# *The Oxidation of Phenylhydrazones. Part IV.**

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(*a*) The acid-catalysed rearrangements of benzylazoxybenzene have been studied.

(*b*) " Bisazoxybenzyl " (Bamberger and Renauld, *Ber.*, 1897, **30**, 2278) has been shown to be ω-azoxytoluene.

(*c*) The phenylhydrazones of certain aromatic and heterocyclic aldehydes and ketones have been oxidised with perphthalic acid.

Oxidation of benzaldehyde phenylhydrazone with perbenzoic or perphthalic acid yields benzylazoxybenzene (Part I, *J.*, 1953, 2517; Witkop and Kissman, *J. Amer. Chem. Soc.*, 1953, **75**, 1975). The present paper reports further investigation of similar compounds.

Bergmann, Ulpts, and Witte (*Ber.*, 1923, **56**, 679) found that benzylazoxybenzene rearranges to *N*-benzoyl-*N'*-phenylhydrazine in acetic acid at 150° (for milder conditions, see Experimental section); this rearrangement is closely similar to both the isomerisation of primary nitro-compounds to hydroxamic acids in hot sulphuric acid (Lippincott and Mass, *Ind. Eng. Chem.*, 1939, **31**, 118) and the conversion of primary aliphatic azoxy-compounds into *N*-acyl-*N'*-alkylhydrazines in hot hydrochloric acid (Langley, Lythgoe, and Rayner, *J.*, 1952, 4191). Although Bergmann *et al.* (*loc. cit.*) state that benzylazoxybenzene is unaffected by boiling hydrochloric acid, we have found that it is converted into benzaldehyde (40%) and benzoylazobenzene (45%) on prolonged treatment with 10N-hydrochloric or sulphuric acid.

The formation of these products may be explained by assuming that part of the benzylazoxybenzene is first converted into *N*-benzoyl-*N'*-phenylhydrazine (Bergmann *et al.*, *loc. cit.*) and that this is oxidised by unchanged benzylazoxybenzene forming benzoylazobenzene and benzaldehyde phenylhydrazone; the phenylhydrazone would then hydrolyse forming benzaldehyde:

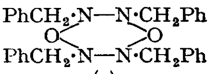
$$\mathrm{PhCH_2{\cdot}N(O){:}NPh \longrightarrow PhCO{\cdot}NH{\cdot}NHPh}$$

$$\mathrm{PhCH_2{\cdot}N(O){:}NPh + PhCO{\cdot}NH{\cdot}NHPh \longrightarrow PhCO{\cdot}N{:}NPh + PhCH{:}N{\cdot}NHPh}$$

$$\mathrm{PhCH{:}N{\cdot}NHPh + H_2O \longrightarrow PhCH{:}O + PhNH{\cdot}NH_2}$$

This reaction sequence is analogous to the interaction of hydrazobenzene and azoxybenzene, with the formation of two molecules of azobenzene (Freundler, *Bull. Soc. chim.*, 1904, **31**, 459). Confirmatory evidence results from the formation of benzoylazobenzene in excellent yield when benzylazoxybenzene is refluxed with *N*-benzoyl-*N'*-phenylhydrazine in ethanolic hydrochloric acid.

In order to prepare benzylazoxybenzene by an alternative method, we attempted its synthesis from *N*-benzylhydroxylamine and nitrosobenzene. This reaction has already been studied by Bamberger and Renauld (*Ber.*, 1897, **30**, 2278), who obtained a product " bisazoxybenzyl," m. p. 210°, to which they assigned structure (I) ($C_{28}H_{28}O_2N_4$). Repetition of this work gave a product having the properties described by Bamberger and Renauld (*loc. cit.*), but our molecular-weight determinations indicate the molecular formula $C_{14}H_{14}ON_2$. It was shown to be identical (mixed m. p.) with ω-azoxytoluene, prepared (in 30% and 14% yield, respectively) by the peracid oxidation of both ω-azotoluene and benzaldehyde benzylhydrazone. As azoxybenzene was also isolated from the reaction, it appears that the products are formed by a mutual oxidation–reduction process :


(I)

$$\mathrm{2PhCH_2{\cdot}NH{\cdot}OH + 2PhN{:}O \longrightarrow PhCH_2{\cdot}N(O){:}N{\cdot}CH_2Ph + PhN(O){:}NPh}$$

Such behaviour is common in these systems (cf. Taylor and Baker, " Sidgwick's Organic Chemistry of Nitrogen," Oxford, 1942, p. 432), although we used alkaline conditions, which

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* Part III, *J.*, 1954, 1650.

favour the formation of unsymmetrical azoxy-compounds (cf. Bamberger and Bernays, *Ber.*, 1902, **35**, 1624; Aston and Jenkins, *Nature*, 1951, **167**, 863; Anderson, *J.*, 1952, 1722).

In addition to the azoxy-compounds described in Part I (*loc. cit.*), we have found that oxidation of the phenylhydrazones of several *ortho*-substituted benzaldehydes, and of thiophen-2-aldehyde phenylhydrazone, with perphthalic acid gives excellent yields of the corresponding azoxy-compounds. Furfuraldehyde phenylhydrazone gave a fair yield of azoxy-compound (cf. Bergmann *et al.*, *loc. cit.*) but *p*-dimethylaminobenzaldehyde phenylhydrazone gave a hygroscopic product which could not be purified satisfactorily. In this case, it is likely that *N*-oxide formation has also occurred at the tertiary nitrogen atom, as in the similar oxidation of *p*-dimethylaminophenylazobenzene (Angeli, *Atti R. Accad. Lincei*, 1915, **24**, 1190).

When benzaldehyde *N*-methylphenylhydrazone was oxidised with perphthalic acid, only a small yield of nitrosobenzene could be isolated. Oxidation of this hydrazone obviously cannot give an azoxy-compound. Only acetophenone was isolated from the peracid oxidation of acetophenone *N*-methylphenylhydrazone.

## EXPERIMENTAL

(M. p.s are corrected. Microanalyses were performed under the direction of Dr. K. W. Zimmermann.)

*Reactions of Benzylazoxybenzene in Acid.*—(a) *Acetic acid.* Benzylazoxybenzene (3 g.) in glacial acetic acid (25 ml.) was refluxed (15 min.) and the solution poured into ice-water (100 ml.). The precipitate was crystallised from aqueous ethanol, giving needles (1·8 g.) of *N*-benzoyl-*N'*-phenylhydrazine, m. p. and mixed m. p. 168°.

(b) *Mineral acid.* Benzylazoxybenzene (2 g.) and 10N-hydrochloric or sulphuric acid (100 ml.) were refluxed (6 hr.). The mixture was distilled and the distillate added to a solution of 2 : 4-dinitrophenylhydrazine in hydrochloric acid. The precipitate was crystallised from glacial acetic acid, giving orange needles (0·90 g.), m. p. 234—236° (decomp.), undepressed on admixture with authentic benzaldehyde 2 : 4-dinitrophenylhydrazone.

The brilliant blue residue was dissolved in benzene–ethanol (1 : 1) and purified by chromatography on alumina, giving red plates (0·76 g.), m. p. 32—33°, identical with authentic benzoylazobenzene, which on reduction with zinc dust in acetic acid gave *N*-benzoyl-*N'*-phenylhydrazine, m. p. and mixed m. p. 168°.

(c) *Dehydrogenation of* N*-benzoyl-*N'*-phenylhydrazine.* Benzylazoxybenzene (1 g.) and *N*-benzoyl-*N'*-phenylhydrazine (1 g.) were refluxed (1 hr.) with 10N-hydrochloric acid (20 ml.) in ethanol (40 ml.). The solution was steam-distilled and the residue basified and extracted with ether. After evaporation and crystallisation of the residue from light petroleum (b. p. 30—90°), benzoylazobenzene (0·90 g.), m. p. 32°, was obtained.

*Per-acid Oxidations.*—(a) *Phenylhydrazones.* The phenylhydrazones listed below were oxidised by perphthalic acid in ethyl ether to the corresponding *azoxy*-compounds, as described in Part I (*loc. cit.*). The azoxy-compounds were crystallised from ethanol–pyridine.

| Phenylhydrazone oxidised | Yield (%) | M. p. (decomp.) | Found (%) | | | Required (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | C | H | N | C | H | N |
| *o*-Tolualdehyde | 80 | 188° | 74·2 | 6·0 | 12·5 | 74·3 | 6·2 | 12·4 |
| *o*-Chlorobenzaldehyde | 87 | 188 | — | — | 11·5 | — | — | 11·4 |
| Salicylaldehyde | 76 | 114·5 | 68·6 | 4·9 | — | 68·4 | 5·4 | — |
| Furfuraldehyde | 35 | *ca.* 110—130 | — | — | — | — | — | — |
| Thiophen-2-aldehyde | 70 | 148·5 | 60·3 | 4·5<br>(S, 14·7) | — | 60·5 | 4·6<br>(S, 14·7) | — |

(b) N*-Methylphenylhydrazones.* Benzaldehyde *N*-methylphenylhydrazone (4 g.) and perphthalic acid (3·5 g.) in ethyl ether (50 ml.) were set aside for 4 days. Residual acids were removed in the usual manner, and the ether was evaporated. A portion (0·5 g.) of the residue (3·0 g.) was refluxed (30 min.) with aniline (0·5 ml.) in acetic acid (5 ml.). *trans*-Azobenzene (0·1 g.), m. p. and mixed m. p. 68°, was obtained after evaporation and crystallisation from ethanol.

Acetophenone *N*-methylphenylhydrazone (5 g.) was added to a solution of perphthalic acid (3·6 g.) in ethyl ether (100 ml.), and the solution shaken vigorously. After the solution had been set aside for 1 hr., phthalic acid was removed in the usual way. The ethereal solution was extracted with 2N-hydrochloric acid at 0°, and the acid layer was basified and extracted with ether. Evaporation of this extract gave an oil which would not form a picrate. Evaporation of the original ether solutions and distillation of the residue gave acetophenone, b. p. 200° (phenylhydrazone, m. p. and mixed m. p. 105°).

(c) ω-*Azotoluene and benzaldehyde benzylhydrazone.* ω-Azotoluene [prepared by a method analogous to that used by Langley, Lythgoe, and Rayner (*loc. cit.*) for ω-azo-*p*-chlorotoluene] (2·8 g.) was added to a solution of perphthalic acid (5·5 g.) in ethyl ether (200 ml.), and the mixture was set aside in the refrigerator for 3 days. The precipitate was crystallised from *o*-xylene–ethanol, giving needles (1·0 g.) of ω-*azoxytoluene*, m. p. 209° (decomp.) (Found: C, 74·25; H, 6·2; N, 12·2. $C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%).

Similar oxidation of benzaldehyde benzylhydrazone gave the above azoxy-compound in 14% yield.

*Attempted Synthesis of Benzylazoxybenzene.*—*N*-Benzylhydroxylamine hydrochloride (Jones and Sneed, *J. Amer. Chem. Soc.*, 1917, **39**, 674) (4 g.), nitrosobenzene (4 g.), and sodium hydroxide (2 g.) in ethanol (200 ml.) were warmed to 40°, the solution becoming red-brown. The mixture was cooled and the precipitate crystallised from *o*-xylene, giving needles (2·5 g.), m. p. 209° (decomp.) undepressed on admixture with ω-azoxytoluene [Found: C, 74·4; H, 5·6%; *M* (Rast), 196. Calc. for $C_{14}H_{14}ON_2$: *M*, 226]. *trans*-Azoxybenzene, m. p. and mixed m. p. 36°, was isolated from the filtrate after evaporation and crystallisation from ethanol.

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