Oxidations with Phenyl Iodosoacetate. Part IV. The Oxidation of Substituted* o-*Nitroanilines.*

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Some substituted *o*-nitroanilines have been oxidised with phenyl iodosoacetate in benzene, and the nature of the products has been determined. The mechanism of the reaction is discussed.

o-NITROANILINE, 4-methyl- and 4-chloro-2-nitroaniline, and 2 : 4-dinitroaniline are converted into the corresponding benzofurazan oxides, in excellent yield, by phenyl iodosoacetate in benzene (cf. Part II, *J.*, 1953, 1989).

We have now found that 5-methyl-, 5-chloro-, and 5-methoxy-2-nitroaniline are similarly oxidised in yields of 90—93%. The products are identical with those obtained by the oxidation of either the 4- or 5-substituted 2-nitroanilines with alkaline sodium hypo-

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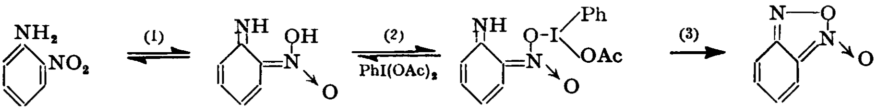
* Part III, *J.*, 1954, 3122.

chlorite by Green and Rowe's method (*J.*, 1912, **101**, 2452). When 1-nitro-2-naphthylamine was oxidised, both 1 : 1′-dinitro-2 : 2′-azonaphthalene (3%) and naphthofurazan oxide (86%) were obtained. Similarly, the oxidation of 2-nitro-1-naphthylamine yielded 2 : 2′-dinitro-1 : 1′-azonaphthalene (3%) and the same naphthofurazan oxide, but in only 7% yield. From the oxidation of 4-methoxy-2-nitroaniline, the only isolable product was, surprisingly, 4 : 4′-dimethoxy-2 : 2′-dinitroazobenzene in 5% yield. The corresponding benzofurazan oxide was, however, obtained in quantitative yield when 4-methoxy-2-nitroaniline was oxidised with alkaline sodium hypochlorite.

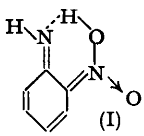
We therefore suggest the following mechanism for the formation of benzofurazan oxides from *o*-nitroanilines :

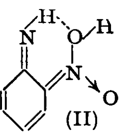


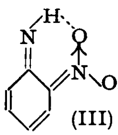
Stage (1) is comparable with that proposed by Green and Rowe (*loc. cit.*) as the first stage in the oxidation by sodium hypochlorite. The position of the equilibrium of this ketamine–enamine tautomerism would be affected by substituents. Those substituents which either withdraw electrons from the amino-group or increase the electron density on the nitro-group would favour the formation of the *aci*-nitro-compound which, it is suggested, is then oxidised to the benzofurazan oxide. If *aci*-nitro-compound formation is not favoured, " normal " oxidation to the azo-compound will presumably take place according to the mechanism proposed in Part II.

On this basis, the marked difference in behaviour between 4- and 5-methoxy-2-nitroanilines can now be interpreted. In 5-methoxy-2-nitroaniline, the methoxyl group should decrease the electron density on the amino-group and increase the electron density on the nitro-group, thus favouring *aci*-nitro-compound formation. In 4-methoxy-2-nitroaniline, the methoxyl group should increase the electron density on the amino-group and decrease the electron density on the nitro-group. Furazan oxide could not then be obtained, and only a low yield of the corresponding azo-compound is isolated.

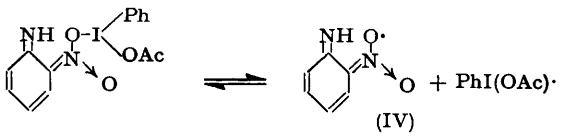
The intermediate *aci*-nitro-compound would be expected to show marked hydrogen bonding in the forms (I), (II), or (III). Pauling (" Nature of the Chemical Bond," Oxford Univ. Press, 1950, p. 307) has noted that, in general, the greater the electronegativity of an atom, the greater its power to form hydrogen bonds. The relative order of stability should therefore be (III) > (II) > (I). The hydrogen attached to oxygen is thus less strongly bonded than the hydrogen attached to nitrogen. It has been shown in the reaction of glycols with lead tetra-acetate (Cordner and Pausacker, *J.*, 1953, 102) and of nitrophenols with phenyl iodosoacetate (Part I; *J.*, 1953, 107) that hydrogen atoms involved in hydrogen bonding are not readily attacked by these reagents. This is now further confirmed as it has been found that *o*-nitroacetanilide and *N*-methyl-*o*-nitroaniline do not react with phenyl iodosoacetate. Thus stage (2), which is the esterification step already proposed in Part I for the oxidation of glycols by the same reagent, should take place at the O–H and not the N–H bond.

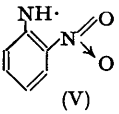

(I)


(II)

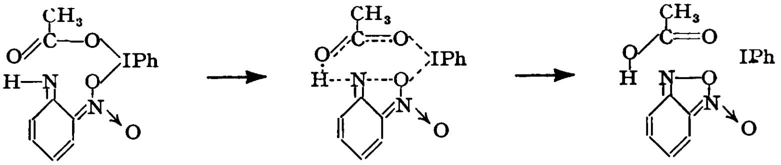

(III)

Stage (3) cannot involve a simple homolytic fission of the type discussed in Part I :

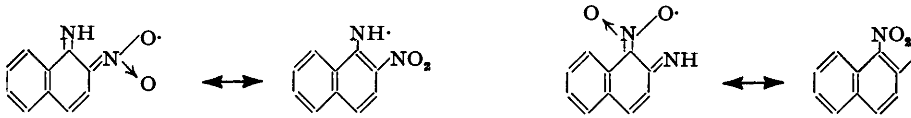

(IV)


(V)

for (IV) is merely one contributing form of a resonance hybrid, another of whose forms would be (V). As this is the type of intermediate postulated in Part I as a precursor in the formation of azo-compounds, the results described above could not be explained satisfactorily. Stage (3) probably takes place in an intramolecular fashion :



1-Nitro-2-naphthylamine and 2-nitro-1-naphthylamine are the only compounds which give a mixture of the azo-compound and the furazan oxide. The yield of azo-compound from each is very low (*ca.* 3%), but the furazan oxide is formed in excellent yield (86%) from 1-nitro-2-naphthylamine and in low yield (7%) from 2-nitro-1-naphthylamine. Here it may be possible that homolytic fission of the " ester " initially formed may take place (cf. Part I) to form the radicals (VI*a* and VI*b* ; VII*a* and VII*b*) :



(VI*a*) (VI*b*) (VII*a*) (VII*b*)

The furazan oxide could still be formed from the intermediates as described above [or possibly from (VI*a*) and (VII*a*)], whereas azo-compounds would result from dimerisation and further oxidation of (VI*b*) and (VII*b*) (cf. Part II). The greater stability of (VI*b*) compared with (VII*b*), explains the lower yield of naphthofurazan oxide obtained from 2-nitro-1-naphthylamine. Admittedly, the yield of azo-compound from this latter substance is not very high, but it has been found (Part II) that α-naphthylamine is oxidised to 1 : 1′-azonaphthalene in a yield of only 3%.

When acetic acid was used as solvent, in place of benzene, *o*-nitroaniline, 4-chloro-2-nitroaniline, and 1-nitro-2-naphthylamine were oxidised to the corresponding azo-compounds without the formation of furazan oxide (Part III). This is in accord with Green and Rowe's results (*J.*, 1912, **101**, 2449, 2455) that oxidation of *o*-nitroaniline with alkaline sodium hypochlorite gives benzofurazan oxide, but the neutral reagent gives only 2 : 2′-dinitroazobenzene. The *aci*-nitro-form of the *o*-nitroamines may be suppressed in acetic acid because of interference with the internal hydrogen bonding.

EXPERIMENTAL

Melting points are corrected unless stated otherwise. Analyses are by Dr. W. Zimmermann.

All oxidations with phenyl iodosoacetate in benzene were performed as described in Part II. The results of oxidations yielding only a benzofurazan oxide are shown below; the products crystallised from ethanol or light petroleum (b. p. 40—69°) as pale yellow prisms.

Subst. in 2-nitroaniline	5-Me	5-Cl	5-OMe
$PhI(OAc)_2$ uptake, mol.	1·08	1·04	1·04
M. p. of benzofurazan oxide	96°	48°	115° *
Yield, %	93	92	90

* Found : C, 50·9 ; H, 3·7. Calc. for $C_7H_6O_3N_2$: C, 50·6 ; H, 3·6%.

Oxidation of 4-Methoxy-2-nitroaniline.—The oxidation of 4-methoxy-2-nitroaniline (2·70 g.) yielded, in addition to a brown, benzene-insoluble substance which could not be crystallised, 4 : 4′-dimethoxy-2 : 2′-dinitroazobenzene (0·126 g.), which crystallised from benzene as orange-red rods, m. p. 267° (lit., m. p. 259°) (Found : C, 50·7 ; H, 3·7 ; N, 17·1. Calc. for $C_{14}H_{12}O_6N_4$: C, 50·6 ; H, 3·6 ; N, 16·9%).

Oxidation of 1-*Nitro*-2-*naphthylamine*.—The oxidation of 1-nitro-2-naphthylamine (1·495 g.) yielded (*a*) 1 : 1′-*dinitro*-2 : 2′-*azonaphthalene* (0·040 g.), which crystallised from benzene as orange-red rods, m. p. 305—306° (uncorr.) (Found : C, 64·7; H, 3·3. $C_{20}H_{12}O_4N_4$ requires C, 64·5; H, 3·25%), and (*b*) naphthofurazan oxide (1·270 g.), needles (from ethanol), m. p. and mixed m. p. 126°.

Oxidation of 2-*Nitro*-1-*naphthylamine*.—The oxidation of 2-nitro-1-naphthylamine (1·203 g.) yielded, in addition to a brown benzene-insoluble substance, (*a*) 2 : 2′-*dinitro*-1 : 1′-*azonaphthalene* (0·039 g.), which crystallised from benzene as orange-red rods, m. p. 219° (Found : C, 64·9; H, 3·2. $C_{20}H_{12}O_4N_4$ requires C, 64·5; H, 3·25%), and (*b*) naphthofurazan oxide, m. p. 126°, identical with the product obtained from 1-nitro-2-naphthylamine.

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