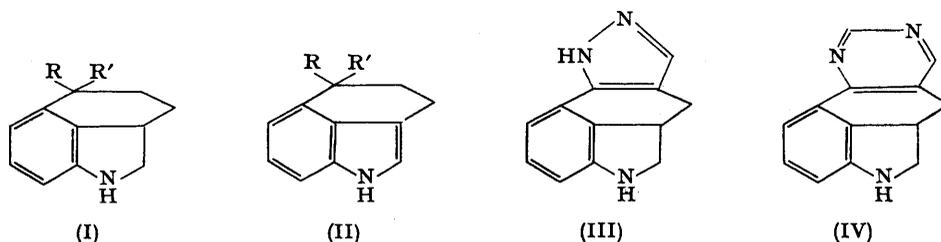


1067. *The Dehydrogenation of Indolines to Indoles with Manganese Dioxide.*

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Some simple and also tricyclic indoles, *e.g.* (II), have been prepared by dehydrogenation of the corresponding indolines with manganese dioxide.

A CONVENIENT route to various derivatives of 1,3,4,5-tetrahydrobenz[*cd*]indole (II; R = R' = H), which were required for a pharmacological study of this interesting ring system that occurs in the ergot alkaloids, appeared to exist from relatively accessible indolines, *e.g.* (I), provided that a satisfactory method for their dehydrogenation could be found.



The choice of reagent is limited by the tendency of the tricyclic system to become naphthalenoid and by the ease with which indoles undergo oxidative polymerisation. The indoline-ketone (I; RR' = :O) had been dehydrogenated to the indole-ketone (II; RR' = :O) with palladium-charcoal in small yield,¹ a result we were unable to improve on (or even quite to equal). We also obtained the same ketone in equally poor yield (7%) from the alcohol (I; R = H, R' = OH). In our search for a better dehydrogenating agent, the indoline-ketone (I; RR' = :O) was treated separately with deactivated Raney nickel in the presence of hydrated sodium arsenate,¹ mercuric acetate, potassium ferricyanide, chloranil, 9,10-phenanthraquinone,³ 2,3-dichloro-5,6-dicyano-1,4-benzoquinone,^{3,4} and nickel peroxide.² Only the last two reagents gave rise to the desired indole (II; RR' = :O), the quinone in less than 5% and nickel peroxide in about 30% yield.

¹ E. C. Kornfeld, E. J. Fornfeld, G. B. Kline, M. J. Mann, D. E. Morrison, R. G. Jones, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1956, **78**, 3087.

² K. Nakagawa, R. Konaka, and T. Nakata, *J. Org. Chem.*, 1962, **27**, 1597.

³ E. A. Braude and R. P. Linstead, *J.*, 1954, 3544 *et seq.*

⁴ D. Burn, V. Petrov, and G. O. Weston, *Tetrahedron Letters*, 1960, 14; D. Burn, D. N. Kirk, and V. Petrov, *Proc. Chem. Soc.*, 1960, 14.

Better success rewarded our efforts with manganese dioxide, a versatile reagent⁵ whose reactions with heterocyclic systems have been little studied. The indoline-ketone (I; RR' = :O) was converted into the indole-ketone (II; RR' = :O) at best in 64% yield, and the alcohol (I; R = H, R' = OH) into the same ketone in 32% yield. No naphtholic material⁶ could be detected in the product. Optimum conditions for the reaction consisted in shaking together the indoline-ketone and finely divided manganese dioxide⁷ in the ratio of 1:4 at room temperature in methylene chloride for 24 hr.

By this technique 1,2,2a,3,4,5-hexahydrobenz[cd]indole (I; R = R' = H) and its 5-piperidino- and 5-morpholino-derivatives were smoothly dehydrogenated to the corresponding indoles as were the alcohols (I: R = OH; R' = Me and Et), but dehydrogenation of the alcohol (I; R = OH, R' = Ph) was only partially successful, leading to an amorphous product with the spectral characteristics of an indole. The compounds (III) and (IV), which we prepared by interaction of 1-benzoyl-4-formyl-5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole with hydrazine and formamide, respectively, followed by hydrolytic benzoylation, were unaffected by the reagent. Some simple indolines, such as indoline* itself and ethyl β -indolin-3-ylpropionate, could also be dehydrogenated smoothly by manganese dioxide, but 2-methyl- and 2,3-dimethyl-indoline gave uncharacterisable gummy products. The 1-benzoyl derivative of the indoline-ketone (I; RR' = :O) and that of β -indolin-3-ylpropionic acid did not react with the reagent.

EXPERIMENTAL

Ultraviolet spectra were determined in ethanol.

5-Hydroxy-1,2,2a,3,4,5-hexahydrobenz[cd]indole (I; R = H, R' = OH).—(a) A solution of 5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole¹ (1.33 g.) in ethanol (10 ml.) was treated at 50° with a solution of sodium borohydride (0.25 g.) in 50% ethanol (4 ml.) and then kept at room temperature overnight. Most of the ethanol was removed under reduced pressure from the mixture which had been acidified with dilute hydrochloric acid, and water (10 ml.) was added. After treatment with charcoal the solution was added dropwise to *n*-sodium hydroxide solution (50 ml.), giving a white precipitate (1.01 g.) of the 5-hydroxy-compound, m. p. 213—214° (from benzene-ether) (Found: C, 75.1; H, 7.4; N, 8.05. C₁₁H₁₃NO requires C, 75.4; H, 7.5; N, 8.0%). The 1,5-diacetyl derivative had m. p. 156.5—158° (from ethyl acetate) (Found: C, 69.4; H, 6.6; N, 5.6. C₁₅H₁₇NO₃ requires C, 69.5; H, 6.6; N, 5.4%).

(b) A mixture of 1-benzoyl-5-hydroxy-1,2,2a,3,4,5-hexahydrobenz[cd]indole¹ (0.22 g.), sodium hydroxide (0.25 g.), water (3 ml.), and ethanol (2 ml.) was heated under reflux for 4 hr. On cooling, the 5-hydroxy-compound was obtained as prisms (0.08 g.), m. p. 209—211° undepressed by admixture with the product obtained in (a).

5-Oxo-1,3,4,5-tetrahydrobenz[cd]indole (II; RR' = :O).—(a) *From 5-hydroxy-1,2,2a,3,4,5-hexahydrobenz[cd]indole and palladium-charcoal.* A mixture of the indoline-alcohol (2.2 g.), 5% palladium-charcoal (3.0 g.), and *p*-cymene (30 ml.) was refluxed for 1 hr., and the solvent then removed under reduced pressure. The residue was digested with benzene (200 ml.) and the filtered solution washed with dilute hydrochloric acid (2 × 50 ml.), water, and dried (Na₂SO₄). Removal of the solvent yielded the indole-ketone (0.155 g., 7.1%), m. p. 160—162° undepressed on admixture with authentic material, λ_{\max} . 224, 244, 324, and 365 μ . (ϵ 13,850, 14,850, 4470, and 3690).

(b) *From 5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.* A solution of the quinone (0.44 g.) in dry benzene (25 ml.) was added to a solution of the indoline-ketone (0.33 g.) in dry benzene (15 ml.), and the solid which precipitated was filtered off. The washed (dil. NaOH, dil. HCl, and water) and dried (Na₂SO₄) filtrate was evaporated to a gum which was chromatographed on alumina with benzene. The resulting yellow solid (0.015 g., 4.6%), m. p. 142—150°, was identified as the required ketone by its infrared and ultraviolet spectra.

* After this work had been completed, a similar dehydrogenation of indoline was reported by E. F. Pratt and T. P. McGovern, *J. Org. Chem.*, **1964**, **29**, 1540.

⁵ See R. M. Evans, *Quart. Rev.*, **1959**, **13**, 61.

⁶ C. A. Grob and P. Payot, *Helv. Chim. Acta*, **1953**, **36**, 839.

(c) *From 5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole and nickel peroxide.* A solution of the indoline-ketone (1.0 g.) in dry benzene (25 ml.) containing finely powdered nickel peroxide (2.0 g.) was shaken for 24 hr. at room temperature. The nickel peroxide was filtered off and the filtrate washed with dilute hydrochloric acid (2 × 50 ml.), water, and dried (Na₂SO₄). Removal of the solvent *in vacuo* afforded the indole-ketone (0.33 g., 33.4%), m. p. 154–158°.

(d) *From 5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole and manganese dioxide.* The indoline-ketone (30.0 g.) in dry methylene chloride (600 ml.) was shaken for 24 hr. with manganese dioxide⁷ (120 g.), after which the mixture was filtered and the solid extracted in a Soxhlet apparatus for 7 hr. with methylene chloride. The combined liquors were washed with dilute hydrochloric acid (from which 2.65 g. of starting ketone was recovered on basification) and water, dried (MgSO₄), and evaporated *in vacuo*. The residue was recrystallised from benzene–light petroleum (b. p. 60–80°), to give the indole-ketone (17.3 g., 64% based on unrecovered starting material), m. p. 160–161°.

(e) *From 5-hydroxy-1,2,2a,3,4,5-hexahydrobenz[cd]indole and manganese dioxide.* A solution of the indoline-alcohol (0.5 g.) in chloroform (60 ml.) was shaken with manganese dioxide (5.0 g.) at room temperature for 2 days. The mixture was worked up as above, save that the liquor was evaporated to dryness to give a gum (0.42 g.) which, after chromatography on alumina, gave the indole-ketone (0.16 g., 32.7%), m. p. 156–159°.

1,2,2a,3,4,5-Hexahydrobenz[cd]indole (I; R = R' = H).—A mixture of 5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole (2.04 g.), hydrazine hydrate (85%; 1.6 ml.), potassium hydroxide (2.24 g.), and diethylene glycol (16 ml.) was kept at 200° for 4 hr., cooled, and poured into water. The precipitated indoline (1.54 g., 82.1%) had m. p. 55–56° [from light petroleum (b. p. 40–60°)] (Found: C, 83.4; H, 8.3; N, 8.6. C₁₁H₁₃N requires C, 83.0; H, 8.2; N, 8.8%).

1,3,4,5-Tetrahydrobenz[cd]indole (II; R = R' = H).—The preceding indoline (2.5 g.), in benzene (125 ml.), was shaken with manganese dioxide (10.0 g.) at room temperature for 2 days. The mixture was worked up in the usual way, to give a brown gum which was chromatographed on alumina with ether–light petroleum (b. p. 60–80°). The resulting semi-solid was recrystallised from light petroleum (b. p. 40–60°), to give the indole (0.96 g., 38.9%), which was identified by comparison of its m. p. (50–52°) and ultraviolet spectrum with recorded^{8,9} data.

1-Benzoyl-5-piperidino-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—A solution of 1-benzoyl-5-bromo-1,2,2a,3,4,5-hexahydrobenz[cd]indole¹ (3 g.) and piperidine (2.25 ml.) in dry benzene (120 ml.) was refluxed in an atmosphere of nitrogen for 3 hr., and then set aside at room temperature overnight. The solution was filtered from piperidine hydrobromide, washed with iced water, and extracted with iced *n*-hydrochloric acid (3 × 75 ml.). The extract was added dropwise to 2*N*-sodium hydroxide (300 ml.), with stirring, whereupon the 5-piperidino-compound was precipitated (2.22 g., 73.1%), m. p. 129.5–130.5° [from ethyl acetate–light petroleum (b. p. 40–60°)] (Found: C, 80.15; H, 7.6; N, 7.8. C₂₃H₂₆N₂O requires C, 79.7; H, 7.6; N, 8.1%).

5-Piperidino-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—A mixture of the 1-benzoyl derivative (6.15 g.), sodium hydroxide (3.0 g.), ethanol (50 ml.), and water (50 ml.) was refluxed overnight, diluted with water (100 ml.), and cooled in ice. The piperidino-compound (4.065 g., 94.5%) separated as an oil which crystallised, m. p. 99–102.5°, raised to 109–110.5° after several recrystallisations from light petroleum (b. p. 80–100°) (Found: C, 79.7; H, 8.8; N, 11.3. C₁₆H₂₂N₂ requires C, 79.3; H, 9.15; N, 11.6%).

5-Piperidino-1,3,4,5-tetrahydrobenz[cd]indole.—A mixture of the above indoline (0.5 g.), manganese dioxide (2.0 g.), and benzene (10 ml.) was shaken at room temperature for 3 days, and then worked up as usual but with omission of the acid washing. A solid (0.215 g., 43.3%), m. p. 127–130°, was obtained from the gummy residue by trituration with light petroleum (b. p. 60–80°) containing a little ether. Recrystallisation from light petroleum (b. p. 80–100°)–benzene gave the indolamine, m. p. 128–130°, λ_{max}. 225, 283, and 293 mμ (ε 22,400, 6000, and 5400) (Found: C, 79.8; H, 8.4; N, 11.4. C₁₆H₂₀N₂ requires C, 79.95; H, 8.4, N, 11.7%).

1-Benzoyl-5-morpholino-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—The procedure described for the piperidino-analogue was repeated, using morpholine (2.25 ml.). The resulting product (68%) was recrystallised from ethyl acetate–light petroleum (b. p. 40–60°), to give the 5-morpholino-compound, m. p. 132–133.5° (Found: C, 75.7; H, 7.1; N, 8.1. C₂₂H₂₄N₂O₂ requires C, 75.8; H, 6.9; N, 8.0%).

⁷ J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J.*, 1952, 1094.

⁸ W. A. Jacobs and R. G. Gould, jun., *J. Biol. Chem.*, 1937, **120**, 141.

⁹ F. C. Uhle, *J. Amer. Chem. Soc.*, 1949, **71**, 761.

5-Morpholino-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—The 1-benzoyl derivative (5.07 g.) was hydrolysed with aqueous ethanolic sodium hydroxide as above, to give the *morpholinoindoline* (3.015 g., 84.9%), which formed prisms, m. p. 129—130°, from light petroleum (b. p. 80—100°)—benzene (Found: C, 74.0; H, 8.3; N, 11.2. $C_{15}H_{20}N_2O$ requires C, 73.7; H, 8.25; N, 11.5%).

5-Morpholino-1,3,4,5-tetrahydrobenz[cd]indole.—The above indoline (1.41 g.), in benzene (25 ml.), was treated with manganese dioxide (5.65 g.) and worked up as in the piperidino-series except that the used oxide was extracted with chloroform (2 × 25 ml.) and then boiling benzene (3 × 50 ml.). The combined extracts yielded, on evaporation, a buff solid (1.26 g.), m. p. 155—160°, which was chromatographed on alumina with benzene and recrystallised from benzene—light petroleum (b. p. 60—80°), to give the *indolamine* (0.88 g., 62.9%), m. p. 172—174°. Further recrystallisation raised the m. p. to 177—179°, λ_{max} . 225, 283.5, and 292.5 μ (ϵ 25,800, 6050, and 5600) (Found: C, 74.2; H, 7.7; N, 11.8. $C_{15}H_{18}N_2O$ requires C, 74.4; H, 7.5; N, 11.6%).

1-Benzoyl-5-hydroxy-5-methyl-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—A solution of 1-benzoyl-5-oxo-1,2,2a,3,4,5-hexahydrobenz[cd]indole (7.5 g.), in benzene (45 ml.), was added during 20 min. to a refluxing solution of methylmagnesium iodide (from 2.6 ml. of methyl iodide and 1 g. of magnesium) in ether (7.5 ml.), and the mixture was refluxed for 1 hr. Ice-cold saturated ammonium chloride solution (50 ml.) was added, and the organic layer was separated, washed with water, and dried (Na_2SO_4). Removal of the solvent under reduced pressure, followed by trituration of the residue with ether, gave the *alcohol* (5.55 g., 70%), m. p. 164.5—165.5° (from methanol) (Found: C, 77.6; H, 6.4; N, 5.0. $C_{19}H_{19}NO_2$ requires C, 77.8; H, 6.5; N, 4.8%).

5-Hydroxy-5-methyl-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—A mixture of the preceding alcohol (1 g.), sodium hydroxide (1 g.), ethanol (7 ml.), and water (7 ml.) was heated under reflux for 4 hr. The crystalline solid (0.29 g., 42.9%) which formed on cooling gave needles of the *amino-alcohol*, m. p. 203—205° (decomp.) from pentyl acetate (Found: C, 72.9; H, 7.8; N, 7.4. $C_{12}H_{15}NO, \frac{1}{2}H_2O$ requires C, 72.7; H, 8.1; N, 7.1%).

5-Hydroxy-5-methyl-1,3,4,5-tetrahydrobenz[cd]indole.—A mixture of the preceding alcohol (0.25 g.), manganese dioxide (1.25 g.), and ethyl acetate (120 ml.) was shaken at room temperature for 30 min., and worked up as in previous experiments save that the solution was washed with 10% acetic acid in place of hydrochloric acid. Elution of the resulting gum from alumina with 3:1 ether—benzene yielded the crude indolic alcohol (0.18 g.), m. p. 105—115°, which was estimated to be 56% pure by comparison of its ultraviolet and infrared spectra with those of an authentic specimen.¹⁰

1-Benzoyl-5-ethyl-5-hydroxy-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—The procedure already described for the 5-methyl compound was followed with ethylmagnesium iodide. The crude *alcohol* (2.56 g.), m. p. 95—100°, which was obtained by chromatography on alumina, was recrystallised from cyclohexane—benzene, followed by extraction (Soxhlet) with ether, to give prisms (1.5 g., 18%), m. p. 120.5—122° (Found: C, 78.15; H, 6.8; N, 4.75. $C_{20}H_{21}NO_2$ requires C, 78.1; H, 6.9; N, 4.6%).

5-Ethyl-5-hydroxy-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—A mixture of the preceding alcohol (0.78 g.), sodium hydroxide (1 g.), ethanol (5 ml.), and water (6 ml.) was heated under reflux for 5.5 hr. Next morning, crystals (0.26 g., 50%) of one of the epimeric forms of the *amino-alcohol* had separated, m. p. 176—177° (from benzene) (Found: C, 76.9; H, 8.4; N, 7.3. $C_{13}H_{17}NO$ requires C, 76.8; H, 8.4; N, 6.9%). Evaporation of the hydrolysis liquor gave a solid (0.13 g., 25%), m. p. 134—140°, which, after several recrystallisations from ethanol, yielded the other epimer, m. p. 151—151.5° (Found: C, 76.4; H, 8.3; N, 6.9%).

5-Ethyl-5-hydroxy-1,3,4,5-tetrahydrobenz[cd]indole.—A mixture of the above alcohol (0.1 g.), manganese dioxide (0.5 g.), and benzene (15 ml.) was shaken at room temperature for 1.5 hr. and worked up in the usual way. The crude product (0.079 g., 79.8%) was triturated with benzene—light petroleum (b. p. 60—80°) and then recrystallised from the same solvent mixture, to give the indolic alcohol, m. p. 138—140.5°, which was identified by comparison of its infrared and ultraviolet spectra with those of an authentic specimen,⁶ m. p. 142—144°, and by mixed m. p. determination.

1-Benzoyl-5-hydroxy-5-phenyl-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—The method described for the 5-methyl compound was followed using phenylmagnesium bromide. Recrystallisation of the crude product from ethyl acetate gave the *alcohol* as plates (3.39 g., 35.3%), m. p. 206—208° (Found: C, 80.6; H, 6.0; N, 4.1. $C_{24}H_{21}NO_2$ requires C, 81.1; H, 6.0; N, 3.9%).

5-Hydroxy-5-phenyl-1,2,2a,3,4,5-hexahydrobenz[cd]indole.—The above alcohol (2.3 g.) was

¹⁰ E. Hardegger and H. Corrodi, *Helv. Chim. Acta*, 1955, **38**, 468.

hydrolysed as described for the 5-methyl compound, to give the *amino-alcohol* (1.35 g., 83%), m. p. 182—184° (from benzene) (Found: C, 81.15; H, 6.8; N, 5.6. $C_{17}H_{17}NO$ requires C, 81.2; H, 6.8; N, 5.6%).

4-Benzoyl-5,5a,6,9-tetrahydro-4H-indolo[3,4-fg]indazole.—Hydrazine hydrate (5 ml.) was added to a solution of 1-benzoyl-4-formyl-5-oxo-1,2,2a,3,4,5-hexahydrobenz[*cd*]indole¹ (2.5 g.) in *n*-sodium hydroxide (50 ml.) at 45°, and the mixture was kept at room temperature overnight. The *benzoylindazole* (2.1 g., 85%) formed needles, m. p. 252—253° from methanol (Found: C, 75.8; H, 5.1; N, 14.2. $C_{19}H_{15}N_3O$ requires C, 75.7; H, 5.0; N, 13.95%). The pale yellow *acetyl derivative* had m. p. 196—198° (from ethyl acetate) (Found: C, 73.5; H, 5.0; N, 12.25. $C_{21}H_{17}N_3O_2$ requires C, 73.45; H, 5.0; N, 12.2%).

5,5a,6,9-Tetrahydro-4H-indolo[3,4-fg]indazole (III).—A mixture of the benzoylindazole derivative (0.9 g.), sodium hydroxide (0.5 g.), ethanol (5 ml.), and water (5 ml.) was refluxed (3 hr.) until all the solid had dissolved. On cooling, the *indazole* separated as its crystalline *dihydrate* (0.26 g., 37.3%), m. p. 82—84° (from benzene-ether) (Found: C, 62.5; H, 6.5; N, 18.1. $C_{12}H_{11}N_3 \cdot 2H_2O$ requires C, 61.8; H, 6.5; N, 18.0%). The *hydrochloride monohydrate* (from ethanol-ether) decomposed slowly above 210° (Found: C, 57.4; H, 5.8; Cl, 13.8; N, 16.7. $C_{12}H_{11}N_3 \cdot HCl \cdot H_2O$ requires C, 57.3; H, 5.6; Cl, 14.1; N, 16.7%). The *diacetyl derivative* had m. p. 223.5—225.5° (from ethyl acetate) (Found: C, 68.3; H, 5.45; N, 15.1. $C_{16}H_{15}N_3O_2$ requires C, 68.3; H, 5.4; N, 14.9%).

4-Benzoyl-4,5,5a,6-tetrahydroindolo[3,4-gh]quinazoline.—A solution of 1-benzoyl-4-formyl-5-oxo-1,2,2a,3,4,5-hexahydrobenz[*cd*]indole (1 g.) in formamide (10 ml.) was added dropwise to boiling formamide (20 ml.), and refluxing was continued for a further 2 hr. The cooled mixture was diluted with water (20 ml.) and extracted with chloroform (3 × 40 ml.). The dried (Na_2SO_4) extract was evaporated under reduced pressure and the residue crystallised on trituration with ether. The *quinazoline* (0.42 g., 41%) formed pale yellow prisms, m. p. 207.5—209° from propan-2-ol (Found: C, 76.3; H, 5.1; N, 13.1. $C_{20}H_{15}N_3O$ requires C, 76.7; H, 4.8; N, 13.4%).

4,5,5a,6-Tetrahydroindolo[3,4-gh]quinazoline (IV).—A mixture of the benzoylquinazoline (2.49 g.), concentrated hydrochloric acid (20 ml.), and glacial acetic acid (5 ml.) was refluxed for 7 hr. The precipitated benzoic acid was filtered off and the filtrate was evaporated to dryness under reduced pressure, leaving the dihydrochloride as a dark green solid (1.94 g., 86.8%) which decomposed above 225° after recrystallisation from ethanol-ether. Treatment of an aqueous solution of the salt with alkali and crystallisation from benzene gave lemon yellow crystals of the *quinazoline base*, m. p. 158° (Found: C, 74.5; H, 5.5; N, 19.85. $C_{13}H_{11}N_2$ requires C, 74.6; H, 5.3; N, 20.1%).

Indole.—A mixture of indoline (2.07 g.), manganese dioxide (10.0 g.), and benzene (75 ml.) was shaken overnight, and the product (1.14 g., 56%) which was isolated in the usual way and distilled, b. p. 144°/32.5 mm., m. p. 47—49°, was identified as indole by mixed m. p. and spectrographic comparison.

Ethyl β-Indol-3-ylpropionate.—Ethyl β-indolin-3-ylpropionate¹¹ (0.45 g.) in benzene (10 ml.) was shaken with manganese dioxide (2.0 g.) for 2.5 days. The crude product (0.386 g., 86.5%), m. p. 31—37°, after passage in ether through a short column of alumina followed by trituration with ether-light petroleum (b. p. 40—60°), did not depress the m. p. (41—42°) of an authentic sample prepared by esterification of β-indol-3-ylpropionic acid.

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¹¹ B. K. Blount and R. Robinson, *J.*, 1931, 3158.