Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.17. Found: C, 30.07; H, 4.27.

The dibromide was dehydrobrominated by refluxing 7.56 g. of material in 10 ml. of 30% alcoholic potassium hydroxide for 12 hours. Addition of water caused 4.09 g. (78%) of product to separate. Distillation of the dried material yielded 3.55 g. (68%) of material that was identified as 1-bromocyclohexene from its physical properties, b.p. 65.7–66.0° (26 mm.), n^{25}D 1.5112.

Five mole per cent. of diphenylamine and ferric chloride were used in experiments 5 and 6 in an attempt to promote ionic addition.[29] In these experiments 90% of the unreacted I was isolated from the deep red solution.

Addition of Hydrogen Bromide to 1-Methylcyclohexene.—A typical experiment is as follows: Experiment 15: Hydrogen bromide was added to 19.25 g. (0.2 mole) of III in 150 g. of pentane according to method B. Dry hydrogen bromide was passed through the solution for 1.25 hours as the solution was being irradiated. After removal of the hydrogen bromide with solid sodium carbonate the solution was filtered and fractionated. After the removal of the solvent and unreacted III the remaining material was completely distilled and collected in three fractions.

Fraction	B.p., °C. (21.5 mm.)	g.	n^{25}D	*t*-Bromide, %
1	70.0–72.3	6.57	1.4898	32.6, 32.3
2	72.3–73.3	7.30	1.4905	20.3, 20.9
3	73.3–73.5	5.44	1.4908	12.3, 12.2

The composition of each fraction was determined by analyzing for tertiary bromide in the presence of secondary bromide by the method of Walling, Kharasch and Mayo.[15] Analyses were carried out in duplicate on a 0.1–0.3-g. sample. In this experiment the tertiary bromide amounts to 22.3% of the total product.

In order to check the method of analysis, pure cyclohexyl bromide and 1-bromo-1-methylcyclohexane were analyzed. These analyses showed < 1% tertiary bromide for the former compound and 100% tertiary bromide for the latter.

The fractions were combined and total halogen determined by the method described by Bacon.[30]

Anal. Calcd. for $C_7H_{13}Br$: Br, 45.13. Found: Br, 45.38, 45.11.

The yield of analytically pure material was 19.3 g. (54.5%).

The addition product was dehydrohalogenated as follows: A solution of 11.4 g. of the addition product in 25 ml. of dry pyridine was refluxed for 8 hours and then poured into 100 ml. of water. The solution was neutralized with dilute hydrochloric acid and steam distilled until the distillate contained no unsaturated material. About 15 ml. of distillate was collected. The organic layer was separated and dried and weighed 4.82 g. (78%). This material was distilled yielding 3.23 g. (52.3%) of volatile material, n^{25}D 1.4478. This product was identified as 1-methylcyclohexene containing 1.1% 3-methylcyclohexene by a combination of chemical and infrared analysis. When pure 3-methylcyclohexene was submitted to the conditions of dehydrobromination it was recovered unchanged in 90.8% yield. The experiments summarized in Tables II and III were carried out in a similar manner.

In experiment 18, anhydrous hydrogen bromide was passed through a solution of 15.0 g. of III and 0.15 g. of diphenylamine in 50 ml. of glacial acetic acid. The product was isolated by diluting the solution with water and extracting with pentane. The organic layer was washed with sodium bicarbonate solution and dried over sodium sulfate. Fractionation yielded 23.2 g. (84%) of material, b.p. 66.7–67.7° (23 mm.), n^{25}D 1.4866–1.4868. This material was found to be 100% tertiary halide and appears to be identical with the product obtained from 1-methylcyclohexanol.

Infrared Analysis.—The quantitative determination of 3-methylcyclohexene in III was carried out with a Baird Associates Recording Spectrophotometer with sodium chloride prisms. From the spectra of the pure isomers and of synthetic mixtures containing small amounts of 3-methylcyclohexene, peaks at 13.92 μ and at 14.9 μ were found to be suitable, on the basis of sensitivity and freedom from interference, for the analysis of small amounts of 3-methylcyclohexene in III. As the samples obtained in the dehydrohalogenations contained small and varying amounts of an unidentified impurity absorbing at 14.86 μ the 13.92 μ peak was used for the analysis. A 0.1-mm. cell was used and was calibrated using synthetic mixtures. Beer's law and additivity of absorbencies of solvent and solute were assumed for concentrations of < 6% 3-methylcyclohexene.

MADISON, WISCONSIN

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[29] M. S. Kharasch, J. A. Norton and F. R. Mayo, *J. Org. Chem.*, **3**, 48 (1938).

[30] C. W. Bacon, THIS JOURNAL, **31**, 49 (1909).

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

Condensation of Saturated Halides with Unsaturated Compounds. IX. Halogen Exchange between *t*-Butyl Halides and Aluminum Halides during the Condensation with Ethylene[1]

BY LOUIS SCHMERLING AND JAMES P. WEST

RECEIVED JUNE 11, 1951

The condensation of *t*-butyl chloride with ethylene in the presence of aluminum bromide at −40 to −50° results in the formation of 1-bromo- and 1-chloro-3,3-dimethylbutane in 15 and 32% yields, respectively. A similar halogen exchange occurs during the condensation of *t*-butyl bromide with ethylene in the presence of aluminum chloride. Interaction of the alkyl chloride with the catalyst is indicated by these experiments which thus lend support to the carbonium ion theory of metal halide activity. A chain mechanism, involving abstraction of a chloride ion by a carbonium ion, is proposed to explain the data.

The condensation of *t*-butyl chloride with ethylene in the presence of aluminum chloride at −15 to −10° results in a 75% yield of 1-chloro-3,3-dimethylbutane.[2] This reaction presumably occurs by way of polarization of the alkyl halide *via* the formation of a complex with the catalyst. Hence, if the halogen atoms in the catalyst are different from the one in the alkyl halide, it may be expected that at least part of the halogen in the final product will be that of the catalyst rather than of the original *t*-butyl halide

$$(CH_3)_3CCl + AlBr_3 \rightleftharpoons (CH_3)_3C^+(AlBr_3Cl)^- \quad (1)$$

$$(CH_3)_3C^+(AlBr_3Cl)^- + CH_2{=\!=}CH_2 \rightleftharpoons (CH_3)_3CCH_2CH_2^+(AlBr_3Cl)^- \quad (2)$$

$$(CH_3)_3CCH_2CH_2^+(AlBr_3Cl)^- \rightleftharpoons (CH_3)_3CH_2CH_2Br + AlBr_2Cl \quad (3)$$

That such exchange of halogen does occur was shown by an experiment in which ethylene was bubbled into a well-stirred mixture of *t*-butyl

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[1] Preceding paper in this series, THIS JOURNAL, **74**, 2885 (1952).

[2] L. Schmerling, *ibid.*, **67**, 1152 (1945).

chloride (1.03 moles), aluminum bromide (0.33 mole) and *n*-pentane diluent at −40 to −50°. 1-Bromo- and 1-chloro-3,3-dimethylbutane were formed in 15 and 32% yields, respectively. The amount of bromohexane formed by the exchange reaction was thus approximately one-third of the condensation product rather than one-half as calculated on a statistical basis. Similarly, the reaction of *t*-butyl bromide (1.02 moles) with ethylene in the presence of aluminum chloride (0.34 mole) under the same conditions resulted in a 58% yield of 1-bromo-3,3-dimethylbutane and only 13% of the 1-chloro-3,3-dimethylbutane formed by interaction with the catalyst.

The fact that the halogen which predominated in the product was the same as that in the *t*-butyl halide throws additional light on the mechanism of the reaction. It indicates that the condensation occurs not only in the manner shown above but also by the chain-carrying exchange reaction

$$(CH_3)_3CCH_2CH_2^+(AlBr_3Cl)^- + (CH_3)_3CCl \longrightarrow (CH_3)_3CCH_2CH_2Cl + (CH_3)_3C^+(AlBr_3Cl)^- \quad (4)$$

The *t*-butyl carbonium ion reacts with ethylene as shown in equation 2. The chain is terminated by the reaction of equation 3.

The exchange of halogen between alkyl halides in the presence of aluminum halides was confirmed experimentally by showing that *t*-butyl chloride and *t*-pentyl bromide are obtained in 36 and 50% yields, respectively, when a mixture of *t*-butyl bromide and *t*-pentyl chloride is treated with a catalytic amount of aluminum chloride at −30 to −25°. Similarly, the reaction of *t*-butyl chloride with *t*-pentyl bromide under the same conditions resulted in the formation of about 30% each of *t*-butyl bromide and *t*-pentyl chloride.

On the other hand, little or no halogen exchange occurred when *t*-butyl bromide was treated with 1-chloro-3,3-dimethylbutane and aluminum chloride at temperatures ranging from −45 to 0°. Also, there was little reaction between *t*-butyl chloride and 1-bromo-3,3-dimethylbutane in the presence of aluminum bromide at −20 to −10°. These results might at first thought seem to be proof that the exchange reaction expressed by equation 4 does not occur. Actually, however, they furnish evidence in support of the equation by showing that it is substantially irreversible. The *t*-butyl halides form complexes when treated with aluminum halides much more rapidly than do the 1-halo-3,3-dimethylbutanes. The resulting *t*-butyl carbonium ions do not abstract halogen held by primary carbon atoms, a principle which finds analogy in the observation that the aluminum chloride-catalyzed exchange of halogen for hydrogen between alkyl halides and alkanes takes place in appreciable yield only with alkanes containing a tertiary carbon atom, presumably because alkyl carbonium ions do not readily abstract hydrogen held by primary and secondary carbon atoms.[3] However, a chain reaction seems to be involved to only a minor extent in this hydrogen–halogen exchange; the interaction of *t*-butyl chloride with excess isopentane in the presence of an equimolecular amount of aluminum bromide yielded *t*-pentyl bromide (as well as some 2-bromo-3-methylbutane) and only a small amount of *t*-pentyl chloride.

$$(CH_3)_3C^+(AlBr_3Cl)^- + CH_3CH_2(CH_3)_2CH \rightleftarrows (CH_3)_3CH + CH_3CH_2(CH_3)_2C^+(AlBr_3Cl)^- \quad (5)$$

$$CH_3CH_2(CH_3)_2C^+(AlBr_3Cl)^- \longrightarrow CH_3CH_2(CH_3)_2CBr + AlBr_2Cl \quad (6)$$

$$CH_3CH_2(CH_3)_2C^+(AlBr_3Cl)^- + (CH_3)_3CX \longrightarrow CH_3CH_2(CH_3)_2CX + (CH_3)_3C^+(AlBr_3Cl)^- \quad (7)$$

$$(X = Cl \text{ or } Br)$$

The reaction of equation 6 apparently predominates over the chain-carrying reaction indicated by equation 7. On the other hand, the difference may be due to the experimental conditions. The hydrogen–halogen exchange reactions were carried out at room temperature and the aluminum bromide was in solution in the isopentane. Hence, the reaction of equation 1 was the most rapid reaction and only a small amount of the *t*-butyl halide was available for reaction 7; furthermore, if *t*-pentyl chloride did form, most of it was rapidly converted to *t*-pentyl bromide by reaction with the catalyst. The reaction temperatures in the condensation and the halogen–halogen exchange experiments described in the present paper were, respectively, −50 to −40° and −30 to −25° and the catalyst was present chiefly in the undissolved state.

Experimental

Condensation of *t*-Butyl Chloride with Ethylene in the Presence of Aluminum Bromide.—Ethylene was bubbled through a stirred mixture of 95 g. (1.03 moles) of *t*-butyl chloride, 89 g. (0.33 mole) of aluminum bromide and 125 g. of *n*-pentane at −40 to −50° until absorption was very slow (1.5 hours). The increase in weight of the mixture, 38 g., corresponded to 1.3 moles of reacted and dissolved ethylene. The water-white upper layer was decanted from the bright yellow, pasty catalyst layer, washed with water (additional pentane being added to facilitate handling), dried and distilled. There was obtained 39.5 g. (0.33 mole) of 1-chloro-3,3-dimethylbutane, b.p. 61–63° at 117 mm. (117–119° at 760 mm.), $n^{20}D$ 1.4180; and 25.0 g. (0.15 mole) of 1-bromo-3,3-dimethylbutane, b.p. 54–57° at 42 mm. (137–140° at 760 mm.), $n^{20}D$ 1.4446.

Condensation of *t*-Butyl Bromide with Ethylene in the Presence of Aluminum Chloride.—Ethylene was bubbled through a well-stirred mixture of 140 g. (1.02 moles) of *t*-butyl bromide, 50 g. of *n*-pentane and 45 g. (0.34 mole) of aluminum chloride at −40 to −50°. Rapid absorption took place during the first one-half hour. Thereafter it became quite slow, little or no absorption occurring at the end of one hour. The flask content gained 34 g., corresponding to 1.2 moles of ethylene. The liquid product (205 g.) was decanted from the 64 g. of the yellow, granular catalyst layer, washed with water, dried and distilled. Fractionation and refractionation of the product yielded 16 g. (0.13 mole) of 1-chloro-3,3-dimethylbutane, boiling chiefly at 52–53° at 70 mm. (117–118° at 760 mm.), $n^{20}D$ 1.4189. There was also obtained 99 g. (0.59 mole) of 1-bromo-3,3-dimethylbutane, the major portion of which boiled at 65–66° at 68 mm. (137 to 138° at 760 mm.), $n^{20}D$ 1.4444.

The identity of the 1-chloro-3,3-dimethylbutane was confirmed by comparison of its infrared spectrum with that of a sample prepared by the condensation of *t*-butyl chloride with ethylene in the presence of aluminum chloride.

Halogen Exchange between *t*-Butyl and *t*-Pentyl Halides.—A solution of 69 g. (0.5 mole) of *t*-butyl bromide and 53 g. (0.5 mole) of *t*-pentyl chloride was added during 90 minutes to a stirred mixture of 61 g. of *n*-pentane and 5.0 g. of aluminum chloride at −25 to −30°. Stirring was continued for one hour after all of the halide solution had been added, the mixture was then cooled to −40°, and the liquid product was decanted from the 6 g. of solid catalyst, washed, dried, and distilled through an efficient fractionating column.

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[3] P. D. Bartlett, F. E. Condon and A. Schneider, THIS JOURNAL, **66**, 1534 (1944).

The distillation data and the infrared spectra of the fractions indicated that the product consisted of 16.5 g. (0.18 mole) of *t*-butyl chloride, 23 g. (0.17 mole) of *t*-butyl bromide, 19 g. (0.18 mole) of *t*-pentyl chloride and 37.5 g. (0.25 mole) of *t*-pentyl bromide.

Under similar conditions, the reaction of 0.33 mole each of *t*-butyl chloride and *t*-pentyl bromide resulted in the formation of 0.11 mole of *t*-butyl bromide and 0.10 mole of *t*-pentyl chloride.

Attempted Halogen Exchange between *t*-Butyl Halides and 1-Halo-3,3-dimethylbutanes.—Very little reaction occurred when 68 g. (0.5 mole) of *t*-butyl bromide was added during 40 minutes to a stirred mixture of 3.0 g. of aluminum chloride and 60 g. (0.5 mole) of 1-chloro-3,3-dimethylbutane dissolved in 62 g. of *n*-pentane at −45 to −40° or at −5 to 0°. Attempts to cause the halogen exchange by carrying out the reaction in the presence of larger quantities of aluminum chloride (22 g.) at −45 to −40° or at −20 to −10° were also unsuccessful. The catalyst was converted to red-brown sludge (32 and 70 g., respectively); distillation of the washed upper layer in each case yielded only the unreacted alkyl halides.

Similarly, no 1-chloro-3,3-dimethylbutane was isolated from the product obtained by the addition of 0.2 mole of *t*-butyl chloride to 0.2 mole of 1-bromo-3,3-dimethylbutane and 5.0 g. of aluminum bromide in 60 g. of *n*-pentane at −20 to −10°.

RIVERSIDE, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Chlorination of Dimethyl Sulfide and Some of Its Derivatives with Sulfuryl Chloride and Thionyl Chloride[1]

BY WILLIAM E. TRUCE, G. H. BIRUM AND E. T. MCBEE

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Sulfuryl chloride and thionyl chloride have been found to be new chlorinating agents for alkyl sulfides. All nine of the possible chlorinated dimethyl sulfides have been prepared by chlorination of dimethyl sulfide and trithiane with sulfuryl chloride. Thionyl chloride is a less vigorous chlorinating agent than sulfuryl chloride, but it affords good yields of mono-, di- and trichlorodimethyl sulfides from dimethyl sulfide, and almost a quantitative yield of α,α'-dichlorodimethyl sulfide from trithiane. In the chlorination of dimethyl sulfide, it has been found that all three hydrogens of one carbon atom are replaced by chlorine before the second methyl group is chlorinated. Thionyl chloride has been used to introduce one, two and three chlorine atoms on the methyl group of *t*-butyl methyl sulfide. Evidence is provided to support an ionic mechanism for the chlorination of sulfides. Chromic anhydride has been employed for the oxidation of α-chlorosulfides, and all nine of the chlorodimethyl sulfones have been thus prepared. The chlorine in several of the chlorodimethyl sulfides, having three chlorine atoms on at least one carbon atom, has been replaced by fluorine. The sulfones of some of these fluorodimethyl sulfides have been prepared.

The present investigation has been principally concerned with the chlorination of dimethyl sulfide and its chloro-derivatives with sulfuryl chloride and thionyl chloride, two new chlorinating agents for organic sulfides.[2a] A few of the chlorodimethyl sulfides have been prepared previously by chlorination of dimethyl sulfide with chlorine. Riche[2b] was the first to report that dimethyl sulfide can be chlorinated with chlorine, but he gave no structures or physical properties for his products except a boiling point for a substance that analyzed for hexachlorodimethyl sulfide. James[2c] suggested that this boiling point was much too low for hexachlorodimethyl sulfide and that the product was probably perchloromethyl mercaptan; this suggestion has been confirmed by the present work. Feichtinger and Moos[3] reported that the same tetrachlorodimethyl sulfide was obtained by the reaction of chlorine with dimethyl sulfide as was obtained by the reaction of α,α'-dichlorodimethyl sulfide with chlorine, but they gave no structure for their product. Because of the nature of the decomposition products when tetrachlorodimethyl sulfide was chlorinated further, they believed that penta- and hexachlorodimethyl sulfide were formed, but they were unable to isolate these postulated more highly chlorinated sulfides. Bohme[4] prepared monochlorodimethyl sulfide from paraformaldehyde, methyl mercaptan, and hydrogen chloride, and, also, by the reaction of chlorine with dimethyl sulfide in carbon tetrachloride at −20°. He gave no yield by the latter method. α,α'-Dichlorodimethyl sulfide has been prepared by chlorination of trithiane with sulfur monochloride[5] and sulfur dichloride.[6]

The only chlorodimethyl sulfides that had been definitely isolated, identified, and characterized previous to the present work were monochlorodimethyl sulfide and α,α'-dichlorodimethyl sulfide. Nothing has been known of the order of replacement of the remaining hydrogen atoms upon further chlorination. This lack of knowledge of the chlorination of dimethyl sulfide has, no doubt, been due in large part to the difficulty of controlling the reaction with chlorine. The present investigation of the chlorination of dimethyl sulfide has been greatly facilitated by the use of sulfuryl chloride and thionyl chloride as the chlorinating agents. By the reaction of sulfuryl chloride with dimethyl sulfide and trithiane, all of the nine possible chlorodimethyl sulfides have been prepared. The identification of many of the products has been greatly aided by finding that chromic anhydride in glacial acetic acid is a convenient reagent for oxidizing α-chlorosulfides to sulfones.

Chlorination of Dimethyl Sulfide with Sulfuryl Chloride.—Sulfuryl chloride reacts vigorously with dimethyl sulfide according to the equation

$$CH_3SCH_3 + SO_2Cl_2 \longrightarrow CH_2ClSCH_3 + HCl + SO_2$$

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[1] Taken from G. H. Birum's Ph.D. thesis. Presented at the Milwaukee Meeting of the American Chemical Society, April 2, 1952.

[2] (a) F. G. Bordwell and co-workers recently observed analogous results (private communication). (b) M. A. Riche, *Ann. chim. phys.*, [iii] **43**, 283 (1855). (c) J. W. James, *J. Chem. Soc.*, **51**, 273 (1887).

[3] H. Feichtinger and J. Moos, *Ber.*, **81**, 371 (1948).

[4] H. Bohme, H. Fischer and R. Frank, *Ann.*, **563**, 54 (1949).

[5] I. Bloch and F. Hohn, *Ber.*, **55B**, 53 (1922).

[6] F. G. Mann and W. J. Pope, *J. Chem. Soc.*, **123**, 1172 (1923).