THERMAL REARRANGEMENTS OF 8-AZA- AND 8-OXA-3,4-DIAZATRICYCLO-[5.1.0.$0^{2,6}$]OCT-4-ENES

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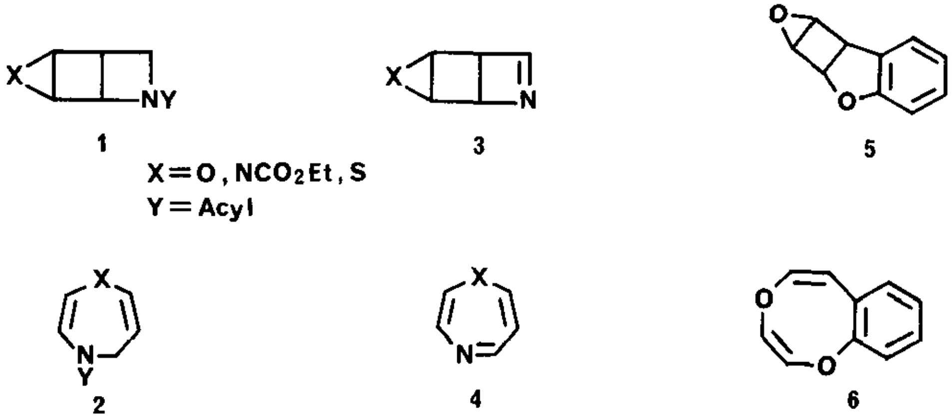
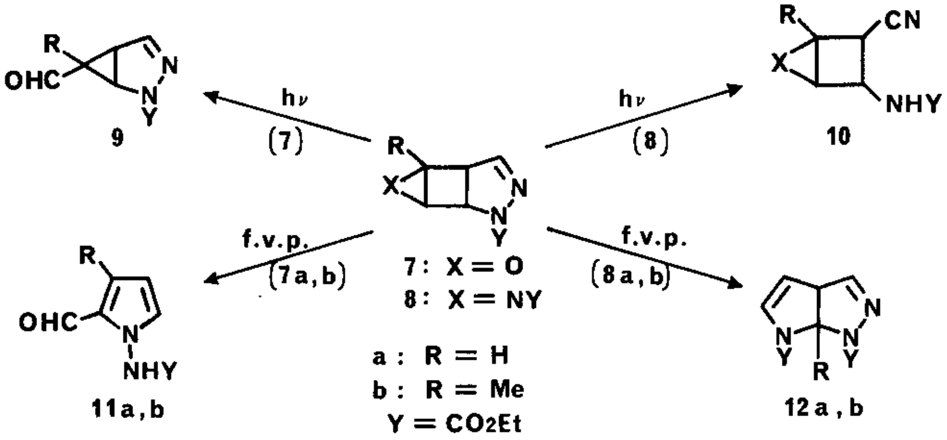
Abstract — Flash vacuum pyrolysis of the 8-oxa-3,4-diazatricyclo-[5.1.0.$0^{2,6}$]oct-4-enes (7) resulted in rearrangement to give the 1-amino-2-formylpyrroles (11), presumably via the 1,4,5-oxadiazocines (14), whereas that of the 8-aza analogues (8) gave the 3a,6a-dihydropyrrolo[2,3-c]pyrazoles (12) by a different type of rearrangement.

It has shown that the tricyclic compounds with a highly strained bicyclopentane ring system can be used as synthons for seven- and eight-membered heterocycles.[1-4] For example, the thermolysis or photolysis of 3-azatricyclo[4.1.0.$0^{2,5}$]-heptanes (1)[2] and -heptenes (3)[3] resulted in valence isomerization with ring opening to give the corresponding 1,4-dihydro seven-membered ring compounds (2) and (4). The tetrahydro-oxirenocyclobutabenzofurans (5), upon pyrolysis, afforded the 1,4-benzodioxocins (6).[4] These results prompted us to examine the ring opening of the 8-oxa- (7) and 8-aza-3,4-diazatricyclo[5.1.0.$0^{2,6}$]oct-4-enes (8),[5] prepared



Scheme 1

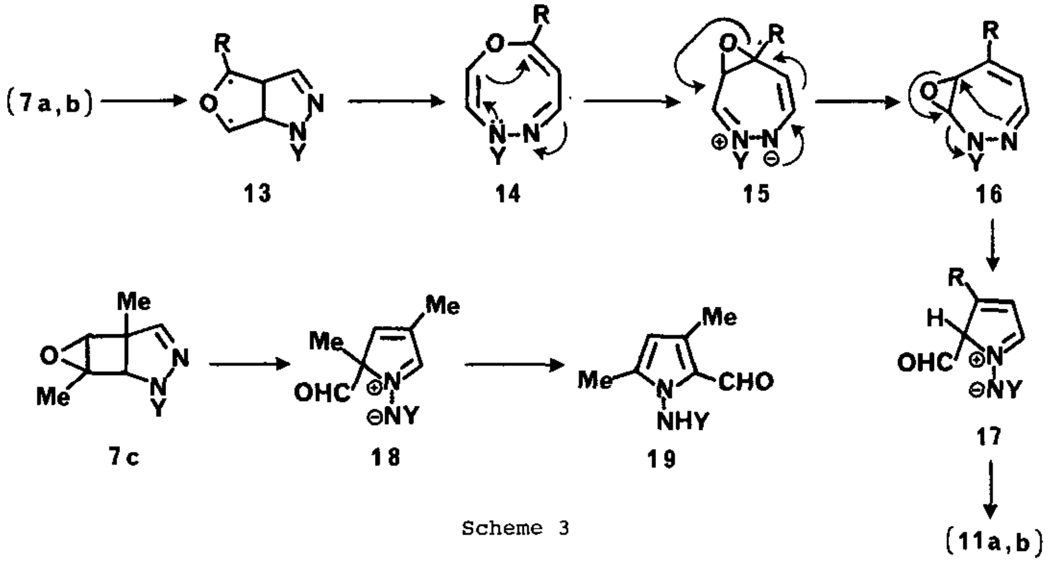


Scheme 2

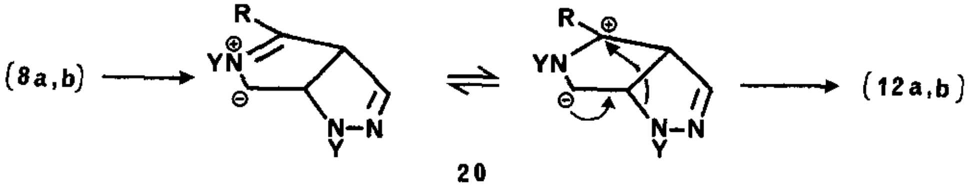
from 2,3-dihydro-1H-1,2-diazepines[6] *via* four steps. And we have reported[5] that the photolysis of 7 and 8 afforded the ring contraction products (9) and (10), respectively, although the expected ring expansion products such as oxadiazocines and triazocines could not be obtained. However, upon heating in solvents at 100-160 °C, the 8-oxa compounds (7) were not changed and the 8-aza compounds were decomposed to give complex mixtures, but no characterizable product. We report here that the flash vacuum pyrolysis of 7 and 8 gave interesting rearrangement products.

Flash vacuum pyrolysis of the 8-oxa compounds (8a,b) at 390 °C (3×10^{-5} mmHg) gave complex mixtures, from which the rearrangement products (11),[7] 1-amino-2-formylpyrroles, were isolated by chromatography as the sole characterizable products. On the other hand, the pyrolysis of the 8-aza compounds (8a,b) under similar conditions gave the different type of rearrangement products (12),[8] 3a,6a-dihydropyrrolo[2,3-c]pyrazoles, in 20-30% yields.

A possible mechanism for the pyrolysis of the 8-oxa compounds (7) is shown in Scheme 3. The pyrolysis may proceed by initial formation of the expected 1,4,5-oxadiazocines (14) *via* the biradical intermediates (13) by analogy with the case of 5. The oxadiazocines (14) might rearrange to the pyrrolinium imides (17), presumably *via* the oxiranes (15) and (16) successively, then the imides (17) are aromatized to give the products (11). The presence of the imide intermediates (17) was confirmed by the following results. In the pyrolysis of the 8-oxa-1,6-dimethyl compound (7c), the imide (18)[9] could be isolated in *ca*. 10% yield,



Scheme 3



Scheme 4

together with 1-ethoxycarbonyl-2-formyl-3,5-dimethylpyrrole (**19**).[10] Further heating the N-imide (**18**) in xylene at 140 °C for 4 days resulted in migration of the formyl group to give the pyrrole (**19**) in 85% yield. On the other hand, the ring conversion of the 8-aza compounds (**8**) into **12** may proceed *via* initial C-C bond fission in the aziridine ring to the ionic intermediates (**20**), which may undergo such rearrangement as shown in Scheme 4 to give **12**.

The difference in pyrolysis between **7** and **8** may depend on the different mode of the initial bond fission in the three-membered ring. The pyrolysis of the oxiranes (**7**) may proceed *via* homolytic fission only at a high temperature, thus does not proceed in solution at 160 °C. On the contrary, the aziridines (**8**) might undergo ionic bond cleavage even at a lower temperature (100-160 °C), but the intermediates would decompose preferentialy in solution, and the rearrangement products (**12**) could be obtained only by the flash vacuum pyrolysis.

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7. Satisfactory elemental analyses and spectral data were obtained for all new compounds reported; *e.g.*, (**11a**): mp 64-65 °C; ir (KBr): 3360 (NH), 1730 and 1660 (C=O) cm^{-1}; ^{1}H-nmr δ (CDCl$_3$): 1.28 and 4.34 (3H, t, and 2H, q, CO$_2$Et), 6.44 (1H, dd, 4-H), 7.16 (1H, dd, 3-H), 7.26 (1H, dd, 5-H), 8.68 (1H, br, NH), $J_{3,5}$= 2, $J_{3,4}$= 4, $J_{4,5}$= 3 Hz; (**11b**): mp 77-79 °C. The structures of **11** were characterized by spectral comparison with 2-formylpyrroles [T.J. Batterham, "NMR Spectra of Simple Heterocycles," John Wiley & Sons, N.Y., 1973, p. 146].
8. Compound (**12a**): viscous oil; ir (neat): 1730 (C=O) cm^{-1}; ^{1}H-nmr δ (CDCl$_3$): 1.28 and 4.22 (3H, t, and 2H, q, CO$_2$Et), 1.32 and 4.30 (3H, t, and 2H, q, CO$_2$Et), 4.48 (1H, m, 3a-H), 5.04 (1H, dd, 4-H), 6.54 (1H, d, 6a-H), 6.72 (1H, dd, 5-H), 6.93 (1H, d, 3-H), $J_{3,3a}$= 1, $J_{3a,4}$= 3, $J_{3a,5}$= 2, $J_{3a,6a}$= 8, $J_{4,5}$= 4 Hz; ^{13}C-nmr (ring carbons): 57.12 (d, 3a-C), 74.77 (d, 6a-C), 104.01 (d, 4-C), 132.07 (d, 5-C), 146.01 (d, 3-C).
9. Compound (**18**): mp 86-88 °C; ir (KBr): 1730 and 1690 (C=O) cm^{-1}; ^{1}H-nmr δ (CDCl$_3$): 1.36 and 4.36 (3H, t, and 2H, q, CO$_2$Et), 1.43 (3H, s, 2-Me), 1.83 (3H, d, 4-Me), 5.28 (1H, m, 3-H), 6.95 (1H, d, 5-H), 9.60 (1H, s, CHO), $J_{3,5}$=2, $J_{3,4\text{-Me}}$= 1.5 Hz.
10. Compound (**19**): mp 90.5-91.5 °C; ir (KBr): 3360 (NH), 1740 and 1650 (C=O) cm^{-1}; ^{1}H-nmr δ (CDCl$_3$): 1.28 and 4.32 (3H, t, and 2H, q, CO$_2$Et), 2.15 (3H, s, 3-Me), 2.27 (3H, s, 5-Me), 5.82 (1H, s, 4-H), 7.83 (1H, br, NH), 9.58 (1H, s, CHO). The structure of **19** was further confirmed by crystal X-ray analysis.

Received, 20th July, 1987