Azimines as 1,3-Dipoles [1]

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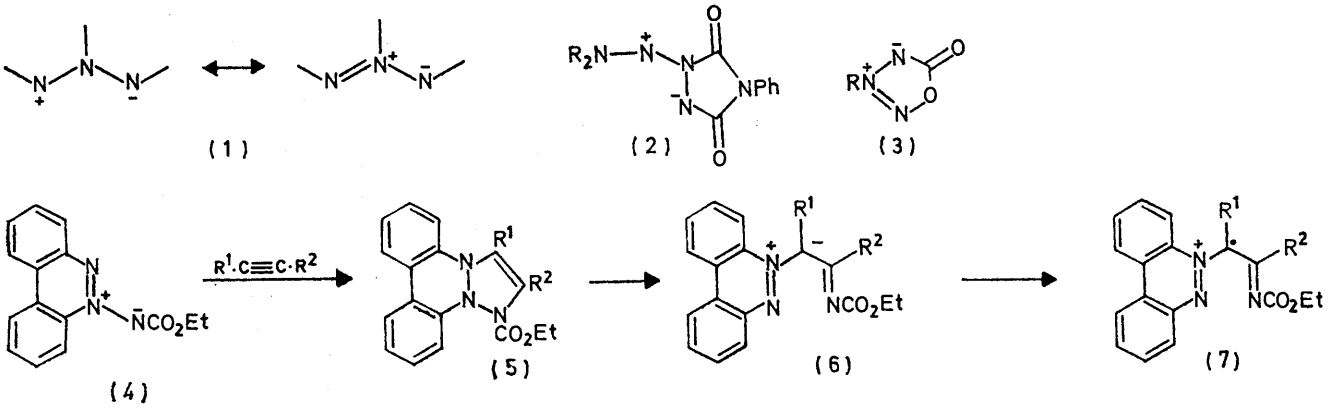
Benzocinnoline *N*-ethoxycarbonylimides [*e.g.* (4)] react with acetylenic esters and dicyanoacetylene to give the stable azomethine imines [*e.g.* (6)] by initial 1,3-dipolar cycloaddition and spontaneous electrocyclic ring opening of the triazolines so formed. The regiospecificity observed with 3-methoxybenzocinnoline 6-ethoxycarbonylimide (14) confirms this reaction sequence. The *N*-imide (4) reacts with olefins to give benzocinnoline presumably by decomposition of the unstabilised adducts which were not isolated. The azomethine imines (6) are readily oxidised to stable radical cations (7).

Benzocinnoline *N*-benzoylimide (4; COPh for CO_2Et) undergoes the same 1,3-dipolar cycloaddition reactions.

It is now over ten years since Huisgen formalised the concept of 1,3-dipolar cycloaddition.[2] During this time the three-nitrogen azimine system (1) has remained one of the few 1,3-dipoles based on carbon, oxygen, and nitrogen for which cycloadditions have not been observed. Although several azimines are known [3,4] the only reported attempts to observe such cycloadditions involved the aminoazimines (2; R = alkyl or aryl) [4] and the oxatriazolones (3; R = cyclohexyl or decyl).[5] The former did not react with phenyl isocyanate or acetylenedicarboxylic esters and the latter gave a rearrangement product, the 1-substituted 1,2,3-triazole, with diphenylacetylene at high temperatures. The benzocinnoline *N*-imides, *e.g.* (4),[6] which possess the three-nitrogen 4π and 372 nm (ε 49,000, 32,600, and 10,000)] which is typical of benzocinnolines, benzocinnoline *N*-oxides, and benzocinnolinium ylides. Its i.r. spectrum shows three carbonyl absorptions at 1645, 1690, and 1730 cm^{-1} in chloroform solution, the first two of which show the expected shifts to higher frequency in the picrate salt of (6). The n.m.r. spectrum of a freshly prepared solution of this ylide in deuteriochloroform shows 8 aromatic protons and 3 ester groups. On gentle warming of the solution the aromatic absorptions broaden and finally disappear irreversibly. This is not compatible with a temperature dependent conformational effect but seems more consistent with paramagnetic relaxation due to delocalisation of an unpaired electron over the aromatic



electron azimine system are therefore of interest as possible 1,3-dipoles, and we have investigated their reactions with dipolarophiles.

The *N*-amide (4) reacted exothermically with an equivalent amount of dimethyl or diethyl acetylenedicarboxylate in benzene or dimethylformamide at room temperature to give dark green adducts (6) quantitatively. Physical and chemical properties of these adducts are inconsistent with the expected triazoline structure (5) but fully support the highly stabilised azomethine imine structure (6). Thus for example the ylide (6; $R^1 = R^2 = CO_2Et$) has a u.v. spectrum [$\lambda_{max.}$ (EtOH) 256, 309, system. We therefore attribute the effect to the formation of a small proportion of the highly stabilised radical cation (7) which is in rapid equilibrium with (6). The presence in chloroform of a radical species whose concentration increases on warming was confirmed by e.s.r. spectroscopy. It is possible that the chloroform itself acts as electron acceptor in the oxidation of (6); such electron transfer has been suggested as a key step in the reaction of amines with polyhalogenoalkanes.[7] In the non-oxidising solvent acetonitrile, the e.s.r. signal was less intense and probably resulted from adventitious atmospheric oxidation. Complete oxidiation of (6) to (7) was effected by addition of an equimolar amount of

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

[2] R. Huisgen, *Festschrift zur Zehnjahresfeier des Fonds der Chemischen Industrie, Dusseldorf*, 1960, 73; *Proc. Chem. Soc.*, 1961, 357; *Chem. Weekblad*, 1963, **59**, 89; *Angew. Chem. Internat. Edn.*, 1963, **2**, 565, 633.

[3] L. Hoesch, M. Karpf, E. Dunkelblum, and A. S. Dreiding, *Chimia*, 1971, **25**, 245; R. C. Kerber, *J. Org. Chem.*, 1972, **37**, 1587; R. C. Kerber and P. J. Heffron, *ibid.*, p. 1592.

[4] K. H. Koch and E. Fahr, *Angew. Chem. Internat. Edn.*, 1970, **9**, 634; K. H. Koch, Dissertation, Universität, Würzburg, 1969.

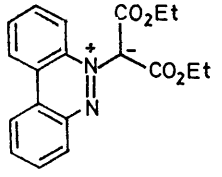
[5] R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, 1968, **101**, 536.

[6] S. F. Gait, M. E. Peek, C. W. Rees, and R. C. Storr, *J.C.S. Perkin I*, 1974, 1248.

[7] J. R. Lindsay Smith and Z. A. Malik, *J. Chem. Soc.* (*B*), 1970, 617, 920.

the stable radical cation, tris-(*p*-bromophenyl)ammonumyl hexachloroantimonate.[8]

The properties of the analogous azomethine imine (8), synthesised by treatment of the quaternary salt obtained from benzocinnoline and diethyl bromomalonate with aqueous sodium hydroxide, also provide strong evidence for the proposed structure (6). The ylide (8) is very similar in all respects (including ready conversion into a radical cation) to the azomethine imine (6) obtained from the cycloaddition. Further chemical support comes from the formation of benzocinnoline by thermal decomposition of (6) in refluxing diglyme. Also 1 equiv. of hydrogen is taken up on catalytic hydrogenation to give



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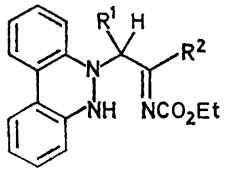

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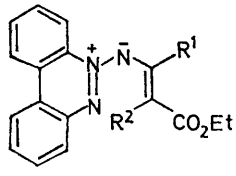

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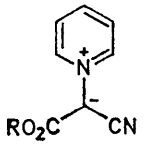

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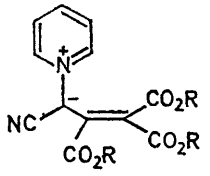

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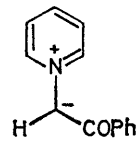


(13)

a product, presumably the imine (9) or the isomeric enamine, which could not be isolated owing to its ready reoxidation by atmospheric oxygen.

This last evidence, in particular, rules out an azimine structure (10) for the 1 : 1 adduct since benzocinnoline *N*-imides cleave readily on catalytic hydrogenation to give benzocinnoline.[6] Such a structure had to be considered in view of the reported formation of the azomethine ylide (12) from the pyridinium ylide (11) and acetylenedicarboxylic esters in acetonitrile.[9] A 'cationotropic' shift of CO_2Me in an intermediate zwitterion, resulting from initial Michael-like addition, was suggested to account for this reaction.

Similar cycloadditions were observed with ring substituted benzocinnoline *N*-ethoxycarbonylimides (see later) and with the *N*-benzoylimide (4; COPh for CO_2Et) and acetylenedicarboxylic esters.

Methyl propiolate gave an analogous adduct (6; $R^1 = CO_2Me$, $R^2 = H$) with (4). Evidence for the proposed orientation of this adduct is the low field signal (δ 9·52) of the side chain proton, which also does not exchange with D_2O. In contrast, the side chain proton in ylide (13) appears at δ 6·8 and exchanges slowly with D_2O. This orientation has been proved, indirectly, by an *X*-ray structure determination of the product of further reaction of adduct (6; $R^1 = CO_2Me$, $R^2 = H$) with diethyl acetylenedicarboxylate.* Adducts were readily obtained with dicyanoacetylene but less reactive dipolarophiles such as but-2-yne and diphenylacetylene did not react.

The most reasonable mechanism for the formation of the 1 : 1 adducts (6) is initial 1,3-dipolar cycloaddition to give the cycloadducts (5). These would rapidly undergo fission of the weak N–N bond † *via* an allowed 6π electrocyclic reaction (retro-1,5-dipolar cyclisation)[10] to give the highly stabilised ylides (6) as the observed products. These reactions therefore provide the first example of the 1,3-dipolar cycloaddition of an azimine.[1]

Cycloaddition of the methoxybenzocinnoline *N*-imide (14) is regiospecific in the sense shown.[11] Establishment of this specificity, which is consistent with the reaction sequence proposed above, is important since formally similar ylides (18) result from the reaction of phenanthridine *N*-oxides [12] and related ylides [13,14] with acetylenic esters. Although the mechanism of these *N*-oxide reactions is not known, an analogous mechanism for the reaction of our benzocinnoline *N*-imides would have led either to a regiospecificity opposite to that observed or to a non-regiospecific reaction. This latter possibility arises since a plausible mechanism for the addition of phenanthridine *N*-oxide to acetylenedicarboxylic esters is *via* the isoxazoline (16) and the aziridine (17), as shown, and in the benzocinnolinium reactions the diaziridine intermediate (19), analogous to (17), could cleave by breaking either of the two C–N bonds. 1,3-Dipolar cycloaddition to give isoxazolines is a probable first step since these can be

* We thank Dr. A. F. Cameron for this *X*-ray structure determination which will be published separately.

† Significantly very few five-membered ring compounds with three adjacent saturated nitrogen atoms have ever been reported (*cf.* P. J. Abbott, R. M. Acheson, M. W. Foxton, N. R. Raulins, and G. E. Robinson, *J.C.S. Perkin I*, 1972, 2182).

[8] F. A. Bell, A. Ledwith, and D. C. Sherrington, *J. Chem. Soc.* (*C*), 1969, 2719.

[9] C. Leonte and I. Zugrăvescu, *Tetrahedron Letters*, 1972, 2029.

[10] H. Reimlinger, *Chem. Ber.*, 1970, **103**, 1900.

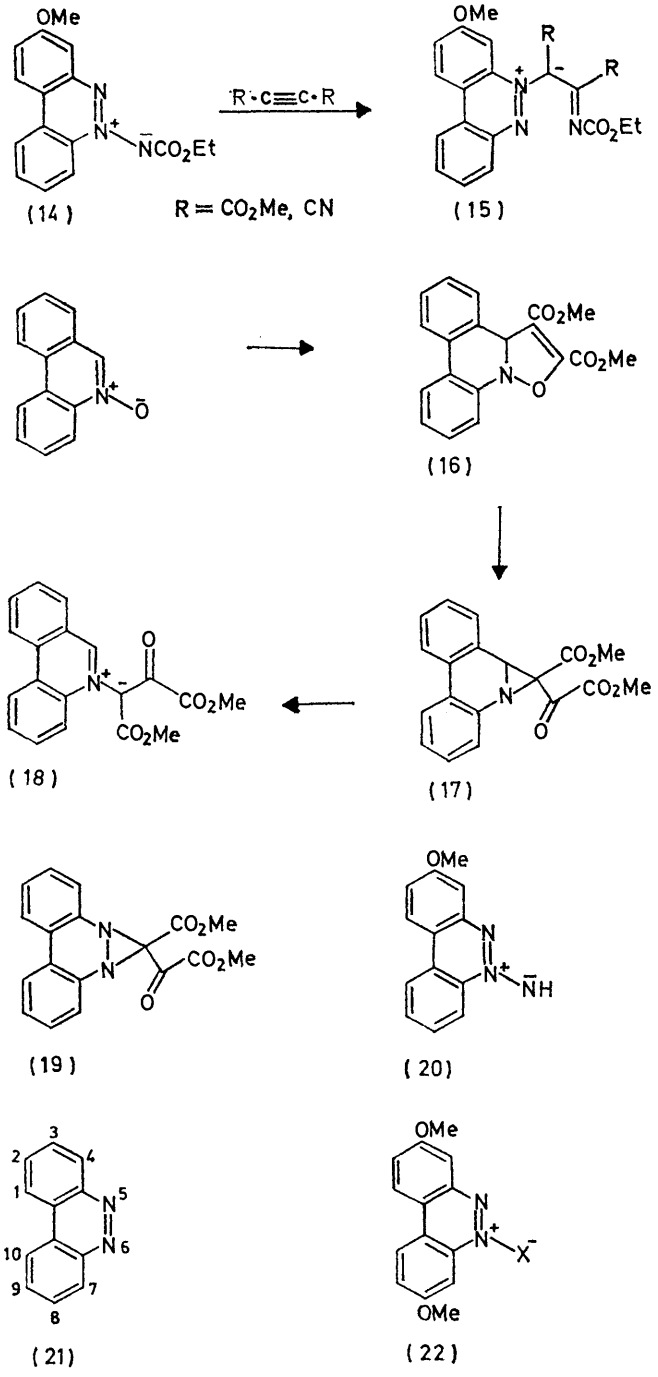
[11] S. R. Challand, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1973, 837.

[12] R. M. Acheson, A. S. Bailey, and I. A. Selby, *J. Chem. Soc.* (*C*), 1967, 2066 and references therein; R. Huisgen, H. Seidl, and J. Wulff, *Chem. Ber.*, 1969, **102**, 915.

[13] S. Takahashi and H. Kano, *J. Org. Chem.*, 1965, **30**, 1118.

[14] H. Seidl, R. Huisgen, and R. Knorr, *Chem. Ber.*, 1969, **102**, 904.

isolated in the reaction of 3,4-dihydroisoquinoline *N*-oxide and propiolic esters and shown to rearrange to analogous ylides.[14] The ready thermal rearrangement of



isoxazolines to 2-acylaziridines has also been demonstrated.[15] Significantly the isoxazolines, *e.g.* (16), cannot undergo a simple retro-cyclisation to give a 1,5-dipole *

* We use the term 1,5-dipole as an extension of Huisgen's definition of a 1,3-dipole. The 1,5-dipole is a 6π electron system isoelectronic with a pentadienide anion and the formal positive and negative centres are interchangeable.

[15] J. E. Baldwin, R. G. Pudussery, A. K. Qureshi, and B. Sklarz, *J. Amer. Chem. Soc.*, 1968, **90**, 5325.

such as we propose for our triazoline system, since this would lead to a zwitterion having a saturated carbon atom within the system.

An alternative mechanism for the above nitrone additions involves deoxygenation of the *N*-oxide by the acetylene to give an α-ketocarbene which then recombines with the deoxygenated heterocycle. Such a mechanism has received support in a recent communication.[16] A corresponding sequence for the azimine reaction involving 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 the *N*-imide (4) was allowed to react with dimethyl acetylenedicarboxylate in the presence of an excess of 3,8-dimethoxybenzocinnoline there was no ' cross-over '; only ylide (6) was formed and none of the dimethoxy-ylide corresponding to (6) could be detected.

The regiospecificity was established as follows. 3-Methoxybenzocinnoline *N*(6)-imide (20) was obtained by thermal rearrangement of 3-methoxy-5*H*-dibenzo[*d*,*f*]-[1,2,3]triazepine.[6] Structural assignment for this *N*-imide is based on the close similarity of its ^{1}H and ^{13}C n.m.r. spectra with those of 3-methoxybenzocinnoline 6-oxide, produced unambiguously by methylation of 3-hydroxybenzocinnoline 6-oxide.[6,17] The fine structure of the ^{1}H spectra is particularly useful in this respect. 3,8-Dimethoxybenzocinnoline *N*(5)-imide (22; X = NH) was obtained by rearrangement of 3,8-dimethoxydibenzotriazepine and also by direct amination of 3,8-dimethoxybenzocinnoline with *O*-mesitylsulphonylhydroxylamine.[6] The *N*-imides (20) and (22; X = NH) were converted into their ethoxycarbonyl derivatives with ethyl chloroformate.

In the ^{13}C n.m.r. spectra of aromatic compounds a methoxy-group is expected to shift an *ortho*-carbon signal *ca.* 15·5 p.p.m. to higher field.[18] It is apparent that the 2,9 and 4,7 pairs of carbon atoms in benzocinnoline (21) are not affected equally by the introduction of 3,8-methoxy-groups. The high field signal at 108·5 p.p.m. in the dimethoxybenzocinnoline must correspond to one of these pairs; we arbitrarily assume this to be the 4,7 pair, but the following arguments are equally valid if it is the 2,9 pair.

In the 3,8-dimethoxybenzocinnoline 5-oxide (22; X = O) [19] C(4) and C(7) are different and have chemical shifts of 106·0 and 101·9 p.p.m., respectively. Assignment of the 106·0 p.p.m. signal to C(4) follows from the appearance of a single absorption at 106·6 p.p.m. for 3-methoxybenzocinnoline 6-oxide. 3,8-Dimethoxybenzocinnoline *N*(5)-imide (22; X = NH) similarly shows absorptions at 102·2 and 101·3 p.p.m.; 3-methoxybenzocinnoline *N*(6)-imide (20) shows only one at 102·3

[16] R. A. Abramovitch and I. Shinkai, *J.C.S. Chem. Comm.*, 1973, 569.

[17] E. Waldau and R. Pütter, *Angew. Chem. Internat. Edn.*, 1972, **11**, 826.

[18] J. B. Stothers, ' Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, p. 197.

[19] F. E. Kempter and R. N. Castle, *J. Heterocyclic Chem.*, 1969, **6**, 523.

p.p.m., again corresponding to the lower field signal of the dimethoxy pair.

The azomethine imine [22; X = $C(CO_2Me)\cdot C(CO_2Me)$:NCO_2Et] obtained by cycloaddition of 3,8-dimethoxybenzocinnoline 5-ethoxycarbonylimide (22; X = NCO_2Et) shows signals at 106·3 and 98·9 p.p.m. for C(4) and C(7). Significantly the azomethine imine derived from addition of 3-methoxybenzocinnoline 6-ethoxycarbonylimide (14) has an absorption at 99·9 p.p.m. corresponding to the *higher* field one of the pair for the dimethoxy-analogue. Assuming that the O, N, and C side chains in these isoelectronic dipolar systems exert parallel substituent effects, this result shows that, during the course of the addition, the side chain has migrated from one benzocinnoline nitrogen to the other.

^{1}H N.m.r. spectra could not be used in this assignment because while the two methoxy-groups in 3,8-dimethoxybenzocinnoline 5-oxide and in 3,8-dimethoxybenzocinnoline 5-imide have different chemical shifts, those in the 3,8-dimethoxyazomethine imines [22; X = $C(R)\cdot C(R)$:NCO_2Et, R = CO_2Me or CO_2Et] are isochronous. With dicyanoacetylene, the dimethoxy-*N*-imide (22; X = NCO_2Et) gave an azomethine imine [22; X = $C(CN)\cdot C(CN)$:NCO_2Et] with resolved ^{1}H methoxy-absorptions at τ 5·86 and 5·95. The dimethoxy-*N*-imide (22; X = NH) has methoxy-signals at τ 6·04 and 6·11. 3-Methoxybenzocinnoline 6-imide (τ_{OMe} 6·11) gives an azomethine imine (τ_{OMe} 5·83) again indicating that a change in side chain position has occurred. Pure 3-methoxybenzocinnoline 5-imide was not available. Amination of 3-methoxybenzocinnoline with *O*-mesitylsulphonylhydroxylamine gave an inseparable mixture of 3-methoxy-5- and -6-imines.[6] The mixture of ethoxycarbonylazimines derived from these imines was also inseparable but gave a mixture of regioisomeric azomethine imines with dimethyl acetylenedicarboxylate. This shows that the regiospecificity observed with the pure 3-methoxyiminobenzocinnoline 6-ethoxycarbonylimide (14) was not the result of a dominating substituent effect.

Only acetylenic dipolarophiles can give cycloadducts with (4) which are capable of electrocyclic ring opening to stabilised ylides. Treatment of (4) with a variety of olefins (maleic anhydride, and maleic, fumaric, and cinnamic esters) gave no characterisable 1 : 1 adducts. Instead, benzocinnoline was formed under much milder conditions than in the absence of olefins. Thus reaction has occurred between the *N*-imide (4) and the olefin and this too is presumably initiated by dipolar cycloaddition. No cycloaddition to the *N*-imide (4) was observed with anisaldehyde or phenyl isocyanate.

EXPERIMENTAL

Reaction of Benzocinnoline N-*Ethoxycarbonylimide* [6] (4) *with Acetylenic Esters.*—The acetylene (1 equiv.) was added to a solution of the *N*-imide in the minimum volume of benzene. The solution became dark green as a rapid exothermic reaction occurred. After 2 h the adduct was filtered off and recrystallised. When the reaction was carried out in dimethylformamide the adduct was precipitated by addition of the mixture to water.

Reaction of the *N*-imide (4) and diethyl acetylenedicarboxylate gave 1-(5-*benzo*[c]*cinnolinio*)-1,2-*bisethoxycarbonyl*-2-*ethoxycarbonyliminoethanide* (6; $R^1 = R^2 = CO_2Et$) (90%) as dark green plates, m.p. 216—218·5° (from ethanol) (Found: C, 63·0; H, 5·4; N, 9·6. $C_{23}H_{23}N_3O_6$ requires C, 63·1; H, 5·3; N, 9·6%); $\nu_{max.}$ (Nujol) 1725, 1690, and 1660 cm^{-1}, $\lambda_{max.}$ 256 (ε 49,000), 309 (32,600), 372 (10,200), and 533 nm (950), τ 1·25—1·70br (4H, m), 1·95—2·38br (4H, m), 5·50 (2H, q, *J* 7 Hz), 5·92 (2H, q, *J* 7 Hz), 6·09 (2H, q, *J* 7 Hz), 8·52 (3H, t, *J* 7 Hz), 8·90 (3H, t, *J* 7 Hz), and 9·05 (3H, t, *J* 7 Hz), *m/e* 437, 180, and 152.

The *N*-imide (4) and dimethyl acetylenedicarboxylate gave 1-(5-*benzo*[c]*cinnolinio*)-2-*ethoxycarbonylimino*-1,2-*bismethoxycarbonylethanide* (6; $R^1 = R^2 = CO_2Me$) (95%) as dark green plates, m.p. 225—228° (decomp.) (from benzene) (Found: C, 61·7; H, 4·75; N, 10·3. $C_{21}H_{19}N_3O_6$ requires C, 61·6; H, 4·7; N, 10·3%), $\nu_{max.}$ 1735, 1692, and 1660 cm^{-1}, $\lambda_{max.}$ 256 (ε 44,000), 311 (29,200), 374 (10,000),

^{13}C N.m.r. data for benzocinnolines (chemical shifts in p.p.m. from Me_4Si)

Benzocinnoline (21)	144·6,[a] 130·8, 130·6, 128·5, 120·8, 120·2 [a]
3-Methoxybenzocinnoline [b]	159·5,[a] 146·2,[a] 144·4,[a] 130·9, 130·5, 127·1, 122.9, 122·0, 120·4, 114·6,[a] 108·9, 55·5
3,8-Dimethoxybenzocinnoline	158·5,[a] 146·0,[a] 123·5, 121·1, 115·4,[a] 108·5,[c,d] 55·5
Benzocinnoline 5-oxide	142·5,[a] 137·3,[a] 133·0, 130·9, 130·1, 129·2, 126·4, 122·8, 122·4, 121·7, 119·6,[a] 118·3 [a]
3-Methoxybenzocinnoline 6-oxide [b]	162·0,[a] 144·7,[a] 136·9,[a] 133·1, 129·2, 122·9, 122·8, 122·3, 120·3, 112·7,[a] 106·6,[c] 55·4
3,8-Dimethoxybenzocinnoline 5-oxide (22; X = O) [b]	161·8,[a] 160·8,[a] 143·6,[a] 137·7,[a] 124·8, 123·6, 122·1, 120·5, 113·0, 106·0,[c] 101·9,[d] 55·7, 55·3
Benzocinnoline 5-imide [b]	143·3,[a] 132·1,[a] 130·6, 129·4, 128·1, 127·1,[a] 123·5, 121·5, 120·7, 120·5, 115·3 [a]
3-Methoxybenzocinnoline 6-imide (20) [b]	160·5,[a] 145·0,[a] 130·8, 127·4,[a] 127·0, 121·8, 121·2, 120·8, 114·1, 109·3,[a] 102·3,[c] 55·3
3,8-Dimethoxybenzocinnoline 5-imide (22; X = NH) [b]	159·8,[a] 158·7,[a] 144·0,[a] 131·9,[a] 122·4, 121·7, 121·2, 114·3, 109·6,[a] 102·2,[c] 101·3,[d] 55·7, 55·2
(6; $R^1 = R^2 = CO_2Me$) [b]	167·6,[a] 163·1,[a] 159·9,[a] 143·7,[a] 139·2,[a] 138·5, 133·5, 132·9, 132·3, 131·5, 128·1,[a] 125·2,[a] 123·0, 122·4, 122·2, 107·5,[a] 60·7, 52·4, 51·2, 14·5
(15; R = CO_2Me)	167·8,[a] 163·0,[a] 161·7,[a] 159·7,[a] 143·1,[a] 141·1,[a] 137·7, 131·3, 130·6, 127·2,[a] 126·1, 125·4,[a] 125·0, 123·6, 122·0, 107·1,[a] 99·9,[c] 60·5, 56·3, 52·3, 51·1, 14·4
[22; X = $C\cdot(CO_2Me)\cdot C(CO_2Me)$:$NCO_2Et$] [e]	168·0,[a] 163·2,[a] 162·4,[a] 160·5,[a] 156·9,[a] 145·2,[a] 140·6,[a] 131·5, 127·8,[a] 126·0, 124·6, 124·0,[a] 123·3, 121·3,[a] 107·1,[a] 106·3,[c] 98·9,[d] 60·5, 56·3, 55·9, 52·3, 51·2, 14·4

[a] Tentatively assigned as quaternary C on the basis of peak intensity. [b] One peak obscured by overlapping. [c] C(4). [d] C(7). [e] This sample contained an impurity. Additional low intensity peaks were observed at 161·7, 159·7, 118·8, 115·9, 106·7, and 94·2 p.p.m. These have been assigned to the impurity on the basis of their low intensity and lack of correlation with absorptions of ethanides (6) and (15) although in some cases this assignment is clearly not unambiguous.

and 554 nm (825), τ 1·00—1·66br (4H, m), 1·78—2·40br (4H, m), 5·88 (3H, s), 6·02 (2H, q, *J* 7 Hz), 6·40 (3H, s,) and 9·07 (3H, t, *J* 7 Hz), *m/e* 409, 180, and 152; *picrate*, yellow plates, m.p. 205—206° (from ethanol) (Found: C, 50·7; H, 3·55; N, 12·9. $C_{27}H_{22}N_6O_{13}$ requires C, 50·7; H, 3·45; N, 13·2%), $\nu_{max.}$ 1747, 1717, and 1630 cm^{-1}. When this cycloaddition was carried out in the presence of 3,8-dimethoxycinnoline only the ethanide (6; $R^1 = R^2 = CO_2Me$) was formed; no ethanide [22; X = C(CO_2Me):NCO_2Et)] was detected by t.l.c.

The *N*-imide (4) and methyl propiolate gave 1-(5-*benzo*[c]*cinnolinio*)-2-*ethoxycarbonylimino*-1-*methoxycarbonylethanide* (6; $R^1 = CO_2Me$, $R^2 = H$) (95%), as dark green plates, m.p. 192—193° (from benzene) (Found: C, 64·95; H, 4·9; N, 11·7. $C_{19}H_{17}N_3O_4$ requires C, 64·95; H, 4·9; N, 12·0%), $\nu_{max.}$ 1690 and 1653 cm^{-1}, $\lambda_{max.}$ 285 (ε 42,800), 299 (30,500), 374 (9350), and 554 nm (830), τ 0·48 (1H, s), 1·05—1·82br (4H, m), 1·85—2·49br (4H, m), 5·90 (2H, q, *J* 7 Hz), 6·25 (3H, s), and 8·88 (3H, t, *J* 7 Hz).

Benzocinnoline *N*-benzoylimide [6] (4; COPh for CO_2Et) and dimethyl acetylenedicarboxylate gave 1-(5-*benzo*[c]*cinnolinio*)-2-*benzoylimino*-1,2-*bismethoxycarbonylethanide* (6; $R^1 = R^2 = CO_2Me$; COPh for CO_2Et) (64%) as green plates, m.p. 124—126° (from benzene) (Found: C, 68·2; H, 4·5; N, 9·3. $C_{25}H_{19}N_3O_5$ requires C, 68·0; H, 4·3; N, 9·5%), $\nu_{max.}$ 1735 and 1695 cm^{-1}, τ 1·0—1·6br (4H, m), 1·6—2·3br (4H, m), 2·5—3·5 (5H, complex m), 5·85 (3H, s), and 6·30 (3H, s).

3,8-Dimethoxybenzocinnoline 5-ethoxycarbonylimide [6] (21; X = NCO_2Et) and dimethyl acetylenedicarboxylate gave 1-(3,8-*dimethoxy*-5-*benzo*[c]*cinnolinio*)-2-*ethoxycarbonylimino*-1,2-*bismethoxycarbonylethanide* [22; X = C(CO_2Me)·C(CO_2Me):NCO_2Et] (61%) as brown crystals, m.p. 248—249° (from benzene) (Found: C, 58·65; H, 4·9; N, 8·7. $C_{23}H_{23}N_3O_8$ requires C, 58·8; H, 4·9; N, 8·9%), $\nu_{max.}$ 1730, 1700, and 1658 cm^{-1}, τ 1·66 (2H, dd), 2·24 (1H, d), 2·39 (1H, t), 2·58—3·0 (2H, m), 5·92 (3H, s), 5·96 (6H, s), 5·99 (2H, q, *J* 7 Hz), 6·39 (3H, s), and 9·07 (3H, t, *J* 7 Hz), *m/e* 469 (M^+).

3-Methoxybenzocinnoline 6-ethoxycarbonylimide (14) [6] and dimethyl acetylenedicarboxylate gave 2-*ethoxycarbonylimino*-1-(3-*methoxy*-5-*benzo*[c]*cinnolinio*)-1,2-*bismethoxycarbonylethanide* (83%) as brown crystals, m.p. 240—241° (from benzene) (Found: C, 59·9; H, 4·8; N, 9·6. $C_{22}H_{21}N_3O_7$ requires C, 60·1; H, 4·8; N, 9·6%), $\nu_{max.}$ 1733, 1696, and 1660 cm^{-1}, τ 1·4—1·6 (3H, m), 2·0—2·18 (3H, m), 2·6—2·8 (1H, m), 5·9 (3H, s), 5·93 (3H, s), 5·98 (2H, q, *J* 7 Hz), 6·38 (3H, s), and 9·01 (3H, t, *J* 7 Hz), *m/e* 439 (M^+).

3,8-Dimethoxybenzocinnoline 5-ethoxycarbonylimide (22; X = NCO_2Et) and diethyl acetylenedicarboxylate gave 1-(3,8-*dimethoxy*-5-*benzo*[c]*cinnolinio*)-1,2-*bisethoxycarbonyl*-2-*ethoxycarbonyliminoethanide* [22; X = C(CO_2Et)·C(CO_2Et):NCO_2Et] (48%), m.p. 229—231° (from benzene) (Found: C, 60·3; H, 5·4; N, 8·2. $C_{25}H_{27}N_3O_8$ requires C, 60·3; H, 5·4; N, 8·4%), $\nu_{max.}$ 1732, 1697, and 1659 cm^{-1}, τ 1·64br (2H, d), 2·2—2·9 (4H, m), 5·45 (2H, q, *J* 7 Hz), 5·82 (2H, q, *J* 7 Hz), 5·94 (6H, s,) 5·99 (2H, q, *J* 7 Hz), 8·50 (3H, t, *J* 7 Hz), 8·84 (3H, t, *J* 7 Hz), and 9·03 (3H, t, *J* 7 Hz), *m/e* 497 (M^+).

The *N*-imide (14) and diethyl acetylenedicarboxylate gave 1,2-*bisethoxycarbonyl*-2-*ethoxycarbonylimino*-1-(3-*methoxy*-5-*benzo*[c]*cinnolinio*)*ethanide* (42%), m.p. 215—217° (from benzene) (Found: C, 61·1; H, 5·4; N, 9·0. $C_{24}H_{25}N_3O_7$ requires C, 61·6; H, 5·35; N, 9·0%), $\nu_{max.}$ 1727, 1688, and 1655 cm^{-1}, τ 1·4—1·75br (3H, d), 2·05br (3H, s), 2·7 (1H, m), 5·44 (2H, q, *J* 7 Hz), 5·84 (2H, q, *J* 7 Hz), 5·95 (3H, s), 6·00 (2H, q, *J* 7 Hz), 8·51 (3H, t, *J* 7 Hz), 8·85 (3H, t, *J* 7 Hz), and 9·01 (3H, t, *J* 7 Hz), *m/e* 467 (M^+).

The *N*-imide (4) and dicyanoacetylene [20] gave 1-(5-*benzo*[c]*cinnolinio*)-1,2-*dicyano*-2-*ethoxycarbonyliminoethanide* (6; $R^1 = R^2 = CN$) (62%), m.p. >280° (Found: C, 66·1; H, 3·8. $C_{19}H_{13}N_5O_2$ requires C, 66·4; H, 3·8%), $\nu_{max.}$ 2240 and 1684 cm^{-1}.

The *N*-imide (21; X = NCO_2Et) and dicyanoacetylene gave 1,2-*dicyano*-1-(3,8-*dimethoxy*-5-*benzo*[c]*cinnolinio*)-2-*ethoxycarbonyliminoethanide* [22; X = C(CN)·C(CN):NCO_2Et] (50%), m.p. >280° (Found: C, 60·9; H, 4·3. $C_{21}H_{17}N_5O_4$,0·5H_2O requires C, 61·15; H, 4·4%), $\nu_{max.}$ 2220 and 1665 cm^{-1}, τ 1·2—2·5 (7H, m), 5·86 (3H, s), 5·9 (2H, q, *J* 7 Hz), 5·95 (3H, s), and 8·72 (3H, t, *J* 7 Hz).

The *N*-imide (14) and dicyanoacetylene gave 1,2-*dicyano*-2-*ethoxycarbonylimino*-1-(3-*methoxy*-5-*benzo*[c]*cinnolinio*)-*ethanide* (65%), m.p. >300° (Found: C, 63·6; H, 4·1. $C_{20}H_{15}N_5O_3$ requires C, 63·4; H, 4·0%), $\nu_{max.}$ 2220 and 1660 cm^{-1}, τ 1·3—2·8 (7H, m), 5·83 (3H, s), 5·85 (2H, q, *J* 7 Hz), and 8·83 (3H, t, *J* 7 Hz).

A mixture of 3-methoxybenzocinnoline 5- and 6-ethoxycarbonylimides was obtained by ethoxycarbonylation of the mixed imines formed by amination of 3-methoxybenzocinnoline with *O*-mesitylsulphonylhydroxylamine.[6] The mixture was allowed to react with dimethyl acetylenedicarboxylate and the crude adduct mixture was isolated. The n.m.r. spectrum of this fraction indicated clearly that it was a mixture of isomeric adducts: τ 1·4—1·9 (3H, complex m), 2·0—2·9 (4H, complex m), 5·9—6·0 (8H, 2 unresolved s and overlapping q), 6·38 (3H, s), and 8·95 and 9·05 (2 overlapping t).

Reaction of the N-*Ethoxycarbonylimide* (4) *with Olefins*.—The *N*-imide and a slight excess of olefin in dimethylformamide were maintained at 90° for 16 h. With diethyl maleate and fumarate and with ethyl cinnamate t.l.c. indicated little reaction, and benzocinnoline was the only recognisable product.

The *N*-imide and diethyl maleate were heated under reflux in solution in dimethylformamide for 1 h. The resulting mixture was poured into water to give a precipitate of benzocinnoline (78%), m.p. and mixed m.p. 153—155°. A control experiment showed that very little decomposition of imide occurred in the absence of olefin.

Hydrogenation of Azomethine Imine (6; $R^1 = R^2 = CO_2Me$).—The azomethine imine in ethanol was hydrogenated using Adams catalyst. Hydrogen (1 equiv.) was rapidly absorbed and the dark green solution became pale yellow. No further uptake of hydrogen was observed over several hours. Re-exposure of the solution to the atmosphere resulted in rapid oxidation (within 10 min) to give the initial azomethine imine.

Pyrolysis of the Azomethine Imine (6; $R^1 = R^2 = CO_2Me$).—The azomethine imine (425 mg) was heated in refluxing diglyme for 16 h. The solution was poured into water and the resulting precipitate was chromatographed on basic alumina. Elution with ether gave benzocinnoline (152 mg) (85%), m.p. and mixed m.p. 153—156°.

Hydrolysis of the Azomethine Imine (6; $R^1 = R^2 = CO_2Me$).—The azomethine imine (300 mg) was heated under reflux in 2N-hydrochloric acid for 3 h. The cooled, filtered solution was basified with sodium carbonate to give benzocinnoline (100 mg, 74%), m.p. and mixed m.p. 153—155°.

[20] A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, 1945, **10**, 149.

Reduction of Tris-(p-*bromophenyl*)*ammoniumyl Hexachloroantimonte.*[8]—Addition of tris-(*p*-bromophenyl)ammoniumyl hexachloroantimonate (1 equiv.) to ylide (**6**; R^1 = CO_2Me, R^2 = H) in $CDCl_3$ solution in an n.m.r. tube caused the virtual disappearance of the n.m.r. spectrum of the ylide (**6**) and gave the characteristic AA'BB' quartet of tris-(*p*-bromophenyl)amine. The ammoniumyl salt gave no n.m.r. signal in $CDCl_3$ in the absence of the ylide (**6**).

(5-*Benzo*[c]*cinnolinio*)*bisethoxycarbonylmethanide* (**8**).—Benzocinnoline (1·8 g) and diethyl bromomalonate (2·4 g) were heated in refluxing ethanol for 24 h. The ethanol was removed by distillation under reduced pressure and the residue was dissolved in water. The aqueous solution was basified with sodium hydroxide and then extracted with dichloromethane. The dichloromethane extracts were dried and evaporated to give the *ylide* (**8**) (220 mg, 7%), dark green plates, m.p. 180—181° (from benzene–petroleum) (Found: C, 67·7; H, 5·45; N, 8·5. $C_{19}H_{18}N_2O_4$ requires C, 67·4; H, 5·4; N, 8·3%), $\nu_{max.}$ 1680, 1600, and 1580 cm^{-1}, τ 1·00—1·68br (4H, m), 1·78—2·33br (4H, m), 5·77 (4H, q, *J* 6·5 Hz), and 8·80 (6H, t, *J* 6·5 Hz).

We thank Drs. R. J. Abraham, R. D. Lapper, A. Ledwith, and P. J. Russell for helpful discussion and the S.R.C. for fellowships (S. R. C. and M. J. R.) and a studentship (S. F. G.).

[4/957 *Received*, 16*th May*, 1974]