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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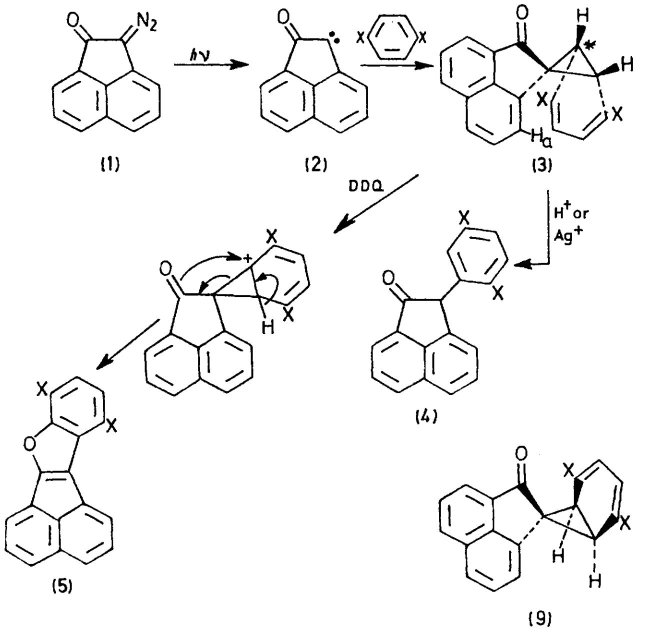
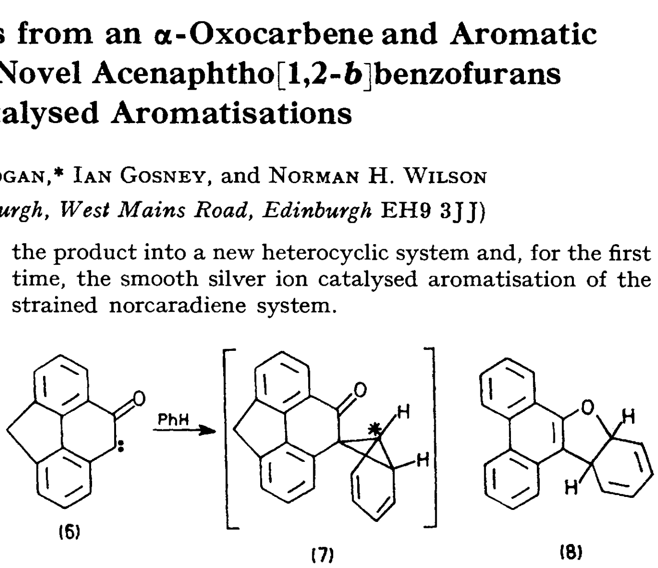
Summary Photolysis of 2-diazoacenaphthen-1-one in benzene gives spiro[acenaphthene-1,7′-*cis*-norcara-2′,4′-diene]-2-one (**3**) which rapidly isomerises to 2-phenylacenaphthen-1-one under silver perchlorate catalysis and gives the novel acenaphtho[1,2-*b*]benzofuran (**5**; X = H) in the presence of 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 the product into a new heterocyclic system and, for the first time, the smooth silver ion catalysed aromatisation of the strained norcaradiene system.



Scheme 1



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 rings[1] 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

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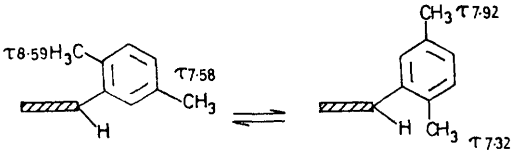
† New compounds had correct m.s., n.m.r., and analytical characteristics.

dihydrofuran (**8**) (Scheme 2). The difference in behaviour can be attributed to the greater accessibility of the ketone group with respect to the bridgehead carbon atom marked with an asterisk (*) in (**7**) compared with (**3**). In this connection ^{1}H n.m.r. spectroscopy shows clearly that (**3**; X = H or Me) is the *endo*-isomer,‡ as depicted in Scheme 1, rather than the *exo*-form (**9**). In particular the adducts (**3**; X = H, Me) exhibit first-order doublets at τ 3·1—3·2 attributable to the shielded proton H_a.



Scheme 3

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

[1] L. A. Paquette, *Accounts Chem. Res.*, 1971, **4**, 280.
[2] B. M. Trost and P. L. Kinson, *Tetrahedron Letters*, 1973, 2675.