The Production of Acridines by a Nitrene Insertion Reaction

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Summary Thermal decomposition of 2-azido-2′-methoxydiphenylmethane gives predominantly acridans and acridines, as well as the expected azepinoindoles, while 2-azido-4′-methoxydiphenylmethane and 2-azido-2′-methyldiphenylmethane give azepinoindoles with no trace of acridans or acridines.

NITRENE insertion reactions leading to the production of five- or seven-membered heterocyclic rings have often been reported.[1] The only aromatic azide decomposition reactions proceeding through a nitrene intermediate and leading to six-membered heterocycles are those in which the nitrene inserts into the C–H bond of a suitably placed methyl or methylene group (giving dihydrophenanthridines[2] or tetrahydroquinolines[3]) and those leading to phenothiazines.[4,5] When an alkyl nitrene substitutes in an aromatic ring to give a dihydrophenanthridine,[6] the yield is low. We now report a case where nitrene insertion leads predominantly to acridine derivatives, as well as to azepinoindoles.

The product from thermal decomposition† of the parent azide (**1**) was the azepinoindole (**2**).[7] Similarly, 2-azido-4′-methoxydiphenylmethane (**3**) gave the methoxyazepinoindole (**4**).‡ However, decomposition of 2-azido-2′-methoxydiphenylmethane (**5**) gave a mixture of ten components.

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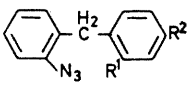
† All decompositions were performed in trichlorobenzene under a nitrogen atmosphere, at 180—200°.

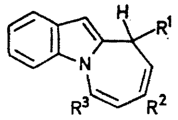
‡ All compounds mentioned were fully characterised and gave satisfactory analyses unless otherwise stated.

The principal products and their percentage yields estimated by g.c. were as follows: the methoxyazepinoindole (**6**) and the azepinoindolone (**7**) (7·7%); acridan (**8**) (10%) and acridine (**9**) (2·8%); 1-methoxyacridan (**10**) (26%) and 1-methoxyacridine (**11**) (7%).§ Acridine derivatives make up approximately 46% of the total products, and over 80% of those separable by g.c.;¶ most of the compounds can be derived from the two azanorcaradiene intermediates shown in the Scheme. Comparison with the reaction producing methoxylated phenothiazines would have suggested the isomeric 4-methoxyacridan as the most likely product.[5]

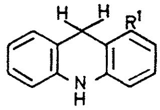
The methoxyacridan (**10**) is extremely readily oxidised; rigid exclusion of oxygen during decomposition and work-up suggests that an internal oxidation–reduction system is responsible for the production of 1-methoxyacridine (**11**). The new insertion process is not due to an *ortho* (steric) effect, since decomposition of 2-azido-2′-methyldiphenylmethane (**14**) gave as the main characterised product the azepinoindole (**15**). Examination of the crude mixture of products by n.m.r. spectroscopy showed no trace of acridan or acridine products.



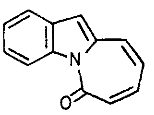
(1) $R^1 = R^2 = H$
(3) $R^1 = H, R^2 = OMe$
(5) $R^1 = OMe, R^2 = H$
(14) $R^1 = Me, R^2 = H$



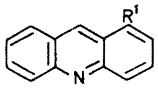
(2) $R^1 = R^2 = R^3 = H$
(4) $R^1 = R^3 = H, R^2 = OMe$
(6) $R^1 = R^2 = H, R^3 = OMe$
(15) $R^1 = Me, R^2 = R^3 = H$
(16) $R^1 = OMe, R^2 = R^3 = H$



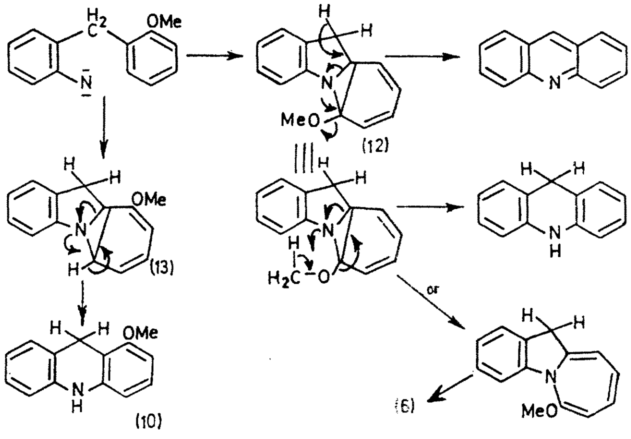
(8) $R^1 = H$
(10) $R^1 = OMe$



(7)



(9) $R^1 = H$
(11) $R^1 = OMe$



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§ Identical with a synthetic sample supplied by Professor E. Ritchie.

¶ Also shown to be present by g.l.c.–m.s. examination were 2-amino-2′-methoxydiphenylmethane, and the methoxyazepinoindole (**16**).

[1] See, for example, R. K. Smalley and H. Suschitzky, *Chem. and Ind.*, 1970, 1338.
[2] G. Smolinsky, *J. Amer. Chem. Soc.*, 1960, **82**, 4717; *ibid.*, 1961, **83**, 2489.
[3] G. Smolinsky and B. I. Feuer, *J. Org. Chem.*, 1964, **29**, 3097.
[4] P. A. S. Smith, B. B. Brown, R. K. Putney, and R. F. Reinisch, *J. Amer. Chem. Soc.*, 1953, **75**, 6335.
[5] J. I. G. Cadogan and S. Kulik, *Chem. Comm.*, 1970, 792 and references therein.
[6] R. A. Abramovitch and E. P. Kyba, *Chem. Comm.*, 1969, 265.
[7] G. R. Cliff, E. W. Collington, and G. Jones, *J. Chem. Soc.* (*C*), 1970, 1490.