404. *Oxidations with Phenyl Iodosoacetate. Part II.* The Oxidation of Primary Aromatic Amines.*

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Some primary aromatic amines have been oxidised by phenyl iodosoacetate in benzene and the nature of some of the products has been examined.

ALTHOUGH primary aromatic amines have been oxidised with a number of different reagents, there is relatively little evidence concerning the effect of structure on the nature of the product. The only investigation of this nature is by Saunders *et al.* (see *J.*, 1951, 3433, for preceding references), who have investigated the action of hydrogen peroxide, catalysed by the enzyme peroxidase, on several primary aromatic amines. In the present work, fifteen primary aromatic amines have been oxidised by phenyl iodosoacetate in benzene solution.

In preliminary experiments, the amine (*ca.* 5 × 10^{-4} mole) and phenyl iodosoacetate (*ca.* 15 × 10^{-4} mole) were dissolved in dry benzene (25 ml.) and 1-ml. aliquots were withdrawn daily and titrated with *ca.* 0·05N-sodium thiosulphate after the addition of acidified potassium iodide. In addition, it was found that characteristic colours were obtained when *ca.* 1 mg. of amine was added to 2 ml. of a 1% solution of phenyl iodosoacetate in glacial acetic acid. The results are in Table 1.

TABLE 1.

Compound	$PhI(OAc)_2$ consumed (mol.)	Days reqd. for completion	Immediate colour	Colour after 1 hr.
Aniline	1·92	2	Transient purple, then deep green, becoming brown	Dark brown
o-Toluidine	1·62	2	Purple, becoming mauve	Deep carmine
m- ,, ...	1·58	1	Transient pink, then dark brown	Dark brown
p- ,, ...	1·94	1	Light brown	Light brown
o-Chloroaniline	1·51	4	Pale brown	Light brown
m- ,, ...	1·13	1	Wine-red	Deep red-brown
p- ,, ...	1·62	2	Pink	Red
o-Anisidine	1·67	2	Dark brown	Dark brown
p- ,, ...	1·56	1	Purple slowly appearing	Deep carmine
o-Nitroaniline	1·16	2	Yellow	Yellow
m- ,, ...	1·05	2	Yellow	Light brown
p- ,, ...	1·16	2	Yellow	Dark yellow
α-Naphthylamine ...	1·60	1	Blue green, rapidly becoming brown	Light brown
β- ,, ...	1·89	1	Light brown	Red brown

When the amines were treated with phenyl iodosoacetate, in the ratios shown, the corresponding azo-compounds were the only products that could be isolated from the following (percentage yields in parentheses): aniline (95); *o*-toluidine (42); *m*-toluidine (56); *p*-toluidine (6); *o*-chloroaniline (39); *m*-chloroaniline (66); *p*-chloroaniline (55); *o*-anisidine (3); *m*-nitroaniline (65); *p*-nitroaniline (53); and α-naphthylamine (3).

When *o*-nitroaniline was oxidised, benzofurazan oxide was formed in 81% yield. Green and Rowe (*J.*, 1912, **101**, 2449) have reported that *o*-nitroaniline is converted into benzofurazan oxide by alkaline sodium hypochlorite but into the corresponding azo-compound under neutral conditions (*J.*, 1912, **101**, 2455). Similarly, phenyl iodosoacetate converted 4-methyl- and 4-chloro-2-nitroaniline and 2 : 4-dinitroaniline into the corresponding benzofurazan oxides in yields of 96%, 91%, and 94% respectively.

β-Naphthylamine is oxidised to 1 : 2 : 6 : 7-dibenzophenazine (28%) and a product, $C_{25}H_{20}O_5N_2$, which has a green metallic lustre, gives a deep blue solution in nitrobenzene, and resembles that obtained by Liebermann (*Annalen*, 1876, **183**, 265) on oxidation of β-naphthylamine by ferric chloride. 1 : 2 : 6 : 7-Dibenzophenazine has previously been

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* Part I is considered to be " The Oxidation of Glycols by Aryl Iodosoacetates," *J.*, 1953, 107.

obtained (Claus and Jaeck, D.R.-P. 78,748) by the oxidation of β-naphthylamine with calcium hypochlorite.

Although *p*-anisidine and *p*-phenetidine were converted into the azo-compounds in yields of 5% and 7% respectively, several other compounds could be isolated. The products from *p*-anisidine differed from those reported by Daniels and Saunders (*J.*, 1951, 2112). A study of the oxidation of alkoxy- and aryloxy-amines will be reported later.

Pausacker (*loc. cit.*) suggested that the azo-compounds are formed as follows:

$$2\text{PhI(OAc)}_2 + 2\text{Ar}\cdot\text{NH}_2 \rightleftharpoons 2\text{PhI(OAc)}\cdot\text{NHAr} + 2\text{AcOH}$$

$$2\text{PhI} + 2\text{AcOH} + \text{Ar}\cdot\text{N}\vdots\text{N}\cdot\text{Ar} \longleftarrow 2\text{PhI(OAc)}\cdot + \text{Ar}\cdot\text{NH}\cdot\text{NH}\cdot\text{Ar} \longleftarrow 2\text{Ar}\cdot\text{NH}\cdot + 2\text{PhI(OAc)}\cdot$$

Partial confirmation comes in oxidation of hydrazobenzene to azobenzene in 92% yield by phenyl iodosoacetate. This type of free-radical mechanism can also be extended to explain the formation of 1 : 2 : 6 : 7-dibenzophenazine from β-naphthylamine and of benzofurazan oxide from *o*-nitroaniline.

EXPERIMENTAL

Analyses are by Dr. W. Zimmermann.

The amount of phenyl iodosoacetate indicated in Table 1 was dissolved in dry thiophen-free benzene (30 ml. per g.), and the amine (*ca.* 1—2 g.) added. After the required time at room temperature, the solution was concentrated and chromatographed on alumina, with benzene as eluant. The azo-compound (or benzofurazan oxide) was in the bottom band. Azobenzene was identified by m. p. (68°) and mixed m. p. The m. p.s and analyses of the other azo-compounds are in Table 2.

TABLE 2.

Substituents in azobenzene	M. p. found	M. p. lit.	Solvent	Found (%): C	Found (%): H	Found (%): N	Calc. (%): C	Calc. (%): H	Calc. (%): N
2 : 2′-Me_2	52°	55°	Ethanol	—	—	12·9	—	—	13·3
3 : 3′-Me_2	50	55	Methanol	—	—	13·2	—	—	—
4 : 4′-Me_2	142	143	Ethanol	—	—	13·0	—	—	—
2 : 2′-Cl_2	136	137	Benzene	57·1	3·2	10·8	57·5	3·2	11·15
3 : 3′-Cl_2	103	101	,,	57·5	3·3	10·9	—	—	—
4 : 4′-Cl_2	184	184	,,	57·4	3·4	10·8	—	—	—
3 : 3′-$(NO_2)_2$	152	153	*cyclo*Hexane	53·2	3·0	21·0	52·95	2·9	20·6
4 : 4′-$(NO_2)_2$	219	220	Benzene	53·0	2·9	21·0	—	—	—
2 : 2′-$(OMe)_2$	154	153	Methanol	—	—	11·5	—	—	12·0
4 : 4′-$(OMe)_2$	163	164	,,	—	—	11·6	—	—	—
4 : 4′-$(OEt)_2$	160	160	Ethanol	71·5	7·1	10·4	71·1	6·7	10·4
1 : 1′-Azonaphthalene	190	190	Light petroleum (b. p. 80—100°)	85·3	5·0	9·9	85·1	5·0	9·9

Table 3 summarises the data for the products formed on oxidation of the *o*-nitroanilines and crystallised from light petroleum (b. p. 40—60°).

Substituent in benzofurazan oxide	M. p. found	M. p. lit.	Found (%): C	Found (%): H	Found (%): N	Calc. (%): C	Calc. (%): H	Calc. (%): N
—	70°	72°	53·5	3·1	20·2	53·0	2·9	20·6
5-Cl	48	48	42·5	2·0	—	42·2	1·8	—
5-NO_2	67	72	39·9	1·7	—	39·9	1·7	—
5-Me	96	97	56·3	4·0	19·1	56·0	4·0	18·7

Oxidation of β-*Napthylamine.*—β-Naphthylamine (1·40 g.) was added to phenyl iodosoacetate (6·7 g.) in dry thiophen-free benzene (200 ml.). After 2 days at room temperature, the solution was filtered, yielding a compound (0·92 g.) with a green metallic lustre. This was insoluble in most organic solvents and could only be crystallised from nitrobenzene in which it formed a deep blue solution; it had m. p. >300° (Found: C, 69·8, 69·6; H, 4·4, 4·4; N, 6·6, 6·5. Calc. for $C_{25}H_{20}O_5N_4$: C, 70·0; H, 4·7; N, 6·5%). The initial filtrate was concentrated and chromatographed on alumina. A red band was obtained which yielded 1 : 2 : 6 : 7-dibenzophenazine (0·40 g.; m. p. 286°; lit. m. p. 284°) after crystallisation from benzene (Found: C, 85·3; H. 4·3: N, 10·1. Calc. for $C_{20}H_{12}N_2$: C, 85·7; H, 4·3; N, 10·0%).

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