mixture was stirred for 3 hr during which time it slowly warmed to −20° and was flash-distilled into a Dry Ice–acetone trap. The distillate after drying ($CaSO_4$) was shown by glpc (column A) to contain a 69:31 ratio of 3-chloro-1-butene and 1-chloro-2-butene in an overall yield of 92%. Concentration of the solution followed by preparative glpc (column P) gave 4.6 g (48%) of (−)-chloride **13**: a^{30}D −30.8° (neat) (50.4% optically pure[11]); nmr (CCl_4) δ 1.58 (d, 3, J = 6.5 Hz, methyl), 4.42 (m, 1, consisting of a quartet, J = 6.5 Hz, each line of which is further split into a doublet of doublets, J = 7.0 and 0.8 Hz, methine), 5.00 (d of d, 1, J = 10.0 and 0.8 Hz, terminyl vinyl), and 5.86 (m, 1, consisting of a doublet of doublets, J = 10.0 and 7.0 Hz, each line of which is further split into a 1:1:1 triplet, J = 2.5 Hz, internal vinyl).

Reaction of Optically Active 3-Chloro-*cis*-1-butene-*1-d* (13) with Phenyllithium.—Optically active (−)-chloride **13**, 4.0 g (0.044 mol), in ether was added to 0.8 *N* phenyllithium in ether according to the general procedure of the previous paper.[2] Analysis of the crude reaction mixture by glpc (column B) revealed a 73% yield of three hydrocarbons in a ratio of 86.0:13.5:0.5. Preparative glpc (column Q) of a small portion of the crude product led to isolation of the major component, 1-phenyl-*trans*-2-butene-*1-d* (15), identified by comparison with unlabeled material and by its nmr spectrum (CCl_4) δ 1.65 (m, 3, methyl), 3.2 (m, 1, methine), 5.4 (m, 2, vinyl), and 7.0 (m, 5, aromatic). A small sample of the next most abundant product was similarly isolated and identified as 1-phenyl-*cis*-2-butene-*1-d* (16). The third component was not present in sufficient quantity to permit isolation, but its structure was confirmed as 3-phenyl-1-butene (presumably deuterated at C_1 with cis geometry, **17**) by glpc comparison (columns B, C, and D) with authentic unlabeled material.

Distillation of the crude product yielded 2.80 g of a mixture of **15**, **16**, and 17 in a ratio of 86.0:13.5:0.5, bp 62–64° (10 mm). A 2.500-g portion of this distillate was diluted to 9.500 g with a mixture of optically inactive compounds in exactly the same ratio. Careful distillation through a spinning band column gave 5.15 g of a mixture containing only hydrocarbons **15** and **16** in a ratio of 86.5:13.5 which was then diluted to twice its weight with 5.15 g of the identical mixture of unlabeled materials. This mixture (containing 13.2% of deuterated optically active hydrocarbons) was separated into two portions.

A 5.0-g portion (0.038 mol) was reduced by diimide [formed by treatment of 30.0 g of anhydrous hydrazine in 50 ml of ethanol (containing a few crystals of $CuSO_4$) with oxygen, 30 ml/min for 24 hr].[20] After the usual work-up, the organic layer was distilled through a 6-in. Vigreux column yielding 2.94 g (59%) of 1-phenylbutane-*1-d* (**18a**): bp 62° (10 mm); $[a]^{27}$D −0.780° (neat).

From a 5.3-g portion, preparative glpc (column Q) gave 4.30 g of pure trans olefin **15** which was reduced with diimide to 2.30 g (53%) of 1-phenylbutane-*1-d* (**18b**): bp 62° (10 mm); $[a]^{27}$D −1.02° (neat).

Registry No.—6, 29333-27-5; 7, 29333-28-6; 8, 29333-29-7; 9, 29333-30-0; 10, 29333-31-1; (+)-**11**, 29333-32-2; (+)-**12**, 29453-55-2; (−)-**13**, 29333-33-3; (−)-**18**, 29453-61-0; (+)-**18**, 14159-12-7; phenyllithium, 591-51-5.

(20) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Lett.*, 347 (1961).

Reductions of Some Aliphatic β Diketones with Lithium Aluminum Hydride

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The reduction of β diketones with lithium aluminum hydride ($LiAlH_4$) under forcing conditions affords products of elimination as well as the expected 1,3-diols. The elimination products (unsaturated alcohols) are obtained in yields which correspond to the enol content of the starting diketone. The reaction is highly stereospecific, giving rise to trans olefins exclusively. The unsymmetrical diketone, 2,4-hexanedione, affords two unsaturated alcohols, 3-hexen-2-ol and 2-hexen-4-ol, with the former predominating. The ratio of these two products and their stereochemistry are discussed in light of the most likely reaction mechanism.

The reduction of enolizable β-keto esters,[1,2] malonic enolates,[3] and β diketones[1,4–6] with lithium aluminum hydride ($LiAlH_4$) gives rise to products of elimination as well as the expected 1,3-diols. In discussing the mechanism of the reaction, Dreiding and Hartman[1] proposed that the elimination products (unsaturated alcohols) resulted from the action of $LiAlH_4$ on the enol forms of the compounds, the diols arising from the nonenolized portions. The applicability of Dreiding and Hartman's mechanism to systems other than alicyclic or aromatic β-dicarbonyl compounds has been questioned by other investigators. Marshall, Andersen, and Hochstetler[3] reported that the proposed mechanism could not account for the saturated mono-

alcohols observed by them in the reduction of malonic enolates and suggested a considerably more complicated reaction scheme. Pohoryles, Sarel, and Ben-Shoshan[5] reacted acetylacetone with lithium aluminum hydride under forcing conditions and observed a higher ratio of elimination product to diol than would be expected from the enol content of acetylacetone. None of these investigators report on the stereochemistry of the unsaturated reaction products.

We have examined the reductions of acetylacetone and 2,4-hexanedione with $LiAlH_4$ in some detail. We were especially interested in identifying all reaction products, in determining the direction of the elimination in the case of the unsymmetrical dione, and in elucidating the stereochemistry of the reaction. This report describes our results and their bearing on the mechanism of the reduction–elimination reaction. Of especial interest is the stereochemical control exhibited during the elimination. The unsaturated reaction products are exclusively trans (Scheme I).

Results

Acetylacetone was a logical choice for most of our studies, because it is the most readily available, sym-

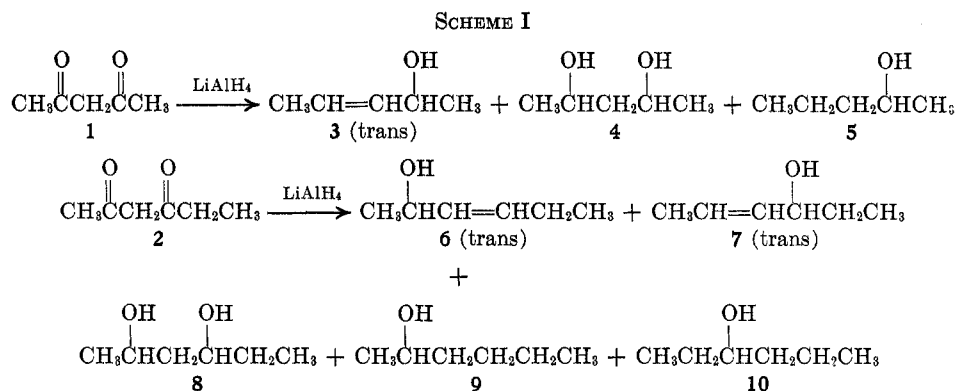(1) A. S. Dreiding and J. A. Hartman, *J. Amer. Chem. Soc.*, **75**, 939 (1953).

(2) E. Romann, A. J. Frey, P. A. Stadler, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1900 (1957).

(3) (a) J. A. Marshall, N. H. Andersen, and A. R. Hochstetler, *J. Org. Chem.*, **32**, 113 (1967); (b) W. J. Bailey, M. E. Humes, and W. A. Klein, *ibid.*, **28**, 1724 (1963); (c) W. F. Gannon and E. A. Steck, *ibid.*, **27**, 4137 (1962).

(4) A. S. Dreiding and J. A. Hartman, *J. Amer. Chem. Soc.*, **75**, 3723 (1953).

(5) L. A. Pohoryles, S. Sarel, and R. Ben-Shoshan, *J. Org. Chem.*, **24**, 1878 (1959).

(6) (a) G. Stork and F. H. Clarke, Jr., *J. Amer. Chem. Soc.*, **83**, 3114 (1961); (b) A. Luttringhaus and N. Engelhard, *Angew. Chem.*, **73**, 218 (1961).

Scheme I

$$
\underset{\textbf{1}}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3} \xrightarrow{LiAlH_4} \underset{\textbf{3 (trans)}}{CH_3CH=CH\overset{OH}{\overset{\|}{C}}HCH_3} + \underset{\textbf{4}}{CH_3\overset{OH}{\overset{\|}{C}}HCH_2\overset{OH}{\overset{\|}{C}}HCH_3} + \underset{\textbf{5}}{CH_3CH_2CH_2\overset{OH}{\overset{\|}{C}}HCH_3}
$$

$$
\underset{\textbf{2}}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3} \xrightarrow{LiAlH_4} \underset{\textbf{6 (trans)}}{CH_3\overset{OH}{\overset{\|}{C}}HCH=CHCH_2CH_3} + \underset{\textbf{7 (trans)}}{CH_3CH=CH\overset{OH}{\overset{\|}{C}}HCH_2CH_3}
$$

$$
+
$$

$$
\underset{\textbf{8}}{CH_3\overset{OH}{\overset{\|}{C}}HCH_2\overset{OH}{\overset{\|}{C}}HCH_2CH_3} + \underset{\textbf{9}}{CH_3\overset{OH}{\overset{\|}{C}}HCH_2CH_2CH_2CH_3} + \underset{\textbf{10}}{CH_3CH_2\overset{OH}{\overset{\|}{C}}HCH_2CH_2CH_3}
$$

metrical 2,4 diketone and because the products of the reduction–elimination reaction are easily separated and identified. The selection of 2,4-hexanedione as a model of an unsymmetrical system was dictated not only by its convenience but also because we were interested in this compound in another connection.

The LiAlH₄ reduction of these diones proceeds well only under forcing conditions. A sixfold excess of hydride and 16 hr in refluxing ether were required to complete the reaction.

The results of the LiAlH₄ reductions carried out in this study are given in Table I. The data obtained

Table I

Reduction–Eliminations with LiAlH₄[a]

Product	% of product isolated[b]	% yield[b]
Acetylacetone (1) (Excess LiAlH₄)		
trans-3-Penten-2-ol (3)	85.5	82.5
2,4-Pentanediol (4)	11.5	11.0
2-Pentanol (5)	3.0	3.0
Acetylacetone (1) (Stoichiometric LiAlH₄)[c]		
trans-3-Penten-2-ol (3)	78	
3-Penten-2-one (12)	20	
2,4-Pentanediol (4)	2	
2-Pentanol (5)	Trace	
2,4-Hexanedione (2) (Excess LiAlH₄)		
trans-3-Hexen-2-ol (6)	52.0	41.0
trans-2-Hexen-4-ol (7)	21.0	17.0
2,4-Hexanediol (8)	18.5	14.5
2-Hexanol (9)	6.5	5.0
3-Hexanol (10)	2.0	1.5
3-Penten-2-one (Methyl Propenyl Ketone, 12)		
3-Penten-2-ol[d]	95.5	
2-Pentanol (5)	3.5	
1,3-Pentadiene[e]	1.0	
cis-3-Penten-2-ol		
cis-3-Penten-2-ol	100	
trans-3-Penten-2-ol (3)	0	
2-Pentanol (5)	0	
2,4-Pentanediol (4)		
2,4-Pentanediol (4)	100	
3-Penten-2-ol (3)	0	
2-Pentanol (5)	0	

[a] Similar reaction conditions for all reductions. [b] Expressed as mole per cent. [c] Product breakdown was not obtained accurately, since more than 90% of the starting material was recovered. Ratio of 3-penten-2-ol to 3-penten-2-one was 3.5:1. Presence of a trace of 2-pentanol was indicated but not confirmed. No yield data were obtained. [d] Stereochemistry undetermined. [e] Apparently an artifact arising from pyrolysis of the 3-penten-2-ol in the entry port of the gas chromatograph.

for acetylacetone and 2,4-hexanedione were confirmed in duplicate experiments. The reaction of LiAlH₄ with acetylacetone was especially clean. Only three compounds were obtained, *trans* 3-penten-2-ol (3), 2,4-pentanediol (4), and 2-pentanol (5), and these accounted for 96% of the starting material. The reduction of 2,4-hexanedione was more complicated. Two unsaturated and two saturated alcohols are possible as well as the diol[7] and all were observed.
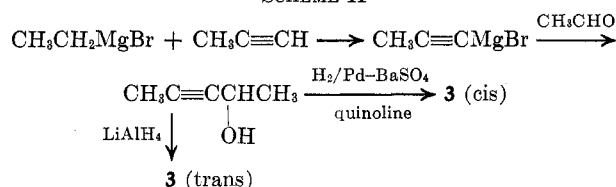
The various reaction products were identified by direct comparison of their gas chromatographic behavior and spectral properties with those of authentic samples. The cis and trans isomers of 3 were prepared as shown in Scheme II.

Scheme II

$$
CH_3CH_2MgBr + CH_3C\equiv CH \longrightarrow CH_3C\equiv CMgBr \xrightarrow{CH_3CHO}
$$

$$
\underset{\underset{\textbf{3 (trans)}}{\Big\downarrow LiAlH_4}}{CH_3C\equiv C\overset{OH}{\overset{\|}{C}}HCH_3} \xrightarrow[\text{quinoline}]{H_2/Pd\text{–}BaSO_4} \textbf{3 (cis)}
$$

The corresponding isomers of both 3-hexen-2-ol (6) and 2-hexen-4-ol (7) were synthesized in an analogous fashion. The cis and trans forms of the various unsaturated alcohols are readily separable by gas chromatography.[8] The nmr spectra (see Table II) allowed an unambiguous assignment of the stereochemistry of the double bonds of all of the alcohols. The olefinic protons for the trans configuration are grouped at τ 4.43–4.50 while the olefinic protons for the cis configuration are at τ 4.62. The ir spectra provided confirmatory evidence for our assignments. The structures of all intermediates leading to those olefin alcohols which we synthesized were confirmed by their nmr and ir spectra.

The amount of elimination *vs.* reduction correlates very well with the enol content of the two diones under the reaction conditions (Table III). The per cent of the enol form in ether and CDCl₃ was estimated from the nmr spectra by comparing the integrated intensities of the singlets due to the enol (τ 7.97 in CDCl₃,

(7) A referee has pointed out that 2,4-hexanediol (8) can exist as a mixture of erythro and threo forms. We recognize this possibility but have obtained no evidence that such a mixture actually exist in this instance. We did observe what appeared to be a mixture of diastereomers for 2,4-pentanediol (4) in the nmr spectrum and on thin layer plates. Since the character of these mixtures is not important to our discussion, we have chosen to avoid confusion by referring to 4 and 8 in the singular throughout this paper.

(8) The cis forms have somewhat longer retention times. For example, *cis*-3-penten-2-ol has a retention time about 2 min longer than the trans isomer on a 12-ft Carbowax 20M column at 40°. Further details on the chromatography of these materials are given in the Experimental Section.

TABLE II
TABULATION OF NMR SPECTRA

Compd (solvent)	Registry no.	Chemical shift, τ (multiplicity,[a] coupling constant[b])					
		a	b	c	d	e	f
$CH_3COCH_2COCH_3$ (CDCl₃) a b c ⇅		7.79 (s)	6.37 (s)	7.79 (s)			
$CH_3COCH=COHCH_3$ a b c d	1522-20-9	7.97 (s)	4.42 (s)		7.97 (s)		
$CH_3COCH_2COCH_2CH_3$ (CDCl₃) a b c d ⇅		7.81 (s)	6.43 (s)	7.48 (q, J_{cd} = 7 Hz)	8.98 (t, J_{cd} = 7 Hz)		
$CH_3COCH=COHCH_2CH_3$ a b c d e	29494-98-2	7.99 (s)	4.46 (s)		7.71 (q, J_{de} = 7 Hz)	8.90 (t, J_{de} = 7 Hz)	
$CH_3C{\equiv}CCHOHCH_3$ (CDCl₃) a b c d	27301-54-8	8.21 (d, J_{ab} = 2 Hz)	5.53 (qq, J_{ab} = 2 Hz, J_{bd} = 6.5 Hz)	6.06 (s)	8.62 (d, J_{bd} = 6.5 Hz)		
$CH_3C{\equiv}CCHOHCH_2CH_3$ (CDCl₃) a b c d e	20739-59-7	8.18 (d, J_{ab} = 2 Hz)	5.75 (tq, J_{bd} = 7 Hz, J_{ab} = 2 Hz)	6.05 (s)	8.32 (dq, J_{bd} = 7 Hz, J_{de} = 7 Hz)	9.03 (t, J_{de} = 7 Hz)	
$CH_3CH_2C{\equiv}CCHOHCH_3$ (CDCl₃) a b c d e	109-50-2	8.88 (t, J_{ab} = 7.5 Hz)	7.79 (dq, J_{ab} = 7.5 Hz, J_{bc} = 2 Hz)	5.49 (qt, J_{ce} = 7.5 Hz, J_{bc} = 2 Hz)	5.99 (s)	8.59 (d, J_{ce} = 7.5 Hz)	
trans-$CH_3CH=CHCHOHCH_3$ (CCl₄) a b b' c d e		8.36 (dd, J_{ab} = 5 Hz, $J_{ab'}$ = 1 Hz)	4.48 (m)	5.85 (m)	5.64 (s)	8.86 (d, J_{ce} = 6.5 Hz)	
cis-$CH_3CH=CHCHOHCH_3$ (CCl₄) a b b' c d e	24652-50-4	8.38 (d, J_{ab} = 5 Hz)	4.62 (m)	5.44 (dq, $J_{b'c}$ = 6 Hz, J_{ce} = 6 Hz)	5.73 (s)	8.84 (d, J_{ce} = 6 Hz)	
trans-$CH_3CH=CHCHOHCH_2CH_3$ a b b' c d e f (CCl₄)		8.34 (dd, J_{ab} = 5 Hz, $J_{ab'}$ = 0.5 Hz)	4.50 (m)	6.13 (dt, $J_{b'c}$ = 6 Hz, J_{ce} = 6 Hz)	5.76 (s)	8.48 (m)	9.14 (t, J_{ef} = 7 Hz)
cis-$CH_3CH=CHCHOHCH_2CH_3$ a b b' c d e f (CCl₄)	29478-30-6	8.37 (d, J_{ab} = 5 Hz)	4.62 (m)	5.73 (dt, $J_{b'c}$ = 6 Hz, J_{ce} = 6 Hz)	5.96 (s)	8.48 (m)	9.14 (t, J_{ef} = 7 Hz)
trans-$CH_3CH_2CH=CHCHOHCH_3$ a b c c' d e f (CCl₄)		9.02 (t, J_{ab} = 7 Hz)	7.98 (m)	4.43 (m)	5.78 (m)	6.23 (s)	8.80 (d, J_{df} = 6 Hz)
cis-$CH_3CH_2CH=CHCHOHCH_3$ a b c c' d e f (CCl₄)	29478-31-7	9.04 (t, J_{ab} = 7 Hz)	7.93 (m)	4.63 (m)	5.41 (m)	6.58 (s)	8.82 (d, J_{df} = 6H)
trans-$CH_3CH=CHCOCH_3$ (CDCl₃) a b c d		8.27 (dd, J_{ab} = 6.5 Hz, J_{ac} = 1.5 Hz)	3.27 (dq, J_{ab} = 6.5 Hz, J_{bc} = 16 Hz)	3.92 (dq, J_{ac} = 1.5 Hz, J_{bc} = 16 Hz)	7.80 (s)		
$CH_3CHOHCH_2COCH_3$ (CDCl₃) a b c d e	4161-60-8	8.83 (d, J_{ab} = 6 Hz)	5.80 (tq, J_{ab} = 6 Hz)	5.80 (s)	7.44 (d, J_{bd} = 6 Hz)	7.85 (s)	
$CH_3CHOHCH_2CHOHCH_3$ a b c d b c a (CDCl₃)ᶜ		8.82 (d, J_{ab} = 6 Hz)	6.04 (tq, J_{ab} = 6 Hz, J_{bd} = 6 Hz)	5.21 (s)	8.49 (t, J_{bd} = 6 Hz)		
$CH_3CH_2CHOHCH_2CHOHCH_3$ a b c d e c d f (CCl₄)ᶜ		9.09 (t, J_{ab} = 6.5 Hz)	8.40 (m)	6.14 (m)	5.16 (s)	8.52 (t, J_{ce} = 6.5 Hz)	8.83 (d, J_{cf} = 6.5 Hz)

[a] s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. [b] The absolute values of the coupling constant are given to ±0.5 Hz. [c] Probably a mixture of diastereomers.

TABLE III
CORRELATION OF ENOL CONTENT AND ELIMINATION vs. REDUCTION

Compd	Elimination products, %[a]	Enol contents, %[b]		Lit.
		Ether	CDCl₃	
Acetylacetone	88.5	88.5	84.0	81,[c] 91,[d] 94[e]
2,4-Hexanedione	81.5	80[f]	80[f]	

[a] Includes unsaturated alcohols and saturated monoalcohols. [b] Solutions 10% in dione. [c] In cyclohexane: L. W. Reeves, *Can. J. Chem.*, **35**, 1351 (1957). [d] In hexane: J. B. Conant and A. F. Thompson, Jr., *J. Amer. Chem. Soc.*, **54**, 4039 (1932). [e] In ether: K. H. Meyer, *Ber.*, **47**, 826 (1914). [f] Accurate determination is difficult because of multiplicity of peaks and overlapping of signals.

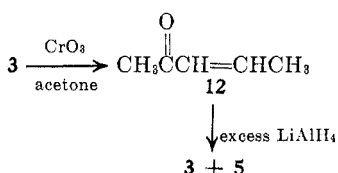τ 8.05 in ether) and keto (τ 7.79 in CDCl₃, τ 7.88 in ether) methyls, the keto methylenes (τ 6.39 in CDCl₃,

obscured in ether), and the enol –CH= (τ 4.42 in CDCl₃, τ 4.55 in ether).

The direction of elimination with the unsymmetrical 2,4-hexanedione (2) was in the favor of the ethyl-substituted olefin, 3-hexen-2-ol (6). This isomer predominated over 2-hexen-4-ol (7) by 2.5:1. This ratio was constant throughout several repetitive experiments.

The stereochemistry of the elimination is especially interesting; the products were trans in all cases. None of the cis olefins were observed, indicating an extraordinary degree of stereochemical control. The trans forms of the olefins are apparently the primary reaction products and do not result from rearrangement of the cis isomers, since cis-3-penten-2-ol was recovered unchanged when treated with LiAlH₄ under the same conditions employed for reduction of the dione. The corresponding keto alcohols and 1,3-diols were similarly
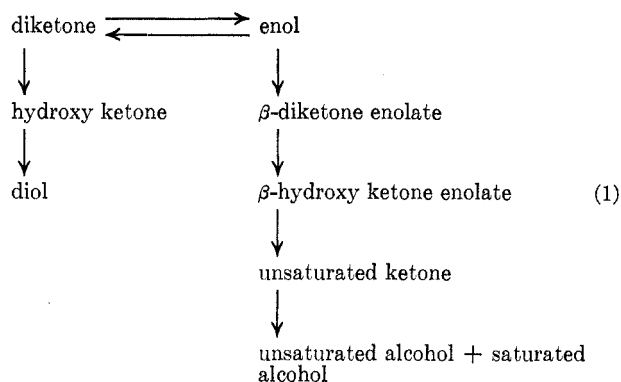
excluded as precursors of the transolefinic alcohols. Reduction of 4-hydroxy-2-pentanone (11) with excess LiAlH$_4$ gave a quantitative yield of 2,4-pentanediol (4).[9] No unsaturated alcohol was observed. In a separate experiment, 4 was recovered unchanged under the conditions of the reduction–elimination reaction.

Methyl propenyl ketone (3-penten-2-one, 12), however, could not be excluded as an intermediate to 3-penten-2-ol (3). In fact, evidence for its transitory presence during the reaction was obtained. When acetylacetone was treated with a limited quantity of LiAlH$_4$, 12 was obtained along with 3 in the ratio of 1:3.5.[12] In addition, when 12, prepared by chromic acid oxidation of 3, was allowed to react with LiAlH$_4$ under the reduction–elimination conditions, both 3 penten-2-ol (3) and 2-pentanol (5) were isolated. The stereochemistry of the double bond of all of these compounds was found by their nmr spectra (see Table II) to be trans and to remain so during all transformations. The amount of 5 (3%) was virtually the same as that obtained from the reduction–elimination of acetylacetone (Table I). The possibility that 5 might have arisen from 3 must be considered, since reduction of allyl alcohol to 1-propanol has been observed under forcing conditions.[13] However, 3 was recovered unchanged when subjected to the reaction conditions which produced 5 from both 1 and 12.

$$3 \xrightarrow[\text{acetone}]{CrO_3} CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH=CHCH_3$$
$$12$$
$$\downarrow \text{excess LiAlH}_4$$
$$3 + 5$$

Discussion

Our results are consistent with reaction path 1. The two forms of the diketones appear to react independently, the enolic portions giving rise predominantly to the elimination products 3, 6, and 7 along with the saturated alcohols 5, 9, and 10, while the diketo forms are reduced normally to the diols. This scheme is supported by the data in Table III and by the fact that we have shown that the intermediates which lead to the diols, *i.e.*, the hydroxy ketones, or the diols themselves are not converted to elimination products

(9) The 4-hydroxy-2-pentanone (11) was prepared in surprisingly good yield (50–60%) by the partial hydrogenation of acetylacetone over platinum black. Previous attempts to hydrogenate acetylacetone to the ketol in which other catalysts were employed have met with varying success. Poor yields were obtained using Raney nickel[10] while rhodium on carbon was more effective.[11] We found no difficulty in stopping at the ketol stage. Only under forcing conditions was some 2,4-pentanediol observed. It appears that good yields of hydroxy ketones such as 11 can be obtained by taking advantage of the high enol content of the diketone. The olefinic function apparently can be reduced preferentially. Our results suggest that platinum black in ethanol is a good choice of catalyst and solvent for this transformation.

(10) P. S. Stutsman and H. Adkins, *J. Amer. Chem. Soc.*, **61**, 3303 (1939).

(11) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, pp 265–266.

(12) The unsaturated ketone 12 was identified by gas chromatography (retention time identical with an authentic sample) and time-of-flight mass spectrometry. The intensity ratios of *m/e* 69:41 of near unity and the fact that the intensity of the parent peak (*m/e* 84) is about 30% of the *m/e* 69 peak strongly suggests the trans configuration for 12; see A. Cornu and R. Massot, "Compilation of Mass Spectral Data," Heyden and Sons Ltd., London, 1966.

(13) F. A. Hochstein and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3483 (1948).

diketone $\rightleftharpoons$ enol

$\downarrow$ $\downarrow$

hydroxy ketone   β-diketone enolate

$\downarrow$ $\downarrow$

diol   β-hydroxy ketone enolate   (1)

                       $\downarrow$

                unsaturated ketone

                       $\downarrow$

                unsaturated alcohol + saturated alcohol

under the conditions of the reaction. We also demonstrated that compounds resulting from reduction of the enol forms, the unsaturated ketones or unsaturated alcohols, do not give rise to any appreciable quantities of diols.[14]

The saturated alcohols 5, 9, and 10 arise from 1,4 addition of hydride to the enones 12, 16, and 17 which appear to be true intermediates in the reaction scheme. Several pieces of evidence point strongly in this direction. In the first place, compounds such as 12, 16, and 17 with carbonyl functions conjugated to double bonds, frequently afford 1,4 addition products when reduced by LiAlH$_4$ under forcing conditions.[13,15,16] Secondly, a trace of 12 was actually isolated in some of the acetylacetone reductions. Finally, when 12 was reduced under the same conditions as acetylacetone, 2-pentanol (5) was obtained in the identical amount, relative to 3-penten-2-ol (3), as in the case of the diketone. It appears that elimination of one oxygen occurs before reduction at the second.

Dreiding and Hartman postulated analogous intermediates in the reduction–elimination of alicyclic and aromatic β-dicarbonyl compounds.[1,4] However, their proposed mechanism has been criticized as failing to account for the formation of fully saturated products obtained in the reduction of malonic enolates, and evidence was given for a somewhat more complicated reaction scheme.[3a] In the case of malonic enolates, the reaction may take a somewhat different course.

In the case of the unsymmetrical dione (2), the reaction is somewhat more complicated as indicated by Scheme III. Here we have used a convenient cyclic representation for the intermediate enolate 13 although a noncyclic form involving two complexed aluminum atoms would serve as well. The initial hydride can be attached either to a or b, and it is this which ultimately determines the product distribution (*e.g.*, relative amounts of 6 and 9 *vs.* 7 and 10). The predominant attack occurs at b (adjacent to the ethyl group) which is the more electropositive site. An alternate scheme would involve representing the two possible enols 18 and 19 as existing and reacting separately. The relative amounts of 6 and 7 would then

(14) It has been suggested by a reviewer that the enolate of a β-hydroxy ketone, *e.g.*, 14 or 15, could be reduced to the corresponding diol. We feel this occurs to a very small extent if at all. We have no direct evidence for this but others[2,3a,4] have reported the complete absence of such reductions in the case of pre-formed enolates.

(15) N. B. Gaylord, "Reduction with Complex Metal Hydrides," Interscience, New York, N. Y., 1956, Chapter 15.

(16) J. C. Richer and R. Clarke, *Tetrahedron Lett.*, 935 (1964); M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, **19**, 1042 (1952); W. R. Jackson and A. Zurquiyah, *J. Chem. Soc.*, 5280 (1965).

SCHEME III

13

14

15

16

17

MH	MH
7 + 10	6 + 9
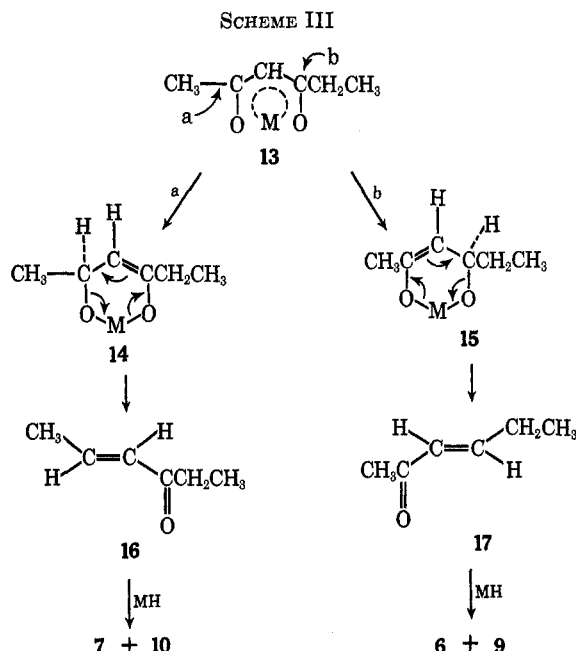
reflect the proportion of the two enolic forms (an allylic rearrangement occurs during the reaction so that **18** gives rise to **7** and **19** to **6**). Our results do not permit a choice between these two schemes.

18

19

16 ──→ 7 + 10	17 ──→ 9 + 6
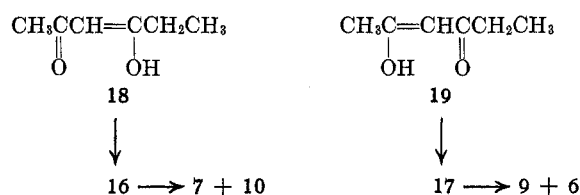
One of the most interesting aspects of the reaction is its high degree of stereospecificity. All of the unsaturated alcohols obtained were trans with no trace of the cis isomers observed. As discussed above, the configuration of the double bond in the final products is fixed by the elimination step (**14** → **16** or **15** → **17** in Scheme III). An examination of models as illustrated in structures **20** and **21** shows that there is considerably less crowding when the confirmation around the incipient double bond is trans than if it were cis. The transition state (**21**) for the formation of *cis*-**16** forces

21

20
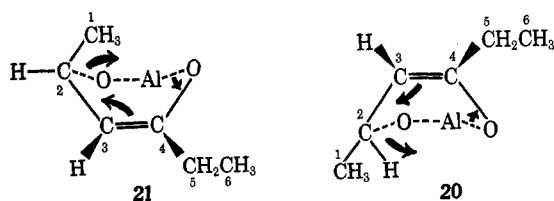
the 1-methyl group into close proximity to the oxygen at carbon 4 with the result of rather severe steric interactions. In the transition state (**20**) for the formation of *trans*-**16**, it is the hydrogen at carbon 2 that interacts with the oxygen at carbon 4, with a resulting reduction of steric crowding. An additional factor is the aluminum–oxygen bonding which we feel would constrain the intermediate **14** or **15** in a cyclic configuration and into a pseudoboat conformation. This would accentuate the interactions described above. It is most probably the formation of the aluminum–oxygen bonds

that provides most of the driving force for this elimination reaction.

The synthetic utility of the reduction–elimination reaction has been recognized in only a few instances[6,17] and in these cases the stereochemistry was not important. Because of its stereospecificity, however, the reaction should have considerable value in the preparation of pure trans-unsaturated alcohols. In such syntheses the yield of elimination product can be improved by conditions favoring a high degree of enolization in the parent dicarbonyl compound. This can frequently be accomplished by converting the starting material to its enolate prior to reduction with LiAlH$_4$[2,3,17] or by addition of substances to the reaction which stabilize the enol form of the dicarbonyl compound.[18] It should be emphasized that the effect of such additions on the stereochemical control of the reduction–elimination is not known.[19]

Experimental Section[20]

General.—Commercial acetylacetone (Matheson Co.) and 2,4-hexanedione (Eastman Kodak) were used without purification. Lithium aluminum hydride was obtained from Ventron, Inc., Beverly, Mass. The 2-pentanol, 2-hexanol, and 3-hexanol were obtained from the Matheson Co.; the 2,4-pentanediol from Frinton Laboratories. Authentic samples of *trans*-3-penten-2-ol and *trans*-2-hexen-4-ol were obtained from Aldrich Chemical Co. and J. T. Baker Chemical Co., respectively. The assigned stereochemistry of these samples was confirmed by independent synthesis and by comparison of their infrared traces with published spectra.[21] The reduction–elimination products were identified by comparison of gas chromatographic retention times and, where appropriate, ir and nmr spectra with those of authentic samples.

Reduction–Elimination of Acetylacetone (1) with LiAlH$_4$.— To a slurry of 13.0 g of LiAlH$_4$ in 100 cc of ether was added, dropwise, a solution of 10.0 g (0.1 mol) of acetylacetone in 100 cc of ether. The resulting mixture was refluxed for 16 hr after which the unreacted LiAlH$_4$ was decomposed by the successive addition of 13 ml of water, 10 ml of 20% NaOH, and 20 ml of water. The inorganic salts were filtered and washed with ether. The ether washings were combined and dried over MgSO$_4$, and the solvent was removed. An oily residue (9.4 g) remained. A 1.0-g portion of the residue was removed and analyzed by gas–liquid partition chromatography (glpc). The results are given in Table I. The remaining product was distilled. Two fractions were obtained. The first (6.1 g, bp 115–121.5°) was analyzed by glpc and found to contain 96% *trans*-3-penten-2-ol (**3**) and 4% 2-pentanol (**5**). No other materials were detected. The second fraction (pot residue, 2.0 g) was analyzed by glpc and nmr. The two methods were in excellent agreement and showed that the residue contained 50–52% *trans*-3-penten-2-ol (**3**) and 48–50% of what was probably a mixture of diastereomeric 2,4-pentanediols (**4**). After adjusting for the aliquot removed these two fractions amounted to a 96% recovery of products. A duplicate experiment gave virtually identical results.

(17) J. A. Marshall and N. Cohen, *J. Amer. Chem. Soc.*, **87**, 2773 (1965); J. A. Marshall and N. Cohen, *J. Org. Chem.*, **30**, 2475 (1965); J. A. Marshall and R. D. Carroll, *Tetrahedron Lett.*, 4223 (1965).

(18) For example, L. W. Reeves [*Can. J. Chem.*, **35**, 1351 (1957)] has shown that acetylacetone is converted totally to its enol form in the presence of triethylamine.

(19) Triethylamine, for example, forces enolization by coordinating strongly with the enol hydroxy group of acetylacetone.[18] This may inhibit formation of intermediates such as **15** and thereby reduce the stereospecificity of the reaction. In addition, as discussed above, the mechanism may be different in the case of pre-formed enolates.

(20) The nmr spectra were obtained on a Varian A-60 spectrometer and the infrared spectra on a Perkin-Elmer Model 137 spectrophotometer. Gas chromatographic separations were made on either a F & M 500 (tc detector), F & M 609 (flame ionization), or P & E 226 (capillary) gas chromatograph. A summary of columns used and retention times is given in Table IV.

(21) R. Heilmann, G. de Gaudemaris, and P. Arnaud, *Bull. Soc. Chim. Fr.*, 119 (1957).

TABLE IV

GAS CHROMATOGRAPHY DATA

Compd	A[c]	B[c]	C[d]	D[d]	E[e]	F[e]	G[e]
cis-3-Hexen-2-ol	21.5[f]			37.5[f]			
trans-3-Hexen-2-ol (6)	21.6[f]	9.8[g]	42.0[h]	33.5[f]	12.2[i]		
cis-4-Hexene-3-ol	22.7[f]						
trans-4-Hexen-3-ol (7)	20.4[f]	9.0[g]	40.0[h]		12.2[i]		4.0[i]
2-Hexanol (9)					9.5[i]		3.0[i]
3-Hexanol (10)					8.0[i]		2.8[i]
2,4-Hexanediol (8)							5.5[i]
cis-3-Penten-2-ol			22.5[h]		7.5[i]		
trans-3-Penten-2-ol (3)			21.0[h]	6.2[i]	7.0[i]	0.8[k]	
2-Pentanol (5)			14.0[h]	4.8[i]	5.0[i]		
2,4-Pentanediol (4)						5.0[k]	
Acetylacetone (1)					2.1[i]		
3-Penten-2-one (12)					6.0[i]		

[a] Column A, 50-ft capillary (0.02 in. i.d.) support coated with Carbowax 1540; B, 50-ft capillary (0.02 in. i.d.) support coated with Carbowax 600; C, 12-ft stainless steel Chromosorb W; D, 10-ft stainless steel (0.25 in. i.d.) packed with 10% Carbowax 20M on Chromosorb W; E, 10-ft stainless steel (0.25 in. i.d.) packed with 10% Carbowax 20M on Chromosorb W; F, 6-ft stainless steel (0.25 in. i.d.) packed with 10% Carbowax 20M on Chromosorb W; G, 4-ft stainless steel (0.25 in. o.d.) packed with 10% Carbowax 20M on Chromosorb W. [b] Du Pont Model 310 curve resolver was used in resolution. [c] Used in P & E Model 226 capillary gas chromatograph, flame ionization detector. [d] Used in F & M Model 609 gas chromatograph, flame ionization detector. [e] Used in F & M Model 500 gas chromatograph, tc detector. [f] At 50°. [g] At 70°. [h] At 40°. [i] At 75°. [j] At 100°. [k] At 125°.

Reduction–Elimination of 2,4-Hexanedione (2) with LiAlH₄.— The reduction was carried out with 11.4 g (0.1 mol) of 2,4-hexanedione (2) and 6.5 g of LiAlH₄ as described above except that the entire reaction mixture was distilled. (Before distillation the crude mixture was analyzed by glpc. The results are shown in Table I.) Three fractions were collected, weighed, and analyzed by glpc. The first (0.55 g, bp 100–139°) consisted of 60% of a mixture of unsaturated alcohols 6 and 7 and a small amount of 2- and 3-hexanol (9) and (10), 40% of solvent, and a small amount of unreacted 2. Fraction two (6.0 g, bp 139.5–140°) consisted of 90% of the two unsaturated alcohols, 8.5% of 9 and 2.0% of 10, and less than 0.5% of trace impurities. The third fraction was the pot residue; it was analyzed by glpc and nmr and was shown to be 95% 2,4-hexanediol (8) (probably a mixture of erythro and threo forms)[7] and 5% of a mixture of unsaturated and saturated alcohols similar to fraction two. The product recovery amounted to 79%. The two unsaturated alcohols, 6 and 7, were not separable readily by distillation. Each of the above fractions and the crude product mixture were analyzed by glpc using various columns and conditions (see Table IV). In every case the mixture consisted of 71% *trans*-3-hexen-2-ol (6) and 29% *trans*-4-hexen-3-ol (7). None of the corresponding cis isomers were detected.

The reaction was repeated with similar results except that only a 65% recovery of reaction products was obtained.

Reduction of 12 with LiAlH₄.—To 2.2 g of LiAlH₄ in 25 ml of anhydrous ether was added 2.0 g of 12 in 25 ml of anhydrous ether. The reaction was refluxed overnight and worked up as described above. The product was shown by glpc to contain 95.5% 3, 3.5% 5, and 1% 1,3-pentadiene (see footnote e, Table I).

4-Hydroxy-2-pentanone was prepared by reduction of 40 g of 1 in 150 ml of absolute ethanol over a total of 5.5 g of PtO₂. The catalyst was added in five equal portions during the uptake of 1 molar equiv of hydrogen. The product was distilled after

removal of the catalyst and solvent. It amounted to a 92% yield, bp 110–112° (90 mm) [lit.[22] bp 74–75° (18 mm)].

Reaction of 2,4-Pentanediol (4) with LiAlH₄.—The diol 4, in ether, was refluxed overnight with excess LiAlH₄. The reaction was worked up as described above and the crude mixture was analyzed by glpc. Only unchanged starting material was isolated.

Reduction of 4-Ketopentanol-2 (11) with LiAlH₄.—To a vigorously stirred suspension of 3.2 g of LiAlH₄ in 50 ml of ether was added, dropwise, 2.5 g of 11. The resulting mixture was refluxed overnight and worked up as described. The crude reaction mixture was shown by glpc analysis to contain only 2,4-pentanediol (4).

Reaction of *cis*-3-Penten-2-ol with LiAlH₄.—A solution of 1.3 g of *cis*-3-penten-2-ol (contaminated with 15% of the trans isomer) in 10 ml of ether was dropped into a vigorously stirred slurry of 1.8 g of LiAlH₄ in 20 ml of ether. The resulting mixture was refluxed overnight and worked up as described above. The solvent was removed by distillation and the residue was analyzed by glpc (Table IV). It contained the identical mixture of *cis*-(85%) and *trans*- (15%) 3-penten-2-ol as the starting material.

(22) V. I. Esafov, *Zh. Obshch. Khim.*, **33**, 3755 (1963).