Synthesis of the First Examples of 1,4-Benzodioxocines

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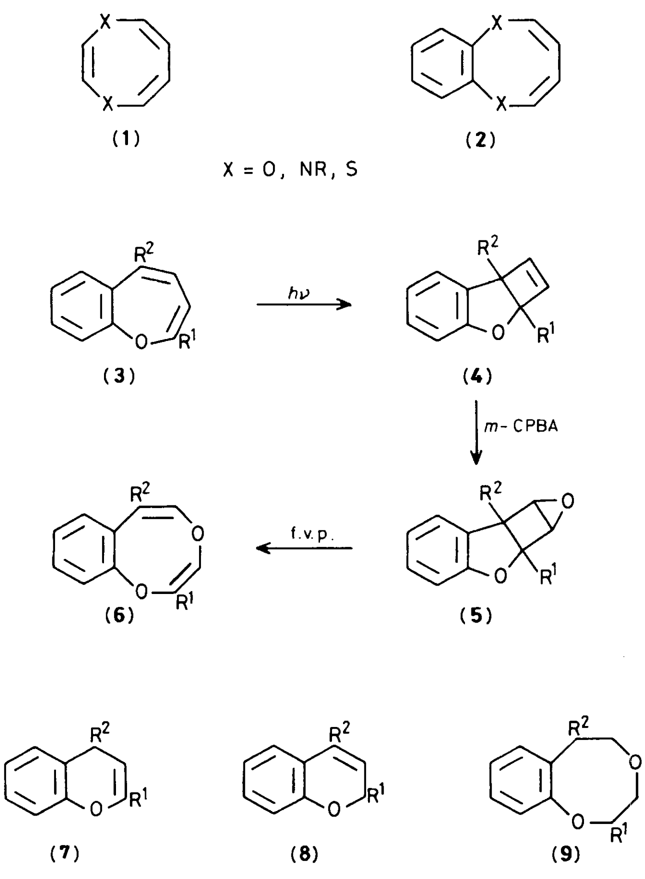
Flash vacuum pyrolysis of the 1a,1b,6b,6c-tetrahydro-oxireno[2′,3′ : 3,4]cyclobuta[1,2-*b*][1]benzofurans (**5**), prepared from the benzoxepines (**3**) *via* two steps, results in ring-opening to give the novel 1,4-benzodioxocines (**6**), whose spectral data indicate that they are non-aromatic.

The new dihetero eight-membered ring compounds, isoelectronic with the cyclo-octatetraene dianion,[1] have recently been of considerable interest as ten-π-electron systems.[2] Monocyclic diheterocines of the type (**1**) such as 1,4-dioxocines,[3] 1,4-dithiocines,[4] 1,4-diazocines,[5] and 1,4-oxazocines[6] have already been synthesized mainly by valence bond isomerizations of *cis*-diheterobis-σ-homobenzenes or cyclobutene ring systems, and their molecular structures and properties have been studied. As for the benzo-series, the 1,6-benzodiheterocines (**2**: X = O,[7] S,[8] and NR[9]) are known, but other isomers, *viz.* the 1,4-benzodiheterocines, have not been reported. Here we report the synthesis of the first examples of 1,4-benzodioxocines (**6**) by a new route for heterocines.

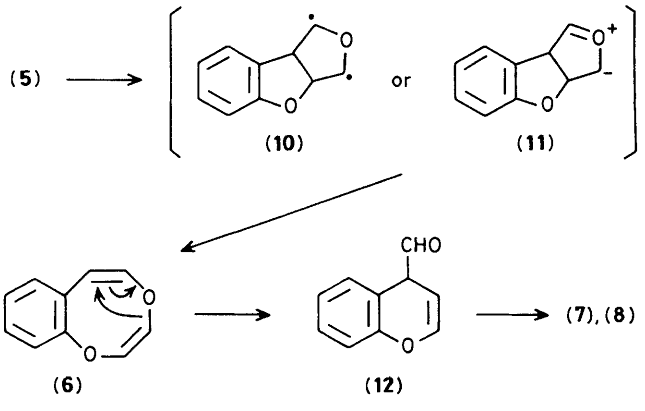
The benzoxepines (**3a**—**c**) prepared by the reaction[10] of pyridazine *N*-oxides with benzyne were irradiated to give the tricyclic compounds (**4**) (70—80% yields), which were treated with *m*-chloroperbenzoic acid (*m*-CPBA) to afford the oxirane compounds (**5**)[†] in *ca.* 80% yields (Scheme 1).

Recently, we have shown that thermolysis of some heterotricycloheptanes having a similar bicyclopentane system to (**5**) in refluxing toluene or xylene resulted in ring-opening to give the corresponding 1,4-dihetero seven-membered ring compounds.[11] Although the tricyclo-octanes (**5**) were heated in solvents at 250 °C, no reaction occurred. However, flash vaccum pyrolysis (f.v.p.) of (**5**) at 550 °C (3 × 10^{-5} mmHg) resulted in valence bond isomerization with ring expansion to give the desired novel 1,4-benzodioxocines (**6a**—**c**)[‡] in 15—25% yields, together with the benzopyrans[12] (**7**) (10—25%) and (**8**) (10—20%). Hydrogenation of (**6**) with Pd–C gave the tetrahydrodioxocines (**9**)[§] in 90% yields (see Scheme 1).



a; R¹ = R² = H
b; R¹ = H, R² = Me
c; R¹ = R² = Me

Scheme 1



Scheme 2

[†] Satisfactory elemental analyses and spectral data were obtained for (**5**); *e.g.*, (**5a**): yellow oil; δ (^{1}H) ($CDCl_3$) 3.80—4.14 (3H, m, 1-, 6-, and 7-H), 4.90 (1H, t, 2-H), 6.9—7.3 (4H, m, Ph-H), $J_{2,6}$ 4, and $J_{1,7}$ 2 Hz. The stereochemistry of (**5**) is not known at present.

[‡] Satisfactory elemental analyses and spectral data were obtained for the new dioxocines (**6**); *e.g.*, (**6a**): colourless oil; δ (^{1}H) ($CDCl_3$) 6.34 (1H, d, 2-H), 5.93 (1H, d, 3-H), 6.30 (1H, d, 5-H), 5.46 (1H, d, 6-H), 7.14 (4H, br, Ph-H), $J_{2,3}$ 3.4, and $J_{5,6}$ 7.8 Hz; δ (^{13}C) ($CDCl_3$) 142.8 (d, C-2), 133.2 (d, C-3), 136.4 (d, C-5), 107.7 (d, C-6), Ph-C [121.7 (d), 125.4 (d), 128.6 (d), 128.9 (s), 131.1 (d), and 155.2 (s)]. (**6b**): colourless oil; δ (^{1}H) 1.94 (3H, d, 6-Me), 5.78 (1H, d, 3-H), 6.12 (1H, d, 2-H), 6.21 (1H, m, 5-H), 6.9—7.4 (4H, m, Ph-H), $J_{5,6\text{-Me}}$ 1 and $J_{2,3}$ 3.5 Hz; δ (^{13}C) 137.5 (d, C-2), 133.3 (d, C-3), 130. 1 (d, C-5), 124.9 (s, C-6), Ph-C [122.2 (d), 125.4 (d), 127.6 (d), 129.4 (d), 132.5 (s), and 152.9 (s)]. The spectral assignments were performed by spin-decoupling or selective hetero-decoupling experiments. It is well known that the geminal coupling constants have an approximately linear dependence on the electronegativity of substituents in vinyl compounds (ref. 13); therefore, the small coupling constant (3.4 Hz) for the O–CH=CH–O function in (**6**) seems to be reasonable.

[§] Satisfactory elemental analyses and spectral data were obtained for (**9**); *e.g.*, (**9a**): colourless oil; *m/z* 164 (M^+); δ (^{1}H) ($CDCl_3$) 2.91 (2H, m, 6-H), 3.67 (2H, m, 3-H), 3.78 (2H, m, 5-H), 4.08 (2H, m, 2-H), and 6.9—7.3 (4H, m, Ph-H).

The ring conversion of (**5**) into (**6**) may proceed *via* cleavage of the C–C bond in the oxirane ring to the biradical (**10**) or the ionic intermediate (**11**), followed by ring-opening of the furan ring (Scheme 2). The benzopyrans (**7**) and (**8**) are derived from the initially formed dioxocines (**6**); this was confirmed by further pyrolysis of (**6**) under the same conditons to give (**7**) and (**8**) (30—40% yields). Although the detailed mechanism is not known, we assume that the formation of (**7**) and (**8**) from (**6**) proceeds *via* [1,3]-sigmatropic rearrangement or homolytic C(3)–O bond fission to the formyl intermediate (**12**) followed by decarbonylation (see Scheme 2).

The structures of (**6**) are based mainly on the n.m.r. spectral data. The ^{1}H n.m.r. signals (δ 5.46—6.34) of the heterocyclic ring protons in (**6**) lie in the olefinic range and the vicinal coupling constants ($J_{2,3}$ 3.4 and $J_{5,6}$ 7.8 Hz) are relatively small. Moreover, compounds (**6**) exhibit ^{13}C resonances at relatively low field strength for all the eight-membered ring carbon atoms. These spectral properties are similar to those of the non-aromatic monocyclic 1,4-dioxocines[3] and 1,6-benzodioxocines[7] and are different from those of the monocyclic 1,4-diazocines[5] and 1,4-oxazocines,[6,9] which are known to have a planar structure and aromatic character. The above data lead to the conclusion that the 1,4-benzodioxocines (**6**) possess no substantial diamagnetic ring current due to the lower tendency of the oxygen atom to π-electron delocalization and are thus non-aromatic.

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