with that of authentic *dl-erythro*-1,2,3-butanetriol triacetate. Its retention time on gas chromatography at 195° using a column packed with 30% of Viton A-HV[30] on 80–100 mesh Chromosorb W, was 16.1 min., identical with that of an authentic sample of *dl-erythro*-1,2,3-butanetriol triacetate. The *threo* isomer, which under these conditions had a retention time of 18.4 min., was absent in the chromatogram of **13** obtained from Fungichromin.

Synthesis of *dl-erythro*-1,2,3-Butanetriol Triacetate.—The *trans*-crotyl alcohol used in this preparation had b.p. 120°, $n^{25}D$ 1.4262 (lit.[31] b.p. 121.2°, $n^{25}D$ 1.4262). Its infrared spectrum was the same as that published.[32] However, gas chromatography of its acetate at 85° on a column packed with 30% of a saturated solution of silver nitrate in tetraethylene glycol on 60–80 mesh Chromosorb showed it to be a mixture of 92% of the *trans* and 8% of the *cis* isomer. To a solution of 6.53 g. of this (largely) *trans*-crotyl alcohol in 10 ml. of glacial acetic acid was added slowly, with stirring, 21.6 g. of 40% peracetic acid.[33] After stirring for 1 hr., acetic anhydride (20 g.) and concentrated sulfuric acid (1 ml.) were added, and the mixture was stirred at 70° for 2 hr. After cooling to room temperature it was poured on ice, and extracted with four 20-ml. portions of chloroform. The combined extracts were washed free of acid with 10% sodium carbonate solution, and dried over magnesium sulfate. Analysis by gas chromatography showed that only partial acetylation had occurred. The chloroform was removed, and the residue (17.1 g.) was mixed with 30 ml. of pyridine and 15 g. of acetic anhydride. The mixture was allowed to stand at room temperature for 3 days and then was poured on ice and extracted with three 20-ml. portions of chloroform. The combined extracts were washed with 20% sulfuric acid, 10% sodium carbonate solution and saturated sodium chloride solution, and dried (magnesium sulfate). Removal of the solvent and distillation of the residue gave 7.83 g. (37% yield) of impure *dl-erythro*-1,2,3-butanetriol triacetate. Redistillation afforded a sample, b.p. 70° (0.2 mm.), $n^{25}D$ 1.4273, which was contaminated only by 1% of the *threo* isomer as shown by gas chromatography.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.94. Found: C, 51.96; H, 6.63.

Synthesis of *dl-threo*-1,2,3-Butanetriol Triacetate.—To a vigorously stirred mixture of 1.45 g. of *trans*-crotyl acetate (b.p. 130–131°, $n^{25}D$ 1.4149, containing 8% of the *cis* isomer; see above), 38 ml. of glacial acetic acid, 0.36 ml. of water and 5.36 g. of silver acetate was added finely ground iodine (3.24 g.) over a period of 50 min. Stirring was continued at room temperature for 1 hr., then at 95° for 5 hr. The cooled mixture was filtered and the filter cake was washed with glacial acetic acid. The combined filtrate and washings were concentrated to *ca.* 6 ml. by distillation through a semi-micro column (at 35 mm. and a bath temperature of 55–60°). To the filtered residue were added 15 g. of acetic anhydride and 30 ml. of pyridine. The mixture was allowed to stand at room temperature overnight and then was poured on ice and extracted with three 30-ml. portions of ether. The combined extracts were washed with ice-cold 20% sulfuric acid, 5% sodium bicarbonate solution, sodium thiosulfate solution and concentrated sodium chloride solution, and dried over magnesium sulfate. Distillation through a semi-micro column afforded 2.27 g. (77%) of a mixture, b.p. 82° (0.2 mm.), $n^{25}D$ 1.4286, containing 82% of *dl-threo*-1,2,3-butanetriol triacetate and 18% of the *erythro* isomer. A sample further enriched (92%) in the higher boiling *threo* isomer was obtained by fractionation using a short spinning band column.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 51.72; H, 6.94. Found: C, 51.96; H, 6.83.

Pure *dl-threo*-1,2,3-butanetriol triacetate was isolated from this sample by preparative gas chromatography at 195°, using a column packed with 30% of Viton A-HV on 80–100 mesh Chromosorb W. It had $n^{25}D$ 1.4287; its infrared spectrum (carbon disulfide solution) was very similar to that of the *erythro* isomer, the most prominent difference being a band of medium intensity at 1140 cm.$^{-1}$ which was absent in the spectrum of the *erythro* isomer. The latter had a similar band at 1165 cm.$^{-1}$, not found in the spectrum of the *threo* isomer.

(30) Kindly supplied by the Elastomer Chemicals Department, E. I. du Pont de Nemours and Co., Wilmington, Del.

(31) L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 727 (1950).

(32) C. F. Hiskey, H. L. Slates and N. L. Wendler, *J. Org. Chem.*, **21**, 429 (1956).

(33) The temperature rose to 80° during the addition. The yield of the triacetate could probably be improved considerably by keeping the temperature between 30 and 40°.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIF.]

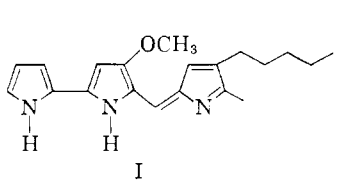
2,2′-Bipyrrole

BY HENRY RAPOPORT AND NEAL CASTAGNOLI, JR.[1]

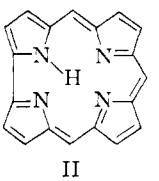
RECEIVED DECEMBER 23, 1961

Interest in the 2,2′-bipyrrole system has led to an examination of several methods of synthesizing this compound. One method, the condensation of 2-pyrrolidinone with pyrrole followed by dehydrogenation of the resulting pyrroline, is of particular interest, since it gives a good yield and is potentially applicable to a wide variety of compounds in this little investigated area of polypyrrole chemistry.

In view of the importance of 2,2′-bipyrrole in naturally occurring compounds as well as the general lack of information available on the chemistry of this system, we have undertaken an examination of several syntheses of the unsubstituted 2,2′-bipyrrole which potentially are applicable to problems involving specifically substituted bipyrroles. Naturally occurring compounds which contain the bipyrrole nucleus are prodigiosin (I) and related pigments[2a,b] and vitamin B_{12},[3] the



I



II

parent aromatic ring system of which is corrole (II). Although several bipyrroles have been reported in the literature, most of the synthetic methods used are of a limited nature, employing drastic coupling-type reactions and resulting in highly substituted, symmetrical bipyrroles.[4] As

(1) Public Health Service Predoctoral Research Fellow of the Division of General Medical Sciences.

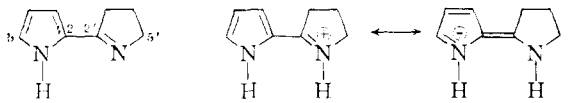
(2) (a) H. Rapoport and K. G. Holden, *J. Am. Chem. Soc.*, **84**, 635 (1962); (b) H. H. Wasserman, J. E. McKeon, L. Smith and P. Forgione, *ibid.*, **82**, 506 (1960).

(3) R. Bonnett, J. R. Cannon, V. M. Clark, A. W. Johnson, L. F. J. Parker, E. L. Smith and A. Todd, *J. Chem. Soc.*, 1158 (1957).

(4) *E.g.*, H. Fischer and A. Stackel, *Z. physiol. Chem.*, **258**, 121 (1939); J. L. A. Webb and R. R. Threlkeld, *J. Org. Chem.*, **18**, 1406 (1953).

part of the work on the synthesis of prodigiosin, the first synthesis of 2,2′-bipyrrole recently was reported.[2a] These studies were taken as the starting point of the present investigation.

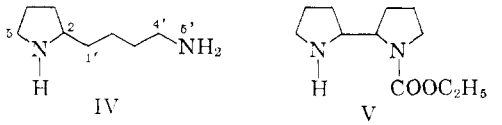
Rapoport and Holden[2a] synthesized bipyrroles by catalytic dehydrogenation of 2,2′-pyrrolidinylpyrroles, the latter compounds being obtained by the condensation of 1-pyrroline with pyrrole or a substituted pyrrole. This procedure was examined in greater detail in order to determine optimum reaction conditions for 2,2′-bipyrrole itself. It was found that the palladium-catalyzed dehydrogenation of 2,2′-pyrrolidinylpyrrole in refluxing xylene gave bipyrrole in 25% yield and two additional basic compounds. The less polar of these two compounds was obtained in 45% yield and has been assigned the structure of 2,2′-(1′-pyrrolinyl)-pyrrole (III) on the following evidence. Strong infrared absorption at 3485 and 1618 cm.$^{-1}$ correspond to a pyrrolic N—H and a C=N stretch, respectively. The ultraviolet absorption of this material in alkali is similar to that of bipyrrole and shows a bathochromic shift upon acidification (Fig. 1). This shift is to be expected, since protonation of the imino nitrogen results in the formation of an extended π-system (IIIa). Confirmation of the location of the double bond was obtained from the nuclear magnetic resonance spectrum (Table I) which displayed three high field (methylene) signals, three low field (aromatic) signals, and one very low signal for the pyrrolic N–H.



III IIIa

The second basic compound, isolated in 5% yield from the dehydrogenation reaction, was an oil. This compound has been shown[5] to be 2-(4′-aminobutyl)-pyrrole (IV) by (1) analysis of the amine and its 2,4-dinitrophenyl derivative, (2) formation of a tosylate which was soluble in alkali, (3) infrared absorption at 3495 (pyrrolic N–H) and 3275 cm.$^{-1}$ (amino N–H), and (4) its nuclear magnetic resonance spectrum which showed the expected differences from pyrrolidinylpyrrole and bipyrrole (Table I).

Considering the poor yield of the desired bipyrrole from the dehydrogenation reaction, 2,2′-(1′-ethoxycarbonylpyrrolidinyl)-pyrrole (V) was prepared by N-carbethoxylation of pyrrolidinylpyrrole. Since V cannot form a 1-pyrrolinyl intermediate on dehydrogenation, it was hoped that a better yield of bipyrrole might be realized. However, V did not undergo dehydrogenation even



IV V

when exposed to refluxing diisopropylbenzene (205°). This is a strong indication that the 1-pyrroline III is an intermediate in the conversion of pyrrolidinylpyrrole to bipyrrole.

(5) The isolation and structure determination of this substance was done in conjunction with K. Holden.

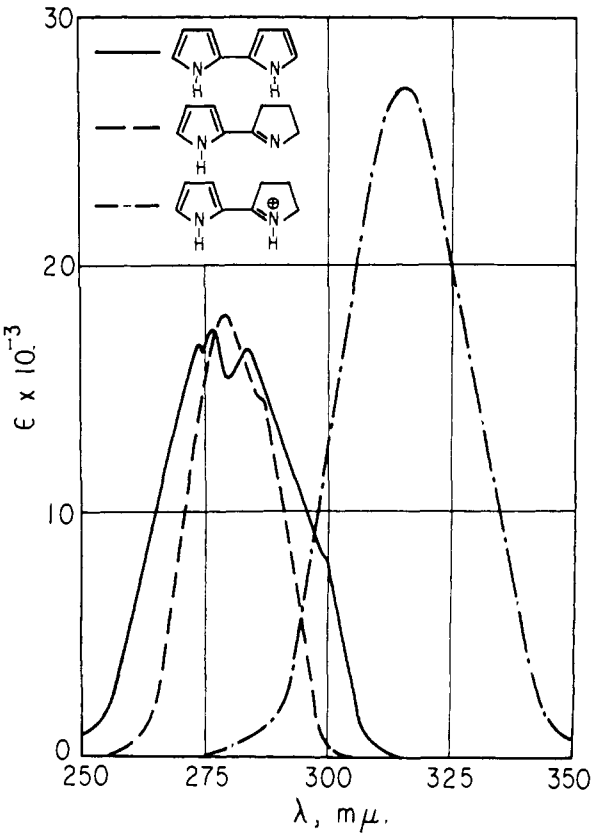


Fig. 1.—Ultraviolet absorption spectra in methanol of 2,2′-bipyrrole and 2,2′-(1′-pyrrolinyl)pyrrole (III, IIIa).

Application of the foregoing method to the synthesis of substituted bipyrroles is limited to pyrroles that are not strongly deactivated by electron-withdrawing substituents, since 1-pyrroline will not condense with a deactivated pyrrole nucleus.[2a] This limitation might be overcome by increasing the reactivity of the electrophilic component in the condensation. Recently,[6] it has been shown that 1-pyrroline-1-oxides undergo nucleophilic attack more readily than the corresponding 1-pyrroline. With this in mind, 1-pyrroline-1-oxide (VI)[7] was heated with an equimolar amount of pyrrole in chloroform. None of the expected hydroxylamine VII was formed, and starting material was recovered.

VI VII

The most fruitful procedure developed for the synthesis of bipyrrole is patterned after the Vilsmeier reaction.[8] This reaction as it is usually effected involves the formation of a complex be-

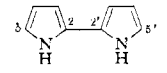
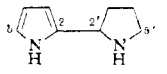
(6) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland and A. Todd, *J. Chem. Soc.*, 2094 (1959).

(7) J. Thesing and W. Sirrenberg, *Ber.*, **92**, 1748 (1959).

(8) The Vilsmeier reaction has been reviewed by O. Bayer in "Methoden der Org. Chemie," E. Müller, editor, 4th Ed., Vol. VII (1), G. Thieme Verlag, Stuttgart, 1954, p. 29.

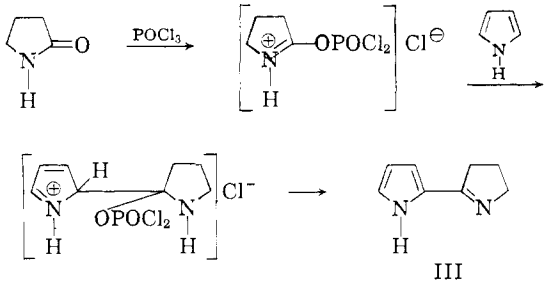
TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME SUBSTITUTED PYRROLES

Compound	Proton peaks, τ-values,[a] and position of H atom								
	1	3	4	5	1′	2′	3′	4′	5′
 2,2′-Bipyrrole[b]		3.78		3.34			3.78		3.34
III[c]	−0.32	3.58	3.93	3.08			6.50	8.83	7.78
 2,2′-Pyrrolidinylpyrrole	−0.50	3.78		3.20	7.37	5.75	7.90		6.88
IV[c]	0.95	3.90 4.10		3.40	7.35	8.45	7.35		8.15

[a] Measured in deuteriochloroform using a Varian model A-60 spectrometer. [b] In liquid sulfur dioxide. [c] See text for formula.

tween dimethylformamide and phosphorus oxychloride which then attacks a nucleophilic aromatic system.[9] Although di-N-substituted amides other than dimethylformamide have been used successfully in this reaction,[10,11] previous to this study secondary amides had not been investigated. Relating to our problem, should 2-pyrrolidinone form an analogous complex with phosphorus oxychloride, the following reaction sequence might take place



III

The anticipated product, 2,2′-(1′-pyrrolinyl)-pyrrole (III), had already been obtained from the partial dehydrogenation of pyrrolidinylpyrrole and was known to be stable.

This reaction was first carried out according to the general procedure used in the preparation of pyrrole-2-carboxaldehyde.[12] Isolation of the basic fraction from the reaction mixture gave two compounds, the desired pyrrolinylpyrrole (40% yield) and a by-product having the same properties as those reported[13] for the self-condensation product of 2-pyrrolidinone in the presence of phosphorus oxychloride. When the pyrrolidinone–phosphorus oxychloride adduct was formed in the presence of an excess of pyrrole, this side reaction was avoided and pure pyrrolinylpyrrole III was obtained in 80% yield.

It was already indicated from our previous observations that pyrrolinylpyrrole could be converted to bipyrrole by catalytic dehydrogenation. Various solvents and catalysts were tested, and the best yield was realized when pyrrolinylpyrrole was heated at 200° for 2 hours in di-*n*-hexyl ether in the presence of 100 mole per cent. of 10% or 30% palladium-on-charcoal. Sulfur dehydrogenation in dimethylformamide and chloranil oxidation[14] were also briefly examined as methods of aromatizing pyrrolinylpyrrole but proved ineffective.

Experimental[15]

Dehydrogenation of 2,2′-Pyrrolidinylpyrrole.—A mixture of 2,2′-pyrrolidinylpyrrole[16] (3.0 g., 22 mmoles), 5% palladium-on-charcoal (1.5 g., 1.7 mmoles) and xylene (75 ml.) was heated under reflux with vigorous stirring and a nitrogen sweep. After 4 hours, the hot solution was filtered, and the catalyst was digested twice with hot chloroform. The combined solutions were cooled to room temperature and were extracted with *p*H 4 phosphate buffer (3 × 25 ml.). Alkalization to *p*H 10 gave a flocculant precipitate which was extracted into ether and the ether solution was dried over magnesium sulfate.

The xylene solution, which contained the bipyrrole, was dried, the xylene was evaporated, and the residue was digested with 10 ml. of chloroform. Filtration of this mixture and sublimation of the insoluble portion at 90° (0.2 mm.) followed by crystallization from benzene yielded 0.83 g. (25%) of **2,2′bipyrrole**, m.p. 189–190° (reported[2a] 187°).

The ether solution, containing the basic products, was evaporated, and a solid residue (1.56 g.) was obtained which was chromatographed on 50 g. of activity III alumina. Elution with benzene–hexane (1:1) gave 1.38 g. (46%) of **2,2′-(1′-pyrrolinyl)-pyrrole (III)**, melting at 162–163° after sublimation at 80° (0.2 mm.); ultraviolet absorption in 1 *N* methanolic potassium hydroxide: λ_{max} 287 mμ, sh (ε 14,490), 278 (17,900); in 0.1 *N* methanolic hydrochloric acid: λ_{max} 316 (27,200).

Anal. Calcd. for $C_8H_{10}N_2$: C, 71.6; H, 7.5; N, 20.9. Found: C, 71.7; H, 7.4; N, 21.1.

Continued elution of the column with benzene and benzene–chloroform mixtures gave 0.15 g. of **2-(4′-aminobutyl)-pyrrole (IV)** which was distilled (short-path) at 90° (5 mm.); ultraviolet absorption: 217 mμ (ε 4,720).

Anal. Calcd. for $C_8H_{14}N_2$: C, 69.5; H, 10.2; N, 20.3, equiv. wt., 138. Found: C, 69.8; H, 9.9; N, 20.1; equiv. wt., 136.

2-(4′-*p*-Toluenesulfonylaminobutyl)-pyrrole was prepared from 2-(4′-aminobutyl)-pyrrole (IV) and *p*-toluenesulfonyl chloride in pyridine. It was an oil which was purified on alumina (activity III), eluting with benzene–chloroform

(9) G. F. Smith, *J. Chem. Soc.*, 3842 (1954).

(10) G. G. Kleinspehn and A. E. Briod, *J. Org. Chem.*, **26**, 1652 (1961).

(11) W. C. Anthony, *ibid.*, **25**, 2049 (1960).

(12) R. M. Silverstein, E. E. Ryskiewicz and C. Willard, *Org. Syntheses*, **36**, 74 (1956).

(13) H. Bredereck and R. Bredereck, *Ber.*, **94**, 2278 (1961).

(14) L. M. Jackman in "Advances in Organic Chemistry," R. A. Raphael, E. C. Taylor and H. Wynberg, editors, Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 329.

(15) All melting points are corrected and were taken in evacuated capillaries; microanalyses were performed by V. Tashinian, Microchemical Laboratory, University of California, Berkeley. Infrared spectra were taken in chloroform, and ultraviolet spectra were taken in methanol.

(16) 2,2-Pyrrolidinylpyrrole was prepared with minor modifications[2a] by the method of D. W. Fuhlhage and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).

(1:1). It was freely soluble in 1 *M* sodium hydroxide and precipitated on neutralization with phosphoric acid.

The N-2,4-dinitrophenyl derivative of 2-(4′-aminobutyl)-pyrrole (IV) was prepared by boiling for 1 hour a solution of 53 mg. (0.38 mmole) of the amine in 10 ml. of benzene containing 1 ml. of triethylamine and 75 mg. (0.40 mmole) of 2,4-dinitrofluorobenzene. The solvents were evaporated and the residue was chromatographed on alumina (4 g., activity III), giving 75 mg. (0.25 mmole, 64% yield) of product, eluted with benzene, which was crystallized from acetone–hexane; m.p. 79–79.5°; ultraviolet absorption: λ_{max} 347 mμ (ε 17,200), 259 (7,900), 214 (19,200).

Anal. Calcd. for $C_{14}H_{16}O_4N_4$: C, 55.3; H, 5.3; N, 18.4. Found: C, 54.9; H, 5.5; N, 18.5.

2,2′-(1′-Ethoxycarbonylpyrrolidinyl)-pyrrole (V).—2,2′-(Pyrrolidinyl)-pyrrole (5 g., 36.7 mmoles) was dissolved in 100 ml. of 50% aqueous methanol, the solution was cooled to 5°, and 4 ml. (37 mmoles) of ethyl chloroformate was added rapidly with stirring, followed by the dropwise addition of 3.90 g. (37 mmoles) of sodium carbonate in 25 ml. of water over a 1-hour period. After the addition was complete, the reaction mixture was stirred at room temperature for an additional 3 hours. The mixture was then extracted with three 50 ml. portions of ether, each extract being washed with 10 ml. of *p*H 4 phosphate buffer. From the acid washes, 1.55 g. (31%) of starting material was recovered. The ether layer was dried over sodium carbonate and, after solvent was removed, distillation of the residue at 103° (0.2 mm.) gave 4.0 g. (52.3% yield) of product.

Anal. Calcd. for $C_{11}H_{16}N_2O_2$: C, 63.4; H, 7.7; N, 13.5. Found: C, 63.1; H, 7.8; N, 13.3.

2,2′-(1′-Pyrrolinyl)-pyrrole (III) from 2-Pyrrolidinone and Pyrrole.—To 20 g. (0.3 mmole) of pyrrole, maintained at 0.5° in a nitrogen atmosphere, was added with stirring 9.0 g. (60 mmoles) of phosphorus oxychloride over a 30-minute period, followed by the addition of 6.0 g. (70 mmoles) of 2-pyrrolidinone over a 1-hour period. After the addition was complete, the reaction mixture was stirred an additional 30 minutes at room temperature. Then 25 ml. of chloroform was added, the solution was poured into an ice-cold solution of 40 g. (0.3 mole) of sodium acetate in 100 ml. of water, and 10*M* potassium hydroxide was added slowly while maintaining the temperature at 0° (by adding ice) until the *p*H reached 10. A white precipitate formed and dissolved into the chloroform. The chloroform layer was separated and washed twice with water and the aqueous layer was extracted three times with 50-ml. portions of chloroform, each chloroform portion being washed twice with water. The combined chloroform solutions were then extracted three times with 50-ml. portions of *p*H 4 phosphate solution, and the combined aqueous phase was basified to *p*H 10 and extracted with chloroform. Drying and evaporating of the chloroform left 7.2 g. (92.4% yield) of a white solid which was sublimed at 80° (0.2 mm.) and crystallized from ethanol, yielding 6.2 g. (80% yield) of pure 2,2′-(1′-pyrrolinyl)-pyrrole (III), m.p. 162–163°.

2,2′-Bipyrrole by Catalytic Dehydrogenation of 2,2′-(1′-Pyrrolinyl)-pyrrole (III).—A mixture of 2,2′-(1′-pyrrolinyl)-pyrrole (2.17 g., 16 mmoles), 10% palladium-on-charcoal (7.5 g., 16 mmoles of palladium), and di-*n*-hexyl ether (250 ml.) was heated at 200° with vigorous stirring for 2 hours, continuously sweeping with nitrogen. The hot mixture then was filtered, the filtrate was cooled to room temperature, 500 ml. of hexane was added, and the solution was stored at −80° for 12 hours. The precipitated bipyrrole was collected, washed with hexane, and sublimed (80° (0.2 mm.)) to give 0.8 g., 38% yield, of pure bipyrrole, m.p. 189–190°.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISC., AND OF STANFORD UNIVERSITY, STANFORD, CALIF.]

Stereochemical Control of the Angular Methylation of Fused Ring Ketones[1]

BY WILLIAM S. JOHNSON,[2] DUFF S. ALLEN, JR., RAYMOND R. HINDERSINN, GEORGE N. SAUSEN AND RAPHAEL PAPPO

RECEIVED NOVEMBER 10, 1961

Methylation of 2-benzylidene-1-decalone (II), with potassium *t*-butoxide and methyl iodide, gives a mixture of epimeric angularly methylated products: *cis*-(III) and *trans*-(IV) in a ratio of 3/1. Similar stereoselective behavior has been noted in a number of other cases, and the method is accordingly stereochemically unfavorable for the synthesis of *trans*-fused rings, *e.g.*, the C/D ring systems of the steroids. The present study reports attempts to find variables controlling this *cis/trans* ratio in favor of the *trans* isomer. The empirical approach, *i.e.*, altering conditions, etc., failed to uncover any such variable. Two hypotheses then were examined: that the geometry of the transition state approximates (1) that of the products and (2) that of the reactants. Experiments to test hypothesis 1 gave increases in some cases but no significant decrease in the *cis/trans* ratio. Thus this ratio was 3.5/1 for the methylation of the furfurylidene derivative of XIV; 9/1 for XXVII; at least 3/2 for the C_4-epimer of XXVII; and about 8/1 for the tetrahydropyranyl ether furfurylidene derivative of XXXVIII. Experiments designed to test hypothesis 2 led to successful results. On the premise that introduction of an olefinic bond at 6, 7 in the decalone system (Fig. 1) would remove one axial hydrogen at 7 interfering with the *trans* approach of the methyl group, the methylation of XLII was examined and found to give the *trans* product in at least 56% yield. Similarly, methylation of XLVII (R = H) afforded XLVII (R = CH_3) in 69% yield. The latter was in turn converted to a steroid XLIX, the total synthesis of which was thus stereoselective at every step. The principle has also been applied to a stereoselective total synthesis of estrone since methylation of LI (R = H) gave a preponderance of LI (R = CH_3). It was noted that with olefinic bonds in the 3,4- or 5,6-position of 1-decalone (Fig. 1), the effect of eliminating an axial hydrogen on the *trans*-approach side was overshadowed by angular distortion favoring *cis* approach. Thus methylation of LIV and of LVII gave *cis* products exclusively.

Certain previous total syntheses of steroids, namely estrone,[3] epiandrosterone,[4] 3β,11β-dihydroxyandrostane-17-one[5] and testosterone,[6,1a] have embodied a common sequence for the elaboration of ring D involving as key intermediates the corresponding 18-nor-D-homo compounds (*e.g.*, formula XLV). This angular methylation–ring contraction sequence is typified, in its simplest form, by the conversion of 1-decalone (I) into *trans*-8-methyl-1-hydrindanone (VI).[7] Thus the former substance was converted, by condensation with

(1) (a) This represents paper XIII of the series entitled "Steroid Total Synthesis—Hydrochrysene Approach." For part XII, see W. S. Johnson, W. A. Vredenburgh and J. E. Pike, *J. Am. Chem. Soc.*, **82**, 3409 (1960). (b) For a preliminary report of part of this work, see W. S. Johnson and D. S. Allen, Jr., *ibid.*, **79**, 1261 (1957).

(2) To whom inquiries should be directed, Department of Chemistry, Stanford University, Stanford, Calif.

(3) W. S. Johnson, D. K. Banerjee, W. P. Schneider, C. D. Gutsche, W. E. Shelberg and L. J. Chinn, *J. Am. Chem. Soc.*, **74**, 2832 (1952).

(4) W. S. Johnson, B. Bannister and R. Pappo, *ibid.*, **78**, 6331 (1956).

(5) W. S. Johnson, R. Pappo and W. F. Johns, *ibid.*, **78**, 6339 (1956).

(6) W. S. Johnson, B. Bannister, R. Pappo and J. E. Pike, *ibid.*, **78**, 6354 (1956).

(7) W. S. Johnson, *ibid.*, **65**, 1317 (1943); **66**, 215 (1944).