

benzoate recrystallized from a 50-50 mixture of petroleum ether and benzene; m. p. 118-119°. A mixed m. p. with the tribenzoate of β -phenylglycerol gave a m. p. of 104-106°, showing that the two are different.

Anal. Calcd. for $C_{46}H_{38}O_8$: C, 75.20; H, 5.18. Found: C, 75.52, 75.12; H, 4.99, 5.19.

Hydrolysis of this product gave back the mono-ether of β -phenylglycerol, m. p. 155.5-156°. It is therefore the tetrabenzoate of another mono-ether of β -phenylglycerol and is certainly different from the one obtained in small quantities from the distillate of the main reaction product.

The yield of the β -phenylglycerol amounted to about 12.2% while that of its mono-ethers amounted to about 4.5%. A considerable amount of the cinnamyl alcohol went over to a resin as well as benzaldehyde and glycerinaldehyde, both of which were isolated.

Summary

1. The hydroxylation of certain unsaturated substances with functional groups using hydrogen

peroxide in *t*-butyl alcohol and osmium tetroxide as the catalyst has led to the production of a number of useful glycols.

2. From ethyl crotonate, diethyl maleate, and diethyl fumarate, the corresponding hydroxylated esters were obtained in fairly good yields.

3. From mesityl oxide, 2-methylpentanediol-2,3-one-4 was obtained in about 23% yield.

4. From vinyl acetate, divinyl ether, and vinyl bromide, glycolaldehyde was obtained in yields of 60, 96, and 12.5%, respectively.

5. From oleic acid a yield of 60% of the high melting dihydroxy stearic acid was obtained.

6. From cinnamyl alcohol was obtained β -phenylglycerol and two different new mono ethers of this glycerol. The tetrabenzoates of the ethers were prepared and analyzed.

CAMBRIDGE, MASS.

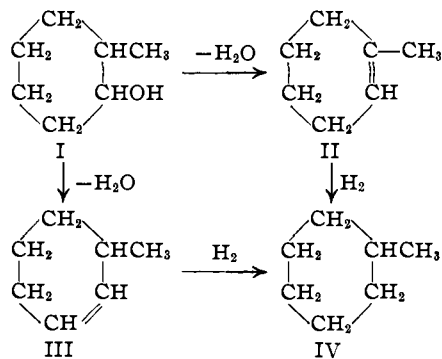
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

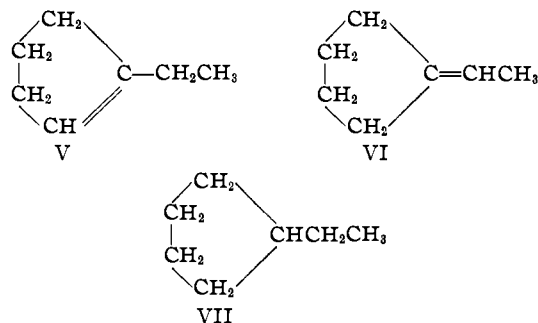
The Dehydration of *trans*-2-Methylcyclohexanol

BY CHARLES C. PRICE

It recently has been reported¹ that the dehydration of 2-methylcyclohexanol with phosphoric anhydride, followed by hydrogenation of the olefin thus obtained, yielded a methylcyclohexane differing in its physical properties from any previously reported. It was suggested that this material was a new isomer, arising from the non-planar nature of the cyclohexane ring. Since the properties reported for the cyclo-olefin and cycloparaffin closely resembled those of 1-ethyl-1-cyclopentene and ethylcyclopentane, respectively, and since ring contraction could conceivably occur during the dehydration, the olefin intermediate in the transformation of the alcohol to the cycloparaffin has been examined carefully.



(1) Vogel, *J. Chem. Soc.*, 1323 (1938).



An examination of Table I reveals the similarity in physical properties of the cycloolefin obtained by Vogel with the cycloolefins III and V, as well as the similarity between his cycloparaffin and VII.

The dehydrations of *trans*-2-methylcyclohexanol carried out in this Laboratory, however, using phosphoric anhydride at temperatures varying from 140 to 230°, always resulted in the formation of a mixture containing only compounds II and III. The mixtures contained 35 to 50% of II; the components could be separated by fractional distillation.

The structures of the cycloolefins were determined by oxidation of the crude mixture with aqueous potassium permanganate. The products isolated were ϵ -ketoheptanoic acid (as its semi-

TABLE I
 PHYSICAL PROPERTIES OF THE VARIOUS HYDROCARBONS

	B. p., °C.	n_D^{20}	d_4^{20}	M^{20}_D (found)	M^{20}_D (calcd.)
1-Methyl-1-cyclohexene (II) ^a	111 -112	1.4496	0.8110	31.85	31.87
3-Methyl-1-cyclohexene (III) ^b	106 -107	1.4423	.799	31.90	
1-Ethyl-1-cyclopentene (V) ^c	106.5-107	1.4426	.8000	31.85	
Cycloolefin (Vogel)	106 -106.5	1.4462	.7938	32.32	32.34
Ethylidenecyclopentane (VI) ^d	114	1.4481	.8020	32.12	
Methylcyclohexane (IV) ^e	100.8	1.4231 (d_{He})	.7694	32.40	
Cycloparaffin (Vogel)	102 -103	1.4231	.7679	32.56	32.34
Ethylcyclopentane (VII) ^e	103 -103.2	1.4201	.7669 (15°)		
Ethylcyclopentane (VII) ^f	100.5-101	1.4184 (d_{He})	.7610	32.55	

^a Wallach, *Ann.*, **359**, 297 (1908). ^b Wallach, *ibid.*, **329**, 371 (1903). ^c Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927). ^d Wallach, *Ann.*, **365**, 274 (1909). ^e Wibaut, *Chem. and Ind.*, 753 (1938). ^f Eisenlohr, *Fortschritte der Chemie, Physik, physikal. Chem.*, **18**, 521 (1925).

carbazon) from II and succinic acid² from III. In spite of careful examination, no oxidation products corresponding to V or VI could be detected. Ring contraction on dehydration must therefore be negligible, if it occurs at all.

It was found that 1-methyl-1-cyclohexene (II) was quite sensitive to exposure to air and moisture, its physical properties changing appreciably in a day or so even when the material was loosely stoppered. Over 10% of high boiling material was isolated from a sample of the pure olefin which had been standing in a glass-stoppered bottle for several months. The boiling point and index of refraction indicated that this material consisted chiefly of methylcyclohexanol and cyclohexylcyclohexene.

Considerable difficulty was encountered in attempting to hydrogenate the olefin mixture using Raney nickel or Adams platinum catalyst, even after repeated distillation.³ Conversion to the saturated compound was readily accomplished, however, after the crude olefin had been distilled with alcohol, with which it forms an azeotropic mixture boiling at 70-72°. Removal of the catalyst poison in this manner yielded material which absorbed hydrogen readily to form methylcyclohexane identical in every respect with an authentic sample prepared from cyclohexanone by treatment with methylmagnesium chloride followed by dehydration and hydrogenation. The pure methylcyclohexane, moreover, showed no change in physical properties, even after standing a month.

Experimental

trans-2-Methylcyclohexanol (I).—The material employed was a commercial grade. It was redistilled and the

(2) The primary oxidation product, α -methyladipic acid, has a tertiary hydrogen atom α to a carboxyl group. Such a structure is not stable toward alkaline potassium permanganate.

(3) Vogel also noted this difficulty in attempting to hydrogenate his cycloolefin.

portion boiling from 164-166°, n_D^{20} 1.5625, was used. The unrecrystallized phenylurethan, prepared by treating the alcohol with phenyl isocyanate, had a melting point of 102-103°, indicating that the starting material must have consisted of more than 95% of the *trans*-isomer.⁴

Dehydration of I.—To 115 g. of the alcohol in a 500-cc. modified Claisen flask was added 60-80 g. of phosphoric anhydride rapidly and the flask immediately stoppered. The mixture boiled vigorously and considerable olefin distilled. After the initial vigorous reaction the mixture was heated gradually to 210-220°; 65-75 g. (68-78%) of olefin was obtained. In other experiments, the reaction mixture was kept cool during the addition of the phosphoric anhydride and then gradually heated. Olefin was evolved continuously at reaction mixture temperatures from 130-250°. The composition of olefin from different experiments and at different temperatures did not vary greatly, consisting of 35 to 50% II, the remainder being III. The percentage of the two constituents was determined by refractive index and density measurements as well as separation of the components by repeated fractional distillation. The purest sample of 3-methyl-1-cyclohexene (III) separated from this mixture by repeated fractional distillation had the following properties: b. p. 106-106.5°; n_D^{20} 1.4426; d_4^{20} 0.7986; M^{20}_D (found) 31.85; M^{20}_D (calcd.) 31.87.

A typical distillation of the crude olefin mixture gave fractions as follows.

B. p., °C.	Cc.	n_D^{20}	d_4^{20}	M^{20}_D
105-108	3.5	1.4448	0.8009	31.87
108-109	2.0	1.4458	.8033	31.85
109-110	3.5	1.4469	.8058	31.84
110-111	2.5	1.4480	.8063	31.86

Oxidation.—Ten grams of olefin mixture (40% II as determined by the index of refraction) was oxidized with 40 g. of potassium permanganate in 250 cc. of water at 0° for twenty-four hours with vigorous mechanical stirring. After filtration and ether extraction, 50 cc. of concentrated hydrochloric acid and 200-300 g. of ammonium sulfate were added. Ten extractions with 10-15 cc. portions of ether followed by evaporation of the ether left 8 g. of water-soluble acids as a yellow oil. On treatment with saturated semicarbazide solution this formed a precipitate of 2.5 g. (60%) of ϵ -ketoheptanoic acid semicarbazone, m.

(4) Vavon, Perlin and Horeau, *Bull. soc. chim.*, [4] **51**, 648 (1932).

p. 142-143.⁵ Extraction of this mother liquor with ether recovered 6 g. of the straw-yellow oil, the major portion of which crystallized. Dried on a clay plate, the crystalline material had the correct melting point (m. p. 183-185°) and neutral equivalent (neut. equiv. 62) for succinic acid.

Hydrogenation.—Five grams of olefin mixture (distilled with alcohol, washed with water to remove the alcohol and then fractionated, 30% II) was dissolved in 25 cc. of alcohol and 2-3 g. of Raney nickel added. Hydrogenation at three atmospheres pressure was complete in three or four hours. The product had the following properties: b. p. 101-101.5°; n_D^{20} 1.4230; d_4^{20} 0.7712; M^{20}_D (found) 32.36; M^{20}_D (calcd.) 32.34.

1-Methyl-1-cyclohexene (II).—This compound was obtained by dehydration of 1-methyl-1-cyclohexanol prepared from cyclohexanone and methylmagnesium chloride. Its properties agreed with those reported in the literature: b. p. 110-110.5°; n_D^{20} 1.4500; d_4^{20} 0.8103; M^{20}_D (found) 31.84; M^{20}_D (calcd.) 31.87.

(5) Wallach, *Ann.*, **329**, 371 (1903).

Oxidation.—Oxidation of 0.7 g. of this olefin (II) with permanganate as above yielded 0.6-0.7 g. (50%) of the semicarbazone of ϵ -ketoheptanoic acid, m. p. 142-143°.

Hydrogenation.—Hydrogen added readily to this olefin (II) using Adams catalyst in alcohol at three atmospheres pressure. The product had the same properties as the methylcyclohexane prepared from III: b. p. 101.5-102°; n_D^{20} 1.4234; d_4^{20} 0.7711; M^{20}_D (found) 32.35; M^{20}_D (calcd.) 32.34.

Summary

The dehydration of *trans*-2-methylcyclohexanol with phosphoric anhydride yielded a mixture of 1-methyl-1-cyclohexene and 3-methyl-1-cyclohexene. The methylcyclohexane obtained by hydrogenation of this olefin mixture was found to be identical in every respect with other authentic samples of this hydrocarbon.

URBANA, ILLINOIS

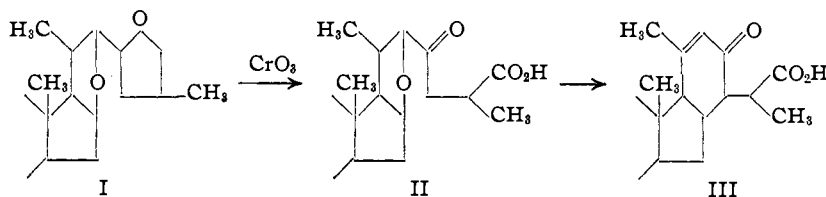
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Sarsasapogenin. IV. Further Observations Concerning Sarsasapogenoic Acid and Related Compounds

BY LOUIS F. FIESER, EDWARD M. FRY¹ AND R. NORMAN JONES²

From the work of Jacobsen in this Laboratory³ it was concluded that anhydrosarsasapogenoic acid has the partial structure III and that its formation from sarsasapogenin by oxidation to sarsasapogenoic acid and treatment of the latter with alcoholic alkali is most plausibly interpreted by regarding these substances as having the structures I and II, first tentatively suggested by Tschesche and Hagedorn.⁴ The structure III for the anhydro compound was based upon the re-



sults of oxidation and reduction experiments and upon spectrographic evidence⁵ of the presence of an α,β -unsaturated carbonyl system. The spectrographic evidence has now been extended by a determination of the ultraviolet absorption spec-

trum of the methyl ester acetate of anhydrosarsasapogenoic acid in absolute alcohol⁵ (curve 1, Fig. 1). This and the other determinations reported were made by one of us (R. N. J.) by a technique which will be described in a future paper (measurements at room temperature, slit width 0.12 mm.). Both the principal and the secondary absorption bands at 243 $m\mu$ ($\log \epsilon = 4.13$) and 303 $m\mu$ ($\log \epsilon = 1.86$) correspond in position and intensity with those characteristic of α,β -unsaturated ketones,⁶ in conformity with formula III. The dibasic acid $C_{27}H_{40}O_7$ ^{3b} resulting from the permanganate oxidation of anhydrosarsasapogenoic acid was regarded as having two carbonyl groups.

The absorption spectrum of the dimethyl ester of this acid (curve 2, Fig. 1) definitely has carbonyl characteristics and lacks the original feature of conjugation, but it is hardly possible from the spectrographic evidence to distinguish between a monoketo and diketo carboxylic acid.

The spectrum of the acetate of sarsasapogenoic acid (curve 2, Fig. 2) is characterized by the ap-

- (1) Du Pont Research Fellow.
- (2) Commonwealth Fund Fellow.
- (3) Fieser and Jacobsen, *THIS JOURNAL*, **60**, (a) 28, (b) 2753, (c) 2761 (1938).
- (4) Tschesche and Hagedorn, *Ber.*, **68**, 1412, 2247 (1935).
- (5) Fieser and Jones, *THIS JOURNAL*, **61**, 532 (1939).

- (6) For example, see Mohler, *Helv. Chim. Acta*, **20**, 289 (1937).