Anal. Calcd. for $C_{26}H_{38}O_5$: C, 72.52; H, 8.90. Found: C, 72.40; H, 8.78.

The allylic rearrangement of 17aβ-vinyl-D-homoetiocholane-3α,17aα-diol-11-one 3-acetate[1] under identical conditions also gave XVI in comparable yield. Identity was confirmed by infrared analysis.

The ozonolysis of 1.50 g. of pure XVI in acetone solution at 0°, followed by reduction of the ozonide with Raney nickel gave 1.24 g. of material melting at 164–166° (theory for 17a-ketone was 1.26 g.). One recrystallization from methanol gave 1.14 g. of D-homoetiocholane-3α-ol-11,17a-dione 3-acetate, m.p. and mixed m.p. 171–172.5°, infrared spectrum confirmatory.

The saponification of XVI by means of aqueous methanolic potassium carbonate solution gave **D-homopregn-17a-(20)-ene-3α,21-diol-11-one**, rosettes of long, slender needles from methanol, m.p. 236.8–245.4°,[30] $[\alpha]D$ −24.4° (*c* 1.0 in acetic acid).

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.25; H, 9.89. Found: C, 76.22; H, 9.70.

D-Homopregnane-3α,17aα,21-triol-11,20-dione 3,21-Diacetate (XVII).—To a solution of 62.0 g. of XVI (0.144 mole) in 3600 ml. of dry *t*-butyl alcohol was added 98.0 g. (0.304 mole) of phenyl iodosoacetate and 440 ml. of dry pyridine. The mixture was stirred until solution of the phenyl iodosoacetate was complete, and there was then added a solution of 720 mg. of osmium tetroxide in 18 ml. of water. After standing at room temperature for 22 hours[31] the solution was saturated with hydrogen sulfide gas and allowed to stand a further 4 hours. The black solution was steam distilled to remove *t*-butyl alcohol and iodobenzene and the residue was taken up in chloroform and water. After filtration of the chloroform–water mixture through a Filtercel pad, the chloroform layer was separated and washed with 2 *N* nitric acid, water, sodium bisulfite solution, water and sodium bicarbonate solution. Evaporation of the chloroform solution yielded a light brown colored solid. The material was chromatographed on 1800 g. of silica gel. Preliminary elution gave traces of resins; elution with 35–40% ether–*n*-pentane gave 7.74 g. (12.5%) of recovered XVI. Further elution with the same eluate gave 15.13 g. (28.6%) of the side-chain cleavage product, D-homoetiocholane-3α-ol-11,17a-dione 3-acetate. Further elution removed a series of resinous fractions, followed by a series of crystalline fractions on elution with 100% ether. The latter fractions gave, on recrystallization from acetone and from ethyl acetate, 21.0 g. (31.6% yield) of XVII as short, blunt needles, m.p. 224.6–226.0°, $[\alpha]D$ +78.3°.

Anal. Calcd. for $C_{26}H_{38}O_7$: C, 67.51; H, 8.28. Found: C, 67.46; H, 8.12.

D-Homopregnane-3α,17aα,21-triol-11,20-dione (XVIII).—To a stirred suspension of 18.70 g. (0.0404 mole) of finely powdered XVII in 1600 ml. of C.P. methanol, in an atmosphere of nitrogen, was added a solution of 23.80 g. (0.238 mole) of potassium bicarbonate in 150 ml. of water. The mixture was heated to 45° and stirred at this temperature until solution of the XVII was complete (1 hour). After standing overnight at room temperature the solution, still under nitrogen, was treated with excess glacial acetic acid and concentrated *in vacuo* to remove the methanol. The residual slurry was diluted with water, filtered, and the insoluble solid was washed thoroughly with water. After drying at 70° there was obtained 15.83 g. of a highly solvated form of XVIII, m.p. 121–129°, $[\alpha]D$ +50.6°. The material could not be obtained crystalline in the anhydrous form, nor could satisfactory analyses of the solvate be obtained. However, the solvate gave pure XVII on reacetylation with acetic anhydride–pyridine.

Methanolysis of XVII by means of 0.27 *N* perchloric acid in methanolic solution[32] failed to quantitatively remove the 3-acetate group.

D-Homopregnane-17aα,21-diol-3,11,20-trione (XIX).—To a solution of 2.00 g. of XVIII (solvate) in 10 ml. of acetone was added a solution of 1.09 g. of N-bromoacetamide, 0.4 ml. of pyridine and 1.5 ml. of water in 25 ml. of methanol. The mixture was allowed to stand in the dark overnight at room temperature. To the resulting deep orange-colored solution was added 10 ml. of glacial acetic acid and 0.4 g. of zinc dust, the mixture was stirred at room temperature for one hour, filtered and the zinc pad was washed with acetone. Concentration of the combined filtrates to dryness *in vacuo* gave a yellow resin, which crystallized when triturated with ethyl acetate. Recrystallization from methanol gave 0.62 g. of XIX as slender needles of m.p. 218.6–225.2°, $[\alpha]D$ +63.2° (*c* 0.2 in acetic acid).

Anal. Calcd. for $C_{22}H_{32}O_5$: C, 70.18; H, 8.57. Found: C, 70.24; H, 8.33.

Acetylation of XIX with acetic anhydride–pyridine (18 hr. at 25°) gave a quantitative yield of D-homopregnane-17aα,21-diol-3,11,20-trione 21-acetate (VIIIa), identified by mixed m.p. and a comparison of the infrared spectra.

(31) The consumption of the phenyl iodosoacetate was followed titrimetrically with sodium thiosulfate. The reaction was essentially complete in 8–10 hours.

(32) *Cf.* J. Fried, *et al.*, *Chemistry & Industry*, 1232 (1956).

RENSSELAER, NEW YORK

[CONTRIBUTION FROM THE MERCK SHARP & DOHME RESEARCH LABORATORIES]

D-Homo Rearrangement of Cortical Steroids. Interrelationship of D-Homo Derivatives in the 11-Oxygenated Pregnane Series[1]

BY N. L. WENDLER AND D. TAUB

RECEIVED FEBRUARY 3, 1958

Chemical proof is provided to substantiate the 17a-keto structure for D-homo systems arising from cortical steroids through the agency of Lewis acids.

The structure and stereochemistry of the four D-homo systems derivable from 17-hydroxy-20-keto steroids have been established recently by partial synthesis.[2] From this work it was observed that 3α-acetoxy-17α-hydroxypregnane-11,20-dione (VIII) on D-homoannulation with Lewis acids produced 3α-acetoxy,17α-hydroxy-17β-methyl-D-homoetiocholane-11,17a-dione (V-II) as the major product. Consequently, it was inferred[3] that Lewis acid-catalyzed D-homoannulation products of 17α-hydroxy-21-acetoxy-20-keto systems should correspondingly possess the 17a-ketone structure. The present account describes the chemical confirmation of this structural assignment and with it a complete correlation of the D-homo steroids in the 11-oxygenated pregnane series.

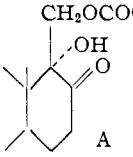
D-Homoannulation of 17α-hydroxy-21-acetoxy-pregnane-3,11,20-trione (III) with aluminum alkoxide yielded the 17a-ketone IV. Bromination

(1) A preliminary account of this work was reported in *Chemistry & Industry*, 822 (1957).

(2) N. L. Wendler, D. Taub, S. Dobriner and D. K. Fukushima, THIS JOURNAL, **78**, 5027 (1956).

(3) Reference 2, footnote 22.

of IV at C-4 and then dehydrobromination *via* the semicarbazone procedure produced the Δ^4-derivative II which was identical with a sample obtained by D-homoannulation of cortisone acetate (I). The structure of this individual and its close relatives had previously been assigned incorrectly the isomeric 17-ketone structure, part structure A[4]; this assignment resulted from an extrapolation

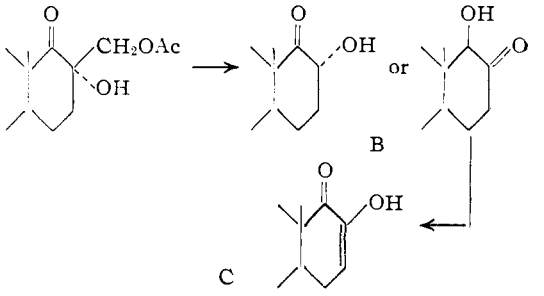


A

of conclusions based on earlier work[5] in the field which has since been revised.[2,6]

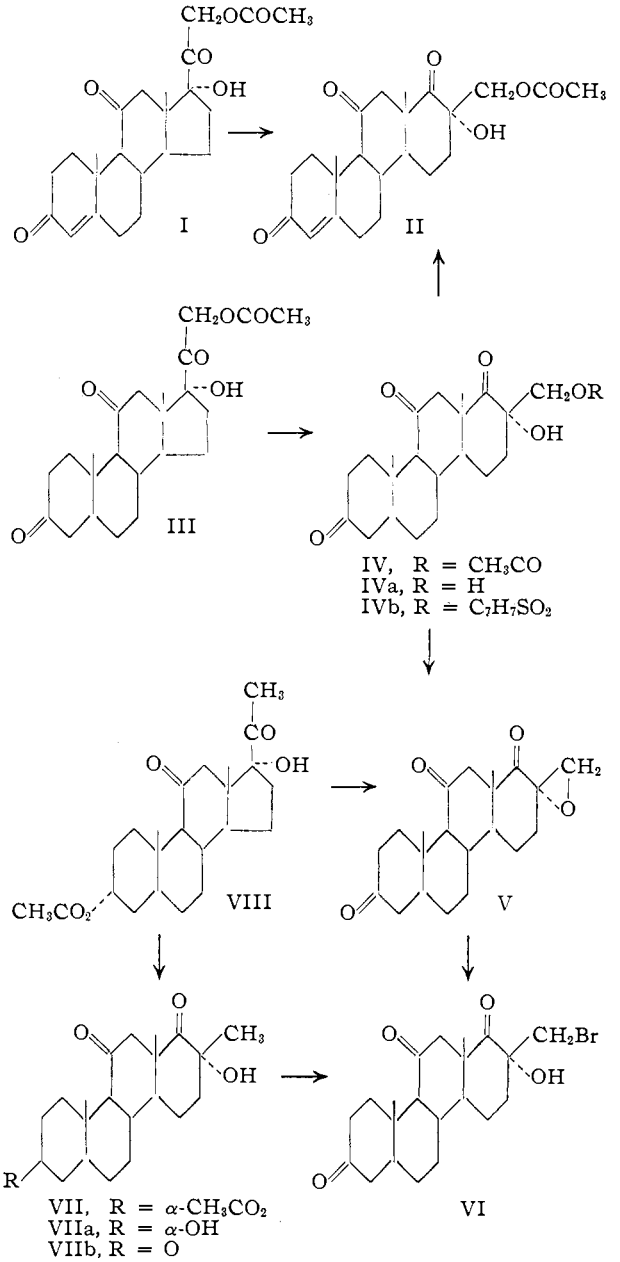
Saponification of the D-homo derivative IV followed by treatment with *p*-toluenesulfonyl chloride in pyridine afforded the primary *p*-toluenesulfonic ester IVb. Reaction of the latter with methanolic potassium hydroxide resulted in formation of the 17α,21-oxide derivative V. Cleavage of the oxide with 15% hydrogen bromide in acetic acid proceeded at the primary position as anticipated to yield the bromohydrin VI. The latter was smoothly debrominated by hydrogenation over 25% palladium-on-calcium carbonate to afford 17α-hydroxy-17β-methyl-D-homoetiocholane-3,11,17a-trione (VIIb). This product, VIIb, was identical with an authentic sample prepared from 3α-acetoxy-17α-hydroxy-17β-methyl-D-homoetiocholane-11,17a-dione (VII) by saponification at C-3 to give VIIa followed by oxidation at that position with N-bromacetamide. The structure of VII had been established previously[2] by partial synthesis.

An interesting side reaction which appears to accompany the D-homoannulation of 17α-hydroxy-21-acetoxy cortical steroids with aluminum alkoxides is the loss of the acetoxymethylene residue with resultant formation of the 17,17a-ketol, part structure B.[7] This degradation was observed to



occur with both cortisone (I) and its dihydro derivative III and is considered to result from acetate removal through ester exchange with the catalyst followed by loss of formaldehyde *via* retroaldolization. In the case of cortisone (I) the degraded ketol B was further oxidized to the diosphenol C.

The foregoing completes the interrelationship of the D-homo systems arising in the 11-ketopregnane series from members differing in degree of oxygenation in the side chain component. In all instances the Lewis acid-catalyzed D-ring expansion was found to proceed with preponderant formation of the 17a-ketone structure and to possess identical stereochemistry at C-17 (17α-OH).



Experimental[8]

3α,17α-Dihydroxy-17β-methyl-D-homoetiocholane-11,-17a-dione (VIIa).—A solution of 1 g. of 3α-acetoxy-17α-hydroxy-17β-methyl-D-homoetiocholane-11,17a-dione[2] (VII) in 25 cc. of methanol was treated with 1 g. of potassium hydroxide in 5 cc. of water and the reaction mixture refluxed for 1 hr. At the end of this time the solvents were concentrated *in vacuo* until solid separated, whereupon the organic material

(4) (a) V. Georgian and N. Kundu, *Chemistry & Industry*, 431 (1954); (b) E. Batres, G. Rosenkranz and F. Sondheimer, THIS JOURNAL, **76**, 5171 (1954).

(5) R. B. Turner, *ibid.*, **75**, 3484 (1953).

(6) (a) D. K. Fukushima, S. Dobriner, M. S. Heffler, T. H. Kritchevsky, F. Herling and G. Roberts, *ibid.*, **77**, 6585 (1955); (b) R. B. Turner, M. Perelman and K. T. Park, Jr., *ibid.*, **79**, 1108 (1957).

(7) The configuration of the OH is indicated in its more stable equatorial orientation, a consequence reasonably to be anticipated from the considered mode of formation of this substance.

(8) All melting points were taken on a micro hot-stage and are corrected.

was extracted with ethyl acetate. The ethyl acetate extract was washed with water and saturated salt solution, dried, concentrated *in vacuo* and the residue crystallized from acetone–ether, m.p. 174–175°, wt. 800 mg.

Anal. Calcd. for $C_{21}H_{32}O_4$: C, 72.41; H, 9.20. Found: C, 72.66; H, 9.30.

17α-Hydroxy-17β-methyl-D-homoetiocholane-3,11,17a-trione (VIIb).—A solution of 348 mg. of VIIa in 1 cc. of *t*-butyl alcohol and 0.7 cc. of pyridine was treated with a solution of 360 mg. of N-bromoacetamide in 1.5 cc. of *t*-butyl alcohol and 4–5 drops of water. The reaction mixture was allowed to stand at room temperature for 16 hr. during which time the reaction solution took on an orange coloration accompanied by product crystallization in the form of prisms. The product was filtered and washed with ether. Crystallization from acetone afforded a first crop of 210 mg. of VIIb, m.p. 220–225°; λ_{max} 2.84 μ (OH), 5.84 μ (C=O).

Anal. Calcd. for $C_{21}H_{30}O_4$: C, 72.83; H, 8.67. Found: C, 72.87; H, 8.83.

D-Homoannulation of 17α-Hydroxy-21-acetoxypregnane-3,11,20-trione (III) with Aluminum Alkoxide to Give 17α-Hydroxy-17β-acetoxymethyl-D-homoetiocholane-3,11,17a-trione (IV).—A solution of 6 g. of III in 100 cc. of dioxane, 100 cc. of toluene and 50 cc. of cyclohexanone was refluxed with a water separator until 25 cc. had been collected. The reaction mixture was cooled somewhat and treated with 6 g. of aluminum isopropoxide. The system was flushed with nitrogen and allowed to reflux for 1 hr. At the end of this period of reflux, the reaction mixture was cooled, treated with 300–400 cc. of water and allowed to stand overnight. The solvents were distilled *in vacuo* to leave the product as a gum. The latter was treated with 50 cc. of 10% hydrochloric acid and extracted with ethyl acetate. The ethyl acetate extract was washed with dilute potassium bicarbonate and salt solution, dried and evaporated to dryness *in vacuo*. The residue was acetylated in 15 cc. each of acetic anhydride and pyridine at room temperature. The acetylated product, *ca.* 7 g., was chromatographed on 250 g. of acid-washed alumina. The material (280 mg.) eluted with 10–20% ether in benzene gave a strong, immediate test for enolizable ketols with blue tetrazolium reagent and proved to be the corresponding degraded ketol (B) as its acetate derivative, m.p. 229–235°; no OH in infrared, no maximum in ultraviolet. $[\alpha]^{chf}D$ +28° (*c* 0.875 g./100).

Anal. Calcd. for $C_{22}H_{30}O_5$: C, 70.59; H, 8.02. Found: C, 70.42; H, 8.02.

Additional amounts of this compound were present in mixed chromatographic fractions as indicated by paper chromatography to a maximum extent of *ca.* 125 mg.

The fractions eluted with 50% ether in benzene and ether alone afforded 1.5 g. of IV which gave only a delayed test with blue tetrazolium reagent. Crystallization of IV was effected from acetone–ether, m.p. 144–146°, with phase change prisms → needles melting at 171–173°; λ^{chf}_{max} 2.8–2.84 μ (OH), 5.73 μ (OAc) and 5.82 μ (C=O); $[\alpha]^{chf}D$ +87.4° (*c* 1.175 g./100).

Anal. Calcd. for $C_{23}H_{32}O_6$: C, 68.31; H, 7.92. Found: C, 68.43; H, 7.90.

Additional amounts of IV were present in mixed chromatographic fractions as indicated by paper chromatography to a maximum extent of *ca.* 750 mg.

17α-Hydroxy-17β-hydroxymethyl-D-homoetiocholane-3,11,17a-trione (IVa).—A solution of 800 mg. of IV in 25 cc. of methanol at 0–5° was treated with 225 mg. of potassium hydroxide in 5 cc. of water. The reaction mixture was allowed to stand at room temperature for 2 hr. then acidified with 0.3–0.4 cc. of acetic acid and concentrated to dryness *in vacuo* below 40°. The product was extracted with ethyl acetate and crystallized from the same solvent in 90% yield as prisms, m.p. 212–215°.

Anal. Calcd. for $C_{21}H_{30}O_5$: C, 69.61; H, 8.29. Found: C, 69.50; H, 8.10.

Formation of the 17α,21-Oxide V.—A solution of 800 mg. of IVa in 5 cc. of pyridine was treated at 0° with 420 mg. of *p*-toluenesulfonyl chloride. The reaction mixture was allowed to stand for 16–18 hr. in the ice-box. At the end of this time the reaction mixture was treated with ice-water and the oil which separated extracted with ethyl acetate. The ethyl acetate extract was washed successively with 5% hydrochloric acid, water, three times with potassium bicarbonate solution and finally salt solution. The dried ethyl acetate solution of IVb yielded a non-crystallizable oil on evaporation. The latter was dissolved in 25 cc. of methanol and treated with 1 g. of potassium hydroxide in 3 cc. of water. The reaction mixture was allowed to stand at room temperature for 1 hr. during which time the product oxide V crystallized in part as flat, square plates. The reaction mixture was concentrated *in vacuo* and the residue extracted with ethyl acetate. The crystalline residue after evaporation of the solvent was crystallized from acetone to afford 300 mg. of oxide V, m.p. 264–268°.

Anal. Calcd. for $C_{21}H_{28}O_4$: C, 73.26; H, 8.14. Found: C, 72.92; H, 8.22.

17α-Hydroxy-17β-bromomethyl-D-homoetiocholane-3,-11,17a-trione (VI).—A solution of 150 mg. of oxide V in 8 cc. of glacial acetic acid was treated with 2 cc. of 15% hydrogen bromide in acetic acid at 10–15°. The reaction mixture was allowed to stand 45 minutes after which it was evaporated to dryness *in vacuo* and flushed several times with benzene. The bromohydrin VI crystallized from acetone–hexane as prisms, m.p. 225–230° (darkening).

Anal. Calcd. for $C_{21}H_{29}O_4Br$: C, 59.29; H, 6.82; Br, 18.83. Found: C, 59.71; H, 6.93; Br, 18.46.

Conversion of Bromohydrin VI to 17α-Hydroxy-17β-methyl-D-homoetiocholane-3,11,17a-trione (VIIb).—A 100-mg. sample of VI in 15 cc. of methanol and 1 ml. of water was treated with hydrogen at 1 atm. pressure and 22° over 200 mg. of 25% Pd-on-$CaCO_3$ catalyst. Hydrogen uptake was complete within 10 minutes. The mixture was filtered, the filtrate concentrated to dryness and the crystalline residue crystallized from acetone–ether to give 72 mg. (88%) of 17α-hydroxy-17β-methyl-D-homoetiocholane-3,11,17a-trione (VIIb) as prisms, m.p. 220–225°, undepressed with an authentic sample (m.p. 220–225°) prepared by D-homo rearrangement of VIII (see above). The respective infrared spectra likewise were identical.

D-Homoannulation of Cortisone Acetate (I).—A 6.7-g. sample of cortisone acetate (I) was D-homoannulated in the manner described by Batres, Rosenkranz and Sondheimer,[4b] and acetylated with acetic anhyhride in pyridine at room temperature. Chromatography of the product afforded 100 mg. of the corresponding degraded diosphenol C as its diacetate derivative on elution with 20% ether in benzene, crystallized from acetone–ether, m.p. 246–251°, $\lambda^{CH_3OH}_{max}$ 236 mμ, ε 21000.

Anal. Calcd. for $C_{22}H_{26}O_5$: C, 71.38; H, 7.03. Found: C, 71.09; H, 7.30.

Elution with ether afforded II which was crystallized from methanol, m.p. 198–199.5° (reported[4b] 199–201°); λ^{chf}_{max} 2.78 μ (OH), 5.7 and 8 μ (OAc), 5.95 and 6.09 μ (Δ^4-3-ketone).

Anal. Calcd. for $C_{23}H_{30}O_6$: C, 68.61; H, 7.52. Found: C, 68.73; H, 7.39.

Conversion of IV to II.—A solution of 808 mg. of IV in 25 cc. of glacial acetic acid containing 200 mg. of *p*-toluenesulfonic acid monohydrate was brominated at 20° with 320 mg. of bromine in 10 cc. of acetic acid containing 181 mg. of sodium acetate. After complete addition of bromine, a solution of 175 mg. of sodium acetate in 10 cc. of water was added followed by 150 cc. of water. The brominated product was extracted with chloroform and the chloroform extract washed with dilute potassium bicarbonate solution, dried and concentrated.

The crude bromination product was allowed to react in 20 cc. of acetonitrile with 1.1 g. of semicarbazide free base dissolved in 10 cc. of acetonitrile and 3.5 cc. of acetic acid for a period of 16–18 hours. At the end of this time the reaction mixture was concentrated *in vacuo*, treated with water and extracted with chloroform. The chloroform extract was washed with dilute potassium bicarbonate solution, dried and concentrated to a residue (wt. 600 mg., λ_{max} 269 mμ ($\epsilon^{1\%}_{1cm}$ 375), 235 mμ ($\epsilon^{1\%}_{1cm}$ 200)).

The above crude semicarbazone was dissolved in 300 cc. of acetic acid, treated with 3.0 cc. of pyruvic acid and 10 cc. of water and allowed to stand 18 hr. at room temperature. At the end of this period the reaction mixture was concentrated *in vacuo*, diluted with chloroform and water and the chloroform layer separated and washed with potassium bicarbonate solution. Concentration of the chloroform extract followed by room temperature acetylation of

the residue provided material that was chromatographed on neutral alumina. That fraction eluted with chloroform and crystallized from acetone–ether; m.p. 194–197° was not depressed on mixed m.p. with II obtained from cortisone acetate (I). The infrared spectra of the two samples were identical.

RAHWAY, N. J.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

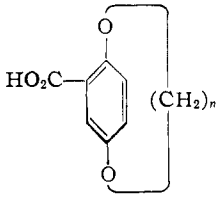
Many-membered Carbon Rings. XVII. A Paracyclophane Possessing Two *gem*-Dimethyl Groups[1,2]

BY A. T. BLOMQUIST AND F. JAFFE[3]

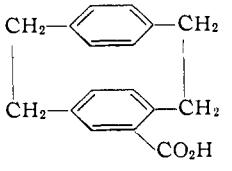
RECEIVED JANUARY 28, 1958

The acyloin cyclization of dimethyl *p*-phenylene-bis-(β,β-dimethylvalerate) has given 3,3,8,8-tetramethyl-5-keto-6-hydroxy[10]paracyclophane in 31% yield, together with a dimeric cyclic acyloin (*ca.* 10% yield). The dimethyl ester named above was synthesized from benzene and other simple intermediates.

Our general concern with the chemistry of many-membered carbon rings has included, among other things, a particular interest in the stereoisomerism attendant with certain kinds of these carbocycles. For example, we have indicated previously that the conformations of molecules such as cyclononane and *trans*-cyclononene are dissymmetric[4,5] and suitable derivatives of these should, under the circumstances of restricted rotation at room temperature, be resolvable into optical antipodes. It is also true that certain *o*-substituted paracyclophanes would possess molecular dissymmetry as a consequence of restricted rotation of the benzene nucleus with respect to the polymethylene bridge. Molecular dissymmetry arising from such circumstances has in fact been demonstrated by Lüttringhaus in his resolution of the polymethylene ethers of gentisic acid (I and II).[6] Further, a similar kind



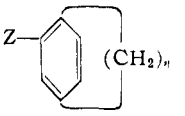
I, $n = 8$
II, $n = 9$



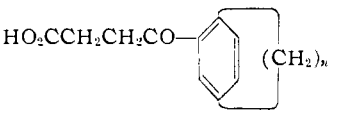
III

of origin of molecular dissymmetry was shown by Cram in his resolution of the paracyclophanecarboxylic acid III.[7]

From a consideration of modern molecular models one would expect to be able to resolve suitable derivatives of nuclearly-substituted paracyclophanes such as IV provided the polymethylene bridge had a chain of eight to ten carbon atoms. Accordingly, studies were carried out to test this

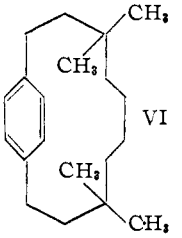


IV, $n = 8$, 9 and 10



V, $n = 9$ and 10

thesis. The first work done toward this end, synthesis and attempted resolution of the acids V,[8] was not encouraging. It seemed desirable therefore to develop the synthesis of a very highly hindered paracyclophane such as VI and to then attempt resolution of suitable *o*-substituted derivatives of it.



VI

While the study of syntheses leading to VI was in progress it was discovered in this Laboratory[9] that the discouraging results obtained with the acids V were due to the fact that the compounds V were not at hand at all and that the succinoylation of [9]- and [10]paracyclophane rearranged the *para*-polymethylene bridge to a *meta*-polymethylene bridge. The development of syntheses leading to VI was nevertheless continued and the results obtained in the synthesis of the acyloin precursor for VI are presented in this article. A subsequent account will be given of the resolution studies of this hydrocarbon.

A condensed outline of the total synthesis of 3,3,8,8-tetramethyl-5-keto-6-hydroxy[10]paracyclophane (XII) is given.

The acylation of benzene with β,β-dimethylglutaric anhydride, reported to give an almost

(1) For the preceding paper in this series see A. T. Blomquist and Y. C. Meinwald, THIS JOURNAL, **80**, 630 (1958).

(2) For a discussion of the "cyclophane" system of nomenclature for bridged benzene rings see W. M. Schubert, W. A. Sweeney and H. K. Latourette, *ibid.*, **76**, 5462 (1954), and D. J. Cram and J. Abell, *ibid.*, **77**, 1179 (1955).

(3) This article is an abstract of part of the dissertation presented by F. Jaffe in September, 1957, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).

(5) A. T. Blomquist, E. S. Wheeler and Y. Chu, *ibid.*, **77**, 6307 (1955).

(6) A. Lüttringhaus and H. Gralheer, *Ann.*, **557**, 108, 112 (1947); A. Lüttringhaus and G. Eyring, *Angew. Chem.*, **69**, 139 (1957); *Ann.*, **604**, 111 (1957).

(7) D. J. Cram and N. L. Allinger, THIS JOURNAL, **77**, 6289 (1955).

(8) R. E. Stahl, Thesis, Cornell University, Ithaca, N. Y., 1954; K. L. Lockwood, Thesis, Cornell University, Ithaca, N. Y., 1955.

(9) A. T. Blomquist and Y. C. Meinwald, unpublished results.