"THE ANISOMETRIC REARRANGEMENT AND OPTICAL ROTATION

OF $\gamma$-ETHYL-$\alpha$-METHYLALLYL ALCOHOL".

A thesis offered for the Ph.D. degree

of London University by

## Contents

### Part I. Theoretical.

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Introduction</td>
<td>1.</td>
</tr>
<tr>
<td>Section I</td>
<td>The Optical-Rotatory Properties of Substituted Allyl Derivatives</td>
<td>3.</td>
</tr>
<tr>
<td>Section II</td>
<td>Parachor Determinations and the Structure of Allylic Alcohols</td>
<td>6.</td>
</tr>
<tr>
<td>Section III</td>
<td>The Reactivity of Allylic Alcohols and their Derivatives I.</td>
<td>15.</td>
</tr>
<tr>
<td></td>
<td>(i) General characteristics of the compounds</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ii) Alkyl-oxygen fission in derivatives of allylic alcohols</td>
<td></td>
</tr>
<tr>
<td>Section IV</td>
<td>The Reactivity of Allylic Alcohols and their Derivatives II.</td>
<td>24.</td>
</tr>
<tr>
<td></td>
<td>Rearrangements</td>
<td></td>
</tr>
<tr>
<td>Section V</td>
<td>The Reactivity of Allylic Alcohols and their Derivatives III.</td>
<td>36.</td>
</tr>
<tr>
<td></td>
<td>Rearrangements, continued</td>
<td></td>
</tr>
<tr>
<td>Section VI</td>
<td>( \gamma )-Ethyl-( \alpha )-methylallyl Alcohol</td>
<td>50.</td>
</tr>
<tr>
<td></td>
<td>(3-Hexen-2-ol)</td>
<td></td>
</tr>
<tr>
<td>Section VII</td>
<td>( \alpha )-( \gamma )-Dimethylallyl Alcohol</td>
<td>71.</td>
</tr>
</tbody>
</table>

### Part II. Experimental.

- References: 102

### Appendix.

- Methods of Analysis of the Hexenol Mixtures: 105
INTRODUCTION.

For many years it has been realised that on account of the ease of electron-shift in the three-carbon allyl system, rearrangement may occur during reactions of the type:

$$\gamma = \frac{c^a}{x} \rightarrow \gamma = \frac{c^a}{y} \quad \text{or} \quad \frac{y}{c^a} = \frac{c^a}{y}$$

or the rearrangements may be internal:

$$\gamma = \frac{c^a}{x} - \frac{c^a}{x} \quad \xrightarrow{-} \quad \frac{y}{c^a} = \frac{c^a}{x}$$

In studies of optically-active derivatives of substituted alcohols it was found that optical activity is retained during internal rearrangements, and a number of hypotheses about the structure of these alcohols have been based on these and other observations. The use of optically active esters also made it possible to observe the occurrence of alkyl-oxygen fission and to obtain further information bearing on the mechanism of the reactions of substituted allyl derivatives.

The following properties of the alcohols and their derivatives have been examined:

1. Parachor
2. Optical rotation
3. Reactions involving alkyl-oxygen fission
4. Rearrangement reactions of both alcohols and esters.
The present work is mainly concerned with the rearrangement reactions in the system:

\[
\begin{align*}
\text{Me} & \quad \text{Et} \\
\text{CH} = \text{CH} & \quad \text{CH} = \text{CH} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

\(\text{-ethyl-}\gamma\text{-methylallyl} \quad \gamma\text{-ethyl-}\alpha\text{-methylallyl}
\)

\(\text{alcohol} \quad \text{alcohol}
\)

I \quad II.

Airs, Dalfo and Kenyon (1) showed that the carbinal I changed into its isomer II with substantial retention of its optical activity, and they advanced a view of the constitution of the carbinal. Airs (2) and Dalfo and Kenyon (3) made the further deduction that the system I \(\rightarrow\) II would reach equilibrium with a slight preponderance of the \(\gamma\)-methyl isomer.

The testing of these conclusions and the determination of the optical-rotatory power of II, \(\alpha\)-methyl-\(\gamma\)-ethyldiallyl alcohol, form the main objects of the present investigation.
I. THE OPTICAL-ROTATORY PROPERTIES OF SUBSTITUTED ALKYL DERIVATIVES.

The allyl alcohols listed in Table I have been resolved into their optically-active forms by fractional crystallisation of alkaloidal salts of their hydrogen phthalic esters.

Their optical properties have not been investigated in great detail. The table is a summary of the information at present available. Levene (4, 5, 6) has examined the rotatory dispersions of some members of the series, using a wide range of wave-lengths, and showed that all the compounds he had examined had complex rotatory dispersions. In all other cases, the specific rotations were determined over too narrow a range of wave-lengths for a similar conclusion to be unequivocally drawn, but the indication, where any can be found, is towards complexity.
<table>
<thead>
<tr>
<th>Alcohol</th>
<th>([\alpha]_{6893})</th>
<th>([\alpha]_{5461})</th>
<th>([\alpha]_{4353})</th>
<th>Dispersion Ratio ([\alpha]_{4353})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+) CH_2:CH:CHOH:CH_3 (\alpha)-methylallyl</td>
<td>33.89°</td>
<td>40.33°</td>
<td>72.39°</td>
<td>2.17</td>
<td>7</td>
</tr>
<tr>
<td>(+) CH_2:CH:CHOH:C_2H_5 (\alpha)-ethylallyl</td>
<td>35.20°</td>
<td>42.14°</td>
<td>76.13°</td>
<td>2.13</td>
<td>7</td>
</tr>
<tr>
<td>(-) CH_2:CH:CHOH:C_3H_7 (\alpha)-n-propylallyl</td>
<td>-23.92°</td>
<td>-34.55°</td>
<td>-62.70°</td>
<td>2.17</td>
<td>7</td>
</tr>
<tr>
<td>(-) CH_2:CH:CHOH:C_4H_9 (\alpha)-n-butyllallyl</td>
<td>-26.20°</td>
<td>-31.53°</td>
<td>-57.39°</td>
<td>2.19</td>
<td>7</td>
</tr>
<tr>
<td>Note ((-) CH_2:CH:CHOH:C_11 (\alpha)-n-amylallyl (1)</td>
<td>-25.00°</td>
<td>-23.82°</td>
<td>-55.35°</td>
<td>2.21</td>
<td>6</td>
</tr>
<tr>
<td>(+) CH_3:CH:CH:CHOH:CH_3 (\gamma)-dimethylallyl</td>
<td>0.50°</td>
<td>0.84°</td>
<td>3.04°</td>
<td>6.1</td>
<td>10</td>
</tr>
<tr>
<td>(+) CH_3:CH:CH:CHOH:C_2H_5 (\gamma)-methyl-(\alpha)-ethylallyl</td>
<td>13.1°</td>
<td>14.1°</td>
<td>29.9°</td>
<td>2.23</td>
<td>1</td>
</tr>
<tr>
<td>Note (+) CH_3:CH:CH:CHOH:C_3H (2) (\gamma)-methyl-(\alpha)-propylallyl</td>
<td>3.65°</td>
<td>4.58°</td>
<td>8.98°</td>
<td>2.38</td>
<td>9</td>
</tr>
<tr>
<td>Note (-) CH_3:CH:CH:CHOH:C_1 (\gamma)-methyl-(\alpha)-butylallyl (3)</td>
<td>-3.0°</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>(+) C_2H_5:CH:CH:CHOH:C_2H_5 (\gamma)-diethylallyl</td>
<td>5.59°</td>
<td>6.81°</td>
<td>12.25°</td>
<td>2.19</td>
<td>43</td>
</tr>
<tr>
<td>(+) CH_3:CH:CH:CHOH:C_3H (\gamma)-methyl-(\alpha)-allylallyl</td>
<td>23.00°</td>
<td>22.00°</td>
<td>50.43°</td>
<td>2.20</td>
<td>12</td>
</tr>
<tr>
<td>Note (+) Ph.CH:CH:CHOH:CH_3 (\gamma)-phenyl-(\alpha)-methylallyl (4)</td>
<td>16.8°</td>
<td>21.8°</td>
<td>45.0°</td>
<td>2.63</td>
<td>8</td>
</tr>
<tr>
<td>Note (-) CH_3:CH:CH:CHOH:Ph (\gamma)-methyl-(\alpha)-phenylallyl (5)</td>
<td>20.16°</td>
<td>-33.59°</td>
<td>-64.00°</td>
<td>--</td>
<td>11</td>
</tr>
</tbody>
</table>
Measurements were made on the homogeneous alcohol at 25°C, except as shown in the foot-notes.

Note (1) Temperature 25°C; at wave-lengths 5070, 5461, 4350A, respectively, in heptane solution.

(2) Temperature 15°C.

(3) Temperature 24°C.

(4) In acetone solution, c = 5.

(5) The rotation recorded in the λ5000 column was read at λ5700.

Levene and Fotheron (6) also record a large range of [α]

for α,α-dimethylallyl and α-α-butylllallyl alcohols, for specimens with, approximately, 90% of the optical activity of the specimens listed in the table.

It is reasonable to suppose that the complex rotatory dispersions of these compounds are due to induced asymmetry, or anisotropy, in the molecule. The conception of "asymmetry", which postulates an induced semi-polar state of a double bond (i.e., here \( \alpha = \beta \) becomes \( \alpha - \beta \)) is usually regarded as implying a highly-irreproducible disturbance of the electrons between the two carbon atoms. "Anisotropy", in the special sense of the word when applied to this double-bonded type of group, is a less simple idea, involving the \( \pi \)-electrons of the double bond; such electrons will be influenced by the substituent groups of the molecule, not to approach one or other of the atomic nuclei, but into different energy levels,
with consequent disturbance of the symmetry of the double bond.

Kenyon and Fartridge (14) studied the addition of bromine to \( \gamma \)-phenyl-\( \alpha \)-methylallyl alcohol, and found that the saturation of the double bond occurred in such a way that the induced anisotropy was responsible for the appearance of new optically-active centres or centres in the system.

In each case, the reaction product was a mixture of two optically-active dibromo alcohols, separable by fractional crystallisation. Oxidation of each separated product yielded an optically-active dibromo-ketone. These reactions may be represented thus:

\[
\begin{align*}
\text{Br}_2 & \rightarrow \text{ketone} \\
\text{CH}_3\text{CH} = \text{CH}-\beta \gamma & \rightarrow \text{ketone} \\
\end{align*}
\]
In these cases, the optical activity was originally centred on the α-carbon atom. Addition of bromine not only destroys the double bond, but creates asymmetric centres at the β- and γ-carbon atoms. When a dibromo alcohol is oxidized, the original asymmetric centre is destroyed; since the resulting ketone is optically-active, the bromine addition must result in the fixation on the β- or γ-atom of optical activity induced by the original active α-carbon atom.
II. PARAETHER DETERMINATIONS AND THE STRUCTURE OF ALPHLIC ALCOHOLS.

Hills, Kenyon and Phillips (13) measured the parachor of a number of allyl alcohols and their esters. The parachor ($\alpha$) is a quantity defined by Sugden as equal to:

$$\frac{\gamma^2}{D-d}$$

where $D$ = molecular weight of a non-associated liquid.

$\gamma$ = the surface tension of the liquid.

$D$ = the density of the liquid.

$d$ = the density of the vapour at the temperature of the experiment.

The relation is practically constant over wide ranges of temperature, and has been considered an essentially additive property. Thus, if the effect of each structural unit of a compound is known, i.e. if the components of a parachor contributed by each atom and bond can be calculated accurately, the parachor of a compound can be used to distinguish between alternative structures. For example, quinone can be formulated in the following ways:

$$\begin{align*}
\text{Parachor 236.1} & \\
\text{(Sugden)} & \\
\text{Parachor 219.0}
\end{align*}$$
The observed parachor is 236.0, indicating the diketone structure to be the more probable.

It was hoped that similarly useful information could be derived from observations on allyl derivatives, but later evidence has been obtained showing that the property is not strictly additive. Munford and J. W. C. Phillips (15), and, later, Sibling (16, 17, 18, 19), have recalculated the original "structural constants" of Sugden, and have demonstrated that these values are quite sensitive to the influence of nearby atoms and bonds. Sibling has shown that, in addition to the mutual influence of groups and atoms, the length of the chain of carbon atoms involved has an effect on the parachor. He expresses the increasing contribution of each extra link by multiplying values calculated by simple addition by a factor of \( f^n \), where \( f = 1.0034163 \), approximately, and \( n \) = the number of carbon atoms in the carbon chain. The contributions of groups are calculated in a similar manner to the values of Sugden. When the parachors are calculated in this way, the agreement with observed values is good. As with other systems, however, the calculated are much higher than the observed values for alcohols.

The parachors of allyl alcohol and its substituted homologues, as well as allylic esters and ethers have been studied by Kenyon and his co-workers.

Bills, Kenyon and Phillips (13) found that the observed
parachors for various specimens of (+), (-), and (di) γ-dimethylallyl alcohol ranged from 226 to 233.8, whereas the calculated value is 233.2 (Sugden's constants) or 233.6 (Smith-Phillips constants). Using Gibling's system, the value is 244.8. In contrast to this, the observed parachors of nine esters and others of the carbinal did not differ significantly from the calculated values. In the same paper, observations on allyl alcohol itself and some homologues (α-ethyl, α-n-butyl-, and γ-phenyl-) are recorded. All, except the parent allyl alcohol, showed low values in the same way as did γ-dimethylallyl alcohol; the 'normal' value of the parent substance has been corrected to a lower figure in a later paper (1), and the discrepancy is attributed to incomplete drying. This later paper recorded observations on allyl acetate, γ-methylα-ethylallyl alcohol, its acetate and benzoate, α-phenyl-γ-methylallyl and γ-phenyl-α-methylallyl alcohols. The parachor of each of these alcohols was lower than calculated, but that of the esters normal. Duveen and Keynon (10) found that α-allyl-γ-methylallyl alcohol and its esters showed analogous behaviour.

The explanation first advanced of these facts was that of a postulated cyclic form, e.g. of α-γ-dimethylallyl alcohol:

\[ \text{I} \quad \text{II} \quad \text{III} \]
This suggestion is in harmony with the anomalous optical-
rotatory dispersion of the alcohol, since such a cyclic
structure would contain two asymmetric centres, whereas the
cyclic isomer of α-butyllallyl alcohol, for example, would have
only one asymmetric carbon atom, and therefore would show
simple rotatory dispersion, as, in fact, it does. Isomerisation
of this type would be, moreover, necessarily confined to
hydroxylic compounds, so that the esters and ethers of those
alcohols might be expected to be normal, open-chain structures
showing no parachor anomaly.

Consideration of other experimental observations is,
however, less favourable to the theory. For example, the (+)
alcohol from optically-pure α,β-dimethylallyl hydrogen phthalate
had a parachor corresponding to more than 50% cyclisation.
Isomeride III would therefore be present in considerable
proportion, and, on re-esterification, would be expected to
yield an optically-inactive hydrogen phthalic ester, since it
is internally compensated. In actual fact, the re-formed ester
had a rotatory power very little less than that of the
optically-pure compound. Similarly, α- or γ-substituted allyl
alcohols would each be expected to yield mixtures of α- and
γ-substituted compounds on esterification, and this does not
occur, e.g. α-methylallyl (29) and cinnamyl (21, 22) alcohols
give their respective acetates unmixed with isomers when warmed
with acetic anhydride. The parachor of cinnamyl alcohol would
indicate considerable cyclisation.
Similarly, on hydrogenation, optically-pure allyl alcohols are reduced to optically-pure saturated alcohols, e.g. \((-\))-\(n\)-butylallyl alcohol gives \((+)\) ethyl \(n\)-butyl carbinol.

Airs, Salfi and Kenyon (1) have re-examined the evidence which led to the introduction of this theory of cyclised forms. They pointed out that low pararhor values are a normal property of all alcohols, but from an investigation of the effect of temperature on these values for both saturated and unsaturated alcohols, they showed that the approach to calculated values of pararhors with rising temperature was faster with saturated than with unsaturated alcohols. The difference is not very great, however, the maximum being 1.2 units for \(n\)-amyl alcohol against a minimum of 0.2 units for \(\gamma\)-dimethylallyl alcohol over the range 15 - 40°C. Later unpublished observations by Mrs. W. G. Wright on the molecular weight of \(\gamma\)-methyl-\(\gamma\)-ethylylyl alcohol (from its depression of the freezing-point of benzene) have shown that the alcohol is strongly associated at room temperature, so that much of the pararhor anomaly, in this case at least, can be attributed to the normal reason, viz. association.

Sibbing considers that the departures of observed from calculated values of the pararhors of these alcohols may be conveniently expressed as a 'packing fraction', or percentage, presumably representing the loosening of the structural
contribution of hydroxyl groups by the formation of hydrogen bonds:

\[
\text{H-O-H}
\]

Calculations of some of these packing percentages are given in the following table.

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>calc. ((F))</th>
<th>obs. ((P))</th>
<th>calc. ((F)) - obs. ((P))</th>
<th>Packing (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>94.5</td>
<td>83.2</td>
<td>6.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Ethyl</td>
<td>133.8</td>
<td>126.6</td>
<td>7.2</td>
<td>5.2</td>
</tr>
<tr>
<td>(n)-Amyl</td>
<td>253.7</td>
<td>241.2</td>
<td>12.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Allyl</td>
<td>108.9</td>
<td>153.0</td>
<td>0.9</td>
<td>5.6</td>
</tr>
<tr>
<td>(\alpha)-n-Butylallyl</td>
<td>315.0</td>
<td>328.0</td>
<td>3.1</td>
<td>2.0</td>
</tr>
<tr>
<td>(\gamma)-Phenylallyl</td>
<td>333.6</td>
<td>324.4</td>
<td>14.2</td>
<td>4.2</td>
</tr>
<tr>
<td>(\alpha)-Ethylallyl</td>
<td>235.1</td>
<td>220.1</td>
<td>7.0</td>
<td>3.0</td>
</tr>
<tr>
<td>(\gamma)-Methyl-(\alpha)-allyl-allyl</td>
<td>309.1</td>
<td>205.4</td>
<td>15.7</td>
<td>4.4</td>
</tr>
<tr>
<td>(\gamma)-Methyl-(\alpha)-ethyl-allyl</td>
<td>289.7</td>
<td>267.2</td>
<td>15.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Methyl (\beta)-methyl-allyl carbinol</td>
<td>277.7</td>
<td>263.4</td>
<td>9.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Packing \(\% = \frac{100 (F)}{(P)} \) - \((P)\)
It is plain that the association of the unsaturated alcohols is quite similar in magnitude to that of saturated alcohols, and that there is, in consequence, no evidence of cyclisation.

The Raman spectra, studied by Dupont et al. (23), and the molecular refractivities (Arcus and Penyon (9)) of certain allyl alcohols also suggest that the typical molecule is the unsaturated open-chain form and that the cyclic isomer or isomers can be present in only very small proportions, if at all.
III. THE REACTIVITY OF ALKYL ALCOHOLS AND THEIR DERIVATIVES - I.

(1) General characteristics of the compounds.

(11) Alkyl-oxygen fission in derivatives of allylic alcohols.

(1). General Characteristics.

The allyl alcohol system

\[
\text{CH}_2 = \text{CH.CH}_2 + \text{X}
\]

where X is -OH, -OR, or -O = S=OR, has considerable reactivity, because of the ease with which electrons are made available to the anionic group X, and for this reason allyl halides are much more easily hydrolysed than n-propyl halides. Substitution of certain groups for the hydrogen atom of the allyl group promotes the reactivity.

Burton and Ingold dealt with the subject in their well-known paper of 1920 (84), and their conclusions, together with later deductions, are as follows.

A parallelism exists between the power of a group substituted in the allyl chain to confer mobility on the anionic group X, and the power of the same group of o-p direction in aromatic substitution. The mechanism of the action of various groups may vary, e.g., \( \text{CO}_2 \text{R} \), alkoxyl, by means of the "lone pair", and \( \text{H}_2 \text{C} = \text{S} \), methyl, by the "hyperconjugation" effect, but the results are similar.
Burton and Ingold point out that these effects are of a latent character, i.e., a substituent group can only facilitate the breaking of the bond joining the allyl group to the allyl chain; if the tendency to dissociate did not already exist in the system, the substituent would not cause such a tendency to originate.

The position of substitution in the allyl chain is also of importance in determining the magnitude of the effect produced. The kinetic study of the case of rearrangement of \( \alpha-, \beta-, \) and \( \gamma- \) substituted allyl alcohols by Fraun and Jones (25, 26), showed that the effect produced by allyl substitution in the \( \alpha- \) position is considerable, in the \( \beta- \) position less, and in the \( \gamma- \) position greatest of all. They consider that the very noticeably increased effect in the latter case is due to a change in the type of effect. In the \( \alpha- \) position an allyl group has a general inductive effect, but when in the \( \gamma- \) position, the effect is tautomeric, with the polarisable double bond providing an additional source of electrons:

\[
R \rightarrow \overset{\text{\( \gamma \)}}{\text{\( \alpha \)}} \rightarrow \text{CH} \\

v. Ingold (27). If there is disubstitution in the \( \gamma- \) position, there is an even greater increase in the mobility of the system, though the quantitative effect of the second substituent group is not so great as the first, presumably because the polarisability of the double bond decreases when already partially polarised.
The effect in \( \beta \)-substitution is lessened by the greater distance of the substituent from the hydroxyl group (cf. the reactivities of \( n \)-propyl and isopropyl derivatives). There is also the possibility that the substituent can exert an influence

\[
\text{R} \quad \text{CH}_2 \rightarrow \quad \text{C} - \text{CH}_2 - \text{X}
\]

The more stable of the two isomers

\[
\text{R}' \rightarrow \text{CH} = \text{CH} - \text{CH} \left\langle - \text{R}'' \right. \quad \text{and} \quad \text{R}' \rightarrow \text{CH} = \text{CH} \left\langle - \text{R}'' \right. \quad \text{X} \quad \text{X}
\]

is that which has the more powerfully electron-releasing substituent in the \( \gamma \)-position, e.g. \( \gamma \)-phenyl-\( \alpha \)-methylallyl derivatives are more stable than their \( \alpha \)-phenyl-\( \gamma \)-methylallyl isomers. The work of Brando and Jones leads to the conclusion that the \( \gamma \)-phenyl compounds should be more reactive. No contradiction is implied, however, since a compound may well be more stable thermodynamically than another, but its energy of activation less, and so it is more 'reactive'.

The anionic group \( X \) also exerts an important effect on the reactivity of an allyl derivative. Burton and Ingold (loc. cit.) concluded that the more stable \( -X \) is in the form of the anion \( X^\text{-} \), the more mobile becomes the system to which it is attached. The spontaneous ionisation of substituted allyl derivatives is easily observed in the case of optically-active compounds, as racemisation occurs when the substituted allyl group is released as a carbonium ion. The ionic character of such racemisation
has been demonstrated by the fact that α-γ-dimethylallyl hydrogen phthalate remains optically unchanged during three months in methyl-alcoholic solution at 31°C, but changes rapidly, with considerable decomposition as well as racemisation, in nitromethane solution during a two-months period at the same temperature. The dielectric constant, and hence the ionising power, of the solvent nitromethane is considerably greater than that of methanol.

(ii). Alkyl-oxygen Fission in Ethers of Allylic Alcohols.

When carboxylic esters are hydrolysed or solvolyised, two alternative modes of fission are possible:

(1) \[ R'\cdot CH\cdot O\cdot CH\cdot R'' \]

alkyl-oxygen fission

(2) \[ R'\cdot CH\cdot O\cdot \cdot \cdot CH\cdot R'' \]

acyl-oxygen fission.

(2) is the normal kind of disruption, but (1) will occur if the group \( R'' \) has sufficiently strong electron-releasing properties, and if the external conditions, especially the solvent medium, are favourable. The dielectric constant of the medium, and its ability to stabilise the carbonium ion \( R'' \) by solvation, will determine whether the ion \( R'' \) is actually released.

The existence of the alkyl-oxygen fission mechanism can be demonstrated:–

(a) if the group \( R'' \) is optically-active, when racemisation will occur, or

(b) if there is β unsaturation in an allylic \( R'' \) with respect to the carbon atom attached to oxygen, then rearrangement will occur,
In mechanism (2), where the allylic group is never detached from the oxygen atom, the valencies of the asymmetric carbon atom cannot rearrange, so neither racemisation nor rearrangement is possible.

The group R" may be written, in the cases to be discussed as:

\[
R_1.CH = CH.CH.R_2,
\]

where \( R_1 \) and \( R_2 \) are alkyl or aryl groups.

When fission occurs, \( R'' \) is liberated as an ion

\[
\text{R}_1.CH.CH.CH.R_2
\]

and optical activity is thereby destroyed. When this carbonium cation becomes attached again to an anion \( X^\ominus \), the newly-formed covalent bond may be either at the original point of attachment (\( \alpha- \)) or a new one (\( \gamma- \)). Rearrangement is not a necessary consequence of the process. The relative electron-releasing powers of \( R_1 \) and \( R_2 \) will affect the relative stabilities of the two possible compounds, and the proportions of each which are formed will vary. In practice, e.g., with phenyl methyl allyl derivatives, one compound may be formed to almost complete exclusion of the other.

Partial racemisation has been observed in the hydrolysis of \( \gamma \)-phenyl-\( \alpha \)-methylallyl (8), \( \alpha \gamma \)-dimethylallyl (11), and \( \gamma \)-methyl-\( \alpha \)-ethylallyl (1) hydrogen phthalates.

In addition, rearrangement has been observed in the
hydrolysis of α-phenyl-γ-methyallyl hydrogen phthalate (11). The alcohol formed was γ-phenyl-α-methyallyl; none of the α-phenyl-γ-methyallyl alcohol was detected.

Dalfo, Hils, Kenyon, Phillips and Platt (23) described a series of experiments with the optically-active hydrogen phthalates and benzoates of αγ-dimethyallyl alcohol, and collated the evidence from investigations of other substituted allyl alcohols. The reagents employed were alcohols and organic acids. The results of the reactions had two characteristic features:—

1. Extensive racemisation of the product.

2. The racemisation of the recovered portion of the ester, if the reaction is halted before completion.

In cases where the conditions were suitable, rearrangement also took place. Both the characteristic features indicate alkyl-oxygen fission; the fact that the esters racemise more quickly than they react agrees with the known SN1 mechanism of such reactions (Hughes et al. (23)).

The reactions investigated or collected together, in the work recorded by this paper, and others, are summarised in Table III.
<table>
<thead>
<tr>
<th>Hydrogen Phthalate Reagent</th>
<th>Product</th>
<th>% Optical Purity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>of</td>
<td>of recovered</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>product</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>unreacted ester.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table III.**

<table>
<thead>
<tr>
<th>Product</th>
<th>% Optical Purity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**cy-dimethylallyl alcohol**

<table>
<thead>
<tr>
<th>formic acid</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) 5 mins. formate at 100°</td>
<td>0</td>
</tr>
<tr>
<td>(2) 15 mins. at 100°</td>
<td>1*</td>
</tr>
<tr>
<td>(3) 30 mins. at 90°</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>acetic acid</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>65 days at 97°</td>
<td>acetate</td>
</tr>
<tr>
<td>3 hrs. at 90°</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>methyl alcohol</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>21 hrs. at methyl 64°</td>
<td>other</td>
</tr>
<tr>
<td>3 months</td>
<td>no reaction</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>n-butanol</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 hrs. at n-butyl 90°</td>
<td>other</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>cy-dimethylallyl alcohol</th>
<th>benzyl alcohol</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 hrs. at benzyl 90°</td>
<td>other</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>phenol</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 phenols</td>
<td>1 ester,</td>
</tr>
<tr>
<td>1 phenol:</td>
<td>1 ester,</td>
</tr>
<tr>
<td>Hydrogen Pthalate Reagent of</td>
<td>Product of</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>(D benzate)</td>
<td></td>
</tr>
<tr>
<td>1 -dimethylallyl alcohol</td>
<td></td>
</tr>
<tr>
<td>a-formic acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>acetic acid</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>1-phenyl -γ-methylallyl alcohol</td>
<td>methyl</td>
</tr>
<tr>
<td></td>
<td>acetic acid</td>
</tr>
<tr>
<td>n-propyl-γ-methylallyl</td>
<td>benzoic acid</td>
</tr>
<tr>
<td></td>
<td>formic acid</td>
</tr>
<tr>
<td></td>
<td>formic acid</td>
</tr>
<tr>
<td>Hydrogen Phthalate Reagent of</td>
<td>Product</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>a-ethyl-γ-methylallyl</td>
<td>methyl alcohol</td>
</tr>
<tr>
<td>a-phenylallyl</td>
<td>methyl alcohol</td>
</tr>
<tr>
<td>do.</td>
<td>ethyl alcohol</td>
</tr>
<tr>
<td>do.</td>
<td>formic acid</td>
</tr>
<tr>
<td>do.</td>
<td>acetic acid</td>
</tr>
</tbody>
</table>

* = inversion of configuration.

▽ = (1) high proportion of acid (2) medium proportion of acid (3) low proportion of acid.
This section is concerned with the anisotropic type of rearrangement:

\[
\text{CH}_3\text{CH}(:\text{CH})\text{CH}_2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CH}(:\text{CH})\text{CH}(_2\text{CH}_2\text{OH})
\]

Young, Lane and their collaborators, continuing the earlier work of Provenz (31) on the same subject, have contributed a long series of papers on the system:

\[
\text{MeCHCHCH}_2\text{Me} \rightarrow \text{CHCHCH}(_2\text{Me})\text{Me}
\]

III crotyl

IV methylnylearbinyl

They have found (32) that if either of the pure alcohols is treated with hydrogen bromide, an equilibrium mixture of the two isomeric bromides is formed. They concluded that there are two operative mechanisms; the first is the normal bimolecular process, while the second involves ionization followed by reaction of the liberated carbocation ion, as described in Section III (Hughes-Ingold \textit{S}_2 and \textit{S}_1 respectively).

The hydrolysis of the halides was also studied. The secondary chloride (methylnylearbinyl) reacted entirely by a mechanism independent of the hydroxide ion concentration, but

* A prototropic rearrangement \(\text{CH}_3\text{CH}(:\text{CH})\text{CH}(\text{CH})\text{OH} \rightarrow \text{CH}_3\text{CH}(:\text{CH})\text{CH}(_2\text{CH}_2\text{OH})\) of these alcohols, described by Tiffenau in 1907 is a typical example of the general "pinacolic" system of Ingold and Shore.

* A prototropic rearrangement \(\text{CH}_3\text{CH}(\text{CH})\text{CH}(\text{CH})\text{OH} \rightarrow \text{CH}_3\text{CH}(_2\text{CH}_2\text{OH})\) of these alcohols, described by Tiffenau in 1907 is a typical example of the general "pinacolic" system of Ingold and Shore and will not be considered here.
affected by the nature of the solvent used i.e. the reaction proceeds by way of a solvated carbonium ion. The primary crotyl chloride seemed to react both by this and the bimolecular mechanism; the proportions of the two mechanisms depended on the hydroxide concentration.

From either chloride, the hydrolytic product consisted of a mixture of the two carbinals; the methylvinylcarbinal halide gave practically the same proportions of the two whatever the hydroxide concentration, while the crotyl chloride gave an increasing proportion of crotyl alcohol with increasing alkalinity of the reaction conditions.

The bimolecular $S_n$ mechanism seemed in this case to result entirely in reaction without isomerisation,

\[
\text{V} \quad \text{VI}
\]

The possibility also existed that isomerisation could result by what Catchpole, Hughes and Ingold (35, 34) have called the $S_n$ mechanism:

\[
\text{VII} \quad \text{VIII}
\]

Roberts, Young and Winstead (33) studied the reactions of the two chlorides with ethoxide ions in ethyl-alcoholic solution and with acetate ions in acetic acid. In no case could they obtain a pure first order reaction, but acetyls which involved a first order reaction always led to mixtures of acetates.
Heterogeneous substitution by silver acetate gave almost the same mixture of isomeric acetates from either chloride. They succeeded in isolating a pure second-order reaction for both chlorides on alcoholysis; the ethyl ether products were in each case those corresponding to the original halide. Acetylation in homogeneous conditions with acetate ions in acetic acid gave analogous results.

Catchpole and Hughes (33, 34), in recent work on the ethanalysis of α- and γ-methylallyl halides, obtained similar results. It may be concluded that under ordinary conditions i.e. where steric hindrance by disubstitution of the α-carbon atom does not impede bimolecular attack, no isomerisation occurs during a bimolecular reaction of this type.

The liability of this system is, therefore, dependent on the nature of the migrating group. If the group is a powerful electron-attractor e.g. halogen, the system can be rearranged easily by way of the intermediate carbonium ion:

\[
\text{CH}_3-\text{CH}(:\text{CH})_2^+\]

If the group is the less powerful hydroxyl, the ion is never released, and the compound reacts by a bimolecular mechanism which does not allow of rearrangement.

Burton (21, 22) observed that α-phenylallyl p-nitrobenzoate is converted smoothly into cinnamyl p-nitrobenzoate in acetic anhydride, but, in the presence of acetic acid, cinnamyl acetate is formed. Other α-phenylallyl esters behave similarly in the
presence of organic acids, and Burton concluded that preliminary ionisation of the ester is necessary for interconversion.

Kaiser and Bunting (36, 37) made quantitative studies of the reaction of cinnamyl chloride with acetate ion, in the presence, or absence, of various metallic acetates. In acetic anhydride, potassium acetate yielded only cinnamyl acetate and the order of reaction was nearly 2. In pure acetic acid, almost equal quantities of 'normal' (cinnamyl) and 'abnormal' (o-phenylallyl) acetates were formed, and the order of reaction was intermediate between 1 and 2. When water was added to the acetic acid, thus raising the dielectric constant of the medium, the proportion of normal product was higher, but the order remained between 1 and 2.

In acetic anhydride solution, reaction proceeds almost exclusively by the attack of acetate ion on cinnamyl chloride in a similar manner to the hydroxide ion attack on a crotyl halide.

In acetic acid, this mechanism continues to operate, but is supplemented by a $S_{N1}$ ionisation process yielding a mixed product. When the dielectric constant of the medium is raised, the formation of the more strongly ionisable 'abnormal' product from the ions will be retarded relative to the formation of the 'normal'. This accounts for the effect of the addition of water to the reaction mixture.
A different type of allyl rearrangement is involved in the Claisen reaction (v. Tarbell (38)). The essential change

\[ \text{C} - \text{O} - \text{C} - \text{CH} = \text{C} \quad \rightarrow \quad \text{C} = \text{O} \]

has been explained by Burd and Pollack (39) in terms of a mechanism involving a partial ionic fission of the oxygen atom from the allyl system grouping. For example, they consider that the normal mode of change is

\[ \text{This ketone may then enolise} \]

A similar mechanism has been formulated for the so-called 'abnormal' cases, e.g. \(\gamma\)-ethylallyl phenyl ether, where rearrangement gives an isomer of the expected product (here \(\sigma\)-dimethylallyl phenol)
If the Ω-positions are blocked, rearrangement to the p-position occurs. This is believed to happen by a process involving complete ionisation.

A similar rearrangement is shown by the diallyl system

\[
\text{CH}_3\text{CH} = \text{C} - \text{C} - \text{C} - \text{C} = \text{C} \\text{CH}_3
\]

Gope, Hoyle and Seyl (40) described reactions of the type:

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{C} - \text{C} & \text{COOH} \\
\text{CH}_2\cdot\text{CH}_2 & \rightarrow \\
\text{CH}_3\text{CH} - \text{C} & \text{C} - \text{C} \text{COOH} \\
\text{CH}_2\cdot\text{CH}_2
\end{align*}
\]

VII

VIII
Although this result in the transfer of a hydrocarbon radical from the \( \alpha \)- to the \( \gamma \)-carbon of an allyl group, and of the double bond of this group from \( \beta \gamma \)- to \( \alpha \beta \)- with respect to the activating anionic group or groups, the resemblance to the other rearrangements considered in this and succeeding sections is probably only superficial. The process in the diallyl system has been demonstrated to be unimolecular. Opps, Hofman and Hardy (41) proved that it was truly intramolecular by mixing two compounds of this type, and allowing them to rearrange; they separated the product of the reaction into two constituents only, these being the substances which would have been obtained by rearrangement of the two compounds separately.

The diallyl system closely resembles that required for Claisen rearrangement, only differing in the substitution of an oxygen atom by a carbon atom.

\[
\begin{align*}
\text{Diallyl} & : c - \overset{\circ}{c} - \overset{\circ}{c} - c = \text{} \\
\text{Claisen} & : c - c - \overset{\circ}{c} - \overset{\circ}{c} = \text{}
\end{align*}
\]

Both types of reaction are unaffected by hydrogen ions, whereas the anisotropic rearrangements proper are strongly influenced e.g. substituted alcohols of the mono-allyl series rearrange only in the presence of acid. It is probable that the diallyl system tends to rearrange because of the usual tendency to conjugation of double bonds, with consequent reduction of the free energy of the molecule.
The simpler mono-allyl compounds owe their power of rearrangement to the ease with which the anion can detach itself from the allylic group.

If the second double bond in the diallyl system is replaced by a triple bond, the electrical conditions are altered once more, and the six-carbon chain behaves very similarly to an allyl three-carbon chain substituted by saturated alkyl, or aryl, groups. The investigations of Jones, Heilbron, McCombie and their collaborators have yielded much information on this new unsaturated system.

If, for example, γ-methyl-α-ethynylallyl alcohol (IX) is shaken with a 31 sulphuric acid solution at room temperature, it rearranges quantitatively within 14 hours to α-methyl-γ-ethynylallyl alcohol (X), (Ref. 42).

\[ \text{CH}_3\text{CH} = \text{CH} = \text{CHCH}_2 \rightarrow \text{CH} = \text{CH} = \text{CHCH}_2\]

\( \text{IX} \rightarrow \text{X} \)

This reaction occurs with many other γ-substituted -ethynylallyl alcohols, and also with diols of the general formula:-
The rearrangement of the diols gives

by a change of the same kind, to compounds wherein the double and triple bond have become conjugated (43).

Jones and McCombie (42) studied the effect of temperature and also of acid concentration on the reaction. They compared their results with those of Kenyon, Partridge and Phillips (11) on α-phenyl-γ-methylallyl alcohol, which differs from the carbinol IX only by having a phenyl group instead of an ethynyl as the substituent in the α-position of the allyl chain.

The comparison showed that the ethynyl is a stronger attractor of electrons than the phenyl group, but that the latter confers much greater mobility on the system; the ability of the two groups to stabilise a positive charge on a neighbouring carbon atom differs considerably. Their deductions agree with those of Ingold (44) based on different evidence; this worker pointed out that the phenyl group is capable of promoting both anionotropic and prototropic changes:
Since the ethynyl group can only promote anionotropic changes, a simple comparison in terms of inductive effect is inadequate.

The quantitative work of Braude and Jones was previously mentioned in Section III (25, 26). It also included kinetic measurements on the effect of hydrogen ion activity (i.e. taking the effect of added electrolytes into account and of the solvent. Their results showed that the hydrogen ion concentration is always a determining factor in the change, while the solvent sometimes plays a part also. They regard the mechanism as intramolecular.

When the solvent does not participate in the reaction, no products other than the rearranged carbinols have been detected even at high-acid concentrations, and isomerisation and racemisation of an optically-active specimen of the alcohol IX were found to take place at exactly the same rate. The activation energy of these reactions was deduced to be between 19 and 24 kilocalories per gram-molecule, which is too low to correspond either to the covalent $\sigma$ or the ionic fission $\sigma$ of the carbon-oxygen bond. They propose a mechanism in which water is the mobile entity, as follows:
This series of reactions is that proposed for α-ethynylallyl alcohols (and the related diols) with alkyl substituents only. When the substituents are aryl, a modified scheme is proposed wherein the solvent medium is involved.

A solvated ion is first formed which can decompose to give the original carbinol or rearrange, by an internal movement of electrons, to a second ion which decomposes to yield a compound of the rearranged system; in an alcoholic solvent the product is the mixed ether of the isomerised carbinol and the solvent. If the solvent is non-hydroxylic, solvation may still occur, although the formation of an ether is no longer possible. For example, solution in dioxan causes a marked decrease in the energy of activation of the rearrangement of α-phenyl-substituted alcohols of this type.

These mechanisms are regarded as intramolecular by Braude
and Jones, as in the rate-determining step of the first mechanism, where the water molecule moves from the region of the α-carbon to that of the γ-carbon of the allyl chain, it does so under the complete control of the carbonium ion, and is not influenced appreciably by other water molecules in the solvent medium. This is not like the intramolecular process in e.g. the Claisen rearrangement (v. P. 23) where the breaking of the first bonds and the formation of the second occurs with little or no relative movement of the atoms. It has more resemblance to the benzidine change, where the relative position of the atoms alter. The term 'intramolecular' seems to be in need of more precise definition. Rearrangements, whether of atoms or electrons, cannot occur in these cases without the breaking of bonds, and, although the momentarily-formed pair of molecules may never escape from virtually complete control each of the other's movements, the pair can only be said, by definition, to form a single molecule. If this is accepted, the processes of the Braude-Jones mechanism are intramolecular.

However, there is a definite and complete fission of bonds resulting in racemisation when the starting compound is optically-active, so that some other mechanism must be involved in the rearrangement of simpler allyl alcohols, since some of these retain their optical activity on isomerisation.
Ingold, Hsu and Wilson (45) considered the mechanism of prototropic rearrangements, and studied the influence of constitutional factors on the rate of racemisation of prototropic compounds. The system

\[ R_1 \xrightleftharpoons[3]{\text{A}} R_2 + B = \text{C} \xrightarrow{\text{A}} R_3 \]

where \( A \) may be \( H \), i.e., a prototropic or an anion, i.e., an anionotrophic system.

\[ \text{*} = \text{asymmetric atom} \]

might or might not retain optical activity if the interconversion took place by way of an intermediate ion.

They investigated both prototropic and anionotropic systems for a suitable subject for study of this point, and chose the azomethine

\[ \text{Ph} \xrightarrow{\text{C}} \text{C}_{6}\text{H}_{4}\text{Cl(p)} \]

\[ \text{Ph} \xrightarrow{\text{C}} \text{C} = \text{H.C(II)} \]

\[ \text{Ph} \xrightarrow{\text{C}} \text{C}_{6}\text{H}_{4}\text{Cl(p)} \]

The initial substance I was optically-active. On allowing it to rearrange, it was found that the equilibrium mixture contained only the racemic form of II. These authors were not satisfied that racemisation was occurring at the same time as ionisation, but did not find evidence to the contrary.

Kenyon, Partridge and Phillips (11) investigated the anionotropic system wherein \( \alpha \)-phenyl-\( \gamma \)-methylallyl derivatives
are converted into \( \gamma \)-phenyl-\( \alpha \)-methylallyl compounds. They noted that the tendency of \( \text{C}_4 \text{H}_4 \text{C} = \text{C} = \text{CH}_2 \) to pass over into \( \text{C}_4 \text{H}_4 \text{C} = \text{C} = \text{CH}_2 \) was affected by the stability of \( \gamma \) as an anion, in accordance with the general considerations of reactivity noted in Section III.

The hydrogen phthalate and other esters of \( \alpha \)-phenyl-\( \gamma \)-methylallyl alcohol isomerised much more readily than the parent alcohol. Solid (-) hydrogen phthalic ester kept at room temperature liquefied and resolidified into a mixture of (+) and (cl) forms of \( \gamma \)-phenyl-\( \alpha \)-methylallyl hydrogen phthalate. In solution, the change occurred still more easily.

Observations of the rate of interconversion were carried out by kinetic measurements of the rotatory powers of solutions of (-) hydrogen phthalic ester in benzene or carbon disulphide. It was found that the isomerisation was a unimolecular reaction, and the deduced energy of activation was 28.8 kilocalories per gram-molecule. This is comparable with the 19 to 34 kilocalories activation energy found by Grado and Jones (Section IV) for rearrangement of ethynylallyl alcohols. The effect of raising temperature was found to be considerably greater than that of a rise in the dielectric constant of the solvent used, a fact which is at variance with the theory that the mechanism of these reactions is of a simple ionisation type, and also with Burton's finding (21, 22) that \( \alpha \)-phenylnallyl-\( \gamma \)-nitrobenzoate changed into the cinnamyl ester in two days in
benzonitrile (dielectric constant high), but took thirteen days in benzene (dielectric constant low).

Further observations on α-phenyl-γ-methylallyl alcohol derivatives may be summarised as follows:

1. The salts of the (-) hydrogen phthalic ester were much more stable than the parent ester e.g. the ammonium salt stayed unchanged for 9 days, before partial decomposition rendered further observations of optical activity impossible; the pyridine and quinoline salts were stable for months.

2. The p-xenylurethane isomerised in much the same way as the hydrogen phthalate, changing in the solid state into its isomer with an even greater retention of optical activity (more than 90% against 70%).

3. Neutral esters were more stable than the acid esters.

4. The racemic p-nitrobenzoate was stable at room temperature. On melting, it became metastable, changing only on inoculation with a crystal of γ-phenyl-α-methylallyl p-nitrobenzoate. The corresponding (-) ester changes similarly into (dl) and (+) γ-phenyl-α-methylallyl ester, the mixture possessing about 50% of its maximum activity.

5. The (-) acetate was changed, with free acetic acid present, into (dl) and (+) acetate of γ-phenyl-α-methylallyl alcohol. The product retained about 1% of its optical activity.

Of these, (3) is of the type of reaction discussed in Section III.
where the major part of the rearrangement proceeds by a preliminary ionisation of the ester, rearrangement of the carbonium ion, and its recombination into a racemic and rearranged acetate. Reactions (1) to (4), and the minor part of (5) presumably take place by other mechanisms. Kenyon, Partridge and Phillips (11) advanced an explanation of these observations by supposing that the carboxylic esters (hydrogen phthalate, p-nitrobenzoate) exist in a quasi-cyclic form, which is spatially possible, and favours reversal of the sign of optical rotation if the anion migrates:

\[ \text{X, here, is } -C_6H_4\text{COCH (o-) or } -C_6H_4\text{NO}_2 (p-) \]

When isomerisation takes place, a new link is formed along the line here dotted. If an external anion, say methoxide, approaches along the line of the dotted arrow, this reaction may be forestalled by the formation of a rearranged methyl ether, with optical activity of the same sign as the original ester. This has been done experimentally (loc. cit.) by the reaction of methyl alcohol with the (-) p-nitrobenzoate. If the internal anion is rather more firmly attached, isomerisation will occur first, and the methyl alcohol reacts by an ordinary bimolecular mechanism with the rearranged ester with a Walden
inversion occurring as is usual in such cases. This also has been observed experimentally, (+) hydrogen phthalic ester reacting slowly with methanol to give a (−) ether.

Hughes has suggested another mechanism is involved in the rearrangements of the esters (33, 34). In its latest form it is

\[
\begin{align*}
\text{R - CH = CH - CH - R'} & \quad \text{R - CH = CH - CH - R'} \\
\text{CO - C}_3\text{H}_4\cdot\text{CC} & \quad \text{CO - C}_3\text{H}_4\cdot\text{CC} \\
\end{align*}
\]

It involves a proton transfer between the two \(-\text{C-CO-}\) groups in the molecule (an internal acid catalysis), and, in the view of the proposer, need not lead to racemisation.

The mechanism proposed by Kenyon does not require complete separation of the anion. Burton had considered that this was necessary in such cases, because for example when tetramethylammonium acetate reacted with \(\alpha\)-phenylallyl \(p\)-nitrobenzoate, cinnamyl acetate was obtained (21, 22). This, in Kenyon's view, could be due either to an isomerisation followed by the attack of acetate ion, or a direct attack by acetate ion on the \(\gamma\)-carbon atom of the \(\alpha\)-phenylallyl compound. Catchpole, Hughes and Inghold (34) criticise the contention of Kenyon that this is a replacement and not an isomerisation on the ground that carbonium ion formation is generally agreed to be necessary to a rearrangement of the allyl system, and should therefore be common to both replacement-with-rearrangement and isomerisation.
reactions. They add a proviso that the intramolecular change could be so rapid as to allow the ionisation no time to occur, but that then Burton would have been unable to divert the reaction.

The ionic attack on the γ-carbon atom is that labelled \( S_{\alpha} \) by Hughes et al., and has been shown not to occur in several cases investigated (Section IV). Their objection to the formulation of the mechanism of the Burton findings as an isomerisation followed by ionic attack seems, however, less valid. Burton caused his isomerisation to occur in the presence of a high concentration of acetate ion, thus predisposing the conditions towards reaction of a bimolecular character. It seems possible that the isomerisation of a substituted allyl ester could proceed in such a way that when the reaction (with regard to one molecule) was nearly complete, that molecule would be in such a condition with respect to internal energy and electronic distribution that the bimolecular attack of an external ion would be highly favoured.

Catchpole, Hughes and Ingold (loc. cit.) regard the isomerisations of the hydrogen phthalic (and presumably also the p-xenylurethane) esters of substituted allyl alcohols as a special case; they cite Roberts, Young and Winstein (35) for another example of the same kind. Crotyl alcohol reacts with thionyl chloride to give mainly methylvinylecarbinyl
chloride; conversely, methyl vinyl carbinal reacts to give mainly crotyl chloride. This type of change is formulated by: 

\[ R - CH = CH = CH - R' \quad \xrightarrow{O - SO - Cl} \quad R - CH = CH - CH - R' \quad \rightarrow \quad SO_2 \quad Cl \]

They conclude that the general mode of isomerisation is that which proceeds by way of an intermediate carbonium ion, leading to racemisation if the original compound was optically active, but that certain esters may isomerise by way of the above mechanism (which they call Sn!). In the solid state, it or Kenyon's alternative formulation, will be operative.

Investigations of allyl alcohols where neither R' nor R'' is aromatic in character present many points of interest. Their general characteristics differ in some respects from those of the semi-aromatic alcohols. For example, the availability of electrons is much reduced if no phenyl group is present, so that the changes, if not always sluggish, are considerably slower than in the earlier examples given. Of the alkyl groups, methyl and ethyl have approximately the same power of electron-release; lengthening of the carbon causes a falling-off, but branching a considerable increase, of electron-availability. In these alkyl-substituted allyl systems, investigations have been on the whole more concerned with the alcohols than with their derivatives.

The first of these compounds was \( \alpha \gamma \)-dimethylallyl alcohol. This has certain peculiarities which will be discussed later.

(Sect. VII.) It has the further disadvantage that its possible
rearrangement reactions cannot be followed by changes in optical activity, as the symmetrical substitution does not permit the detection of a change of attachment of an anionic group from $\alpha$- to $\gamma$-carbon. Similarly, $\alpha\gamma$-diethylallyl alcohol (46) cannot be studied from the point of view of rearrangement.

An asymmetrically substituted allyl alcohol of aliphatic type was prepared by Arcus and Kenyon (9). An $\alpha$-$\beta$-propyl-$\gamma$-methylallyl alcohol was resolved optically by recrystallisation of the strychnine salt of its hydrogen phthalic ester. The optically-active hydrogen phthalate was hydrolysed, (13) and the resulting optically-active carbinol (III) was hydrogenated. The product was completely racemic. If rearrangement had occurred at any stage to give $\alpha$-methyl-$\gamma$-$n$-propylallyl derivatives with retention of optical activity, the carbinol (V) on hydrogenation would have yielded optically-active methyl $n$-emyl carbinol (VI), so it was concluded that optically-active $\alpha$-$n$-propyl-$\gamma$-methylallyl alcohol did not rearrange without racemisation.

\[
\begin{align*}
\text{III} & \quad \text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2 \\
& \quad \text{CH}_3\cdot\text{CH}:\text{CH}:\text{CH}(\text{CH}) \\
& \quad \downarrow \quad \quad \quad \downarrow \\
& \quad \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3 \\
& \quad \text{CH}:\text{CH}:\text{CH}(\text{CH})\text{CH}_3 \\
\end{align*}
\]

$\* = \text{asymmetric atom}$
The esters of purely aliphatic allyl alcohols do not easily rearrange. The hydrogen phthalic esters, and the p-nitrobenzoates of both α-n-propyl-γ-methylallyl and its isomer γ-propyl-α-methylallyl alcohol were unaffected by heating with pyridine on the steam-bath for two hours. The action of concentrated alkali on these esters was to produce the parent alcohol. On the other hand, hydrolysis of the optically-active esters by dilute alkali or by sodium acetate solution gave a racemic mixture of carbinols. It appeared that the ion \(\text{CHMeC}n\text{CH}_3\text{CO}^+\) was released, and this must have happened during the hydrolysis, since neither carbinol will rearrange in the presence of alkali.

Miers, Balfe and Kenyon (1) prepared optically-active γ-methyl-α-ethylallyl alcohol, and found that it behaved in many respects like γ-methyl-α-n-propylallyl alcohol. For example, hydrolysis of the optically-active hydrogen phthalic ester with dilute alkali was accompanied by racemisation, whereas if alkali of strength 5N and upwards was used, retention of optical activity was complete. This retention was proved by hydrogenation of the product to the saturated ethyl n-propyl carbinol, which had \([\alpha]_D^{20} = +7.1^\circ\) \(5993\), homogeneous, as compared with the (+) carbinol prepared by Kenyon (53), with \([\alpha]_D^{20} = -421^\circ\). Similarly, conversion of the hydrogen phthalic ester of the alcohol into the methyl ether resulted in almost complete loss of optical activity, whereas the reaction
of the potassic-derivative of the active carbinal with methyl iodide yielded an ether of much higher rotatory power.

The carbinal, however, possessed properties not previously recorded in alcohols of this type. Specimens of (+) and (−) alcohols exhibited mutarotation on standing. The change of rotatory power was of such a kind that other allyl alcohols were re-examined and Hulfe, Hills, Kenyon, Phillips and Platt (23) found that a four-year-old specimen of 1-γ-methyl-α-n-propylallyl alcohol had changed its rotation from \( [\alpha]_{D}^{170} = -4.4^\circ \)

to \( [\alpha]_{D}^{200} = 5.40^\circ \). The hydrogen phthalates corresponding had

\( [\alpha]_{D}^{5461} = -0.3^\circ \) and \(-2.9^\circ \) respectively, in ethyl-alcoholic solution. This mutarotation is probably due to a rearrangement similar to that undergone by γ-methyl-α-ethylallyl alcohol.

The rate of mutarotation of γ-methyl-α-ethylallyl alcohol varied with different specimens, and was found to be sensitive to traces of acid. Old samples were found to have become acid, and differences in the rate of formation of this impurity were thought to account for the varying rates of mutarotation. The specific rotations of mutarotated specimens were lower than the rotation of the original, but the carbinals obtained by hydrogenation of the former had high rotatory powers; the hydrogen phthalic ester prepared from one of the reduced carbinals had a higher rotatory power than optically-pure ethyl n-propyl carbinal hydrogen phthalate. Furthermore, in one case, the rotatory power of the carbinal was observed to rise
at first before falling.

The mutarotation was accompanied by rearrangement. A specimen of (dl) $\gamma$-methyl-$\alpha$-ethylallyl alcohol which had been kept for two years was converted into p-xenylurethane, and the mixed ester was crystallised fractionally. The hydrogenation-product of this same carbinol, treated similarly, yielded fractions identifiable as the p-xenylurethanes of ethyl n-propyl carbinol and methyl n-amyl carbinol.

The mutarotation seemed therefore to consist of a rearrangement to $\alpha$-methyl-$\gamma$-ethylallyl alcohol, which was optically-active, and also partly to a racemic material. It was found possible to analyse the mixture as regards the constituents:

1. $\gamma$-methyl-$\alpha$-ethylallyl alcohol (optically-active)
2. $\alpha$-methyl-$\gamma$-ethylallyl alcohol (also optically-active)
3. Racemic material.

The ratio of the specific rotation of (+) ethyl n-propyl carbinyl hydrogen phthalate (in 5% solution in chloroform) to the observed rotation of the (+) carbinol (homogeneous) in a 1 dm. tube at $20^\circ C$ at $\lambda 5893$ is 1.7. For methyl n-butyl carbinyl hydrogen phthalate and carbinol, the corresponding ratio is 4.6. The ratios for mixtures of the two species were determined, and a graph constructed showing the variation of the ratio with the composition of the mixture. The percentage of racemic material was deduced after the proportions of
optically-active isomers were found, by calculating the optical-rotatory power of a mixture of optically-pure alcohols of that composition and comparing it with the observed rotatory power of the mixture.

The hexenol mixture after mutarotation was hydrogenated, and the composition deduced by observations on the hexenol mixture produced. The method rested on several assumptions. The specific rotation of each hydrogen phthalate and of each carbinol was assumed to be unaffected by dilution with its isomeride; it was further assumed that significant amounts of other optically-active substances were not present. (+)-Ethyl n-propyl carbinol was known to be related to (+)-γ-methyl-α-ethylyallyl alcohol, as the process of hydrogenation by which interconversion took place was unlikely to cause any configurational change. On the other hand, α-methyl-γ-ethylallyl alcohol was unknown, and its corresponding relationship to methyl n-butyl carbinol unproven. A further necessary assumption was that α-methyl-γ-ethylallyl alcohol was formed as the (+) isomeride.

A specimen of (+) γ-methyl-α-ethylallyl alcohol which had been standing for 1156 days was, by this method of analysis, shown to consist of 41% of (+) γ-methyl-α-ethylallyl alcohol, 33% of α-methyl-γ-allyl alcohol, and 27% of racemic material. The original alcohol had been 92.5% optically-pure. The racemic material probably contained both racemic alcohols, but
the high retention of optical activity was the most remarkable feature. The initial rise in totatory power, previously mentioned, also occurred with this specimen.

Alrfs, Balfe and Kenyon (loc. cit.) postulated an intramolecular change which was preceded by a form of internal association:

\[
\begin{align*}
\text{R} &\quad\text{O} &\quad\text{CH} &\quad\text{R}^* \\
\text{R}^* &\quad\text{O} &\quad\text{OH} &\quad\text{R}
\end{align*}
\]

This co-ordination would be likely to favour the retention of a high proportion of the optical activity when isomerisation took place. The objections raised to the inner-ether theory did not apply in this case, and such association would account for the low value of the pararhor. The process involved a certain amount of 'fixing' of position inside the molecule, and is similar to the mechanism proposed for the esters of this type of carbinal, which however results in inversion of sign on isomerisation. The nature of the co-ordination was not particularised by these authors, but Young, Nozaki and Warner (61) had previously called attention to the fact that acid catalysis is a feature of these changes (cf. Jones' work, Sections III and IV). They considered that the probable mode of isomerisation involved oxonium ions formed by co-ordination of proton with the alcohols:
The implications of this mechanism are dealt with in the next section.
VI. \( \gamma \)-ETHYL-\( \alpha \)-METHYL ALLYL ALCOHOL (\( \gamma \)-HEXYL-2-OL).

Introduction.

This section deals particularly with two points:

1. The determination of the rotatory power of \( \gamma \)-methyl-\( \gamma \)-ethylallyl alcohol, which Mrs. Balf and Kenyon (loc. cit.) suggested should be higher than that of \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol, to account for the initial rise in rotatory power during the rearrangement of the latter.

2. The determination of the total composition of the equilibrium rearrangement product of \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol. Mrs. Balf and Kenyon did not determine this; their analysis was of the optically active components of the rearranged products. The determination, also, of the composition of rearranged products from \( \alpha \)-methyl-\( \gamma \)-ethylallyl alcohol, for comparison with those from \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol.

(1) PREPARATION AND THE OPTICAL ROTATION OF \( \alpha \)-METHYL-\( \gamma \)-ETHYLALLYL ALCOHOL.

\( \alpha \)-methyl-\( \gamma \)-ethylallyl alcohol has been previously described by Frevost (48), who prepared it by the reaction of methyl magnesium bromide with 2-pentenal. The aldehyde was obtained by converting 1:3 pentadiene to a mixture of
dibromides, hydrolysing this to a mixture of diols, and dehydrating the latter with 25% sulphuric acid by heating. The mixture of aldehydes was fractionally distilled. The overall yield by this method was very low. The method adopted in the present investigation gave better, but still low, overall yields. Firstly, propionaldehyde was condensed with acetone in the presence of alkali to yield an aldol:

\[
\text{C}_2\text{H}_5\cdot\text{CHO H} + \text{CH}_2\cdot\text{CO.CH}_3 \rightarrow \text{CH}_2\text{H}_5\cdot\text{CHCH} \quad \text{(CH}_2\cdot\text{CO.CH}_3
\]

which was then dehydrated by slow distillation from anhydrous oxalic acid to yield 3-hexen-2-one. This ketone was prepared by Grignard and Fluchaire (40) in 50% yields on the propionaldehyde used, by the same method. In the present experiments, 30% was never exceeded, in spite of various alterations which were tried in the experimental conditions.

The ketone was reduced by the Meerwein-Ponndorf method

\[
3 \text{C}_2\text{H}_5\cdot\text{CHCH.CO.CH}_3 + \text{Al}(-\text{C-CH.CH.CH}_2\text{H}_5)_3 \rightarrow \text{Al}(-\text{C-CH.CH.CH}_2\text{H}_5)_3 \quad \text{CH}_3 + 3 \text{CH}_3\cdot\text{CO.CH}_3
\]

The yield at this stage was 35% (average), so that the overall yield was about 10%.

On reaction with phthalic anhydride in the presence of pyridine, the alcohol yielded its hydrogen phthalic ester as an uncrystallisable oil, which was converted into its brucine salt. Recrystallisation of the salt three times from acetone, and decomposition with acid gave a laevorotatory ester
\( [\alpha]_{D}^{25^\circ} = -17.9^\circ \), in chloroform solution. The ester, on hydrolysis with an excess of 5N alkali, gave a (-) carbinol \( [\alpha]_{D}^{25^\circ} = -0.64^\circ \) (homogeneous). The hydrogen phthalate re-formed by the digestion of this (-) carbinol with pyridine and phthalic anhydride at room temperature had \( [\alpha]_{D}^{25^\circ} = 2.2^\circ \), in chloroform. The 3-hexen-2-yl radical seemed therefore to be rather unusually reactive. Tests were carried out to determine whether 3-hexen-2-yl hydrogen phthalate could undergo alkyl oxygen fission. Slow reaction with \( \frac{1}{2} \) equivalents of 0.33N sodium bicarbonate solution at room temperature resulted in the formation of no di-3-hexen-2-yl phthalate, and there was no visible reaction between the sodium salt of 3-hexen-2-yl hydrogen phthalate and sodium p-toluenesulphinate in the course of several weeks. These results may be contrasted with the corresponding reactions of the hydrogen phthalates of anisyl methyl carbinol and p-methoxybenzhydryl respectively (50).

The preparation and resolution of the hydrogen phthalate was repeated. The brucine salt of the ester was recrystallised five times and, on decomposition, yielded a hydrogen phthalate \( [\alpha]_{D}^{25^\circ} = -20.8^\circ \), in chloroform. This was hydrolysed with a large excess of 10N sodium hydroxide solution, yielding 3-hexen-2-ol \( [\alpha]_{D}^{25^\circ} = -4.8^\circ \) (homogeneous). The (-) carbinol was then hydrogenated at 1.5 atmospheres pressure using platinic oxide catalyst, and a hexanol was obtained \( [\alpha]_{D}^{25^\circ} = -11.0^\circ \) (homogeneous).
This was converted into a hydrogen phthalate $[\alpha]^{25}_{{\lambda} = 5893} = -40.8^\circ$ in chloroform. Pickard and Kenyon (47) give the rotatory powers for 2-hexanol at 25°C as $11.48^\circ$ and its hydrogen phthalate as $43.59^\circ$ for $\lambda = 5893$. Calculation of the ratio:

$$[\alpha]$$ Hydrogen phthalate in chloroform solution

$\alpha$ Carbinol (homogeneous)

for $\lambda = 5893$ in the case of the carbinol and hydrogen phthalate prepared as just described, is $4.56$. Airs, Dafle and Kenyon (1) give the ratio for pure 2-hexanol and its hydrogen phthalate as $4.60$. It may be concluded that the (-) 3-hexen-2-ol prepared was 93-99% 3-hexen-2-ol, and 96% optically pure. 10N sodium hydroxide solution had therefore been effective in preventing racemisation during hydrolysis of the (-) hydrogen phthalate.

The full optical-rotatory power of the (-) 3-hexen-2-ol is calculated to be $-4.25^\circ|^{25}_{{\lambda} = 5893}$. Similarly the full rotatory power of 3-hexen-2-yl hydrogen phthalate is $-21.7^\circ|^{25}_{{\lambda} = 5893}$.

The specific rotatory power of $\gamma$-ethyl-$d$-methylallyl alcohol, though low, is of the same order of magnitude as that of $\gamma$-methyl-$d$-$n$-propylallyl alcohol (9). Table I shows that the further substitution of an alkyl group in the $\gamma$-position of an $d$-substituted allyl alcohol often results in a considerable reduction of rotatory power. The optical rotation of 3-hexen-2-ol was determined for a range of wave-lengths. The
dispersion ratios are \([a]_{4350}/[a]_{5461} = 1.63\); \([a]_{5350} = 2.41\)

The observed rotatory powers fit a one-term Brude equation

\[
[a]_{25^\circ} = \frac{1.150}{\lambda^2 - 0.28132}
\]

whence \(\lambda = 2414\) \(\text{\AA}\). 2-Hexen-1-ol (Airs, Belfe and Konyon (1)), and 3-Hepten-3-ol (Platt (46)), have rotatory powers similarly fitting one-term equations, with \(\lambda\), respectively equal to 2225 \(\text{\AA}\) and 2400 \(\text{\AA}\). There is good reason to suppose that the rotations of these substituted allyl alcohols are only apparently simple, and that the complexity would be revealed if observations were made at lower wave-lengths (v. refs. (6) and (9)).

The known value of the optical-rotatory power of 2-hexen-4-ol (1) and the determined value of the rotatory power of 3-hexen-2-ol enable one to calculate the rotatory power of the mixture of carbinals obtained by Airs, Belfe and Konyon (1) on allowing (-) 2-hexen-4-ol to rotate for 1156 days. If the assumption be made that each component of the mixture contributes to the rotatory power without effect on the other's contribution, then the observed rotation in the 2.5 cm. tube after 1156 days should have been 2.52°. The observed rotation was 3.35°. This suggests that some other optically-active substance or substances is present. These may be the oxonium ions formed in the intermediate stages of the rearrangement e.g.

\[
\text{Me} - \text{CH} \quad \text{CH}_2 \quad \text{O} \quad \text{CH}_2 \text{Et}
\]
If this is so, it would also account for the initial rise of rotatory power observed in the mutarotation of 2-hexen-4-ol (1). The explanation suggested by the authors of the paper, viz., that the rise was due to the formation of optically-active 3-hexen-2-ol must be invalid, since the latter carbinol has been found to have an optical rotatory power lower than that of 2-hexen-4-ol.

(3) THE REARRANGEMENT OF γ-METHYL-α-ETHYLALLYL ALCOHOL

Airs, Balfie and Kenyon (1), in the work described in Section V, showed that optically-active γ-methyl-α-ethyl-allyl alcohol rearranges to α-methyl-γ-ethylallyl alcohol with considerable retention of optical activity. They deduced that the rearrangement of (+) carbinol led to the formation of the (+) form of its isomer, and were able partially to analyse the resulting mixture.

Balfie and Kenyon (3), in a review of anisotropic rearrangements, suggested that the carbinol mixture would come to an equilibrium composition, and Airs (2) expected that the equilibrium mixture would contain a slightly greater proportion of the γ-methyl than of the α-methyl isomer.

The present work in connection with the rearrangement of these carbinols was therefore directed towards the investigation of the following points:
(1) The establishment of a method for the analysis of mixtures of the racemic carbinols.

(2) The use of this method of analysis in following the change of composition of such mixtures with time.

(3) The study of the effect of acids and alkalis on the rearrangement, and of the concurrent decomposition to a diene by loss of water.

It was found that the hydrogenation of the carbinol mixture to a mixture of hexanols, and the conversion of this into a mixed p-xenylurethane, gave a product whose melting-point was a fairly accurate indication of the composition of the mixture of hexanols.*

The mixture of hexanol p-xenylurethane, formed directly from the carbinols, was not a satisfactory substance on which to make observations, as a cutectic mixture was formed between the two components, and the mixture of esters, over most of the composition range, had a low and rather indefinite melting-point. The mixture of saturated esters, on the other hand, showed a nearly perfect range of solid solutions. There was a slight inflexion in the curve melting-point v. composition of mixture which indicated the formation of a molecular compound of incongruent melting-point, at a composition of about 1:1.

*The Appendix describes attempts to establish another method of analysis.
Specimens of (dl) \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol were stored under various conditions. Small samples were withdrawn from time to time and hydrogenated to form a mixture of hexanols. This was converted to a mixed \( p \)-xenylurethane, whose melting-point was determined.

The substances added to the various specimens were as follows:

(i) None.
(ii) 1\% of glacial acetic acid.
(iii) Anhydrous potassium carbonate (2.5\% by weight of the carbinol).
(iv) Ammonia, to saturation.

A specimen of \( \alpha \)-methyl-\( \gamma \)-ethylallyl alcohol was allowed to stand without additions.

It was found that all specimens isomerised on standing with the exception of that in contact with potassium carbonate.

That to which acid had been added remained colourless, but rearranged to the extent of 10\% in 64 days, 15\% in 145 days, 23\% in 283 days, 41\% in 355 days, 49\% in 412 days, 53\% in 523 days and 54\% in 591 days.

The specimen stored without additions became discoloured (yellow) fairly rapidly, and deposited water to an extent indicating 34\% decomposition of the carbinol in 425 days. The composition, as regards the relative proportions of the two carbinols present, was found to be 53\% of \( \alpha \)-methyl isomer after
393 days, and later observations at 405 days and 573 days gave the same proportion.

The specimen stored with ammonia gradually discoloured. After 93 and 150 days it had apparently changed 1.5%, and after 346 days, 2%.

The specimen stored with potassium carbonate did not discolour, and no change in composition could be detected after 93, 147 or 273 days.

The α-methyl-γ-ethylallyl alcohol rearranged to the extent of 14% in 174 days, 23% in 222 days, 28% in 349 days, 32% in 415 days, 43% in 510 days, and had attained equilibrium in 532 days with 43% isomerisation, as an observation at 650 days gave an identical result.

The work of Airs, Balfes and Kenyon (1) showed that (+) γ-methyl-α-ethylallyl alcohol after 1150 days had changed to a mixture of 41% (+) γ-methyl-α-ethylallyl alcohol, 32% of (+) α-methyl-γ-ethylallyl alcohol and 27% racemic material. The present results indicate that an equilibrium is reached at 53% α-methyl-γ-ethylallyl alcohol in 530 days. From this, the composition of the racemic material obtained previously can be deduced, as the mixture should have reached equilibrium with respect to the total amounts of each alcohol present after 1150 days.

The racemic material should contain $(43 - 41) = 4$ parts of $(41) \gamma$-methyl-$\alpha$-ethylallyl alcohol to $(53 - 32) = 23$ parts of $(32) \alpha$-methyl-γ-ethylallyl alcohol.
of (dl) α-methyl-γ-ethylallyl alcohol. The mixture after
1156 days standing therefore consisted of:

- 41% (+) γ-methyl-α-ethylallyl alcohol
- 4% (dl) γ-a
- 32% (+) α-γ
- 23% (dl) α-γ

The considerable disparity in the proportions of the racemic
carbinal present can be accounted for either by supposing that
α-methyl-γ-ethylallyl alcohol racemises much more rapidly than
its isomer, or that racemisation accompanies the formation of
this alcohol by isomerisation. The latter view is the more
likely, as the behaviour of α-methyl-γ-ethylallyl alcohol on
standing is very similar to that of its isomer, rearranging to
the extent of 20% with no acid added, and therefore needing to
develop acidity before starting to change, in 343 days, whereas
the γ-methyl compound with 1% acid changed 20% in 200 days.
The matter is discussed later in this section in connexion with
the mechanism of isomerisation.

As well as being practically identical in reactivity, the
two carbinals are present in almost equal proportions in the
equilibrium mixture. This is to be expected, as the electron-
releasing powers of the ethyl and methyl groups are very
similar. It is in strong contrast to other cases. For
example, γ-phenyl-α-methylallyl derivatives may be regarded as
coming to equilibrium with their α-phenyl-γ-methyl-allyl
isomers, but are so much more stable than the latter that the
proportions of the \( \alpha \)-phenyl isomers in the equilibrium mixture are extremely small. It is probable that when allyl alcohols or their esters are disubstituted in the \( \alpha \)- and \( \gamma \)-positions by electron-releasing substituents, an equilibrium tends to be set up, wherein the isomer with the more powerfully electron-releasing group in the \( \gamma \)-position is in excess. Since methyl and ethyl differ little in this respect, an equilibrium near the proportions 1:1 would be expected.

The retention of optical activity led Airs, Balfour and Kenyon (1) to suggest that there was some kind of internal bonding involved, represented by:

\[
\begin{align*}
\text{H} & \quad \text{CH} \quad \text{H} \\
\text{II} & \quad \text{C} & \quad \text{II} \\
\text{N} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

but they did not give any indication of the nature of the bond. The evidence for such a link was based on parachor determinations, (Section II), and is not of a very substantial character. This bonding would result in a certain amount of steric strain, which should be detectable by its effect on physical characteristics, but these carbinols are not noticeably unlike other unsaturated alcohols.

The schemes of isomerisation proposed by Young, Bosani and Warner (31), and by Braunss and Jones (25), depend upon acid catalysis, which has been shown by the present work to be essential for the change to occur.
The simpler Young mechanism:

\[ \begin{array}{c}
R'\underset{\text{CH}}{\text{O}}\underset{\text{CH}}{\text{C}}\underset{\text{CH}}{\text{R}}^+ + H^+ \\
\text{H} & \text{H} & \text{H}
\end{array} \quad \text{\(\leftrightarrow\)} \quad \begin{array}{c}
R'\underset{\text{CH}}{\text{O}}\underset{\text{CH}}{\text{C}}\underset{\text{CH}}{\text{R}}^-
\text{H} & \text{H} & \text{H}
\end{array} \]

supposes that the function of the acid catalyst is to be found in the supplying of a proton to form the oxonium ion of the carbinol. The creation of a strongly-positive centre on the oxygen atom, together with the electron-concentration in the region of the \(\gamma\)-carbon, leads to a ready explanation of the ease of change into, firstly, the oxonium ion of the isomeric carbinol, and thence by the loss of a proton to this carbinol itself.

The Braude-Jones mechanism has been referred to in Section V. It is a more complicated concept, of a system differentiated into two modes, the "alkyl" and the "aryl". The "alkyl" mode, which will operate when the substituents in the allyl chain are alkyl groups, is very similar to the Young mechanism, except that the approach of the oxygen atom to the \(\gamma\)-carbon is not explained in terms of electrostatic attraction, but as a complete severance of the oxygen from
the α-carbon atom in a neutral water molecule; this is supposed to occur with the water molecule never moving outside the field of influence of the carbonium ion from which it is momentarily detached.

The "aryl" mode, which is less relevant to the present discussion, occurs when the γ-substituent (or more rarely the α- or β-substituent, is phenyl or a similar group, involves the attachment of a solvent molecule to the γ-carbon atom (in solvation) and the subsequent detachment of the anion attached to the α-carbon atom.

Fraude (52) has recently reconsidered these mechanisms in greater detail. The modes which are here designated 'alkyl' and 'aryl' he considers to be intra- and intermolecular respectively. He suggests that, apart from the actual substituents present in the allyl system, the mechanism operating will depend on the relative probabilities of reaction of the intermediate complex

$$\begin{align*}
\left[\gamma = \text{OH}_2 \right]^+ & \rightleftharpoons \left[\text{OH}_2\right]^+
\end{align*}$$

with the "internal" water or an external molecule. The transition from one mechanism to another would be gradual, depending on ambient conditions such as the concentration of water in the solvent used. This transition could not be detected by the kinetic criteria so far applied.

He remarks that retention of optical activity, used as a
criterion of the intramolecular nature of uncatalysed rearrangements (cf. Kenyon, Partridge and Phillips (11); Leif and Kenyon (3)) is inapplicable in the hydrogen-ion-catalysed reaction since the migrating positive charge will destroy any asymmetry produced by the orientated approach of the migrating water molecule on one side of the γ-carbon atom. This is probably true, but the possibility must be examined that there is a mechanism analogous to that proposed by Ingold and Hughes (33) for the rearrangement of certain esters (Section V).

This mechanism supposes that, under suitable conditions, viz. a sufficiently high concentration of rearranging substance, retention of optical activity would be possible even in an intermolecular rearrangement. There might be preliminary ionisation of a small proportion of the allyl ester, followed by the attack of the anion thus formed on a neighbouring ester molecule, setting up a chain reaction

\[ R-X \rightarrow R^+ + X^- \]

\[ X^- \ldots \ldots X-X \rightarrow X-R + X^- \]

This is the \( S_{N}2 \) mechanism, which they have demonstrated does not operate under conditions of greater dilution.

The attacking entity, if this type of mechanism applies to the rearrangement of alcohols, can only be a water molecule which has been released from the influence of its carbonium ion, and which then reacts with either a carbinol molecule or the complex formed by the latter with a proton. The attack on a
carbinol molecule is not likely, as the formation of the isomer would mean the loss of a hydroxide group from the a-carbon atom, and also that of a hydrogen atom from the region of the γ-carbon atom, probably both as ions. A very high energy of activation would be expected for such reactions.

\[
\begin{align*}
-\hat{\mathbf{\cdot}} & = \mathbf{\cdot} - \hat{\mathbf{\cdot}} \quad \rightarrow \quad -\hat{\mathbf{\cdot}} & \cdot & \hat{\mathbf{\cdot}} = \mathbf{\cdot} \\
\text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O}
\end{align*}
\]

The attack on the carbinol-proton complex is, in effect, the 'aryl' mode, except that there is no free carbonium ion involved, so that optical activity could be retained. The slow rearrangement of γ-methyl-α-ethylallyl alcohol is compatible with this mechanism, as it can only operate when a water molecule approaches a carbinol-proton complex from certain directions.

There is the serious objection, however, that the 'alkyl' mode should operate for methyl-ethyl-allyl alcohols. The conditions under which the latter carbinols were rearranged differed from those used by Braude, Jones et al. in the fact that there was much less water present, so that the likelihood of the 'alkyl' mode operating was greater than for the ethynylallyl alcohols. Since Braude's theory was founded on the rearrangement of the latter in the presence of much water, and also of a much higher hydrogen-ion concentration than Airs, Balfe and Kenyon employed, the probability of this 'aryl mode' type of mechanism operating with retention of optical activity may be discounted.

The Braude-Jones mechanism, therefore, though most probably
applicable to many cases of anionotropic rearrangement, does not account for the optical retention in others, and some other process must act in these.

The Young mechanism, on the other hand, presents no difficulty in visualising the retention of optical activity, since the oxonium ions could be inter-converted with the positive charge carried in the entity moved along the carbon chain from the α-to the γ-carbon atom. If this charge is always seated on the oxygen atom, which is attracted to the vicinity of the γ-carbon atom by the electron concentration there, the formation of the partial bonds in the intermediate state takes place when there is a considerable steric 'fixing' of the atoms in an entity:

\[ R'\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{R}'' \]

where \( \ldots \ldots \) denotes a partial bond.

It gives a reasonable explanation of the source of the energy required for the steric deformation in intermediate states without demanding that the carbinol itself should have an unusual structure.

Balfe and Kenyon (3) in their review of asymmetric syntheses, gave this change as an example. In general, in such reactions, if a second asymmetric carbon atom is formed in a molecule already containing an optically-active centre, the new asymmetric atom is also optically-active. Such an intermediate entity as formulated above would account for the
formation of only one diastereoisomeride.

It may be pointed out that the oxonium ion first formed could well be a preliminary step in a Brønsted-Jonas type of change. If the second step occurred i.e. the positive charge moved on to the carbon chain, a water molecule might then break off, and a proton be lost from the carbonium ion, instead of recombining with a water molecule. This would result in the formation of a diene. The loss of water was observed to occur quite readily with the specimen of γ-methyl-α-ethylallyl alcohol stored without catalyst, decomposition being as much as 24% in 425 days. The break-down to diene and water is probably not quite so simple a process as here visualised; the material of the storage bottle, in this case an ordinary brown bottle-glass, may be a further necessary catalyst, as no decomposition of this kind was observed to occur in specimens which had been kept in Pyrex glass.

It is probable that the first step in the rearrangement of decomposition of a disubstituted allyl alcohol consists of the attachment of a proton to the oxygen atom, forming an oxonium ion. This ion will then behave in a manner depending on the nature of the substituents and (probably) on external factors like the surface of the vessel in which it is contained.
It may rearrange directly into the oxonium ion of the isomeric carbinol, which is then released by the loss of a proton from the ion. This process can, and in the case of the methyl ethyl allyl alcohols does, result in the retention of optical activity.

Otherwise, especially if an aryl substituent is present, it may transfer the positive charge from the oxygen atom to the carbon chain. A water molecule will then break off; if it remains within the influence of the carbonium ion, the isomeric oxonium ion is formed as before, but with optical activity lost. If solvation at the \(\gamma\)-carbon atom by a hydroxylic solvent occurs, an ether of the isomeric carbinol is formed, again with loss of optical activity. If the water escapes from the influence of the carbonium ion, decomposition to dienes, proton and water occurs.
\* = asymmetric carbon atom. \( R', R'' = H \) or alkyl or aryl group

\[ R'.CH_2.CH = CH.CH.CH_2.R'' \]

\( \text{OH} \)

\(+H^+ / \quad \)

\[ R'.CH_2.CH = CH.CH_2.R'' \]

\( \text{H} \)

\( \text{O} \)

Rearranged carbinol
(Optically active)

Rearranged carbinol
(racemic)

Dienes
In the case of \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol, when the (+) carbinol had been allowed to stand for 1153 days, the proportions of carbinols present were

\[
\begin{align*}
41\% & \ (\text{dl}) \ \gamma \text{-methyl-\( \alpha \)-ethylallyl alcohol} \\
4\% & \ (\text{dl}) \ \gamma \ 
\end{align*}
\]

It can be deduced that the carbinols only become racemic on rearrangement. Since the reactivity of each is approximately equal, the disproportionate preponderance of racemic rearranged carbinol indicates its formation during the rearrangement. The situation, however, is more complex than the above analysis suggests. The hydrocarbons formed were not estimated by Mrs. Salfe and Kenyon, so that a true weight balance is not possible on the information available. It can be said, however, that the ratio of the proportions of the racemic carbinols is not what one would expect after so long a period of standing. There is far too little (dl) \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol, which, after less than half the period had elapsed, should have been formed at a greater rate than its racemic isomer. It may be that the \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol is more easily dehydrated to a mixture of dienes than is its isomer. This supposition would also account for the observation that the specimen of \( \gamma \)-methyl-\( \alpha \)-ethylallyl alcohol stored without acid in brown glass reached equilibrium with
respect to the proportions of carbinols present in a shorter
time than the specimen stored with added acid in Pyrex glass,
since 24% decomposition to water and hydrocarbons took place
in the former specimen, and no apparent decomposition in the
latter.
VII. \( \gamma \)-DIMETHYLLALLYL ALCOHOL.

The optical-rotatory power of \( \gamma \)-dimethylallyl alcohol (13) is low \([\alpha]_b^{5461} + 1.14^\circ\); it is extremely sensitive to temperature changes and solvent influence. Mutarotation occurs in a highly erratic manner. When the (+) carbinol is reduced with hydrogen and platinic oxide, the resulting methyl \( n \)-propyl carbinol yields a (+) hydrogen phthalic ester of almost full rotatory power. These reactions were carried out under conditions unlikely to lead to loss of activity, so that the original (+) dimethylallyl alcohol was probably almost optically-pure. When the (+) carbinol is treated in the cold with pyridine and phosphorus trichloride, a (-) chloride is formed, with \([\alpha]_b^{20^\circ} \) varying in different experiments from \(-1^\circ\) to \(-19^\circ\) (53, 13). This (-) chloride racemises on standing, either alone or when dissolved in benzene. On hydrolysis with a suspension of calcium carbonate in water, it yields an alcohol (laevorotatory) \([\alpha]_b^{100^\circ} \) \(-1.43^\circ\), which was converted quantitatively into a racemic hydrogen phthalic ester. The original (+) alcohol, under the same conditions, gave a hydrogen phthalate \([\alpha]_b^{5461} + 23.5^\circ\).

The laevor-alcohol can also be converted into a racemic dibrom-addition product, i.e. it does not contain the normal form of (-) \( \gamma \)-dimethylallyl alcohol. Optically-active derivatives have been prepared, however. The acetate
[\alpha]_{5461}^{\text{D}} = -0.02^3 \text{ and the hydrogen-reduction product } [\alpha]_{5461}^{\text{D}} = 0.3^3 

have each rotatory powers about 2\% of those of the corresponding products from (+) \text{\textgamma}-\text{dimethylallyl alcohol.}

These peculiarities of \text{\textgamma}-\text{dimethylallyl alcohol} together with its parascholar have caused certain suggestions to be made regarding its structure, and that of \textit{allyl} alcohols in general. Since it has been concluded in the present thesis that these alcohols exist in open-chain form, and not in the cyclic form postulated by these suggestions, it is desirable to consider the especial characteristics of this alcohol in more detail.

Balfe, Hills, Kenyon, Phillips and Platt (54) suggested that the observations on the anomalous laever-alcohols are best explained by supposing that the hydrolytic product of the (-) chloride to consist chiefly of (dl) alcohol, but to contain a small proportion of some laeverotatory substance. The appearance, or non-appearance, of optical activity in products of reaction of the carbinal would then be due to preferential attack on the reagent on one of the other constituent of the mixture, complicated by the possible removal of one product or the other during purification.

Consideration of the evidence of mutarotation of (+) \text{\textgamma}-\text{dimethylallyl alcohol} makes it probable that the (-) substance is already present in apparently optically-pure (+) carbinal, and does not itself mutarotate. The mutarotation, however erratic, always led eventually to a reversal of sign, and the
(+)-alcohol when reacted with half-an-equivalent of phenyl carbimide left a (-)-alcohol as unreacted substance. When half-an-equivalent of phenyl carbimide reacted with a carbimide which had become laevorotatory by mutarotation, the unreacted carbimide was again laevorotatory.

A possible substance to be present would be (-)-methyl allyl carbimide, which answers well to the requirements of the situation. It has E.P. 115-116° and [α]_20^0^-4.4^0. This rotation was calculated by comparison of the rotatory power of the reduction product of a partially-resolved alcohol and that of optically-pure methyl n-propyl carbimide (Richard and Kenyon (47)). A careful distillation of (+)-dimethylallyl alcohol showed that the first runnings had a lower rotatory power than the main fraction (E.P. 110-112°). As the rotatory power of the anomalous carbimide is low in value, and the dispersion complex, the composition may well be as suggested, although no direct evidence in the form of a derivative of methyl allyl carbimide has been found.

The mechanism of isomerisation to produce the (-)-carbimide was suggested to be as in the scheme:

```
CH_2=CHCH=CHCH_2CH_3 \rightarrow CH_2=CHCH=CHCH_2CH_3 \leftarrow CH_3
```

It was suggested that it occurred under the influence of the electron-releasing methyl group (Baker and Nathan, (55));
Hughes, Ingold and Takeda, (56)). It seems, however, unlikely that the α-methyl group could control the molecule in this way, since the γ-methyl is more able to polarize the double bond and so cause electron-movements in the opposite sense. It may be said that, whatever the constitution of the (−) substance, if it exists, in γ-dimethylallyl alcohol, it is a minor constituent, and most of the alcohol consists of the normal open-chain form, as do other allyl alcohols.
PART 2. EXPERIMENTAL.

3-Hexen-2-ol. (α-Methyl-γ-ethylallyl alcohol).

This substance has been previously described by Frévelet (43). It was prepared in this investigation by the reduction of the corresponding ketone, 3-hexen-2-one. The latter was prepared by the method of Grignard and Muchaire (43).

Acetone, distilled from anhydrous calcium chloride, (200 g) was mixed with ether (80 g) and 2.5N sodium hydroxide solution (100 ml), and the mixture cooled to 5°C. More of the freshly-distilled acetone (200 g) was mixed with redistilled propionaldehyde (200 g), and added, with vigorous stirring, to the cooled mixture over a period of five hours. The temperature of the reaction mixture was kept below 15°C, and stirring continued for one hour after addition was complete. The ethereal layer was separated, and the aqueous layer extracted three times with 30-40 ml. portions of ether. The ethereal solutions were united, washed with 3% acetic acid solution until the washings were acid, and then with water until the acid was removed. The solution was then dried over anhydrous sodium sulphate, and the other, acetone and unreacted propionaldehyde distilled. The orange liquid remaining (c. 200 g.) was distilled slowly from 8 g. of anhydrous oxalic acid. The fraction boiling 150-153°C was collected, dried over anhydrous potassium carbonate and redistilled. The fraction boiling 153-157°C was collected. The yield was variable,
but was usually rather less than 60 gms. (15% on the propionaldehyde used). Grignard and Fluchaire state that their yield was 50%.

Distillation of the crude product without the addition of anhydrous oxalic acid, followed by drying and redistillation as before, gave yields varying from 15% to 35%, the highest yields being obtained when the scale of the reaction was reduced. The French authors state specifically that very low yields result if the crude aldol is distilled without a dehydrating agent.

Further investigations were made in attempts to improve the yields. As the reaction depends on the efficient admixture of two immiscible liquid phases, it was thought that ineffective stirring might be responsible for the poor result. Experiment with various patterns of stirrer ended with the adoption of a type consisting of a thistle-funnel with pierced sides. The efficiency of mixing was then high, the mixture taking two or three minutes to separate completely into two layers. It was found that the improved stirring had no appreciable effect on the yield.

The use of lower temperatures during the condensation (40° to 60°) also altered the yield very little.

Some specimens of the ketone were prepared similarly, but the pure aldol was separated before dehydration, as it was found that the dehydration of the pure product could be effected
rather more smoothly than that of the crude. The aldel, 4-hydroxyhexan-2-one, was obtained in 80-90% yield from the crude reaction-product. It is a pale-yellow liquid, B.P. 63-93°/15 mm., 110-120°/23 mm. It decomposed very easily on warming with 4% by weight of anhydrous oxalic acid, giving 60-70% yields of ketone, i.e., 24-32% overall.

The ketone thus prepared had B.P. 45-50°/18 mm., 60-65°/15 mm., 136-137°/760 mm. n\textsubscriptD 1.4457. d\textsubscript2\textsuperscript{20} 0.8874. It was slightly contaminated with impurities giving it a yellowish tinge and a faintly acrid odour. The impurities were removable by distilling the ketone with an equal volume of dry benzene. The product, after removal of substances boiling below 150° at atmospheric pressure, was distilled at 10 mm. pressure—B.P. 44-45°. The ketone was then nearly colourless and had a pleasant odour.

Derivatives of 3-Hexan-2-one.

Semicarbazone.

3-Hexan-2-one (1.8 g) was added to a saturated solution of semicarbazide hydrochloride (2 g) in water, and ethyl alcohol (0.5 ml.) added drop by drop until the mixture was homogeneous. The mixture was then warmed for 15 minutes on the water-bath, cooled, and the white crystals which separated filtered. These crystals were recrystallized twice from alcohol to M.P. 138-137°C. A similar product was obtained when sodium acetate (1 g) was added as a buffer to the reaction mixture.
A solution of 3-hexen-2-one (2 g) and 2:4 dinitrophenylhydrazine (2 g) in glacial acetic acid (4 ml) was added to a solution of sodium acetate (1 g) in water (10 ml). Alcohol was added drop by drop until the mixture was homogeneous. The reaction mixture was then warmed for 15 minutes on the water-bath. After cooling, the red crystals which had separated were filtered and washed on the filter with hot water. Four recrystallisations from alcohol gave needle-shaped crystals of M.P. 130-131°C, which was unaltered by a further recrystallisation from alcohol.

Analysis:-- Found Calculated for C_{12}H_{14}N_{4}O_N 27·1% N 19·2% Recrystallisation three times more from alcohol, followed by standing of the crystals in a vacuum desiccator for three months, gave a substance M.P. 132·5°C.

Analysis:-- Found Calculated N 19·6% N 20·1%

Similar discrepancies of analysis, presumably due to solvent retention, for the 2:4 dinitrophenylhydrazone of the near homologue, 3-hepten-2-one, were reported by Eccott and Linstead (57).

Reduction of 3-Hexen-2-one.

Isopropyl alcohol was dried by refluxing the 99% grade for five hours over quicklime. It was then distilled (S.P.
82.7°C, and a 60% middle fraction used for the reaction.

Aluminium turnings were cleaned by warming in sodium hydroxide solution until the evolution of hydrogen was brisk, then washing well with water. They were then, in earlier preparations, treated with 1% mercuric chloride solution for 10 minutes, washed again with water, and finally dried in a current of warm air. Later, it was found that the addition of mercuric chloride in the quantities necessary (0.1 g. or less) to the reaction mixture produced no deleterious effect.

A typical charge for the reaction was isopropyl alcohol (550-600 ml), dry, cleaned aluminium turnings (12 g.) and mercuric chloride (0.1 g.). Evolution of hydrogen started almost immediately, becoming so violent that cooling of the flask was necessary. After some time, it subsided so that heating under reflux on the water-bath was required to complete the reaction. A dark-grey precipitate, very bulky, though small in weight, was formed in addition to a clear solution. The whole mixture could be used for the next stage of the reaction.

3-Hexen-2-one (60 g.) was added to the reaction-mixture and the whole was heated gently on a water-bath. Acetone slowly distilled through a fractionating column surmounted by a methyl alcohol 'cold-finger'. The evolution of this acetone slackened after one hour, but continued to be distilled for five to seven hours more. When the distillate no longer gave
a positive reaction with a 0.1% solution of 2:4 dinitrophenyl-hydrazine in 2N hydrochloric acid, the unchanged isopropyl alcohol was removed by distillation at somewhat reduced pressure (300 mm.). The residual complex was decomposed by cooling well, and adding a slight excess of hydrochloric acid (300 ml. of 6N). The organic constituents were removed by extraction with four portions (50 ml.) of ether, and the united ethereal solutions washed free of acid. The mixture was then dried over anhydrous potassium carbonate, the ether was distilled at atmospheric pressure, and the carbinol at reduced pressure (b.p. 47-48°/12 mm.; 55-57°/16 mm.; 73-75°/35 mm.). The yield varied from 30-40% on 60 g. of ketone up to 45% on 25 g. of ketone.

The procedure was changed in the preparation of later specimens of the carbinol to accelerate the process. Vapour was distilled past the 'cold-finger' until the volume of liquid remaining in the reaction mixture was reduced to one-third of its original volume. An equal volume of dry isopropyl alcohol was added, and distillation continued until the reaction mixture became very viscous. Decomposition and isolation of the carbinol was carried out as before. The yield by this procedure was about 35%.

The carbinol was a colourless liquid with a pleasant odour and was slightly irri\textquotesingle;atory.
Analysis:- Calculated for C₆H₁₂O: C 72.0%; H 12.0%

Found: C 71.7%; H 11.8%

Density: $\rho_{20}^0 = 0.8330; \rho_{25}^0 = 0.8333; \rho_{27}^0 = 0.8316.$

Refractive index: $n_2^0 = 1.4324.$

The carbinol decomposed on distillation at atmospheric pressure, the main product of decomposition, distilling at c. 70°, being probably mainly 1:3 hexadiene.

The higher-boiling materials formed simultaneously with the carbinol in the reduction of the ketone were mostly highly polymeric, but there was a fraction (c. 10% yield) b.p. 85-90°/35 mm., which was a practically colourless, odourless oil. It was unsaturated, and may have been a dimer of 1:3 hexadiene.

The Hydrogen Phthalic Ester of 3-Hexen-2-ol.

3-Hexen-2-ol (20 g.), dried over anhydrous potassium carbonate, freshly distilled phthalic anhydride (29 g.) and dry, redistilled pyridine (20 ml.) were mixed together and allowed to stand for 15 hours. The mixture was then warmed to 40° to dissolve the remaining phthalic anhydride, and allowed to cool. It was then cooled further to 0°, and dilute hydrochloric acid was added (25 ml. concentrated acid diluted to 200 ml.) together with crushed ice. The oil which separated was dissolved in 100 ml. of ether, washed with more dilute hydrochloric acid, and then shaken with a saturated
solution of sodium bicarbonate in about 10% excess (200-220 ml.).

The solution of the sodium salt of the ester was decomposed, after separating off the ethereal layer, by the addition of hydrochloric acid until the solution was acid to Congo-red. The precipitated ester was dissolved in ether, washed free of acid, and the ethereal solution dried over anhydrous sodium sulphate. After removal of the ether, with or without the addition of light-petroleum (40-60°C), the ester separated as a yellow oil. Attempts to purify it by forming the sodium salt, washing the aqueous solution of the salt with ether, and decomposing again, effected no improvement of the colour; use of the ammonium salt in a similar manner resulted in a darkened product. The ester could not be made to crystallise.

The yield of hydrogen phthalic ester varied from 60-70%, so the ethereal solution obtained in the first purification with bicarbonate was evaporated, and the oil obtained quantitatively saponified. The excess of alkali was titrated with standard acid. The deduced composition of the oil corresponded closely with that of the hydrogen phthalic ester.

The hydrogen phthalic ester appeared to be fairly stable; specimens were completely soluble in chloroform two months after formation, but six months later crystals of phthalic acid had deposited.
Reactions of the Hydrogen Phthalic Ester.

These tests were carried out in further investigation of the tendency of the ester to alkyl-oxygen fission (v.p. 52).

1) The ester (1 g.) was dissolved in its equivalent (13.5 ml.) of 0.3N sodium hydroxide solution. There was no visible change after one month.

2) The ester (3.3 g.) was dissolved in 1.5 equivalents of saturated sodium bicarbonate solution (150 ml. of 0.33N), and the solution allowed to stand for one month. Oily drops slowly settled out. These were extracted with two 25 ml. portions of ether, the solvent removed and the oil weighed (0.305 g.). The oil was saponified with excess ethyl-alcoholic sodium hydroxide solution, and the excess alkali titrated with acid. The ester content of the oil was negligible; it was concluded that the reaction with sodium bicarbonate solution was entirely a hydrolysis to 3-hexen-2-ol and sodium phthalate.

3) A solution of the sodium salt was prepared as in reaction (1), and warmed to 35°C with sodium p-toluenesulphinate (0.7 g.). There was no visible reaction on standing.

Optical Resolution of 3-Hexen-2-yl Hydrogen Phthalate.

The hydrogen phthalic ester was kept in a vacuum desiccator for three days after preparation; its molecular
weight was then determined by hydrolysis by excess alkali, and titration with acid, to be 247 (theor. 248).

The ester (40 g.) was dissolved in dry acetone (300 ml.) and the solution poured on to anhydrous brucine (82 g.). The mixture was warmed to 50°C to dissolve the alkaloid. The solution was allowed to stand until about one-half of the alkaloid salt had deposited. The crystals of the salt were redissolved in acetone and crystallisation allowed to occur again. The process was repeated, and the crop of crystals obtained in the third crystallisation (12 g.) used in the next stage of the investigation.

In the second resolution, the quantities used in this stage were:
- Hydrogen phthalic ester 80 g.
- Brucine (anhydrous) 95.3 g.
These were dissolved in 400 ml. of acetone, and the resolution carried on as above. There were five crystallisations, with the recovery of a final crop of least soluble brucine salt of 8.9 g.

As the brucine salt was found to be very soluble in acetone, other solvents, including chloroform and methyl acetate, were tried. In all of them the salt was very soluble. The salts of the ester with other alkaloids (quinidine, cinchonidine) were also prepared, but were found to be even more soluble and tended to deposit from solution as oils.
Decomposition of the Brucine Salt.

Brucine salt of the hydrogen phthalate (13 g.) was dissolved in chloroform (70 ml.) and the solution shaken with ten 75 ml. portions of 2.5N hydrochloric acid at 10°C. The liberated hydrogen phthalic ester was then washed with water in chloroform solution, and the solution dried with anhydrous sodium sulphate. The chloroform was then removed at 70°C/20 mm. to leave the ester (4.4 g.) as an almost colourless oil, \([\alpha]_{5893} = -17.9^\circ\) (c, 2.5; l, 0.5) in chloroform.

Similar decomposition of the brucine salt obtained in the second resolution yielded ester (3.3 g.), with the following rotatory powers:-

(c, 2.45; l, 0.5), in chloroform solution. Temperature 25.0°C

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>([\alpha])</th>
</tr>
</thead>
<tbody>
<tr>
<td>6473</td>
<td>-17.7(5)^\circ</td>
</tr>
<tr>
<td>5893</td>
<td>-23.6</td>
</tr>
<tr>
<td>5780</td>
<td>-22.6</td>
</tr>
<tr>
<td>5480</td>
<td>-23.9</td>
</tr>
<tr>
<td>5380</td>
<td>-26.5</td>
</tr>
<tr>
<td>4800</td>
<td>-44.6</td>
</tr>
<tr>
<td>4353</td>
<td>-63.1</td>
</tr>
</tbody>
</table>

The dispersion ratio \([\alpha]_{4353}[\alpha]_{5480}\) is 2.15.
The Specific Optical Rotation of 3-Hexen-2-\(\gamma\) Hydrogen Phthalate $[\alpha]_D = 0.5 \text{ dm}, c = 4.9$ in chloroform, vs. Wavelength.
Hydrolysis of the Eubron Phthalate Ester.

The ester \([\alpha]_{500}^\circ = 23.5^\circ\) was treated with 6 ml. (2.0 equivalent) of 2N sodium hydroxide solution, heated in an oil-bath at 100°C for 30 minutes, and the carbinol then distilled over in a current of steam, the yield being 1.5 g. from 3.0 g. of ester. The carbinol was salted out with potassium carbonate, and dried for 15 hours over an anhydrous portion of the same salt; \([\alpha]_{21}^\circ = -0.64^\circ\) (homogeneous substance; \(\lambda = 0.24\)).

Reconversion of this carbinol to the hydrogen phthalic ester, by the method described above, gave an ester

\([\alpha]_{500}^\circ = 23.5^\circ\) (\(\lambda = 0.5\); \(\delta = 2.8\), in chloroform)

Hydrolysis of the ester \([\alpha]_{500}^\circ = 23.5^\circ\) was carried out using 10N sodium hydroxide solution (5 ml., 3.8 equivalents). The carbinol obtained had \(\alpha_4^{25} = 0.005\); its optical-rotatory power were as below:

<table>
<thead>
<tr>
<th>(\lambda)</th>
<th>([\alpha]_{500}^\circ)</th>
<th>([\alpha]_{5401}^\circ)</th>
<th>([\alpha]_{500}^\circ) corr. for optical purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>6436</td>
<td>-3.54(5)°</td>
<td>-3.62°</td>
<td></td>
</tr>
<tr>
<td>5003</td>
<td>-4.00</td>
<td>-4.25</td>
<td></td>
</tr>
<tr>
<td>5700</td>
<td>-4.30</td>
<td>-4.40</td>
<td></td>
</tr>
<tr>
<td>5401</td>
<td>-4.00</td>
<td>-5.10</td>
<td></td>
</tr>
<tr>
<td>5303</td>
<td>-3.90</td>
<td>-6.15</td>
<td></td>
</tr>
<tr>
<td>4200</td>
<td>-6.77</td>
<td>-7.05</td>
<td></td>
</tr>
<tr>
<td>4333</td>
<td>-3.83</td>
<td>-9.40</td>
<td></td>
</tr>
</tbody>
</table>

Homogeneous state, 1, 0.25, temperature 25.0°C.

The dispersion ratio \([\alpha]_{6000}^\circ/[\alpha]_{5401}^\circ\) is 1.22; \([\alpha]_{6585}^\circ/[\alpha]_{5003}^\circ\) = 2.22.
Graph of $\lambda^2$ vs. $1/[a]^{25\circ}$
Reduction of *Leuco-3-Hexen-2-ol.*

(*Leuco-*) 3-hexen-2-ol (1.0 g.) was dissolved in dry ether (10 ml.), Adams' platinic oxide catalyst (0.1 g.) was added, and reduction was carried out with hydrogen at 1.5 atmospheres pressure. There was an induction period of 5-10 minutes while the catalyst was being reduced, followed by a rapid absorption of hydrogen by the carbinol. After 20 minutes, absorption of hydrogen ceased. The catalyst was filtered off, and the ether distilled.

The carbinol obtained by reduction of the hexenol

\[
[a]_{5893} = -0.6\degree \text{ had } [\alpha]_{5893} = 13.0 - 1.7\degree, \text{ homogeneous, } l = 0.25. 
\]

The carbinol similarly obtained from the hexenol

\[
[a]_{5893} = 25.0 - 4.8\degree \text{ had a density } 0.8130, \quad 25.0 \text{ and } [\alpha]_{5893} = 25.0 - 11.0\degree, \text{ homogeneous, } l = 0.25. \text{ Pickard and Kenyon (47) give the corresponding values for optically pure 2-hexanol as } 0.8120 \text{ and } -1143\degree, \text{ respectively.}
\]

**The Hydrogen Phthalate of the Reduced Carbinol.**

Reduced carbinol \([\alpha]_{5893} = -11.0\degree (0.71 g.)\) and phthalic anhydride (1.35 g.) were heated together in a sealed tube for 6 hours at 100\degree C. The product was readily and completely soluble in chloroform; \([\alpha]_{5893} = -49.6\degree, c = 5.02, l = 1.0.\) Pickard and Kenyon (loc. cit.) give 45.3\degree as the specific rotatory power of optically-pure 2-hexanyl hydrogen phthalate.
The ratio of Airs, Balfes andKenyon (1), viz.

\[
\frac{[\text{\text{CH}_3}_3 \text{ of the hydrogen phthalate}]}{d_{\text{\text{C}_6}^\circ \text{ of carbinol (homogenouse)}}}
\]

is 4.88 for the reduced carbinol and its hydrogen phthalate prepared as described above at 25°C; the ratio for pure 2-hexanal and its hydrogen phthalate is 4.6 at 25°C.

2-Hexen-4-ol (α-methyl-γ-ethylallyl alcohol).

This carbinol was prepared by the reaction of crotonaldehyde (0.9 equivalent) with methylmagnesium iodide (1.0 equivalent), in 80-85% yield, bp. 39-42°C/0 mm., 339/33 mm.;
\(d_{21}^\circ 0.9331, \, n_{5893}^\circ 1.4223\).

Four portions of the twice-distilled carbinol were set aside.

1. 6.9 g. were allowed to stand without additions in a bottle of ordinary brown glass. A certain amount of discoloration occurred, accompanied by the separation of water (5.0 ml. after 14 months).

2. 10 g. were stored with 0.1 ml. of glacial acetic acid added, in a small pyrex flask.

3. 10 g. were stored similarly to (2), but with 0.25 g. of anhydrous potassium carbonate.

4. 10 g. were stored similarly to (2), but with 0.5 ml. of concentrated ammonium hydroxide solution.

The reason for employing two different alkaline addenda, in specimens (3) and (4), was the possibility that water also
exerted a catalytic effect on the reaction, therefore specimens were stored under both moist and anhydrous alkaline conditions.

3-hexen-2-ol (10 g.) was also stored, without additions, in a Pyrex flask.

2-Hexanol and 3-Hexanol.
These were prepared by the appropriate Grignard reaction, 0.9 equivalent of aldehyde being added to 1.0 equivalent of Grignard compound at 5°C.

2-Hexanol. n-Butylmagnesium bromide and acetaldehyde.
Yield 70%.

3-Hexanol. Ethylmagnesium chloride and n-butyraldehyde.
Yield 70-80%.
Both were dried over anhydrous potassium carbonate, and distilled to constant boiling-point:

2-hexanol 136-137°C; d_4^20 0.8158.
3-hexanol 138°C; d_4^20 0.8190.

The Preparation of p-Xenylurethanse.

The method used was to warm the anhydrous carbinitol with p-xenylcarbimide for 1 hour at 70°C. In the case of saturated carbinols, the use of approximately equivalent proportions (viz. 1 of carbinol to 2 of carbimide by weight) was convenient, but the dehydrating action of the carbimide made it advisable to use proportions of approximately 1:1 by weight for the unsaturated alcohols.
Voluminous quantities of di-p-xenyl urea were always deposited when the reaction mixture was extracted with ether (15 ml. for each 0.2 g. of carbimol used). This di-p-xenylurea represented 15-20% of the original p-xenylcarbimide. The precipitate was filtered off, and the ethereal solution allowed to stand in a damp atmosphere for 24 hours to allow any unreacted carbimide to form di-p-xenyl urea and be precipitated. No precipitate was usually formed; when any had appeared, it was filtered off and the ethereal solution of p-xenylurethane mixed with 5 ml. of light petroleum (40-60°C) and the p-xenylurethane allowed to crystallise.

**2-Hexanyl Ester.**

After two recrystallisations from ether and light petroleum, the ester consisted of small white needles m.p. 90-91°C.

Analysis: Found: N 4.70%
Calculated: N 4.71%

**3-Hexanyl Ester.**

Similarly, after two recrystallisations, the p-xenylurethane was a felted mass of long white needles m.p. 136-137°C.

Analysis: Found: N 4.68%
Calculated: N 4.71%

**3-Hexen-2-yl Ester.**

Reaction of 0.4 g. carbimol with 0.45 g. p-xenylcarbimide yielded a p-xenylurethane, which after three recrystallisations
formed a mass of very small white crystals M.P. 71°C.

Analysis:- Found:- N 4.67%
Calculation:- N 4.75%

2-Hexen-4-yl Ester.

Reaction of 1.0 g. of carbanol with 1.0 g. p-xenyl-carbamide yielded an ester which, after three recrystallisations, consisted of white crystals M.P. 102°C.

Analysis:- Found:- N 4.70%
Calculation:- N 4.75%

The Melting-Point Curves for Mixtures of p-Xenylurethanes.

(1) 2-Hexenyl and 3-Hexenyl Esters.

Quantities of the pure p-xenylurethanes were weighed, and mixed by solution in dry ether; the ether was then distilled off and the solid mixture left in the vacuum desiccator for 24 hours before its melting-point was taken. The values tabulated below are those at which the first sign of definite, easily-observable melting was noted. They corresponded, in the cases of mixtures of lower melting-point, to the first-observed temperatures of complete fluidity. In mixtures with melting-points near the higher end of the range, they represent the temperature when a partial fluidity was seen.
<table>
<thead>
<tr>
<th>% of 2-Isomer.</th>
<th>M.P. °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>90-91</td>
</tr>
<tr>
<td>87.0</td>
<td>93</td>
</tr>
<tr>
<td>73.5</td>
<td>95-96</td>
</tr>
<tr>
<td>61.7(5)</td>
<td>99-100</td>
</tr>
<tr>
<td>50.0</td>
<td>103-104</td>
</tr>
<tr>
<td>37.3(5)</td>
<td>111</td>
</tr>
<tr>
<td>24.7</td>
<td>119-120</td>
</tr>
<tr>
<td>12.3</td>
<td>125-127</td>
</tr>
<tr>
<td>0</td>
<td>135-137</td>
</tr>
</tbody>
</table>

(2) 3-Hexen-2-yl and 2-Hexen-4-yl Esters.

The preparation of mixtures was carried out in a similar way to those described above. Melting-points tabulated are in general those of complete melting.

<table>
<thead>
<tr>
<th>% of 3-Hexen-2-yl Isomer.</th>
<th>M.P. °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>71</td>
</tr>
<tr>
<td>89.2</td>
<td>56-57</td>
</tr>
<tr>
<td>81.8</td>
<td>58</td>
</tr>
<tr>
<td>68.7</td>
<td>59</td>
</tr>
<tr>
<td>60.4</td>
<td>61-62</td>
</tr>
<tr>
<td>48.5</td>
<td>72-73</td>
</tr>
<tr>
<td>30.2</td>
<td>73</td>
</tr>
<tr>
<td>22.8</td>
<td>85-88</td>
</tr>
<tr>
<td>10.0</td>
<td>94</td>
</tr>
<tr>
<td>0</td>
<td>102</td>
</tr>
</tbody>
</table>
The Melting-points of Mixtures of Xylylurethanes of 2-Hexanol and 3-Hexanol.
The Melting-points of Mixtures of the Xylenolurethanes of 3-Hex-2-ol and 2-Hexen-4-ol.
The Analysis of Mixtures of 2-Hexanol and 3-Hexanol.

A. Mixtures of Known Composition.

(1). 2-hexanol (0.713 g.) and 3-hexanol (0.623 g.) were mixed and heated with p-xenylcarbimide (2.62 g.) for 1 hour at 70°C. The mixture was cooled and extracted with ether (70 ml.). The ethereal solution was allowed to stand for 24 hours in a damp atmosphere, the precipitated di-p-xenylurea filtered off, and light petroleum (40-60°C, 15 ml.) added. The solution was allowed to evaporate until about 0.5 ml. of liquid remained, when the solid was filtered off, washed on the filter with two 1 ml. portions of light petroleum, and then kept in a vacuum desiccator for 43 hours. The melting-point of the mixed ester was 103-104°C., corresponding to 45-50 5% of 2-hexanol (actually present 51.1%).

(2). This was carried out as in (1), but with the quantities:

- 2-Hexanol: 0.227 g.
- 3-Hexanol: 0.514 g.
- p-Xenylcarbimide: 1.44 g.

The mixed ester had a melting-point 115-115.5°C., corresponding to 25.5-30.0% 2-hexanol (actually present 30.7%).
3. Mixtures of Carbinols formed on Standing.

(1) 2-hexen-4-ol, after 325 days standing.

The specimen was dried for 24 hours over anhydrous potassium carbonate; 0.52 g. was heated with p-xenylcarbinide (0.65 g.) for 1 hour at 70°C. Extraction, etc., was carried out as described in the last section. The mixed ester consisted of greasy crystals of rather indefinite melting-point (65-70°C, corresponding to either 0.6-7.3% or to 48.5-54.3% 3-hexen-2-yl ester).

(2) Hydrogenated Mixtures of Carbinols.

It was decided that the direct esterification of the mixture of hexanols, as above, would lead to the formation of mixed esters of less sharp melting-point than those formed from the mixture of hexanols obtained by hydrogenation of the hexanol mixture.

The method followed in the experiments tabulated below was as follows:-

A small portion (0.5-1.0 g.) was withdrawn from the carbinol mixture to be examined. It was then neutralised, if acid, and also dried, by standing it for 12 hours with anhydrous potassium carbonate. In cases where ammonium hydroxide was the addendum to the specimen, ammonia remaining in solution in the dried carbinol was removed by drawing a current of dry air through the carbinol.
The dry carbinol was then dissolved in dry ether (10 ml.), and hydrogenated as described above (p.90). The mixture of hexanols obtained was heated with 0.9-1.1 equivalent of p-xylene carbimide at 70°C. for 1 hour, and the mixed ester extracted as previously described. The results are contained in the tables below. It has been assumed that the mixture of hexanols formed by hydrogenation contained the same proportion of 2-hydroxy- to 3-hydroxy-compound as that existing in the mixture of hexanols from which it was derived.

### 2-hexen-4-ol (stored without additions).

<table>
<thead>
<tr>
<th>Period of storage</th>
<th>M.P. of mixed ester</th>
<th>% 3-hexen-2-ol of reduced carbinol. in specimen.</th>
</tr>
</thead>
<tbody>
<tr>
<td>393 days</td>
<td>101.5-102°C</td>
<td>53-55%</td>
</tr>
<tr>
<td>435 &quot;</td>
<td>101-101.5</td>
<td>55-56%</td>
</tr>
<tr>
<td>573 &quot;</td>
<td>101-101.5</td>
<td>55-56%</td>
</tr>
</tbody>
</table>

### 2-hexen-4-ol (with 1% acetic acid added).

<table>
<thead>
<tr>
<th>Period of storage</th>
<th>M.P. of mixed ester</th>
<th>% 3-hexen-2-ol of reduced carbinol. in specimen.</th>
</tr>
</thead>
<tbody>
<tr>
<td>84 days</td>
<td>123-123.5°C</td>
<td>9.5-10%</td>
</tr>
<tr>
<td>143 &quot;</td>
<td>126-127</td>
<td>11.5-13%</td>
</tr>
<tr>
<td>239 &quot;</td>
<td>116-117</td>
<td>25-28%</td>
</tr>
<tr>
<td>355 &quot;</td>
<td>108-108.5</td>
<td>40-41%</td>
</tr>
<tr>
<td>412 &quot;</td>
<td>104.5-105</td>
<td>47-48%</td>
</tr>
<tr>
<td>520 &quot;</td>
<td>102-102.5</td>
<td>52.5-53.5%</td>
</tr>
<tr>
<td>531 &quot;</td>
<td>101.5-102</td>
<td>53-55%</td>
</tr>
</tbody>
</table>
2-hexen-4-ol (stored over anhydrous $\text{K}_2\text{CO}_3$).

<table>
<thead>
<tr>
<th>Period of storage</th>
<th>M.P. of mixed ester of reduced carbinol</th>
<th>% 3-hexen-2-ol in specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>68 days</td>
<td>136-136.5°C</td>
<td>0.5-1.0%</td>
</tr>
<tr>
<td>147 &quot;</td>
<td>136-136.5</td>
<td>0.5-1.0%</td>
</tr>
<tr>
<td>273 &quot;</td>
<td>136-136.5</td>
<td>0.5-1.0%</td>
</tr>
</tbody>
</table>

2-hexen-4-ol (with 2% ammonium hydroxide added).

<table>
<thead>
<tr>
<th>Period of storage</th>
<th>M.P. of mixed ester of reduced carbinol</th>
<th>% 3-hexen-2-ol in specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>96 days</td>
<td>134.5-134.8°C</td>
<td>1.5-2.0%</td>
</tr>
<tr>
<td>150 &quot;</td>
<td>134.5-135</td>
<td>1.5-1.5%</td>
</tr>
<tr>
<td>345 &quot;</td>
<td>134.5-135</td>
<td>1.5-1.5%</td>
</tr>
</tbody>
</table>

3-hexen-2-ol (stored without additions).

<table>
<thead>
<tr>
<th>Period of storage</th>
<th>M.P. of mixed ester of reduced carbinol</th>
<th>% 3-hexen-2-ol in specimen</th>
</tr>
</thead>
<tbody>
<tr>
<td>174 days</td>
<td>92.5-93.5°C</td>
<td>84-89%</td>
</tr>
<tr>
<td>222 &quot;</td>
<td>94-94.5</td>
<td>73-81</td>
</tr>
<tr>
<td>343 &quot;</td>
<td>95.5-96</td>
<td>73-74</td>
</tr>
<tr>
<td>415 &quot;</td>
<td>97-97.5</td>
<td>67-69.5</td>
</tr>
<tr>
<td>510 &quot;</td>
<td>99.5-100</td>
<td>60-61</td>
</tr>
<tr>
<td>532 &quot;</td>
<td>100.5-101</td>
<td>57-63</td>
</tr>
<tr>
<td>653 &quot;</td>
<td>100.5-101</td>
<td>57-63</td>
</tr>
</tbody>
</table>

It is apparent that water does not catalyse isomerisation of 2-hexen-4-ol in the absence of acid, as the specimen with ammonium hydroxide solution added did not change detectably in composition.
References.

(9) Arcus and Kenyon, J.C.S., 1939, 3112.
(15) Kumford and Phillips (J.), J.C.S., 1929, 2112.
(20) Grédy and Piaux, Compt. rend., 1934, 2255, (1934).
(21) Burton, J.C.S., 1939, 1650.
(22) Do., do., 1939, 455.
(23) Dupont and others, Bull. soc. chim., 1939, 1239, 1215.
(24) Burton and Ingold, J.C.S., 1923, 704.
(25) Braude and Jones, J.C.S., 1944, 436.
(27) Ingold, J.C.S., 1933, 1120.
(32) Young, Lane et al., J.A.C.S., 69, 847, (1933).
(33) Hughes and Ingold, J.C.S., 1943, 2.
(34) Catchpole and Hughes, J.C.S., 1943, 1.
(35) Roberts, Young and Winstein, J.A.C.S., 64, 2157, (1942).
(41) Cope, Hoffman and Hardy, J.A.C.S., 63, 1933, (1941).
(42) Jones and Mccombie, J.S., 1943, 281.
(43) Neillbron, Jones and Raphael, J.C.S., 1943, 266.
(45) Ingold, Hau and Wilson, J.C.S., 1935, 1715.
(47) Pickard and Kenyon, J.C.S., 93, 49, (1911).
(49) Grignard and Fluchaire, Ann. chim., 2, 5, (1928).


(52) Braude, *J.C.S.*, 1945, 794.


(56) Hughes, Ingold and Taher, *J.C.S.*, 1940, 949.


APPENDIX.

METHODS OF ANALYSIS OF THE HEXENOL MIXTURES.

Although it was clear from the beginning of the investigation that the method finally adopted, viz. the conversion of the mixture of carbinols into a mixture of derivatives of convenient melting-point, would provide a means of determining the composition of the mixture of 2-hexen-4-ol with 3-hexen-2-ol, an attempt was made to find a more precise method.

It would be expected that the physical characteristics of the carbinols:

\[
\begin{align*}
\text{2-hexen-4-ol} & : \quad \text{CH}_3\left(\text{CH}=\text{CH}\right)_2\text{CH}_{\text{II}} \\
\text{3-hexen-2-ol} & : \quad \text{C}_2\text{H}_5\text{CH}=\text{CH}\text{CH}_3
\end{align*}
\]

would be so similar that methods such as determinations of density or refractive index, or by fractional distillation would be impractical (e.g. the boiling-points of the carbinols are given in the literature as 135.5° (ref. 1) and 136° (ref. 43) respectively.

Certain chemical methods, such as the determination of the rate of addition of iodine to the double bonds, or of esterification of the alcohols, seemed equally unpromising, since the characteristics most affecting these properties are those of the group \(-\text{CH} = \text{CH} \cdot \text{CHOH}\), which is present in both carbinols.
Consideration was also given to the oxidative fission of the molecules as a possible method. Ozonolysis leads in the first instance to the formation of acetic and propionic acids respectively from the two carbinols, together with two keto-acids:

\[
\begin{align*}
\text{CH}_3\cdot\text{CH} = \text{CH}\cdot\text{CH} \cdot \text{C}_2\text{H}_5 & \rightarrow \text{CH}_3\cdot\text{COCH} + \text{C}_2\text{H}_5\cdot\text{CO} \cdot \text{COOH} \\
\text{C}_2\text{H}_5\cdot\text{CH} = \text{CH}\cdot\text{CH} \cdot \text{CH}_3 & \rightarrow \text{C}_2\text{H}_5\cdot\text{COCH} + \text{CH}_3\cdot\text{CO} \cdot \text{COOH}
\end{align*}
\]

The keto-acids are not volatile in steam, so that the mixture of acetic and propionic acids could be analysed by the Duclaux method (Ann. chim. phys. (5), 2, 239, (1874); Analyst, 42, 125, (1874)). In this, the mixture of acids to be analysed is dissolved in a standard volume of water, and then a certain proportion by volume of the solution is distilled off, collected, and titrated with alkali. The volatilities in steam of the simpler aliphatic acids have been determined, and it is possible to calculate from the titration value that proportions of the acids were present in the original solution.

Unfortunately, the control of the oxidation would probably not be rigid enough to prevent further oxidation of the keto-acids to carbon dioxide and acetic and propionic acids. Also Boekhout and De Vries (Research Journal of the Royal Netherlands Agricultural Station, 20, 79, (1917)) have shown that the method is quite unreliable with more than two
3nH2n+1·COOH acids present, and it was thought very likely that the keto-acids, though themselves not volatile in steam, would affect the relative volatilities of the aliphatic acids. The method was therefore not considered further.

The reduced mixture of carbinols i.e. of two hexanols is less reactive, and powerful reagents may be employed with some hopes of quantitative results. On the other hand, the carbinols are so stable that few reagents, except those possessing oxidative properties, can be used. Treatment with alkali hypochlorite was investigated, on the assumption that 3-hexanol would be oxidised only to 3-hexanone, but that 2-hexanol, after conversion to 2-hexanone, would undergo a haloform reaction to produce n-butyric acid and the appropriate haloform.

\[
\begin{align*}
C_3H_7·CHOH·C_2H_5 & \xrightarrow{NaOH} C_3H_7·CO·C_2H_5 \\
C_4H_9·CHOH·C\ & \xrightarrow{NaOH} C_4H_9·CO·C \ & \xrightarrow{NaOH} C_4H_9·COOH·CHX_3
\end{align*}
\]

The first step in the investigation was to test whether it could be used for the quantitative estimation of 2-hexanol.

Weighed amounts of 2-hexanol (0.5-1.0 g.) were mixed with 10 ml. of aqueous sodium hydroxide solution (2.5N) and potassium iodide (1 g.). A weighed excess of iodine crystals (upwards of 40%) was then added. The mixture was stirred vigorously while 25 ml. of dioxan was added, to bring the mixture into homogeneous solution.

The mixture was then warmed on the water-bath for periods varying from 2 to 30 minutes; heating was then stopped, and
the reaction-mixture allowed to stand for 15 minutes longer on the water-bath. It was then cooled to room temperature, diluted with 50 ml. of water, acidified with sulphuric acid, and the excess iodine titrated with N/10 thiosulphate solution.

Usually, iodoform crystals separated on dilution with water, but on several occasions no crystals appeared; instead, a dark-brown oil was obtained, possibly methylene iodide containing dissolved iodine. When the oil appeared, the solution was not titrated.

The mixtures from which iodoform separated were found to contain too much iodine i.e. the amount of carbinol calculated from the titration figures to have been present was too low, varying from 32 to 96% of the true figure.

Variation of the time of warming, or of the excess of iodine used, did not affect the results in a consistent manner. For example, two results were obtained giving respectively 83·3 and 88·2% of the true amount of hexanol used. In each case, the excess of iodine used was 40%. When the excess of iodine was increased to 60%, with the same time of warming, the result indicated only 58% of the true amount of hexanol present.

One reason for the failure of the method under these conditions is probably the dismutation of the hypohalite:

$$3 \text{NaCl} \rightarrow \text{NaClO}_2 + 2 \text{NaI}$$
Schwicker (Zeit. phys. Chem., 16, 3032, (1895)) found that the period of half-change of sodium hypojodite at dilution 0.016N and in the presence of excess hydroxide ion, to be only 25 minutes at 12°C. Since the reaction was carried out at 60-70°C, the loss of hypojodite by conversion to iodate and iodide must be at least comparable to that used in the oxidative processes. However, one would expect that the greater the excess of iodine used, the more nearly would the reaction of the hexanol approach completion, and this was found not to be the case.

The rate of reaction of iodine with dioxan was found to be low (10 ml. of 0.01 ml. N/10 iodine solution in 30 minutes at 22°C). The effect of this factor would have been to favour a high rather than a low result.

Methyl alcohol is more generally used as a solvent in this type of reaction. Bates, Mullally and Walker (J.C.S. 1923, 401) gave a correction of 0.5 ml. of N/10 iodine solution for every 20 ml. of methyl alcohol at room temperature. This is of the same order of velocity as the reaction of the hexanols, so methyl alcohol seems an unsuitable solvent for the carbinols in this reaction.

It was intended that the investigation should have continued with the hexanol and the hypojodite present in much lower concentrations viz. with approximately 1% hexanol solution in dioxan and N/10 iodine and sodium hydroxide
solutions. Similar concentrations have been used by
Cuculescu (Bull. soc. st. Cernauti, 2, 143, (1923)). His
method was repeated in the present investigation. 16 ml. of
a 1% solution of a ketone (in this case methyl benzy1 ketone)
in methyl alcohol was added drop by drop to 20 ml. of 2.5%
sodium hydroxide solution. 90 ml. of N/10 iodine solution
(approximately a 50% excess) was then added, and the solution
allowed to stand at room temperature until the turbidity
cleared with the crystallisation and deposition of iodoform.
The solution was then carefully just acidified with sulphuric
acid, excess N/5 thiosulphate solution added, and the excess
titrated with N/10 iodine solution with starch indicator.
The use of methyl alcohol as solvent in this case was
justifiable because of the much quicker reaction of the ketone
with the hypoidite.

The results ranged between 3 and 8%, too high, even when
the correction for the reaction of methyl alcohol was applied.
The high results were possibly due to the iodination of
methylene groups in benzy1 radicals.

The reproducibility of the results was however only ±1%
Though it seemed quite probable that the use of a 1% solution
of hexanol in dioxan and of a very large excess of N/10
hypoidite solution at 20°C would allow estimations of hexanol
with a similar accuracy, this reproducibility was approximately
the same as that given by the determination of the melting-
point of the mixture of xenylurethanes prepared from the mixture of hexanols. It was therefore decided that the investigation of the hypoiodite method should be discontinued, and the melting-point method was adopted.