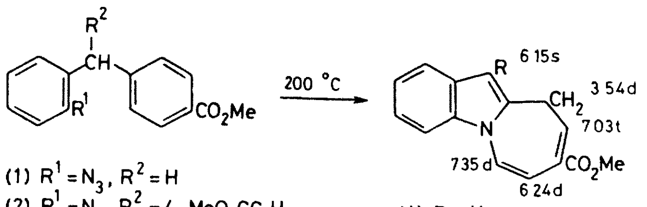
Ring Expansion of an Electron-deficient Benzene by a Nitrene

By PETER C. HAYES and GURNOS JONES*
(*Chemistry Department, University of Keele, Keele, Staffs* ST5 5BG)

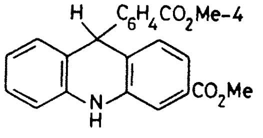
Summary Thermal decomposition of 4-(2-azidobenzyl)-methoxycarbonylbenzene (**1**) and the triphenylmethyl analogue (**2**) gives azepinoindoles, by nitrene insertion into the electron-deficient benzene ring.

CONSPICUOUSLY absent from the now extensive list of nitrene reactions is an insertion into an electron-deficient benzene ring, with subsequent expansion to give an azepine. Methanesulphonylnitrene, apparently in the singlet state, has been shown to attack benzene rings with electron-withdrawing substituents, but no ring expansion was observed, the products being anilides.[1] Our experience of intramolecular nitrene insertions[2] led us to expect ring expansion from the combination of high energy (thermal generation at 200 °C) and favourable geometry, and we have now shown that insertion–expansion does occur.

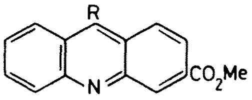


(1) $R^1 = N_3$, $R^2 = H$
(2) $R^1 = N_3$, $R^2 = 4\text{-}MeO_2CC_6H_4$
(3) $R^1 = NH_2$, $R^2 = H$

(4) R = H
(5) $R = 4\text{-}MeO_2CC_6H_4$



(6)



(7) R = H
(8) $R = 4\text{-}MeO_2CC_6H_4$

We have prepared 4-(2-azidobenzyl)methoxycarbonylbenzene (**1**) and the triphenylmethane (**2**).† Both decomposed cleanly in trichlorobenzene at 200 °C. From the azide (**1**) the products were the azepinoindole (**4**) (34%), the amine (**3**) (1·4%), and the acridine (**7**) (1%). From the azide (**2**) the products were the azepinoindole (**5**) (34%) the acridan (**6**) (10%), and the acridine (**8**) (5%). Chemical shifts and multiplicities for the protons on the azepinoindole (**4**) are shown with the formula; important features are the 2H doublet at δ 3·54 and the indolic β-hydrogen at δ 6·15, establishing the 10*H*-azepinoindole structure. Important spectral points for the acridines were a doublet at δ 8·99 (*J* 1·2 Hz, 4-H), which showed a large downfield shift with Eu(fod)$_3$. The small coupling constant proves that the methoxycarbonyl group is at position 3, and that no rearrangement has taken place.

We thank the S.R.C. and Glaxo (Research) Ltd., for a CASE award (to P.C.H.).

(*Received*, 19*th June* 1980; *Com.* 666.)

---

† The azides (**1**) and (**2**) were obtained from the corresponding amines by diazotisation and subsequent treatment with sodium azide, by previously reported procedures (ref. 2). All new compounds gave satisfactory microanalyses.

[1] R. A. Abramovitch, G. N. Knaus, and V. Uma, *J. Org. Chem.*, 1974, **39**, 1101.

[2] G. R. Cliff and G. Jones, *J. Chem. Soc. (C)*, 1971, **3418**; R. N. Carde and G. Jones, *J. Chem. Soc., Perkin Trans.* 1, 1974, 2066; R. N. Carde, G. Jones, W. McKinley, and C. J. Price, *ibid.*, 1978, 1211.