Pericyclic Transformations in 1,5-Dipolar Iminoazimines

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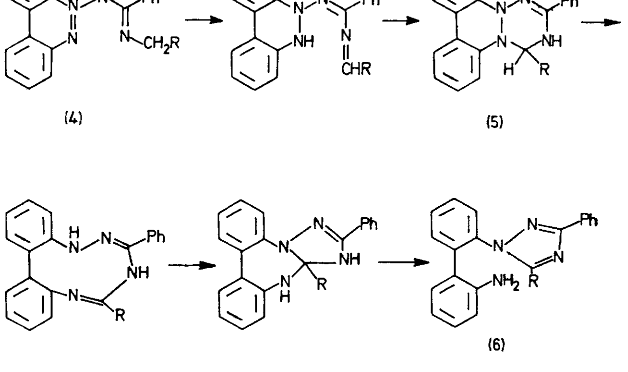
Summary On heating, benzocinnoline *N*-arylbenzaminimides (**1**) undergo 1,5-dipolar cyclisation and retro-dipolar cycloaddition to give benzocinnoline *N*-arylimides (**3**); in contrast the *N*-alkyl analogues (**4**) are much less stable and undergo a 1,6-H shift leading ultimately to 1-(2′-aminobiphenyl-2-yl)-3-phenyl-1,2,4-triazoles (**6**).

IMINOAZIMINES (**1**) are of interest as potential sources of iminonitrenes and as extended dipolar systems in which a variety of pericyclic reactions are possible.

They are readily obtained when benzocinnoline *N*-imide[1] and imidochlorides are allowed to react in acetonitrile in the presence of solid potassium carbonate. The iminoazimines (**1**; Ar = Ph, *o*-tolyl, and *p*-nitrophenyl) (m.p. 221—222°, 163—165°, and 221—222° respectively) produced in this way are stable, yellow to orange, crystalline solids for which n.m.r. and u.v. spectral data support the open 1,5-dipolar structures rather than the alternative cyclic structures (**2**). In this respect they resemble the recently reported iminoazimine (**1**; H for Ar)[2] and the analogous alkoxycarbonyl and acylazimines.[1]

On pyrolysis in refluxing 1,2,4-trichlorobenzene (20 min) or in the melt at 220° these iminoazimines gave *N*-arylazimines (**3**) (up to 85%) and benzonitrile, presumably by 1,5-dipolar cyclisation followed by retro 1,3-dipolar cycloaddition. This contrasts with the behaviour of the corresponding alkoxycarbonyl and acylazimines which do not give benzocinnoline *N*-oxide but rather benzocinnoline, by N–N bond cleavage, and *N*-substituted carbazoles, by rearrangement and loss of nitrogen. The above sequence provides an attractive synthesis of benzocinnoline *N*-arylimides (**3**) which can also be obtained, although in much lower yield, from benzocinnoline *N*-imide with benzenediazonium chloride (for **3**; Ar = Ph), and with *p*-chloronitrobenzene (for **3**; Ar = *p*-$NO_2C_6H_4$).



SCHEME

In contrast with *N*-aryliminoazimines (**1**) the *N*-alkyl derivatives (**4**; R = H and Me) are unstable and only the former is isolable. The azimine (**4**; R = H) rearranges slowly at room temperature and rapidly and quantitatively at 80° in acetonitrile to give the aminotriazole (**6**; R = H), m.p. 139—140°; ν_{max} (Nujol) 3455 and 3340 cm^{-1} (NH_2). Attempts to prepare the *N*-ethyliminoazimine (**4**; R = Me) led to spontaneous formation of the analogous aminotriazole (**6**; R = Me), m.p. 144—145°, (45%) together with benzocinnoline (35%). The acetyl derivative of this amine is identical with that previously reported by an alternative route.[2]

This unexpected rearrangement, which is not catalysed by added base, can be rationalised as shown in the Scheme. The first step involves a sigmatropic 1,6-H shift through the 1,5-dipole π-system, analogous to the antarafacial 1,7-shift which occurs in the precalciferol–calciferol interconversion;[3] this is followed by a series of intramolecular additions and H-migrations before final aromatisation. For the *N*-isopropyliminoazimine, initial H-shift and cyclisation are possible but the subsequent steps are precluded. However, reaction of benzocinnoline *N*-imide with *N*-isopropylbenzimidoyl chloride followed by gentle warming gave benzocinnoline (75%) as the only recognisable product. No intermediate such as the *gem*-dimethyl species corresponding to (**5**) was detected.

Sigmatropic H-migrations in polyenes are well documented.[4] Observation of this 1,6-shift together with the few examples of 1,4-shifts reported for 1,3-dipoles[5] suggests that such processes must be considered as important in dipolar systems in general. Indeed, a 1,6-H shift in a vinylogous azomethine imine accounts for the anomalous cycloadducts from benzocinnoline *N*-alkylimides and acetylenic esters.[6]

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