Polyhalogenoheterocyclic Compounds. Part XXVIII.[1] Polychloroindoles

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5,7-Di-, 5,6,7-tri- (3), and 3,5,6,7-tetra-chloroindoles have been characterised on the basis of ^1H coupling constants. Further chlorination of compound (3), with phosphorus pentachloride, gave 2,3,3,4,5,6,7-heptachloro-3*H*-indole (5), characterised with the aid of ^{13}C n.m.r., and identical with a sample prepared by pyrolysis of *N*-pentachlorophenyltrichloroacetimidoyl chloride (7). Compound (5) reacted with sodium isopropoxide or amines to give substitution products, whereas with sodiomalonic ester or sodium benzenethiolate products were obtained which indicate that initial attack takes place on chlorine.

IN exploring the chemistry of highly halogenated heterocyclic compounds, we have previously reported syntheses of perchlorinated derivatives of pyridine, diazines, and the corresponding benzo-derivatives;[2] and of perchlorobenzo[*b*]thiophen.[3] Here we describe syntheses of some polychloroindoles.

It was reported [4] that chlorination of sodium *N*-acetyl-indoline-2-sulphonate (1) gave a mixture of di- and tri-chloroindoles, although these were not fully characterised. We have found that chlorination of (1) under

carefully controlled conditions (−2 to +2 °C), followed by treatment with sodium hydroxide below 10 °C, gave 5,7-dichloroindole (2), identical with a sample prepared by an unambiguous synthesis.[5] When the chlorination was allowed to proceed further, by warming to 15 °C, then work-up as before gave 5,6,7-trichloroindole (3), identified on the basis of ^1H coupling constants. The 2-proton resonance was identified from the relative shifts in absorption on changing solvents, since it has been demonstrated [6-8] that changing from non-polar

[1] Part XXVII, R. D. Chambers, W. K. R. Musgrave, and P. G. Urben, *J.C.S. Perkin I*, 1974, 2584.

[2] See earlier parts of this series.

[3] G. M. Brooke and R. King, *Tetrahedron*, 1974, **30**, 857.

[4] J. Thesing, G. Semlar, and G. Mohr, *Chem. Ber.*, 1962, **95**, 2205.

[5] B. Heath-Brown and P. G. Philpott, *J, Chem. Soc.*, 1965, 7185.

[6] R. V. Jardine and R. K. Brown, *Canad. J. Chem.*, 1963, **41**, 2067.

[7] M. G. Reineke, H. W. Johnson, and J. F. Sebastian, *Chem. and Ind.*, 1964, 151; *J. Amer. Chem. Soc.*, 1969, **91**, 3817.

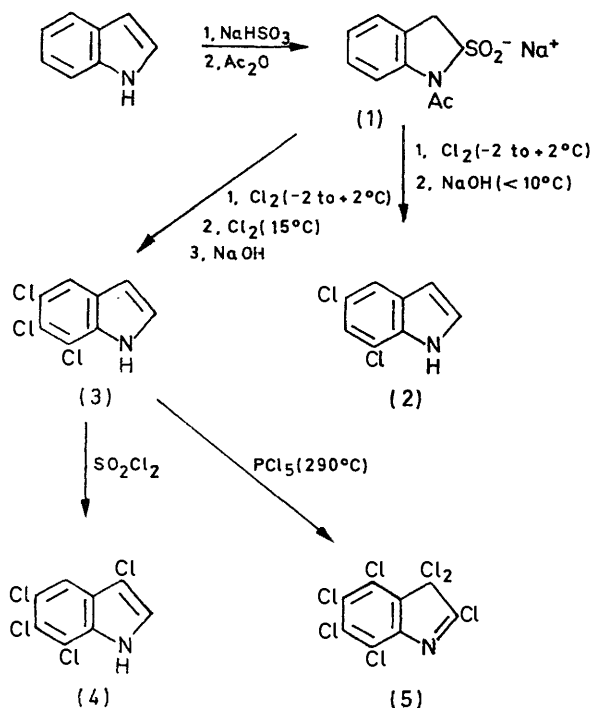[8] J. Ronayne and D. H. Williams, *J. Chem. Soc. (B)*, 1967, 805.

to a polar solvent leads to a significantly greater down-field shift for the resonance arising from the 2-proton

Cl$_2$(-2 to +2°C); 2. NaOH(<10°C)

1. Cl$_2$(-2 to +2°C); 2. Cl$_2$(15°C); 3. NaOH

(1) 1. NaHSO$_3$ / 2. Ac$_2$O → SO$_2^-$ Na$^+$ (Ac)

(3) (2)
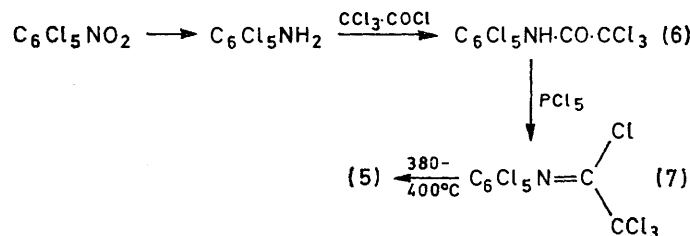
SO$_2$Cl$_2$ PCl$_5$(290°C)

(4) (5)

than for other resonances in indoles. Coupling con-stants have been assigned completely for indole,[9] and appropriate values correspond closely with values observed for the dichloro-derivative (2), from which we conclude that chlorine substitution does not affect these values significantly. The values observed for compound (3) closely parallel those for indole and the dichloro-derivative (2), where the 1-proton couples only with the 2-, 3-, and 4-protons. These coupling constants estab-lish the presence of the 3- and 4-protons and therefore the structure (3).

described above. This argument is still regarded as valid in the presence of the 3-chloro-substituent because 3-bromo- and 3-methyl-indoles each show an effect similar to that of indole itself.[6] Likewise the presence of the 4-proton was deduced from the observation of 1,4-proton coupling.

Further chlorination of the trichloro-derivative (3) with phosphorus pentachloride at 290 °C gave a per-chloro-compound which, in principle, could have either the 3H-indole (5) or the N-chloroindole structure. U.v. data for the polychlorinated compounds which we have prepared appear to distinguish between a 1H- and a 3H-indole structure since only the latter has no broad absorption in the region 275—325 nm. Other workers have shown that 1H-indole and N-chloroindole have closely similar spectra,[10,11] and 2,3-dimethyl-1H-indole and 3-chloro-2,3-dimethyl-3H-indole have distinguish-able spectra.[12] Conclusive evidence for the structure of (5) was, however, obtained from the ^{13}C n.m.r. spectrum. A variety of recorded ^{13}C n.m.r. data[13] on polychloro-compounds indicate that a CCl$_2$ signal occurs at sig-nificantly higher field than that of aromatic or vinylic $=C$Cl$-$. The spectrum of (5) is clearly defined, showing seven absorptions between 169 and 125 p.p.m. (downfield from Me$_4$Si), together with one absorption at 81.6 p.p.m. which firmly establishes the presence of CCl$_2$ and, therefore, the 3H-indole structure (5). Other workers have also argued for a 3H-indole structure.[14]

Since our work[15] began, other workers[16] have synthesised perchloro-3H-indole (5) by pyrolysis of N-pentachlorophenyltrichloroacetimidoyl chloride (7); a sample of (5) prepared by pyrolysis of (7) was identical with the sample prepared as described above. A con-venient synthesis of (7) was achieved by the reaction of pentachloroaniline with trichloroacetyl chloride, followed by the reaction of the amide (6) with phosphorus pentachloride.

Reactions of Heptachloro-3H-indole (5).—Heptachloro-3H-indole (5) reacts with a variety of nucleophiles at

C$_6$Cl$_5$NO$_2$ → C$_6$Cl$_5$NH$_2$ CCl$_3$·COCl → C$_6$Cl$_5$NH·CO·CCl$_3$ (6)

PCl$_5$

(5) ←$\frac{380-400°C}$ C$_6$Cl$_5$N=C$\overset{Cl}{\underset{CCl_3}{}}$ (7)

A tetrachloroindole (4) was obtained by reaction of the trichloro-derivative (3) with sulphuryl chloride in ether and the continued presence of a 2-proton was deduced by a solvent-induced proton chemical shift, as

room temperature; this is consistent with the activating influence of the nitrogen atom and it is reasonable to assume that attack occurs in the heterocycle ring.

Potassium isopropoxide displaces chlorine to give an

[9] P. J. Black and M. L. Hefferman, *Austral. J. Chem.*, 1965, **18**, 353.
[10] J. Derkosch, O. E. Polansky, E. Rieger, and G. Derflinger, *Monatsh.*, 1961, **92**, 1131 (*Chem. Abs.*, 1962, **57**, 13307).
[11] M. De Rosa, *J.C.S. Chem. Comm.*, 1975, 482.
[12] P. G. Gassman, G. A. Campbell, and G. Mehta, *Tetrahedron*, 1972, **28**, 2749.
[13] G. E. Hawkes, R. A. Smith, and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 1276.

[14] E. Degener, Farbenfabriken Bayer A.-G., lecture to the 2nd International Symposium on Polyhalogeno-compounds, Salford, 1971, and personal communication.
[15] R. A. Storey, unpublished work, 1965—1966; R. D. Cham-bers, R. A. Storey, and W. K. R. Musgrave, B.P. 1 177 628 (Cl.CO7d)/1970 (*Chem. Abs.*, 1970, **72**, 100501).
[16] H. Holdschmidt, E. Degener, H. G. Schmelzer, H. Tarnow, and W. Zecher, *Angew. Chem. Internat. Edn.*, 1968, **7**, 856 (*Chem. Abs.*, 1966, **65**, 18567b).

ether, and methylamine and dimethylamine give the corresponding amines; the u.v. spectra of these products are typical of polychlorinated 3H-indole structures. Also, the ^{1}H n.m.r. spectra indicated a single isomer in each case. The position of nucleophilic attack is not proven but because of the known activating influence of a nitrogen atom, the 2-position seems more likely than displacement from CCl_2. Surprisingly, treatment of (5) with sodiomalonic ester or with sodium benzenethiolate led only to reduction, giving 2,3,4,5,6,7-hexachloroindole (9) and no nucleophilic substitution product. Hexachloroindole (9) was also obtained by reaction of (5)

Nuc = PhS$^-$ or $\bar{C}H(CO_2Et)_2$
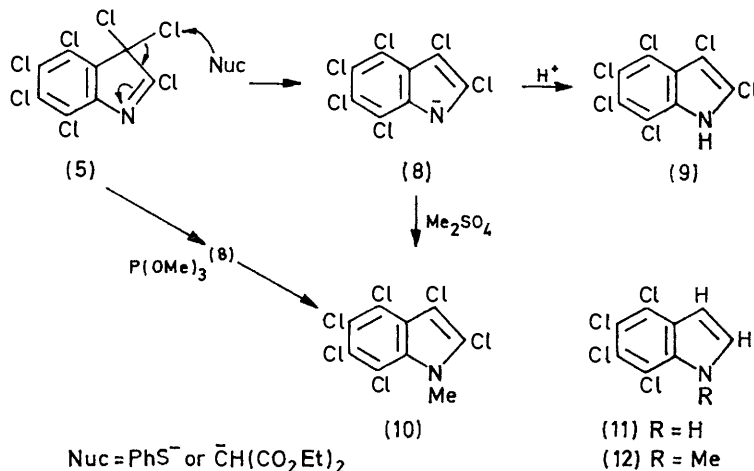
with butyl-lithium or magnesium, followed by hydrolysis, although the reaction of the metal derivatives with dimethyl sulphate gave the N-methyl derivative (10). A mechanism for the formation of (9) was indicated by the observation that, in the presence of dimethyl sulphate, reaction of (5) with sodiomalonic ester or sodium benzenethiolate gave the N-methyl derivative (10), which demonstrates the intermediacy of the hexachloroindole anion (8). The mechanism apparently involves nucleophilic attack on chlorine, which is unusual, and the driving force in this case is clearly the formation of the aromatic anion (8). In addition, the nature of the nucleophile is important, and the observed nucleophilic attack on carbon in (5) by oxygen and nitrogen nucleophiles but on chlorine by the carbon and sulphur nucleophiles is a reflection of the strengths on the corresponding bonds to chlorine. Confirmation of the mechanism comes from the reaction of (5) with trimethyl phosphite, giving the N-methyl derivative (10); this is closely analogous to the reaction of hexachlorocyclopentadiene with this reagent.[17]

Catalytic reduction offered the possibility of a means of identifying substitution products from (5), by ^{1}H n.m.r. However, while reduction of (5) or (9) and the N-methyl derivative (10) occurred readily, giving compounds (11) and (12), respectively, other derivatives did not undergo this reaction.

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* We are indebted to Dr. Heath-Brown for providing a sample for comparison (see ref. 5).

EXPERIMENTAL

5,7-*Dichloroindole* (2).—The crude sulphonate (1)[4] (212.1 g) was dissolved in a mixture of water (2 l) and ice (500 g); the solution was filtered to remove impurities and chlorine was passed through at -2 to $+2$ °C with stirring. When absorption of chlorine was complete, nitrogen was passed to remove the excess of chlorine. Then the green solution was carefully treated with aqueous sodium hydroxide (600 ml, 20% w/w) at <10 °C. The precipitate (57.6 g) was filtered off, washed, dried, and sublimed (80°; 0.05 mmHg) to give crude product (54.4 g). This material (10 g) was recrystallised [petroleum (b.p. 40—60°] several times to give the dichloro-derivative (2) (1 g), m.p. 53.5—

54.0°; i.r. spectrum identical with that of a sample * prepared by an unambiguous synthesis,[5] δ_H (Me$_2$CO) ca. 10.3 (H-1), 7.45 (H-2), 6.56 (H-3), 7.57 (H-4), and 7.22 (H-6), δ_H (CCl$_4$) ca. 7.9 (H-1), 6.95 (H-2), 6.32 (H-3), 7.35 (H-4), and 7.05 (H-6), $J_{1,2}$ ca. 2.4, $J_{1,3}$ 2.1 $J_{1,4}$ 0.7, $J_{2,3}$ 3.1, $J_{2,6}$ 0.4, $J_{4,6}$ 1.7 Hz.

5,6,7-*Trichloroindole* (3).—Compound (1) (prepared from 100 g of indole) was treated as described above. The chlorination was continued at 15 °C for a further 30 min and the crude product (58.4 g) was isolated as before. Recrystallisation [petroleum (b.p. 60—80°)] gave pure 5,6,7-*trichloroindole* (3) (47 g), m.p. 97.5—98.0° [Found: C, 43.5; H, 1.9; Cl, 48.3; N, 6.5%; M^+ (^{35}Cl), 219. C$_8$H$_4$Cl$_3$N requires C, 43.6; H, 1.85; Cl, 48.25; N, 6.35%; M, 219]; $\lambda_{max.}$ (cyclohexane) 279, 292, and 304 nm (ε 7 100, 5 600, and 3 200); ν_{NH} 3 400 cm^{-1}; δ_H (Me$_2$CO) ca. 10.5 (H-1), 7.43 (H-2), 6.50 (H-3), and 7.65 (H-4), δ_H (CCl$_4$) ca. 8.0 (H-1), 7.08 (H-2), 6.36 (H-3), and 7.48 (H-4), $J_{1,2}$ 2.4, $J_{1,3}$ 2.1, $J_{1,4}$ 0.7, $J_{2,3}$ 3.1 Hz.

3,5,6,7-*Tetrachloroindole* (4).—Sulphuryl chloride (0.4 ml) in dry ether (100 ml) at 5 °C was added dropwise to a solution of compound (3) (0.5 g) in dry ether (100 ml) at 0 °C. The solution was stirred at this temperature for 1 h, heated under reflux (30 min), cooled to <10 °C, and then poured onto ice–water. The organic phase was washed with water (2 × 100 ml), then an excess of aqueous sodium hydrogen carbonate, and dried (MgSO$_4$), and the ether was removed by distillation to leave a solid (0.54 g). This crude product (159 mg) was separated by chromatography on silica gel (chloroform as eluant) and recrystallisation

[17] V. Mark, *Tetrahedron Letters*, 1961, 295; D. T. Clark, W. J. Feast, M. Foster, and D. Kilcast, *Nature Phys. Sci.*, 1972, **68**, 236.

[petroleum (b.p. 60—80°)] gave 3,5,6,7-*tetrachloroindole* (4) (107 mg), m.p. 128.5—129° [Found: C, 37.9; H, 1.4; Cl, 55.3; N, 5.6%; M^+ (^{35}Cl), 253. $C_8H_3Cl_4N$ requires C, 37.7; H, 1.2; Cl, 55.65; N, 5.5%; M, 253]; $\lambda_{max.}$ (cyclohexane) 286, 294, 302, and 307 nm (ε 6 100, 5 800, 4 700, and 4 200); ν_{NH} 3 400 cm^{-1}; δ_H (Me$_2$CO) *ca.* 10.9 (H-1), 7.50 (H-2), and 7.60 (H-4), δ_H (CCl$_4$) *ca.* 8.1 (H-1), 7.10 (H-2), and 7.53 (H-4), $J_{1,2}$ 2.5, $J_{1,4}$ 0.7 Hz.

2,3,3,4,5,6,7-Heptachloro-3H-indole (5).—A mixture of compound (3) (10 g) and phosphorus pentachloride (70 g) was heated in an autoclave to 290 °C for 6 h. The autoclave was opened, the gases were vented, and volatile materials were removed under vacuum. The residue was extracted with benzene, and the product, after removal of benzene, was sublimed (90—100 °C; 0.03 mmHg) to give crude (5) (11.3 g). The sublimate was recrystallised [petroleum (b.p. 60—80°)] to give 2,3,3,4,5,6,7-*heptachloro-3H-indole* (5) (7.5 g), m.p. 123.5—124.5° [Found: C, 26.8; Cl, 69.3; N, 3.9%; M^+ (^{35}Cl), 355. C_8Cl_7N requires C, 27.05; Cl, 69.65; N, 4.0%; M, 355]; $\lambda_{max.}$ (cyclohexane) 241, 249, and 257 nm (ε 21 700, 27 600, and 26 600).

Pentachloroaniline.—A mixture of pentachloronitrobenzene (100 g) and methanol (2 l) was heated under reflux, and hydrochloric acid (11N; 50 ml) and coarse iron filings (85 g in 1 g portions) were added. More hydrochloric acid (11N; 210 ml) was added and the mixture was stirred under reflux for 17 h. Methanol was removed by distillation, water (1 l) was added, and the mixture was filtered. The solid was dissolved in ether (*ca.* 1.5 l) and the solution was washed with water (500 ml), dried (MgSO$_4$), and distilled. The residue was recrystallised (CCl$_4$) to give pentachloroaniline (70 g), m.p. 231.5—232.5° [Found: C, 26.8; H, 1.1; Cl, 67.1; N, 5.3%; M^+ (^{35}Cl), 263. Calc. for $C_6H_2Cl_5N$: C, 27.15; H, 0.75; Cl, 66.8; N, 5.3%; M, 263].

A mixture of pentachloroaniline (20 g), trichloroacetyl chloride (40 ml), and sulphuric acid (d 1.84; 1 ml) was heated under reflux under nitrogen for 3 days. The mixture was cooled, diluted with water (200 ml), and extracted with ether (400 ml). The extract was washed with aqueous sodium hydrogen carbonate, dried (MgSO$_4$), and evaporated and the residue was recrystallised from carbon tetrachloride to give the N-trichloroacetyl derivative (6) (21.7 g), m.p. 233.0—233.5° [Found: C, 23.1; H, 0.2; Cl, 68.6; N, 3.1%; M^+ (^{35}Cl), 407. Calc. for C_8HCl_8NO: C, 23.4; H, 0.25; Cl, 69.05; N, 3.4%; M, 407].

N-*Pentachlorophenyltrichloroacetamidoyl Chloride* (7).[16]—Compound (6) (1 g) and phosphorus pentachloride (2 g) were sealed under vacuum in a Carius tube and heated at 160 °C for 5 h. The contents of the tube were dissolved in carbon tetrachloride, the solution was filtered and evaporated to dryness, and the residue was separated by chromatography on silica gel (chloroform) and recrystallised [petroleum (b.p. 60—80°)] to give the product (7) (0.46 g), m.p. 127.5—128.5° [Found: C, 22.4; Cl, 74.6; N, 3.6%; M^+ (^{35}Cl), 425. Calc. for C_8Cl_9N: C, 22.4; Cl, 74.35; N, 3.25%; M, 425].

Pyrolysis of the Imidoyl Chloride (7).[16]—Compound (7) (1 g) was heated under reflux at 380—400 °C in a slow stream of nitrogen for 7.5 h. The effluent gas was passed through a liquid air trap to collect the evolved chlorine. The residue in the reaction vessel was separated by chromatography on silica gel (carbon tetrachloride) and the second major component was sublimed (80 °C; 0.03 mmHg) and recrystallised [petroleum (b.p. 60—80°)] to give pale yellow crystals of compound (5) (443 mg), m.p. 122—123°,

identical (i.r. spectrum) with a sample prepared as described above.

Reactions of 2,3,3,4,5,6,7-*Heptachloro*-3H-*indole* (5).— (a) *With potassium isopropoxide.* Potassium isopropoxide (0.91M in propan-2-ol; 0.75 ml) was added dropwise with stirring to compound (5) (0.18 g) in dry propan-2-ol (30 ml). After 15 min the mixture was poured into water (100 ml), acidified (4N-HCl), and extracted with ether; the extracts were dried (MgSO$_4$) and evaporated. The residue (0.2 g) was separated by chromatography on silica gel [chloroform–carbon tetrachloride (50% v/v)]. The major component (0.1 g) was decolourised [charcoal in petroleum (b.p. 60—80°)] and recrystallised [petroleum (b.p. 60—80°)] to give a hexachloro(isopropoxy)-3H-indole, m.p. 126.5—127.0° [Found: C, 34.4; H, 2.2; Cl, 55.4; N, 3.7%; M^+ (^{35}Cl), 379. Calc. for $C_{11}H_7Cl_6NO$: C, 34.6; H, 1.85; Cl, 55.7; N, 3.65%; M, 379]; $\lambda_{max.}$ (cyclohexane) 239, 245.5, and 253.5 nm (ε 26 800, 31 400, and 27 200).

(b) *With methylamine.* Methylamine in ethanol (0.073M; *ca.* 32 ml) was added dropwise with rapid stirring under nitrogen to compound (5) (0.41 g) in ethanol (80 ml). The solution was stirred (1 h) and evaporated to dryness and the residue (0.52 g) separated by chromatography on silica gel (chloroform) to give two components. The first major component (0.31 g) was recrystallised [petroleum (b.p. 60—80°)] to give a hexachloro(methylamino)-3H-indole, chars *ca.* 180° [Found: C, 31.3; H, 1.1; Cl, 60.5; N, 8.2%; M^+ (^{35}Cl), 350. Calc. for $C_9H_4Cl_6N_2$: C, 30.65; H, 1.15; Cl, 60.3; N, 7.95%; M, 350]; $\lambda_{max.}$ (cyclohexane) 258 and 261 nm (ε 32 000 and 25 600).

(c) *With dimethylamine.* Dimethylamine (0.036M in ethanol; 30 ml) was added dropwise with stirring under nitrogen to compound (5) (0.18 g) in ethanol (20 ml). The solution was evaporated and the remaining solid (0.23 g) was separated by chromatography on silica gel (chloroform). The major component (0.19 g) was recrystallised (carbon tetrachloride) to give a hexachloro(dimethylamino)-3H-indole (0.16 g), chars *ca.* 180 °C [Found: C, 32.6; H, 2.0; Cl, 57.5; N, 7.4%; M^+ (^{35}Cl), 364. Calc. for $C_{10}H_6Cl_6N_2$: C, 32.75; H, 1.65; Cl, 58.0; N, 7.65%; M, 364]; $\lambda_{max.}$ (cyclohexane) 259.5 nm (ε 31 300).

(d) *With diethyl sodiomalonate.* Compound (5) (0.18 g) in tetrahydrofuran (10 ml) was added to diethyl sodiomalonate in tetrahydrofuran (0.11M; 5 ml) and the mixture was stirred for 30 min at room temperature. The solution was poured into water and extracted with ether (2 × 100 ml), the extracts were dried (MgSO$_4$) and evaporated, and the residue (0.36 g) was separated by chromatography on silica gel [chloroform–carbon tetrachloride (50 : 50 v/v)]. The major component (0.14 g) was recrystallised [petroleum (b.p. 60—80°)] to give 2,3,4,5,6,7-hexachloroindole (9) (see later).

(e) *With sodium benzenethiolate.* The reaction of compound (5) with benzenethiol and sodium hydride, under conditions similar to those described above, also gave compound (9).

(f) *With magnesium.* A mixture of magnesium turnings (0.5 g), compound (5) (0.36 g), and dry tetrahydrofuran (10 ml) was placed in a dry flask and ethylene dibromide (0.5 ml) was added. The mixture was warmed slightly, to initiate the reaction, stirred at 35—40 °C for 2 h, and finally heated under reflux for 15 min. Water (50 ml) was added and the mixture was extracted with ether; the extracts were dried (MgSO$_4$) and evaporated, and the residue (0.33 g) was separated by chromatography on silica

gel (chloroform). The major component (0.27 g) was recrystallised (carbon tetrachloride) to give 2,3,4,5,6,7-hexachloroindole (9), m.p. 189.5—190.5° [Found: C, 29.9; H, 0.6; Cl, 66.2; N, 4.6%; M^+ (^{35}Cl), 321. C_8HCl_6N requires C, 29.65; H, 0.3; Cl, 65.7; N, 4.35%; M, 321], $\lambda_{max.}$ (cyclohexane) 293 nm (ε 10 000).

(g) *With n-butyl-lithium.* The reaction of compound (5) with n-butyl-lithium in tetrahydrofuran at −70 °C, followed by hydrolysis, gave compound (9).

(h) *With lithium aluminium hydride.* Reaction of compound (5) with lithium aluminium hydride in tetrahydrofuran at room temperature gave compound (9).

2,3,4,5,6,7-*Hexachloro*-N-*methylindole* (10).—A solution of trimethyl phosphite (0.067 ml) in dry ether (10 ml) was added dropwise with stirring to a solution of compound (5) (0.2 g) in dry ether (30 ml) at 0 °C. The solution was allowed to reach room temperature over 1 h, then poured into water, and acidified with hydrochloric acid (4N). The mixture was extracted with ether and the combined extracts were dried ($MgSO_4$) and evaporated; the residue (0.26 g) was separated by chromatography on silica gel (carbon tetrachloride). The major component (0.18 g) was recrystallised [petroleum (b.p. 60—80°)] to give 2,3,4,5,6,7-*hexachloro*-N-*methylindole* (10), m.p. 236.5—237.0° [Found: C, 32.1; H, 1.2; Cl, 62.5; N, 3.8%; M^+ (^{35}Cl), 335. $C_9H_3Cl_6N$ requires C, 32.0; H, 0.9; Cl, 62.95; N, 4.15%; M, 335], $\lambda_{max.}$ (cyclohexane) 303 nm (ε 9 500).

In reactions (e)—(h) (above) treatment with dimethyl sulphate before hydrolysis gave compound (10).

Catalytic Hydrogenations.—(a) 2,3,3,4,5,6,7-*Heptachloro*-3H-*indole* (5). A mixture of compound (5) (0.27 g), magnesium oxide (0.46 g), 10% palladium–charcoal (0.3 g), and dry tetrahydrofuran (40 ml) was shaken in hydrogen at room temperature. The solution was filtered and evaporated and the residue (0.22 g) was separated by chromatography on silica gel (carbon tetrachloride). The major component (0.08 g) was recrystallised [petroleum (b.p. 60—80°)] to give 4,5,6,7-*tetrachloroindole* (11), m.p. 177.0—177.5° [Found: C, 38.0; H, 1.4; Cl, 55.9; N, 5.8%; M^+ (^{35}Cl), 253. $C_8H_3Cl_4N$ requires C, 37.7; H, 1.2; Cl, 55.65; N, 5.5%; M, 253], $\lambda_{max.}$ (cyclohexane) 283, 294.5, and 306 nm (ε 8 100, 6 300, and 2 900); δ_H (Me_2CO) 7.33 (H-2) and 6.61 (H-3), δ (CCl_4) 7.20 (H-2) and 6.63 (H-3), $J_{1,2}$ 2.6, $J_{1,3}$ 2.2, $J_{2,3}$ 3.2 Hz.

(b) 2,3,4,5,6,7-*Hexachloroindole* (9).—Hydrogenation of compound (9) (0.09 g) similarly gave compound (11) (0.03 g).

(c) 2,3,4,5,6,7-*Hexachloro*-N-*methylindole* (10).—Hydrogenation of compound (10) (0.12 g) similarly gave 4,5,6,7-*tetrachloro*-N-*methylindole* (12) (0.08 g), m.p. 211.5—212.5° [Found: C, 40.5; H, 1.6; N, 5.1%; M^+ (^{35}Cl), 267. $C_9H_5NCl_4$ requires C, 40.2; H, 1.85; N, 5.2%; M^+, 267]; $\lambda_{max.}$ (cyclohexane) 292 and 312 nm (ε 6 500 and 4 700).