Reaction of Benzo[*c*]cinnolinium-5-(*N*-acyl- and *N*-benzimido-imides) with Diphenylcyclopropenone

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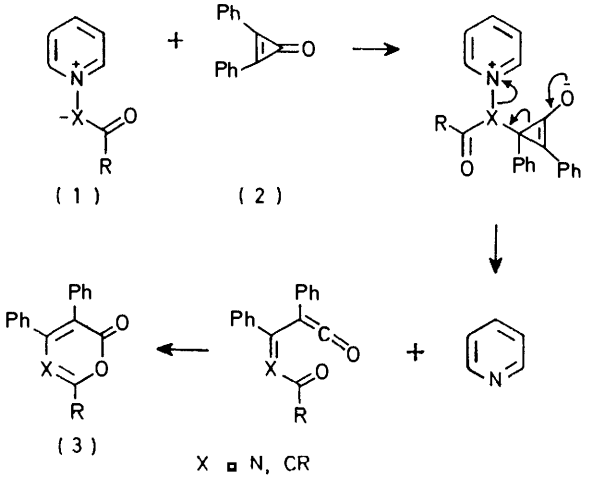
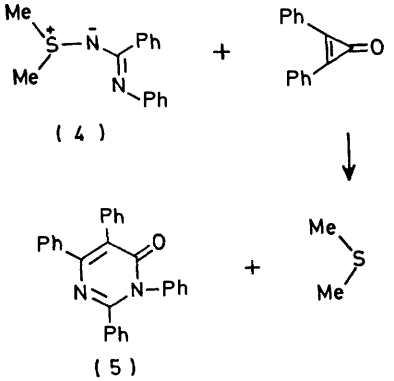
Benzo[*c*]cinnolinium-5-(*N*-acylimides) (6; R = Ph, OEt, or Me) give benzo[*c*]cinnoline and 2-substituted-4,5-diphenyloxazin-6-ones (7) on reaction with diphenylcyclopropenone. In contrast, the related benzo[*c*]cinnolinium-5-(*N*-benzimidoimides) (11; R = H, Ph, or *p*-tolyl) give stable adducts (12), which on pyrolysis yield benzo[c]-cinnoline and 1-substituted-2,5,6-triphenylpyrimidin-4-ones.

REACTION of pyridiniumacylmethylides [1] (1; X = CR) and acylimides [2] (1; X = N) with diphenylcyclopropenone (2) (DPCP) gives pyridine together with pyrones (3; X = CR) or oxazinones (3; X = N), respectively.



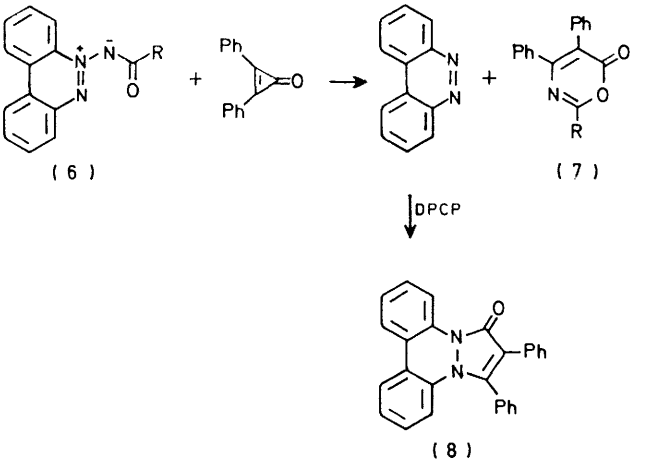
SCHEME 1

No stable intermediates are detected in these reactions and the most plausible mechanism is shown in Scheme 1. This type of reaction also occurs with the sulphoximide (4) which gives pyrimidone (5) and dimethyl sulphide [3] spontaneously on reaction with DPCP. However, during the course of our studies with extended dipoles



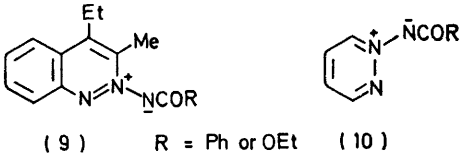
based on benzocinnoliniumimides we have observed an alternative mode of reaction leading to stable 1 : 1 adducts from the imides (11) and DPCP.

With the benzocinnolinium-*N*-acylimides (6; R = Ph, OEt, and Me), the reaction in hot dimethylformamide or benzene follows the expected course giving benzo[*c*]cinnoline and oxazinones (7) as shown in Scheme 2. Triphenyloxazin-6-one (7; R = Ph) [4] and 2-ethoxy-4,5-diphenyloxazin-6-one (7; R = OEt) from DPCP and the benzoyl- (6; R = Ph) and ethoxycarbonyl-imides (6; R = OEt), respectively, were identified by comparison with authentic samples. 2-Methyl-4,5-diphenyloxazin-6-one formed from the acetylimide (6; R = Me) showed a characteristic carbonyl absorption at 1 735 cm^{-1} in the i.r. spectrum and had the required mass-spectral and analytical data. The reaction is complicated by the fact that benzo[*c*]cinnoline itself reacts readily with DPCP to give the cycloadduct (8).[5] Thus equimolar



SCHEME 2

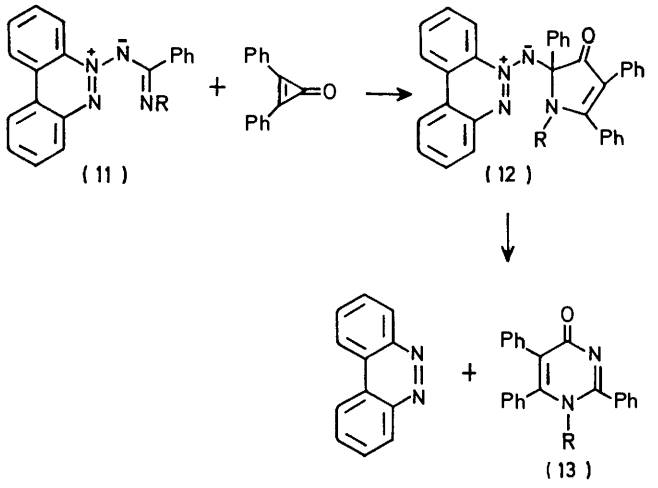
proportions of the reactants gave oxazinone (7), benzo-[*c*]cinnoline, and adduct (8) together with unchanged ylide (6) but an excess of DPCP gave only oxazinone and



adduct. Similar reactions were observed with the cinnolinium and pyridazinium ylides (9) and (10).[6]

In contrast to the benzo[*c*]cinnolinium *N*-acylimides the *N*-benzimidoimides (11) give a completely different

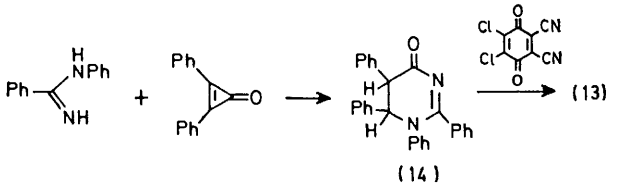
reaction with DPCP. Thus on heating with DPCP in refluxing benzene for 24 h, the *N*-phenylimide (11; R = Ph) gave a yellow, insoluble 1 : 1 adduct in high yield (90%) to which we assign structure (12). This structure assignment is based on the following evidence.



The carbonyl absorption observed at 1 685 cm^{-1} in the i.r. spectrum is reasonable for the five-membered cyclic vinylogous amide and compares favourably with the carbonyl frequency of 1 660 cm^{-1} observed for the similar vinylogous urea (8). The colour and u.v. spectrum are consistent with the benzo[*c*]cinnolinium-*N*-imide structure, so also is the 220-MHz ^1H n.m.r. spectrum which shows the fine structure characteristic of this class of compounds.[7] A parent ion is not observed in the mass spectrum but the base peak at *m/e* 400 corresponds to loss of benzo[*c*]cinnoline, again a characteristic of benzo[*c*]-cinnolinium-*N*-imides. Addition of DPCP to the C=N of simple imines has been reported [8] and benzo[*c*]-cinnolinium-*N*-benzimidoimides have been found to behave as reactive imines in their cycloadditions to ketens.[9] The adducts are clearly not related to the novel type of adduct reported recently from pyridinium-methylides and DPCP.[10] Further support for the structure of these 1 : 1 adducts comes from their pyrolysis (see later). Analogous adducts are formed from the imides (11; R = H and *p*-tolyl) and DPCP and from the imide (11; R = Ph) and diphenylcyclopropenethione. No adducts were observed with the *N'*-alkylbenzimido-ylides (11; R = Me and Et) [11] which rearrange at temperatures lower than those required for reaction with DPCP.

The formation of different types of products from the *N*-acyl- (6) and *N*-benzimido-ylides (11) is a result of a difference in the preferred site of attack by the electrophilic cyclopropenone. In the acyl ylides (6), the inner side-chain nitrogen is the nucleophilic site, whereas in the *imido*-ylides (11) it is the terminal nitrogen. A similar trend is observed in the reaction of these ylides with diphenylketen.[9,12] Interestingly, the imidoyl sulphimide (4) which incorporates the same ' amidine ' side chain moiety as the ylides (11), suffers attack at the inner nitrogen. This difference possibly reflects the difference between a simple ylide (4) and a delocalised mesoionic π-system (11) where the largest HOMO coefficients are to be expected at the termini.

On pyrolysis by heating at the melting point for 15—20 min or in refluxing trichlorobenzene for 12 h, the 1 : 1 adducts (12) gave benzo[*c*]cinnoline and the pyrimidones (13) in good yield. The pyrimidones were characterised by analytical, mass-spectral, and i.r. spectral data ($\nu_{max.}$ *ca.* 1 650 cm^{-1}). In the case of adduct (12; R = H), triphenylpyrimidone was identified by comparison with an authentic specimen, prepared independently,[13] thereby establishing the pyrimidone structure. For the products from adducts (12; R = Ph and *p*-tolyl) the assignment of a 1-substituted-1,3-pyrimidin-4-one rather than the isomeric 1-substituted-1,3-pyrimidin-6-one is somewhat more tentative and rests largely on the fact that the pyrimidone from (12; R = Ph) is different from but isomeric with that from DPCP and sulphoximide (4). In addition, 5,6-dihydro-1,2,5,6-tetraphenyl-4-pyrimidone (14) has been reported from the reaction of *N*-



phenylbenzamidine and DPCP.[14] Dehydrogenation of this dihydropyrimidone with dichlorodicyanobenzoquinone gave a tetraphenylpyrimidone identical with that produced by pyrolysis of the adduct (12; R = Ph).

The results indicate that the nature of the cationic portion of an ylide can profoundly effect the character of an ambident anionic portion. This has obvious implications in the use of such ylides in synthesis.

EXPERIMENTAL

Reaction of Benzo[c]*cinnolinium*-5-(N-*acylimides*) *with Diphenylcyclopropenone*.[15]—(a) *Benzo*[c]*cinnolinium*-(N-*benzoylimide*) (6; R = Ph).[7] A mixture of the imide (6; R = Ph) (120 mg, 0.4 mmol) and diphenylcyclopropenone (165 mg, 0.8 mmol) in dimethylformamide (10 ml) was heated at 100 °C for 24 h. The mixture was then concentrated by evaporation under reduced pressure and 2,3-diphenylpyrazolo[1,2-*a*]benzo[*c*]cinnolin-1-one (8), m.p. 278—279 °C, was filtered off. The residue was subjected to preparative t.l.c. on silica gel. Elution with 70% petroleum–ether gave 2,4,5-triphenyl-1,3-oxazin-6-one (7; R = Ph) (26 mg, 20%), m.p. and mixed m.p. 207—208 °C (lit.,[4] 207—208 °C), and further 2,3-diphenylpyrazolo[1,2-*a*]-benzo[*c*]cinnolin-1-one (8) (total yield 97 mg, 63%). The pyrazolobenzocinnolinone (8) prepared by the method of Lown and Matsumoto [5] from benzocinnoline and diphenylcyclopropenone initially had m.p. 264—265 °C (lit.,[5] 264—265 °C) but this was raised to 278—279 °C after two crystallisations from dichloromethane. The yield of oxazinone (7; R = Ph) was variable due to its susceptibility to hydrolysis during chromatography.

(b) *Benzo*[c]*cinnolinium*-(N-*ethoxycarbonylimide*) (6; R = OEt).[7] When treated as above the ethoxycarbonylimide (6; R = OEt) gave 2-ethoxy-4,5-diphenyloxazin-6-one (7; R = OEt) (40 mg, 55%), m.p. and mixed m.p. 94—95 °C (lit.,[2] 94—95 °C) and the pyrazolobenzocinnoline (8) (40%), m.p. and mixed m.p. 278—279 °C.

(c) *Benzo*[c]*cinnolinium*-(N-*acetylimide*) (6; R = Me).[7] A mixture of the acetylimide (6; R = Me) (237 mg, 1 mmol) and diphenylcyclopropenone (412 mg, 2 mmol) was heated under reflux in dry benzene for 24 h. After cooling the pyrazolobenzocinnoline (8) was filtered off (270 mg, 70%). The mother-liquors were concentrated and subjected to preparative t.l.c. on silica gel to give 2-*methyl*-4,5-*diphenyl*-1,3-*oxazin*-6-*one* (7; R = Me) (60 mg, 25%), m.p. 163—165 °C from dichloromethane–hexane (Found: C, 77.9; H, 5.2; N, 5.4. $C_{17}H_{13}NO_2$ requires C, 77.6; H, 4.9; N, 5.3%), $\nu_{max.}$ (Nujol) 1 735 cm^{-1}, *m/e* 263 (M^+) and 219.

Reaction of Benzo[c]*cinnolinium*-5-(N-*benzimidoylimides*) (11) *with Diphenylcyclopropenone*.—(a) *Benzo*[c]*cinnolinium*-(N-*benzimidoylimide*) (11; R = H).[11] A mixture of the imide (11; R = H) (2.98 g, 10 mmol) and diphenylcyclopropenone (2.06 g, 10 mmol) was heated under reflux in benzene (150 ml) for 24 h. After cooling the resulting yellow solid was filtered off, dried, and recrystallised from tetrahydrofuran–hexane to give the *adduct* (12; R = H) (3.72 g, 65%) as yellow needles, m.p. 230 °C (Found: C, 80.8; H, 4.8; N, 11.0. $C_{34}H_{24}N_4O$ requires C, 80.9; H, 4.8; N, 11.1%); $\nu_{max.}$ (Nujol) 1 680, 1 600, and 1 560 cm^{-1}; *m/e* 324 ($M^+ - 180$).

(b) *Benzo*[c]*cinnolinium*-[N-(N′-*phenylbenzimidoyl*)-*imide*] (11; R = Ph).[11] The same procedure with the imide (11; R = Ph) and diphenylcyclopropenone gave the adduct (12; R = Ph) (90%) as yellow crystals from tetrahydrofuran–hexane, m.p. 266—267 °C (Found: C, 83.1; H, 5·3; N, 9.4. $C_{40}H_{28}N_4O$ requires C, 82.7; H, 4.85; N, 9.65%); $\nu_{max.}$ (Nujol) 1 685, 1 590, and 1 560 cm^{-1}; *m/e* 400 ($M^+ - 180$).

(c) *Benzo*[c]*cinnolinium*-[N-(N′-p-*tolylbenzimidoyl*)*imide*] (11; R = p-*tolyl*).[11] The same procedure with imide (11; R = *p*-tolyl) gave the *adduct* (12; R = *p*-tolyl) (57%), as yellow needles from tetrahydrofuran–hexane, m.p. 278—279 °C (Found: C, 82.85; H, 5.2; N, 9.5. $C_{41}H_{30}N_4O$ requires C, 82.8; H, 5.05; N, 9.4%); $\nu_{max.}$ (Nujol) 1 685, 1 600, and 1 580 cm^{-1}; *m/e* 594 (M^+) and 414 (base peak, $M^+ - 180$).

Reaction of Benzo[c]*cinnolinium*-5′-[N-(N′-*phenylbenzimidoyl*)*imide*] *with Diphenylcyclopropenethione*.[16] A mixture of the imide (11; R = Ph) (374 mg, 1 mmol) and diphenylcyclopropenethione (222 mg, 1 mmol) in benzene (35 ml) was heated under reflux for 2 h. After cooling, the resulting red solid was filtered off, washed with benzene, dried, and recrystallised from tetrahydrofuran–hexane to give the *adduct* (12; S for O, R = Ph), (97%), as red prisms, m.p. 179—180 °C (Found: C, 80.4; H, 4.85; N, 9.5. $C_{40}H_{28}N_4S$ requires C, 80.5; H, 4.7; N, 9.4%); $\nu_{max.}$ (Nujol) 1 590 and 1 585 cm^{-1}; *m/e* 596.

Pyrolysis of the Adducts (12).—(a) The adduct (12; R = H) (100 mg), was maintained at its m.p. for 25 min. The cooled pyrolysate was extracted with benzene and the insoluble residue was collected and recrystallised from dichloromethane–hexane to give 2,5,6-triphenylpyrimidone (13; R = H) (56 mg, 89%), identical with an authentic specimen. The benzene soluble portion was purified by chromatography on silica gel, elution with ether giving benzo[*c*]cinnoline (28 mg, 78%), m.p. and mixed m.p. 155—156 °C.

(b) The adduct (12; R = Ph) (200 mg) was maintained at its m.p. for 15 min. Extraction of the cooled pyrolysate with benzene as above gave the insoluble 1,2,5,6-*tetraphenylpyrimidin*-4-*one* (13; R = Ph) (105 mg, 76%) as crystals, m.p. 315—317 °C (from dichloromethane–hexane) (Found: C, 83.5; H, 5.0; N, 6.6. $C_{28}H_{20}N_2O$ requires C, 84.0; H, 5.0; N, 7.0%); $\nu_{max.}$ (KBr) 1 650 cm^{-1}; *m/e* 400 (M^+). The benzene-soluble fraction yielded, after chromatography on silica gel, benzocinnoline (45 mg, 73%).

The adduct (12; R = Ph) was also heated under reflux in 1,2,4-trichlorobenzene (225 °C) for 12 h. The trichlorobenzene was removed by distillation under reduced pressure and the residue was chromatographed on silica gel. Elution with ether gave benzocinnoline (90%) and 1,2,5,6-tetraphenylpyrimidin-4-one (80%).

(c) The adduct (12; R = *p*-tolyl) (149 mg) was maintained at its m.p. for 25 min. After cooling the pyrolysate was subjected to preparative t.l.c. on silica gel using ether–acetone (9 : 1) as eluant. This gave benzocinnoline (41 mg, 91%) and 1-p-*tolyl*-2,5,6-*triphenylpyrimidin*-4-*one* (78 mg, 76%), crystals from dichloromethane–hexane, m.p. 204—205 °C (Found: C, 83.6; H, 5.3; N, 6.8. $C_{29}H_{22}N_2O$ requires C, 84.05; H, 5.3; N, 6.8%); $\nu_{max.}$ (Nujol) 1 640 cm^{-1}, *m/e* 414 (M^+).

Dehydrogenation of 5,6-*Dihydro*-1,2,5,6-*tetraphenylpyrimidin*-4-*one* (14).—The dihydropyrimidone (14), prepared as described by Eicher and his co-workers [14] (402 mg, 1 mmol), and dichlorodicyanobenzoquinone (454 mg, 2 mmol) were heated together in dry dioxan (40 ml) at 110 °C for 48 h. The cooled mixture was filtered to give 5,6-dichloro-2,3-dicyanohydroquinone (415 mg, 91%), m.p. 265 °C, and the filtrate was concentrated and chromatographed on neutral alumina. Elution with ethyl acetate gave tetraphenylpyrimidin-4-one (13; R = Ph) (280 mg, 70%), m.p. and mixed m.p. 315—317 °C, identical with the sample obtained from pyrolysis of (12; R = Ph).

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