing a hydroaromatic compound by oxidizing it with benzene has given excellent results.[4] However, uniformly good yields were not obtained in attempting to duplicate results and extend the method. For example, in testing catalysts in the conversion of dicyclohexyl to diphenyl, *i.e.*

$$C_6H_{11}C_6H_{11} + 2C_6H_6 \xrightarrow[350°]{Ni} C_6H_5C_6H_5 + 2C_6H_{12}$$

the yield of diphenyl after reaction for two hours varied from 1 to 90%.

The variability in yields was found to depend upon the quality of the benzene used. Fractionation of a sample of benzene which gave good results showed that the lower boiling fractions were better than the higher boiling ones. A number of false leads were followed which, however, led to the discovery that the addition of 25 mg. of tetramethyl tin or of carbon tetrachloride to 20 ml. of benzene and 2 g. of catalyst improved the yield of diphenyl so that the conversion was approximately 80%. The fruitful observation was made that the more thoroughly the benzene was purified from thiophene the poorer were the yields of diphenyl obtained. It was then found that the addition of a suitable amount of thiophene to pure benzene gave excellent yields of diphenyl. For example, the per cent. conversions of dicyclohexyl to diphenyl were with varying amounts of thiophene

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[1] Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

[2] Allied Chemical and Dye Corporation Fellow 1941–1942.

[3] Monsanto Chemical Company Fellow 1942–1943.

[4] Adkins, Richards and Davis, THIS JOURNAL, 63, 1320 (1941).