Acknowledgment.—The authors are indebted to Mr. C. W. Nash for microanalyses.

Experimental

1-Methyl-4-phenyl-4-acetoxypiperidine (Using H_3PO_4).—To a stirred mixture of 240 g. (4.0 moles) of glacial acetic acid and 51 g. (0.50 mole) of acetic anhydride was slowly added with external cooling 58 g. (0.50 mole) of 85% orthophosphoric acid. After the exothermic reaction had ceased there was added with cooling 65 g. (0.50 mole) of N,N′,N″-trimethyltrimethylenetriamine followed by 59 g. (0.50 mole) of α-methylstyrene. The mixture was stirred at 115° for 4 hr., allowed to stand 2 days, diluted with 500 ml. of water, extracted with benzene and made basic with sodium carbonate. The amine was taken up in benzene, dried over anhydrous potassium carbonate and distilled to give 35 g. (30.1%) of 1-methyl-4-phenyl-4-acetoxypiperidine, b.p. 100–120° (0.85 mm.). This crystallized and melted at 62–64° after recrystallization from heptane.

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.96; H, 8.34; N, 5.97.

The hydrochloride melted at 211–212° after recrystallization from acetone (lit.[4] m.p. 212–213°).

Anal. Calcd. for $C_{14}H_{20}NO_2Cl$: C, 62.33; H, 7.47; N, 5.19; Cl, 13.1. Found: C, 62.26; H, 7.59; N, 5.19; Cl, 13.2.

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[4] A. Ziering, L. Berger, S. D. Heineman and J. Lee, *J. Org. Chem.*, **12**, 894 (1947).

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The Stereochemistry of the Debromination of *meso*-1,2-Dibromo-1,2-dideuteroethane by Iodide Ion

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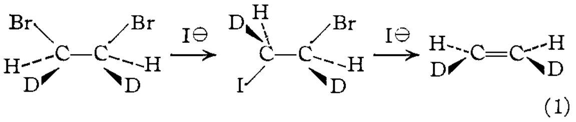
Recently, Hine and Brader have concluded that the debromination of ethylene bromide by iodide ion proceeds by a rate-controlling step of SN2 displacement by iodide ion, followed by a faster step of *trans* elimination on the intermediate bromoiodide.[1] The over-all result of this path would be *cis* removal of the bromine atoms (eq. 1). The conclusion was based on a comparison of substitution and elimination rates of a number of halides and involved a number of reasonable assumptions.



(1)

Since *meso*-1,2-dibromo-1,2-dideuteroethane was available in these laboratories from a previous study on the stereochemistry of debromination,[2] it was decided to determine directly the steric course of bromine elimination with iodide ion in this system.

As predicted for the reaction path proposed by Hine and Brader, the net steric course of the reaction in 90% aqueous methanol at 59° was one of exclusive *cis* elimination, within experimental error. *cis*-Ethylene-d_2 was isolated in about 60% yield (Table I). In a control experiment, treatment of *trans*-ethylene-d_2 with an appropriate mixture of iodide ion, iodine and bromine, under the reaction conditions gave a negligible amount of isomerization to *cis*-olefin. It was confirmed that treatment of *meso*-1,2-dibromo-1,2-dideuteroethane with zinc in water yielded the *trans* elimination product,[2] *trans*-ethylene-d_2, and that *dl*-2,3-dibromobutane with iodide ion gave *trans* elimination[3] (in contrast to ethylene dibromide), yielding greater than 95% of *cis*-2-butene and less than 5% *trans*-2-butene.

TABLE I

Compound	Reagents	*cis* in olefin mixture, %
95% *meso*-5%-*dl*-CHDBrCHDBr	KI in 90% CH_3OH (59°)	94.0, 93.0
trans-Ethylene-d_2	KI + I_2 + Br_2 in 90% CH_3OH (59°)	2.0
dl-2,3-Dibromobutane	KI in 90% CH_3OH (59°)	95–100

Experimental

Materials.—*trans*-Ethylene-d_2, *meso*-1,2-dibromo-1,2-dideuteroethane and *dl*-2,3-dibromobutane were prepared as previously described.[2,4] Infrared analysis of the *meso*-1,2-dibromo-1,2-dideuteroethane showed it to contain 5% of the *dl*-isomer.[4]

Debromination Procedures.—A mixture of *meso*-1,2-dibromo-1,2-dideuteroethane (0.0132 g.), methanol (1 ml.), water (0.1 ml.) and potassium iodide (0.75 g.) was heated in a sealed tube at 59° for 24 hr. in the dark. The tube was broken and the ethylene isolated in about 60% yield. The infrared analysis was carried out as before.[2] The same procedure was used for *dl*-2,3-dibromobutane.

The debromination of *meso*-1,2-dibromo-1,2-dideuteroethane with zinc metal and analysis of the olefin product was carried out as before.[2]

Control Experiment.—A mixture of *trans*-ethylene-d_2 (3 ml., gas), methanol (1 ml.), water (0.1 ml.), iodine (0.03 g.) and bromine (0.02 g.) was heated at 59° in a sealed tube for 24 hr. The olefin was isolated and analyzed as above.

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[1] J. Hine and W. H. Brader, Jr., THIS JOURNAL, **77**, 361 (1955).

[2] W. M. Schubert, B. S. Rabinovitch, N. R. Larson and V. A. Sims, *ibid.*, **74**, 4590 (1952).

[3] S. Winstein, W. G. Young and D. Pressman, *ibid.*, **61**, 1645 (1939).

[4] H. J. Bernstein, A. D. E. Pullin, B. S. Rabinovitch and N. R. Larson, *J. Chem. Phys.*, **20**, 8 (1952).

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Reactions in Sunlight. XVIII. Dimerization of *o*-Phthalaldehyde

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Thiele and Günther[1] state that although *o*-phthalaldehyde (I) is stable in the dark, upon exposure to sunlight it forms a mixture of colorless substances which is crumbly in character. We have found that a solution of I in benzene, exposed to sunlight for one day (July), forms a colorless crystalline photodimer III which reduces ammoniacal silver nitrate solution. The photo-dimer forms a crystalline monophenylhydrazone and a monoöxime. On heating under reduced pressure, III dissociates to give a colorless sublimate, which was identified as phthalide II. The photo-dimer should, therefore, be either III or IIIa; IIIa is ruled out by the infrared absorption spectrum.

Absorption bands were observed in the infrared spectrum of the photodimer at 2820, 1739, 1368, 1290, 1213 and 910 cm.$^{-1}$, arising from an aromatic aldehyde; at 1748, and 1287 cm.$^{-1}$ from a carbonyl

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[1] J. Thiele and O. Günther, *Ann.*, **347**, 107 (1906).