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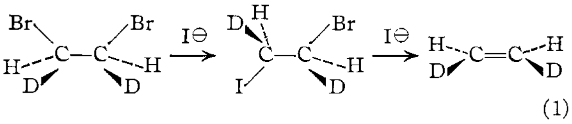
The Stereochemistry of the Debromination of *meso*-1,2-Dibromo-1,2-dideuteroethane by Iodide Ion

BY W. M. SCHUBERT, HARVEY STEADLY AND
B. S. RABINOVITCH

RECEIVED JUNE 11, 1955

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

BY ALEXANDER SCHÖNBERG AND AHMED MUSTAFA

RECEIVED APRIL 25, 1955

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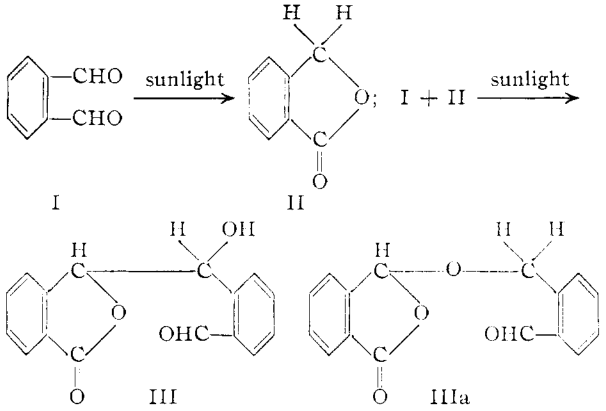
(1) J. Thiele and O. Günther, *Ann.*, **347**, 107 (1906).

in a strained ring; at 3465, 1420, 1309 and 1070 cm.$^{-1}$ from a secondary alcohol in which the –OH group is free and non-bonded as indicated by the high frequency and the sharpness of the 3465 cm.$^{-1}$ band; at 1333 and 1344 cm.$^{-1}$ from the two → C–H groupings; and at 1611, 1597, 1498, 1196, 1112, 1022, 967, 766, 763 and 704 cm.$^{-1}$ from *o*-disubstituted benzene groupings, the doublet at 766 and 763 cm.$^{-1}$ indicating that two such groupings are present. These groupings are compatible with formula III, but not with formula IIIa, since they do not contain an aliphatic ether (C–O–C) grouping.

The photochemical addition of I to II yielding III is parallel to the photochemical addition of diphenylmethane to benzophenone,[2] xanthene to benzophenone, and xanthene to xanthone.[3] In all these cases the hydrogen of a methylene group migrates under the influence of sunlight to a carbonyl group. The formation of II from III by the action of heat is comparable to the formation of xanthene from the xanthene–xanthone adduct, corresponding to III, under similar conditions.



Experimental

Action of Sunlight on *o*-Phthalaldehyde (I).—The air in a Schlenk tube,[4] containing 1 g. of I[5] in 25 ml. of dry, thiophene-free benzene, was displaced by dry carbon dioxide and the tube sealed. The reaction mixture was exposed to sunlight for one day (July). The colorless crystals that separated during exposure melt at around 184° (dec., yellow melt).[6] Crystals from xylene contained xylene of crystallization which was readily lost when the sample was dried at 100° for 6 hr. The yield was almost quantitative.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.5; H, 4.4. Found: C, 71.3; H, 4.3.

Compound III is soluble in hot xylene, but difficultly soluble in cold benzene, ethyl alcohol and ether; it gives an orange color with sulfuric acid. III (0.2 g.) was heated (steam-bath) with 2 ml. of phenylhydrazine for 0.5 hr.; the resulting colorless crystals were washed with ether and recrystallized from xylene; yield 0.12 g., m.p. 220° (yellow melt).

Anal. Calcd. for $C_{22}H_{18}N_2O_3$: C, 73.7; H, 5.0; N, 7.8; mol. wt., 358. Found: C, 73.4; H, 4.9; N, 7.7; mol. wt. (micro-Rast), 365.

The addition of a few ml. of ether to the filtrate of the reaction mixture gave more of the hydrazone derivative.

A solution of 0.3 g. of III and 0.2 g. of hydroxylamine hydrochloride in 30 ml. of ethyl alcohol, containing a few drops of pyridine, was refluxed for 3 hr. The reaction mixture was set aside overnight at room temperature, rendered just acidic with dilute hydrochloric acid and concentrated. The oily residue was then washed several times with light petroleum (b.p. 50–60°) and the resulting solid crystallized from dilute alcohol; yield 0.18 g., m.p. 139°.

Anal. Calcd. for $C_{16}H_{13}NO_4$: C, 67.8; H, 4.6; N, 4.9. Found: C, 67.3; H, 4.5; N, 4.7.

Thermal Decomposition.—The pyrolysis was carried out in a 15-ml. flask which was connected to a working oil-pump through a delivery tube containing two bulbs which were cooled externally. When the reaction flask, containing 1 g. of III, was heated at 150° (bath-temp.), colorless crystalline sublimate was formed. Upon recrystallization from petroleum ether (b.p. 50–60°), the sublimate yielded 0.31 g. of phthalide which was identified by m.p. and mixed m.p. The residual mass in the reaction vessel was crystallized from benzene as almost colorless crystals, m.p. 278°.

Spectra.—The rock salt infrared (2 to 15 μ) spectrum of the photo-dimer was measured in the solid state as a Nujol mull of capillary thickness with a Perkin–Elmer model 21 double beam, automatic recording infrared spectrophotometer.

Acknowledgment.—The authors are indebted to Dr. David N. Kendall for the infrared spectrum and its interpretation.

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[2] E. Paternò and G. Chieffi, *Gazz. chim. ital.*, **39**, II, 419 (1909).

[3] A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 67 (1944).

[4] W. Schlenk and A. Thal, *Ber.*, **46**, 2840 (1913).

[5] *o*-Phthalaldehyde obtained from Dr. Theodor Schuchardt (Munich) was crystallized from light petroleum (b.p. below 40°) m.p. 57°.

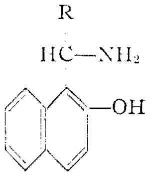
[6] The control experiment which was run in the dark, but otherwise under identical conditions, showed no reaction.

Studies on Sterically Hindered Phenols. I. Instability of 1-Triphenylmethyl-β-naphthol toward Acids

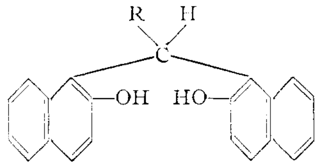
BY ALEXANDER SCHÖNBERG, AHMED MUSTAFA AND AHMED FATHY ABDEL MAUGOUD SHALABY

RECEIVED APRIL 25, 1955

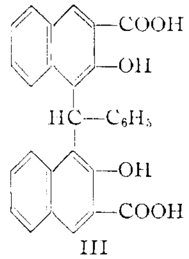
Some derivatives of 1-methyl-2-hydroxynaphthalene are readily hydrolyzed with the rupture of the C–C bond between the naphthalene ring and the methyl carbon atom. Thus, compounds of types I and II were hydrolyzed to yield naphthol and the corresponding aldehyde[1,2]; III yielded 2-hydroxy-3-naphthoic acid and benzaldehyde.[3]



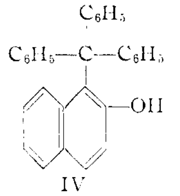
I



II



III



IV

Since all three types of substances (I, II, III) have one or two hydroxyl groups and one hydrogen atom

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[2] M. S. Kharasch and J. Porsche, *J. Org. Chem.*, **1**, 265 (1936).

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