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A FREE RADICAL PATHWAY TO BENZYNE: THE DECOMPOSITION OF N-(2-IODOPHENYL)-N-NITROSOBENZAMIDE

by

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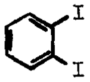
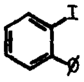
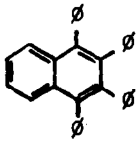
We have previously reported (1) that the photolysis of 1,2-diiodobenzene at 2537 Å gives products characteristic of both 2-iodophenyl radicals and benzyne. These observations prompted us to suggest a free radical pathway to benzyne involving the elimination of an iodine atom from the 2-iodophenyl radical. Others have reported similar observations on the photolysis (2), thermal decomposition (3), and zinc reduction (4) of 1,2-diiodobenzene. Because of the mechanistic ambiguities involved in these reactions, we sought alternative sources of 2-iodophenyl radicals. This paper reports the behavior of 2-iodophenyl radicals generated from a classical free radical source under mild conditions.

N-(2-Iodophenyl)-N-nitrosobenzamide (I), m.p. 79-80° (dec.), was prepared in 80% yield by the reaction of nitrosyl chloride with N-(2-iodophenyl)-benzamide in Ac_2O/HOAc containing 10% pyridine (5), followed by low temperature recrystallization of the crude product from methanol. The purity (97-99%) of the material was routinely assayed by spectrophotometric determination of the yield of the azo coupling product with β-naphthol (6). The coupling product was identical in all respects with that prepared from β-naphthol and diazotized 2-iodoaniline.

The nitroso compound (I) decomposes readily in solution. Products under several conditions are described in the Table. All decompositions were carried out for 12 hrs. at 50° in carefully deoxygenated systems; the concentrations of I were *ca.* 3.8 x 10^{-2} *M*. All products shown were isolated and characterized by comparison with authentic materials. Yields were determined by v.p.c. using internal standard methods.

TABLE

	% Yields				
Solvent/ Conditions	ØCO$_2$H	ØI			
Benzene	75	0.9	14	57	---
Benzene/ tetracyclone[a]	64	---	18	40	7.7
Cyclohexene	55	43	<0.4[b]	--	c
Cyclohexene/ tetracyclone[a]	51	38	<0.4[b]	--	0.7

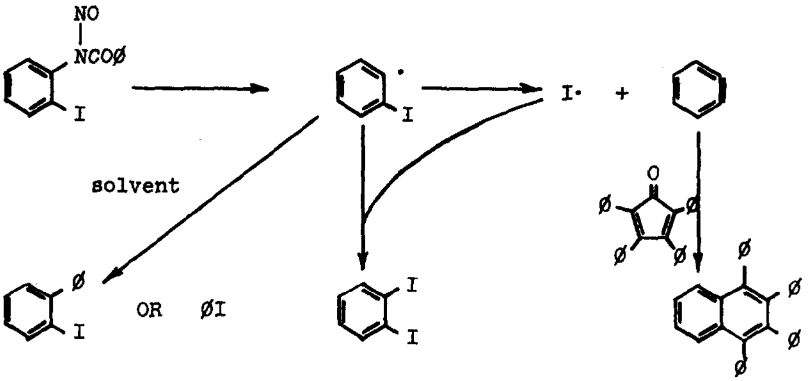
[a] 4.7 x 10^{-2} *M* tetraphenylcyclopentadienone (tetracyclone)

[b] Limit of detectability

[c] <1% yield[b] of 3-phenylcyclohexene, a known product of reaction of benzyne with cyclohexene (7)

Although the detailed mechanism of decomposition of nitroso acylanilides has only recently been clarified (8), there is general agreement that aryl radicals are formed (8, 9). The products described in the Table are readily discussed in terms of the reactions shown in the Chart. The critical step in this scheme involves the fragmentation of the 2-iodophenyl radical into benzyne and an iodine atom.

CHART



As expected, 2-iodophenyl radicals in benzene react primarily with solvent to give 2-iodobiphenyl. A significant fraction of the iodophenyl radicals, however, are recovered as 1,2-diiodobenzene. This unexpected product is reasonably formed by the reaction of iodophenyl radicals with iodine and constitutes circumstantial evidence for the benzyne producing elimination reaction. Concrete support for the formation of benzyne is given by the isolation of tetraphenylnaphthalene from the decomposition of I in the presence of tetracyclone, a known benzyne scavenger (10). The scheme in the Chart predicts identical yields of diiodobenzene and tetraphenylnaphthalene if both scavenging reactions are equally efficient. Tetracyclone, however, is not very soluble in benzene and is not a very good benzyne scavenger (11).

The decompositions in cyclohexene offer compelling evidence for the radical nature of the steps leading to benzyne and diiodobenzene. As shown in the Chart, iodophenyl radicals are partitioned between solvent capture and elimination. In the presence of cyclohexene, the yields of the products associated with the elimination pathway, diiodobenzene and tetraphenylnaphthalene, are dramatically reduced. Cyclohexene is more reactive toward aryl radicals than benzene and efficiently interrupts the elimination process by diverting iodophenyl radicals to other products.

Competing decompositions of I in benzene, *e.g.* radical *vs.* ionic (12) or radical *vs.* cyclic (13), could explain the formation of both iodophenyl radicals and benzyne. However, the data require that the ratio of these competing pathways be sensitive to a solvent change from benzene to cyclohexene. This seems rather unlikely; a more satisfactory explanation involves the formation of benzyne from 2-iodophenyl radicals.

A bimolecular disproportionation reaction of 2-iodophenyl radicals could explain the formation of diiodobenzene and benzyne by a radical pathway. However, a ten-fold change in the concentration of I in benzene has no significant effect on the yield of diiodobenzene (13-17%). In addition, the product of coupling of iodophenyl radicals, 2,2'-diiodobiphenyl, could not be detected by v.p.c. of reaction mixtures from the decomposition of I in benzene. These observations mitigate the probability of a bimolecular pathway involving iodophenyl radicals. We conclude that benzyne is formed by a unimolecular radical elimination of iodine from 2-iodophenyl radicals.

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