Cyclisations of Azidoformates. Cyclisation of Aryl Azidoformates

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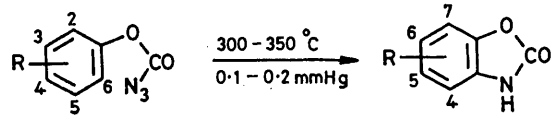
Summary Phenyl azidoformates give benzoxazolones on 'spray pyrolysis' by direct nitrene attack at the *ortho*-position and α-naphthyl azidoformate gives a naphthoxazolone only by β-attack; biphenyl-2-yl azidoformate gives both 7-phenylbenzoxazolone and an azepine by nitrene attack of the adjacent ring while 2,6-dimethylphenyl azidoformate gives the *endo*-Diels–Alder dimer of 6-isocyanato-2,6-dimethylcyclohexa-2,4-dienone under the same conditions.

WE recently demonstrated that benzyl azidoformates decompose to yield oxazoloazepines and subsequently dimers therefrom by intramolecular nitrene attack.[1] We herein report a preliminary study of the intramolecular nitrene reactions of aryl azidoformates.

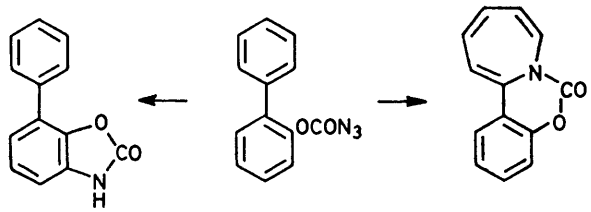


(1) (2)

a; R = H
b; R = Me
c; R = Cl
d; R = Ph

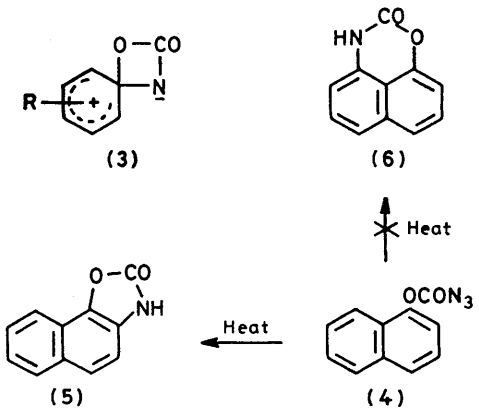
In an unpublished observation,[2] German workers noted that phenyl azidoformate (**1a**) undergoes vapour phase pyrolysis to give benzoxazolone (**2a**), in high yield. We confirm this result using our 'spray pyrolysis' technique[1,3] and note that the reaction does not involve a spiro-intermediate (**3**)[4] since 4-substituted phenyl azidoformates (**1b**) and (**1c**) give the corresponding unrearranged benzoxazolones (**2b**) and (**2c**), in good yields. Thus, 4-methylphenyl azidoformate (**1b**) gave the known[5] 5-methylbenzoxazolone (**2b**) (98%) as confirmed by unambiguous synthesis from the corresponding aminophenol and phosgene. α-Naphthyl azidoformate (**4**) gave solely the product of β-attack (**5**; m.p. 237—239 °C, 50%) with no sign of the *peri*-derived product (**6**), which we have unambiguously synthesised from 8-amino-1-naphthol and phosgene.[6]

Biphenyl-2-yl azidoformate (**1d**) has two potential sites for attack: (i) the vacant *ortho*-position and (ii) the 1,2-bond of the phenyl substituent. In fact both pathways are followed since two products (**7**) and (**8**) are isolated in 24

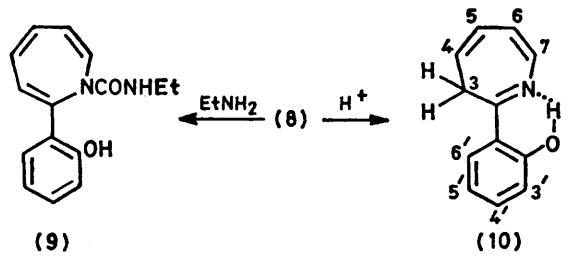


(7) (1d) (8)

and 46% yield, respectively. The former, m.p. 185 °C, shows a typical NH and carbonyl absorption of a benzoxazolone (3200br, 1765, and 1720 cm^{-1}) and an appropriate ^1H n.m.r. spectrum.† The latter azepine (**8**), an orange crystalline solid (m.p. 86·5—88 °C) shows no NH absorption but a carbonyl signal (1760, 1720 cm^{-1}) in its i.r. spectrum and characteristic olefinic absorptions in its ^1H n.m.r. spectrum [δ ($CDCl_3$) 5·4—5·8 (m, 3H), 5·8—6·0 (m, 2H,



(3) (6) (4) (5)

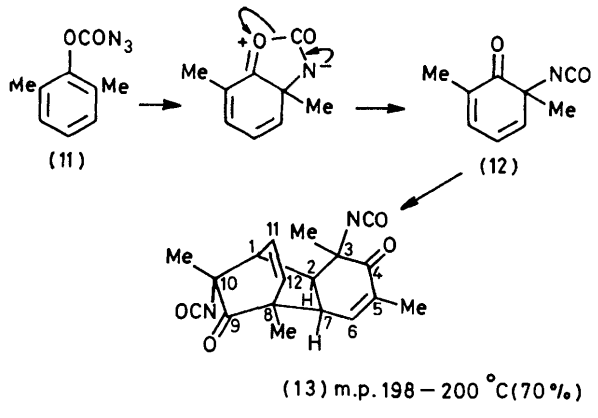


(9) (10)

azepine ring protons) and 6·9—7·45 (m, 4H, Ar-H)]. The cyclic urethane (**8**) is rapidly cleaved in cold ethylamine in ether solution to give the azepine (**9**)‡ as a yellow solid in 90% yield (m.p. 121—122 °C) while acidic hydrolysis converts it into the 3*H*-azepine (**10**)‡ (yellow liquid).

† The europium shift reagent $Eu(fod)_3$ with benzoxazolones appears to complex with the ring oxygen. With the biphenyl derivative (**7**), an equivalent pair of protons (assigned to 2′-H and 6′-H) with *ortho*- and *meta*-coupling are brought to lower field.

‡ For (**9**); ν_{max} (Nujol) 3400 and 3150br (NH and OH), 1640 cm^{-1}(CO); δ ($CDCl_3$) 0·92(t, CH_3), 3·13 (quint., CH_2), 4·77br (t, NH), 5·0—6·6(m, 3H + 2H, azepine protons), 6·6—7·4(m, 4H, Ar-H), and 9·85(br, OH). For (**10**) ν_{max} (Nujol) 3600—2000br (OH), 2850 and 2925 (CH_2), 1600 (C=N), and 740 cm^{-1} (*o*-C_6H_4); δ ($CDCl_3$) 2·93(d, CH_2, $J_{3,4}$ 7 Hz), 5·36(d of q, 4-H, $J_{4,5}$ 8 Hz), 6·2—6·55(m, 2H, 5-H and another), 6·7—7·1(m, 2H), 7·15—7·5(m, 2H), and 7·68(d of d, 7-H, *J* 8 and 12 Hz).



SCHEME

Finally, 2,6-dimethylphenyl azidoformate (**11**) shows another unexpected type of reaction, in which a dimer (**13**), derived by *endo*-Diels–Alder dimerisation of the cyclohexadienone (**12**), is isolated as shown in the Scheme. Related dimeric cyclohexadienones have been noted particularly from Wessely oxidation of *e.g.* 2,6-dimethylphenols.[7] Warm ethanol converts the bis-isocyanate (**13**) into the corresponding bis-urethane. The spectra of the isocyanate (**13**) are particularly definitive: ν_{max} (Nujol) 2250, 2220 (NCO), 1720 (CO), and 1680 cm^{-1} (C=C); δ ($CDCl_3$ at 220 MHz): 1·38, 1·43, and 1·48 (3×s, 3-Me, 8-Me, and 10-Me), 1·88 (t, 5-Me, $J_{Me\text{-}6} = J_{Me\text{-}7} = 1{\cdot}5$ Hz), 2·87 (m, 7-H, $J_{6,7}$ 4·0 Hz), 2·96 (d of d, 2-H, $J_{2,7}$ 8·5 Hz, $J_{1,2}$ 1·5 Hz), 3·20 (d of t, 1-H, $J_{1,11}$ 6·5 Hz, $J_{1,12}$ 1·5 Hz), 5·64 (d of d, 12-H, $J_{11,12}$ 8·5 Hz), 6·28 (dd, 11-H), and 6·33 (br d, 6-H).

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[4] *Cf.* 5-membered spiro-intermediates: J. I. G. Cadogan, *Acc. Chem. Res.*, 1972, **5**, 303. For 6-membered spiro-intermediates see ref. **3**.
[5] W. J. C. Burris, *J. Am. Chem. Soc.*, 1949, **71**, 1266.
[6] This assignment corrects an erroneous statement in a lecture summary: O. Meth-Cohn, *Heterocycles*, 1980, **14**, 1497.
[7] For a review ('Cyclohexadienones') see A. J. Waring, *Adv. Alicyclic Chem.*, 1966, **1**, 129.