Formation of Benzynes by Photolysis of 1,2-Di-iodoarenes

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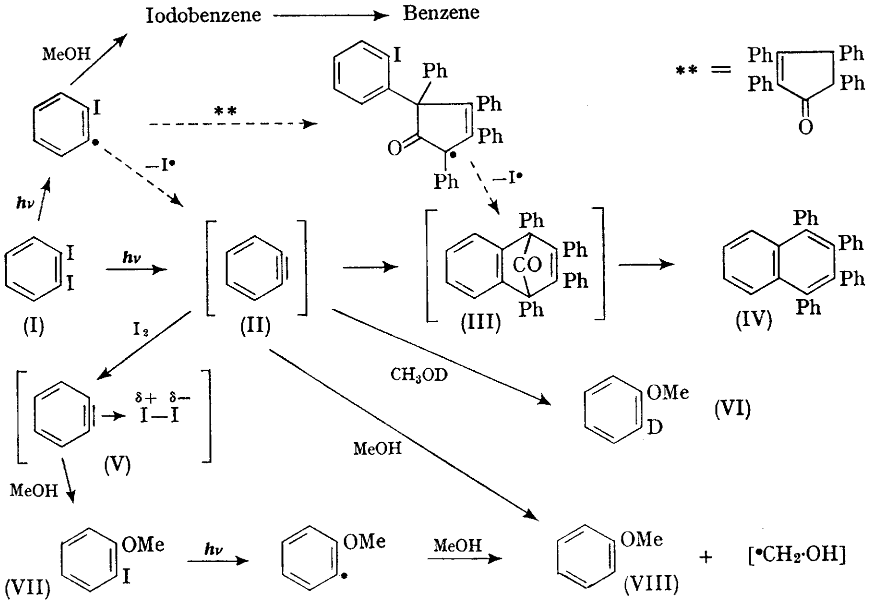
KAMPMEIER and HOFFMEISTER[1] have given evidence, based on adduct formation with tetracyclone and furan (Scheme), that benzyne was formed on photolysis of solutions of 1,2-di-iodobenzene. However, the possibility that the adducts result from two-step radical additions was not completely excluded. We now report conclusive evidence that benzynes are intermediates in the photolysis of 1,2-di-iodobenzene and 3,4-di-iodotoluene. The novel formation of 2-iodoanisole, presumably by methanolysis of a π-complex of iodine with benzyne, is also reported.

It is known[2–4] that alcohols add to benzynes to form aryl alkyl ethers, *e.g.*, anisole (VIII) by addition to benzyne, and that the isomeric tolyl ethers are formed by additions of ethanol to 3-methylbenzyne. Furthermore, Kharasch and Friedman[5] showed that photolysis of iodo-aromatic compounds in methanol (and other H-donor solvents) leads to transfer of hydrogen to the aryl radical formed by photolysis of the iodo-aromatic compound ($ArI \rightleftharpoons Ar\cdot + I\cdot$). In the case of methanol, the α-hydrogen was abstracted to form the hydroxymethyl radical, which was subsequently converted into formaldehyde and dimethoxymethane.

If no other route to the anisoles was available, their presence as products could serve as definitive proof for benzyne intermediates in the photolysis of 1,2-di-iodoarenes in methanol. Another possible demonstration for benzyne intermediate, the formation of biphenylene, was ruled out by Kampmeier and Hoffmeister,[1] and this was also confirmed by Kharasch and his co-workers[6] for photolysis of 1,2-di-iodobenzene (I) in benzene solution. Presumably, iodine present in the reaction mixture acts as a trap for benzyne, and precludes formation of biphenylene.

Photolysis of 0·33 g. of *o*-di-iodobenzene in 20 ml. of methanol, for 24 hr., using a low pressure, cold cathode mercury arc, in "Vycor", gave 35% anisole, 32% iodobenzene, 4% *o*-iodoanisole, and appreciable amounts of benzene (*cf.* Scheme). The formation of anisole was anticipated, but not that of *o*-iodoanisole and its presence complicated the interpretation because it could lead to anisole



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by photolytic conversion into *o*-methoxyphenyl radicals, and subsequent abstraction of hydrogen from methanol. In order to differentiate between this route for anisole formation and that involving benzyne, the photolysis of (I) was carried out in CH_3OD. Anisole was isolated by preparative gas–liquid chromatography, and mass spectral analysis, using low ionizing voltage, showed it to contain 63·8% of monodeuteroanisole (VI). This must have arisen by addition of CH_3OD to benzyne, and its formation unequivocally establishes the presence of benzyne intermediate in the photolysis of *o*-di-iodobenzene under the conditions used in the present work.

A logical route to *o*-iodoanisole would involve electrophilic attack by iodine on benzyne, resulting in a "π-complex" (V), which by reaction with methanol could yield *o*-iodoanisole. An alternative possible route to *o*-iodoanisole might be through solvolysis of 1,2-di-iodobenzene by methanol. This appears unlikely from mechanistic considerations, and also from the fact that by photolysis of iodobenzene in methanol only a trace (less than 0·1%) of anisole was found.

To substantiate further the formation of a benzyne intermediate, the photolysis of 3,4-di-iodotoluene in methanol was studied, in which the resulting 3-methylbenzyne should lead, by addition of methanol, to *p*- and *m*-methylanisole, both of which were found in a combined yield of 28%. The approximate ratio *p*- : *m*-isomers was as expected from 3-methylbenzyne,[3] though the exact analysis was not made, and it is not yet known whether the competing reaction (*cf.*, II yielding VII) significantly changes the product ratios of the *m*- and *p*-methylanisoles. Whether formation of benzyne from 1,2-di-iodoarene occurs by concerted elimination of two iodine atoms, or by a two-step process *via* 2-iodophenyl radical, also remains to be settled.

The availability of a wide variety of 1,2-di-iodoaromatic compounds makes these attractive as general sources for conversions into arynes. Studies to detect other arynes by photolysis of selected dihalogenoarenes and of dihalogenoheterocyclic compounds are in progress.

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