1,5- *versus* 1,3-Dipolar Reactivity of Azomethine Imines

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Summary The azomethine imines (**1**) function as 6π-electron 1,5-dipoles rather than 4π-electron 1,3-dipoles in their cycloaddition to acetylenedicarboxylic esters.

The azomethine imines (**1**)[1] are of interest since in cycloaddition they can, in principle, act as 4π-electron 1,3-dipoles, 6π-electron 1,5-dipoles,† or 8π-electron 1,7-dipoles.

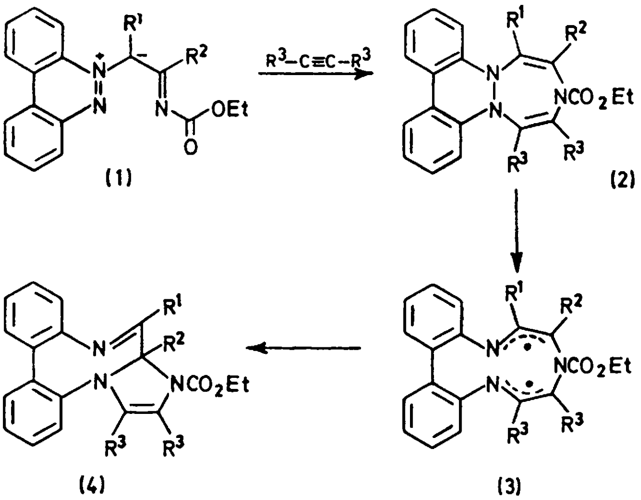
1,3-Dipolar cycloaddition of azomethine imines is well known.[2] In this respect the benzocinnolinium ylide (**5**)[1] functions as expected to yield the adduct (**6**) when treated with dimethyl acetylenedicarboxylate in dimethylformamide at 70° for 30 min. The n.m.r. spectrum of adduct (**6**) shows two different CO_2Me groups and two identical CO_2Et groups and its u.v. spectrum (λ_{max} 262 and 394 nm; ϵ 30,000 and 12,000) is consistent with an almost planar biphenyl chromophore.

In contrast the azomethine imines (**1**) do not give the analogous 3 + 2 cycloadducts (**7**). Reaction of (**1**; $R^1 = R^2 = CO_2Me$) with dimethyl acetylenedicarboxylate in dimethylformamide at 70° for 30 min gave a colourless adduct (60%), tentatively assigned structure (**4**; $R^1 = R^2 = R^3 = CO_2Me$). However, when the reaction was carried out at room temperature over 24 h a second isomeric yellow adduct (**2**; $R^1 = R^2 = R^3 = CO_2Me$) was isolated together with (**4**). Adduct (**2**) rearranges under mild conditions to (**4**) (>95% conversion in 15 min in dimethylformamide at 70°). The reaction of (**1**; $R^1 = R^2 = CO_2Et$) with dimethyl acetylenedicarboxylate and of (**1**; $R^1 = R^2 = CO_2Me$) with diethyl acetylenedicarboxylate at 70° gave an identical mixture of products (**4**) which are stable under these conditions. Thus all, or substantially all, of (**4**) is formed *via* the symmetrical adduct (**2**) which is therefore the primary product.

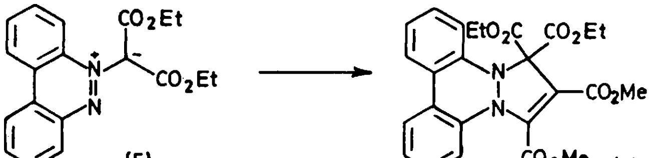
The symmetrical structure for (**2**) was confirmed by its n.m.r. spectrum which shows three different types of ester group in the ratio 2 : 2 : 1, and a symmetrical distribution of aromatic protons. The more tentative assignment of structure (**4**) is based on the availability of a reasonable mechanistic route from (**2**) *via* the stabilised diradical (**3**), and on the fact that (**4**; $R^1 = R^2 = R^3 = CO_2Me$) shows five different ester groups. The alternative structure (**7**) for this adduct is eliminated since its u.v. spectrum (λ_{max} 231, 254sh, and 290 nm; ϵ 26,000, 19,500, and 9,500) differs significantly from that of (**6**) and is consistent with a twisted‡ biphenyl structure.

Entirely analogous reactions are observed with the azomethine imine (**1**; $R^1 = CO_2Me$, $R^2 = H$) obtained by cycloaddition of *N*-ethoxycarbonyliminobenzocinnoline[1] to methyl propiolate. As expected the methine proton in (**2**; $R^2 = H$) appears at δ 8·04 p.p.m. thus excluding the alternative aziridine structure (**8**) for the initial adduct.

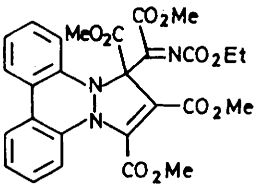
We have thus established that the azomethine imines (**1**) function as 6π-electron 1,5-dipoles, rather than as 4π-electron 1,3-dipoles. If the symmetry ordering of the π-orbitals in (**1**) parallels that in the isoelectronic pentadienyl anion, a concerted $\pi^6s + \pi^2s$ cycloaddition is disallowed; adduct (**2**) probably arises by a stepwise mechanism



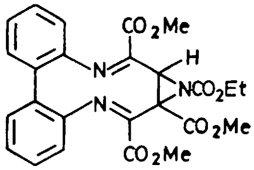
(1) (2) (3) (4)



(5) (6)



(7)



(8)

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† We use the term 1,5-dipole as an extension of Huisgen's definition of a 1,3-dipole. A 1,5-dipole has the same relationship to a pentadienyl anion as a 1,3-dipole to an allyl anion. The concept of 1,5-dipoles, and their cyclisations, have been thoroughly discussed (H. Reimlinger, *Chem. Ber.*, 1970, **103**, 1900 *et seq.*). 1,5-Dipolar cycloaddition reactions, however, are very rare (*cf.* R. Huisgen, *Angew. Chem. Internat. Edn.*, 1968, **7**, 321).

‡ Dreiding models indicate a dihedral angle of *ca.* 75°.

most reasonably initiated by nucleophilic attack by the ylide side chain through nitrogen, on the acetylene. Formation of the expected 3 + 2 adduct from the simpler ylide (**5**) may be the result of a concerted 1,3-dipolar cycloaddition since the side chain oxygen atom in (**5**) is less nucleophilic than the nitrogen atom in (**1**).

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[1] S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1972, 688.

[2] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 580.