Photochemical Ring Contraction of 8-Aza- and 8-Oxa-3,4-diazatricyclo[5.1.0.$0^{2,6}$]oct-4-enes

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Photolysis of the 8-oxa-3,4-diazatricyclo[5.1.0.$0^{2,6}$]oct-4-enes (**7**) results in a ring transformation to give the 6-formyl-2,3-diazabicyclo[3.1.0]hex-3-enes (**9**), whereas the 8-aza compounds (**8**) give the 2-amino-3-cyano-5-azabicyclo[2.1.0]pentanes (**12**) by cleavage of the N–N bond.

We have previously reported that the thermolysis of the 3-azatricyclo[4.1.0.$0^{2,5}$]heptanes (**1**) results in ring expansion with valence isomerization to give the corresponding seven-membered ring compounds.[1] The 3,4-diazatricycloheptanes (**2**)[2] and the dioxatricyclo-octanes (**3**)[3] have also been shown to undergo thermal ring opening giving 2,5-dihydro-1*H*-1,2-diazepines and 1,4-benzodioxocines, respectively. These results prompted us to examine the ring opening of the title compounds (**7**) and (**8**), but the thermolysis of them afforded complex mixtures and no characterizable products. However, the photolysis of the tricyclo-octenes (**7**) and (**8**) gave interesting results, although the expected ring expansion products could not be obtained.

The title tricyclo-octenes (**7**) and (**8**) were synthesized from the 2,3-diazabicyclo[3.2.0]hept-6-enes (**4**),† prepared by photocyclization of 2,3-dihydro-1*H*-1,2-diazepines[4] *via* the tricyclo-octanes (**5**) and (**6**), as shown in Scheme 1.

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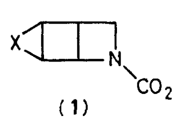
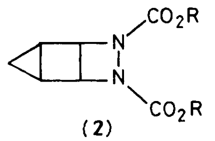
† Satisfactory elemental analyses and spectral data were obtained for all new compounds: (**7a**) m.p. 70—71 °C; i.r. $\nu_{max.}$ (KBr) 1700 (C=O) cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$) 3.84 (1H, m, 2-H), 4.07 (2H, m, 1- and 7-H), 4.64 (1H, m, 6-H), 6.82 (1H, d, *J* 1 Hz, 5-H), 1.34 and 4.23 (3H, t, and 2H, q, CO$_2$Et); (**7b**) m.p. 76—78 °C; (**8a**) oil; i.r. $\nu_{max.}$ (CHCl$_3$) 1720 (C=O) cm^{-1}; ^{1}H n.m.r. δ (CDCl$_3$) 3.38 (2H, m, 1- and 7-H), 3.80 (1H, m, 2-H), 4.60 (1H, m, 6-H), 6.87 (1H, d, *J* 1 Hz, 5-H), 1.34 and 1.36 (each 3H, t, CO$_2$CH$_2$C*H*$_3$), 4.26 and 4.32 (each 2H, q, CO$_2$CH$_2$–); (**8b**) oil.


(1)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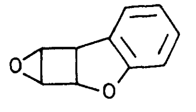
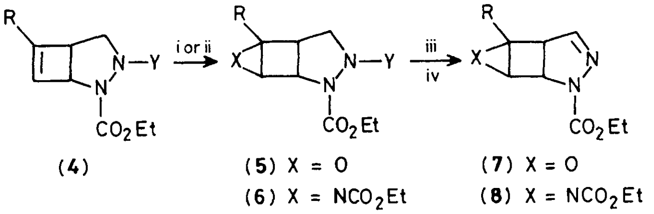

(3)

X = O, NCO_2R, S, CH_2



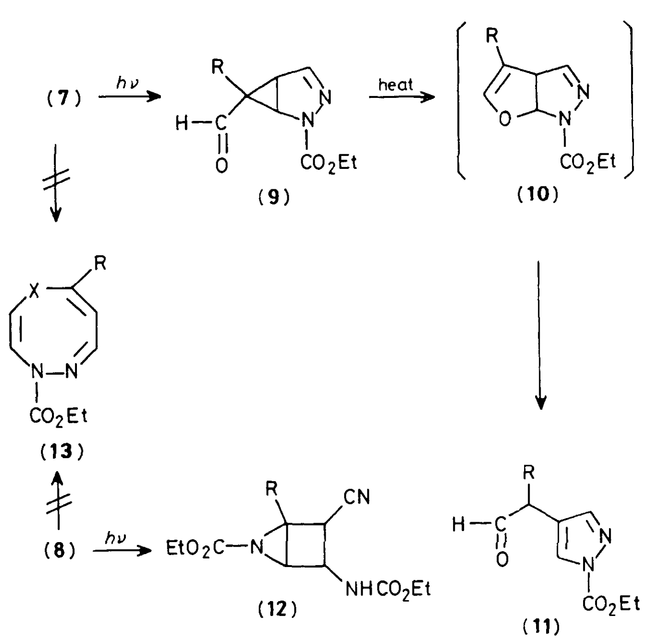
a; R = H
b; R = Me

Y = CO_2CH_2Ph

Scheme 1. *Reagents:* i, *m*-chloroperbenzoic acid; ii, *p*-$NO_2C_6H_4$-SO_3NHCO_2Et-Et_3N; iii, H_2/Pd–C; iv, Bu^{t}OCl-1,8-diazabicyclo-(5.4.0)undec-7-ene.

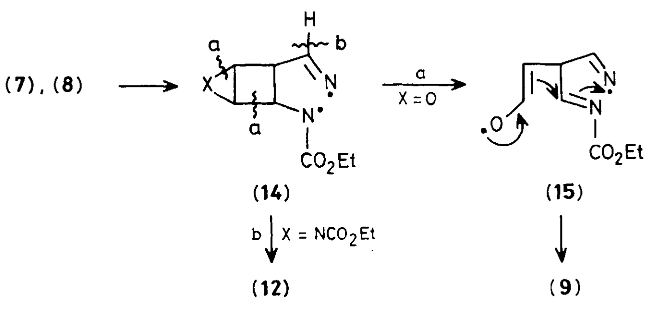
Irradiation (30 W, low-pressure Hg lamp; quartz) of the 8-oxa compounds (**7a,b**) (u.v. λ 242 nm) for 10—15 min in acetonitrile with ice cooling resulted in a ring transformation to give the 6-formyl-2,3-diazabicyclo[3.1.0]hex-3-enes (**9**) as colourless oils in 30—40% yields: (**9a**) [i.r. $\nu_{max.}$ ($CHCl_3$) 1710 (br., 2 × C=O), 2720 and 2840 (O=C–H) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.50 (1H, m, 6-H), 3.38 (1H, m, 5-H), 4.82 (1H, dd, *J* 2 and 6 Hz, 1-H), 7.15 (1H, s, 4-H), 9.93 (1H, d, *J* 2 Hz, CHO), 1.36 and 4.34 (3H, t, and 2H, q, CO_2Et); (**9b**) i.r. $\nu_{max.}$ ($CHCl_3$) 1710 (br., 2 × C=O), 2720 and 2840 (O=C–H) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.00 (3H, s, 6-Me), 3.38 (1H, d, *J* 6 Hz, 5-H), 4.74 (1H, d, *J* 6 Hz, 1-H), 7.04 (1H, s, 4-H), 9.83 (1H, s, CHO), 1.38 and 4.38 (3H, t, and 2H, q, CO_2Et)]. The spectral data are consistent with the proposed structures (**9**), which was also confirmed by thermolysis of (**9**) in toluene at 60—70 °C, which afforded the pyrazoles (**11**)‡ in 30—40% yields *via* the unstable dihydrofuropyrazoles (**10**).§

In contrast, the 8-aza compounds (**8a,b**), upon irradiation under the same conditions for 10 min, underwent only N—N bond fission to give the nitrile compounds (**12**) in 50—60% yields [(**12a**) m.p. 98—100 °C; i.r. $\nu_{max.}$ (KBr) 3300 (NH), 2250 (CN), 1720 (C=O), and 1680 (C=O) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 3.28 (1H, d, *J* 4 Hz, 3-H), 3.43 and 3.50 (each 1H, m, 1- and 4-H), 4.05 (1H, m, 2-H), 5.90 (1H, br d, *J* 8 Hz, NH), 1.28 and 1.35 (each 3H, t, $CO_2CH_2CH_3$), 4.19 and 4.27 (each 2H, q, CO_2CH_2–); (**12b**) m.p. 120—121 °C; i.r. $\nu_{max.}$ (KBr) 3250 (NH), 2250 (CN), 1720 (C=O), and 1680 (C=O) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.62 (3H, s, 4-Me), 3.28 (1H, br, 1-H), 3.32 (1H, d, *J* 4 Hz, 3-H), 4.05 (1H, m, 2-H), 5.80 (1H, br d, *J* 8 Hz, NH), 1.27 and 1.33 (each 3H, t, $CO_2CH_2CH_3$), 4.17 and 4.24 (each 2H, q, CO_2CH_2–)]. In the photolysis of both of (**7**) and (**8**), the formation of the expected eight-membered ring compounds (**13**) was not observed.



a; R = H
b; R = Me

Scheme 2



Scheme 3

Although the detailed mechanisms are not clear, we assume that the photo-induced ring contractions proceed by initial homolytic N–N bond fission to the diradical intermediates (**14**). In the case of the 8-oxa compounds (**7**), the intermediates (**14**) would undergo synchronous homolytic ring contraction of the cyclobutane and the oxirane rings to give the formyl products (**9**) *via* (**15**). In the case of the 8-aza compounds (**8**), an intramolecular transfer of the hydrogen atom of the imine group to the aminyl centre may occur to give the nitrile products (**12**). The difference between (**7**) and (**8**) may depend on the different reactivity of C–O and C–N bonds toward homolytic fission. In the case of (**8**), the less reactive C–N bond may not favour synchronous ring contraction to give (**15**) and thus the transfer of the hydrogen atom becomes predominant.

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References

1 J. Kurita, K. Iwata, M. Hasebe, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1983, 941.
2 H.-D. Martin, H. Höchstetter, and A. Steigel, *Tetrahedron Lett.*, 1984, **25**, 297.
3 J. Kurita, S. Yamada, H. Sakai, and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.*, 1985, 1254.
4 T. Tsuchiya and V. Snieckus, *Can. J. Chem.*, 1975, **53**, 519.

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‡ (**11a**) oil; i.r. $\nu_{max.}$ ($CHCl_3$) 1730 and 1750 (C=O) cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 3.64 (2H, br d, *J* 1 Hz, CH_2CHO), 7.63 (1H, s, 5-H), 8.12 (1H, s, 3-H), 9.74 (1H, t, *J* 1 Hz, CHO), 1.44 and 4.50 (3H, t, and 2H, q, CO_2Et); (**11b**) oil.

§ The presence of the intermediates (**10**) was confirmed by ^1H n.m.r. spectral analysis when the reaction was carried out in an n.m.r. sample tube: *e.g.*, (**10a**) δ ([$^2H_8$] toluene) 3.92 (1H, m, 5-H), 4.36 (1H, t, 6-H), 5.95 (1H, m, 7-H), 6.00 (1H, d, *J* 8 Hz, 1-H), and 6.10 (1H, br s, 4-H).