5. *Reactions of (+)- and (—)-γ-Methyl-α-ethylallyl Alcohols and their Derivatives.*

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From a study of the mutarotation of γ-methyl-α-ethylallyl alcohol it is concluded that there is a steady transformation by anionotropic change into α-methyl-γ-ethylallyl alcohol, the sign of rotation of the isomeric alcohol produced being similar to that of the original alcohol. Evidence from parachors suggests some peculiarity of structure in the allylic alcohols, and a pseudo-cyclic configuration is proposed which is in harmony with the retention of asymmetry on anionotropic change. The chloride of γ-methyl-α-ethylallyl alcohol gives a mixture of γ-methyl-α-ethylallyl and α-methyl-γ-ethylallyl alcohols on hydrolysis, mainly *via* dissociation with extensive racemisation.

A method for analysis of mixtures of optically active methyl-*n*-butyl- and ethyl-*n*-propyl-carbinols is introduced, which may be applicable to mixtures of other optically active substances.

The acid phthalic *ester* of γ-methyl-α-ethylallyl alcohol can be separated, by fractional crystallisation of its brucine salt, into (+)- and (—)-forms. Table I gives the rotatory powers of the (+)-phthalate in various solvents; the characteristic diagram (Lowry, "Optical Rotatory Power," 1935, p. 418) plotted from these data indicates slightly complex dispersion. The (+)- and the (—)-γ-methyl-α-ethylallyl alcohol are obtained from these esters by saponification with 5N-sodium hydroxide. As with other αγ-disubstituted allyl alcohols, partial racemisation occurs if more dilute alkali is used (Balfe and Kenyon, *Nature*, 1941, **148**, 196). Table II gives the rotatory powers of the (+)-alcohol at different temperatures in the homogeneous state. The observations at 15° fit a one-term Drude equation $[\alpha]_\lambda^{15^\circ} = 3{\cdot}78(\lambda^2 - 0{\cdot}0638)$, which has a characteristic frequency of 2525 A. This is close to the characteristic frequency, 2690 A., found for γ-methyl-α-*n*-propylallyl alcohol by Arcus and Kenyon (J., 1938, 312) who, nevertheless, from other evidence, concluded that the dispersion was not truly simple. In view

TABLE I.

Specific rotatory powers of (+)-γ-methyl-α-ethylallyl hydrogen phthalate in various solvents.

Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
H_2O *	10·0	+20·2°	+21·7°	+26·0°	+60·3°	C_5H_5N	10·0	+18·1°	+19·7°	+22·5°	+46·0°
	5·0	20·7	22·0	26·5	60·1		5·0	17·8	19·0	22·1	48·0
	2·5	20·0	21·1	23·9	56·4		2·5	17·4	18·8	20·8	49·0
EtOH	10·0	26·6	27·8	32·5	65·7	C_6H_6	5·0	10·6	11·0	12·9	27·4
	5·0	27·5	28·8	33·4	68·5	$CHCl_3$	5·0	11·5	13·0	15·0	32·9
	2·5	27·2	29·7	32·5	68·0	CS_2	10·0	−12·4	−13·0	−14·5	−24·7
$CH_3{\cdot}NO_2$	10·0	18·8	20·3	23·3	48·5		5·0	13·9	14·5	16·1	28·2
	5·0	21·4	22·8	26·2	53·0		2·5	14·4	14·8	16·2	27·8
	2·5	23·6	24·4	29·0	60·0						

* The sodium salt of the acid ester was used in this solvent.

TABLE II.

Influence of temperature on the rotatory power of (+)-γ-methyl-α-ethylallyl alcohol (in the homogeneous state; $l = 0{\cdot}5$).

Temp.	$d_4^{t^\circ}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	Temp.	$d_4^{t^\circ}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
15°	0·8431	+13·5°	+14·1°	+16·1°	+29·9°	40°	0·8218	+11·4°	+12·0°	+13·7°	+25·5°
20	0·8389	13·1	13·7	15·7	29·0	50	0·8131	10·5	11·1	12·7	23·8
30	0·8303	12·2	12·8	14·7	27·3	60	0·8047	9·7	10·2	11·8	22·1

of their unsaturation, it is probable that extension of the observations for both alcohols to shorter wave-lengths would show the necessity for a second term in the equations, as is indicated by the observations of Levene and Haller (*J. Chem. Physics*, 1937, **5**, 980), who found that two-term equations were required to fit the rotatory dispersion of αγ-dimethylallyl alcohol and other unsaturated secondary alcohols.

Reduction of the (+)-alcohol with hydrogen gives (+)-ethyl-*n*-propylcarbinol, which has $[\alpha]_{5893}^{20^\circ} + 7{\cdot}09^\circ$ (homogeneous) and gives a hydrogen phthalate having $[\alpha]_{5893}^{20^\circ} + 9{\cdot}70^\circ$ in chloroform solution. The maximum values given by Kenyon (J., 1914, **105**, 2226) are, for the (−)-carbinol $[\alpha]_{5893}^{20^\circ} - 4{\cdot}21^\circ$, and for its phthalate, $[\alpha]_{5893}^{20^\circ} - 5{\cdot}76^\circ$. The ratio between the rotation of the carbinol and that of the phthalate is the same (1·37) in both sets of results, indicating that the higher values now found are not due to impurity, and we are of the opinion that the (+)-carbinol and its ester are optically pure.

(−)-γ-Methyl-α-ethylallyl hydrogen phthalate (having 40% of the maximum rotatory power) reacts with methyl alcohol to afford a *methyl hexenyl ether* of $\alpha_{5461}^{21^\circ} - 0{\cdot}18^\circ$ (l, 0·5). From the alcohol obtained from the same specimen of phthalate, by a reaction which does not disturb the bonds of the asymmetric carbon atom (reaction of the potassium derivative of the alcohol with methyl iodide), methyl γ-methyl-α-ethylallyl ether is obtained with $\alpha_{5461}^{23^\circ} + 6{\cdot}88^\circ$ (l, 0·5). This result affords further evidence of the extensive racemisation which occurs in replacement reactions of derivatives of the αγ-disubstituted allyl alcohols (Arcus and Kenyon, J., 1938, 1912; Balfe and Kenyon, *loc. cit.*). Rearrangement may also have occurred during the replacement reaction, but practical difficulties prevented its detection.

(+)- and (−)-γ-Methyl-α-ethylallyl alcohols undergo mutarotation at rates varying with different specimens (Table III). The rate is increased by addition of a trace of acid, and since old specimens were found to have become acid, variations in the amount of acid formed may account for the variations in rates of mutarotation. The mutarotation is not due to simple racemisation, since the rotatory power of the hexanol obtained by reduction of the alcohol after mutarotation is higher than would be expected if racemisation alone had occurred. The hydrogen phthalate of this hexanol has, in fact, a specific rotation higher than that of optically pure ethyl-*n*-propylcarbinyl hydrogen phthalate. The mutarotation is probably attributable to an anionotropic rearrangement, with formation of α-methyl-γ-ethylallyl alcohol, since by fractional crystallisation of the p-*xenylurethane* of a 2-years old specimen of γ-methyl-α-ethylallyl alcohol, the urethane of the α-methyl-γ-ethylallyl isomeride was obtained. Confirmatory evidence of the rearrangement is given by the density of the hexanol formed by reduction of γ-methyl-α-ethylallyl alcohol. During storage of the unsaturated alcohol the density of its reduction product—prepared after different intervals—gradually alters from that of ethyl-*n*-propylcarbinol to a value intermediate between those of ethyl-*n*-propyl- and methyl-*n*-butyl-carbinols.

The ratio between the specific rotation of (+)-ethyl-*n*-propylcarbinyl hydrogen phthalate (in chloroform solution) and the observed rotation of the (+)-carbinol (homogeneous; l, 1) at λ_{5893} is 1·7. For methyl-*n*-butylcarbinol the corresponding ratio is 4·6. On account of the difference between these two ratios it becomes possible to deduce the proportions of the different optically active species present in a mixture of ethyl-*n*-propyl- and methyl-*n*-butyl-carbinols by observing the rotatory power of the mixture and

TABLE III.

Mutarotation of γ-methyl-α-ethylallyl alcohol (transferred at intervals from stoppered bottles to a 0·5-dm. polarimeter tube).

(i) Specimen of (+)-γ-methyl-α-ethylallyl alcohol.

Time, days.	t.	α_{5893}.	α_{5780}.	α_{5461}.	α_{4358}.	$\alpha_{5461}^{20^\circ}$ (calc.).
0	21·0°	+4·87°	+5·12°	+5·94°	+11·15°	+5·97°
1	21·0	4·93	—	5·97	11·09	5·98
3	19·0	5·00	5·26	6·12	11·28	6·09
6	19·0	5·03	5·25	6·06	11·23	6·03
8	21·0	—	5·12	5·94	—	5·96
22	18·0	5·05	—	6·21	11·41	6·14
24	18·0	5·04	—	6·16	11·46	6·10
42	19·5	4·98	—	6·05	11·04	6·05
59	19·5	4·92	5·22	6·00	11·05	6·00
119	27·5	4·04	4·26	4·96	9·26	5·14
122	19·0	—	4·56	5·26	9·85	5·23
125	20·0	—	4·51	5·14	9·64	5·14
129	24·0	4·21	4·47	5·13	9·50	5·23
132	23·5	—	4·30	4·89	9·30	4·97
134	22·0	—	4·31	4·95	9·33	5·00
136	22·0	4·05	4·30	4·95	9·30	5·00
174	18·3	4·00	4·15	4·75	9·06	4·70
188	19·0	3·86	4·01	4·64	8·70	4·62
198	20·0	3·86	4·04	4·64	8·66	4·64
223	20·0	—	4·01	4·69	8·50	4·69
370	19·0	3·66	3·94	4·50	8·40	4·47
594	18·5	3·53	3·77	4·32	8·00	4·29
987	19·0	3·35	3·55	4·07	7·58	4·05
1156	21·5	3·33	3·41	4·04	7·49	4·06

(ii) Specimen of (—)-γ-methyl-α-ethylallyl alcohol.

Time, days.	t.	α_{5893}.	α_{5780}.	α_{5461}.	α_{4358}.	Time, days.	t.	α_{5893}.	α_{5780}.	α_{5461}.	α_{4358}.
0	19·5°	−4·98°	−5·19°	−5·95°	−10·95°	919	19·0°	−4·90°	—	−5·96°	−10·88°
300	19·5	4·99	5·23	5·98	10·50	1634	21·0	4·90	−5·20°	5·90	11·10
524	17·5	4·94	5·22	5·97	11·05						

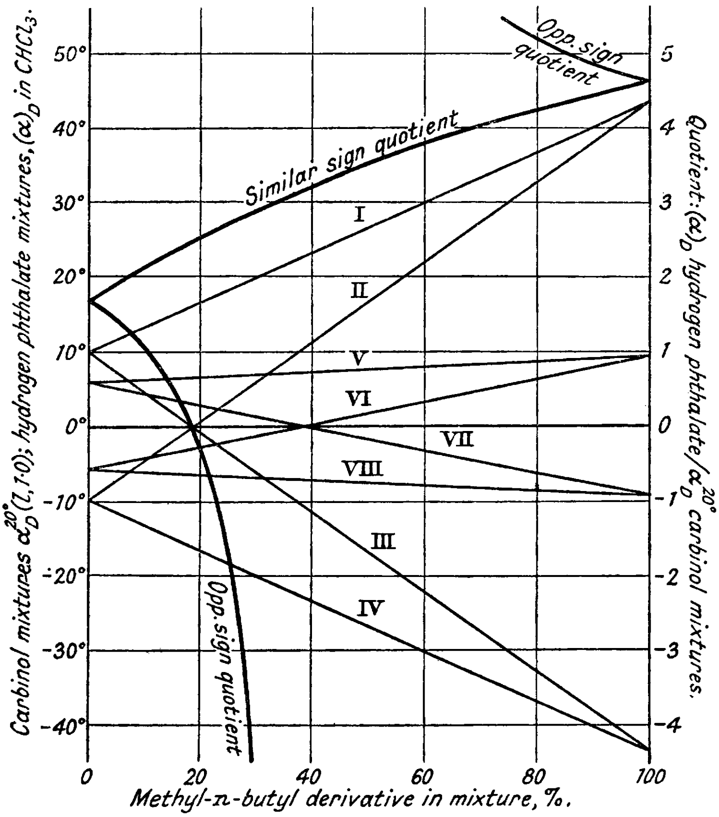
(iii) Specimen of (+)-γ-methyl-α-ethylallyl alcohol.

0	20·5	+5·40	+5·75	+6·66	+12·20		(1% Formic acid added.)				
736	21·0	5·36	5·60	6·50	11·85	757	20·0	+5·16	+5·25	+6·15	+11·15

of the mixture of hydrogen phthalic esters prepared from it. (The method may be applicable to the analysis of mixtures of other optically active compounds, and its application might be extended by the use of physical properties other than optical rotatory power.) If the mixture of hexanols has been obtained by reducing a mixture of γ-methyl-α-ethylallyl and α-methyl-γ-ethylallyl alcohols, the results of the calculation can be used to deduce the composition of the mixture of hexenols. In applying this procedure two assumptions are made, *viz.*, that the specific rotation of each phthalate or of each alcohol is not altered by dilution with its isomeride, and that significant amounts of other optically active substances are not present in the mixture of alcohols. The method is best illustrated by an example.

In the figure the observed rotatory powers (l, 1; λ_{5893}) of mixtures of (+)- and (—)-ethyl-*n*-propyl- and -methyl-*n*-butyl-carbinols and the specific rotations (in chloroform) of their hydrogen phthalates are plotted against the composition of the mixture, giving straight lines. The curve shows how the ratio of specific rotation of phthalate mixture to rotation of carbinol mixture varies according to the composition of the mixture. The data for methyl-*n*-butylcarbinol and its hydrogen phthalate are taken from the results of Pickard and Kenyon (J., 1911, **99**, 45), and those for ethyl-*n*-propylcarbinol and its ester were determined with material obtained by reduction of freshly prepared (+)-γ-methyl-α-ethylallyl alcohol. The first specimen of this alcohol referred to in Table III was reduced to hexanol after the last observation of rotatory power quoted (1156 days) had been made. The hexanol had $\alpha_{5893}^{20^\circ}$ + 5·0° (l, 1·0) and its hydrogen phthalate had $[\alpha]_{5893}^{20^\circ}$ + 16·7° in chloroform solution. The ratio between these two rotations is 3·34 which, according to the curve in the figure, corresponds to a mixture of 56% of ethyl-*n*-propyl- and 44% of methyl-*n*-butyl-carbinol, both of the same sign and therefore both dextrorotatory, since the mixture is dextrorotatory. Now a mixture of the optically pure (+)-carbinols in this proportion would have $\alpha_{5893}^{20^\circ}$ + 7·4° (l, 1·0). The observed rotatory power, + 5·0°, thus shows that the optically active carbinols make up 67·5% of the mixture. The composition of the mixture is therefore 37·8% of (+)-ethyl-*n*-propyl, 29·7% of (+)-methyl-*n*-butyl-carbinol, and 32·5% of optically inactive material, presumably a mixture of both carbinols.

(+)-Ethyl-*n*-propylcarbinol is related in configuration to (+)-γ-methyl-α-ethylallyl alcohol, from which it is obtained by reduction, a process which cannot cause change in configuration. The relation between sign of rotation and configuration of methyl-*n*-butylcarbinol and α-methyl-γ-ethylallyl alcohol has not been directly determined, but it can be deduced that in this case also similar signs of rotation indicate similar configurations. The α-methyl-γ-ethylallyl alcohol formed during the mutarotation of (+)-γ-methyl-α-ethylallyl alcohol must be dextrorotatory because the dispersion ratio ($\alpha_{4358}/\alpha_{5893}$) does not alter during the process of mutarotation; formation of the (−)-tautomeride would cause the rotatory dispersion of the mixture to become complex (or anomalous) and so alter the dispersion ratio. This (+)-α-methyl-γ-ethylallyl alcohol gives, on reduction, (+)-methyl-*n*-butylcarbinol, as shown above.



I. *Hydrogen phthalates of* d-*methyl*-n-*butyl- and* d-*ethyl*-n-*propyl-carbinols.*
II. ,, ,, d- ,, ,, l- ,, ,, ,,
III. ,, ,, l- ,, ,, d- ,, ,, ,,
IV. ,, ,, l- ,, ,, l- ,, ,, ,,
V. d-*Methyl*-n-*butyl- and* d-*ethyl*-n-*propyl-carbinols.*
VI. d- ,, ,, l- ,, ,, ,,
VII. l- ,, ,, d- ,, ,, ,
VIII. l- ,, ,, l- ,, ,, ,,

Optical rotatory powers *of mixtures of ethyl*-n-*propyl- and methyl*-n-*butyl-carbinols and of mixtures of their hydrogen phthalates ; also ratios of rotations to those of carbinol mixtures.*

The results previously calculated can now be applied to ascertain the composition of the mixture formed during the mutarotation of (+)-γ-methyl-α-ethylallyl alcohol, a correction being applied for the fact that the alcohol used in this experiment had only 92·5% of the maximum rotatory power. The final calculation shows that during the mutarotation (1156 days) racemisation occurred to the extent of 27%, 41% of (+)-γ-methyl-α-ethylallyl alcohol remained, and 32% of (+)-α-methyl-γ-ethylallyl alcohol was formed. Although the racemic portion of the product probably contains both isomerides, the noteworthy feature of the result is the very high retention of optical activity, even if the rearrangement is irreversible; if it involves a state of equilibrium, the retention of optical activity becomes still more remarkable. There is some evidence that the rearrangement is reversible. Although it results in an eventual decrease in rotatory power, in the initial stages the rotatory power rises [see section (i), Table III]. The most likely explanation for this is that the rearrangement occurs to a preponderating extent with retention of optical activity, but that it is reversible, and is accompanied by a certain amount of racemisation. On this basis, the initial rise in rotatory power would be ascribed to conversion of (+)-γ-methyl-α-ethyl- into (+)-α-methyl-γ-ethyl-allyl alcohol; the rate of increase is diminished as equilibrium is approached, and a decrease sets in when the irreversible loss of rotatory power, due to racemisation, becomes appreciable.*

Kenyon, Partridge, and Phillips (J., 1937, 207) suggested a cyclic configuration in order to explain the retention of optical activity during the anionotropic conversion of (—)-α-phenyl-γ-methylallyl hydrogen phthalate into the (+)-γ-phenyl-α-methylallyl ester. This suggestion can be extended to cover the present observations. The notion of such a cyclic configuration for the substituted allyl alcohols recalls the cyclic structure for αγ-dimethylallyl alcohol discussed by Hills, Kenyon, and Phillips (J., 1936, 576) as a result of parachor determinations. We have therefore re-examined the question of the parachors of the substituted allyl alcohols. The parachor of γ-methyl-α-ethylallyl alcohol is 267·2, different specimens, when pure, all giving values within 0·3 unit of this. Hills, Kenyon, and Phillips (*loc. cit.*) recorded the parachor of αγ-dimethylallyl alcohol as varying between 226 and 233, but we find the freshly purified alcohol to have a parachor of 230·2 and again ascribe variations to the presence of impurity; *e.g.*, after 6 months' storage the parachor changes to 228·8. Hills, Kenyon, and Phillips (*loc. cit.*) give the parachor of allyl alcohol as 159, in close agreement with the value calculated from Sugden's constants ("Parachor and Valency," 1930). We now find, however, a value of 153·9 for allyl alcohol and consider that the higher figure previously recorded was due to incomplete drying of the material, a difficult process for this alcohol (Tornoe, *Ber.*, 1891, **24**, 2670).

Table IV summarises the results of the parachor determinations. Allyl alcohol and two α-substituted, one γ-substituted, and five αγ-disubstituted allyl alcohols, as well as methyl-β-methylallylcarbinol, all have parachors below the values calculated from Sugden's constants (*op. cit.*) and, with the exception of allyl alcohol, below those calculated from Mumford and Phillips's constants (J., 1929, 2113). A low parachor value is not, however, peculiar to unsaturated alcohols, for it is shown also by saturated alcohols, and in this case is ascribed to association (Sugden, *op. cit.*). Hills, Kenyon, and Phillips concluded that the low parachor of the unsaturated alcohols was not due to association, because they found the parachor of allyl alcohol to be normal, and although this evidence was unsatisfactory, we consider, for the following reason, that their conclusion was justified. The parachors of saturated alcohols increase with rise of temperature, as is to be expected if the parachor anomaly is due to

TABLE IV.

Parachors of unsaturated alcohols and their esters, and of saturated alcohols.

Substance.	Observed [*P*].			Observed	Calc. [*P*]
Unsaturated.	15°.	20°.	40°.	$[P]_{40^\circ} - [P]_{15^\circ}$.	(Sugden).
Allyl alcohol [1]	153·9	—	154·2	0·3	160·2
α-Ethylallyl alcohol [2]	—	228·1	—	—	238·2
α-*n*-Butylallyl alcohol [2]	—	305·9	—	—	316·2
γ-Phenylallyl alcohol [2]	—	324·4	—	—	331·2
αγ-Dimethylallyl alcohol [1]	230·2	—	230·4	0·2	238·2
γ-Methyl-α-ethylallyl alcohol [1]	267·2	—	267·5	0·3	277·2
α-Phenyl-γ-methylallyl alcohol [3]	—	360·6	—	—	372·1
γ-Phenyl-α-methylallyl alcohol [3]	—	367·4	—	—	372·1
γ-Methyl-α-allylallyl alcohol [1]	295·4	—	295·9	0·5	301·8
Methyl-β-methylallylcarbinol [1]	268·4	—	268·6	0·2	277·2
Allyl acetate [1]	245·1	—	245·3	0·2	244·0
γ-Methyl-α-ethylallyl acetate [1]	362·1	—	361·5	0·4	361·0
γ-Methyl-α-ethylallyl benzoate [1]	490·2	—	490·5	0·3	494·9
Saturated.					
Methyl alcohol [4]	88·2	88·3	88·7	0·5	93·2
Ethyl alcohol [4]	126·8	126·9	127·5	0·7	132·2
n-Amyl alcohol [1]	241·2	—	242·4	1·2	249·2

[1] Determinations made in present work. [2] Hills, Kenyon, and Phillips (*loc. cit.*). [3] Kenyon, Partridge, and Phillips (*loc. cit.*). [4] From data given by Sugden (*op. cit.*). Values at 15° and 40° interpolated.

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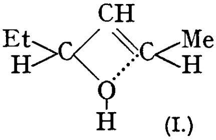
* This argument assumes that (+)-α-methyl-γ-ethylallyl alcohol has a higher specific rotatory power than the isomeric alcohol. The rotatory power of the former is apparently not on record and we have not had an opportunity to determine it or to measure the rate at which the rearrangement proceeds—a desirable datum.

association (Sugden, *op. cit.*). The amount of this increase varies with the molecular weight of the alcohol; Owen, Quale, and Beavers (*J. Amer. Chem. Soc.*, 1939, **61**, 900) find that the parachors of saturated tertiary alcohols increase by about 0·2% for every 10° rise in temperature, and a similar increase is shown by the three saturated *n*-alcohols given in Table IV. The parachors of unsaturated alcohols also increase with rise of temperature, but to a much less extent than those of saturated alcohols and independently of the variation in molecular weight. For example, the parachor of *n*-amyl alcohol (*M*, 88) increases by 1·2 units between 15° and 40°, whereas that of αγ-dimethylallyl alcohol (*M*, 86) increases by only 0·2 unit in the same temperature range. The low parachors of allyl alcohol and its α- and γ-substituted derivatives are therefore unlikely to be due to association, and we regard them as evidence of some structural peculiarity in the alcohols. The assumption that this peculiarity involves some form of co-ordination between the hydroxyl group and the C_γ atom brings the parachor observations into line with the phenomena associated with the mutarotation of γ-methyl-α-ethylallyl alcohol, and such an intramolecular association may be expected to be affected by temperature to a lesser extent than the intermolecular association of saturated alcohols. Hills, Kenyon, and Phillips (*loc. cit.*) considered the possibility that the substituted allyl alcohols were equilibrium mixtures of open-chain and cyclic (propylene oxide) tautomerides. Raman-spectra observations (Dupont *et al.*, *Bull. Soc. chim.*, 1939, **5**, 1208, 1215) on a substituted allyl alcohol indicate that the molecule is unsaturated, and the molecular refractivities of a number of such alcohols (Arcus and Kenyon, J., 1938, 312) suggest that the cyclic structure can only be present in a very small proportion of molecules, if any. Accordingly, we propose for γ-methyl-α-ethylallyl alcohol a structure which can be represented as (I). Against the possibility of a cyclic structure for αγ-dimethylallyl alcohol, Hills, Kenyon, and Phillips (*loc. cit.*) argued that, as a result of *cis–trans*-isomerisation, two stereochemical modifications of structure about the C_γ atom should exist, a possibility which was inconsistent with certain of their observations. This argument does not hold against the suggestion now put forward, since the mutarotation experiments described above show that one of the stereoisomeric modifications of the C_γ atom is formed to a preponderating extent.



(I.)

The essential feature of the formulation (I) is that it implies some form of attraction (or interaction) between the oxygen atom and the γ-carbon atom, in spite of the fact that the distance between these two atoms is greater than the carbon–oxygen covalent length. This attraction, it is suggested, alters the molecular volume of the alcohol, and holds the oxygen atom in such a position that, when rearrangement occurs, one of the two possible stereoisomeric forms of the new asymmetric carbon atom is formed to a greater extent than the other. In the esters of the substituted allyl alcohols, there may be a similar attraction between the doubly-bonded oxygen of the esterified carboxyl group and the γ-carbon atom. This would explain the retention of asymmetry during the anionotropic rearrangement of certain of these esters (Balfe and Kenyon, *Trans. Faraday Soc.*, in press), but in this case there is no need to assume any modification of molecular volume, because the normal interatomic dimensions, in a six-membered pseudo-cyclic configuration, bring the two atoms in question into proximity. Hence, no parachor anomaly is found in the esters. Hills, Kenyon, and Phillips record the parachors of five esters, three ethers, and the chloride of αγ-dimethylallyl alcohol; with one exception, which they ascribe to impurity, these compounds have values close to those calculated from Sugden's constants. Similarly, Table IV shows that *γ-methyl-α-ethylallyl acetate* and *benzoate* and allyl acetate have parachors close to the calculated values.

γ-Methyl-α-ethylallyl alcohol is converted into the *chloride* by the action of thionyl chloride and quinoline, the (+)-alcohol giving a (−)-chloride. The optically active chloride exhibits slightly complex dispersion in the visible spectrum. Different specimens of the chloride varied in rotatory power, suggesting the occurrence of some racemisation during its preparation, but in all cases the rotatory power was comparatively high, rendering extensive racemisation improbable. The chloride is chemically unstable (it evolves hydrogen chloride after a few days) and for this reason observations of its mutarotation were not undertaken; all experiments were done with freshly prepared chloride.

The chloride is hydrolysed by water in the presence of calcium carbonate. It is less easily hydrolysed than the chloride of αγ-dimethylallyl alcohol and more easily than that of γ-methyl-α-*n*-propylallyl alcohol. Hydrolysis of the (−)-chloride gives a hexenol of very low lævorotation; this, on reduction, gives a slightly dextrorotatory hexanol which is optically inactive at λ_{4358}, indicating anomalous dispersion. This hexanol and the hexenol from which it was prepared both yielded hydrogen phthalates of low dextrorotation. The *p*-xenylurethane of the hexenol obtained by hydrolysis of the *dl*-chloride can be separated into two fractions, one of which is the *p*-xenylurethane of γ-methyl-α-ethylallyl alcohol (m. p. 102°) whilst the *other* (m. p. 82°) is presumably that of α-methyl-γ-ethylallyl alcohol. The hydrogen phthalate prepared from this hexenol does not crystallise, indicating that it is a mixture. The hexanol obtained from this hexenol yields a hydrogen phthalate and a *p*-xenylurethane, both of which can be separated into derivatives of ethyl-*n*-propyl- and methyl-*n*-butyl-carbinols. It being thus established that on hydrolysis of γ-methyl-α-ethylallyl chloride the corresponding alcohol and the anionotropic isomeride are formed, we have applied to the product the method of analysis described above. It is found that, starting with (+)-γ-methyl-α-ethylallyl alcohol, the product of hydrolysis of its chloride consists of 7·4% of (+)-γ-methyl-α-ethylallyl alcohol, 0·6% of (−)-α-methyl-γ-ethylallyl alcohol, and 92% of *dl*-material, which probably contains both isomerides in comparable amounts, since derivatives of both were isolated in substantial yield from the hydrolytic product of *dl*-hexenyl chloride.

The most significant feature of this result is the high proportion of racemisation, indicating that the chloride anion separates from the molecule before the hydroxyl ion becomes attached. The contrast of this behaviour with the high retention of optical activity in the intramolecular mutarotation rearrangement is marked. With regard to the optically active components of the product, the γ-methyl-α-ethylallyl alcohol has the same configuration as the original alcohol, because it is derived from it by two successive reactions of the type which cause inversion of configuration (accompanied by racemisation). The proportion of (−)-α-methyl-γ-ethylallyl alcohol formed is so small as to be of doubtful significance; it may be observed, however, that the small degree of optical activity retained on the C_γ atom is not likely to be due to shielding of this atom by the chlorine atom, since this, by analogy with the mutarotation reaction, would produce the (+)-alcohol.

EXPERIMENTAL.

dl-γ-Methyl-α-ethylallyl alcohol, prepared in 50% yield by the interaction of crotonaldehyde (0·9 mol.) and ethylmagnesium chloride, and dried over potassium carbonate, was distilled first in a vacuum and then at atmospheric pressure (Found: C, 72·9; H, 12·3. Calc.: C, 72·0; H, 12·1%). If the first distillation was omitted, the crude alcohol decomposed during the other distillation, water being eliminated. B. p. 44—45°/13 mm., 135—135·5°/760 mm.; $n_D^{23°}$ 1·4325, $d_{4°}^{25°}$ 0·8346. Reif (*Ber.*, 1906, **39**, 1603; 1908, **41**, 2739) gives b. p. 133—134°/760 mm., $d_{4°}^{25°}$ 0·8409, $n_D^{25°}$ 1·4312.

dl-*γ-Methyl-α-ethylallyl Hydrogen Phthalate.*—The *dl*-alcohol, phthalic anhydride, and pyridine in molecular proportions, were heated on a steam-bath for 1 hour. The cold homogeneous reaction mixture, when stirred with dilute hydrochloric acid and ice, yielded an oil which soon solidified (yield 80%). After being washed and dried, this product was sufficiently pure for resolution. It separates from carbon disulphide–light petroleum in small plates, m. p. 52—53° (Found, by titration: *M*, 245. $C_{14}H_{16}O_4$ requires *M*, 248). The *phthalate* remains unchanged when kept at room temperature for several months, or at 100° for 1½ hours, or when warmed at 80° for 2 hours in the presence of a trace (2½%) of phthalic acid. It slowly decomposes at room temperature in solution (*e.g.*, in benzene or carbon disulphide), depositing small quantities of phthalic acid after several months.

(+)-*γ-Methyl-α-ethylallyl Hydrogen Phthalate.*—Brucine (235 g.) was dissolved in a hot solution of the foregoing *dl*-ester (150 g.) in acetone (400 c.c.). The crystalline salt which separated was obtained optically pure after nine recrystallisations, each effected by adding acetone to the hot, concentrated solution of the salt in chloroform. Decomposition of the brucine salt occurs during recrystallisation if the materials are not thoroughly dried. *l*-Brucine (+)-γ-methyl-α-ethylallyl phthalate has m. p. 168°. (+)-γ-Methyl-α-ethylallyl hydrogen phthalate, obtained by decomposition of the brucine salt with hydrochloric acid, and crystallised from ether–light petroleum, has m. p. 70·5°; $[\alpha]_{5461}$ + 15·0° (*l*, 2; *c*, 5·0 in chloroform). A specimen of brucine salt which had been recrystallised only three times was decomposed and the resulting dextro-phthalate crystallised four times from ether light–petroleum; by this procedure also optically pure (+)-γ-methyl-α-ethylallyl hydrogen phthalate was obtained.

(−)-*γ-Methyl-α-ethylallyl Hydrogen Phthalate.*—After concentration, the first three mother-liquors from the brucine salt described above yielded a crop of crystals; these after three crystallisations from acetone had m. p. 125—126°, and when decomposed with hydrochloric acid yielded a hydrogen phthalate of m. p. 68—69°, $[\alpha]_{5461}$ − 14·7°. By three crystallisations of this ester from ether–light petroleum, optically pure (−)-γ-methyl-α-ethylallyl hydrogen phthalate, m. p. 70·5°, $[\alpha]_{5461}$ − 15·0° (*l*, 2; *c*, 5·0 in chloroform), was obtained.

(+)- *and* (−)-*γ-Methyl-α-ethylallyl Alcohols.*—The (+)- and the (−)-hydrogen phthalate were separately hydrolysed with sodium hydroxide (2·5 mols. of 5N) and heated in a current of steam. The alcohols were extracted with ether, dried with potassium carbonate, and distilled in a vacuum. The (+)-alcohol had $[\alpha]_{5983}$ + 12·38°, $[\alpha]_{5461}$ + 14·24°, $[\alpha]_{4358}$ + 28·65° (*l*, 2; *c*, 5·0 in carbon disulphide).

Reduction of γ-Methyl-α-ethylallyl Alcohol.—The alcohol was reduced with hydrogen at 2 atm. in dry ether with a platinum catalyst (Short, *J. Soc. Chem. Ind.*, 1936, **55**, 14T). (i) *dl*-Alcohol, freshly prepared from the hydrogen phthalate, yielded ethyl-*n*-propylcarbinol, b. p. 132·5—133·5°, $d_{4°}^{20°}$ 0·8193. (ii) *dl*-Alcohol, prepared from the hydrogen phthalate and kept for 2 years, yielded a hexanol, b. p. 131—133°, $d_{4^\circ}^{20^\circ}$ 0·8181; Pickard and Kenyon (J., 1913, **103**, 1923) give $d_{4^\circ}^{20^\circ}$ 0·8213; Ginnings and Webb (*J. Amer. Chem. Soc.*, 1938, **60**, 1389) give b. p. 134·5—135°/760 mm., $d_{4^\circ}^{25^\circ}$ 0·8143. (iii) (+)-Alcohol, having $[\alpha]_{5461}^{21^\circ}$ + 14·91° (96% optically pure), yielded (+)-ethyl-*n*-propylcarbinol, b. p. 131—133°. $[\alpha]_{5893}^{20^\circ}$ + 6·81°, $[\alpha]_{5461}^{20^\circ}$ + 7·79°, $[\alpha]_{4358}^{20^\circ}$ + 12·41° (*l*, 0·25).

*Ethyl-*n*-propylcarbinyl Hydrogen Phthalate.*—(i) The *dl*-carbinol described in (i) above was heated with phthalic anhydride (1 mol.) at 110—120° for 7 hours; the ester thereby obtained was crystallised from ether–light petroleum, m. p. 75—76°. Pickard and Kenyon (*loc. cit.*) give m. p. 76—77°. (ii) The ester similarly prepared from the (+)-carbinol described in (iii) above had m. p. 48—49°, $\alpha_{5893}^{20^\circ}$ + 9·31°; $\alpha_{5780}^{20^\circ}$ + 10·19°; $\alpha_{5461}^{20^\circ}$ + 11·26°; $\alpha_{4358}^{20^\circ}$ + 18·26° (*l*, 2; *c*, 5·0 in chloroform).

*Methyl-*n*-butylcarbinyl Hydrogen Phthalate.*—The *dl*-carbinol, b. p. 137—140°, $d_{4^\circ}^{20^\circ}$ 0·8150 (Pickard and Kenyon, J., 1911, **99**, 45, give b. p. 136°, $d_{4^\circ}^{20^\circ}$ 0·8150), was prepared by the interaction of acetaldehyde and *n*-butylmagnesium bromide. The hydrogen phthalate, prepared in the usual manner, crystallised in needles, m. p. 48°, from ether–light petroleum.

dl-*γ-Methyl-α-ethylallyl acetate*, prepared by Einhorn's method, had b. p. 54—56°/17 mm., 152—154°/760 mm., $n_D^{19^\circ}$ 1·4230, $d_{4^\circ}^{15^\circ}$ 0·8931 (Found : C, 66·9; H, 9·8. $C_8H_{14}O_2$ requires C, 67·5; H, 9·9%), and the *benzoate*, prepared similarly, had b. p. 144—145°/20 mm., $n_D^{19^\circ}$ 1·5076; $d_{4^\circ}^{19^\circ}$ 1·0055 (Found : C, 76·4; H, 7·8. $C_{13}H_{16}O_2$ requires C, 76·45; H, 8·0%).

dl-*γ-Methyl-α-ethylallyl chloride* was prepared by the slow addition of thionyl chloride (1·1 mols.) to a mixture of the *dl*-alcohol with quinoline (1 mol.) in ether at 0°, the solution being filtered while cold. It has b. p. 30°/13 mm., 100°/370 mm., and 123—124°/760 mm. (slight decomp.); $n_D^{20^\circ}$ 1·4400 (Found : C, 61·0; H, 9·6; Cl, 28·2. $C_6H_{11}Cl$ requires C, 60·7; H, 9·4; Cl, 29·9%). The corresponding (—)-chloride, prepared from the (+)-alcohol having $[\alpha]_{5461}^{20\cdot5^\circ}$ + 15·8°, had $\alpha_{5893}^{19^\circ}$ — 11·25°, $\alpha_{5780}^{19^\circ}$ —12·65°, $\alpha_{5461}^{19^\circ}$ — 14·75°, $\alpha_{4358}^{19^\circ}$ — 28·3° (*l*, 0·5).

Hydrolysis of dl-*γ-Methyl-α-ethylallyl Chloride.*—Over a period of 3 days calcium carbonate (5 g.) was added to a mixture of the chloride (6 g.) and water (15 g.) with occasional shaking. The resulting hexenol was dried with potassium carbonate and distilled in a vacuum; 20% had b. p. up to 47°, 60% b. p. 47—49°, 20% b. p. 49—50°/12 mm. All the fractions had $n_D^{19\cdot5^\circ}$ 1·4345. Total yield, 4 g.

The *p*-xenylurethane of *dl*-*γ*-methyl-α-ethylallyl alcohol was prepared by heating the freshly prepared *dl*-alcohol (0·5 g.) with *p*-xenylcarbimide (1 g.) at 100° for 1 hour and extraction with ether. It separated from ether–light petroleum in long colourless needles, m. p. 102°. When prepared from *dl*-carbinol that had stood for 2 years, it afforded on fractional crystallisation two crops of crystals; the major crop had m. p. 102—103°, and a small quantity (25%) was obtained with an apparently constant m. p. 84—86°.

p-*Xenylurethane of the Product of Hydrolysis of* dl-*γ-Methyl-α-ethylallyl Chloride.*—The hexenol (5 g.) and *p*-xenylcarbimide (10 g.) were treated as before, and after extraction with ether the product was fractionally crystallised from ether–light petroleum. The higher-melting crop had m. p. 102—103°, and mixed m. p. with the p-*xenylurethane* (see above) of authentic *dl*-*γ*-methyl-α-ethylallyl alcohol, 102° (Found : C, 78·9; H, 7·4. $C_{19}H_{21}O_2N$ requires C, 77·3; H, 7·2%). The other final crop had m. p. 81—82° (Found : C, 77·9; H, 7·4%).

The p-*xenylurethanes* of *dl*-ethyl-*n*-propylcarbinol and *dl*-methyl-*n*-butylcarbinol separated from ether–light petroleum in colourless needles, m. p. 135° (Found : N, 4·7. $C_{19}H_{23}O_2N$ requires N, 4·7%), and m. p. 91—92° (Found : N, 4·7%), respectively.

p-*Xenylurethane of the Reduced Product of Hydrolysis of* dl-*γ-Methyl-α-ethylallyl Chloride.*—The hexenol (4 g.) was reduced with hydrogen, distilled, converted into the *p*-xenylurethane, and fractionally crystallised from ether–light petroleum. One crop had m. p. 132—133°, and, when mixed with the *p*-xenylurethane of *dl*-ethyl-*n*-propylcarbinol, m. p. 131—132°; the other had m. p. 91—92° and, when mixed with the *p*-xenylurethane of *dl*-methyl-*n*-butylcarbinol, m. p. 90—91°.

Hydrogen Phthalate of the Reduced Product of Hydrolysis of dl-*γ-Methyl-α-ethylallyl Chloride.*—The reduced product (3·8 g.), heated with phthalic anhydride (5·7 g.) at 110—120° for 7 hours, gave the hydrogen phthalate which was purified *via* its sodium salt and fractionally crystallised from ether–light petroleum. One crop had m. p. 73° and, when mixed with dl-*ethyl-*n*-propylcarbinyl hydrogen phthalate*, m. p. 73—74·5° (*M*, by titration, 251. $C_{14}H_{18}O_4$ requires *M*, 250). The other crop had m. p. 46—48° and, when mixed with dl-*methyl-*n*-butylcarbinyl hydrogen phthalate*, m. p. 45—47° (Found : *M*, 252).

Hydrolysis of (—)-γ-Methyl-α-ethylallyl Chloride.—The (—)-chloride (5·5 g.), having $\alpha_{5461}^{18\cdot5^\circ}$ — 6·55° (*l*, 0·5) [prepared from the (+)-alcohol (10 g.) having $[\alpha]_{5461}^{21^\circ}$ + 6·56°], was hydrolysed as before, giving a hexenol having $\alpha_{5893}^{18^\circ}$ — 0·11°, $\alpha_{5780}^{18^\circ}$ — 0·10°, $\alpha_{5461}^{18^\circ}$ — 0·07°, $\alpha_{4358}^{18^\circ}$ — 0·03°, (*l*, 0·5). This was reduced to the hexanol (1·5 g.) having b. p. 132—137°, $\alpha_{5893}^{20^\circ}$ + 0·04°, $\alpha_{5461}^{20^\circ}$ + 0·02°, $\alpha_{4358}^{20^\circ}$ ± 0·00° (*l*, 0·25). This gave a hydrogen phthalate having (without recrystallisation) $[\alpha]_{5893}$ + 0·20°, $[\alpha]_{5461}$ + 0·07° in chloroform (*l*, 2; *c*, 7·5). The ethereal washings from the alkaline solution of this hydrogen phthalate were optically inactive.

The quotient for λ 5893, 0·20/0·16 = 1·25, corresponds with the ratio 93% of *d*-ethyl-*n*-propylcarbinol to 7% of *l*-methyl-*n*-butylcarbinol, and such a mixture of optically pure components would have $\alpha_{5893}^{20^\circ}$ + 4·7° (*l*, 1·0) (see figure). The initial (+)-carbinol was 42% optically pure, so that for optically pure starting material the rotation of the final hexanol would be $\alpha_{5893}^{20^\circ}$ + 0·38° (*l*, 1·0) or 8% of the theoretical. Hence, on tautomerisation of (+)-α-ethyl-γ-methylallyl alcohol by conversion into the chloride and subsequent hydrolysis, there was 92% racemisation, 7·4% unchanged, and 0·6% converted into (−)-α-methyl-γ-ethylallyl alcohol.

Methyl γ-Methyl-α-ethylallyl Ether.—(i) *From γ-methyl-α-ethylallyl alcohol.* To the alcohol (5 g., $\alpha^{22^\circ}_{5461}$ − 2·5°; *l*, 0·5) in dry ether (30 c.c.), potassium (1·6 g.) was added; after standing overnight, the unreacted potassium was removed, and methyl iodide (7 g.) added to the solution. When the rapid reaction was complete, the solution was washed with water, dried, the ether evaporated, and the residue distilled at normal pressure. To remove unchanged alcohol, the distillate (2·6 g.) was warmed with phthalic anhydride (3 g.) and pyridine (2 g.), and the hydrogen phthalic ester removed by extraction with sodium carbonate. The residual *methyl γ-methyl-α-ethylallyl ether* was distilled at normal pressure, b. p. 110—115°, yield 1·5 g.,' $n_D^{20^\circ}$ 1·4110, $\alpha^{23^\circ}_{5461}$ + 6·88° (*l*, 0·5) (Found : C, 72·5; H, 12·3. $C_7H_{14}O$ requires C, 73·7; H, 12·3%).

(ii) *From (−)-γ-methyl-α-ethylallyl hydrogen phthalate.* The phthalate {8 g., $[\alpha]_{5461}$ − 6·0° in chloroform; the same specimen from which the alcohol used in (i) was obtained by hydrolysis} was heated under reflux with anhydrous methyl alcohol (50 g.) for 32 hours, and the reaction mixture distilled at ordinary pressure. The distillate, diluted with twice its volume of dry ether, was mixed with powdered calcium chloride (60 g.) and left overnight. After filtration, and removal of the ether by evaporation, the residual methyl hexenyl ether was distilled; b. p. 110—112°, $n_D^{22^\circ}$ 1·4180, $\alpha^{21^\circ}_{5461}$ − 0·18° (*l*, 0·5); yield 1·0 g.

dl-*γ-Methyl-α-ethylallyl* p-*nitrobenzoate*, prepared from the alcohol (5 g.) by Einhorn's method, separates from light petroleum in pale yellow flakes (5 g.), m. p. 35—37° (Found : N, 5·4. $C_{13}H_{15}O_4N$ requires N, 5·6%).

Surface tensions were determined by the method of maximum bubble pressure (Sugden, *op. cit.*), the apparatus being calibrated by means of benzene.

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