513. *The Oxidation of Phenylhydrazones with Perphthalic Acid. Part I.*

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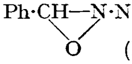
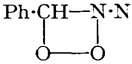
It has been shown that benzaldehyde phenylhydrazone reacts with perphthalic acid forming benzylazoxybenzene. Similar oxidation of a number of substituted benzaldehyde phenylhydrazones has also been investigated.

BERGMANN, ULPTS, and WITTE (*Ber.*, 1923, **56**, 679) found that benzaldehyde phenylhydrazone, $C_{13}H_{12}N_2$, was oxidized by perbenzoic acid (we have used perphthalic acid) to a compound, $C_{13}H_{12}ON_2$, m. p. 201°, to which they assigned structure (I). This structure resembles that (II) proposed by Busch and Dietz (*Ber.*, 1914, **47**, 3277) for the autoxidation


(I)


(II)

Ph·N:N·CHPh·O·OH
(III)

product of benzaldehyde phenylhydrazone, which has since been shown to be (III) (Pausacker, *J.*, 1950, 3478; Criegee and Lohaus, *Chem. Ber.*, 1951, **84**, 219). By analogy, it might be expected that the per-acid oxidation product would be Ph·N:N·CHPh·OH, which would immediately rearrange forming *N*-benzoyl-*N'*-phenylhydrazine. However, as this has m. p. 168°, it is obviously not the product (cf. Bergmann, Ulpts, and Witte, *loc. cit.*). Two other simple possibilities are benzylazoxybenzene (IV) and ω-phenylazoxytoluene (V).

$Ph{\cdot}CH_2{\cdot}N(O){:}NPh$
(A) (IV) (B)

$Ph{\cdot}CH_2{\cdot}N{:}N(O)Ph$
(A) (V) (B)

$Ph{\cdot}CH_2{\cdot}N(O){:}N{\cdot}C_6H_4Br\text{-}p$
(VI)

The infra-red absorption spectrum of the per-acid oxidation product (kindly measured by courtesy of Professor J. D. Roberts of the Massachusetts Institute of Technology) has strong bands at 6·73 and 6·91 μ, and less intense bands at 7·57 and 7·67 μ. This indicates the possibility of an azoxy-structure as Langley, Lythgoe, and Rayner (*J.*, 1952, 4193) found that characteristic vibrations of the azoxy-group (in azoxymethane) are in the 6·55 and the 7·45 μ region and that C–H deformation modes occur at 7·24 and 6·96 μ. Furthermore, no significant absorption is present in the regions 2·88—3·28 and 5·89—6·00 μ, indicating the absence of $-NH-$ and $>C{=}N-$ groups respectively.

Confirmatory evidence results from reduction of the per-acid oxidation product to benzaldehyde phenylhydrazone in excellent yield by lithium aluminium hydride. This is in accord with Brown and Nystrom's finding (*J. Amer. Chem. Soc.*, 1948, **70**, 3738) that the reduction of azoxybenzene by lithium aluminium hydride yields azobenzene quantitatively.

As would be expected on the basis of the azoxy-structure, neither acetophenone nor benzaldehyde *N*-methyl-*N*-phenylhydrazone could be oxidized by perphthalic acid to a product containing an oxygen atom; some reaction did, however, take place (as shown by the titration of " active " oxygen), and it is intended to investigate these reactions in detail.

Bromination was used to distinguish between (IV) and (V), as in the recorded elucidations of the structures of unsymmetrical azoxy-compounds (cf. Angeli and Valori, *Atti R. Accad. Lincei*, 1912, (v), **21**, 155; Bigiavi and Sabatelli, *Gazzetta*, 1927, **57**, 559). Bromination readily occurred and this indicates that structure (IV) is correct as the benzene ring (B) in (IV) would be the only one that would be substituted readily. The bromination product was assigned structure (VI) as it was found to be identical (mixed m. p.) with the per-acid oxidation product of benzaldehyde *p*-bromophenylhydrazone.

If the mechanism of the per-acid oxidation is assumed to be:

$$Ph{\cdot}CH{:}N{\cdot}NHPh \rightleftharpoons \underset{(VII)}{Ph{\cdot}CH_2{\cdot}N{:}NPh} \longrightarrow Ph{\cdot}CH_2{\cdot}N(O){:}NPh$$

then structure (IV) is also more likely than (V) since the nitrogen atom attached directly to the benzyl group in (VII) is the more basic, and it has been shown (Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692) that per-acids are electrophilic reagents. Furthermore, (IV) would be stabilized by resonance between the azoxy-group and the phenyl group (B) whereas this is not possible in (V).

A number of nuclear-substituted benzaldehyde phenylhydrazones have been oxidised by perphthalic acid and the yields determined, as it is intended to investigate this reaction kinetically.

Langley, Lythgoe, and Rayner (*loc. cit.*) have stated that they have investigated the compound obtained by the action of perbenzoic acid on benzaldehyde phenylhydrazone and " whatever its structure, it was not the expected azoxy-compound." No experimental evidence is given to support this statement. However, these authors found that primary aliphatic azoxy-compounds reacted with mineral acid to yield a carboxylic acid and a hydrazine. This further supports structure (IV) as Bergmann, Ulpts, and Witte (*loc. cit.*) found that the per-acid oxidation product reacts with acetic acid forming *N*-benzoyl-*N'*-phenylhydrazine.

EXPERIMENTAL

(M. p.s are corrected. Microanalyses are by Dr. W. Zimmermann.)

Per-acid Oxidation of Substituted Benzaldehyde Phenylhydrazones.—Perphthalic acid (5×10^{-3} mole) in ether (20 ml.) was added to the appropriate benzaldehyde phenylhydrazone (5×10^{-3} mole). After 2 days the product was filtered off. Phthalic acid was removed from the filtrate by extraction with sodium hydrogen carbonate solution, and a further amount of product obtained by evaporation of the ether under reduced pressure. Yields, m. p.s, and analyses of the *azoxy*-compounds are shown in the following Table; primed numerals (2', etc.) refer to positions in the benzene ring B.

				Found (%)			
Substituent	Yield (%)	M. p. (with decomp.)	Solvent	C	H	N	Cl
—	96	201°	Pyridine	—	—	—	—
3-Me	94	177	,,	74·8	5·9	12·5	—
4-Me	98	180	,,	74·2	6·0	12·3	—
3'-Me	98	172	Ethyl acetate	74·1	6·1	12·2	—
4'-Me	96	187	Ethanol–pyridine	74·2	5·8	12·4	—
	$C_{14}H_{14}ON_2$ requires C, 74·3; H, 6·2; N, 12·4%.						
3-OMe	100	173	Ethanol–pyridine	69·7	5·7	11·7	—
4-OMe	94	176	,,	69·4	5·8	11·8	—
3'-OMe	92	168	,,	69·4	5·8	11·7	—
4'-OMe	96	173	,,	69·5	5·5	11·8	—
	$C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8; N, 11·6%.						
3-Cl	95	186·5	Ethanol–pyridine	—	—	11·4	14·4
4-Cl	97	182·5	,,	—	—	11·3	14·4
3'-Cl	97	163·5	Pyridine	—	—	11·5	13·9
4'-Cl	99	186·5	,,	—	—	11·1	14·3
	$C_{13}H_{11}ON_2Cl$ requires N, 11·4; Cl, 14·4%.						
3-NO_2	90	169	Ethanol–pyridine	60·7	3·9	16·1	—
4-NO_2	94	135	,,	60·6	4·4	16·5	—
3'-NO_2	90	192	Ethyl acetate	61·0	4·5	16·4	—
	$C_{13}H_{11}O_3N_3$ requires C, 60·7; H, 4·3; N, 16·3%.						
4'-Br	97	203	Pyridine	53·9	3·8	9·3	—
	$C_{13}H_{11}ON_2Br$ requires C, 53·6; H, 3·8; N, 9·6%.						
Ph·CH:N·NH·$C_{10}H_7$-β	95	172·5	Ethyl acetate	77·6	5·0	10·8	—
	$C_{17}H_{14}ON_2$ requires C, 77·9; H, 5·4; N, 10·7%.						

Reduction of (IV) *with Lithium Aluminium Hydride.*—The azoxy-compound (IV) (0·45 g.) in dry ether (500 ml.) was refluxed (8 hr.) with lithium aluminium hydride (0·05 g., in 50 ml. of dry ether). Excess of hydride was destroyed with moist ether (100 ml.), the aluminium hydroxide filtered off, and the filtrate dried (Na_2SO_4). Upon evaporation and crystallization from aqueous ethanol, benzaldehyde phenylhydrazone (0·35 g.) was obtained, having m. p. 156—157°, and mixed m. p. with authentic material 157—158°.

Bromination.—Bromine (3 g.) in pyridine (20 ml.) was added to the azoxy-compound (IV) (1·25 g.) in pyridine (100 ml.), and the mixture refluxed for 10 min. and then set aside for 3 days. The precipitate (1·6 g.) formed on addition of ethanol (100 ml.) was filtered off and crystallized from pyridine. It had m. p. 202—203° (decomp.), mixed m. p. with (IV) 190—194°, and mixed m. p. with (VI) 202—203° (decomp.).

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