Benzo[c]cinnoline *N*-Oxides as 1,3-Dipoles

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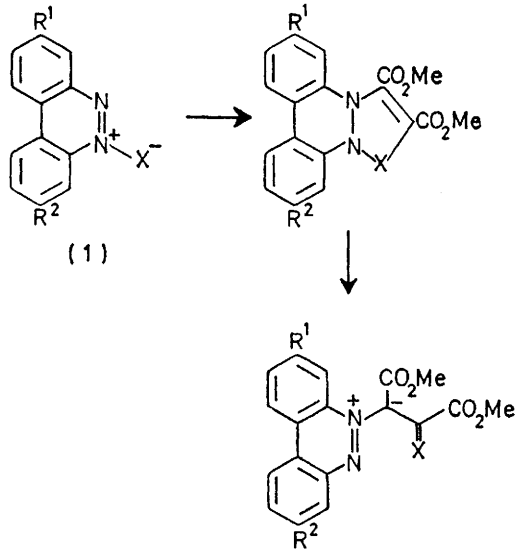
Summary Benzocinnoline *N*-oxides give azomethine ylides with dimethyl acetylenedicarboxylate at elevated temperatures, most probably by 1,3-dipolar cycloaddition which is unprecedented for azoxy compounds, followed by electrocyclic ring opening; this mechanism is confirmed for the same reactions of the closely related *N*-iminobenzocinnolinium ylides.

ALTHOUGH their potential 1,3-dipolar character has long been recognised[1] there have been no reported cycloaddition reactions of azoxy-compounds.

Several benzocinnoline *N*-oxides, conformationally rigid azoxy-compounds, have now been found to give 1:1 adducts with dimethyl acetylenedicarboxylate (DMAD) albeit in very low yield. Slow addition of 3 moles of DMAD to the benzocinnoline *N*-oxides (**1**; X=O; R^1=R^2=H; R^1=OMe, R^2=H; R^1=R^2=OMe) in nitrobenzene at 190°

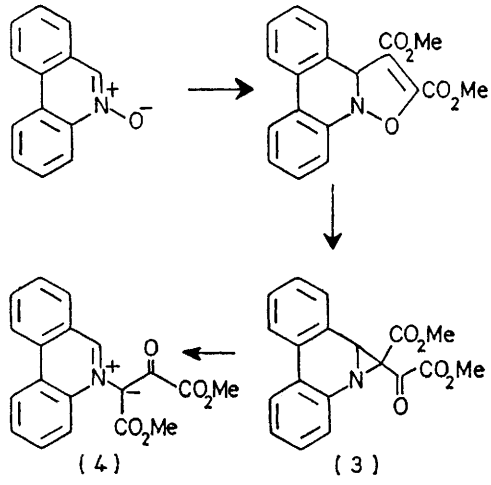


(1) (2)

over 3 h gave the adducts (**2**; X=O) in 2, 5, and 7% yield, respectively. 2,9-Dimethoxybenzocinnoline *N*-oxide gave an adduct in 8% yield. A considerable amount of unreacted *N*-oxide was recovered in each case (the yields based on *N*-oxide consumed being 15, 22, 38, and 51% respectively) but the reactions were not reversible. The above yields were not improved by variation of solvent, temperature, and reaction time.

The adducts were assigned the structures (**2**; X = O) on the basis of analytical data and spectral comparison with the adducts (**2**; X = NCO_2Et) formed from *N*-iminobenzocinnolinium ylides and DMAD.[2] Benz[*cd*]indazole *N*-oxide and 4,4'-bis(dimethylamino)azoxybenzene did not react under the above conditions.

Formation of the ylides (**2**; X = O) can be explained by 1,3-dipolar cycloaddition, unprecedented for azoxy-compounds, followed by electrocyclic ring opening, exactly as postulated for the analogous reaction of *N*-iminobenzocinnolinium ylides (**1**; X = NCO_2Et). That the latter involves such a mechanism is strongly supported by the regiospecific reaction of azimine (**1**; X = NCO_2Et, R^1 = OMe, R^2 = H) with DMAD to give ylide (**2**; X = NCO_2Et, R^1 = OMe, R^2 = H), as shown by a comparative analysis of the n.m.r. spectra of all the *N*-oxides, azimines, and the derived ylides.†



(4) (3)

SCHEME

This observation is important since it removes a doubt concerning the above rationalisation of the azimine cycloadditions. This is raised by the formation of ylides (*e.g.* **4**) from phenanthridine *N*-oxides[3] and related cyclic nitrones[4,5] with acetylenic esters in what is formally an analogous reaction but which clearly cannot involve such a sequence.

The *N*-oxide reactions could involve rearrangement of an initial 1,3-dipolar cycloadduct (in the case of dihydroisoquinoline *N*-oxide such an adduct has been isolated and shown to rearrange to the corresponding ylide[5]) probably (*cf.* ref. 6) as shown in the Scheme. In the azimine cycloadditions, intervention of a diaziridine analogous to (**3**) would have led to non-regiospecific addition.‡ An alternative possibility involves deoxygenation of the *N*-oxide by the acetylene to give an α-ketocarbene which then recom-

† The C(7) ^{13}C n.m.r. absorptions of (**1**; X = NCO_2Et, R^1 = OMe, R^2 = H) and the corresponding *N*-oxide (**1**; X = O, R^1 = OMe, R^2 = H) correlate very closely with the lower field absorption of the C(4)–C(7) pair observed for the 3,8-dimethoxy-derivatives. Since the above azimine gives an azomethine imine which displays an absorption corresponding to the higher field one of the pair of the dimethoxy-azomethine imine, the side chain must now be attached to the other ring nitrogen, assuming only that the O, N, and C side chains exert parallel substituent effects. A similar pattern of shifts was observed for the ^{13}C MeO absorptions in the above compounds and for the ^1H MeO absorptions in the corresponding reactions with dicyanoacetylene. Full details of these spectral assignments will be given in the full paper.

‡ (**1**; X = NCO_2Et, R^1 = H, R^2 = OMe) was only available in admixture with its 8-methoxy-isomer (**1**; X = NCO_2Et, R^1 = OMe, R^2 = H). However, this mixture gave a mixture of adducts (**2**: X = NCO_2Et, R^1 = H, R^2 = OMe) and (**2**; X = NCO_2Et, R^1 = OMe, R^2 = H) thus showing that the regiospecificity observed with the pure azimine was not the result of an over-riding substituent effect.

bines with the deoxygenated heterocycle, a mechanism which has received support in a recent communication.[7] A corresponding mechanism for the azimine reaction, *via* an α-iminocarbene, would again lead to non-regiospecific addition, and also to the possibility of interception of the carbene by a more nucleophilic benzocinnoline. However when (**1**; X = NCO_2Et, $R^1 = R^2 = H$) was allowed to react with DMAD in the presence of an excess of 3,8-dimethoxybenzocinnoline no "cross-over" was observed; only ylide (**2**; X = NCO_2Et, $R^1 = R^2 = H$) was formed and no ylide (**2**; X = NCO_2Et, $R^1 = R^2 = OMe$) could be detected.

Significantly 1,5-dipolar electrocyclic ring opening of an initial cycloadduct is possible for azimines and azoxy compounds but not for nitrones.

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