Azimines as 1,3-Dipoles

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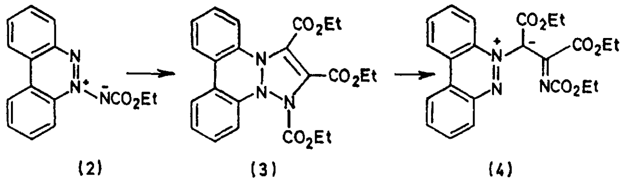
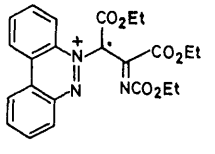
Summary The first examples of 1,3-dipolar cycloaddition of an azimine (**1**) are provided by the reactions of *N*-iminobenzocinnolinium ylides, *e.g.* (**2**), with acetylenedicarboxylic esters to give azomethine imines, *e.g.* (**4**).

In his classic review of 1,3-dipolar cycloaddition, Huisgen identified all the possible 1,3-dipoles based on carbon, oxygen, and nitrogen.[1] The three-nitrogen azimine system (**1**) stands out as one of the few for which cycloadditions have not yet been observed. The benzocinnolinium ylides, *e.g.* (**2**), which we recently described[2] are now shown to undergo cycloaddition in complete accord with Huisgen's prediction.

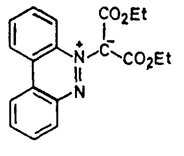
(1)



(2) (3) (4)



(5)



(6)

The ylide (**2**) reacts exothermally with an equivalent amount of dimethyl or diethyl acetylenedicarboxylate, in benzene or dimethylformamide at room temperature, to give green 1:1 adducts (**4**)† quantitatively. Spectral evidence fully supports the azomethine imine structure (**4**).‡ There are three main absorption bands in the u.v. spectrum [λ_{max} (EtOH) 256 (ϵ 49,000), 309(23,000), and 372 nm (10,000)] characteristic of benzocinnoline, benzocinnoline *N*-oxides, and benzocinnolinium ylides (**2**), together with a broad weak band at *ca.* 550 nm (ϵ *ca.* 900) which accounts for the colour. The i.r. spectrum shows three carbonyl absorptions at 1645, 1690, and 1730 cm^{-1} in chloroform solution, the first two of which show the expected shifts to higher frequency in the picrate salt of (**4**). The n.m.r. spectrum of a freshly prepared solution in deuteriochloroform shows 8 aromatic protons and 3 ester groups. On warming the solution, the aromatic absorptions broaden and finally disappear irreversibly, although the ester absorptions remain unaffected. We attribute this to the formation from (**4**) of a small proportion of the highly stabilised radical cation (**5**), which is in rapid equilibrium with (**4**), the solvent chloroform acting as oxidant. The presence in chloroform of a radical species whose concentration increases on warming was confirmed by e.s.r. spectroscopy. Complete oxidation of (**4**) to (**5**) was effected by

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† Only reactions in the diethyl ester series are illustrated.

addition of an equimolecular amount of the stable radical cation, tris-(*p*-bromophenyl)aminium hexachloroantimonate.[3]

Further strong evidence for the suggested structure (**4**) comes from the synthesis of the azomethine imine (**6**) by treatment of the quaternary salt obtained from benzocinnoline and diethyl bromomalonate with aqueous sodium hydroxide. The ylide (**6**) is completely analogous in all respects, including its ready conversion into a radical cation, to the azomethine imine (**4**) obtained from the cycloaddition reaction.

We believe that the only satisfactory mechanism for the formation of the 1:1 adduct (**4**) is initial 1,3-dipolar cycloaddition to give the cyclic adduct (**3**). The latter, which has three adjacent saturated nitrogen atoms, should be unstable and rapidly undergo N–N bond fission to give the highly stabilised benzocinnolinium ylide (**4**), the observed product. Entirely analogous 1,3-dipolar cycloadditions were observed with the *N*-benzoyl ylide (**2**; CO_2Et replaced by COPh).

Although acetylenic dipolarophiles can give the stabilised ylides (**4**), olefinic dipolarophiles cannot, and in agreement with this, treatment of the ylide (**2**) with a variety of olefins gave no characterisable 1:1 adducts. However, benzocinnoline was formed, under much milder conditions than in the absence of olefin.[2] Thus reaction has occurred between the ylide and the olefins and this too is presumably initiated by dipolar cycloaddition.

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[1] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565, 633.

[2] S. F. Gait, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1971, 1545.

[3] F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc.* (*C*), 1969, 2719.