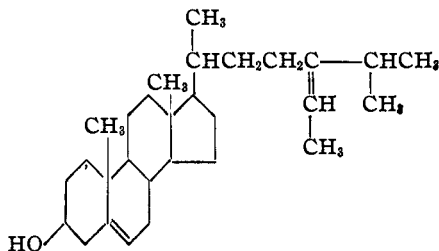


hormones, the complete elucidation of its structure seemed desirable.

It was decided, first of all, to reinvestigate the ozonization reaction. The failure of Heilbron, *et al.*,¹ to isolate ethylisopropylacetaldehyde cannot be considered conclusive evidence for the lack of unsaturation in the side chain, since the later work of this author on zymosterol⁴ has shown that side chain double bonds in sterols may occupy positions other than 22-23. The result of our study showed that fucosterol indeed presents a similar case. In two separate experiments acetaldehyde could be isolated as the *p*-nitrophenylhydrazone from the products of the ozonolysis. The yield of aldehyde was over 30% in both cases, which precludes the possibility that it may have been derived from an impurity or formed in a secondary reaction. Since position 24-28 for the double bond in question is the only one which would account for the formation of acetaldehyde by ozonolysis, it is suggested that the structure of fucosterol is best represented by the accompanying formula.



Experimental

Isolation of Fucosterol.—The material used for this work was obtained from a quantity of *Fucus vesiculosus* gathered along the New Jersey coast. About 22.5 kg. of the dried sea weed was ground and percolated thoroughly with ether. After evaporation of the solvent 650 g. of extracted material remained. The residue was saponified overnight at room temperature and on purification yielded 40 g. (0.18%) of sterol. Several recrystallizations from methanol gave pure fucosterol, the physical properties of which agreed quite closely with those given by Heilbron,¹ as shown in the following table

	MacPhillamy M. p., °C.	[α] _D	Heilbron M. p., °C.	[α] _D
Sterol	124	-41	124	-38.4
Acetate	118	-45	118-119	-43.8
Benzoate	121	-16	120	..

Ozonization of Fucosterol.—A finely divided suspension of 1.15 g. of fucosterol in 12 cc. of glacial acetic acid was ozonized for one-half hour at an ozone concentration of about 2%, the exit gases being led through 50 cc. of water.

(4) B. Heath-Brown, I. M. Heilbron and E. R. H. Jones, *J. Chem. Soc.*, 1482 (1940).

Over-ozonization had to be avoided as it results in low if not negligible yields. The reaction mixture, combined with the wash water, was distilled through an efficient fractionating column. After approximately 20 cc. of distillate had been collected, the receiver was removed, and a solution of 500 mg. of recrystallized *p*-nitrophenylhydrazine in 20 cc. of 50% acetic acid was gradually added. The hydrazone crystallized out immediately. It was filtered, washed with cold water, and after drying weighed 175 mg. (33.6%); m. p. 124-125°. After three recrystallizations from dilute alcohol the substance had a constant m. p. of 128-129°. The melting point of a mixture with authentic acetaldehyde *p*-nitrophenylhydrazone showed no depression.

Anal. Calcd. for C₃H₉N₃O₂: C, 53.63; H, 5.06; N, 23.45. Found: C, 53.58; H, 4.89; N, 23.69.

The author wishes to thank Dr. O. Wintersteiner for his interest and advice during this investigation.

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RECEIVED MAY 20, 1942

Olefin Rearrangements. The Equilibrium of Olefins from Pinacolyl Alcohol¹

BY ROBERT KINSEL SMITH

The dehydration of saturated alcohols and the attendant rearrangement of olefins formed during the reaction have long been investigated experimentally. The mechanisms of these rearrangements have been studied intensively on the basis of experimental results. The absence of thermodynamical data has in general prevented the calculation of equilibrium constants for the ratios of different olefins obtained from a particular dehydration. Recently, thermal data have been published^{2,3} concerning the heats of hydrogenation of 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene and the relative heat contents of 2,2-dimethylbutane and 2,3-dimethylbutane. These provide a basis for the calculation of the equilibrium mixture of these olefins produced in the dehydration of methyl-*t*-butylcarbinol. The equilibrium values for the ratios of the olefins obtained in this reaction are of importance because widely variant results are obtained through the use of different catalysts to effect the dehydration.

Meunier and Whitmore⁴ dehydrated methyl-*t*-butylcarbinol with phosphoric acid on silica gel

- (1) Original manuscript received August 7, 1941.
- (2) (a) Dolliver, Gresham, Kistiakowsky and Vaughan, *THIS JOURNAL*, **59**, 831 (1937); (b) Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 142 (1936).
- (3) Rossini and Prosen, *ibid.*, **62**, 2250 (1940).
- (4) Meunier and Whitmore, *ibid.*, **55**, 3721 (1933).

at 350° and obtained 90% rearrangement. The products formed were 1.5% of *t*-butylethylene (I) which is the normal dehydration product, 34.5% of 2,3-dimethyl-1-butene (II) and 64% of 2,3-dimethyl-2-butene (III). Whitmore, Laughlin and Nash⁵ passed (II) and (III) separately over the same catalyst and found 3% of (I), 31% of (II) and 61% of (III). This indicated that approximate equilibrium had been obtained.

Cramer and Glasebrook⁶ dehydrated methyl-*t*-butylcarbinol over activated alumina at 350°. The results obtained by this procedure were greatly different from those obtained by Whitmore and co-workers with a more acidic catalyst.^{4,5} Cramer and Glasebrook found alumina yielded 64.4% of (I), 27% of (II) and 8.6% of (III). When the more acidic aluminum sulfate was used as a catalyst, the proportions were 3.5% of (I), 34% of (II) and 62.5% of (III). These latter check closely with the results obtained with the phosphoric acid catalyst of Whitmore.^{4,5}

Calculations.—The calculation of the equilibrium constant requires the experimental determination of the heat of reaction and the evaluation of the entropy change of the system.

The heats of hydrogenation and the heat of isomerization of the resulting saturated hydrocarbons as determined by the differences in their heat content provide a simple method for the evaluation of the heats of isomerization of the olefins. The values for the heats of hydrogenation of I, II and III have been found^{2a,b} to be 30.341, 27.997 and 26.633 kcal./mole, respectively, at 355°K. The heat contents of 2,2-dimethylbutane and 2,3-dimethylbutane have been found³ to be -2016 and -4095 cal., respectively, when compared to the heat content of normal hexane. In the subsequent calculations, the heat of isomerization has been assumed to remain essentially constant with change in temperature. This assumption is justified by the knowledge that the difference in the heat content of saturated isomeric hydrocarbons is little changed by temperature over the range involved here.

With these values, the complete calculation of the equilibrium constants is possible if the difference in entropy of the olefins is known. The entropies of (I) and (III) have been determined⁷

(5) Whitmore, Laughlin and Nash, *THIS JOURNAL*, **56**, 1395 (1934).

(6) Cramer and Glasebrook, *ibid.*, **61**, 230 (1939).

(7) Parks, Shomate and Kennedy, *ibid.*, **60**, 1508 (1938).

through calorimetric measurements up to 298° K. The value for (II) was not found and thus estimations must be made to calculate the complete equilibria conditions.

The equation for the translational and rotational entropy of any molecule in the gas phase at a given temperature, *T*, and a pressure, *P*, may be expressed by

$$S = 8/2 R \ln T - R \ln P + 3/2 R \ln M + R/2 \ln ABC - R \ln \sigma + 265.35 \quad (1)$$

The products of the moments of inertia were calculated by the method of Eidinoff and Aston.⁸ The ordinary atomic distances of C-H as 1.09 Å., C-C as 1.54 Å., and C=C as 1.33 Å. were used in the calculations with the angle C-C-C taken as 109°28' and the C=C-C angle as 124°20'.

The entropy due to hindered rotation and internal rotation must be separately determined by Pitzer's method.⁹ The expression which has been developed for the internal rotational entropy is

$$S_{i,r} = R(-0.767 + 1/2 \ln T + 1/2 \ln I_r \times 10^{-40} - \ln n) - (S_i - S) \quad (2)$$

where I_r is the reduced moment of the two rotating groups, *n* is the number of potential minima and ($S_i - S$) is determined by the potential barrier restricting rotation, the temperature, the reduced moment and *n*.

The potential barrier restricting rotation of a methyl group was assumed to be 3200 cal. except in the instances wherein a double bond was adjacent to the methyl group where the hindering potential was taken to be 2000 cal. The rotation of two alkyl groups about each other was assumed to have a potential barrier of 8500 cal. unless one of the carbons in the bond about which rotation was being considered has a double bond in which the potential was assumed to be 7500 cal.

The vibrational entropy involved has not been determined spectroscopically. A self-consistent method of approximating wave lengths was used and the results adjusted so that the final entropy of the compound agreed reasonably well with heat capacity data for the entropy of the gas at the boiling point. The approximations made are listed in Table I with values obtained for different molecular properties.

The entropy change from I to III is then 3.31 e. u. and the heat of isomerization is

$$-30,341 + 4095 - 2,016 + 26,633 = -1,629 \text{ kcal.} \quad (3)$$

(8) Eidinoff and Aston, *J. Chem. Phys.*, **3**, 379 (1935).

(9) Pitzer, *ibid.*, **5**, 46 (1937).

The free energy change is

$$\Delta F = -1629 - 3.31T \quad (4)$$

$$K_{623} = 20.1 \quad (4a)$$

The corresponding changes for II to III are

$$-27.997 + 26.633 = -1.664 \text{ kcal. and } -1.10 \text{ e. u.}$$

$$\Delta F = -1664 + 1.10T \quad (5)$$

$$K_{623} = 1.81 \quad (5a)$$

TABLE I

Assignment Compound.....	No.	Wave no. I		Wave no. II		Wave no. III	
		No.	No.	No.	No.	No.	No.
C—C—C	6	316	8	400	4	400	
C—C=C	2	160	4	180	8	180	
C—C—H	4	640	4	640			
C—C	4	950	4	900	4	900	
At.....		315°K.		345°K.			
<i>S</i> _{vib.}	14.88					21.30	
<i>S</i> _{int. rot.}	5.75					5.60	
<i>S</i> _{rot. trans.}	63.13					61.10	
Total <i>S</i>	83.76					88.00	
Obs. <i>S</i> ^a	83.92					88.00	
<i>C</i> _v (gas) ^{calcd.}	34.7					32.3	
<i>C</i> _v (liq) ^b _{obs.}	41.8					39.2	
At.....		673°K.		673°K.		673°K.	
<i>S</i> _{vib.}	31.59		35.88			37.86	
<i>S</i> _{int. rot.}	4.65		5.18			4.4	
<i>S</i> _{trans.}	68.58		68.22			65.92	
Total <i>S</i>	104.87		109.28			108.18	

^a Observed entropies⁷ extrapolated to boiling point by continuing *C*_v curves from 298°K. and adding 29.6 e. u.

^b According to Kincaid and Eyring, *J. Chem. Phys.*, **6**, 620 (1938) the difference between *C*_v(liq.) and *C*_v(gas) is normally between 6 and 7 cal./mole deg. for complex materials. The differences observed here are 7.1 for I and 6.9 for III, which is quite reasonable. *C*_v(liq.) was found by using the value from entropy data⁷ and subtracting an approximate factor obtained from the Landolt-Börnstein "Tabellen" in the following manner:

$$C_p - C_v = T\alpha^2 V/\beta = 3 \text{ cal./mole deg.}$$

The constant for the same reaction at 350° as calculated from the data of Whitmore and co-workers⁵ was 20.3 for the ratio of III to I and 1.96 for the ratio of III to II. The results of Cramer and Glasebrook⁶ were 18 and 1.81, respectively.

Discussion.—The results obtained by these methods cannot be regarded as final inasmuch as the calculations involving the vibrational entropy are not exact. However, assuming that the internal potential barriers for rotation are those assigned, little change in the relative entropy would be observed when the vibrational frequencies are consistently changed. The agreement of the calculated and observed entropy and the reasonable approximation of the specific heat

of the perfect gas at the boiling point indicate that the assigned vibrations must be of the right order of magnitude.

Changes in the hindering potentials of the various groups by 500 cal. would change the difference in entropy by no more than 0.1 e. u. for I to III and even less for II to III.

The values for the vibrational frequencies were assigned by comparison of the molecules involved with similar olefins reported in Kohlrausch, "Der Smekal-Raman Effekt" and data in Hibben. The frequency assignments were made on the basis of similar work done on methylacetylene.¹⁰

Conclusion.—The rearrangement of these olefins using acidic materials as catalysts has been found to proceed in agreement with estimated thermodynamic values. The comparison of the dehydrations using acidic catalysts and those which do not furnish hydrogen ions indicates that the latter catalysts act merely in the removal of an equivalent of a water molecule with no effect upon the isomerization of the compounds formed. On the other hand, the catalytic action of hydrogen ion in the isomerization of olefins is definitely indicated.

The author wishes to thank Dr. F. C. Whitmore and Dr. J. G. Aston of the Pennsylvania State College and Dr. H. Eyring of this Laboratory for their assistance.

(10) Bryce Crawford, *J. Chem. Phys.*, **7**, 140, 555 (1939).

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RECEIVED MARCH 16, 1942

The Utilization of Aliphatic Nitro Compounds. IV. Nitrodiols (Nitroglycols) Prepared from Simple Aldehydes¹

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In a recent paper³ the authors discussed the condensation of nitroparaffins with aldehydes to form nitroalcohols. In a continuation of this work nitromethane has been condensed with aldehydes to form nitrodiols. Any primary nitroparaffin condenses with formaldehyde to form a nitrodiol,⁴ but only nitromethane condenses with

(1) Presented before the Division of Organic Chemistry at the Memphis meeting of the American Chemical Society, in April, 1942. Abstracted from a thesis presented to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1941.

(2) Present address: Emery Industries, Inc., Cincinnati, Ohio.

(3) Sprang and Degering, *THIS JOURNAL*, **64**, 1063 (1942).

(4) Pauwels, *Rec. trav. chim.*, **17**, 27 (1898).