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Formation of Norcaradiene Derivatives from an α-Oxocarbene and Aromatic Compounds: Their Conversion into Novel Acenaphtho[1,2-b]benzofurans and their Silver Ion Catalysed Aromatisations

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Summary Photolysis of 2-diazoacenaphthen-1-one in benzene gives spiro[acenaphthene-1,7'-cis-norcara-2',4'-diene]-2-one (3) which rapidly isomerises to 2-phenylacenaphthen-1-one under silver perchlorate catalysis and gives the novel acenaphtho[1,2-b]benzofuran (5; X = H) in the presence of dicyanodibenzoquinone (DDQ), other aromatic receptors giving similar results.

ADDITION of α -oxocarbenes to aromatic systems to give isolable norcaradienes has not been reported. We now record the first example and also describe the conversion of



† New compounds had correct m.s., n.m.r., and analytical characteristics.

the product into a new heterocyclic system and, for the first time, the smooth silver ion catalysed aromatisation of the strained norcaradiene system.



SCHEME 2

Thus, photolysis in Pyrex or quartz of 2-diazoacenaphthen-1-one (1) in benzene gives the spiro-compound (3; X = H; 84%),† presumably via the α -oxocarbene (2), as stable pink rods which isomerised to compound (4; X = H; 66%) after 3 days in boiling *p*-xylene. This aromatisation was catalysed by toluene-p-sulphonic acid and, significantly, occurred very rapidly with the production of a transient red colour, under the influence of silver perchlorate (4%), thus providing the first extension of the silver ion catalysed cleavage of strained rings¹ to the norcaradiene system. Reaction of the norcaradiene (3; X = H) with DDQ in toluene gave the new heterocycle acenaphtho[1,2-b]benzofuran (5; X = H; 68%). Similar reactions were effected in p-xylene and toluene instead of benzene. The isomeric spirocycloheptatriene derivatives were not detected. Reactions as in Scheme 1 are likely possibilities.

Formation of the norcaradiene (3) from the oxocarbene is doubtless a function of the inability of the latter to undergo a Wolff ring contraction but it is of interest not only for its rarity, but also in comparison with the oxocarbene (6), which also is reluctant to undergo a Wolff reaction.² In the latter case, in contrast, the corresponding norcaradiene (7) was not detected, and the product is the dihydrofuran (8) (Scheme 2). The difference in behaviour can be attributed to the greater accessibility of the ketone



SCHEME 3

group with respect to the bridgehead carbon atom marked with an asterisk (*) in (7) compared with (3). In this connection ¹H n.m.r. spectroscopy shows clearly that (3; X = H or Me) is the *endo*-isomer,[‡] as depicted in Scheme 1,

‡ endo- and exo- are used here in relation to the acenaphthene aromatic rings.

² B. M. Trost and P. L. Kinson, Tetrahedron Letters, 1973, 2675.

rather than the *exo*-form (9). In particular the adducts (3; X = H, Me) exhibit first-order doublets at $\tau 3 \cdot 1 - 3 \cdot 2$ attributable to the shielded proton H_{a} .

Finally it is noteworthy that considerable steric crowding in the aromatised product (4; X = Me) leads to a conformational effect observable on the n.m.r. time scale. Thus singlets at 28 °C attributable to aromatic methyl groups (τ 7.68br, and 7.85) sharpen considerably at 60 °C and progressively broaden at lower temperatures and eventually split into doublets at -50 °C (τ 7.58, 7.92; 7.32, 8.59) (Scheme 3).

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¹ L. A. Paquette, Accounts Chem. Res., 1971, 4, 280.