Two Novel Indole Rearrangements

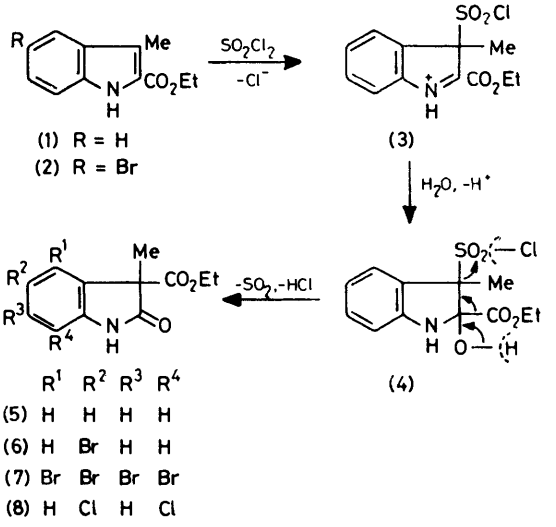
By R. Morrin Acheson,* Richard J. Prince, and Garry Procter, Department of Biochemistry, South Parks Road, Oxford OX1 3QU

Ethyl 3-methylindole-2-carboxylate is rearranged by sulphuryl chloride to ethyl 3-methyl-2-oxoindoline-3-carboxylate, and similar transformations accompanied by halogenation are effected by bromine, or ethyl *NN*-dichlorocarbamate, in aqueous acetic acid. The last reagent converted both *NN*-dimethylindole-2- and -3-carboxamides into 3,5,7-trichloro-*NN*-dimethyl-2-oxoindoline-3-carboxamide.

1-Hydroxyindole is a very reactive substance which is obtained by the careful reduction of 2-nitrophenylacetaldehyde.[1,2] A number of derivatives, particularly those bearing a carboxy-group at position 2, are relatively stable under ordinary laboratory conditions and most have been obtained by similar reductive cyclisations.[3,4] The occurrence of 1-methoxyindoles in plants [1,2] is interesting, for they could be formed *via* *N*-oxidation.[5-7] *N*-Chlorination of indole takes place,[8] as does 1-nitrosation of tryptophan,[9] so it seems possible that an *N*-oxidation of an indole might occur in plants and be followed by *O*-methylation. Pea seedlings are alleged [10] to metabolise indole-3-acetic acid to the 1-hydroxy-derivative but this claim is based only on weak chromatographic evidence. All attempts to oxidise indoles to 1-hydroxyindoles by chemical methods have failed, except that 1-hydroxy-2-phenylindole has been detected as an intermediate in the oxidation of 2-phenylindoline to 2-phenylisatogen.[11] The report [12] that sulphuryl chloride in acetic acid and subsequent treatment with water converted ethyl 3-methylindole-2-carboxylate into the 1-hydroxy-derivative was thought therefore to be worth reinvestigation.

Ethyl 3-methylindole-2-carboxylate when treated successively with sulphuryl chloride and water gave a compound with the properties previously noted.[12] The additional spectral data which we have now obtained are inconsistent with a 1-hydroxyindole formulation. The i.r. spectrum shows no OH vibration, while the presence of frequencies corresponding to both ester and secondary amide type carbonyl groups, and comparison of the ^{1}H n.m.r. spectrum with those of known indolin-2-ones [13,14] and 1-hydroxyindoles,[2,15,16] shows that the compound must have structure (5). The indolinone (5) was decarboxylated by refluxing hydrobromic acid to 3-methylindolin-2-one, and its structure confirmed by synthesis. 2-Chloronitrobenzene with sodium diethyl malonate gave the ester (9) which was converted into (10) by methyl iodide and sodium ethoxide. Hydrogenation, over Raney nickel, gave the desired indolinone (5), but the use of palladised charcoal yielded the 1-hydroxyindolinone (11). This gave a deep purple colour with methanolic iron(III) chloride, while 1-hydroxyindolin-2-one gives a blue colour.[17]

The mechanism of this rearrangement is thought to be similar to that proposed [14] for the conversion of trimethyl 1-methylindole-2,3,4-tricarboxylate into trimethyl 5-bromo-1-methyl-2-oxoindoline-3,3,4-tricarboxylate by bromine in aqueous acetic acid, and involves attack of the sulphuryl chloride at position 3 to give (3), addition of water leading to (4) and rearrangement as shown in the Scheme. The indole (1) on treatment with bromine and aqueous acetic acid at 5 °C gave the bromoindole (2), while at 50 °C with more bromine a mixture of (2) and the rearrangement product (6) was obtained; rearrangement



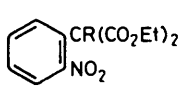
	R^1	R^2	R^3	R^4
(5)	H	H	H	H
(6)	H	Br	H	H
(7)	Br	Br	Br	Br
(8)	H	Cl	H	Cl

probably follows 5-substitution. Under more vigorous conditions (2) gave the tetrabromoindolinone (7). Ethyl *NN*-dichlorocarbamate similarly converted (1) into the dichloroindolinone (8). It is noteworthy that sulphuryl chloride is the only reagent which we have found which causes the ester-shift without introducing halogen atoms. Because of this it does not appear to be a source of electrophilic chlorine under these conditions.

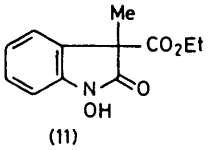
The melting point of the bromoindole (2), even after purification by high-pressure liquid chromatography, was significantly lower than that of synthetic material, although the i.r. and n.m.r. spectra were superimposable. The isomeric 4- and 6-bromo-isomers were also synthesised by Fischer's method and their properties were quite different from those of (2).

A number of rearrangements involving the movement of an ester group are known, but the only reported amide shifts are the conversion of 4-phenyl-2,3-dioxobutyramide into 2-carbamoyl-2-hydroxy-3-phenylpropionic acid caused by base,[18] the related rearrangement of 2,3,4-trioxo-1,2,3,4-tetrahydroquinoline,[18] and a 1,5-

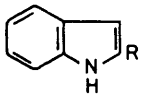
photochemical shift of a carboxamide group.[19] The effect of ethyl *NN*-dichlorocarbamate in aqueous acetic acid on the indoles (12)—(14) was therefore examined. Only the dimethylamide (12) gave a tractable product which was identified, from its u.v., i.r., and n.m.r. spectra, as a mixture of the indolinones (15) and (16). Similar treatment of *NN*-dimethylindole-3-carboxamide gave an identical mixture, the mass and other spectra being superimposable. Further chlorination of both mixtures gave the trichloroindolinone (16) which showed the expected spectral similarities with the spectra of methyl 3,5,7-trichloro-2-oxoindoline-3-carboxylate.[20]



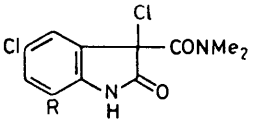
(9) R = H
(10) R = Me



(11)



(12) R = $CONMe_2$
(13) R = $CONH_2$
(14) R = CN



(15) R = H
(16) R = Cl

The amide shift presumably occurs through a positively charged chlorine atom attacking position 3 of (12) to give an intermediate [*cf.* (3)] which rearranges along the lines shown in the Scheme and is preceded and/or followed by further chlorination.

EXPERIMENTAL

The instruments and chromatographic procedures used have been described previously;[21] n.m.r. i.r., and u.v. spectra were measured for $CDCl_3$, $CHCl_3$ and MeOH solutions, unless otherwise stated, and are recorded as τ values and in cm^{-1} and nm (ε) respectively.

Ethyl 3-Methylindole-2-carboxylate (1).—This was obtained as described [12] from aniline and ethyl 2-ethyl-3-oxobutyrate in 45% overall yield, m.p. 134—136 °C, identical to that reported; i.r. 3 465s (NH), 1 700infl., and 1 690 (CO); u.v. 229 (24 800) and 296 (21 500), unchanged on addition of aqueous sodium hydroxide; n.m.r. 1.24 (1-H), 5.63 (q, 2-CO_2CH_2Me), 8.61 (t, *J* 7 Hz, 2-CO_2CH_2Me), 7.44 (3-Me), 2.75—3.00 (m, 4-, 5-, and 6-H), and 2.37 (dd, *J* 6 and 2 Hz, 7-H).

Ethyl 3-Methyl-2-oxoindoline-3-carboxylate (5).—(i) The indole (1) with sulphuryl chloride and work-up as described [12] gave a yellow oil (35% yield) which eventually crystallised from ether—light petroleum (b.p. 40—60 °C) giving the indolinone (5) as irregular rhombs, m.p. 86—88 °C (lit.,[12] 87—88 °C) (Found: C, 65.9; H, 5.9; N, 6.4. Calc. for $C_{12}H_{13}NO_3$: C, 65.8; H, 5.9; N, 6.4%); i.r. 3 440s (NH), 3 220br (bonded NH), 1 715—1 750br (CO), and 1 615; the unbonded NH was not observed for a Nujol mull; u.v. 252 (6 500); n.m.r. 0.58br (1-H), 8.32 (3-Me), 5.89 (q, 3-CO_2CH_2Me), 8.86 (t, *J* 7 Hz, 3-CO_2CH_2Me), and 2.65—3.20 (m, 4-, 5-, 6-, and 7-H).

This indolinone (5) (0.23 g) was heated at 100 °C for 45 min with 48% aqueous hydrogen bromide (1 ml) and acetic acid (9 ml). After cooling, dilution with water and extraction with ethyl acetate gave 3-methylindolin-2-one as an oil with an n.m.r. spectrum identical to that published.[22]

(ii) 2-Chloronitrobenzene (15.7 g) with diethyl malonate (16.8 g) and sodium hydride, using the procedure [20] employed for 2,4-dichloronitrobenzene and dimethyl malonate, gave diethyl 2-nitrophenylmalonate (9) (8.8 g), b.p. 126—128 °C at 0.2 Torr (lit.,[23] b.p. 150—190 °C at 0.3—2.5 Torr with decomposition). A solution of sodium (1 g) in ethanol (50 ml) with ethyl acetate (0.5 ml) (procedure from ref. 24) was added over 2 h to a stirred mixture of the ester (9) (8.8 g) and methyl iodide, and stirring was continued for 2 h. After solvent removal *in vacuo* water was added when the *ester* (10) precipitated (8.0 g); recrystallisation from light petroleum (b.p. 40—60 °C) gave rhombs, m.p. 49—51 °C (Found: C, 57.0; H, 5.8; N, 4.8. $C_{14}H_{17}NO_6$ requires C, 57.0; H, 5.8; N, 4.7%).

This ester (1.0 g) in ethanol (50 ml) was hydrogenated over Raney nickel (0.25 g) at 4 atm and room temperature for 3 days. Filtration and evaporation gave the indolinone (5) (0.8 g) which after recrystallisation had the same m.p., mixed m.p., and i.r. and n.m.r. spectra as the analysed sample.

Ethyl 1-Hydroxy-3-methyl-2-oxoindoline-3-carboxylate (11).—The nitro-compound (10) (1.0 g) was hydrogenated in ethanol over 5% palladium on charcoal and gave the 1-*hydroxyindolinone* (11) (0.55 g), rhombs from ether–light petroleum (b.p. 40—60 °C), m.p. 113—115 °C (Found: C, 61.5; H, 5.5; N, 6.1. $C_{12}H_{13}NO_4$ requires C, 61.3; H, 5.5; N, 6.0%); i.r. 3 140br (OH), 2 850br (OH), 1 740 (CO), 1 705 (CO), and 1 615; u.v. 262 (6 200), 285 (4 600), and, after addition of base, 289 (10 200); n.m.r. −0.35br (OH), 8.39 (3-Me), 5.98 (q, 3-CO_2CH_2Me), 8.93 (t, *J* 7 Hz, 3-CO_2CH_2Me), and 2.55—3.10 (m, 4-, 5-, 6-, and 7-H).

Bromination of Ethyl 3-Methylindole-2-carboxylate (1).—(i) Bromine (1 ml) in acetic acid (7 ml) was added to the indole (1) (2.3 g) in acetic acid (25 ml) containing 10% of water at 5 °C (*cf.* ref. 14). After 2 h the mixture was poured into water, the solid collected and recrystallisation (MeOH) gave yellow needles (2.1 g) of (2), m.p. 150—152 °C, identical spectroscopically to the synthetic specimen. High-pressure liquid chromatography removed the yellow contaminant and raised the m.p. to 158—159 °C, but synthetic material had the lit.[25] m.p. of 163°; i.r. 3 460s (NH), 3 430w,br, 1 710s,infl., and 1 695; u.v. 234 (28 500), 240infl. (26 200), and 300 (18 500) unchanged by addition of sodium hydroxide; n.m.r. 1.2br (1-H), 7.49 (2-Me), 5.67 (q, 3-CO_2CH_2-Me), 8.61 (t, *J* 7 Hz, 3-CO_2CH_2Me), 2.28 (d, 4-H), 2.68 (dd, 6-H), and 2.87 (d, $J_{4,6}$ 1.5; $J_{6,7}$ 8.5 Hz, 7-H).

(ii) Bromine (0.5 ml) in acetic acid was added to the indole (1) (0.5 g) in aqueous acetic acid essentially as just described except that the mixture was heated at 50 °C for 3 h before being worked up. Fractional recrystallisation (from MeOH) of the product gave ethyl 5-bromo-2-methylindole-3-carboxylate (2) (0.4 g) and the *indolinone* (6) (0.1 g), m.p. 128—130 °C (Found: C, 48.1; H, 4.0; N, 4.8. $C_{12}H_{12}BrNO_3$ requires C, 48.3; H, 4.0; N, 4.7%); i.r. (Nujol) 3 170w, 1 725infl., 1 715s (CO), and 1 610; u.v. 247 (13 900) 296 (1 420), and, after addition of base, 267 (12 000) and 276 (10 700); n.m.r. 0.45br (1-H), 8.34 (3-Me), 5.89 (q, 3-CO_2CH_2Me), 8.84 (t, *J* 7 Hz, 3-CO_2CH_2Me), 2.71 (d, 4-H), 2.68 (dd, 6-H), and 3.21 (d, $J_{4,6}$ 2; $J_{6,7}$ 9 Hz, 7-H).

Ethyl 4,5,6,7-Tetrabromo-3-methyl-2-oxoindoline-3-carb-

oxylate (7).—The 5-bromoindole (2) (0.5 g) in acetic acid (25 ml) containing water (10%) was stirred at 0 °C, bromine (5 ml) in acetic acid added (2 h) and the mixture kept at 50 °C for 4 h. Pouring into water precipitated the *tetrabromoindolinone* (7) (0.3 g), pale yellow needles (from aqueous dimethyl sulphoxide), which sublime at 280 °C (Found C, 27.2; H, 1.9; Br, 60.1; N, 2.6. $C_{12}H_9Br_4NO_3$ requires C, 26.9; H, 1.7; Br, 59.8; N, 2.6%); i.r. (Nujol) 3 150br, 1 750 (CO), 1 720 (CO), and 1 590; u.v. 230 (31 500), 262 (8 700), 315br (2 060), and after addition of base 234 (24 600), 288 (14 100), and 335infl. (3 150); n.m.r. [$(CD_3)_2SO$] −1.4 (1-H), 8.36 (3-Me), 5.90 (q, 3-CO_2CH_2Me), and 8.90 (t, J 7 Hz, 3-CO_2CH_2Me).

Ethyl 5-Bromo-3-methylindole-2-carboxylate (2).—This was obtained from 4-bromoaniline and ethyl 2-ethyl-3-oxobutyrate as described,[25] except that the phenylhydrazone (10 g) in ethanol (50 ml) was cyclised by concentrated sulphuric acid (7 ml) using the procedure of Elks *et al.*[12] The indole (7.1 g), yellow needles (from methanol), had m.p. 163 °C, identical to that reported,[25] and spectra identical to those of the specimen obtained from the bromination of (1).

Ethyl 4- and 6-Bromo-3-methylindole-2-carboxylate.—3-Bromoaniline, by the foregoing procedure, gave a *ca.* 1 : 1 mixture of the 4- and 6-isomers which showed signs of separating on t.l.c. using ether–light petroleum (b.p. 40—60 °C), 1 : 1 v/v, as eluant. High-pressure liquid chromatography with this solvent over Merck Kieselgel 60 (230—400 mesh) eluted first the *6-bromo-ester*, needles (from ether), m.p. 172—174 °C (Found: C, 51.2; H, 4.2; N, 5.1. $C_{12}H_{12}BrNO_2$ requires C, 51.1; H, 4.3; N, 5.0%); i.r. (Nujol) 3 350s (NH), 1 680s (CO), and 1 612w; u.v. 231 (29 000) and 307 (20 200) unchanged on addition of base; n.m.r. 1.3br (1-H), 5.65 (q, 2-CO_2CH_2Me), 8.60 (t, J 7 Hz, 2-CO_2CH_2Me), 7.48 (3-Me), 2.87 (dd, 4-H), 2.56 (d, 5-H), and 2.56 (d, $J_{4,5}$ 8.5; $J_{5,7}$ 1.5 Hz, 7-H).

The *4-bromo-indole*, needles (from ether), was eluted next, m.p. 152—155 °C (Found: C, 51.2; N, 4.2; N, 5.0. $C_{12}H_{12}BrNO_2$ requires C, 51.1; H, 4.3; N, 5.0%); i.r. (Nujol) 3 325s (NH), 1 675s (CO), and 1 608w; u.v. 234 (35 000), 299 (22 600), and 328infl. (8 500), unchanged on addition of base; n.m.r. 1.2br (1-H), 5.62 (q, 2-CO_2CH_2Me), 8.58 (t, J 7 Hz, 2-CO_2CH_2Me), 7.15 (3-Me), and 2.68—3.1 (m, 5-, 6-, and 7-H).

Reaction of Ethyl 3-Methylindole-2-carboxylate (1) *with Ethyl* NN-*Dichlorocarbamate.*—The carbamate (0.8 ml) was added dropwise into a solution of the indole (1) (0.6 g) in 25 ml of acetic acid containing 10% of water at 0 °C, and after 12 h at room temperature the mixture was poured into ice–water. Recrystallisation of the precipitate from benzene gave *ethyl 5,7-dichloro-3-methyl-2-oxoindoline-3-carboxylate* (8) (0.34 g), m.p. 154—155 °C (Found: C, 50.2; H, 3.9; N, 5.0. $C_{12}H_{11}Cl_2NO_3$ requires C, 50.0; H, 3.8; N, 4.9%); i.r. (Nujol) 3 150, 3 080 (NH), 1 725 (CO), and 1 610; u.v. 257 (11 700), 300 (1 800) and, after addition of base, 279 (14 400), and 315infl. (2 150); n.m.r. 1.11 (1-H), 8.32 (3-Me), 5.88 (q, 3-CO_2CH_2Me), 8.82 (t, J 7 Hz, $CO_2CH_2CH_3$), 2.79 [d, 4- (or 6-)H], and 2.93 [d, $J_{4,6}$ 1.5 Hz, 6- (or 4-)H].

Indole-2-carboxamides.—Indole-2-carbonyl chloride[26] in ether with excess of liquid ammonia gave the amide (13), m.p. 234—236 °C (lit.,[27] 235—237 °C); i.r. (Nujol) 3 460 (indole N–H), 3 200br ($CONH_2$), 1 650 (CO), 1 620 and 1 590; n.m.r. [$(CD_3)_2SO$] −1.3 (1-H), 2.05br ($CONH_2$), and 2.4—3.2 (5 H, m, ArH). With excess of anhydrous dimethylamine in ether the acid chloride gave the *NN*-dimethylamide (12), m.p. 182.5—183 °C (lit.,[28] 181—182 °C); i.r. (Nujol) 3 295 (N–H, shifts to 3 450 in $CHCl_3$), 1 610 (CO), and 1 575; n.m.r. [$(CD_3)_2SO$] −1.4 (1-H) 6.84 (NMe_2), and 2.3—3.2 (5 H, m, ArH).

The 2-amide (13) gave the nitrile (14), m.p. 101 °C, by the procedure described;[27] i.r. 3 450 (NH), 2 210 (CN), 1 620, and 1 600; n.m.r. [$(CD_3)_2SO$] −1.2 (1-H) and 2.4—3.8 (5 H, m, ArH).

NN-*Dimethylindole-3-carboxamide.*—Purified thionyl chloride (15 g) was added to indole-3-carboxylic acid (10 g) suspended in chloroform (250 ml) and after 2 h under reflux (water bath) the solvent was removed *in vacuo*, chloroform added, and the evaporation repeated. The residue, in chloroform (200 ml), with excess of dimethylamine in ether gave the corresponding amide, needles (5.8 g) (from MeOH), m.p. 235—236 °C (lit.,[29] 236 °C); i.r. (Nujol) 3 220 (NH) (shifts to 3 450 in $CHCl_3$), 1 620 (CO), 1 580, and 1 560; n.m.r. −1.4 (exchanges with D_2O, 1-H), 6.92 (2-$CONMe_2$), and 2.1—3.1 (5 H, m, ArH).

Reactions of the Indoles (12)—(14) *with Ethyl* NN-*Dichlorocarbamate.*—The indole (12), (13), or (14) (5.3 mmol) was dissolved in acetic acid containing 10% of water (50 ml) and ethyl *NN*-dichlorocarbamate[20] (7.9 mmol) added dropwise with stirring near 0 °C. After 2 h stirring the mixture was poured into ice–water (200 ml), and the resulting precipitate collected, washed, and dried *in vacuo*.

(i) *NN*-Dimethylindole-2-carboxamide (12) (1.0 g) gave a product, recrystallized (1.3 g) from acetonitrile, m.p. 185—191 °C, containing only two compounds (t.l.c.; 2% MeOH in $CHCl_3$; R_F 0.4 and 0.5); i.r. (Nujol) 3 100—3 300 (NH, shifts to 3 410 in $CHCl_3$), 1 750 (oxindole CO), and 1 650 ($CONH_2$); n.m.r. [$(CD_3)_2SO$] −1.37 (1-H), 7.16 (2-$CONMe_2$), 2.65 (d, 4-H), 2.57 (q, 6-H), and 2.95 (d, $J_{4,6}$ 2.5; $J_{6,7}$ 8 Hz, 7-H); corresponding to (15), together with resonances due to (16) as in the next paragraph.

The mixture from the dimethylamide (1 g) was heated under reflux with further dichlorocarbamate (0.8 g) in the aqueous acetic acid (25 ml) for 1 h and worked up as before to give *3,5,7-trichloro*-NN-*dimethyl-2-oxoindoline-3-carboxamide* (16) (1.0 g, 58% from the initial indole), m.p. 205—207 °C (from acetonitrile) (Found: C, 43.2; H, 2.9; N, 9.2. $C_{11}H_9Cl_3N_2O_2$ requires C, 42.9; H, 2.9; N, 9.1%); i.r. (Nujol) 3 100 (NH, shifts to 3 410 in $CHCl_3$), 1 750 (2-CO), 1 640 (3-CO), and 1 285; n.m.r. [$(CD_3)_2SO$] −1.77 (1-H), 7.20 (3-$CONMe_2$), 2.65 (d, 4-H), and 2.40 (d, $J_{4,6}$ 2.5 Hz, 6-H); u.v. (MeOH containing 10% H_2O) 228 (22 900), 266 (4 700), and 324 (1 200).

(ii) *NN*-Dimethylindole-3-carboxamide, treated as for the 2-isomer (12), gave an identical mixture of (15) and (16), which was similarly converted (61% yield from the initial indole) by further ethyl *NN*-dichlorocarbamate into (16), identical in spectra with the analysed sample.

(iii) Indole-2-carboxamide (13) gave only polymeric products while indole-2-carbonitrile (14) gave a very unstable product showing C≡N, but no N–H, i.r. absorptions and only aromatic protons in the n.m.r. spectrum which may have been an *N*-chloro- (or 3-chloro-3*H*)-indole which could not be characterised further.

[8/474 *Received*, 15*th March*, 1978]

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