nmr data. Infrared analysis showed conclusively that III rather than IV is the correct structure. The infrared spectrum of the compound in question was identical in every detail with the spectrum of *cis*-bicyclo[3.3.0]oct-2-ene published by Germain and Blanchard.[14]

Corroboration of structure III was obtained from the hydrogenation of the compound over palladium on charcoal (1.01 mole of hydrogen per mole of III was consumed). The resulting product was *cis*-bicyclo[3.3.0]octane whose infrared spectrum was identical with that published by Roberts and Gorham for the authentic material.[15] It should be noted that the infrared spectrum for *trans*-bicyclo[3.3.0]octane differs considerably from that of the *cis* compound.[15]

Hydrogenation of 2-Pentyne.—One-hundred mmoles of 2-pentyne in 40 ml of THF was hydrogenated at 190° under 1600 psi of hydrogen in the presence of 20 mmoles of a metal hydride catalyst. With sodium hydride catalyst and a 1.0-hr reaction time, the product composition was 1,2- and 2,3-pentadiene, 4.4%; *n*-pentane, 0.7%; 1-pentene, 2.3%; *cis*-2-pentene, 19.0%; *trans*-2-pentene, 1.9%; and 2-pentyne, 71.7%. With potassium hydride catalyst and a 0.7-hr reaction time, the product composition was 1,2- and 2,3-pentadienes, 13.2%; *n*-pentane, 9.0%; 1-pentene, 16.8%; *cis*-2-pentene, 3.6%; *trans*-2-pentene, 1.0%; 2-pentyne, 56.4%; and dimer, trace. With lithium hydride catalyst and a 0.5-hr reaction time, the product composition was *n*-pentane, 3.0%; 1-pentene, 0.4%; *cis*-2-pentene, 23.5%; *trans*-2-pentene, 2.0%; and 2-pentyne, 71.1%.

Hydrogenation of 1,3-Pentadiene. Tracer Studies.—The hydrogenation of the substrate over lithium deuteride is described in the text. The relative amounts of the deuterated pentenes were determined by mass spectrometry. A 96.5% conversion of the diene into 20% *n*-pentane and 80% pentenes was obtained in 0.3 hr. The *n*-pentane was composed of 85% C_5H_{12}, 14% $C_5H_{11}D$, and 1% $C_5H_{10}D_2$. See text for the pentene analysis.

Fifty mmoles of the diene in 40 ml of THF was treated with deuterium gas (685 psi) at 190° in the presence of 224 mmoles of lithium hydride. After 1.3 hr, 43.5% of the diene had been converted into a mixture of pentenes. The deuterium content of the latter was C_5H_{10}, 7.1%; C_5H_9D, 34%; $C_5H_8D_2$, 49%; $C_5H_7D_3$, 7.3%; $C_5H_6D_4$, 1.6%; $C_5H_5D_5$, 0.5%; and $C_5H_4D_6$, 0.1%.

With similar quantities of reagents, 1,3-pentadiene was 100% converted mainly into pentenes in 2.6 hr at 190–225° in the presence of deuterium gas and sodium hydride. The pentene consisted of 1.9% C_5H_{10}, 17% C_5H_9D, 65% $C_5H_8D_2$, 13.5% $C_5H_7D_3$, 2.1% $C_5H_6D_4$, and 0.6% $C_5H_5D_5$.

The product from a similar experiment with potassium hydride (0.2 hr) gave a pentene product which consisted of 4.3% C_5H_{10}, 27% C_5H_9D, 49.5% $C_5H_8D_2$, 16% $C_5H_7D_3$, 2.8% $C_5H_6D_4$, 0.4% $C_5H_5D_5$, and 0.1% $C_5H_4D_6$.

Hydrogenation of Bicyclo[2.2.1]heptadiene.—Twenty mmoles of a metal hydride catalyst was used for the hydrogenation of 100 mmoles of the topic diene in 40 ml of THF. With sodium hydride at 190°, the diene was 90% converted in 5.5 hr into a product consisting of 50.1% bicyclo[2.2.1]heptene, 42.9% nortricyclene, and 7.0% unidentified dimers. With potassium hydride at 190°, the diene was 91% converted in 0.3 hr into a product having a similar composition as above. With potassium hydride at 150° for 2.3 hr, a 100% conversion was obtained; the product consisted of 76% bicyclo[2.2.1]heptene, 23% nortricyclene, and 0.8% dimer.

The isomerization of bicyclo[2.2.1]heptene to nortricyclene also was examined. One-hundred mmoles of the olefin and 20 mmoles of potassium hydride in 40 ml of THF were heated at 190° for 1.3 hr. Only 4.8% of the olefin was converted into nortricyclene.

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[14] J. E. Germain and M. Blanchard, *Bull. Soc. Chim. France*, 473 (1960).

[15] J. D. Roberts and W. F. Gorham, *J. Am. Chem. Soc.*, **74**, 2278 (1952).

The Reduction of Malonic Enolates with Lithium Aluminum Hydride

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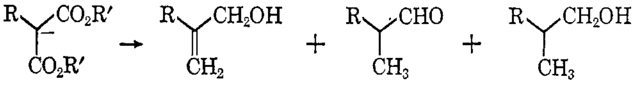
Diethyl cyclohexylmalonate (**1**) and the corresponding sodio derivative **3** were reduced with lithium aluminum hydride. The free ester afforded 2-cyclohexylpropane-1,3-diol in 95% yield, whereas the derived enolate **3** gave a mixture of 2-cyclohexylpropanal (**4**), 2-cyclohexyl-2-propen-1-ol (**5**), and 2-cyclohexylpropan-1-ol (**7**). The relative amounts of these products varied with the method of work-up. A reaction scheme which accommodates these findings is presented and critically examined.

Enolizable 1,3-dicarbonyl compounds frequently afford products of reduction and elimination upon treatment with lithium aluminum hydride. This reaction, first recognized for β-keto esters and β-keto aldehydes by Dreiding and Hartman,[3] also takes place with β-diketones[4] and, less readily, with malonic esters.[5] Dreiding and Hartman[3] correctly surmised that the reduction–elimination reaction depended upon the initial formation of an enolate. Subsequently, Eschenmoser and his co-workers showed that the enolate prepared from a β-keto ester with sodium hydride underwent reduction with nearly exclusive formation of the elimination product.[6] We applied this modified reduction–elimination procedure to monosubstituted malonic esters and thereby were able to prepare allylic alcohols possessing key structural features of certain natural products.[7] However, the yields of desired materials usually suffered owing to the formation of aldehydes and saturated alcohols as significant by-products in these reductions. Similarly, we also noted



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[1] National Science Foundation Predoctoral Fellow, 1964–1966.

[2] National Institutes of Health Predoctoral Fellow 1965–present.

[3] A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953); J.-C. Richer and R. Clarke, *Tetrahedron Letters*, **No. 16**, 935 (1964).

[4] *Cf.* G. Stork and F. H. Clarke, Jr., *J. Am. Chem. Soc.*, **83**, 3114 (1961); A. S. Dreiding and J. A. Hartman, *ibid.*, **75**, 3723 (1953).

[5] W. J. Bailey, M. E. Hermes, and W. A. Klein, *J. Org. Chem.*, **28**, 1724 (1963). For a particularly favorable case, see W. F. Gannon, and E. A. Steck, *ibid.*, **27**, 4137 (1962).

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

[7] J. A. Marshall and N. Cohen, *J. Am. 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 Letters*, 4223 (1965).

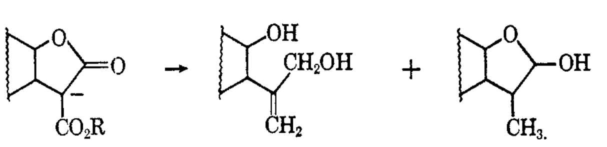
TABLE I

REDUCTION OF DIETHYL SODIOCYCLOHEXYLMALONATE (3)[a]

Entry	$LiAlH_4$[b]	Time, hr	Work-up[c]	U[d]	Products, %				1,4 redn,[e] %	1,2 redn,[e] %
					Esters 1 and 10	Aldehyde 4	Allylic Alcohol 5	Satd alcohol 7		
1[f]	3.7	3–4	A	5	...	1	70	24	26.5	73.5
2[f]	2.6	4	A	2	...	1	72	25	27	73
3[f]	2.0	4	A	4	...	5	73	18	25	75
4	2.1	4	A	5	...	2	72	21	24	76
5	0.8	10	A	10	12, 1	14	62	1	19	81
6	2.1	4	A_i	6	...	16	70	8	25	75
7[f]	2.1	4	B	6	...	5	86[g]	3[g]	9	91
8	0.8	9.5	B	8	16, ..	7	68[g]	1[g]	10	90
9[f]	2.1	4	C_m	8	...	4	78[h]	10[h]	16	84
10	2.1	4	C_e	7	...	5	77[h]	11[h]	17	83

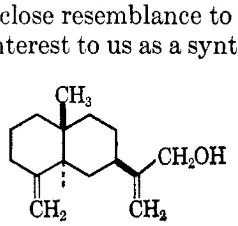
[a] Reductions were performed in refluxing 1,2-dimethoxyethane. [b] Moles of $LiAlH_4$ per mole of malonate 3. [c] A = direct addition of water, A_i = inverse addition of water, B = addition of ethyl formate, C_m = addition of dimethyl carbonate, C_e = addition of diethyl carbonate. [d] Total amount of extraneous materials observed as three to four peaks in the gas chromatograms (see the Experimental Section). [e] Excluding the extraneous materials. [f] Duplicate experiments. Agreement to ±2% was generally observed. [g] Adjusted to account for the formation of the corresponding formate. [h] Adjusted to account for the formation of the corresponding carbonate.

that reductions of α-carboalkoxy-γ-butyrolactone enolates afford appreciable quantities of lactols.



Since the postulated mechanism for reduction–elimination reactions[3] fails to account for the formation of the observed saturated products, we decided to examine the malonic enolate reduction more closely in the hope of shedding some light on the various reaction pathways. This report presents a scheme for the genesis of these by-products and describes an experimental modification for improving the yields of allylic alcohols.

Diethyl cyclohexylmalonate (1) seemed well suited for these studies since the expected products could be easily prepared, readily identified, and precisely analyzed. Moreover, the expected major product, allylic alcohol **5**, bears a close resemblance to costol,[8] a natural product of some interest to us as a synthetic objective.[9]



costol

Before investigating the reduction of malonic enolate **3** we looked into the behavior of the free ester **1** toward lithium aluminum hydride. As expected, this ester afforded 2-cyclohexylpropane-1,3-diol (**2**) as the principal reduction product. In contrast, reduction of the corresponding enolate **3** gave a mixture of products containing mainly allylic alcohol **5** along with lesser amounts of aldehyde **4** and saturated alcohol **7** (Table I). In addition, small quantities of unidentified components were detected. These substances appear to arise chiefly from minor impurities in the starting material and, to a lesser extent, from hydrogenolysis of the alcoholic products. Authentic samples of the major reduction products were secured from the product mixtures as follows (see Scheme I). The entire mixture was first treated with manganese dioxide[10] giving a mixture rich in unsaturated aldehyde **11**. After purification *via* the semicarbazone derivative, aldehyde **11** was reduced with ethereal lithium aluminum hydride thus affording an authentic sample of allylic alcohol **5**. Catalytic hydrogenation smoothly converted unsaturated aldehyde **11** into its dihydro derivative **4**. Saturated alcohol **7** was obtained *via* hydrogenation of the malonic enolate reduction mixture. The spectral properties of these compounds supported their assigned structures (see the Experimental Section). Comparison of these substances with the products obtained from the reductions of malonic enolate **3** was achieved through gas chromatography by peak enhancement and the identities of the various peaks were substantiated by preparative gas chromatography.

SCHEME I

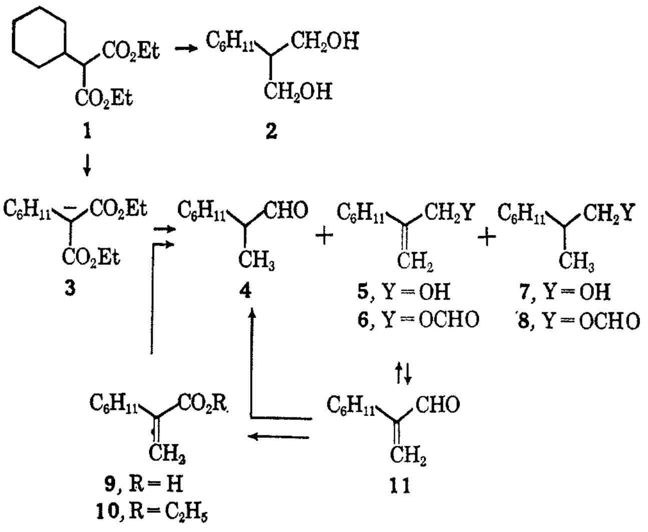


Table I summarizes experiments conducted with diethyl sodiocyclohexylmalonate in order to determine the effects of certain variables on the product distribution. Only slight variations in product composi-

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(8) V. Benešová, V. Herout, and F. Šorm, *Collection Czech. Chem. Commun.*, **24**, 2365 (1959).

(9) J. A. Marshall, M. Pike, and R. D Carroll, *J. Org. Chem.*, **31**, 2933 (1965).

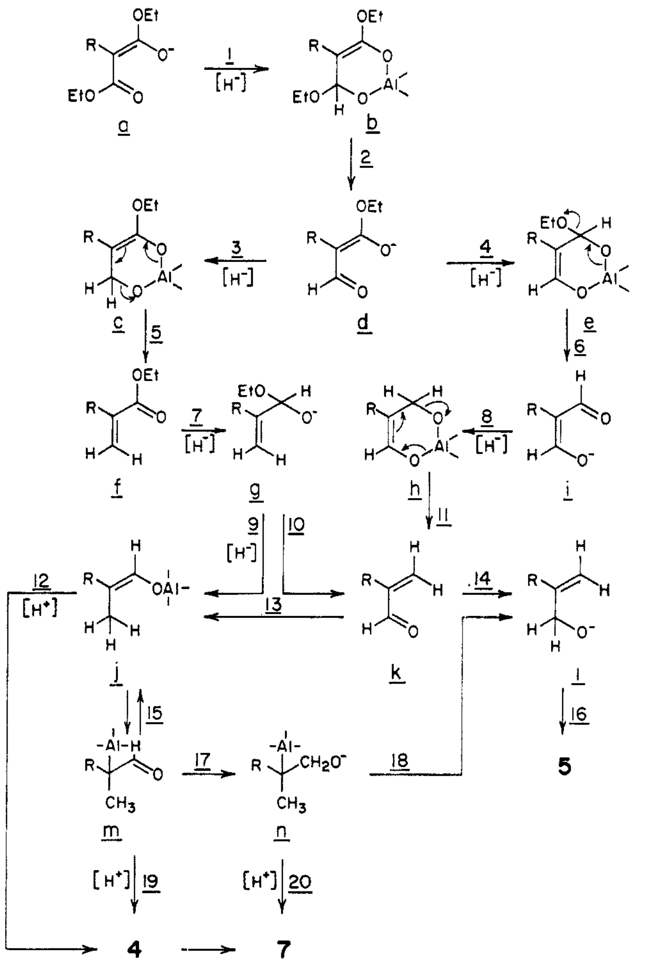
(10) D. Herbst and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 4337 (1960).

tion were noted for changes in the molar ratio of lithium aluminum hydride to malonic enolate **3** ranging from 3.7 to 2.0 (entries 1–4). In experiments employing less than the stoichiometric quantity of reducing agent (entry 5) the percentage of saturated alcohol **7** decreased markedly and the amount of aldehyde **4** increased correspondingly. These observations raised the possibility that the enolate of aldehyde **4**[11] might undergo sufficiently rapid protonation upon addition of water during the work-up procedure to enable the resulting aldehyde to compete favorably with water for the excess hydridic species which might still be present. In testing for this possibility, we quenched a sample of a reduction mixture containing excess reducing agent by injection into rapidly stirred ice–water (entry 6). Here, as in the experiment where insufficient hydride was employed (entry 5), aldehyde **4** predominated over saturated alcohol **7**.

Hoping to destroy the excess lithium aluminum hydride and other active hydridic species while maintaining an aprotic reaction medium, we treated the sodiomalonate reduction mixture with ethyl formate before adding water (entry 7).[12] In keeping with the aforementioned postulate, the percentage of saturated alcohol **7** decreased markedly when this modification was made. Surprisingly, the percentage of aldehyde **4** likewise decreased, whereas the percentage of allylic alcohol **5** sharply increased. Thus, the ratio of 1,2 to 1,4 reduction appears significantly affected by the work-up procedure. Table I shows that this ratio (*ca.* 75:25) remains essentially constant when reaction mixtures are quenched with water whereas a higher proportion of 1,2-reduction products (*ca.* 90:10) results when ethyl formate is similarly used, even with insufficient reducing agent (entry 8). Carbonic esters likewise suffice, but less efficiently (entries 9 and 10). These findings point to the unexpected conclusion that nonenolizable esters can essentially convert aldehyde **4** (most likely in the form of its enolate) into allylic alcohol **5** under work-up conditions. The superiority of ethyl formate over diethyl carbonate suggests that steric and/or electronic factors may influence such conversions. In fact, the somewhat higher ratio of 1,2- to 1,4-reduction products obtained using insufficient hydride followed by an aqueous work-up (entry 5) may also reflect this same phenomenon since here a portion of the starting ester (as enolate **3**) remained in the reduction mixture. The small percentage of saturated alcohol which stubbornly persists even under the most favorable 1,2-reduction conditions, could result in part from reduction of aldehyde **4** by the residual alkoxyaluminohydrides upon addition of water, or possibly *via* a direct pathway (see below).

Scheme II shows various stepwise reduction pathways by which the observed products **4**, **5**, and **7** can arise from malonic enolate **3**. For the sake of clarity, some of the species are depicted as cyclic aluminum structures although two aluminum (and/or lithium) atoms could actually be involved in a noncyclic intermediate. Steps 1 and 2 portray the first stage of reduction in which malonic enolate a affords formylacetic anion d *via* the tetrahedral intermediate b. This intermediate could subsequently react with hydride at the aldehyde grouping (step 3) giving the tetrahedral intermediate c which could then undergo elimination to unsaturated ester f as pictured for step 5. Alternatively, enolate d could react at the ester grouping (step 4) *via* intermediate e to give the malonic dialdehyde enolate i (step 6) which upon subsequent reduction (step 8) and elimination (step 11) affords the unsaturated aldehyde k. Unsaturated ester f could also give k by the usual reduction sequence (steps 7 and 10). According to this scheme, the ultimate reduction products of malonic enolate **3** should be obtainable solely from unsaturated ester **10** and unsaturated aldehyde **11**.

SCHEME II



In fact, under the conditions used to reduce enolate **3**, aldehyde **11** afforded allylic alcohol **5** as virtually the exclusive product (Table II, entry 1). In sharp contrast, unsaturated ester **10** gave only 10% **5** and appreciable amounts of saturated aldehyde **4** (48%) and saturated alcohol **7** (40%) under these conditions (Table II, entry 2). Thus it appears that the predominant reduction pathway for malonic enolate **3** proceeds *via* unsaturated aldehyde **11** (k in Scheme I) without passing through unsaturated ester **10** (f in Scheme II).

The question remains as to the genesis of aldehyde **4** and alcohol **7**. As noted above, alcohol **7** seems to

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(11) Ketone enolates resist reduction by lithium aluminum hydride.[8] See, also, W. G. Dauben and J. F. Eastham, *ibid.*, **75**, 1718 (1953).

(12) Control experiments showed that ethyl formate consumed three of the four hydrides of lithium aluminum hydride. Presumably, then, lithium trialkoxyaluminohydrides are formed at this stage of the work-up and the ultimate suppression of alcohol **7** still depends upon the affinity of these hydrides for aldehyde **4** *vs.* water in the second stage of the work-up. *Cf.* H. C. Brown and N. M. Yoon, *ibid.*, **88**, 1464 (1966); H. C. Brown and C. J. Shoaf, *ibid.*, **86**, 1079 (1964).

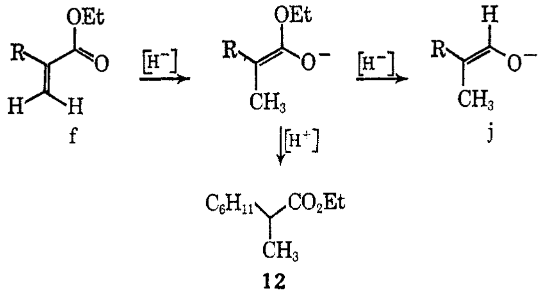
Table II

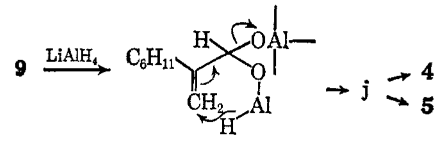
Reduction of Conjugated Carbonyl Compounds[a]

				Products, %					
Entry	Substrate	$LiAlH_4$[b]	Work-up[c]	U[d]	Aldehyde **4**	Allylic alcohol **5**	Satd alcohol **7**	1,4 redn,[e] %	1,2 redn,[e] %
1[f]	Aldehyde **11**	3.5	A	...	..	98	2	2	98
2[f]	Ester **10**	2.1	A	3	48	9	40	91	9
3[f]	Ester **10**	2.1	B	1	63	24[g]	12[g]	75	25
4[f]	Acid **9**	2.3	A	1	8	46	45	54	46
5[f]	Acid **9**	2.3	B	2	21	64[g]	13[g]	35	65

[a] Reductions were performed in refluxing 1,2-dimethoxyethane for 2 hr. [b] Moles of $LiAlH_4$ per mole of substrate. [c] A = direct addition of water, B = direct addition of excess ethyl formate followed by water. [d] Total amount of unidentified material observed as three to four peaks in the gas chromatogram. [e] Excluding the unidentified materials. [f] Duplicate experiments. Agreement to ±2% was generally observed. [g] Adjusted to account for the formation of the corresponding formate.

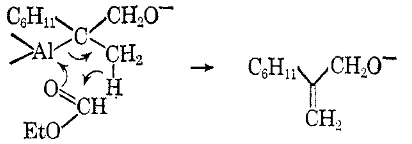
stem mainly from aldehyde **4** when water is used in the reduction work-up (Table I, compare entries 1–4 with 5–7). Referring to Scheme II, step 13 appears unimportant as a route to j, the enolate precursor of aldehyde **4**, since authentic aldehyde **11** shows little tendency to undergo 1,4 reduction. In considering alternative pathways to j we can suggest two possibilities starting from unsaturated ester f. The first of these involves initial 1,2 reduction of ester f followed by SN2′ hydrogenolysis (step 9) of the tetrahedral intermediate g. Alternatively, f could undergo 1,4 reduction giving the enolate related to the corresponding ester (*i.e.*, **12**) which would undergo subsequent reduction as depicted. In view of the known resistance of enolates to the reducing action of lithium aluminum hydride[3] and our failure to isolate significant amounts of the saturated ester **12**, this latter pathway to aldehyde **4** appears unlikely. Moreover, we obtained appreciable amounts of aldehyde **4** and saturated alcohol **7** from reductions of the unsaturated acid **9** with lithium aluminum hydride (Table II, entries 4 and 5). In this case conjugate addition of hydride to the corresponding salt appears *a priori* less attractive than SN2′ hydrogenolysis of the intermediate corresponding to g (Scheme II) as shown below. Evidently, this process occurs less readily with acids than with esters.





In keeping with the trend observed for malonic enolate **3** (*cf.* Table I, entry 4 *vs.* 7), the addition of ethyl formate to reduction mixtures derived from unsaturated ester **10** resulted in a higher ratio of 1,2- to 1,4-reduction products as well as a larger percentage of aldehyde **4** than when water was added directly (Table II, entry 2 *vs.* 3). Again, the formation of saturated alcohol **7** could not be completely suppressed.

These observations implicate an intermediate which can directly yield saturated alcohol **7** (favored when water is added) or allylic alcohol **5** (favored when ethyl formate is added) depending on the work-up procedure. An intermediate such as n arising *via* reduction (step 17) of species m, the aluminum tautomer[13] of aldehyde enolate j, accommodates these findings. The enolate resulting from 1,4 reduction of unsaturated ester f could likewise afford n. Protonation of this organoaluminum would then yield saturated alcohol **7** directly whereas allylic alcohol **5** could arise by the elimination process depicted below.[14] The aldehyde enolate j could arise through an analogous elimination process.



Evidence supporting the postulated enolate j and also compatible with m and n was secured through deuterium labeling experiments. Thus addition of deuterium oxide to the reduction mixtures from malonic enolate **3** and unsaturated ester **10** afforded typical mixtures of aldehyde **4**, allylic alcohol **5**, and saturated alcohol **7**. These product mixtures were treated with lithium aluminum hydride and the saturated alcohol was isolated by means of preparative gas chromatography. The mass spectrum indicated the predominant incorporation of one deuterium atom whose placement at C-2 was clearly indicated by the nmr spectrum (see the Experimental Section).

In the final analysis, malonic enolate reductions proceed through a fairly complex series of steps. The derived α,β-unsaturated esters (*e.g.*, f) and α,β-unsaturated aldehydes (*e.g.*, k) are very likely intermediates with the latter playing the principal role. The former appear to account for the anomalous reduction products, namely aldehyde **4** and saturated alcohol **7** in the case at hand. Aldehyde **4** comes primarily from unsaturated ester **10** *via* a two-step reduction process as pictured in Scheme II (f → j), whereas the majority of saturated alcohol **7** arises from aldehyde **4** in a post-reduction step which takes place during

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(13) A similar intermediate has been postulated in reductions of enol acetates with lithium aluminum hydride.[11] See also, M. M. Rogic, *Tetrahedron*, **21**, 2823 (1965).

(14) For an analogy involving alkylboranes, see B. M. Mikhailov, Y. N. Bubnov, and V. G. Kiselev, *J. Gen. Chem., USSR*, **36**, 62 (1966).

hydrolytic work-up. An alkylaluminum species (*cf.* n in Scheme II) may also yield a small percentage of alcohol **7**. The most surprising finding of this study concerns the direct influence of the work-up procedure over the ratio of 1,2- to 1,4-reduction products. Though unexpected, this finding can be explained within the framework of Scheme II (n → l).[15]

Undoubtedly the picture is made even more complex by the presence of mixed hydrides (alkoxyaluminohydrides)[12] whose reducing properties vary with the nature and number of alkoxy substituents. We are very likely dealing with complexes which have limited solubility in the reduction medium, particularly where insufficient hydride is employed. Consequently, product ratios may depend upon the concentration of reagents, the reaction temperature, and the nature of the solvent. In fact, unsaturated ester **10** gives up to 52% allylic alcohol **5** when the reduction is carried out in ether followed by ethyl formate, whereas only 24% of this product is obtained under similar conditions in 1,2-dimethoxyethane.

Finally it should be mentioned that allylic alcohol **5** on prolonged refluxing (48 hr) with lithium aluminum hydride is partially converted into saturated alcohol **7**. However, under the reduction conditions employed in Tables I and II, this pathway can account for no more than a 2% yield of **7**.

Experimental Section[16]

Reductions of Diethyl Sodiocyclohexylmalonate 3 with Lithium Aluminum Hydride.—The following procedures were employed for the reductions summarized in Table I.

A solution of 3.68 g of diethyl cyclohexylmalonate[17] in 25 ml of 1,2-dimethoxyethane was stirred with 0.88 g of 50% sodium hydride–mineral oil dispersion at reflux until gas evolution ceased (1–2 hr). To the cooled mixture was added lithium aluminum hydride (0.8–3.7 mole equiv of hydride calculated on the basis that reduction of **3** theoretically requires 1 mole of $LiAlH_4$) after which the reflux temperature was maintained with stirring. After the stated time, the mixture was cooled and subjected to one of the following work-up procedures.

A.—A 75-ml portion of ether was added followed by aqueous sodium hydroxide.[16a] The granulated salts were filtered and the filtrate was analyzed by gas chromatography. The following retention times were observed using the $^1/_8$ in. × 20 ft column[16b] at 200° with a helium flow rate of 22 cc/min: aldehyde **4**, 8.7; alcohol **7**, 17.0; and allylic alcohol **5**, 20.6 min. Material balances of 80–90% were obtained when these mixtures were distilled.

A$_1$.—A portion of the reaction mixture was removed with a hypodermic syringe and slowly injected into rapidly stirred ice–water. The mixture was thoroughly extracted with ether after the addition of Rochelle's salt to complex the aluminum gel.

B.—An ethereal solution containing *ca.* 2 molar equiv of ethyl formate (based on initial hydride) was added. After 15–20 min, aqueous sodium hydroxide[16a] was added and method A was followed. Under these conditions, two new peaks were observed in the gas chromatogram at 12.8 and 13.6 min. These were probably the formates **8** and **6**, respectively, since treatment with lithium aluminum hydride or saponification caused their disappearance with a corresponding increase in the quantities of alcohols **7** and **5**. These formates were formed in about 10% yield and appear in Table I as the related alcohols **7** and **5**.

C.—Diethyl carbonate was used to consume the excess hydride in the manner of work-up B. Carbonates analogous to formates **6** and **8** were observed in the gas chromatograms of the resulting products. These materials gave the respective alcohols **5** and **7** upon reduction with lithium aluminum hydride. They appear as their related alcohols in Table I.

Reductions of 2-Cyclohexylpropenal (11), Ethyl 2-Cyclohexylpropenoate (10), and 2-Cyclohexylpropenoic Acid (9) with Lithium Aluminum Hydride.—The following procedures were employed for the reductions outlined in Table II for unsaturated aldehyde **11**, ester **10**, and acid **9**.

To a refluxing solution of lithium aluminum hydride in 1.7 ml of 1,2-dimethoxyethane was added by hypodermic syringe, 1 mmole of the carbonyl compound in 1 ml of the same solvent. After 2 hr, the mixture was subjected to one of the work-up procedures outlined above for the reduction of malonic enolate **3**. The results of these experiments appear in Table II.

When the above procedure was followed with ester **10** using ether as the solvent a mixture of aldehyde **4** (36%), alcohol **5** (31%), and alcohol **7** (32%) was obtained *via* work-up A. Work-up B afforded aldehyde **4** (35%), alcohol **5** (52%), and alcohol **7** (10%).

2-Cyclohexylpropane-1,3-diol (2).—A mixture containing 0.98 g of diethyl cyclohexylmalonate (**1**)[17] and 0.3 g of lithium aluminum hydride in 80 ml of anhydrous ether was stirred at room temperature for 16 hr. Work-up with aqueous sodium hydroxide[16a] gave 0.59 g (91%) of diol **2**, mp 80–86°. The analytical specimen, mp 91–92°, was obtained after two recrystallizations from ethyl acetate: λ_{max}^{KBr} 3.01 (OH), 8.98, 9.54, 9.79, 10.13, and 10.46 μ.

Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47. Found: C, 68.3; H, 11.5.

2-Cyclohexylpropanal (4).—A mixture containing 1.08 g of unsaturated aldehyde **11**, 10 ml of ethanol, and 0.20 g of 5% palladium on carbon was stirred in an atmosphere of hydrogen until the theoretical volume had been taken up. The mixture was filtered and distilled giving 0.83 g (76%) of aldehyde **4**: bp 75° (bath temperature) (15 mm); λ_{max}^{film} 3.69 (aldehyde CH), 5.80 (CO), 9.94, and 11.24 μ; $\delta_{TMS}^{CCl_4}$ 9.54 (CHO, doublet, J = 2 cps), and 1.01 ppm (CH_3, doublet, J = 7 cps). The 2,4-dinitrophenylhydrazone exhibited mp 110–111° (lit.[18] mp 110–111°).

2-Cyclohexyl-2-propen-1-ol (5). A. From the Malonic Enolate 3.—To a stirred suspension of 12 g of 50% sodium hydride–mineral oil dispersion in 340 ml of 1,2-dimethoxyethane was added 50.0 g of diethyl cyclohexylmalonate (**1**). The mixture was maintained at reflux and stirred for 6 hr, whereupon 20.5 g of lithium aluminum hydride was added to the cooled mass. After the initial reaction had subsided, the mixture was brought to reflux and stirred for 3 hr. The cooled slurry was diluted with 1 l. of ether, 110 ml of water was carefully added, and the precipitated salts were rendered granular by stirring. After filtration the mixture was distilled, bp 90° (25 mm) to 100° (15 mm), affording 25.2 g (87%). Analysis by gas chromatography[16b] gave the composition of this material as aldehyde **4** (1%), allylic alcohol **5** (71%), saturated alcohol **7** (26%), and unidentified materials (2%).

The **phenylurethan** derivative was recrystallized from hexane. The analytical sample exhibited mp 59–60.5°.

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.49; H, 7.77; N, 5.41. Found: C, 74.4; H, 8.1; N, 5.3.

The above procedure was carried out on 12.0 g of malonate **2** except that 18.5 g of ethyl formate was added after the reduction was complete. Work-up as above followed by reduction of the formates ($LiAlH_4$) and distillation afforded 6.0 g (86%), bp

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[15] Alternatively, aldehyde m could undergo elimination to unsaturated aldehyde k by an analogous process (see above).

[16] (a) Unless otherwise stated, lithium aluminum hydride reduction mixtures were decomposed by adding 2.0 ml of water and 1.6 ml of 10% aqueous sodium hydroxide for each 1 g of the reducing agent. The mixture was stirred until the salts became granular, then it was filtered, and the solvent was removed from the filtrate under reduced pressure. When 1,2-dimethoxyethane was employed as the solvent, the reaction mixture was diluted with twice its volume of ether before the aqueous base was added. (b) Gas chromatographic analyses were performed on an F & M Model 700 instrument using a $^1/_8$ in. × 20 ft column packed with 16% Carbowax 20 M on 60–80 Diatoport S or on a Model 720 instrument using a 0.25 in. × 16 ft column packed with the same material. The Model 700 instrument was equipped with a Disc integrator. The values obtained on this instrument agreed closely with those secured from the Model 720. With the latter, the percentage compositions were calculated according to the method of J. C. Bartlet and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960). Both instruments were equipped with thermal conductivity detectors and employed helium as the carrier gas. (c) Combustion analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., or Miss H. Beck, Northwestern University.

[17] G. S. Hiers and R. Adams, *J. Am. Chem. Soc.*, **84**, 2385 (1962). The material used in the present study was prepared according to G. S. Fonken and W. S. Johnson, *ibid.*, **74**, 831 (1952).

[18] G. Ferrari and C. Casagrande, *Farmaco* (Pavia) *Ed. Sci.*, **18**, 780 (1963); *Chem. Abstr.*, **60**, 2811*d* (1964).

84–87° (4 mm). Gas chromatography indicated the presence of **5** (88.3%), **7** (6.4%), and unidentified materials (5.2%).

The principal unidentified material (*ca.* 2–5% of the total mixture) was isolated by preparative gas chromatography. Its infrared spectrum was superimposable with that of 2-cyclohexylethanol. This material evidently arises from ethyl 2-cyclohexylacetate, a minor contaminant of the starting diethyl cyclohexylmalonate (**1**). The remaining unidentified materials were judged to be hydrocarbons from their retention times.

B. **From Unsaturated Aldehyde 11.**—To a stirred mixture of 130 mg of lithium aluminum hydride in 20 ml of ether was added 138 mg of unsaturated aldehyde **11**. The mixture was stirred for 2 hr and treated with aqueous base[16a] giving 136 mg (97%) of unsaturated alcohol **5**: bp 90° (bath temperature) (12 mm); $n^{29}\text{D}$ 1.4822; $\lambda_{\max}^{\text{film}}$ 3.00 (OH), 6.07 (C=C), 9.70, and 11.20 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.07 (CH_2OH), 4.86, and 5.03 ppm (C=CH_2, two doublets, J = 1 cps). The gas chromatogram indicated a purity of 99.8%. The phenylurethan had mp 59–60°, undepressed upon admixture with a sample prepared in part A above.

With 1,2-dimethoxyethane as the solvent the reduction gave a 98:2 mixture of unsaturated alcohol **5** and saturated alcohol **7**.

2-Cyclohexylpropan-1-ol (**7**).—A 3.78-g sample of a mixture containing 4% aldehyde **4**, 72% allylic alcohol **5**, and 19% alcohol **7** (prepared from malonate **1** as described above) was stirred with 0.4 g of 5% palladium on carbon in 23 ml of ethanol under an atmosphere of hydrogen until no more gas was taken up. The solvent was removed from the filtered solution and a 3.5-g sample of the residue was treated with ethereal lithium aluminum hydride. The reaction mixture was decomposed with aqueous base[16a] and the product was distilled giving 3.31 g (89%) of alcohol **4**: bp 110–111° (16 mm); $n^{19}\text{D}$ 1.4722; $\lambda_{\max}^{\text{film}}$ 2.98 (OH), 9.56, and 11.24 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 3.5 (CH_2O, partially resolved ABX pattern), 4.0 (OH), and 0.88 ppm (CH_3, doublet, J = 6 cps). The gas chromatogram indicated a purity of 95%.

Anal. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.8; H, 12.7.

When the reduction described in Table I (entry 2) was allowed to proceed for 48 hr, the product contained 2% aldehyde **4**, 40% propenol **5**, and 54% propanol **7**. Starting from authentic propenol **5**, a similar reduction experiment afforded a 90:10 mixture of **5** and **7** after 26 hr.

2-Cyclohexylpropenoic Acid (**9**).—The procedure of Clark, *et al.*,[19] was employed. A solution containing 2.75 g of sodium hydroxide in 110 ml of water was added dropwise over 45 min to a rapidly stirred solution of 1.72 g of aldehyde **11** and 2.75 g of silver nitrate in 50 ml of 1:1 aqueous ethanol. After 5 hr, the mixture was filtered, the filtrate was washed with ether, and the aqueous phase was acidified with dilute hydrochloric acid and extracted thoroughly with ether. Distillation afforded 1.68 g (88%) of acid **9**: bp 80° (bath temperature) (0.1 mm); $n^{29}\text{D}$ 1.4827; $\lambda_{\max}^{\text{film}}$ 3.0–4.0 (OH), 5.90 (conjugated C=O), 6.14 (conjugated C=C), 7.74, 8.03, 8.36, 8.56, and 11.17 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 12.32 (CO_2H), 6.29 (H_a—C=C), doublet, J = 1.2 cps) and 5.57 ppm (H_b—C=C, triplet, J = 1.2 cps). The gas chromatogram indicated a purity of 96%.

Anal. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.9; H, 9.4.

This material crystallized, mp 35–36°, after prolonged refrigeration.

Ethyl 2-Cyclohexylpropenoate (**10**).—Ethereal diazoethane was added to a solution of 5.9 g of acid **9** in 75 ml of ether until a persistent yellow color was observed. The color was discharged with several drops of acetic acid and the solution was filtered. The filtrate was washed with aqueous sodium bicarbonate and saturated brine, dried, and distilled affording 5.5 g (79%) of ester **10**: bp 106–108° (12 mm); $\lambda_{\max}^{\text{film}}$ 5.80 (CO), 6.02 (C=C), 7.81, 8.09, 8.42, 8.65, 8.92, 9.70, and 10.60 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 6.19 (H_a—C=C, doublet, J = 1.5 cps), 5.54 (H_b—C=C, triplet, J = 1.4 cps), 4.26 (OCH_2CH_3, quartet, J = 7.5 cps), and 1.30 ppm (CH_3-CH_2O, triplet, J = 7.5 cps). The analytical sample was obtained by preparative gas chromatography followed by short-path distillation, $n^{20}\text{D}$ 1.4646.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.7; H, 10.1.

2-Cyclohexylpropenal (**11**).—A 35.2-g sample of a mixture containing 1% aldehyde **4**, 72% allylic alcohol **5**, 25% alcohol **7**, and 2% unidentified components (prepared from malonate **1** as described above) in 2.4 l. of chloroform was stirred with 275 g of activated manganese dioxide[20] for 5.5 hr. The mixture was filtered, the filter cake was washed with ether, and the combined filtrates were distilled affording 15.02 g: bp 74–75° (12 mm); $\lambda_{\max}^{\text{film}}$ 3.33 (=C—H), 3.70 (aldehyde C—H) 5.89 (conjugated CO), 6.15 (conjugated C=C), 8.17, 10.45–10.58, 11.02, 11.19, and 11.42 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 9.57 (CHO), 6.21 (H_a—C=C, triplet, J = 0.8 cps), and 5.97 ppm (H_b—C=C, doublet, J = 0.6 cps). The fraction contained 98.9% aldehyde **4** and 1.1% four other compounds.[16b]

A second fraction of 16.38 g, bp 80–104° (12 mm), contained 5% aldehyde **11**, 43% allylic alcohol **5**, 49% alcohol **7**, and 3% unidentified components.

Material from fraction 1 was converted into a semicarbazone derivative which exhibited mp 208–209° after several recrystallizations from methanol.

Anal. Calcd for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.77; N, 21.50. Found: C, 61.8; H, 8.9; N, 21.3.

A 5.0-g sample of the semicarbazone derivative of aldehyde **11** and 6.0 g of phthalic anhydride in 12 ml of methanol and 60 ml of water was heated at reflux for 0.5 hr and distilled with steam.[21] The distillate was saturated with sodium chloride and extracted with ether. Aldehyde **11** was isolated by distillation, bp 70° (bath temperature) (7 mm). Material thus secured (99.8% pure according to the gas chromatogram) was used to prepare acid **9** and aldehyde **4**, and for the reduction studies in Table II.

In another experiment 9.8 g of a mixture containing 93% of alcohol **5** was treated with 130 g of manganese dioxide in 800 ml of chloroform for 7 hr using vigorous mechanical stirring. Distillation gave aldehyde **11** (purity 90%) in 92% yield.

Ethyl 2-Cyclohexylpropanoate (**12**).—A 227-mg sample of ester **10** was hydrogenated over 40 mg of reduced platinum oxide in 15 ml of absolute ethanol. Hydrogen uptake (1 equiv) was complete in 0.4 hr and the mixture was filtered. Distillation afforded 202 mg (88%) of colorless oil: bp 65–68° (bath temperature) (2.2 mm); $n^{20}\text{D}$ 1.4489; $\lambda_{\max}^{\text{film}}$ 5.77 (C=O), 8.51, and 8.69 μ.

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.7; H, 11.0.

2-Deuterio-2-cyclohexylpropan-1-ol (**7-D**).—Malonic ester **1** (3.7 g) was converted to enolate **3** and reduced with lithium aluminum hydride (1.1 g) as described above. Work-up A was employed using deuterium oxide in place of water. The crude material (5% unknown, 7% **4**, 71% **5**, and 16% **7**)[16b] was reduced with lithium aluminum hydride and the distilled product, 1.8 g (86%), bp 60–75° (bath) (0.3 mm) (5% unknown, 73% **5**, and 22% **7**)[16b] was subjected to preparative gas chromatography. The saturated alcohol (**7-D**) which was collected exhibited $\lambda_{\max}^{\text{film}}$ 3.0 (OH), 4.69 (C—D), 9.56, and 11.24 μ; $\delta_{\text{TMS}}^{\text{CCl}_4}$ 4.33 (OH), 3.41 (CH_2OH, AB quartet, J = 11 cps), and 0.85 ppm (CH_3CD singlet). The mass spectrum[22] showed no parent peak but calculations based on the M − H_2O and M − CH_2OH peaks indicated 4.2% D_0, 93.8% D_1, and 2.0% D_2 species.

Similar results were obtained starting from unsaturated ester **10**.

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