Benzo[*c*]cinnoline *N*-Imides [1]

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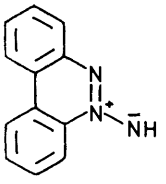
Benzo[*c*]cinnoline *N*-imide (1) is formed quantitatively by mild thermal isomerisation of dibenzo[*d*,*f*][1,2,3]-triazepine (2), or directly from 2,2'-diaminobiphenyl by aprotic diazotisation without isolation of the intermediate triazepine (2). The *N*-imide (1) is also formed by amination of benzocinnoline, preferably with *O*-mesitylsulphonylhydroxylamine. The *N*-imide (1) is readily converted into *N*-alkyl, -aryl, -acyl, and -alkoxycarbonyl derivatives (5), and the spectroscopic and chemical properties of all the *N*-imides are in accord with the presence of the proposed stable 1,3-dipolar 4 π-electron azimine system. Photolysis of the *N*-imides gave benzocinnoline and the nitrene, R–N̈:. Pyrolysis of the parent *N*-imide (1) gave carbazole exclusively whereas the *N*-methylimide gave only benzocinnoline. The *N*-benzoyl-, *N*-acetyl-, and *N*-ethoxycarbonyl-imides gave both *N*-substituted carbazoles and benzocinnoline. The results of ^{15}N-labelling and other experiments, including conversion of the *N*-imide (1) into carbazole, suggest that isomerisation of the triazepine (2) into the *N*-imide (1) is reversible, and involves the ring-opened, diazo-imine form of the triazepine as intermediate (Scheme 2).

In a recent paper [2] we described the formation of benzocinnoline *N*-imide (1) in the diazotisation of 2,2'-diaminobiphenyl. It was formed as the major product of aprotic diazotisation by diphenylnitrosamine or pentyl nitrite in benzene and was shown to arise by thermal rearrangement of dibenzo[*d*,*f*][1,2,3]triazepine (2). 2-Amino-2'-azidobiphenyl and benzocinnoline, which were also formed in the diazotisations, probably arose by reaction of the *N*-imide (1) with the ' masked diazonium ' triazepine (2). The *N*-imide (1) was produced in lower yield, together with a variety of other products, in the aqueous diazotisation of 2,2'-diaminobiphenyl in 2N-hydrochloric acid.



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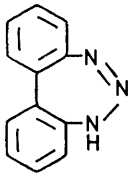


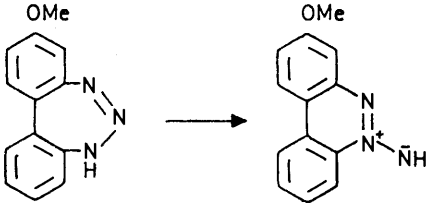
(2)

The *N*-imide (1) is a stable, yellow, crystalline solid. Its structure is strongly supported by spectral data. Thus a sharp N–H stretching absorption is observed at 3160 cm^{-1} and the base peak in the mass spectrum is at *m*/*e* 180 ($M^+ - NH$). The u.v. spectrum is characteristic of a benzocinnoline or, more particularly, a benzocinnoline *N*-oxide, showing three main absorptions at 254 (ε 37,500), 297 (8930), 310 (7700), 323 (6900) and 367 nm (9120). It therefore contrasts with the isomeric triazepine (2) which absorbs at 239 (ε 27,300), 265 (9750), and 294 (5850) nm.[2] Finally, the ^{1}H n.m.r. spectrum of the *N*-imide (1) is virtually identical with that of the isoelectronic *N*-oxide.

The chemical behaviour of the *N*-imide (1) is also in complete accord with the proposed structure. A stable hydrochloride is formed with hydrochloric acid. Deamination occurs readily with nitrous acid at 0° or with pentyl nitrite at room temperature. Catalytic hydrogenation gives dihydrobenzocinnoline, which is readily oxidised to benzocinnoline on exposure to air.

The *N*-imide (1) can also be produced from benzocinnoline by direct amination with hydroxylamine-*O*-sulphonic acid [3] or, in much higher yield, with *O*-mesitylsulphonylhydroxylamine.[4,5] Indeed this last reaction is now the method of choice for its preparation.

Several analogous benzocinnoline *N*-imides have been obtained by the above methods. Thus 3-methyl-, 3-methoxy-, and 3,9-dimethoxy-dibenzotriazepines are converted into the corresponding *N*-imides on heating in benzene. The 3-methoxytriazepine (3) gave only 3-methoxybenzocinnoline *N*(6)-imide (4), showing that substituents can control the direction of this isomerisation. Direct amination of 3-methoxybenzocinnoline gave an inseparable mixture of benzocinnoline *N*(5)- and *N*(6)-imides in which the 5-isomer predominated (n.m.r. spectroscopy indicated a 3 : 2 mixture). The orientational assignment for these methoxy-*N*-imides is based on the close similarity of the ^{1}H and ^{13}C n.m.r. absorptions of the 3-methoxy-*N*(6)-imide to those of 3-methoxybenzocinnoline *N*(6)-oxide, obtained by



(3) (4)

methylation of 3-hydroxybenzocinnoline, *N*(6)-oxide which was prepared unambiguously.[6]

The *N*-imide (1) is readily converted into a variety of *N*-substituted derivatives [5; R = Ac, Bz, CO·CHPh$_2$, CO$_2$Me, CO$_2$Et, CO·NHPh, C$_6$H$_4$·NO$_2$-*p*, 2,4-(NO$_2$)$_2$C$_6$H$_3$, Ph, Me, or Et]. The acyl, ethoxycarbonyl, and activated aryl derivatives were formed by treatment of the *N*-imide with the appropriate

[1] Preliminary communications, S. F. Gait, C. W. Rees, and R. C. Storr, *Chem. Comm.*, 1971, 1545; S. F. Gait, M. E. Peek, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1972, 982.

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

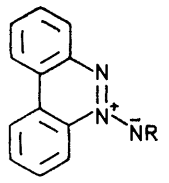
[3] R. Gösl and A. Meuwsen, *Chem. Ber.*, 1959, **92**, 2521.

[4] L. A. Carpino, *J. Amer. Chem. Soc.*, 1960, **82**, 3133; G. Krause, *Synthesis*, 1972, 140.

[5] Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, and M. Ikeda, *J. Org. Chem.*, 1973, **38**, 1239.

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

chloride in the presence of base. The carbamoyl and diphenylacetyl derivatives were obtained by treatment with phenyl isocyanate and diphenylketen, respectively. Benzocinnoline *N*-phenylimide was obtained in low



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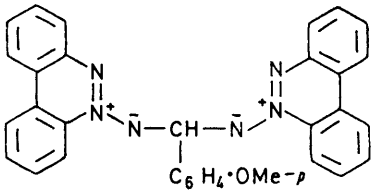

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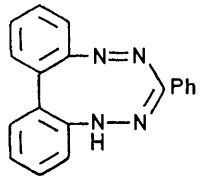

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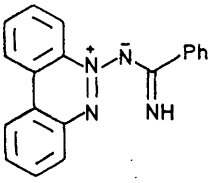


(7)

yield together with benzocinnoline and phenyl azide by treatment of the *N*-imide (1) with benzenediazonium chloride in the presence of a copper catalyst (see later).

Certain of these derivatives have been reported recently by Neugebauer and Fischer [7] in a paper describing an alternative route to azimines; they showed that the previously reported cyclic formazan (6) [8] had the *N*-benzimidoylimide structure (7).

Treatment of the *N*-imide (1) with sodamide in liquid ammonia followed by an alkyl iodide gave the alkyl derivatives. With anisaldehyde, the condensation product (8) was formed. The stability of a wide range of derivatives, particularly the bis-*N*-imide (8), illustrates the 1,3-dipolar character of these *N*-imides. They are delocalised 4 π-electron systems which in valence bond terms may be written with the exocyclic nitrogen atom bearing either a formal positive or negative charge. They are examples of the rare azimine 1,3-dipolar system.[9]

The *N*-substituted derivatives have ^{1}H n.m.r. spectra which are similar to that of the *N*-imide (1) and all show a mass spectral base peak at *m/e* 180. A low-frequency carbonyl stretching absorption is observed for the acyl and alkoxycarbonyl derivatives (1660, 1590, and 1605 cm^{-1} for the ethoxycarbonyl, acetyl, and benzoyl derivatives, respectively); this occurs *ca.* 90 cm^{-1} to higher frequency in the spectra of the picrate salts. A similar effect has been noted for substituted pyridine *N*-imides.[10] The u.v. spectra are as expected for benzocinnoline *N*-imides, with a main absorption at *ca.* 250 nm (ε *ca.* 35,000) and the wavelengths of the two longer-wavelength absorptions varying with the nature of the substituent. Catalytic reduction of the benzoyl and ethoxycarbonyl derivatives gave benzocinnoline together with benzamide and ethyl carbamate, respectively. Similar reductive cleavage of benzocinnoline *N*-imides was reported by Neugebauer and Fischer.[7]

On pyrolysis in refluxing bis-(2-methoxyethyl) ether or *o*-dichlorobenzene, the *N*-imide (1) unexpectedly gave carbazole almost quantitatively. In contrast the *N*-methyl derivative (5; R = Me) behaved as expected, undergoing N–N bond cleavage in refluxing 1,2,4-trichlorobenzene to give benzocinnoline. Similar fragmentation to give benzocinnoline and, at least formally, the appropriate nitrene occurred with the *N*-acetyl-, *N*-benzoyl-, and *N*-ethoxycarbonyl-imides in refluxing bis-(2-methoxyethyl) ether or 1,2,4-trichlorobenzene, but in each case *N*-substituted carbazoles were also formed (see Table). The results of thermolysis in bis-(2-methoxyethyl) ether are complicated by the presence of peroxides. Thus in the heavily peroxidised ether (strong positive indication in test with acidified potassium iodide), the *N*-imide (1) gave benzocinnoline (60%) and only a trace of carbazole, a complete reversal of the normal product distribution. Addition of benzoyl peroxide to pure, peroxide-free bis-(2-methoxyethyl) ether also led to this reversal of product distribution. *N*-Benzoylcarbazole formation was also suppressed in the case of the *N*-benzoylimide (5; R = Bz) in the peroxidised ether. Significantly the rate of decomposition of the *N*-benzoylimide was also greater in the ether than in *o*-dichlorobenzene at the same temperature.

Fragmentation reactions of the *N*-imides (5)

	Pyrolysis in solution [a]		Photolysis [h]	
N-Imide (5)	Benzocinnoline	Carbazole	Benzocinnoline	Carbazole
H	Trace	95;[b] 80 [c]	68	5
H	60 [d]	Trace		
CO_2Et	50	35 [e]	35	0
Ac	17	52 [f]		
Bz	21	60 [g]	38	0
Me	96	0		

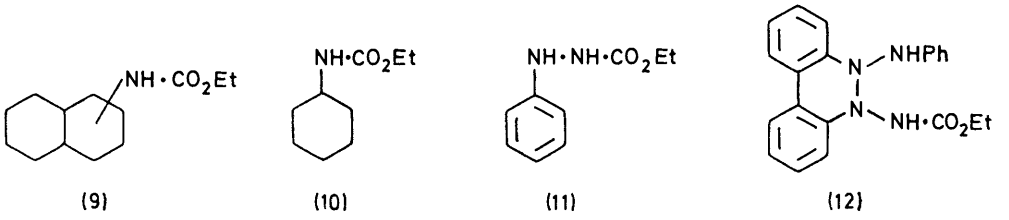
[a] In refluxing 1,2,4-trichlorobenzene except where stated otherwise. [b] In refluxing peroxide-free bis-(2-methoxyethyl) ether. [c] In refluxing *o*-dichlorobenzene. [d] In refluxing peroxidised bis-(2-methoxyethyl) ether. [e] Mixture of 9-ethoxycarbonylcarbazole and carbazole. [f] 9-Acetylcarbazole. [g] 9-Benzoylcarbazole. [h] Sensitised with benzophenone.

On u.v. irradiation, the *N*-imide (1) and its derivatives all underwent fragmentation to give benzocinnoline.

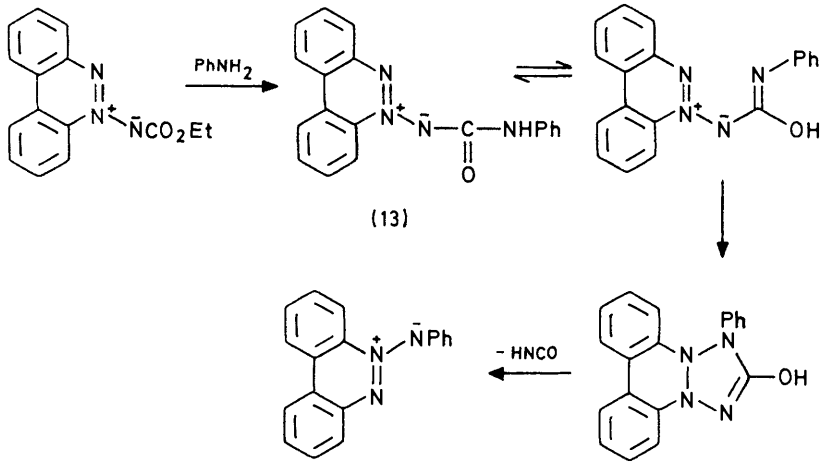
There are several examples of N–N bond cleavage in heterocyclic *N*-imides leading to the heterocycle and a formal nitrene fragment, mostly induced photochemically.[11] The nature of the nitrene fragment has been the subject of speculation and discussion but no clear

[7] F. A. Neugebauer and H. Fischer, *Chem. Ber.*, 1973, **106**, 1589.
[8] D. Jerschel and W. Elder, *Chem. Ber.*, 1955, **88**, 1284.
[9] S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, *J.C.S. Chem. Comm.*, 1972, 688; S. R. Challand, S. F. Gait, M. J. Rance, C. W. Rees, and R. C. Storr, following paper; L. Hoesch, M. Karpf, E. Dunkelblum, and A. S. Dreiding, *Chimia (Switz.)*, 1971, **25**, 245; R. C. Kerber, *J. Org. Chem.*, 1972, **37**, 1587; R. C. Kerber and P. J. Heffron, *ibid.*, p. 1592.
[10] T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432.
[11] V. Sniekus, *Chem. Comm.*, 1969, 831; A. Balasubramanian, J. M. McKintoch, and V. Sniekus, *J. Org. Chem.*, 1970, **35**, 433; V. Sniekus and G. Kan, *Chem. Comm.*, 1970, 172.

picture has emerged.[12] In our system, the nitrene has been intercepted only with the *N*-ethoxycarbonylimide (5; R = CO_2Et). Pyrolysis in refluxing decalin gave a mixture of the three expected isomeric C–H insertion products (9).[13] The mixture was not separated but characteristised by analytical and spectral data; three broad N–H signals and signals for three ethyl groups were observed in the n.m.r. spectrum. Photolysis of the *N*-ethoxycarbonylimide in cyclohexane gave the cyclohexylcarbamate (10), identical with an authentic specimen prepared from cyclohexylamine and ethyl chloroformate. With other *N*-imides the ' nitrene ' fragment was not detected. In particular



(9) (10) (11) (12)



SCHEME 1

atives into carbazoles pose interesting mechanistic problems.

Three mechanisms can be envisaged for the triazepine-to-*N*-imide isomerisation (Scheme 2). Mechanism (a) was readily eliminated by a ^{15}N-labelling experiment. Treatment of 2,2'-diaminobiphenyl with pentyl [^{15}N]-nitrite should proceed through a [6-^{15}N]triazepine. The *N*-imide (1) produced by this reaction by using 30% labelled pentyl nitrite was exclusively labelled at the exocyclic nitrogen atom as indicated by its mass spectrum, in which the molecular ion peak showed 30% incorporation. The base peak corresponding to $M^+ -$ NH showed no label. Deamination of this *N*-imide with nitrous acid gave unlabelled benzocinnoline. Mechanism (a) is further excluded by the observation that the *N*-methyltriazepine did not isomerise to the *N*-methylimide. There is no reason why this should not occur by route (a), whereas routes (b) and (c) both require migration of the *N*-substituent. At present we cannot distinguish with certainty between route (b), involving ring closure of the 6*H*-triazepine tautomer to give the triaziridine (14) which opens to give the *N*-imide, and route (c), which involves an electrocyclic reaction of the ring-opened diazoimine isomer of the dibenzotriazepine to give (15), followed by hydrogen migration. Both routes are consistent with the labelling results. However we strongly favour route (c) since 3-methoxydibenzotriazepine rearranges to give 3-methoxybenzocinnoline *N*(6)-imide exclusively.

no trace of benzofurazan *N*-oxide was observed in thermolysis or photolysis of the *N*-2,4-dinitrophenylimide [5; R = 2,4-$(NO_2)_2C_6H_3$].

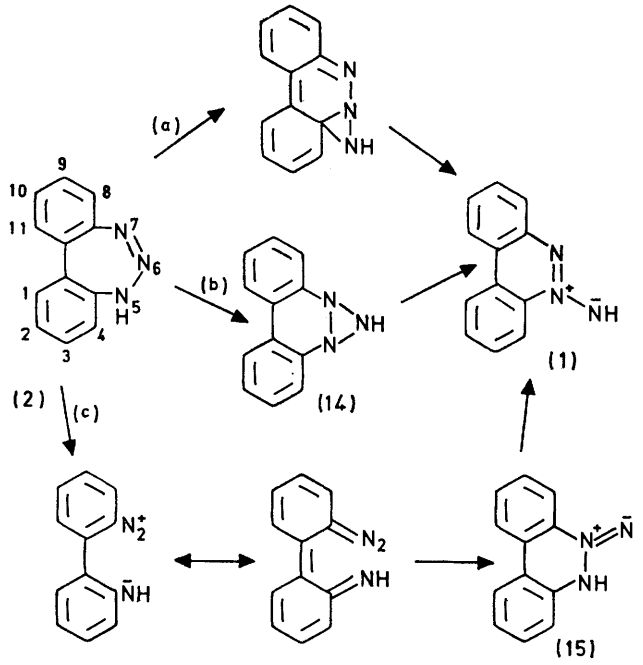
When attempts were made to intercept ethoxycarbonylnitrene as its N–H insertion product (11) by pyrolysis in aniline, the *N*-phenylimide ylide (5; R = Ph) was formed in low yield. This probably results from conjugate addition to give (12) followed by elimination of ethyl carbamate. The reasonable alternative mechanism shown in Scheme 1 was also considered, but this seems much less likely since the *N*-carbamoylimide (13) formed independently from the imide (1) and phenyl isocyanate did not give the *N*-phenylimide on pyrolysis.

Both the conversion of the triazepine (2) into the *N*-imide (1) and that of the *N*-imide (1) and its deriv-

[12] C. W. Bird, D. Y. Wong, G. V. Boyd, and A. J. H. Summers, *Tetrahedron Letters*, 1971, 3187.

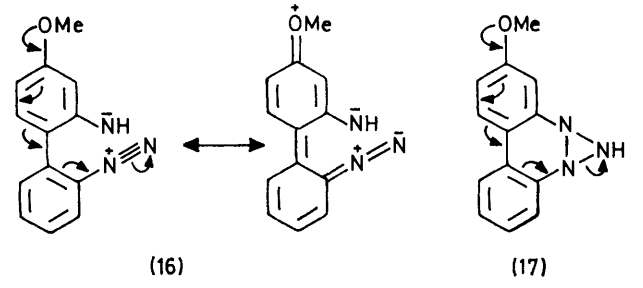
[13] W. Lwowski in ' Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 185.

This is to be expected in route (c) since electron delocalisation (16) should favour cleavage of the triazepine ring in the sense shown. On the other hand the



SCHEME 2

methoxy-group should direct opening of the triaziridine (17) to give the alternative *N*-imide.



The above discussion refers to the thermal uncatalysed isomerisation of triazepine to *N*-imide. The triazepine is converted into the *N*-imide in dilute aqueous acid, and the formation of 2-amino-2′-azidobiphenyl and benzocinnoline when the *N*-imide (1) is adsorbed on warm silica gel suggests that the interconversion can also be acid-catalysed and reversible (see ref. 2, p. 1252).

Formation of carbazole by decomposition of the *N*-imide (1) in boiling bis-(2-methoxyethyl) ether or dichlorobenzene may be closely related mechanistically. Such loss of molecular nitrogen also implies that the triazepine-to-*N*-imide isomerisation is reversible and that carbazole is produced by decomposition of a small equilibrium proportion of triazepine at this relatively high temperature. Formation of *N*-methylcarbazole from *N*-methyldibenzotriazepine is in accord with this postulate. Alternatively carbazole formation could occur by extrusion of nitrogen from the intermediate (15) on route (c). Lack of methylcarbazole formation from the *N*-methylimide and formation of exclusively unlabelled carbazole from labelled *N*-imide (exocyclic ^{15}N) is in agreement with either mechanism.

We presume that in bis-(2-methoxyethyl) ether containing peroxides an alternative pathway leading to benzocinnoline results from oxidative attack of peroxides on the exocyclic nitrogen atom. This reaction dominates the rearrangement to the triazepine which leads ultimately to carbazole, and possibly also dominates the uncatalysed N–N bond cleavage leading to benzocinnoline.

Formation of both benzocinnoline and *N*-substituted carbazoles from the *N*-imides (5; R = Ac, Bz, or CO_2Et) indicates that acyl group migration can occur with surprising facility. That migration had occurred was confirmed by the formation of unlabelled *N*-benzoylcarbazole from *N*-benzoyl[^{15}N]imide.

The *N*-imide (1) and its derivatives are examples of the rare 1,3-dipolar azimine system. The following paper describes an investigation of the cycloaddition reactions of these *N*-imides.

EXPERIMENTAL

Common reaction products such as carbazole and benzocinnoline were always characterised by mixed m.p. determination and i.r. spectral comparison; literature m.p.s for these are not recorded. U.v. spectra are for solutions in ethanol and n.m.r. spectra for solutions in deuteriochloroform unless otherwise stated. ^{13}C N.m.r. data are quoted as downfield shifts from tetramethylsilane.

Benzocinnoline N-*Imide* (1).—The formation of the *N*-imide (1) by diazotisation of 2,2′-diaminobiphenyl and by thermal rearrangement of 5*H*-dibenzo[*d*,*f*][1,2,3]triazepine and its detailed physical properties have been described.[2]

Amination of Benzo[c]*cinnoline with O-Mesitylsulphonylhydroxylamine.* *O*-Mesitylsulphonylhydroxylamine was prepared by the method of Tamura and his co-workers.[5] In order to minimise the risk of its decomposition, the aminating agent was normally used freshly prepared without thorough drying.

A mixture of *O*-mesitylsulphonylhydroxylamine (10 g) and benzocinnoline (5 g) in dichloromethane was stirred overnight. The resulting solid was filtered off and stirred with an excess of aqueous sodium hydroxide. The liberated benzocinnoline *N*-imide was filtered off and recrystallised from ether–petroleum to give yellow needles (3·7 g, 70%), m.p. 126°.

Deamination of Benzo[c]*cinnoline* N-*Imide* (1).—(*a*) A solution of the *N*-imide (200 mg) and pentyl nitrite (0·5 ml) in benzene (30 ml) was heated under reflux for 16 h. The mixture was passed through a short alumina column (ether as eluant) to give benzocinnoline (172 mg, 96%).

(*b*) Sodium nitrite (175 mg, 2·5 mmol) in water (10 ml) was added dropwise to the *N*-imide (500 mg, 2·5 mmol) in 2N-sulphuric acid (25 ml) at 0°. After 15 min at 0—5° the mixture was basified and benzocinnoline (440 mg, 98%) was collected.

Benzo[c]*cinnoline* N-*Imide Hydrochloride.*—Concentrated

hydrochloric acid (5 drops) was added to a solution of *N*-imide (300 mg) in warm ethanol (20 ml). After 30 min the mixture was concentrated and the pale yellow *hydrochloride* crystallised; m.p. 162—164° (decomp.) (Found: C, 62·1; H, 4·3; N, 17·7. $C_{12}H_{10}ClN_3$ requires C, 62·3; H, 4·3; N, 18·0%).

Reduction of Benzo[c]*cinnoline* N-*Imide* (1).—A methanolic solution of the *N*-imide was shaken under hydrogen in the presence of 10% palladium–charcoal at room temperature. After 10 min, the solution was filtered and evaporated to give benzocinnoline (94%).

Disproportionation of the N-*Imide* (1) *on Silica Gel.*—The *N*-imide (280 mg) was adsorbed on silica gel and maintained at 80° for 10 min. The products were then eluted from a silica gel column. Elution with 20% ether–petroleum gave carbazole (10 mg, 4·5%), m.p. and mixed m.p. 245°. Further elution gave 2-amino-2′-azidobiphenyl (125 mg, 42%), identical with an authentic specimen. 50% Ether–petroleum eluted benzocinnoline (116 mg, 45%).

3-*Methoxybenzo*[c]*cinnoline* N(6)-*Imide* (4).—3-Methoxy-5*H*-dibenzo[*d*,*f*][1,2,3]triazepine (3) was heated under reflux in benzene for 1 h. Benzene was removed by evaporation under reduced pressure and the residue was chromatographed on alumina to give the N-*imide* (4) (80%) as yellow prisms (from benzene), m.p. 144—145° (Found: C, 68·9; H, 5·0; N, 18·7. $C_{13}H_{11}N_3O$ requires C, 69·3; H, 4·9; N, 18·6%); *m/e* 225 (M^+), 210 (M — NH), 198, and 182; $\nu_{max.}$ 3150 (N–H) 1610, 1587, 1335, 1315, 1260, 1210, 1175, 1039, 840, 775, 760, and 720 cm^{-1}; τ 1·3br (1H, d), 1·7—2·7 (5H, complex m), 3·0—3·2 (2H, m, includes NH), and 6·11 (3H, s); ^{13}C δ 55·6, 103·1, 110·1, 114·9, 121·8, 122·1, 122·8, 128·0, 128·3, 131·7, 146·1, 161·8, and 167·4 p.p.m. The ^1H and ^{13}C n.m.r. spectra were very similar to those of 3-methoxybenzocinnoline *N*(6)-oxide synthesised unambiguously.

3-*Methoxybenzo*[c]*cinnoline* N(5)- *and* N(6)-*Imides.*—3-Methoxybenzocinnoline *N*(6)-oxide was obtained from 3-hydroxybenzocinnoline *N*(6)-oxide [6] by methylation with dimethyl sulphate. It was also obtained from 4-methoxy-2,2′-dinitrobiphenyl [14] by reduction with sodium sulphide in refluxing aqueous ethanol, and had m.p. 147—150° (from ethanol), $\nu_{max.}$ 1613, 1586, 1367, 1349, 1287, 1203, 1041, 787, and 724 cm^{-1}; τ 1·39br (1H, d), 1·85—2·60 (4H, m), 2·76—2·97 (2H, m), and 6·12 (3H, s); ^{13}C δ 55·4, 106·6, 112·7, 120·3, 122·3, 122·8, 122·9, 129·2, 133·1, 136·9, 144·7, and 162·0 p.p.m.

3-Methoxybenzocinnoline *N*(6)-oxide (1 g) in triethyl phosphite was maintained at 130—140° for 12 h. After cooling, ether was added to give a yellow precipitate of 3-*methoxybenzo*[c]*cinnoline* (74%), yellow plates, m.p. 150—151° (from chloroform–petroleum) (Found: C, 74·4; H, 4·9; N, 13·2. $C_{13}H_{10}N_2O$ requires C, 74·3; H, 4·8; N, 13·3%); *m/e* 210 (M^+), 182 (M — N_2), 167, 152, 151, and 150; $\nu_{max.}$ 1621, 1297, 1205, 1087, 1032, 830, and 765 cm^{-1}; τ 1·25—2·73 (7H, m) and 5·96 (3H, s).

Amination of 3-methoxybenzocinnoline by the method described for benzocinnoline gave a mixture (88%) of *N*(5)- and *N*(6)-imides. N.m.r. data for the 5-imide were obtained by subtraction of the spectrum of the 6-isomer: τ 1·8—2·1, 2·6—2·8, 3·2, and 6·05 (OMe). The ratio of integrals of methoxy-peaks indicated a 3 : 2 ratio of 5- to 6-imide.

3,8-*Dimethoxybenzo*[c]*cinnoline* N(5)-*Imide.*—(*a*) 3,9-Dimethoxy-5*H*-dibenzo[*d*,*f*][1,2,3]triazepine was heated under reflux in benzene for 1 h. Evaporation followed by chromatography of the residue on alumina gave the N-*imide* (30%), m.p. 153—154°, *m/e* 255 (M^+), 240 (M — NH) 225, and 197; $\nu_{max.}$ 3370, 1610, 1345, 1270, 1215, 1165, 1040, 840, and 820 cm^{-1}; τ ($CDCl_3$) 1·75—2·1 (3H, m), 2·8—3·1 (4H, m), 6·05 (3H, s), and 6·11 (3H, s); ^{13}C δ 55·2, 55·7, 101·3, 102·2, 109·6, 114·3, 121·2, 121·7, 122·4, 131·9, 144·0, 158·7, and 159·8 p.p.m. Elemental analysis was carried out on the ethoxycarbonyl derivative (below).

(*b*) Amination of 3,8-dimethoxybenzocinnoline [15] with *O*-mesitylsulphonylhydroxylamine by the standard method gave 3,8-dimethoxybenzocinnoline *N*(5)-imide (72%).

3-*Methylbenzo*[c]*cinnoline* N(6?)-*Imide.*—3-Methyl-5*H*-dibenzo[*d*,*f*][1,2,3]triazepine was heated under reflux in benzene for 1 h. Evaporation followed by chromatography of the residue on alumina gave the *N-imide* (73%), yellow needles, m.p. 116—119° (from benzene) (Found: C, 74·5; H, 5·3; N, 20·0. $C_{13}H_{11}N_3$ requires C, 74·6; H, 5·3; N, 20·1%) *m/e* 209 (M^+), 194 (M — NH), and 182; $\nu_{max.}$ 3145, 1601, 1572, 1320, 1250, 1201, 1165, 1012, 835, 760, and 720 cm^{-1}. T.l.c. and n.m.r. spectroscopy indicated that this was a single isomer and it was therefore presumed to be the 6-imide by analogy with the rearrangement of 3-methoxydibenzotriazepine.

Derivatives of Benzo[c]*cinnoline* N-*Imides.*—*Benzo*[c]*cinnoline* N-*ethoxycarbonylimide.* Ethyl chloroformate (2·75 g, 5 equiv.) was added dropwise to benzocinnoline *N*-imide (500 mg) and triethylamine (255 mg) in dichloromethane or dry tetrahydrofuran (15 ml). The mixture was heated under reflux for 16 h, cooled, evaporated, and chromatographed on alumina. Elution with 50% ether–petroleum gave unchanged *N*-imide and 5% ethyl acetate–ether gave the N-*ethoxycarbonylimide* (76%) as yellow needles, m.p. 128—129° (from benzene–petroleum) (Found: C, 67·2; H, 4·9; N, 15·6. $C_{15}H_{13}N_3O_2$ requires C, 67·4; H, 4·9; N, 15·6%); *m/e* 267 (M^+), 222, 180, and 152; $\nu_{max.}$ 1660, 1466, 1380, 1232, 1095, 771, 722, and 690 cm^{-1}; $\lambda_{max.}$ 253 (ε 31,100), 300 (8720), and 426 nm (13,400); τ 1·0—1·15 (1H, m), 1·5—2·6 (7H, m), 5·67 (2H, q, *J* 7 Hz), and 8·60 (3H, t, *J* 7 Hz); *picrate*, yellow needles, m.p. 158—160° (from benzene) (Found: C, 51·0; H, 3·4; N, 16·6. $C_{21}H_{16}N_6O_9$ requires C, 50·8; H, 3·3; N, 16·9%); $\nu_{max.}$ 1745 cm^{-1} (C=O).

Hydrogenation. The *N*-ethoxycarbonylimide (250 mg) in methanol was stirred under hydrogen in the presence of 10% palladium–charcoal for 10 min. The mixture was filtered and evaporated and the residue was chromatographed on silica gel. Elution with 15% ether–petroleum gave ethyl carbamate (17 mg, 20%), m.p. and mixed m.p. 47—49°. 50% Ether–petroleum eluted benzocinnoline (89 mg, 53%).

3-*Methoxybenzo*[c]*cinnoline* N(6)-*ethoxycarbonylimide.* This *N*-imide was obtained (92%) by the above procedure as a yellow crystalline *solid*, m.p. 170—171° (from benzene) (Found: C, 64·4; H, 4·8; N, 14·1. $C_{16}H_{15}N_3O_3$ requires C, 64·6; H, 5·0; N, 14·1%); *m/e* 297 (M^+), 252, 225, 210, and 167; $\nu_{max.}$ 1660, 1615, 1233, 1096, 782, and 758 cm^{-1}; τ 0·95br (1H, d), 1·5—2·7 (6H, complex m), 5·62 (2H, q, *J* 7 Hz), 6·05 (3H, s), and 8·57 (3H, t, *J* 7 Hz).

3,8-*Dimethoxybenzo*[c]*cinnoline* N(5)-*ethoxycarbonylimide.* This was obtained (90%) as a yellow crystalline *solid*, m.p. 152—154° (from benzene) (Found: C, 68·5; H, 5·8; N,

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10·4. $C_{17}H_{17}N_3O_4,C_6H_6$ requires C, 68·15; H, 5·7; N, 10·4%); *m/e* 327 (M^+), 282, 255, 240, 197, and 169; $\nu_{max.}$ 1665, 1625, 1300, 1223, 1090, 1045, and 830 cm^{-1}; τ 1·6—1·95 (3H, m), 2·45—2·7 (3H, m), 2·72 (s, benzene), 5·54 (2H, q, *J* 7 Hz), 5·99 (3H, s), 6·06 (3H, s), and 8·56 (3H, t, *J* 7 Hz).

Benzo[c]*cinnoline* N-*benzoylimide*. Benzoyl chloride (410 mg, 3 mmol) was added to a suspension of benzocinnoline *N*-imide (500 mg, 2·5 mmol) in aqueous potassium hydroxide. The mixture was shaken for 10 min and the resulting solid was filtered off and recrystallised from ethanol to give the *N*-benzoylimide (711 mg, 95%) as yellow plates, m.p. 212—214° (lit.,[7] 211—212°) (Found: C, 76·0; H, 4·4; N, 14·0. Calc. for $C_{19}H_{13}N_3O$: C, 76·2; H, 4·4; N, 14·0%), *m/e* 299 (M^+), 257, 222, 180, and 152; $\nu_{max.}$ 1605 cm^{-1} (C=O); $\lambda_{max.}$ 248 (ε 37,500) and 434 nm (10,900); τ 0·86—1·00 (1H, m) and 1·35—2·65 (13H, m); *picrate*, yellow needles, m.p. 183—185°; $\nu_{max.}$ 1675 cm^{-1} (C=O).

Hydrogenation. Catalytic hydrogenation as described for the *N*-ethoxycarbonylimide gave benzocinnoline (65%) and benzamide (98%), m.p. and mixed m.p. 127—129°, separated by chromatography on silica gel.

Benzo[c]*cinnoline* N-*acetylimide*. A mixture of benzocinnoline *N*-imide (500 mg, 2·5 mmol) and acetic anhydride (500 mg, 4·9 mmol) in pyridine was stirred at room temperature for 2 h. The *N*-acetylimide was precipitated with pentane and recrystallised from benzene–petroleum to give yellow plates (510 mg, 80%), m.p. 207—208 (lit.,[7] 208—209°) (Found: C, 70·8; H, 4·9; N, 17·7. Calc. for $C_{13}H_{11}N_2O$: C, 70·9; H, 4·7; N, 17·7%), *m/e* 237 (M^+), 222, 180, and 152; $\nu_{max.}$ 1590 (C=O) cm^{-1}; $\lambda_{max.}$ 249 (ε 34,700), 347 (7880), and 414 nm (6560); τ ($CDCl_3$) 0·86—1·00 (1H, m), 1·32—2·22 (7H, m), and 7·63 (3H, s); *picrate*, m.p. 176—178°, $\nu_{max.}$ 1715 cm^{-1} (C=O).

Benzo[c]*cinnoline* N-*diphenylacetylimide*. A mixture of benzocinnoline *N*-imide (100 mg) and an excess of diphenylketen in dry dichloromethane (15 ml) was set aside for 1·5 h. The resulting solid was filtered off and washed with ether to give the *diphenylacetylimide* (90%) as a yellow crystalline solid, m.p. 236—238° (Found: C, 79·7; H, 4·95; N, 10·5. $C_{26}H_{19}N_3O$ requires C, 80·2; H, 4·9; N, 10·8%); $\nu_{max.}$ 1620 (C=O) cm^{-1}.

Benzo[c]*cinnoline* N-(*phenylcarbamoyl*)*imide* (13). A small excess of phenyl isocyanate (119 mg) was added to benzocinnoline *N*-imide (100 mg) in dichloromethane (15 ml). The resulting red solid which crystallised was filtered off to give the *carbamoylimide* (85%), m.p. 189—190° (Found: C, 71·9; H, 4·5; N, 17·7. $C_{19}H_{14}N_4O$ requires C, 72·6; H, 4·5; N, 17·8%); $\nu_{max.}$ 3300 (NH) and 1645 (C=O) cm^{-1}.

Benzo[c]*cinnoline* N-(4-*nitrophenyl*)*imide*. Benzocinnoline *N*-imide (500 mg, 2·5 mmol) was stirred with sodium hydride (125 mg; 50% dispersion; 2·5 mmol) in dry dimethylformamide (15 ml) at 60° for 1 h. 4-Chloronitrobenzene (380 mg, 2·5 mmol) was then added and the mixture stirred at 40° for 3 h. The mixture was poured into water and extracted with dichloromethane, and the extracts were washed, dried, and evaporated. The residue was chromotographed on alumina. Elution with 50% ether–petroleum gave unchanged benzocinnoline *N*-imide (24%). 60% Ether–petroleum eluted the N-(4-*nitrophenyl*)*imide* (6%) as red needles, m.p. 238—238·5° (from ethanol) (Found: C, 68·4; H, 4·0; N, 17·5. $C_{18}H_{12}N_4O_2$ requires C, 68·4; H, 3·8; N, 17·7%), *m/e* 316 (M^+) 270, 180, and 152; $\nu_{max.}$ 1575, 1507, 1470, 1392, 1330, 1275, 1115, 858, 770, 760, and 721 cm^{-1}. Elution with ether gave benzocinnoline (68%).

Benzo[c]*cinnoline* N-(2,4-*dinitrophenyl*)*imide*.—Benzocinnoline *N*-imide (2 g, 10 mmol) and 1-fluoro-2,4-dinitrobenzene (1·9 g, 10 mmol) were heated under reflux in ethanol (60 ml) in the presence of sodium carbonate. After 3 h the mixture was filtered and the residue washed thoroughly with dichloromethane. The combined filtrate and washings were evaporated and the residue was crystallised from ethanol to give the N-(2,4-*dinitrophenyl*)*imide* (70%) as red plates, m.p. 232—233·5° (Found: C, 59·8; H, 3·2; N, 19·3. $C_{18}H_{11}N_5O_4$ requires C, 59·8; H, 3·1; N, 19·4%), *m/e* 361 (M^+), 315, 269, 180, and 152; $\nu_{max.}$ 1590, 1535, 1510, 1400, 1310, 1288, 1210, 1141, 842, 766, 750, 738, and 720 cm^{-1}. The 2,4-dinitrophenylimide was also obtained by using 1-chloro-2,4-dinitrobenzene.

Benzo[c]*cinnoline* N-*phenylimide*. (*a*) A solution of benzocinnoline *N*-ethoxycarbonylimide (500 mg) in aniline (5 ml) was maintained at 130° for 30 min. The aniline was removed by distillation under reduced pressure and the residue was chromatographed on alumina. Elution with 20% ether–petroleum gave the N-*phenylimide* (13%) as bright orange needles, m.p. 129—131° (from ether–petroleum) (Found: C, 79·3; H, 4·6; N, 15·6. $C_{18}H_{13}N_3$ requires C, 79·6; H, 4·8; N, 15·4%), *m/e* 271 (M^+), 241, 219, 180, and 152; $\nu_{max.}$ 1378, 1275, 778, 776, 728, and 695 cm^{-1}. Elution with ether gave benzocinnoline (60%).

(*b*) Sodium nitrite (175 mg, 2·5 mmol) was added to a solution of aniline (233 mg, 2·5 mmol) in N-hydrochloric acid (10 ml) at 0°. The resulting solution was added to a mixture of benzocinnoline *N*-imide (500 mg, 2·5 mmol) and copper bronze in N-hydrochloric acid and the mixture was stirred overnight. After basification the products were extracted with dichloromethane and separated by chromatography on alumina to give (eluant in parentheses phenyl azide (40%) (2% ether–petroleum), benzocinnoline *N*-phenylimide (15%) (10% ether–petroleum), benzocinnoline *N*-imide (10%) (20% ether–petroleum), and benzocinnoline (30%) (ether).

The same products were formed in the absence of copper, which was added to maximise the yield of the *N*-phenylimide.

Benzo[c]*cinnoline* N-*methylimide*. Sodium (300 mg) was added to liquid ammonia (200 ml) at −78° containing a trace of iron(III) nitrate. After disappearance of the blue colour, benzocinnoline *N*-imide (490 mg, 2·5 mmol) in dry dimethylformamide (5 ml) was added to give a deep red solution. After 10 min, dry methyl iodide (2 ml) was added, the mixture was extracted with ether, and the combined extracts were chromatographed on alumina. Elution with 10% ether–petroleum gave the *N*-methylimide (80%) as yellow needles, m.p. 92° (from petroleum) (lit.,[7] 88—89°) (Found: C, 74·4; H, 5·2; N, 19·9. Calc. for $C_{13}H_{11}N_3$: C, 74·6; H, 5·3; N, 20·1%), *m/e* 209 (M^+), 181, 167, 157, and 152; $\nu_{max.}$ 1612, 1591, 1475, 1379, 1330, 1268, 1142, 1120, 775, 762, 725, 686, and 660 cm^{-1}; $\lambda_{max.}$ 252 (ε 29,000), 294 (7180), 304 (7840), 317 (4900), and 376 nm (6700); τ 1·2—1·45 (1H, m), 1·7—3·1 (7H, m), and 6·4 (3H, s).

Benzocinnoline N-*ethylimide*. This was prepared exactly as for the *N*-methyl derivative, with ethyl iodide in place of methyl iodide. Elution with 15% ether–petroleum gave the N-*ethylimide* (87%) as yellow needles, m.p. 105—106° (from petroleum) (Found: C, 75·5; H, 6·1; N, 18·7. $C_{14}H_{13}N_3$ requires C, 75·3; H, 5·9; N, 18·8%), *m/e* 223 (M^+)

207, 180, and 152; $\nu_{max.}$ 1600, 1518, 1470, 1411, 1336, 776, 758, and 721 cm^{-1}; $\lambda_{max.}$ 255 (ε 33,000), 295sh (10,000), 305 (10,800), 319sh (7650), and 387 nm (10,800); τ 1·23—1·60 (1H, m), 1·8—3·2 (7H, m), 6·35 (2H, q, *J* 7 Hz), and 8·50 (3H, t, *J* 7 Hz).

NN'-*Bis*(*benzo*[c]*cinnolin-5-io*)-p-*methoxybenzylidene diaminide* (8). A small crystal of iodine was added to a mixture of benzocinnoline *N*-imide (500 mg) and anisaldehyde (500 mg) in ethanol (10 ml) which was maintained at 50° for 30 min. After cooling, the precipitate was filtered off and recrystallised from benzene to give the *diaminide* (8), m.p. 105—109° (Found: C, 75·5; H, 4·8; N, 16·7. $C_{32}H_{24}N_6O$ requires C, 75·6; H, 4·8; N, 16·5%), *m/e* 328 [*M* − 180 (benzocinnoline)] and 180; τ 0·1—1·1 (m), 1·6—3·2 (m), and 6·1 (s, OMe).

Pyrolyses.—(i) *Benzocinnoline* N-*imide*. (*a*) The *N*-imide (100 mg) was heated under reflux in *o*-dichlorobenzene (4 ml) for 1 h. After cooling, addition of pentane gave a precipitate of carbazole (74 mg, 80%).

(*b*) The *N*-imide (200 mg) was heated under reflux in bis-(2-methoxyethyl) ether (5 ml) for 3 h. The cooled solution was poured into water to give a precipitate of carbazole (95%). Similar pyrolysis in bis-(2-methoxyethyl) ether which showed a positive indication in a test for peroxides gave an oil when the solution was poured into water. Extraction with dichloromethane and chromatography of the extracts on alumina gave benzocinnoline (60%) and a trace of carbazole.

(*c*) Pyrolysis of the *N*-imide hydrochloride in peroxide-free bis(2-methoxyethyl) ether for 1 h gave carbazole (92%).

(ii) *Benzocinnoline* N-*ethoxycarbonylimide*. (*a*) The *N*-imide (500 mg) was heated under reflux in 1,2,4-trichlorobenzene (20 ml) for 2 h. Trichlorobenzene was then distilled off under reduced pressure and the residue was chromatographed on silica gel. Elution with 10% ether–petroleum gave a fraction containing carbazole and 9-ethoxycarbonylcarbazole [16] (i.r. spectral comparison with authentic samples). Elution with ether gave benzocinnoline (168 mg, 50%). The total carbazole–9-ethoxycarbonylcarbazole fraction was hydrolysed with aqueous ethanolic sodium hydroxide to give carbazole (106 mg, 34%). 9-Ethoxycarbonylcarbazole is reported to undergo thermal decomposition to carbazole at high temperature.[16]

(*b*) A solution of the *N*-imide in decalin was maintained at 165° for 2 h (at 125° decomposition was very slow). The solvent was removed by distillation under reduced pressure and the residue was chromatographed on silica gel. Elution with 15% ether–petroleum gave a mixture of 1-, 2-, and 5-(ethoxycarbonylamino)decalin as an oil (19%) (Found: C, 69·3; H, 10·3; N, 6·1. Calc. for $C_{13}H_{23}NO_2$: C, 69·3; H, 10·3; N, 6·2%), *m/e* 225 (M^+), 196, and 136; $\nu_{max.}$ 3360, 2980, 1721, 1712, 1695, 1545, 1457, 1238, 1110, 1058, 784, and 772 cm^{-1}; τ 2·35, 2·95, and 3·10 (broad singlets, total 1H), 6·05 (2H, q, *J* 7 Hz), and 7·9—9·5 (20H, m). Elution with ether gave benzocinnoline.

(*c*) The *N*-imide was recovered largely unchanged after refluxing in cyclohexane for 1 week.

(iii) *Benzocinnoline* N-*acetylimide*. Pyrolysis of the *N*-acetylimide in 1,2,4-trichlorobenzene as described for the ethoxycarbonyl derivative gave, after chromatography on silica gel, 9-acetylcarbazole (52%), m.p. and mixed m.p. 68°, and benzocinnoline (17%).

(iv) *Benzocinnoline* N-*benzoylimide*. Similar pyrolysis in 1,2,4-trichlorobenzene gave *N*-benzoylcarbazole (50%), m.p. and mixed m.p. 95—96°, and benzocinnoline (21%), separated by chromatography on silica gel.

(v) *Benzocinnoline* N-*methylimide*. Similar pyrolysis in 1,2,4-trichlorobenzene gave benzocinnoline (96%). No trace of *N*-methylcarbazole was detected by t.l.c.

(vi) *Benzocinnoline* N-(*2,4-dinitrophenyl*)*imide*. The 2,4-dinitrophenylimide was heated under reflux in bis-(2-methoxyethyl) ether for 20 h and the resulting solution was poured into water to give a brown precipitate. This was chromatographed on alumina to give benzocinnoline (5%) on elution with ether and an unidentified, highly fluorescent, yellow substance. No benzofurazan *N*-oxide was detected in this reaction by t.l.c.

(vii) NN'-*Bis*(*benzocinnolin-5-io*)-p-*methoxybenzylidene diaminide*. This was heated under reflux in oct-2-ene for 1·5 h. The solvent was removed by distillation under reduced pressure and the residue was chromatographed on alumina. Elution with 75% ether–petroleum gave 4-cyanoanisole (45%), m.p. 58° (lit.,[17] 59°), and ether eluted benzocinnoline (52%).

Photolyses.—Irradiations were carried out on solutions of the substrate (1—3 mmol) in acetonitrile (200 ml) (except where stated) with a Hanovia medium-pressure 125 W lamp fitted with a quartz filter. Products were separated by chromatography as described above. Photolyses were conducted either with or without added benzophenone (4 g) as sensitiser.

(i) Benzocinnoline *N*-imide gave (*a*) by direct photolysis (24 h) 2-aminobiphenyl (12%), m.p. and mixed m.p. 47—50°, carbazole (5%), and benzocinnoline (40%); (*b*) by sensitised photolysis (24 h) benzocinnoline (68%).

(ii) Benzocinnoline *N*-ethoxycarbonylimide gave (*a*) by sensitised photolysis in cyclohexane (24 h), after chromatography on silica gel, ethyl *N*-cyclohexylcarbamate (29%), m.p. and mixed m.p. 55—56° (lit.,[18] 56 °), and benzocinnoline (35%); (*b*) by direct photolysis in cyclohexane (24 h) a trace of ethyl *N*-cyclohexylcarbamate and benzocinnoline (10%).

(iii) Benzocinnoline *N*-benzoylimide gave by sensitised photolysis (1 week) benzocinnoline (38%).

Labelling Studies.—^{15}N-Labelled compounds were prepared and handled as described for the unlabelled analogues. ^{15}N Incorporation was determined by mass spectrometry and the results are described in the Discussion section. Pentyl [^{15}N]nitrite was obtained from commercially available labelled sodium nitrite by the method described by Vogel.[19]

We thank the S.R.C. for research studentships (to S. F. G. and M. E. P.) and Mr. J. J. Barr and Mr. S. Alsop for experimental assistance.

[4/1152 *Received*, 13*th June*, 1974]

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