188°; *Anal.* Found: C, 61.99; H, 3.69; N, 4.44; Cl, 1.09; $\lambda_{\max}^{\text{Nujol}}$ 5.79 μ). Although nitration of this chloroester gave V (R = CH_3; X = Cl) (m.p. 231° dec. *Anal.* Found: C, 54.9; H, 3.2; N, 7.4; Cl, 9.6) which could be converted *via* palladium-catalyzed reduction to VII (R = CH_3; X = Cl) (m.p. 306° dec. *Anal.* Found: C, 61.47; H, 3.03; N, 9.15; Cl, 11.6), dechlorination of these compounds was impracticable and it was therefore necessary to proceed as follows. Reduction of IV (R = CH_3; X = Cl) with sodium borohydride removed the chlorine and reduced the benzo[f]-quinoline to corresponding 1,4-dihydroderivate, VI (R = CH_3) (m.p. 218° dec. *Anal.* Found: 68.9; H, 5.08; N, 4.74; infrared in Nujol, 3.05, 5.83 and 6.03 μ) which was aromatized with palladium-charcoal in xylene to IV (R = CH_3; X = H) (m.p. 150°. *Anal.* Found: C, 69.17; H, 4.50; N, 4.89; infrared, 5.75 and 5.80 μ). Nitration of the latter compound in analogy with Jacobs' experiments[5] on similarly constituted compounds, led almost exclusively to V (R = CH_3; X = H) (m.p. 204°. *Anal.* Found: C, 59.86; H, 3.66; N, 8.5), and subsequent reduction and lactam ring closure, using palladium-charcoal in acetic acid,[8] afforded compound VII (R = CH_3; X = H) (*Anal.* Found: C, 69.04; H, 3.68; N, 10.06), identical, in respect to melting point (302°), mixed melting point (undepressed), infrared spectrum (identical, with ester and lactam peaks at 5.80 and 5.84 μ, respectively), and ultraviolet spectrum with an authentic specimen[2,9] of that compound. Hydrolysis gave the corresponding acid,[2] VII (R = X = H) (m.p. > 360°. *Anal.* Found: C, 68.0; H, 3.2; N, 10.6) which has been converted[2] to dihydrolysergic acid.

A full account of this work and related studies will appear in the future. We wish to express our sincere appreciation to Mr. Louis Dorfmann and his entire staff for microanalytical and spectral data, and to Dr. E. Schlittler for unfailing encouragement.

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(8) G. N. Walker, *J. Am. Chem. Soc.*, **77**, 3844 (1955).

(9) We are greatly indebted to Dr. Frederick C. Uhle of Harvard Medical School for a generous sample of this compound. The ultraviolet spectrum has been published (*cf.* ref. 6).

Substitution Reactions of Derivatives of 2-Anthrol at the 1- and 3-Positions[1]

Sir:

Discrepancies contained in recent work[2,3] on the Fries rearrangement of 2-anthryl acetate (I) prompt us to publish briefly the preliminary results obtained in our independent study[4] of this reaction and of the formylation of 2-methoxyanthracene (II). Thus, both the hydroxyketone (III), m.p. 218–219° dec., obtained[3] in 83% yield from the high-temperature rearrangement of I, and the hydroxyketone (IV), m.p. 112–113°, obtained[2] in unspecified low yield from rearrangement in nitrobenzene at room temperature, are reported to be methyl 2-hydroxy-1-anthryl ketone, an apparently rigorous proof of structure having been offered in each case.

Both III and IV have been obtained independently in this Laboratory[4] under roughly similar conditions but in greatly different yields. Thus, the Fries rearrangement of I in nitrobenzene (0.5 hr. at room temperature) produced IV, m.p. 115–116.5°, in yields of about 60%, whereas the high temperature reaction (1.5 hr. at 140°, no solvent) produced III, m.p. 226–227° dec., in yields of 3–13%. Mixture melting points of the methyl ethers and acetates of III and IV have shown that they are different isomers, and repeated attempts to obtain III in higher yield have failed.

The proof of structure described by Shah and Sethna[2] was independently employed by us,[4] and their assignment of the 2,1 orientation to IV is confirmed. The 2,3 orientation is assigned to III, since infrared spectra[5] revealed strong intramolecular hydrogen bonding. The Dakin oxidation of III to 1,2-anthradiol, which Jain and Seshadri[3] advanced as proof of structure, conceivably could be explained by contamination with IV, which also is formed in low yield from the high-temperature Fries rearrangement.

Formylation of II with *N*-methylformanilide and phosphorus oxychloride has afforded a mixture (about 70% yield) of approximately equal amounts of two difficultly separable methoxyaldehydes, m.p. 192–194.5° and 116–117°. Separate demethylations produced, respectively, the known 2-hydroxy-1-anthraldehyde[3] (V), m.p. and mixed m.p. 166.5–167°, and a new hydroxyaldehyde (VI), m.p. 228–231° dec., most probably the 3,2 isomer since infrared spectra[5] revealed strong intramolecular hydrogen bonding. The 1,2 orientation of both IV and V was confirmed by proton magnetic resonance spectra.[6]

The above work apparently represents the first two examples of the formation of comparable

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(1) This study was supported, in part, by Grant G-7640 from the National Science Foundation and by a grant from the Research Corp.

(2) N. H. Shah and S. Sethna, *J. Org. Chem.*, **24**, 1783 (1959).

(3) A. C. Jain and T. R. Seshadri, *J. Sci. Industr. Res.*, **15B**, 61 (1956).

(4) J. L. Ferrari and I. M. Hunsberger, Abstracts of Papers, 136th Meeting of the American Chemical Society, Sept. 1959, p. 21 P.

(5) Determined at the University of Illinois through the courtesy of Dr. H. S. Gutowsky.

(6) Determined at the University of Illinois through the courtesy of Dr. H. S. Gutowsky and Dr. A. L. Porte.

amounts of 2,3- and 2,1- isomers by substitution into a 2-substituted anthracene. A rigorous chemical proof of structure of III and IV is in progress and will be reported later, along with details of the above reactions and evidence (derived from infrared and proton magnetic resonance spectra) concerning the bond structure of anthracene.

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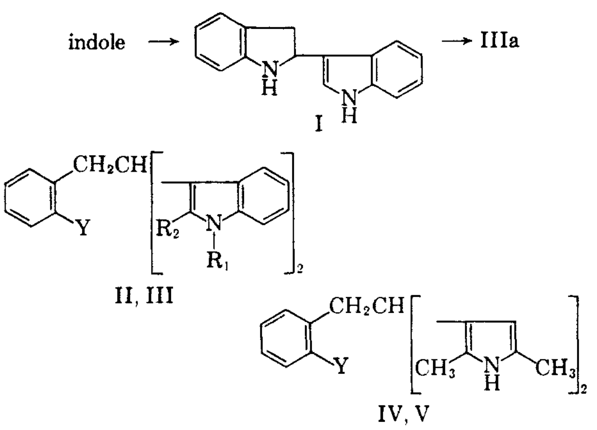
The Synthesis of Triindole, and Mixed Indole and Indole:Pyrrole Trimers

Sir:

The structure of triindole, the stable terminal product from the acid-catalyzed polymerization of indole, remained an enigma from the time of its discovery in 1913[1] until 1954, when a structure was proposed which could be derived through a plausible electronic mechanism.[2] Based on the discovery that it forms a Schiff base with benzaldehyde, and, therefore, must contain a primary amino group, Smith proposed the bisindole structure IIIa for triindole. The mechanism proposed for the formation of triindole[3] involves diindole as an intermediate. The correct structure for diindole (I), first proposed in 1954,[2] was confirmed by degradation in 1957.[4] We have now confirmed structure IIIa for triindole by an independent synthesis.

In the manner common for formation of bisindoles, by condensation of indoles with aldehydes,[5] an excess of indole condensed with *o*- nitrophenylacetaldehyde[6] in warm acetic acid solution (100°, 2 hr.) to give 3,3′-[2-(2-nitrophenyl)ethylidene]-bisindole (IIa) in 85% yield, light yellow crystals from ethanol water, m.p. (softens above 205°) 208–209°; *Anal.* Calcd. for $C_{24}H_{19}N_3O_2$ (381.42): C, 75.57; H, 5.02: N, 11.02. Found: C, 75.64; H, 5.20; N, 11.10; ν_{NH} 3450, ν_{NO_2} 1522, 1347 cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 223 mμ (log ϵ 4.84), 275 (4.12), 282 (4.13), 291 (4.08). Hydrogenation of IIa at 2 atm. in methanol over Raney nickel catalyst gave triindole (IIIa) in 77% yield, m.p. and mixed m.p. with an authentic sample,[7] 169–170.5°. The infrared spectra of the two samples in Nujol were identical in every respect.



II, IV. Y = NO_2
III, V. Y = NH_2
IIa, IIIa. $R_1 = R_2 = H$
IIb, IIIb. $R_1 = H$, $R_2 = CH_3$
IIc, IIIc $R_1 = R_2 = CH_3$

In a similar manner (except at 50°, 17 hr.) were prepared 2,2′-dimethyl-3,3′-[2-(2-nitrophenyl)-ethylidene]bisindole (IIb) in 87% yield, pale yellow crystals from 95% ethanol, m.p. 231–232.5°; *Anal.* Calcd. for $C_{25}H_{23}N_3O_2$ (409.47): C, 76.26; H, 5.66; N, 10.26; Found: C, 75.98; H, 5.89; N, 10.49; ν_{NH} 3380, ν_{NO_2} 1530, 1365 cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 228 mμ (4.80), 283 (4.18), 292 (4.14); 1,1′,2,2′-tetramethyl-3,3′-[2-(2-nitrophenyl)ethylidene]bisindole (IIc) in 99% yield, yellow crystals from 95% ethanol, m.p. 180–181.5°; *Anal.* Calcd. for $C_{28}H_{27}N_3O_2$ (437.52): C, 76.86; H, 6.22; N, 9.61; Found: C, 76.94; H, 6.31; N, 9.83; ν_{NO_2} 1523, 1357 (also strong bands at 1381 and 1371) cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 230 mμ (4.81), 287 (4.16), 294 (4.16); and 2,2′,5,5′-tetramethyl-3,3 -[2-(2-nitrophenyl)ethylidene]bispyrrole (IV) in 90% yield, golden yellow crystals from 95% ethanol, m.p. (darkens above 185°) 217–218°; *Anal.* Calcd. for $C_{20}H_{23}N_3O_2$ (337.41): C, 71.19; H, 6.87; N, 12.45; Found: C, 70.89; H, 7.06; N, 12.69; ν_{NH} 3330, ν_{NO_2} 1518, 1340 cm.$^{-1}$ in Nujol; ultraviolet spectrum in 95% ethanol contains only rising end absorption.

Hydrogenation as with triindole gave the corresponding amines: IIIb in 79% yield, colorless crystals from methanol water, m.p. (softens at 175°) 245–246°; *Anal.* Calcd. for $C_{26}H_{25}N_3$ (379.48): C, 82.29; H, 6.64; N, 11.07; Found: C, 82.28; H, 6.72; N, 10.99; ν_{NH} 3420 (strongest), 3350, 3190 cm.$^{-1}$ in Nujol; λ_{max} in 95% C_2H_5OH: 229 mμ (4.82), 285 (4.18), 292 (4.15); IIIc in 79% yield, colorless crystals from methanol water, m.p. 182–183°; *Anal.* Calcd. for $C_{28}H_{29}N_3$ (407.54): C, 82.51; H, 7.17; N, 10.31; Found: C, 82.57; H, 7.24; N, 10.06; ν_{NH} 3480, 3390 cm.$^{-1}$ in Nujol;

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