A Note on Three Routes to Benzyne: Decomposition of Diphenyliodonium Acetate, Nitrosation of *N*-Phenylphosphylamidates, and Deoxygenation of Benzenediazotoluene-*p*-sulphonate *N'*-Oxide (Cupferron Tosylate) by Phosphorus Trichloride

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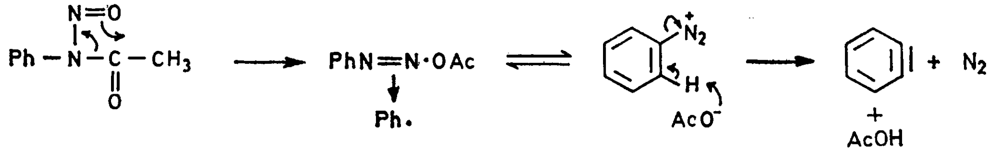
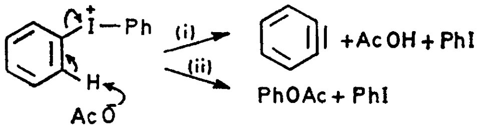
Thermolysis of diphenyliodonium acetate in benzene, nitrosation, *via p*-chlorobenzoyl nitrite, of diethyl and dipheny *N*-phenylphosphoramidates, ethyl-*NN'*-diphenylphosphonodiamidate, and *NN'N''*-triphenylphosphoric triamide, and deoxygenation of benzenediazotoluene-*p*-sulphonate *N'*-oxide by phosphorus trichloride all give benzyne in 4—20% yields, by mechanistically similar pathways, as shown by trapping with tetraphenylcyclopentadienone.

THE formation of benzyne by elimination from benzenediazonium acetate, formed directly or *in situ* by rearrangement of *N*-nitrosoacetanilide is now well established (Scheme 1).[1] We now briefly describe three routes to benzyne which are mechanistically related to Scheme 1.



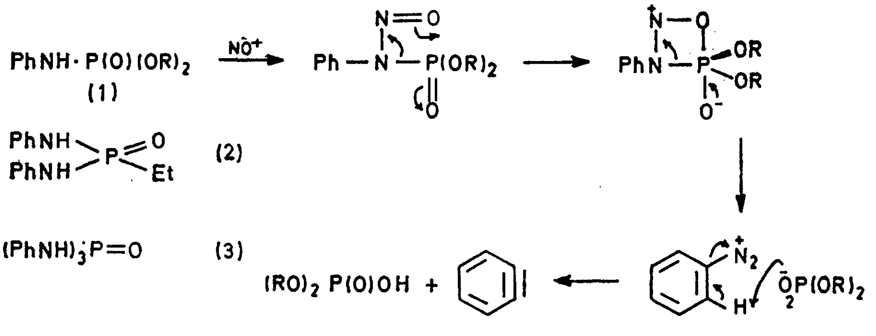
SCHEME 1



SCHEME 2

Thermolysis of Diphenyliodonium Acetate.—The analogy between production of benzyne by this route [Scheme 2, route (i)] and from benzenediazonium acetate (Scheme 1) is obvious, and recalls the relationship between diazotised anthranilic acid and *o*-(phenyliodonio)benzoate as sources of benzyne.[2] In the event diphenyliodonium acetate, directly or prepared *in situ* from the iodide and potassium acetate at 80°, in benzene gave benzyne in 3% yield as measured by trapping with tetraphenylcyclopentadienone. The major product was phenyl acetate [Scheme 2, route (ii)]. Various substituted diphenyliodonium salts behave similarly, the best yield (12%) of benzyne adduct being derived from the mono-*m*-nitro-derivative.

Nitrosation of N-*Phenylphosphoramidates.*—It is known that *N*-nitroso-*N*-phenylphosphoramidates rapidly and quantitatively rearrange to give benzenediazonium phosphates,[3] presumably by a route related to Scheme 1 which is even more favoured as a result of the propensity with which pentaco-ordinate phosphorus can accommodate a four-membered ring (Scheme 3). In accord



SCHEME 3

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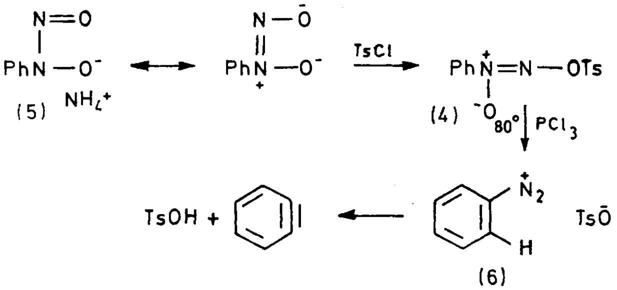
[1] (*a*) J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, **4**, 186; (*b*) C. Ruchardt and C. C. Tan, *Angew. Chem. Internat. Ed.*, 1970, **9**, 522; (*c*) B. D. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.

[2] F. M. Beringer and S. J. Huang, *J. Org. Chem.*, 1964, **29**, 445, 1637.

[3] (*a*) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 1304; (*b*) J. I. G. Cadogan, *ibid.*, 1957, 1079.

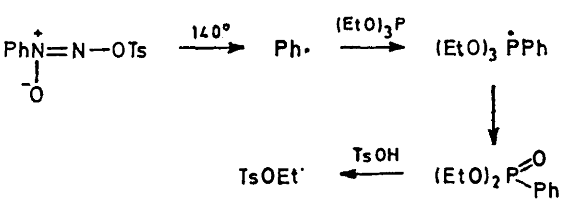
with the foregoing, nitrosation, with *p*-chlorobenzoyl nitrite,[1c] of diphenyl and diethyl *N*-phenylphosphoramidate (1; R = Ph or Et), ethyl-*NN*′-diphenylphosphonodiamidate (2), and *NNN*′-triphenylphosphoric triamide (3) gave benzyne in 13, 20, 12, and 5% yields, respectively, as shown by trapping with tetraphenylcyclopentadienone.

*Deoxygenation of Benzenediazotoluene-*p*-sulphonate* N′-*Oxide* (*Cupferron Tosylate*) *with Phosphorus Trichloride*.—The rationale of this reaction is apparent from Scheme 4.



Scheme 4

Benzenediazotoluene-*p*-sulphonate *N*′-oxide (4), prepared by reaction of the readily available reagent Cupferron [the ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine (5)] with toluene-*p*-sulphonyl chloride,[4] is an azoxy-compound which in theory can be deoxygenated by tervalent phosphorus reagents [5] to give benzenediazonium tosylate (6). This in turn might be expected to decompose to give benzyne and toluene-*p*-sulphonic acid by analogy with Scheme 1. In the event this occurred to the extent of 7%, at 80° in benzene, as shown by trapping with tetraphenylcyclopentadienone, on deoxygenation by phosphorus trichloride, which was preferred over triethyl phosphite since the latter reacts with the dienone. A major by-product was radical-derived biphenyl. Deoxygenation by triethyl phosphite in the presence of furan and 1,1-diphenylethylene as a benzyne promoter [6] gave, instead of benzyne, diethyl phenylphosphonate (20%), formed by radical phenylation,[7] and



Scheme 5

ethyl toluene-*p*-sulphonate (56%), formed by ethylation of toluene-*p*-sulphonic acid. These results suggest that reaction takes place as in Scheme 5, where direct thermolysis of the parent tosylate (4) to give phenyl radicals is the dominant process. In accord with this, thermolysis of the tosylate (4) in benzene alone at 140° gave biphenyl (48%).

EXPERIMENTAL

Materials.—Diaryliodonium chlorides and bromides were prepared as previously described,[8] as were *p*-chlorobenzoyl nitrite,[1b] and diethyl and diphenyl *N*-phenylphosphoramidates.[3] *NN*′*N*″-Triphenylphosphoric triamide had m.p. 209—210° (lit.,[9] 211—214°). *N*-Nitroso-*N*-phenylhydroxylamine tosylate [4] had m.p. 135—136° (decomp.) (heating at 1° per min) [lit.,[4] 136—137° (decomp.)]. Ethyl-*NN*′-diphenylphosphonamidate had m.p. 147°.[3b]

Formation and Trapping of Benzyne.—(i) via *Nitrosation of* N-*phenylphosphoramidates*. *p*-Chlorobenzoyl nitrite (1·9 g, 10 mmol) in dry benzene (50 ml) was added during 1 h to a boiling mixture of diethyl *N*-phenylphosphoramidate (1·15 g, 5 mmol) and tetraphenylcyclopentadienone (2·85 g, 7·5 mmol) in benzene (100 ml). The mixture was kept at the b.p. for 15 h, then maleic anhydride (1 g, 10 mmol) was added and the resulting mixture was boiled for a further 5 h. Removal of benzene and chromatography on alumina (dry column technique) gave biphenyl (13%) and 1,2,3,4-tetraphenylnaphthalene (20%), identical with an authentic specimen.[1c]

Reactions of diphenyl *N*-phenylphosphoramidate, ethyl *NN*′-diphenylphosphorodiamidate, and *NN*′*N*‴-triphenylphosphoric triamide similarly gave 1,2,3,4-tetraphenylnaphthalene in 13, 12, and 5% yields, respectively.

(ii) via *Thermolysis of diaryliodonium acetates*. The iodonium chloride or iodide (1 mmol), tetraphenylcyclopentadienone (1 mmol), and freshly fused potassium acetate (1·2 mmol) were stirred in boiling benzene under nitrogen for 6 h. Standard work-up gave the corresponding 1,2,3,4-tetraphenylnaphthalenes, as shown by comparison with authentic specimens.[1c] Diphenyliodonium bromide or iodide in this way gave the naphthalene in 3% yield, *m*-nitrophenyl(phenyl)iodonium chloride gave 5-nitro-1,2,3,4-tetraphenylnaphthalene (12%) and a trace of 1,2,3,4-tetraphenylnaphthalene, and *p*-methyl-, *p*-bromo-*p*-nitro, and *o*-nitrophenyl(phenyl)iodonium chlorides or bromides gave 2—4% yields of the corresponding substituted tetraphenylnaphthalenes, as did bis-*m*-nitrophenyliodonium chloride.

(iii) via *Deoxygenation of Benzenediazotoluene-*p*-sulphonate* N′-*oxide by phosphorus trichloride*. The tosylate (0·29 g, 1 mmol) and tetraphenylcyclopentadienone (0·5 g, 1·3 mmol) were boiled under reflux with phosphorus trichloride (2·5 mmol) in dry benzene under nitrogen for 18 h. Dry column chromatography gave 1,2,3,4-tetraphenylnaphthalene (7%) and biphenyl (22%), identified by comparison with authentic specimens.

A corresponding reaction carried out with triethyl phosphite and furan in benzene in the presence of 1,1-diphenylethylene as a benzyne promoter,[6] at 60 or 140°, gave no 1,4-epoxy-1,4-dihydronaphthalene. G.l.c.–mass spectrometry

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[4] T. E. Stevens, *J. Org. Chem.*, 1964, **29**, 311.

[5] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

[6] J. I. G. Cadogan, C. D. Murray, and J. T. Sharp, *J.C.S. Chem. Comm.*, 1974, 901.

[7] J.-J. L. Fu and W. G. Bentrude, *J. Amer. Chem. Soc.*, 1972, **94**, 7710.

[8] F. M. Beringer, *J. Amer. Chem. Soc.*, 1953, **75**, 2705; 1959, **81**, 342.

[9] L. F. Audrieth and A. D. F. Toy, *J. Amer. Chem. Soc.*, 1942, **64**, 1553.

established the identity of biphenyl (3%), diethyl phenylphosphonate (20%), and ethyl toluene-*p*-sulphonate (56%) as products of the reaction at 140°. At 60° the starting material did not react.

Reaction of the tosylate with triethyl phosphite in benzene at 140° gave biphenyl (17%), diethyl phenylphosphonate (40%), and the tosyl ester (28%); reaction in the absence of the phosphite gave biphenyl (48%).

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