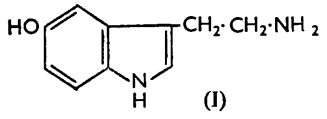
389. *The Synthesis of Some Indolylalkylamines.*

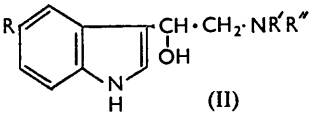
By D. E. Ames, R. E. Bowman, D. D. Evans, and W. A. Jones.

Attempts to synthesise the serotonin analogues (II) are described. The use of lithium borohydride for the reduction of 3-indolyl ketones to the corresponding alcohols has been examined.

The pharmacological importance of serotonin (I) and other indolylalkylamines [1] led us to examine the synthesis of some compounds of type (II), containing an adrenaline-like side-chain, for biological evaluation. As far as we are aware the only compound of this type which has been described is the parent (II; R = R′ = R″ = H), whose picrate is reported



(I)



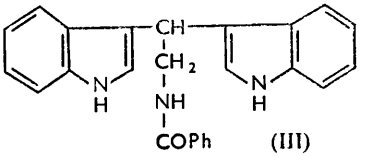
(II)

by Majima and Kotake.[2] Attempts to repeat this work could not be pursued as condensation of 1-acetyl-3-formylindole with nitromethane gave only a very small yield of 1-acetyl-3-(1-hydroxy-2-nitroethyl)indole. When the compound (II; R = R′ = R″ = H) was ultimately obtained by a different method it differed markedly from that described by these authors.

The first route investigated was the condensation of indolylmagnesium iodide with benzamidoacetaldehyde. None of the desired product (II; R = R′ = H, R″ = Bz) could be isolated, however, the only crystalline product being the bis-compound (III). Majima and Kotake [3] similarly obtained di-3-indolylphenylmethane from indolylmagnesium iodide and benzaldehyde.

[1] Erspamer, *Pharmacol. Rev.*, 1954, **6**, 425.
[2] Majima and Kotake, *Ber.*, 1925, **58**, 2037.
[3] *Idem, ibid.*, 1922, **55**, 3865.

An alternative approach to the synthesis of compounds of type (II) consists of reduction of the cyanohydrin of 3-formylindole. Attempts to prepare this cyanohydrin by addition of potassium cyanide to the aldehyde in acetic acid or in bisulphite solution were unsuccessful. This lack of reactivity is consistent with Thesing's view [4] that 3-formylindole may be regarded as the vinylogue of an amide.



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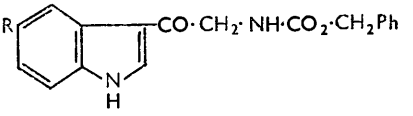


(IV)

The reduction of 3-indolyl ketones was next examined as a means of introducing the hydroxyl group into the side-chain. 3-Acetylindole has been reduced by sodium ethoxide at a high temperature [5] and with lithium aluminium hydride,[6] the sole product being 3-ethylindole in each case. Similarly, reduction of 3-formylindole with lithium aluminium hydride gives only skatole,[6] but 3-hydroxymethylindole has recently been obtained by the use of potassium borohydride for this reduction.[7] Before the latter method was published we had reduced 3-formylindole and various 3-indolyl ketones with lithium borohydride in tetrahydrofuran. 3-Formylindole was thus reduced in high yield to 3-hydroxymethylindole, and 1-acetyl-3-formylindole gave 1-acetyl-3-hydroxymethylindole which could readily be deacetylated. 3-Formyl-1-methylindole yielded 3-hydroxymethyl-1-methylindole as an oil, but some di-1-methylindolylmethane was also obtained (though this may have been an artifact formed during distillation). Reduction of 3-acetylindole with lithium borohydride in cold tetrahydrofuran gave 3-1′-hydroxyethylindole but much starting material was always recovered, and when the reduction was carried out in refluxing solvent only 3-ethylindole was isolated. Similar results were obtained in the case of 1 : 3-diacetylindole, about half the starting material being recovered.

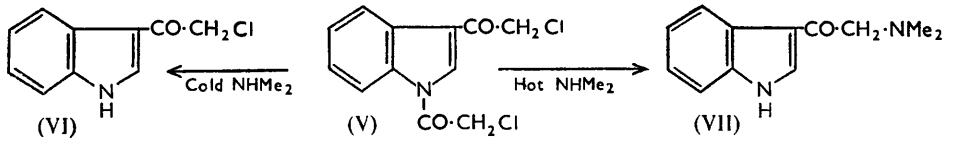
Despite the difficulty of achieving this reduction without effecting hydrogenolysis of the oxygen–carbon bond, application of this method to the preparation of hydroxy-amines (II) was investigated. Benzyloxycarbonylglycyl chloride was condensed with indolylmagnesium bromide to give the ketone (IV; R = H) which was reduced with lithium borohydride, the alcohol (II; R = R′ = H, R″ = CO_2·CH_2Ph) being obtained in good yield. Catalytic hydrogenation furnished the hydroxy-amine (II; R = R′ = R″ = H), isolated as the picrate; attempts to isolate the free amine or the hydrochloride failed. The colourless solution of the hydrochloride, obtained from the picrate by ion-exchange, rapidly became dark red on concentration in the cold. A similar synthesis starting with benzyloxycarbonylsarcosyl chloride yielded the compound (II; R = R′ = H, R″ = Me), also isolated as the picrate. Sarcosine was conveniently prepared on a considerable scale from ethyl chloroacetate and benzylmethylamine.

Condensation of 5-benzyloxyindolylmagnesium bromide with benzyloxycarbonylglycyl chloride yielded the ketone (IV; R = CH_2Ph·O) but the corresponding alcohol (II; R = CH_2Ph·O, R′ = H, R″ = ·CO_2·CH_2Ph), obtained by lithium borohydride reduction, was a glass. Catalytic debenzylation of this material gave an amorphous solid from which the alcohol (II; R = OH, R′ = R″ = H) could not be obtained pure or crystalline.

Finally it was hoped to prepare the alcohol (II; R = H, R′ = R″ = Me) by reduction of the dimethylamino-ketone (VII). Reaction between indolylmagnesium bromide and chloroacetyl chloride furnished a di(chloroacetyl)indole which is formulated as (V) on the basis of the following evidence. On treatment with dimethylamine in cold ethanol it yields an insoluble chloroacetylindole, m. p. 230°, converted by catalytic hydrogenation in the presence of a base into the known 3-acetylindole. The intermediate chloroacetylindole must therefore be the 3-isomer; fractional crystallisation of the products from the Grignard

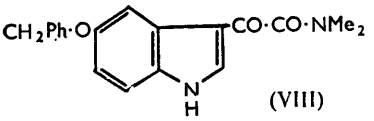
[4] Thesing, *Chem. Ber.*, 1954, **87**, 507.
[5] Alberti, *Gazzetta*, 1937, **67**, 238.
[6] Leete and Marion, *Canad. J. Chem.*, 1953, **31**, 775.
[7] Silverstein, Ryskiewicz, and Chaikin, *J. Amer. Chem. Soc.*, 1954, **76**, 4485.

reaction yielded more of this product, but the di(chloroacetyl)indole was the main product even when equimolar proportions of reactants were employed. Previous work [3,8] on this condensation, however, has been stated to give a 3-chloroacetylindole, m. p. 214°. Mingoia [9] also obtained material, m. p. 214°, but, in addition, isolated an " isomer," m. p.



230°, which he considered was the 2-isomer since it gave indole-2-carboxylic acid on fusion with potassium hydroxide. Speeter and Anthony [10] have recently pointed out that such evidence is valueless as 3- as well as 2-substituted indoles give the 2-carboxylic acid on alkali fusion. It is therefore suggested that Mingoia's product, m. p. 230°, was actually 3-chloroacetylindole and that the specimens, m. p. 214°, of earlier workers were impure and probably contained some 1 : 3-di(chloroacetyl)indole.

Treatment of either 3-chloroacetylindole or 1 : 3-di(chloroacetyl)indole with dimethylamine in ethanol–methoxyethanol gave the required 3-dimethylaminoacetylindole (VII). Repeated attempts to reduce this ketone with lithium borohydride were unsuccessful, most of the ketone being recovered, although it evidently formed a complex with the borohydride. Reduction with approximately the calculated amount of lithium aluminium hydride gave a complex mixture from which the required alcohol could not be isolated.



(VIII)

When this work was nearly complete Dr. R. F. Parcell (Parke, Davis and Co., Detroit) kindly informed us that in unpublished work he had obtained the phenol (II; R = OH, R′ = R″ = Me) by reduction of the ether (VIII) with lithium aluminium hydride in dioxan–ether followed by catalytic debenzylation (contrast Speeter and Anthony [10]).

Experimental

Reaction between Indolylmagnesium Iodide and Benzamidoacetaldehyde.—Ethereal indolylmagnesium iodide (15 c.c.; 1M) was added to a stirred suspension of benzamidoacetaldehyde (4·1 g.) in ether (25 c.c.), and the mixture stirred for 5 hr. Decomposition of the complex with ammonium chloride solution and extraction with ether furnished an oil which was washed with boiling light petroleum (b. p. 60—80°). The gum was triturated with ether, to give a small amount of 1-*benzamido*-2 : 2-*di*-3′-*indolylethane* (III), m. p. 187—190° (Found : C, 78·9; H, 5·5; N, 10·9. $C_{25}H_{21}ON_3$ requires C, 79·1; H, 5·6; N, 11·1%).

Reductions with Lithium Borohydride. General Procedure.—Lithium borohydride (1 g.) was added to a suspension of the ketone (5 g.) in tetrahydrofuran (40 c.c.; dried over CaH_2), and the mixture left at room temperature for 2 hr. with occasional shaking. After addition of ammonium chloride solution and extraction with ethyl acetate, the extracts were washed with water, dried (Na_2SO_4), and evaporated *in vacuo* (bath <40°), the residue being crystallised or distilled.

Thus were prepared 3-hydroxymethylindole (5·2 g. from 5·8 g. of 3-formylindole), m. p. 89—91° (varies with rate of heating [7]) (Found : C, 73·6; H, 6·4. Calc. for C_9H_9ON : C, 73·5; H, 6·2%), and 1-*acetyl*-3-*hydroxymethylindole* (0·5 g. from 1·0 g. of 1-acetyl-3-formylindole [2]), needles, m. p. 137—139°, from benzene–ethyl acetate (Found : C, 69·8; H, 5·9; N, 7·6. $C_{11}H_{11}O_2N$ requires C, 69·8; H, 5·9; N, 7·4%). In another experiment the crude reduction product from 1-acetyl-3-formylindole (2·0 g.) was dissolved in ethanol (20 c.c.) and treated with ethanolic dimethylamine (3 c.c.; 33%) at room temperature for 1 hr. Evaporation *in vacuo*, addition of water, and isolation with ether furnished 3-hydroxymethylindole (0·7 g.), m. p. 95—98°.

[8] Majima and Kotake, *J. Chem. Soc. Japan*, 1922, **43**, No. 12; Sanna, *Gazzetta*, 1929, **59**, 838.
[9] Mingoia, *ibid.*, 1931, **61**, 646.
[10] Speeter and Anthony, *J. Amer. Chem. Soc.*, 1954, **76**, 6208.

3-Hydroxymethyl-1-methylindole.—3-Formyl-1-methylindole (6·4 g.) was reduced by the general procedure and the product distilled, two fractions being separated : (i) *3-hydroxymethyl-1-methylindole*, b. p. 150—160°/2 mm. (Found : C, 74·7; H, 7·1; N, 8·8. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·9; N, 8·7%); and (ii) a resinous gum, b. p. 215—220°/0·4 mm. The latter crystallised on trituration with methanol and recrystallisation from the same solvent afforded *di-(1-methyl-3-indolyl)methane*, prisms m. p. 105—109° (Found : C, 83·0; H, 6·8; N, 10·6. $C_{19}H_{18}N_2$ requires C, 83·2; H, 6·5; N, 10·2%).

Reduction of 3-Acetylindole.—(*a*) When 3-acetylindole (6·4 g.) was reduced with lithium borohydride (1·0 g.), starting material (2·8 g.) was recovered and *3-1'-hydroxyethylindole* (1·6 g.) was obtained as an orange oil (Found : C, 74·1; H, 7·3; N, 8·4. $C_{10}H_{11}ON$ requires C, 74·5; H, 6·9; N, 8·7%). (*b*) Starting material (0·5 g.) was again recovered when the ketone (6·4 g.) and lithium borohydride (1·0 g.) in tetrahydrofuran (25 c.c.) were refluxed for 50 min. Distillation of the product, isolated in the usual manner, gave 3-ethylindole (2·3 g.), b. p. 128—129°/5 mm., m. p. 33—35° (Found : C, 82·8; H, 7·7; N, 9·8. Calc. for $C_{10}H_{11}N$: C, 82·7; H, 7·6; N, 9·7%).

Reduction of 1 : 3-Diacetylindole.—The diacetylindole (2·0 g.) was reduced by the general procedure, 0·8 g. being recovered unchanged on trituration with ether–ethyl acetate. Evaporation of the mother-liquors *in vacuo* yielded a brown gum which appeared to be mainly *1-acetyl-3-1'-hydroxyethylindole* (Found : C, 70·3; H, 6·7; N, 6·2. $C_{12}H_{13}O_2N$ requires C, 70·9; H, 6·5; N, 6·9%).

3-Benzyloxycarbonylaminoacetylindole.—A suspension of *N*-benzyloxycarbonylglycine (10 g.) in ether (100 c.c.) was treated with oxalyl chloride (15 g.) at room temperature for 2 days; the solution was decanted into benzene (250 c.c.) and evaporated to dryness *in vacuo* (bath <30°). The residual acid chloride in ether was rapidly added to a vigorously stirred, ice-cooled solution of indolylmagnesium bromide (from indole, 5·9 g.) in ether (1 l.). After 30 min. saturated ammonium chloride solution (300 c.c.) was added and stirring continued until the red gummy complex had decomposed to give a white solid. Separated by filtration and washed with water and ether, the crude ketone (3·7 g.) had m. p. 215—220°. Extraction of the filtrate with ethyl acetate and trituration of the resulting gum with ether yielded more material, m. p. 215—220° (0·2 g.). The *ketone* separated from ethanol in plates, m. p. 227—230° (Found : C, 70·0; H, 5·2; N, 9·4. $C_{18}H_{16}O_3N_2$ requires C, 70·1; H, 5·2; N, 9·1%).

3-(2-Benzyloxycarbonylamino-1-hydroxyethyl)indole.—The foregoing crude ketone (5·0 g.) was reduced by the general procedure; the resulting *alcohol* (4·1 g.) crystallised from benzene as plates, m. p. 116—117° (Found : C, 69·8; H, 6·0; N, 9·2. $C_{18}H_{18}O_3N_2$ requires C, 69·7; H, 5·9; N, 9·0%).

3-(2-Amino-1-hydroxyethyl)indole.—The alcohol (6·3 g.) in ethanol (80 c.c.) was hydrogenated in the presence of 5% palladised charcoal (1 g.) until absorption ceased. The filtered solution was concentrated to small volume under reduced pressure and treated with picric acid (3·5 g.) in methanol–water (2 : 1; 40 c.c.); the precipitated picrate (5·6 g.) decomposed above 95° without melting. Recrystallisation from aqueous methanol gave plates which decomposed at 100° without melting (Found : C, 47·6; H, 3·9; N, 17·7. Calc. for $C_{16}H_{15}O_8N_5$: C, 47·4; H, 3·7; N, 17·3%). Majima and Kotake [2] claimed to have prepared this picrate as orange crystals, m. p. 188°. The product prepared as described above was bright yellow but became orange, owing to decomposition, during attempts to recrystallise it from high-boiling solvents.

In another experiment, the alcohol (0·5 g.) was hydrogenated similarly and the crude product treated with periodic acid (0·5 g.) in aqueous methanol. After 1 hr. the mixture was concentrated and diluted with water; recrystallisation of the precipitate from aqueous ethanol gave 3-formylindole, m. p. 186—188° undepressed by admixture with authentic material (the infrared spectra of the samples were identical).

Sarcosine.—Ethyl chloroacetate (216 g.) was added during 1 hr. to stirred, refluxing benzylmethylamine (430 g.) and heating continued for a further ½ hr. Isolated in the usual manner and fractionally distilled through a short Fenske column, ethyl *N*-benzyl-*N*-methylaminoacetate (306 g.) was obtained as a colourless oil, b. p. 103—108°/15 mm., n_D^{20} 1·4999 (Mannich and Kuphal [11] give b. p. 138°/13 mm.). The ester (306 g.) in ethanol (400 c.c.) was refluxed with 5N-sodium hydroxide solution (400 c.c.) for 6 hr. After addition of water (400 c.c.), ethanol was removed by distillation. The solution was adjusted to pH 6·5 with hydrochloric acid and evaporated to dryness under reduced pressure; repeated extraction of the residue with hot

[11] Mannich and Kuphal, *Ber.*, 1912, **45**, 314.

chloroform–ethanol (2 : 1) gave *N*-benzylsarcosine (197 g.), m. p. 184—190°. Recrystallisation from the same solvents furnished needles, m. p. 190—191° (lit.,[11] m. p. 189—190°). The amino-acid (36 g.) in ethanol (300 c.c.) and water (100 c.c.) was hydrogenated in the presence of 5% palladised charcoal (2 g.), absorption being complete in 3·5 hr. Concentration of the filtered solution to small volume followed by dilution with ethanol and then acetone yielded sarcosine (16·9 g.), m. p. 198—204° (decomp.).

N-*Benzyloxycarbonylsarcosine*.—Sarcosine (14·2 g.) was dissolved in 2N-sodium hydroxide (80 c.c.), and the mixture stirred and cooled while sodium hydroxide solution (80 c.c.; 2N) and benzyl chloroformate (27 g.) were added simultaneously during 30 min. After being stirred for a further 30 min. and washed with ether (3 × 100 c.c.), the aqueous layer was cooled and acidified with concentrated hydrochloric acid (25 c.c.). Isolated with ethyl acetate, the *acid* was a viscous gum (Found : C, 59·1; H, 6·1; N, 6·3. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·9; N, 6·3%).

3-(N-*Benzyloxycarbonylsarcosyl*)*indole*.—The foregoing acid in ether (100 c.c.) was treated with oxalyl chloride (25 g.) as in the previous example, and the crude acid chloride similarly condensed with indolylmagnesium bromide (from indole, 17·6 g.) in ether (1 l.). Decomposition of the complex with ammonium chloride solution gave only a little amorphous solid which was discarded. By extraction of the filtrate with ethyl acetate, washing with water, drying ($MgSO_4$), and evaporation *in vacuo*, a gum was obtained which crystallised on trituration with ether–ethyl acetate. This crude product (3·8 g.) had m. p. 150—160°; recrystallisation from ethyl acetate gave the *ketone*, plates, m. p. 164—166° (Found : C, 70·6; H, 6·0; N, 8·9. $C_{19}H_{18}O_3N_2$ requires C, 70·8; H, 5·6; N, 8·7%).

2-(2-N-*Benzyloxycarbonyl*-N-*methylamino*-1-*hydroxyethyl*)*indole*.—Reduction of the ketone (2·5 g.) with lithium borohydride according to the general procedure gave the *alcohol* (1·9 g.) which separated from benzene in needles, m. p. 105—106° (Found : C, 70·6; H, 6·4; N, 8·6. $C_{19}H_{20}O_3N_2$ requires C, 70·4; H, 6·2; N, 8·6%).

3-(1-*Hydroxy*-2-*methylaminoethyl*)*indole Picrate*.—The benzyloxycarbonyl compound (0·4 g.) in ethanol (30 c.c.) was hydrogenated with 5% palladised charcoal (0·5 g.), and the resulting amine isolated as the *picrate* from aqueous methanol. It decomposed at *ca.* 90° without melting (Found : C, 48·9; H, 4·1; N, 16·9. $C_{17}H_{17}O_8N_5$ requires C, 48·7; H, 4·1; N, 16·7%). The bright yellow picrate darkened to orange during attempts to recrystallise it, even from methanol, and analytical data on the products were unsatisfactory.

5-*Benzyloxy*-3-*benzyloxycarbonylaminoacetylindole*.—Finely powdered 5-benzyloxyindole[12] (11 g.) was added to a stirred, ice-cold, ethereal solution of ethylmagnesium bromide (from 1·2 g. of magnesium). After 15 minutes' stirring, benzyloxycarbonylglycyl chloride (from the acid, 10·5 g.) was added and the mixture refluxed for 1 hr. Addition of ammonium chloride solution and extraction with ethyl acetate yielded a gum, which partially crystallised on trituration with a little ethyl acetate, to give material (2·1 g.), m. p. 172—176°. The *ketone* crystallised from ethyl acetate (charcoal) in prisms, m. p. 181—183° (Found : C, 72·0; H, 5·3; N, 6·8. $C_{25}H_{22}O_4N_2$ requires C, 72·5; H, 5·4; N, 6·8%).

3-(2-*Amino*-1-*hydroxyethyl*)-5-*hydroxyindole*.—The foregoing ketone (1·0 g.) in tetrahydrofuran (20 c.c.) was reduced with lithium borohydride (0·4 g.). Isolated in the usual manner, 5-*benzyloxy*-3-(2-*benzyloxycarbonylamino*-1-*hydroxyethyl*)*indole* was a gum (Found, after drying at 30°/0·1 mm. for 1 hr. : C, 72·2; H, 5·8. $C_{25}H_{24}O_4N_2$ requires C, 72·1; H, 5·8%).

The alcohol (from 4·4 g. of ketone) in ethanol (60 c.c.) was shaken in hydrogen with 5% palladised charcoal (2 g., 1 g., 1 g. portions) until 2 mol. had been absorbed. Evaporation of the filtered solution gave a gum. Amorphous solid (1·3 g.) was obtained by dissolution in butanol, followed by addition of toluene to the filtered (charcoal) solution. Reprecipitation in the same manner yielded an almost colourless solid which was dried at 57°/0·1 mm. for 8 hr.; it decomposed at *ca.* 110° without melting (Found : C, 63·1; H, 6·1; N, 12·6. $C_{10}H_{12}O_2N_2$ requires C, 62·5; H, 6·3; N, 14·6%). This product presumably consisted mainly of the *phenol* (II; R = OH, R′ = R″ = H) but it could not be obtained crystalline and attempts to purify it further were unsuccessful.

1 : 3-*Di*(*chloroacetyl*)*indole*.—Indolylmagnesium bromide (from indole, 23·4 g.) in ether (1 l.) was stirred vigorously at 0° while chloroacetyl chloride (15 c.c.) in ether (100 c.c.) was added rapidly. After the mixture had been stirred for a further 30 min., saturated ammonium chloride solution (800 c.c.) was added. The insoluble colourless product [12·3 g.; m. p. 165—175° (decomp.)] was collected and washed with water and ether. Recrystallisation of a portion from

[12] Boehme, *J. Amer. Chem. Soc.*, 1953, **75**, 2502.

methanol–ethyl acetate (1 : 1) gave stout needles of 1 : 3-*di(chloroacetyl)indole* m. p. 175—176° (Found : C, 53·3; H, 3·4; N, 5·3; Cl, 26·0. $C_{12}H_9O_2NCl_2$ requires C, 53·4; H, 3·4; N, 5·2; Cl, 26·2%). In one experiment the ethereal layer was separated, washed with water and evaporated *in vacuo*. On standing at 0° crystallisation occurred; trituration with ether followed by recrystallisation from ethanol–ethyl acetate (charcoal) gave a small quantity of 3-chloroacetylindole, yellow needles, m. p. 229—230° (decomp.) (Found : C, 61·4; H, 4·1; N, 7·3; Cl, 18·5. Calc. for $C_{10}H_8ONCl$: C, 62·0; H, 4·2; N, 7·2; Cl, 18·3%). This sample did not depress the m. p. of that described below. No other crystalline products could be isolated from the reaction mixture.

3-*Chloroacetylindole*.—Dimethylamine (1 c.c. of 33% ethanolic solution) was shaken with the di(chloroacetyl)indole (0·5 g.) suspended in ethanol (5 c.c.), at room temperature for 1·5 hr. Filtration afforded colourless solid (0·3 g.), m. p. 225—227° (decomp.), which, on recrystallisation from ethanol, gave 3-*chloroacetylindole*, m. p. 230—232° (decomp.) (Found : C, 61·9; H, 4·0; N, 7·6; Cl, 18·3%).

3-Chloroacetylindole (0·5 g.) in ethanol (25 c.c.) was hydrogenated in the presence of triethylamine (0·5 g.) and palladised charcoal (0·5 g.; 10% Pd). Reduction was initially rapid but became very slow after 1 mol. had been absorbed in *ca.* 5 min. Concentration of the filtered solution and addition of water yielded 3-acetylindole (0·35 g.), m. p. 183—186° raised to 188—190° by recrystallisation from ethanol. The m. p. was undepressed by admixture with authentic material.[13]

3-*Dimethylaminoacetylindole*.—A suspension of 1 : 3-di(chloroacetyl)indole (16·5 g.) in 2-methoxyethanol (100 c.c.) was treated with ethanolic dimethylamine (100 c.c.; 33%), and the mixture refluxed (bath 140°) for 2 hr. The solution was filtered (charcoal) at the b. p. and, on cooling, the product (9·2 g.), m. p. 205—210°, separated. Recrystallisation from ethanol–methoxyethanol gave colourless rods, m. p. 209—211°, of the *amino-ketone* (Found : C, 71·1; H, 7·2; N, 13·8. $C_{12}H_{14}ON_2$ requires C, 71·3; H, 7·0; N, 13·9%). The *methiodide* (prepared in methoxyethanol solution) formed needles (from methoxyethanol), m. p. 222—224° (decomp.) (Found : C, 45·3; H, 4·9; I, 36·9. $C_{13}H_{17}ON_2I$ requires C, 45·3; H, 5·0; I, 36·9%). The *picrate* crystallised from ethanol in yellow needles, m. p. 182—184° (decomp.) (Found : C, 50·2; H, 4·1; N, 16·3. $C_{18}H_{17}O_8N_5$ requires C, 50·1; H, 4·0; N, 16·2%).

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[13] Saxton, *J.*, 1952, 3592.