Studies on 2-Iodophenyl Radicals: the Decomposition of 2-Iodophenylazotriphenylmethane

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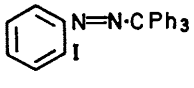
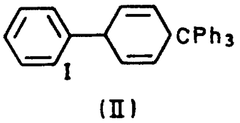
Summary The homolytic decomposition of 2-iodophenylazotriphenylmethane gives 2-iodophenyl radicals, but does not give detectable amounts of benzyne.

WE have reported the apparent formation of benzyne in the photolysis of 1,2-di-iodobenzene[1] and in the thermal decomposition of *N*-(2-iodophenyl)-*N*-nitrosobenzanilide.[2] Characteristic reactions of 2-iodophenyl radicals and benzyne are observed in both cases. 4-Methylbenzene is firmly established as a product of the decomposition of *N*-(2-iodo-4-methylphenyl)-*N*-nitrosobenzanilide in t-butyl alcohol[3] by the formation of 3- and 4-tolyl t-butyl ethers in 1·45 ratio. Essentially the same ratio of products is obtained from accepted 4-methylbenzyne sources, diazotized 2-amino-4-methylbenzoic acid,[3] and 5- and 6-methylbenzo-1,2,3-thiadiazole 1,1-dioxides.[4] The apparent formation of benzyne from two very different sources of 2-iodophenyl radicals led us to conclude that benzyne is formed by elimination of an iodine atom from a 2-iodophenyl radical.[2] We now report observations on the behaviour of 2-iodophenyl radicals derived from 2-iodophenylazotriphenylmethane.



(I)



(II)

The azo-compound is prepared from 2-iodoaniline[5] by way of 2-iodophenylhydrazine [m.p. as the hydrochloride, 158—161° (decomp.)] and *N*-(2-iodophenyl)-*N*′-triphenylmethylhydrazine [m.p. 155—165° (decomp.)]. Oxidation of the crude triphenylmethylhydrazine with Ag_2O–$MgSO_4$ in benzene and recrystallization of the crude product from $CHCl_3$–MeOH at room temperature gives (I), m.p. 118° (decomp.),† λ_{max} (cyclohexane) 431 nm, ϵ 168. T.l.c. on Silica Gel-G with four solvent systems shows single uniform spots; 0·01% of the precursor hydrazine would have been detected.

Decomposition of (I) (*ca.* 3×10^{-2} M) in degassed solutions in benzene at 72° gives a complex mixture of products which was resolved and analysed by a combination of column, thin and thick layer,[6] and vapour phase chromatographic techniques. Iodobenzene (*ca.* 0·3%), biphenyl (1—2%), 1,2-di-iodobenzene (2—4%), and 2-iodobiphenyl (1—2%) were identified by comparison with authentic samples. The major product of the reaction, m.p. range 156—186°, 87—89%, was isolated by chromatography on alumina and was homogeneous by t.l.c. with four solvent systems. This material is assigned as a mixture of stereoisomers of 1-(2-iodophenyl)-4-triphenylmethylcyclohexa-2,5-diene (II). Pyrolysis of the reaction product (II) at 260° in a sealed tube or in a g.l.c. inlet at 300° gives 2-iodobiphenyl and triphenylmethane as the only products detectable by t.l.c. and g.l.c.; the products were characterized by chromatographic comparisons with authentic samples. Oxidation of (II) with 2,3-dichloro-5,6-dicyanoquinone in benzene[7] yields (88%) a product assigned as 2-iodo-4′-triphenylmethylbiphenyl,† m.p. 186—189°. The latter compound was reduced with $LiAlH_4$ in benzene–tetrahydrofuran to give 4-triphenylmethylbiphenyl (66%), identical with authentic material.[8]

Decomposition of (I) at 72° in benzene solutions saturated with oxygen gives 2-iodobiphenyl (83%), triphenylmethyl peroxide (42—46%), benzophenone (18—26%), triphenylmethanol (18–25%), 1,2-di-iodobenzene (3—5%), iodobenzene (*ca.* 0·1%), and biphenyl (*ca.* 0·5%). Photodecompositions of (I) in degassed benzene solutions at 254 nm (quartz, low pressure mercury resonance lamp) or at

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† These compounds gave satisfactory combustion analyses.

>310 nm (Pyrex, medium pressure mercury lamp) gives product mixtures qualitatively similar to those obtained from the thermal decompositions. In particular, (II) is the major product (54%) of the photodecomposition in degassed benzene solutions. The products of the decomposition of (I) are analogous to those reported from phenylazotriphenylmethane[8] and establish (I) as a source of 2-iodophenyl radicals.

Thermal decompositions of (I) in benzene containing tetracyclone, in the presence or absence of oxygen, does not give 1,2,3,4-tetraphenylnaphthalene. T.l.c. proved to be the most satisfactory analytical method: control experiments showed that 0·1% yield of the benzyne tetracyclone adduct would have been detected. Photodecompositions of (I) at 254 nm and >310 nm in degassed benzene solutions containing tetracyclone gives comparable results.‡ Authentic tetraphenylnaphthalene is not destroyed under the photolysis conditions. Thermal decompositions of (I) in furan in the presence or absence of oxygen followed by hydrolytic work-up with methanolic hydrochloric acid failed to give detectable quantities of α-naphthol.[9] Control experiments showed that the work-up and t.l.c. analysis would have detected the presence of a 0·1% yield of α-naphthol.

The evidence outlined above indicates that the homolytic decomposition of (I) gives 2-iodophenyl radicals, but does not give benzyne. Our earlier conclusion[2] that benzyne is formed by a unimolecular radical elimination of iodine from 2-iodophenyl radicals must, therefore, be viewed with scepticism. It seems necessary to look further for the explanations for the formation of benzyne and/or benzyne adducts in the photolysis of 1,2-di-iodobenzene and the thermal decomposition of *N*-(2-iodophenyl)-*N*-nitrosobenzanilide.

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‡ Control experiments showed that <1% yield of adduct would have been detected.

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