702. *Indoles. Part II.* The Structure of Indole Dimer.*

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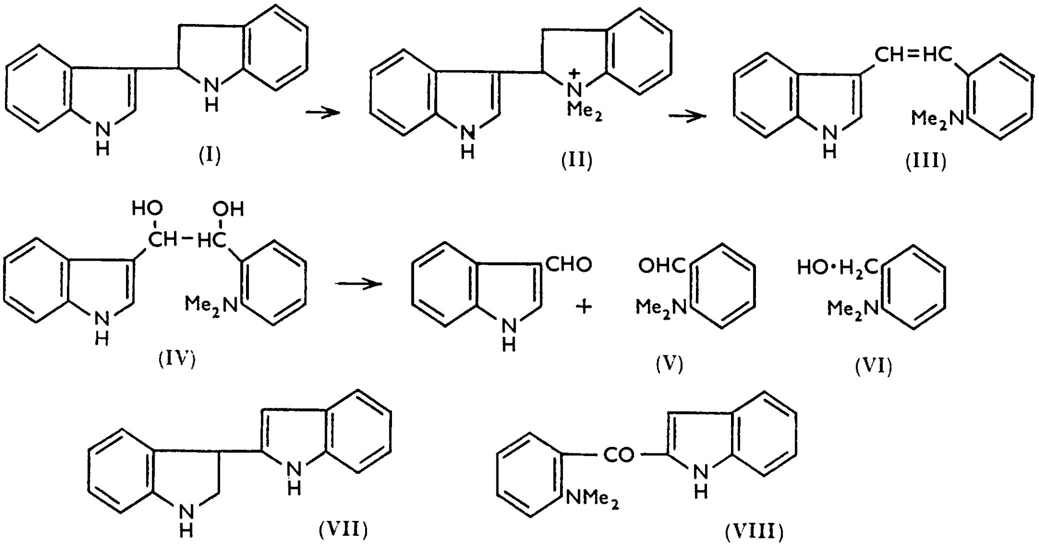
Structure (I) for indole dimer [1] is substantiated by a degradation.

In a previous communication,[1] structure (I) was proposed for indole dimer, on the basis of mechanistic arguments. We have now confirmed it by a degradation. The dimer was converted by methyl iodide and anhydrous potassium carbonate in acetone into the methyl methiodide (as II), which underwent normal Hofmann degradation to the methine (III). With osmium tetroxide this yielded the crystalline diol (IV), which with periodate gave 3-formylindole in 82% yield and a liquid base, presumably *o*-dimethylaminobenzaldehyde (V); the base was reduced by sodium borohydride to 2-dimethylaminobenzyl alcohol (VI), characterised as the picrate. Authentic 2-dimethylaminobenzyl alcohol



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* Part I, Smith, *J.*, 1954, 3842.

[1] Smith, *Chem. and Ind.*, 1954, 1451.

was prepared by reduction of methyl *NN*-dimethylanthranilate with lithium aluminium hydride.

The structure (VII) proposed by Schmitz-DuMont *et al.*[2] for indole dimer would have required the above degradation to lead to formaldehyde and the ketone (VIII).

EXPERIMENTAL

M. p.s are corrected.

2-3′-*Indolyl*-1 : 1-*dimethylindolinium iodide* (as II). Indole dimer (3 g.) in dry acetone (100 c.c.) was refluxed for 6 hr. with methyl iodide (10 g.) and potassium carbonate (10 g.). After evaporation under reduced pressure, the residue was washed with ether, then very thoroughly with cold water. Crystallisation from methanol yielded the *iodide* as prisms, m. p. 195—197° (3·8 g., 86%) (Found: C, 55·05; H, 4·9; N, 6·6. $C_{18}H_{19}N_2I$ requires C, 55·4; H, 4·9; N, 7·15%).

3-2′-*Dimethylaminostyrylindole picrate* (cf. III). The iodide (2·83 g.) was refluxed for 15 min. in 15% aqueous-ethanolic sodium hydroxide (100 c.c.), most of the ethanol removed under reduced pressure, and the residue treated with water (30 c.c.) and extracted with ether (3 × 30 c.c.). The combined, dried (K_2CO_3) extracts gave a pale brown liquid (1·92 g.), which from methanol solution gave a *picrate* (3·57 g., 82%), orange prisms, m. p. 145—149° (from acetone) (Found: C, 58·4; H, 4·25; N, 14·0. $C_{18}H_{18}N_2,C_6H_3O_7N_3$ requires C, 58·65; H, 4·3; N, 14·25%). The base, liberated from the picrate, did not crystallise.

2′-*Dimethylaminophenyl*-1-3′-*indolylethane*-1 : 2-*diol* (IV). The methine (62·5 mg.) in dry ether (2 c.c.) containing 3 drops of pyridine was treated at 0° with osmium tetroxide (100 mg.) in dry ether (10 c.c.). After being kept overnight at room temperature, the brown osmate–pyridine complex was filtered off, washed with ether, dissolved in methylene chloride (15 c.c.), and shaken with 10% aqueous mannitol (20 c.c.) containing 1% of potassium hydroxide. The methylene chloride solution was separated and the aqueous layer extracted further with methylene chloride (5 × 10 c.c.). The combined dried extracts yielded the *diol* (58·7 mg.) which crystallised from methanol as prisms, m. p. 183—185° (50·0 mg., 70·5%) (Found: C, 72·5; H, 6·9; N, 9·6. $C_{18}H_{20}O_2N_2$ requires C, 72·9; H, 6·8; N, 9·5%).

Periodate fission. The diol (80 mg.) in aqueous ethanol was treated at 0° with sodium metaperiodate (70 mg.) in water (1 c.c.). After 2 hr. at 0°, the ethanol was boiled off under reduced pressure, and the residue diluted with water (5 c.c.) and extracted with ether (4 × 10 c.c.). The combined extracts were divided into basic and non-basic fractions. The non-basic fraction (41 mg.) crystallised, to give a pinkish solid, m. p. 188—193°. Sublimation, followed by crystallisation from aqueous methanol, gave 3-formylindole as colourless plates, m. p. and mixed m. p. 194—196° (32 mg., 82%). The basic fraction (18·5 mg.) was treated in methanol (3 c.c.) with sodium borohydride (35 mg.) and kept at 40° for 2 hr. The methanol was boiled off under reduced pressure, water (10 c.c.) was added, and the whole was extracted with ether (3 × 10 c.c.). The combined, dried extracts yielded a colourless liquid (16·0 mg.) which with picric acid (24 mg.) in benzene yielded a picrate, m. p. 120—127°. One crystallisation from methanol gave yellow elongated prisms, m. p. 128—130°, undepressed on admixture with 2-dimethylaminobenzyl alcohol picrate. The free base, recovered from the picrate and distilled at 80° (oil-bath)/0·01 mm., had an infrared spectrum (liquid film) identical with that of authentic 2-dimethylaminobenzyl alcohol.

2-*Dimethylaminobenzyl alcohol* (VI).—Methyl *NN*-dimethylanthranilate[3] (10 g.) in dry ether (100 c.c.) was treated dropwise with an excess of ethereal lithium aluminium hydride. After 4 hr. at room temperature, the mixture was slowly treated with water (15 c.c.), 40% aqueous sodium hydroxide (30 c.c.) was added, the whole shaken, and the ether layer separated. This yielded 2-*dimethylaminobenzyl alcohol* (7·7 g., 96%), b. p. 115°/8 mm. (Found: C, 71·6; H, 8·6; N, 9·7. $C_9H_{13}ON$ requires C, 71·5; H, 8·65; N, 9·3%). The *picrate* forms yellow prisms (from ethanol), m. p. 129—130° (Found: C, 47·5; H, 4·65; N, 14·6. $C_9H_{13}ON,C_6H_3O_7N_3$ requires C, 47·35; H, 4·25; N, 14·75%).

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[2] Schmitz-DuMont, Hamann, and Geller, *Annalen*, 1933, **504**, 1.

[3] Willstätter and Kahn, *Ber.*, 1904, **37**, 408.