

## Use of Benzyne Promoters in the Conversion of Benzenediazonium Acetate into Benzyne

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**Summary** The observations that 1,1-diphenylethylene and a series of related alkenes act as promoters for the formation of benzyne from benzenediazonium acetate even in the presence of furan, which otherwise promotes the competing radical reaction, leads also to an explanation of the hitherto puzzling promoting effect of tetraphenylcyclopentadienone.

THE simple one-pot conversion of anilines into aryne depends on acetate induced elimination from the arenediazonium ion, produced *via in situ* diazotisation.<sup>1,2</sup> Major limitations of the reaction are that, in contrast to benzenediazonium acetate, some substituted diazonium salts prefer to decompose *via* the "normal" radical chain route [Scheme: steps (ii) and (iii)], rather than give an aryne [step (i)], while furan, despite being a good aryneophile, also reacts very readily *via* the radical chain route, even in the unsubstituted case.<sup>1c,3</sup> Further, there has been no satisfactory explanation of the diversion by tetraphenylcyclopentadienone (tetracyclone) of the decom-

position of benzenediazonium acetate from the normal radical route to give benzyne.<sup>1c,4</sup>

TABLE. Decomposition of *N*-nitrosoacetanilide in benzene-furan at 60° in the presence of benzyne promoters (1 mol. equiv.)

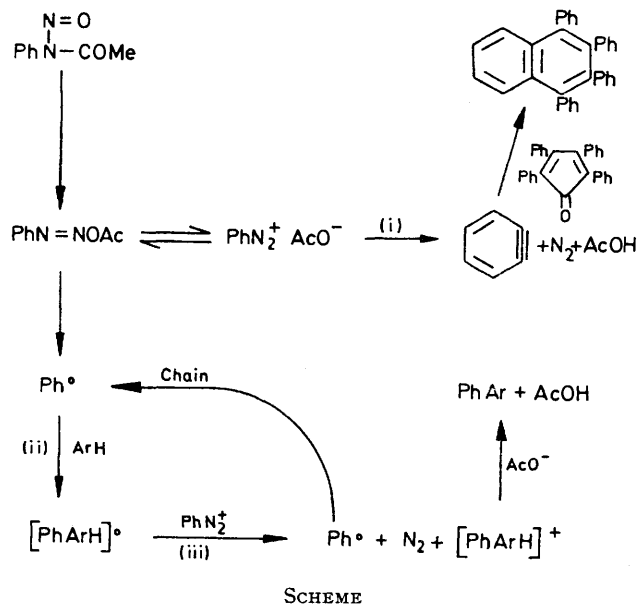
Promoter	Benzyne <sup>a</sup> (%)	Phenyl radicals <sup>b</sup> (%)
None .. .. .	7	60
(1) .. .. .	37	10
(2) .. .. .	43	17
(3) .. .. .	23	36
(PhCO) <sub>2</sub> .. .. .	11	52
<i>trans</i> -PhCH=CHPh .. .. .	32	23
Ph <sub>2</sub> C=CHPh .. .. .	27	31
PhCH=CH <sub>2</sub> .. .. .	42	11
Ph <sub>2</sub> C=CH <sub>2</sub> .. .. .	46	8

<sup>a</sup> Trapped with furan.

<sup>b</sup> Measured as biphenyl + 2-phenylfuran.

A possible explanation of the latter is that tetracyclone acts by trapping a phenyl radical to give a relatively long-lived radical which suppresses the unwanted chain reaction [(ii) and (iii)], rather than reacts with the diazonium cation

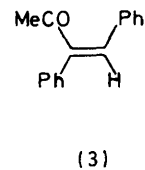
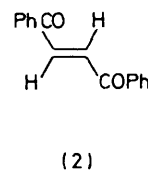
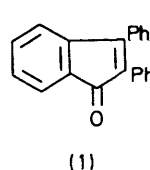
thus leading to promotion of the benzyne-forming reaction (i). If this is so then olefins, such as those in the Table, capable of reacting with phenyl radicals to give long-lived radicals should also act as promoters of the benzyne-forming reaction.



We now describe the realisation of this expectation (Table), even in the presence of furan, hitherto unsuccessful as a benzyne trap in these systems.

The best promoter so far discovered is 1,1-diphenyl-

ethylene which may be functioning *via* the radical ( $\text{Ph}_2\dot{\text{C}}\text{CH}_2\text{Ph}$ ) judging by the isolation of triphenylethylene as a by-product. The argument would then require this radical, being very much delocalised than the cyclohexadienyl radical ( $\text{PhArH}\cdot$ ), to be much longer lived, even in the presence of the diazonium cation.



Regardless of mechanistic detail however, these results show that 1,1-diphenylethylene has considerable potential as an aryne promoter in those cases where substituted diazonium salts prefer to react *via* the radical route even in the presence of tetracyclone,<sup>2</sup> and we have shown that *p*-*t*-butylbenzenediazonium acetate, in benzene-furan, gives an aryne:radical ratio of only 1:20, whereas in the presence of 1,1-diphenylethylene the ratio is greatly improved to 2.5:1.

Finally, these results suggest that the promoting effect of tetracyclone is due to a similar addition of phenyl radicals leading to a chain inhibiting long-lived radical, and hence to predominance of step (i). Unlike the alkenes listed in the Table, however, tetracyclone is also a very efficient aryne trap and therein lies a possible explanation of its special effect.

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<sup>1</sup> (a) D. L. Brydon, J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *Chem. Comm.*, 1967, 727; (b) D. L. Brydon, J. I. G. Cadogan, J. Cook, M. J. P. Harger, and J. T. Sharp, *J. Chem. Soc. (B)*, 1971, 1996; (c) J. I. G. Cadogan, *Accounts Chem. Res.*, 1971, 4, 186; (d) C. Rüchardt and C. C. Tan, *Angew. Chem. Internat. Edn.*, 1970, 9, 522.

<sup>2</sup> B. D. Baigrie, J. I. G. Cadogan, J. R. Mitchell, A. K. Robertson, and J. T. Sharp, *J.C.S. Perkin I*, 1972, 2563.

<sup>3</sup> V. Hassmann, C. Rüchardt, and C. C. Tan, *Tetrahedron Letters*, 1971, 3885.

<sup>4</sup> J. I. G. Cadogan, D. M. Smith, and J. B. Thomson, *J.C.S. Perkin I*, 1972, 1296.