Photocyclisation of 1-Styrylimidazoles. A Novel Route to *N*-Bridgehead Compounds

By G. Cooper and W. J. Irwin,* Department of Pharmacy, University of Aston in Birmingham, Gosta Green, Birmingham B4 7ET

The photoisomerisation of *trans*-1-styrylimidazole and derivatives to the *cis*-isomers is described. The *cis*-compounds undergo a stereospecific photodehydrocyclisation involving the 2-position of the imidazole ring to give imidazo[2,1-*a*]isoquinoline, benzimidazo[2,1-*a*]isoquinoline, and derivatives. The reverse mode of cyclisation, involving 2-styrylbenzimidazoles in C–N bond formation, is also demonstrated; benzimidazo[1,2-*a*]quinoline and its 2,3,10-trimethyl derivative have been obtained from the corresponding 2-styryl compounds.

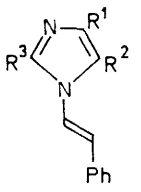
THE photodehydrocyclisation of *trans*-stilbene to yield phenanthrene [1,2] *via* the intermediate *cis*-isomer was first demonstrated in 1950. It was shown that the reaction probably proceeds *via* oxidation of the primary photoproduct, dihydrophenanthrene. Since that time the reaction has been widely exploited and many simple and condensed derivatives of stilbene, aza-analogues of stilbene (*e.g.* styrylpyridines,[3] styrylpyrimidines,[4] and azobenzene [5]), and related compounds such as furyl- and thienyl-ethylenes [6] have been found to undergo similar photocyclisations. This type of reaction has also been the subject of several reviews.[7]

This paper describes studies of the photochemical behaviour of 1-styrylimidazoles available from earlier work.[8]

Irradiation of *trans*-1-styrylimidazole (1) with Pyrex-filtered light was monitored by u.v. spectroscopy. A family of spectra was obtained with an isosbestic point at 249 nm. This suggested that a simple process involving only one product was probably taking place and thus indicated that the reaction was an isomerisation, with no photodegradation of *cis*-1-styrylimidazole (15). The reaction was repeated on a large scale and a crude oil was isolated. The n.m.r. spectrum showed an AB quartet for the olefinic protons (J 9 Hz), thus confirming the *cis*-stereochemistry of the product, in conjunction with lower $\lambda_{max.}$ and $\varepsilon_{max.}$ values. The *trans*-isomer

[1] N. J. Turro, 'Molecular Photochemistry,' Benjamin, New York, 1967, p. 30; D. C. Neckers, 'Mechanistic Organic Photochemistry,' Reinhold, New York, 1967.
[2] C. O. Parker and P. E. Spoerri, *Nature*, 1950, **166**, 603.
[3] C. E. Loader and C. J. Timmons, *J. Chem. Soc.*, 1966, 1078.
[4] H. H. Perkampus and T. Bluhn, *Tetrahedron*, 1972, **28**, 2099.
[5] G. E. Lewis, *Tetrahedron Letters*, 1960, 12.
[6] C. E. Loader and C. J. Timmons, *J. Chem. Soc.*, 1967, 1677; R. M. Kellog, M. B. Groen, and H. Wynberg, *J. Chem. Soc.*, 1967, 3093.
[7] F. R. Stermitz, *Org. Photochem.*, 1967, **1**, 247; E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, **23**, 482; S. T. Reid, *Adv. Heterocyclic Chem.*, 1970, **11**, 1.
[8] G. Cooper, W. J. Irwin, and D. L. Wheeler, *Tetrahedron Letters*, 1971, 4321; W. J. Irwin and D. L. Wheeler, *Tetrahedron*, 1972, **28**, 1113; G. Cooper and W. J. Irwin, *J.C.S. Perkin I*, 1973, 911; 1975, 798.

appeared to be absent (n.m.r. and t.l.c.). The compositions of the isomerisation mixture at intermediate times were calculated from measurements of absorbances of the mixture and extinction coefficients of the two



	R^1	R^2	R^3
(1)	H	H	H
(2)	CO_2Me	CO_2H	H
(3)	CO_2Me	CO_2Me	H
(4)	CO_2Me	H	H
(5)	Ph	Ph	H
(6)	H	H	Me
(7)	H	H	Ph
(8)	CO_2Me	H	Me

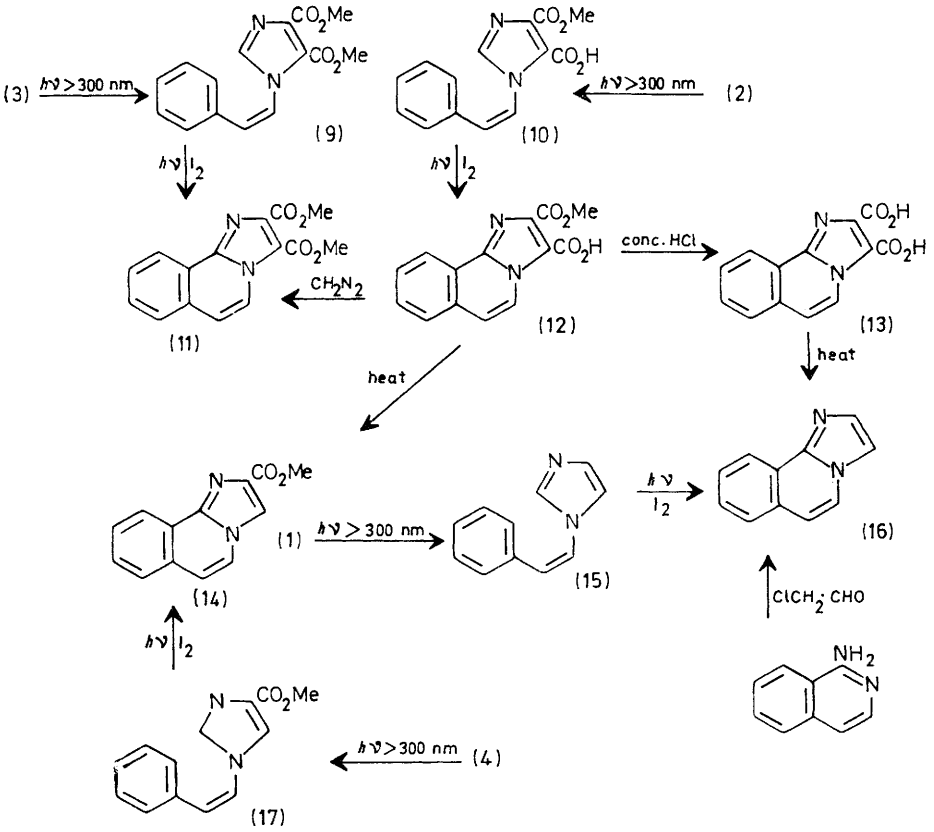
isomers at two wavelengths. Similar data were obtained from isomerisation experiments with the *trans*-1-styrylimidazoles (4), (6)—(8), and (18). Plots of log [*trans*-isomer] *vs.* time yielded straight lines and demonstrated the first-order dependence of the isomerisation. The differences in rates of isomerisation of the six compounds (Table) could be due to inherent structural differences or to differing absorption characteristics. A measure of the absorptivity of each compound is the area under the u.v. absorption spectrum of each *trans*-isomer above 300 nm, *i.e.* the region that is irradiated by light transmitted through Pyrex. In general the compound with the greatest area of absorption (from frequency scan) above 300 nm also had the greater rate of isomerisation. A correlation coefficient calculated for all the points (r 0.89) indicates that there is a linear relationship.

Rates of isomerisation of *trans*-1-styrylimidazoles

trans-Olefin	(1)	(5)	(6)	(7)	(8)	(18)
$10^3k/s^{-1}$	7.74	21.2	25.5	20.4	54.1	81.6

The families of u.v. spectra from the irradiation of 4-methoxycarbonyl-*trans*-1-styrylimidazole-5-carboxylic acid (2) and the dimethyl ester (3) under identical conditions did not, however, produce similar results. An isosbestic point was not observed although similar reductions in $\lambda_{max.}$ and $\varepsilon_{max.}$ were seen.

In the hope of devising a simple synthetic route to *N*-bridgehead systems, we extended our study to the photoreactions of *cis*-1-styrylimidazoles. A methanolic 0.03mM-solution of the *trans*-isomer containing iodine (0.02mM), in a quartz cuvette, was irradiated with a Hanovia 100 W medium-pressure mercury lamp, at a constant distance, and the reaction was monitored by u.v. spectroscopy. The family of spectra obtained during irradiation of the half ester (2) through Pyrex show the development of intense absorption at 246 nm, indicating



the formation of a cyclic compound similar to phenanthrene ($\lambda_{max.}$ 247 nm). A similar increase in the peak at 246 nm can be generated with 1 or 0.1 mol equiv. of iodine. This peak also appears, although much less efficiently, if the experiment is conducted in the absence of iodine, oxygen being the oxidant. Methanol as solvent gave better results than ether or cyclohexane. A reaction on a preparative scale with Pyrex-filtered light (20 h) gave the imidazo[2,1-*a*]isoquinoline (12) in 55% yield.

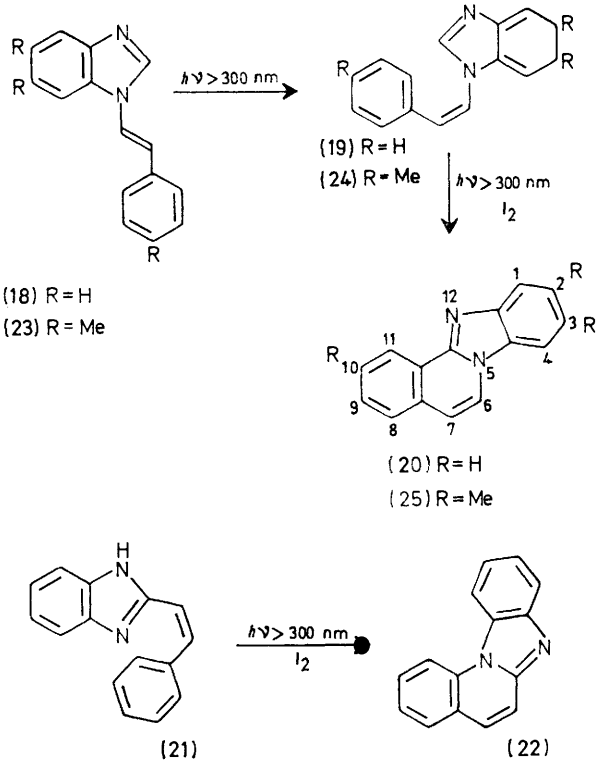
The i.r. spectrum of the product indicated the presence of an ester (ν_{CO} 1 720 cm^{-1}) and a carboxy-group (ν_{CO} 1 640; ν_{OH} 2 650 cm^{-1}) and the mass spectrum showed a molecular ion at *m/e* 270, confirming that dehydrocyclisation had occurred. Hydrolysis with refluxing concentrated hydrochloric acid gave the corresponding diacid, which on heating in diethylene glycol afforded the parent imidazo[2,1-*a*]isoquinoline (16). The m.p. and i.r. and u.v. spectra of this compound were identical with those reported [9] for the product of condensation of 1-aminoisoquinoline with chloroacetaldehyde. The acid (12) was esterified with diazomethane to give the diester (11) and decarboxylated, in refluxing dimethylformamide, to give the monoester (14).

The u.v. spectra of the imidazo[2,1-*a*]isoquinolines were all similar: $\lambda_{max.}$ 245—256 nm (ε 55 000—62 000). The n.m.r. spectra all showed a low-field multiplet, at τ *ca.* 1.3, assigned to the 10-proton (close to the basic 1-nitrogen atom and on a π-deficient ring). This is useful in analysis of mixtures of the olefin [τ *ca.* 2.0 (s, H-2 of imidazole)] and the cyclic product. The absorptions assigned to the 5- and 6-protons were observed as an AB quartet (*J* 7 Hz), showing deshielding by a 3-carboxy- or ester-group.

The u.v. spectra obtained by monitoring the photodehydrocyclisation of the *trans*-1-styrylimidazole diester (3) with Pyrex-filtered light, by comparison with the spectrum of the expected product, indicated that photodehydrocyclisation was the major reaction. This was confirmed by the isolation of the imidazoisoquinoline (11) in 44% yield from a preparative-scale experiment. These photodehydrocyclisations could, without the occurrence of rearrangements, only involve the vacant 2-position of the imidazole ring. However both the monoester (4) and *trans*-1-styrylimidazole (1) itself have unsubstituted 2- and 5-positions at which photodehydrocyclisation could occur.

Pyrex-filtered light, as mentioned previously, isomerises the olefins (1) and (4), but to cyclise the *cis*-olefins it was necessary to use unfiltered light (*i.e.* a quartz vessel). Irradiation of the *cis*-olefins with unfiltered light caused some *cis* ⟶ *trans* isomerisation before cyclisation; thus the proportions of *cis*- and *trans*-isomers constituting the photostationary state produced by unfiltered light were different from those produced under Pyrex-filtered light. Comparison with the u.v. spectra of the imidazo[2,1-*a*]isoquinolines indicated that the major reaction was at the 2-position. Analysis of the crude reaction mixture from preparative scale experiments by n.m.r. spectroscopy and t.l.c. showed the presence of only one product in each case. The low yield of imidazo[2,1-*a*]isoquinoline (16) in the preparative experiment was thought to be due to the fact that the product absorbed light at 254 nm very intensely, and this happened to be the major wavelength of radiation below 300 nm emitted by the lamp. Extensive photolysis of the product occurred as a result. Attempts to obtain rate constants from the u.v. spectra were unsuccessful owing to difficulties in determining concentrations accurately. Analysis on the assumption that only *cis*- and *trans*-olefins, imidazo[2,1-*a*]isoquinoline, and iodine were present did not produce a self-consistent picture and suggests that a more complex sequence is involved.

trans-1-Styrylbenzimidazole (18) was isomerised under Pyrex-filtered light in the presence of 1 mol. equiv. of



iodine. The resulting *cis*-isomer was then irradiated through quartz. Cyclisation was observed, and benzimidazo[2,1-*a*]isoquinoline (20) was subsequently isolated from a preparative-scale experiment in 53% yield. The properties of the product (20) were identical with those reported for the product of condensation of 1-fluoro-2,4-dinitrobenzene with 1-aminoisoquinoline with subsequent reduction and deamination,[10] and also the product of photolysis or thermolysis of 1-(1-isoquinolyl)-benzotriazole.[11] Benzimidazo[2,1-*a*]isoquinoline showed a similar pattern of n.m.r. absorption to that described

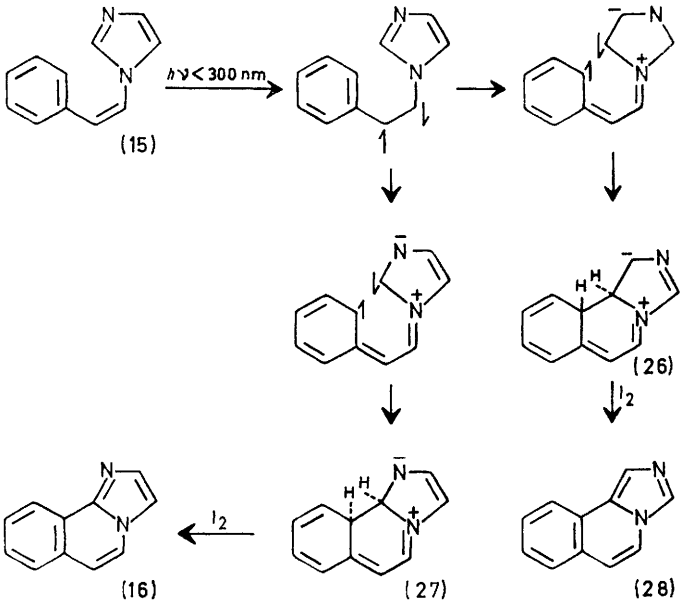
[9] A. J. Hubert and H. Reimlinger, *Chem. Ber.*, 1970, **103**, 3811.
[10] G. Morgan and J. Stewart, *J. Chem. Soc.*, 1939, 1057.
[11] A. J. Hubert, *J. Chem. Soc.*, 1969, 1334

for the imidazo[2,1-*a*]isoquinolines. A low-field multiplet at τ 1.35 was assigned to the 1-proton, and an AB quartet (J 7 Hz) to the 5- and 6-protons.

Evidence has been presented [7,12] for the intermediary dihydrophenanthrenes in the photocyclisation of stilbenes. A possible pathway for the photocyclisation of 1-styrylimidazoles is shown in the Scheme. *cis*-1-Styrylimidazole (15) must undergo polarisation of the imidazole ring in order to form a dihydro-intermediate [(26),(27)]. Polar species of this type have been suggested as the products of irradiation of imidazoles.[13] The selectivity of the photocyclisation may be due to the relative stabilities or ease of formation of the dihydro-intermediates [(26),(27)]. Compound (27), in which the negative charge is delocalised over carbon and nitrogen atoms, would be expected to be more stable than compound (26), in which delocalisation can only occur over carbon atoms. Hence a preponderance of imidazo[2,1-*a*]-isoquinoline (16) would be expected rather than its isomer (28). The photodehydrocyclisation of 2-methyl- (6) and 2-phenyl- (7) *trans*-1-styrylimidazoles could only afford 3-methyl- and 3-phenyl-imidazo[5,1-*a*]isoquinoline. Although both compounds, in cuvette experiments, underwent isomerisation, in the presence of iodine, with Pyrex-filtered light, no evidence of photodehydrocyclisation was observed on irradiation with unfiltered light. Only tars were recovered from prolonged irradiation in preparative experiments. The failure of these reactions may be due to the instability of the polar intermediates similar to structure (26). We considered that these intermediates might be stabilised by an electron-withdrawing substituent at the 4-position of the imidazole ring [*e.g.* (8)]. To test this possibility, the 4-ester (8) was irradiated. Cuvette experiments revealed that *trans* ⟶ *cis* isomerisation occurred readily under Pyrex-filtered light; however, no new absorption bands appeared on irradiation in the presence of iodine with unfiltered light. Only gradual destruction of the olefin was observed.

The isomerisation and photodehydrocyclisation of *trans*-1-styrylimidazoles has thus been shown to occur readily and with complete specificity, in the examples described, for the 2-position of the imidazole ring. An inverse process, the isomerisation and photodehydrocyclisation of *trans*-2-styrylimidazoles, involving a novel bond formation between the *ortho*-position of the phenyl ring and a nitrogen atom of the imidazole ring, was also considered to be feasible. The u.v. spectrum of *trans*-imidazole, $\lambda_{max.}$ 322 nm, obtained from *o*-phenylenediamine and cinnamic acid [14] showed a loss of intensity even under normal illumination and this, presumed to be due to isomerisation, occurred very rapidly when a solution was irradiated under Pyrex-filtered light to give a photostationary state. Irradiation of the *cis*-olefin (21) with Pyrex-filtered light in the presence of iodine caused the slow appearance of absorptions at 249, 257, and 267 nm and also in the region 345—370 nm. This change was monitored in a preparative-scale experiment and the development of intense fluorescence was also observed. A photostationary state was reached after 88 h and the solution yielded a product with the properties reported [15] for benzimidazo[1,2-*a*]quinoline (22).

In an attempt to obtain more data for the analysis of the n.m.r. spectrum of this system, 2,9,10-trimethylbenzimidazo[1,2-*a*]quinoline (25) was synthesized



SCHEME

[12] Th. J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, 1972, **94**, 5914; F. B. Mallory and C. W. Mallory, *ibid.*, p. 6041.

[13] G. Leandri, A. Mangini, F. Montanari, and R. Passerini, *Gazetta*, 1955, **85**, 769.

[14] T. R. Govindachari and K. Nagerajan, *Indian J. Chem.*, 1964, **2**, 169.

[15] G. Morgan and J. Stewart, *J. Chem. Soc.*, 1939, 1057.

by the same route. Condensation of the hydrochloride of 4,5-dimethyl-*o*-phenylenediamine with *p*-methylcinnamic acid gave the *trans*-olefin (23) in 50% yield. The u.v. spectrum of this product is similar to that of *trans*-2-styrylbenzimidazole, and the *trans*-olefin (23) also behaved similarly upon irradiation, first giving the *cis*-olefin (24), then the cyclic product (25) in 27% yield. Because of the symmetrical structure of the olefin, only one product of photodehydrocyclisation could be produced. The u.v. spectra of the benzimidazo-[1,2-*a*]quinolines (22) and (25) are similar as are the n.m.r. spectra although the complexity in the latter case is greatly reduced.

EXPERIMENTAL

I.r. spectra were determined for Nujol mulls, unless otherwise stated, with a Unicam SP 200 spectrophotometer. N.m.r. spectra were determined for solutions in deuteriochloroform, unless otherwise stated, with tetramethylsilane as internal standard, on a Varian A60-A spectrometer, or on a Varian HR220 spectrometer by the Physico-Chemical Measurements Unit, Harwell. Mass spectra were determined on an A.E.I. MS9 spectrometer, operating at 100 μA and 70 eV. U.v. spectra were determined for solutions in methanol on a Beckmann Acta V spectrophotometer. Reaction temperatures quoted are those of an external oil bath. Light petroleum refers to the fraction of boiling range 60—80°. Photochemical reactions were performed in a Hanovia 1 l reactor, with a 100 Watt medium-pressure mercury arc.

Photoisomerisation Reactions.—The photoisomerisations of the *trans*-1-styrylimidazoles were carried out on methanolic 30 μM-solutions in a quartz cuvettes 10 cm from the lamp, fitted with a Pyrex filter. U.v. spectra were determined at intervals and the curves were analysed by a least-squares technique.

cis-1-*Styrylimidazole* (15).—*trans*-1-Styrylimidazole (1.0 g) was irradiated in methanol (1 l) through Pyrex until u.v. spectroscopy indicated no further reaction (24 h). The solvent was evaporated off and the residue was extracted with boiling light petroleum. The extract was evaporated to yield the *cis*-olefin as a mobile yellow oil, $\nu_{max.}$ 1 650 cm^{-1} (C=C); τ ($CDCl_3$) 2.58 (1 H, s, 2-H), 2.88 (5 H, m, Ph), 3.0 (1 H, d, *J* 1 Hz, 4-H), and 3.2 (1 H, d, *J* Hz,=C*H*Ph); $\lambda_{max.}$ 250 nm (ε 9 000).

2-*Methoxycarbonylimidazo*[2,1-a]*isoquinoline*-3-*carboxylic Acid* (12).—A stirred solution of 4-methoxycarbonyl-*trans*-1-styrylimidazole-5-carboxylic acid (2) (2.0 g) and iodine (0.17 g) was irradiated in methanol (1 l) through Pyrex. When u.v. spectroscopy indicated complete reaction (20 h) any free iodine was neutralised with sodium thiosulphate solution and the solution was evaporated to low bulk to precipitate the *imidazoisoquinoline* (1.1 g, 55%), m.p. 202—203° (with decarboxylation), as feathery white needles (from methanol) (Found: C, 61.95; H, 3.65; N, 10.15. $C_{14}H_{10}N_2O_4$ requires C, 62.35; H, 3.7; N, 10.35%); $\nu_{max.}$ 1 640 (C=O), 1 720 (C=O), and 2 650 cm^{-1} (O–H); τ ($CDCl_3$; 220 MHz) 0.5 (1 H, d, *J* 7.5 Hz, 5-H), 1.23 (1 H, m, 10-H), 2.25 (3 H, m, 7-,8-, and 9-H), 2.63 (1 H, d. *J* 7.5 Hz, 6-H), and 5.8 (3 H, s, CH_3); $\lambda_{max.}$ 318 (ε 4 420) and 256 nm (61 440).

Imidazo[2,1-a]*isoquinoline* (16).—(*a*) A stirred solution of *trans*-1-styrylimidazole (1.0 g) and iodine (0.15 g) in methanol (1 l) was irradiated through quartz. When u.v. spectroscopy indicated complete reaction (7 h) any free iodine was neutralised with sodium thiosulphate solution and the solvent was evaporated off. The residue was extracted with boiling light petroleum and the solution was refrigerated to yield imidazo[2,1-*a*]isoquinoline (0.12 g, 12%), identical with that synthesized by hydrolysis and decarboxylation of the half ester (12).

(*b*) The half ester (12) (0.2 g) was heated under reflux in concentrated hydrochloric acid (10 cm^3) for 2 h. The solution was cooled to precipitate imidazo[2,1-*a*]isoquinoline-2,3-dicarboxylic acid (0.19 g, 100%), m.p. 240° (with decarboxylation); $\nu_{max.}$ ε 1 600br cm^{-1} (CO_2^-) $M^{+\cdot}$ 256. The diacid (0.18 g) was heated under reflux in diethylene glycol (5 cm^3) for 1 min. The cooled solution was poured into water (50 cm^3) and extracted with chloroform. The extract was washed with water and dried ($MgSO_4$). Evaporation gave imidazo[2,1-*a*]isoquinoline (0.08 g, 64%), m.p. 93—94° (lit.,[15] 94—96°), as needles (from light petroleum) (Found: C, 78.15; H, 4.85; N, 16.5. Calc. for $C_{11}H_8N_2$: C, 78.55; H, 4.75; N, 16.65%); τ ($CDCl_3$) 1.3 (1 H, m, 10-H), 2.2 (1 H, d, *J* 7.5 Hz, 5-H), 3.07 (1 H, d, *J* 7.5 Hz, 6-H), 2.4 (3 H, m, 7-, 8-, and 9-H), 2.43 (1 H, d, *J* 1 Hz, 2-H), and 2.5 (1 H, d, *J* 1 Hz, 3-H); $\lambda_{max.}$ 294 (ε 4 700), 280 (7 130), 252 (54 480), and 243 nm (38 700) [lit.,[15] $\lambda_{max.}$ 294 (4 700), 280 (7 300), 252 (55 000), 243 (38 000), and 214 nm (8 000)]; *m/e* 169 (13%), 168 (100), 167 (5), 141 (7), 140 (5), 128 (7), 115 (5), 114 (20), 113 (5), 84 (6), and 43 (8),*m** 118.3 (168 ⟶ 141), 97.52 (168 ⟶ 128), and 92.17 (141 ⟶ 114).

Dimethyl Imidazo[2,1-a]*isoquinoline*-2,3-*dicarboxylate* (11).—(*a*) A stirred solution of the *trans*-olefin (3) (0.25 g) and iodine (0.03 g) in methanol (1 l) was irradiated through Pyrex. When u.v. spectroscopy indicated complete reaction (15 h) any free iodine was neutralised with sodium thiosulphate solution and the solvent was evaporated off. The residue was triturated with ether to yield the *cyclised diester* (0.11 g, 44%), identical with that synthesized by esterification of the half ester (12).

(*b*) The half ester (12) (0.5 g) was added in small amounts to ethereal diazomethane (0.5 g) and the solution was allowed to evaporate with stirring. The residue was filtered from the minimum of ether to yield the *diester* (11) (0.48 g, 91%), m.p. 165—166°, as needles (from benzene–light petroleum) (Found: C, 63.2; H, 4.2; N, 9.7. $C_{15}H_{12}N_2O_4$ requires C, 63.4; H, 4.25; N, 9.85%); $\nu_{max.}$ 1 710 (C=O) and 1 730 cm^{-1} (C=O); τ ($CDCl_3$) 1.25 (1 H, d, *J* 7.5 Hz, 5-H), 1.35 (1 H, m, 10-H), 2.4 (3 H, m, 7-, 8-, and 9-H), 2.85 (1 H, d, *J* 7.5 Hz, 6-H), 5.96 (3 H, s, 2-OCH_3), and 6.04 (3 H, s, 3-OCH_3); $\lambda_{max.}$ 333 (ε 4 310), 318 (4 540), 304 (3 630), 259sh (33 800), and 245 nm (62 600); $M^{+\cdot}$ 284 (42%).

Methyl Imidazo[2,1-a]*isoquinoline*-2-*carboxylate* (14).—(*a*) A stirred solution of the monoester (4) (1.14 g) and iodine (0.127 g) in methanol (1 l) was irradiated through quartz. When u.v. spectroscopy indicated complete reaction (14 h) any free iodine was neutralised with sodium thiosulphate solution and the solvent was evaporated off. The residue was dissolved in chloroform and washed with water. The dried ($MgSO_4$) solution was evaporated and the residue triturated with ether to yield the ester (14) (0.48 g, 44%), identical with that synthesized by decarboxylation of the half ester (12).

(*b*) The half ester (12) (0.2 g) was heated under reflux in diurethylformamide (5 cm^3) for 15 min. Water was added (to 20 cm^3) and the solution was refrigerated to yield the *ester* (0.13 g, 81%), m.p. 193—194°, as pale yellow needles

(from benzene) (Found: C, 69.2; H, 4.35; N, 12.15. $C_{13}H_{10}N_2O_2$ requires C, 69.0; H, 4.45; N, 12.4%); $\nu_{max.}$ 1 720 cm^{-1} (C=O); τ ($CDCl_3$) 1.2 (1 H, m, 10-H), 1.84 (1 H, s, 3-H), 2.13 (1 H, d, J 7 Hz, 5-H), 3.05 (1 H, d, J 7 Hz, 6-H), 2.35 (3 H, m, 7-, 8-, and 9-H), and 6.0 (3 H, s, CH_3); $\lambda_{max.}$ 248 (ε 55 680), 251sh (44 240), and 256sh nm (40 880); $M^{+\cdot}$ 226 (98%).

Benzimidazo[2,1-a]*isoquinoline* (20).—A stirred solution of *trans*-l-styrylbenzimidazole (0.8 g) and iodine (0.09 g) in methanol (1 l) was irradiated through quartz. When u.v. spectroscopy indicated complete reaction (15 h) any free iodine was neutralised with sodium thiosulphate solution and the solvent was evaporated off. The residue was extracted with boiling light petroleum to yield benzimidazo-[2,1-*a*]isoquinoline (0.42 g, 53%), m.p. 129—130° (lit.,[15] 129–130°), as pale yellow prisms (from light petroleum) (Found: C, 82.45; H, 4.8; N, 12.65. Calc. for $C_{15}H_{10}N_2$: C, 82.55; H, 4.6; N, 12.85%); τ ($CDCl_3$) 1.35 (1 H, m, 11-H), 2.1 (1 H, m, 1-H), 2.55 (1 H, d, J 7 Hz, 6-H), 2.7 (6 H, m, 2-, 3-, 4-, 8-, 9-, and 10-H), and 3.5 (1 H, d, J 7 Hz, 7-H); $\lambda_{max.}$ 349 (ε 6 100), 332.5 (7 500), 316 (8 560), 279 (49 440), 268 (35 800), and 257.5 nm (23 750); *m/e* 219 (17%), 218 (100), 217 (8), 109 (12), and 77 (5), *m* * 166 (218 ⟶ 190).

Benzimidazo[1,2-a]*quinoline* (22).—A stirred solution of *trans*-2-styrylbenzimidazole (0.5 g) and iodine (0.06 g) in methanol (1 l) was irradiated through Pyrex. When u.v. spectroscopy indicated complete reaction (88 h) any free iodine was neutralised with sodium thiosulphate solution and the solvent was evaporated off. The residue was extracted with boiling light petroleum and the solution was clarified and evaporated at room temperature to yield a white solid. Recrystallisation gave the benzimidazoquinoline (0.32 g, 64%), m.p. 101—102° (sintering at 75°) (lit.,[15] 102—103°) as needles [from ethanol–water (1 : 1)] of the hemihydrate [Found: C, 79.3; H, 4.65; N, 12.1. Calc. for $(C_{15}H_{10}N_2)_2H_2O$: C, 79.3; H, 4.85; N, 12.35%]; $\lambda_{max.}$ 366 (ε 6 000), 350 (10 300), 330 (12 200), 266 (24 700), 257 (28,400), 248.5 (32 700), and 236 nm (28 500); fluorescence: absorption $\lambda_{max.}$ 350 nm, emission $\lambda_{max.}$ 396 nm; τ ($CDCl_3$; 220 MHz) 1.65 (1 H, d, J 8.5 Hz, 11-H), 1.78 (1 H, d, J 8.5 Hz, 1-H), 2.02 (1 H, d, J 7 Hz, 4-H), 2.33 (1 H, q $J_{8,9}$ 8, $J_{8,10}$ 1.5 Hz, 8-H), 2.48 (2 H, s, 6- and 7-H), and 2.39—2.72 (4 H, m, 2-, 3-, 9-, and 10-H).

5,6-*Dimethyl*-1-(trans-p-*methylstyryl*)*benzimidazole* (23).—The hydrochloride of 4,5-dimethyl-*o*-phenylenediamine (3.44 g, 0.02 mol) was finely ground with *trans*-*p*-methylcinnamic acid (3.2 g, 0.02 mol). The resultant powder was heated at 180 °C for 1 h. A melt formed which solidified. The solid was washed with chloroform and dissolved in methanol. The solution was added to an excess of potassium hydrogen carbonate solution (200 cm^3) to precipitate the *olefin* (2.5 g, 50%), m.p. 234—235°, as needles (from ethyl acetate) (Found: C, 82.65; H, 6.8; N, 10.6. $C_{18}H_{18}N_2$ requires: C, 82.45; H, 6.85; N.10.7%); τ ($CDCl_3$) 2.5—3.1 (8 H, m, aromatic and olefinic), 6.67 (6 H, s, 5- and 6-CH_3), and 7.7 (3 H, s, *p*-CH_3); $\lambda_{max.}$ 360sh (ε 24 000), 344 (39 000), 268 (12 700), 259sh (10 300), 238sh (10 300), and 208 nm (36 300); *m/e* 263 (5%), 262 (40), 261 (100), 260 (5), 246 (5), 245 (8), 132 (10), 131 (8), 124 (9), 118 (14), 117 (16), 116 (7), 92 (5), 65 (5), and 39 (5), *m** 260 (262 ⟶ 261).

2,3,10-*Trimethylbenzimidazo*[1,2-a]*quinoline* (25).—A stirred solution of 5,6-dimethyl-1-(*trans*-*p*-methylstyryl)benzimidazole (23) (1.0 g) and iodine (0.05 g) in methanol (1 l) was irradiated through Pyrex. When u.v. spectroscopy indicated complete reaction (1 week) any free iodine was neutralised with sodium thiosulphate solution and the solvent was evaporated off. The residue was extracted with chloroform and the extract washed with water, dried ($MgSO_4$), and evaporated to an oil which was purified by elution through a column of neutral alumina with chloroform. The fast-running yellow band was collected and the solvent was evaporated off to yield the *benzimidazo*[1,2-a]*quinoline* (0.27 g, 27%), m.p. 177—178°, as pale yellow needles (from ether) (Found: C, 82.85; H, 6.2; N, 10.7. $C_{18}H_{16}N_2$ requires C, 83.1; H, 6.15; N, 10.75%); τ ($CDCl_3$; 220 MHz) 2.02 (1 H, s, 11-H), 2.19 (1 H, s, 1-H), 2.37 (1 H, s, 4-H), 2.54 (1 H, d, J 8 Hz, 8-H), 7.5 (3 H, s. 10-CH_3), 7.6 (3 H, s, 3-CH_3), and 7.65 (3 H, s, 2-CH_3); $\lambda_{max.}$ 373 (ε 7 400), 354.5 (12 900), 338 (14 650), 283sh (6 300), 253 (34 700), and 244.5 nm (36 200).

We thank the S.R.C. for a post-graduate research studentship (to G. C.).

[5/1047 *Received*, 2nd *June*, 1975]