Decomposition of Some Substituted Azidoindoles and Azidohexahydrocarbazoles

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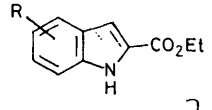
Photolytic and thermal decomposition of some substituted azidoindoles and azidohexahydrocarbazoles in nucleophilic solvents yields synthetically useful *o*-substituted aminoindoles. The conversion of 9-acetyl-7-azidohexahydrocarbazole in secondary amines on irradiation into an indoloazepine provides the first example of the expansion of a tricyclic hetero-system *via* a nitrene intermediate. Some cycloaddition reactions of these azides with dimethyl acetylenedicarboxylate are also reported.

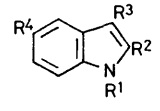
We report the results of a study of the photolytic and thermal decomposition of some substituted azidoindoles and azidohexahydrocarbazoles in nucleophilic solvents. This work was carried out to establish whether these azides would ring expand to pyrroloazepines under these conditions (like typical monocyclic aromatic azides [1]) or yield *o*-substituted amines (like typical bicyclic aromatic azides [2]).

The new azidoindoles (1a—d), (4), and (7) were prepared in two steps from the corresponding nitroindoles (2a—d), (5), and (8) (obtained by Fischer cyclisation) by reduction to the amines (3a—d), (6), and (9) followed by diazotisation and treatment with sodium azide to give the azidoindoles. The azide (4) was made from ethyl 5-nitroindole-2-carboxylate by methylation at the 1-position, accompanied by hydrolysis, and subsequent re-esterification with acidic ethanol.

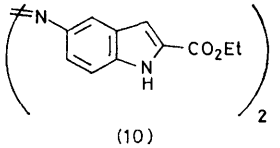
Photolytic decomposition of ethyl 5-azidoindole-2-carboxylate (1b) in a large excess of morpholine using a medium-pressure mercury lamp with a Pyrex filter, gave



(1a—d) R = N_3
(2a—d) R = NO_2 } 4-,5-,6-, and 7- isomers, respectively
(3a—d) R = NH_2

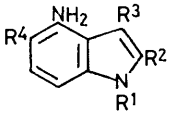


(4) R^1 = Me, R^2 = CO_2Et, R^3 = H, R^4 = N_3
(5) R^1 = Me, R^2 = CO_2Et, R^3 = H, R^4 = NO_2
(6) R^1 = Me, R^2 = CO_2Et, R^3 = H, R^4 = NH_2
(7) R^1 = COMe, R^2 = R^3 = Me, R^4 = N_3
(8) R^1 = COMe, R^2 = R^3 = Me, R^4 = NO_2
(9) R^1 = COMe, R^2 = R^3 = Me, R^4 = NH_2

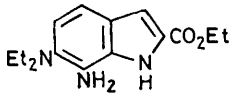


(10)

ethyl 4-amino-5-morpholinoindole-2-carboxylate (11) in 69% yield. Photolysis of this azide in other secondary amines also produced these rather less easily accessible *o*-dialkylamino-substituted aminoindole derivatives (12)—(16), in yields of 30—69%. The structures assigned to



(11) R^1 = R^3 = H, R^2 = CO_2Et, R^4 = O(morpholino)-N-
(12) R^1 = R^3 = H, R^2 = CO_2Et, R^4 = Et_2N
(13) R^1 = R^3 = H, R^2 = CO_2Et, R^4 = Pr^n_2N
(14) R^1 = R^3 = H, R^2 = CO_2Et, R^4 = C_4H_8N
(15) R^1 = R^3 = H, R^2 = CO_2Et, R^4 = $C_5H_{10}N$
(16) R^1 = R^3 = H, R^2 = CO_2Et, R^4 = $C_6H_{12}N$
(17) R^1 = Me, R^2 = CO_2Et, R^3 = H, R^4 = Et_2N
(18) R^1 = Me, R^2 = CO_2Et, R^3 = H, R^4 = O(morpholino)-N-



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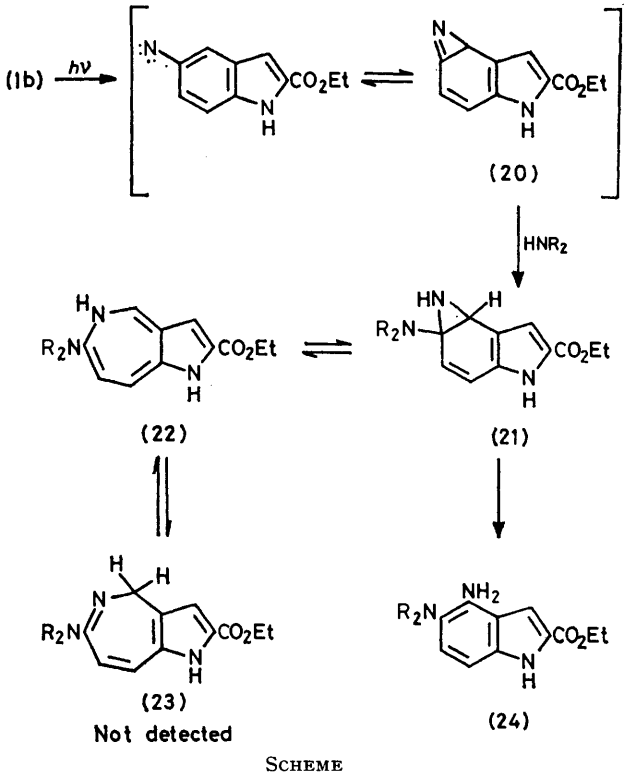
these diamines are based on spectroscopic data. 4-Amino-5-morpholinoindole-2-carboxylate (11) has i.r. absorptions at 3 450 and 3 350 (NH_2), 3 320 (indole >N–H), and 1 690 cm^{-1} (>C=O). Broad signals in the n.m.r. spectrum at τ 6.34 (β-CH_2) and 7.31 (α-CH_2) indicate the incorporation of morpholine. The aromatic region shows two AB doublets at τ 3.36 and 3.14 assigned to 6- and 7-H respectively, whilst the 3-H signal appears as a singlet at τ 2.68. The mass spectrum gave the correct molecular ion, M^+ 289. The above spectral data did not allow us to distinguish between structure (11) and the isomeric ethyl 5-amino-4-morpholinoindole-2-carboxylate. However, irradiation at the frequency of the amino protons (τ 4.82) resulted in a 20% increase in intensity of the signal of the 3-proton (τ 2.68), while the intensity of the 6-proton signal remained unchanged, which confirms the proposed structure (11) [nuclear Overhauser effect (n.O.e.)].

Photolysis of ethyl 5-azidoindole-2-carboxylate in diethylamine gives approximately the same yield of diamine (12) whether a Pyrex filter or quartz is used. In the presence of pyrene, a singlet sensitiser for photolysis of 2-azidobiphenyl,[3] the yield of (12) was unaffected, which is consistent with a recent observation on decomposition of monocyclic aryl azides.[4] The 5-azido-1-

methylindole-2-carboxylate (4) behaved like (16) on photolysis in diethylamine and morpholine and gave similar yields of the corresponding diamines (17) and (18), but the azidoindole (7) formed only intractable tars on photolysis in diethylamine.

Photolysis of ethyl 6-azidoindole-2-carboxylate (1c) in diethylamine gave the diamine (19) in 55% yield, identified from its i.r., n.m.r., and mass spectra. Irradiation at the frequency of the 7-amino group (τ 5.76) induced an n.O.e. enhancement (18%) in the indole N–H proton



SCHEME

signal at τ 1.32. The 4- and the 7-azidoindoles (1a) and (1d), on photolysis in diethylamine, did not give the anticipated diamines. The former gave intractable tars, whilst the 7-azido-isomer gave (3d); primary arylamines as products from aryl azide photolysis are ascribed to decomposition *via* triplet nitrenes.

Formation of the *o*-diamines is believed to occur as in the Scheme. Nucleophilic attack by the solvent (a secondary amine) on the benzazirine (20) takes place rapidly to give the aziridine (21) which may rearomatise to give the observed *o*-diamine products (24). Alternatively, the aziridine (21) may ring-expand to the azepine (22) which may then rearrange to the azepine (23). No evidence for pyrroloazepine products of the types (22) and (23) from the decomposition of the above azidoindoles has been found, although reaction mixtures were examined very carefully because such azepines have been found in other bicyclic aromatic azide decompositions.[5] The Scheme also accommodates the observed formation of the diamine (19) on photolysis of ethyl 6-azidoindole-2-carboxylate, where the azido group is again β to the ring junction (naphthalene nomenclature). On the other hand, on photolysis in diethylamine, 4- and 7-azidoindoles (1a) and (1d), in which the azido groups are α to the ring junction, do not give *o*-diamines as might be expected, but mainly tars.

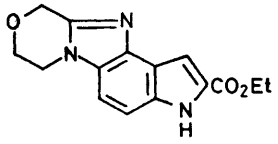
In order to examine the generality of the nucleophilic attack in the Scheme, *i.e.* conversion of (20) into (21), ethyl 5-azidoindole-2-carboxylate (1b) was decomposed in some other nucleophilic solvents. Irradiation of (1b) in butane-1-thiol gave ethyl 4-amino-5-(butylthio)-indole-2-carboxylate (40%), one of the few examples of an aryl azide reacting with a sulphur nucleophile,[6] together with a trace of the triplet-derived product (3b). Photolytic decomposition of (1b) in aniline gave the azo-compound (10) (3%) and azobenzene. No other azo-compounds were found.

Thermolysis does not appear to provide a synthetically useful alternative method of converting azidoindoles into *o*-diamines.

Several *o*-azido-*N*-alkylaminoquinolines have been decomposed (thermally and photolytically) to give imidazoquinolines in synthetically useful yields.[7] By analogy, ethyl 4-azido-5-morpholinoindole-2-carboxylate [prepared from (11) by diazotisation followed by addition of sodium azide] on thermolysis in bromobenzene gave the imidazo[4,5-*e*]indole (25) which demonstrates the synthetic utility of these diamines. The intermediate dihydroimidazoindole would spontaneously aromatise.

The absence of any azepines as products from these azidoindole decompositions may be attributed [2] mainly to the effect of the annelated pyrrole ring upon the azidobenzene ring undergoing decomposition. To test this view the azidohexahydrocarbazoles (26a—c), in which no aromatic ring is fused to the benzene ring, were decomposed in a series of secondary amines. These azides were prepared from the corresponding aminohexahydrocarbazoles (27a—c) obtained by a new convenient one-stage reduction procedure involving hydrogenation at 50 atm and 25 °C of the corresponding nitrotetrahydrocarbazole (27d) over 5% Pd–C in ethyl acetate–ethanol. All the new amines and azides shared the expected spectral and analytical data. Photolytic decomposition of 9-acetyl-5-azido-1,2,3,4,4a,9a-hexahydrocarbazole (26a) in morpholine or diethylamine produced dark polymeric material. Only 9-acetyl-6-amino-1,2,3,4,10,11-hexahydrocarbazole (27b) could be isolated from the photolysis of the corresponding azide in several secondary amines. In contrast, 9-acetyl-7-azido-1,2,3,4,4a,9a-hexahydrocarbazole (26c) on irradiation in secondary amines, gave a series of dialkylaminohexahydroazepino[3,4-*b*]indoles (28)—(31) in good yields. The structures of these azepines were assigned from spectroscopic data. For instance, the i.r. spectrum of (29) is devoid of any N–H stretching absorption and shows a large band at 1 650 cm^{-1} (>C=O) as well as an absorption at 1 610 cm^{-1} (>C=N). The n.m.r. spectrum contains a broad multiplet between τ 7.90 and 9.20 which corresponds to the four methylenes of the cyclohexane ring. The 5b- and 9a-protons give broad singlets at τ 6.68 and 5.90 and the

acetyl signal is at τ 7.85. A large singlet at τ 6.39 is assigned to the four methylenes of the morpholino group.



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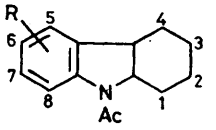
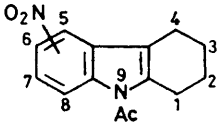
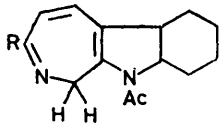


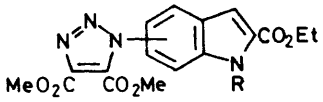
(26 a—c) R = N_3, 5-, 6-, and 7- isomer, respectively
(27 a—c) R = NH_2, 5-, 6-, and 7- isomer, respectively



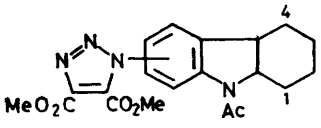
(27d)



(28) R = Et_2N-
(29) R = 
(30) R = $C_5H_{10}N$-
(31) R = C_4H_8N-



(32a) R = H ; 5- isomer
(32b) R = H ; 6- isomer
(32c) R = H ; 7- isomer
(33) R = Me 5- isomer



(34a) 6 - isomer
(34b) 7 - isomer

The 4- and 5-H (seven-membered ring) give two vicinal coupled doublets at τ 2.95 and 4.32, respectively ($J_{4,5}$ 8 Hz). The two CH_2 protons at the 1-position give two doublets at τ 5.38 and 7.55 which show typical geminal coupling (J 13 Hz). One of these signals (τ 7.55) appears at a high field owing to the anisotropic shielding effect of the adjacent carbonyl group. Confirmation that these two protons were coupled to each other was obtained by irradiation at τ 7.55 when the doublet at τ 5.38 collapsed to a singlet. This provides the first example of a tricyclic system undergoing ring expansion by this method.

Many examples are known of azides behaving as 1,3-dipoles in addition reactions with dipolarophiles (*e.g.* acetylenic esters).[8] This reaction was extended to some of the new azidoindoles (1b), (1d), and (4) and azidohexahydrocarbazoles (26b and c) to provide some novel triazole systems. The azides were heated in refluxing chloroform with dimethyl acetylenedicarboxylate which gave the 1-substituted 1,2,3-triazoles (32)—(34) in quantitative yield.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer and ^1H n.m.r. spectra on a Varian EM360 or a Perkin-Elmer R32 instrument (tetramethylsilane as internal standard). Low resolution mass spectra were recorded on an A.E.I. MS12 and high resolution spectra on an A.E.I. MS9 spectrometer.

Light petroleum refers to the fraction of b.p. 60—80 °C.

Azides were photolysed with a medium-pressure mercury vapour lamp with a Pyrex filter unless stated otherwise.

Yields quoted are based on starting material consumed.

Spectral data of the new aminoindoles, azidoindoles, and azido- and amino-hexahydrocarbazoles are available as supplementary Publication No. SUP 22332 (6 pp.).*

Nitroindoles (2a—d).—These were prepared from the appropriate nitrophenylhydrazones by the Fischer cyclisation method.[9] Yields and m.p.s are given in Table 1.

1-Methyl-5-nitroindole-2-carboxylic Acid.—Dimethyl sulphate (56.7 g) was added dropwise to a stirred solution of ethyl 5-nitroindole-2-carboxylate (52.2 g, 0.223 mol) in a mixture of acetone (360 ml) and aqueous 50% potassium hydroxide (101.7 g). The mixture was refluxed for 3 h and cooled. The precipitated potassium salt was collected by filtration, washed with a small volume of cold acetone, and dissolved in hot water (2 l). The solution was filtered while hot and acidified with concentrated hydrochloric acid. On cooling, a white crystalline solid precipitated which was filtered off, washed with water, and dried to yield the *acid* (34.4 g, 70%), m.p. 265—266° (from benzene–ethanol), $\nu_{max.}$ (Nujol) 1 710 cm^{-1} (C=O), τ ($CDCl_3$) 7.48br (CO_2H), 5.92 (s, NMe_3), 2.62 (s, 4-H), 2.38 and 1.95 (d, J 9 Hz, 6- and 7-H), and 1.40 (s, 3-H), *m/e* 220 (M^+) (Found: C, 54.2; H, 3.6; N, 12.8. $C_{10}H_8N_2O_4$ requires C, 54.55; H, 3.7; N, 12.7%).

Ethyl 1-Methyl-5-nitroindole-2-carboxylate (5).—1-Methyl-5-nitroindole-2-carboxylic acid (31.0 g) was refluxed in ethanol (750 ml) and concentrated sulphuric acid (20 ml). After 70 h no starting material remained (t.l.c.). The ethanol was removed on a rotary evaporator and ice–water added. The crude product was filtered off under vacuum and dried to afford the *ethyl ester* (28.4 g, 81%), m.p. 155—156° (from ethanol) (Found: C, 57.9; H, 4.8; N, 11.35. $C_{12}H_{12}N_2O_4$ requires C, 58.05; H, 4.85; N, 11.3%).

2,3-Dimethyl-5-nitroindole was prepared by a known method [10] from 4-nitrophenylhydrazone (69%); m.p. 184° (lit., 184°). 1-Acetyl-2,3-dimethyl-5-nitroindole (8) was prepared by the method of Simpson and his co-workers; [11] yield 87%, m.p. 108—109° (lit.,[11] 109°).

Aminoindoles.—General procedure. The appropriate nitro-compound (12 g) was dissolved in ethyl acetate (200 ml) and ethanol (400 ml) and reduced, at room temperature in an autoclave, under 50 atm of hydrogen, using 5% palladium–charcoal as catalyst. After 24 h the mixture was removed from the autoclave and the catalyst was filtered off. Removal of the solvent gave the amine, which was then recrystallised. Yields and m.p.s for the products are given in Table 1 and spectroscopic data appear in the Supplementary Publication.

Azidoindoles.—General procedure. The appropriate amino compound (4 g) was dissolved in dilute hydrochloric acid (30 ml; conc. HCl–H_2O 1 : 1 v/v) and cooled rapidly to form a fine suspension of the hydrochloride. The mixture was

* See Notice to Authors No. 7 in *J.C.S. Perkin I*, 1977, Index issue.

diazotized at 0 °C with aqueous sodium nitrite (30%; 8 ml). Addition of the diazonium salt to a cooled solution of sodium azide (excess) and sodium acetate (large excess) precipitated the azide. The azide was extracted with chloroform (3 × 200 ml) and the extracts were combined, decolourised with carbon, and dried ($MgSO_4$). Removal of the solvent gave the azide. All the azides were purified by column chromatography. Yields and m.p.s for the products are given in Table 1 and spectroscopic data appear in the Supplementary Publication.

Photolysis of Azidoindole Derivatives in Amines.—General procedure. The secondary amines were distilled and dried over caustic alkali pellets before use. A solution of the azide (1 g) in the amine (100 ml) was prepared and purged with nitrogen for at least 10 min prior to photolysis. The stirred solution was irradiated at room temperature under nitrogen, using a water-cooled immersion well containing a medium-pressure mercury arc. Each reaction was monitored by observing the disappearance of the azide i.r. band. After the azide peak had disappeared the amine was distilled off under vacuum and the residue was chromatographed on alumina (type H).

Photolysis of Ethyl 5-Azidoindole-2-carboxylate (1b).—(a) *In diethylamine.* The azide in diethylamine (1% solution) was irradiated for 10 h. Chromatography of the product [light petroleum–benzene (1 : 1) as eluant] gave *ethyl 4-amino-5-(diethylamino)indole-2-carboxylate* (12) (0.26 g, 27%), m.p. 106° (from ethanol), $\nu_{max.}$ (Nujol) 3 305 (NH), 3 385 and 3 130 (NH_2), and 1 710 cm^{-1} (C=O), τ ($CDCl_3$) 9.02 (t, *J* 7 Hz, ethyl Me), 8.53 (t, *J* 7 Hz, ester Me), 7.00 (q, *J* 7 Hz, ethyl CH_2), 5.52 (q, *J* 7 Hz, ester CH_2), 5.50br (exchangeable, NH_2), 3.17 and 2.83 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.74 (3-H), 0.38br (exchangeable H, NH), *m/e* 275 (M^+) (Found: C, 65.55; H, 7.7; N, 15.2. $C_{15}H_{21}N_3O_2$ requires C, 65.4; H, 7.7; N, 15.3%). Elution with benzene–ether (1 : 1) gave *diethyl 5,5′-azoindole-2,2′-dicarboxylate* (10) (0.012 g, <1%), m.p. 315° (from ethanol), $\nu_{max.}$ (Nujol) 3 335 (NH) and 1 695 cm^{-1} (C=O), τ ($CDCl_3$–DMSO) 8.60 (t, *J* 7 Hz, Me), 5.60 (q, *J* 7 Hz, CH_2), 6.50 (s, exchangeable, NH), 2.70 (4-H), 2.40 and 1.90 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), and 1.41 (3-H), *m/e* 404 (M^+) (Found: C, 65.3; H, 5.0; N, 13.9. $C_{22}H_{20}N_4O_4$ requires C, 65.3; H, 5.0; N, 13.9%).

(b) *In dipropylamine.* The azide in dipropylamine (1% solution) was irradiated for 10 h. Chromatography of the product using light petroleum–benzene (1 : 1) as eluant gave *ethyl 4-amino-5-dipropylaminoindole-2-carboxylate* (13) 0.33 g, 31%), m.p. 107—108° (from light petroleum), $\nu_{max.}$ (Nujol) 3 310 (NH), 3 480 and 3 370 (NH_2), and 1 695 cm^{-1} (C=O), τ ($CDCl_3$) 9.15 (t, *J* 7 Hz, propyl Me), 8.60 (m, ester Me and propyl β-CH_2), 7.13 (t, *J* 7 Hz, propyl α-CH_2), 5.54 (q, *J* 7 Hz, ester CH_2), 5.40br (exchangeable, NH_2), 3.20 and 2.84 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.77 (3-H), and 0.83br (exchangeable, NH), *m/e* 303 (M^+) (Found: C, 67.3; H, 8.4; N, 14.0. $C_{17}H_{25}N_3O_2$ requires C, 67.3; H, 8.3; N, 13.9%). Elution with benzene gave diethyl 5,5′-azoindole-2,2′-dicarboxylate (0.05 g, 3.5%), identical with the product obtained in (a).

(c) *In morpholine.* The azide in morpholine (1% solution) was irradiated for 10 h and the product purified as described in (a). *Ethyl 4-amino-5-morpholinoindole-2-carboxylate* (11) (0.69 g, 69%), had m.p. 176—177° (from benzene), $\nu_{max.}$ (Nujol) 3 320 (NH), 3 450 and 3 350 (NH_2), and 1 690 cm^{-1} (C=O), τ (DMSO) 8.72 (t, *J* 7 Hz, ethyl Me), 7.31 (m, NCH_2), 6.34 (m, OCH_2), 5.77 (q, *J* 7 Hz, ethyl CH_2), 4.82br (exchangeable, $NH)_2$, 3.36 and 3.14 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.68 (3-H), 0.69br (exchangeable, NH), *m/e* 289 (M^+) (Found: C, 62.3; H, 6.6; N, 14.5. $C_{15}H_{19}N_3O_3$ requires C, 62.3; H, 6.6; N, 14.5%); the *acetyl derivative* (61%) had m.p. 229—230° (from methanol), $\nu_{max.}$ (Nujol) 3 315 (indole NH), 3 365 (amide NH), and 1 690—1 705 cm^{-1} (acetyl C=O and ester C=O), τ ($CDCl_3$) 8.69 (t, *J* 7 Hz, ethyl Me), 7.76 (s, acetyl Me), 7.30 (m, NCH_2), 6.31 (m, OCH_2), 5.75 (q, *J* 7 Hz, ethyl CH_2), 3.30 and 3.09 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.61 (3 H), 1.82br (exchangeable, amide NH), 0.74br (exchangeable, indole NH), *m/e* 331 (M^+) (Found: C, 62.05; H, 6.45; N, 12.6. $C_{17}H_{21}N_3O_4$ requires C, 61.6; H, 6.4; N, 12.7%).

(d) *In piperidine.* The azide in piperidine (1% solution) was irradiated for 12 h and treated as described in (a). *Ethyl 4-amino-5-piperidinoindole-2-carboxylate* (15) (0.41 g, 41%), m.p. 160—161° (from benzene), $\nu_{max.}$ (Nujol) 3 310 (NH), 3 390 and 3 250 (NH_2), and 1 700 cm^{-1} (C=O), τ [$(CD_3)_2CO$] 8.60 (t, *J* 7 Hz, ethyl Me), 8.34br (β- and γ-CH_2), 7.16br (α-CH_2), 5.59 (q, *J* 7 Hz, ethyl CH_2), 5.10br (ex-

TABLE 1

Nitro-, amino-, and azido-indoles

Compound	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(1b)	25	141—143	57.4	4.25	24.3	$C_{11}H_{10}N_4O_2$	57.4	4.4	24.3
(4)	78	64—65	59.2	4.9	22.9	$C_{12}H_{12}N_4O_2$	59.0	4.95	22.9
(7)	51	93—94	63.3	5.1	24.7	$C_{12}H_{12}N_4O$	63.15	5.3	24.55
(1a)	17	123—125	57.4	4.3	24.5	$C_{11}H_{10}N_4O_2$	57.4	4.4	24.3
(1c)	22	136—137	57.4	4.2	24.3	$C_{11}H_{10}N_4O_2$			
(1d)	22	113—115	*d*			$C_{11}H_{10}N_4O_4$			
(2b)	73	224—225 [a]							
(5)	81	155—156	57.9	4.8	11.35	$C_{12}H_{12}N_2O_4$	58.1	4.9	11.3
(8)	87	108—109 [b]							
(2a)	34	228—230 [a]							
(2c)	23	194—196 [a]							
(2d)	63	91—92 [a]							
(3b)	94	126—127 [c]							
(6)	97	79—80	65.9	6.6	12.9	$C_{12}H_{14}N_2O_2$	66.0	6.5	12.8
(9)	90	96—98	71.4	6.9	13.8	$C_{12}H_{14}N_2O$	71.3	7.0	13.85
(3a)	92	121—122	64.6	6.0	13.8	$C_{11}H_{12}N_2O_2$	64.7	5.9	13.7
(3c)	94	130—131	64.5	5.9	13.9	$C_{11}H_{12}N_2O_2$			
(3d)	89	108—109	64.8	5.8	13.6	$C_{11}H_{12}N_2O_2$			

[a] S. M. Parmerter, A. G. Cook, and W. B. Dixon, *J. Amer. Chem. Soc.*, 1958, **80**, 4621. [b] C. M. Atkinson, J. C. E. Simpson, and A. Taylor, *J. Chem. Soc.*, 1954, 165. [c] H. Lindwall and G. J. Mantell, *J. Org. Chem.*, 1953, **18**, 345. [d] Did not give a satisfactory analysis.

changeable, NH_2), 3.12 and 2.80 ($J_{6,7}$ 9 Hz, 6- and 7-H), 2.60 (3-H), and 1.10br (exchangeable, NH), *m/e* 287 (M^+) (Found: C, 67.1; H, 7.4; N, 14.65. $C_{16}H_{21}N_4O_2$ requires C, 66.9; H, 7.4; N, 14.6%).

(e) *In pyrrolidine.* The azide in pyrrolidine (1% solution) was irradiated for 10 h. *Ethyl 4-amino-5-pyrrolidin-1-yl)-indole-2-carboxylate* (14) (0.31 g, 33%), had m.p. 189—190° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3 335 (NH), 3 430 (NH of NH_2; second absorption masked by indole NH), and 1 675 cm^{-1} (C=O), τ ($CDCl_3$) 8.67 (t, *J* 7 Hz, ethyl Me), 8.10br (β-CH_2), 7.10br (α-CH_2), 5.70 (q, *J* 7 Hz, ethyl CH_2), 5.85br (exchangeable, NH_2), 2.90 (m, 3- and 7-H), 3.38 (d, $J_{6,7}$ 9 Hz, 6-H), and 1.10br (exchangeable, NH), *m/e* 273 (M^+) (Found: C, 66.1; H, 7.2; N, 15.2. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%).

(f) *In perhydroazepine.* The azide in hexamethyleneimine (1% solution) was irradiated for 9 h. *Ethyl 4-amino-5-(perhydroazepin-1-yl)indole-2-carboxylate* (16) (0.37 g, 35%), had m.p. 148° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3 340 (NH), 3 460 (NH of NH_2; second absorption masked by indole NH), and 1 685 cm^{-1} (C=O), τ ($CDCl_3$) 8.69 (t, *J* 7 Hz, ethyl Me), 8.31br (β- and γ-CH_2), 7.05br (α-CH_2), 5.69 (q, *J* 7 Hz, ethyl CH_2), 5.20br (exchangeable, NH_2), 3.25 and 2.95 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.82 (3-H), and 1.09br (exchangeable, NH), *m/e* 301 (M^+) (Found: C, 68.2; H, 7.9; N, 13.9. $C_{17}H_{23}N_3O_2$ requires C, 67.75; H, 8.0; N, 13.9%); the *acetyl derivative* (56%) had m.p. 179—180° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3 335 (NH; NH of amide masked by indole NH), and 1 680—1 700 cm^{-1} (acetyl C=O and ester C=O), *m/e* 343 (M^+) (Found: C, 66.5; H, 7.5; N, 12.1. $C_{19}H_{25}N_3O_3$ requires C, 66.65; H, 7.1; N, 12.3%).

(g) *In diethylamine with pyrene.* Pyrene was added to a 1% solution of the azide in diethylamine (2 mol of pyrene to 1 mol of azide) which was irradiated for 10 h as described for (a). The pyrene was recovered quantitatively by chromatography of the reaction residue, using light petroleum (b.p. 60—80°) as eluant. Further elution with light petroleum–benzene (1 : 1) gave a product (0.25 g, 26%) identical with that obtained in (a).

(h) *In diethylamine.* The azide in diethylamine (1% solution) was irradiated for 10 h as described above, but using a quartz filter. The product (0.19 g, 20%) was identical with that obtained in (a).

(i) *In butane-1-thiol.* The azide was relatively insoluble in butane-1-thiol. Therefore, a 1% solution was prepared in dichloromethane–butane-1-thiol (1 : 1). The solution was irradiated for 40 h; chromatography of the product [benzene–diethyl ether (1 : 1) as eluant] gave *ethyl 4-amino-5-(butylthio)indole-2-carboxylate* (0.41 g, 40%), b.p. 237—240° at 0.1 mmHg, $\nu_{max.}$ (Nujol) 3 330 (NH), 3 450 (NH of NH_2; second absorption masked by indole NH), and 1 700 cm^{-1} (C=O), τ ($CDCl_3$) 8.2—9.4 (m, butyl CH_2CH_2Me and ethyl Me), 7.32 (t, *J* 7 Hz, SCH_2), 5.97br (exchangeable. NH_2), 5.70 (q, *J* 7 Hz, ethyl CH_2), 3.35 and 2.92 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.79 (3-H), and 0.30br (exchangeable, NH) (Found: M^+, 292.1244. $C_{15}H_{20}N_2O_2S$ requires *M*, 292.1245). Elution with benzene–diethyl ether (1 : 1) gave a trace of diethyl 5,5′-azoindole-2,2′-dicarboxylate, identical with the product obtained in (a).

(j) *In aniline.* The azide in aniline (1% solution) was irradiated for 10 h to give azobenzene (0.04 g). Elution with benzene–diethyl ether (1 : 1) gave diethyl 5,5′-azoindole-2,2′-dicarboxylate (0.04 g, 3.0%), identical with the product obtained in (a).

Photolysis of Ethyl 5-Azido-1-methylindole-2-carboxylate.—(a) *In diethylamine.* The azide in diethylamine (1% solution) was irradiated for 5 h to afford *ethyl 4-amino-5-diethylamino-1-methylindole-2-carboxylate* (17) (0.28 g, 30%), m.p. 63—64° (from light petroleum), $\nu_{max.}$ (Nujol) 3 480 and 3 380 (NH_2) and 1 700 cm^{-1} (C=O), τ ($CDCl_3$) 9.05 (t, *J* 7 Hz, ethyl Me), 8.63 (t, *J* 7 Hz, ester Me), 7.07 (q, *J* 7 Hz, ethyl CH_2), (s, NMe), 6.00 (q, *J* 7 Hz, ester CH_2), 5.60br (exchangeable, NH_2), 3.27 and 2.86 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), 2.75 (3-H), *m/e* 289 (M^+) (Found: C, 66.3; H, 8.0; N, 14.6. $C_{16}H_{23}N_3O_2$ requires C, 66.4; H, 8.0; N, 14.5%). Elution with benzene gave *diethyl 5,5′-azo-1,1′-dimethylindole-2,2′-dicarboxylate* (0.03 g, 2%), m.p. 218° (from benzene), $\nu_{max.}$ (Nujol) 1720 cm^{-1} (C=O), τ ($CDCl_3$) 8.58 (t, *J* 7 Hz, ethyl Me), 5.89 (s, NMe), 5.59 (q, *J* 7 Hz, ethyl CH_2), 2.56 (4-H), 2.69 and 1.94 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), and 1.72 (3-H), *m/e* 432 (M^+) (Found: C, 66.6; H, 6.67; N, 12.75. $C_{24}H_{24}N_4O_4$ requires C, 66.65; H, 5.56; N, 12.95%).

(b) *In morpholine.* The azide in morpholine (1% solution) was irradiated for 5 h. *Ethyl 4-amino-1-methyl-5-morpholinoindole-2-carboxylate* (18) (0.65 g, 65%), had m.p. 155—156° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3 450 and 3 360 (NH_2) and 1 705 cm^{-1} (C=O), τ ($CDCl_3$) 8.63 (t, *J* 7 Hz, ethyl Me), 7.14 (m, NCH_2), 6.15 (m, OCH_2), 5.61 (q, *J* 7 Hz, ethyl CH_2), 6.02 (s, NMe), 5.60br (exchangeable, NH_2), 3.30 and 2.86 (d, $J_{6,7}$ 9 Hz, 6- and 7-H), and 2.76 (3-H), *m/e* 303 (M^+) (Found: C, 63.9; H, 7.0; N, 13.8. $C_{16}N_{21}N_3O_3$ requires C, 63.35; H, 7.0; N, 13.85%).

Photolysis of 1-Acetyl-5-azido-2,3-dimethylindole in Diethylamine.—The azide in diethylamine (1% solution) was irradiated for 13 h. Chromatography of the residue gave intractable material.

Photolysis of Ethyl 6-Azidoindole-2-carboxylate in Diethylamine.—The azide in diethylamine (1% solution) was irradiated for 7 h. The product, *ethyl 7-amino-6-(diethylamino)indole-2-carboxylate* (19) (0.53 g, 55%), had m.p. 132—133° (from benzene–light petroleum), $\nu_{max.}$ (Nujol) 3 320 (NH), 3 410 and 3 230 (NH_2), and 1 680 cm^{-1} (C=O), τ ($CDCl_3$) 8.98 (t, *J* 7 Hz, ethyl Me), 8.60 (t, *J* 7 Hz, ester Me), 6.80 (q, *J* 7 Hz, ethyl CH_2), 5.76br (exchangeable, NH_2), 5.58 (*J* 7 Hz, ester CH_2), 2.61 and 3.30 (d, $J_{4,5}$ 9 Hz, 4- and 5-H), 2.78 (3-H), and 1.32br (exchangeable, NH), *m/e* 275 (M^+) (Found: C, 65.4; H, 7.7; N, 15.2. $C_{15}H_{21}N_3O_2$ requires C, 65.4; H, 8.0; N, 15.3%).

Photolysis of Ethyl 4-Azidoindole-2-carboxylate in Diethylamine.—The azide in diethylamine (1% solution) was irradiated for 2½ h. Chromatography of the residue gave intractable polymeric material.

Photolysis of Ethyl 7-Azidoindole-2-carboxylate in Diethylamine.—The azide in diethylamine (1% solution) was irradiated for 2 h. The product, ethyl 7-aminoindole-2-carboxylate (3d) (0.16 g, 23%), was identical with that prepared previously.

Thermolysis of Ethyl 5-Azidoindole-2-carboxylate.—(a) *In diethylamine.* A solution of the azide (0.8 g, 0.0035 mol) in diethylamine (50 ml) was purged with nitrogen and heated at 140 °C in a pressure vessel. After 24 h the reaction was discontinued and the amine was distilled off under vacuum. The residue was chromatographed on an alumina (type H) column, yielding only intractable polymeric material.

(b) *In perhydroazepine.* A solution of the azide (0.8 g, 0.0035 mol) in perhydroazepine (50 ml) was purged with nitrogen and heated under reflux until all the azide had decomposed (6 h) (i.r. solution spectra). The amine was dis-

tilled off under vacuum and the residue chromatographed on alumina (type H). Elution with benzene gave ethyl 4-amino-5-perhydroazepin-1-yl)indole-2-carboxylate (0.037 g, 3.5%). Elution with benzene–diethyl ether (1 : 1) gave ethyl 5-aminoindole-2-carboxylate (0.056 g, 8%).

(c) *In morpholine.* A solution of the azide (0.8 g, 0.0035 mol) in morpholine (50 ml) was treated as in (b) for 6 h. Chromatography with benzene as eluant gave ethyl 4-amino-5-morpholinoindole-2-carboxylate (0.04 g, 4%). Elution with benzene–diethyl ether (1 : 1) gave ethyl 5-aminoindole-2-carboxylate (0.071 g, 10%).

7,8-*Dihydro*-5H-[1,4]*oxazino*[4,3-a]*imidazo*[4,5-e]*indole* (25).—Ethyl-4-azido-5-morpholin-4-yl)indole-2-carboxylate (0.09 g) was dissolved in bromobenzene (10 ml) and added dropwise to boiling bromobenzene (40 ml). After 4 h the solvent was removed and the residue chromatographed on alumina. Elution with ethyl acetate gave the *imidazo*[4,5-e]*indole* (25) (0.04 g, 40%), m.p. 229—231° (from ethanol), $\nu_{max.}$ (Nujol) 3 310 (NH) and 1 690 cm^{-1} (C=O), τ ($CDCl_3$) 8.82 (t, J 7 Hz, Me), 6.32 (q, J 7 Hz ethyl CH_2), 8.60 s, NCH_2), 6.43 (s, OCH_2), 5.75 (s, exchangeable, NH), 3.50—4.10 (m, aromatic), *m/e* 285 (M^+) (Found: C, 63.3; H, 5.2; N, 14.9. $C_{15}H_{15}N_3O_3$ requires C, 63.15; H, 5.3; N, 14.7%).

Tetrahydronitrocarbazoles (2d).—6-Nitro-1,2,3,4-tetrahydrocarbazole (93%), prepared by the method of Deorha *et al.*,[10] had m.p. 175—176 °C (lit.,[10] m.p. 177 °C). 5-Nitro-1,2,3,4-tetrahydrocarbazole (34%), prepared by the method of Barclay *et al.*,[12] had m.p. 155—156 °C (lit.,[12] m.p. 155—156 °C). 7-Nitro-1,2,3,4-tetrahydrocarbazole (17%), prepared by the method of Barclay *et al.*,[12] had m.p. 170—171 °C (lit.,[12] m.p. 171—172 °C). 9-Acetyl-6-nitro-1,2,3,4-tetrahydrocarbazole (87%) had m.p. 244 °C (lit.,[13] m.p. 244 °C), 9-acetyl-7-nitro-1,2,3,4-tetrahydrocarbazole (88%) had m.p. 172—173 °C (lit.,[13] m.p. 174 °C), and 9-*acetyl*-5-*nitro*-1,2,3,4-*tetrahydrocarbazole* (79%) had m.p. 152—154 °C, $\nu_{max.}$ (Nujol) 1 700 cm^{-1} (C=O), τ ($CDCl_3$) 8.16 and 6.96br (β- and γ-CH_2, respectively), 7.32 (s, acetyl Me), 2.79 (t, $J_{6.7} = J_{7.8}$ = 9 Hz, 7-H), 2.34 (d, $J_{6.7}$ 9 Hz, 6-H), and 1.60 (d, $J_{7.8}$ 9 Hz, 8-H), *m/e* 258 (M^+) (Found: C, 65.2; H, 5.4; N, 10.8. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.5; N, 10.85%).

9-*Acetyl*-5-, 6-, *and* 7-*amino*-1,2,3,4,4a,9a-*hexahydrocarbazoles.—General procedure.* The appropriate nitro-compound (12 g) was dissolved in ethyl acetate (200 ml) and ethanol (400 ml) and reduced, at room temperature in an autoclave, under 50 atm of hydrogen, using palladium–charcoal as catalyst. After 24 h the mixture was removed from the autoclave and the catalyst filtered off. Removal of the solvent gave the amine which was then recrystallised. Data for the products are given in Table 2.

Azidohexahydrocarbazoles.—These were prepared by the same general procedure as for the azidoindoles. Data for the products are given in Table 2.

Photolysis of Azidohexahydrocarbazole Derivatives in Secondary Amines.—General procedure. The same procedure was employed for photolysis as for the azidoindole derivatives.

Photolysis of 9-*Acetyl*-6-*azido*-1,2,3,4,4a,9a-*hexahydrocarbazole in Diethylamine.*—The azide in diethylamine (1% solution) was irradiated for 10 h as described to give 9-acetyl 6-amino-1,2,3,4,4a,9a-hexahydrocarbazole (0.56 g, 78%). This product was identical with the sample prepared previously. Addition of pyrene before photolysis gave a similar result, as did irradiation with a quartz filter and other secondary amines.

Photolysis of 9-*Acetyl*-7-*azido*-1,2,3,4,4a,9a,*hexahydrocarbazole.*—(a) *In diethylamine.* The azide in diethylamine (1% solution) was irradiated for 8 h. Chromatography of the product using benzene–chloroform (1 : 1) as eluant gave 10-*acetyl*-3-*diethylamino*-5b,6,7,8,9,9a-*hexahydro*-1H-*azepino*[3,4-b]*indole* (28) (0.70 g, 74%), m.p. 90—91° (from light petroleum), $\nu_{max.}$ (Nujol) 1 650 (C=O), and 1 610 cm^{-1} (C=N), τ ($CDCl_3$) 7.70—9.00 (m, CH_2s of cyclohexane), 8.91 (t, J 7 Hz, ethyl Me), 7.85 (s, acetyl Me), 5.70—7.00 (m, ethyl CH_2 and 5b- and 9a-H), 4.90 and 8.10 (d, J 13 Hz, 7-H_2), and 2.94 and 4.40 (d, $J_{3.4}$ 8 Hz, 3- and 4-H), *m/e* 301 (M^+) (Found: C, 71.6; H, 9.2; N, 14.0. $C_{18}H_{27}N_3O$ requires C, 71.7; H, 9.0; N, 13.9%).

(b) *In morpholine.* The azide in morpholine (1% solution) was irradiated for 8 h to give 10-*acetyl*-5b,6,7,8,9,9a-*hexahydro*-3-*morpholino*-1H-*azepino*[3,4-b]*indole* (29) (0.75 g, 76%), m.p. 133—135° (from light petroleum), $\nu_{max.}$ (Nujol) 1 650 (C=O) and 1 610 cm^{-1} (C=N), τ ($CDCl_3$) 7.90—9.20 (m, CH_2s of cyclohexane), 7.85 (s, acetyl Me), 6.39 (s, CH_2s of morpholino), 6.68 and 5.90 (5b- and 9a-H), 5.38 and 7.55 (d, J 13 Hz, 7-H_2), and 2.95 and 4.32 (d, $J_{3.4}$ 8 Hz, 3- and 4-H), *m/e* 315 (M^+) (Found: C, 68.3; H, 8.2; N, 13.3. $C_{18}H_{25}N_3O_2$ requires C, 68.5; H, 8.0; N, 13.3%).

(c) *In piperidine.* The azide in piperidine (1% solution) was irradiated for 8 h and gave 10-acetyl-5b,6,7,8,9,9a-*hexahydro*-10-*piperidino*-1H-*azepino*[3,4-b]*indole* (30) (0.73 g, 75%), m.p. 104—105° (from light petroleum), $\nu_{max.}$ (Nujol) 1 650 (C=O) and 1 610 cm^{-1} (C=N), τ ($CDCl_3$) 7.90—9.20 (m, CH_2s of cyclohexane), 8.46br (β- and γ-CH_2 s of piperidino), 6.42br (α-CH_2s of piperidino), 7.85 (s, acetyl Me), 6.65

TABLE 2

Azido- and amino-hexahydrocarbazoles and substituted triazoles

Compound	Yield (%)	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N
(26a)	43	91—93	*a*			$C_{12}H_{14}N_4O$			
(26b)	95	102—103	65.4	6.35	21.7	$C_{14}H_{16}N_4O$	65.6	6.3	21.9
(26c)	90	87—88	65.7	6.3	21.8	$C_{14}H_{16}N_4O$			
(27a)	98	142—143	73.2	7.8	12.2	$C_{14}H_{17}N_2O$	73.0	7.9	12.2
(27b)	98	161—162[b]							
(27c)	91	158—159	73.5	8.0	12.1				
(32a)	98	160—162	54.9	4.3	15.05	$C_{17}H_{16}N_4O_6$	54.8	4.3	15.05
(32b)	97	197—199	55.0	4.0	15.0	$C_{17}H_{16}N_4O_6$			
(32c)	98	150—152	55.1	4.35	15.0	$C_{17}H_{16}N_4O_6$			
(33)	98	209—211	55.85	4.7	14.55	$C_{18}H_{18}N_4O_6$	56.0	4.7	14.5
(34a)	98	137—139	60.1	5.5	13.9	$C_{20}H_{22}N_4O_5$	60.3	5.6	14.05
(34b)	98	144—145	60.1	5.6	13.95	$C_{20}H_{22}N_4O_5$			

[a] Did not give a satisfactory analysis. [b] N. Kuroki and K. Konishi, *J. Synthetic Org. Chem., Japan*, 1954, **12**, 29.

and 5.95 (5b- and 9a-H), 5.06 and 7.81 (d, J 13 Hz, 7-H_2), and 2.94 and 4.37 (d, $J_{3,4}$ 8 Hz, 3- and 4-H), *m/e* 313 (M^+) (Found: C, 72.65; H, 8.8; N, 13.4. $C_{19}H_{27}N_3O$ requires C, 72.8; H, 8.7; N, 13.4%).

(d) *In pyrrolidine.* Irradiation for 8 h gave 10-*acetyl*-5b, 6,7,8,9,9a-*hexahydro*-10-(*pyrrolidin*-1-*yl*)-1H-*azepino*[3,4-b]-*indole* (31) (0.69 g, 74%), m.p. 121—123° (from light petroleum), $\nu_{max.}$ (Nujol) 1 650 (C=O) and 1 625 cm^{-1} (C=N), τ ($CDCl_3$) 7.90—9.20 (m, CH_2 s of cyclohexane), 8.16br (β-CH_2s of the pyrrolidino), 6.48br (α-CH_2 s of the pyrrolidino), 7.87 (s, acetyl Me), 6.75 and 5.95 (5b- and 9a-H), 5.72 and 7.22 (d, J 13 Hz, 7-H_2), and 2.95 and 4.44 (d, $J_{3,4}$ 8 Hz, 3- and 4-H), *m/e* 299 (M^+) (Found: C, 72.3; H, 8.4; N, 14.0. $C_{18}H_{25}N_3O$ requires C, 72.2; H, 8.4; N, 14.0%).

Photolysis of 5-*Azido*-1,2,3,4,4a,9a-*hexahydrocarbazole* (26a) *in Diethylamine.*—The azide in diethylamine (1% solution was irradiated for 17 h. Chromatography of the residue gave intractable material.

Cycloaddition Reactions of Azidoindole and Azidohexahydrocarbazole Derivatives.—General procedure. The azide (0.5 g) in chloroform (50 ml) was heated under reflux with a slight excess of dimethyl acetylenedicarboxylate. Each reaction was monitored by i.r. spectrophotometry. When the azide peak had gone, the chloroform was removed under vacuum and the remaining solid triazole was recrystallised. Data for the products are given in Table 2.

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