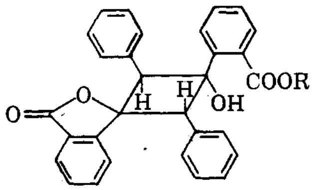
methyl ester hydrogen signals at τ 6.23 (p.p.m.), two one-proton singlets located at τ 4.52[12] and τ 5.50 (p.p.m.), the positions being invariant upon dilution. Only the ester III can give rise to such a spectrum, and hence, the structure of the photodimer must be Ia.



II, R=H
III, R=CH_3

The large difference in chemical shift between the two cyclobutane ring hydrogens appears to be the consequence of shielding effects exerted on these by the various phenyl groups, being particularly sensitive to the steric relationships between the substituents on the ring. Opening of one lactone ring appears to increase the shielding (by about 0.7 p.p.m.) experienced by, the vicinal *cis* proton, but causes a deshielding effect (by about 0.3 p.p.m.) on the *trans* hydrogen. The latter is probably the result of the altered rotational equilibrium position of the *cis* phenyl group, effected by the added steric interaction which opening of the lactone ring introduces.

Experimental

Photodimerization of 3-Benzylidenephthalide.—Solid 3-benzylidenephthalide (15 g.) was irradiated in frequently turned thin layers, for about 2 weeks with a G. E. 275-w. sunlamp. Total solid was triturated with cold benzene (75 ml.) and the filtered remaining solid (4 g., 27%) was recrystallized twice from large volumes of benzene to give the photodimer Ia as stubby needles, m.p. 294–296°. The benzene soluble solid (10 g.) was shown to be starting material.

Anal. Calcd. for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54; mol. wt., 444. Found: C, 80.81; H, 4.43; mol. wt., 451.

Base Hydrolysis of the Photodimer. Formation of II.—The photodimer (5.0 g.) was stirred with alcoholic 5% sodium hydroxide (50% water–ethanol) for 4 hr. The clear solution was cooled and neutralized with cold 10% hydrochloric acid. The precipitated solid (4.55 g.) was air-dried and was shown to consist of the monocarboxylic acid–lactone II and large amounts of starting material. II readily reverted to starting material on standing; it was not obtained in a pure state, but was converted to the methyl ester III immediately.

More vigorous hydrolysis by refluxing the basic solution for 6 hr. led to the formation of a different acid–lactone, m.p. 244–246°, characterized as being isomeric with II. The methyl ester had infrared bands at 5.65, 5.80, and 5.93 (sh) μ. It is evident that cyclobutane ring cleavage takes place under these conditions.

Preparation of III. Methyl Ester of II.—An ether suspension of II was treated with diazomethane until the color of diazomethane persisted. The considerable amount of unchanged solid remaining consisted of photodimer, to a large part formed during the diazomethane treatment. The methyl ester III was obtained in small yields from the ether solution by evaporation of the solvent *in vacuo*. Fast recrystallization from boiling benzene–petroleum ether afforded, after the less soluble photodimer had crystallized, in subsequent crops, III as small prisms. The melting point of III was that of the photodimer, with a crystalline change being observable at 180° on slow heating. The infrared spectrum of a melted sample was identical to that of the photodimer. Reversion to photodimer also took place at moderate speeds in solution; stability as a solid was good.

Anal. Calcd. for $C_{31}H_{24}O_5$: C, 78.13; H, 5.08. Found: C, 78.56; H, 5.34.

Acknowledgment.—The author gratefully acknowledges a postdoctoral fellowship from the U. S. Public Health Service, Division of General Medical Sciences, 1959–1961.

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[12] This proton signal is not sharp, but is unresolvable.

Synthesis of a Derivative of Indolo[3,2-*b*]carbazole

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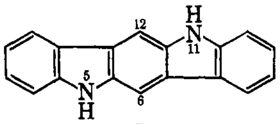
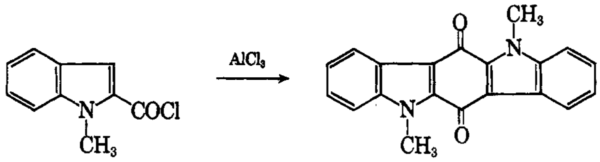
Efforts in the indolocarbazole area recently have been summarized by Grotta, *et al.*[1] (*cf.* also ref. 2), who prepared 5,11-dihydroindolo[3,2-*b*]carbazole (I) by cyclodehydrogenation of N,N′-diphenyl-*p*-phenylenediamine. Noland, *et al.*,[3,4] suggested that the condensation products resulting from the reaction of 1-methylindole with methyl isobutyl ketone and that of indole with acetophenone may be derivatives of 5,6,11,12-tetrahydroindolo[3,2-*b*]carbazole.



I

We have found that a derivative of this difficultly accessible ring system resulted readily when a solution of 1-methylindole-2-carbonyl chloride (II) in 1,2-dichloroethane was treated with aluminum chloride.[5] This reaction led to 5,11-dimethylindolo[3,2-*b*]carbazole-6,12(5*H*,11*H*)-dione (III) in 41% yield. The assignment of this structure is supported by analytical data, and ultraviolet and infrared spectra.



II III

In connection with this problem we had occasion to examine the reduction of "urorosein sulfate" with lithium aluminum hydride. Early literature related to this compound was reviewed by Fearon and Boggust,[6] who prepared urorosein sulfate by heating indole-3-carboxaldehyde with sulfuric acid, and proposed structure IV for the free base. On the other hand, Harley-

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[1] H. M. Grotta, C. J. Riggle, and A. E. Bearse, *J. Org. Chem.*, **26**, 1509 (1961).

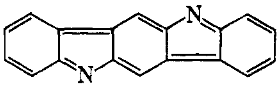
[2] *Cf.* R. J. Brunton, F. K. Drayson, S. G. P. Plant, and M. L. Tomlinson, *J. Chem. Soc.*, 4783 (1956).

[3] W. E. Noland, C. G. Richards, H. S. Desai, and M. R. Venkiteswaran, *J. Org. Chem.*, **26**, 4254 (1961).

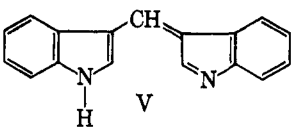
[4] W. E. Noland and M. R. Venkiteswaran, *ibid.*, **26**, 4263 (1961).

[5] *Cf.* the reaction of benzoyl chloride with aluminum chloride which afforded a small amount of anthraquinone: S. Coffey and J. vanAlphen in "Chemistry of Carbon Compounds," E. H. Rodd, Ed., Vol. IIIB, Elsevier Publishing Co., New York, N. Y., 1956, p. 1376.

[6] W. R. Fearon and W. A. Boggust, *Biochem. J.*, **46**, 62 (1950).



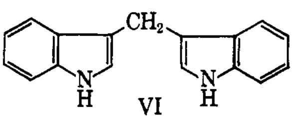
IV



V

Mason and Bu'lock[7] presented evidence that favored structure V for urorosein.[8]

We have found that reduction of urorosein sulfate with lithium aluminum hydride afforded 3,3′-methylenebisindole (VI), which was identical with an authentic sample. This result provides support for the formulation[7] of urorosein sulfate as a salt of structure V.[9]



VI

Experimental[10,11]

1-Methylindole-2-carbonyl Chloride (II).—1-Methylindole-2-carboxylic acid[12] was converted to the corresponding acid chloride using phosphorus pentachloride and ether.[13] The analytical sample melted at 84–85° (from Skellysolve B). Ultraviolet spectrum showed λ_{max} 234 (16,200); 314 mμ (ϵ 23,050). Infrared spectrum showed =CH: 3080; C=O: 1780, 1735, 1675 w; C=C: 1615, 1515 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; Cl, 18.31; N, 7.23. Found: C, 62.64; H, 4.25; Cl, 17.67; N, 7.38.

5,11-Dimethylindolo[3,2-*b*]carbazole-6,12(5*H*,11*H*)-dione (III).—Aluminum chloride (4 g., 0.03 mole) was added during 5 min. to a solution of II (2.9 g., 0.015 mole) in 20 ml. of 1,2-dichloroethane. The resulting dark solution was stirred at room temperature for 30 min. Ice (10 g.) was added, followed by 6 ml. of concentrated hydrochloric acid in 32 ml. of water. The mixture was stirred in the cold for 1 hr. It was then filtered and the red solid washed with water; 1 g. (41% yield), m.p. 365°. Crystallization from dimethylformamide afforded red needles of the same melting point. Ultraviolet spectrum (in dimethylformamide–ethanol) showed sh 268 (21,250), 279 (34,900), 295 (49,600), 346 (10,700), 403 mμ (ϵ 10,550). Infrared spectrum showed =CH: 3040; C=O: 1640; C=C: 1615, 1575, 1540, 1502, 1495 cm.$^{-1}$.

Anal. Calcd. for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found: C, 76.38; H, 4.46; N, 9.20.

Reduction of Urorosein Sulfate.—Urorosein sulfate[6] (9.2 g.) was added portionwise over 15 min. to a suspension of lithium aluminum hydride (18.4 g.) in 500 ml. of tetrahydrofuran. The mixture was refluxed for 2.5 hr., and was then decomposed by the addition of 19 ml. of water followed by 920 ml. of 10% sulfuric acid. The organic layer was separated and the aqueous layer was extracted with three 100-ml. portions of ether. The combined organic extract was dried over magnesium sulfate and evaporated to dryness. The resulting solid (6.4 g.) was dissolved in 400 ml. of ether and treated with Darco G-60; the resulting solution was concentrated until crystallization began; yield, 3.39 g.; m.p. 163–164°. The second crop amounted to 0.9 g., m.p. 162–163°. Ultraviolet spectrum showed λ_{max} 225 (66,200), sh 276 (11,000), 282 (11,900), 291 mμ (ϵ 10,600). Infrared spectrum showed =CH: 3060, 3040; C=C/C=N: 1620, 1595, 1545, 1490; C–N: 1220, 1160, 1090, 1060, 1035, 1010; ring: 795, 740, 725 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.99; H, 5.87; N, 11.21.

This compound was identical with an authentic sample of 3,3′-methylenebisindole (VI) as determined by mixture melting point and comparison of ultraviolet and infrared spectra. The authentic sample of VI was prepared from indole, paraformaldehyde, and zinc chloride according to Leete and Marion,[14] and purified by chromatography on silica using 20% ethyl acetate–Skellysolve B as eluent.

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(7) J. Harley-Mason and J. D. Bu'lock, *Biochem. J.*, **51**, 430 (1952).

(8) *Cf.* also G. F. Smith, *J. Chem. Soc.*, 3842 (1954), and H. von Dobeneck, W. Lehnerer, and G. Maresch, *Z. Physiol. Chem.*, **304**, 26 (1956).

(9) Grotta, *et al.*,[1] obtained 60 mg. of I by tin–hydrochloric acid reduction of 1 g. of urorosein sulfate. In view of the above conclusion this result was perhaps due to hydrolytic cleavage of urorosein to give indole-3-carboxaldehyde which, followed by dimerization, dehydration, and reduction, would give rise to I. We thank the referee for this suggestion.

(10) Melting points were taken in a capillary tube and are uncorrected. Ultraviolet spectra (recorded in mμ) were determined in 95% ethanol using a Cary spectrophotometer Model 19. Infrared spectra (recorded in cm.$^{-1}$) were determined in Nujol using a Perkin-Elmer recording infrared spectrophotometer Model 21. Skellysolve B is commercial hexane, b.p. 60–70°, made by Skelly Oil Co., Kansas City, Mo. Silica was 50–200 mesh, manufactured by G. Frederick Smith Chemical Co., Columbus, Ohio.

(11) The author is indebted to Mr. W. A. Struck and his associates for microanalyses, to Mrs. Betty Zimmer and Miss L. M. Pschigoda for ultraviolet and infrared spectra, and to Mr. L. G. Laurian for laboratory assistance.

(12) H. R. Snyder and P. L. Cook, *J. Am. Chem. Soc.*, **78**, 969 (1956).

(13) J. R. Johnson, R. Hasbrouck, J. D. Dutcher, and W. F. Bruce, *ibid.*, **67**, 423 (1945).

(14) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).