

TABLE I  
CLEAVAGE OF ISOMERIC 1,3-DIOLS

Cpd.	1,3-propanediol	Precipitation time	Yield, %
(IIa)	$\alpha$ -1-Phenyl-2-methyl-3,3-diethyl	4 min.	17.1
(IIb)	$\beta$ -1-Phenyl-2-methyl-3,3-diethyl	2 min.	32.6
(IIIa)	$\alpha$ -1,1,3-Triphenyl-2-methyl	10 sec.	88.9
(IIIb)	$\beta$ -1,1,3-Triphenyl-2-methyl	75 sec.	65.4

$\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionic Acid (IVa).—To 28.05 g. of potassium hydroxide in 50 ml. of ethanol and 100 ml. of water was added 52.1 g. of ethyl  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionate. The mixture was refluxed for one hour, diluted with water and ether extracted. The aqueous phase was cooled and acidified with 400 ml. of ice cold 20% hydrochloric acid and ether extracted. The ether extracts after drying and concentrating yielded 46.3 g. of an oil which crystallized. Eleven fractional crystallizations from 1:1 benzene-petroleum ether (60–90°) yielded 8.75 g., m.p. 96.5–97.5°, whose melting point was not altered by continued recrystallization. Recrystallization of non-oily material from water yielded the same melting point. From the filtrates could be isolated additional product having this melting point. The reported<sup>3,4,6</sup> melting point for this isomer is 95°.

$\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionic Hydrazide (IVa).—To a solution of 4.0 g.  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionic acid, m.p. 96.5–97.5°, in ether was added an ethereal solution of excess diazomethane. Removal of the ether by distillation left 4.35 g. of colorless oil which crystallized to give solid, m.p. 43–46°. This methyl  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionate was used directly in the reactions with hydrazine hydrate and Grignard reagents.

A mixture of 1 g. of methyl  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionate, 0.75 ml. of hydrazine hydrate (85%) and 1 ml. of ethanol was refluxed on the steam-bath for 30 minutes. On cooling, a solid separated and was filtered and washed with a little ethanol; yield 0.71 g. (71%) of  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionic hydrazide, m.p. 199–200°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>: N, 14.42; C, 61.83; H, 7.27. Found: N, 14.54; C, 61.71; H, 7.50.

**Curtius Rearrangement of  $\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionic Hydrazide (IVa).**—One-half gram of  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionic hydrazide, m.p. 199–200°, was suspended in 5.0 ml. of water and 0.44 ml. of 50% hydrochloric acid added with mechanical stirring to the mixture cooled to 5°. Then 4.0 ml. of ether was added. Finally, a cold solution of 0.20 g. of sodium nitrite in 2.0 ml. of water was added dropwise with stirring over five minutes keeping the temperature at 5°. The ether phase was separated and the aqueous phase ether extracted three times. The ether

phase was diluted with 20 ml. of benzene and dried over sodium sulfate for ten minutes. The ether was removed by distillation and the benzene solution remaining was refluxed on the steam-bath for one-half hour. Removal of the benzene under reduced pressure left an oil which crystallized m.p. 100–110°; 0.35 g. (78% crude). Comparison of the infrared spectrum of the product with the spectra of the two pure isomers of 4-methyl-5-phenyl-2-oxazolidones (m.p. 96° and 146°)<sup>16</sup> showed it to be essentially pure lower melting isomer (96°). Both isomers and the product contained a carbonyl absorption band at 5.67  $\mu$ ; however, the product exhibited a weak band also at 5.95  $\mu$  which may be due to an impurity of unreacted hydrazide. The spectrum of the higher melting isomer (146°) contained absorption bands at 7.43 and 9.99  $\mu$ . These were lacking in the spectrum of the Curtius product and that of the pure lower melting isomer (96°). An absorption band at 9.82  $\mu$  was present only in the spectrum of the product and that of the lower melting isomer. Otherwise, except for some smaller differences, the three spectra were identical.

The Curtius product was saponified on the steam-bath with 5 ml. of 20% aqueous sodium hydroxide. At the end of 70 minutes, the mixture was made definitely acid with 20% hydrochloric acid and ether extracted and then made basic with 20% sodium hydroxide solution and benzene extracted and dried over sodium sulfate. The ether extracts yielded only a very small amount of non-crystalline material. Concentration of the benzene extracts left 0.16 g. of solid, m.p. 71–75°. One recrystallization from ether-petroleum ether (30–60°) brought the melting point of the *dl*-nor- $\psi$ -ephedrine to 76.8–77.5°; further recrystallization did not change this.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>NO: N, 9.26. Found: N, 9.13.

Fifty mg. of the *dl*-nor- $\psi$ -ephedrine was dissolved in 5 ml. of dry ether and anhydrous hydrogen chloride gas was passed into the solution to give a white precipitate weighing 48 mg., m.p. 172–173°. The melting point was not altered by recrystallization from ethanol.

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>NOCl: N, 7.46; Cl, 18.89; C, 57.60; H, 7.52. Found: N, 7.66; Cl, 19.05; C, 57.45; H, 7.62.

**Reaction of Methyl  $\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylpropionate (Va) with Ethylmagnesium Bromide and Phenylmagnesium Bromide.**—These reactions were run exactly as described above for the corresponding ethyl ester Ia,b except on a much smaller scale. From the reaction with ethylmagnesium bromide only the  $\alpha$ -isomer of 1-phenyl-2-methyl-3-ethyl-1,3-pentanediol, m.p. 138°, was isolated while from the reaction with phenylmagnesium bromide only the  $\alpha$ -isomer of 1,1,3-triphenyl-2-ethyl-1,3-propanediol, m.p. 131°, was obtained. The yields were 37 and 31%, respectively.

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[CONTRIBUTION NUMBER 1171 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

## The Cleavage Reaction of 1,3-Diols. III. The Synthesis of a Pair of Diastereomeric Ditertiary 1,3-Diols and an Effect of Configuration on Mode of Cleavage<sup>1</sup>

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The diastereomeric 2-phenyl-3-methyl-4-ethyl-2,4-hexanediols have been synthesized by several approaches, including one which is stereospecific. The results of the acid-catalyzed cleavage reaction of these compounds are explicable on the basis of the mechanism proposed in this paper.

The ease with which the cleavage reaction of 1,3-diols<sup>2–5</sup> proceeds to give olefins and ketones or

(1) Taken from the dissertation presented by H. E. Zimmerman to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. We are indebted to the E. I. du Pont de Nemours Company for a fellowship in support of this work.

(2) F. Brucher and J. English, Jr., *THIS JOURNAL*, **74**, 4279 (1952).

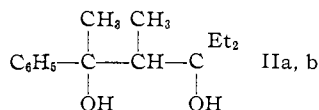
(3) H. E. Zimmerman and J. English, Jr., *ibid.*, **75**, 2367 (1953).

(4) *Ibid.*, **76**, 2285 (1954).

(5) *Ibid.*, **76**, 2291 (1954).

aldehydes has been shown<sup>5</sup> in the case of the diastereomeric 1,1,3-triphenyl-2-methyl-1,3-propanediols to depend on the configuration of the 1,3-diol. The present paper deals with a somewhat more striking case of differing behavior of diastereomers in the cleavage reaction, that is, with the isomeric 2-phenyl-3-methyl-4-ethyl-2,4-hexanediols (IIa, b).

For the preparation of these compounds (IIa, b) three different synthetic approaches were used.



The first began with the Reformatsky reaction of acetophenone and ethyl  $\alpha$ -bromopropionate to yield ethyl  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyrate<sup>6</sup> (Ia, b). Treatment of this product with excess ethylmagnesium bromide gave a mixture of the two diastereomers of 2-phenyl-3-methyl-4-ethyl-2,4-hexanediol (IIa, b). By crystallization from ethanol the major product,  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol (IIa), m.p. 121°, was obtained. By slow crystallization from benzene of the lower melting solid fraction obtained from the filtrates of the major product and manual separation of the crystals a small amount of  $\beta$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol (IIb), m.p. 117°, was obtained. The non-identity of the two materials was shown by a large (over 15°) mixed melting point depression. The infrared spectra of IIa and IIb were in general very similar; nevertheless, in the 8–12  $\mu$  region there were differences.

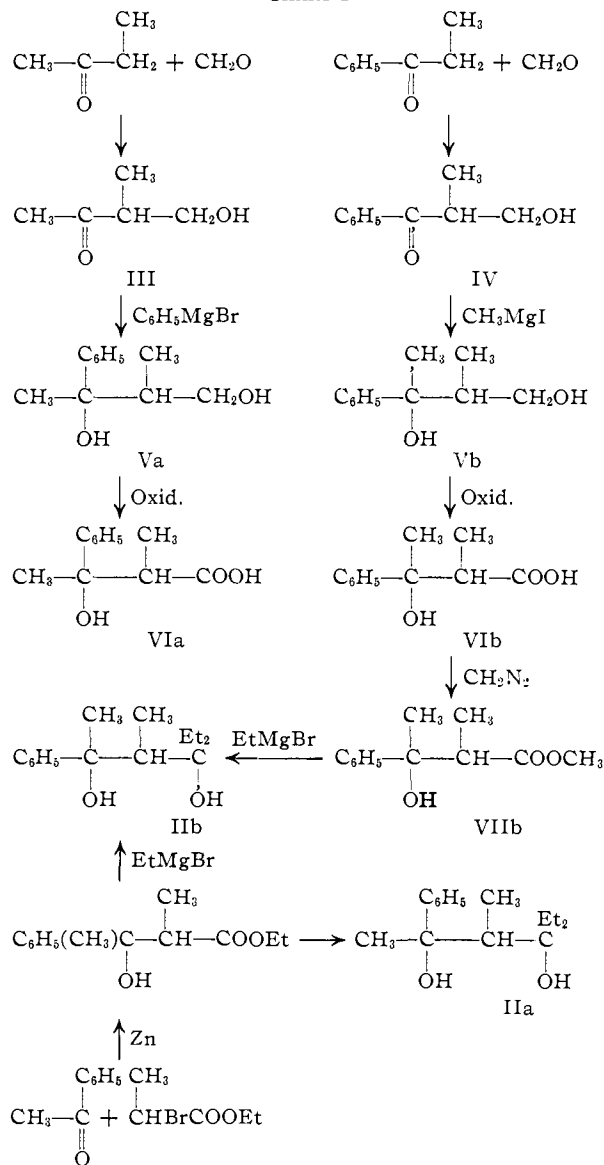
Although the Reformatsky approach had yielded both isomers of the desired 1,3-diol, it was nevertheless of interest to try a stereospecific synthesis making use of Tiffeneau's rule,<sup>7–13</sup> which was first formulated by Tiffeneau and co-workers<sup>7–10</sup> in an extensive series of papers and which may be stated as follows: The reaction of a ketone (or aldehyde)  $\text{A}-\text{CO}-\text{R}'$ , where A is a group containing an asymmetric center, with the Grignard reagent  $\text{R}''\text{MgX}$  yields predominantly one of the two possible diastereomeric alcohols, while the reaction of the ketone  $\text{A}-\text{CO}-\text{R}''$  with the Grignard reagent  $\text{R}'\text{MgX}$  produces the other. The application of this rule has been mainly to the reactions of carbonyl compounds carrying either no second functional group or an alpha hydroxyl, amino or methoxyl group. The present synthesis applies this principle to a case where the ketone contains a beta hydroxyl group.

The ketones needed were 4-hydroxy-3-methyl-2-butanone (III) and 3-hydroxy-1-phenyl-2-methyl-1-propanone (IV). The first compound III was prepared without much difficulty by the aldol condensation of formaldehyde with methyl ethyl ketone using a modification of the method of Morgan and Holmes.<sup>14</sup> The second compound IV has been prepared by Fuson and co-workers<sup>15</sup> by the reaction of propiophenone with paraformaldehyde in methanol with potassium carbonate as a catalyst. We were unable to isolate any of the desired product under these conditions. Since it had been

found by Long and Troutman in syntheses in the chloromycetin series<sup>16</sup> that the conditions of Fuson gave poor yields of monocondensation products of formaldehyde with amidoacetophenones, which might be expected to be similar in reactivity to propiophenone, the procedure of Long and Troutman, which employs a sodium bicarbonate catalyst, was used to give IV in reasonable yield.

According to Tiffeneau's rule the reactions of III with phenylmagnesium bromide and of IV with methylmagnesium iodide should yield  $\alpha$ - and  $\beta$ -isomers<sup>17</sup> of 2-methyl-3-phenyl-1,3-butane-diol (Va, b), respectively. These reactions were carried out to give Va, m.p. 69°, and Vb, an oil, b.p. 111–112° at 0.16–0.18 mm. The infrared spectra of these compounds were very similar, but

CHART I



(6) "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 17.

(7) M. Tiffeneau and J. Levy, *Compt. rend.*, **178**, 1724 (1924).

(8) M. Tiffeneau and J. Levy, *Bull. soc. chim.*, **41**, 1351 (1927).

(9) A. McKenzie, E. Luis, M. Tiffeneau and P. Weill, *ibid.*, **45**, 414 (1929).

(10) M. Tiffeneau, J. Levy and E. Ditz, *ibid.*, **2**, 1848 (1935).

(11) R. Roger, *J. Chem. Soc.*, 108 (1939).

(12) D. Curtin, E. Harris and E. Meislich, *THIS JOURNAL*, **74**, 2901 (1952).

(13) D. Cram and F. Abd Elhafez, *ibid.*, **74**, 5828 (1952).

(14) G. Morgan and E. Holmes, *J. Chem. Soc.*, 2667 (1932).

(15) R. Fuson, W. Ross and C. McKeever, *THIS JOURNAL*, **60**, 2935 (1938).

(16) L. Long and H. Troutman, *ibid.*, **71**, 2471 (1949).

(17) The  $\alpha$  and  $\beta$  nomenclature for Va, b is adjusted to fit Tiffeneau's convention, in which the diastereomer obtained from the more bulky Grignard reagent is designated  $\alpha$  and also to agree with the nomenclature used for the  $\alpha$ - and  $\beta$ -isomers of II.

they showed definite shifts in certain maxima. All efforts to induce the  $\beta$ -isomer to crystallize were fruitless. Without doubt, it contained some  $\alpha$ -isomer, for it is unlikely that the Grignard reaction was completely stereospecific; the results of the next step indicate however that any such contamination was minor.

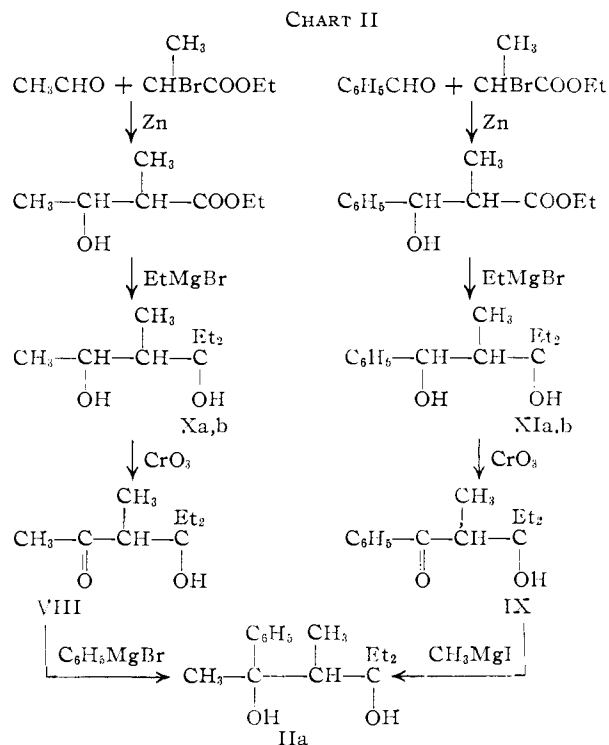
Both  $\alpha$ - and  $\beta$ -2-methyl-3-phenyl-1,3-butanediol (Va and Vb) were successfully oxidized in suspension by dilute aqueous potassium permanganate to the corresponding diastereoisomeric  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric acids (VIa and b), respectively. The oxidation of Va gave  $\alpha$ - $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric acid (VIa) m.p. 67°. This is apparently the same compound reported by Spasov and Kurtev.<sup>18</sup> The oxidation of Vb gave  $\beta$ , $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric acid (VIb), m.p. 122°. The infrared spectra of these isomers differ appreciably. That Vb (an oil) was essentially homogeneous was indicated by comparison of the infrared spectrum of the crude oxidation product from Vb (ca. 80% yield), which had been purified only to the extent of removing non-acidic material, with the spectrum of the recrystallized oxidation product (VIb); no differences could be detected.

In order to relate the configurations of these acids (VIa and b) to those of the isomeric 2-phenyl-3-methyl-4-ethyl-2,4-hexanediols (IIa and b) one of the acids (VIb) was treated with diazomethane to give  $\beta$ -methyl  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyrate (VIIb), m.p. 53°. Reaction of VIIb with excess ethylmagnesium bromide yielded  $\beta$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol, m.p. 117°, which had already been obtained as the minor product in the Reformatsky approach, thus showing that the  $\beta$ -1,3-diol obtained in the Reformatsky approach is indeed configurationally related to the  $\beta$ -compounds of the Tiffeneau approach.

In view of the success of Tiffeneau's rule, it was of interest to obtain the  $\alpha$ - and  $\beta$ -isomers of 2-phenyl-3-methyl-4-ethyl-2,4-hexanediol (IIa and b) by another reaction sequence which would employ the same reaction principle. This would involve the reaction of phenylmagnesium bromide with 4-hydroxy-3-methyl-4-ethyl-2-hexanone (VIII) to give one isomer and that of methylmagnesium iodide with 3-hydroxy-1-phenyl-2-methyl-3-ethyl-1-pentanone (IX) to give the other. The former is formally derived from the aldolization of methyl ethyl ketone with diethyl ketone and the latter from propiophenone and diethyl ketone. Actually, the preparation of these compounds by the aldol condensation seemed quite unlikely and a general method for synthesis of  $\beta$ -hydroxyketones of this type was desirable. The oxidation of the corresponding secondary-tertiary 1,3-diols (X and XI) with chromic anhydride was considered a reasonable possibility. As a test of the method 1,1,3-triphenyl-1,3-propanediol<sup>4,19</sup> (XII) was oxidized in good yield to the known<sup>20</sup>  $\beta$ -hydroxy- $\beta$ , $\beta$ -diphenylpropiophenone (XIII) with one equivalent of chromic anhydride in acetic acid at room temperature. The method was then applied to the 1,3-

diols, X and XI. The former was obtained from the reaction of ethylmagnesium bromide with ethyl  $\beta$ -hydroxy- $\alpha$ -methylbutyrate<sup>21</sup> while the preparation of the latter has been described in an earlier paper.<sup>5</sup> Although both X and XI may exist in two diastereoisomeric forms, no attempt was made to separate isomers before oxidation, since the second center of asymmetry is destroyed in the reaction.

Unexpectedly the reactions of VIII with phenylmagnesium bromide and of IX with methylmagnesium iodide did not yield different isomers of II as would be predicted by Tiffeneau's rule. Instead,  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol (IIa) was obtained from both reactions. The identity of the products with the  $\alpha$ -isomer was shown by mixed melting point determinations and infrared comparisons.



The cleavage reaction of the very similar but non-diastereoisomeric 2-phenyl-4-methyl-2,4-pentane-diol has already been reported<sup>2</sup> to give a 55% yield of acetone. The course of this reaction is in accord with a previous generalization<sup>4</sup> that the major cleavage product arises by fission of the carbon-oxygen bond of the more highly-substituted (especially by aromatic groups) carbinol group. Hence it was anticipated that (IIa and IIb) would yield diethyl ketone; analogy with the 1,1,3-, triphenyl-2-methyl-1,3-propanediols<sup>5</sup> suggested, however, the likelihood of a difference in ease of formation of this product.

Under the usual conditions<sup>4,5</sup> there was isolated directly from the reaction medium in the cleavage of the  $\beta$ -isomer (IIb) a 75% yield of the expected dinitrophenylhydrazone of diethyl ketone in a practically pure state. The increased yield over that

(18) A. Spasov and B. Kurtev, *C. A.*, **44**, 3439 (1950).

(19) A. McKenzie and G. Martin, *J. Chem. Soc.*, **112** (1913).

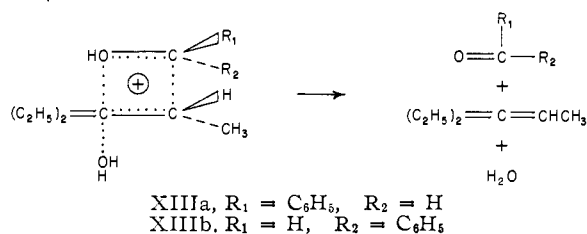
(20) D. Vorländer, J. Osterburg and O. Meyer, *Ber.*, **56**, 1136 (1923).

(21) E. Blaise and I. Herman, *Ann. chim.*, **20**, 187 (1910).

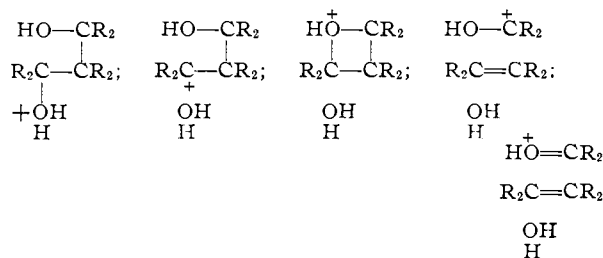
of the analogous case mentioned above may be partially due to a difference in dehydration conditions. Under the same conditions the  $\alpha$ -isomer (IIa) gave an impure dinitrophenylhydrazine that was found on purification to be the acetophenone derivative (17% yield). Since this was indicative only of the minimum amount of cleavage and since no diethyl ketone 2,4-dinitrophenylhydrazone could be isolated, the reaction was run on a larger scale with no 2,4-dinitrophenylhydrazine present to give 5% of diethyl ketone, 35% of acetophenone and 46% of a product which appears to be an allyl ether. In the runs made in the presence of 2,4-dinitrophenylhydrazine the  $\alpha$ -isomer required 30 seconds for precipitation of the derivative to begin while the  $\beta$ -isomer required only 5 seconds. That this difference in precipitation time was not due to different rates of derivative formation of diethyl ketone and acetophenone was showed by addition to a similar hot solution of 2,4-dinitrophenylhydrazine of small samples of each ketonic product; in each case the precipitation of the derivative was instantaneous.

The most striking aspect of the cleavage of these two isomers (IIa and b) is the different course taken by the cleavage reaction of the two diastereomeric 1,3-diols. Also of interest is the difference in time required for the beginning of derivative precipitation. This difference is not due to a difference in solubilities of the two derivatives, for the acetophenone 2,4-dinitrophenylhydrazone is less soluble than the diethyl ketone derivative and would be expected to precipitate at a lower concentration; the much more rapid precipitation of diethyl ketone 2,4-dinitrophenylhydrazone must then be attributed to a greater rate of ketone formation.

The observations in this and the preceding papers on the effect of structure and configuration on the cleavage reaction are all in accord with a mechanism involving a four-membered cyclic transition state as previously suggested.<sup>1,22</sup> The geometry of such a transition state rationalizes the increased tendency of  $\alpha$ -1,1,3-triphenyl-2-methyl-1,3-propanediol of proven configuration<sup>5</sup> to undergo cleavage to benzaldehyde as compared to the  $\beta$ -isomer

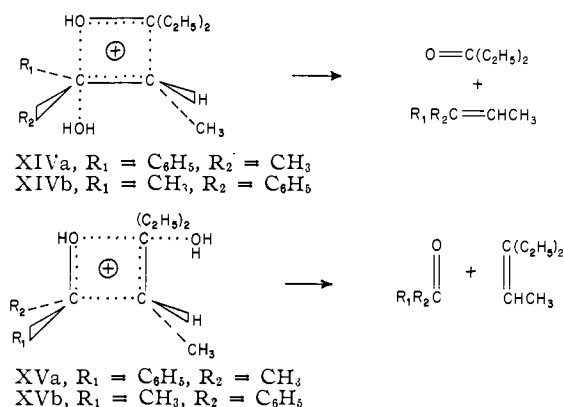


(22) Contributors to this transition state would be



The transition state in case of the  $\alpha$ -isomer (XIIIa) is sterically more favored since the phenyl group is *trans* to the methyl group while in the  $\beta$  case (XIIIb) these groups bear a *cis* relationship. The observed increased rate and higher yield in the cleavage of the  $\alpha$ -form may be interpreted on this basis.

The differing behavior of the isomeric 2-phenyl-3-methyl-4-ethyl-2,4-hexanediols (IIa, b) may be similarly explained. In this case since two products, diethyl ketone and acetophenone, are observed, two transition states must be considered for each isomer (XIVa, XVa for one isomer (A) and XIVb, XVb for the other (B)).



A consideration of these isomeric transition states leads to the prediction that one isomer, B (from which XIVb and XVb are derived), would be expected to yield predominantly diethyl ketone, since this transition state XIVb is more favored sterically than the alternative XVb; the other isomer A would similarly be expected to yield acetophenone as the main product. The experimental observation that IIb forms chiefly diethyl ketone and IIa, acetophenone suggests a tentative assignment of configuration B to IIb and A to IIa.<sup>23</sup> It is hoped that an independent establishment of the configurations of IIa and IIb will add more convincing evidence for, or against, these views.

### Experimental

**4-Hydroxy-3-methyl-2-butanone.** Modified Procedure of Morgan and Holmes.<sup>14</sup>—To a liter three-neck flask equipped with Hershberg stirrer and thermometer was added 267 ml. (3 moles) of 2-butanone and 200 ml. (2.46 moles) of 37% aqueous formaldehyde. The reaction was begun by adjusting the pH to 9 by addition of 2.5 ml. of 2 N sodium hydroxide solution. The temperature was kept at 30°; cooling in ice was necessary, since the reaction was somewhat exothermic. More base was added as necessary to keep the pH of the solution between 8 and 9 (3 additional ml. of 2 N base was added). At the end of four hours the odor of formaldehyde had disappeared, and the reaction was allowed to stand at room temperature overnight. The reaction mixture was then made slightly acid by addition of acetic acid and the entire mixture was subjected to vacuum distillation at room temperature and water-pump vacuum with a Dry Ice-cooled receiver until only 191 g. remained and little more material was distilling. The residue was

(23) Superimposed on the steric factors in XIV and XV there would be expected an electrical effect favoring the formation of diethyl ketone. This seems less important here than in the 1,1,3-triphenyl-2-methyl-1,3-propanediol (XIII) case although the ratio of diethyl ketone to acetophenone in the cleavage of IIb compared to the acetophenone to diethyl ketone ratio in IIa might suggest the operation of such an effect.

then distilled at 15 mm. to give 62.5 g., b.p. (80—) 86–87° and much higher boiling residue. The former was redistilled to give three fractions: I, 76.5–77.0° at 8.5 mm.,  $n_{20}^{25}$  1.4299, 7.16 g.; II, 77.0° at 8.5 mm.,  $n_{20}^{25}$  1.4309, 35.23 g.; and III, 77.0° at 8.5 mm.,  $n_{20}^{25}$  1.4310, 11.75 g. (reported<sup>24</sup>  $n$  1.4320). Fractions II and III were pure 4-hydroxy-3-methyl-2-butanone.

**$\alpha$ -2-Methyl-3-phenyl-1,3-butanediol.**—To 0.60 mole of phenylmagnesium bromide in 225 ml. of ether in a liter three-neck flask equipped with Hershberg stirrer, reflux condenser and dropping funnel was added 36 g. (0.2 mole) of 4-hydroxy-3-methyl-2-butanone in 50 ml. of ether with stirring and cooling in ice. The addition required two hours, and at the end of this time the reaction gave a positive Gilman test for excess Grignard. The reaction mixture was allowed to warm to room temperature and stirred for an additional half-hour. The reaction mixture was then poured onto ice and saturated ammonium chloride solution. The ether extracts were dried over sodium sulfate and then concentrated by distillation on the steam-bath. The residue was distilled to give 4.20 g., b.p. 105–108° at 0.08–0.09 mm. (bath temp. 147–150°); 9.35 g., b.p. 107.5–108° at 0.085 mm. (bath temp. 147–156°); and 7.49 g., b.p. 108° at 0.085 mm. (bath temp. 151–159°). The total weight was 21.04 g. All three fractions crystallized when treated with seed obtained by cooling a benzene-petroleum ether solution in Dry Ice. The first fraction was somewhat oily; the second and third fractions crystallized completely and melted at 54–59°. Recrystallization of fraction I from benzene-petroleum ether (30–60°) gave 2.74 g. of solid, m.p. 60–64° which on further recrystallization melted at 68–69°. Recrystallization of fractions II and III gave 10.60 g., m.p. 60–66°. Further recrystallization brought the melting point to 68–69°; this was pure  $\alpha$ -2-methyl-3-phenyl-1,3-butanediol. The oily filtrates crystallized slowly to yield more of the same isomer and no other solid material could be isolated. Infrared analysis showed the presence of hydroxyl absorption band (2.79 and 3.00  $\mu$ ) and the absence of carbonyl bands.

*Anal.* Calcd. for  $C_{11}H_{16}O_2$ : C, 73.30; H, 8.95. Found: C, 73.59; H, 8.88.

**3-Hydroxy-1-phenyl-2-methyl-1-propanone.**—To a 300-ml. three-neck flask fitted with thermometer, Hershberg stirrer, reflux condenser and Glas-col heater was added 40.2 g. (0.3 mole) of propiophenone, 18 g. (0.06 mole) of para-formaldehyde, 200 ml. of methanol and 0.80 g. of sodium bicarbonate. Stirring at 50° was continued for 24 hours. The reaction mixture was then poured into 500 ml. of water, acidified with 1 ml. of acetic acid and extracted with benzene. The combined benzene extracts were washed with water and dried over sodium sulfate. The benzene was removed by distillation on the steam-bath under water-pump vacuum. The residue was distilled to give 14.90 g. of impure propiophenone, b.p. 63–72° at 2 mm. and 20.05 g. (65.4% based on unrecovered propiophenone) of 3-hydroxy-1-phenyl-2-methyl-1-propanone, b.p. 116–117° at 1.5–2.0 mm. (bath temp. 155–161°). This preparation was run several times and the yield was essentially constant, except that on a larger scale the yields were slightly lower. Infrared analysis of the product indicated the presence of hydroxyl and carbonyl functions (at 2.90 and 5.98  $\mu$ , respectively).

Under the conditions of Fuson<sup>15</sup> no product was isolated. The present experimental is an adaptation from that used<sup>16</sup> in the chloramphenicol series for the condensation of formaldehyde with amidoacetophenones.

**$\beta$ -2-Methyl-3-phenyl-1,3-butanediol.**—To 0.34 mole of methylmagnesium iodide in 120 ml. of ether (formed from iodine-free methyl iodide) in a 300-ml. three-neck flask fitted with reflux condenser, Hershberg stirrer and dropping funnel was added 14 g. (0.0843 mole) of 3-hydroxy-1-phenyl-2-methyl-1-propanone (twice redistilled) in 80 ml. of dry ether with stirring and cooling in ice. The addition was made during 100 minutes. The reaction mixture, which gave a positive Gilman test at this point, was then allowed to warm to room temperature and stir for an additional 45 minutes. During this time a crystalline complex separated. The reaction mixture was decomposed on ice and saturated aqueous ammonium chloride. After drying over sodium sulfate, the ether solution was concentrated by distillation on

the steam-bath under atmospheric pressure. The residue was distilled to give 3.4 g., b.p. 111–112° at 0.16 mm. and 5.0 g., b.p. 112° at 0.175 mm. (bath temps. 159–200°). The total yield of  $\beta$ -2-methyl-3-phenyl-1,3-butanediol was 8.4 g. The infrared spectrum was almost identical with that of  $\alpha$ -2-methyl-3-phenyl-1,3-butanediol except for minor shifts in maxima; for example, the tertiary C–O stretching vibration was at 9.03  $\mu$  for the  $\alpha$ -isomer and at 9.10 for the  $\beta$ . Seeding the  $\beta$ -isomer with the  $\alpha$ -isomer did not cause crystallization. The  $\beta$ -isomer could not be induced to crystallize at all.

*Anal.* Calcd. for  $C_{11}H_{16}O_2$ : C, 73.30; H, 8.95. Found: C, 73.10; H, 8.67.

**$\alpha,\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric Acid.**<sup>18</sup>—To a liter flask equipped with a Hershberg stirrer were added 4.6 g. (0.029 mole) of potassium permanganate, 2.3 g. of anhydrous sodium carbonate, 460 ml. of distilled water and 2.0 g. (0.011 mole) of finely powdered  $\alpha$ -2-methyl-3-phenyl-1,3-butanediol. Stirring was begun and continued at room temperature for 21 hours. The reaction mixture was then treated with sodium bisulfite until a clear colorless solution was obtained. The solution was made distinctly basic by addition of a small amount of 10% sodium hydroxide and then ether extracted to remove non-acidic material. The aqueous phase was acidified and ether extracted. The ether extract was dried over sodium sulfate and the ether removed on the steam-bath under water-pump vacuum to leave 1.59 g. of colorless oil which crystallized when seeded with a small amount of solid product. (The oil obtained in the first run crystallized only after weeks of standing.) The  $\alpha,\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric acid which had thus crystallized was recrystallized from benzene-petroleum ether (30–60°) to give a m.p. of 65–67°. The infrared spectrum of the recrystallized product showed hydroxyl and carbonyl absorption bands and was identical with that of the oil obtained after removal of the ether. The product is apparently the compound reported by Spasov and Kurtev,<sup>18</sup> who did not state the method of preparation. They reported<sup>18</sup> m.p. 65–67°.

*Anal.* Calcd. for  $C_{11}H_{14}O_3$ : C, 68.02; H, 7.24. Found: C, 67.76; H, 7.37.

**$\beta,\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric Acid.**—To a liter flask equipped with a Hershberg stirrer was added 2.3 g. (0.0146 mole) of potassium permanganate, 1.15 g. of anhydrous sodium carbonate and 230 ml. of distilled water. One gram of  $\beta$ -2-methyl-3-phenyl-1,3-butanediol (an oil) was mixed thoroughly with 20 g. of washed and pyrolyzed beach sand; this having been done, the beach sand was only slightly moistened by the oil. This was then added to the reaction flask and stirring begun. Stirring of the mixture kept the sand nicely dispersed. The reaction was allowed to proceed at room temperature for 28 hours. Enough sodium bisulfite was added to decolorize the reaction mixture and the mixture was made definitely basic by addition of a small amount of 10% sodium hydroxide. The sand was filtered off and the filtrate was ether extracted to remove non-acidic material. The aqueous solution was then acidified with concentrated hydrochloric acid and the cloudy solution ether extracted. The ether extract was dried over sodium sulfate and then concentrated by distillation of the ether under reduced pressure at room temperature. An oil remained which weighed 0.85 g. and quickly crystallized. One recrystallization from ether-petroleum ether (30–60°) gave a melting point of 93–97°. Further recrystallization brought the melting point to 121.5–122.0°. The infrared spectrum of this pure sample of  $\beta,\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric acid was identical with that obtained with the unrecrystallized material obtained by removal of the ether from the ether extracts. No other isomer could be isolated.

*Anal.* Calcd. for  $C_{11}H_{14}O_3$ : C, 68.02; H, 7.27. Found: C, 68.24; H, 7.49.

Infrared spectra of	Maxima, $\mu$
Pure $\alpha$ -acid	7.22, 7.23, . . . , 9.14, 9.39, 10.07
Pure $\beta$ -acid	7.27, . . . , 8.90, . . . , 9.36, 9.97
Crude oxidation product, m.p. 93–97°	7.25, . . . , 8.90, . . . , 9.36, 9.98

**$\beta$ -Methyl  $\beta$ -Hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyrate.**—To 1.95 g. of  $\beta,\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyric acid in 50

(24) G. Morgan, N. Megson and K. Pepper, *Chemistry and Industry*, 887 (1938).

ml. of ether was added an ethereal solution of distilled diazomethane (prepared from 7.36 g. of N-methyl-N-nitroso-N'-nitroguanidine by reaction with KOH) with swirling until the yellow color persisted and no more nitrogen was evolved. The solution was allowed to stand open in the hood until colorless. The ether solution was then dried over sodium sulfate and finally concentrated in vacuum to leave 1.98 g. of crystalline  $\beta$ -methyl- $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyrate, m.p. 50–53°. Recrystallization from petroleum ether (30–60°) brought the melting point to 52–53°. The entire product was utilized in a later experiment.

**$\alpha$ - and  $\beta$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—To 1.84 moles of ethylmagnesium bromide in 670 ml. of ether in a 2-liter three-neck flask fitted with reflux condenser, Hershberg stirrer and dropping funnel was added dropwise with stirring and cooling in ice 81.6 g. (0.37 mole) of ethyl  $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyrate prepared according to "Organic Reactions"<sup>6</sup> in 75 ml. of dry ether. The addition was made during 75 minutes. The reaction mixture was then allowed to warm to room temperature and stir for an additional half hour. The mixture was cooled again in ice and a saturated solution of ammonium chloride was added dropwise with cooling in ice and stirring until precipitation of a magnesium salt had begun. The reaction mixture was then poured into a saturated ammonium chloride solution containing ice. The ether extracts were dried over sodium sulfate and the ether removed on the steam-bath under water-pump vacuum. The residue (about 85 ml.) was subjected to vacuum distillation in a wide side-arm Claisen flask to give five fractions: I, 10.47 g., b.p. 44–81° at 0.65–1.30 mm.; II, 5.55 g., b.p. 88–105° at 0.44–0.58 mm.; III, 18.27 g., b.p. 109–121° at 0.40–0.45 mm.; IV, 40.57 g., b.p. 127–130° at 0.22–0.32 mm.; and V, 2.23 g. solid scraped from side-arm and column of distilling flask, m.p. 109–116° (no m.p. depression with pure  $\alpha$ -isomer). Fractions I and II did not crystallize when seeded with either isomer. Fraction III crystallized only partially to yield 0.84 g. of impure  $\alpha$ -isomer, m.p. 110–117° (mixed melting point). Fraction IV crystallized essentially completely giving a melting point of 99–111° (no depression with  $\alpha$ -isomer). The solid fractions combined weighed 43.64 g. This was dissolved in 50 ml. of hot 95% ethanol and allowed to cool slowly to room temperature, whereupon 20.04 g. of  $\alpha$ -isomer, m.p. 116–120°, separated. The filtrate on being cooled in the refrigerator yielded 6.96 g., m.p. 108–115°, which on recrystallization from ethanol yielded 4.94 g., m.p. 116–120°. One recrystallization of the 116–120° melting material yielded pure  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol, m.p. 120–121°. The filtrates tended to oil; they were therefore concentrated in vacuum and dissolved in ether-petroleum ether (30–60°). Crystallization from this solvent mixture yielded a first crop of solid, m.p. 96–108°. This on recrystallization from ethanol yielded more pure  $\alpha$ -isomer. A total of 25.34 g. of pure  $\alpha$ -2-phenyl-3-methyl-4-ethyl-1,3-hexanediol obtained by the above procedure and recrystallization to constant melting point. The ether-petroleum ether filtrate yielded several small crops of impure  $\alpha$ -isomer leaving a filtrate which yielded material melting 93–108°. This was dissolved in benzene containing approximately half its volume of ether and allowed to stand in an open erlenmeyer flask on the desk-top. Two types of crystals could be discerned; the  $\alpha$ -isomer crystallized out in flat plates which were sometimes long enough to be considered rods. The  $\beta$ -isomer crystallized out in huge 14-sided crystals which had a hexagonal cross-section. By manually separating out the  $\beta$ -isomer and repeating the process 0.91 g. of pure  $\beta$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol, m.p. 116–117°, was obtained. The infrared spectra of the two isomers were very similar; however, they did exhibit significant differences. The  $\beta$ -isomer showed a mixed m.p. depression with the  $\alpha$ -isomer.

*Anal.* Calcd. for  $C_{15}H_{24}O_2$ : C, 76.22; H, 10.24. Found for  $\alpha$ -isomer: C, 76.01; H, 10.18. Found for  $\beta$ -isomer: C, 76.00; H, 10.20.

**$\beta$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—Repetition of the above experiment on a smaller scale using 1.90 g. of pure  $\beta$ -methyl- $\beta$ -hydroxy- $\alpha$ -methyl- $\beta$ -phenylbutyrate yielded 1.68 g. of solid and oil after removal of the ether. Filtration gave 0.41 g. of solid, m.p. 96–110°. One recrystallization from aqueous ethanol yielded 0.32 g., m.p. 115–117°, which showed no depression when melted with the  $\beta$ -isomer obtained from the previous experiment. Mixed

with  $\alpha$ -2-phenyl-3-methyl-4-hexanediol it gave a melting point of 93–97°. Further recrystallization brought the melting point to 116–117° (0.24 g. plus 0.06 g., m.p. 114.5–116.0°). All the filtrates were combined and chromatographed on alumina on a 1.5 × 22 cm. column using 4% methanol in benzene throughout. In addition to a non-crystallizing oily fraction 0.14 g. of  $\beta$ -isomer was recovered. From this experiment only the  $\beta$ -isomer of 2-phenyl-3-methyl-4-ethyl-2,4-hexanediol was isolated.

**$\beta$ -Hydroxy- $\beta$ , $\beta$ -diphenylpropiophenone.**<sup>20</sup>—To three grams (0.01 mole) of 1,1,3-triphenyl-1,3-propanediol (not completely dissolved) in 100 ml. of acetic acid was added a solution of 0.67 g. (0.0067 mole) of chromic anhydride in 50 ml. of acetic acid containing 1 ml. of water. The mixture darkened immediately. The reaction mixture was allowed to stand at room temperature for seven hours; at the end of this time the solution was green and no further change in color was occurring. The reaction mixture was placed in a distilling flask equipped with capillary, dropping funnel and Dry Ice cooled receiver. The acetic acid was then removed by distillation under oil-pump vacuum at or below room temperature. The distilling flask was kept near room temperature by heating with a beaker of warm water. The acetic acid solution was added continuously from the dropping funnel until the entire reaction mixture had been concentrated to a dry solid. This was then treated with 300 ml. of water and ether extracted. The ether extracts were dried over sodium sulfate and the ether removed *in vacuo* leaving 3.10 g. of solid smelling of acetic acid. Recrystallization from aqueous ethanol yielded a first crop of plates, m.p. 118–119.5°. A second recrystallization brought the melting point of the  $\beta$ -hydroxy- $\beta$ , $\beta$ -diphenylpropiophenone to 119–120° (reported<sup>20</sup> by Vorländer and co-workers, who used another approach to this compound, was 119°).

**3-Hydroxy-1-phenyl-2-methyl-3-ethyl-1-pentanone.**—To a solution of 3.70 g. (0.0166 mole) of a mixture of diastereomers of 1-phenyl-2-methyl-3-ethyl-1,3-pentanediol<sup>8</sup> dissolved in 160 ml. of glacial acetic acid was added a solution of 1.10 g. (0.011 mole) of chromic anhydride dissolved in 80 ml. of glacial acetic acid containing 1.6 ml. of water. The dark solution was kept at room temperature for 3.5 hours during which time the solution gradually turned greenish blue. The acetic acid was removed at room temperature under oil-pump vacuum as described previously. The residue was treated with 300 ml. of water and ether extracted. The ether extracts were dried over sodium sulfate and then concentrated *in vacuo*. The residual oil was distilled from a small flask fitted with a capillary to give 1.98 g. of 3-hydroxy-1-phenyl-2-methyl-3-ethyl-1-pentanone boiling at 125–131° (bath temperature) at 0.025–0.040 mm. Infrared analysis substantiated the structural assignment, showing hydroxyl and carbonyl bands of comparable intensities. The product would not form a crystalline phenylhydrazone or a semicarbazone.

*Anal.* Calcd. for  $C_{14}H_{20}O_2$ : C, 76.32; H, 9.15. Found: C, 75.56; H, 8.73.

**$\alpha$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—To 0.06 mole of methylmagnesium iodide (prepared from iodine free methyl iodide) in 22 ml. of ether in a 100-ml. three-neck flask equipped with reflux condenser, stirrer and dropping funnel was added 1.37 g. (0.006 mole) of 3-hydroxy-1-phenyl-2-methyl-3-ethyl-1-pentanone dissolved in 10 ml. of dry ether. The addition was made dropwise during 1.5 hours with stirring and cooling in ice. The reaction mixture was then allowed to warm to room temperature and stirred for an additional half-hour. The mixture was poured onto ice and ammonium chloride solution and ether extracted. The ether extracts were dried over sodium sulfate and concentrated *in vacuo*. The residual oil was seeded with  $\beta$ -isomer. The thick oil crystallized slowly to give 0.97 g. of slightly oily solid. Recrystallization from aqueous ethanol yielded 0.45 g. of  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol, m.p. 115–116° (mixed m.p. with  $\alpha$  was 116.5–117.0°, mixed m.p. with  $\beta$  was 93–95°). Infrared analysis indicated that the product was indeed the  $\alpha$ -isomer of 2-phenyl-3-methyl-4-ethyl-2,4-hexanediol.

**3-Methyl-4-ethyl-2,4-hexanediol.**—To 1.0 mole of ethylmagnesium bromide in 375 ml. of ether in a liter three-neck flask equipped with Hershberg stirrer, dropping funnel and reflux condenser was added dropwise with stirring and cooling in ice 30.21 g. (0.21 mole) of ethyl  $\beta$ -hydroxy- $\alpha$ -methylbutyrate<sup>21</sup> dissolved in 100 ml. of dry ether. The addition re-

quired two hours; the mixture was then allowed to warm to room temperature and stirred for an additional half-hour. The reaction mixture was poured onto ice and saturated ammonium chloride solution and ether extracted. The ether extracts were dried over sodium sulfate and then concentrated. The residue (about 30 ml.) was distilled to give 19.39 g. (59%) of 3-methyl-4-ethyl-2,4-hexanediol, b.p. 98–101° at 2.0 mm. Infrared analysis showed strong hydroxyl absorption and an impurity of a carbonyl compound.

**4-Hydroxy-3-methyl-4-ethyl-2-hexanone.**—To a solution of 3.2 g. (0.02 mole) of 3-methyl-4-ethyl-2,4-hexanediol in 200 ml. of glacial acetic acid was added a solution of 1.33 g. ( $0.02 \times 0.67 = 0.013$  mole) of chromic anhydride in 100 ml. of glacial acetic acid containing 2 ml. of water. The mixture was allowed to stand at room temperature for 12 hours by which time the color had turned green. The acetic acid was then removed under oil-pump vacuum at room temperature as previously described. The residue was treated with 100 ml. of water and ether extracted. The ether extracts were dried over sodium sulfate and then concentrated *in vacuo*. The residue was then distilled to give 1.70 g. of 4-hydroxy-3-methyl-4-ethyl-2-hexanone, b.p. (bath temp.) 80–85° at 2 mm. The infrared spectrum was consistent with the structural assignment, showing hydroxyl and carbonyl absorption bands (2.90 and 5.89  $\mu$ , respectively). The product formed a semicarbazone, m.p. 152–153°, by reaction with an aqueous-alcoholic solution of semicarbazide hydrochloride and sodium acetate.

*Anal.* Calcd. for  $C_{10}H_{21}O_2$ : C, 55.79; H, 9.83; N, 19.52. Found: C, 55.54; H, 9.36; N, 19.69.

**$\alpha$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—To 0.06 mole of phenylmagnesium bromide in 22 ml. of ether in a 100-ml. three-neck flask equipped with reflux condenser, stirrer and dropping funnel was added dropwise with stirring 1.58 g. (0.01 mole) of 4-hydroxy-3-methyl-4-ethyl-2-hexanone in 10 ml. of dry ether. The addition was made with cooling in ice and required 40 minutes. The reaction mixture was then allowed to warm to room temperature and was stirred for an additional 105 minutes. The mixture was worked-up by pouring onto ice and saturated ammonium chloride solution and ether extracting. The ether extracts were dried over sodium sulfate and concentrated *in vacuo*; a residue of 2.43 g. of oily solid remained. The solid was filtered free of oil and weighed 1.20 g., m.p. 112–117°. Recrystallization from aqueous ethanol yielded a first crop of 1.04 g. of pure  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol, m.p. 118–119° (mixed m.p. with  $\alpha$ -isomer was 118.5–120.0°; mixed m.p. with  $\beta$ -isomer was 94–107°. The filtrates yielded 0.10 g. more of less pure  $\alpha$ -isomer, m.p. 113–115°; mixed m.p. with authentic  $\alpha$ -isomer was 116–118°. The original oily filtrate was distilled to a bath temperature of 115° at 0.3 mm. and the residue yielded 0.1 g. of solid when diluted with petroleum ether (30–60°); this had a melting point of 114–117° after one recrystallization and did not depress the melting point of pure  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol. No  $\beta$ -isomer could be isolated in this experiment.

**Dehydration of  $\alpha$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—To a hot mixture of 10 ml. of 95% ethanol, 1 ml. of concentrated sulfuric acid and 0.418 g. (0.0021 mole) of 2,4-dinitrophenylhydrazine was added 0.5 g. (0.0021 mole) of finely powdered  $\alpha$ -2-phenyl-3-methyl-4-ethyl-2,4-hexanediol. The mixture was kept at the boiling point for five minutes.

At the end of the first 30 seconds, measured from the moment of addition of the diol, the separation of an orange solid began. The mixture was allowed to cool and was filtered to give 0.37 g. of orange solid which on recrystallization from benzene (or instead extraction with hot ethanol) gave 0.11 g. (17.4% minimum yield) of acetophenone 2,4-dinitrophenylhydrazone, m.p. 240–241°. A mixed melting point with an authentic sample was not depressed and an infrared comparison with an authentic sample showed no differences. This experiment was run several times with essentially the same results.

**Dehydration of  $\beta$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—This was run exactly as in the preceding experiment except that the  $\beta$ -isomer of 2-phenyl-3-methyl-4-ethyl-2,4-hexanediol was used. In this case the precipitation of the orange derivative began in five seconds. The filtered derivative weighed 0.42 g. (74.7% cleavage) and was essentially pure diethyl ketone 2,4-dinitrophenylhydrazone, m.p. 152.5–154.5°. Recrystallization from aqueous ethanol brought the melting point to 153–154.5°. Mixed melting point determination and infrared comparison confirmed the structural assignment.

**Larger Scale Dehydration of  $\alpha$ -2-Phenyl-3-methyl-4-ethyl-2,4-hexanediol.**—To a mixture of 100 ml. of 95% ethanol and 10 ml. of concentrated sulfuric acid in a 250-ml. ground glass erlenmeyer flask fitted with a reflux condenser was added 23.6 g. (0.1 mole) of  $\alpha$ -2-phenyl-3-methyl-4-ethyl-1,3-hexanediol. The mixture was refluxed on the steam-bath for ten minutes and then cooled in ice and neutralized to phenolphthalein pink with 10% sodium hydroxide. Three hundred ml. of water was added and the entire mixture ether extracted. The ether extracts were dried over sodium sulfate. The benzene was slowly distilled off at atmospheric pressure to a vapor temperature of 80°. The residue was distilled in a small Podbielniak column to give: I, 0.47 g., b.p. 84–87.5°, smelling like diethyl ketone; II, 0.08 g., b.p. 65–81° at 58 mm.; III, 3.76 g., b.p. 94–104° at 3½ mm.; IV, 2.51 g., b.p. 103–117° at 34 mm.; and V, 8.52 g., b.p. 125–147° at 34 mm. Fractions I and II were added to 1.0 g. of 2,4-dinitrophenylhydrazine in 20 ml. of ethanol containing 2 ml. of concentrated sulfuric acid to give 1.3 g. of orange solid, m.p. 149–152° (5% cleavage to minor prod.) which on recrystallization from ethanol gave pure diethyl ketone 2,4-dinitrophenylhydrazone, m.p. 155–156° (no mixed m.p. dep.). Fractions III, IV and V were combined and fractionated in a vacuum jacketed Podbielniak column to give the following fractions: I, 0.91 g., b.p. 74–95° at 39 mm. (bath temp. 125–130°); II, 4.20 g. of acetophenone, b.p. 97–99.5° at 30 mm. (bath temp. 129–147°), 35% cleavage; III, 8.07 g. of material, b.p. 141–143° at 30 mm. (bath temp. 156–175°); and IV, 1.17 g., b.p. 146–147° at 30 mm. (bath temp. 183–188°, forced distillation), analyzing for  $C_{30}H_{42}O$  (an allyl ether). Fraction II gave a 2,4-dinitrophenylhydrazone, m.p. 241–242°; recrystallization brought the melting point to 244–245°. This fraction also gave a semicarbazone, m.p. 199.5–200.5° (reported for acetophenone semicarbazone is 200°). The infrared spectra of fractions III and IV were almost identical except for a carbonyl impurity in III. No hydroxyl absorption bands (2.7–3.1  $\mu$ ) were present; however, there were two strong bands in the carbon-oxygen stretching region (at 9.40 and 9.75  $\mu$ ). Also, an absorption band at 6.15  $\mu$  indicated unsaturation.

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