[Contribution from the George Herbert Jones Laboratory, University of Chicago]

# REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XV. THE ADDITIONS OF BROMODICHLOROMETHANE AND DIBROMODICHLOROMETHANE TO OLEFINS. THE PREPARATION OF 2-ALKENALS

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Further investigation of the peroxide-induced and photochemical reactions of heterohalomethanes with olefins was suggested by previous studies of the additions of carbon tetrachloride, carbon tetrabromide, chloroform, bromoform, and bromotrichloromethane to olefins (1). The addition reactions of bromodichloromethane with olefins, and the stepwise reaction of one molecule of dibromodichloromethane with two molecules of olefin are described in this paper. The possibility that the organic halides so formed might be hydrolyzable to 2-alkenals and $\alpha,\alpha'$-dienones stimulated interest in these addition reactions.

*Reactions of bromodichloromethane with olefins.* Acetyl peroxide-induced reactions of bromodichloromethane with propylene, isobutylene, and octene yielded the expected one-to-one molecular addition products, which were identified (as described in the experimental part) as 1,1-dichloro-3-bromoalkanes. The similar reaction with vinyl acetate yielded 1-bromo-3,3-dichloropropyl acetate.

With regard to ease of initiation, product yields, the nature of products formed, the reactions of bromodichloromethane resemble those of bromoform rather than those of chloroform. On the basis of product identification, and by analogy with the reaction mechanisms proposed for reactions previously studied, the following reaction chain is suggested for the bromodichloromethane addition reactions.

$$\text{(I)}\quad CHCl_2Br + \cdot CH_3 \rightarrow CH_3Br + HCl_2C\cdot$$

$$\text{(II)}\quad HCl_2C\cdot + RCH{=}CH_2 \rightarrow \cdot CHRCH_2CHCl_2$$

$$\text{(III)}\quad CHCl_2Br + \cdot CHRCH_2CHCl_2 \rightarrow BrCHRCH_2CHCl_2 + HCl_2C\cdot$$

Together, the reactions of chloroform, bromoform, and bromodichloromethane establish the following order of reactivity toward free radicals: Br > H > Cl.

*Reactions of dibromodichloromethane with olefins.* Acetyl peroxide-induced reactions of dibromodichloromethane with propylene, isobutylene, and 1-octene also yielded one-to-one molecular addition products. With regard to ease of initiation and product yields, these reactions resemble those of carbon tetrabromide and bromotrichloromethane rather than those of carbon tetrachloride. On this basis the following reaction scheme is proposed, and product structures are assigned accordingly.

$$\text{(Ia)}\quad Cl_2CBr_2 + \cdot CH_3 \rightarrow CH_3Br + BrCl_2C\cdot$$

$$\text{(IIa)}\quad BrCl_2C\cdot + RCH{=}CH_2 \rightarrow \cdot CHRCH_2CBrCl_2$$

$$\text{(IIIa)}\quad Cl_2CBr_2 + \cdot CHRCH_2CBrCl_2 \rightarrow BrCHRCH_2CBrCl_2 + BrCl_2C\cdot$$

The addition products of dibromodichloromethane with propylene and isobutylene were induced to undergo similar addition reactions with the respective olefins. It is believed that the principal products obtained have the structures suggested by the following reaction scheme.

(Ib) $RCHBrCH_2CCl_2Br + \cdot CH_3 \rightarrow CH_3Br + \cdot CCl_2CH_2CHBrR$

(IIb) $\cdot CCl_2CH_2CHBrR + RCH{=}CH_2 \rightarrow \cdot CHRCH_2CCl_2CH_2CHBrR$

(IIIb) $RCHBrCH_2CCl_2Br + \cdot CHRCH_2CCl_2CH_2CHBrR \rightarrow \cdot CCl_2CH_2CHBrR + BrCHRCH_2CCl_2CH_2CHBrR$

The difficulty in definitely identifying these products by the usual methods arises from the multiplicity of products obtained in the sodium ethoxide reactions. Even in the cases of the bromodichloromethane addition products, which yield chiefly the 2-alkenals, there are also low-boiling halogenated by-products, indicating side-reactions of the type:

$RCHBrCH_2CHCl_2 \rightarrow RCH{=}CHCHCl_2 \rightarrow RCH{=}C{=}CHCl$ and/or $R'CH{=}CH{-}CH{=}CHCl$

With the addition products (one molecule of dibromodichloromethane to two molecules of the olefin) such side reactions predominate over the desired reactions which would lead to diethyl ketals of disubstituted divinyl ketones.

## EXPERIMENTAL PART[1]

*The preparation of bromodichloromethane.* Bromodichloromethane was prepared in the counterdistillation apparatus shown in Figure 1.[2] In a typical experiment, a solution containing bromoform (532 gr.; 2.1 moles), chloroform (800 gr.; 6.7 moles) and aluminum chloride (10 g.) was placed in flask *A*. It was heated to reflux for 30 minutes, and then stopcock *B* was opened to allow the distillate from the reaction mixture to flow through trap *C* which contained Florosil to remove traces of aluminum chloride. Finally, this distillate drained into flask *D*.

Distillation was continued until the temperature in the still-head above flask *A* reached 72–74°. At this time, flask *D* was heated to start distillation through fractionating column *E* (packed with single-turn glass helices). Pure chloroform was taken off at the top of the column, and returned through stopcock *F* and a connecting tube *G* to flask *A*. Stopcock *F* was adjusted so that the return of chloroform maintained a temperature of 72–74° above flask *A*.

After operating in this way for 40 hours, the volume of the reaction mixture (flask *A*) decreased to about 100 ml. Chloroform from the fractionating column was then drained

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[1] The term Ag equiv. is defined as the number of grams of the halogen-containing compound which react with one mole of silver nitrate, in accordance with the reaction:

$$Ag^+ + X^- \rightarrow AgX$$

[2] This apparatus has been applied to the preparation of bromotrichloromethane in 90% yield by a similar method. It is also applicable to ester-exchange reactions (as in the conversion of ethyl to methyl esters), and to the Meerwein oxidation of high-boiling alcohols with the aid of acetone and aluminum *t*-butoxide.

rapidly into flask *A* until a volume of 500 ml. was reached. Counter-distillation was continued for another 8 hours. During this time, the distilling temperature above flask *A* dropped to 63°.

The solution in flask *D* was then distilled without further treatment. After unreacted chloroform had distilled, bromodichloromethane (b.p. 88°; $n_D^{20}$ 1.4962; 903 g.; 87% yield) was obtained. The remaining solution was then distilled at reduced pressure. Dibromochloromethane (b.p. 62° at 120 mm.; $n_D^{20}$ 1.5469; 70 g.; 11% yield) distilled next. A residue (15 g.) remained in the distilling flask.

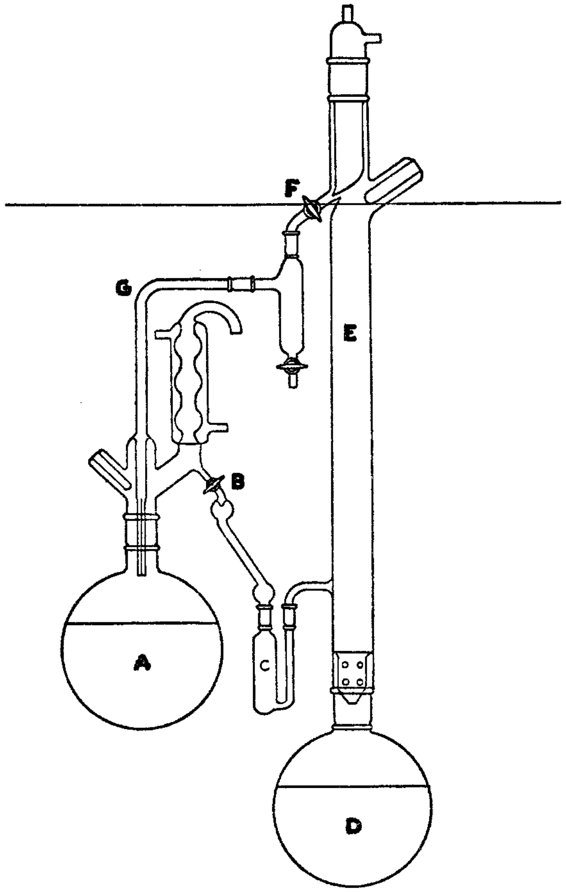

FIGURE 1

*Reaction of bromodichloromethane with 1-octene in the presence of acetyl peroxide.* A solution of bromodichloromethane (417.0 g.; 2.54 moles; $n_D^{20}$ 1.4962) and 1-octene (56 g.; 0.5 mole; $n_D^{20}$ 1.4090) held at 90° for 4 hours was treated with acetyl peroxide (5.4 g.; 0.046 mole) in two equal portions. After unchanged bromodichloromethane had been distilled, a product shown to be 1,1-dichloro-3-bromononane (110.1 g.; b.p. 65° at 0.03 mm.; $n_D^{20}$ 1.4842) was recovered.

*Anal.* Calc'd for $C_9H_{17}BrCl_2$: Ag equiv., 92.0. Found: Ag equiv., 92.3.

A residue (17.5 g.) remained in the still pot.

*Identification of the bromodichloromethane-1-octene addition product (1,1-dichloro-3-*

*bromononane).* The bromodichloromethane-1-octene addition product (96.0 g.; 0.35 mole) was dropped into a sodium ethoxide solution (prepared by the reaction of 46 g. of sodium with 400 ml. of absolute ethanol) containing potassium iodide (5 g.). An exothermic reaction occurred, and a white solid separated. The reaction mixture was held at its reflux temperature for 10 hours.

After it had cooled, the white precipitate (81.g.; expected sodium salts, 93 g.) was separated on a filter. Ethanol was then removed by distillation through a 12-plate column until the volume of undistilled material was about 125 ml. Ligroin (b. 35°; 300 ml.) was added, and the resulting solution was washed with water. It was vigorously stirred with hydrochloric acid (3%) for 2 hours, and was then separated, washed with water, and dried over sodium sulfate.

After the ligroin had been removed by distillation, the reaction product was distilled through a 35-plate Podbielniak column. Fractions distilling first (b.p. 30–45° at 0.4 mm.; 12. g.) were unsaturated products containing halogen. The principal reaction product (b.p. 54–56° at 0.2 mm.; 34.1 g.; $n_D^{20}$ 1.4501) then distilled. These physical constants correspond to those given in the literature for 2-nonenal.

Further confirmation for this identification was obtained by the preparation of the 2,4-dinitrophenylhydrazone (m.p. 124–25°; melting point of mixture with authentic 2,4-dinitrophenylhydrazone of 2-nonenal, 124–25°) and its *p*-nitrophenylhydrazone (m.p. 107–108°; melting point of mixture with authentic *p*-nitrophenylhydrazone of 2-nonenal, 107°). 2-Nonenal for this comparison was prepared according to the method of Scanlan and Swern (2).

*Reaction of bromodichloromethane with vinyl acetate in the presence of acetyl peroxide.* To a solution of vinyl acetate (50. g.; 0.58 mole; b.p. 72°; $n_D^{28}$ 1.3951) in bromodichloromethane (375 g.; 2.29 moles) held at 65°, a solution of acetyl peroxide (2.5 g.) in bromodichloromethane (30 g.) was added slowly over a period of 4 hours. Following completion of the addition, the reaction mixture was heated for another 2 hours.

A mixture of unchanged vinyl acetate and bromodichloromethane (b.p. 40–48° at 100 mm.; 350 g.) was recovered by distillation through a 10-inch Vigreux column. Further distillation at lower pressures yielded a colorless liquid product (60 g.; b.p. 58–9° at 0.2 mm.; $n_D^{20}$ 1.4785). This product gave a halogen analysis consistent with that expected for the bromodichloromethane-vinyl acetate addition product, 1-bromo-3,3-dichloropropyl acetate.

*Anal.* Calc'd for $C_5H_7BrCl_2O_2$: Ag equiv., 83.3. Found: Ag equiv., 82.9.

A residue (16.5 g.) remained in the distilling flask.

*Identification of the bromodichloromethane-vinyl acetate addition product (1-bromo-3,3-dichloropropyl acetate).* A portion (1 g.) of the bromodichloromethane-vinyl acetate addition product was treated with a solution of 2,4-dinitrophenylhydrazine (1.5 g.) and concentrated hydrochloric acid (2 ml.) in ethanol (95%; 30 ml.). The orange needles that separated melted at 162° after three recrystallizations from ethanol. This substance gave the halogen analysis expected for the 2,4-dinitrophenylhydrazone of β,β-dichloropropionaldehyde.

*Anal.* Calc'd for $C_9H_8Cl_2N_4O_4$: Cl, 23.1. Found: Cl, 22.9.

Attempts to prepare β,β-dichloropropionaldehyde by the hydrolysis of this addition product failed, presumably because of its instability. Hydrolysis at room temperature with dilute sulfuric acid (5%) yielded only polymeric products. A similar result was obtained upon hydrolysis with dilute sodium bicarbonate solution. Accordingly, an attempt was made to hydrolyze, and then oxidize the resulting aldehyde to more stable products using a suspension of silver oxide in water.

A mixture containing the bromodichloromethane-vinyl acetate addition product (23 g.), silver oxide (62 g.) and water (150 g.) was shaken in a brown bottle for 6 hours at room temperature.

The mixture was filtered, and the filtrate was extracted several times with ether. The ether solution was dried over sodium sulfate and distilled, distillation yielding a high-boiling, tarry product (7.6 g.).

The filtrate and the precipitate were recombined, and the resulting mixture was saturated with potassium carbonate. After standing overnight, the precipitate was removed, and the filtrate was acidified with hydrochloric acid. It was then extracted several times with ether, and the ether solution was dried over sodium sulfate.

The ether left a dark, viscous residue (4 g.). White needle-like crystals (0.2 g.) sublimed from this residue when it was warmed under high vacuum. This substance melted at 78-79°. The melting point given in the literature for β-chloroacrylic acid is 80°.

*Reaction of isobutylene with bromodichloromethane in the presence of acetyl peroxide.* A solution of acetyl peroxide (2.3 g.) in bromodichloromethane (100 g.) was placed in the stainless steel bomb of a Parr hydrogenation apparatus. The apparatus was thoroughly swept with isobutylene, and the bomb and its contents were brought under a gauge pressure of 35 pounds of isobutylene. By means of an electrical heating jacket, the temperature of the reaction mixture was brought to 60°. The pressure of isobutylene was maintained at 35 pounds, and this temperature was held for 8 hours.

Unchanged bromodichloromethane (55 g.; b.p. 88°) was removed by distillation. The residual reaction product was distilled at reduced pressure. A colorless oil (b.p. 71-73° at 12 mm.; 34.6 g.; $n_D^{20}$ 1.4950), which gave the halogen analysis expected for the bromodichloromethane-isobutylene addition product, was obtained.

*Anal.* Calc'd for $C_5H_9BrCl_2$: Ag equiv., 73.3. Found: Ag equiv., 72.0.

A tarry residue (5 g.) remained in the distilling flask.

*Identification of the bromodichloromethane-isobutylene addition product (1,1-dichloro-3-methyl-3-bromobutane).* A portion (14 g.) of the bromodichloromethane-isobutylene addition product was dropped slowly into a sodium ethoxide solution prepared by dissolving sodium (9 g.) in absolute ethanol (200 ml.). The reaction mixture warmed, and a white precipitate appeared. The reaction mixture was heated under reflux for 12 hours. After it cooled, the precipitated salts (9.5 g.; 12.1 g. expected) were separated and the filtrate was distilled under reduced pressure (100 mm.) to remove ethyl alcohol. When the volume of the mixture in the distilling flask reached 50 ml., ligroin (b. 35°; 150 ml.) was added. The ligroin solution was washed with water, dilute hydrochloric acid, and again with water, and was dried over sodium sulfate.

After the ligroin had been removed by distillation, an oily product remained. It distilled from 50° to 70° at 50 mm. (6 g.; $n_D^{20}$ 1.4446). This oil was shown to contain β,β-dimethylacrolein by conversion to its dark red 2,4-dinitrophenylhydrazone (m.p. 178.5-179°; melting point of mixture with authentic 2,4-dinitrophenylhydrazone of β,β-dimethylacrolein, 178.5-179°).

β,β-dimethylacrolein used for comparison was prepared by the method of Fischer, Ertel, and Loewenberg (3).

*Reaction of bromodichloromethane with propylene in the presence of acetyl peroxide.* A solution of acetyl peroxide (2.2 g.) in bromodichloromethane (167.4 g.; 1.02 mole) was treated with propylene in a Parr bomb apparatus in a manner similar to that described for the isobutylene reaction. A pressure of 45 pounds and a reaction temperature of 60° were maintained for 10 hours.

The reaction mixture was distilled through a 10-inch Vigreux column. After unchanged bromodichloromethane (b.p. 25-28° at 30 mm.; 114. g.) had been removed, a colorless oil (34.3 g.; b.p. 75-76° at 30 mm.; $n_D^{20}$ 1.4912), which gave a halogen analysis consistent with 1,1-dichloro-3-bromobutane, distilled.

*Anal.* Calc'd for $C_4H_7BrCl_2$: Ag equiv., 68.6. Found: Ag equiv., 68.5.

A residue (11.3 g.) remained in the distilling flask.

*Identification of the bromodichloromethane-propylene addition product (1,1-dichloro-3-bromobutane).* A portion (30 g.) of the bromodichloromethane-propylene addition product was dropped into a solution of the sodium salts of ethylene glycol prepared by the reaction of 19 g. of sodium with 250 g. of ethylene glycol held at 90-100°, and the resulting reaction mixture was held at 110° for 5 hours. After cooling, the mixture was acidified with dilute hydrochloric acid (5%), and the resulting solution was distilled under vacuum (110 mm.). An aqueous solution (73 ml.), smelling strongly of an aldehyde, was obtained. An aliquot portion (5 ml.) of this solution was treated with an excess of 2,4-dinitrophenylhydrazine. A crimson precipitate (0.4523 g.; yield, 28%) was obtained. This material was shown to be the 2,4-dinitrophenylhydrazone of crotonaldehyde (m.p. 189° after three recrystallizations from a benzene-ligroin solution; melting point of mixture with an authentic sample, 189°).

*Reaction of dibromodichloromethane with propylene in the presence of acetyl peroxide.* A solution of acetyl peroxide (2 g.) in dibromodichloromethane (203.4 g.; b.p. 68° at 88 mm.; $n_D^{20}$ 1.5509) was placed in the bomb of the Parr hydrogenation apparatus. After the apparatus was thoroughly swept with propylene, a pressure of 30 pounds of propylene was maintained, and the reaction mixture was held at 80° for 4 hours.

The reaction mixture (wt. after reaction, 232 g.) was distilled at reduced pressure. Unchanged dibromodichloromethane (16 g.; b.p. 68° at 88 mm.) distilled first. The reaction product (b.p. 36° at 0.05 mm.; 214.7 g.; $n_D^{20}$ 1.5369) was a colorless oil which gave the correct halogen analysis and molecular weight for the dibromodichloromethane-propylene addition product (1,1-dichloro-1,3-dibromobutane).

*Anal.* Calc'd for $C_4H_6Br_2Cl_2$: Ag equiv., 69.7; mol. wt., 279.
Found: Ag equiv., 69.2; mol. wt., 275.

A residue (10 g.) remained.

This substance was also prepared by photochemically-induced additon. Dibromodichloromethane (300 g.) was placed in a tube illuminated internally with a mercury-vapor discharge tube. Propylene was slowly passed into the solution while heat from the light maintained the reaction mixture at 50°. These conditions were maintained for 60 hours. 1,1-Dichloro-1,3-dibromobutane (145.5 g.) was obtained by distillation.

*Reaction of 1,1-dichloro-1,3-dibromobutane with propylene in the presence of acetyl peroxide.* In 1,1-dichloro-1,3-dibromobutane (120.0 g.) prepared in the previous reaction, acetyl peroxide (2 g.) was dissolved, and the solution was placed in the steel bomb of the Parr apparatus. The reaction mixture was held at 80° for 10 hours under a 40-pound pressure of propylene.

The reaction mixture was distilled without further treatment under high vacuum. Unchanged 1,1-dichloro-1,3-dibromobutane (53.5 g.; b.p. 36–49° at 0.5 mm.) was removed. A colorless oil (b.p. 75–78° at 0.5 mm.; 58.5 g.; $n_D^{20}$ 1.5282) then distilled. It gave the halogen analysis and molecular weight expected for 2,6-dibromo-4,4-dichloroheptane.

*Anal.* Calc'd for $C_7H_{12}Br_2Cl_2$: Ag equiv., 81.7; mol. wt., 326.
Found: Ag equiv., 81.3; mol. wt., 321.

A residue (7 g. ) remained in the distilling flask.

*Reaction of 1,1-dichloro-1,3-dibromobutane with 1-octene in the presence of acetyl peroxide.* A solution of acetyl peroxide (2 g.) in 1,1-dichloro-1,3-dibromobutane (285 g.; 0.69 mole) and 1-octene (20.0 g.; 0.18 mole) was held at 70° for 10 hours, and then at 100° for 3 hours.

The reaction mixture was then distilled. About 6.0 g. of 1-octene (b.p. 32–40° at 43 mm.) was recovered. Unchanged 1,1-dichloro-1,3-dibromobutane (206. g.; 0.52 mole; b.p. 62–67° at 1 mm.) distilled next. The residual reaction product (44.1 g.; 62% yield) had too high a boiling point to permit of distillation at 0.1 mm. through the Vigreux column. Accordingly, it was distilled in a molecular still at a pressure of $10^{-5}$ mm. Hg. A colorless oil (41.2 g.; $n_D^{20}$ 1.5120), which gave a halogen analysis and a molecular weight consistent with 2,6-dibromo-4,4-dichlorododecane, was obtained.

*Anal.* Calc'd for $C_{12}H_{22}Br_2Cl_2$: Ag equiv., 99.3; mol. wt., 397.
Found: Ag equiv., 99.5; mol. wt., 396.

*Reaction of dibromodichloromethane with isobutylene in the presence of acetyl peroxide.* A solution of acetyl peroxide (2.8 g.) in dibromodichloromethane (143. g.) was placed in the steel bomb of the Parr apparatus. A small amount of isobutylene introduced into the bomb dissolved completely. The bomb and its contents were slowly warmed to 50°, and pressure in the bomb increased from 0 to 18 pounds. At this point, the pressure rose suddenly to 45 pounds and then dropped to 0. At the same time, the reaction mixture increased in temperature to 90°. The bomb heater was turned off, and the temperature of the reaction mixture was maintained at 70° by the slow introduction of isobutylene. Finally, it was necessary to turn on the bomb heater to hold the reaction temperature at 70°, and a pressure of 20 pounds of isobutylene was maintained for two hours.

The reaction mixture was distilled through a 10-inch Vigreux column. Unchanged dibromodichloromethane (15 g.; b.p. 65° at 80 mm.) was recovered. Then a colorless oil (143 g., b.p. 53° at 0.3 mm.; $n_D^{20}$ 1.5385), which gave a halogen analysis consistent with 1,1-dichloro-1,3-dibromo-3-methylbutane, distilled.

*Anal.* Calc'd for $C_5H_8Br_2Cl_2$: Ag equiv., 74.7. Found: Ag equiv., 74.5.

A residue (9 g.) remained in the distilling flask.

*Reaction of 1,1-dichloro-1,3-dibromo-3-methylbutane with isobutylene in the presence of acetyl peroxide.* A solution of acetyl peroxide (3.6 g.) in 1,1-dichloro-1,3-dibromo-3-methylbutane (110 g.) was placed in the steel bomb of the Parr apparatus. The temperature of the reaction mixture was held at 65°, and the isobutylene pressure was maintained at 23 pounds for 12 hours.

The reaction mixture was distilled through a 10-inch Vigreux column. Unchanged 1,1-dichloro-1,3-dibromo-3-methylbutane (b.p. 50–53° at 0.3 mm.; 95 g.) distilled first. Since on further distillation, decomposition of the residue (30 g.) occurred, it was distilled in a Hickman molecular still. A colorless oil (22 g.; $n_D^{20}$ 1.5342), which gave a halogen analysis corresponding to 2,6-dibromo-2,6-dimethyl-4,4-dichloroheptane, was obtained.

*Anal.* Calc'd for $C_9H_{16}Br_2Cl_2$: Ag equiv., 88.7. Found: Ag. equiv., 88.5.

A residue (7 g.) remained in the still.

*Attempts to identify the 1,1-dichloro-1,3-dibromo-3-methylbutane-isobutylene addition product.* A solution containing this addition product (38. g.; 0.107 mole) in 95% ethanol (100 ml.) was placed in a 500-ml. round-bottomed flask fitted with a Tru-Bore stirrer. The flask was immersed in an ice-water bath, and the solution was vigorously stirred. Ethanolic potassium hydroxide solution (236 ml.; 0.904 *N*; 0.2133 mole KOH) was slowly dropped in over a period of 1 hour. A white precipitate formed. After the addition was completed the reaction mixture was allowed to stand at room temperature for 16 hours.

Water (300 ml.) was then added to the reaction mixture, and the resulting mixture was extracted 5 times with 200-ml. portions of ligroin (b. 60°). The ligroin solution was then washed three times with water, and was dried over sodium sulfate.

An aliquot portion of the combined wash liquors was analyzed for halogen content. It was found that 0.2133 equivalent of halide ion had been removed in the hydrolysis (theoretical amount based upon potassium hydroxide used, 0.2133 equivalent). Further analysis indicated that this solution contained 0.06012 equivalent of chloride ion, and 0.1533 equivalent of bromide ion.

Ligroin was removed by distillation through a 25-plate Podbielniak column. The remaining reaction product was then distilled through a 10-inch Vigreux column. Four fractions which boiled over a range from 55° to 110° at 24 mm. were obtained (combined wt., 14.5 g.). Fraction 3 (5.5 g.; $n_D^{20}$ 1.4821; b.p. 87–96° at 24 mm.) was analyzed for chlorine.

*Anal.* Calc'd for $C_9H_{14}Cl_2$: Cl, 36.8. Found: Cl, 34.3.

The apparent chlorine content obtained by analysis of a substance $C_9H_{14}BrCl$ would be 34.4.

## SUMMARY

1. In peroxide-induced reactions with 1-alkenes, bromodichloromethane closely resembles bromoform (rather than chloroform) in its behavior.

2. Based upon experimental evidences of structure, it is concluded that bromodichloromethane adds in good yield (50–80%) to 1-alkenes to give the following products: with 1-octene, 1,1-dichloro-3-bromononane; with propylene, 1,1-dichloro-3-bromobutane; with isobutylene, 1,1-dichloro-3-bromo-3-methylbutane; and with vinyl acetate, 1-bromo-3,3-dichloropropyl acetate.

3. Dibromodichloromethane reacts with propylene in the presence of acetyl

peroxide, or under illumination, to give 1,1-dichloro-1,3-dibromobutane. This product reacts with propylene under the same conditions to give 2,6-dibromo-4,4-dichloroheptane. It reacts with 1-octene to give 2,6-dibromo-4,4-dichlorododecane.

4. Free-radical chain mechanisms for these reactions are discussed.

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