Pathways for the Decomposition of Arenediazonium Ions: the Question of Aryne Participation

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Summary 1-Phenyl-3,3-dimethyltriazene (**1**; X = H) is a stable source for the benzenediazonium ion which is in equilibrium with the betaine (**2**) and hence can give rise to products derived from benzyne and phenyl radicals: on the other hand, the analogous 2,3,4,5-tetrahalogenophenyltriazenes (**1**; X = F or Cl) do not lead to arynes.

The decomposition of arenediazonium salts is complex and can lead to aryl cations,[1] aryl radicals,[1,2a] or in certain cases to arynes.[2] We became interested in the mechanisms involved because of our inability to generate the tetrahalogenobenzynes[3] from 2,3,4,5-tetrahalogenobenzenediazonium salts. Several mechanisms have been suggested to account for the formation of arynes from arenediazonium salts. These include E_1 eliminations in the case of sterically hindered diazonium salts,[2a,b] and E_1cB,[2a,c] and E_2[2d] reactions.

We found that the triazenes (**1**; X = F or Cl) were recovered quantitatively after attempted reactions carried out at 135° in *p*-xylene in the presence of either trichloroacetic acid or *O*-deuterioacetic acid and sodium acetate. In contrast, the reaction of 1-phenyl-3,3-dimethyltriazene (**1**; X = H) with sodium trichloroacetate (2 mol) and trichloroacetic acid (2 mol) in benzene containing tetraphenylcyclopentadienone gave 1,2,3,4-tetraphenylnaphthalene and biphenyl in 35 and 18% yield, respectively. A reaction of (**1**; X = H) in 1,2-dichloroethane with sodium trichloroacetate (2 mol) and trichloroacetic acid (1 mol) in the presence of anthracene gave triptycene (15%), together with 9-phenylanthracene (31%).

We therefore decided to seek evidence for the betaine (**2**) (Scheme) in reactions of benzenediazonium salts which are known[2] to lead to products derived from benzyne and the phenyl radical. A reaction of [2-^{2}H]benzenediazonium chloride (81% [2-^{2}H]†) with potassium acetate (4 mol) and

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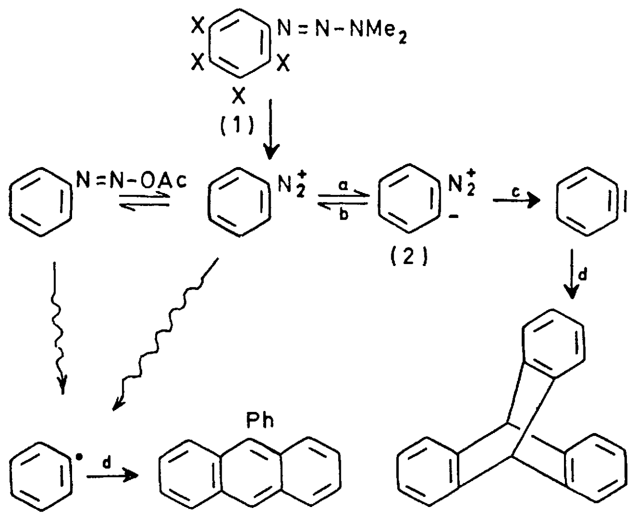
† Prepared from [2-^{2}H]aniline [R. Harrison, H. Heaney, J. M. Jablonski, K. G. Mason, and J. M. Sketchley, *J. Chem. Soc.* (*C*), **1969**, 1684] and determined by mass spectrometry as [2-^{2}H]acetanilide and 4′-hydroxy[2-^{2}H]azobenzene.

acetic acid (0·3 mol) in 1,2-dichloroethane in the presence of anthracene (0·5 mol) gave 9-phenylanthracene (36% [^{2}H]) and (7% [$^2H_2$]) together with triptycene (18% [^{2}H]). Thus extensive removal of the *ortho* deuterium together with some replacement of *ortho* protium by deuterium occurs before the benzenediazonium ion decomposes either to phenyl radicals or benzyne. These results show that the benzenediazonium ion is in equilibrium with the betaine (**2**) as originally suggested by Cadogan's group[2] and exclude the E_2 elimination mechanism for the formation of benzyne since this would have presumably resulted in the retention of significantly more than one half of the effective deuterium content. The arenediazoacetate—arenediazonium acetate pair equilibrium is well established,[4] and thus explains the presence of a di-deuteriated product derived from phenyl radicals.



SCHEME. a, AcO$^-$; b, AcOH; c, $-N_2$; d, Anthracene.

Although the above results show that the betaine (**2**) is involved they do not, on their own, prove that benzyne is formed from the betaine since a similar loss of deuterium would be expected by an E_1 mechanism. In a series of control experiments in which we used benzenediazonium chloride in 1,2-dichloroethane in the presence of potassium acetate (2 mol), anthracene (0·5 mol), and acetic acid (0, 0·5, 1·0, and 2·0 mol), the ratios of 9-phenylanthracene to triptycene were 1·3, 2·6, 2·9, and 3·8. The effect of increasing the acetic acid concentration clearly results in the equilibria being moved towards the benzenediazoacetate–benzenediazonium ion system. The fact that the ratio of phenyl radical to benzyne derived products increases with increasing acetic acid concentration shows that the benzyne is not formed directly from the benzenediazonium ion by an E_1 mechanism. The two sets of data show that benzyne is formed from the benzenediazonium ion by an E_1cB mechanism as shown in the Scheme. Presumably the presence of electron-withdrawing substituents in arenediazonium salts not only increases the electrophilicity of the diazonium function but also reduces the extent to which aryl radical precursors can revert back to the arenediazonium ion. This explains our failure to generate tetrahalogenobenzynes from arenediazonium salts.

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