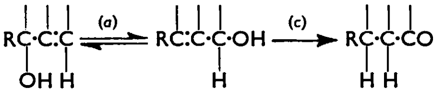
638. *The Rearrangement of αβ-Unsaturated Alcohols to Saturated Aldehydes and Ketones. Part I. The Preparation of αβ-Unsaturated Alcohols and 1 : 2-Diols and their Prototropic Change.*

By M. B. Green and W. J. Hickinbottom.

The recorded acid-catalysed isomerisms of αβ-unsaturated alcohols are reviewed. The behaviour of these alcohols when heated with sulphuric acid in water or in water–dioxan is studied and a comparison made with the behaviour of the corresponding 1 : 2-diols. The preparation of αβ-unsaturated alcohols and 1 : 2-diols is reported.

The characteristic changes which αβ-unsaturated alcohols can undergo in contact with aqueous mineral acid are (*a*) reversible oxotropic change, (*b*) dehydration to a diene, or (*c*) prototropic change with formation of a saturated aldehyde or ketone.



$$\mathrm{R\overset{|}{\underset{OH}{C}}\cdot\overset{|}{\underset{H}{C}}:\overset{|}{C} \xrightleftharpoons{(a)} R\overset{|}{C}:\overset{|}{C}\cdot\overset{|}{\underset{H}{C}}\cdot OH \xrightarrow{(c)} R\overset{|}{\underset{H}{C}}\cdot\overset{|}{\underset{H}{C}}\cdot\overset{|}{C}O}$$

Oxotropic rearrangement of these alcohols is well known.[1] Prototropic change, has, however, been observed only occasionally.

2-Methylprop-2-en-1-ol is converted into *iso*butyraldehyde by hot aqueous mineral

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[1] See Braude, *Quart. Rev.*, 1950, **4**, 407.

acid [2,3]; other examples of the prototropic change are the formation of 2-methylbutan-1-al from 2-ethylprop-2-en-1-ol, of 3-methylbutan-2-one from 3-methylbut-3-en-2-ol,[4] and of 2 : 4-dimethylpentan-3-one from 2 : 4-dimethylpent-1-en-3-ol.[5] These alcohols are substituted allyl alcohols; allyl alcohol itself undergoes prototropic change only sluggishly —when heated at 100° with dilute hydrochloric acid it gives some propionaldehyde together with diallyl ether, propylene glycol, allyl chloride, and condensation products.[6]

Since completion of our work Dreiding and Hartman [7] have described the conversion of 2-methylene*cyclo*hexanol into 2-methyl*cyclo*hexanone with hot dilute sulphuric acid.

The isomerisation [8] of αβ-unsaturated alcohols to carbonyl compounds can also be achieved over nickel at 210° or over copper at 300°. This catalytic transformation is probably no more than a disproportionation. The change promoted by aqueous mineral acid admits no such obvious explanation and the object of our work was to study the conditions and causes of the change.

Preliminary experiments were carried out with 2-methylprop-2-en-1-ol. The product of the rearrangement was identified as *iso*butyraldehyde by its physical constants and by comparison of its semicarbazone with that of an authentic specimen. The effect of varying the concentration of acid is shown in Table 1; 500 c.c. of acid of different concentrations and 20 g. of the alcohol were used in each experiment. The effect of varying the ratio of alcohol to acid, 0·4N-sulphuric acid being used, is shown in Table 2. The yields are based on the weight of pure material isolated. With 0·4N-sulphuric acid the change was substantially complete after 8—12 hours' refluxing. As a result of these experiments standard conditions were devised (see Experimental) for comparing the behaviour of 42 αβ-unsaturated alcohols and their capacity for prototropic change. The results are recorded in Tables 3—7. The yields recorded are for the pure fractionated products; the loss during isolation is mostly " column hold-up " and amounts to about 10% when 20 c.c. of alcohol are used.

TABLE 1.

	Concentration of sulphuric acid (N)							
Yield, wt. %	0·2	0·1	0·2	0·4	0·8	1·2	2·0	4
Aldehyde	61	91	92	91	90	86	79	68
Cyclic acetal	—	—	—	—	—	5	8	20
Unchanged alcohol	30	—	—	—	—	—	—	—

TABLE 2.

	Volume of 0·4N-acid						
Yield, wt. %	2000	1000	400	200	100	40	20
Aldehyde	91	91	90	60	39	16	6
Cyclic acetal	—	—	—	26	48	75	63
High-boiling products	5	5	5	5	5	10	20

TABLE 3. *Primary alcohols* $\text{RCH:CH}\cdot\text{CH}_2\cdot\text{OH}$.

Alcohol	Product	Yield, wt. %	Alcohol	Product	Yield, wt. %
$\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{OH}$	$\text{CH}_3\cdot\text{CH}_2\cdot\text{CHO}$	*ca.* 0·5	$\text{Pr}^i\text{CH:CH}\cdot\text{CH}_2\cdot\text{OH}$	$\text{Et}\cdot\text{CO}\cdot\text{Pr}^i$	*ca.* 0·5
$\text{MeCH:CH}\cdot\text{CH}_2\cdot\text{OH}$	$\text{Me}\cdot\text{CO}\cdot\text{Et}$		$\text{Bu}^t\text{CH:CH}\cdot\text{CH}_2\cdot\text{OH}$	$\text{Et}\cdot\text{CO}\cdot\text{Bu}^t$	

TABLE 4. *Primary alcohols* $\text{CH}_2\text{:CR}\cdot\text{CH}_2\cdot\text{OH}$.

Alcohol	Product	Yield, wt. %	Alcohol	Product	Yield, wt. %
$\text{CH}_2\text{:CMe}\cdot\text{CH}_2\cdot\text{OH}$	$\text{Me}_2\text{CH}\cdot\text{CHO}$	91	$\text{CH}_2\text{:CPr}^i\cdot\text{CH}_2\cdot\text{OH}$	$\text{Pr}^i\text{MeCH}\cdot\text{CHO}$	89
$\text{CH}_2\text{:CEt}\cdot\text{CH}_2\cdot\text{OH}$ ...	$\text{EtMeCH}\cdot\text{CHO}$	90	$\text{CH}_2\text{:CBu}\cdot\text{CH}_2\cdot\text{OH}$	$\text{BuMeCH}\cdot\text{CHO}$	90
$\text{CH}_2\text{:CPr}\cdot\text{CH}_2\cdot\text{OH}$	$\text{PrMeCH}\cdot\text{CHO}$	92	$\text{CH}_2\text{:CBu}^t\cdot\text{CH}_2\cdot\text{OH}$	$\text{Bu}^t\text{MeCH}\cdot\text{CHO}$	88

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[2] Scheschukov, *J. Russ. Phys. Chem. Soc.*, 1884, **16**, 479.
[3] Hearne, Tamele, and Converse, *Ind. Eng. Chem.*, 1941, **33**, 805; F.P. 763,286; U.S.P. 2,010,076.
[4] Kondakov, *J. Russ. Phys. Chem. Soc.*, 1885, **17**, 290.
[5] Umnova, *ibid.*, 1910, **42**, 1530.
[6] Solonina, *ibid.*, 1887, **19**, 302; Nef, *Annalen*, 1904, **335**, 308.
[7] Dreiding and Hartman, *J. Amer. Chem. Soc.*, 1956, **78**, 1216.
[8] Delaby *et al.*, *Compt. rend.*, 1925, **180**, 1278; *Bull. Soc. chim. France*, 1926, **39**, 1582.

TABLE 5. *Secondary alcohols* CH_2:CR·CHR′·OH.

Alcohol	Product	Yield, wt. %	Alcohol	Product	Yield, wt. %
CH_2:CMe·CHMe·OH	CH_3·CHMe·CO·Me	92	CH_2:CEt·CHBu·OH	CH_3·CHEt·CO·Bu	92
CH_2:CMe·CHEt·OH	CH_3·CHMe·CO·Et	89	CH_2:CPr·CHEt·OH	CH_3·CHPr·CO·Et	91
CH_2:CMe·CHPr·OH	CH_3·CHMe·CO·Pr	90	CH_2:CPr^i·CHEt·OH	CH_3·CHPr^i·CO·Et	90
CH_2:CMe·CHBu·OH	CH_3·CHMe·CO·Bu	91	CH_2:CBu^t·CHEt·OH	CH_3·CHBu^t·CO·Et	86
CH_2:CEt·CHEt·OH	CH_3·CHEt·CO·Et	87			

In the changes recorded in this Table, traces of aldehydes were present in the product They were removed by treatment with silver oxide before fractionation. The two alcohols CH_2:CH·CHPr^i·OH and CH_2:CH·CHBu^t·OH gave only minute traces of ketones.

TABLE 6. *Primary alcohols* RCH:CR′·CH_2·OH.

Alcohol	Product	Yield, wt. %	Alcohol	Product	Yield, wt. %
MeCH:CMe·CH_2·OH	EtCHMe·CHO	25	EtCH:CEt·CH_2·OH	PrEtCH·CHO	26
	$CHMe_2$·CO·Me	63		MeCHEt·COEt	61
EtCH:CMe·CH_2·OH	PrCHMe·CHO	15	PrCH:CEt·CH_2·OH	BuCHMe·CHO	19
	$CHMe_2$·CO·Et	71		MeCHEt·CO·Pr	69
MeCH:CEt·CH_2·OH	$CHEt_2$·CHO	36			
	EtMeCH·COMe	52			

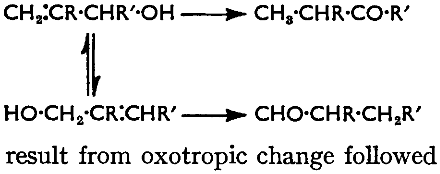
TABLE 7. *Secondary alcohols* RCH:CR′·CHR″·OH.

Alcohol	EtCH:CMe·CHEtOH	PrCH:CEt·CHPr·OH	MeCH:CMe·CHEt·OH
Product	PrCHMe·CO·Et·	BuCHEt·CO·Pr	EtCHMe·CO·Et + Et_2CH·CO·Me

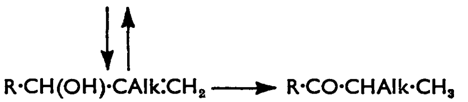
The alcohols MeCH:CH·CHEt·OH and MeCH:CH·CHBu·OH gave no ketonic products.

The following alcohols gave only dienes: CMe_2:CMe·CH_2·OH, CH_2:CMe·CMe_2·OH, CMe_2:CMe·CHMe·OH, CMe_2:CMe·CMe_2·OH, CH_2:CH·CEt_2·OH, CMe_2:CH·CHMe·OH, CH_2:CEt·CEt_2·OH, CHMe:CMe·CMe_2·OH, CH_2:CH·CMe_2·OH, CMe_2:CH·CH_2·OH, CHMe:CH·CMe_2·OH.

Comparison of the results in Tables 3 and 4 shows that a C_β-alkyl group has considerable effect in promoting prototropic change. Allyl alcohol and its linear homologues undergo prototropic change only with difficulty; the β-substituted allyl alcohols do so readily and practically quantitatively. With secondary alcohols it is possible to get some measure of the competing oxotropic reaction

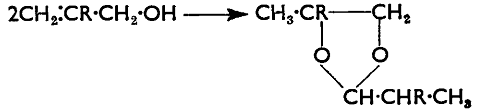


Any aldehyde formed must result from oxotropic change followed by prototropic change. It is seen from Table 5 that only traces of aldehyde are formed; oxotropic change, therefore, plays no important part. If, however, the unsaturated γ-carbon of the allyl alcohol carries an alkyl group, oxotropy is the predominant reaction (Table 6).



With the alcohols RR′C:CR″·CH_2·OH there was no clear evidence of prototropic change: instead, dehydration occurred to the diene obtained from the isomeric tertiary alcohol RR′C(OH)·CR″:CH_2.

The observed prototropic changes could be explained by the formation of a glycol from the unsaturated alcohol, since there are recorded observations of the formation of glycols under these conditions,[6] and it has been established in this work, by varying the conditions of the reaction, that excellent yields of cyclic acetals can be obtained: indeed this provides a convenient method of preparing the glycols.



Alternatively, the well-known formation of carbonyl compounds from glycols under acid conditions and the prototropic change of αβ-unsaturated alcohols might both proceed through a common transient intermediate.

$$\begin{tikzcd} \mathrm{CHR{:}CR'\cdot CHR''\cdot OH} \arrow[r] \arrow[d] & \mathrm{CH_2R\cdot CR'(OH)\cdot CHR''\cdot OH} \arrow[dl, leftrightarrow] \\ {[\mathrm{A}]} \arrow[r] & \mathrm{CH_2R\cdot CHR'\cdot COR''} \end{tikzcd}$$

A number of 1 : 2-diols were therefore prepared corresponding to the expected hydration products of the αβ-unsaturated alcohols. Their behaviour was examined under conditions precisely comparable with those used for αβ-unsaturated alcohols. The glycols $\mathrm{HO\cdot CRR'\cdot CH_2\cdot OH}$ were converted almost quantitatively into the aldehydes $\mathrm{CHRR'\cdot CHO}$ (Table 8).

TABLE 8.

Glycol	Product	Yield, wt. %	Glycol	Product	Yield, wt. %
$\mathrm{HO\cdot CMe_2\cdot CH_2\cdot OH}$	$\mathrm{CHMe_2\cdot CHO}$	92	$\mathrm{HO\cdot CBuMe\cdot CH_2\cdot OH}$	$\mathrm{CHBuMe\cdot CHO}$	90
$\mathrm{HO\cdot CEtMe\cdot CH_2\cdot OH}$	$\mathrm{CHEtMe\cdot CHO}$	89	$\mathrm{HO\cdot CBu^tMe\cdot CH_2\cdot OH}$	$\mathrm{CHBu^tMe\cdot CHO}$	86
$\mathrm{HO\cdot CPrMe\cdot CH_2\cdot OH}$	$\mathrm{CHPrMe\cdot CHO}$	91	$\mathrm{HO\cdot CEt_2\cdot CH_2\cdot OH}$	$\mathrm{CHEt_2\cdot CHO}$	91
$\mathrm{HO\cdot CPr^iMe\cdot CH_2\cdot OH}$	$\mathrm{CHPr^iMe\cdot CHO}$	88			

Conversion of the glycols $\mathrm{HO\cdot CR_2\cdot CHR'\cdot OH}$ into the ketones $\mathrm{CHR_2\cdot COR'}$ was substantially complete although small amounts (1% or less) of the isomeric aldehydes $\mathrm{CR_2R'\cdot CHO}$ were also formed (Table 9).

Under the conditions used glycols $\mathrm{HO\cdot CHR\cdot CH_2\cdot OH}$ (R = Me, Pr, Pr^i, and Bu^t) gave only a small yield of the expected aldehyde; no carbonyl compound was detected when $\mathrm{HO\cdot CHMe\cdot CHPr^i\cdot OH}$ was refluxed with 0·4N-sulphuric acid.

A tentative hypothesis to account for these results is considered in the following paper. It accords with the results of a study [9] of the conversion of [1-^{14}C]methallyl alcohol into *iso*butyraldehyde.

TABLE 9.

Glycol	Product	Yield, %	Glycol	Product	Yield, %
$\mathrm{HO\cdot CMe_2\cdot CHMe\cdot OH}$	$\mathrm{CHMe_2\cdot COMe}$	89	$\mathrm{HO\cdot CEt_2\cdot CHMe\cdot OH}$	$\mathrm{CHEt_2\cdot COMe}$	90
$\mathrm{HO\cdot CMe_2\cdot CHPr\cdot OH}$	$\mathrm{CHMe_2\cdot COPr}$	88	$\mathrm{HO\cdot CEtMe\cdot CHMe\cdot OH}$	$\mathrm{CHEtMe\cdot COMe}$	89
$\mathrm{HO\cdot CMe_2\cdot CHBu\cdot OH}$	$\mathrm{CHMe_2\cdot COBu}$	87			

The required αβ-unsaturated alcohols (Table 11) were conveniently prepared by reduction of αβ-unsaturated aldehydes with lithium aluminium hydride. Some secondary alcohols were also prepared from unsaturated aldehydes and alkylmagnesium halides.

The Mannich reaction provided a useful route to α-alkylacraldehydes (Table 10). The method, originally employed by Marvel, Meyers, and Saunders,[10] depends on thermal decomposition of the base formed by the condensation of a saturated aldehyde with formaldehyde and dimethylamine.

$$\mathrm{RCH_2\cdot CHO + CH_2O + NHMe_2 \longrightarrow RCH(CH_2\cdot NMe_2)\cdot CHO \longrightarrow CH_2{:}CR\cdot CHO + NHMe_2}$$

The unsaturated aldehydes $\mathrm{CHR{:}CR'\cdot CHO}$ were most satisfactorily prepared by crotonaldehyde condensation in alkali; with suitable control of the experimental conditions

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[9] Currell and Fry, *J. Amer. Chem. Soc.*, 1956, **78**, 4377.

[10] Marvel, Myers, and Saunders, *ibid.*, 1948, **70**, 1694.

good yields were obtained. In condensations between two different aldehydes the yields were understandably less, but under suitable conditions they were sufficiently good to make the method useful.

TABLE 10. *α-Alkylacraldehyde* $CH_2{:}CR{\cdot}CHO$.

R	Yield, %	B. p.	Found, % C	Found, % H	Calc., % C	Calc., % H
Me[a]	66	67—68°	68·4	8·5	68·6	8·6
Et[a]	75	91—92	71·6	9·6	71·4	9·6
Pr[a]	73	116—118	73·6	10·4	73·4	10·2
Pr^i	55	106—108	73·4	10·3	73·4	10·2
Bu	78	138—139	75·1	10·7	75·0	10·8
Bu^t	69	125—126	75·2	10·8	75·0	10·8

[a] Sommelet, *Ann. Chim. Phys.*, 1906, **9**, 526.

TABLE 11. *Unsaturated alcohols* $R{\cdot}CH{:}CR'{\cdot}CH_2{\cdot}OH$.

Alcohol	Yield, %	B. p.	Found, % C	Found, % H	Calc., % C	Calc., % H
But-2-en-1-ol[a]	70	117—118°	66·8	11·3	66·6	11·2
2-Methylprop-2-en-1-ol[b]	81	113—114	66·7	11·2	66·6	11·2
2-Ethylprop-2-en-1-ol[c]	83	133—134	69·9	11·7	69·7	11·7
2-Propylprop-2-en-1-ol	87	151—152	72·0	12·1	72·0	12·1
2-*iso*Propylprop-2-en-1-ol	84	146—147	72·0	12·1	72·0	12·1
2-Butylprop-2-en-1-ol	88	170—171	73·6	12·3	73·6	12·4
2-*tert.*-Butylprop-2-en-1-ol	78	161—162	73·8	12·5	73·6	12·4
2-Methylbut-2-en-1-ol[d]	84	123—124	70·0	11·6	69·7	11·7
2-Ethylbut-2-en-1-ol	87	138—139	71·9	12·0	72·0	12·1
2-Methylpent-2-en-1-ol[e]	86	140—141	72·0	12·1	72·0	12·1
2-Ethylpent-2-en-1-ol	82	66—67/25 mm.	73·8	12·2	73·6	12·4
2-Ethylhex-2-en-1-ol	89	85—86/25 mm.	74·9	12·5	74·9	12·6

[a] Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197. [b] Ref. 2. [c] Kondakov, *J. Russ. Phys. Chem. Soc.*, 1888, **20**, 147. [d] Herzig, *Monatsh.*, 1882, **3**, 123. [e] Lieben and Zeisel, *ibid.*, 1883, **4**, 28; 1886, **7**, 54.

TABLE 12. *Esters* $HO{\cdot}CRR'{\cdot}CO_2Et$.

R	R′	Yield, %	B. p.°/25 mm.	R	R′	Yield, %	B. p.°/25 mm.
Me	Me	63	48—50	Me	Bu	78	91—93
Me	Et	71	68—70	Me	Bu^t	66	79—81
Me	Pr	74	80—82	Et	Et	80	76—78
Me	Pr^i	73	73—75				

TABLE 13.

R	R′	Yield, %	B. p.°/25 mm.	Found, % C	Found, % H	Calc., % C	Calc., % H
			Glycols $HO{\cdot}CRR'{\cdot}CH_2{\cdot}OH$.				
Me	Me[a]	78	76—78	53·4	11·4	53·3	11·2
Me	Et[b]	83	85—87	57·8	11·7	57·7	11·6
Me	Pr	85	96—98	61·2	11·9	61·0	11·9
Me	Pr^i[c]	81	91—93	61·1	11·9	61·0	11·9
Me	Bu	86	107—108	63·7	12·4	63·6	12·2
H	Pr^i[d]	83	84—85	57·9	11·7	57·7	11·6
Me	Bu^t	75	94—96	63·8	12·1	63·6	12·2
Et	Et[e]	84	90—92	61·1	12·1	61·0	11·9
			Glycols $HO{\cdot}CR_2{\cdot}CHR'{\cdot}OH$				
Me	Me[f]	74	81—82	57·8	11·8	57·7	11·6
Me	Et[e]	76	91—92	61·0	12·0	61·0	11·9
Me	Pr[g]	79	104—105	63·8	12·2	63·6	12·2
Me	Bu[h]	77	116—117	65·8	12·5	65·7	12·4
Et	Me[i]	80	98—99	63·7	12·3	63·6	12·2

[a] Nevole, *Bull. Soc. chim. France*, 1877, **27**, 63. [b] Kling, *ibid.*, 1904, **31**, 18. [c] Couturier, *Ann. Phys. Chim.*, 1892, **26**, 473. [d] Flavitski, *Annalen*, 1875, **179**, 351. Henry, *Compt. rend.*, 1907, **144**, 1405. Wurtz, *Ann. Phys. Chim.*, 1859, **55**, 458. [g] Kapron, *ibid.*, 1948, **3**, 117. [h] Meerwein, *Annalen*, 1919, **419**, 136. [i] Tiffeneau and Dorlencourt, *Bull. Soc. chim. France*, 1907, **1**, 1209.

Most of the required 1 : 2-diols (Table 13) were prepared from α-hydroxy-carboxylic esters (Table 12) either by hydrogenation with copper chromite [11] or by reaction with appropriate alkylmagnesium halides.

EXPERIMENTAL

Distillation Technique.—The column (50 cm. long × 3 cm. diam.) was packed with L-shaped pieces of nickel gauze and wound externally with Nichrome wire covered with asbestos lagging 2 cm. thick. The distillation head was of total reflux type with intermittent take off through a ball valve operated by a solenoid. The column had an efficiency of 20 plates at 30 c.c./hr. with a reflux ratio of 1 : 12; the hold-up was about 2 c.c. For distillation under reduced pressure a mercury manostat was used with an infinitely variable contact, and there was pressure equalisation across the column.

The distillation vessel, a pear-shaped flask with nitrogen leak, was immersed in a thermostatically controlled electrically heated oil-bath.

The amounts thus distilled were generally not less than 20 c.c. and often considerably more. Under these conditions constancy of boiling point and satisfactory analyses provided a reasonable guarantee of purity. It should be added that when oxidisable or hygroscopic materials are handled as in the work described later, determination of refractive index is not a reliable or satisfactory indication of purity.

General Procedure for Reaction of αβ-Unsaturated Alcohols with Acid.—The unsaturated alcohol (20 g.) was refluxed with 0·4N-sulphuric acid (1000 c.c.) under nitrogen for 48 hr. The solution was then saturated with salt, the product extracted with ether, and the extract washed, dried, and distilled. If the solubility of the alcohol was too low to permit a homogeneous solution, the aqueous acid was replaced by a 0·4N-solution of sulphuric acid in dioxan–water (1 : 3 v/v).

The carbonyl compounds were identified by comparison of their semicarbazones with authentic specimens.

α-Alkylacraldehydes.—Dimethylammonium chloride (1·2 moles), formaldehyde (40% soln.; 1·2 moles) and the appropriate saturated aldehyde (1·0 mole) were stirred at 70° for 24 hr. and then steam-distilled. The distillate was extracted with ether and the extract dried and fractionated. Compounds thus obtained are shown in Table 10.

Unsaturated Aldehydes, RCH:CR′·CHO.—The aldehyde (6·0 moles) or mixture of two aldehydes (3·0 moles of each) was added during 15 min. to vigorously stirred N-sodium hydroxide (200 c.c.). The mixture was then quickly chilled in ice and the product extracted with ether and distilled. The following were thus prepared : 2-Methylbut-2-en-1-al [10] (from acetaldehyde and propionaldehyde), b. p. 117—118°, yield 53% (Found : C, 71·6; H, 9·7. Calc. for C_5H_8O : C, 71·4; H, 9·6%). 2-Ethylbut-2-en-1-al [12] (from acetaldehyde and butyraldehyde), b. p. 36—37°/25 mm., yield 41% (Found : C, 73·4; H, 10·3. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%). 2-Methylpent-1-en-1-al [13] (from propionaldehyde), b. p. 38—39°/25 mm., yield 71% (Found : C, 73·4; H, 10·1. Calc. for $C_6H_{10}O$: C, 73·4; H, 10·3%). 2-*Ethylpent*-2-*en*-1-*al* (from propionaldehyde and butyraldehyde), b. p. 52—53°/25 mm., yield 42% (Found : C, 75 2; H, 10·6. $C_7H_{12}O$ requires C, 75·0; H, 10·8%). In this and the following preparation the reactants were added to N-sodium hydroxide at 80°. 2-Ethylhex-2-en-1-al [14] (from butyraldheyde), b. p. 66—67°/25 mm., yield 85% (Found : C, 76·2; H, 11·2. Calc. for $C_8H_{14}O$: C, 76·1; H, 11·2%).

Unsaturated Primary Alcohols.—The appropriate unsaturated aldehyde (1·0 mole) in dry ether (100 c.c.) was added to a stirred solution of lithium aluminium hydride (0·3 mole) in dry ether (300 c.c.) at such a rate as to produce gentle refluxing. 15 min. after addition was completed, water was added carefully and the mixture poured on ice and 10% sulphuric acid. The ether layer was separated, washed, dried, and distilled. Compounds obtained by this method are shown in Table 11.

3-*Methylbut*-2-*en*-1-*ol*,[15] b. p. 54—55°/25 mm., was prepared in 78% yield by reduction

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[11] Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 3121.

[12] Cox, U.S.P. 2,175,556.

[13] Lieben and Zeisel, *Monatsh.*, 1883, **4**, 28; 1886, **7**, 54.

[14] Raupenstrauch, *ibid.*, 1887, **8**, 112.

[15] Courtot, *Bull. Soc. chim. France*, 1906, **35**, 660, 978.

of ββ-dimethylacrylic acid with lithium aluminium hydride (1·25 mol.) (Found: C, 69·8; H, 11·7. $C_5H_{10}O$ requires C, 69·7; H, 11·7%). 2 : 3-*Dimethylbut*-2-*en*-1-*ol*,[16] b. p. 61—62°/25 mm., was similarly prepared from αββ-trimethylacrylic acid in 83% yield (Found: C, 72·9; H, 12·3. $C_6H_{12}O$ requires C, 72·0; H, 12·1%).

Unsaturated Secondary Alcohols.—The aldehyde (0·8 mole) in ether (250 c.c.) was added during 1 hr. to a solution prepared from magnesium (1 g.-atom), an alkyl bromide (1·0 mole) and ether (250 c.c.) cooled to 0°. The mixture was stirred throughout the addition and for 3 hr. thereafter at room temperature. It was then poured on ice in saturated ammonium chloride solution. The ether layer was separated, washed, dried, and distilled. The following were thus prepared: 4-Methylpent-1-en-3-ol [17] (from acraldehyde and *iso*propyl bromide), b. p. 124—125°, yield 74% (Found: C, 72·0; H, 12·1. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·1%). 4 : 4-*Dimethylpent*-1-*en*-3-*ol* (from acraldehyde and *tert.*-butyl bromide), b. p. 51—52°/25 mm., yield 78% (Found: C, 73·6; H, 12·3. $C_7H_{14}O$ requires C, 73·6; H, 12·4%). Hex-4-en-3-ol [18] (from crotonaldehyde and ethyl bromide), b. p. 133—135°, yield 81% (Found: C, 72·1; H, 12·1. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·1%). Oct-2-en-4-ol [19] (from crotonaldehyde and butyl bromide), b. p. 79—80°/25 mm., yield 79% (Found: C, 75·1; H, 12·7. Calc. for $C_8H_{16}O$: C, 74·9; H, 12·6%). 3-Methylbut-3-en-2-ol [4] (from 2-methylprop-2-en-1-ol and methyl bromide), b. p. 116—117°, yield 68% (Found: C, 69·7; H, 11·6. Calc. for $C_5H_{10}O$: C, 69·7; H, 11·7%). 2-*Methylpent*-1-*en*-3-*ol* (from 2-methylprop-2-en-1-al and ethyl bromide), b. p. 134—135°, yield 73% (Found: C, 72·1; H, 12·1. $C_6H_{12}O$ requires C, 72·0; H, 12·1%). 2-*Methylhex*-1-*en*-3-*ol* (from 2-methylprop-2-en-1-al and propyl bromide), b. p. 153—154°, yield 75% (Found: C, 73·5; H, 12·2. $C_7H_{14}O$ requires C, 73·6; H, 12·4%). 2-*Methylhept*-1-*en*-3-*ol* (from 2-methylprop-2-en-1-al and butyl bromide), b. p. 77—78°/25 mm., yield 77% (Found: C, 75·0; H, 12·5. $C_8H_{16}O$ requires C, 74·9; H, 12·6%). 2-*Ethylpent*-1-*en*-3-*ol* (from 2-ethylprop-2-en-1-al and ethyl bromide), b. p. 64—65°/25 mm., yield 86% (Found: C, 73·7; H, 12·5. $C_7H_{14}O$ requires C, 73·6; H, 12·4%). 2-*Ethylhept*-1-*en*-3-*ol* (from 2-ethylprop-2-en-1-al and butyl bromide), b. p. 91—92°/25 mm., yield 83% (Found: C, 76·0; H, 12·7. $C_9H_{18}O$ requires C, 76·0; H, 12·8%). 2-*Propylpent*-1-*en*-3-*ol* (from 2-prop-2-en-1-al and ethyl bromide), b. p. 83—84°/25 mm., yield 78% (Found: C, 75·1; H, 12·3. $C_8H_{16}O$ requires C, 74·9; H, 12·6%). 2-iso*Propylpent*-1-*en*-3-*ol* (from 2-*iso*propylprop-3-en-1-al and ethyl bromide), b. p. 75—76°/25 mm., yield 73% (Found: C, 74·9; H, 12·4. C_8H_{16} requires: C, 74·9; H, 12·6%). 2-tert.-*Butylpent*-1-*en*-3-*ol* (from 2-*tert.*-butylprop-2-en-1-al and ethyl bromide), b. p. 81—82°/25 mm., yield 71% (Found: C, 76·0; H, 12·5. $C_9H_{18}O$ requires C, 76·0; H, 12·8%). 4-*Methyl*-4-*hexen*-3-*ol* (from 2-methylbut-2-en-1-al and ethyl bromide), b. p. 66—67°/25 mm., yield 76% (Found: C, 73·5; H, 12·3. $C_7H_{14}O$ requires C, 73·6; H, 12·4%). 4-*Ethylhept*-4-*en*-3-*ol* (from 2-methylpent-2-en-1-al and ethyl bromide), b. p. 88—89°/25 mm., yield 75% (Found: C, 76·1; H, 12·8. $C_9H_{18}O$ requires C, 76·0; H, 12·8%). 5-*Ethylnon*-5-*en*-4-*ol* (from 2-ethylhex-2-en-1-al and propyl bromide), b. p. 110—111°/25 mm., yield 78% (Found: C, 77·8; H, 13·0. $C_{11}H_{22}O$ requires C, 77·6; H, 13·0%).

The following were prepared by reduction of the corresponding unsaturated ketones by lithium aluminium hydride under the conditions previously described: 4-*Methylpent*-3-*en*-2-*ol*, b. p. 58—59°/25 mm., yield 88% (Found: C, 72·1; H, 12·1. $C_6H_{12}O$ requires C, 72·0; H, 12·1%). 3 : 4-*Dimethylpent*-3-*en*-2-*ol*, b. p. 65—66°/25 mm., yield 86% (Found: C, 73·6; H, 12·3. $C_7H_{14}O$ requires C, 73·6; H, 12·4%).

Tertiary Unsaturated Alcohols.—The following were prepared by condensation of the appropriate unsaturated ester with an alkylmagnesium bromide: 2-Methylbut-3-en-2-ol,[20] b. p. 98—99°, yield 81% (Found: C, 69·7; H, 11·6. Calc. for $C_5H_{10}O$: C, 69·7; H, 11·7%). 3-Ethylpent-1-en-3-ol, b. p. 124—125°, yield 71% (Found: C, 73·8; H, 12·1. Calc. for $C_7H_{14}O$: C, 73·6; H, 12·4%). 2-Methylpent-3-en-2-ol,[18] b. p. 112—113°, yield 79% (Found: C, 72·1; H, 11·9. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·1%). 2 : 3-Dimethylbut-3-en-2-ol,[15] b. p. 117—118°, yield 76% (Found: C, 72·1; H, 12·2. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·1%). 2 : 3-*Diethylpent*-1-*en*-3-*ol*, b. p. 41—42°/25 mm., yield 81% (Found: C, 76·0; H, 12·7. $C_9H_{18}O$ requires C, 76·0; H, 12·8%). 2 : 3-*Dimethylpent*-3-*en*-2-*ol*,[21] b. p. 40—41°/25 mm., yield 75%

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(Found: C, 73·8; H, 12·3. Calc. for $C_7H_{14}O$: C, 73·6; H, 12·4%). 2:3:4-*Trimethylpent-3-en-2-ol*, b. p. 56—57°/25 mm., yield 78% (Found: C, 75·0; H, 12·6. $C_8H_{16}O$ requires C, 74·9; H, 12·6%).

Semicarbazones of Saturated Aldehydes.—The unsaturated aldehyde (20 g.) in 80% aqueous alcohol (75 c.c.) was hydrogenated at 40 lb./sq. in. in presence of palladium chloride (1% soln.; 20 c.c.) and gum arabic (2% soln.; 29 c.c.). The mixture was then poured into water and the aldehyde extracted with ether. The dried extract was evaporated and the residue heated for 1 hr. on a steam-bath with Girard P reagent (10% soln. in alcohol; 1·5 equiv.). The mixture was poured on ice and exhaustively extracted with ether. The remaining aqueous solution was then acidified with sufficient hydrochloric acid to make it normal. The aldehyde was extracted with ether after storage overnight and the ether extract converted directly into the semicarbazone.

The following semicarbazones were thus obtained:

		Found, %		Calc., %	
Semicarbazone of	M. p.	C	H	C	H
$CHMe_2$·CHO	125—126°	46·6	8·6	46·5	8·6
CHMeEt·CHO	104—105	50·4	9·2	50·4	9·1
CHMePr·CHO	100—101	53·4	9·6	53·5	9·6
$CHMePr^i$·CHO	110—111	53·6	9·5	53·5	9·6
*CHMeBu·CHO	92—93	56·1	9·8	56·1	9·9
*$CHMeBu^t$·CHO	118—119	56·0	9·8	56·1	9·9
$CHEt_2$·CHO	98—99	53·6	9·5	53·5	9·6
*CHEtPr·CHO	88—89	56·1	9·7	56·1	9·9
*CHEtBu·CHO	81—82	58·5	10·2	58·4	10·3

* New compounds. The m. p. of the semicarbazones of the other aldehydes are in substantial agreement with those recorded in the literature.

Semicarbazones of Saturated Ketones.—The unsaturated secondary alcohol (20 g.) was hydrogenated in ethyl alcohol (100 c.c.) at 40 lb./sq. in. and room temperature, 1% of Pd–C catalyst being used. The mixture was poured into water, the secondary alcohol taken up in ether, and the solution dried and evaporated. The residue, in acetic acid (50 c.c.), was oxidised at 40° by chromium trioxide in acetic acid. The mixture was then diluted with water, the ether solution of the product heated with Girard P reagent as described above, and the ketones converted into semicarbazones. (See following Table.)

		Found, %		Calc., %	
Semicarbazone of	M. p.	C	H	C	H
$CHMe_2$·CO·Me	113—114°	50·3	9·2	50·4	9·1
$CHMe_2$·CO·Et	92—93	53·5	9·5	53·5	9·6
$CHMe_2$·CO·Pr	118—119	56·0	9·9	56·1	9·9
$CHMe_2$·CO·Bu	110—111	585	10·1	58·4	10·3
CHMeEt·CO·Me	95—96	53·4	9·6	53·5	9·6
CHMeEt·CO·Et	107—108	56·0	9·8	56·1	9·9
CHMeEt·CO·Pr	101—102	58·4	10·4	58·4	10·3
CHMeEt·CO·Bu	89—90	60·4	10·6	60·3	10·6
$CHEt_2$·CO·Me	133—134	56·0	9·8	56·1	9·9
CHMePr·CO·Et	97—98	58·4	10·2	58·4	10·3
*$CHMePr^i$·CO·Et	108—109	58·3	10·3	58·4	10·3
*CHMeBu·CO·Et	85—86	60·3	10·5	60·3	10·6
*$CHMeBu^t$·CO·Et	99—100	60·4	10·6	60·3	10·6
*CHEtBu·CO·Pr	91—92	63·5	11·1	63·4	11·0

* New compound.

α-Hydroxycarboxylic Esters.—Sodium pyrosulphite (380 g.; 2 moles) in water (500 c.c.) was added at 30—40° during 15 min. to a vigorously stirred mixture of the appropriate ketone or aldehyde (3 moles), sodium cyanide (98%; 165 g., 3·2 moles), ice (400 g.), and water (50 c.c.). After being stirred for a further 15 min., the mixture was cooled to 0° and the cyanohydrin decanted off. From the residue, a further amount of cyanohydrin was obtained by adding 100 c.c. of water.

The crude cyanohydrin was dried ($CaCl_2$), filtered, diluted with ethyl alcohol (250 c.c.), and saturated with hydrogen chloride at 0°. This solution was kept overnight, then poured on ice, and the hydroxy-ester extracted with ether. The yields and b. p.s of α-hydroxy-esters HO·CRR′·CO_2Et are given in Table 12.

Glycols HO·CRR′·CH$_2$·OH.—The appropriate α-hydroxy-ester (100 g.), ethyl alcohol (100 c.c.), and copper chromite (50 g.) were hydrogenated in a rocking stainless steel autoclave at 200° and 5000 lb./sq. in. The reduction was generally complete in 1—3 hr. The product was removed with ethanol, and the solution filtered and distilled. The compounds thus obtained are shown in Table 13.

Glycols HO·CR$_2$·CHR′·OH.—The appropriate hydroxy-ester (0·3 mole) in dry ether (150 c.c.) was added to a stirred solution of the appropriate Grignard reagent [from magnesium (1 g.-atom) and the alkyl bromide (1 mole) in dry ether (500 c.c.)] kept at 0°. The mixture was stirred for 3 hr. at room temperature after the addition was completed, and then poured on ice and saturated ammonium chloride. The ether layer was separated and combined with those obtained by extracting the aqueous layer overnight with ether in a continuous extractor. Distillation of the dried solutions gave the required glycol. The results are summarised in Table 13.

4-*Methylpentane*-2 : 3-*diol*.—This *diol*, b. p. 92—93°/25 mm. (Found : C, 61·2; H, 11·9. $C_6H_{14}O_2$ requires C, 61·0; H, 11·9%), was prepared by adding a solution of 4-methylpent-2-ene in *tert.*-butyl alcohol (200 c.c.) to a 7% solution of hydrogen peroxide in *tert.*-butyl alcohol cooled to 0°, followed by osmium tetroxide (0·5% solution in *tert.*-butyl alcohol; 5 c.c.). After 3 days at 0° the mixture was distilled, giving 19 g. of diol.

4-Methylpent-2-ene was obtained in 90% yield by reduction of 4-methylpent-2-yne (41 g.) by sodium (25 g.) in liquid ammonia (500 c.c.) and the subsequent addition of ammonium nitrate.

Ethylhexane-1 : 2-*diol*, b. p. 116—117°/25 mm. (Found : C, 65·7; H, 12·6. $C_8H_{18}O_2$ requires C, 65·7; H, 12·4%), was obtained similarly from 2-ethylhex-1-ene in 40% yield.

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