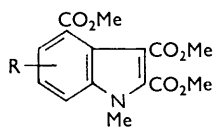


354. *Addition Reactions of Heterocyclic Compounds. Part XIV.**
The Pyrolysis† and Hydrolysis of Tetramethyl 3a,7a-Dihydro-1-
methylindole-2,3,3a,4-tetracarboxylate.

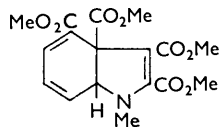
By R. M. ACHESON and J. M. VERNON.

Pyrolysis of tetramethyl 3a,7a-dihydro-1-methylindole-2,3,3a,4-tetracarboxylate (IV) with palladium-charcoal gave trimethyl 1-methylindole-2,3,4-tricarboxylate (I) and tetramethyl 1-methylindoline-2,3,3,4-tetracarboxylate (V), the latter through a 1,2-shift of the angular ester group; pyrolysis in diphenyl ether gave tetramethyl 1-methylindole-2,3,6,7-tetracarboxylate (XI) and trimethyl 1-methylpyrrole-2,3,4-tricarboxylate. Alkaline hydrolysis of the ester (IV) and treatment with diazomethane gave trimethyl 6,7-dihydro-1-methylindole-2,3,4-tricarboxylate which was oxidised to the indole (I) and with dimethyl acetylenedicarboxylate gave a mixture of 1-methylindole-tetra- and penta-carboxylic esters.

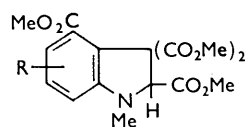
1-METHYLPYRROLE and dimethyl acetylenedicarboxylate give the 1:2 molar adduct (IV) or in other conditions a mixture of products including one unidentified compound¹ which has now been obtained along with trimethyl 1-methylindole-2,3,4-tricarboxylate (I) in variable yield by heating the adduct (IV) with palladium-charcoal. This compound, the indoline (V), was isomeric with the adduct but unlike the latter it resisted hydrogenation, and also heating with dimethyl acetylenedicarboxylate or with silver oxide in boiling light petroleum. With methanolic bromine the adduct (IV) aromatised¹ to trimethyl 1-methylindole-2,3,4-tricarboxylate, but the indoline (V) gave a monobromination product (VI) from which it was regenerated by catalytic hydrogenation. The bromo-derivative, on hydrolysis and esterification, afforded a trimethyl bromomethylindoletricarboxylate (II), decarboxylation and oxidation having taken place at some stage. Hydrogenation of this bromo-ester gave the known indole (I) which established the presence of this structural grouping in the preceding compounds of the degradation. The reactions of the



(I ; R = H)
 (II ; R = 5- or 7-Br)
 (III ; R = 6-Br)



(IV)



(V ; R = H)
 (VI ; R = 5- or 7-Br)

indoline (V) strongly suggested that it possessed a benzene ring and that further aromatisation by loss of hydrogen atoms only was impossible. The blue fluorescence and ultraviolet absorption spectrum of methyl *m*-dimethylaminobenzoate were extremely similar to those of the indoline (V), and although this model compound gave a normal methoxyl analysis the anomalously high results obtained with the indoline (V) and its bromo-derivative (VI) in the Zeisel determination are understandable since partial demethylation of methylaminobenzoic acids can occur under these conditions.² It therefore appeared that the isomer of the adduct (IV) possessed structure (V) or (VII).

Since carboxylic acid and ester groups have a similar deshielding effect on the protons of the α -carbon atom,³ the nuclear magnetic resonance of the methylene hydrogen atoms of

* Part XIII, preceding paper.

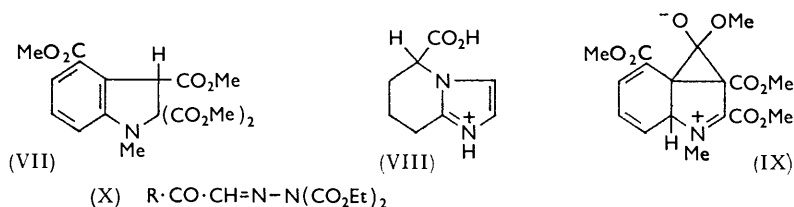
† Cf. Acheson and Vernon, *Proc. Chem. Soc.*, 1962, 277.

¹ Acheson and Vernon, *J.*, 1962, 1148.

² Goldschmiedt, *Monatsh.*, 1906, 27, 651.

³ Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon, London, 1959, p. 53.

phenylacetic acid (τ 6.4) may be used as a model for the isolated proton of structure (VII). The single proton resonance of the imidazole (VIII), and that of the methylene protons of imidazol-1-ylacetic acid (τ 4.7 and 4.8, respectively) ⁴ similarly would correspond to that expected for the isolated proton of structure (V). The nuclear magnetic resonance spectrum of the isomer of the adduct (IV) included absorption due to four *O*-methyl (τ 6.1—6.3) and one *N*-methyl group (τ 7.0), an isolated hydrogen atom (τ 4.7), and an irregular group of lines at low field; the spectrum of the bromo-derivative (VI), discussed later, is similar. Structure (V) is therefore preferred to structure (VII) for the dihydro-indole.



Elimination of the 3 α -substituent of the adduct (IV) yielding the indole (I), and its migration to the 3-position accompanied by partial aromatisation of the nucleus, are alternative reactions since independent conversion of the indoline (V) into the indole (I) did not occur. Isomerisation of the adduct (IV) to the indoline (V) may take place through nucleophilic attack of the 3-position to the 3 α -carbonyl group leading to the intermediate (IX). Opening of the cyclopropane ring and movement of the 7 α -hydrogen atom complete the sequence which accounts for the formation of the product. The intermediate (IX) is similar to the cyclopropanone intermediate suggested ⁵ for the Favorskii rearrangement and it is not impossible that the cyclopropanone of this base-catalysed reaction adds an anion yielding a species exactly comparable with structure (IX). The only other 1,2-shift of an ester group found in the literature occurs in the reaction between various diazo-ketones and diethyl azodicarboxylate: ⁶ products of structure (X) are formed and a similar mechanism involving a diaziridine intermediate can be written. Analogies are also apparent with the 1,3-shift of the ester group in the abnormal Michael reaction ⁷ and with the Stevens rearrangement. ⁸

Bromination of the indole triester (I) gave a monosubstitution product, the nuclear magnetic resonance spectrum of which showed absorption due to *O*- and *N*-methyl groups (τ 6.1—7.0) and a quartet (about τ 2.0) due to two aromatic protons. The coupling constant (1.5 c./sec.) showed that the hydrogen atoms are *meta* to each other, ⁹ and therefore bromination must have occurred at position 6, as is also the case with ethyl indole-3-carboxylate. ¹⁰ This 6-bromoindole (III) was not identical with an isomeric compound (II) obtained from the bromination product (VI) of the indoline (V). The nuclear magnetic resonance spectrum of this bromination product (VI) showed *O*- and *N*-methyl absorption (τ 6.1—6.3, and 7.0, respectively), an isolated proton (τ 5.0), and a simple quartet (τ 3.1) corresponding to an AB type of spectrum with a coupling constant (8.3 c./sec.) appropriate to adjacent benzenoid protons. ⁹ The bromine atom is therefore at position 5 or 7.

Pyrolysis of the adduct (IV) in diphenyl ether gave tetramethyl 1-methylindole-2,3,6,7-tetracarboxylate (XI) and some trimethyl 1-methylpyrrole-2,3,4-tricarboxylate,

⁴ Bishop, appendix to Abraham and Trown, *Biochem. J.*, in the press.

⁵ Lofffield, *J. Amer. Chem. Soc.*, 1951, **73**, 4707.

⁶ Fahr and Scheckenbach, *Annalen*, 1962, **655**, 86.

⁷ Bergmann, Ginsburg, and Pappo, *Org. Reactions*, 1959, **10**, 179.

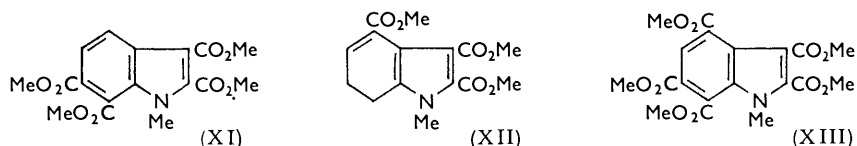
⁸ Hauser and Kantor, *J. Amer. Chem. Soc.*, 1951, **73**, 1437.

⁹ Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance Spectroscopy," McGraw-Hill, New York, 1959, p. 264.

¹⁰ Majima and Kotake, *Ber.*, 1930, **63**, 2237.

both of which had previously been obtained¹ from 1-methylpyrrole and dimethyl acetylenedicarboxylate. Scission of the 3,3a-bond in the adduct (IV) and re-attachment of the side chain at the old 7 position followed by dehydrogenation could account for the formation of the indole (XI) in a way which resembles the thermal rearrangement of some Diels-Alder adducts described by Woodward and Katz.¹¹

Hydrolysis of the adduct (IV), acidification, and treatment with diazomethane gave a dihydrotrimethyl-1-methylindole-2,3,4-tricarboxylate which with bromine or palladium-charcoal was oxidised to the indole (I). Both the dihydroindole and the trimethyl 4,5,6,7-tetrahydro-1-methylindole-2,3,4-tricarboxylate obtained on hydrogenation gave the Ehrlich reaction. Their ultraviolet absorption spectra and that of diethyl 4,5-dimethylpyrrole-2,3-dicarboxylate¹² were very similar and closely resembled those of other pyrroles not possessing additional unsaturated substituents at the α -positions; unsaturated substituents at β -positions have a comparatively small effect on the pyrrole spectrum.¹² This suggests that the dihydroindole possesses structure (XII). With dimethyl acetylenedicarboxylate the dihydroindole (XII) gave a mixture of 1-methylindole-tetra- and -penta-carboxylic esters whose failure to give an Ehrlich reaction suggests the presence of substituents in the 2,3-position. The ultraviolet absorption spectrum of the pentaester



is particularly like that of the tetraester (XI) and is consistent with structure (XIII), which could be formed by addition of the acetylenic ester across the 5,7a-positions of the dihydroindole (XII) followed by the elimination of the 6,7-carbon atoms as ethylene.

Ultraviolet absorption spectra in methanol.

Compound	Absorption maxima (\AA) ($10^{-4} \epsilon$)					
<i>Reduced indoles</i>						
(V)	2280	(1.85)	2640	(0.56)	3440	(0.31)
(VI)	2280 *	(3.06)	2770	(1.21)	3360	(0.29)
6,7-Dihydro-1-methylindole-2,3,4-tricarboxylic acid hydrate	2560	(0.90)	2980	(1.00)		
(XII)	2500	(0.60)	2880	(0.90)		
4,5-Dihydro-(XII)	2510	(0.56)	2890	(0.96)		
Me ₂ 6,7-dihydro-1-methylindole-3(?),4-dicarboxylate	2370	(0.90)	2610 †	(0.40)		
<i>Indoles</i>						
(II)	2280	(3.04)	3020	(1.28)		
(III)	2300		3210			
(XIII)	2500	(3.16)	3140	(1.23)		
Me ₄ 1-methylindole-tetracarboxylate, m. p. 200°	2425	(3.83)	3115	(1.12)		
Me ₂ 1-methylindole-3(?),4-dicarboxylate	2200	(3.27)	2485	(0.92)	2930	(0.98)
<i>Reference compounds</i>						
Me <i>m</i> -dimethylaminobenzoate	2295	(2.37)	2630	(0.99)	3425	(0.22)
Et ₂ 4,5-dimethylpyrrole-2,3-dicarboxylate †... ..	2130	(0.80)	2500	(0.45)	2930	(1.05)

* Not max., absorption at this wavelength. † Infection. ‡ In ethanol; see ref. 12.

The thermal elimination of an ethano-bridge leading to an aromatic structure is a common reaction and the initial addition suggested is analogous to those of maleic anhydride to 2-vinylfuran¹³ and to 2-vinylthiophen.¹⁴

¹¹ Woodward and Katz, *Tetrahedron*, 1959, **5**, 70.

¹² Cookson, *J.*, 1953, 2789.

¹³ Paul, *Compt. rend.*, 1939, **208**, 1028.

¹⁴ Scully and Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 6329.

Selective decarboxylation of 6,7-dihydro-1-methylindole-2,3,4-tricarboxylic acid, esterification, and dehydrogenation gave the same product as that obtained from the triester (I) by partial hydrolysis and decarboxylation. The 2-carboxyl group is probably lost.¹⁵

EXPERIMENTAL

Alumina used for chromatography was Spence's grade H, deactivated by being shaken with 5% of its weight of 10% aqueous acetic acid. Ehrlich's reagent was *p*-dimethylaminobenzaldehyde (2%) in concentrated hydrochloric acid-ethanol-water (*ca.* 1 : 3 : 6 v/v).

The nuclear magnetic resonance spectra were measured at 29.91 Mc./sec. with chloroform, deuteriochloroform, or nitromethane as solvent and tetramethylsilane as internal standard; the model compounds were measured in trifluoroacetic acid with cyclohexane (τ 8.56) as internal standard. The infrared spectra were measured for Nujol mulls and inflections are marked with an asterisk.

Pyrolysis of Tetramethyl 3a,7a-Dihydro-1-methylindole-2,3,3a,4-tetracarboxylate (IV).—(i) 5% Palladium-charcoal (Light's, 5 g.) was washed with dilute hydrochloric acid, sucked dry, and further dried at 140° for 10 min. It was intimately mixed with the dihydroindole (IV) (5.0 g.) and after being heated at 180° for 6 hr. the mixture was extracted with ether (Soxhlet). The partially crystalline ether-soluble material was dissolved in benzene and chromatographed on alumina (100 ml.) prepared in light petroleum (b. p. 40–60°). Elution with 1 : 1 v/v light petroleum (b. p. 40–60°)-benzene (1.8 l.) and evaporation gave *tetramethyl 1-methylindoline-2,3,3,4-tetracarboxylate* (V), which crystallised from methanol in large hexagonal prisms (0.2 g., 4%), m. p. 107°, identical in mixed m. p. and infrared absorption spectrum with the unidentified material of m. p. 107° (Found: C, 56.0; H, 5.3; N, 3.9; OMe, 38.6; total *N*-Me and *O*-Me, 20.3%; *M*, 401, 351. C₁₇H₁₉NO₈ requires C, 55.9; H, 5.3; N, 3.8; 4OMe, 34.0; total *O*-Me and *N*-Me, 20.5%; *M*, 365) which was obtained earlier¹ from 1-methylpyrrole and dimethyl acetylenedicarboxylate. Its infrared absorption spectrum for paraffin paste (ν_{\max} . 5.69, 5.72, 5.79, 5.87, 6.26, 6.80*, 7.00, 7.36, 7.70, 7.82, 8.10, 8.21, 8.37, 8.62, 8.88, 9.37, 9.56, 9.73, 9.92, 10.07, 10.60, 11.17, 11.21, 11.57, 12.01, 12.21, 13.05, 13.23, 13.60, and 14.60 μ), but not for chloroform solutions, had an unusual quartet of peaks in the carbonyl region which was particularly useful for identification. In benzene, chloroform, or methanol it showed a strong blue fluorescence. It gave no Ehrlich reaction and did not react in acetic acid with hydrogen over Adams catalyst, with silver oxide in refluxing light petroleum (b. p. 60–80°), or with dimethyl acetylenedicarboxylate at 190° for 2–3 hr.

Further elution with benzene (1.2 l.), evaporation, and crystallisation of the residue from methanol gave needles of trimethyl 1-methylindole-2,3,4-tricarboxylate (I) (0.4 g., 9%), m. p. and mixed m. p. 123–124° with an authentic specimen.¹

The above procedure gave the most reproducible results. The use of different batches of palladium-charcoal previously washed with alkali or suspended in methanol and shaken under hydrogen, or untreated catalyst, or a shorter reaction time gave very variable yields (0–30%) of the indoline (V) together with the indole (I) and, in one case, some trimethyl 1-methylpyrrole-2,3,4-tricarboxylate, m. p. and mixed m. p. 162° (1%) with a sample prepared earlier,¹ was also formed.

(ii) The dihydroindole (IV) (5.0 g.) was added in portions to refluxing diphenyl ether. After 10 min., when some darkening had taken place, the mixture was cooled and the insoluble material collected and washed with ether. Recrystallisation of the solid from methanol (charcoal) gave trimethyl 1-methylpyrrole-2,3,4-tricarboxylate (0.2 g., 6%), m. p. and mixed m. p. 163°.

The dark tarry solution obtained on concentration of the combined filtrate and washings showed no infrared acetylenic absorption and slowly deposited a solid. Crystallisation of this from methanol gave tetramethyl 1-methylindole-2,3,6,7-tetracarboxylate (XI) (0.5 g., 10%), of identical m. p., mixed m. p., and infrared absorption spectrum with a specimen obtained previously.¹

Degradation of Tetramethyl 1-Methylindoline-2,3,3,4-tetracarboxylate (V). This indoline (0.5 g.) in methanol (10 ml.) at 40° was treated with bromine (0.25 g.) in methanol (1 ml.). The colour faded rapidly and after 1 hr. at room temperature the solution was evaporated.

¹⁵ Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience Publ., Inc., New York, 1960, p. 69.

The residue crystallised on trituration with ether, giving *tetramethyl 5(or 7)-bromo-1-methylindoline-2,3,3,4-tetracarboxylate* (VI) which separated from light petroleum (b. p. 60—80°) in colourless prisms (0.45 g., 74%), m. p. 97—98° (Found: C, 45.0; H, 4.2; N, 3.6; Br, 17.1; OMe, 31.6. $C_{17}H_{18}BrNO_8$ requires C, 46.0; H, 4.1; N, 3.2; Br, 18.0; 4OMe, 28.0%), ν_{max} . 5.72, 5.78*, 6.32, 7.00*, 7.43, 7.85, 7.95*, 8.01, 8.17, 8.35, 8.50*, 8.97, 9.23, 9.52, 9.90, 10.20, 10.95, 11.80, 12.33, 12.75, 13.20, and 13.65 μ . This bromo-compound (30 mg.) in methanol (3 ml.) with palladised charcoal was shaken under hydrogen (3 atm.) for 19 hr. Filtration, evaporation, and crystallisation of the residue from methanol gave back the original indoline (V) (15 mg.), m. p. 106°, identical with an authentic specimen in mixed m. p. and infrared absorption spectrum.

The bromo-compound (VI) (0.38 g.) was refluxed with potassium hydroxide (1.2 g.) in water (0.6 ml.) and methanol (3 ml.) for 6 hr. After cooling, the precipitate was collected. It dissolved in water and after acidification the resulting solution was extracted continuously with ether. The dried ($MgSO_4$) extract was evaporated and the residue treated with ethereal diazomethane. Evaporation gave a glass which crystallised from methanol (after 6 months), yielding *trimethyl 5(or 7)-bromo-1-methylindole-2,3,4-tricarboxylate* (II) as colourless prisms (40 mg.), m. p. 177° (Found: C, 46.7; H, 3.8; N, 3.6; OMe, 24.2. $C_{15}H_{14}BrNO_8$ requires C, 46.8; H, 3.7; N, 3.7; 3OMe, 24.1%), ν_{max} . 5.72, 5.83, 6.23, 6.54, 7.01, 7.11, 7.40, 7.51, 7.92, 8.03, 8.24, 8.56, 9.27, 9.86, 10.00, 10.35, 10.61, 11.38, 12.35, 12.52, 12.65, 13.01, and 13.33 μ . It gave no colour on prolonged heating with Ehrlich's reagent.

This bromoindole (II) (8 mg.) was shaken in methanol (2 ml.) with hydrogen (3 atm.) over palladium on charcoal for 16 hr. Filtration and evaporation gave *trimethyl 1-methylindole-2,3,4-tricarboxylate* (I), m. p. 121—122°, mixed m. p. with an authentic specimen 122—123° with which it was identical in infrared absorption spectrum.

Bromination of Trimethyl 1-Methylindole-2,3,4-tricarboxylate (I).—Bromine (2.0 g.) in glacial acetic acid (5 ml.) was added slowly with swirling to the indole (I) (2.4 g.) in glacial acetic acid (12 ml.) at 10° and after 2 hr. the mixture was poured into cold water. After $\frac{1}{2}$ hr. the precipitate was collected; it crystallised from methanol as a mixture of matted needles and colourless prisms. In warm methanol the needles dissolved more rapidly than the prisms, which remained on decantation. The needles melted, at 150—160°, after further crystallisation from methanol, but subsequent crystallisation from light petroleum (b. p. 60—80°)-benzene gave *trimethyl 6-bromo-1-methylindole-2,3,4-tricarboxylate* (III) as matted needles (0.8 g.), m. p. 157—159° (Found: C, 46.8; H, 3.9; N, 3.5; Br, 19.7; OMe, 24.9. $C_{15}H_{14}BrNO_8$ requires C, 46.9; H, 3.7; N, 3.7; Br, 20.8; 3OMe, 24.2%).

The prisms crystallised from methanol, yielding another compound, m. p. 187°, which is under investigation.

The 6-bromoindole (III), when shaken in methanol with palladium-charcoal and hydrogen, was debrominated to the original indole (I), identified by mixed m. p. and infrared absorption spectrum comparisons.

Methyl m-Dimethylaminobenzoate.—*m*-Dimethylaminobenzoic acid with ethereal diazomethane gave the ester, a colourless oil with a blue fluorescence, b. p. 72°/0.03 mm., 278°/7.34 mm. (lit.,¹⁶ 270°), n_D^{20} 1.559 (Found: C, 66.7; H, 7.3; N, 7.8; OMe, 17.5; *O*-Me + *N*-Me, 24.5. Calc. for $C_{10}H_{13}NO_2$: C, 67.1; H, 7.3; N, 7.8; OMe, 17.3; *O*-Me + *N*-Me, 25.2%). With bromine in methanol it gave a *dibromo-derivative*, crystallising from methanol in prisms, m. p. 150° (decomp.) (Found: C, 35.5; H, 3.9; N, 4.0; OMe, 9.7. $C_{10}H_{11}Br_2NO_2$ requires C, 35.6; H, 3.3; N, 4.2; OMe, 9.2%).

Trimethyl 6,7-Dihydro-1-methylindole-2,3,4-tricarboxylate (XII).—The dihydroindole (IV) (6 g.) and potassium hydroxide (7.2 g.) in water (7 ml.) and methanol (50 ml.) were refluxed for 12 hr. The precipitate was collected and dissolved in the minimum of water. Addition of concentrated hydrochloric acid caused evolution of carbon dioxide and precipitation of *6,7-dihydro-1-methylindole-2,3,4-tricarboxylic acid monohydrate* (2.65 g., 57%), which crystallised from aqueous ethanol as a white powder, darkening on heating, m. p. 229° (decomp.) (Found: C, 50.7; H, 4.6; N, 5.0%; *M*, by potentiometric titration, 290. $C_{12}H_{13}NO_7$ requires C, 50.9; H, 4.6; N, 5.0%; *M*, 283). It gave a purple Ehrlich colour when heated.

The *triester* (XII), obtained with diazomethane in ether, separated from a large volume of light petroleum (b. p. 40—60°) as prisms, m. p. 98° (Found: C, 58.8; H, 5.6; N, 4.6; OMe, 30.3. $C_{15}H_{17}NO_8$ requires C, 58.7; H, 5.5; N, 4.6; 3OMe, 30.3%).

¹⁶ Griess, *Ber.*, 1873, 6, 585.

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Oxidation of Trimethyl 6,7-Dihydro-1-methylindole-2,3,4-tricarboxylate.—(i) Bromine (0.08 g.) was added to the triester (XII) (0.3 g.) in methanol (3 ml.). The colour was discharged and after 1 hr. the precipitate was collected. Crystallisation from methanol gave trimethyl 1-methylindole-2,3,4-tricarboxylate (I) (0.27 g., 90%) as prisms, m. p. and mixed m. p. 122—124°.

(ii) The triester (XII) (50 mg.) and 5% palladium-charcoal (50 mg.) were heated at 140° for 45 min. Extraction with hot methanol yielded trimethyl 1-methylindole-2,3,4-tricarboxylate (20 mg.), m. p. and mixed m. p. 122—123°.

Trimethyl 4,5,6,7-Tetrahydro-1-methylindole-2,3,4-tricarboxylate.—The dihydroindole (XII) (0.5 g.) in methanol (20 ml.) was shaken with 10% palladium-charcoal (0.1 g.) under hydrogen (5 atm.) for 30 hr. Filtration and evaporation gave a colourless oil which largely solidified. Recrystallisation from ether-light petroleum (b. p. 40—60°) gave needles of an unidentified material (50 mg.), m. p. 146—147° (Found: C, 55.5; H, 5.8; N, 4.0%), and concentration of the filtrate from this gave *trimethyl 4,5,6,7-tetrahydro-1-methylindole-2,3,4-tricarboxylate* (0.35 g., 70%) which separated as irregular prisms, m. p. 95° (Found: C, 58.1; H, 6.2; N, 4.7. $C_{15}H_{19}NO_6$ requires C, 58.3; H, 6.2; N, 4.5%). It gave a dark violet colour on prolonged heating with Ehrlich's reagent. It was very similar in m. p. and in ultraviolet and infrared absorption spectra to the original dihydroindole (XII) but a mixed m. p. was depressed.

Trimethyl 6,7-Dihydro-1-methylindole-2,3,4-tricarboxylate and Dimethyl Acetylenedicarboxylate.—The triester (XII) (1.0 g.) and the acetylene (1.0 g.) were heated at 200° for 1½ hr. The resulting tar was dissolved in benzene and chromatographed on alumina (200 ml.). Elution with equal volumes of light petroleum (b. p. 40—60°)—benzene (1.2 l.) gave a trace of yellow oil. Elution with benzene (800 ml.) gave a non-indolic product (30 mg.), having m. p. 119—120° after crystallisation from methanol (Found: C, 48.7; H, 4.4; N, 1.2; OMe, 45.1%), λ_{max} 2760 Å with a shoulder at ca. 2550 Å. Further elution with benzene (1.2 l.) and 5 : 1 benzene-ether (400 ml.) gave solid A of unsharp m. p. (120 mg.). Finally elution with 5 : 1 benzene-ether (400 ml.) gave an unorientated *tetramethyl 1-methylindole-tetracarboxylate* (70 mg.), long needles (from methanol), m. p. 200° (Found: C, 56.4; H, 4.7; N, 3.9; OMe, 34.1. $C_{17}H_{17}NO_8$ requires C, 56.1; H, 4.7; N, 3.9; 4OMe, 34.2%).

Solid A was rechromatographed on alumina (10 ml.). After elution with 1 : 1 light petroleum (b. p. 40—60°)—benzene (800 ml.), benzene (400 ml.) eluted the original dihydroindole (XII) (42 mg.), m. p. and mixed m. p. 95—98° (from methanol). More benzene (1.6 l.) eluted *pentamethyl 1-methylindole-2,3,4,6,7-pentacarboxylate* (XIII) (26 mg.) which crystallised from methanol as matted needles, m. p. 187° (Found: C, 54.1; H, 4.7; OMe, 36.7. $C_{19}H_{19}NO_{10}$ requires C, 54.2; H, 4.5; 5OMe, 36.8%).

Dimethyl 1-Methylindole-3(?),4-dicarboxylate.—(i) Trimethyl 1-methylindole-2,3,4-tricarboxylate (I) (3.0 g.) and sodium hydroxide (0.40 g.) in methanol (40 ml.) and water (1 ml.) were refluxed for 4 hr., the solution evaporated to dryness, and the residue extracted with water (20 ml.). After filtration from unchanged triester (I), acidification precipitated a *dimethoxycarbonyl-1-methylindolecarboxylic acid* which separated from methanol in flakes (2.0 g., 70%), m. p. 180° (Found: C, 57.6; H, 4.6; N, 5.0; OMe, 21.5. $C_{14}H_{13}NO_6$ requires C, 57.1; H, 4.5; N, 4.8; 2OMe, 21.3%).

This acid (0.5 g.) was heated with precipitated copper powder (0.1 g.) in quinoline (2 ml.). Decarboxylation began at about 160° and was rapid at 180°, where the temperature was held for ½ hr. After cooling, an excess of dilute hydrochloric acid and ether (30 ml.) were added. The ether-soluble material crystallised from methanol (charcoal) giving *dimethyl 1-methylindole-3(?),4-dicarboxylate* (0.1 g., 24%) as colourless rods, m. p. 120—121° (Found: C, 63.6; H, 5.4; N, 5.7; OMe, 24.9. $C_{13}H_{13}NO_4$ requires C, 63.2; H, 5.3; N, 5.7; 2OMe, 25.1%). A mixed m. p. with the original triester (I) was considerably depressed and the compound with hot Ehrlich's reagent gave a purple colour which faded on cooling.

(ii) 6,7-Dihydro-1-methylindole-2,3,4-tricarboxylic acid hydrate (1.2 g.) was heated with concentrated hydrochloric acid (15 ml.) for 15 min. on a steam-bath while carbon dioxide was expelled and, after cooling, the insoluble material (0.6 g.) of m. p. 249° (decomp.) was collected. It gave an Ehrlich reaction when heated. This solid reacted with diazomethane in ether, and the product was purified with charcoal from methanol solution. Crystallisation of the methanol-soluble material from light petroleum (b. p. 60—80°) now gave *dimethyl 6,7-dihydro-1-methylindole-3(?),4-dicarboxylate* as colourless crystals, m. p. 103—103.5° (Found: C, 63.3; H, 6.0; N, 5.8; OMe, 24.3. $C_{13}H_{13}NO_4$ requires C, 62.7; H, 6.0; N, 5.6; 2OMe, 24.9%).

This diester (20 mg.) was heated with 5% palladium-charcoal (20 mg.) at 130° for 35 min.

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Extraction with methanol gave dimethyl 1-methylindole-3(?),4-dicarboxylate, identical in mixed m. p. and infrared absorption spectrum with the specimen obtained as under (i).

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DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF OXFORD.

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