Dichotomy in the Reaction of Phthalimidonitrene with Activated Benzenoid Compounds

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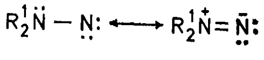
Summary Activated aromatic compounds react with phthalimidonitrene (**1**) generated from the aziridine (**2**), to give mostly 3*H*-azepines (**3**), but with the nitrene from lead tetra-acetate oxidation of *N*-aminophthalimide to give mostly the insertion products (**5**).



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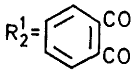

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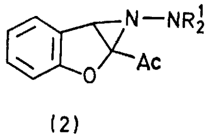

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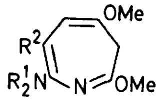

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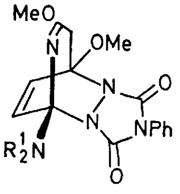

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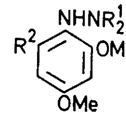

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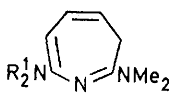

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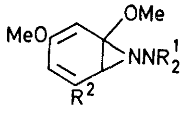

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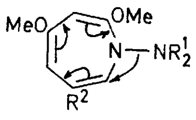

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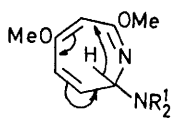

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Although nitrenes usually react with aromatic compounds,[1] phthalimidonitrene (**1**) fails to react significantly with either benzene or anisole. This may be attributed to a reduced electrophilicity of the nitrene associated with charge delocalisation as in (**1**). Accordingly we tested the reaction of (**1**) generated by oxidation of *N*-aminophthalimide,[2] and thermal dissociation of the aziridine (**2**)[3] with more nucleophilic benzenoid compounds.

With 1,3-dimethoxybenzene in boiling benzene the aziridine (**2**) gave the 3*H*-azepine (**3**; $R^2 = H$). Whilst the n.m.r. spectrum of (**3**; $R^2 = H$) shows the methylene protons as a slightly broadened singlet (τ 7·02) and the vinyl protons as doublets (J 6·5 Hz) at τ 3·94 and 4·55, the spectrum of the derived phenyltriazolinedione adduct (**4**) shows the methylene protons as an AB system centred at τ 6·74 (J_{AB} 18 Hz) and the vinyl protons as doublets (J 10 Hz) at τ 3·06 and 3·84. In addition to (**3**; $R^2 = H$) (2·0—2·5 parts) the n.m.r. spectrum of the crude product indicated the presence of the insertion product (**5**; $R^2 = H$) (1 part).

Reaction of (**2**) with 1,3-dimethoxy-5-methylbenzene, 3,5-dimethoxybenzyl cyanide, and 1,3,5-trimethoxybenzene gave the azepines (**3**; $R^2 = Me$), (**3**; $R^2 = CH_2CN$), and (**3**: $R^2 = OMe$) respectively. In accord with the assigned structures the *C*-methyl resonance in (**3**; $R^2 = Me$) and the CH_2CN resonance in (**3**; $R^2 = CH_2CN$) showed no allylic coupling. Dissociation of (**2**) in the presence of *NN*-dimethylaniline gave the azepine (**6**) whose structure was confirmed by 90 MHz n.m.r. spectroscopy with spin decoupling. The azepines (**3**) and (**6**) are presumably formed *via* aziridinobenzenes like (**7**) and 1*H*-azepines (**8**) by 1,7-shift of the phthalimido group (**8**; arrows)† and 1,5-hydrogen shift (**9**; arrows). The related 1,7-shift of OMe in tropone dimethylacetal is easy[4] and the 1,3-shift of a phthalimido-group in the rearrangement of 1-phthalimido-1*H*-azirines is apparently spontaneous.[5]

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† The reaction may involve heterolytic cleavage of the N–N bond to give an azatropylium cation which recombines with phthalimide anion at C-2.

Phthalimidonitrene generated by lead tetra-acetate oxidation of *N*-aminophthalimide reacted with a large excess of 1,3-dimethoxybenzene to give the insertion product (**5**; $R^2 = H$) (28—37%) and only a trace (n.m.r.) of the azepine (**3**; $R^2 = H$); similarly 1,3,5-trimethoxybenzene gave (**5**; $R^2 = OMe$) as the only isolable product (53%). Since traces of acid are thought to be important in determining the product distribution in the reactions of nitrenes with aromatic compounds[6] it seemed likely that the acetic acid produced in the oxidative generation of (**1**) diverted the aziridinobenzene (**7**) to the aromatic product (**5**).[1a] This effect was in part imitated by generating (**1**) from (**2**) in the presence of acetic acid (1 equiv.). Under these conditions reaction of (**1**) with 1,3-dimethoxybenzene gave mostly the insertion product (**5**; $R^2 = H$) (2 parts) at the expense of the azepine (**3**; $R^2 = H$) (1 part).

Satisfactory analytical and spectral data have been obtained for all the new compounds described.

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