

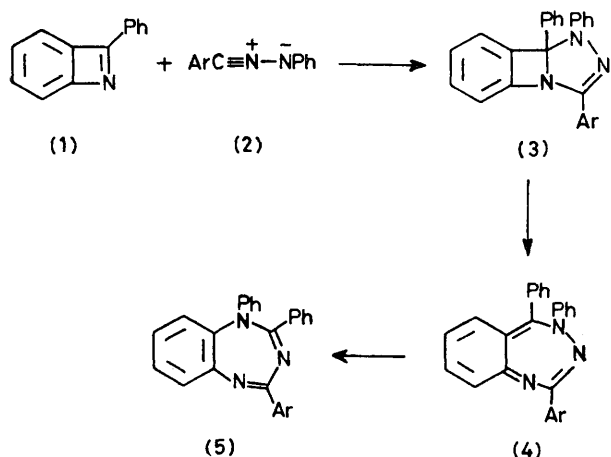
Benzazetes as Precursors for Benzotriazepines

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Summary The primary cycloadducts from 2-phenylbenzazete (1) and diarylnitrile imines (2) rearrange spontaneously to 1,2,4-triarylbenzo[*f*]-1,3,5-triazepines (5); the isolable but labile adduct from the azete (1) and diazomethane is transformed into the azidostyrene (8) thermally, and into a mixture of 2- and 3-phenylindoles and the ketone (11) in the presence of acidic catalysts.

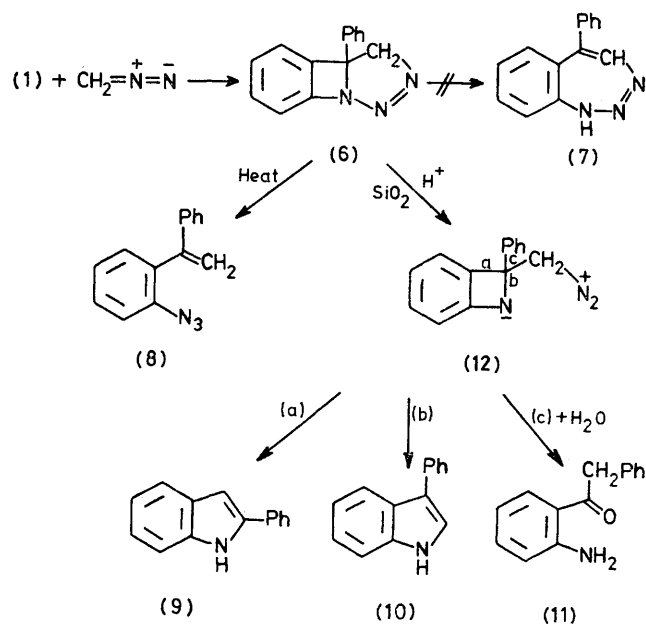
The synthetic potential of benzazetes (*e.g.* 1) is well illustrated by consideration of the 1,3-dipolar cycloaddition of linear dipolar systems containing two nitrogens, nitrile imines and diazo-compounds. The initial cycloadducts are benzo-fused bicyclic valence isomers of triazepines. Electrocyclic ring opening of the unstable four-membered ring would give *o*-quinonoid benzotriazepines which can achieve stabilisation by H-migration or C-N transposition. If sydrones, where loss of CO₂ from the initial adduct is to be expected, are included with the above dipoles several of the possible benzotriazepine systems become potentially available. We report here our preliminary studies in this area.



Addition of the nitrile imines (2) to 2-phenylbenzazete (1)¹ is expected to proceed through the adducts (3) which on ring opening would give the benzo[*e*]-1,2,4-triazepines (4). By analogy with the reaction previously observed with nitrile oxides,² (4) should rearrange to give benzo[*f*]-1,3,5-triazepines (5) by electrocyclic ring closure to a diaziridine, a 1,5-NAr shift, and ring opening. This overall transformation (1) + (2) → (5)[†] does indeed proceed spontaneously

and in good yield when the nitrile imines (2; Ar = Ph, *p*-MeC₆H₄, *p*-ClC₆H₄, and *p*-NO₂C₆H₄) are generated *in situ* from the α -chlorohydrazone and triethylamine in the presence of 2-phenylbenzazetes, thus providing a route to this unknown system.[‡] In contrast with the nitrile oxide reaction² no initial adducts were isolable.

With diazomethane the expected regioselectivity of addition would lead to (6), which by H-migration and ring cleavage might produce 1*H*-, 3*H*, or 5*H*-benzo[*f*]-1,2,3-triazepines (*e.g.* 7)³ while the alternative regioisomer could lead to benzo[*f*]-1,2,4-triazepines. Addition of diazomethane to 2-phenylbenzazete at -80 °C, followed by non-chromatographic work up,[§] gave the expected adduct (6) for which an AB quartet, *J* 19 Hz, was observed at δ 4.43 and 4.94 in its n.m.r. spectrum (CCl₄). The adduct (6) is transformed quantitatively into the azidostyrene (8)



on heating in benzene at 50 °C for *ca.* 1 h. On treatment with acid or attempted chromatography on silica (6) gave a mixture of 2- and 3-phenylindoles (9) and (10) and the amino-ketone (11), the unexpected 2-phenylindole (9) being the predominant product. While 3-phenylindole

[†] The reaction is carried out below *ca.* -30 °C in CH₂Cl₂ solution. After warming to room temperature the orange benzotriazepines are isolated by chromatography to give, for example, (5; Ar = Ph), m.p. 198–201 °C, λ_{max} (EtOH) 242 (ϵ 26,267), 268 (30,414) and 340 (5069) nm; (5; Ar = *p*-MeC₆H₄), m.p. 195–196 °C, gave 1-phenyl-2-*p*-tolylbenzimidazole on acidic hydrolysis.

[‡] No simple derivatives are known, the only reported examples involve 1,3,5-benzotriazepinones, thiones, and imides; see F. E. King, R. M. Acheson, and P. C. Spensley, *J. Chem. Soc.*, 1948, 1366; R. M. Acheson and N. F. Taylor, *ibid.*, 1956, 4727; M. Israel, L. C. Jones, and E. J. Modest, *Tetrahedron Letters*, 1968, 4811; G. Doleschall, G. Hornyak, B. Agai and K. Lampert, *Tetrahedron*, 1976, 32, 57.

[§] Etheral diazomethane is added to (1) in CH₂Cl₂ and the mixture allowed to warm to room temperature. The solvent is removed under reduced pressure and (6) extracted into hexane below room temperature.

could conceivably have arisen by loss of nitrogen from the benzo-1,2,3-triazepine (7), isolation of (9) and (11) suggests that N-N cleavage proceeds as shown in (12), and migration of bonds (a), (b), or (c) to the developing positive carbon then accounts for all three products. There is no evidence for conversion of (6) into the unknown system (7); for example, 4-phenylcinnoline *N*-imides, possible rearrangement products of (7), are not observed and no *N*-methyl derivative of (7) could be isolated from treatment of (6) with base and methyl iodide.

Sydnonones might lead to 2*H*-benzo[*e*]-1,2,4-triazepines or 3*H*-benzo-1,2,3-triazepines by cycloaddition, ring cleavage, and extrusion of CO₂. However, 3,4-diphenyl- and 3-*p*-chlorophenyl-sydnones are insufficiently reactive to intercept (1) prior to its dimerisation.

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