one. The mother liquors were chromatographed on silica gel and two fractions were eluted. The first yielded 77 mg. of 3β-acetoxyallopregnane-20-one (II), after two recrystallizations from methanol, m.p. 144–145°; $[\alpha]^{26}D$ +78°; infrared spectrum identical with that of an authentic sample. The second fraction afforded 54 mg. of starting material, III.

Reaction of 3β,17α-Dihydroxyallopregnane-20-one (Ia) with Zinc–Acetic Acid.—One hundred and forty-five milligrams of Ia afforded a crystalline product which was acetylated with acetic anhydride–pyridine at room temperature. Chromatography on silica gel yielded three fractions. Fraction A was rechromatographed on 10 g. of silica gel and three compounds were eluted: 12 mg. of 3β-acetoxyallopregnane-20-one (II), infrared spectrum identical with authentic II, m.p. 145–146° after one recrystallization from methanol; 14 mg. of a mixture of II and 3β-acetoxy-17α-hydroxyallopregnane-20-one; 20 mg. of IV, infrared spectrum identical with that of 3β-acetoxy-17aβ-methyl-D-homoandrostane-17-one, m.p. 161–169° after one recrystallization from methanol. Fraction B was recrystallized once from methanol, m.p. 188–190°, and was shown by infrared spectrometry to be the 3-monoacetate of Ia. Fraction C was again chromatographed but was poorly resolved; the monoacetate of Ia was the only substance identified.

Reaction of 3β-Acetoxy-17aα-hydroxy-17aβ-methyl-D-homoandrostane-17-one (V) with Zinc–Acetic Acid.—From 140 mg. of V, after chromatography, 104 mg. (78%) was obtained. The infrared spectrum was identical with that of 3β-acetoxy-17aβ-methyl-D-homoandrostane-17-one (IV). One recrystallization from methanol yielded IV, m.p. 172–173°, $[\alpha]^{26}D$ −60° (Ramirez[18] reported m.p. 171–173° and $[\alpha]^{25}D$ −52° ($CHCl_3$)). The mother liquor afforded impure IV, m.p. 164–167°.

Treatment of 3β-Acetoxy-17aβ-hydroxy-17aα-methyl-D-homoandrostane-17-one (VI) with Zinc–Acetic Acid.—Of 250 mg. of VI subjected to the standard treatment, 221 mg. of unreacted VI was recovered. There was no evidence for any other product.

Reaction of 3β,17α-Diacetoxy-17β-methyl-D-homoandrostane-17a-one (VII) with Zinc–Acetic Acid.—From 300 mg. of VII after chromatography on silica gel, 227 mg. of VIII were obtained; the infrared spectrum was identical with 3β-acetoxy-17α-methyl-D-homoandrostane-17a-one (VIII).[15] The substance was recrystallized once from methanol, 174 mg., m.p. 170–171°, $[\alpha]^{26}D$ −30° (acetone) (Prins and Sloppee[14] report a melting point of 171° and $[\alpha]D$ −32° (acetone) for this compound). The mother liquors yielded impure VIII, m.p. 168–171°, $[\alpha]^{26}D$ −24° (acetone).

Acknowledgment.—The support and interest of Dr. T. F. Gallagher in this investigation is gratefully acknowledged.

(18) F. Ramirez and S. Stafiez, THIS JOURNAL, **78**, 644 (1956).

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

Syntheses in the Terpene Series. III.[1] A Synthesis of 4,4,9-Trimethyl-*trans*-decal-8-one

BY FRANZ SONDHEIMER AND DOV ELAD

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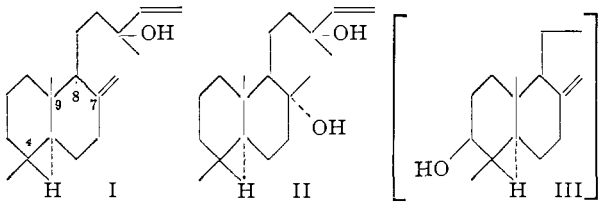
4,4,9-Trimethyl-*trans*-decal-8-one (XIIa), a substance of potential utility for the synthesis of certain di- and triterpenes, has been synthesized from the readily accessible 9-methyl-Δ^4-octalin, -3,8-dione (VI) by a seven-step sequence. 9-Methyl-Δ^4-octal-7ξ-ol-3-one (XIX) has been prepared in the course of an investigation into routes to 4,4,9-trimethyl-*trans*-decal-7-one (XXa).

We have recently embarked upon the synthesis of certain of the di- and triterpene alcohols, such as manool (I),[2] sclareol (II)[2] and α-onocerin (I-II).[3] The carbon skeleton of all of these substances as well as of some of the diterpene acids such



as cativic acid,[4] eperuic acid[5] and labdanolic acid[6] contains the 4,4,9-trimethyl-*trans*-decalin system bearing alkyl or alkylidine substituents at the C-7 and C-8 positions. We considered that suitable starting materials would be the unknown 4,4,9-trimethyl-*trans*-decal-8-one (XIIa) and the corresponding 3β-hydroxy compound XIIb, or alternatively the C-7 ketones XXa and XXb, since the carbonyl group in ring B would make possible the introduction of an alkyl or alkylidine group in the adjacent position and could itself subsequently also be converted to an alkyl or alkylidine function. Such bicyclic ketones moreover could be of value as intermediates in the synthesis of the polycyclic di- and triterpenes containing more than two rings.[7] In the present paper we record the synthesis of 4,4,9-trimethyl-*trans*-decal-8-one (XIIa) by a method which should permit also the preparation of the corresponding 3β-hydroxy compound XIIb. After completion of this work (for a preliminary account, *cf.* footnote 1a), Cocker and Halsall[8] in a preliminary communication reported the synthesis of XIIa by a method similar to our own, while King, Ritchie and Timmons[9] announced the synthesis of the corresponding 3β-ol XIIb (as the benzoate) by a different method. We also undertook some exploratory experiments aimed at the synthesis of 4,4,9-trimethyl-*trans*-decal-7-one (XXa), an account of which is given.

(1) (a) The paper by D. Elad and F. Sondheimer, *Bull. Research Council Israel*, **5A**, 269 (1956), is to be considered Part I of this series; (b) for Part II, see D. Elad and F. Sondheimer, *Proc. Chem. Soc.*, 206 (1957).

(2) *Cf.* W. Klyne, *J. Chem. Soc.*, 3072 (1953).

(3) D. H. R. Barton and K. H. Overton, *ibid.*, 2639 (1955); K. Schaffner, R. Viterbo, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 174 (1956).

(4) F. W. Grant and H. H. Zeiss, THIS JOURNAL, **76**, 5001 (1954).

(5) F. E. King and G. Jones, *J. Chem. Soc.*, 658 (1955).

(6) J. D. Cocker and T. G. Halsall, *ibid.*, 4262 (1956).

(7) *Cf.* R. Rüegg, J. Dreiding, O. Jeger and L. Ruzicka (*Helv. Chim. Acta*, **33**, 889 (1950)), who prepared the optically active 7-methyl derivative of IIa by the degradation of α-amyrin.

(8) J. D. Cocker and T. G. Halsall, *Chemistry & Industry*, 1275 (1956).

(9) F. E. King, C. F. Ritchie and C. J. Timmons, *ibid.*, 1230 (1956).

The starting material for the synthesis of XIIa was 9-methyl-Δ^4-octalin-3,8-dione (VI),[10] prepared readily by the Michael condensation between 2-methylcyclohexane-1,3-dione (V) and 1-diethylaminobutan-3-one (IV).[11] In the diketone VI it was necessary to protect the saturated keto grouping so that the unsaturated ketone could be dimethylated without the occurrence of ring cleavage or methylation at C-7. Use was made of the fact that at room temperature manganese dioxide smoothly oxidizes allylic alcohols to the corresponding ketones, whereas saturated alcohols are stable.[12] Consequently VI was reduced with lithium aluminum hydride to a mixture of 9-methyl-Δ^4-octalin-3β,8β-diol (VIIa) and the 3α,8β-diol VIIb[13] which without purification was oxidized directly in chloroform solution with manganese dioxide. The resulting non-crystalline 9-methyl-Δ^4-octal-8β-ol-3-one (VIIIa), obtained in 74% yield, formed a hydrate, m.p. 59°, agreeing well in properties with that obtained by Birch, *et al.*,[14] by a more involved method. An optical antipode of VIIIa has also been reported recently to be formed by a microbiological reduction of VI.[15]

The next step involved the introduction of the 4,4-dimethyl grouping. Woodward, Barton, *et al.*,[16] have shown that the direct methylation of Δ^4-cholesten-3-one with methyl iodide and potassium *t*-butoxide in boiling *t*-butyl alcohol leads to the corresponding 4,4-dimethyl-Δ^5-3-one and we have found this reaction to occur very readily even at room temperature. Treatment of 9-methyl-Δ^4-octal-8β-ol-3-one (VIIIa) under these conditions did not result in simple dimethylation; only oily products were obtained which showed no hydroxyl band in the infrared; doubtlessly ring B of the vinylogous aldol VIIIa had been cleaved under the strongly alkaline conditions. After considerable experimentation this difficulty was overcome by the simple expedient of subjecting the benzoate VIIIb, m.p. 97°, to the methylation reaction at room temperature, whereby 4,4,9-trimethyl-Δ^{10}-octal-8β-ol-3-one benzoate (IXa), m.p. 87°, was obtained in about 60% yield. The structure of this substance was confirmed by the infrared spectrum, which no longer showed the band at 1660 cm.$^{-1}$ (α,β-unsaturated ketone) present in the precursor VIIIb, and by the ultraviolet spectrum which was that to be expected of a simple benzoate. A second compound (m.p. 93°), less polar than IXa, was formed in the methylation step in 15% yield. Its spectral properties were very similar to those of the 4,4-dimethylated ketol benzoate IXa and it is probably the 2,4,4-trimethylated product IXb; the elemental analysis does not, however, allow the 2,2,4,4-tetramethyl formulation to be excluded with certainty. It is interesting to note that over-methylation had occurred in spite of the relatively mild conditions used in the methylation step.

The ketol benzoate IXa contains oxygen functions at the C-3 and C-8 positions necessary for its conversion to the 3β-hydroxy-8-ketone XIIb. Our first goal however was the 3-desoxy-8-ketone XIIa and for this purpose it was necessary to effect the removal of the oxygen at C-3. This was done most conveniently by subjecting IXa to the Huang-Minlon[17] modification of the Wolff–Kishner reduction, whereby 4,4,9-trimethyl-Δ^{10}-octal-8β-ol (X), m.p. 123°, was produced in 78% yield; the reaction conditions had brought about saponification of the ester at C-8 as well as reduction of the ketone at C-3. The double bond in X was saturated through hydrogenation in acetic acid over platinum, a reaction which yielded 73% of 4,4,9-trimethyl-*trans*-decal-8β-ol (XI), m.p. 75°. The *trans* configuration is assigned to this compound since a model of X reveals the β-side to be considerably more hindered (by the axial 4- and 9-methyl groups) than the α-side.[18] Finally, oxidation of XI with chromium trioxide produced the desired 4,4,9-trimethyl-*trans*-decal-8-one (XIIa), m.p. 42°, in about 90% yield.

While investigating routes to 4,4,9-trimethyl-*trans*-decal-7-one (XXa) and its 3β-hydroxy derivative XXb, we prepared 9-methyl-Δ^4-octal-7ξ-ol-3-one (XIX). The starting material, 2-methyl-4-benzoyloxycyclohexanone (XVIIa), has been prepared previously by the methylation of 4-benzoyloxycyclohexanone (XVI) *via* the enamine derivative.[19] We found a convenient method to involve the hydrogenation of toluhydroquinone (XIII) to a mixture of stereoisomeric 2-methylcyclohexane-1,4-diols (XIV),[20] which on differential benzoylation at C-4 followed by chromium trioxide oxidation furnished a stereoisomeric mixture of the keto-ester XVIIa, one isomer of which (m.p. 70°) crystallized in *ca.* 35% yield. This sequence is analogous to the conversion of hydroquinone to 4-benzoyloxycyclohexanone.[21] That the preferential benzoyl-

(10) P. Wieland and K. Miescher, *Helv. Chim. Acta*, **33**, 2215 (1950); C. A. Friedmann and R. Robinson, *Chemistry & Industry*, 777 (1951); N. L. Wendler, H. L. Slates and M. Tishler, THIS JOURNAL, **73**, 3816 (1951); N. K. Chandhuri and P. C. Mukharji, *J. Indian Chem. Soc.*, **33**, 81 (1956).

(11) Prof. M. S. Newman of the Ohio State University, Columbus, Ohio, has developed this sequence into a high yield reaction and has very kindly provided us with the experimental details prior to publication.

(12) *Cf.* (a) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952); (b) O. Mancera, G. Rosenkranz and F. Sondheimer, *ibid.*, 2189 (1953); (c) F. Sondheimer, C. Amendolla and G. Rosenkranz, THIS JOURNAL, **75**, 5930 (1953).

(13) *Cf.* W. G. Dauben, R. A. Micheli and J. F. Eastham (*ibid.*, **74**, 3852 (1952)) for the steric course of the lithium aluminum hydride reduction of steroidal Δ^4-3-ketones. The 8β-hydroxy configuration has been assumed for these and subsequent compounds by analogy with similar reductions in the steroid series. These stereochemical considerations are however not of importance since the asymmetric centers at C-3 and C-8 are later eliminated.

(14) A. J. Birch, J. A. K. Quartey and H. Smith, *J. Chem. Soc.*, 1768 (1952).

(15) V. Prelog and W. Acklin, *Helv. Chim. Acta*, **39**, 748 (1956).

(16) (a) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives and R. B. Kelly, THIS JOURNAL, **76**, 2852 (1954); *J. Chem. Soc.*, 1131 (1957). See also (b) V. Petrow, *et al.*, *ibid.*, 2998 (1955); 4490 (1956); (c) H. J. Ringold and G. Rosenkranz, *J. Org. Chem.*, **22**, 602 (1957).

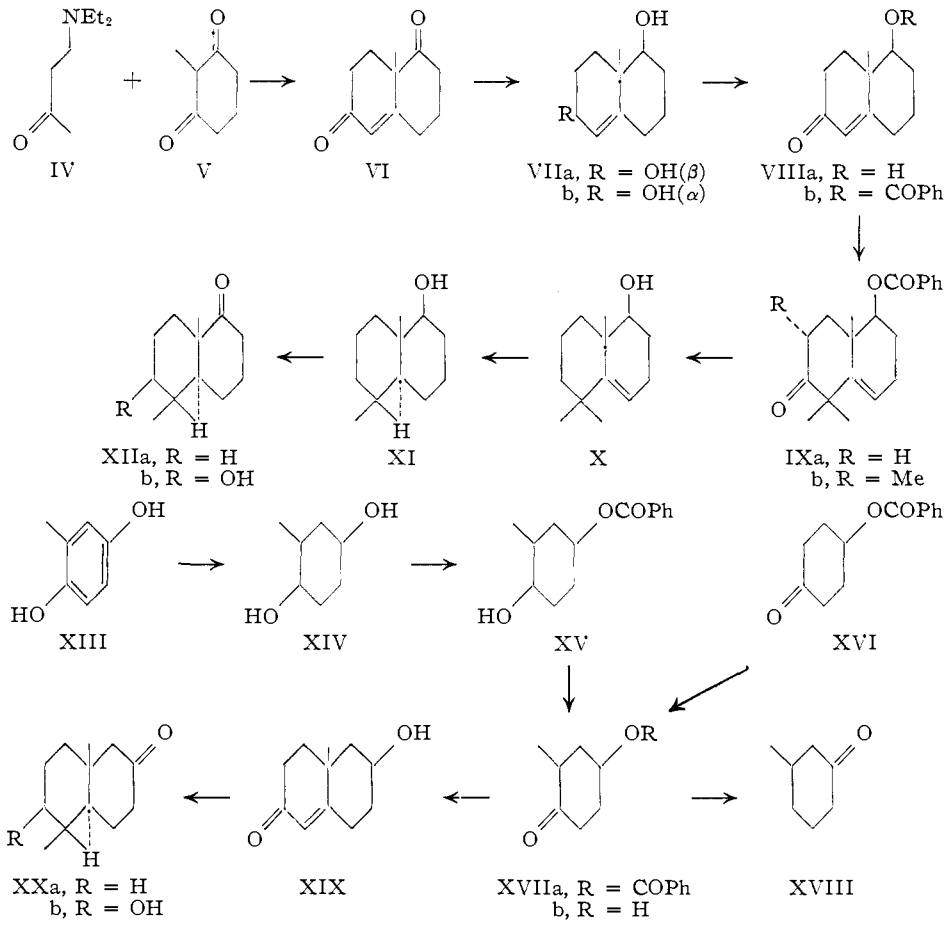
(17) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

(18) It has been shown by J. L. Beton, T. G. Halsall, E. R. H. Jones and P. C. Phillips [*J. Chem. Soc.*, 753 (1957); see also footnote 16c] that the hydrogenation of steroidal 4,4-dimethyl-Δ^4-3-ones leads to the *trans* configuration, but these cases cannot be used for predicting results in the decalin series in view of the absence of the C and D rings in the latter.

(19) G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

(20) The formulas XIV, XV, XVIIa, XVIIb and XIX are not intended to specify the stereochemical configurations.

(21) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).



ation had occurred at C-4 and not at C-1 and that the keto-ester was therefore the required XVIIa and not 3-methyl-4-benzoyloxycyclohexanone, was shown through successive Wolff–Kishner–Huang-Minlon reduction and chromium trioxide oxidation of XVIIa, whereby 3-methylcyclohexanone (XVIII) (and not 2-methylcyclohexanone) was obtained.

Saponification of the keto-ester XVIIa, m.p. 70°, by means of sodium methoxide in methanol produced the liquid 2-methyl-4-hydroxycyclohexanone (XVIIb),[22] which on condensation with 1-diethylaminobutan-3-one methiodide in benzene–methanol in the presence of sodium methoxide[23] furnished 9-methyl-Δ^4-octal-7ξ-ol-3-one (XIX), m.p. 103°, in only very poor yield.[24] The yield could not be improved appreciably by changing the reaction conditions and the further transformation of XIX to XXa or XXb was not investigated.

Acknowledgments.—We would like to express our thanks to Prof. G. Stork of Columbia University and Dr. T. G. Halsall of the University of Oxford for interesting discussions and correspondence, and to Prof. M. S. Newman of the Ohio State University for providing the experimental details for the preparation of 9-methyl-Δ^4-octalin-3,8-dione.

Experimental[25]

9-Methyl-Δ^4-octal-8β-ol-3-one (VIIIa).—9-Methyl-Δ^4-octalin-3,8-dione (VI) (55 g., m.p. 49–50°)[10,11] dissolved in 1 l. of dry ether was added dropwise with stirring to a solution of 28 g. of lithium aluminum hydride in 1.2 l. of dry ether at such a rate as to maintain a slow reflux. The mixture was stirred for a further 30 minutes, cooled and the excess reagent was destroyed by the careful addition of ethyl acetate. Saturated sodium sulfate solution was added dropwise until the precipitate began to adhere to the side of the flask, followed by solid magnesium sulfate. The precipitate was collected, washed well with ethyl acetate and ether and the combined filtrates were evaporated to dryness. The semi-solid residue (54.6 g.), consisting of the crude diols VIIa and VIIb, showed no appreciable carbonyl absorption in the infrared.

The crude diol mixture, dissolved in 3 l. of chloroform, was shaken with 550 g. of manganese dioxide[12b,26] for 15 hours. The dioxide was collected and extracted with boiling chloroform in a Soxhlet extractor until no more organic material was removed. The combined chloroform extracts on evaporation gave 53.2 g. of the crude ketol VIIIa which was purified most efficiently by chromatography on 1.5 kg. of alumina. Ether–chloroform (1:1) eluted the pure anhydrous ketol (40.2 g., 74% from VI) as an oil which crys-

(22) Partial inversion of the methyl group must have occurred during this ester interchange reaction, since benzoylation of XVIIb regenerated the keto-ester XVIIa again as a steroisomeric mixture.

(23) *Cf.* Y. Abe, T. Harukawa, H. Ishikawa, T. Miki, M. Sumi and T. Toga, THIS JOURNAL, **75**, 2567 (1953).

(24) Prof. G. Stork of Columbia University, New York City, has kindly informed us that he and Dr. J. Szmuszkovicz have also found this reaction to proceed in only poor yield.

(25) Melting points are uncorrected. Ultraviolet spectra were measured in 95% ethanol solution on a Unicam model S.P. 500 spectrophotometer and infrared spectra in chloroform solution on a Perkin–Elmer model 12C single beam spectrophotometer with sodium chloride prism. Analyses were carried out in our microanalytical laboratory under the direction of Mr. Erich Meier.

(26) F. Sondheimer, O. Mancera, M. Urquiza and G. Rosenkranz, THIS JOURNAL, **77**, 4145 (1955), footnote 17.

tallized slowly on contact with moist air. Crystallization of a sample from ether containing a few drops of water yielded the pure hydrated form, m.p. 58–59°, λ_{max} 240 mμ (ε 14,800), ν_{max} 1661 cm.$^{-1}$ and free hydroxyl band; Birch, *et al.*,[14] give m.p. 59–60°.

Anal. Calcd. for $C_{11}H_{16}O_2 \cdot H_2O$: C, 66.64; H, 9.15. Found: C, 66.68; H, 9.07.

9-Methyl-Δ⁴-octal-8β-ol-3-one Benzoate (VIIIb).—The anhydrous ketol VIIIa (34 g.) and benzoyl chloride (200 cc.) in dry pyridine (400 cc.) were allowed to stand overnight at room temperature. The product, isolated with ether in the usual way, was dissolved in a 1:1 mixture of benzene and petroleum ether and filtered through 1.5 kg. of alumina. This procedure yielded 49.4 g. (92%) of the benzoate VIIIb which after crystallization from petroleum ether showed m.p. 96–97°, λ_{max} 232 mμ (ε 31,500), ν_{max} 1710 and 1660 cm.$^{-1}$, no hydroxyl band.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.07; H, 7.15.

4,4,9-Trimethyl-Δ¹⁰-octal-8β-ol-3-one Benzoate (IXa) and 2,4,4,9-Tetramethyl-Δ¹⁰-octal-8β-ol-3-one Benzoate (IXb).—*Potassium (27 g.) was dissolved in 750* cc. *of dry t-butyl* alcohol under nitrogen and a solution of 43.5 g. of the ketol benzoate VIIIb in 150 cc. of *t*-butyl alcohol was added during 5 minutes at room temperature, with stirring. Methyl iodide (180 cc.) was then added during 5 minutes and the solution was stirred for 1 hour at room temperature under nitrogen. Dilute hydrochloric acid was added and the product was isolated with ether in the usual way. Chromatography on 1.5 kg. of alumina and elution with petroleum ether–benzene (1:1) yielded first an oil and then 27.1 g. (57%) of the 4,4-dimethylated ketone IXa which after crystallization from petroleum ether showed m.p. 86–87°, λ_{max} 230 mμ (ε 13,700), ν_{max} 1703 cm.$^{-1}$ (superimposed benzoate and saturated ketone).

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.96; H, 7.79.

The oil eluted from the column before the required IXa gradually crystallized on being allowed to stand for several weeks. Crystallization from pentane gave 7.5 g. (15%) of what is probably the 2,4,4-trimethylated ketone IXb, m.p. 91–93° (large depression on admixture with IXa as well as with VIIIb), λ_{max} 230 mμ (ε 13,900), ν_{max} 1703 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 76.91; H, 8.21.

4,4,9-Trimethyl-Δ¹⁰-octal-8β-ol (X).—A mixture of 25 g. of the methylated ketol benzoate IXa, 45 cc. of 100% hydrazine hydrate, 40 g. of potassium hydroxide and 450 cc. of diethylene glycol was boiled under reflux for 2 hours. The mixture was then distilled until the internal temperature reached 200°, the distillate being collected. Boiling under reflux was then continued for a further 4 hours. The cooled mixture together with the distillate was diluted with water and the resulting precipitate was collected. The filtrate was extracted well with ether and the further quantity of solid obtained by evaporation of the ether extract was combined with the material obtained directly. Crystallization from petroleum ether furnished 12.1 g. (78%) of the unsaturated alcohol X, m.p. 122–123°, ν_{max} free hydroxyl band.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.16; H, 11.35.

4,4,9-Trimethyl-*trans*-decal-8β-ol (XI).—The unsaturated alcohol X (11 g.) dissolved in 150 cc. of glacial acetic acid was shaken in hydrogen over 1.5 g. of platinum oxide catalyst at room temperature and atmospheric pressure. After *ca.* 3 hours the absorption of gas had stopped. The catalyst was removed, the filtrate was diluted with water and the product was extracted with ether. The oily residue obtained by evaporation of the ether was dissolved in a little pentane and cooled in a Dry Ice–acetone-bath. The resulting crystalline saturated alcohol XI (8.1 g., 73%) showed m.p. 69–72° and was of sufficient purity for use in the next step. The analytical sample, obtained by repeated sublimation at 120° (0.2 mm.), showed m.p. 74–75°, ν_{max} free hydroxyl band.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.48; H, 12.53.

4,4,9-Trimethyl-*trans*-decal-8-one (XIIa).—A solution of 7.5 g. of chromium trioxide in 18 cc. of water and 60 cc. of acetic acid was added to a stirred solution of 7.2 g. of the alcohol XI in 90 cc. of acetic acid during 10 minutes, with water cooling. The mixture was allowed to stand overnight at room temperature and was then diluted with water. Extraction with ether followed by distillation produced 6.5 g. (88%) of the saturated ketone XIIa, b.p. 113–115° (3.5 mm.), m.p. 40–42°, ν_{max} 1700 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.13; H, 11.49.

2-Methyl-4-benzoyloxycyclohexanone (XVIIa) from Toluhydroquinone (XIII).—Toluhydroquinone (84 g.) in 110 cc. of methanol was shaken in hydrogen with 20 g. of Raney nickel at 150° and 150 atmospheres. After 2 hours the theoretical amount of gas had been absorbed and uptake stopped. The catalyst was collected, washed well with hot methanol and the solvent was evaporated under reduced pressure. The residual oily mixed glycols XIV (88.4 g.) showed no appreciable absorption in the ultraviolet. They were dissolved in 250 cc. of chloroform (free of ethanol) and 190 cc. of pyridine, cooled to 0°, and a solution of 96 g. (1 equivalent) of benzoyl chloride in 200 cc. of chloroform was then added dropwise with stirring during 5 hours, the internal temperature being kept at 0–5° by continued cooling. The mixture was allowed to stand at room temperature overnight and was then washed successively with water, dilute sulfuric acid sodium bicarbonate solution and water. Drying, evaporation of solvent and distillation of the residue gave 102 g. (64% from XIII) of the monobenzoate XV as a mixture of stereoisomers, b.p. 146–150° (0.2 mm.).

The above monobenzoate (22.5 g.) was dissolved in 45 cc. of glacial acetic acid and a solution of chromium trioxide (14 g.) in 9 cc. of water and 35 cc. of acetic acid was added with stirring and cooling, the temperature not being allowed to rise above 30°. The mixture was set aside at room temperature overnight and then diluted with ether and water. The organic layer was washed with potassium hydroxide solution and water and was then dried and evaporated. The residue (16.2 g.) partially crystallized on being allowed to stand for several days. Trituration with cold hexane gave 8.0 g. (36%) of one isomer of the keto-benzoate XVIIa with m.p. 63–66°, which after repeated crystallization from hexane showed m.p. 69–70°, ν_{max} 1708 cm.$^{-1}$ (superimposed benzoate and saturated ketone).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.33; H, 7.33.

The mother liquors (8.2 g., 37%), which could not be induced to crystallize further, showed an infrared spectrum almost identical with that of the crystalline material and probably consisted of a stereoisomeric mixture of XVIIa.

3-Methylcyclohexanone (XVIII) from 2-Methyl-4-benzoyloxycyclohexanone (XVIIa).—The Wolff–Kishner–Huang-Minlon reduction of 2.5 g. of the crystalline keto-benzoate XVIIa was carried out by means of 2.5 cc. of 100% hydrazine hydrate, 4.5 g. of potassium hydroxide and 25 cc. of diethylene glycol, exactly as described above for the reduction of the keto-benzoate IXa to X. The resulting crude 3-methyl cyclohexanol (1.1 g.), which showed a hydroxyl but no carbonyl bands in the infrared, was dissolved in 5 cc. of acetic acid and a solution of 1.5 g. of chromium trioxide in 2 cc. of water and 8 cc. of acetic acid was added, with cooling. The solution was allowed to stand overnight at room temperature and the product was isolated with ether in the usual way. The resulting crude 3-methylcyclohexanone (XVIII) (0.85 g.) yielded a 2,4-dinitrophenylhydrazone with m.p. 155–157° undepressed on admixture with an authentic sample (m.p. 155–157°) but giving a large depression on admixture with a sample of 2-methylcyclohexanone 2,4-dinitrophenylhydrazone (m.p. 134–135°). Similarly the semicarbazone, m.p. 181–182°, gave no depression on admixture with a sample of 3-methylcyclohexanone semicarbazone (m.p. 181–182°) but did depress the m.p. of 2-methylcyclohexanone semicarbazone (m.p. 191–192°).

9-Methyl-Δ⁴-octal-7ξ-ol-3-one (XIX).—The crystalline keto-benzoate XVIIa (3 g.) was boiled under reflux with 20 cc. of dry methanol containing 0.15 g. of sodium for 15 hours. Water (0.4 cc.) was added, the cooled solution was saturated with carbon dioxide and the methanol was then taken off under reduced pressure. The residue was extracted well with warm ether and the ether extract was washed repeatedly with water. The ether solution, containing methyl benzoate, was discarded and the combined

aqueous extracts were evaporated to dryness under reduced pressure. Distillation of the residue gave 1.2 g. (73%) of 2-methyl-4-hydroxycyclohexanone (XVIIb), b.p. 119–120° (4 mm.). Benzoylation of this material regenerated the keto-benzoate XVIIa as a mixture of isomers which again only crystallized partially.

Sodium (0.12 g.) was dissolved in 6 cc. of dry methanol and this solution was added to a stirred mixture of 0.77 g. of the above hydroxy-ketone XVIIb and 1-diethylaminobutan-3-one methiodide (prepared from 0.95 g. of IV and 0.9 g. of methyl iodide) in 7 cc. of dry benzene, the operation being conducted under nitrogen. The reaction mixture was stirred overnight at room temperature and then for 1.5 hours under reflux. Acetic acid (1 cc.) was added and the product was then isolated with ether in the usual way. The oily product (0.75 g.) was chromatographed on 30 g. of alumina. The fractions eluted with ether–chloroform (1:1) on crystallization from hexane–benzene gave *ca.* 30 mg. of the unsaturated keto-alcohol XIX, m.p. 102–103°, λ_{max} 242 mμ (ϵ 15,100).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H. 8.95. Found: C, 73.05; H, 8.96.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

An Attempted Synthesis of the Pentalene Ring System

BY MARSHALL GATES AND S. PAUL MALCHICK[1]

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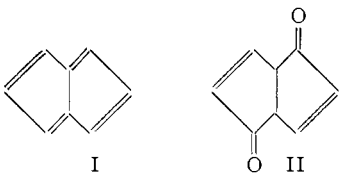
A synthetic approach to the pentalene ring system starting with dicyclopentadiene has been explored. Two isomeric vinyl substituted bicyclo[3.3.0]octadienes have been shown to yield what appears to be azulene on dehydrogenation.

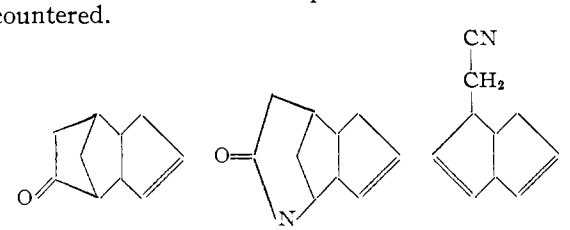
The as-yet-unknown hydrocarbon pentalene[2] (I) is of great theoretical interest and has been the subject of a number of quantum mechanical treatments,[3] the most refined of which[3c] suggests that the hydrocarbon will not have aromatic stability. In agreement with this conclusion is the failure of a number of attempts to produce it by dehydrogenation of either saturated or unsaturated bicyclo-[3.3.0]octane derivatives[4] and the complete failure of the unsaturated diketone II to exhibit enolic properties.[5]



I O II

We wish to record yet another failure to obtain the pentalene system by dehydrogenation together with the additional observation that ethyl- or vinyl-pentalene apppears to be thermodynamically unstable relative to azulene.

The unsaturated *exo*-ketone III, easily available from dicyclopentadiene (*endo*)[6] and containing the bicyclo[3.3.0]octane system pre-formed,[7] served as starting material. Its oxime[6a] on Beckmann rearrangement yields a mixture of the lactam IV and the nitrile V, the latter the result of second-order Beckmann rearrangement, and both of these substances were used in subsequent operations.[8] As shown below, they have the same carbon skeleton, that with a two carbon atom side chain in the 1-position of the bicyclo[3.3.0]octane system. The isomeric substances with two single carbon atom substituents in the 1- and 3-positions were not encountered.



III IV V

The nitrile V, which was characterized by conversion to the corresponding unsaturated and saturated acids, yields the amine VI on reduction with lithium aluminum hydride. Methylation of VI, successively with formaldehyde–formic acid and methyl iodide, yielded the methiodide VIII through the tertiary amine VII. The saturated compounds X and XI were similarly produced from the saturated amine IX obtained by hydrogenation of VI.

Hofmann degradation of the quaternary base corresponding to VIII gave a triply unsaturated hydrocarbon (XII) in insufficient quantity to purify rigorously but which showed infrared maxima at 10.07 and 11.01 μ associated with the vinyl group. Further, the presence of conjugation in the hydrocarbon was clearly shown by its maximum at 238 mμ in the ultraviolet. This conjugation must have been introduced during the degradation inasmuch as the doubly unsaturated amine VII shows no maximum in the ultraviolet.

The unsaturated hydrocarbon XIII produced similarly from XI also exhibits infrared absorption at 10.1 and 11.02 μ attributable to the vinyl group

(1) Celanese Corporation Fellow, 1951–1952.

(2) J. W. Armit and R. Robinson, *J. Chem. Soc.*, **121**, 827 (1922).

(3) (a) C. A. Coulson and G. A. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36**, 193 (1940); (b) D. P. Craig and A. Maccoll, *J. Chem. Soc.*, 964 (1949); (c) D. P. Craig, *ibid.*, 3175 (1951); R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).

(4) (a) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 611 (1936); C. T. Blood and R. P. Linstead, *ibid.*, 2255, 2263 (1952); (b) J. D. Roberts and W. F. Gorham, THIS JOURNAL, **74**, 2278 (1952).

(5) H. J. Dauben, Jr., Victor R. Ben and S. H. K. Chiang, Abstracts of Papers Presented at Los Angeles, Calif., March 15 to March 19, 1953, American Chemical Society.

(6) (a) H. A. Bruson and T. W. Reiner, THIS JOURNAL, **67**, 723 (1945); (b) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

(7) Several other approaches from dicyclopentadiene also appear promising and some have been investigated. The action of performic acid on dicyclopentadiene yields a rearranged glycol of no immediate use; *cf.* M. Gates and S. P. Malchick, *ibid.*, **76**, 1378 (1954).

(8) The double bonds of III and IV and their derivatives have been assigned the position shown on the assumption that the hydration-rearrangement by which the precursor of III is formed from dicyclopentadiene[6b] is favored when the double bond is in the allylic position to that undergoing rearrangement. This assignment is, of course, not rigorous, nor is the assignment of the positions of the double bonds in V.