

CCCLXXVIII.—*The Preparation and Hydrolysis of the  
Isomeric Azoxybenzyl Bromides.*

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As a result of recent work on the hydrolysis of substituted benzyl halides by aqueous alcohol it may be stated that, in a series of isomeric benzyl halides, those isomerides in which the  $-\text{CH}_2\text{Hal}$

group is attached to the carbon atom of the benzene nucleus which is attacked during substitution of the corresponding benzene derivative are the ones from which the halogen is most readily removed by the hydrolysing agent named (compare Olivier, *Rec. trav. chim.*, 1923, 42, 775). This rule holds for the relatively simple OMe, CH<sub>3</sub>, F, Cl, Br, I, NO<sub>2</sub>, and CO<sub>2</sub>H derivatives;  $\omega$ -bromo-*o*-toluic acid, however, is an exception because of steric influences (see Olivier, *loc. cit.*; Lapworth and Shoesmith, J., 1922, 121, 1391; Shoesmith and Slater, this vol., p. 214).

It has now been found that the rule also holds for the more complicated azoxybenzyl bromides of the general formula CH<sub>2</sub>Br·C<sub>6</sub>H<sub>4</sub>· $\overline{\text{N}\cdot\text{O}\cdot\text{N}}$ ·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>Br. Azoxybenzene, on treatment with nitric acid, gives the *o*- and *p*-nitro-derivatives (Zinin, *Annalen*, 1860, 114, 218), and therefore, according to the above rule, the rates of hydrolysis of the bromides should be *o* and *p* > *m*. This is so, for the rates in aqueous propyl-alcoholic solution are in the order *o* > *p* > *m*. This, incidentally, is the first case in which the ortho-compound is the most readily hydrolysable isomeride.

#### EXPERIMENTAL.

*o*-Azoxybenzyl Bromide.—*o*-Nitrobenzyl alcohol (Shoesmith and Hetherington, J., 1924, 125, 1316) in aqueous-alcoholic solution was reduced with zinc dust to the hydroxylamine (Bamberger, *Ber.*, 1903, 36, 837), which, without being isolated, was oxidised to *o*-azoxybenzyl alcohol (needles, m. p. 123°, from benzene) by hydrogen peroxide or air. The azoxy-alcohol was dissolved in hot benzene, and dry hydrogen bromide passed through the solution; the syrup that separated crystallised when kept under alcohol and was the hydrobromide of an unknown, complex base. When the solution was saturated (three passages of hydrogen bromide were essential), the benzene was almost completely removed *under diminished pressure* on the water-bath. Towards the end of the operation, the temperature was not allowed to rise above that of the room, otherwise violent decomposition of the bromide always took place. The residue crystallised from a small quantity of alcohol in colourless, long plates of *o*-azoxybenzyl bromide, m. p. 105° (violent decomp. at 106°) (Found: hydrolysable Br, 41.3. C<sub>14</sub>H<sub>12</sub>ON<sub>2</sub>Br<sub>2</sub> requires Br, 41.7%).

*m*-Azoxybenzyl Bromide.—*m*-Nitrobenzyl alcohol, prepared from *m*-nitrobenzaldehyde, was converted into *m*-azoxybenzyl alcohol, m. p. 86° (Carré, *Compt. rend.*, 1905, 141, 595), in the above manner and further into the corresponding azoxybenzyl bromide in hot benzene solution by means of dry hydrogen bromide, the operation

proceeding quite smoothly with separation of a small quantity of resin. *m*-Azoxybenzyl bromide crystallises from alcohol in pale yellow plates, m. p. 119° (Found : hydrolysable Br, 41.3%).

*p*-Azoxybenzyl Bromide.—*p*-Nitrobenzyl alcohol (m. p. 92°) was converted by the above method into *p*-azoxybenzyl alcohol, which crystallised from benzene (or much water) in pale yellow needles, m. p. 167° (Found : N, 10.7.  $C_{14}H_{14}O_3N_2$  requires N, 10.9%). A mixture of the azoxy-alcohol (2 g.) and phosphorus pentabromide (6 g.) in bromoform (20 c.c.) was heated for 3 hours on the water-bath, and the bromoform (10 c.c.) then distilled off. The crude *p*-azoxybenzyl bromide which separated from the residue crystallised from acetone in pale yellow needles, m. p. 203° (Found : Br, 42.0%).

*Hydrolysis of the Isomeric Azoxybenzyl Bromides.*—Owing to the slight solubility of the *p*-isomeride in ethyl alcohol, the hydrolyses were carried out in aqueous propyl alcohol. Approximately 0.05 g. of the bromide was rapidly dissolved in 20 c.c. of propyl alcohol on the water-bath, 2 c.c. of water were added, and the whole was placed in the vapour of carbon tetrachloride for a definite time. In the table, *w* is the weight in grams of the bromide, *t* the time in hours from the addition of the alcohol, and *x* the percentage of the bromide changed, estimated by titration of the liberated hydrobromic acid with *N*/20-ammonia.

<i>t.</i>	<i>o</i> -Isomeride.		<i>m</i> -Isomeride.		<i>p</i> -Isomeride.	
	<i>w.</i>	<i>x.</i>	<i>w.</i>	<i>x.</i>	<i>w.</i>	<i>x.</i>
0.6	0.0496	60	—	—	—	—
1	0.0483	97	0.0530	22	0.0500	32
2	0.0564	100	0.0535	40	0.0470	53
4	—	—	0.0544	63	0.0500	77
8	—	—	0.0522	88	0.0506	96

A slight colour change was noticeable in the *o*-isomeride, but not in the other two.

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