

glycol which boiled at 120–125° (4 mm.) and melted at 39–43°.

Hydrogenation of Hydroxyacetic Acid.—The procedures for hydrogenation and product isolation were similar to

those used for adipic acid. The product, ethylene glycol, had b.p. 76° (5.5 mm.), refractive index at 25° of 1.4300, and m.p. –13°.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Quantitative Studies with Lithium Aluminum Hydride. The Reduction of Butenolides

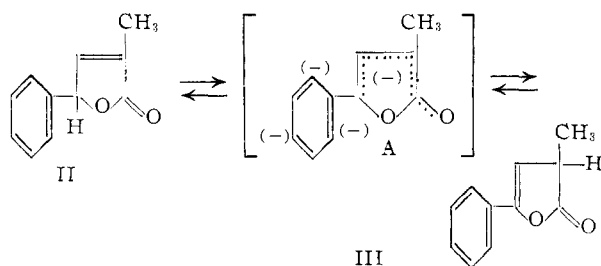
BY FAUSTO RAMIREZ AND MORDECAI B. RUBIN¹

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The lithium aluminum hydride reduction of the tautomeric unsaturated lactones α -methyl- γ -phenyl- $\Delta^{\alpha,\beta}$ -butenolide (II) and α -methyl- γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide (III) has been examined quantitatively. The effect of varying the hydride-butenolide mole ratio and of varying the reduction time at several mole ratios, have been studied. The reduction of the α,β -unsaturated butenolide II yielded the keto alcohol IV, the unsaturated dialcohol VI, and the saturated dialcohol V. The β,γ -unsaturated butenolide III yielded the keto alcohol IV and small amounts of the saturated dialcohol V. The formation of the common reduction products, IV and V from both butenolides suggests that a common hybrid anion A is formed during the reductions. This study indicates that variations in the hydride-butenolide ratios result in the formation of different complexes which, however, yield the same products on hydrolysis.

Examination of the literature on lithium aluminum hydride² discloses the reduction of one pair of tautomeric butenolides. Thus, Hochstein³ reported a 65% yield of γ -acetylpropanol ($\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{OH}$) from α -angelica lactone (γ -methyl- $\Delta^{\beta,\gamma}$ -butenolide) and a 10% yield of 1,4-pentane-diol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)⁴ from β -angelica lactone (γ -methyl- $\Delta^{\alpha,\beta}$ -butenolide).

We have investigated the action of lithium aluminum hydride on two tautomeric crystalline butenolides, namely, α -methyl- γ -phenyl- $\Delta^{\alpha,\beta}$ -butenolide (II) and α -methyl- γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide (III), interconvertible through a common hybrid anion A. The effect of varying the hydride-butenolide mole ratio and of varying the reduction time at several mole ratios, were studied. The composition of the reduction products was established by spectrophotometric methods in the infrared and ultraviolet and by chemical means.



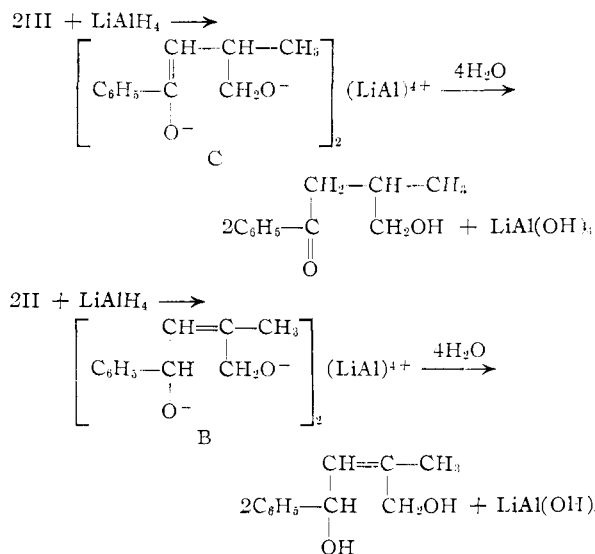
By analogy with the reduction of other lactones,² the stoichiometry of the reduction of butenolides II and III may be represented as

(1) Union Carbide and Carbon Fellow, 1952–1953. From part of the Ph.D. Thesis of M. B. Rubin. Presented at the 126th National Meeting of the Amer. Chem. Soc., September, 1954.

(2) (a) W. G. Brown in "Organic Reactions," Vol. VI, R. Adams, Editor, John Wiley and Sons, Inc., New York, N. Y., 1951, Ch. 10; (b) U. Solms, *Chimia*, **5**, 25 (1951); (c) B. C. L. Weedon, *Ann. Rep.*, **49**, 139 (1952).

(3) F. A. Hochstein, *THIS JOURNAL*, **71**, 305 (1949).

(4) The original reference³ gives "2,4-pentanediol" as the only product of the reduction of β -angelica lactone. This appears to be a misprint.



It has been stated that simple enolate anions (such as C) generally resist reduction by LiAlH_4 ,⁵ although anions derived from β -dicarbonyl compounds are susceptible to reduction by the hydride.^{5a,b} The behavior of anions such as A remains to be explored.⁶

Examples of *partial reductions* of saturated lactones to hydroxyaldehydes^{7a} and of ortho esters^{7b} to aldehydes have been reported. Such partial reductions, if possible with unsaturated lactones,

(5) (a) A. S. Dreiding and J. A. Hartman, *THIS JOURNAL*, **75**, 939 (1953); (b) *ibid.*, **75**, 3723 (1953); (c) W. G. Dauben and J. P. Eastham, *ibid.*, **75**, 1718 (1953); (d) R. E. Lutz and J. S. Gillespie, *ibid.*, **72**, 2002 (1950); (e) R. L. Wears, *ibid.*, **73**, 2390 (1951).

(6) That the hydrogen in the type of butenolides here considered is significantly acidic and, therefore, capable of reacting with LiAlH_4 to generate anion A, is shown by the facile isomerization of III into II by triethylamine (*vide infra*). The action of LiAlH_4 on active hydrogens has been reviewed (H. E. Zaugg and B. W. Horrom, *Anal. Chem.*, **20**, 1026 (1948); F. A. Hochstein, *THIS JOURNAL*, **71**, 305 (1949); T. H. Higuchi in "Organic Analysis," Vol. II, Interscience Publishers, New York, N. Y., 1954).

(7) (a) G. A. Arth, *THIS JOURNAL*, **75**, 2413 (1953); (b) C. J. Claus and J. L. Morgenthau, *ibid.*, **73**, 5005 (1951).

would open new routes to γ -hydroxy- α,β -unsaturated aldehydes (from II) and γ -ketoaldehydes (from III).

Preparation of the Butenolides and Characterization of the Reduction Products.—Chart I summarizes the transformations carried out during the synthesis of the butenolides and the characterization of the reduction products. The unknown butenolides were prepared from β -benzoyl- α -methylpropionic acid (I) in the usual manner.⁸ Thus, treatment of the keto acid I with hot acetic anhydride gave α -methyl- γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide (II), while the action of sulfuric acid-acetic acid-acetic anhydride on the keto acid I yielded α -methyl- γ -phenyl- $\Delta^{\alpha,\beta}$ -butenolide (III). In this series the α,β -isomer is the stable form and can also be obtained from the β,γ -isomer on treatment with triethylamine.⁹ The structures of the isomeric butenolides II and III follow from (1) their ultraviolet^{8b} and infrared¹⁰ absorption spectra as described in the Experimental and (2) their chemical properties: II resisted hydrogenation in the presence of platinum and failed to form a 2,4-dinitrophenylhydrazone, whereas III absorbed 2-mole equivalents of hydrogen and readily formed a 2,4-dinitrophenylhydrazone, under comparable conditions.

The reduction of α -methyl- γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide (III) with *excess hydride* in diethyl ether at 25° yielded β -(hydroxymethyl)-butyrophenone (IV) in 43% yield. The keto alcohol IV could not be induced to crystallize and was characterized through crystalline derivatives and spectral data. That the keto alcohol IV is capable of further reduction with lithium aluminum hydride was proven in an independent experiment.

The reduction of α -methyl- γ -phenyl- $\Delta^{\alpha,\beta}$ -butenolide (II) with *excess hydride* yielded the crystalline unsaturated diol *cis*-2-methyl-4-phenyl-2-butene-1,4-diol (VI) in 70% yield. VI had absorption maxima in the OH-region of the infrared but no maxima in the 5.5–6.1 μ region; it decolorized bromine and formed a crystalline mono-3,5-dinitrobenzoate which still exhibited OH-absorption in the infrared.

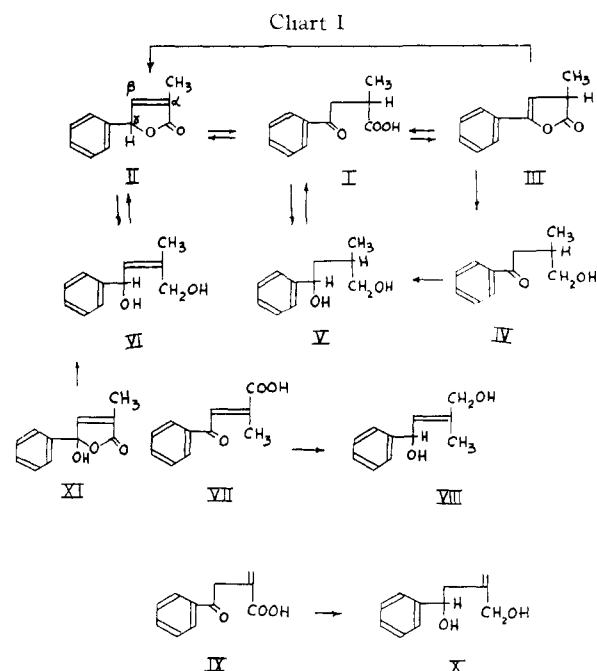
The *cis*-unsaturated diol VI was also isolated from the lithium aluminum hydride reduction of *cis*- β -benzoyl- α -methylacrylic acid (XI) recently

(8) (a) E. Walton, *J. Chem. Soc.*, 438 (1940); (b) A. W. Nineham and R. A. Raphael, *ibid.*, 118 (1949); (c) E. Shaw, *THIS JOURNAL*, **68**, 2510 (1940); (d) F. A. Kuehl, Jr., R. P. Linstead and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950).

(9) This is in contrast to the observed behavior of the closely related system lacking the α -methyl group in which the β,γ -isomer (*viz.*, γ -phenyl- $\Delta^{\beta,\gamma}$ -butenolide) is the stable form. The reversal of the stability of the isomeric butenolides must be attributed to the α -methyl group and is perhaps associated with hyperconjugation. (Cf. M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 103). In the aliphatic and alicyclic series the α,β -butenolides in which the C=C and C=O are conjugated, are the stable forms. (W. Cocker and S. Hornsby, *J. Chem. Soc.*, 1157 (1947); M. S. Newman and C. O. Van der Werf, *THIS JOURNAL*, **67**, 233 (1945)). We have observed (F. Ramirez and M. Rubin, *THIS JOURNAL*, **77**, 2905 (1955)) that α -methyl- γ -(β -naphthyl)- $\Delta^{\alpha,\beta}$ -butenolide is the only form which can be isolated from the corresponding keto acid.

(10) $\Delta^{\alpha,\beta}$ -Butenolides exhibit a carbonyl band around 5.72 μ whereas the $\Delta^{\beta,\gamma}$ -isomers absorb at ca. 5.56 μ . (W. G. Dauben and P. D. Hance, *THIS JOURNAL*, **75**, 3352 (1953); W. Cocker, B. E. Cross and D. H. Hayes, *Chemistry and Industry*, 314 (1952); J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951)).

prepared by Lutz and co-workers.¹¹ Independent evidence for the structure of the unsaturated diol VI was provided by the isolation of the α,β -butenolide II from the chromic anhydride-pyridine¹² oxidation of VI. β -Benzoyl- α -methylpropionic acid (I) was recovered unchanged under similar oxidative conditions.



Quantitative Experiments.—The results of a number of quantitative experiments in which (a)

TABLE I
REDUCTION OF α -METHYL- γ -PHENYL- $\Delta^{\beta,\gamma}$ -BUTENOLIDE (III)
(500 MG.) WITH LiAlH_4 IN DIETHYL ETHER AT ROOM
TEMPERATURE

Run no.	Molar ratio ^b	Time	Product, mg.	Composition of product, ^a %	
				α,β -Butenolide II ^c	Keto alcohol IV
1	0.25	3 hr.	460	43	49 ^d
2 ^e	.25	11 min.	476	38	(54)
5	.50	3 hr.	431	11	49
3	.50	11 min.	411	7	68, 69 ^f
4	.50	11 min.	445	4	70
6	1.2	3 hr.	486	3	59
7	1.2	40 hr.	431	1	45, 43
8 ^g	1.2	8 days	1781	0	45, 44
				124	

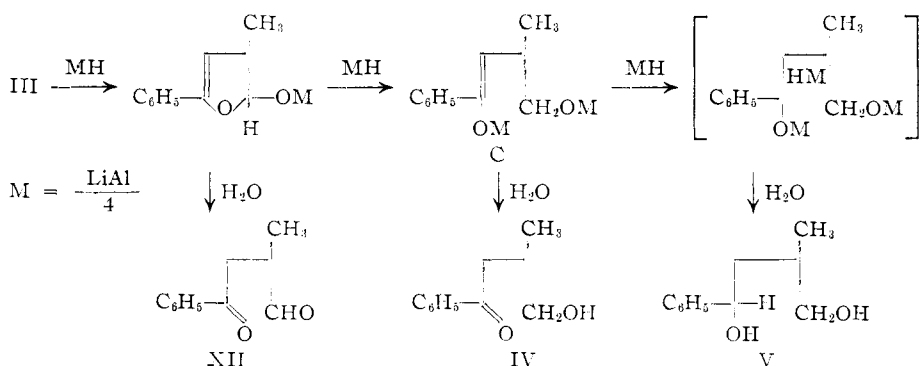
^a The figures are considered significant to within ± 3 –4%.
^b Hydride/butenolide. ^c During hydrolysis an isomerization III \rightarrow II takes place (see Experimental). ^d Spectrophotometrically. ^e α,β -Butenolide isolated and characterized. ^f Gravimetrically as dinitrophenylhydrazone. Product compared with authentic sample. ^g Amount of β,γ -butenolide III used, 2.200 g. From the usual moist-ether hydrolysis, 1.781 g. of product was isolated; further treatment of solids with aqueous HCl in chloroform solution gave additional 0.124 g. of product. Products combined for analysis.

(11) R. E. Lutz, P. S. Bailey, C. K. Dien and J. W. Rinker, *THIS JOURNAL*, **75**, 5039 (1953). Lutz and co-workers have shown that *cis*- β -aroyl- α - and β -methylacrylic acids are largely cyclic and give cyclic derivatives.

(12) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, *THIS JOURNAL*, **75**, 722 (1953).

the hydride-butenolide mole ratio and (b) the reduction time, were varied, are summarized in Tables I and II. In these experiments, an ether solution of the hydride was added, with efficient stirring, to the undissolved butenolide, which reacted rapidly; this practice was found to permit reproducible results.

It can be seen from Table I (runs 1 and 2) that the mole ratio stoichiometrically required for partial reduction of the β,γ -butenolide III to γ -ketoaldehyde XII led, instead, to keto alcohol IV. The amount of keto alcohol IV formed corresponds closely to the butenolide recovered and is near the expected value of 50%. It appears that the complex (or complexes) initially formed (corresponding to XII) is rapidly reduced to a complex (or complexes) from which keto alcohol IV is obtained on hydrolysis. In the system under study, then, no partial reduction to XII appears feasible. All four hydrogens of the LiAlH_4 can be utilized for reduction under these conditions.¹³



In 3 hours, an increase in initial mole ratio from 0.25 to 0.50 (runs 1 and 5) did not markedly increase the proportion of keto alcohol IV in the product, in spite of the fact that the amount of butenolide recovered decreased considerably. In other words, the complex(es) from which keto alcohol IV is formed on hydrolysis is further reduced by the hydride. On the other hand, in 3 hours, a further increase in initial mole ratio from 0.50 to 1.2 (runs 5 and 6) did not decrease the proportion of keto alcohol IV in the product.¹⁴ These observations suggest that more than one type of complex capable of yielding keto alcohol IV on hydrolysis are involved in the reductions. The type of complex and its susceptibility to further reduction by excess hydride probably depend on the mole ratio initially used.

Evidence was obtained showing that at least some of the material balance consists of 2-methyl-4-phenyl-4-butanediol (V) (see Experimental) which represents a *third-stage* reduction product.

At an initial 0.5 mole ratio, a decrease in reaction time from 3 hours to 11 minutes (runs 5 and 3) led to a considerable increase in the proportion of keto alcohol formed. In fact, the optimum conditions among those studied for the preparation of keto al-

(13) In the reduction of enol-acetates⁵⁰ with LiAlH_4 , not all of the hydride hydrogen atoms seemed to be available.

(14) A 1.2 mole ratio actually led to slightly more keto alcohol IV. It should be noted that keto alcohol IV would result from a *simple* enolate anion.

cohol IV are those of run 3 (*cf.* run 4). It seems that, in the environment provided by the initial 0.5 mole ratio, the complex(es) from which keto alcohol is formed on hydrolysis is capable of further reduction on standing.¹⁵

Since at a 1.2 mole ratio an increase in reaction time (runs 7 and 6) led to a significant decrease in the proportion of keto alcohol IV formed, it was of interest to allow the reaction to proceed for a much longer period of time. Run 8 shows that the product composition under these circumstances did not vary appreciably (compare with run 7). Again, a reasonable explanation lies in the possibility that two (or more) types of complexes capable of yielding keto alcohol on hydrolysis are initially formed, one of them being more susceptible to further reduction by excess hydride than the other(s). It should be noted that in runs 6, 7 and 8 the final reduction mixture was a clear and colorless solution with no precipitate present. The resistance of the keto alcohol complex(es) to further reduction under

these conditions is, thus, not due to solubility considerations.

Examination of infrared spectra (not shown) revealed that the reduction of the α,β -butenolide II with limited amounts of LiAlH_4 resulted in complex mixtures of products. In addition to recovered butenolide (column 5 of Table II) the presence of

four substances was demonstrated.

TABLE II
REDUCTION OF α -METHYL- γ -PHENYL- $\Delta\alpha,\beta$ -BUTENOLIDE (II)
(500 MG.) WITH LiAlH_4 IN DIETHYL ETHER AT ROOM
TEMPERATURE

Run no.	Molar ratio ^b	Time	Product, mg.	Composition of product, ^a %	Carbonyl component IV ^c
9	0.25	3 hr.	460	41	17
10	.25	3 hr.	440	37	13
12	.50	3 hr.	445	7	29
11	.50	11 min.	435	4	26
13 ^d	1.2	3 hr.	(510) ^e	1	15
14	1.2	3 hr.	480	1	17

^a The figures are considered significant to within $\pm 4\%$ although the values obtained for carbonyl component probably are closer to the true values. ^b Hydride/butenolide. ^c Spectrophotometrically. ^d 70% of *cis*-unsaturated diol VI isolated by crystallization. ^e Combined weight of product from hydrolysis by water and by aqueous HCl.

(1) *cis*-2-Methyl-4-phenyl-2-butene-1,4-diol (VI).—No satisfactory analytical procedure for the determination of unsaturated diol VI was developed, but it was possible to isolate crystalline VI

(15) At an initial 0.25 mole ratio a decrease in time from 3 hr. to 11 minutes did not significantly change the product composition (runs 1 and 2), a result which emphasizes the relative rapidity with which some LiAlH_4 reductions occur.

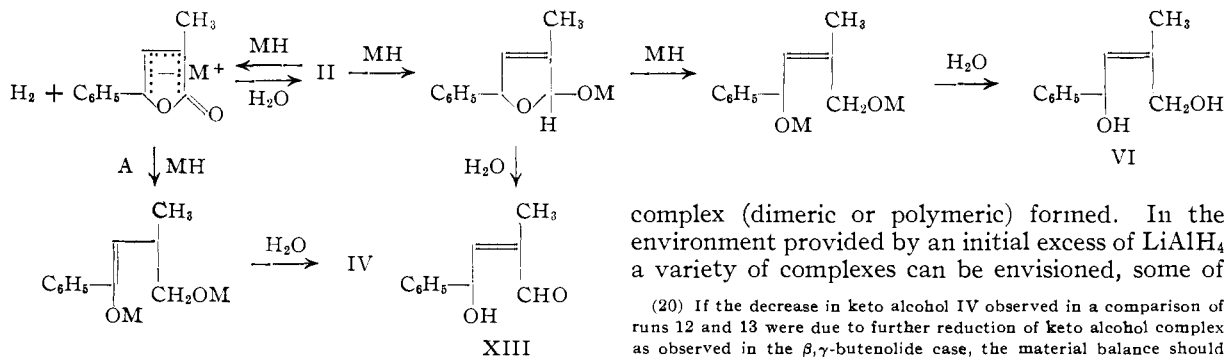
in amounts which in one instance (run 13, excess LiAlH_4) closely approached the material balance.

(2) **2-Methyl-4-phenyl-1,4-butanediol (V).**—Small amounts of this substance were shown to be present by isolation of its 3,5-dinitrobenzoate. The formation of this saturated diol may be the result of a sluggish attack at room temperature and in diethyl ether of a $\text{C}=\text{C}$ bond not conjugated with an aromatic ring, or it may originate from other intermediates (*vide infra*).

(3) **β -(Hydroxymethyl)-butyrophenone (IV).**—The presence of this substance was suggested by the benzoyl-type of chromophore observed both in the infrared and in the ultraviolet. The presence of keto alcohol IV was verified by isolation of its 2,4-dinitrophenylhydrazone. The values of column 6 in Table II were calculated on the assumption¹⁶ that the keto alcohol IV was the only phenyl ketone present in the products.

The isolation of keto alcohol IV from the reduction of the α,β -butenolide II is taken as an indication that some anion A is, indeed, formed by the action of LiAlH_4 (acting as a base) on the $\text{C}-\text{H}$ bond,¹⁷ and that *the anion A is further reduced by the hydride*. The reduction of II is, thus, thought to occur by two paths: (a) by direct reduction of the butenolide and (b) by reduction of the anion A.¹⁸

(4).—A fourth substance having a carbonyl group *not conjugated with the benzene ring* was shown to be present in very small amounts by the isolation of a 2,4-dinitrophenylhydrazone exhibiting an absorption maximum at $361 \text{ m}\mu$, which is typical of unconjugated carbonyl derivatives of this type.¹⁹



(16) Justified by a failure to detect other phenyl ketone 2,4-dinitrophenylhydrazones upon chromatographic analysis.

(17) That attack of LiAlH_4 on a $\text{C}-\text{H}$ bond may successfully compete with reduction of certain functional groups such as $\text{C}\equiv\text{N}$ has been suggested (L. H. Amundsen and L. S. Nelson, *THIS JOURNAL*, **73**, 242 (1951)).

(18) In the absence of a proton source no obvious course for an isomerization of the α,β -butenolide II is apparent, since H_2 is evolved in the formation of anion A from the butenolide. Utilization of some II as proton source would not be consistent with the results of Table II. It has been pointed out that the hydrogen liberated by enolizable substances under the action of LiAlH_4 should correspond very closely to the true enol content, due to a freezing of the tautomeric interconversion as a result of a very rapid reaction of both forms (keto form with reduction and enol form with hydrogen evolution) (ref. 2a, p. 473; J. A. Krynitsky, J. E. Johnson and H. W. Carhart, *THIS JOURNAL*, **70**, 486 (1948); E. Hofling, H. Lieb and W. Schoniger, *Monatsh.*, **83**, 60 (1952). Unlike the situation of three-carbon tautomerism represented by the butenolides ($\text{II} \rightleftharpoons \text{III}$), the keto \rightleftharpoons enol system involves action of the hydride on $\text{C}-\text{H}$ and $\text{O}-\text{H}$, respectively. (Cf. M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 104.)

(19) F. Ramirez and A. F. Kirby, *THIS JOURNAL*, **76**, 1037 (1954).

The structure and origin of this substance is not clear at this time.

It can be seen from Table II (runs 9 and 10) that the mole ratio stoichiometrically required for partial reduction of the α,β -butenolide II to γ -hydroxy- α,β -unsaturated aldehyde XIII resulted, instead, in recovery of about 50% of the original butenolide II. This suggests that the complex(es) formed in the *first-stage* reduction is in turn rapidly reduced and that partial reduction of the type $\text{II} \rightarrow \text{XIII}$ is not feasible in this system.

In 3 hours, an increase in the initial mole ratio from 0.25 to 0.50 (runs 9 and 12) led to a small but significant *increase* in the proportion of keto alcohol IV in the product, but further increase in the initial mole ratio to 1.2 resulted in a *decrease* in the amounts of keto alcohol IV (run 13 or 14).²⁰

At an initial 0.5 mole ratio, an increase in reaction time from 11 minutes to 3 hours (runs 11 and 12) did not affect the proportion of butenolide II and of keto alcohol IV in the product, which is an indication of the relative rapidity with which certain LiAlH_4 reductions may take place.

An extensive discussion of the complexes involved in the reductions is not warranted at this time, since details of even simple reductions with LiAlH_4 are not clear.²¹ When limited amounts of LiAlH_4 are present, simple complexes are perhaps formed. The facile two-stage reductions of the butenolides ($\text{III} \rightarrow \text{IV}$ and $\text{II} \rightarrow \text{VI}$) under these conditions may involve chelates of sparing ether solubility as a result of the absence of $\text{Al}-\text{H}$ bonds. Dilution may play a role in determining the type of

complex (dimeric or polymeric) formed. In the environment provided by an initial excess of LiAlH_4 a variety of complexes can be envisioned, some of

(20) If the decrease in keto alcohol IV observed in a comparison of runs 12 and 13 were due to further reduction of keto alcohol complex as observed in the β,γ -butenolide case, the material balance should contain considerable saturated diol V. However, in run 13 as much as 70% of crystalline *cis*-unsaturated diol VI could be isolated, indicating the presence of relatively small amounts of other products. An explanation could lie in the possibility, already discussed, that different types of complexes are formed in the dissimilar environments provided by the various mole ratios.

(21) The assumption that the reactive species in LiAlH_4 reductions in ether solutions is the AlH_4^- ion, and that the hydrogen is transferred as hydride in a bimolecular nucleophilic displacement of unspecified details has been advanced (cf. ref. 9a and L. W. Trevoy and W. G. Brown, *THIS JOURNAL*, **71**, 1675 (1949)). Others have utilized this picture (*inter alia*, reference 4b; E. L. Eliel and J. P. Freeman, *ibid.*, **74**, 923 (1952); R. Fuchs and C. A. Vander Werf, *ibid.*, **74**, 5917 (1952); A. Feldstein and C. A. Vander Werf, *ibid.*, **76**, 1626 (1954)). A recent suggestion, which considers the reactions of LiAlH_4 as those of hydride anions and which ascribes a role to the solvent used, has been made (cf. N. L. Paddock, *Nature*, **167**, 1070 (1951); M. L. Paddock, *Chemistry and Industry*, 63 (1953)). Details of this work are not available. In this connection the work of Wiberg (E. Wiberg and A. John, *Z. Naturforsch.*, **7**, 581 (1952)) utilizing ether solutions of aluminum hydride should be mentioned. J. E. Johnson, R. H. Blizzard and H. W. Carhart (*THIS JOURNAL*, **70**, 3654 (1948)) have shown that toward alkyl halides, not all four hydrogens of LiAlH_4 show the same reactivity (cf. ref. 5c).

them of considerable ether solubility as a result of the presence of Al-H bonds.

Experimental²²

β -Benzoyl- α -methylpropionic Acid (I). (a).—The keto acid I was prepared from methylsuccinic anhydride,²³ benzene and aluminum chloride as described.²³

(b).—The following alternate procedure for the preparation of the keto acid I was developed. A solution of 65 g. of potassium cyanide in 100 ml. of water was added dropwise to a stirred solution containing 64 g. of crotonophenone,²⁴ 450 ml. of 95% ethanol and 29 ml. of acetic acid, kept at 55°. Most of the ethanol was removed by distillation and the residue was treated with an aqueous solution containing 90 g. of sodium hydroxide. The mixture was heated under reflux for 3 hr. and allowed to stand overnight. Addition of 150 ml. of concentrated hydrochloric acid to the cool, well stirred solution gave a solid in a form suitable for filtration. The crude acid was dissolved in hot sodium carbonate solution treated with Norit and reprecipitated by dropwise addition of 150 ml. of concentrated hydrochloric acid. The yield of air-dried acid I was 60 g., m.p. 140–141°, not raised by recrystallization from chloroform-carbon tetrachloride or benzene; reported¹⁸ for I, m.p. 140°.

The 2,4-dinitrophenylhydrazone of methyl β -benzoyl- α -methylpropionate was obtained directly from a methanolic solution of the keto acid I; orange crystals, m.p. 130–131° (methanol-ethyl acetate), $\lambda_{\text{max}}^{\text{CHCl}_3}$ 379 m μ (ϵ 27,700), bands at 3.00, 5.80, 6.15 and 6.23 μ (chloroform).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_6$: C, 56.0; H, 4.7; N, 14.5. Found: C, 56.1; H, 4.7; N, 14.5.

α -Methyl- γ -phenyl- $\Delta\alpha,\beta$ -butenolide (II).—A mixture of keto acid I (10 g.), acetic anhydride (40 ml.), acetic acid (40 ml.) and concentrated sulfuric acid (10 drops) was kept at room temperature for 24 hr. The mixture was cooled and filtered. The crystalline material so obtained was washed with carbon tetrachloride; yield of II, 3.1 g. (34%), m.p. 221–223°. The analytical sample of II was obtained from chloroform-carbon tetrachloride as colorless crystals, m.p. 226–227°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.69 μ , $\lambda_{\text{max}}^{\text{EtOH}}$ only end absorption.

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_2$: C, 75.8; H, 5.8. Found: C, 76.1; H, 6.0.

Heating of the above mixture for 3 hr. on the steam-bath led to essentially the same yield of butenolide II.

Keto acid I (0.07 g.) was obtained from butenolide II (0.10 g.) on refluxing with 10% aqueous potassium hydroxide for 2 hr.

The butenolide II gave no precipitate with an aqueous methanolic solution of 2,4-dinitrophenylhydrazinium sulfate.

No hydrogen uptake was noted at atmospheric pressure when an ethanolic solution of II was kept in contact with platinum oxide catalyst.

α -Methyl- γ -phenyl- $\Delta\delta,\gamma$ -butenolide (III).—A mixture of keto acid I (10 g.), and acetic anhydride (40 ml.) was heated for 3 hr. on the steam-bath. The cool mixture was added to a solution of sodium carbonate in water. The precipitate was filtered and dissolved in ether. The dry ether solution was concentrated and chilled. The yield of butenolide III was 7 g. (77%), m.p. 52–70°. This material had $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.58 μ . After two recrystallizations from ether II had m.p. 84–86°, $\lambda_{\text{max}}^{\text{CHCl}_3}$ 5.58 μ , and $\lambda_{\text{max}}^{\text{EtOH}}$ 261 m μ (ϵ 10,900) and end absorption at 215 μ .

Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_2$: C, 75.8; H, 5.8. Found: C, 75.6; H, 5.9.

The butenolide III absorbed 2.05 mole equivalents of hydrogen at atmospheric pressure in ethanolic solution with platinum oxide as catalyst.

Treatment of the butenolide III in methanolic solution with 2,4-dinitrophenylhydrazine reagent gave the 2,4-dinitrophenylhydrazone of methyl β -benzoyl- α -methylpropionate.

(22) Analyses by Micro-Tech Laboratories, Skokie, Ill., and Schwarzkopf Microanalytical Laboratories, Woodside, New York. All melting points are corrected.

(23) G. S. Dixon, H. Gregory and L. F. Wiggins, *J. Chem. Soc.*, 2131 (1949); G. A. Oppenheim, *Ber.*, **34**, 4227 (1901).

(24) R. C. Foson, R. F. Christ and G. M. Whitman, *This Journal*, **68**, 2151 (1936).

β -(Hydroxymethyl)-butyrophenone (IV).—A suspension of 4.0 g. of α -methyl- γ -phenyl- β,γ -butenolide (III) and 1.5 g. of lithium aluminum hydride in 125 ml. anhydrous ether was held at room temperature for 5 hours with occasional shaking. Four ml. of water was then added to the clear colorless solution, the mixture stirred for 1 hour and filtered. The inorganic residue was washed with ether. The ether solutions were combined, dried over sodium sulfate and concentrated *in vacuo* to yield 3.2 g. of crude β -(hydroxymethyl)-butyrophenone, $\lambda_{\text{max}}^{\text{EtOH}}$ 243 m μ , ϵ 6,300. Molecular distillation at 0.0002 mm., 78° bath temperature, yielded a viscous oil ϵ_{max} 8,950, λ 243 m μ , which did not analyze satisfactorily. The infrared spectrum showed strong absorption at 2.93 and 5.96 μ . On the basis of an ϵ value of 13,200 for isovalerophenone at 243 m μ , the yield of IV was 43%.

The 2,4-dinitrophenylhydrazone of the keto alcohol IV was obtained in methanol solution in 43% yield based on butenolide III; red-orange crystals m.p. 126–127° (methanol), $\lambda_{\text{max}}^{\text{CHCl}_3}$ 380 m μ (ϵ 24,400), bands at 3.00, 6.15 and 6.23 μ , no bands in the 5–6 μ region, in chloroform.

Anal. Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_4\text{O}_6$: C, 57.0; H, 5.1; N, 15.6. Found: C, 57.2; H, 5.0; N, 15.6.

The 3,5-dinitrobenzoate of the keto alcohol IV was obtained as colorless plates, m.p. 86–87° (90% ethanol); it showed bands at 5.89 and 5.69 μ , but no band in the 2.9–3.0 μ region, in chloroform.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_7$: C, 58.1; H, 4.3; N, 7.5. Found: C, 58.2; H, 4.6; N, 7.7.

2-Methyl-4-phenyl-1,4-butanediol-A (V).—A mixture of 4.0 g. of β -benzoyl- α -methylpropionic acid (I), 3.0 g. of lithium aluminum hydride and 125 ml. of anhydrous diethyl ether was heated under reflux for 2.5 hr. Water was added to the cooled mixture. The ether layer obtained upon filtration and separation gave 3.0 g. of thick, colorless oil which slowly crystallized at –20° under carbon tetrachloride. The yield of crystalline diol (V) of m.p. 52–66° was 1.9 g. The analytical sample melted at 75–76° (carbon tetrachloride) and exhibited a band at 3.00 μ but no bands in the 5–6 μ region, in chloroform.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{O}_2$: C, 73.3; H, 8.9. Found: C, 73.4; H, 8.9.

The bis-3,5-dinitrobenzoate of V was prepared from 3,5-dinitrobenzoyl chloride in pyridine solution. Recrystallization from chloroform-carbon tetrachloride gave white plates, m.p. 165.6–167.4°.

Anal. Calcd. for $\text{C}_{25}\text{H}_{20}\text{O}_4\text{N}_4$: C, 52.8; H, 3.5; N, 9.8. Found: C, 52.9; H, 3.6; N, 9.7.

Oxidation of the saturated diol V with the chromic anhydride-pyridine reagent gave β -benzoyl- α -methylpropionic acid (I) in rather poor yield (30 mg. of keto acid from 100 mg. of diol).

***cis*-2-Methyl-4-phenyl-2-butene-1,4-diol (VI).**—Two hundred and fifty ml. of 0.134 *M* lithium aluminum hydride solution (in ether) was added to 4.9 g. of α,β -butenolide II. In contrast to the reduction of the β,γ -butenolide III the initial reaction was much less vigorous here. After 3 hr. standing at room temperature, moist ether was added with stirring, the resultant precipitate was filtered off, washed with ether and the combined ether solutions evaporated to dryness to give 0.5 g. of amorphous solid. The precipitated solid from the moist ether decomposition was suspended in chloroform and shaken with 5% hydrochloric acid. The layers were separated and the acid layer washed three times with chloroform. The combined chloroform extracts were washed once with water, dried over magnesium sulfate, and evaporated to dryness to give 3.9 g. of amorphous solid. The two fractions were combined (4.4 g., total yield), dissolved in chloroform and let stand in the deep freeze for two days to give 3.1 g. (70% of total recovered material) of white crystals, m.p. 146–148°. A sample recrystallized twice from chloroform-carbon tetrachloride and three times from ethyl acetate-hexane gave white prisms of *cis*-2-methyl-4-phenyl-2-butene-1,4-diol, m.p. 148.8–149.4°.

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.1; H, 7.9. Found: C, 74.2; H, 7.9.

A mono-3,5-dinitrobenzoate of VI, obtained upon treatment of VI with 3,5-dinitrobenzoyl chloride and pyridine for 2 days at room temperature, had m.p. 162.9–163.4° (chloroform-methanol), λ 2.9 μ .

Anal. Calcd. for $C_{18}H_{18}N_2O_7$: C, 57.8; H, 4.3; N, 7.5. Found: C, 58.1; H, 4.2; N, 7.4.

α -Methyl- γ -phenyl- $\Delta\alpha,\beta$ -butenolide (II) from *cis*-2-Methyl-4-phenyl-2-butene-1,4-diol (VI).—A solution containing 240 mg. of the unsaturated diol VI in 3 ml. of anhydrous pyridine was added to a mixture of chromic anhydride (720 mg.) and pyridine (7.2 ml.). Immediate darkening was observed. After 24 hr. at room temperature the mixture was poured into water (25 ml.) and filtered. The inorganic solids were washed with benzene-ether (1:1) and the organic wash used to extract the aqueous filtrate. Removal of the solvents left an oily residue (250 mg.) from which 95 mg. of α -methyl- γ -phenyl- $\Delta\alpha,\beta$ -butenolide (II) was obtained after one recrystallization (chloroform-carbon tetrachloride). The identity of II was established by mixed m.p. determination and infrared spectra.

From a mixture of β -benzoyl- α -methylpropionic acid (I) (300 mg.) and chromic anhydride (300 mg. in 3 ml. of pyridine), which stood at room temperature for 24 hr., it was possible to recover 260 mg. of keto acid I. Further indication that the keto acid I did not react under the conditions used was the lack of discoloration of the solution.

Reduction of *trans*- β -Benzoyl- α -methylacrylic Acid (VII) with $LiAlH_4$.—From 1.5 g. of VII¹¹ and 200 ml. of 0.11 M $LiAlH_4$ solution (2 hours reflux) there was isolated, after the usual work-up, 0.28 g. (20%) of crystalline *trans*-2-methyl-4-phenyl-2-butene-1,4-diol (VIII), m.p. 114.0–115.8° (chloroform-carbon tetrachloride).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 73.9; H, 7.7.

Reduction of β -Benzoyl- α -methylenepropionic Acid (IX) with $LiAlH_4$.—From 5 g. of IX¹¹ and 3 g. of $LiAlH_4$ in 150 ml. of ether (2 hours reflux) there was isolated 1.9 g. of yellow oil, from which 0.4 g. (9%) of crystalline 2-methylene-4-phenyl-1,4-butanediol (X) could be obtained. Analytically pure X had m.p. 97.2–97.6° (carbon tetrachloride).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.1; H, 7.9. Found: C, 74.6; H, 7.8.

Reduction of *cis*- β -Benzoyl- α -methylacrylic Acid (XI) with $LiAlH_4$.—Treatment of XI¹¹ (1.7 g.) with lithium aluminum hydride (1.3 g.) in diethyl ether solution (200 ml.) gave 0.22 g. of a thick oil from which 0.07 g. of crystalline VI, m.p. 146–147°, was obtained upon recrystallization from carbon tetrachloride. A mixed m.p. determination with the sample of unsaturated diol VI obtained from II showed no depression.

γ -Phenyl- $\Delta\beta,\gamma$ -butenolide.—The only isolable product from the reaction of β -benzoylpropionic acid with a mixture of acetic anhydride-acetic acid (1:1) containing a few drops of concentrated sulfuric acid was γ -phenyl- $\Delta\beta,\gamma$ -butenolide, m.p. 89–90° (ligroin), $\lambda^{E_{OH}^{max}}$ 218 μ (ϵ 14,000), 260 μ (ϵ 14,500), band at 5.55 μ , in chloroform. This butenolide had been previously obtained from β -benzoylpropionic acid and acetic anhydride; reported^{8b} m.p. 91–92°.

γ -Phenyl- $\Delta\beta,\gamma$ -butenolide was recovered unchanged from a solution in ligroin containing some triethylamine, heated several hours. In this experiment no evidence for the isomeric $\Delta\alpha,\beta$ -butenolide was obtained.

General Procedure for the Quantitative Experiments.—The butenolides were freshly recrystallized and dried *in vacuo* over P_2O_5 . Approximately 0.05 M solutions of $LiAlH_4$ in ether were prepared, handled and transferred in a dry nitrogen atmosphere. The convenient iodimetric procedure of Felkin²⁵ was used to standardize the $LiAlH_4$ solutions.

The reductions were performed with 0.500-g. (2.87 mmoles) samples of the butenolides in a 250-ml. modified erlenmeyer type flask fitted with a magnetic stirrer and adapters leading to a reflux condenser, a water-jacketed buret and a mercury seal to provide a closed system adjustable to atmospheric pressure. The calculated volume of hydride solution could be introduced from the buret into the reaction vessel containing the butenolide in a nitrogen atmosphere. At the end of the desired reaction time, 100 ml. of moist ether was added, the mixture was carefully filtered and the collected solids washed with ether. The combined ether solutions were carefully evaporated to dryness and the crude product dried to constant weight over phosphorus pentoxide, *in vacuo*.

Analysis. (1).—It was initially established that the unreacted butenolide recovered in the reduction of either α,β -

butenolide II or β,γ -butenolide III was the α,β -isomer II. Consequently, it was necessary to analyze the reaction product for α,β -butenolide II only, in order to determine unreacted starting material. Since the isomeric butenolides (II and III) gave different products on reduction, the isomerization III \rightarrow II was not brought about by the hydride solution but occurred upon addition of water.¹⁸ This point was substantiated by showing that a lithium aluminate mixture (obtained by addition of water to an ether solution of $LiAlH_4$) rapidly converted the β,γ -isomer III into the α,β -isomer II. The α,β -butenolide II was assayed by a spectrophotometric method in the infrared (chloroform solution) in the usual manner.

(2) **Keto Alcohol IV.** (a) **Gravimetric Determination.**—A weighed sample of the reduction product was dissolved in methanol and allowed to stand overnight with a solution prepared by dissolving 1 g. of 2,4-dinitrophenylhydrazine in 60 ml. of concentrated sulfuric acid, diluted to 1 l. with water.²⁶ The precipitate of 2,4-dinitrophenylhydrazone was filtered, dried and weighed. The identity of the hydrazone was confirmed by comparisons (infrared spectra, mixed melting point) with authentic β -(hydroxymethyl)-butyrophenone-2,4-dinitrophenylhydrazone previously reported.

(b) **Spectrophotometric Determination.**—A weighed amount of reduction product was dissolved in a known volume of 95% ethanol and analyzed in a Beckman model DU spectrophotometer. The concentration of keto alcohol IV in solutions of crude product was determined from the equation $D_{250} \mu m = 10,300 C_{IV}$ where C_{IV} represents the concentration of keto alcohol in moles per liter, $D_{250} \mu m$ is the observed optical density at 250 μm and 10,300 is the extinction coefficient of isovalerophenone, taken as model, at 250 μm ; at this wave length the extinction coefficient of the α,β -butenolide II (800) was negligible for our purposes.

Unsaturated Diol, VI.—Although no analytical procedure for VI was developed, the relatively high melting point of VI (m.p. 148–149°) permitted its isolation in some experiments by recrystallization. The total crude reaction mixture was dissolved by boiling in a small volume of chloroform, and carbon tetrachloride was added slowly to the hot solution until crystallization began. After standing at -20° the crystalline product was collected, dried and weighed.

In several experiments the presence, although not the amounts, of substances not analyzable by the methods described above was demonstrated by actual isolation and comparison with authentic samples (*vide infra*).

The results of the analyses are summarized in Tables I and II. The following observations were made: (Table I), in runs 1 and 2 an immediate yellow color followed by a precipitate developed upon addition of the hydride solution to the β,γ -butenolide. Both color and precipitate persisted throughout the reaction. In runs 3, 4 and 5 a transient yellow color developed. The color disappeared after some time and a colorless precipitate remained throughout the reaction. In runs 6, 7 and 8 the transient yellow color was noticed; it quickly faded and gave way to a clear, colorless solution. *No precipitate was apparent in runs 6, 7 or 8.*

Table II: In runs 9, 10, 11 and 12 a white precipitate was noted throughout the entire reaction. In runs 13 and 14 a clear solution was formed during the first stages of the reaction; after some time (*ca.* 15 min.) a white precipitate formed. At no time was a yellow color observed in the reduction of the α,β -butenolide.

Reduction of β,γ -Butenolide III with Excess Hydride: Preparation and Chromatography of 3,5-Dinitrobenzoates.—A mixture of β,γ -butenolide III (3.4 g., 19.5 mmoles) and $LiAlH_4$ in anhydrous ether (200 ml. of a solution containing 0.9 g. or 23.4 mmoles of the hydride) was kept 3 hr. at room temperature. After hydrolysis with moist ether, 2.8 g. (83%) of oil was obtained. To 1.8 g. of this oil there was added 5 g. of freshly recrystallized 3,5-dinitrobenzoyl chloride and 20 ml. of anhydrous pyridine. After 24 hr. at room temperature the mixture was poured into water and extracted with chloroform. Evaporation of the washed chloroform solution gave 4 g. of oil which was taken up in 75 ml. of anhydrous benzene and placed on a 21 \times 5 cm. column of florisil. By successive elutions (benzene and 1:1

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benzene-chloroform) it was possible to isolate 400 mg. of a substance shown to be identical to 2-methyl-4-phenyl-1,4-butanediol-(V) bis-3,5-dinitrobenzoate by comparison of the infrared spectra.

Reduction of α,β -Butenolide II with Excess Hydride: Preparation and Chromatography of 3,5-Dinitrobenzoates.—A mixture of α,β -butenolide II (4.9 g., 28.1 mmoles), LiAlH_4 (1.4 g., ca. 34 mmoles) and anhydrous ether (152 ml.) was allowed to stand at room temperature for 3 hr. The mixture was treated with moist ether, the precipitate was filtered and the ether was removed. The solid obtained in the filtration was suspended in chloroform and the suspension was shaken with dilute hydrochloric acid. Removal of the chloroform gave a residue which was combined with the previous portion obtained from the ether. The combined crystalline product (4.5 g., 92%) was dissolved in chloroform and treated, while hot, with carbon tetrachloride. Upon cooling several days in the refrigerator, 3.2 g. (65%) of crystalline *cis*-2-methyl-4-phenyl-2-butene-1,4-diol (VI), m.p. 146–147°, was collected. The mother liquid from which the unsaturated diol VI crystallized was evaporated to dryness and yielded 1.3 g. of material. This was treated with 3,5-dinitrobenzoyl chloride (2 g.) and pyridine (15 ml.). After 24 hr. at room temperature, the solution was poured into water and extracted with chloroform. Evaporation of the washed chloroform solution gave 2.1 g. of oily mixture of 3,5-dinitrobenzoates. The oil was taken in anhydrous benzene (75 ml.) and placed in a 20 × 5 cm. column of florisil. By successive elutions (benzene, 1:1 benzene-chloroform) it was possible to isolate 200 mg. of a substance shown to be identical to 2-methyl-4-phenyl-1,4-butanediol-(V)-bis-3,5-dinitrobenzoate by means of infrared spectra. Other fractions from the chromatogram had infrared spectra similar to but not identical with that of the saturated diol benzoate.

Reduction of One Mole of α,β -Butenolide II with 0.5 Mole of Hydride: Preparation and Chromatography of 2,4-Dinitrophenylhydrazones.—In the apparatus previously described, the α,β -butenolide (2.5 g., 14.4 mmoles) was

treated with 65 ml. of a 0.11 *M* LiAlH_4 solution in ether (7.2 mmoles of hydride). After 15 min. at room temperature moist ether was added. In the usual manner (moist ether hydrolysis), 1.9 g. (76%) of crystalline product was isolated. From the acidic treatment of the inorganic products of the hydrolysis, 0.61 g. (24%) of additional crystalline product was obtained. The 1.9 g. of product gave upon recrystallization from chloroform-carbon tetrachloride 0.4 g. (16%) of *cis*-2-methyl-4-phenyl-2-butene-1,4-diol (VI), m.p. 144–148°. The mother liquid was evaporated to dryness leaving 1.4 g. of gummy solid which was dissolved in methanol (10 ml.) and treated with a solution of 2,4-dinitrophenylhydrazinium sulfate in aqueous methanol. The red oil which formed was freed of liquid by centrifugation and decantation and was dried *in vacuo*. A solution of the 2,4-dinitrophenylhydrazone mixture in benzene was placed in a 9 × 3 cm. column of silicic acid (2 parts)-Celite (1 part). The column was eluted with benzene under a small positive pressure of nitrogen. From the first 50 ml. of benzene, a small amount of unreacted 2,4-dinitrophenylhydrazone was obtained. The second fraction (50 ml.) gave after evaporation, 0.14 g. of yellow crystalline solid (fraction A). Elution with more benzene (100 ml.) followed by 2:1 benzene-chloroform (250 ml.) gave no product. Elution with chloroform gave 0.175 g. of red oil (fraction B), $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}}$ 380 μ ; fraction B was rechromatographed from chloroform as before. In this manner fraction B yielded 0.135 g. of a red substance shown to be identical in all respects (m.p. 124–126°; no depression upon admixture with authentic sample; identity of infrared and ultraviolet spectra) with β -(hydroxymethyl)-butyrophenone-(IV)-2,4-dinitrophenylhydrazone previously reported.

Fraction A obtained above was recrystallized from chloroform-methanol to yield 75 mg. of yellow-orange crystals, m.p. 234.4–234.8°, $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}}$ 361 μ . *Anal.* Found: C, 50.5; H, 3.7; N, 20.8. This substance was not further investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Metalation of 2,6-Diisopropylanisole and 1,3-Diisopropylbenzene¹

BY CHESTER E. CLAFF, JR.²

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Amylsodium with sodium *t*-pentoxide metalates 1,3-diisopropylbenzene and 2,6-diisopropylanisole in the ring positions *meta* to the alkyl groups. In separate metalations or in competition experiments the hydrocarbon is metalated more easily than the ether. Both 2,6-diisopropylanisole and triethylamine retard the metalation of 1,3-diisopropylbenzene. Electrostatic complexing of the sodium cation is postulated.

Introduction

Previous workers have shown that metalation of a heterosubstituted aromatic ring by organosodium reagents takes place *ortho* to the hetero atom if the position is available. Metalations of phenyl alkyl ethers,³ sodium and potassium phenoxides,⁴ sodium benzoate,⁵ sodium anilide⁶ and dimethylaniline⁷ by amylosodium took place in the *ortho* positions. This paper will discuss the effects of blocking the *ortho* positions of anisole with alkyl substituents. 2,6-Diisopropylanisole was chosen in the hope of

sterically preventing coordination at the ether oxygen and of limiting the position of metalation to the carbon atom *para* to the methoxy group. The isopropyl group of cumene severely restricts metalations at adjacent positions in the ring.^{8,9} The metalation of 1,3-diisopropylbenzene at the 5-position, which is sterically identical with the 4-position of 2,6-diisopropylanisole, also was studied for comparison purposes.

Metalation of 2,6-Diisopropylanisole.—This ether was prepared from the sodium salt of 2,6-diisopropylphenol¹⁰ by treatment with methyl *p*-toluenesulfonate. Bromination gave 2,6-diisopropyl-4-bromoanisole which was converted to the Grignard reagent and treated with carbon dioxide to give 3,5-diisopropyl-4-methoxybenzoic acid.

2,6-Diisopropylanisole was added to a slight excess of amylosodium containing sodium *t*-pent-

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