Cycloaddition of Benzocinnoline *N*-Acylimides to Diphenylketen

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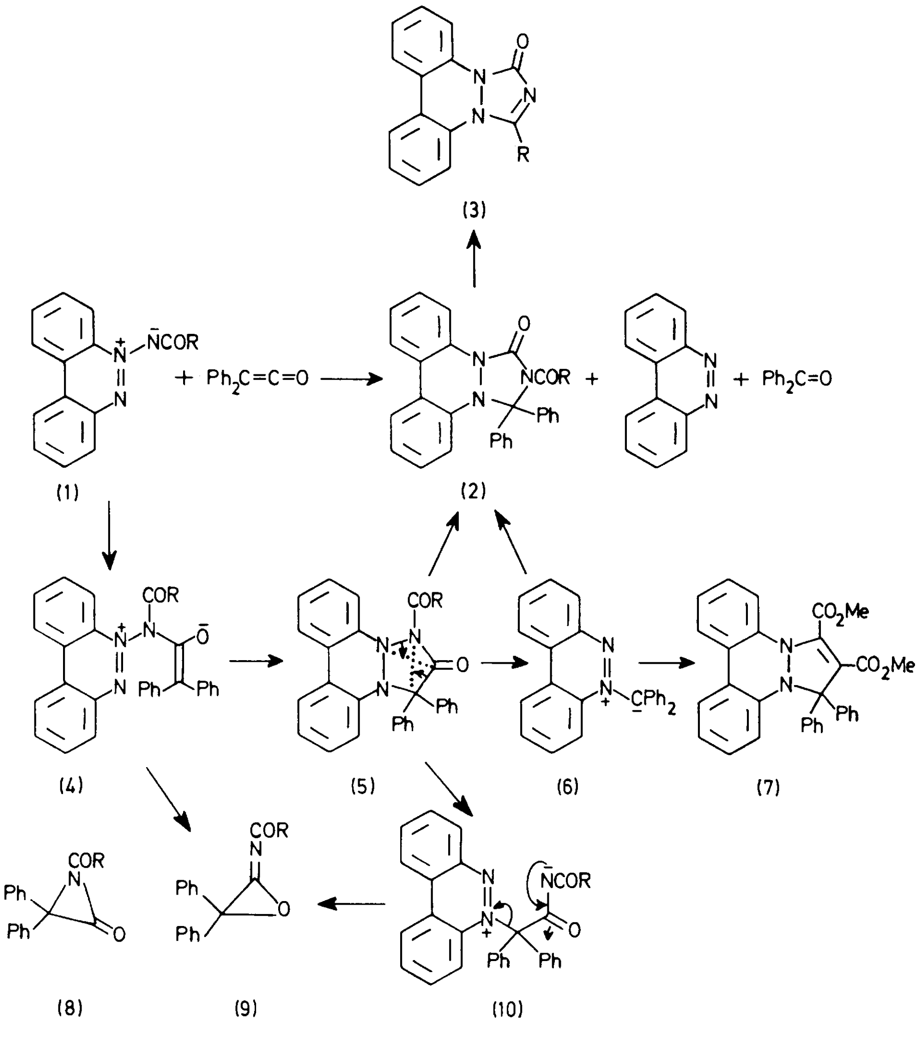
Summary Benzo[*c*]cinnoline *N*-acylimides (**1**) give the rearranged adducts (**2**) with diphenylketen; the ylide (**6**) can be intercepted in this reaction suggesting that the expected 1,3-dipolar cycloadduct (**5**) is formed initially and rearranges to (**2**) both intramolecularly and by dissociation–recombination.

DURING the course of our studies on cycloadditions of extended dipolar systems[1] we have uncovered an unexpected mode of reaction of the azimines (**1**) with ketens which involves an unusual type of rearrangement.

Addition of diphenylketen (1·2 equiv.) to a solution of benzo[*c*]cinnoline *N*-acetylimide (**1**, R = Me) in benzene gave a dark coloured solution which gradually lightened over 2h. Work up by chromatography on neutral alumina gave benzophenone (50%), benzo[*c*]cinnoline (40%) and the rearranged 1 : 1 adduct (**2**) (12%), m.p. 200–201 °, ν_{max} 1745 and 1720 cm^{-1}; ^{13}C n.m.r. spectrum: $\delta(CDCl_3)$ 168·6 (MeCO) and 148·3 (N–CO–N) p.p.m. Similar reactions were observed with the azimines (**1**, R = Ph, *p*-$NO_2C_6H_4$, or OEt).



The structure of the adducts was unambiguously determined for (**2**, R = Me) by *X*-ray crystallography. Exposure of a small crystal to graphite-monochromated Mo–K *X*-radiation on a Hilger and Watts Y290 diffractometer yielded 1957 independent data. The structure was resolved by direct-phasing techniques, and refined by least squares calculations to a final *R* of 0·05.

Crystal data: $C_{28}H_{21}N_3O_2$, *M* 431·2, monoclinic, a = 8·679(1), b = 18·317(2), c = 13·689(2) Å, β = 100·94(4)°, U = 2136 Å^3, D_m = 1·37 g cm^{-3}, Z = 4, D_c = 1·34 g cm^{-3}, F (000) = 904, space group $P2_1/n$, Mo-K_α *X*-radiation, λ = 0·71069 Å, μ(Mo-K_α) = 0·93 cm^{-1}.

The adducts (**2**) were not converted into benzophenone and benzocinnoline under the reaction or work up conditions but heating of (**2**, R = Ph) in refluxing chlorobenzene gave these products in high yield. Acid catalysed hydrolysis of (**2**, R = Ph or Me) gave the triazolines (**3**) and benzophenone.

The most likely route to the adducts (**2**) involves the initial formation of the expected 1,3-dipolar cycloadduct (**5**). This would be unstable by virtue of its three saturated N atoms and could rearrange intramolecularly to (**2**) as shown. Alternatively, dissociation to the benzocinnolinium ylide (**6**) and acyl isocyanate followed by recombination with the opposite regioselectivity would also give (**2**). The feasibility of this latter mechanism is demonstrated by the formation of the same adducts in good yield by the reaction of acyl isocyanates with the ylide

(**6**).† Also, when the reaction of the imide (**1**, R = Ph) with diphenylketen was conducted in dimethyl acetylenedicarboxylate (DMAD) as solvent, the ylide (**6**) was intercepted as the adduct (**7**) (14%) in addition to the rearranged adduct (**2**, 15%, *cf.* 36% in benzene). Although control experiments indicated that the reactivity of acyl isocyanates towards (**6**) is *ca.* ten times greater than that of DMAD we would anticipate almost complete conversion into (**7**) if dissociation–recombination were the exclusive mechanism. We therefore conclude that if (**5**) is an intermediate, its rearrangement to (**2**) is to some extent intramolecular, and is either concerted or proceeds *via* dissociation and recombination within a solvent cage.

The origin of the benzophenone and benzocinnoline in the cycloaddition also presents an interesting problem. The ylide (**6**) is a conceivable source but can be ruled out as the important precursor in our system since the yields of benzophenone obtained when (**6**) is generated alone‡ are significantly lower ($\leqslant 10\%$) than in the azimine–keten cycloadditions. Indeed with the ylide (**1**, Me replaces COR) the yields of benzocinnoline and benzophenone are almost quantitative. Another possible route involves the zwitterion (**4**) which could collapse to give benzocinnoline and the α-lactam (**8**) or imino-oxiran (**9**). The latter is particularly attractive as a precursor for benzophenone and indeed such species are presumed intermediates in the thermal conversion of α-lactams into ketones and isocyanides.[2] In our system direct formation of the imino-oxiran would appear to be necessary since conversion of the α-lactam into benzophenone *via* the imino-oxiran is unlikely at room temperature and has been ruled out for the α-lactam (**8**, R = OEt)§ which is thermally stable up to 130 °C. An alternative source of the benzophenone is the initial adduct (**5**) in which N–N bond cleavage can lead to the zwitterion (**10**) and hence imino-oxiran (**9**) as well as to (**6**) and acyl isocyanate. This last mechanism has the advantage that if the fragmentation of (**5**) to (**9**) is considered as approaching a concerted $\sigma^2 + \sigma^2 + \pi^2$ process it offers an explanation for the lack of α-lactam formation.

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† Generated by treatment of the quaternary salt from benzocinnoline and benzhydryl bromide with base.

‡ Careful deoxygenation of the solvent and reactants in the azimine–keten cycloadditions has little or no effect on the yield of benzophenone.

§ The α-lactam (**8**; R = OEt), m.p. 106–107 °C, $\nu_{max.}$ 1830 and 1690 cm^{-1}, was obtained by application of the method of M. Miyoshi, *Bull. Chem. Soc. Japan*, 1973, **46**, 212.

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[2] I. Lengyel and J. C. Sheehan, *Angew Chem. Internat. Edn.*, 1968, **7**, 25.