The experimental procedure involved the dissolving of suitable amounts of the crystalline solute in 250-ml. portions of water. The initial temperature of this water was generally in the 22-23° region and the subsequent temperature lowerings varied in the different experiments from 1.578° down to 0.236°. The values for the heats of solution thus obtained were then adjusted to the standard temperature of 25° by use of Kirchhoff's law with a suitable estimate for ΔC_p, the difference between the heat capacity of the dissolved and crystalline solute. In making this estimate the specific heat of the dissolved solute was assumed to be the same as that found by Gibson and Giauque[3] for liquid glycerol, while the specific heats for the crystalline alcohols were derived from the measurements of Parks and co-workers.[4]

The samples of polyhydroxy alcohols were C.P. products of the Pfanstiehl Chemical Co. The *d*-mannitol material was recrystallized from distilled water, then dried in an electric oven for two days at 100°, and finally subjected to vacuum desiccation over anhydrous magnesium perchlorate for two weeks. The melting point of the product thus obtained and that of the original sample were both 166.1°. The samples of *i*-erythritol and dulcitol were similarly treated, without recrystallization, to this oven-drying process and vacuum desiccation.

Heats of Solution.—Mannitol samples were dissolved in water in an initial series of eight experiments. The solutions thereby obtained varied from 0.3634 to 0.1140 molal. The experimental results are summarized in Table I, with the observed temperature lowerings in column 3 and the ΔH_{298} of solution values, expressed in calories per gram of solute, in the last column. An estimated maximum error of 0.002° in ΔT here introduces uncertainties of 0.04 to 0.12 cal. in the individual ΔH_{298} results. With due allowance for such uncertainties, the heat of solution of mannitol is evidently independent of the concentration in conformity with the requirements of a perfect solution.

TABLE I

HEATS OF SOLUTION OF *d*-MANNITOL IN WATER AT 25°

Experiment no.	Molality of resulting solution	$-\Delta T$ of solution	ΔH_{298} of solution (cal. per gram)
1	0.3634	1.496	29.59
2	.2960	1.219	29.57
3	.2817	1.153	29.56
4	.2726	1.119	29.53
5	.2531	1.040	29.53
6	.1313	0.550	29.65
7	.1212	0.503	29.62
8	.1140	0.474	29.70
Mean result			29.59 (±0.05)

Similarly, the heats of solution of *i*-erythritol and dulcitol were measured in six and eight experiments, respectively. Again the resulting data showed no change of the heat effect with the concentration of the solution. The molal heats of solution for these three polyhydroxy alcohols are now reported in Table II.

TABLE II

SUMMARY OF HEATS OF SOLUTION IN WATER AT 25°

Substance	Formula	No. of experiments	Mean ΔH_{298} of solution, kcal. per mole
i-Erythritol	$C_4H_6(OH)_4$	6	5.57 (±0.01)
d-Mannitol	$C_6H_8(OH)_6$	8	5.39 (±0.01)
Dulcitol	$C_6H_8(OH)_6$	8	7.09 (±0.04)

For comparison with our present results the literature contains only early values obtained for all three substances by Berthelot[5] and a value obtained for mannitol by Speyer.[6] The Berthelot data, when computed to 25°, differ from ours by +0.4, −3.7 and −8.5%, respectively. Speyer's value is 0.6% lower than our mannitol result.

Discussion

The heats of combustion of crystalline erythritol, mannitol and dulcitol, as well as of liquid ethylene glycol and glycerol, have been measured previously in this Laboratory.[7] These experimental results are here recorded in columns 2 and 3 of Table III.

TABLE III

HEATS OF COMBUSTION, $-\Delta H_c$, FOR FIVE POLYHYDROXY ALCOHOLS (IN KCAL. PER MOLE AT 25°)

Substance	$-\Delta H_c$, experimental Crystals	Liquid	$-\Delta H_c$, calcd. Liquid
Ethylene glycol	....	284.32	284.47
Glycerol	....	395.63	395.34
i-Erythritol	500.18	(505.75)	506.21
d-Mannitol	722.93	(728.32)	727.95
Dulcitol	720.63	(727.72)	727.95

Our present data for the heats of solution can now be combined with such combustion values for the crystalline alcohols so as to yield the heats of combustion for the hypothetical liquid forms at 25°, which are given parenthetically in Col. 3. Thus we have comparable data, with uncertainties of not over 0.07% in any case, for five polyhydroxy alcohols, and from a study of these results we have deduced the empirical general equation to express

$$-\Delta H_c = 62.73 + 110.87n$$

the heat of combustion, in kilocalories, of such compounds as a function of the number of carbon atoms n. The values thereby calculated for the five alcohols are recorded in column 4.

In this connection it should be noted that the experimental data in Table III show a difference of only 0.60 kcal. for the heats of combustion of the isomers, mannitol and dulcitol, in the liquid form, although the values for the respective crystals differ by 2.30 kcal. This situation is striking evidence as to how greatly crystal forces may influence such thermal data, and supports our general conclusion that comparisons in any homologous series should preferably be based on data referring to the liquid state.

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[3] G. E. Gibson and W. F. Giauque, THIS JOURNAL, **45**, 93 (1923).

[4] G. S. Parks and C. T. Anderson, *ibid.*, **48**, 1506 (1926); G. S. Parks and H. M. Huffman, *ibid.*, **48**, 2788 (1926).

[5] M. Berthelot, *Ann. chim. phys.*, [6] **21**, 409 (1890); *ibid.*, [5] **9**, 313 (1876).

[6] C. L. Speyer, THIS JOURNAL, **18**, 146 (1896).

[7] G. S. Parks, T. J. West, B. F. Naylor, P. S. Fujii and L. A. McClaine, *ibid.*, **68**, 2524 (1946).

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Steroids. XXXIII.[1] Δ^7-Allopregnene-3β,17α-diol-20-one and Related Compounds

BY J. PATAKI, G. ROSENKRANZ AND CARL DJERASSI[2]

RECEIVED JANUARY 28, 1952

Kritchevsky and Gallagher's method[3] for the introduction of a 17α-hydroxy group, which involves formation of an enol acetate of a 20-keto steroid followed by treatment with perbenzoic acid, has so far not been applied to a 20-keto steroid which possesses a double bond. Since Δ^7-allopregnene-3β, 17α-diol-20-one (Ia) was required for biological

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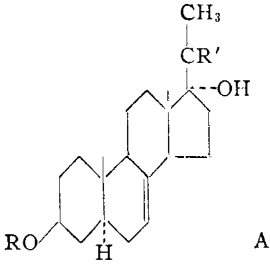
[1] Paper XXXII, C. Djerassi, O. Mancera, M. Velasco, G. Stork and G. Rosenkranz, THIS JOURNAL, **74**, 3321 (1952).

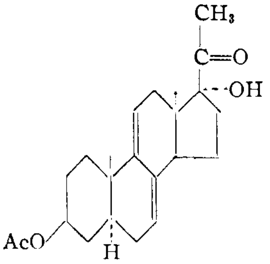
[2] Department of Chemistry, Wayne University, Detroit, Michigan.

[3] T. H. Kritchevsky and T. F. Gallagher, *J. Biol. Chem.*, **179**, 507 (1949); THIS JOURNAL, **73**, 184 (1951).

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 $\Delta^{7,9(11)}$-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' = $\left\langle\begin{matrix}H\\OH\end{matrix}\right.$



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 **$\Delta^{7,17}$-allopregnadiene-3β,20-diol diacetate** with m.p. 138–140°, $[\alpha]^{20}\text{D}$ +5°, $\lambda_{\max}^{\text{nujol}}$ 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°, $[\alpha]^{20}\text{D}$ −73° $\lambda_{\max}^{\text{nujol}}$ 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°, $[\alpha]^{20}\text{D}$ −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°, $[\alpha]^{20}\text{D}$ −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]

$\Delta^{7,9(11)}$-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°, $[\alpha]^{20}\text{D}$ +7°, $\lambda_{\max}^{\text{EtOH}}$ 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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[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.

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The Structure of Cyclooctatetraene*

BY WILLIS B. PERSON, GEORGE C. PIMENTEL AND KENNETH S. PITZER

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

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[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.