

[CONTRIBUTION NUMBER 1090 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Acid-catalyzed and Thermal Cleavage Reactions of Di-tertiary-1,3-diols¹

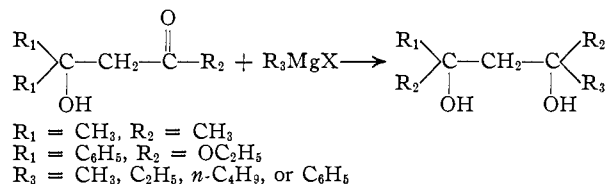
BY JAMES ENGLISH, JR., AND FREDERICK V. BRUTCHER, JR.

RECEIVED JANUARY 17, 1952

A number of di-tertiary-1,3-diols have been prepared and dehydrated under various conditions. In all cases except one in which the diol system was part of a six-membered ring, a cleavage of the molecules into ketones and olefins was observed. In mixed aliphatic-aromatic diols, the products are aliphatic ketones and aromatic olefins. The mechanism of the reaction is discussed.

It was recently observed² in this Laboratory that the dehydration of 1,3-diphenyl-1-cyclohexyl-1,3-butanediol resulted in the cleavage of the molecule, chiefly into phenyl cyclohexyl ketone and α -methylstyrene. This cleavage, together with the well known³⁻⁶ cleavage of hexamethyl-1,3-propanediol^{7,8} into acetone and tetramethylethylene constitute the only well defined evidence we have found in the literature of this interesting behavior of di-tertiary-1,3-diols on dehydration.⁹

In an effort to determine the generality of this cleavage reaction and gain some information bearing on its mechanism, a study of the dehydration of a series of di-tertiary-1,3-diols has been initiated. As a preliminary step a series of diols was synthesized by the action of Grignard reagents on β,β -diphenyl- β -hydroxypropionic ester¹⁰ and on diacetone alcohol.



The diols in all cases (except VI) were found to be solids, easily purified by crystallization, and were dehydrated with potassium hydrogen sulfate at 150–200°, with the results shown in Table I.

The percentage yields are based on pure material isolated from the mixture by distillation or as crystalline derivatives and are minimum values. That the extent of cleavage is somewhat greater is indicated by the hydroxylamine titration¹¹ analyses of cleavage products of compounds II and III (Table I); these show the presence of considerably larger amounts of ketone than could be isolated in pure form.

(1) Taken in part from the dissertation presented by F. V. Brutcher to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) J. English, C. A. Russell and F. V. Brutcher, *THIS JOURNAL*, **72**, 1653 (1950).

(3) R. Criegee, *Ber.*, **68B**, 665 (1935).

(4) A. Barbot, *Bull. soc. chim.*, [5] **2**, 1438 (1935).

(5) F. C. Whitmore and E. E. Stahly, *THIS JOURNAL*, **67**, 2158 (1945).

(6) H. C. Brown and R. S. Fletcher, *ibid.*, **71**, 1845 (1949).

(7) A. Slawjanov, *Chem. Zentr.*, **78**, II, 134 (1907).

(8) A. Kalishev, *J. Russ. Phys. Chem. Soc.*, **46**, 427 (1913).

(9) Many aliphatic tertiary-primary-1,3-diols apparently dehydrate without cleavage to unsaturated alcohols (*cf.* St. Pfau and Plattner, *Helv. Chim. Acta*, **15**, 1250 (1932)). A tertiary-secondary-1,3-diol, 2-methyl-2,4-pentanediol, has been reported to cleave to acetaldehyde and isobutylene in low yield (2% and 4%, respectively) (see S. A. Ballard, R. T. Holm and A. N. Williams, *THIS JOURNAL*, **72**, 5734 (1950), for most recent report).

(10) H. Rupe and E. Busalt, *Ber.*, **40**, 4537 (1907).

(11) A. M. Trozzolo and E. Lieber, *Anal. Chem.*, **22**, 764 (1950).

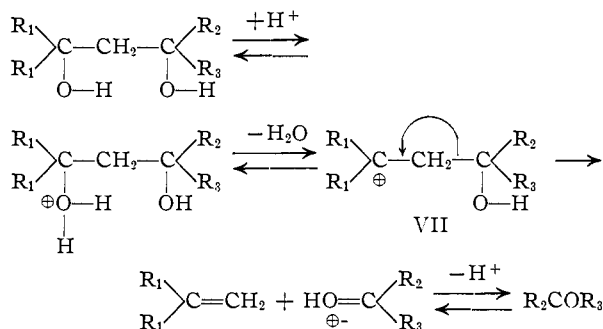
TABLE I¹²

DEHYDRATION OF $\begin{array}{c} \text{R}_1 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_1 \end{array} - \text{CH}_2 - \begin{array}{c} \text{R}_2 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{R}_3 \end{array}$ WITH KHSO₄

	R ₁	R ₂	R ₃	Products	Yield, %
I	C ₆ H ₅	C ₆ H ₅	C ₆ H ₅	(C ₆ H ₅) ₂ C=CH ₂ (C ₆ H ₅) ₂ C=O	56 61-79 (97 ^b)
II	C ₆ H ₅	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	(C ₄ H ₉) ₂ C=O (C ₆ H ₅) ₂ C=O	68 (95 ^a) 5
III	C ₆ H ₅	C ₂ H ₅	C ₂ H ₅	(C ₆ H ₅) ₂ C=CH ₂ (C ₂ H ₅) ₂ C=O (C ₆ H ₅) ₂ C=O	56 66 (86 ^a) 1
IV	C ₆ H ₅	CH ₃	CH ₃	(CH ₃) ₂ C=O	67
V	CH ₃	CH ₃	C ₆ H ₅	(CH ₃) ₂ C=O CH ₃ COC ₆ H ₅	55 3
VI	CH ₃	CH ₃	CH ₃	(CH ₃) ₂ C=O	15 (43 ^b)

^a Determined by hydroxylamine titration of reaction mixture. ^b Dehydration by solution in concentrated H₂SO₄ at room temperature.

It seems most reasonable to assume, in accord with Whitmore's cleavage hypothesis,⁵ that the acid-catalyzed cleavage reaction proceeds by an ionic mechanism under the conditions of Table I as shown below.



In each case, the olefinic product is derived from the (phenyl substituted) carbinol carbon which might be expected to lose its hydroxyl group more readily on acid attack, while the ketonic cleavage product is derived from the other hydroxyl group. This results almost exclusively in the formation of aromatic olefins and aliphatic ketones from these diols.

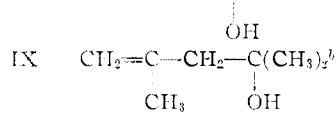
The decomposition of the carbonium ion intermediate, VII, should lead to terminal olefin formation. In agreement with this the previously reported ozonolysis² of the small amount of olefin formed in the dehydration of 1,3-diphenyl-1-cyclohexyl-1,3-butanediol indicated the presence of 90% terminal olefin, α -cyclohexylstyrene.

(12) It is interesting to note that compounds I, III, IV and VI have been previously reported by investigators in the older literature, who reported low boiling dehydration products, but failed to identify them.

The virtually quantitative cleavage of I in concentrated sulfuric acid at room temperature is consistent with the mechanism above as is the observation that even in a dilute alcoholic sulfuric acid solution of 2,4-dinitrophenylhydrazine, III readily gave a precipitate of diethyl ketone-2,4-dinitrophenylhydrazone on gentle warming.

The β -carbonium ion VII has been assumed to cleave directly to an olefin and conjugate acid of a ketone. An alternate path for VII would involve ejection of a proton to yield a α,β - or β,γ -unsaturated alcohol which might subsequently re-add a proton to give VII which in turn would cleave. To test this possibility two representative unsaturated alcohols (VIII and IX, Table II) were prepared and their dehydration products examined.

TABLE II
Unsaturated alcohols
VIII $(C_6H_5)_2C=C(H)-C(OH)(C_6H_5)_2^a$



Unsatd. alcohol	Dehydration products	
	KHSO ₄	Conc. H ₂ SO ₄
VIII	No $(C_6H_5)_2C=O$	No $(C_6H_5)_2C=O$
IX	No CH_3COCH_3	31% CH_3COCH_3

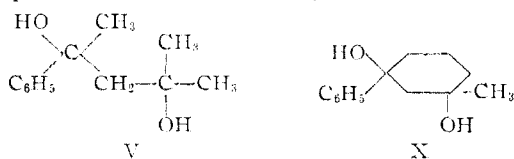
^a W. Schlenk and E. Bergmann, *Ann.*, **463**, 237 (1938).

^b A. Franke and M. Kohn, *Monatsh.*, **28**, 1002 (1907).

VIII yielded no detectable amount of benzophenone on dehydration under the same conditions which effected 61–97% cleavage of the corresponding diol I. Triphenylindene was the only dehydration product isolated from this unsaturated alcohol. On this basis it is concluded that VIII is not an intermediate in the cleavage of the parent diol I.

2,4-Dimethyl-4-pentene-2-ol (IX), a β,γ -unsaturated alcohol, a hypothetical intermediate in the dehydration of the diol VI, was found to yield no acetone under the same conditions which yielded 15% acetone from this diol. In concentrated sulfuric acid at room temperature, this unsaturated alcohol cleaved to form acetone but in lower yield than VI.¹³ It is concluded that IX is not a necessary intermediate in the cleavage of VI even though both undoubtedly undergo fission through the common carbonium ion intermediate $(CH_3)_2^+C-CH_2-C(OH)(CH_3)_2$.

Should the cleavage reaction proceed by way of a concerted *trans* elimination involving migration of an electron pair *trans* to the leaving hydroxyl group, it would be expected that steric factors would alter the course of the reaction. To obtain some information on this point, 1-methyl-3-phenyl-1,3-cyclohexanediol (X) was prepared, dehydrated and compared with an analogous open chain diol V.



(13) The allyl alcohol, $(CH_3)_2C=CH-C(OH)(CH_3)$, has been reported to dehydrate smoothly to dienes (*cf.* von Fellenberg, *Ber.*, **37**, 3578 (1904)) and was not investigated in this work.

The dehydration of X with potassium bisulfate gave rise to no detectable amounts of carbonyl compounds, although V gave 55% of cleavage products under the same conditions. No solid derivatives of carbonyl compounds could be isolated nor could appreciable amounts be detected by hydroxylamine titration. It thus appears that in a cyclic diol the cleavage reaction is suppressed and the normal dehydration process is favored. This finds an explanation based on the proposals of Barton concerning the conformation of the cyclohexane ring.^{14,15}

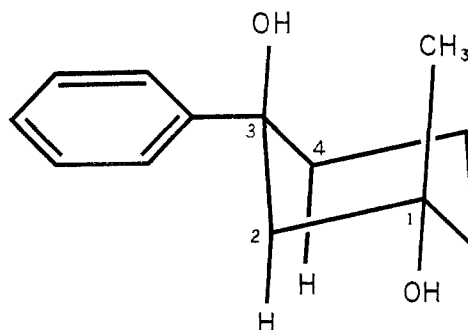


Fig. 1.

According to this hypothesis, the large phenyl group would assume preferentially an equatorial position (Fig. 1) while the hydroxyl group attached to the same carbon (C-3) would be polar. Since carbons 2 and 4 bear polar hydrogen atoms *trans* to the hydroxyl on carbon 3, normal *trans* 1,2-elimination of water is favored. Cleavage is suppressed because the electron pair bonding carbons 1 and 2 can be arranged *trans* to the hydroxyl only by twisting of the molecule from this favored arrangement. It thus appears from a study of molecular models that steric factors would be expected to influence the cleavage reaction of 1,3-diols.

It is recognized that the reaction may be reversible and that the cyclic form X would be heavily favored as observed in the somewhat analogous case of citronellal.¹⁶ The reverse of this cleavage reaction would closely resemble the condensations reported by Prins.¹⁷ Further studies on other types of 1,3-diols are in progress in the hope of gaining more information on this point.

An alternative explanation of the failure of the cyclic diol X to cleave might be the requirement of the formation of some sort of cyclic intermediate involving the two hydroxyls. Of a number of possibilities perhaps the most reasonable one is the proposal of Barbot⁴ that trimethylene oxides are the first products in the dehydration of 1,3-diols. In the case of X the formation of a trimethylene oxide ring would be expected to be more difficult¹⁸ than in open chain analogs.

(14) D. H. R. Barton, *Experientia*, **VI**/8, 316 (1950).

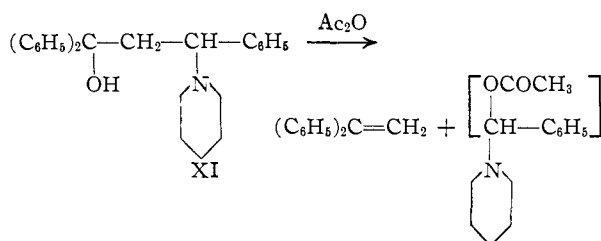
(15) We are indebted to Mr. William Lucey for the execution of the line drawing.

(16) C. C. Price and M. L. Dickman, *Ind. Eng. Chem.*, **40**, 257 (1948).

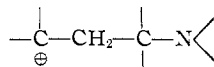
(17) A. Prins, *Chem. Weekblad*, **14**, 627 (1917).

(18) Although trimethylene oxide structures in cyclic systems of this sort have occasionally been postulated (Geissman and Morris, *This Journal*, **66**, 717 (1944); Moubasher, *ibid.*, **73**, 3245 (1951)) no rigorous proof of their existence has been given.

It is of some interest to note that a closely analogous cleavage reaction has recently been reported by Adamson.¹⁹ The cleavage of XI pre-



sumably proceeds through a β -carbonium-ion



in which a nitrogen atom rather than an oxygen atom is attached to the β -carbon.

Several experiments on the thermal pyrolysis of ditertiary-1,3-diols were performed to study their behavior at high temperatures and in the absence of strong acid catalysts. It was found that passage of IV over glass wool at 500° yielded 47% of benzophenone while none of this ketone was obtained in the potassium bisulfate dehydration of the same diol. Similar results were obtained with III which gave 28% of benzophenone as compared to 1% with potassium bisulfate. It is clear that the 1,3-diol system is capable of fission in other ways under thermal conditions, although the mechanism of such a cleavage is undoubtedly complex.

Experimental²⁰

1,1,3,3-Tetraphenyl-1,3-propanediol.—A solution of 60 g. (0.22 mole) of ethyl β -hydroxy- β , β -diphenylpropionate in 300 ml. of dry benzene was slowly dropped with stirring into a solution of 1.5 moles of phenylmagnesium bromide in 300 ml. of dry ether. The addition required two hours and the mixture was allowed to stand seven hours more. The mixture was decomposed with ammonium chloride in the usual way and the product extracted with ether, the extract dried over sodium sulfate, and solvents removed in vacuum. The crude 1,1,3,3-tetraphenyl-1,3-propanediol was recrystallized from ether to give 45.8 g. (55%) of white needles, m.p. 124–125°. ²¹

Anal. Calcd. for $\text{C}_{27}\text{H}_{24}\text{O}_2$: C, 85.3; H, 6.30; active H, 0.53. Found: C, 85.7; H, 6.65; active H, 0.55.

1,1-Diphenyl-3-*n*-butyl-1,3-heptanediol.—This substance was prepared as described above for the tetraphenyl analog using *n*-butylmagnesium bromide. The crude product (85% yield) was washed with petroleum ether and finally recrystallized from a mixture of benzene and petroleum ether (b.p. 30–60°), to yield 43% of the theoretical amount of pure 1,1-diphenyl-3-*n*-butyl-1,3-heptanediol, m.p. 81–82°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{32}\text{O}_2$: C, 81.3; H, 9.40. Found: C, 81.1; H, 9.62.

1,1-Diphenyl-3-ethyl-1,3-pentanediol prepared as above from ethyl- β -hydroxy- β , β -diphenylpropionate and ethylmagnesium bromide crystallized slowly on standing and was recrystallized from petroleum ether (b.p. 80–100°) to a constant m.p. 75.5–76°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{24}\text{O}_2$: C, 80.5; H, 8.45; active hydrogen, 0.70. Found: C, 80.6; H, 8.6; active hydrogen, 0.70.

1,1-Diphenyl-3-methyl-1,3-butanediol was prepared as above except that the reaction mixture was extracted with

benzene after decomposition with ammonium chloride solution. The pure diol²² recrystallized from benzene was obtained in 64% yield, m.p. 116–117°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_2$: C, 79.7; H, 7.82; active hydrogen, 0.78. Found: C, 79.5; H, 7.93; active hydrogen, 0.75.

1,3-Dimethyl-1-phenyl-1,3-butanediol.—To a Grignard reagent prepared from 13.8 g. (0.58 mole) of magnesium and 67.3 g. (0.43 mole) of bromobenzene in 200 ml. of dry ether was added slowly with stirring over a period of one hour 100 ml. of an ether solution containing 16.3 g. (0.14 mole) of freshly distilled diacetone alcohol. The mixture was stirred at room temperature for an additional one-half hour and decomposed as usual with ammonium chloride. On removal of the solvent an oil was obtained which crystallized slowly on seeding; the seed crystals were obtained by a small scale sublimation at 0.001 mm. A total of 5.8 g. of crystals (21.4% of theoretical), m.p. 52–53°, was obtained on recrystallization from petroleum ether (b.p. 60–100°).

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_2$: C, 74.3; H, 9.28; active hydrogen, 1.03. Found: C, 74.2; H, 9.07; active hydrogen, 0.90.

2,4-Dimethyl-2,4-pentanediol.—This substance was prepared according to the method of Lemaire²³ by the action of methylmagnesium iodide on diacetone alcohol. The purified product, b.p. 64° (2 mm.), n_D^{20} 1.4378 was analyzed for active hydrogen.

Anal. Calcd. for $\text{C}_7\text{H}_{16}\text{O}_2$: H, 1.52. Found: H, 1.4.

Dehydration Procedure.—All of the diols in Table I and the unsaturated alcohols in Table II were dehydrated in the following manner. They were mixed with an equal weight of fused potassium bisulfate and heated in a bath at temperatures of 150–180° for periods of 3–4 hours. Longer periods of heating had little effect on the yields of ketonic products and most of the reaction seemed to be completed in less than this time as judged by the evolution of water and volatile products. In these cases in which acetone or diethyl ketone was evolved these substances were allowed to distil from the reaction flask and caught directly in a cooled receiver containing a little alcohol. This solution of the distillate was then treated with 2,4-dinitrophenylhydrazine in 10% alcoholic sulfuric acid and acetone and diethyl ketone identified as their 2,4-dinitrophenylhydrazones which were purified to the literature m.p. and weighed. Mixed melting points were carried out with authentic 2,4-dinitrophenylhydrazones in all cases and no depressions were observed.

The less volatile cleavage products (see Table I), were identified by carrying out the dehydration reaction under reflux, cooling and extracting the residue with ether. After removal of the solvent this extract was distilled and diphenyl ketone and acetophenone identified, and estimated as their 2,4-dinitrophenylhydrazones. Dibutyl ketone was isolated in a similar manner as its semicarbazone. Diphenylethylene was isolated by distillation from the ether extract obtained as above as a liquid, b.p. 276–277°, n_D^{20} 1.6093. These properties agree with those recorded²⁴ in the literature for this hydrocarbon.

TABLE III

CLEAVAGE PRODUCTS FROM NaHSO_4 DEHYDRATIONS

Diol, Sec	Table I g.	Cleavage product, g.	Isolated as ^a	Properties B.p. or m.p., °C.
I	8.6	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}$	2.38	B 276, n_D^{20} 1.6085
		$(\text{C}_6\text{H}_5)_2\text{CO}$	2.45	2,4D M 238
II	2.0	$(\text{C}_6\text{H}_5)_2\text{CO}$	0.57	Semi M 90
		$(\text{C}_6\text{H}_5)_2\text{C}=\text{O}$	0.10	2,4D M 239
III	28.0	$(\text{C}_6\text{H}_5)_2\text{C}=\text{CH}_2$	10.0	B 276, n_D^{20} 1.6083
		$(\text{C}_2\text{H}_5)_2\text{CO}$	5.59	2,4D M 156
		$(\text{C}_6\text{H}_5)_2\text{CO}$	0.13	2,4D M 239
IV	2.5	$(\text{CH}_3)_2\text{CO}$.39	2,4D M 124–125
V	2.0	$(\text{CH}_3)_2\text{CO}$.33	2,4D M 125
		$\text{CH}_3\text{COCH}_2\text{CH}_3$.04	2,4D M 243
VI	2.0	$(\text{CH}_3)_2\text{CO}$.11	2,4D M 125

^a "2,4D" refers to 2,4-dinitrophenylhydrazone. "Semi" refers to semicarbazone. In all cases mixed melting points were carried out with authentic samples and no depressions observed.

(22) M. I. Berberianu (ref. 21) reports this m.p. as 114°.

(23) J. Lemaire. *Chem. Zentr.*, **80**, I, 1982 (1909).

(24) "Beilstein," Vol. 5, p. 308.

(19) D. W. Adamson, *Nature*, **164**, 500 (1949).

(20) All melting and boiling points are corrected.

(21) M. I. Berberianu, *Bul. Soc. romane. stin.*, **22**, 11 (1914). *C. A.*, **8**, 1423 (1914), prepared this compound in a similar manner and reports m.p. 121–123°.

Dehydrations in concentrated sulfuric acid solution were carried out by dissolving the diols (I and VI, Table I) in about 50 times their weight of sulfuric acid at room temperature. After standing (I for 40 hours, VI for 20 minutes) at room temperature the reaction mixtures were poured on ice and the products extracted with ether and benzene. The combined extracts were washed free of acid, evaporated and the ketones isolated from the residues as their 2,4-dinitrophenylhydrazones in the usual manner.

Hydroxylamine Titration.—In two cases, II and III of Table I dehydrations were carried out as described above under reflux. The ether extracts of the cooled reaction mixtures were washed with sodium bicarbonate and water until neutral. Aliquots (50 ml.) of these solutions were treated with 50 ml. of the hydroxylamine reagent of Trozzolo and Lieber.¹² A blank was run on the ether used as solvent in each case. The solutions were warmed gently until the ether was mostly removed and then refluxed vigorously for one hour. At the end of this time they were cooled and titrated with a pH meter to an end-point at pH 3.9. The total amount of mixed ketones present was estimated according to Trozzolo and Lieber's method.

Dehydration of 1,1,3,3-Tetraphenyl-2-propene-1-ol.—This reaction was carried out over potassium bisulfate at 170–190° for five hours. The reaction product was an ether insoluble solid which was dissolved in hot benzene. Treatment of this solution with alcoholic dinitrophenylhydrazine gave no benzophenone derivative. On evaporation and recrystallization from ethanol there was obtained 1.73 g. of slightly yellow triphenylindene, m.p. 135°. Further recrystallization from benzene gave a colorless product m.p. 135° giving a depression of 25° with the starting material. 1,1,3-Triphenylindene has been obtained by rearrangement in acid of tetraphenylallene, the normal dehydration product of 1,1,3,3-tetraphenyl-2-propene-1-ol and reported to melt at 135°.¹⁶ The identity of our reaction product with this substance was further confirmed by its infrared spectrum which showed no bonds corresponding to OH, C=O, or aliphatic C=C groups, and by its analysis.

Anal. Calcd. for C₂₇H₂₆: C, 94.2; H, 5.82. Found: C, 94.0; H, 6.07.

3-Phenyl-3-cyclohexanol-1-one.—To a Grignard reagent from 62.8 g. (0.4 mole) of bromobenzene in 250 ml. of dry ether was added slowly 15 g. (0.13 mole) of dihydroresorcinol²⁶ in 50 ml. of anhydrous tetrahydrofuran. The temperature was kept below 0° and the mixture was stirred 1.5 hours. At this time the mixture became solid and was decomposed with ice and ammonium chloride in the usual way. After separation of the ether layer the aqueous phase was extracted with six 100-ml. portions of ethyl acetate and these extracts combined with the ether and dried over sodium sulfate. On removal of solvents at room temperature there was obtained a yellow oil which when triturated with ether yielded 3-phenyl-3-cyclohexanol-1-one as a white crystalline material, m.p. 154–155°. 1,3-Diphenylcyclohexadiene and 3-phenyl-2-cyclohexene-1-one were isolated from the mother liquors as described by Woods and Tucker, the former as a solid, m.p. 98–99°, and the latter as its bright red 2,4-dinitrophenylhydrazone, m.p. 228–229°. The maximum yield of 3-phenyl-3-cyclohexanol-1-one obtained in a series of 11 runs under different conditions, was obtained under the conditions specified (17%).

¹²⁵ D. Vorlander and C. Siebert, *Ber.*, **39**, 1024 (1906).

¹²⁶ R. B. Thompson, *Org. Syntheses*, **27**, 21 (1947).

¹²⁷ C. F. Woods and I. W. Tucker, *This Journal*, **70**, 2174 (1948).

1-Methyl-3-phenyl-1,3-cyclohexanediol.—This substance was prepared by dropping a slurry of 5 g. (0.026 mole) of 3-phenyl-3-cyclohexanol-1-one in 500 ml. of warm benzene into an ether solution of methylmagnesium iodide, prepared from 18.5 g. (0.13 mole) of methyl iodide in 150 ml. of ether. The addition was carried out over a period of 1.5 hours at 0° during which time considerable foaming was observed. After the addition was complete stirring was continued at 0° for five hours more when the mixture was decomposed in ice and ammonium chloride solution. The aqueous layer was extracted with three 200-ml. portions of ether and the extracts combined, dried and evaporated at room temperature. A sirupy semi-solid mass (4.9 g.) was obtained which was dissolved in warm benzene, treated with Norite, and cooled to yield crystalline 1-methyl-3-phenyl-1,3-cyclohexanediol. This was recrystallized from benzene-petroleum ether (b.p. 30–60°) to give 2.03 g. (38%) of pure diol, m.p. 75°.

Anal. Calcd. for C₁₃H₁₈O₂: C, 75.7; H, 8.70; active hydrogen, 0.97; mol. wt., 206. Found: C, 75.9; H, 9.09; active hydrogen, 0.94, 0.97; mol. wt. (ethyl acetate), 204.

Dehydration of 1-Methyl-3-phenyl-1,3-cyclohexanediol.—A sample (0.48 g.) was heated for six hours at 180–200° with potassium hydrogen sulfate under reflux and the ether extract of the cooled reaction mixture analyzed for carbonyl compounds by the hydroxylamine titration method. Only 2% of the theoretical amount of mixed carbonyl compound was detected by this method. In other runs no solid derivatives could be obtained.

Similarly a sample (0.22 g.) was dissolved in 5 ml. of concd. sulfuric acid, allowed to stand two hours, diluted with ice, extracted with ether, washed with NaHCO₃, and aliquots evaporated and analyzed by the hydroxylamine method; a negligible amount of carbonyl compound was demonstrated in this analysis.

The only product observed in these dehydrations was an unsaturated liquid, presumably a hydrocarbon, boiling at about 145°. Its absorption spectrum showed strong absorption at 243–237 m μ , increasing to 249–250 m μ on further dehydration, indicative of the probable presence of a conjugated system; insufficient material made the positive identification of this substance impossible.

Pyrolysis.—1,1-Diphenyl-3-methyl-1,3-butanediol and 1,1-diphenyl-3-ethyl-1,3-pentanediol were subjected to pyrolysis by passing them through a tube (10 × 130 mm.) loosely packed with glass wool and heated in an oven at 500°. The diols were introduced into the heated zone at a pressure of 0.5–1.0 mm. by tilting the tube and allowing the molten substance or the finely powdered solid to flow gradually from a small flask into the tube. About one hour was required for the pyrolysis. The products were caught in traps cooled with Dry Ice, taken up in ether, dried and distilled. Unchanged diol was recovered from the non-volatile fractions by crystallization from petroleum ether and the ketones were isolated from the distillates as 2,4-dinitrophenylhydrazones.

1,1-Diphenyl-3-methyl-1,3-butanediol (5 g.) gave benzophenone 2,4-dinitrophenylhydrazone, m.p. 238°, in 47% yield (3.0 g.).

1,1-Diphenyl-3-ethyl-1,3-pentanediol (18 g.) gave 28% benzophenone 2,4-dinitrophenylhydrazone (4.0 g.), m.p. 231°, and 36% diethyl ketone 2,4-dinitrophenylhydrazone, (308 g.); m. p. 252–256°, 11.4 g. of starting material was recovered.

NEW HAVEN, CONN.