THE REACTIONS AND STRUCTURE OF
\( \alpha \chi \)-SUBSTITUTED ALLYL ALCOHOS.

A STUDY OF THE REACTIONS AND OPTICAL PROPERTIES
OF ETHYLPROPENYLICARBINOL
AND SOME OF ITS DERIVATIVES.

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ABSTRACT OF THESIS.

Ethylpropenylcarbinol (α-ethyl-γ-methylallyl alcohol) has been resolved into its d- and l-forms by fractional crystallisation of the brucine salt of the hydrogen phthalic ester. Reduction of the optically active alcohol has provided data which revise the figures published for the specific rotatory powers of ethyl n-propylcarbinol and its hydrogen phthalic ester.

Parachor determinations on substituted allyl alcohols and derivatives have indicated that the alcohols possess a cyclic configuration. The absence of association in allylic alcohols has been demonstrated by comparison of the effects of temperature on the parachors of these alcohols and of saturated alcohols which are known to be associated.

In comparison with that of methylpropenylcarbinol (αγ-di-methylallyl alcohol) the mutarotation of ethyl-
propenylcarbinol is regular, and the formation of optically active methylbutenyloarbinol (\(\alpha\)-methyl-\(\gamma\)-ethylallyl alcohol) has been shown to occur by anionotropic change. The cyclic configuration referred to above permits an explanation for the retention of asymmetry on already established principles.

The chloride of ethylpropenyloarbinol has been prepared and has been shown to give a mixture of ethylpropenylcarbinol and methylbutenyloarbinol on hydrolysis. These products have been identified by reduction and separation of derivatives of the resulting ethylpropyl- and methyl \(n\)-butylcarbinols by fractional crystallisation. Optically active ethylpropenyloarbinyl chloride suffers extensive racemisation on hydrolysis. Thus there is usually separation of the chloride anion before attachment of the hydroxyl group, the liberation of a mesomeric kation during this process leading to racemisation and isomerisation.

The problems arising from the data already published on \(\alpha\)-\(\gamma\)-di-methylallyl alcohol are discussed in the light of the results obtained in this work.
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INTRODUCTION

In 1936 Hills, Kenyon and Phillips (J.C.S., 1936, 576) resolved $\alpha\gamma$-dimethylallyl alcohol (methylpropenylcarbinol) which was found to undergo mutarotation and possess a low parachor value. The alcohol obtained by hydrolysis of its chloride exhibited unusual optical properties. Since then other optically active $\alpha\gamma$-di-substituted allyl alcohols have been examined in an attempt to explain the abnormalities of $\alpha\gamma$-dimethylallyl alcohol as well as for their own intrinsic interest. Among these are $\alpha$-methyl-$\gamma$-phenylallyl alcohol (Kenyon, Fartridge and Phillips, J.C.S., 1936, 85), $\alpha$-phenyl-$\gamma$-methylallyl alcohol (Kenyon, Fartridge and Phillips, J.C.S., 1937, 207) and $\alpha$-m-propyl-$\gamma$-methylallyl alcohol (Arcus and Kenyon, J.C.S., 1938, 1912).

The present investigation continues these researches by studying $\alpha$-ethyl-$\gamma$-methylallyl alcohol (ethylpropenylcarbinol), the preparation and physical properties of which are to be found in the experimental section of this work.
(I) Optical properties of ethylpropenylcarbinol and certain of its derivatives.

No anomalous rotatory dispersion was observed with ethylpropenylcarbinol and the maximum rotation obtained gave in the homogeneous state for light in the visible spectrum, a one term Drude equation:

\[ [\alpha] = \frac{3.780}{(\lambda^2 - 0.0638)} \]

with a characteristic frequency of about 2525 Å. Levene and Hailer (J.Chem.Phys.1937,5,980) have found with similar alcohols that an analysis of the dispersion over a wide range of wave-lengths shows the necessity for a two-term Drude equation to account for the dispersion. The rotation of the alcohol decreased regularly with rise in temperature and extrapolation indicated that the dispersion would not be anomalous at the boiling point. The characteristic frequency found here for ethylpropenylcarbinol is very close to that reported for \( \text{\text{-p-}} \)propylpropenylcarbinol by Arcus and Kenyon (loc.cit.) viz. 2690 Å.

The hydrogen phthalic ester gave a characteristic diagram (Armstrong and Walker, Proc. Roy.Soc.,1913,A,88,388) for rotatory powers in various solvents which indicated very slightly complex dispersion and in the parachor section of this work a tendency to ring formation in the similarly
constituted benzoate is suggested. This is brought about by the proximity of the carboxyl oxygen and the γ-carbon atom with the powerful electromeric effect of the benzene nucleus. The maximum obtainable specific rotation of the hydrogen phthalic ester was definite but there was some variation in that of the alcohol obtained therefrom by hydrolysis which indicated slight racemisation during this hydrolysis. A similar result has been reported in the hydrolysis of the hydrogen phthalic ester of α-methyl-γ-phenylallyl alcohol by Kenyon, Partridge and Phillips, (J.C.S., 1936,85) who found that saponification with 5N sodium hydroxide gave the alcohol in a state approaching optical purity and less concentrated solutions of sodium hydroxide caused increasing racemisation. An explanation for this phenomenon has been put forward by Arcus and Kenyon (J.C.S., 1938,1917) which involves the liberation of the carbonium kation $\text{CHR}_1 . \text{CH}_2 . \text{CHR}_2$ with consequent racemisation to an extent dependent on the strength of the alkali used. Normal saponification which maintains asymmetry must proceed without breaking the $\text{O-R}$ bond and in strongly alkaline solution the existence of the hydrogen phthalic ester as an ion favours such a course of reaction.

[Diagram]

\[ \text{CO}_2^- \quad \text{CO}_\text{OR} \]
When the alkali is insufficiently strong, thus permitting the existence of appreciable amounts of undissociated ester-acid, the electron attracting nature of the undissociated carboxyl group promotes the tendency to the formation of the above mentioned carbonium kation.

\[
\text{CO} \rightarrow \text{CHR}_1 \rightarrow \text{CH} = \text{CHR}_2 \rightarrow \text{CHR}_1 \cdot \text{CH} \cdot \text{CHR}_2
\]

When a specimen of the d-alcohol was reduced the rotation of the ethyl \( n \)-propylcarbinol obtained was greater than that published by Pickard and Kenyon (J.C.S., 1913, 103, 1923) and also greater than Kenyon (J.C.S., 1914, 105, 222&ted after further investigation \( \beta \)-binol reduced had not the 226). The specimen of ethylpropenylcarbinol reduced had not the maximum rotation obtainable but by correcting for the amount of racemic material present in that reduced the specific rotation obtained for the optically pure d-ethyl \( n \)-propylcarbinol is \( [\alpha]_D^{20} = +7.09^\circ \). The d-ethyl \( n \)-propylcarbinol was converted to the hydrogen phthalate which in chloroform solution had a specific rotation (similarly corrected) \( [\alpha]_D = +9.70^\circ \). The previous maximum figures reported (loc. cit.) were for ethyl \( n \)-propylcarbinol \( [\alpha]_D^{20} = -4.21^\circ \) and for the hydrogen phthalate in chloroform solution \( [\alpha]_D = -5.76^\circ \). It is
therefore concluded that the rotatory power of optically pure ethylpropenylcarbinol is $[\alpha]_D^{20} = +7.09^\circ$ and that the figures given by Pickard and Kenyon are too low. The ratio of the specific rotation of the hydrogen phthalate to that of the carbinol is 1.37 in both cases. The revised figure is still in line with the generalisation made by these workers on the rotatory powers of the ethyl series of carbinols. The $\alpha$-ethylpropenylcarbinol used for reduction was freshly prepared from the hydrogen phthalate and thus no mutarotation had occurred.

A simple substitution reaction on ethylpropenylcarbinol was found to cause extensive racemisation with a small amount of inversion. Optically active (laevo) ethylpropenylcarbinol was converted to the potassio derivative with potassium metal in ether and the product mixed with methyl iodide. After filtering off the potassium iodide there was obtained the methyl ether possessing a large dextro rotation. The configuration of this ether is the same as that of the original carbinol as the linkage between the hydroxyl oxygen and the asymmetric carbon atom remains intact throughout the reaction.

The same ether was then prepared by a method which involved substitution. A specimen of the hydrogen phthalic ester of the ethylpropenylcarbinol used previously (also
laevorotatory) was refluxed with methyl alcohol. The configurations of the 1-carbinol and of the 1-hydrogen phthalic ester from which it was obtained by hydrolysis are necessarily identical because the oxygen to carbon linkage is not broken during normal hydrolysis. (Polanyi and Szabo, Trans. Faraday Soc., 1934, 30, 508). The methyl ether recovered from the product was in this case laevorotatory but with only 2.6% of the rotatory power of the ether made by the potassio derivative intermediate. Thus substitution of the methoxy radicle for the acid phthalyl radicle had involved inversion with over 97% racemisation. This extensive racemisation in similar reactions has been noted before and appears characteristic when inversion occurs with allylic compounds. Arcus and Kenyon (J.C.S., 1938, 1939) give the following data:

<table>
<thead>
<tr>
<th>Optical Purity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHMe:CH.CHMe</td>
</tr>
<tr>
<td>CO₂H.C₆H₄.CO.O</td>
</tr>
<tr>
<td>CHMe:CH.CHFr</td>
</tr>
<tr>
<td>CO₂H.C₆H₄.CO.O</td>
</tr>
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<td></td>
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</tbody>
</table>
In the last example the benzoate was shown to be a mixture. The result obtained with ethylpropenylcarbinyl hydrogen phthalate is exactly in line with those tabulated above.

The mechanism of the replacement of groups in aliphatic compounds containing an asymmetric carbon atom has been shown to depend on two main principles. (Kenyon, Phillips, Trans. Faraday Soc., 1930, 26, 45; Hughes, Ingold et alia, J.C.S., 1937, 1252). When the entering group becomes attached to the asymmetric carbon atom before the displaced group is detached then there is inversion of configuration with a small amount of racemisation.

\[
A - X + Y^{-} \rightarrow Y^{-} A - X \rightarrow A - Y + X^{-}
\]

The controlling stage in this reaction is bimolecular. If however the displaced group is detached before the entering group becomes attached, racemisation is considerable. Should there be any retention of optical activity due to the shielding action of the receding ion then inversion occurs.

\[
A - X \rightarrow A^{+} + X^{-}
\]

\[
A^{+} + Y^{-} \rightarrow A - Y
\]

This is a two stage process and the controlling stage is monomolecular. It follows that in all the above cases the
phthalyl radicle leaves the molecule as an anion and the reactions are mainly two stage processes. The residual unstable carbonium kation as has been pointed out by Arcus and Kenyon (loc. cit.), is effectively planar and thus immediately racemised on formation. It was not found possible to show that the methyl ether was a mixture, owing to the difficulties in analysis of mixtures of isomeric ethers and to the experience obtained when attempts were made to isolate pure specimens of ethers for parachor determinations. There was a marked tendency to form constant boiling point mixtures even with solvents and this prevented the application of the refractive index method used by Young and Lane. (J.A.C.S., 1937, 59, 2051).

Ethylpropenylcarbinol exhibited mutarotation in an apparently erratic manner on standing. One d-specimen in 1,156 days had lost 34% of its optical activity while another l-specimen after standing 1,634 days had only lost 1% activity. Yet another d-specimen only lost 2% activity in 736 days but with the subsequent addition of 1% of formic acid it lost 6% activity in a further 21 days.

The first specimen on reduction with hydrogen in the presence of platinum catalyst gave a hexanol of greater optical rotatory power than would be expected from the specific rotation of ethylpropylcarbinol obtained by the
reduction of freshly prepared ethylpropenylcarbinol. The rotation obtained (correcting for the optical purity of the carbinol before mutarotation) was 93% of that of optically pure ethylpropylcarbinol, whereas the activity of the ethylpropenylcarbinol had decreased to 66% on standing. The increased optical activity was due to the presence of an alcohol as the hydrogen phthalate of this reduced product had a much greater specific rotation than that of optically pure ethylpropylcarbinyl hydrogen phthalate. Thus as well as some racemisation there had been a tautomeric conversion to another carbinol with retention of optical activity. With this extensive loss of activity on standing the dispersion constant had not changed, suggesting that the new carbinol formed was very similar to the original ethylpropenylcarbinol. There are very good grounds for postulating the formation of α-methyl-γ-ethylallyl alcohol (methylbutenylcarbinol) in these circumstances, that is a migration of the hydroxyl group from the α- to the γ-carbon atom. A specimen of dl-ethylpropenylcarbinol which had stood about two years was redistilled and converted to the p-xenyl urethane. After fractional crystallisation a small quantity of crystals having melting point of the p-xenyl urethane of α-methyl-γ-ethylallyl alcohol was obtained. The density of the reduced ethylpropenylcarbinol of similar age was found to lie between the values for ethylpropylcarbinol and methyl-
$\alpha$-butylcarbinol.

An isomeric change in which the hydroxyl anion migrated from the $\alpha$- to the $\gamma$-carbon atom as suggested above would cause the formation of methylbutenylcarbinol, but it is shown later that some type of ring tautomerism is necessary to explain the large proportion of asymmetry induced in the $\gamma$-carbon atom. The cyclic configuration (p.29) for ethylpropenylcarbinol evidenced by parachor measurements, is in favour of the tautomeric change while it also provides the conditions for propagation of asymmetry. It is only necessary that the linkage between the hydroxyl oxygen and the $\gamma$-carbon atom should become a true covalent linkage and leave the original oxygen to $\alpha$-carbon atom as a dative bond. This would occur under the positive inductive influence of the $\alpha$-ethyl group if the hydroxyl, in tending to ionise off, moved sufficiently far from the retaining field of the $\alpha$-carbon atom. An actual transfer of electrons from one linkage of the $\beta$-carbon atom to the other would occur simultaneously, thus generating the methylbutenylcarbinol molecule without any complete ionisation. As in the case of ethylpropenylcarbinol the positive inductive effect of the ethyl group is greater than that of the methyl group, the ultimate equilibrium mixture would therefore be expected to contain more methylbutenylcarbinol than ethylpropenylcarbinol and there is a definite tendency for the latter
to undergo isomerisation. As a partial ionisation of an anion is involved in this mechanism the attainment of equilibrium should be accelerated by the presence of acid and in a medium of high dielectric constant. In practice the specimen of d-ethylpropenylcarbinol that had lost only 2% of its activity in two years lost another 6% in three weeks after the addition of 1% of formic acid. As all specimens of ethylpropenylcarbinol examined became acid to moist litmus on standing and old specimens were wet when distilled, it would appear that the apparently erratic mutarotation is caused by the varying rate of aerial oxidation on standing. This probably depends largely on the efficiency of purifying in the first place and on the type of bottle used for storage. More irregular mutarotation with change of sign has been observed with methylpropenylcarbinol by Hills, Kenyon and Phillips (loc. cit.).

The fact that the ratios between the specific rotations of ethyl \(n\)-propylcarbinol and its hydrogen phthalate and of methyl \(n\)-butylocarbinol and its hydrogen phthalate are widely different was used to determine approximately the concentrations of the optically active isomers in ethylpropenylcarbinol which had undergone tautomeric change. It is necessary to assume that dilution of one of the saturated isomers by its tautomeric isomer causes no appreciable change in its specific rotation. It is known
that the signs of rotation of the hexanols in the homogeneous state and of the corresponding hydrogen phthalates in chloroform solution are similar. Thus for any mixture of the optically active isomeric hexanols a line showing the change of rotation of a column of the liquid against variation in percentage composition will be generally in the same direction as that for the specific rotations of the corresponding hydrogen phthalates in chloroform solution. The lines however do not make the same angle with the horizontal axis if the rotations are plotted vertically on the same scale. The four possible combinations of the isomers give four pairs of such lines and those involving mixtures of isomers of opposite sign give zero rotation at the appropriate compositions. The scheme is simplified by plotting percentage composition against the quotient obtained by dividing the value for the specific rotation of the hydrogen phthalate mixture by the rotation of the corresponding carbinol mixture. The result is one curve for mixtures of similar sign and another curve which passes through zero and infinity for mixtures of opposite sign. (See fig. p. 16) These curves do not cross one another but only meet at the two points which correspond to 100% ethylpropyl and 100% methylbutyl respectively and are not affected by dilution with optically inactive material provided
that it is to the same extent in both carbinol and hydrogen phthalate. Thence, for a mixture of isomeric hexanols the proportion of optically active isomerides is determined by measurement of the quotient of the rotation of the homogeneous carbinols divided into the specific rotation of the chloroform solution of the total hydrogen phthalate obtained therefrom without any recrystallisation. This measurement also decides whether the isomerides have similar or opposite signs. The proportions of the optically active isomerides being determined, the concentrations of each and their respective signs are found by comparison of the two possible rotations of either carbinol or hydrogen phthalate with the determined rotations. An example of this application is illustrated on page 14. Sodium light was used in all these measurements. The data for methyl n-butylcarbinol were obtained from the constants published by Pickard and Kenyon (J.C.S., 1911, 92, 45) but the values for ethylpropylcarbinol and its hydrogen phthalate were determined on the product of reduction of freshly prepared optically active ethylpropenylcarbinol. The signs of rotation of the saturated and unsaturated carbinols and their hydrogen phthalates were all identical in the last case but the relation between the sign of rotation of methylbutenylcarbinol and of the methylbutylcarbinol obtained by reduction is not known by direct measurement.
All signs of rotation in this case are again probably similar as ethylpropenylcarbinol which has undergone mutarotation has the same dispersion ratio as the freshly prepared carbinol and does not exhibit any anomalous characteristics. A similar condition is found to hold also on the products of reduction of ethylpropenylcarbinol before and after mutarotation. However the configurations of the unsaturated and reduced compounds are necessarily similar whence it follows that the analysis of the saturated mixture of isomerides employing the method outlined above applies directly to the unsaturated isomerides as well.

This method of analysis was applied to the product of reduction of the specimen of α-ethylpropenylcarbinol of which the optical rotatory power had decreased to 66% on standing 1,156 days and which is referred to earlier in this section. The rotatory power of the reduced carbinol was \( \alpha_{589}^2 +5.0^\circ \), \((\mathbf{1,1.0})\) in the homogeneous state and the hydrogen phthalic ester prepared therefrom had \([\alpha]_{589}^2 +16.7^\circ\) in chloroform solution. The quotient \(+16.7/+5.0 = +3.34\) which corresponds with 56% of ethylpropylcarbinol and 44% of methyl n-butylicarbinol. Also the rotatory powers of the carbinols being of similar sign, they must both be dextro-rotatory. (See fig. p. 16). For an optically pure mixture of this composition the rotatory power of the carbinol
would be \( \alpha_{5893}^{20^\circ} + 7.4^\circ (1,1,0) \), so that the optically active constituents totalled 67.5% of the whole. As the \( \delta \)-ethylpropenylcarbinol before mutarotation was 92.5% optically pure it follows that after mutarotation there was retention of 73% of the original optical activity. This was distributed between \( \delta \)-ethylpropenylcarbinol and \( \delta \)-methyl butenylcarbinol in the ratio 56 to 44. Thus of the original \( \delta \)-ethylpropenylcarbinol 27% was racemised, 41% remained and 32% was converted to \( \delta \)-methylbutenylcarbinol.

The anionotropic change which is involved in this mutarotation gives a state of dynamic equilibrium, so that any given molecule may have changed many times and both isomers may have been partly racemised. Nevertheless the amount of optical activity retained in both isomers was substantial and the degree of retention of optical activity in any one change must therefore have been very high.
OPTICAL CHARACTERISTICS OF
MIXTURES OF ETHYL n-PARAFFIN
AND METHYL n-BUTYL CARBINOLS
AND OF THEIR HYDROGEN PHthalates.

[Graph showing the relationship between the percentage composition of MeBu and EtPt and the optical activity (ε) in CHCl₃.]
Parachors of ethylpropenylcarbinol and some of its derivatives and allied compounds.

The molecular volume of a substance when measured in standard circumstances is an additive function of the components of the molecule including any strains caused by the structure. Originally attempts were made to adopt standard conditions for comparison of data by taking molecular volumes at constant temperature or at the boiling point or even at the critical temperature of the substance, but apart from the practical difficulties, such methods made no allowance for the effect on the molecular volumes of the forces due to molecular attractions. These forces are closely related to surface tension and Sugden by application of Macleod's relation between surface tension and density obtained a method for comparison of molecular volumes at what may be termed unit surface tension. Determination of the resulting molecular constant or "parachor" is independent of temperature as long as the substance is liquid and this constant is the sum of the individual atomic parachors with corrections for structural details such as unsaturation, rings and co-ordinate linkages. Sugden's simple method of distributing the parachor equivalents amongst elements and structural features ("The Parachor and Valency", p.33) has been modified by
a scheme worked out by Mumford and (J.W.C.) Phillips (J.C.S., 1929, 2113) which involves corrections for branching chains and groups with contractive influences. In the present work paracho' measurements were used to provide evidence that allylic alcohols tend to form ring structures and thus to justify a mechanism to explain the mutarotation of ethylpropenylcarbinol on established principles. (Ingold and Wilson, J.C.S., 1933, 1493).

Early experiments in tautomeric systems led Ingold and Wilson (loc.cit.) to postulate that when an ion moves from one asymmetric centre to another possible asymmetric centre the product is racemised and that the migration is in itself a racemising effect. They used the mutually interconvertible azo-methines:

\[
\text{Me} \xrightarrow{\text{[H]}} \text{C} \xleftarrow{\text{Me}} \text{N} : \text{C} \quad \xrightarrow{\text{Ph}} \quad \text{Ph} \xleftarrow{\text{Ph}} \text{C} : \text{N} \cdot \text{C} \cdot \text{[H]} \quad \text{C}_6\text{H}_4\text{Cl}
\]

This was a convenient prototropic system and the first isomer in an optically active form was allowed to isomerise in alcoholic solution with sodium ethoxide as the catalyst. The second isomer, phenylmethylenephényl p-chlorphenylazo methine was obtained inactive while the unchaged phenyl p-chlorphenylmethylenemethylphenylazo methine was recovered almost optically pure. They decided that some
key such as a ring structure is necessary to allow the transmission of asymmetry to a new centre generated by such a migration.

The work of Kenyon, Partridge and Phillips on the conversion of \(\alpha\)-phenyl-\(\gamma\)-methylallyl alcohol derivatives into the corresponding derivatives of \(\gamma\)-phenyl-\(\alpha\)-methylallyl alcohol (J.C.S.,1937,207) has confirmed that a cyclic mechanism is required to account for retention of asymmetry. They have postulated a cyclic configuration in the anionotropic system prior to anion migration and a tendency to the probable formation of cyclic bodies in this type of compound has previously been suggested by Hills, Kenyon and Phillips. (J.C.S.,1936,576). This view receives confirmation by parachor evidence obtained in this work.

Hills, Kenyon and Phillips and Kenyon, Partridge and Phillips (loc.cit.) have reported low values for the parachors of \(\alpha\gamma\)-dimethylallyl alcohol, \(\alpha\)-phenyl-\(\gamma\)-methylallyl alcohol and \(\alpha\)-methyl-\(\gamma\)-phenylallyl alcohol as support of a cyclic structure in these compounds. Some variation in the parachor of \(\alpha\gamma\)-dimethylallyl alcohol apparently depending upon the method of preparation has been recorded. An investigation of the parachor of ethylpropenylcarbinol and some of its derivatives and allied compounds has therefore been made, particular attention being paid to the question whether parachor anomalies are
due to association.

Care was taken to ensure a high degree of purity of the compounds on which measurements were made as it was found that all the unsaturated alcohols which were tested, with the exception of allyl alcohol, rapidly became acid to moist litmus on keeping, even in a closed vessel. Therefore as far as possible measurements were taken on freshly prepared and in any case freshly distilled specimens. As large a temperature range as possible was used and in every case parachors at 15°C and 40°C were ultimately evaluated. The surface tension and density values at these temperatures were obtained by plotting the observed data and drawing smooth curves. The curves were sensibly straight lines over the range chosen and this range enabled variations due to association to be detected. In this latter connection the parachor of a saturated alcohol of about the same boiling point and molecular weight as those under review was measured to obtain an indication of the effect of association on the results. n-Amyl alcohol was chosen and its parachor was found to be 241.2 units at 15°C and 242.4 units at 40°C. Both determined values are below the calculated 249.2 using Sugden's atomic constants and 245.4 using Mumford and Phillips' constants. This low parachor value is explained on the basis that an increase in the covalency of the hydroxyl hydrogen resulting from
association causes a decrease in parachor, and the tendency to increase towards the calculated value with rise in temperature is due to the anticipated decrease in association on heating. The observed range of 1.2 units over 25°C temperature range is of the same order as that recorded for other simple saturated alcohols. (Sugden, J.C.S., 1924, 12532).

In Table (I) the parachors of methyl and ethyl alcohols at 15°C and 40°C have been obtained by plotting Sugden's observed values at the other temperatures.

Table (I).  Saturated Alcohols.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Methyl alcohol (M.Wt. 32)</th>
<th>Ethyl alcohol (M.Wt. 46)</th>
<th>n-Amyl alcohol (M.Wt. 88)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>126.4</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>88.2</td>
<td>126.8</td>
<td>241.2</td>
</tr>
<tr>
<td>20</td>
<td>88.3</td>
<td>126.9</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>88.7</td>
<td>127.5</td>
<td>242.4</td>
</tr>
<tr>
<td>70</td>
<td>89.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
<td>128.8</td>
<td>-</td>
</tr>
</tbody>
</table>

\[ [\Phi] \text{Calc. (Sugden)} \begin{array}{l} 93.2 \\
[\Phi]_{40} - [\Phi]_{15} \end{array} \begin{array}{l} 132.2 \\
0.5 \end{array} \begin{array}{l} 249.2 \\
0.7 \end{array} \begin{array}{l} 1.2 \end{array} \]
The differences due to decrease in association for the range 15°C to 40°C are approximately in the ratio of the molecular weights of the respective alcohols and indicate that over this range the effect on the function $\gamma^* / D$ is fairly constant.

The data obtained for the unsaturated alcohols examined (Table (II)) shows no such regularity and the differences are much smaller.

Table (II). Unsaturated Alcohols.

<table>
<thead>
<tr>
<th></th>
<th>Mol.Wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Allyl alcohol</td>
</tr>
<tr>
<td>B</td>
<td>Methylpropenylcarbinol</td>
</tr>
<tr>
<td>C</td>
<td>Ethylpropenylcarbinol</td>
</tr>
<tr>
<td>D</td>
<td>Methyl-β-methylallylcarbinol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>PARACHOR [P] of :-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>15</td>
<td>153.9</td>
</tr>
<tr>
<td>40</td>
<td>154.2</td>
</tr>
</tbody>
</table>

$[F]$ Calc. (Sugden) 160.2 238.2 277.2 277.2

$[F]_{A0} - [F]_{S0}$ 0.3 0.2 0.3 0.2
It is seen that within experimental error the parachor does not vary with temperature over the range used for the unsaturated alcohols examined and thus the low parachor value is not caused by association. However as the parachors of some unsaturated esters are normal it follows that there must be something unusual in the structure of the hydroxyl group to account for the low values given by the alcohols.

The degree of purity of the substance was found to have a large effect on the parachor. Ethylpropenylcarbinol freshly prepared (one day old) from the hydrogen phthalic ester had a parachor of 267.2 at 15°C and 267.5 at 40°C and these values are lower than the calculated 277.2 (Sugden) and 273.6 (Mumford and Phillips). When 2½ months old the values were 267.2 at 15°C and 267.2 at 40°C. Ethylpropenylcarbinol prepared from the Grignard complex and stored 2½ months had a parachor at 15°C of 264.6 and at 40°C of 265.3 units. This specimen when redistilled gave values of 265.7 at 15°C and 266.2 at 40°C. The first fraction obtained by distillation was very wet and it appears that the presence of water causes a marked decrease in parachor, and possibly causes slight association. This is in agreement with the association exhibited by water.

Similar results were obtained with methylpropenylcarbinol.
A specimen of the 1-alcohol that had stood six months and had become acid to moist litmus had a parachor of 228.8 at 15°C and 229.0 at 40°C. After purifying by washing with alkali, drying and redistillation the parachor of this specimen was 230.2 at 15°C and 230.4 at 40°C. A specimen of the same alcohol freshly prepared by hydrolysis of its chloride with water and calcium carbonate had a parachor at 15°C of 230.4 and at 40°C of 230.5 units. Thus again though no association is indicated all these values are much lower than the calculated 238.2 (Sugden) and 233.6 (Mumford and Phillips). Hills, Kenyon and Phillips (J.C.S., 1936, 576) have reported a range of values 226.0 to 233.0 for this alcohol. The variation in parachor appeared to depend upon the method of preparation and even with the nature of the agent used for the hydrolysis of the hydrogen phthalic ester. The fact that, as in the case of ethyl-propenylcarbinol, one of the lowest values was given by a specimen obtained directly from the Grignard reaction and which was probably one of the least pure specimens makes the variation in parachor appear to be a function of the degree of purity and not an indication of variable structure. The very close agreement between the results obtained in this work on purified specimens of methylpropenylcarbinol prepared by hydrolysis of the hydrogen phthalic ester and
of the chloride is noteworthy in this respect, and these figures agree also with the values 230.5 and 230.4 reported by these authors for the respective parachors of specimens of methylpropenylcarbinol prepared by acid and alkaline hydrolysis of the hydrogen phthalic ester. The high value recorded was obtained with a carbinol prepared by the hydrolysis of the hydrogen phthalic ester with aqueous sodium carbonate and sodium acetate.

The parent allyl alcohol has a great affinity for water the last traces of which are difficult to remove. One specimen was dried first with anhydrous copper sulphate and then with potassium carbonate and fractionally distilled, b.p. 96 to 96.7°C at 760mm. Its parachor was 154.1 at 15°C and 154.5 at 40°C. An entirely distinct specimen when dried only with potassium carbonate and fractionally distilled, b.p. 96 to 96.2°C at 760mm, had a parachor 153.9 at 15°C and 154.2 at 40°C. Thus there is very little association in allyl alcohol while the observed values are lower than the calculated 160.2 (Sugden) and close to the calculated 153.6 (Mumford and Phillips). Hills, Kenyon and Phillips (loc.cit.) report a value of 159.0 for allyl alcohol not specially dried.

It is seen that the parachor data published by these authors is contradicted on two points in this work and in each case the effect is to simplify the situation. The
constant value now obtained for the parahor of methyl-
propenylcarbinol removes the necessity to assume that this
substance consists of varying amounts of hypothetical isomers.
Also as allyl alcohol, like methyl- and ethylpropenylcarbinols
is shown to have a low parahor the substituted allyl alcohols
are similar to the parent alcohol in this respect. The
previously reported normal value for allyl alcohol was used
as evidence that there was no association with allylic
alcohols and although this evidence was faulty the conclusion
based thereon was correct, as the present experiments on
the variation of parahor with temperature have shown.

Methyl-β-methylallylcarbinol (freshly distilled
b.p. 43°C at 18mm., n_20° 1.4297) which is isomeric with ethyl-
propenylcarbinol was also found to have a low parahor but
one unit higher than that of ethylpropenylcarbinol. The
values were 268.4 at 15°C and 268.6 at 40°C.

The parahors of two esters of ethylpropenylcarbinol
were determined. The acetate gave values of 362.1 at 15°C
and 361.5 at 40°C. The calculated figures are 361.0
(Sugden) and 361.2 (Mumford and Phillips). The benzoate
gave values of 490.2 at 15°C and 490.5 at 40°C. The
calculated figures are 494.9 (Sugden) and 495.8 (Mumford
and Phillips). A specimen of allyl acetate also was
prepared and the parahor was found to be 245.1 at 15°C
and 245.3 at 40°C. The calculated values are 244.0
(Sugden) and 244.2 (Mumford and Phillips).

No attempt is made in Sugden's atomic parachor constants
to allow for any abnormal strain factors, and thus the differ-
ence between the observed figures and the calculated
parachors using Sugden's method of distribution will
probably give a measure of the extent of abnormality in
structure, particularly as the compounds investigated were
allied. The system of Mumford and Phillips on the other hand
does to some extent allow for discrepancies observed in
various classes of compounds and it appears that the conclu-
sions to be deduced from the vagaries in the particular
case of allylic derivatives might well be masked by the
application of these already partially adjusted constants.
The parachor of \( \alpha \)-ethyl-\( \gamma \)-methylallyl alcohol is 267.3
which is 9.9 units less than the calculated 277.2. The
parachor of \( \alpha \gamma \)-di-methylallyl alcohol is 230.4 or 7.8
units less than the calculated 238.2 while the parachor
of allyl alcohol is 154.2 or 6.0 units less than the
calculated 160.2. Thus the lower the molecular weight in
this series, the less the difference between the calculated
and observed figures. The average value for methyl-\( \beta \)-
methylallylcarbinol is 268.5 or 8.7 units less than the
calculated 277.2. The anomaly here is 1.2 units less than
the anomaly for the isomeric ethylpropenylcarbinol, (\( \alpha \)-ethyl-
\( \gamma \)-methylallyl alcohol).
If for the methyl and ethylpropenylcarbinols the true cyclic structure with a four membered ring postulated by Hills, Kenyon and Phillips (loc.cit.) is examined

The calculated parachor is less than that of the normal unsaturated formula by 11.6 units and thus suggests that the observed figures indicate an equilibrium between the two configurations. However these authors record that optically pure $\alpha\gamma$-di-methylallyl alcohol on reduction yields optically pure methyl $n$-propylcarbinol and they point out that this cannot be reconciled with the symmetry of the cyclic structure for this unsaturated alcohol.

However it is not necessary to postulate a purely covalent cyclic structure to account for the anomalies in allylic derivatives. The difference between the calculated parachor for the double bond structure and that for the four membered ring arises from the difference in molecular volume which in turn is due to release of strain. A structure tending towards the true four membered ring necessarily has a parachor lying between those of the two extremes. It is noteworthy that ethylpropenylcarbinyl acetate and allyl acetate have normal parachors while ethylpropenylcarbinyl
benzoate has a parachor which is lower than the calculated value by a greater amount than experimental error permits. Similar observations have been made on methylpropenylcarbinol by Hills, Kenyon and Phillips (loc.cit.).

The explanation now suggested for the low parachors of the alcohols is given by the formula:

\[
\begin{align*}
R_1 & \quad \text{CH} = C \\
& \quad \text{C} \\
& \quad \text{CH}_3 \\
& \quad \text{H} \\
& \quad \text{OH}
\end{align*}
\]

In this system the inductive effect of the \(\alpha\)-substituent has some influence on the ability of the hydroxyl oxygen to form a dative bond with the \(\gamma\)-carbon atom. In the section dealing with the mutarotation of ethylpropenylcarbinol and the consequent formation of methylbutenylcarbinol evidence is provided in favour of the above formula. It is only necessary to postulate a tautomeric displacement of charge by means of the double bond to allow migration of the hydroxyl anion to the \(\gamma\)-carbon atom. This system provides an essential locking effect to explain the transfer of asymmetry from the \(\alpha\)-carbon atom to the \(\gamma\)-carbon atom in this process.

In the case of the esters, in which an oxygen atom
is linked between two carbon atoms one would not expect this oxygen to tend to attach itself to the γ-carbon atom. In such conditions, which resemble those of an ether linkage, the oxygen is more inert. The doubly linked oxygen of the carbonyl group should be suitably situated for such a purpose as it could take part in forming the stable six-membered ring by so doing and its electronic make-up enables it to act as a donor of electrons. However the circuit would not be completed owing to the inertness of the previously mentioned ether type of linkage and thus though the tendency to form a cyclic structure must be recognised it does not appear to constitute a permanent displacement as in the case of the alcohols. It is likely that the powerful inductive effect of the phenyl nucleus in the benzoate can to a certain extent assist some type of coordinate linkage between the carbonyl oxygen atom and the γ-carbon atom by slight permanent displacement of the charges across the double bond. This is in agreement with the low parachor values recorded for the benzoates of ethylpropenylcarbinol and methylpropenylcarbinol.

The tendency to form a six-membered ring structure in the substituted allyl esters would furnish a simple explanation of the facile isomerisation observed in such cases as α-phenyl-γ-methylallyl hydrogen phthalate (Kenyon, Partridge and Phillips, J.C.S., 1937, 207) wherein
a large proportion of asymmetry is transmitted to the 
\( \gamma \)-carbon atom. Although these workers have suggested a tendency to form a four-membered ring involving the oxygen atom originally contained in the hydroxyl group of the alcohol, it would appear more feasible to assume that the carbonyl oxygen should participate in the isomerisation. This doubly linked carbonyl oxygen atom is the more likely to co-ordinate owing to its known tendency to decrease its covalency with the carbon atom to which it is attached. The result would involve a six-membered ring which on grounds of stability is more likely to be formed than the four-membered ring while the ultimate product would be the same in each case.
(III) Ethylpropenylcarbinyl chloride.

It has been shown by Ingold and Burton that anionotropic tautomerism is frequently very marked in chlorides when compared with the parent alcohols, the chloride ion as a strongly electro negative anion enhancing this tendency by leaving a mesomeric carbonium kation. Ethylpropenylcarbinyl chloride was easily hydrolysed to the carbinol which was found to be a mixture and separation of derivatives of the component alcohols was achieved by fractional crystallisation.

Ethylpropenylcarbinyl chloride was prepared from the alcohol by the action of thionyl chloride in the presence of quinoline. It was obtained in a fair state of purity and could be distilled apparently unchanged at pressures up to half an atmosphere. There was slight decomposition with evolution of hydrogen chloride when distilled at normal pressure. The chloride had a very slight pungent smell but after standing a few days it fumed and smelt strongly of hydrogen chloride. It reacted slowly with water at room temperature, the hydrochloric acid liberated by the reaction being neutralised by the addition of calcium carbonate. It was not as reactive as methylpropenylcarbinyl chloride in this respect (Hills, Kenyon and Phillips, J.C.S.,1936,583.) but more so than propylpropenylcarbinyl.
chloride (Arcus and Kenyon, loc.cit.). Once the reaction started it proceeded fairly rapidly. There appeared to be a period of induction due probably to the necessity to have some alcohol present for rapid hydrolysis to act as a carrier by its property as a solvent for both reactants. The resulting alcohol was recovered, dried and distilled. Attempts to prepare a crystalline hydrogen phthalate of this alcohol were not successful as when left to crystallise there appeared to be slow decomposition with liberation of phthalic acid. Generally the alcohol behaved as a mixture.

The experiment was repeated with optically inactive material and the final mixture of alcohols was converted to the p-xenyl urethane. A solid product was obtained which was then fractionally crystallised from ether and petroleum ether using a scheme similar to that employed in the resolution of a racemic mixture of optically active isomers. Ultimately two distinct crops of crystals were obtained each by the indication of the sharpness of its melting point being a pure substance. The product with the higher melting point was identical with the p-xenyl urethane prepared from pure ethylpropenylcarbinol. The second product had a lower melting point but analysis indicated that the two had identical composition and appeared thus to
be isomers.

In view of the difficulty in preparation of the isomeric \(\alpha\)-methyl-\(\gamma\)-ethylallyl alcohol (methylbutenylcarbinol) and its \(p\)-xenyl urethane with which to compare the second product it was thought wise to reduce the mixture of unsaturated hexenols to the corresponding hexanols and again to attempt separation as the hexanols and their derivatives are fairly readily prepared. Fractional distillation of the mixture of hexanols was tried. Though it was not satisfactory, as the boiling point range was too small for complete separation, the extreme fractions gave \(p\)-xenyl urethanes of very different melting points.

The mixture of hexanols was converted to the mixture of hydrogen phthalic esters and this was subjected to a careful fractional crystallisation. Ultimately two distinct crops of crystals were obtained again each by the indication of the sharpness of its melting point being a pure substance. The equivalents were determined by titration with sodium hydroxide and each corresponded with the hydrogen phthalic ester of a hexanol. The hydrogen phthalic esters of ethylpropylcarbinol and methyl \(n\)-butylcarbinol were prepared and found to have melting points similar to those of the two products of separation of the mixture. The determination of mixed melting points confirmed their identity.
Thus the mixture of hexanols was ethylpropylcarbinol and methylbutylcarbinol so that the mixture resulting from the decomposition of α-ethyl-γ-methylallyl chloride by water consisted of ethylpropenylcarbinol or α-ethyl-γ-methylallyl alcohol and methylbutenylcarbinol or α-methyl-γ-ethylallyl alcohol. Further evidence was obtained by conversion of the mixture of hexanols into their p-xenyl urethanes. Fractional crystallisation of the resulting mixture ultimately yielded two distinct crops of crystals which were respectively identical with the p-xenyl urethanes of ethylpropylcarbinol and methylbutylcarbinol.

The probable explanation of the production of this mixture is the separation of the chloride anion prior to the attachment of the entering hydroxyl group which results in a tautomeric change. The electron repelling property of the ethyl group assists this ionisation, especially in a solvent of high dielectric constant such as water and the α-carbon atom is thus left with a positive charge. The transmitting effect of the double bond induces a deficiency of electronic charge on the γ-carbon atom and the result is a sharing of the positive charge of the carbonium kation between the α- and γ-carbon atoms. The entering hydroxyl group is able to attach itself to either the α- or γ-carbon atom and thus give the mixture of isomers. There arises
again the mesomeric kation but as in the methyl ether formation analysed in section (I) there is also a subsidiary reaction in the hydrolysis of the chloride. This was elucidated by working with optically active material and the results are outlined in connection with the structure and reactions of the compounds studied.

Mixtures have been reported in the products of the hydrolysis of \( \text{n-propylpropenylcarbinyl chloride} \) by Arcus and Kenyon (J.C.S., 1938, 1912). Though there were indications that they were mixtures of isomeric carbinols no separation of derivatives of the unsaturated or reduced material was achieved.

Burton (J.C.S., 1928, 1650; 1934, 1268) has investigated tautomeric change in allylic derivatives on the occasion of substitution of one negative group by another or by ionisation of the negative group in a solvent of high dielectric constant. It was shown that \( \alpha\)-phenylallyl \( \text{p-nitrobenzoate} \) could be transformed to cinnamyl \( \text{p-nitrobenzoate} \) in various solvents at speeds depending upon the type of solvent. By adding tetra-methylammonium acetate and studying the stage at which substitution to give cinnamyl acetate occurred it was also concluded that the separation of the anion, leaving an unstable carbonium kation is essential for the tautomeric change. However, Kenyon, Partridge and Phillips (loc.cit.) as a result of their experiments with optically
active material on the conversion of \( \alpha \)-phenyl-\( \gamma \)-methylallyl alcohol into \( \gamma \)-phenyl-\( \alpha \)-methylallyl alcohol, have concluded that these rearrangements do not involve complete separation of the anion, and that Burton's experiment on the acetate formation may be explained by attachment of the acetate ion to the \( \gamma \)-carbon atom while the \( p \)-nitrobenzoate ion is leaving the \( \alpha \)-carbon atom. This must be reviewed in the light of modern resonance theories. Young and Lane (J.A.C.S., 1936, 62, 647) point out that in the formation of mixtures of bromides by the action of hydrogen bromide on allylic alcohols it is not necessary that the C-O linkage be completely broken. If the oxygen atom moves out a sufficient distance to allow resonance to arise in the rest of the molecule whereby the positive charge is shared between two carbon atoms, before the bromide ion co-ordinates, a mixture may result. This point of view has very wide application and in the hydrolysis of ethylpropenylcarbinyl chloride it appears probable that the distance of separation of the chlorine atom at the time of co-ordination of the hydroxyl group decides the constitution of the product. No doubt there is extensive dissociation, a view which the comparatively high degree of reactivity of the chloride supports. Extensive racemisation of the optically active material on hydrolysis also lends weight to this view but it is shown in the section on that part of the work
that the conception of some co-ordination of a hydroxyl group under the influence of electromeric displacement in the molecule and before complete separation of the chloride ion, is necessary to account for the formation of the products obtained. The elaboration which covers both instances by supposing a variable degree of separation of the anion at the moment of substitution, but allowing a sharp distinction in the product where the distance is sufficient to permit resonance to arise in the carbonium kation, obviates the earlier necessity to assume the simultaneous progress of a distinct subsidiary reaction.

In the preparation of optically active ethylpropenylcarbinyl chloride there was racemisation depending in extent upon the time taken for its preparation. The product showed some complex dispersion and this was due presumably to the asymmetry induced in the \(\gamma\)-carbon atom, which is discussed later in connection with its tautomerism. When hydrolysed with water and calcium carbonate there was much racemisation and the product had a sign of rotation the reverse of that of the starting material. This product, which was a mixture of carbinols exhibited anomalous dispersion, showing that both components were optically active. The hydrogen phthalates of this mixture of alcohols were optically active but were not obtained solid and during their purification
as ammonium salt the ether washings possessed no optical activity. Thus if any optically active ether was formed during the preparation of the chloride it was not present in this mixture of carbinols.

The products of the hydrolysis of optically active ethylpropenylcarbinyl chloride by water and calcium carbonate were analysed by the method employed on ethylpropenylcarbinol that had undergone mutarotation. Owing to the extensive racemisation, the observed rotations were very small but sufficient to confirm the production of a mixture of optically active compounds and to give an approximate value for the proportions of the components. Earlier in this section the results of the hydrolysis of the optically inactive compound are reviewed and it is demonstrated that the products were ethylpropenyl- and methylbutenylcarbinols. As in the separations effected considerable yields of derivatives of both compounds were obtained it is probable that the amounts present were of the same order. The proportions of optically active compounds were very different and there was extensive racemisation with very little propagation of asymmetry to the \( \gamma \)-carbon atom on tautomeric conversion. The optically active components totalled only 8% of the final mixture of carbinols so that 92% racemisation had occurred. Using \( \delta \)-ethylpropenylcarbinol as starting material the optically active portion (8% of the total) of the reduced product of
chloride hydrolysis consisted of 93% \( \alpha \)-ethyl \( n \)-propylcarbinol and 7% \( \beta \)-methyl \( n \)-butylcarbinol. Thus ethylpropenylcarbinyl chloride, like the parent alcohol, also undergoes anionotropic change with some retention of optical activity. The retention is however very small in the case of the chloride, presumably because it occurs mainly by ionisation, rather than by a ring mechanism and the intermediate kation undergoes racemisation.
The structure and reactions of ethylpropenylcarbinol
and its chloride with reference to related compounds.

The work of Ingold and Wilson on the following system has been mentioned in the section on 'Parachors'.

\[
\begin{align*}
R_1^* & \equiv \begin{array}{c}
A-B \equiv C \\
R_2 & \equiv \begin{array}{c}
X \equiv \begin{array}{c}
R_3 \\
R_4
\end{array}
\end{array}
\end{array} & \equiv \begin{array}{c}
A-B \equiv C \\
R_2 & \equiv \begin{array}{c}
X \equiv \begin{array}{c}
R_3 \\
R_4
\end{array}
\end{array}
\end{array}
\end{align*}
\]

I \quad \leftrightarrow \quad II

In this the tautomers were the azo-methines:

\[
\begin{align*}
\text{CH}_3 & \equiv \begin{array}{c}
C_6H_5 \equiv \begin{array}{c}
\text{N}C[H] \\
\end{array}
\end{array} & \equiv \begin{array}{c}
\text{CH}_3 & \equiv \begin{array}{c}
C_6H_5 \equiv \begin{array}{c}
\text{N}C[H] \\
\end{array}
\end{array}
\end{array}
\equiv \begin{array}{c}
C_6H_5 \\
C_6H_4Cl(p.) \\
C_6H_5 \\
C_6H_4Cl(p.)
\end{array}
\end{align*}
\]

III \quad \leftrightarrow \quad IV

These azo-methines were interconvertible in the presence of sodium ethoxide and it was found that after the conversion had proceeded the isomeride IV recovered from the mixture had no perceptible rotatory power. The result was not due to complete racemisation of isomeride III prior to its tautomeric change because the unchanged compound III was recovered with most of its original rotatory power. This complete absence of rotatory power in IV apparently
indicated an entirely different mechanism from that of the established instance of the conversion of linalyl acetate into the optically active $\alpha$-terpinyl ester.

\[
\begin{align*}
\text{[OAc]} & 
\begin{array}{c}
\text{MeCH=CH}_2 \quad \text{CH=CM}_{\text{e}_2} \quad \text{CM}_{\text{e}}=\text{CH-Ch}_{\text{e}}^*\text{CH}_{\text{e}} \quad \text{CM}_{\text{e}}=\text{CH}_{\text{e}} \quad \text{CM}_{\text{e}} \quad \text{[OAc]}
\end{array} \\
\text{CH}_2 & \quad \text{CH}_2 \quad \text{CH}_2 \\
\text{V} & \quad \text{VI}
\end{align*}
\]

It was realised by Ingold and Wilson that in the case $\text{V} \rightarrow \text{VI}$ the migrating centre of asymmetry does not follow the route of the mobile group but this asymmetric synthesis could only be induced by the influence of the centre of asymmetry initially present in the molecule. Also from the mechanistic point of view the two forms of electron displacement for prototropic and anionotropic change are analogous.

\[
\begin{align*}
\text{X-\text{A-}} & \quad \text{B=C} \\
\text{X-\text{A-}} & \quad \text{B=C}
\end{align*}
\]

Thus the reason for the contrast is to be found in the fact that the interconversion $\text{V} \rightarrow \text{VI}$ is a chain-ring change.

Their illustration for an anionotropic system is reproduced in VII. (See fig. p. 43). X and Y mark the intersections between the fixed plane $\text{OAcC}_\alpha \text{C}_\beta$ and the circular locus of $\text{C}_\gamma$. The duplets of the $\text{C}_\beta \text{C}_\gamma$ double bond are indicated.
by a and b. For maximum propagation of asymmetry \( C_y \) would have to be held in such a position as \( C'_y \) and either the a, or the b, electrons would be preferentially coupled with \( C_\infty \) on migration, by the process \( tt \), of the anion \( OAc \). However if rotation of \( C_y \) is not restricted, the symmetrically corresponding point \( C''_y \) (where the relation between the a and b electrons and the electrons which are migrating with the anion is reversed), would on an average be occupied for an equal length of time and cause racemisation. The amount of asymmetry propagated depends upon the ability of the non-equivalence of the external electric fields due to \( R_y \) and \( R_x \) to make it more probable that \( C_y \) should be in one semicircle than the other at the moment of reaction.

It follows that normally the propagation of asymmetry would be very small by such means and some more definite keying action is necessary to assist. Such is given in the conversion V to VI illustrated in VIII. (See fig. p.43). In this system at the moment of conversion the atoms \( C_y C_x C_\alpha \) are effectively fixed at the relative positions necessary for maximum propagation of asymmetry by an effect correlated above with asymmetric synthesis.

The structural formula for ethylpropenylcarbinol suggested by parachor data provides a similar mechanism to that shown in VIII for the propagation of asymmetry.
by tautomeric change on standing.

\[
\begin{align*}
\text{C}_2\text{H}_5 & \quad \text{CH} = \text{C} \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{OH} \\
\text{C}_2\text{H}_5 & \quad \text{H} \\
\text{CH}_3 & \quad \text{C} = \text{CH} \quad \text{C}^\ast \quad \text{CH}_3 \\
\text{OH} & \\
\end{align*}
\]

IX 

X

At the moment of conversion by migration of the hydroxyl anion the \(\gamma\)-carbon atom is held in the correct position for the propagation of asymmetry. This accounts for the relatively high amount of optical activity retained and the mechanism is discussed in the section dealing with the mutarotation of ethylpropenylcarbinol.

Ethylpropenylcarbinyl chloride is probably formed with inversion of configuration as the sign of rotation in the homogeneous state is opposite to that of the carbinol from which it is formed. This has also been observed in the cases of methylpropenylcarbinol and \(n\)-propylpropenylcarbinol the chlorides of which have been prepared by reaction with phosphorus trichloride in the presence of pyridine. In such circumstances the reaction is believed invariably to involve inversion (Frankland, J.C.S., 1913, 103, 713).

As the ethylpropenylcarbinol formed by hydrolysis of the chloride had the same sign of rotation as that of the original carbinol there was also inversion on hydrolysis.
It has been shown that the tautomeric change on hydrolysis of ethylpropenylcarbinyl chloride which caused the formation of a mixture of ethylpropenyl- and methylbutenylcarbinols resulted in a sign of rotation in the methylbutenylcarbinol opposite to that which would be obtained if the ethylpropenylcarbinol used to prepare the chloride had been allowed to tautomerise on standing. The extent of racemisation in the \( \alpha \)-carbon atom was of the same order as that observed with the substitution reaction between methyl alcohol and ethylpropenylcarbinyl hydrogen phthalate but the amount of optical activity transmitted to the \( \gamma \)-carbon atom was a very small proportion of that remaining in the \( \alpha \)-carbon atom. Thus either there was very little of the isomeric methylbutenylcarbinol formed or the change involved the propagation of only a small amount of optical activity. The latter was proved to be the case as fractionation of the inactive product to yield derivatives of both carbinols indicated a similar concentration of both isomeric alcohols after hydrolysis of the chloride.

Arcus and Kenyon (J.C.S., 1938,1912) have studied the products of replacement reactions of the chloride of \( n \)-propylpropenylcarbinol in which asymmetry transmitted to the \( \gamma \)-carbon atom could be detected by reduction of the mixture of isomeric derivatives. After reduction any optical activity must be due to a methyl \( n \)-amylcarbinol
derivative as the di-n-propylcarbinol derivative is symmetrical.

\[
\begin{align*}
\text{CHMe:CH.CH.PrX} & \rightarrow \text{CHMeYCH:CHPr} \rightarrow \text{CHMe}(C_2H_{11})Y \\
& \quad \text{(unsymmetrical)} \\
& \quad \text{H}_2 \\
\text{CHMe:CH.CH.PrY} & \rightarrow \text{CHPr}_2Y \\
& \quad \text{(symmetrical)} \\
& \quad \text{H}_2
\end{align*}
\]

In no case was the reduced product optically active and thus no asymmetry was transferred to the \(\gamma\)-carbon atom. They postulated that as the \textit{dl}-chlordie on hydrolysis was shown to produce a mixture, the carbonium kation \(\text{CHMeCH.CHPr}^+\) was an intermediate in the reactions. This ion being effectively planar would lead to the formation of racemic products. They attributed the small amount of inversion detected on the \(\alpha\)-carbon atom to a subsidiary mechanism of substitution wherein inversion resulted by the substituent group becoming attached to the asymmetric carbon atom before the dissociation of the displaced group.

The circumstances arising in the hydrolysis of ethylpropenylcarbinyl chloride are necessarily similar and the carbonium kation \(\text{CHMeCH.CHPr}^+\) is probably liberated during the reaction. This however would not appear to give rise to the asymmetry detected in the \(\gamma\)-carbon atom even if not effectively planar and if asymmetry could be propagated in
this resonating ion. In the chloride the configuration of the \( \alpha \)-carbon atom is opposite to that in the parent carbinol, and there is no reason to suppose that any induced asymmetry in the \( \gamma \)-carbon atom would not have a configuration opposite to that generated by rearrangement of the parent carbinol. Then as there is inversion on the \( \alpha \)-carbon atom on hydrolysis there would also be inversion on the \( \gamma \)-carbon atom. The result would be a final configuration in the \( \gamma \)-carbon atom similar to that obtained in the molecular rearrangement of the carbinol and this is not the result of experiment.

The optical results obtained can, as in the case of \( n \)-propylpropenylcarbinol, be attributed to a side reaction wherein the mechanism involves substitution of hydroxyl before the dissociation of the chloride anion. This has been treated from the aspect of resonance in the section on ethylpropenylcarbinyl chloride and it was shown there that the migrating ion can oscillate far enough from the residuum to allow association with another ion, while not necessarily far enough to constitute complete dissociation to give in this instance a chloride anion and carbonium kation. When dissociation is not complete the asymmetry of the molecule is preserved though the reaction involves an inversion. An extension using the mechanism for anionotropic systems shown in VII is necessary to account
for the asymmetry transmitted to the $\gamma$-carbon atom. In this case the entering hydroxyl anion becomes associated with the $\gamma$-carbon atom before the chloride anion has left the $\alpha$-carbon atom. These two mechanisms where substitution precedes dissociation may be represented by a combination of:

\[
\begin{align*}
\text{CH}_3\text{CH}=&\text{CHCH}_2\text{H}_5  \\
\text{H}^+ &\text{Cl} &\text{Cl}^{-} &\text{HCl} \\
\text{OH}^- &\text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}=&\text{CHCH}_2\text{H}_5  \\
\text{OH}^- &\text{H}^+ &\text{Cl} &\text{Cl}^{-} &\text{HCl} \\
\text{OH}
\end{align*}
\]

XI and

XII

There is inversion in XI yielding a carbinol of the same configuration as that from which the chloride was prepared. The electronic shift in XII is similar to that involved in the rearrangement of the carbinol on standing and thus gives a configuration opposite to that generated by rearrangement of the parent carbinol. It would appear that the powerful polar nature of the chlorine atom is
sufficient to satisfy the provisos stipulated in the mechanism VII.

The hydrolysis of ethylpropenylcarbinyl chloride gave 9% inversion and transmission of 7% of this amount of activity to the γ-carbon atom. The reaction proceeded smoothly with calcium carbonate and water at room temperature. The hydrolysis of n-propylpropenylcarbinyl chloride however required aqueous sodium carbonate at 65°C and these somewhat severe conditions probably accounted for the detection of only 2% inversion and no transmission of asymmetry to the γ-carbon atom.

Hills and Kenyon (J.C.S., 1936, 576) have reported the formation of an optically active carbinol by the hydrolysis of methylpropenylcarbinyl chloride and this carbinol gave an optically inactive hydrogen phthalic ester but a slightly optically active benzoate. It is now considered that the activity of the carbinol may have been due to an impurity as it was very erratic and no other case of the formation of an inactive hydrogen phthalic ester from optically active methylpropenylcarbinol has been reported. That the carbinol formed by the hydrolysis of this chloride should be inactive is to be anticipated when the mechanism postulated above for ethylpropenylcarbinyl chloride is considered in conjunction with the symmetry of structure of methylpropenylcarbinol.
The symmetrical constitution had added to the difficulty of interpretation of the experimental results obtained with this alcohol. A probable impurity in methylpropenylcarbinylchloride is an ether formed between methylpropenylcarbinol and the methylpropenylcarbinyl chloride during preparation. The above authors comment on the extreme reactivity of the chloride and this impurity would be removed in the crystallisation of the hydrogen phthalic ester. The experimental data show that the benzoate formed from the carbinol in question had very little optical activity while its refractive index (n^20° = 1.5084) was lower than that of the benzoate previously prepared (n^20° = 1.5117). Pure di-pentenyl ether has a low refractive index (n^20° = 1.4290) and a high specific rotation. In this case complete purification of the benzoate from the ether would be very difficult with a small quantity of material as both derivatives are liquids.

The studies of substituted allyl alcohols (present work; Hills, Kenyon and Phillips; Kenyon, Partridge and Phillips; Arcus and Kenyon; etc.) have shown that when the optically active forms of these substances undergo anionotropic change, the products may also be optically active due to a tendency to form a ring configuration, a hypothesis which is suggested by parachor determinations. The derivatives of the alcohols also undergo anionic replacement with remarkable ease but in this case the product,
in which the entering anion may be either on the $\alpha$- or the $\gamma$-carbon atom is usually almost entirely racemised. This is due to extensive ionisation permitting resonance in the mesomeric kation which has been shown to be planar. Asymmetry is only retained when the entering anion is attached at the moment of separation of the replaced anion. Mutarotation of the alcohols is due to anionotropy.

These conclusions, though in some respects novel, are a natural development of previous views on anionotropy and anionic replacements. There remain at present two observations which are difficult to explain.

The first is the optical behaviour of the alcohol obtained by the hydrolysis of methylpropenylcarbinyl chloride and as outlined above the present tendency is to attribute this to an impurity.

The second is the irregular mutarotation of methylpropenylcarbinol as distinct from the steady mutarotation of ethylpropenylcarbinol. It is at present thought possible that this is due to the formation of

$$\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH(OH)} - \text{CH}_3$$

by the somewhat unusual mechanism :-
The anomalies in methylpropenylcarbinol are still under investigation by other workers at Battersea Polytechnic.
EXPERIMENTAL.

Preparation of dl-ethylpropenylcarbinol.

Ethyl magnesium chloride Grignard reagent was prepared from ethyl chloride (130g.) and magnesium (48g.) in dry ether. A crystal of iodine was added to start the reaction and it was essential to have the ether saturated with ethyl chloride and warmed slightly at the beginning. The solution was cooled in ice and salt and crotonaldehyde (127g.) in twice its bulk of ether was added slowly with stirring. The resulting complex was decomposed by pouring the solution on to a mixture of ammonium chloride (250g.) and ice. Any cloudiness was cleared by adding a little dilute hydrochloric acid. The ethereal solution was washed successively with sodium bisulphite solution, dilute sodium carbonate solution and water and dried with potassium carbonate. The ether was removed on the water bath and the alcohol was distilled first in vacuo and then at atmospheric pressure. Omission of the vacuum distillation caused decomposition when distilled at atmospheric pressure, water being eliminated. b.p. 44-45°C/13mm.; 55-56°C/25mm.; 135-135.5°C/760mm. nD^25° 1.4325. d^25° 0.8346. Reif, (Ber. 59,1603 and 41,2739) gives b.p. 133-134°C/760mm.; d^25° 0.8409;
n_20^\circ 1.4312. Yield 50% on the aldehyde. Found C, 72.94;
H, 12.36; C_6H_12O requires C, 72.0; H, 12.08.

The b.p. range noted by Ingold and Wilson (J.C.S.,
1933,1493) of 135 to 142°C/770mm. was not observed on ethyl-
propenylcarbinol that had been purified by vacuum distill-
ation. A sharply boiling product was also obtained by
hydrolysis of the hydrogen phthalate followed by vacuum
distillation. The crotonaldehyde was washed with water,
dried with potassium carbonate and distilled first in vacuo
and then at normal pressure. b.p. 101-103°C.

Preparation of dl-ethylpropenylcarbinyl hydrogen phthalate.

The ethylpropenylcarbinol (200g.) was added with
pyridine (180g.) to phthalic anhydride (296g.) and the
mixture was heated on the water bath until clear (1hr.).
The product was left overnight and then added to a slight
excess of hydrochloric acid in ice very slowly and with
vigorous stirring. The product of fine oily droplets
quickly solidified to a crumbly powder which was filtered off,
thoroughly washed with water and dried. Yield 80%. This
product was sufficiently pure for resolution but for
crystallisation the ester was dissolved in ether and
extracted with sodium carbonate solution. The aqueous
solution was washed with ether and dissolved ether was
then removed by a current of air passed for 20 minutes.
The hydrogen phthalic ester was reprecipitated with hydrochloric acid in ice, washed, dried and crystallised from carbon disulphide and petrol (40-60°C). Small white plates m.p. 52-53°C. Equivalent by titration in alcohol with sodium hydroxide (phenolphthalein indicator) = 245. C14H16O4 requires 248. The ester was crystallised with greater difficulty from ether and petrol (40-60°C) and then had m.p. 51°C.

Resolution of dl-ethylpropenylcarbinyl hydrogen phthalate into d- and l- forms.

Anhydrous brucine free from hydrochloride (235g.) was dissolved in a hot solution of the hydrogen phthalic ester (150g.) in dry acetone (400g.). When cold the partially resolved l-B d-A salt (250g.) separated and was filtered off m.p. approx. 140°C. This was dissolved in dry chloroform (200g.) and concentrated to a syrup and acetone (150g.) was added while hot. When cold the brucine salt which separated (150g.) had m.p. approx. 150°C. Subsequent crystallisations from chloroform and acetone gave m.p. approx. 155-160°C (100g.) and then m.p. approx. 160-163°C (80g.). A further six crystallisations gave the optically pure l-B d-A salt m.p. 168°C. The d-hydrogen phthalic ester was obtained by decomposing the salt with hydrochloric acid and ice in the presence of acetone, extracting with ether, drying
with sodium sulphate and crystallising with the addition of petrol (40-60°C). Glistening white needles m.p. 70.5°C. \([\alpha]_{546}^\circ +15.0°(1,2 \om 5)\) in chloroform solution. These values were unchanged by further crystallisation of the brucine salt or hydrogen phthalate.

It was found practicable to decompose the brucine salt when a m.p. of over 161°C had been reached, thus obtaining the hydrogen phthalic ester \([\alpha]_{546}^\circ +10.0°(1,2 \om 5)\) in chloroform solution. This was purified from the 1-ester by fractional crystallisation from dry ether and petrol (40-60°C) and usually four crystallisations were sufficient to yield the optically pure ester.

The original mother liquor and the subsequent two filtrates were mixed and evaporated to crystallise which gave the partially resolved 1-B 1-A salt m.p. 120-130°C. This was crystallised from dry acetone three times giving a brucine salt m.p. 125-126°C. The hydrogen phthalic ester obtained by decomposition of this salt had m.p. 68-69°C and \([\alpha]_{546}^\circ -14.7°(1,2 \om 5)\) in chloroform solution. Three crystallisations of the ester from dry ether and petrol (40-60°C) gave an optically pure product m.p. 70.5°C. \([\alpha]_{546}^\circ -15.0°(1,2 \om 5)\) in chloroform solution. Further crystallisation did not affect these values.

When recrystallising the brucine salt it was found that a trace of brucine hydrochloride impurity caused extensive decomposition of the salt with separation of
brucine phthalate while the presence of moisture made the filtrations very tedious and reduced the extent of resolution at each crystallisation.

Methyl and ethyl acetates were tried as solvents for the recrystallisation of the 1-B d-A salt but without success as though the products were nicely crystalline resolution was incomplete. A brucine salt m.p. 165-167°C gave on decomposition a hydrogen phthalic ester of m.p. 61-64°C and \([\alpha]_{\text{D}} +12.0^\circ(\text{l}, \text{c}, 5)\) in chloroform solution. When crystallised twice from methyl acetate it had m.p. 168°C and gave a hydrogen phthalic ester of m.p. 67-68°C, \([\alpha]_{\text{D}} +11.5^\circ(\text{l}, \text{c}, 5)\) in chloroform solution. After another crystallisation from methyl acetate it had m.p. 168°C and gave a hydrogen phthalic ester of m.p. 64-67°C, \([\alpha]_{\text{D}} +9.0^\circ(\text{l}, \text{c}, 5)\) in chloroform solution.

The d- and l- ethylpropenylcarbinols.

d-Ethylpropenylcarbinyl hydrogen phthalate (21g.) in 5N sodium hydroxide (45c.c.) was steam distilled. The distillate was extracted with ether and the extract dried with potassium carbonate. After removing the ether on the water bath the d-ethylpropenylcarbinol was distilled in vacuo (5.5g.). It had b.p. 45°C/13mm.; \([\alpha]_{\text{D}}^{18^\circ} +11.75^\circ\), \([\alpha]_{\text{D}}^{18^\circ} +12.17^\circ\), \([\alpha]_{\text{D}}^{18^\circ} +14.30^\circ\), \([\alpha]_{\text{D}}^{18^\circ} +26.65^\circ(\text{l}, \text{c}, 5)\) in...
the homogeneous state and $[\alpha]_{5893} +12.38^\circ$, $[\alpha]_{5780} +12.22^\circ$, $[\alpha]_{5461} +14.24^\circ$, $[\alpha]_{4358} +28.65^\circ$ (1.2 c, 5) in carbon disulphide solution. On another occasion using similar acid phthalic ester a specimen of the carbinol having $[\alpha]_{5893} +13.30^\circ$, $[\alpha]_{5780} +13.75^\circ$, $[\alpha]_{5461} +15.60^\circ$, $[\alpha]_{4358} +29.00^\circ$ (1, 0.5) in the homogeneous state was obtained.

1-Ethylpropenylcarbinyl hydrogen phthalate was hydrolysed similarly and yielded the 1-alcohol having b.p. 55°C/24mm. and $[\alpha]_{5893} +19^\circ$, $[\alpha]_{5780} -11.86^\circ$, $[\alpha]_{5461} -12.36^\circ$, $[\alpha]_{4358} -14.18^\circ$, $[\alpha]_{4358} -26.08^\circ$ (1, 0.5) in the homogeneous state.

The $\gamma$ to $\lambda^2$ relationship curve is given in the fig. p. 60.
$\sqrt{v} \text{ vs } \kappa^2$ Relationship Curves.

Ethyl Propenyl Carbinal
for [0] at 20°C

Ethyl Propenyl Carbinal Chloride for [0] at 19°C (0.5) c

Ethyl Propenyl
Carbinal for [0] at 20°C
The effect of solvent on the rotatory power of \( \delta \)-ethylpropienyl-carbiny1 hydrogen phthalate.

A 2 dm. polarimeter tube was employed. 20cc. of solution of 2g. or 1g. of the ester in the required solvent was prepared and lower concentrations were obtained by dilution in a standard flask.

For the characteristic diagram the specific rotatory power of a solution \((g, 5)\) was used in Patterson's modification of the Armstrong and Walker method of plotting. \((J.C.S., 1916, 109, 1176)\). The standard wave length adopted was 5461 Å and for this wave length specific rotations were plotted on the horizontal axis. At the appropriate point for each solvent on this axis differences between the standard specific rotation and those for other wave lengths were plotted vertically. The characteristic diagram (See fig. p. 63) was then obtained by joining the points associated with individual wave lengths.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration (Wt./100cc.)</th>
<th>5893</th>
<th>5780</th>
<th>5461</th>
<th>4358 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>10.0</td>
<td>+20.2</td>
<td>+21.7</td>
<td>+26.0</td>
<td>+60.3</td>
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<tr>
<td>(Na salt)</td>
<td>5.0</td>
<td>+20.7</td>
<td>+22.0</td>
<td>+26.5</td>
<td>+60.1</td>
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<tr>
<td></td>
<td>2.5</td>
<td>+20.0</td>
<td>+21.1</td>
<td>+23.9</td>
<td>+56.4</td>
</tr>
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</table>
Continued from p. 61.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration (Wt./100cc.)</th>
<th>5893</th>
<th>5780</th>
<th>5461</th>
<th>4358 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl</td>
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<td>+26.6</td>
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<td>+65.7</td>
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<tr>
<td>Alcohol</td>
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<td>+27.5</td>
<td>+28.8</td>
<td>+33.4</td>
<td>+68.5</td>
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<tr>
<td></td>
<td>2.5</td>
<td>+27.2</td>
<td>+29.7</td>
<td>+32.5</td>
<td>+68.0</td>
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<tr>
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<td>-12.4</td>
<td>-13.0</td>
<td>-14.5</td>
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<td>Disulphide</td>
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<td>-14.5</td>
<td>-16.1</td>
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<tr>
<td></td>
<td>2.5</td>
<td>-14.4</td>
<td>-14.8</td>
<td>-16.2</td>
<td>-27.8</td>
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<tr>
<td>Nitro</td>
<td>10.0</td>
<td>+18.8</td>
<td>+20.3</td>
<td>+23.3</td>
<td>+48.5</td>
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<tr>
<td>Methane</td>
<td>5.0</td>
<td>+21.4</td>
<td>+22.8</td>
<td>+26.2</td>
<td>+53.0</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>+23.6</td>
<td>+24.4</td>
<td>+29.0</td>
<td>+60.0</td>
</tr>
<tr>
<td>Pyridine</td>
<td>10.0</td>
<td>+18.1</td>
<td>+19.7</td>
<td>+22.5</td>
<td>+46.0</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>+17.8</td>
<td>+19.0</td>
<td>+22.1</td>
<td>+48.0</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>+17.4</td>
<td>+18.8</td>
<td>+20.8</td>
<td>+49.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>5.0</td>
<td>+10.6</td>
<td>+11.0</td>
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</tr>
<tr>
<td>Chloroform</td>
<td>5.0</td>
<td>+11.5</td>
<td>+13.0</td>
<td>+15.0</td>
<td>+32.9</td>
</tr>
</tbody>
</table>
CHARACTERISTIC DIAGRAM
for ETHYL PROPENYL
CARBONYL HYDROGEN
PATHALATE

25°
30°
35°

20°
15°
10°
5°

5°
10°
15°
20°
25°
30°
35°

5461 A°
5760 A°
5333 A°

Carbon disulfide
Benzene
Hydrogen
Water
Ether

(centigrade)

The effect of temperature on the rotatory power of \( \alpha \)-ethyl-propenylcarbinol.

A 0.5dm. jacketed polarimeter tube was employed. A side arm enabled the thermometer bulb to be immersed in the carbinol and the temperature was varied by circulating a stream of heated water through the jacket. Rotations for four different wave lengths were taken with increasing temperature and the tube was finally allowed to cool for another measurement to verify that heating had not affected the specific rotatory power. The observations are plotted in the Fig. p. 66.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
<th>5893</th>
<th>5780</th>
<th>5461</th>
<th>4358 Å</th>
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</thead>
<tbody>
<tr>
<td>15.0</td>
<td>0.8431</td>
<td>+13.28</td>
<td>+14.12</td>
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<tr>
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<tr>
<td>24.5</td>
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<td>-</td>
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<td>25.8</td>
<td>0.8339</td>
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<td>-</td>
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<td>-</td>
</tr>
<tr>
<td>26.2</td>
<td>0.8336</td>
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<td>+13.20</td>
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<td>26.8</td>
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<td>-</td>
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<td>28.8</td>
<td>0.8313</td>
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<td>29.0</td>
<td>0.8312</td>
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<tr>
<td>30.0</td>
<td>0.8303</td>
<td>-</td>
<td>+13.00</td>
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</table>
Continued from p. 64.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
<th>Specific Rotation for Wave Length</th>
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</thead>
<tbody>
<tr>
<td>30.8</td>
<td>0.8296</td>
<td>5893 - - - +27.10</td>
</tr>
<tr>
<td>32.3</td>
<td>0.8284</td>
<td>5780 +12.24 - -</td>
</tr>
<tr>
<td>37.0</td>
<td>0.8243</td>
<td>5461 - - +14.19 -</td>
</tr>
<tr>
<td>37.5</td>
<td>0.8239</td>
<td>4358 - +12.13 -</td>
</tr>
<tr>
<td>37.8</td>
<td>0.8236</td>
<td>- - +26.46 -</td>
</tr>
<tr>
<td>40.0</td>
<td>0.8218</td>
<td>5893 +11.33 - -</td>
</tr>
<tr>
<td>43.0</td>
<td>0.8191</td>
<td>5780 - - +25.03 -</td>
</tr>
<tr>
<td>43.6</td>
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</tr>
<tr>
<td>44.0</td>
<td>0.8182</td>
<td>4358 - +13.32 -</td>
</tr>
<tr>
<td>53.3</td>
<td>0.8103</td>
<td>5893 +10.25 - -</td>
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<tr>
<td>53.8</td>
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</tr>
<tr>
<td>54.0</td>
<td>0.8096</td>
<td>5461 - +10.87 -</td>
</tr>
<tr>
<td>58.5</td>
<td>0.8060</td>
<td>4358 +9.80 - +11.83 -</td>
</tr>
<tr>
<td>59.0</td>
<td>0.8055</td>
<td>- +10.31 - +21.73</td>
</tr>
<tr>
<td>37.0</td>
<td>0.8243</td>
<td>- - +14.19 -</td>
</tr>
</tbody>
</table>
Effect of Temperature on the Specific Rotatory Power of $\alpha$-Ethyl Propenyl Cardinol.
Mutarotation of ethylpropenylcarbinol.

The specimens of carbinol used for these observations were distilled into glass stoppered bottles for storage at room temperature and they were transferred at intervals to a 0.5 dm polarimeter tube for rotation measurements. Observed rotations and temperatures are tabulated with time of standing.

(I) Specimen of d-ethylpropenylcarbinol.

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Temp. °C</th>
<th>5093</th>
<th>5780</th>
<th>5461</th>
<th>4358</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>19.0</td>
<td>+5.00</td>
<td>+5.26</td>
<td>+6.12</td>
<td>+11.28</td>
</tr>
<tr>
<td>6</td>
<td>19.0</td>
<td>+5.03</td>
<td>+5.25</td>
<td>+6.06</td>
<td>+11.23</td>
</tr>
<tr>
<td>42</td>
<td>19.5</td>
<td>+4.98</td>
<td>-</td>
<td>+6.05</td>
<td>+11.04</td>
</tr>
<tr>
<td>59</td>
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<td>-</td>
<td>+6.00</td>
<td>+11.05</td>
</tr>
<tr>
<td>122</td>
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<td>-</td>
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<td>+5.26</td>
<td>+9.85</td>
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<td>129</td>
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<tr>
<td>136</td>
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<td>+4.95</td>
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<tr>
<td>174</td>
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<tr>
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<tr>
<td>369</td>
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<td>+3.66</td>
<td>+3.94</td>
<td>+4.50</td>
<td>+8.40</td>
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<tr>
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<td>+3.55</td>
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<td>1156</td>
<td>21.5</td>
<td>+3.33</td>
<td>-</td>
<td>+4.04</td>
<td>+7.49</td>
</tr>
</tbody>
</table>
(II) **Specimen of 1-ethylpropenylcarbinol.**

<table>
<thead>
<tr>
<th>Time (Days)</th>
<th>Temp. °C</th>
<th>5893</th>
<th>5780</th>
<th>5461</th>
<th>4358</th>
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(III) **Specimen of d-ethylpropenylcarbinol.**

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<th>Time (Days)</th>
<th>Temp. °C</th>
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<th>5780</th>
<th>5461</th>
<th>4358</th>
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<td>+11.85</td>
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</tbody>
</table>

1% Formic Acid added

757 20.0 +5.16 +5.25 +6.15 +11.15

After mutarotation specimen (I) was taken up in ether, washed with potassium carbonate solution and dried with potassium carbonate. The aqueous solutions possessed no optical rotatory power. The ethereal solution of hexenol was reduced with hydrogen and after drying with potassium carbonate and removing the ether the hexanol was distilled at normal pressure. b.p. 131-133 °C. $\alpha_{5893}^{20^\circ} + 2.50^\circ$, $\alpha_{5461}^{20^\circ} + 2.60^\circ$, $\alpha_{5780}^{20^\circ} + 2.90^\circ$, $\alpha_{4358}^{20^\circ} + 5.00^\circ$ (1, 0.5) in the homogeneous state. Found C, 69.43; H, 13.56; C₆H₄O
requires C,70.6; H,13.7. The starting material, $\left[\alpha\right]_{5461}^{+14.58^\circ}$ was 92.5% optically pure so that for optically pure starting material the rotatory power for a similarly mutarotated product would be $\alpha_{5893}^{20^\circ} + 2.70^\circ (1,0.5)$ or 93% of that of optically pure ethylpropylcarbinol.

The reduced product (0.7g.) was converted to the hydrogen phthalate and after purification by extraction with sodium carbonate solution was precipitated with dilute hydrochloric acid, extracted with ether and dried with sodium sulphate. The total hydrogen phthalate was recovered by removing the ether and leaving in vacuo (0.5g.). It had $[\alpha]_{5893}^{+16.7^\circ}$, $[\alpha]_{5893}^{+16.5^\circ} (1,2.2.5)$ in chloroform solution. The quotient 16.7/5.0 = 3.34 which corresponds with 56% of d-ethylpropylcarbinol and 44% of d-methyl n-butylcarbinol. (See graph p. 6). For an optically pure mixture of this composition the rotatory power of the carbinol would be $\alpha_{5893}^{20^\circ} + 7.4^\circ (1,1.0)$. Thus the optically active constituents (for optically pure starting material) totalled 73% of the whole, indicating that on mutarotation there was 27% racemisation, 41% remained and 32% converted to d-methyl n-butylcarbinol.
**Reduction of dl-ethylpropenylcarbinol.**

Ethylpropenylcarbinol freshly prepared by hydrolysis of the hydrogen phthalate (2.2g.) in dry ether (50c.c.) was reduced with hydrogen at two atmospheres pressure (250c.c.). Platinum catalyst was used and this was introduced as the oxide prepared from chloroplatinic acid by the method given by Short (J.S.C.I., 55, 1936, 141). There was an induction period of 2 minutes after which the oxide was reduced to platinum and reduction of the carbinol was complete in 30 minutes. After filtering off the platinum and drying with potassium carbonate the ether was distilled off leaving ethyl n-propylcarbinol. This was distilled at normal pressure. Yield 1.6g. b.p. 132.5-133.5°C.

\[ d_{20}^o = 0.8193. \]

Another specimen of ethylpropenylcarbinol freshly prepared from the Grignard complex was similarly reduced and the product had b.p. 130-133°C/760mm. and \[ d_{20}^o = 0.8189. \]

When redistilled the fraction b.p. 131-132°C had \[ d_{4}^o = 0.8195 \]

and the fraction b.p. 132-132.5°C had \[ d_{4}^o = 0.8202. \]

Another specimen of ethylpropenylcarbinol which had been prepared by hydrolysis of the hydrogen phthalic ester and had since stood 2 years was similarly reduced and the product had b.p. 131-133°C and \[ d_{20}^o = 0.8181. \]

Pickard and Kenyon (J.C.S., 1913, 103, 1923) give \[ d_{20}^o = 0.8213. \]
Preparation of dl-ethyl n-propylcarbinyl hydrogen phthalate.

Ethyl n-propylcarbinol obtained by the reduction of fresh ethylpropenylcarbinol (2g.) was heated with phthalic anhydride (3g.) at 110-120°C for 7 hours. After dissolving in sodium carbonate solution and extracting three times with ether, the dissolved ether was removed by passing air for \(\frac{1}{2}\) hour and the hydrogen phthalic ester was precipitated by adding excess dilute hydrochloric acid. The product was extracted with chloroform, washed with water, dried with calcium chloride and crystallised after evaporation to dryness from petroleum ether (40-60°C). Yield after two crystallisations 2.2g. m.p. 75-76°C. Pickard and Kenyon (J.C.S., 1913, 102, 1923) give m.p. 76-77°C.

Reduction of d-ethylpropenylcarbinol.

d-Ethylpropenylcarbinol (3.5g.) freshly prepared by hydrolysis of the hydrogen phthalic ester and having \([\alpha]_{546}^{20} = 14.91° \ (1,0.5)\) was reduced as above and the product was distilled at normal pressure. Yield 2.3g. b.p. 131-133°C \([\alpha]_{589}^{20} = 6.81°, \ [\alpha]_{546}^{20} = 7.79°, \ [\alpha]_{435}^{20} = 12.41° \ (1,0.25)\).

The ethylpropenylcarbinol was 96% optically pure and thus for optically pure d-ethyl n-propylcarbinol \([\alpha]_{589}^{20} = +7.09°\).

Kenyon (J.C.S., 1914, 105, 2226) gives \([\alpha]_{589}^{20} = -4.21°\).
for the maximum rotation. This 
relationship curve is given in the fig. p. 60.

Preparation of d-ethyl n-propylcarbinyl hydrogen phthalate.

The procedure was similar to that employed for the dl-hydrogen phthalate but after evaporation to dryness the product was left in a vacuum desiccator for two days to remove traces of solvent. To remove phthalic acid the hydrogen phthalic ester was dissolved in dry chloroform, filtered and again evaporated with vacuum desiccation. The resulting white crystalline solid had m.p. 48-49°C and $\left[\alpha\right]_{D}^{\text{5893}} +9.31^\circ$, $\left[\alpha\right]_{D}^{\text{5700}} +10.19^\circ$, $\left[\alpha\right]_{D}^{\text{5461}} +11.26^\circ$, $\left[\alpha\right]_{D}^{\text{4358}} +18.26^\circ$ (1.2 x 0.5) in chloroform solution. The carbinol was 96% optically pure and as there was no further purification of the hydrogen phthalate, for optically pure d-ethyl n-propylcarbinyl hydrogen phthalate $\left[\alpha\right]_{D}^{\text{5893}} = +9.70^\circ$.

Kenyon (J.C.S., 1914, 105, 2226) gives $\left[\alpha\right]_{D}^{\text{5893}} -5.76^\circ$ for the maximum rotation in chloroform solution.
Preparation of dl-methyl n-butyl carbinol.

n-Butyl magnesium bromide Grignard reagent was prepared from n-butyl bromide (34g.) and magnesium (6g.) in dry ether. The solution was cooled in ice and salt and acetaldehyde (10g.) in twice its bulk of ether was added slowly with stirring. The resulting complex was decomposed by pouring the solution on to a mixture of ammonium chloride (30g.) and ice. The ethereal solution was washed successively with sodium bisulphite solution, dilute sodium carbonate solution and water and dried with potassium carbonate. The ether was removed on the water bath and the methyl n-butyl carbinol was distilled twice at normal pressure. Yield 6g. b.p. 134-141°C. d_{20}^0 0.6150. Pickard and Kenyon (J.C.S., 1911, 99, 45) give b.p. 136°C and d_{20}^0 0.6150.

Preparation of dl-methyl n-butyl carbinyl hydrogen phthalate.

Methyl n-butyl carbinol (2g.) was heated with phthalic anhydride (3g.) at 110-120°C for 7 hours. After dissolving in sodium carbonate solution and extracting three times with ether the dissolved ether was removed by passing air for ½ hour and the hydrogen phthalic ester was precipitated by adding excess dilute hydrochloric acid. The product was extracted with chloroform, washed with
water, dried with calcium chloride and evaporated to dryness. The hydrogen phthalate was recrystallised from ether and petroleum ether (40-60°C) with some difficulty. Colourless prisms, m.p. 48°C. Pickard and Kenyon (J.C.S., 1911, 99, 45) report an oily syrup that would not crystallise.
Preparation of ethylpropenylcarbinyl methyl ether

(I) From 1-ethylpropenylcarbinyl hydrogen phthalate.

1-Ethylpropenylcarbinyl hydrogen phthalate (8g.) of \([\alpha]_{D}^1 = -0.6^\circ\) (1,2 g,5) in chloroform solution was heated under reflux on the water bath with anhydrous methyl alcohol (50g.) for 32 hours. The methyl alcohol had been distilled from calcium. The liquid was distilled off the residual phthalic acid and unchanged hydrogen phthalic ester on the steam bath. Anhydrous calcium chloride (60g.) was added to the distillate and left overnight. After filtering and washing with ether the di-ethyl ether was removed on the water bath and the residue distilled at normal pressure. Yield of ethylpropenylcarbinyl methyl ether 1.0g. b.p. 110-112\(^\circ\)C. \(n_\text{D}^22^\circ = 1.4180\). \(\alpha_{D}^22^\circ = -0.18^\circ\) (1,0,5) in the homogeneous state.

(II) From 1-ethylpropenylcarbinol.

1-Ethylpropenylcarbinol (5g.) having \(\alpha_{D}^22^\circ = -2.5^\circ\) (1,0,5 prepared by hydrolysis of hydrogen phthalic ester similar to that used in method (I) was treated with potassium (1,6g.) in dry ether (30g.). After standing overnight excess potassium was removed and methyl iodide (7g.) was added. After washing three times with ice water and drying with calcium chloride the di-ethyl ether was removed on the water bath. The residue was fractionally distilled at
normal pressure and found to contain unchanged carbinol. To remove this, the total distillate (2.6g.) was warmed with phthalic anhydride (3g.) and pyridine (2g.). The product was dissolved in ether and extracted with sodium carbonate solution. The ether solution was then washed successively with dilute hydrochloric acid and water and dried with calcium chloride. After removing the diethyl ether on the water bath the residue was again fractionally distilled at normal pressure. Yield 1.5g. b.p. 110-115°C. n_D 1.4110. α_23°_D +6.88° (1,0.5) in the homogeneous state.
**Preparation of dl-ethylpropenylcarbinyl p-nitro benzoate.**

p-Nitro benzoyl chloride (9.2g.) was added to a mixture of ethylpropenylcarbinol (5.0g.) and pyridine (4.5g.). The mixture was heated for ½ hour on the water bath and left overnight. The product was extracted with ether, washed successively with ice-cold dilute hydrochloric acid and water and dried with calcium chloride. After distilling off the ether, finally in vacuo, the dl-ethylpropenylcarbinyl p-nitro benzoate was crystallised from petrol (40-60°C). Yield 5g. Pale yellow flakes m.p. 36-37°C.

**Preparation of dl-ethylpropenylcarbinyl acetate.**

Acetyl chloride (5g.) was added to a mixture of ethylpropenylcarbinol (5g.) and pyridine (6g.). After warming gently and standing overnight the mixture was treated with excess ice-cold dilute hydrochloric acid. The product was extracted with ether and the extract was washed with water and dried with sodium sulphate. After removing the ether on the water bath the ester was distilled first in vacuo and then at normal pressure. b.p. 54-56°C/17mm., 152-154°C/760mm. \( n^\circ_{D} \) 1.4230. Found C, 66.91; H, 9.78. \( C_8H_4O_2 \) requires C, 67.5; H, 9.93.
Preparation of dl-ethylpropenylcarbinyl benzoate.

Benzoyl chloride (8g.) was added to a mixture of ethylpropenylcarbinol (5g.) in pyridine (6g.). After warming and standing overnight the mixture was treated with excess ice-cold dilute hydrochloric acid. The product was extracted with ether and the extract was washed with water and dried with sodium sulphate. After removing the ether on the water bath the ester was distilled in vacuo. b.p. 144-145°C/20mm. \( n^\circ_D \) 1.5076. Found C, 76.35; H, 7.81. C\(_{13}\)H\(_{16}\)O\(_2\) requires C, 76.45; H, 7.90.

Purification of Allyl Alcohol.

A specimen was left over anhydrous copper sulphate for one week and then twice fractionally distilled at normal pressure. The fraction b.p. 96.5-97°C was left over potassium carbonate for one week. The result was fractionally distilled and the fraction b.p. 96-96.7°C was collected and sealed for parachor determinations. \( n^\circ_D \) 1.4142. Found C, 61.56; H, 10.23; C\(_3\)H\(_6\)O requires C, 62.0; H, 10.42.

Another specimen of allyl alcohol was left over potassium carbonate for one week and fractionally distilled. The fraction b.p. 95.5-95.7°C was again left over potassium carbonate for one week and fractionally distilled. The fraction b.p. 96-96.2°C was collected for parachor determinations. \( n^\circ_D \) 1.4134.
Preparation of Allyl Acetate.

Acetyl chloride (20g.) was added slowly to a mixture of allyl alcohol (11.5g.) and pyridine (16g.). There was a vigorous reaction and after cooling, the mixture was shaken with ether and dilute hydrochloric acid. The ether extract was washed with water and then potassium carbonate solution. After drying with potassium carbonate the ether was removed on the water bath and the ester was distilled at normal pressure. Yield (after two distillations) 7g. b.p. 103-105°C. n°1 1.4050. Found C, 59.68; H, 8.28. C₅H₈O₂ requires C, 59.68; H, 8.02.

Preparation of Allyl ethyl ether.

Allyl chloride (7.7g.) was added to sodium ethoxide prepared by adding sodium (2.5g.) to absolute alcohol (40g.). The product was warmed on the water bath and left overnight. Water was added and the required ether extracted with di-ethyl ether, washed with water and dried with potassium carbonate. After removing di-ethyl ether on the water bath the allyl ethyl ether was distilled at normal pressure. Yield 3.1g. b.p. 55-56°C. n°1 1.3700. Found C, 61.16; H, 12.49. C₅H₁₀O requires C, 69.70; H, 11.71.
Preparation of \( \text{dl-ethylpropenylcarbinyl chloride} \).

Thionyl chloride (26.4g.) (b.p. 75°C) freshly distilled from linseed oil, in dry ether (80cc.) was added with rapid stirring during one hour to \( \text{dl-ethylpropenylcarbinol} \) (20g.) and quinoline (50g.) in ether (160cc.) while the flask was cooled in a freezing mixture. After standing overnight the ether was removed on the water bath and the product was distilled at normal pressure. Yield 10g., b.p. 30°C/13mm.; 35°C/16mm.; 100°C/370mm. It distilled with slight decomposition and liberation of hydrochloric acid at normal pressure. b.p. 123-124°C. \( \eta^\circ \) 1.4400. Found C, 61.03; H, 9.65; Cl, 28.2. \( \text{C}_6\text{H}_{11}\text{Cl} \) requires C, 60.71; H, 9.36; Cl, 29.93.

It was found necessary to use a small amount of quinoline to avoid a large high boiling residue when the product was distilled as this reduced the yield. Pyridine was first tried but then the product was alkaline after distillation and contained pyridine. When pure the chloride was a colourless liquid with a very faint pungent smell.

Hydrolysis of \( \text{dl-ethylpropenylcarbinyl chloride} \) with water and calcium carbonate.

Precipitated calcium carbonate (2.5g.) was added to a mixture of \( \text{dl-ethylpropenylcarbinyl chloride} \) (6g.) and water
There was slight effervescence and an almost immediate smell of the carbinol. After standing three days with occasional shaking all the calcium carbonate had dissolved and excess was added (2.5g.). There was violent effervescence. The product was extracted with ether and dried with potassium carbonate. After removing the ether on the water bath the product was distilled in vacuo into three fractions. 20% b.p. up to 47°C, 60% b.p. 47-49°C, 20% 49-50°C/12mm. All these fractions had n\_D\textsuperscript{20} 1.4345. Total yield 4g.

**Preparation of the p-xenyl urethane of the product of hydrolysis of dl-ethylpropenylcarbinyl chloride.**

The middle fraction of the above hydrolysis (0.5g.) was heated for 1½ hours with p-xenyl carbimide (1g.) at 100°C. When cold the solid product was dissolved in dry ether, filtered and crystallised by concentrating and adding petroleum ether (40-60°C). The product consisting mainly of white needles had m.p. approx. 75°C. By fractional crystallisation from ether and petrol three crops of crystals were obtained. m.p. 92-93°C, 84°C and 75°C. The second fraction was further fractionated giving m.p. 85-86°C and 75-80°C.
Preparation of the \( p \)-xenyl urethane of \( dl \)-ethylpropenylcarbinol.

\( dl \)-Ethylpropenylcarbinol which had stood 2 years (0.5g) was heated with \( p \)-xenyl carbimide (1g.) as before and the product finally crystallised from ether and petrol. The total yield had m.p. 97-99°C. By fractional crystallisation two crops of crystals were obtained, both in the form of needles. The major fraction had m.p. 102-103°C which was unchanged by further crystallisation. A small quantity (25%) was recovered with an apparently constant m.p. 84-86°C.

Ethylpropenylcarbinol freshly prepared by hydrolysis of the hydrogen phthalic ester yielded a \( p \)-xenyl urethane of long colourless needles m.p. 102°C with two recrystallisations.

Preparation of the hydrogen phthalic ester of the product of hydrolysis of \( dl \)-ethylpropenylcarbinyl chloride.

Hexenol (not redistilled) obtained by hydrolysis of ethylpropenylcarbinyl chloride (3.5g.) was added to a mixture of phthalic anhydride (5.2g.) and pyridine (3.2g.) that had been heated until clear and allowed to cool. After standing four days the hydrogen phthalic ester was extracted as usual with ether and washed with dilute hydrochloric acid, extracted with sodium carbonate solution and reprecipitated with ice cold hydrochloric acid. The
The final solution in ether was washed with water, dried with sodium sulphate and allowed to crystallise. After five months an appreciable white crystalline precipitate had formed but when removed and dried had m.p. over 300°C.

Fractional crystallisation of the p-xenyl urethane of the product of hydrolysis of dl-ethylpropenylcarbinyl chloride.

Hexenol (not redistilled) obtained by hydrolysis of ethylpropenylcarbinyl chloride (5g.) was heated with p-xenyl carbimide (10g.) at 100°C for 1½ hours. The product was extracted with dry ether, filtered and subjected to fractional crystallisation using ether and petroleum ether (40-60°C). The first crop of crystals had m.p. 84-85°C (4g.) and on recrystallisation had m.p. 92-94°C (3g.). The next crystallisation yielded larger crystals (0.7g.) m.p. 100-101°C and this was not increased beyond 102-103°C by subsequent crystallisations. A mixture of this product and authentic ethylpropenylcarbinyl p-xenyl urethane (prepared as above from the carbinol) had m.p. 102°C. Found C, 78.9; H, 7.41. C₁₉H₂₅NO₂ requires C, 77.3; H, 7.17.

The first filtrate on concentration yielded a crystalline product with m.p. 77-80°C (5g.) and this when reduced to 4g. by crystallisation had m.p. 79-83°C. A small amount of higher m.p. material was removed by very
slow concentration of its solution (0.5 g. m.p. 85-89°C) and then 3 g. of crystals with m.p. 80-84°C were obtained. Two further crystallisations yielded a final product of m.p. 81-82°C. Found C, 77.9; H, 7.37. \( \text{C}_9\text{H}_2\text{NO}_2 \) requires C, 77.3; H, 7.17.

**Preparation of the p-xenyl urethane of dl-ethylpropylcarbinol.**

\( \text{dl-Ethylpropylcarbinol (0.5 g.)} \) obtained by reduction of freshly prepared ethylpropynylcarbinol was heated with p-xenyl carbimide (1 g.) at 100°C for 1½ hours. After cooling and extracting with ether the product on crystallisation from ether and petrol had m.p. 135°C and consisted of colourless needles.

**Preparation of the p-xenyl urethane of dl-methyl p-butylicarbinol.**

\( \text{dl-Methyl p-butylicarbinol (0.5 g.)} \) and p-xenyl carbimide (1 g.) treated as with ethylpropylcarbinol yielded the p-xenyl urethane with m.p. 91-92°C.

**Fractional crystallisation of the p-xenyl urethanes of the reduced product of hydrolysis of dl-ethylpropynylcarbinyl chloride.**

Hexenol (4 g.) prepared by the hydrolysis of \( \text{dl-ethyl-} \)
propenylcarbinyl chloride was reduced with hydrogen, dried and distilled to give the corresponding hexanol (1.3g.). This was converted to the p-xenyl urethane and subjected to fractional crystallisation from ether and petroleum ether (40-60°C). The first crop had m.p. 110-120°C which was increased to 129-130°C by two recrystallisations and by two further crystallisations a small quantity of crystals of m.p. 132-133°C was obtained. This constituent was difficult to isolate as although it had the higher melting point it did not necessarily crystallise first. When mixed with authentic ethylpropylcarbinyl p-xenyl urethane the m.p. was 131-132°C.

The first mother liquor yielded on concentration crystals of m.p. 80-90°C which by three recrystallisations was increased to 91-92°C. When mixed with authentic methyl n-butylcarbinyl p-xenyl urethane the m.p. was 90-91°C.

Fractional crystallisation of the hydrogen phthalic ester of the reduced product of hydrolysis of dl-ethylpropenylcarbinyl chloride.

Hexenol (10g.) prepared by the hydrolysis of dl-ethylpropenylcarbinyl chloride was reduced with hydrogen, dried and distilled to give the corresponding hexanol (3.8g.). This was heated with phthalic anhydride (5.7g.) at 110-120°C for 7 hours and the product was taken up in ether and extracted with sodium carbonate solution. After washing with ether
the hydrogen phthalic ester was precipitated with dilute hydrochloric acid and crystallised from chloroform and petrol. This was subjected to fractional crystallisation from ether and petrol (40-60°C). The first crop (2.7g) had m.p. 66-67°C and this was increased to 73°C by six recrystallisations. When mixed with authentic ethylpropylcarbinyl hydrogen phthalate the m.p. was 73-74.5°C. The equivalent (by titration with N/100 sodium hydroxide) was 251. C₁₄H₁₈O₄ requires 250.

The first mother liquor on concentration yielded crystals m.p. 40-50°C (1g). By slow concentration of the solution a crop with m.p. 55-58°C was obtained and the mother liquor from this yielded crystals of m.p. 40-45°C. Two further recrystallisations increased the m.p. to 44-49°C and when mixed with authentic methyl n-butyl carbinyl hydrogen phthalate the m.p. was 43-47°C. A very small quantity was obtained by further crystallisation with m.p. 46-48°C and mixed m.p. with authentic methyl n-butylcarbinyl hydrogen phthalate 45-47°C. The equivalent of the larger fraction (by titration with N/100 sodium hydroxide) was 252. C₁₄H₁₈O₄ requires 250.
Preparation of 1-ethylpropenylcarbinyl chloride.

Freshly distilled thionyl chloride (6.6g.) in dry ether (20cc.) was added slowly (½hr.) to 1-ethylpropenylcarbinol having $[\alpha]_5^{20}_{2} +15.3^\circ$ and quinoline (6.5g.) in ether (35cc.). The mixture was cooled in a freezing mixture and stirred during the addition and the product was at once filtered and washed with ether. After combining the filtrate and washings the ether was removed on the water bath. The residue of chloride was distilled in vacuo. Yield 2.6g. b.p. 35°C/30mm. $\alpha$$_{5893}^{19^\circ} -11.25^\circ$, $\alpha$$_{5780}^{19^\circ} -12.65^\circ$, $\alpha$$_{5^461}^{19^\circ} -14.75^\circ$, $\alpha$$_{4358}^{19^\circ} -28.3^\circ$ (1, 0.5) in the homogeneous state.

The $\alpha$ to $\lambda^2$ relationship curve is given in the fig. p. 60.

Hydrolysis of 1-ethylpropenylcarbinyl chloride.

The above prepared 1-ethylpropenylcarbinyl chloride was added to water (10g.) and calcium carbonate (2g.) and left for a week with occasional shaking. The resulting carbinol was salted out with potassium carbonate, extracted with ether, dried with potassium carbonate and distilled in vacuo after removing the ether on the water bath. Yield 1g. b.p. 55-57°C/20mm. $\alpha$$_{5893}^{18^\circ} -0.24^\circ$, $\alpha$$_{5780}^{18^\circ} -0.20^\circ$, $\alpha$$_{5^461}^{18^\circ} -0.17^\circ$, $\alpha$$_{4358}^{18^\circ} -0.10^\circ$ (1, 0.5) in the homogeneous state. This was converted to the hydrogen phthalate and
purified by washing the ammonium hydroxide extract with ether. The ether washings possessed no optical activity (\(\alpha, 5461, 1, 2\)). After precipitation with dilute hydrochloric acid the hydrogen phthalate was dissolved in ether and dried with calcium chloride. The ether solution was slightly optically active giving \(\alpha, 5461, +0.04^\circ (1, 2)\) but it was not found possible to obtain a solid product by evaporation of the solvent.

Reduction of the carbinol obtained by hydrolysis of 1-ethylpropenylcarbinyl chloride.

The chloride was prepared as before from part d-ethyl-propenylcarbinol (10g.) having \([\alpha]^{21\circ}_{5461} +6.56^\circ (1, 0.5)\) with quinoline (13g.) in ether (50g.) and thionyl chloride (13.2g.) in ether (30g.). The preparation (including distillation) was completed in one hour and the product (5.5g.) had

\[\alpha^{18^\circ}_{5893} -5.13^\circ, \alpha^{18^\circ}_{6780} -5.72^\circ, \alpha^{18^\circ}_{4358} -6.55^\circ, \alpha^{18^\circ}_{4358} -12.60^\circ (1, 0.5)\] in the homogeneous state. The chloride was immediately added to water (15g.) and calcium carbonate (4g.) and left for two weeks. The resulting carbinol was recovered as before and had \(\alpha^{18^\circ}_{5893} -0.11^\circ, \alpha^{18^\circ}_{6780} -0.10^\circ, \alpha^{18^\circ}_{5461} -0.07^\circ, \alpha^{18^\circ}_{4358} -0.03^\circ (1, 0.5)\) in the homogeneous state.

The carbinol was reduced with hydrogen in ether with platinum catalyst, dried with potassium carbonate, and
distilled at normal pressure after removing the ether on the water bath. Yield 1.5g. b.p. 132-137°C. \( \alpha^{20} \_5893 = +0.04^\circ \), \( \alpha^{20} \_5401 = +0.02^\circ \), \( \alpha^{20} \_4356 = +0.00^\circ (1,0.25) \) in the homogeneous state. This reduced carbinol was converted to the hydrogen phthalate, purified by extraction with sodium carbonate solution, precipitated by dilute hydrochloric acid and finally dissolved in ether and dried with sodium sulphate. The total hydrogen phthalate was recovered as a thick syrup which tended to crystallise. It had \([\alpha]_{5893} +0.20^\circ\), \([\alpha]_{5401} +0.07^\circ\), (1,2, 2,7,5) in chloroform solution.

The quotient 0.20/0.16 = 1.25 which corresponds with 93% of \(d\)-ethylpropylene carbinol and 7% of \(1\)-methyl \(n\)-butylcarbinol. (See graph p. 16) For an optically pure mixture of this composition the rotatory power of the carbinol would be \( \alpha^{20} \_5893 +4.7^\circ (1,1.0) \). The starting material (\(d\)-ethylpropylene carbinol) was 42% optically pure and thus for optically pure material subjected to the above process the rotatory power of the reduced carbinol would be \( \alpha^{20} \_5893 +0.38^\circ (1,1.0) \). Hence the optically active constituents (for optically pure starting material) totalled 8% of the whole, indicating that on tautomerisation by formation and hydrolysis of the chloride there was 92% racemisation, 7.4% unchanged and 0.6% converted to \(1\)-methyl \(n\)-butenylcarbinol.
Measurement of the Parachor.

The parachor is given by the formula:

\[ [F] = \frac{M \gamma^\frac{1}{2}}{D - d} \]

derived from Macleod's relationship:

\[ \gamma = C (D - d)^{\frac{1}{2}} \]

(Sugden, "Parachor and Valency")

where \( M \) = molecular weight, \( \gamma \) = surface tension, \( D \) = density of the liquid and \( d \) = density of the vapour.

As \( d \) was negligibly small compared with \( D \) it was omitted, giving the simplified formula:

\[ [F] = \frac{M \gamma^{\frac{1}{2}}}{D} \]

Density measurements were made with a pyknometer of about 0.44cc capacity. This was calibrated with purified benzene and distilled water and a temperature volume curve was plotted for the required range. Observed densities were plotted against temperature (measured to 0.1°C).

Surface tension measurements were obtained by the Maximum Bubble Pressure method described by Sugden (loc.cit.) The apparatus is illustrated (see p. 93) and consisted essentially of two jets with radii approximately 1.5 and
A steady pressure causing air to issue from either of the jets (selected by a tap) was provided by a finely controlled mercury aspirator and the pressure was measured by a tinted absolute alcohol manometer immersed in water. The part of the apparatus containing the jets was lubricated with the liquid under test and could be maintained at steady temperatures by the water bath. A rate of about one bubble bursting per second was used with the small jet and after switching to the large jet the air flow was not changed. For each surface tension measurement the temperature of the liquid was observed and the difference between the maximum pressures for the two sizes of bubbles expressed as c cms. of alcohol at t°C was determined and converted to p dynes per sq. cm. The density of the liquid D at the same temperature was obtained from the density temperature curve described above.

The surface tension is given by the formula:

\[ \gamma = A p \varphi \]

where A, the apparatus constant was determined by calibration with pure benzene. The factor \( \varphi = 1 + 0.69 r g D / p \) where r is the internal radius of the large jet. r was measured with a travelling microscope and the constant \( K = 0.69 r g \) was calculated.
Thus for each observation the formula employed was:

\[ \gamma = A p \left( 1 + \frac{K D}{p} \right) \]

Observed surface tension measurements were plotted against temperature.
Surface Tension by Maximum Bubble Pressure.
Atomic and structural parachors used for calculation of molecular parachors.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Sugden (S.)</th>
<th>Mumford and Phillips (M.P.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4.8</td>
<td>9.2</td>
</tr>
<tr>
<td>H</td>
<td>17.1</td>
<td>15.4 (10.0 in -OH)</td>
</tr>
<tr>
<td>O</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>O₂ (Esters)</td>
<td>60.0</td>
<td>-</td>
</tr>
<tr>
<td>Double Bond</td>
<td>23.2</td>
<td>19.0</td>
</tr>
<tr>
<td>4-membered ring</td>
<td>11.6</td>
<td>6.0</td>
</tr>
<tr>
<td>6-membered ring</td>
<td>6.1</td>
<td>0.8</td>
</tr>
<tr>
<td>Branching chain -CHR₂</td>
<td>-</td>
<td>-3.0</td>
</tr>
<tr>
<td>Ester grouping -COOR</td>
<td>-</td>
<td>-3.0</td>
</tr>
</tbody>
</table>
**n-AMY L ALC OH OL.**  
(Distilled over calcium.)  
(B.Pt. 133.5-134° C/760 mm. n_20° D 1.4125.)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>α</th>
<th>t</th>
<th>Surface Tension (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.8330</td>
<td>7.93</td>
<td>21.0</td>
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<tr>
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<td>7.78</td>
<td>21.2</td>
<td>26.32</td>
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<tr>
<td>17.0</td>
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<td>7.59</td>
<td>21.5</td>
<td>25.68</td>
</tr>
<tr>
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<td>0.8154</td>
<td>7.42</td>
<td>21.7</td>
<td>25.11</td>
</tr>
<tr>
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<td>40.0</td>
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<td>24.06</td>
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<tr>
<td>47.6</td>
<td>0.7994</td>
<td>6.95</td>
<td>22.5</td>
<td>23.52</td>
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</table>

15° C: D 0.8235, γ 25.86, Calc. (S.) 249.2, (M.P.) 245.4
**Diethylpropenyl Carbinol.**

(From hydrogen phthalate. Freshly distilled.)

(B.P. 135-135.5 °C/760 mm.)

Empirical Formula: \(- \text{C}_6\text{H}_{12}\text{O}\)  
M. Wt.: - 100.072

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
<th>(\log_{10} A)</th>
<th>(\log_{10} K)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.8528</td>
<td>3.63172</td>
<td>2.15685</td>
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<td>7.0</td>
<td>0.8491</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.3</td>
<td>0.8405</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.6</td>
<td>0.8322</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.7</td>
<td>0.8255</td>
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<td></td>
</tr>
<tr>
<td>46.0</td>
<td>0.8165</td>
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<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>(D)</th>
<th>(\gamma)</th>
<th>(\log_{10} A)</th>
<th>(\log_{10} K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>0.8522</td>
<td>23.5</td>
<td>26.38</td>
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</tr>
<tr>
<td>13.2</td>
<td>0.8446</td>
<td>23.7</td>
<td>25.84</td>
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</tr>
<tr>
<td>23.2</td>
<td>0.8362</td>
<td>24.0</td>
<td>24.93</td>
<td></td>
</tr>
<tr>
<td>33.5</td>
<td>0.8273</td>
<td>24.5</td>
<td>23.96</td>
<td></td>
</tr>
<tr>
<td>46.2</td>
<td>0.8163</td>
<td>24.8</td>
<td>22.78</td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>(D)</th>
<th>(\gamma)</th>
<th>(\log_{10} A)</th>
<th>(\log_{10} K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 °C</td>
<td>0.8431</td>
<td>25.69</td>
<td>[F] 267.2</td>
<td></td>
</tr>
<tr>
<td>40 °C</td>
<td>0.8216</td>
<td>23.30</td>
<td>[F] 267.5</td>
<td></td>
</tr>
</tbody>
</table>

Calc. (S.) 277.2 (M.P.) 273.6
**Ethyl Phenyl Carbinitol**

(From hydrogen phthalate. Stored 2½ months.)

(B.Pt. originally 136-137°C/760mm.)

**Empirical Formula:** \( \text{C}_6\text{H}_{12}\text{O} \)  
**M.Wt.:** 100.072

**Density.**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>0.1</th>
<th>12.2</th>
<th>21.0</th>
<th>31.7</th>
<th>40.5</th>
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</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.8562</td>
<td>0.8449</td>
<td>0.8382</td>
<td>0.8294</td>
<td>0.8218</td>
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</table>

**Surface Tension**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>a</th>
<th>t</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7</td>
<td>0.8554</td>
<td>7.72</td>
<td>16.8</td>
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<td>9.0</td>
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<td>17.6</td>
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<td>24.0</td>
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<td>18.0</td>
<td>24.93</td>
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<tr>
<td>32.1</td>
<td>0.8292</td>
<td>6.91</td>
<td>18.4</td>
<td>24.10</td>
</tr>
<tr>
<td>39.6</td>
<td>0.8227</td>
<td>6.68</td>
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</tr>
</tbody>
</table>

15°C  
D 0.8429  \( \gamma \) 25.64  [F] 267.2

40°C  
D 0.8223  \( \gamma \) 23.25  [F] 267.2

Calc. (S.) 277.2  (M.P.) 273.6
**ETHYL PROPENYL CARBINOL.**

(From Grignard. Stored 2½ months.)

(B.Pt. originally 136-138° C/760mm.)

---

Empirical Formula: - C₆H₁₂O

M.Wt.: - 100.072

### Density

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>0.2</th>
<th>11.0</th>
<th>20.6</th>
<th>31.3</th>
<th>40.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.8648</td>
<td>0.8560</td>
<td>0.8477</td>
<td>0.8384</td>
<td>0.8312</td>
</tr>
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</table>

### Surface Tension

<table>
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<th>2.9</th>
<th>12.3</th>
<th>21.0</th>
<th>28.6</th>
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<th>40.3</th>
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<tbody>
<tr>
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<td>0.8627</td>
<td>0.8549</td>
<td>0.8473</td>
<td>0.8405</td>
<td>0.8349</td>
<td>0.8310</td>
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<td>a</td>
<td>7.76</td>
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<td>7.48</td>
<td>7.24</td>
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<td>6.77</td>
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<tr>
<td>t</td>
<td>17.3</td>
<td>17.6</td>
<td>18.0</td>
<td>18.5</td>
<td>19.0</td>
<td>19.5</td>
<td>20.0</td>
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<tr>
<td>Surface Tension</td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.05</td>
<td>26.83</td>
<td>26.07</td>
<td>25.23</td>
<td>24.57</td>
<td>24.01</td>
<td>23.58</td>
</tr>
</tbody>
</table>

### Additional Data

| 15° C | D | 0.8526 | γ | 25.81 | [F] 264.6 |
| 40° C | D | 0.8312 | γ | 23.59 | [F] 265.3 |

**Calc. (S.)** 277.2  **(M.F.)** 273.6
DI ETHYLPROPENYL CARBINOL
(From Grignard. Freshly distilled.)
(B.P.t. 136-137°C/760mm.)

Empirical Formula: \( C_6H_{12}O \)
M.Wt.: 100.072

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.8607</td>
<td></td>
</tr>
<tr>
<td>11.3</td>
<td>0.8512</td>
<td></td>
</tr>
<tr>
<td>20.8</td>
<td>0.8436</td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>0.8357</td>
<td></td>
</tr>
<tr>
<td>39.3</td>
<td>0.8281</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>α</th>
<th>t</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.8608</td>
<td>7.67</td>
<td>16.4</td>
<td>26.76</td>
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<tr>
<td>13.0</td>
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<td>7.43</td>
<td>16.9</td>
<td>25.92</td>
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<tr>
<td>22.2</td>
<td>0.8423</td>
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<td>17.3</td>
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<td>31.2</td>
<td>0.8348</td>
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<td>40.4</td>
<td>0.8271</td>
<td>6.72</td>
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<td>23.45</td>
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</table>

15°C  D 0.8483  γ 25.75  [F] 265.7
40°C  D 0.8275  γ 23.48  [F] 266.2
Calc. (S.) 277.2  (M.P.) 273.6
**1-ÁTHYLALCOHOL**

(After standing 6 months.)

(Original B.Pt. 119-122°C/760mm.)

**Empirical Formula:** \( C_6H_{10}O \)  
**M.Wt.:** - 86.08

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>a</th>
<th>t</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.8606</td>
<td>7.71</td>
<td>16.3</td>
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</tr>
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<tr>
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<td>0.8432</td>
<td>7.26</td>
<td>17.0</td>
<td>25.33</td>
</tr>
<tr>
<td>29.7</td>
<td>0.8358</td>
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<tr>
<td>40.0</td>
<td>0.8268</td>
<td>6.71</td>
<td>17.9</td>
<td>23.42</td>
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</table>

15°C: \( D \ 0.8481 \) \( γ \ 25.83 \) [F] 223.8  
40°C: \( D \ 0.8273 \) \( γ \ 23.45 \) [F] 229.0  

Calc. (S.) 238.2 (M.P.) 233.6
1-<wbr/>αYD I M E T H Y L A L L Y L A L C O H O L
(Purified after standing 6 months.)
(B.Pt. 121-122.5°C/760mm.)

**Empirical Formula:** C₅H₁₀O  
**M.Wt.:** 86.08

**Density**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>0.2</th>
<th>10.0</th>
<th>20.4</th>
<th>29.6</th>
<th>40.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.8537</td>
<td>0.8463</td>
<td>0.8377</td>
<td>0.8299</td>
<td>0.8202</td>
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**Surface Tension**

<table>
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<tr>
<th>Temp. °C</th>
<th>D</th>
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<th>1</th>
<th>2</th>
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<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
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<td></td>
<td>0.8299</td>
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<tr>
<td></td>
<td>0.8212</td>
<td>6.68</td>
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**Calc. (S.)** 238.2  (M.P.) 233.6
1-α-DIMETHYLALLYLALCOHOL

(Prep. from chloride.)

(B.Pt. 121.5-122.5°C/760mm.)

Empirical Formula: \(-\text{C}_5\text{H}_{10}\text{O}\)

M.Wt.: 86.08

Density

<table>
<thead>
<tr>
<th>Temp. °C</th>
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<th>10.2</th>
<th>20.0</th>
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<th>40.5</th>
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<tbody>
<tr>
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<td>0.8431</td>
<td>0.8353</td>
<td>0.8255</td>
<td>0.8184</td>
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Surface Tension

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>α</th>
<th>t</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>0.8510</td>
<td>7.58</td>
<td>14.8</td>
<td>26.49</td>
</tr>
<tr>
<td>10.2</td>
<td>0.8431</td>
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<tr>
<td>32.0</td>
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<td>6.89</td>
<td>15.8</td>
<td>24.09</td>
</tr>
<tr>
<td>40.5</td>
<td>0.8184</td>
<td>6.60</td>
<td>16.3</td>
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<table>
<thead>
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</thead>
<tbody>
<tr>
<td>15°C</td>
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<td>40°C</td>
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<td>233.6</td>
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Calc. (S.) 233.2 (M.F.) 233.6
# Allyl Alcohol

**Empirical Formula:** \( \text{C}_3\text{H}_6\text{O} \)  
**M.Wt.:** \( 58.048 \)

<table>
<thead>
<tr>
<th>Temp. (^{\circ}\text{C})</th>
<th>D</th>
<th>t</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.8660</td>
<td>8.21</td>
<td>20.0</td>
</tr>
<tr>
<td>8.7</td>
<td>0.8612</td>
<td>8.03</td>
<td>20.3</td>
</tr>
<tr>
<td>19.2</td>
<td>0.8531</td>
<td>7.80</td>
<td>20.5</td>
</tr>
<tr>
<td>24.2</td>
<td>0.8469</td>
<td>7.68</td>
<td>21.4</td>
</tr>
<tr>
<td>35.3</td>
<td>0.8389</td>
<td>7.31</td>
<td>21.0</td>
</tr>
<tr>
<td>40.1</td>
<td>0.8346</td>
<td>7.20</td>
<td>21.3</td>
</tr>
<tr>
<td>46.1</td>
<td>0.8292</td>
<td>7.04</td>
<td>21.3</td>
</tr>
</tbody>
</table>

**At 15\(^{\circ}\text{C}\):**  
- D: 0.8567 \( y \): 26.76 \( \text{[F]} \): 154.1

**At 40\(^{\circ}\text{C}\):**  
- D: 0.8347 \( y \): 24.39 \( \text{[F]} \): 154.5

**Calc. (s.):** 160.2 \( \text{(M.p.)}: 153.6 \)
**ALLYL ALCOHOL**

(B.Pt. 96-96.2°C/760mm.)

Empirical Formula: \( \text{C}_3\text{H}_6\text{O} \)  
M.Wt.: 58.048

**Density**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.7</td>
<td>0.8668</td>
</tr>
<tr>
<td>11.7</td>
<td>0.8593</td>
</tr>
<tr>
<td>21.4</td>
<td>0.8513</td>
</tr>
<tr>
<td>32.3</td>
<td>0.8417</td>
</tr>
<tr>
<td>42.8</td>
<td>0.8323</td>
</tr>
</tbody>
</table>

**Surface Tension**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( \log_{10} A )</th>
<th>( \log_{10} K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>3.63172</td>
<td>2.15685</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>( D )</th>
<th>( \gamma )</th>
<th>( t )</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>0.8642</td>
<td>8.07</td>
<td>21.6</td>
<td>27.29</td>
</tr>
<tr>
<td>12.1</td>
<td>0.8593</td>
<td>7.91</td>
<td>21.8</td>
<td>26.75</td>
</tr>
<tr>
<td>22.8</td>
<td>0.8499</td>
<td>7.67</td>
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</tr>
<tr>
<td>33.9</td>
<td>0.8401</td>
<td>7.33</td>
<td>22.2</td>
<td>24.81</td>
</tr>
<tr>
<td>43.5</td>
<td>0.8318</td>
<td>7.04</td>
<td>22.4</td>
<td>23.84</td>
</tr>
</tbody>
</table>

\( 15^\circ C \)  
\( D \) 0.8567  
\( \gamma \) 26.58  
\( [F] \) 153.9

\( 40^\circ C \)  
\( D \) 0.8349  
\( \gamma \) 24.19  
\( [F] \) 154.2

Calc. (S.) 160.2  (M.P.) 153.6
METHYL-β-METHYLALLYLCARBINOL.
(B.Pt. 43°C/18mm.)

Empirical Formula: - C₆H₁₂O  M.Wt.: - 100.072

Density

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>0.0</th>
<th>10.5</th>
<th>21.2</th>
<th>23.8</th>
<th>40.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>0.8571</td>
<td>0.8501</td>
<td>0.8411</td>
<td>0.8342</td>
<td>0.8247</td>
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</table>

Surface Tension

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>α</th>
<th>t</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.8570</td>
<td>7.95</td>
<td>17.3</td>
<td>27.69</td>
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<tr>
<td>12.0</td>
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<td>17.8</td>
<td>26.82</td>
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<tr>
<td>20.1</td>
<td>0.8419</td>
<td>7.49</td>
<td>18.2</td>
<td>26.09</td>
</tr>
<tr>
<td>30.7</td>
<td>0.8327</td>
<td>7.14</td>
<td>18.6</td>
<td>24.88</td>
</tr>
<tr>
<td>40.7</td>
<td>0.8241</td>
<td>6.90</td>
<td>19.3</td>
<td>24.04</td>
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</tbody>
</table>

15°C D 0.8463 γ 26.56 [P] 268.4
40°C D 0.8248 γ 24.03 [P] 268.6

Calc. (S.) 277.2 (M.P.) 273.6
Dl-Ethyl Propenylcarbinyl Acetate.
(B.Pt. 152-155°C/760mm.)

Empirical Formula: \( \text{C}_6\text{H}_{14}\text{O}_2 \)
M.Wt.: \( 142.112 \)

**Density**

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9072</td>
</tr>
<tr>
<td>10.1</td>
<td>0.8977</td>
</tr>
<tr>
<td>20.3</td>
<td>0.8885</td>
</tr>
<tr>
<td>30.2</td>
<td>0.8786</td>
</tr>
<tr>
<td>39.4</td>
<td>0.8698</td>
</tr>
</tbody>
</table>

**Surface Tension**

\[
\log_{10} A = 3.64256 \\
\log_{10} K = 2.15685
\]

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>a</th>
<th>(\alpha)</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9072</td>
<td>8.11</td>
<td>16.8</td>
<td>29.23</td>
</tr>
<tr>
<td>10.0</td>
<td>0.8976</td>
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<td>17.3</td>
<td>27.37</td>
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<td>7.50</td>
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<td>26.17</td>
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<tr>
<td>29.3</td>
<td>0.8793</td>
<td>7.18</td>
<td>18.0</td>
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<tr>
<td>41.0</td>
<td>0.8634</td>
<td>6.81</td>
<td>18.5</td>
<td>23.73</td>
</tr>
</tbody>
</table>

\(15^\circ\text{C}\)  \(D\) 0.8931  \(\gamma\)  26.83  \([F]\) 362.1
\(40^\circ\text{C}\)  \(D\) 0.8693  \(\gamma\)  23.90  \([F]\) 361.5

Calc. (s.) 361.0  (M.P.) 361.2
**1-ETHYLPROPENYL CARBINYL BENZOATE.**

(B.Pt. 136-139°C/15mm.)

Empirical Formula: \( C_{13} H_{16} O_2 \)  \[ M.Wt.: - 204.128 \]

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Density</th>
<th>( \gamma )</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.0175</td>
<td>10.32</td>
<td>35.91</td>
</tr>
<tr>
<td>13.4</td>
<td>1.0068</td>
<td>10.02</td>
<td>34.85</td>
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<tr>
<td>21.2</td>
<td>1.0005</td>
<td>9.56</td>
<td>33.26</td>
</tr>
<tr>
<td>29.5</td>
<td>0.9936</td>
<td>9.31</td>
<td>32.38</td>
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<tr>
<td>39.1</td>
<td>0.9858</td>
<td>9.05</td>
<td>31.48</td>
</tr>
<tr>
<td>15 °C</td>
<td>1.0055</td>
<td>( \gamma )</td>
<td>33.98 [ P ] 490.2</td>
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<tr>
<td>40 °C</td>
<td>0.9849</td>
<td>( \gamma )</td>
<td>31.38 [ P ] 490.5</td>
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</table>

Calc. (S.) 494.9 (M.P.) 495.8
**ALLYL ACETATE.**
(B.Pt. 103-105°C/760mm.)

**Empirical Formula:** \( C_5H_8O_2 \)

**M.Wt.** \( 100.064 \)

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>D</th>
<th>e</th>
<th>( \gamma )</th>
<th>Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.9530</td>
<td>8.46</td>
<td>21.9</td>
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<tr>
<td>3.5</td>
<td>0.9433</td>
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<td>22.2</td>
<td>28.19</td>
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<td>10.0</td>
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<td>22.4</td>
<td>27.72</td>
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<tr>
<td>17.0</td>
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<td>7.96</td>
<td>22.6</td>
<td>26.94</td>
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<td>7.71</td>
<td>22.9</td>
<td>26.10</td>
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<td>25.20</td>
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<tr>
<td>39.5</td>
<td>0.9055</td>
<td>7.17</td>
<td>23.6</td>
<td>24.29</td>
</tr>
<tr>
<td>45.8</td>
<td>0.8987</td>
<td>6.95</td>
<td>23.5</td>
<td>23.56</td>
</tr>
</tbody>
</table>

**Surface Tension**

- \( \log_{10} K \) \( 2.15686 \)
- \( \log_{10} \alpha \) \( 3.63172 \)

**Calc. (S.) 244.0 (M.P.) 244.2**