Oxidations with Lead Tetra-acetate. Part II. The Oxidation of Primary Aromatic Amines.*

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Some monosubstituted anilines and α- and β-naphthylamine have been oxidised by lead tetra-acetate in acetic acid.

THE oxidation of primary aromatic amines with phenyl iodosoacetate in benzene (Pausacker, *J.*, 1953, 1989) and in acetic acid (Barlin, Pausacker, and Riggs, *J.*, 1954, 3122) has recently been investigated. The present paper reports a study of the action of lead tetra-acetate in acetic acid.

In preliminary experiments, the amine (*ca.* 1·5—2 × 10^{-4} mole) and lead tetra-acetate (*ca.* 1·5 × 10^{-3} mole) were dissolved in glacial acetic acid (25 ml.), and 1-ml. portions were withdrawn daily and titrated with standardised 0·02N-sodium thiosulphate, after the addition of acidified potassium iodide. An allowance was made for the slight decomposition recorded in a blank experiment. It was also found that intense colours

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* "The Oxidation of Glycols with Lead Tetra-acetate," *J.*, 1953, 102, is considered to be Part I.

were produced immediately a solution of lead tetra-acetate (5%; 2 ml.) was added to the amine (*ca.* 2 mg.). The results are shown in Table 1.

TABLE 1.

Subst. in aniline	—	*o*-Me	*m*-Me	*p*-Me	*o*-Cl	*m*-Cl	*p*-Cl	*o*-OMe
$Pb(OAc)_4$ consumed, mols.	4·40	4·47	3·83	3·02	4·07	1·86	3·22	5·58
Immediate colour	violet	violet	violet	violet	brown	red-violet	red-violet	brown
Subst. in aniline	*p*-OMe	*p*-OEt	*o*-NO_2	*m*-NO_2	*p*-NO_2	α-$C_{10}H_7{\cdot}NH_2$	β-$C_{10}H_7{\cdot}NH_2$	
$Pb(OAc)_4$ consumed, mols.	3·60	3·71	1·46	2·00	1·50	4·50	3·04	
Immediate colour	violet	red-violet	orange	red-brown	orange	deep-red	deep-red	

The initial consumption of lead tetra-acetate was rapid and usually followed by a slow reaction during several days. The molar uptake was, in general, greater than that of phenyl iodosoacetate in either benzene or acetic acid.

In most cases the corresponding azo-compound was formed either alone or with other products. The percentage yields of azo-compounds are shown in parentheses—the second and third figures indicating the yields when phenyl iodosoacetate was used in benzene and in acetic acid, respectively: aniline (5, 95, 0); *o*-toluidine (23, 42, 0); *m*-toluidine (18, 56, 0); *p*-toluidine (4, 6, 0); *o*-chloroaniline (56, 39, 25); *m*-chloroaniline (39, 66, 34); *p*-chloroaniline (35, 55, 24); *o*-anisidine (10, 3, 1); *p*-anisidine (16, 5, 4); *o*-nitroaniline (15, 0, 71); *m*-nitroaniline (40, 65, 61); *p*-nitroaniline (43, 53, 63); α-naphthylamine (0, 3, 0); β-naphthylamine (0, 0, 0); and *p*-phenetidine (26, 7, -).

It can be seen that the three different methods give widely different yields of azo-compound; however, those amines containing electron-attracting groups tend to give relatively higher yields.

It is assumed that the reaction mechanism is analogous to that already proposed (Pausacker, *loc. cit.*) for phenyl iodosoacetate:

$$\begin{tikzcd}
2Pb(OAc)_4 + 2Ar{\cdot}NH_2 \arrow[r, shift left, "\rightleftharpoons", phantom] & 2Pb(OAc)_3{\cdot}NHAr + 2AcOH \arrow[r, phantom, "\rightleftharpoons"] & 2Ar{\cdot}NH{\cdot} + 2Pb(OAc)_3{\cdot} \arrow[d] \\
2Pb(OAc)_2 + 2AcOH + ArN{:}NAr & & ArNH{\cdot}NHAr + 2Pb(OAc)_3 \arrow[ll]
\end{tikzcd}$$

This is partially confirmed since hydrazobenzene is oxidised to azobenzene in 95% yield by lead tetra-acetate in acetic acid. As azobenzene is isolated in only 5% yield from the oxidation of aniline, the intermediate PhNH· radical must enter into side-reactions.

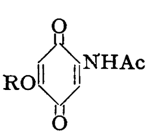
Although benzofurazan oxide was the sole product from the oxidation of *o*-nitroaniline with phenyl iodosoacetate in benzene, it has been found that only 2 : 2′-dinitroazobenzene (15% yield) could be obtained in the present work. This is in accord with the results obtained by using phenyl iodosoacetate in acetic acid, and the explanation is probably that to be given by us elsewhere (*J.*, 1954, in the press). The action on *o*-nitroaniline of lead tetra-acetate in benzene was also studied; the only product isolated was again 2 : 2′-dinitroazobenzene (57% yield). Apparently the formation of the *aci*-nitro-form of *o*-nitroaniline has been repressed (*idem, loc. cit.*) owing to the more polar nature of lead tetra-acetate than of phenyl iodosoacetate.

As stated above, the corresponding azo-compounds were formed during the oxidation of *p*-anisidine and *p*-phenetidine in yields of 16% and 26%, respectively. In addition, compounds *A*, $C_9H_9O_4N$, m. p. 194° (80% yield), and *B*, $C_{10}H_{11}O_4N$, m. p. 216° (59% yield), were also isolated.

Compound *A* contained one acetoxyl and one methoxyl group. It gave a yellow solution in sulphuric acid, but a deep crimson colour with sodium hydroxide solution; this was discharged by addition of zinc dust. After removal of the zinc, a faint pink colour slowly appeared. This suggests a quinonoid structure. During alkaline hydrolysis of compound *A*, 0·97 mole of ammonia was evolved.

Barlin and Riggs (*J.*, 1954, 3125) report the formation (in trace amounts) of a compound, m. p. 216°, from the oxidation of phenacetin with phenyl iodosoacetate in acetic acid. The m. p. of compound *B* is undepressed on admixture with a sample kindly supplied by Dr. Riggs.

On the basis of the above evidence, structure (I) appears most likely for compounds *A* and *B*.



(I; *A*, R = Me; *B*, R = Et)

Dr. Riggs informs us that the ultra-violet absorption spectrum of compound *B* is consistent with the proposed structure (cf. Braude, *J.*, 1945, 490).

The sole product isolated from the oxidation of α-naphthylamine was 1 : 4-naphthaquinone in 16% yield. Oxidation with phenyl iodosoacetate in benzene solution (Pausacker, *loc. cit.*) gave only a low yield (3%) of 1 : 1′-azonaphthalene.

1 : 2-6 : 7-Dibenzophenazine (3% yield), 2-amino-1 : 4-naphthaquinone (25% yield), and 2-acetamido-1 : 4-naphthaquinone 1-β-naphthylamine anil (60% yield) were isolated from the oxidation of β-naphthylamine. 1 : 2-6 : 7-Dibenzophenazine (29%) and an unidentified high-melting substance (66%) were formed by oxidation of β-naphthylamine by phenyl iodosoacetate in benzene (*idem, loc. cit.*), and with phenyl iodosoacetate in acetic acid (Barlin, Pausacker, and Riggs, *loc. cit.*) 2-acetamido-1 : 4-naphthaquinone (34%), 2-acetamido-1 : 4-naphthaquinone 1-β-naphthylamine anil (25%), and an unidentified high-melting substance (14%) are formed.

Thus, although phenyl iodosoacetate and lead tetra-acetate are generally regarded as being oxidising agents of the same type, they may effect widely different oxidations with aromatic amines. It is also apparent that their mode of action is conditioned by the solvent used (cf. Barron, Cavill, Cole, Gilham, and Solomon, *Chem. and Ind.*, 1954, 76).

EXPERIMENTAL

All melting points are corrected. Analyses are by Dr. W. Zimmermann.

Method.—The amine (*ca.* 1—2 g.) and an acetic acid solution of the amount of lead tetra-acetate indicated in Table 1 were set aside at room temperature until reaction was complete. The solvent was removed under reduced pressure and the residue extracted with hot benzene. The cooled benzene extract was filtered, concentrated to *ca.* 50 ml., and chromatographed on alumina, benzene being used as eluant. Azo-compounds were in the bottom band and were identified by m. p. and mixed-m. p. determinations. The results are in Table 2.

Products.—The products of the oxidations are :

Hydrazobenzene yielded azobenzene (95%), m. p. and mixed m. p. 68°.

p-Anisidine (4·03 g.) yielded (*a*) 4 : 4′-dimethoxyazobenzene (0·632 g.), m. p. and mixed m. p. 163° (from methanol), and (*b*) *compound* A (3·21 g.), orange needles (from ethanol), m. p. 194° (Found: C, 55·6, 55·4; H, 4·7, 4·6; N, 7·3; OMe, 15·9; Ac, 21·6%; *M*, 211, 224. $C_9H_9O_4N$ requires C, 55·4; H, 4·6; N, 7·2; 1OMe, 15·9; 1Ac, 22·0%; *M*, 195).

TABLE 2.

Substituents in azobenzene	—	2 : 2′-Me_2	3 : 3′-Me_2	4 : 4′-Me_2	2 : 2′-Cl_2	3 : 3′-Cl_2
M. p., found	68°	53	54	143	135	101
M. p., lit.	68°	55	55	143	137	101

Substituents in azobenzene	4 : 4′-Cl_2	2 : 2′-$(OMe)_2$	2 : 2′-$(NO_2)_2$	3 : 3′-$(NO_2)_2$	4 : 4′-$(NO_2)_2$
M. p., found	184	153	210	152	221
M. p., lit.	184	153	210	153	220

Hydrolysis of compound *A* with sodium hydroxide (20%) gave an alkaline gas which was distilled into standard acid. Back-titration of the excess of acid indicated that 0·97 mole of base had been formed. An aqueous solution of the base showed with ferric sulphate a negative test for hydroxylamine (cf. Meyeringh, *Ber.*, 1877, **10**, 1940), but gave a positive test for ammonia with Nessler's reagent.

p-Phenetidine (1·93 g.) yielded (*a*) 4 : 4′-diethoxyazobenzene (0·502 g.), m. p. and mixed m. p. 160° (from ethanol), and (*b*) *compound* B (1·15 g.), which crystallised from ethanol as mustard-coloured needles, m. p. 216° (Found: C, 57·2, 57·5; H, 5·2, 5·4; N, 6·8; OEt, 17·2. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7; 1OEt, 21·5%).

α-Naphthylamine yielded 1 : 4-naphthaquinone (16%) which, after vacuum-sublimation at 100° and crystallisation from light petroleum (b. p. 90—110°), had m. p. and mixed m. p. 124° (sealed tube). This gave a characteristic red-brown solution in sodium hydroxide.

β-Naphthylamine (6·00 g.) yielded (*a*) 1 : 2-6 : 7-dibenzophenazine (0·169 g.), m. p. and mixed m. p. 283° (from benzene); (*b*) 2-acetamido-1 : 4-naphthaquinone 1-β-naphthylamine anil (3·62 g.), which crystallised from benzene or ethanol as red plates or purple needles, m. p. 209° (Found: C, 77·3, 77·5; H, 4·7, 4·7; Ac, 11·7. Calc. for $C_{22}H_{16}O_2N_2$: C, 77·6; H, 4·7; 1Ac, 12·6%) [the latter compound had properties identical with that obtained from the oxidation of β-naphthylamine with phenyl iodosoacetate in acetic acid (Barlin, Pausacker, and Riggs, *loc. cit.*) and a mixture of the two specimens showed no depression of m. p.]; and (*c*) 2-amino-1 : 4-naphthaquinone (1·48 g.), which had m. p. and mixed m. p. 207° (from benzene or ethanol) (Found: C, 69·8; H, 4·2; N, 8·35. Calc. for $C_{10}H_7O_2N$: C, 69·5; H, 4·05; N, 8·1%).

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