Formation and Thermal Transformations of Extended Dipolar Imidoylazimines [1]

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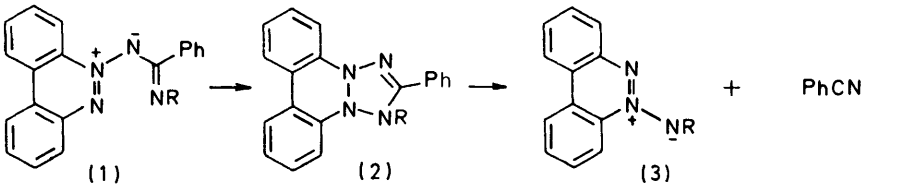
Benzocinnoline *N*-arylbenzimidoylimides (1; R = Ar) are readily obtained from benzocinnoline *N*-imide and imidoyl chlorides and on heating undergo 1,5-dipolar cyclisation and retro dipolar cycloaddition to give benzocinnoline *N*-arylimides. In contrast the *N*-alkyl analogues (1; R = Me, Et) are much less stable and undergo 1,6-H shift leading ultimately to 1-(2'-aminobiphenyl-2-yl)-3-phenyl-1,2,4-triazoles. Attempts to prepare the isopropylimide (1; R = Pr^i) lead to 4,4-dimethyl-2,6-diphenyldihydro-*s*-triazine. Benzocinnoline *N*-benzimidoylimide (1; R = H) is obtained from benzocinnoline *N*-imide and the methiodide salt of thiobenzamide and is converted into the 1,7-dipolar systems (1; R = COR', PhC=NPr^i, or PhC=NPh). On heating, the acyl derivatives give benzocinnoline and oxadiazoles, the isopropylimide gives benzocinnoline and 4-isopropylaminoquinazoline, and the *N*-phenylimide gives benzocinnoline and 1,3,5-triphenyl-1,2,4-triazole and, unexpectedly, diphenylquinazoline, possibly *via* a 1,3,5-benzotriazepine.

THE imidoylazimines (1) are of interest in connection with our studies of extended dipolar cycloadditions.[2] They are isoelectronic with the azomethine ylides (4) for which we have already observed [5 + 2] cycloaddition to acetylenes rather than the expected symmetry allowed [3 + 2] addition, and also with the acyl azimines (5) where only [3 + 2] addition occurs. Replacement of C-3 in the azomethine ylide system by N should therefore give further insight into the factors which control periselectivity in such dipolar systems. Also, knowing that the systems (4) and (5) exist in their open form, it seemed unlikely that cyclisation of the 1,5-dipoles (1) would be a complicating factor as the ring-closed form does not possess any aromatic stabilisation and the low bond energy associated with the three contiguous saturated N atoms would also disfavour the cyclic form (2).



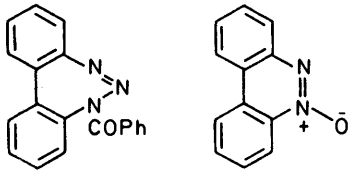
(1) (2) (3) (4) (5) (6) (7)

Benzocinnoline *N*-(arylbenzimidoyl)imides (1; R = Ph, *o*-tolyl, *p*-tolyl, or *p*-$NO_2C_6H_4$) were readily obtained as yellow to orange crystalline solids in good yield from benzocinnoline *N*-imide [3,4] (3; R = H) and the corresponding *N*-arylbenzimidoyl chloride in the presence of potassium carbonate. Acetonitrile proved the best solvent for this reaction.

Physical data strongly support the ylide structure (1) as opposed to the cyclic form (2). The aromatic hydrogens in the ^{1}H n.m.r. spectra show a near identical absorption pattern with those of benzocinnoline *N*-imide and benzocinnoline *N*-oxide. The u.v. spectra also show the characteristic benzocinnoline *N*-imide or *N*-oxide types of chromophore where the biphenyl rings are both planar and conjugated. There are two intense absorptions at about 250 (ε 39 000—52 000) and 400—420 (14 000—15 000) with less intense peaks at 295—298, 307—310, and 321—324 nm. This is to be compared with benzocinnoline *N*-imide which shows absorptions at 254 (ε 37 000), 297 (8 930), and 385 (9 120) nm. The mass spectra show small parent ions in all cases with a base peak at *m/e* 180. Cyclic dihydrobenzocinnoline derivatives in our experience always have a base peak at *m/e* 181 and this appears to be sufficiently consistent for diagnostic purposes. Chemical evidence for the proposed structures comes from catalytic hydrogenation of (1; R = Ph) which gives *N*-phenylbenzamidine and benzocinnoline by the type of reductive N–N bond cleavage observed with other benzocinnoline *N*-imides.[4b] An open structure has also been independently proved for benzocinnoline *N*-benzoylimide (1; R = H) [5] (see later).

Thermal decomposition of the *N*-arylimidoylazimines (1; R = Ar) contrasts with that of the isoelectronic benzocinnoline *N*-benzoylimide (5; R = Ph). Pyrolysis of

the latter in refluxing 1,2,4-trichlorobenzene gave benzocinnoline (6) and *N*-benzoylcarbazole (7).[4b] Benzocinnoline formation is probably associated with oxonitrene formation, although the latter was not intercepted. The expected ethoxycarbonylnitrene insertion products were, however, observed in the pyrolysis of the related ethoxycarbonyl derivative (5; R = OEt). Formation of *N*-benzoylcarbazole is thought to involve either decomposition of a small equilibrium proportion of *N*-benzoyldibenzotriazepine (8) or 1,3-benzoyl migration in the imide (5) and loss of nitrogen.

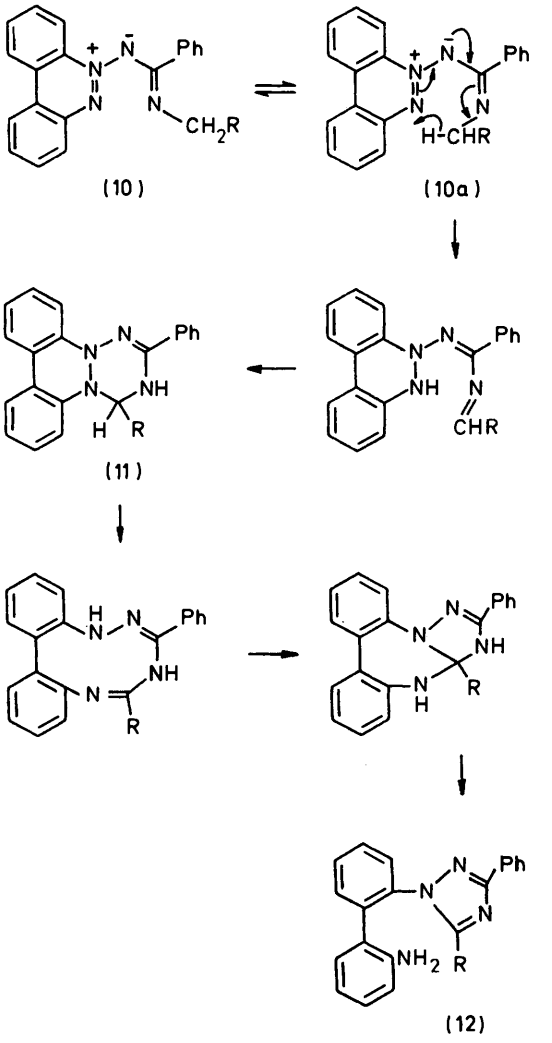


(8) (9) (13)

Pyrolysis of the arylimidoylazimines (1; R = Ph or *p*-$NO_2C_6H_4$), either in the melt or in 1,2,4-trichlorobenzene, led neither to benzocinnoline nor the carbazole derivative but to benzocinnoline *N*-arylimide (3; R = Ph or *p*-$NO_2C_6H_4$) and benzonitrile. These products can be rationalised by 1,5-dipolar cyclisation followed by retro 1,3-dipolar cycloaddition. A careful search in the benzocinnoline *N*-acylimide (5) pyrolysates revealed no benzocinnoline *N*-oxide (9) although this would have been stable under the reaction conditions. The origin of this difference is not clear but may be associated with the greater nucleophilicity of N than O which therefore favours cyclisation. In the case of the *o*-tolyl derivative (1; R = *o*-tolyl) the arylimide (3; R = *o*-tolyl) was isolated in lower yield and unchanged (1) was recovered. In addition some benzocinnoline was isolated from this pyrolysis. The greater resistance of (1; R = *o*-tolyl) to cyclisation and cycloreversion may be attributed to a steric effect of the *o*-methyl on the *N*-aryl group; this also allows N–N bond cleavage leading to benzocinnoline to compete more favourably.

The benzocinnoline *N*-arylimides show remarkable thermal stability as evidenced by their isolation from conditions which the *N*-acyl and ethoxycarbonyl derivatives would not withstand. The above sequence provides an attractive route to the *N*-arylimides (3; R = Ar). Benzocinnoline *N*-phenylimide (3; R = Ph) had previously been obtained in low yield from benzenediazonium chloride and benzocinnoline *N*-imide and the *p*-nitrophenylimide (3; R = *p*-$NO_2C_6H_4$) from 4-nitrochlorobenzene and benzocinnoline *N*-imide.[4b] The availability of both types of route to *N*-arylimides (3; R = Ar) therefore makes it possible to prepare either *N*-arylimide specifically from an unsymmetrically substituted benzocinnoline *N*-imide since the dipolar cyclisation–cycloreversion sequence involves a change in the point of attachment of the exocyclic nitrogen.

One final point which emerged from this study of benzocinnoline *N*-imide decompositions is the sensitivity of the mode of decomposition to the presence of peroxides. Pyrolysis of the imide (1; R = Ph) in unpurified dioxan gave benzocinnoline as the only isolable product. Similar observations were made in the decomposition of the acylimides (5) and unsubstituted imide (3; R = H): decomposition in diglyme [bis-(2-methoxyethyl) ether] which contained peroxides gave benzocinnoline. In pure diglyme (5) gave the expected mixture of acylcarbazole and benzocinnoline and (3; R = H) gave carbazole. Clearly a peroxide-induced mode of decomposition leading to benzocinnoline can intervene in these pyrolyses.



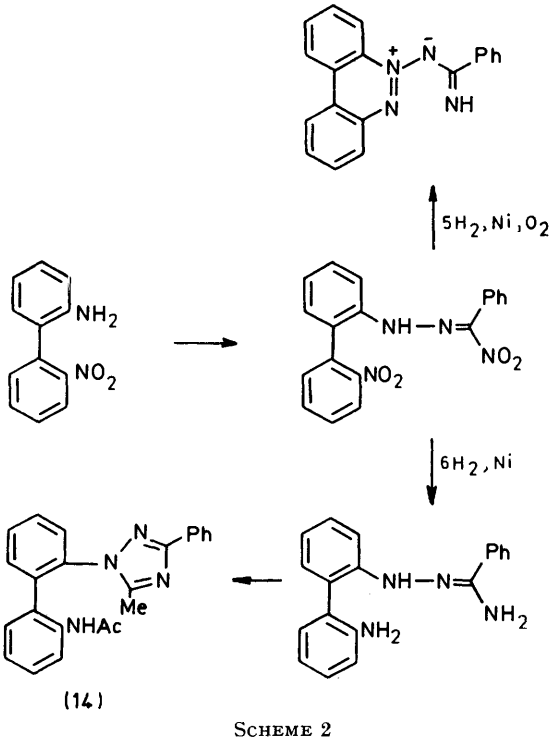
(10) (10a) (11) (12)

SCHEME 1

In contrast with the *N*-arylimidoylazimines, the *N*-alkyl derivatives (1; R = Me or Et) are unstable and only isolable with difficulty. The yellow *N*-(*N*-methylbenzimidoyl)imide (10; R = H) was obtained from benzocinnoline *N*-imide (3; R = H) and *N*-methylbenzimidoyl chloride in acetonitrile but was too unstable for complete characterisation. However the n.m.r. spectrum showed the characteristic benzocinnoline *N*-imide ^1H absorption pattern together with a singlet for the *N*-methyl group. The *N*-ethyl analogue (10; R =

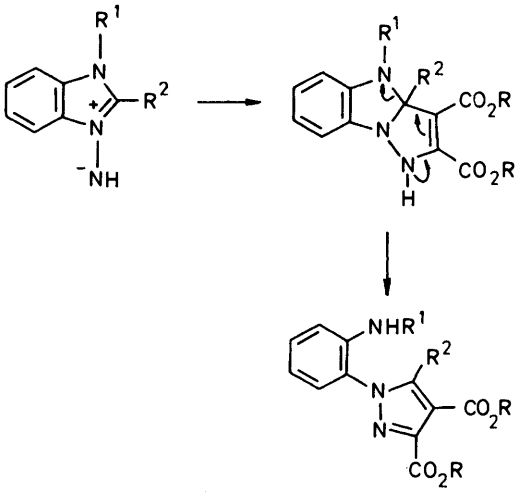
Me) could not be isolated from a similar procedure using *N*-ethylbenzimidoyl chloride but was eventually obtained by a modification in which benzocinnoline *N*-imide reacted with the methiodide salt of *N*-ethylthiobenzamide (13). Displacement of methanethiol gave the hydroiodide salt of the *N*-ethyl derivative (10; R = Me) as a stable red solid. Treatment of this salt with base at low temperature gave the orange, crystalline imide (10; R = Me) for which the ^{1}H n.m.r. spectrum was especially characteristic.

The instability of these alkylimides is associated with isomerisation to the aminobiphenyltriazoles (12; R = H or Me). This isomerisation occurs slowly at room temperature and rapidly and quantitatively at 80 °C in acetonitrile or on melting for the imide (10; R = H); for the imide (10; R = Me) rearrangement is equally ready (45%) but is accompanied by benzocinnoline formation (35%). The aminobiphenyltriazole structures are fully supported by spectral data. Thus (12; R = Me) shows a broad singlet at δ 3.8 (removed by D_2O) in its n.m.r. spectrum and this together with i.r. absorptions at 3 455, 3 330, and 3 218 cm^{-1} is indicative of an amino group. The signal for the methyl on the triazole ring appears at δ 2.1, and u.v. absorptions at 233 (ε 23 500) and 242 nm (21 356) are consistent with a non-planar biphenyl system. Finally (12; R = Me), on treatment with acetic anhydride, gave an acetyl derivative whose physical characteristics were identical with those reported for the acetamidobiphenylyltriazole (14) previously obtained by the sequence shown in Scheme 2.[5] Spectral characteris-



SCHEME 2

tics for the triazole (12; R = H) are very similar, the ^{1}H obscured by those of the aromatic biphenyl protons, as expected.



SCHEME 3

This unexpected rearrangement can be rationalised as shown in Scheme 1. The first step involves a 1,6-sigmatropic H shift through the 1,5-dipolar π-system analogous to the antarafacial 1,7-shift which occurs in the precalciferol–calciferol interconversion [6] and in related systems. This would require the imides (10) to exist in or be easily converted into the *cisoid* configuration (10a). A reasonable pathway allowing interconversion (10) ⇌ (10a) proceeds *via* disrotatory 6π-electrocyclic ring closure to give (2; R = alkyl) followed by rapid inversion at the saturated alkyl substituted N and disrotatory electrocyclic ring opening. That the overall isomerisation is not catalysed by added base (triethylamine, diazabicyclononene) or influenced by change of solvent is consistent withthe rate-determining step being a concerted intramolecular sigmatropic shift.

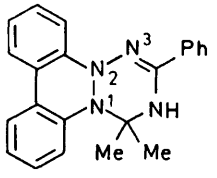
Subsequent steps in the scheme involve, very reasonably, intramolecular nucleophilic addition to an imine, cleavage of a weak N–N single bond, further intramolecular nucleophilic addition and a final aromatisation. This last step is closely related to the rearrangement described by Tamura and his co-workers [7] in the addition of acetylenic esters to benzimidazole *N*-imides (Scheme 3).

Although sigmatropic H-shifts are well documented for polyenes they are much less well known in the isoelectronic dipolar systems. A few examples of 1,4-shifts in 1,3-dipoles (*cf.* 1,5-shifts in dienes) have been reported [8] and in one case H migration has been shown to be intramolecular.[8a] Observation of this 1,6-H shift in a 1,5-dipole supports the contention that sigmatropic shifts in dipolar systems are likely to be very general. In fact a 1,6-shift in a vinylogous azomethine imine accounts for the anomalous cycloadducts from benzocinnoline *N*-alkylimides and acetylenic esters, a reaction in which the overal transformations are very closely related to those described in this paper.[9]

The formation of benzocinnoline in the pyrolysis of the

be explained by an alternative mode of breakdown of the intermediate (11; R = Me) by a $[_{\pi}2_s + _{\pi}2_s + _{\pi}2_s]$ cycloreversion which should also produce benzonitrile and ethylideneamine. However benzonitrile was not observed and attempts to detect ethylideneamine in the pyrolysis by flushing the reaction mixture with nitrogen and passage of the effluent gases through 2,4-dinitrophenylhydrazine solution were unsuccessful.

In the hope of gaining further insight into this reaction, attempts were made to prepare the isopropylimide (1; R = Pr^i) for which 1,6-H shift and cyclisation to (15) is possible but subsequent transformation to triazole is precluded. Attempted preparation using the methiodide



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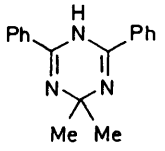

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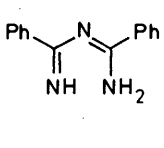
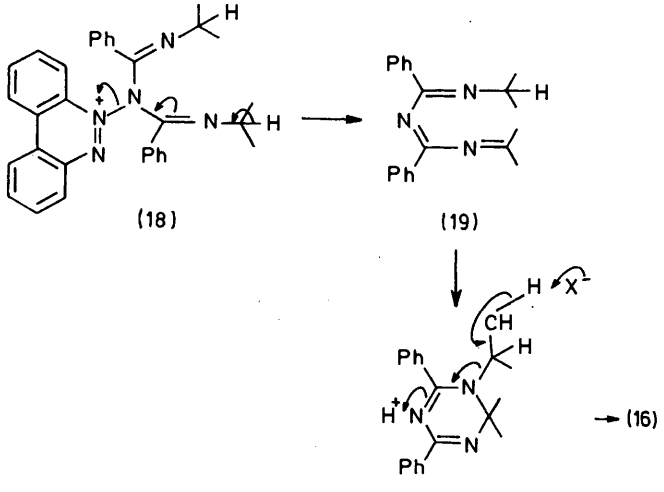


(17)

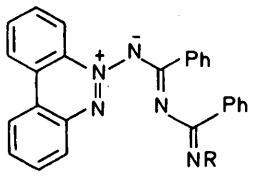
salt of *N*-isopropylthiobenzamide failed but t.l.c. of the reaction mixture from *N*-isopropylbenzimidoyl chloride and benzocinnoline *N*-imide showed the presence of an unstable polar yellow compound with similar R_F to those of the other *N*-alkylimidoylazimines. Attempted isolation of this ylide was unsuccessful and so the reaction mixture was heated. This gave, in addition to unchanged benzocinnoline *N*-imide, benzocinnoline, and 2,6-diphenyl-4,4-dimethyl-1,4-dihydro-*s*-triazine (16). The latter was identified by independent synthesis from the triazapentadiene (17) and acetone. A possible mode of formation involves reaction of the isopropylimidoylazimine with a further mole of the imidoyl chloride to give (18) which undergoes elimination leading to benzocinnoline and the triaza-triene (19). Cyclisation and *N*-dealkylation of this last species would give the *s*-triazine. An alternative route to the triazatriene could



(18) (19) (16)

involve reaction of the cyclic intermediate (15) at N-3 with the imidoyl chloride followed by a retro Diels–Alder reaction. In view of the complexity of this system further speculation is not justified and the origin of the benzocinnoline in the decomposition of (10; R = Me) remains unclear.

1,7-Dipolar Imidoylazimines.—The ylides (10; R = Pr^i or Ph) and (21; R = Me or Ph) were prepared from the corresponding imidoyl chloride or acid chloride and benzocinnoline *N*-benzimidoylimide. The latter had



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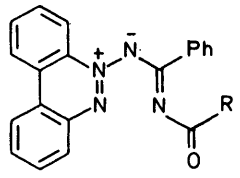
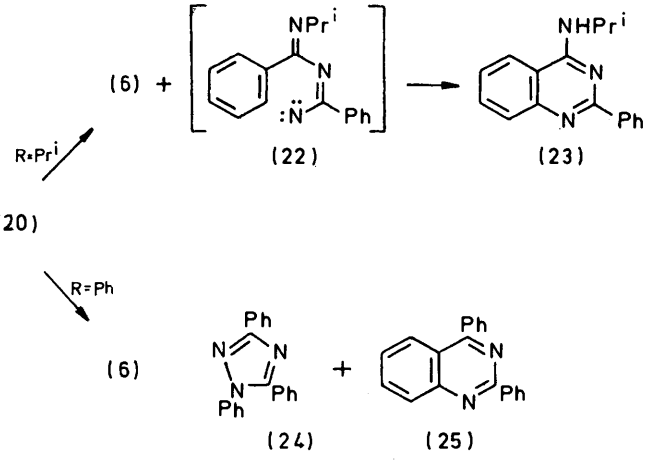


(21)

previously been prepared by Neugebaur and Fischer [5] as shown in Scheme 2. A much simpler procedure involves the reaction of the methiodide salt of thiobenzamide with benzocinnoline *N*-imide (3; R = H) followed by liberation of the free imide with base. The ylide (20) and (21) were red–black solids having the expected physical characteristics. In particular the u.v. spectra were similar to those of the *N*-arylimidoylazimines (1; R = Ar).

The *N*-isopropylimide (20; R = Pr^i) was initially prepared in the hope that 1,5-cyclisation and elimination of benzonitrile would lead to the isopropyl ylide (1; R = Pr^i). However, on pyrolysis at its m.p., this imide gave benzocinnoline and 2-phenyl-4-isopropylaminoquinazoline (23). The latter was synthesised independently from 2-chloro-4-phenylquinazoline and isopropylamine. In this case N–N cleavage leads to benzocinnoline and the nitrene (22), which undergoes intramolecular insertion

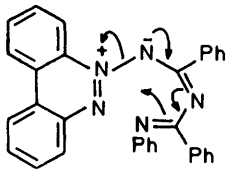


(20) (6) (22) (23) (6) (24) (25)

into the *C*-aryl ring followed by aromatisation. No products indicative of a 1,8-H shift in the 1,7-dipole were apparent; presumably steric and conformational factors militate against such a process.

Thermal decomposition of the imide (21; R = Ph) surprisingly does not follow this pathway but proceeds by two other modes to give benzocinnoline together with triphenyl-1,2,4-triazole (24) and diphenylquinazoline (25). The triazole is probably formed by intramolecular

displacement of benzocinnoline as shown (26) and indeed this is the only mode of decomposition observed with the acyl ylides (21; R = Me, Ph) which give only benzocinnoline and the oxadiazole (27). Diphenylquinazoline



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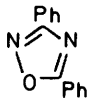
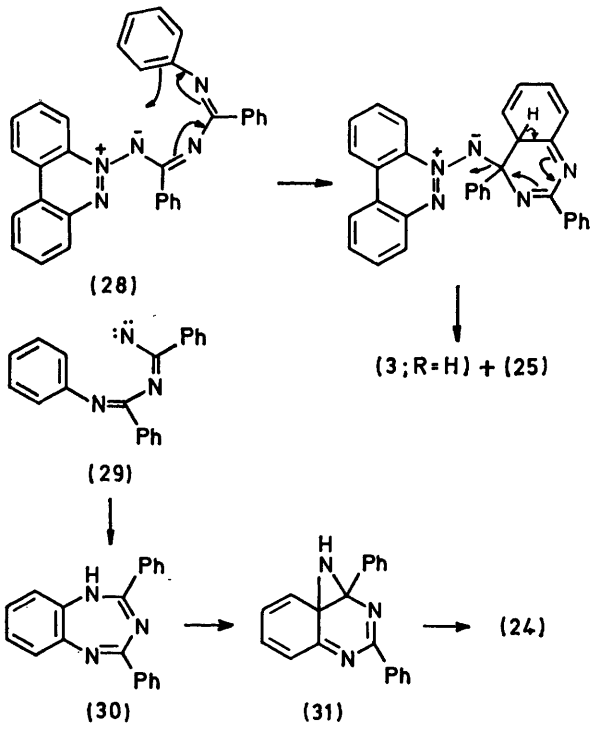


(27)

is a much more interesting product. One possible mechanism for its formation involves electrocyclic ring closure (28) followed by loss of benzocinnoline *N*-imide but we consider this unlikely, as under the pyrolysis conditions the latter is known to give carbazole rather than benzocinnoline. An alternative possibility is formation of the nitrene (29) and insertion into the *N*-phenyl ring to give the 1,3,5-benzotriazepine (30). Under the conditions of the pyrolysis this could undergo electrocyclic ring closure to the aziridine (31) and extrusion of NH.



(28) (3; R=H) + (25) (29) (30) (31) (24)

The differing modes of reaction of the related ylides (20) are puzzling. Factors which almost certainly play a vital role but which are difficult to assess are the conformational and configurational differences between the ylides.

EXPERIMENTAL

Benzo[c]*cinnoline* N-(N-*Arylbenzimidoyl*)*imides* (1; R = Ar): *General Procedure.*—The *N*-arylbenzimidoyl chloride[10] (1.2 mmol) in a small volume of dry acetonitrile was added to a stirred suspension of benzocinnoline *N*-imide[4b] (1 mmol) and a small excess of anhydrous potassium carbonate in the minimum volume of acetonitrile. The mixture was stirred vigorously for 3 h and the resulting deep red solution was filtered. Evaporation of the filtrate and addition of ethanol to the residue gave the *N*-arylimidoylazimines as red-orange solids.

N-Phenylbenzimidoyl chloride gave *benzo*[c]*cinnoline* N-(N-*phenylbenzimidoyl*)*imide* (1; R = Ph) (72%) as deep red prisms, m.p. 221—222 °C (from benzene) (Found: C, 80.7; H, 4.8; N, 14.7. $C_{25}H_{18}N_4$ requires C, 80.2; H, 4.8; N, 15.0%), $\nu_{max.}$ 1 615, 1 594, 1 580, 1 472, 1 450, 1 399, 1 288, 1 272, 1 216, 770, 755, 722, 714, 703, and 696 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 250 (ε 52 320), 295 (13 540), 307 (12 500), 321 (10 420), and 404 nm (14 060), *m/e* 374 and 180.

N-(*p*-Nitrophenyl)benzimidoyl chloride gave *benzo*[c]*cinnoline* N-[N-(p-*nitrophenyl*)*benzimidoyl*]*imide* (1; R = *p*-$NO_2C_6H_4$) (55%) as deep red needles, m.p. 221—222 °C (from benzene–petroleum) (Found: C, 71.7; H, 4.2; N, 16.9. $C_{25}H_{17}N_5O_2$ requires C, 71.6; H, 4.1; N, 16.7%), $\nu_{max.}$ 1 598, 1 585, 1 570, 1 499, 1 464, 1 379, 1 341, 1 304, 1 259, 1 241, 1 221, 1 213, 1 110, 763, 758, 723, 713, and 709 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 249 (ε 39 240), 298 (15 190), 310 (17 720), 324 (19 000), and 420 nm (15 190), *m/e* 419 and 180.

N-(*o*-Tolyl)benzimidoyl chloride gave *benzo*[c]*cinnoline* N-[N-(o-*tolyl*)*benzimidoyl*]*imide* (1; R = *o*-MeC_6H_4) (70%) as orange needles, m.p. 159—160 °C (from benzene–petroleum) (Found: C, 80.0; H, 5.1; N, 14.5. $C_{26}H_{20}N_4$ requires C, 80.4; H, 5.1; N, 14.4%), $\nu_{max.}$ 1 632, 1 604, 1 598, 1 469, 1 388, 1 330, 1 267, 1 261, 1 221, 776, 754, 730, 719, and 707 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 250 (ε 47 200), 295 (12 900), 307 (11 300), 322 (9 200), and 400 nm 12 900), *m/e* 388 and 180.

N-(*p*-Tolyl)benzimidoyl chloride gave *benzo*[c]*cinnoline* N-[N-(p-*tolyl*)*benzimidoyl*]*imide* (1; R = *p*-MeC_6H_4) (62%) as deep red prisms, m.p. 194—195 °C (from benzene) (Found: C, 80.0; H, 5.4; N, 14.7%), $\nu_{max.}$ 1 612, 1 595, 1 510, 1 471, 1 399, 1 338, 1 275, 761, 729, 713, and 701 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 251 (ε 46 000), 297 (7 000), 310 (6 000), 322 (4 000), and 400 nm (14 000), *m/e* 388 and 180.

Hydrogenation of Benzo[c]*cinnoline* N-(N-*Phenylbenzimidoyl*)*imide* (1; R = Ph).—The imidoylazimine (400 mg) in tetrahydrofuran (20 ml) was stirred under hydrogen in the presence of 10% palladium–charcoal (40 mg). Hydrogen uptake ceased after 15 min and the mixture was filtered and concentrated. The residue was chromatographed on neutral alumina. Elution with 80% v/v ether–petroleum gave benzo[*c*]cinnoline (160 mg, 83%), m.p. and mixed m.p. 154—156 °C (lit.,[11] 156 °C). Elution with ethanol gave *N*-phenylbenzamidine (159 mg, 76%), m.p. and mixed m.p. 114—115 °C (lit.,[12] 111—112 °C).

Pyrolysis of Benzo[c]*cinnoline* N-(N-*Arylbenzimidoyl*)*imides* (1; R = Ar).—The imidoylazimines were pyrolysed at their m.p. for 30 min and the residues were chromatographed on alumina (eluant in parentheses).

Benzo[*c*]cinnoline *N*-(*N*-phenylbenzimidoyl)imide (1; R = Ph) gave benzo[*c*]cinnoline *N*-phenylimide (84%), m.p. and mixed m.p. 128—129 °C (lit.,[4b] 129—131 °C) (10% v/v ether–petroleum), and benzonitrile (60%) (10% v/v ether–petroleum).

Benzo[*c*]cinnoline *N*-[*N*-(*p*-nitrophenyl)benzimidoyl]-imide (1; R = *p*-$NO_2C_6H_4$) gave benzonitrile (54%) 10% v/v ether–petroleum) and benzo[*c*]cinnoline *N*-(*p*-nitrophenyl)-imide (72%), m.p. and mixed m.p. 237—238 °C (lit.,[4b] 238 °C) (50% v/v ether–petroleum).

Benzo[*c*]cinnoline *N*-[*N'*-(*o*-tolyl)benzimidoyl]imide (1; R = *o*-$CH_3C_6H_4$) gave (10% vv/ ether–petroleum) *benzo*[c]-*cinnoline* N-(*o-tolyl*)*imide* (33%) as red needles, m.p. 110—112

°C from petroleum (Found: C, 80.0; H, 5.3; N, 15.0. $C_{19}H_{15}N_3$ requires C, 80.0; H, 5.3; N, 14.7%), $\nu_{max.}$ 1 470, 1 439, 1 408, 1 383, 1 274, 764, 751, and 713 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 253 (ε 36 890), 305 (10 110), 319 (8 590), and 420 nm (14 150), *m/e* 285, 270, 219, 181, 180, and 152, together with (50% v/v ether–petroleum unchanged (1; R = *o*-MeC_6H_4) (29%) and (80% v/v ether–petroleum) benzocinnoline (14%), m.p. and mixed m.p. 155—156 °C.

Pyrolysis of the imidoylazimine (1; R = Ph) (150 mg) by heating under reflux in unpurified dioxan (5 ml) for 5 h, followed by removal of solvent and preparative t.l.c. of the residue on Kieselgel PF 254 with 50% ether–petroleum as eluant, gave benzocinnoline (60 mg, 85%) as the only identified product. A similar procedure using 1,2,4-trichlorobenzene gave benzocinnoline *N*-phenylimide and benzonitrile.

Benzo[c]*cinnoline* N-(N-*Methylbenzimidoyl*)*imide* (10; R = H).—*N*-Methylbenzimidoyl chloride [10] (500 mg, 3.3 mmol) was added slowly to a rapidly stirred suspension of benzocinnoline *N*-imide (400 mg, 2 mmol) and an excess of potassium carbonate in dry acetonitrile (5 ml). After 30 min, more imidoyl chloride (100 mg, 0.7 mmol) was added to consume any remaining benzocinnoline *N*-imide (t.l.c.). The mixture was poured into water (30 ml) and the resulting red-brown precipitate was collected and washed with cold ethanol to give *benzo*[c]*cinnoline* N-(N-*methylbenzimidoyl*)*imide* (470 mg, 72%), m.p. 113—114 °C (decomp.), $\nu_{max.}$ 1 610 (C=N), δ ($CDCl_3$) 9.0—7.2 (m, 13 H) and 3.3 (s, 3 H). The fine structure of the aromatic ^1H n.m.r. spectrum was very similar to that observed for the arylimidoylazimines (1; R = Ar). No other data are reported because of the instability of this compound.

Benzo[c]*cinnoline* N-(N-*Ethylbenzimidoyl*)*imide* (10; R = Me).—The methiodide salt of *N*-ethylthiobenzamide [13] (1.7 g, 5.5 mmol) was added to a stirred solution of benzocinnoline *N*-imide (1.0 g, 5.1 mmol) in dry acetonitrile (15 ml) and the mixture was heated under reflux for 2 h. The resulting brown precipitate was filtered off and recrystallised from ethanol to give the *hydroiodide* of *benzo*[c]*cinnoline* N-(N-*ethylbenzimidoyl*)*imide* (1.1 g, 47%) as red-brown prisms m.p. 202—204 °C (Found: C, 55.3; H, 4.2; N, 12.4. $C_{21}H_{19}N_4$ requires C, 55.5; H, 4.2; N, 12.4%). A suspension of this hydroiodide salt and potassium carbonate in ethanol was stirred for 20 min. The resulting deep red solution was filtered and gradual addition of distilled water to the filtrate gave *benzo*[c]*cinnoline* N-(N-*ethylbenzimidoyl*)-*imide* (76%) as orange needles, m.p. 96—98 °C (decomp.) (Found: C, 76.5; H, 5.6; N, 17.7. $C_{21}H_{18}N_4$ requires C, 76.4; H, 5.7; N, 17.8%), $\nu_{max.}$ 1 625, 1 592, 1 470, 1 442, 1 421, 1 398, 1 331, 1 291, 1 269, 1 055, 772, 760, 724, 715, 703 cm^{-1}, δ ($CDCl_3$) 9.05 (m), 8.5—6.6 (m), 4.7 (q), and 1.43 (t).

Pyrolysis of *Benzo*[c]*cinnoline* N-(N-*Alkylbenzimidoyl*)-*imides*.—(a) *Benzo*[c]*cinnoline* N-(N-*methylbenzimidoyl*)-*imide*. The imide (300 mg) was heated under reflux in acetonitrile (10 ml) for 3 h. The solution was evaporated to give an oil which solidified on scratching. Recrystallisation from ether–petroleum gave 1-(2′-*aminobiphenyl*-2-*yl*)-3-*phenyl*-1,2,4-*triazole* (12; R = H) (280 mg, 93%) as prisms, m.p. 139—140 °C (Found: C, 76.9; H, 5.2; N, 18.0. $C_{20}H_{16}N_4$ requires C, 76.9; H, 5.2; N, 17.9%), $\nu_{max.}$ 3 478, 3 360, 1 633, 1 501, 1 460, 1 385, 1 339, 1 312, 1 288, 1 247, 762, 730, and 699 cm^{-1}, $\lambda_{max.}$ 233 (ε 24 120) and 255 nm (24 120), δ ($CDCl_3$) 8.2—6.5 (m, 14 H) and 3.3br (s, 2 H, removed by D_2O), *m/e* 312, 296, 181, 167, and 152. Pyrolysis of the imide at its m.p. for 5 min also gave the triazole (92%).

(b) *Benzo*[c]*cinnoline* N-(N-*ethylbenzimidoyl*)*imide*. (i) This ylide (280 mg) was heated under reflux in acetonitrile (10 ml) for 3 h. Evaporation gave a residue which was chromatographed on neutral alumina. Elution with 80% v/v ether–petroleum gave 1-(2′-*aminobiphenyl*-2-*yl*)-5-*methyl*-3-*phenyl*-1,2,4-*triazole* (12; R = Me) (146 mg, 52%) as prisms, m.p. 144—145 °C from ether–petroleum (Found: C, 77.2; H, 5.5; N, 17.3. $C_{21}H_{18}N_4$ requires C, 77.3; H, 5.5; N, 17.2%), $\nu_{max.}$ 3 455, 3 330, 3 218, 1 631, 1 518, 1 507, 1 487, 1 465, 1 449, 1 379, 1 354, 1 310, 1 122, 759, 726, and 692 cm^{-1}, $\lambda_{max.}$ (CH_2Cl_2) 233 (ε 23 535), 242 (21 356), and 303 nm (3 051), δ ($CDCl_3$) 7.2—6.5 (m, 13 H), 5.8br (s, 2 H, removed by D_2O), and 2.2 (s, 3 H), *m/e* 326, 310, 197, 181, 180, 167, and 152. Elution with ether gave benzocinnoline (45 mg, 29%).

(ii) *N*-Ethylbenzimidoyl chloride [10] (420 mg, 2.5 mmol), benzocinnoline *N*-imide (500 mg, 2.5 mmol), and excess anhydrous potassium carbonate were stirred at room temperature in dry acetonitrile (17 ml) for 1 h. The mixture was then heated under reflux for 1 h. Filtration and evaporation followed by preparative t.l.c. gave 1-(2′-aminobiphenyl-2-yl)-5-methyl-3-phenyl-1,2,4-triazole (270 mg, 32%) and benzocinnoline (117 mg, 23%).

1-(2′-*Acetamidobiphenyl*-2-*yl*)-5-*methyl*-3-*phenyl*-1,2,4-*triazole*.—A mixture of the triazole (12; R = Me) (100 mg, 0.3 mmol) and acetic anhydride (35 mg, 0.3 mmol) in dry pyridine (2 ml) was kept at room temperature for 1 h, then poured into water and extracted with dichloromethane. Preparative t.l.c. of the crude extract gave a solid which after crystallisation from ether–petroleum gave the amide (14) (82 mg, 73%) as prisms, m.p. 141—142 °C (lit.,[5] 141—142 °C) (Found: C, 75.0; H, 5.5; N, 15.3. Calc. for $C_{23}H_{20}N_4O$: C, 75.0; H, 5.5; N, 15.2%).

Attempted Preparation and in situ *Pyrolysis of the* N-(N-*Isopropylbenzimidoyl*)*imide* (1; R = Pr^i).—Benzocinnoline *N*-imide was treated with *N*-isopropylbenzimidoyl chloride [10] as described above for *N*-methylbenzimidoyl chloride. After 1 h at room temperature, t.l.c. indicated the presence of one polar yellow product but chromatography on alumina yielded benzocinnoline (58%) as the only identified product. The mixture was therefore heated under reflux for 2 h and filtered, the filtrate was evaporated and the residue was chromatographed on neutral alumina. Elution with 20% v/v ether–petroleum gave benzocinnoline *N*-imide (10%), 80% v/v ether–petroleum gave benzocinnoline (61%), and ether gave 2,6-diphenyl-4,4-dimethyl-1,4-dihydro-*s*-triazine (16) (13%) as needles, m.p. 169—170 °C (lit.,[14] 169—170 °C) (from benzene–petroleum) (Found: C, 77.5; H, 6.7; N, 15.8. Calc. for $C_{17}H_{17}N_3$: C, 77.5; H, 6.5; N, 16.0%), identical with a sample obtained by the following procedure. 2,4-Diphenyl-1,3,5-triazapenta-1,3-diene hydrochloride [15] (300 mg) was stirred with a suspension of sodium hydrogen carbonate in ether (20 ml). After filtration and evaporation the residual oil was heated under reflux for 3 h in acetone (3 ml) containing a catalytic amount of toluene-*p*-sulphonic acid. Removal of the solvent and preparative t.l.c. of the residue gave the dihydro-*s*-triazine (16) (90 mg, 30%) as crystals, m.p. and mixed m.p. 168—170 °C.

Benzo[c]*cinnoline* N-*Benzimidoylimide* (1; R = H).—A suspension of the methiodide salt of thiobenzamide [13] (1.4 g, 5.2 mmol) and benzocinnoline *N*-imide (1.0 g, 5.1 mmol) in dry acetonitrile (20 ml) was heated under reflux for 2 h. The resulting deep purple precipitate was filtered off and

stirred with ethanolic potassium hydroxide for 15 min. After filtration, water was added to the filtrate to give an orange precipitate which was recrystallised from benzene–petroleum to give benzo[*c*]cinnoline *N*-benzimidoylimide (1; R = H) (1.2 g, 75%), m.p. 127—128 °C (lit.,[5] 127—128 °C).

Benzo[c]*cinnoline* N-(N-*Benzimidoylbenzimidoyl*)*imides* (20).—The imides (20; R = Ph or Pr^i) were prepared from the appropriate imidoyl chloride and benzo[*c*]cinnoline *N*-benzimidoylimide by the procedure used for the preparation of the *N*-arylimidoyl imides from benzo[*c*]cinnoline *N*-imide. (*a*) *N*-Phenylbenzimidoyl chloride gave *benzo*[c]*cinnoline* N-[N-(N-*phenylbenzimidoyl*)*benzimidoyl*]*imide* (20; R = Ph) (30%) as deep red needles, m.p. 182—184 °C (from ethyl acetate–methanol) after column chromatography on neutral alumina (Found: C, 80.5; H, 4.8; N, 14.7. $C_{32}H_{23}N_5$ requires C, 80.5; H, 4.8; N, 14.7%), $\nu_{max.}$ 1 591, 1 556, 1 544, 1 469, 1 451, 1 380, 1 342, 1 313, 1 304, 1 285, 1 235, 1 211, 1 165, 1 141, 1 018, 774, 763, and 701 cm^{-1}, $\lambda_{max.}$ 247 (ε 56 190), 297 (11 650), 310 (10 965), 324, (8 220), and 431 nm (13 020), *m/e* 477, 297, 194, 180, and 152.

(*b*) *N*-Isopropylbenzimidoyl chloride gave, after trituration with ethyl acetate of the residue from the crude reaction mixture, *benzo*[c]*cinnoline* N-[N-(N-*isopropylbenzimidoyl*)*benzimidoyl*]*imide* [20; R = Pr^i] (61%) as deep red prisms, m.p. 232—234 °C, from ethyl acetate–methanol, *m/e* 443 (M^+) 264, 263, 248, 221, 205, 180, and 152, $\nu_{max.}$ 1 592, 1 556, 1 541, 1 491, 1 469, 1 446, 1 407, 1 212, 1 140, and 699 cm^{-1}, $\lambda_{max.}$ 253 (ε 87 590) and 354 nm (19 633), δ ($CDCl_3$) 9.1—6.7 (m, 18 H), 5.25 (q, 1 H), and 1.4 (d, 6 H).

Pyrolysis of Imides (20).—The ylides were maintained at their m.p. for 15 min and the pyrolysates were purified by chromatography on alumina. (*a*) The imide (20; R = Ph) gave 1,3,5-triphenyl-1,2,4-triazole (51%), m.p. and mixed m.p. 104—105 °C (lit.,[16] 104—105 °C), 2,4-diphenylquinazoline (49%), m.p. and mixed m.p. 117—119 °C (lit.,[17] 119—120 °C), and benzocinnoline (59%). (*b*) The imide [20; Pr^i] gave benzocinnoline (76%), and 2-*phenyl*-4-*isopropylaminoquinazoline* (23) (27%) as crystals, m.p. 149—151 °C (from benzene–hexane) (Found: C, 77.7; H, 6.6; N, 16.1. $C_{17}H_{17}N_3$ requires C, 77.6; H, 6.6; N. 16.0%). This was identical with a sample prepared by heating under reflux for 2 h a solution of 2-phenyl-4-chloroquinazoline (1 g) and and isopropylamine (1 g) in acetone. Evaporation of the solvent gave a solid residue of 2-phenyl-4-isopropylaminoquinazoline (92%), m.p. and mixed m.p. 149—151 °C.

Pyrolysis of Benzo[c]*cinnoline* N-(N-*Acylbenzimidoyl*)*imides* (21; R = Me or Ph).—(*a*) The imide (21; R = Me) [5] (500 mg) was maintained at 195 °C for 10 min. The pyrolysate was extracted with chloroform and purified by preparative t.l.c. on silica to give 5-methyl-3-phenyl-1,2,4-oxadiazole (58 mg, 25%), m.p. and mixed m.p. 38—39 °C (lit.,[18] 38—40 °C), and benzocinnoline (210 mg, 80%).

(*b*) The imide (21; R = Ph), m.p. 220—222 °C (from toluene) (230 mg) was maintained at 250 °C for 4 min. Work up as above gave 3,5-diphenyl-1,2,4-oxadiazole (80 mg, 65%), m.p. and mixed m.p. 100—102 °C, and benzocinnoline (70 mg, 70%). T.l.c. of the pyrolysate revealed the presence of a small amount of material having the same R_F as 2-phenyl-4-hydroxyquinazoline.[19]

We thank the S.R.C. for a studentship (to J. J. B.).

[7/2266 *Received*, 28*th December*, 1977]

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