Radical Abstraction of Iodine from Aromatic Iodides: Benzyne Formation from *o*-Iodo-*N*-nitrosoacetanilide

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IN a continuation of our investigations into the decompositions of *o*-substituted *N*-nitrosoacetanilides, one of which had been shown previously to proceed *via* an aryne,[1] it has been observed that *o*-iodo-*N*-nitrosoacetanilide (1 mol.) in benzene (20 mol.) gives, in addition to the expected 2-iodobiphenyl (44%), *o*-di-iodobenzene (12%) and *o*-terphenyl. A reaction carried out in the presence of 2,3,4,5-tetraphenylcyclopentadienone gave, as an additional product, 1,2,3,4-tetraphenylnaphthalene (by m.p. and mixed m.p. and correct infrared spectrum), indicative of the intermediacy of benzyne (*ca.* 1%). It has been further shown, that *m*- and *p*-iodo-*N*-nitrosoacetanilides in benzene give *m*- and *p*-di-iodobenzenes respectively in addition to the expected 3- and 4-iodobiphenyls. The reaction of the *m*-isomer also yielded *m*-terphenyl, *p*-terphenyl was not sought in the *p*-case.

Exemplified by the *o*- case, these results suggest the following in outline:

$$o\text{-I}\cdot C_6H_4\cdot N(NO)Ac \rightarrow o\text{-I}\cdot C_6H_4\cdot \qquad \text{(i)}$$

$$o\text{-I}\cdot C_6H_4\cdot + PhH \rightarrow o\text{-I}\cdot C_6H_4\cdot Ph$$

$$o\text{-I}\cdot C_6H_4\cdot + o\text{-I}\cdot C_6H_4\cdot Ph[\text{or } o\text{-I}\cdot C_6H_4\cdot N(NO)Ac] \rightarrow \underset{\text{(I)}}{o\text{-I}_2\cdot C_6H_4} + \underset{\text{(II)}}{o\text{-Ph}\cdot C_6H_4\cdot[\text{or } o\text{-AcN(NO)}\cdot C_6H_4\cdot]}$$

$$\text{(I) [or (II)]} + PhH \rightarrow o\text{-Ph}_2\cdot C_6H_4$$

This suggests that aryl radicals have a high affinity for iodine in aromatic iodides, a supposition supported by the following observations:

(a) the decomposition of substituted benzoyl peroxides, not containing iodine, (*e.g.*, 4-Cl, 4-Br, 3-Br, 4-Me, 2-Br) or of *p*-chloro-*N*-nitrosoacetanilide, in iodobenzene gave significant yields (0·6—0·95 moles/mole) of the corresponding aryl iodide together with mixtures of 2-, 3-, and 4-iodobiphenyls (30—70% based on the aryl iodide), of isomeric composition expected from radical phenylation of iodobenzene (*e.g.*, 56% 2-; 26% 3-; 18% 4-iodobiphenyl). The corresponding benzoic acids (*ca.* 0·8 mole/mole) were also formed in the reactions of the peroxides.

(b) Significant amounts of *p*-chloro- and *p*-bromoiodobenzene (0·37, 0·36 moles/mole) have been isolated from reactions of *p*-chloro-*N*-nitrosoacetanilide (1 mol.) and *p*-bromobenzoyl peroxide (0·5 mol.) respectively in benzene (20 mol.) admixed with iodobenzene (1 mol.). Other products included 4-bromo- and 4-chloro-biphenyl, and, in each case, biphenyl.

(c) *p*-Iodobenzoyl peroxide (1 mol.) in benzene (20 mol.) gives *p*-di-iodobenzene and *p*-terphenyl in addition to the expected 4-iodobiphenyl.

The formation of phenyl radicals in (a) above, suggests participation of the following sequence, or one similar in the case of *p*-chloro-*N*-nitrosoacetanilide, in the case of the decompositions of aroyl peroxides in the presence of iodobenzene.

$$(\mathrm{ArCO_2})_2 \rightarrow \mathrm{Ar}\cdot + \mathrm{ArCO_2}\cdot + \mathrm{CO_2}$$

$$\mathrm{Ar}\cdot + \mathrm{PhI} \rightarrow \mathrm{ArI} + \mathrm{Ph}\cdot$$

$$\mathrm{Ph}\cdot + \mathrm{PhI} \rightarrow [\mathrm{Ph{\cdot}C_6H_5{\cdot}I}]\cdot \xrightarrow{(\mathrm{ArCO_2})_2} \mathrm{PhC_6H_4I} + \mathrm{ArCO_2H} + \mathrm{ArCO_2}\cdot$$

Reactions described under (b) and (c), in which the iodo-compound is initially present in high dilution in benzene further emphasise the ease of the transfer process.

The formation of a small quantity of benzyne in the case of *o*-iodo-*N*-nitrosoacetanilide could be the result of the loss of an iodine atom from an *o*-iodophenyl radical formed in (i) or the collapse of the intermediate (II), if formed.

The preliminary disclosure of some of our results is prompted by the recent report[2] that decomposition of the related (*N*-2-iodophenyl)-*N*-nitrosobenzamide in benzene gives, in addition to 2-iodobiphenyl, benzyne (7%), and *o*-di-iodobenzene (18%). The following route was favoured, in which benzyne formation was related directly to that of *o*-di-iodobenzene.

$$o\text{-}\mathrm{I{\cdot}C_6H_4}\cdot \rightarrow \text{benzyne} + \mathrm{I}\cdot$$

$$\mathrm{I}\cdot + o\text{-}\mathrm{I{\cdot}C_6H_4}\cdot \rightarrow o\text{-}\mathrm{I_2{\cdot}C_6H_4}$$

The generality of the iodine abstraction reaction demonstrated by us suggests that it is unnecessary to link the formation of benzyne with that of *o*-di-iodobenzene and that formation of the latter by direct abstraction of iodine by an *o*-iodophenyl radical is more likely.

It should be noted that there is one previous report of a reaction similar to those now reported: Harley-Mason and Mann[3] noted without details that a Gomberg reaction of *p*-iodoaniline gave *p*-di-iodobenzene as a side-product. In accord with this the latter has also been obtained recently[4] from the reaction of pentyl nitrite with *p*-iodoaniline in benzene.[5]

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[3] J. Harley-Mason and F. G. Mann, *J. Chem. Soc.*, 1940, 1379.
[4] J. I. G. Cadogan and D. M. Smith, unpublished work.
[5] *cf.*, J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.