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THERMOLYSIS OF 8-AZA- AND 8-OXABENZO[C]TRICYCLO[5.1.0.0^{2,6}]OCTANES: FORMATION OF 3-BENZAZOCINES AND 3-BENZOXOCINS

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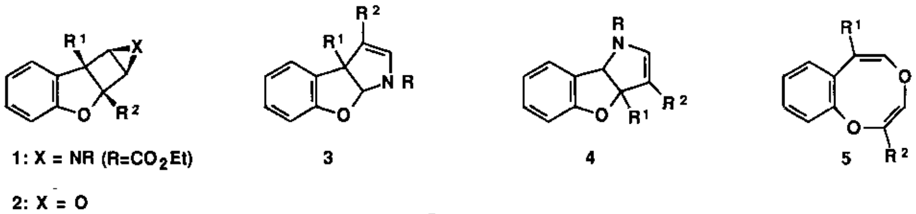
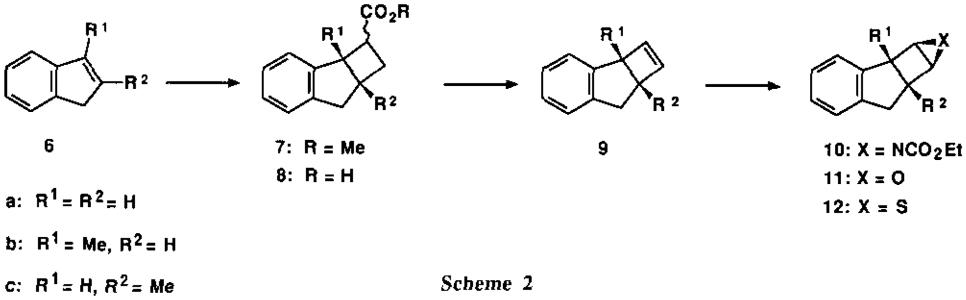
Abstract —— Flash vacuum pyrolysis of 8-aza- (10) and 8-oxabenzo[c]tricyclo[5.1.0.0^{2,6}]octanes (11) resulted in ring-expansion to give the novel 3-benzazocines (14) and 3-benzoxocins (16), respectively. In the case of 11, several kinds of rearrangement products were also obtained.

The ring-opening reactions of highly strained bicyclopentane ring systems[1] and their hetero analogues[2-5] have recently been the object of extensive study. We have reported that the thermolysis of the oxazabenzotricyclo-octanes (1) in xylene at 160 °C resulted in rearrangement to give two kinds of benzofuropyrroles (3) and (4),[4] whereas the flash vacuum pyrolysis (f.v.p.) of the dioxa derivatives (2) resulted in ring-expansion to form the novel 1,4-benzodioxocins (5),[5] although even when the compounds (2) were heated in solvents at 250 °C, no reaction occurred, (Scheme 1). These results prompted us to examine the thermal behavior of the title benzotricyclo-octanes having no oxygen atom in the five-membered ring, and we report here that the f.v.p. of them gave 3,6-dihydro-3-benzazocines and 6H-3-benzoxocins, which are new eight-membered heterocyclic rings, although the synthesis of eight-membered heterocyclic ring systems has recently been widely investigated.[6]



Scheme 1

The synthetic route to the starting benzotricyclo-octanes (10)-(12) used in the present thermolysis is shown in Scheme 2. The methoxycarbonylbenzobicycloheptanes (7a-c), prepared from indenes (6) by photocycloaddition with methyl acrylate, were hydrolyzed to the acids (8), which were oxidatively decarboxylated by treatment with lead tetra-acetate to give the bicycloheptenes (9). The benzotricyclo compounds (10, 11, and 12) were prepared from 9 by treatment with ethoxycarbonylnitrene,[7] m-chloroperbenzoic acid, and succimide-N-sulfenyl chloride followed by $LiAlH_4$,[8] respectively.[9]



6

7: R = Me
8: R = H

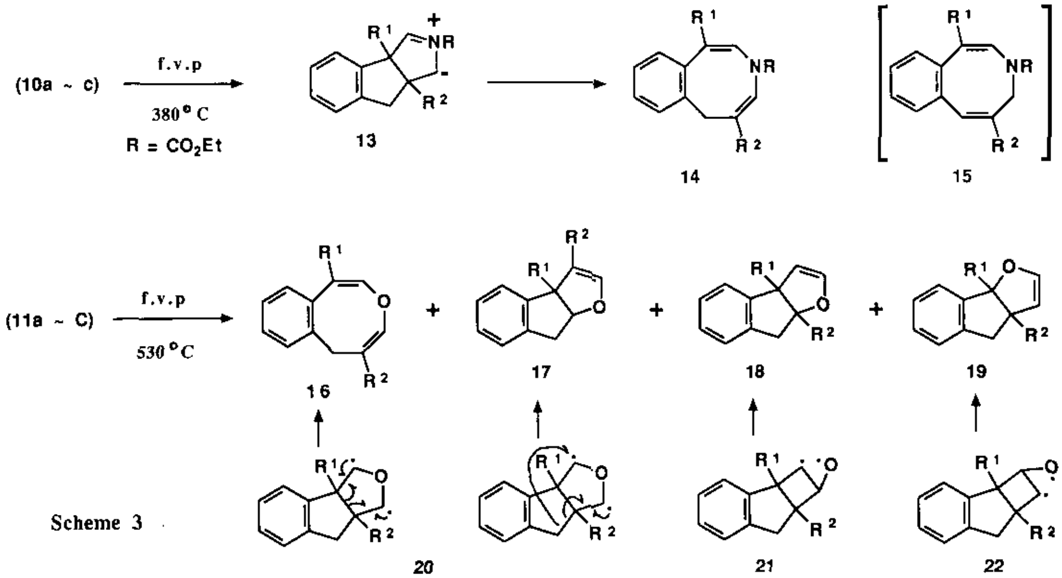
9

10: X = NCO_2Et
11: X = O
12: X = S

a: $R^1 = R^2 = H$
b: $R^1 = Me, R^2 = H$
c: $R^1 = H, R^2 = Me$

Scheme 2

Although heating the aziridine compounds (10a-c) in dichlorobenzene at 180 °C gave complex mixtures and no characterizable products, f.v.p. of them at 380 °C (3×10^{-5} mmHg) gave the expected 3-benzazocines (14)[10] in 60-80% yields as the sole products, probably via the ionic intermediates (13) formed by initial C-C bond fission in the aziridine ring by analogy with the thermolysis of 1.[4]



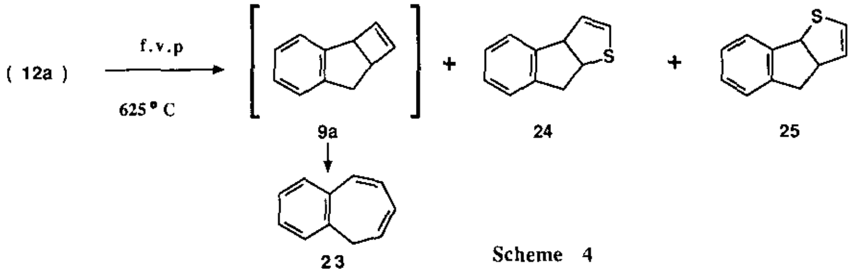
Scheme 3

The structures of the novel 3,6-dihydro-3-benzazocines (14) were characterized by elemental and spectroscopic analyses. For example, in the ^{1}H-nmr spectrum of 14a,[10] signals due to the four heterocyclic ring protons lie in the olefinic range (δ 5.5-6.7) as two pairs of doublets and one of them is further coupled with a methylene signal at δ 3.66. The ^{13}C-nmr spectrum of 14a shows a signal due to the ring methylene carbon at δ 33.36 (t). These spectroscopic data are consistent with the proposed 3,6-dihydro structures (14) for the products and rule out the 3,4-dihydro structures (15).

As compared with the case of the aziridine compounds (10), higher temperatures were needed for the thermolysis of the oxirane compounds (11). F.v.p. of 11a-c at 530 °C also gave the novel 6H-3-benzoxocins (16)[11] in 10-15% yields, but in the case, several kinds of rearrangement products such as indenofurans (17)-(19) were formed in 50-60% yields[12] together with 16. In contrast with the case of the aziridines (10), the thermolysis of the oxiranes (11) may proceed via homolytic bond fission only at a high temperature to give the biradical intermediates (20-22) shown in Scheme 3.[13] The ring-expansion products (16) and the rearrangement products (17) may be derived from 20 formed by C-C bond fission and the biradicals (21) and (22) formed by C-O bond fission might afford the other rearrangement products (18) and (19), respectively.

In addition, heating the thiirane compound (12a) in xylene at 160 °C resulted only in desulfurization to give the cyclobutaindene (9a) in 60-70% yield, whereas f.v.p. of 12a at 625 °C gave 5H-benzocycloheptene (23: 14%) and two rearrangement products (24: 26%) and (25: 11%), but no ring-expansion product. The former product (23) may be derived from initially formed 9a.

The properties of several heterocine monoanions, which are 10π-electron systems, have been reported.[6,14] However, attempts to convert 14 and 16 into their monoanions by removal of a proton have been unsuccessful.



Scheme 4

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9. In the ^{1}H-nmr spectrum of 11b, a nuclear Overhauser effect enhancement (15-20%) was observed only between the methyl (R^1) signal and a proton (R^2) signal; indicating that 11b is the anti-sterostructure shown in Scheme 2, and consequently, all of the tricyclic compounds are considered to be similar stereostructures.
10. 14a: viscous oil; ir (neat) 1730 (C=O) cm^{-1}; ^{1}H-nmr ($CDCl_3$) δ 1.30 and 4.24 (3H, t, and 2H, q, J=7 Hz, CO_2Et), 3.66 (2H, d, J=8 Hz, 6-H_2), 5.52 (1H, d, J=11 Hz, 1-H), 5.72 (1H, dt, J=8 and 8 Hz, 5-H), 6.16 (1H, d, J=8 Hz, 4-H), 6.74 (1H, d, J=11 Hz, 2-H), 7.1-7.3 (4H, m, Ph-H); ^{13}C-nmr (8-membered ring carbons) δ 33.36 (t, 6-C), 112.30 (d, 5-C), 126.01 (d, 4-C), 126.95 (d, 2-C), 128.07 (d, 1-C), 135.83 (s, 6a-C), 139.13 (s, 10a-C); 14b: mp 49-51 °C; 14c: viscous oil.
11. 16a: viscous oil; ^{1}H-nmr ($CDCl_3$) δ 3.58 (2H, dd, J=8 and 1 Hz, 6-H_2), 5.44 (1H, d, J=8 Hz, 1-H), 5.46 (1H, m, 5-H), 6.14 (1H, d, J=8 Hz, 2-H), 6.20 (1H, dd, J= 6 and 1 Hz, 4-H), 7.06 (4H, s, Ph-H); ^{13}C-nmr (8-membered ring carbons): δ 31.59 (t, 6-C), 110.98 (d, 5-C), 118.75 (d, 1-C), 135.2 (s, 6a-C), 139.59 (s, 10a-C), 142.28 and 143.36 (each d, 2- and 4-C); 16b: viscous oil; 16c: viscous oil.
12. Yields and ratios of these rearrangement products were dependent on the methyl group and experimental conditions; details will be published in a full paper.
13. Such difference in thermolysis between aziridine and oxirane rings has been widely observed.[2-5]
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