Cycloadditions of Extended Dipoles: Reaction of Imidoylazimines with Ketens [1]

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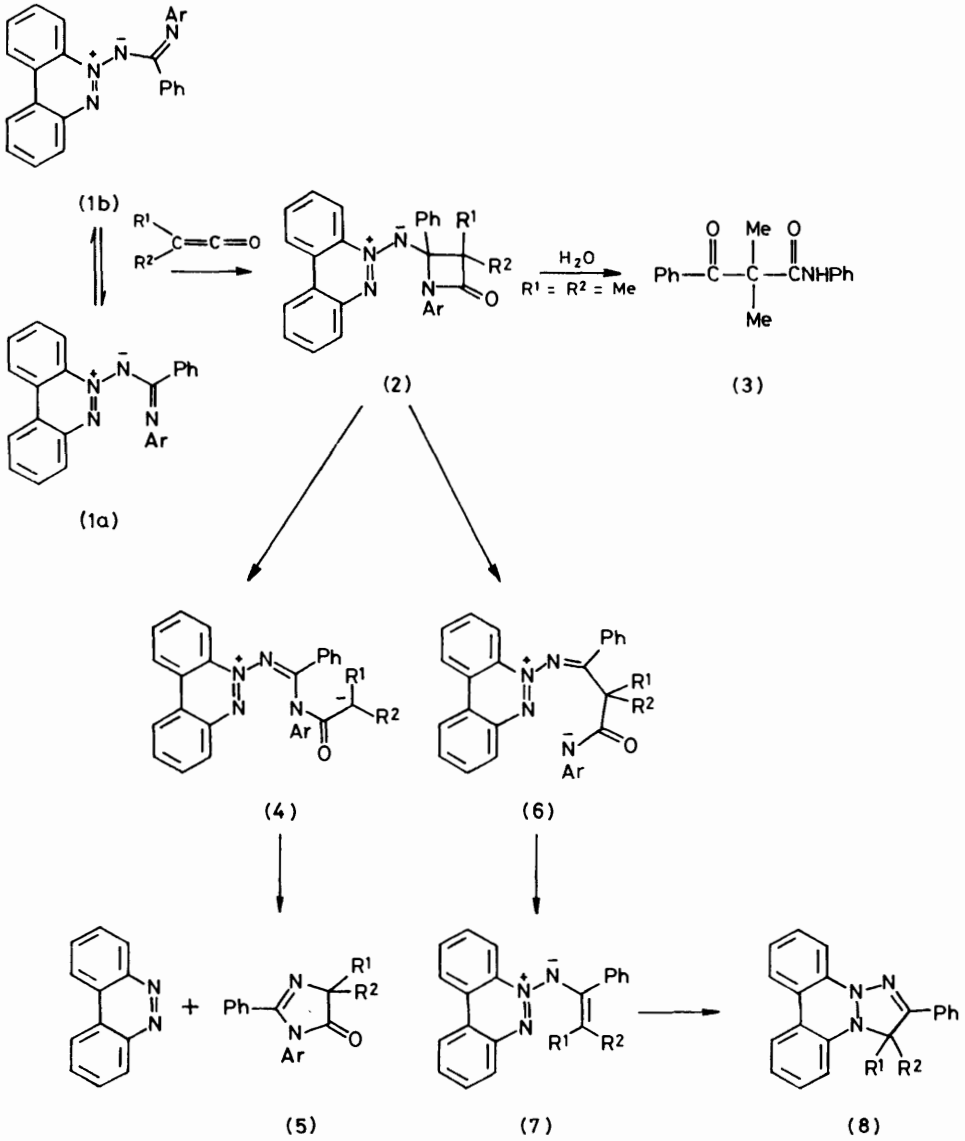
Diphenyl-, phenylmethyl-, and dimethyl-keten undergo 2 + 2 cycloaddition to the C=N bond of benzo[*c*]cinnoline *N*-(*N*-arylbenzimidoyl)imides (1) to give β-lactams (2). On heating, these β-lactams give either benzocinnoline and 1,2,4,4-tetrasubstituted imidazolin-5-ones (5) or triazolobenzocinnolines (8) depending on whether the substituents on the keten or imide stabilise heterolytic C–C or C–N bond cleavage of the β-lactam ring. *p*-Toluonitrile oxide also undergoes addition to the C=N bond of (1) although the initial adduct is not isolable owing to its ready hydrolysis. No products resulting from other modes of cycloaddition to the extended dipoles (1) are observed with dimethyl acetylenedicarboxylate or reactive dienes.

THE imidoylazimines (1) [2] are of interest in cycloaddition since they incorporate 1,3-dipolar, 1,5-dipolar, and dipolarophiles,[4] and also to take part in 2 + 2 cycloadditions to imines.[3,5] This wide ranging reactivity



electron-rich imine character. Ketens are known to function as 1,3-dipolarophiles,[3] less commonly as 1,5- can be attributed to the MO structure of ketens, in particular to the low lying π* orbital orthogonal to the

keten C=C bond. This renders the central carbon highly electrophilic and the molecule susceptible to stepwise cycloadditions with nucleophilic addends. It also possibly stabilises concerted modes of cycloaddition in which the keten acts as an antarafacial component.[6] We report here our studies of the periselectivity of addition of ketens to the imidoazimines (1) and of the thermal transformations of the cycloadducts produced.

Addition of diphenyl-, phenylmethyl-, and dimethyl-keten to the imidoylazimine (1; Ar = Ph) gave rapidly and exclusively the 2 + 2 cycloadducts (2). The diphenylketen used was preformed; phenylmethyl- and dimethyl-keten were generated *in situ* from the appropriate acid chloride and triethylamine. The yellow adducts (2) were unstable and analytical data were not therefore obtained. However all spectral data and the observed reactions were in accord with the proposed structure. Thus n.m.r. spectroscopy shows the characteristic benzocinnoline *N*-imide [7] aromatic ^{1}H absorption pattern and in the case of the cycloadduct from dimethylketen two methyl singlets are apparent at δ 1.5 and 1.3.

Adduct (2)			Pyrolysis product (% yield)		
			Imidazolinone		Triazolobenzocinnoline
R^1	R^2	Ar	(5)	Benzo[*c*]cinnoline	(8)
Ph	Ph	Ph	73	87	0
Ph	Ph	*o*-MeC_6H_4	75	92	0
Ph	Me	Ph	28	51	8
Ph	Me	*o*-MeC_6H_4	35	80	8
Ph	Me	*p*-MeC_6H_4	31	63	7
Ph	Me	*p*-$NO_2C_6H_4$	0	38	50
Me	Me	Ph	0	40	20
Me	Me	*o*-MeC_6H_4	0	28	37
Me	Me	*p*-$NO_2C_6H_4$	0	60	28

The u.v. spectra are consistent with the presence of a benzocinnoline *N*-imide type of chromophore; for example the adduct from phenylmethylketen has main absorptions at 251 (ε 45 890), 296 (7 450), and 372 nm (12 400) compared with benzocinnoline *N*-imide which has absorptions at 254 (37 500), 297 (8 930), and 385 nm (9 120). Strong carbonyl stretching absorptions at 1 740—1 750 cm^{-1} appear in the i.r. spectra of the 1 : 1 adducts and are indicative of the β-lactam structural unit. Finally the mass spectra of the diphenylketen and phenylmethylketen adducts show no parent ion but large fragment ions corresponding to the side chain units are observed at *m/e* 388 and 326 respectively together with the base peaks at 180 corresponding to benzocinnoline. Only one of the two possible diastereoisomeric adducts was observed in the addition to phenylmethylketen; this is presumably the least sterically crowded adduct with the two aryl groups *trans*.

Chemical evidence supporting structure (2) comes from the hydrolysis of the dimethylketen adduct. This gave benzocinnoline *N*-imide and α-benzoyl-αα-dimethylacetanilide (3) which was also synthesised independently for comparison by methylation of α-benzoyl-α-methylacetanilide. This hydrolytic cleavage therefore parallels the usual mode of hydrolysis of β-lactams. Further chemical support for the structure is obtained from the thermal decomposition of the adducts which is described below.

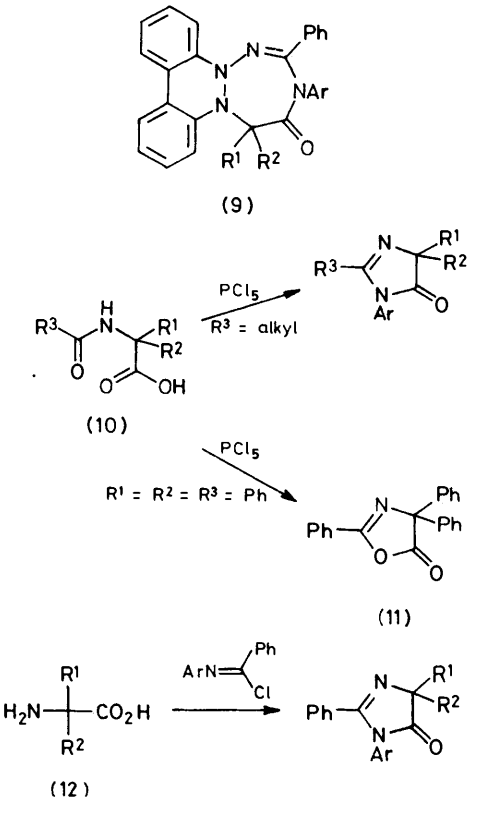
The most likely mechanism for the formation of adducts (2) is nucleophilic attack by the imide terminal nitrogen on the keten to give a stabilised zwitterion (4) which then collapses to give the β-lactam although a concerted $_\pi2_s + _\pi2_a$ cycloaddition cannot be ruled out. Rather disappointingly there is no evidence for formation of the 5 + 2 cycloadduct (9) either by a concerted $_\pi6_s + _\pi2_a$ process or by the alternative mode of collapse of the zwitterion (4) to the seven-membered ring. This was not unexpected since a concerted 5 + 2 addition can only occur with the dipole (1) in a *cisoid* configuration and in conformation (1a) and it is quite possible that (1) exists in a *transoid* form (1b). A stepwise reaction would only result in addition across the 1,5-positions of the dipole (1a or 1b) if the necessary conformational and configurational changes within the zwitterion were faster than ring closure to the β-lactam. More surprising is the absence of products arising from allowed 3 + 2 cycloaddition across the benzocinnoline imide function, as observed with the isoelectronic benzocinnoline *N*-acylimides.[8] Evidently the HOMO orbital coefficients of (1) are such as to favour a one-centre interaction *via* the terminal N-5 rather than a one- or two-centre interaction *via* N-3 or N-1.

Other similar 1 : 1 adducts were clearly obtained from the imidoylazimines (1; Ar = *o*-tolyl) with the three ketens: from (1; Ar = *p*-tolyl) and phenylmethylketen and from (1; Ar = *p*-$NO_2C_6H_4$) and phenylmethyl- and dimethyl-keten. However because of their instability these were not fully characterised but their thermal decomposition was carried out *in situ*. No significant difference was found in cases where adducts were pyrolysed both after isolation or *in situ*.

Thermal Decomposition of the Adducts (2).—Thermal decomposition of the benzocinnoline *N*-oxoazetidinylimides proceeds rapidly in refluxing benzene or toluene. Two modes of decomposition are observed depending on the substituents. One mode involves N–N bond cleavage to give benzocinnoline and the imidazolinone (5), and the second leads to the triazolobenzocinnoline (8). The relative importance of the two processes is apparent from the Table.

Breakdown to benzocinnoline and the imidazolinone could formally involve formation of an oxoazetidinylnitrene which then undergoes ring expansion. This

seems unlikely because higher temperatures than those employed here are required to effect nitrene formation with other benzocinnoline *N*-imides.[7] A more reasonable



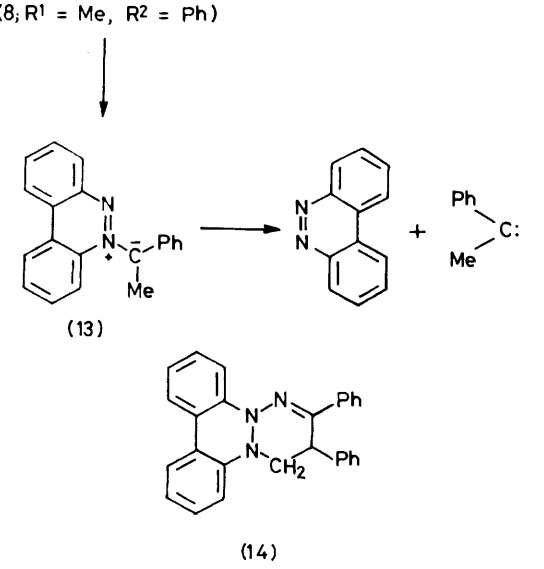
mechanism would be cleavage of the β-lactam C–C bond to give the highly stabilised zwitterion (4), a process assisted by relief of steric strain, followed by internal nucleophilic displacement.

Formation of the triazolobenzocinnoline can be explained by a similar mechanism involving C–N rather than C–C bond cleavage to give the alternative stabilised zwitterion (6). This zwitterion then loses a molecule of isocyanate to give the new ylide (7) which undergoes 1,5-dipolar cyclisation. We were unable however to isolate any isocyanate from these reactions. Perhaps surprisingly no internal displacement in the zwitterion (6) leading to pyrazolinone was observed.

Clearly the preferred mode of reaction of the imides (2) is finely balanced and is dependent on the substituents in a way which is consistent with the above mechanism. When R^1 and R^2 are such that the developing carbanionic centre in (4) derives stabilisation from delocalisation, C–C bond cleavage predominates, but when R^1 and R^2 are electron releasing C–N cleavage leading to triazoline is preferred. As expected introduction of an electron-withdrawing group into the *N*-aryl function (Ar) favours C–N cleavage.

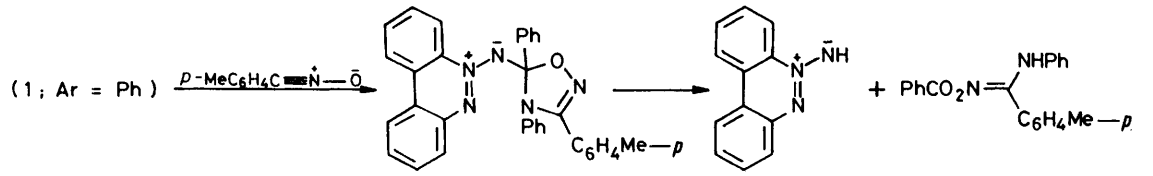
The structures of the tetrasubstituted imidazolinones (5) were confirmed by independent synthesis. The one reported general route to such imidazolinones, involving reaction of amides (10; R^3 = alkyl) with phosphorus pentachloride in the presence of an aromatic amine[9] failed in our hands when R^3 was aryl. Thus attempted preparation of (5; $R^1 = R^2 = Ar = Ph$) by this method gave the oxazolinone (11) by the ready cyclisation of the α-benzamidodiphenylacetic acid. An alternative route involving the action of imidoyl chlorides on the appropriate α-aminoacetic acid (12) in dry pyridine was therefore employed. The spectral characteristics for the imidazolinones were entirely as expected except for the imidazolinone (5; R^1 = Ph, R^2 = Me, Ar = *o*-MeC_6H_4) which showed four peaks in the n.m.r. spectrum in the range δ 3.4—1.7. These peaks correspond to two pairs of singlets for the aryl and imidazoline methyl groups. The two pairs were of unequal intensity and although variable temperature n.m.r. spectra revealed no coalescence up to 125° some variation in chemical shift was apparent. This spectral behaviour is consistent with the presence of (5; R^1 = Ph, R^2 = Me, Ar = *o*-MeC_6H_4) in two diastereoisomeric forms as a consequence of hindered rotation about the N-aryl bond.

The triazolines (8) are derivatives of the rare 1,2-dihydro-1,2,3-triazole system.[10] Evidence for their structure comes from their n.m.r. spectra which no longer show the characteristic benzocinnoline *N*-imide ^1H absorption pattern although their u.v. spectra ($\lambda_{max.}$ 245; ε 33 270 for R^1 = Me, R^2 = Ph) are consistent with a planar biphenyl system. The mass spectra show molecular ions and base peaks at *m/e* 181, the latter again being indicative of a cyclic dihydrobenzocinnoline derivative. Acid-catalysed hydrolysis of the triazoline (8; R^1 = Me, R^2 = Ph) gave benzocinnoline as the only isolated product. Pyrolysis of this compound at its melting point also gave benzocinnoline together with benzonitrile. These products could be explained by retro dipolar cycloaddition to give the azomethine imine (13) which decomposes further at the elevated temperature to give benzocinnoline and phenylmethylcarbene. Such a mechanism seems quite reasonable and in the mass



spectral fragmentation of (8; R^1 = Me, R^2 = Ph) a large peak corresponding to M — PhCN is observed. Attempted trapping of the proposed azomethine imine by pyrolysis in chlorobenzene containing dimethyl acetylenedicarboxylate gave no trace of the expected cycloadduct. Alternative mechanisms such as concerted fragmentation or electrocyclic ring opening to the dipole (7; R^1 = Me, R^2 = Ph) followed by 1,6-H shift [2] and intramolecular nucleophilic addition to give (14) and finally $_o2 + _o2 + _o2$ fragmentation are also possible.

Attempts to synthesise the triazolobenzocinnolines by alternative routes through the 1,5-dipoles (7) have so far been unsuccessful. Thus reaction of benzocinnoline N-imide with 1,2-dibromo-1-phenylethane, in the hope that N-alkylation followed by dehydrohalogenation would give the dipole (7; $R^1 = R^2$ = H), gave only a deep purple solution. Reaction of benzocinnoline N-imide with diethyl ethoxymethylenemalonate similarly gave a deeply coloured reaction mixture from which no pure products were isolated. This latter approach using activated vinyl halides has been used successfully to extend conjugation in pyridinium ylides.[11] It is possible that the two ester groups in (7; $R^1 = R^2 = CO_2Et$) so stabilise the open 1,5-dipolar form as to preclude cyclisation.



(15) (16)

In view of the wide range of periselectivity possible, other cycloadditions to (1) were also investigated. These were disappointing, however, and generally gave either complex intractable mixtures (dimethyl acetylenedicarboxylate) or no reaction (diphenylisobenzofuran and tetraphenylcyclopentadienone). With *p*-toluonitrile oxide, however, there is evidence for cycloaddition across the terminal C=N although the adduct (15) was not isolated. Chromatographic work up gave benzo[*c*]cinnoline N-imide and the amide oxime (16), the expected hydrolysis product.

Although one of the initial objectives of observing extended dipolar cycloadditions to the imidoylazimines (1) was not achieved, the foregoing reactions illustrate that benzocinnoline N-imides are synthetically useful ylides. In principle the reaction of ketens with imidoylazides could lead to imidazolinones and dihydrotriazoles. However such transformations would most likely be precluded by the strong tendency of imidoylazides to exist as aromatic tetrazoles. Benzocinnoline N-imides thus have potential as masked azides.

EXPERIMENTAL

Cycloaddition of the Imidoylazimines (1; Ar = Ph) *with Ketens.*—(a) *Diphenylketen.*[12] The imidoylazimine (1; Ar = Ph) (200 mg, 0.5 mmol) was suspended in dry benzene (10 ml) and freshly distilled diphenylketen (120 mg, 0.6 mmol) in dry benzene was added dropwise to the rapidly stirred mixture. The solution became dark yellow after 0.5 h and evaporation of the solvent followed by trituration of the residual oil with ether–light petroleum gave a flocculent yellow precipitate of benzo[*c*]cinnoline N-(4-oxo-1,2,3,3-tetraphenylazetidin-2-ylimide (2; $R^1 = R^2$ = Ar = Ph) (300 mg, 99%) as yellow needles, m.p. 176—178 °C (decomp.), from ethanol–dichloromethane, *m/e* 568 (M^+), 388, 360, 269, 257, 212, 194, 182, 180, 167, 166, 165, and 152; $\nu_{max.}$ 1 750, 1 601, 1 500, 1 461, 1 384, 1 372, 1 331, 1 323, 1 261, 1 129, and 761 cm^{-1}; $\lambda_{max.}$ 250 (ε 52 117), 297 (9 820), 308 (8 308), 322 (6 798), 392 (13 596), and 412 (10 574) nm. No elemental analysis was obtained because of the ready decomposition of this compound in solution.

(b) *Phenylmethylketen.* 2-Phenylpropionyl chloride [13] (100 mg, 0.6 mmol) was added over 5 min to a rapidly stirred suspension of the imidoylazimine (1; Ar = Ph) (200 mg, 0.5 mmol) in dry benzene (10 ml) containing triethylamine (70 mg, 0.7 mmol). After 0.5 h, triethylamine hydrochloride was filtered off and the yellow filtrate was evaporated. Trituration of the residue with ether–light petroleum gave a yellow precipitate of benzo[*c*]cinnoline N-(3-methyl-4-oxo-1,2,3-triphenylazetidin-2-yl)imide (2; R^1 = Me, R^2 = Ar = Ph) (260 mg, 96%) as yellow crystals, m.p. 164—166 °C (decomp.), from ethanol–dichloromethane, *m/e* 506 (M^+) 326, 298, 223, 181, 180, and 152; $\nu_{max.}$ 1 736, 1 598, 1 499, 1 470, 1 454, 1 444, 1 408, 1 377, 1 361, 769, 757, and 701 cm^{-1}; $\lambda_{max.}$ 251 (ε 45 890), 296 (7 450), 308 (7 450), 322 (6 200), and 374 (12 400) nm; δ($CDCl_3$) 8.95 (m, 1 H), 8.4—6.5 (m, 22 H), and 1.7 (s, 3 H).

(c) *Dimethylketen.* The procedure used was similar to that just described except that an excess of 2-methylpropionyl chloride (5 equiv.) and triethylamine was used. The reaction mixture was kept at 5 °C for 5 h, the solution was concentrated, and triethylamine hydrochloride and the keten dimer were filtered off. Evaporation of the filtrate and trituration of the residue with ether–light petroleum gave benzo[*c*]cinnoline N-(3,3-dimethyl-4-oxo-1,2-diphenylazetidin-2-yl)imide (2; $R^1 = R^2$ = Me, Ar = Ph) (92%) as a yellow-green powder which was insufficiently stable for recrystallisation, $\nu_{max.}$ 1 753, 1 506, 1 478, 1 409, 1 390, 1 384, 1 335, 770, and 758 cm^{-1}; δ($CDCl_3$) 8.9 (m, 1 H), 8.4—6.8 (m, 17 H), 1.5 (s, 3 H), and 1.3 (s, 3 H). This compound was too unstable for realiable determination of other data.

The benzo[*c*]cinnoline N-(oxoazetidinyl)imides (2) from the imidoylazimines (1; Ar = 2-MeC_6H_4, 4-MeC_6H_4, and 4-$NO_2C_6H_4$) were not isolated and reactions carried out on these ylides were performed *in situ*.

Hydrolysis of the Azetidinylimide (2; $R^1 = R^2$ = Me, Ar = Ph).—A solution of the imide (2; $R^1 = R^2$ = Me, Ar = Ph) (200 mg) in undried benzene (10 ml) was maintained at 50 °C for several days. The resulting dark green solution was evaporated and the residue was chromato-

graphed on alumina. Elution with 20% ether–light petroleum gave benzo[*c*]cinnoline *N*-imide (60 mg, 68%) identical with an authentic sample.[7] 33% Ether–light petroleum gave *α-benzoyl-αα-dimethylacetanilide* (3) (70 mg, 58%) as colourless needles, m.p. 109—110 °C, from benzene (Found: C, 76.4; H, 6.4; N, 5.3. $C_{17}H_{17}NO_2$ requires C, 76.4; H, 6.3; N, 5.5%), $\nu_{max.}$(CHCl$_3$) 3 420, 1 693, 1 666, and 1 599 cm^{-1}; δ(CDCl$_3$) 7.9—6.8 (m, 11 H) and 1.6 (s, 6 H); *m/e* 267.

A sample of compound (3) prepared by the following method was identical. α-Benzoyl-α-methylacetanilide [14] (12 g, 48 mmol) was added slowly to a vigorously stirred suspension of sodium hydride (1.2 g; 50% dispersion in oil; 49 mmol) in dry benzene (40 ml)–dimethylformamide (20 ml) at 10 °C. After 0.5 h, methyl iodide (13 g) was added dropwise and stirring was continued for 2 h. Water (100 ml) was then added, and the organic layer was separated, washed with water (3 × 50 ml), dried, and evaporated. The residue was chromatographed on silica gel, elution with ether giving the amide (3) (7 g, 55%).

Pyrolysis of Benzo[c]*cinnoline* N-(*Oxoazetidinyl*)*imides* (2).—The imides (2; R^1 = R^2 = Ar = Ph and R^1 = Me, R^2 = Ar = Ph) were heated under reflux in dry benzene for 6 h. After evaporation of solvent the residues were chromatographed on alumina. The other imides were not isolated but were generated *in situ* as already described and the resulting solutions were heated under reflux in toluene (benzene being removed by distillation). In all cases the triazolocinnoline was eluted with 10% ether–light petroleum, the imidazolinone with 40% ether–light petroleum, and benzo[*c*]cinnoline with 80% ether–light petroleum.

(i) The tetraphenyl compound (2; R^1 = R^2 = Ar = Ph) gave 1,2,4,4-*tetraphenyl-Δ²-imidazolin-5-one* (5; R^1 = R^2 = Ar = Ph) (73%) as prisms, m.p. 156—158 °C from ether–light petroleum (Found: C, 83.7; H, 5.1; N, 7.5. $C_{27}H_{20}N_2O$ requires C, 83.5; H, 5.1; N, 7.5%); $\nu_{max.}$ 1 741 and 1 623 cm^{-1}; *m/e* 388 (*M*$^+$); and benzo[*c*]cinnoline (87%).

(ii) The methyltriphenyl compound (2; R^1 = Me, R^2 = Ar = Ph) gave 1-*methyl*-1,2-*diphenylbenzo*[c]-s-*triazolo*[1,2-a]*cinnoline* (8; R^1 = Me, R^2 = Ph) (8%) as yellow needles, m.p. 195—197 °C, from benzene–light petroleum (Found: C, 83.7; H, 5.5; N, 10.9. $C_{27}H_{21}N_3$ requires C, 83.7; N, 5.4; H, 10.9%), $\nu_{max.}$ 1 501, 1 488, 1 449, 1 358, 1 298, 1 271, 772, 751, 700, 694, and 681 cm^{-1}; $\lambda_{max.}$ 255 (ε 33 270) and 398 (11 770) nm; δ(CDCl$_3$) 7.9—6.6 (m, 18 H) and 2.05 (s, 3 H); *m/e* 387, 284, and 181; 4-*methyl*-1,2,4-*triphenyl-Δ²-imidazolin-5-one* (5; R^1 = Me, R^2 = Ar = Ph) (28%), as prisms, m.p. 127—129 °C, from ether–light petroleum (Found: C, 80.8; H, 5.6, N, 8.7. $C_{22}H_{18}N_2O$ requires C, 81.0; H, 5.5; N, 8.6%); $\nu_{max.}$ 1 749 and 1 620 cm^{-1}; δ(CDCl$_3$) 7.9—6.4 (m, 15 H) and 1.9 (s, 3 H); *m/e* 326 (*M*$^+$); and benzo[*c*]cinnoline (51%).

(iii) The dimethyldiphenyl compound (2; R^1 = R^2 = Me, Ar = Ph) gave 1,1-*dimethyl*-2-*phenylbenzo*[c]-s-*triazolo*-[1,2-a]*cinnoline* (8; R^1 = R^2 = Me) (20%) as orange plates, m.p. 163—165 °C, from benzene–light petroleum (Found: C, 80.9; H, 5.9; N, 13.0. $C_{22}H_{19}N_3$ requires C, 81.2; H, 5.8; N, 12.9%); $\nu_{max.}$ 1 503, 1 489, 1 469, 1 448, 1 376, 1 293, 1 287, 748, and 698 cm^{-1}; $\lambda_{max.}$ 254 (ε 32 230), 260 (31 180), and 388 (7 716) nm; δ(CDCl$_3$) 8.2—6.8 (m, 13 H) and 1.9 (s, 6 H); *m/e* 325, 222, and 181; and benzo[*c*]-cinnoline (40%).

(iv) Benzo[*c*]cinnoline *N*-(4-oxo-2,3,3-triphenyl-1-*o*-tolylazetidin-2-yl)imide (2; R^1 = R^2 = Ph, Ar = *o*-MeC$_6$H$_4$) gave 2,4,4-*triphenyl*-1-o-*tolyl-Δ²-imidazolin-5-one* (5; R^1 = R^2 = Ph, Ar = *o*-MeC$_6$H$_4$) (75%), as prisms, m.p. 136—138 °C, from ether–light petroleum (Found: C, 83.3; H, 5.4; N, 7.2. $C_{28}H_{22}N_2O$ requires C, 83.6; H, 5.5; N, 7.2%); $\nu_{max.}$ 1 749 and 1 613 cm^{-1}; δ(CDCl$_3$) 7.8—6.7 (m, 19 H) and 2.05 (s, 3 H); *m/e* 402 (*M*$^+$); and benzo[*c*]-cinnoline (92%).

(v) Benzo[*c*]cinnoline *N*-(3-methyl-4-oxo-2,3-diphenyl-1-*o*-tolylazetidin-2-yl)imide (2; R^1 = Me, R^2 = Ph, Ar = *o*-MeC$_6$H$_4$) gave the triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph) (8%), m.p. and mixed m.p. 195—197 °C; 4-*methyl*-2,4-*diphenyl*-1-o-*tolyl-Δ²-imidazolin-5-one* (5; R^1 = Me, R^2 = Ph, Ar = *o*-MeC$_6$H$_4$) (35%), m.p. 108—109 °C, from ether–light petroleum (Found: C, 81.5; H, 5.9; N, 8.5. $C_{23}H_{20}N_2O$ requires C, 81.2; H, 5.9; N, 8.2%); $\nu_{max.}$ 1 748 and 1 631 cm^{-1}; δ(CDCl$_3$) 7.9—6.8 (m, 14 H) and 2.3—1.7 (4 peaks, 6 H, see text); *m/e* 340 (*M*$^+$); and benzo[*c*]-cinnoline (80%).

(vi) Benzo[*c*]cinnoline *N*-(3,3-dimethyl-4-oxo-2-phenyl-1-*o*-tolylazetidin-2-yl)imide (2; R^1 = R^2 = Me, Ar = *o*-MeC$_6$H$_4$) gave the triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph) (37%), m.p. and mixed m.p. 195—197 °C, and benzo[*c*]cinnoline (28%).

(vii) Benzo[*c*]cinnoline *N*-(3-methyl-4-oxo-2,3-diphenyl-1-*p*-tolylazetidin-2-yl)imide (2; R^1 = Me, R^2 = Ph, Ar = *p*-MeC$_6$H$_4$) gave the triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph) (7%), m.p. and mixed m.p. 195—197 °C; 4-*methyl*-2,4-*diphenyl*-1-p-*tolyl-Δ²-imidazolin-5-one* (5; R^1 = Me, R^2 = Ph, Ar = *p*-MeC$_6$H$_4$) (31%), as prisms, m.p. 143—145 °C, from ether–light petroleum (Found: C, 81.1; H, 6.1; N, 8.5. $C_{23}H_{20}N_2O$ requires C, 81.2; H, 5.9; N, 8.2%); $\nu_{max.}$ 1 749 and 1 631 cm^{-1}; δ(CDCl$_3$) 7.9—6.9 (m, 14 H), 3.4 (s, 3 H), and 1.95 (s, 3 H); *m/e* 340 (*M*$^+$); and benzo[*c*]cinnoline (63%).

(viii) Benzo[*c*]cinnoline *N*-(3-methyl-1-*p*-nitrophenyl-4-oxo-2,3-diphenylazetidin-2-yl)imide (2; R^1 = Me, R^2 = Ph, Ar = *p*-NO$_2$C$_6$H$_4$) gave the triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph) (50%), m.p. and mixed m.p. 195—197 °C, and benzo[*c*]cinnoline (38%).

(ix) Benzo[*c*]cinnoline *N*-(3,3-dimethyl-1-*p*-nitrophenyl-4-oxo-2-phenylazetidin-2-yl)imide (2; R^1 = R^2 = Me, Ar = *p*-NO$_2$C$_6$H$_4$) gave the triazolobenzocinnoline (8; R^1 = R^2 = Me) (29%), m.p. and mixed m.p. 163—165 °C, and benzo[*c*]-cinnoline (60%).

Independent Synthesis of the Imidazolinones (5).—The appropriate *N*-arylbenzimidoyl chloride (1 equiv.) was added with constant stirring to the appropriate amino acid (1 equiv.) in dry pyridine. After 3 h, pyridine was removed by rotary evaporation and the residue was extracted with boiling ether. Addition of hexane to the ethereal solution precipitated out amide impurities which were filtered off. The filtrate was concentrated and the residue was recrystallised from ether–hexane to give the pure imidazolinone. These were identical with those obtained by pyrolysis of the azetidinylimides (2).

α-Aminodiphenylacetic acid [15] gave compounds (5; R^1 = R^2 = Ar = Ph) (14%) and (5; R^1 = R^2 = Ph, Ar = *o*-MeC$_6$H$_4$) (39%). α-Amino-α-phenylpropionic acid [16] gave compounds (5; R^1 = Me, R^2 = Ar = Ph) (25%), (5; R^1 = Me, R^2 = Ph, Ar = *o*-MeC$_6$H$_4$) (30%), and (5; R^1 = Me, R^2 = Ph, Ar = *p*-MeC$_6$H$_4$) (24%).

Hydrolysis of the Triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph).—The triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph) (71 mg) was heated under reflux for 3 h in ethanol (5 ml) containing conc. hydrochloric acid (0.1 ml). The resulting

solution was diluted with water (5 ml), neutralised with sodium hydrogen carbonate, and extracted with dichloromethane. The extracts were subjected to preparative t.l.c. on silica gel to give benzo[*c*]cinnoline (23 mg, 70%) as the only isolable product.

Pyrolysis of the Triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph).—The triazolobenzocinnoline (8; R^1 = Me, R^2 = Ph) (98 mg) was maintained at its m.p. for 30 min. The residue was then chromatographed on alumina. Elution with 10% ether–light petroleum gave benzonitrile (15 mg, 58%) and elution with ether gave benzo[*c*]cinnoline (38 mg, 83%).

Reaction of the Imidoylazimine (1; Ar = Ph) *with* p-*Toluonitrile Oxide*.—α-Chloro-*p*-tolualdehyde oxime (227 mg, 1.3 mmol) in dry benzene (2 ml) was added to a solution of the imidoylazimine (1; Ar = Ph) (500 mg, 1.3 mmol) and triethylamine (144 mg, 1.4 mmol) in dry benzene (20 ml) and the mixture was stirred for 3 days at room temperature. Triethylamine hydrochloride was filtered off and the filtrate was evaporated to dryness. The residue was chromatographed on alumina. Elution with 10% ether–light petroleum gave di-*p*-tolylfurazan *N*-oxide (42 mg, 23%), m.p. 142—143 °C (lit.,[17] 143—144 °C). 20% Ether–light petroleum gave benzocinnoline *N*-imide (160 mg, 62%), m.p. and mixed m.p. 125—126 °C, and 40% ether–light petroleum gave N-*phenyl*-p-*toluamide* O-*benzoyloxime* (16) (150 mg, 34%) as needles, m.p. 165—167 °C from benzene–light petroleum (Found: C, 76.2; H, 5.5; N, 8.4. $C_{21}H_{18}N_2O_2$ requires C, 76.4; H, 5.5; N, 8.5%); $\nu_{max.}$ 3 320, 1 738, and 1 729 cm^{-1}; *m/e* 330 (M^+). An identical sample of (16) was prepared (86%) by treatment of *N*-phenyl-*p*-toluamide oxime [18] with benzoyl chloride in pyridine. After 30 min the pyridine solution was poured into water, and the resulting precipitate was collected, dried, and recrystallised from benzene–light petroleum.

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