[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Preparation and Structure of a Dimer of *p*-Bromostyrene: 1,3-Di-(*p*-bromophenyl)-1-butene

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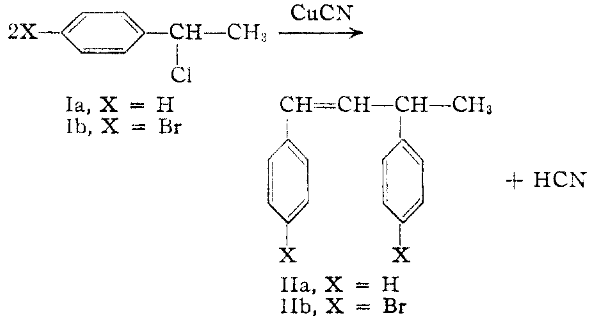
A study has been made of the reaction between α-chloro-α-(*p*-bromophenyl)-ethane and cuprous cyanide. The product isolated has been shown to be 1,3-di-(*p*-bromophenyl)-1-butene by degradative procedures. *p*-Bromohydratropaldehyde, needed as a reference aldehyde in this study, has been synthesized from *p*-bromoacetophenone and ethyl chloroacetate *via* the Darzens glycidic ester condensation.

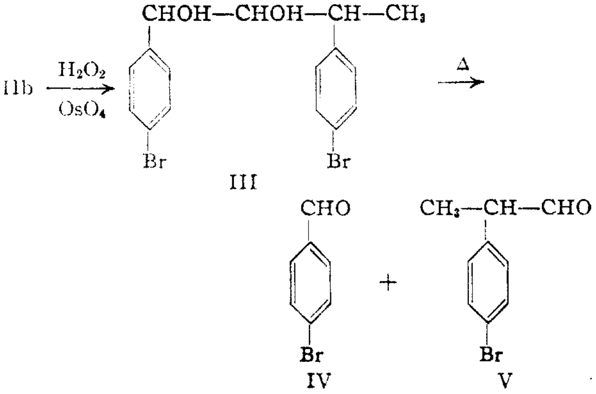
Previous work in this Laboratory[1] has shown that *cis*-1,3-diphenyl-1-butene (IIa) is formed when α-chloroethylbenzene (Ia) and cuprous cyanide are heated together above 130°. A study of the reaction between α-chloro-α-(*p*-bromophenyl)-ethane (Ib) and cuprous cyanide was undertaken in order to extend the reaction. When a mixture of Ib and cuprous cyanide was heated above 125°, a mild reaction occurred with the liberation of hydrogen cyanide.



Ia, X = H
Ib, X = Br

IIa, X = H
IIb, X = Br

The structure IIb was assigned to the solid isolated from the reaction mixture for the following reasons. Bromine analysis agreed with the value calculated for *p*-bromostyrene or a polymer of *p*-bromostyrene. Bromination gave a second solid, m.p. 154–160°, which appears to be the dibromide of IIb and is probably a mixture of diastereoisomers. Attempted molecular weight determinations of IIb by the freezing point method in benzene failed because of the insolubility of IIb in benzene near its freezing point. Degradation of IIb was carried out according to the following sequence of reactions. Hydroxylation of IIb to the glycol III was accomplished by the use of hydrogen peroxide in *t*-butyl alcohol[2] with osmium tetroxide as catalyst. The glycol was destructively distilled under reduced pressure and a series of fractions collected between 76 and 192° at 2 mm. All fractions gave precipitates with 2,4-dinitrophenylhydrazine. The isolation of the 2,4-dinitrophenylhydrazone of *p*-bromobenzaldehyde showed that the latter was one of the degradation products. Fractional precipitation procedures yielded a small quantity of slightly impure *p*-bromohydratropaldehyde-2,4-dinitrophenylhydrazone melting at 118–121°. This established that the second degradation product of IIb was *p*-bromohydratropaldehyde (V). Since IV and V are the degradation products, the position of the double bond must be as indicated in formula IIb.

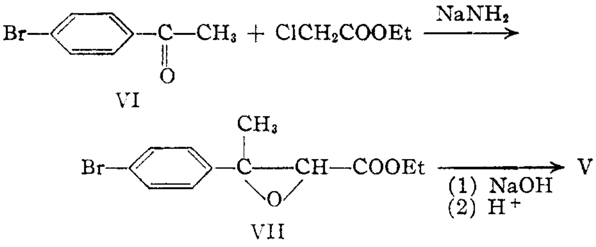


III

IV

V

p-Bromohydratropaldehyde (V), a new compound, was prepared from *p*-bromoacetophenone (VI) *via* the Darzens glycidic ester condensation by a procedure analogous to that for the preparation of hydratropaldehyde from acetophenone,[3] as shown by the equations



VI

VII

Experimental

α-Chloro-α-(*p*-bromophenyl)-ethane (Ib).—*p*-Bromophenylmethylcarbinol was prepared from the mono-Grignard reagent of *p*-dibromobenzene and acetaldehyde by the procedure of Quelet[4] in an average yield of 40%, b.p. 110–123° at 1.5 mm., n^{18}D 1.5728. The pure carbinol was saturated with hydrogen chloride gas at 0°, the aqueous layer separated and the crude chloride dried overnight over calcium chloride in the refrigerator. Distillation through an unpacked column 30 cm. in length gave yields of 80 to 100% of a colorless oil, b.p. 92–105° at 1.5 mm., n^{20}D 1.5687 (reported[5] a pinkish pungent oil, b.p. 115–120° at 11 to 12 mm.). The α-chloro-α-(*p*-bromophenyl)-ethane is stable for as long as six months when stored in a refrigerator at 20°.

1,3-Di-(*p*-bromophenyl)-1-butene (IIb).—In a typical preparation, carried out in a hood, 142.5 g. (0.65 mole) of Ib and 58 g. of cuprous cyanide were placed in a 500-ml., three-necked flask equipped with a reflux condenser, Hershberg stirrer and thermometer. A glass tube connected the top of the condenser to a coil and receiver packed in ice. By means of an oil-bath, the reaction flask was heated to 125°, at which temperature a mild evolution of hydrogen cyanide occurred. When the evolution of hydrogen cyanide had

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(1) G. L. Goerner and W. G. Hines, THIS JOURNAL, **70**, 3511 (1948).

(2) N. A. Milas and S. Sussman, *ibid.*, **58**, 1302 (1936).

(3) C. F. H. Allen and J. Van Allan, *Org. Syntheses*, **24**, 82, 87 (1944).

(4) R. Quelet, *Bull. soc. chim. France*, [4] **45**, 86 (1929).

(5) H. J. Barber, R. Slack and A. M. Woolman, *J. Chem. Soc.*, 99 (1943).

ceased, the oil-bath was removed and the reaction mixture permitted to cool to room temperature. The reaction mass was extracted with three 150-ml. portions of benzene, the benzene removed under the reduced pressure of an aspirator and the residue distilled at 3 mm. pressure through an unpacked column of 30 cm. length. Fractions distilling at 77 to 143° (21.5 g.), 178 to 216° (64.8 g.) and 216 to 225° (5.5 g.) were collected. The fraction distilling at 178 to 216° turned to an oily solid after standing overnight. Recrystallization from methyl alcohol gave 24.1 g. of a white crystalline solid, m.p. 67.5–68°, and 38 g. of a less pure material. The total yield of recrystallized material was 62.1 g. or 51.7%, calculated as IIb.

Anal. Calcd. for $C_{16}H_{14}Br_2$: Br, 43.66. Found: Br, 43.6.

Bromination of 2.5 g. of IIb was carried out in carbon disulfide in the absence of direct light. Evaporation of the carbon disulfide and purification from benzene by precipitation with ligroin gave 3.1 g. of a white solid, m.p. 154–160°. This melting point could not be raised by further recrystallization.

Anal. Calcd. for $C_{16}H_{14}Br_4$: Br, 60.78. Found: Br, 61.0.

Degradation of IIb.—Hydroxylation[2] of IIb was accomplished using excess osmium tetroxide catalyst and only 90% of the theoretical hydrogen peroxide. In 175 ml. of *t*-butyl alcohol there was dissolved 10 g. of IIb and 2 ml. of 0.5% osmium tetroxide catalyst was added. Hydrogen peroxide (14.5 ml. of a 7.36% solution in *t*-butyl alcohol) was added over a period of half an hour. The temperature rise was no more than 3°. After standing overnight, the reaction mixture was shaken with 2 g. of zinc dust and 3 ml. of water to destroy any unreacted hydrogen peroxide and then decanted through glass wool.

The destructive distillation of the glycol III was carried out *in vacuo* in an apparatus consisting of a 50-ml. flask attached to a finger-condenser type distilling head. Solvents were first removed at room temperature with a water aspirator, followed by distillation at 2 mm. pressure. Six fractions were collected in the boiling range of 76 to 192°. From the first fraction, a solid, distilling at 76 to 86°, there was obtained a 2,4-dinitrophenylhydrazone, which after recrystallization from methyl alcohol melted at 257–258°. The 2,4-dinitrophenylhydrazone of *p*-bromobenzaldehyde is reported to melt at 128°[6] and at 260–261°.[7] A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of *p*-bromobenzaldehyde, prepared in this Laboratory and melting at 257–258°, was 257–258°.

The third fraction, a green liquid distilling at 97 to 107° at 2 mm., was converted into the 2,4-dinitrophenylhydrazones in 250 to 300 ml. of methyl alcohol in the conventional manner. Water was added dropwise to the solution to the point of incipient precipitation and the solution permitted to stand overnight. The first crop of crystals, m.p. 235–240°, was removed and the fractional precipitation procedure repeated. The second crop of crystals melted at 185–189°, the third at 118–121°, and the fourth, produced by the addition of excess water, at 109–195°. The third crop of crystals, m.p. 118–121°, when mixed with an authentic sample of the 2,4-dinitrophenylhydrazone of *p*-bromohydratropaldehyde (V), m.p. 123–124°, gave a melting point of 118–119°.

Ethyl β-(*p*-Bromophenyl)-β-methylglycidate (VII).—This procedure is an adaptation of that used by Allen and Van Allan.[3] In a 2-l. three-necked flask equipped with a thermometer, mechanical stirrer and a reflux condenser carrying a soda lime drying tube were mixed 99.5 g. (0.5 mole) of *p*-bromoacetophenone (VI), 66.3 g. (0.5 mole) ethyl chloroacetate and 150 ml. of anhydrous benzene. To this was added 23.6 g. (0.6 mole) of powdered sodamide over a period of two hours, the temperature being maintained at 15–20° by means of an ice-bath. After stirring for two hours, the reaction mixture was poured onto crushed ice and the benzene layer separated. The aqueous layer was extracted twice with benzene. The combined benzene extracts were washed twice with water, once with 10% acetic acid, and dried over anhydrous sodium sulfate. After the removal of the benzene, fractionation gave (a) 21.7 g. of liquid distilling at 38 to 120° at 2.5 mm., which soon solidified and which was mostly unreacted VI and ethyl chloroacetate, (b) 17.5 g. of an intermediate fraction distilling at 125 to 136° at 2 mm. and containing some VI, and (c) 49.1 g. (34.4%) of a straw-colored, viscous oil distilling at 137–146°. The latter is the glycidic ester VII and distilled mostly at 137–140° at 1.5 mm., $n^{20}D$ 1.5360.

Anal. Calcd. for $C_{12}H_{13}BrO_3$: Br, 28.03. Found: Br, 28.0.

***p*-Bromohydratropaldehyde (V).**—To 25.6 g. (0.09 mole) of VII, contained in a 1 l. three-necked flask equipped with a mechanical stirrer, reflux condenser and thermometer, was added a solution of 8.4 g. (0.21 mole) of sodium hydroxide in 25 ml. of water. Almost immediately an exothermic reaction set in and the temperature rose to 65°. The flask was chilled and the temperature maintained at 45–50°. An insoluble white solid precipitated. After stirring for five hours, the reaction mixture was acidified and refluxed for 2.5 hours. Upon cooling an oil separated and was removed and the aqueous layer extracted with benzene. The oil and the benzene extracts were combined, the benzene removed and the residual oil fractionated. Twelve grams of an oil was collected from 90 to 127° at 2 mm., mostly from 98 to 100°, $n^{20}D$ 1.5602, and represented a yield of 62.7% of V.

The 2,4-dinitrophenylhydrazone of V melted at 123–124° after crystallization from methyl alcohol and then from acetic acid.

Anal. Calcd. for $C_{15}H_{13}BrN_4O_4$: Br, 20.32. Found: Br, 20.3.

East Lansing, Mich.

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[6] M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1943, p. 274.

[7] H. R. Snyder and G. R. Handrick, This Journal, 66, 1862 (1944).