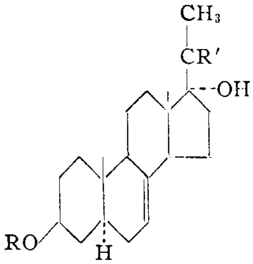
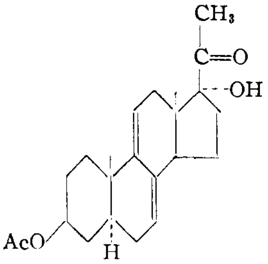
experiments and as an intermediate for some projected syntheses, we have applied Kritchevsky and Gallagher's procedure[3] to Δ^7-allopregnen-3β-ol-20-one[4]; the desired 17α-hydroxy derivative Ia, further characterized by its monoacetate Ib, was isolated without difficulty but in markedly lower yield than recorded earlier,[3,5] for saturated derivatives. Apparently, some reaction occurred with the Δ^7-double bond even though the temperature was kept as low as possible. Dehydrogenation of the acetate Ib with mercuric acetate furnished Δ$^{7,9(11)}$-allopregnadiene-3β,17α-diol-20-one acetate (II), which was required for performic acid oxidation studies[6] as well as for enzymatic oxidations. Lithium aluminum hydride reduction of the diol monoacetate Ib afforded in good yield Δ^7-allopregnene-3β,17α,20-triol (Ic) which has recently[7] been oxidized with periodic acid to Δ^7-androsten-3β-ol-17-one.



Ia, $R = H$; $R_2' = O$
b, $R = Ac$; $R_2' = O$
c, $R = H$; $R_2' = <\!\begin{smallmatrix}H\\OH\end{smallmatrix}$



II

Experimental[8]

Δ^7-Allopregnene-3β,17α-diol-20-one (Ia).—A solution of 7.0 g. of Δ^7-allopregnen-3β-ol-20-one acetate[4] in 40 cc. of acetic anhydride containing 0.35 g. of *p*-toluenesulfonic acid was concentrated to a volume of *ca.* 15 cc. over a period of five hours, poured into ice-water, extracted with ether, washed with sodium bicarbonate solution until neutral, dried and evaporated. A small sample of the resulting oil was crystallized from hexane yielding colorless crystals of **Δ^{7,17}-allopregnadiene-3β,20-diol diacetate** with m.p. 138–140°, $[\alpha]^{20}_D$ +5°, $\lambda^{\text{nujol}}_{\text{max}}$ 1736 cm.$^{-1}$ (acetate band).

Anal. Calcd. for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 75.19; H, 9.37.

The remainder of the material was left in ether solution with 1.2 moles of monoperphthalic acid at 5° for twenty hours whereupon all the peracid had been consumed. After washing with dilute sodium carbonate solution and water, drying and evaporating, there was obtained an oil which was refluxed for 45 minutes with 1.1 g. of sodium hydroxide in 100 cc. of methanol and 20 cc. of water. Dilution with water and two recrystallizations of the resulting precipitate from chloroform–hexane gave 1.36 g. (21%) of **Δ^7-allopregnene-3β,17α-diol-20-one (Ia)** with m.p. 223–225°, $[\alpha]^{20}_D$ −73° $\lambda^{\text{nujol}}_{\text{max}}$ 1704 cm.$^{-1}$ (20-ketone) and free hydroxyl band. Attempts to increase the yield by performing the reaction at room temperature with varying amounts of perphthalic or perbenzoic acid failed.

Anal. Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.53; H, 9.76.

Acetylation in the usual manner (acetic anhydride–pyridine) produced **Δ^7-allopregnene-3β,17α-diol-20-one monoacetate (Ib)** which after recrystallization from methanol showed m.p. 215–217°, $[\alpha]^{20}_D$ −62°.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 74.15; H, 9.21.

Δ^7-Allopregnene-3β,17α,20-triol (Ic).—A solution of 1.55 g. of the monoacetate Ib in 400 cc. of ether was added dropwise to a mixture of 1 g. of lithium aluminum hydride in 100 cc. of the same solvent and then refluxed for 1 hour. After decomposition of the excess reagent with ethyl acetate and washing with dilute hydrochloric acid solution, the dry ether solution was concentrated to incipient crystallization, chilled and the product was collected; yield 1.15 g., m.p. 225–230°. Two recrystallizations from ethyl acetate raised the m.p. to 230–231.5°, $[\alpha]^{20}_D$ −29° (ethanol).

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.09; H, 10.50.

The periodic acid oxidation of this substance to Δ^7-allopregnen-3β-ol-17-one has already been recorded.[7]

Δ$^{7,9(11)}$-Allopregnadiene-3β,17α-diol-20-one Acetate (II).—The mercuric acetate dehydrogenation of Ib was carried out exactly as described earlier for other Δ^7-unsaturated allopregnenes[4,9] and after recrystallization from methanol afforded in 46% yield the diene II with m.p. 196–198°, $[\alpha]^{20}_D$ +7°, $\lambda^{\text{EtOH}}_{\text{max}}$ 234 and 242 mμ, log ε 4.05, 4.11.

Anal. Calcd. for $C_{23}H_{32}O_4$: C, 74.16; H, 8.66. Found: C, 73.89; H, 8.86.

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The Structure of Cycloöctatetraene*

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It has been possible[1] to understand the strain energies of a number of ring molecules by the use of the potential energy functions for related open chain molecules. It is the purpose of this communication to apply the same method to cyclooctatetraene.

There seems to be no doubt but that cyclooctatetraene is a puckered ring with alternating single and double bonds. This is indicated not only by the chemical behavior but also by the infrared and Raman spectra[2] and the majority of the X-ray and electron diffraction investigations.[3] However, two structures have been proposed[2,3] with such a ring, the so-called "tub" and "crown" structures, of symmetry D_{2d} and D_4, respectively.

The tub structure allows each olefinic unit to

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(4) C. Djerassi, J. Romo and G. Rosenkranz, *J. Org. Chem.*, **16**, 754 (1951).

(5) G. Rosenkranz, J. Pataki, St. Kaufmann, J. Berlin and C. Djerassi, THIS JOURNAL, **72**, 4081 (1950).

(6) *Cf.* G. Stork, J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 3546 (1951).

(7) F. Neumann, G. Rosenkranz, J. Romo and C. Djerassi, *ibid.*, **73**, 5487 (1951). Footnote 7 in this paper in referring to the preparation of the triol Ic by mistake gave as reference J. Pataki, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 4055 (1951); the footnote should actually have applied to the present communication.

(8) Melting points are uncorrected. Unless noted otherwise, rotations were measured in chloroform and ultraviolet absorption spectra in 95% ethanol solution. We are grateful to Srta. Paquita Revaque for these measurements and to Srta. Amparo Barba for the microanalyses. Acknowledgment is also due to Srta. Mercedes Velasco for her skillful assistance.

(9) J. Romo, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 5489 (1951).

* This research was supported by The American Petroleum Institute Research Project 44.

(1) K. S. Pitzer, *Science*, **101**, 672 (1945); R. Spitzer and H. M. Huffman, THIS JOURNAL, **69**, 211 (1947).

(2) E. R. Lippincott, R. C. Lord and R. S. McDonald, *ibid.*, **73**, 3370 (1951).

(3) (a) H. S. Kaufman, I. Fankuchen and H. Mark, *Nature*, **161**, 165 (1948); (b) O. Bastiansen and O. Hassel, *Acta Chem. Scand.*, **3**, 209 (1949); (c) K. Hedberg and V. Schomaker, Abstracts for San Francisco Meeting, American Chemical Society, March, 1949.

take a planar configuration, *i.e.*, a doubly bonded pair of carbons and the four atoms singly bonded to them are all in a plane. Thus there is no strain with respect to possible twist in double bonds. The structure is such as to be able to readily adjust to C=C—C angles in the vicinity of 120° so that there is no reason to assume strain from this source. The twist angle about the C–C single bonds is near 90° which presumably prevents any first order conjugation between successive double bonds but does not otherwise cause significant strain. Thus the tub structure is a strain-free configuration.

The heat of formation of cycloöctatetraene measured by Prosen, Johnson and Rossini[4] and converted to the absolute zero with the calculated functions of Lippincott and Lord[5] yields ΔH_f = 76.33 kcal./mole at 0°K. Using the bond energies given recently,[6] and in particular the 81.0 kcal. value appropriate for the C—C single bond in the larger hydrocarbons, one calculates a heat of formation of 86.4 kcal./mole. The difference of 10 kcal./mole can be plausibly ascribed to hyperconjugation in the tub model.

One further check on the tub model is readily made. The lowest totally symmetric vibration at 194 cm.$^{-1}$ is unequivocably identified in the Raman spectrum by its polarization and is far removed from the next higher frequency of the same type at 873 cm.$^{-1}$. Thus a calculation of the lowest totally symmetric bending frequency should offer a significant comparison. The bond distances were assumed constant and the bond angles involving hydrogen were also held constant. The frequency is not sensitive to the exact bond distances or angles—the values used were C–C, 1.51 Å.; C=C, 1.34 Å.; C=C—C angle, 120°; C–H, 1.09 Å.; C=C—H angle, 120°. The potential function for this vibration was assumed to depend almost entirely on the C=C—C angle bending force constant. This constant in other molecules[7] ranges from 0.6 to 1.4 $\times 10^{-11}$ erg./radian^2. The calculated value from the 194 cm.$^{-1}$ frequency is 0.93 $\times 10^{-11}$ erg/radian^2. Similarly in the deuterated cycloöctatetraene the corresponding frequency at 172 cm.$^{-1}$ yields the same potential constant. This potential constant is evidently well within the expected range.

Calculations in the skeletal approximation for all other modes of vibration gave higher frequencies than for this symmetric deformation vibration in agreement with the observed spectrum.

The D_4 or crown model for cycloöctatetraene involves C=C double bonds twisted by about 80°. All normal olefinic compounds involve planar double bonds. Thus there is no precedent for twisted double bonds; indeed one is tempted to say that such bonds would not be double bonds in the ordinary sense. Magee, Shand and Eyring[8] have studied the torsion of double bonds in detail and their results indicate a triplet electronic state to be the most stable in the twisted configuration. On this basis, the crown model would involve four triplet units which would interact in some unknown manner. To be in agreement with the diamagnetism of cycloöctatetraene, this interaction would have to yield a singlet ground state. In view of these considerations it is not possible to make any accurate calculation of the strain energy of the crown structure, but a lower limit of 60 kcal. can be estimated from activation energies for *cis–trans* isomerizations.[8] Also in this structure there would be no reason to expect the typical olefinic C=C stretching frequencies near 1600–1650 cm.$^{-1}$ which are observed very clearly in cycloöctatetraene.

Calculations[9] to the skeletal approximation indicate that for the D_4 model the lowest totally symmetric vibration should be substantially higher than ring deformation vibrations of lower symmetry. This is contrary to the observed Raman spectrum in which the polarized line is at 194 cm.$^{-1}$ and is definitely the lowest of the Raman bands.

In summary, potential energy considerations from related hydrocarbons are in complete agreement with observed facts on the basis of the tub or D_{2d} structure for cycloöctatetraene. The crown or D_4 structure, which has been interpreted as more consistent with certain physical data,[2,3b] is difficult to understand on the basis of the same potential functions and gives the wrong order for the low frequency ring deformation vibrations. Since this manuscript was prepared, Karle[10] has published a further electron diffraction study of cycloöctatetraene and concluded that this molecule has the D_{2d} structure. While the evidence we have presented in this note would not be conclusive, we believe the net balance of all evidence on cyclooctatetraene strongly favors the tub or D_{2d} model.

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[4] E. J. Prosen, W. H. Johnson and F. D. Rossini, THIS JOURNAL, **72**, 626 (1950).

[5] E. R. Lippincott and R. C. Lord, *ibid.*, **73**, 3889 (1951).

[6] K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

[7] J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **38**, 191 (1947); B. Bak, *Kgl. Danske Videnskab. Selskab. Mat-fys Medd.*, **22**, No. 9 (1945); G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., New York, N. Y., 1945, p. 193.

[8] J. L. Magee, W. Shand and H. Eyring, THIS JOURNAL, **63**, 677 (1941); see also R. S. Mulliken, *Phys. Rev.*, **41**, 751 (1932).

[9] Details of this skeletal normal coördinate analysis are presented in the Ph.D. dissertation of Willis B. Person, University of California, 1952.

[10] I. L. Karle, *J. Chem. Phys.*, **20**, 65 (1952).

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Modes of Cleavage of Acylalkylmalonic Esters. Synthesis of *p*-Nitrocaprophenone and *p*-Nitropropiophenone

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The observation of earlier workers[2] that certain crude acyl derivatives of alkylmalonic esters were cleaved by acid at the ketone group to regenerate the carboxylic acid and alkylmalonic ester has been confirmed in the present work with pure acyl derivatives II (X = NO_2, OCH_3 and H). These acyl derivatives, synthesized from the corresponding acid chloride and sodio malonic ester, underwent this mode of cleavage apparently exclusively with dilute sulfuric and acetic acids. For example,

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[1] Carbide and Carbon Chemicals Corp. Fellow, 1950–1952.

[2] *Cf.* R. E. Bowman, *J. Chem. Soc.*, 322 (1950).