1,3-Dipolar Cycloaddition to Benzazetes. Formation of 1,3,5-Oxadiazepines

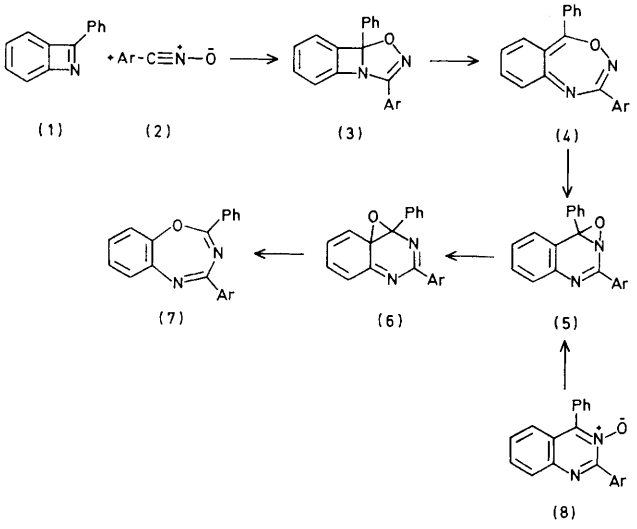
By CHARLES W. REES,* RATNASAMY SOMANATHAN, RICHARD C. STORR,* and ANTHONY D. WOOLHOUSE
(*The Robert Robinson Laboratories, University of Liverpool, P.O. Box* 147, *Liverpool* L69 3BX)

Summary Nitrile oxides react with 2-phenylbenzazete to to give labile initial cycloadducts (**3**) which rearrange very readily to give 1,3,5-oxadiazepines (**7**) presumably *via* an oxaziridine (**5**), thus providing independent support for the widely assumed intermediacy of oxaziridines in photochemical rearrangements of heterocyclic *N*-oxides.

WE recently described the generation of the highly reactive benzazetes and reported several of their Diels–Alder cycloadditions which are of considerable potential in heterocyclic synthesis. The reaction of benzazetes with 1,3-dipoles is also of considerable interest since the initial cycloadducts appear ideally disposed to undergo further transformations; for example, relief of strain in the fused four-membered benzazetine ring could result in the formation of reactive *o*-quinonoid benzo-fused seven-membered heterocyclic systems. We report here the reactions of 2-phenylbenzazete with aryl nitrile oxides which bear out this contention, and disclose a new deep-seated molecular rearrangement.

The nitrile oxides (**2**; Ar = Ph, *p*-tolyl, *p*-Cl.C_6H_4, and *p*-NO_2.C_6H_4) were injected in ether solution at *ca.* −30° on to the pyrolysate from 4-phenylbenzotriazine in which the major component is 2-phenylbenzazete (**1**).[1] This resulted in the rapid discharge of the red colour of the azete; normal work up using preparative t.l.c. gave the highly rearranged yellow 1:1 adducts (**7**) (*ca.* 65%). However, addition of n-pentane to the reaction solution gave a precipitate of the colourless 1:1 adducts (**3**) which were purified by low-temperature crystallisation from ether–light petroleum. Structure (**3**) for these initial adducts is expected by analogy with the known addition of nitrile oxides to imines[2] and is supported by spectral data† and by their subsequent reactions.

On gentle warming in solution or on attempted chromatography or exposure to acid, the adducts (**3**) rearranged quantitatively to the 1,3,5-oxadiazepines (**7**). These same oxadiazepines‡ were obtained by photolysis of the corresponding quinazoline 3-oxides (**8**).[3] This latter reaction probably involves initial formation of the oxaziridine (**5**)



followed by a 1,5-sigmatropic shift to give the epoxide (**6**) which undergoes electrocyclic ring cleavage. Indeed initial oxaziridine formation followed by similar transformations are widely assumed to occur in the photochemical rearrangements of heterocyclic *N*-oxides in general, although oxaziridines have not been directly detected.[4] Significantly, the most reasonable route from initial adduct (**3**) to oxadiazepine (**7**) also involves the oxaziridine (**5**) formed by the purely thermal sequence of azetine ring opening and recyclisation to relieve the *o*-quinonoid ring fusion in (**4**). The ease of the overall transformation (**3**) → (**7**) would suggest that oxaziridines, if produced as initial intermediates in the photolysis of quinazoline *N*-oxides, would indeed be transformed rapidly and exclusively into oxadiazepines by further thermal processes. The six-electron 1,5-sigmatropic shift of oxygen leading to (**6**) and hence (**7**) is clearly favoured over the four-electron electrocyclic process leading to the *N*-oxide (**8**) probably because

of the difference (*ca.* 32 kcal mol^{-1}) in N–O and C–O bond energies.

Attempts to intercept the intermediate (**4**) in the thermal rearrangement of the adduct (**3**; Ar = *p*-tolyl) in the presence of dimethyl acetylenedicarboxylate gave 2-tolyl-4-phenylquinazoline and no oxadiazepine. This unusual and mild deoxygenation also occurs with more conventional deoxygenating agents such as triethyl phosphite, triphenylphosphine and hydrogen–Pd, and probably involves deoxygenation of either the oxaziridine (**5**) or the epoxide (**6**). Deoxygenation is also a common side reaction in the photolysis of heterocyclic *N*-oxides.

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† I.r. spectra confirm the absence of any functional groups inconsistent with the proposed structure, and there is no u.v. absorption at wavelengths longer than 300 nm, ruling out alternative structures such as (**5**); *e.g.* adduct (**3**; Ar = *p*-tolyl), m.p. 85°, ν_{max} (Nujol) 1620, 1600, 1565, 1350, 1285, 1180, 1160, 1150, 1110, 1070, 1010, 985, 940, 915, 855, 805, 785, 770, 750, and 700 cm^{-1}, λ_{max} (Et_2O) 254 (ϵ 14,800) and 275 (9640) nm. Satisfactory analytical data were obtained for all new compounds.

‡ The oxadiazepine structure was confirmed by an *X*-ray crystallographic determination of the structure of (**7**; Ar = *p*-tolyl) by Dr. A. Forbes Cameron of Glasgow University.

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