Decomposition of Unpurified Optically Active 1-Butyl-1-*d* Chlorosulfite in Dioxane.—The chlorosulfite prepared as above from 11.9 g. (0.10 mole) of thionyl chloride and 4.0 g. (0.053 mole) of 1-butanol-1-*d* having $\alpha^{25}D$ −0.142 ± 0.004° (l 4)[1] was dissolved in 25 ml. of dioxane[14] and maintained at 84°. A marked evolution of sulfur dioxide began immediately. After heating for 20 hours the reaction was cooled to room temperature and distilled through a small glass spiral column, collecting 6.1 ml. of 1-butyl-1-*d* chloride, b.p. 78–90°. The distillate was mixed with 5 ml. of pentane and was washed with 4 ml. of water. The organic phase was dried with anhydrous sodium sulfate and distilled through a small column, collecting 3.0 ml. of 1-butyl-1-*d* chloride, b.p. 78–79°, having $\alpha^{25}D$ +0.140 ± 0.003° (l 2).

Decomposition of Distilled Optically Active 1-Butyl-1-*d* Chlorosulfite in Dioxane.—The chlorosulfite was prepared as above from 16.0 g. (0.133 mole) of freshly distilled thionyl chloride and 7.5 g. (0.10 mole) of 1-butanol-1-*d* having $\alpha^{25}D$ +0.145 ± 0.005° (l 4).[16] Distillation through a small Vigreux column gave 12.0 g. (77% yield) of optically active 1-butyl-1-*d* chlorosulfite, b.p. 65–71° (15 mm.).

This material was dissolved in 50 ml. of dioxane[14] and was maintained at 84° for 42 hours. The mixture was distilled through a small glass spiral column and 4.5 ml. of material was collected, b.p. 76–89°. Redistillation of this material through the same column gave 3.0 ml. of 1-butyl-1-*d* chloride, b.p. 77.5–78.5°, having $\alpha^{25}D$ −0.055 ± 0.004° (l 2).

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society.

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[16] This material was the product of a separate preparation to be described in a later paper.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON]

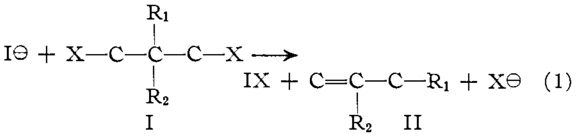
Base-induced Rearrangements. Action of Iodide Ion on Certain 1,3-Dihalides

BY W. M. SCHUBERT AND SIDNEY M. LEAHY, JR.[1]

RECEIVED AUGUST 24, 1956

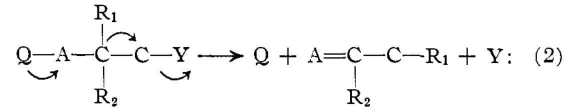
Eight 1,3-dihalides of type I were treated with sodium iodide in dimethylformamide or acetamide at temperatures ranging from 120 to 170°. Six of these dihalides showed the rearrangement–elimination reaction of equation 1, giving moderate yields of either the olefin II, or of an olefin readily obtained by isomerization of II. Both alkyl and hydrogen migration was accomplished, but phenyl migration was not. Qualitative evidence indicates that the rearrangement is "base-induced," with the primary force being an electron "push" on the carbon atom carrying the migrating group.

A study of the reaction, equation 1, of iodide ion with 1,3-dihalides of type I was undertaken to determine whether this reaction is an example of the general "base-induced" rearrangement, equation 2, in which the primary force for rearrangement is an electron push on the carbon atom carrying the migrating group.



$$I^{\ominus} + X-C-\underset{R_2}{\overset{R_1}{C}}-C-X \longrightarrow IX + C{=}\underset{R_2}{C}-C-R_1 + X^{\ominus} \quad (1)$$

I II

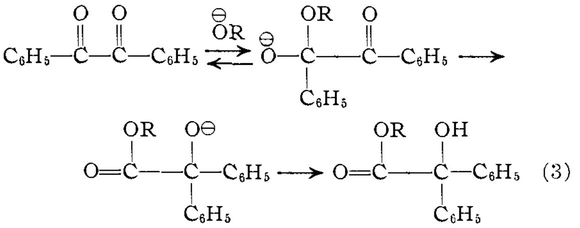


$$Q-A-\underset{R_2}{\overset{R_1}{C}}-C-Y \longrightarrow Q + A{=}\underset{R_2}{C}-C-R_1 + Y: \quad (2)$$

In the general equation 2, Q is an electron pair source, Y is a stable entity (*e.g.*, $Br^{\ominus}$, $:NR_3$) and A is carbon or a hetero atom. Our objective is to find examples of the "base-induced" rearrangement which lend themselves to detailed quantitative kinetic studies. A comparison could then be made between factors promoting the "base-induced" rearrangement and those promoting "acid-induced," Wagner-Meerwein type rearrangements, in which the primary force promoting rearrangement is an electron "pull" exerted from an electron deficient site adjacent to the carbon atom carrying the migrating group.

Possible examples of the "base-induced" rearrangement previously described include the benzilic acid rearrangement,[2–5] the Tiffeneau rearrangement of halomagnesium derivatives of halohydrins[6,7] and the reaction of zinc with 1,3-dihalides such as pentaerythrityl tetrabromide.[8–10]

The benzilic acid rearrangement recently has been found to involve general base participation,[2] equation 3, although previously hydroxide ion was considered to be the only effective base promoting the reaction.[3] In this reaction the electron source (Q of equation 2) is an electron pair on the negative oxygen. The relative degree to which the rearrangement is promoted by a "push" of this electron pair as compared to a "pull" by the carbonyl group[5] is uncertain. However, the rearrangement of a phenyl group is retarded by *p*-methyl and facilitated by *p*- or *m*-chlorine,[3,4] indicating perhaps a predominance of "push."



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 \underset{}{\overset{OR^{\ominus}}{\rightleftarrows}} {}^{\ominus}O-\underset{C_6H_5}{\overset{OR}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 \longrightarrow O{=}\overset{OR}{C}-\underset{C_6H_5}{\overset{O^{\ominus}}{C}}-C_6H_5 \longrightarrow O{=}\overset{OR}{C}-\underset{C_6H_5}{\overset{OH}{C}}-C_6H_5 \quad (3)$$

The Tiffeneau rearrangement may be at least partially base-induced. Geissman and Akawie have proposed a cyclic mechanism for this reaction, equation 4, and believe the rearrangement to be induced by an electrophilic attack of the MgX on the neighboring halogen atoms (*i.e.*, acid-induced).[7]

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[1] Du Pont Fellow, 1954–1955.

[2] W. E. Doering and R. Urban, THIS JOURNAL, **78**, 5938 (1956).

[3] M. T. Clark, E. C. Hendley and O. K. Neville, *ibid.*, **77**, 3280 (1955).

[4] D. G. Ott and G. G. Smith, *ibid.*, **77**, 2325 (1955).

[5] F. H. Westheimer, *ibid.*, **58**, 2209 (1936).

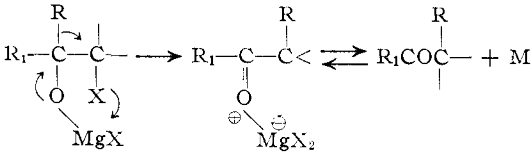
[6] M. Tiffeneau, *Bull. soc. chim.*, [5] **12**, 621 (1945).

[7] T. A. Geissman and R. I. Akawie, THIS JOURNAL, **73**, 1993 (1951).

[8] M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

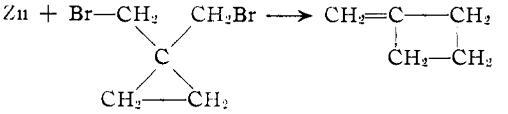
[9] W. Shand, V. Schomaker and J. R. Fischer, *ibid.*, **66**, 636 (1944).

[10] I. Shokor and N. Slobodin, *J. Gen. Chem. U.S.S.R.*, **21**, 2005 (1951).



(4)

When pentaerythrityl tetrabromide or 1,1-bis-(bromomethyl)-cyclopropane (III) is treated with zinc, the main product is methylenecyclobutane.[8-10] This product could conceivably have arisen by a base-induced rearrangement with the electron pair source being zinc metal, equation 5. However, the main force promoting this rearrangement may well be an electrophilic pull by zinc halide at the other halide atom of III. In this connection, Applequist and Roberts found III to be in equilibrium with 1-bromomethyl-1-bromocyclobutane in the presence of zinc bromide.[11]



III

(5)

If an elimination–rearrangement such as that of equation 5 could be brought about by iodide ion in place of zinc, *i.e.* equation 1, such a process would appear much more likely to be an example of a "base-induced" rearrangement. A number of such conversions have now been achieved by the action of sodium iodide on 1,3-dihalides in dimethylformamide or acetamide as the solvent. The conditions required are not mild, however, the temperatures used being 120° or higher.

The 1,3-dihalides used were the following: 1,1-bis-(bromomethyl)-cyclopropane (III), 1,1-bis-(bromomethyl)-cyclohexane, 1,3-dibromo-2,2-dimethylpropane, 1,3-dibromo-2-methylpropane, 1,3-dibromopropane, 1,1-bis-(iodomethyl)-cyclobutane, 1,1-bis-(bromomethyl)-cyclopentane and 1,3-dibromo-2-phenylpropane. The first four of these are known compounds and were prepared by known methods. The fifth is commercially available. The structures of the other dihalides was inferred from their method of preparation, carbon and hydrogen analyses, and their failure to give an iodine coloration when treated with sodium iodide in acetone.[11] All the dibromides except 1,1-bis-(bromomethyl)-cyclohexane and 1,3-dibromo-2,2-dimethylpropane readily gave a white precipitate of sodium bromide when treated with sodium iodide in acetone,[11] hence the elimination–rearrangement reactions with iodide ion may have proceeded *via* the iodobromides or the diiodides. All the dihalides reacted with alcoholic silver nitrate to give precipitates of silver halide.

The following results were obtained in the treatment of the dihalides with sodium iodide at elevated temperature. In dimethylformamide at 150°, 1,1-bis-(bromomethyl)-cyclopropane gave a 31% yield of hydrocarbon mixture. From the infrared spectrum it appeared to be a mixture of about equal parts of methylenecyclobutane and 1-methylcyclobutene. No spiropentane was detected. The presence of methylenecyclobutane was verified by its conversion to the known 1-(hydroxymethyl)-cyclobutanol. The 1-methylcyclobutene probably arose by isomerization of methylenecyclobutane. Under conditions simulating those used on the dihalide, pure methylenecyclobutane gave a hydrocarbon mixture that had an infrared spectrum identical to that of the product from the dihalide.

Treatment of 1,1-bis-(iodomethyl)-cyclobutane with sodium iodide in molten acetamide at 150° gave a 52% yield of methylenecyclopentane, identical in physical properties and infrared spectrum with an authentic sample.[12] In refluxing dimethylformamide, 1,1-bis-(bromomethyl)-cyclopentane and sodium iodide gave a 37% yield of 1-methylcyclohexene, identical with an authentic sample.[13] The 1-methylcyclohexene probably arose by isomerization of first formed methylenecyclohexane. Thus, under conditions simulating the elimination–rearrangement reaction, methylenecyclohexane was practically completely converted to 1-methylcyclohexene.

When 1,1-bis-(bromomethyl)-cyclohexane was heated with sodium iodide in acetamide at 150° for 5 hr., no hydrocarbon product could be obtained and starting dihalide was recovered in 74% yield. A repeat run at 190° for 12 hr. yielded only tar. In dimethylformamide at 120° for 5 hr. 1,3-dibromo-2,2-dimethylpropane and sodium iodide gave a 13% recovery of starting material and a 48% yield (based on recovered dihalide) of volatile hydrocarbon mixture. Careful fractionation gave pure 2-methyl-2-butene and pure 1,1-dimethylcyclopropane in a ratio of about two to one. Under conditions simulating the elimination–rearrangement reaction conditions, 1,1-dimethylcyclopropane was recovered unchanged in 90% yield. This indicates that 1,1-dimethylcyclopropane is not an intermediate in the formation of 2-methyl-2-butene but is formed in a side reaction. The formation of 2-methyl-2-butene probably occurred *via* the readily isomerized 2-methyl-1-butene.

Treatment of 1,3-dibromo-2-methylpropane with sodium iodide in acetamide at 160° for 6 hr. gave back some starting dibromide (6% recovery) and a 57% yield of 2-methylpropene. Methylcyclopropane was evidently not an intermediate in the formation of 2-methylpropene since under conditions simulating the elimination–rearrangement reaction, methylcyclopropane failed to give any 2-methylpropene. When 1,3-dibromopropane was heated with sodium iodide in dimethylformamide at 170°, there was obtained an 18% recovery of 1,3-dibromopropane, a 5% yield of 1,3-diiodopropane and a 56% yield (based on recovered dihalide) of pure propene. Finally, 1,3-dibromo-2-phenylpropane yielded only tar when treated with sodium iodide in formamide at 190°.

In the successful elimination–rearrangement reactions the principal product in each instance is either the olefin expected from equation 1 or an olefin that could readily result by isomerization, under the reaction conditions, of the olefin obtained according to equation 1. The evidence indicates that iodide ion participates (*i.e.*, base participation)

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[11] D. E. Applequist and J. D. Roberts, THIS JOURNAL, **78**, 874 (1956).

[12] R. T. Arnold, R. W. Amidon and R. M. Dodson, *ibid.*, **72**, 2282 (1950).

[13] C. C. Price, *ibid.*, **61**, 1849 (1939).

in the step in which rearrangement occurs and that probably elimination of halogen accompanies rearrangement. Thus, except in one instance, molecular iodine (a conceivable acid catalyst) in the absence of iodide ion was unable to effect detectable rearrangement of the 1,3-dihalides to 1,2-dihalides. In this one instance, treatment of 1,1-bis-(bromomethyl)-cyclopropane with iodine in dimethylformamide at 120° yielded a mixture of 1,1-bis-(bromomethyl)-cyclopropane and 1-bromomethyl-1-bromocyclobutane. Whereas it appears that the elimination–rearrangement reaction is at least partially base-induced, with iodide ion furnishing the necessary "push," the experiments performed do not establish to what degree, if any, a "pull" by iodine or iodine bromide, at the other halogen atom of I, is necessary in the reaction of equation 1.

Since the experiments performed are only qualitative, conclusions as to structural effects are naturally limited. The fact that of the cyclic 1,1-bis-(halomethyl)-cycloalkanes, the cyclohexane failed to give elimination–rearrangement whereas the smaller ring compounds did give the reaction may indicate the reaction is aided by relief of ring and conformational strain. However, relief of ring strain is not necessary for reaction since 1,3-dibromo-2,2-dimethylpropane readily gave elimination–rearrangement. In the examples of 1,3-dibromo-2-methylpropane and 1,3-dibromopropane, it is difficult to account for the results except on the basis of a hydrogen migration (equation 1, R_1 = H).[14,15] Since no product resulting from methyl migration was obtained with 1,3-dibromo-2-methylpropane, it appears that hydrogen migrates more readily than methyl in this instance. In the reaction of 1,3-dibromo-2-phenylpropane, phenyl migration could not be detected. Perhaps elimination–rearrangement could be induced in a suitably substituted phenyl derivative or in 1,3-dibromo-2,2-diphenylpropanes.

Experimental

1,1-Bis-(bromomethyl)-cyclopropane.—This was prepared from the corresponding diol by the method of Zelinski.[16] Contaminating 1-bromomethyl-1-bromocyclobutane was removed by use of a slight modification of the procedure of Applequist and Roberts.[11] The crude dibromide (4.25 g.) was heated with 10 g. of potassium hydroxide pellets to 100° for 20 minutes. The mixture was cooled, diluted with ether and filtered. The filtrate was distilled through a modified Claisen head. The recovery of purified 1,1-bis-(bromomethyl)-cyclopropane was 3.6 g., b.p. 78–80° (16 mm.), n^{25}D 1.5350. Its properties and infrared spectrum were identical with those reported.[11]

1,1,Bis-(hydroxymethyl)-cyclobutane.—1,1-Bis-(carbethoxy)-cyclobutane (62 g., 0.31 m.) in dry ether (150 ml.) was added dropwise, with stirring, to a solution of lithium aluminum hydride (14.0 g., 0.37 mole) in dry ether (500 ml.) at such a rate that gentle refluxing was maintained. The mixture was allowed to stand for 2 hr. and then water (25 ml.) was added dropwise with ice cooling. The sludge was removed by suction filtration and dissolved in 20% sulfuric acid (200 ml.). The acid solution was brought to *p*H 3 by addition of sodium carbonate and then extracted continuously with ether for 24 hr. The ether extract and original filtrate were combined, dried over magnesium sulfate and the ether removed by flash distillation. The residue was distilled through a modified Claisen head. The yield of diol was 24 g. (71%), b.p. 112–115° (3 mm.), n^{25}D 1.4790 (lit.[17] b.p. 145–7 (20 mm.), n^{20}D 1.4758).

Attempts to convert the diol directly to the corresponding dibromide were unsuccessful, either by various procedures using phosphorus tribromide (some with explosive results) or triphenyl phosphite and bromine or thionyl bromide in pyridine (also explosive).

1,1-Bis-(hydroxymethyl)-cyclobutane Dibenzenesulfonate.—Benzenesulfonyl chloride (211 g., 1.2 mole) was added dropwise to a stirred and ice-cooled solution of the diol (56 g., 0.49 mole) in anhydrous pyridine (500 ml.) at such a rate that the temperature did not rise above 5°. The mixture then was stirred at 0° for 2 hr. and allowed to warm to room temperature. The mixture was stirred into ice-cold 3 *N* hydrochloric acid (800 ml.), and the precipitate removed by suction filtration and recrystallized from methanol. Further recrystallization from acetone–ligroin gave 107 g. (55%) of a white solid, m.p. 95–96°. This compound contained sulfur (by sodium fusion) and showed sulfonate absorption in the infrared at 7.30 μ.

Anal. Calcd. for $C_{18}H_{20}O_6S_2$: C, 54.53; H, 5.08. Found: C, 54.38; H, 5.08.

1,1-Bis-(iodomethyl)-cyclobutane.—A mixture of the above dibenzenesulfonate (107 g., 0.27 mole) and sodium iodide (105 g., 0.70 mole) in anhydrous butanone-2 (500 ml.) was heated to reflux for 24 hr. The mixture then was cooled and the salt removed by suction filtration and washed with ether. The combined filtrate was concentrated and the residue distilled through a modified Claisen head, b.p. 110–111° (2.5 mm.). The distillate was badly discolored with iodine which was removed by several washings with 10% sodium thiosulfate. The colorless oil was dried over anhydrous sodium sulfate and fractionated from silver chips, yield 47 g. (52%), b.p. 110–110.5° (2.5 mm.), n^{25}D 1.6201. Sodium fusion revealed iodine to be present, sulfur absent.

Anal. Calcd. for $C_6H_{10}I_2$: C, 21.45; H, 3.00. Found: C, 21.59; H, 2.97.

The compound gave an immediate precipitate of silver iodide when treated with alcoholic silver nitrate. It failed to liberate iodine when treated with potassium iodide in acetone. A vigorous reaction ensued when it was treated with zinc dust in alcoholic solution. The diiodide (3.0 g., 0.009 mole), when heated to reflux with potassium permanganate (6.3 g., 0.04 mole) in 6 *N* sodium hydroxide (30 ml.) for 6 hr., gave as the only isolated product 0.3 g. of starting material. No acidic material was found.

1,1-Bis-(hydroxymethyl)-cyclopentane.—A solution of 1,1-bis-(carbethoxy)-cyclopentane[18] (336 g., 1.6 moles) in dry ether (150 ml.) was added to a stirred solution of lithium aluminum hydride (100 g., 2.6 moles) in dry ether (1500 ml.) at such a rate that gentle reflux was maintained. The mixture was stirred an additional 4 hr. at room temperature. Water (150 ml.) then was added slowly, with stirring and ice cooling. The mixture was filtered by suction and the filtrate set aside. The precipitate was added to cold 20% hydrochloric acid (500 ml.) and the mixture extracted with five 100-ml. portions of ether. The ether extract was combined with the above filtrate, the solution dried over anhydrous magnesium sulfate and the ether removed by flash distillation. The oily residue, which solidified on being cooled, was recrystallized from benzene. The yield of colorless crystals was 101 g. (81%), m.p. 95–96°. An analytical sample was prepared by sublimation at 70° (5 mm.).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.57; H, 10.84. Found: C, 64.53; H, 10.74.

1,1-Bis-(bromomethyl)-cyclopentane.—Phosphorus tribromide (108 g., 0.42 mole) was added slowly to stirred ice-cooled 1,1-bis-(hydroxymethyl)-cyclopentane (26 g., 0.21 mole). The temperature of the mixture was gradually raised to 150° in 3 hr., maintained at 150° for 2 hr., then allowed to cool to room temperature. The mixture was poured over ice (150 g.) and extracted with ether. The extract was dried over anhydrous magnesium sulfate and the ether removed by flash distillation. The residue was distilled to yield 13.1 g. (25%) of the dibromide, b.p. 115–116° (15 mm.), n^{25}D 1.5342. The distillation residue yielded 5.9 g. of starting diol.

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(14) For an example of hydrogen migration in the benzilic acid-type rearrangement see W. E. Doering, T. I. Taylor and E. F. Schoenewaldt, *ibid.*, **70**, 455 (1948).

(15) These examples are being investigated with deuterium on C_2.

(16) N. Zelinski, *Ber.*, **46**, 165 (1913).

(17) N. Zelinski, *ibid.*, **46**, 1094 (1913).

(18) A. I. Vogel, *J. Chem. Soc.*, 1487 (1929).

Anal. Calcd. for $C_7H_{12}Br_2$: C, 32.84; H, 4.73. Found: C, 33.14; H, 4.70.

The dibromide reacted with sodium iodide in acetone to give only a white precipitate and no trace of iodine. Treatment of the dibromide with alcoholic silver nitrate gave silver bromide rapidly.

1,1-Bis-(bromomethyl)-cyclohexane.—The corresponding diol (25 g., 0.18 mole) was converted to the dibromide by the method of Backer and Winter[19]; yield 31 g. (63%). b.p. 95–97° (1 mm.), $n^{25}D$ 1.5374 (lit.[19] b.p. 140° (17 mm.), $n^{20}D$ 1.5390).

Anal. Calcd. for $C_8H_{14}Br_2$: C, 35.55; H, 5.23. Found: C, 35.70; H, 5.47.

The dibromide rapidly gave silver bromide with alcoholic silver nitrate. It failed to liberate iodine or give sodium bromide when treated with sodium iodide in acetone.

1,3-Dibromo-2,2-dimethylpropane.—This was prepared by the method of Whitmore,[20] b.p. 72–73° (16 mm.), $n^{25}D$ 1.5020 (lit.[20] b.p. 84° (28 mm.), $n^{20}D$ 1.5050). The dibromide rapidly gave silver bromide when treated with alcoholic silver nitrate but failed to give either iodine or sodium bromide when treated with sodium iodide in acetone.

1,3-Dibromo-2-methylpropane.—This was prepared by the method of Brewster,[21] b.p. 62–63° (13 mm.), $n^{25}D$ 1.5061 (lit.[21] b.p. 175–177°, $n^{25}D$ 1.5068). The dibromide reacted slowly with alcoholic silver nitrate to form silver bromide. With sodium iodide in acetone it gave a precipitate of sodium bromide but no iodine coloration.

1,3-Dibromo-2-phenylpropane.—Phosphorus tribromide (35 g., 0.13 mole) was added slowly to an ice-cooled, stirred mixture of pyridine (0.1 g.) and 1,3-dihydroxy-2-phenylpropane.[22] The mixture was kept at room temperature for five days, then heated on the steam-bath for 2 hr. The mixture then was poured onto ice (100 g.) and the organic layer washed with 10% sodium bicarbonate, then water, dried over anhydrous magnesium sulfate and fractionated. The yield of dibromide, b.p. 130–132° (3 mm.), $n^{25}D$ 1.5881, was 25.8 g. (71%).

Anal. Calcd. for $C_9H_{10}Br_2$: C, 38.88; H, 3.62. Found: C, 39.02; H, 3.67.

The dibromide rapidly gave a precipitate of sodium bromide on treatment with sodium iodide in acetone but failed to liberate iodine. It gave silver bromide slowly on treatment with alcoholic silver nitrate.

Reaction of 1,1-Bis-(bromomethyl)-cyclopropane with Sodium Iodide.—A mixture of 1,1-bis-(bromomethyl)-cyclopropane (13 g., 0.057 mole), sodium iodide (22.5 g., 0.15 mole) and dimethylformamide (25 ml.) was placed in a reaction flask connected in series to an air-cooled reflux condenser and two Dry Ice–acetone traps. As the temperature of the mixture was raised to 150° a slow gas evolution was observed, accompanied by blackening of the solution due to iodine liberation. The colorless liquid that had collected in the traps after 6 hr. of heating the reaction mixture at 150° was distilled, b.p. 37–41°, no residue, yield 1.2 g. (31% calculated for C_5H_8). The product readily absorbed bromine in carbon tetrachloride. A gas phase infrared spectrum indicated that it consisted of approximately equal parts of methylenecyclobutane, b.p. 41.3,[23] and 1-methylcyclobutene, b.p. 37.1°.[23] Bands appeared at 5.55, 5.95, 7.20 and 8.45 μ (characteristic of methylenecyclobutane[23]) and at 6.10, 7.20, 7.80, 10.10, 12.50 and 13.75 μ (characteristic of 1-methylcyclobutene).[23] There were no bands in the spectrum not characteristic of these compounds; in particular, prominent bands of spiropentane at 4.3, 4.9, 8.6 and 10.0 μ[23] were absent.

Treatment of the olefin mixture (1.2 g.) with performic acid according to the procedure of Roberts and Sauer[24] yielded 0.7 g. (38%) of a 1,2-diol (positive periodic acid test),[25] b.p. 90–95° (6 mm.), $n^{25}D$ 1.4707, which had an infrared spectrum very similar to that reported for 1-(hydroxymethyl)-cyclobutanol[24] (lit.[24] b.p. 93° (6 mm.), $n^{25}D$ 1.4715).

A mixture of authentic methylenecyclobutane[24] (2.0 ml.), sodium iodide (0.5 g.), iodine (0.5 g.) and dimethylformamide was heated in a sealed tube at 160° for 10 minutes. There was recovered 80% of hydrocarbon mixture that had an infrared spectrum identical to that obtained from the reaction of 1,1-bis-(bromomethyl)-cyclopropane with iodide ion.

Treatment of 1,1-Bis-(bromomethyl)-cyclopropane with Iodine.—A mixture of 1,1-bis-(bromomethyl)-cyclopropane (1.0 g.), iodine (0.2 g.) and dimethylformamide (4 ml.) was heated to 120° for 6 hr. The solution then was diluted with water (10 ml.) and extracted with ether. The ether extract was washed with 10% sodium thiosulfate, dried over anhydrous sodium sulfate, the ether evaporated and the residue distilled, b.p. 78–80° (16 mm.), yield 0.35 g. The infrared spectrum, strong absorption at 14.45 and weak absorption at 7.55 μ,[11] indicated it to be a mixture of 1-(bromomethyl)-1-bromocyclobutane (in largest amount) and unchanged 1,1-bis-(bromomethyl)-cyclopropane.

Reaction of 1,1-Bis-(iodomethyl)-cyclobutane with Sodium Iodide.—The procedure was similar to that used on 1,1-bis-(bromomethyl)-cyclopropane except that a constant stream of dry nitrogen was passed through the reaction mixture to entrain volatile products. The diiodide (20 g., 0.06 mole) was added slowly to a solution of sodium iodide (15 g., 0.10 mole) in acetamide (50 g.) at 150°. The mixture was heated at 150° an additional 5 hr. after the addition was completed. The trap contents were combined, washed with ice-water, dried over anhydrous magnesium sulfate and fractionated. The yield was 2.4 g. (52% calculated for C_6H_{10}), b.p. 75–76°, $n^{25}D$ 1.4306 (lit. for methylenecyclopentane,[12] b.p. 74°, $n^{20}D$ 1.4354).

Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found: C, 87.58; H, 12.20.

The infrared spectrum (carbon tetrachloride) of the product was identical to that of an authentic sample of methylenecyclopentane prepared by the method of Arnold, Amidon and Dodson.[12]

When 1,1-bis-(iodomethyl)-cyclobutane (5 g.) was treated with iodine (1 g.) and acetamide (20 g.) at 170° for 48 hr., there was recovered 4.2 g. (84%) of material identical in all respects, including infrared spectrum, with starting diiodide. The diiodide (11 g.) also was recovered unchanged in 81% yield after 48 hr. reflux with zinc chloride (0.5 g.) in ethanol (10 ml.).

Reaction of 1,1-Bis-(bromomethyl)-cyclopentane with Sodium Iodide.—A mixture of the dibromide (10.5 g., 0.04 mole), sodium iodide (15 g., 0.1 mole) and dimethylformamide (50 ml.) was heated to reflux temperature for 6 hr. The mixture was then distilled. The fraction boiling at 90–120° was washed thoroughly with water, dried over anhydrous magnesium sulfate and redistilled. There was obtained 1.4 g. (37%), b.p. 109–111°, $n^{25}D$ 1.4470 (lit.[26] b.p. 109–110°, $n^{20}D$ 1.4498). The infrared spectrum (carbon tetrachloride solution) was identical to that of an authentic sample of 1-methylcyclohexene, prepared by the method of Price.[13]

Methylenecyclohexane[27] (5 g.) was heated with sodium iodide (5 g.), iodine (1 g.) and dimethylformamide (50 ml.) for 2 hr. at reflux temperature. There was recovered 3.9 g. (78%) of hydrocarbon. The infrared spectrum showed it to be practically all 1-methylcyclohexene (strong band at 5.96 μ). Only a trace of the 6.06 μ band of methylenecyclohexane was observed.

Treatment of 1,1-Bis-(bromomethyl)-cyclohexane with Sodium Iodide.—A mixture of the dibromide (8.3 g., 0.03 mole), sodium iodide (15 g., 0.1 mole) and acetamide (50 g.) was heated at 150° for 5 hr. No volatile material was formed. Although the reaction mixture slowly darkened, this was not due to iodine since a carbon tetrachloride extract of a portion of the mixture was colorless. At the end of the heating period, the mixture was diluted with water and repeatedly extracted with ether. After being dried, the ether extract yielded 6.1 g. (74%) of material identical in all respects, including infrared spectrum, with starting material.

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[19] H. J. Backer and H. J. Winter, *Rec. trav. chim.*, **56**, 504 (1937).

[20] F. C. Whitmore, A. H. Popkin, H. I. Bernstein and J. D. Wilkins, This Journal, **63**, 126 (1941).

[21] J. H. Brewster, *ibid.*, **73**, 368 (1951).

[22] H. Adkins and A. R. Billica, *ibid.*, **70**, 3118 (1948).

[23] F. F. Cleveland, M. J. Murray and W. S. Gallaway, *J. Chem. Phys.*, **15**, 745 (1947).

[24] J. D. Roberts and C. W. Sauer, This Journal, **71**, 3927 (1944).

[25] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 129.

[26] F. G. Signaigo and P. L. Cramer, This Journal, **55**, 3329 (1933).

[27] R. T. Arnold and J. F. Dowdall, *ibid.*, **70**, 2591 (1948).

A repeat run at 195° for 12 hr. used up all the starting material and gave tar but no identifiable product.

Reaction of 1,3-Dibromo-2,2-dimethylpropane with Sodium Iodide.—A mixture of the dibromide (55 g., 0.24 mole), sodium iodide (105 g., 0.71 mole) and dimethylformamide was heated at 120° for 5 hr. The contents of the Dry Ice–acetone traps, 6.95 g., was twice fractionated through a 40-plate concentric tube column yielding: fraction A, b.p. 21°, 1.65 g.; fraction B, b.p. 38–39°, 4.1 g.; 1.2 g. of intermediate fractions. The gas phase infrared spectrum (200 mm.) of A was identical to that of an authentic sample of 1,1-dimethylcyclopropane.[28] The spectrum of B (200 mm.) was identical to that of authentic 2-methyl-2-butene. From the original reaction mixture there was recovered, after dilution with water and extraction with ether, 7.1 g. (13% recovery) of starting dibromide.

When 1,1-dimethylcyclopropane (1 ml.) was heated in a sealed tube with sodium iodide (0.5 g.), iodine (0.5 g.) and dimethylformamide (3 ml.) at 150° for an hour, 90% of pure starting material was recovered. No trace of 2-methyl-2-butene was found.

When 1,3-dibromo-2,2-dimethylpropane (5 g.) was heated with iodine (1 g.) in dimethylformamide (10 ml.) at 155° for 15 hr., there was obtained only a 92% recovery of material identical in all respects to the starting material.

Reaction of 1,3-Dibromo-2-methylpropane with Sodium Iodide.—A mixture of dibromide (8 g., 0.037 mole), sodium iodide (15 g., 0.1 mole) and acetamide (50 g.) was heated at 160° for 6 hr. The contents of the Dry Ice–acetone traps was distilled bulb to bulb four times, yielding 1.1 g. (53%) of colorless volatile liquid. Its gas phase infrared spectrum (200 mm.) was identical to that of an authentic sample of 2-methylpropene. From the original reaction flask there was recovered 0.5 g. (6% recovery) of starting dibromide.

When methylcyclopropane (1 ml.) was heated with sodium iodide (1 g.) and iodine (1 g.) in acetamide (3 g.) in a sealed tube at 150–175° for an hour, there was obtained a 75% recovery of volatile material that had the infrared spectrum of pure methylcyclopropane.

When 1,3-dibromo-2-methylpropane (1 g.) was heated with iodine (0.2 g.) and acetamide (3 g.) at 160° for 6 hr., the only product obtained, 0.65 g., was identical in all respects with starting dibromide.

Reaction of 1,3-Dibromopropane with Sodium Iodide.—A mixture of 1,3-dibromopropane (Eastman Kodak Co., redistilled, 40.4 g., 0.2 mole), sodium iodide (60 g., 0.4 mole) and dimethylformamide (200 ml.) was heated at 170° for 5 hr. while a slow stream of dry nitrogen was passed through. The contents of the Dry Ice–acetone traps were distilled bulb to bulb three times giving 3.6 g. of volatile hydrocarbon whose infrared spectrum (gas, 200 mm.) was identical to that of an authentic sample of propylene. From the reaction flask there was recovered 7.1 g. of starting dibromide and 3.1 g. of what was probably 1,3-diiodopropane, b.p. 219–222° (lit.[29] b.p. 224°). The latter contained iodine but not bromine, failed to react with sodium iodide and gave silver iodide when allowed to stand with alcoholic silver nitrate.

When 1,3-dibromopropane (20 g.) was heated with iodine (4 g.) and dimethylformamide (50 ml.) at 170° for 6 hr., no volatile material was formed, and 1,3-dibromopropane was recovered in 90% yield. At room temperature, the dibromide slowly precipitated sodium bromide when treated with sodium iodide in acetone. With alcoholic silver nitrate, the dibromide slowly precipitated silver bromide.

Treatment of 1,3-Dibromo-2-phenylpropane with Sodium Iodide.—A mixture of dibromide (5 g., 0.018 mole), sodium iodide (6 g., 0.04 mole) and acetamide (20 g.) was heated at 190° for 6 hr. A carbon tetrachloride extract of a portion of the darkened reaction mixture was colorless, indicating the absence of iodine. The reaction mixture was diluted with water (100 ml.) and the resultant tarry mixture was extracted with ether. Evaporation of the dried ether extract left no residue. The insoluble tar was subjected to steam distillation, but no water-insoluble distillate was obtained.

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(28) R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. W. Boord, THIS JOURNAL, **70**, 946 (1948).

(29) J. Timmermans and T. J. F. Mattaar, *Bull. soc. chim. Belg.*, **30**, 213 (1921).

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[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY, UNIVERSITY OF NORTH CAROLINA]

The "Element Effect" as a Criterion of Mechanism in Activated Aromatic Nucleophilic Substitution Reactions[1,2]

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RECEIVED JUNE 11, 1956

Rates of condensation of nine 1-substituted-2,4-dinitrobenzenes with piperidine in methanol to form 2,4-dinitrophenylpiperidine (II) have been measured. Three substituents, fluorine, nitro and *p*-toluenesulfonoxy, are displaced very rapidly while six substituents are displaced more slowly with remarkably little variation in rate amongst the six. Since displacement of these six substituents involves the breaking of bonds between carbon and five other elements, this result indicates that bond-breaking has not made significant progress in the rate-determining transition states of these reactions. The strictly SN2-like mechanism is thereby eliminated, but an alternate one-step mechanism is not. However, the facts are most agreeably interpreted in terms of the intermediate complex mechanism with the step in which the complex I is formed being rate determining. This result has the same significance for these nucleophilic substitutions that Melander's observation of the lack of a hydrogen isotope effect in nitration and bromination had for those reactions. Interesting complications were encountered in several of the reactions studied, but these did not prevent satisfactory determination of the desired rate coefficients.

The mechanism of activated[3] aromatic nucleophilic substitution reactions has become a subject of some controversy in recent years. The principal contending points of view are, on the one hand, that the mechanism is a direct, one-step displacement much like the aliphatic SN2 mechanism (equation 1), and on the other hand that the reaction occurs in two steps and involves an intermediate of some stability (equation 2). Both points of view have been advocated at various times through the years, but the strongest arguments have been presented recently by Chapman and his associates,[4] for the one-step, SN2-like mech-

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(1) Research supported by the Office of Ordnance Research, U. S. Army.

(2) Presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1956; preliminary results were described at the Southeastern Regional A.C.S. Meeting, Birmingham, Ala., October, 1954.

(3) It has seemed desirable to distinguish, in discussions of mechanisms, aromatic nucleophilic substitution reactions activated by nitro or other strongly electron-attracting groups from those occurring without activation, as in unsubstituted phenyl or naphthyl halides.

(4) (a) N. B. Chapman and R. E. Parker, *J. Chem. Soc.*, 3301 (1951); (b) E. A. S. Cavell and N. B. Chapman, *ibid.*, 3392 (1953); (c) N. B. Chapman, R. E. Parker and P. W. Soanes, *ibid.*, 2109 (1954).