

127. Isomeric Forms of the Optically Active $\alpha\gamma$ -Dimethylallyl Alcohols.

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UNSATURATED alcohols of the general formula $\text{CHR}'\text{:CH}\cdot\text{CH}(\text{OH})\cdot\text{R}''$ undergo prototropic ($\text{CH}_2\text{R}'\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}''$, Tiffeneau, *Bull. Soc. chim.*, 1907, **1**, 1209; Nomura, *ibid.*, 1925, **37**, 1245) and anionotropic changes [$\text{CHR}'(\text{OH})\cdot\text{CH}\text{:CHR}''$, Gillet, *Bull. Soc. chim. Belg.*, 1922, **31**, 366; Burton and Ingold, J., 1928, 904], indicating that under certain conditions the double bonds are activated. The effect of this activation on the optical properties of (+)- $\alpha\gamma$ -dimethylallyl alcohol is now described and discussed.

dl- $\alpha\gamma$ -Dimethylallyl hydrogen phthalate was resolved by recrystallisation of its brucine salt by Levene and Haller (*J. Biol. Chem.*, 1929, **81**, 705), who isolated the (+)-hydrogen phthalic ester and the corresponding (+)-alcohol, but did not examine them in detail

polarimetrically. We have found that the maximum rotation of the (+)-hydrogen phthalic ester obtained from any such resolution is always $[\alpha]_{5461} + 30.2^\circ$ (c , 5) in chloroform solution. In other solvents the rotatory powers of this ester (Table I) are not abnormal, and when plotted, they fall on a single characteristic diagram (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, *A*, **88**, 388). The (–)- $\alpha\gamma$ -dimethylallyl hydrogen phthalate, $[\alpha]_{5461} - 29.4^\circ$, is obtained by the recrystallisation of its brucine salt, which separates from the concentrated mother-liquors from which the (+)- $\alpha\gamma$ -dimethylallyl hydrogen phthalate has been removed.

TABLE I.

Specific Rotatory Powers, $[\alpha]_{\lambda}^{15-20^\circ}$, of (+)- $\alpha\gamma$ -Dimethylallyl Hydrogen Phthalate in various Solvents.

| Solvent. | c . | $[\alpha]_{5893}$. | $[\alpha]_{5461}$. | $[\alpha]_{4359}$. | Solvent. | c . | $[\alpha]_{5893}$. | $[\alpha]_{5461}$. | $[\alpha]_{4359}$. |
|-------------------------------|-------|---------------------|---------------------|---------------------|---|-------------------|---------------------|---------------------|---------------------|
| H ₂ O (Na salt) | 10.0 | +26.7° | +33.7° | +66.7° | C ₅ H ₅ N | 10.0 | +17.2° | +20.9° | +46.3° |
| | 5.0 | +23.0 | +27.7 | +57.5 | | 5.0 | +17.9 | +21.7 | +47.7 |
| EtOH | 10.0 | +39.0 | +48.5 | +97.6 | CCl ₄ | 2.5 | +19.2 | +23.0 | +49.4 |
| | 5.0 | +38.3 | +49.0 | +97.6 | | 10.0 | +12.8 | +15.9 | +36.1 |
| | 2.5 | +41.0 | +49.2 | +100.2 | | CHCl ₃ | 10.0 | +23.7 | +29.4 |
| Et ₂ O | 1.25 | +41.2 | +52.0 | +104.8 | 5.0 | +23.9 | +30.2 | +62.5 | |
| | 10.0 | +48.75 | +46.7 | +93.5 | 2.5 | +25.4 | +31.4 | +63.4 | |
| | 5.0 | +40.5 | +49.1 | +95.0 | 1.25 | +26.0 | +32.0 | +64.0 | |
| COMe ₂ | 2.5 | +41.8 | +50.0 | +95.6 | C ₂ H ₄ Cl ₂ | 10.0 | +22.3 | +27.1 | +57.1 |
| | 10.0 | +38.5 | +47.1 | +93.7 | 5.0 | +23.2 | +28.4 | +60.9 | |
| | 5.0 | +39.0 | +47.8 | +93.0 | C ₂ H ₄ Br ₂ | 10.0 | +21.0 | +26.0 | +53.6 |
| C ₆ H ₆ | 2.5 | +45.0 | +50.0 | +94.6 | 5.0 | +21.7 | +26.0 | +54.5 | |
| | 10.0 | +22.9 | +27.7 | +58.5 | 2.5 | +22.0 | +26.3 | +55.0 | |
| | 5.0 | +24.0 | +28.8 | +60.0 | 1.25 | +21.6 | +26.4 | +56.0 | |
| | 2.5 | +24.2 | +30.1 | +61.0 | CS ₂ | 10.0 | +10.1 | +10.3 | +14.8 |
| 1.25 | +24.8 | +30.4 | +62.0 | 5.0 | –2.1 | –2.1 | +1.0 | | |

When saponified by alkalis, the (+)-hydrogen phthalic ester gives (+)- $\alpha\gamma$ -dimethylallyl alcohol, the rotatory power of which varies, but is usually close to $[\alpha]_{5461}^{20^\circ} + 0.84^\circ$. As shown in Table II, the rotatory power of this (+)-alcohol changes, and after about 2 months may eventually become laevorotatory to light of λ 5893 and 5461. Similarly, the optically impure (–)-alcohol from the (–)-hydrogen phthalic ester ($[\alpha]_{5461} - 21.4^\circ$ in chloroform) may decrease in laevorotatory power. The behaviour of the (+)- and the (–)- $\alpha\gamma$ -dimethylallyl alcohol is, however, erratic. A specimen of the (–)-hydrogen phthalic ester with $[\alpha]_{5461} - 6.0^\circ$ in chloroform gave a (+)-alcohol with $\alpha_{5461}^{19^\circ} + 0.10^\circ$ (l , 1), which changed to $\alpha_{5461}^{19^\circ} + 2.26^\circ$ (l , 1) after 6 months and then gave a hydrogen phthalic ester with $[\alpha]_{5461} - 5.5^\circ$; after a further 3 months, the alcohol had $\alpha_{5461}^{19^\circ} + 2.04^\circ$ and gave a hydrogen phthalic ester with $[\alpha]_{5461} - 5.6^\circ$, from which on hydrolysis the alcohol was recovered with $\alpha_{5461}^{19^\circ} + 1.0^\circ$ (l , 1). Furthermore, some samples of the alcohols when freshly isolated from the hydrogen phthalic ester changed more rapidly than others: one sample changed from $\alpha_{5461}^{18^\circ} + 0.83^\circ$ to -0.88° (l , 1) in 14 days, and another from $\alpha_{5461}^{18^\circ} - 0.57^\circ$ to $+0.35^\circ$ in 1 day and to $\alpha_{5461}^{18^\circ} + 4.48^\circ$ in 131 days.

TABLE II.

The Mutarotation of (+)- and (–)- $\alpha\gamma$ -Dimethylallyl Alcohols.

| (+)–Alcohol. | | | | (–)–Alcohol. | | | | | |
|--------------|-------|----------------------|-----------------|-----------------|-------------|-------|----------------------|-----------------|-----------------|
| Time, days. | t . | α (l , 1). | | | Time, days. | t . | α (l , 2). | | |
| | | λ 5893. | λ 5461. | λ 4358. | | | λ 5893. | λ 5461. | λ 4358. |
| 0 | 19.6° | +0.23° | +0.46° | +1.82° | 0 | 18.9° | +0.05° | –0.68° | –1.40° |
| 3 | 18.9 | +0.24 | +0.46 | — | 1 | 18.9 | –0.53 | –0.60 | –2.58 |
| 7 | 19.0 | +0.16 | +0.39 | +1.72 | 2 | 19.3 | –0.45 | –0.66 | –2.48 |
| 10 | 16.0 | +0.30 | +0.53 | +2.12 | 5 | 17.0 | –0.50 | –0.76 | –2.51 |
| 32 | 19.2 | +0.02 | +0.18 | +1.27 | 8 | 19.0 | –0.43 | –0.76 | –2.88 |
| 53 | 19.0 | –0.17 | –0.02 | — | 27 | 19.4 | — | –0.43 | — |
| 123 | 24.0 | –0.38 | –0.36 | — | 48 | 19.5 | –0.26 | –0.38 | –2.25 |
| | | α (l , 2). | | | 61 | 20.0 | –0.21 | –0.34 | –2.23 |
| 0 | 20 | +0.60 | +1.02 | +4.05 | 69 | 22.0 | –0.20 | –0.19 | –2.12 |
| 365 | 20 | –0.41 | –0.16 | +1.90 | 118 | 22.0 | –0.02 | –0.03 | –1.77 |

A large quantity of (+)- $\alpha\gamma$ -dimethylallyl hydrogen phthalate was hydrolysed with aqueous sodium hydroxide, and the resulting (+)- $\alpha\gamma$ -dimethylallyl alcohol distilled, b. p. 120—121.5°, through a 6" column: the middle fraction was collected in a clean polarimeter tube with sealed-on end-plates and closed by a well-fitting cork. The readings, taken from a short temperature-rotation curve, were $\alpha_{5893}^{20^\circ} + 0.60^\circ$; $\alpha_{5461}^{20^\circ} + 1.02^\circ$; $\alpha_{4358}^{20^\circ} + 4.05^\circ$ (*l*, 2). After a few weeks the rotatory power began to decrease, and after a year had reached $\alpha_{5893}^{20^\circ} - 0.41^\circ$, $\alpha_{5461}^{20^\circ} - 0.16^\circ$, $\alpha_{4358}^{20^\circ} + 1.90^\circ$ (*l*, 2). A portion of this alcohol yielded a hydrogen phthalic ester with $[\alpha]_{5893}^{20^\circ} + 19.6^\circ$; $[\alpha]_{5461}^{20^\circ} + 25.6^\circ$ (*c*, 5.102; *l*, 2) in chloroform solution.

The erratic character of these changes is to some extent accounted for by the pronounced effect of temperature on the low rotatory power of the alcohol and by its anomalous rotatory dispersion (Table III).

The influence of temperature on the rotatory power of the (+)-alcohol is only partly due to mutarotation; e.g., a (-)-alcohol with $[\alpha]_{5461}^{70^\circ} - 1.33^\circ$ (*l*, 0.5) had $[\alpha]_{5461}^{70^\circ} - 1.61^\circ$ (*l*, 0.5) after having been kept at 70° for 48 hours.

TABLE III.

Specific Rotatory Powers, $[\alpha]_{\lambda}^{\theta}$, of (+)- $\alpha\gamma$ -Dimethylallyl Alcohol and its Derivatives
(in the homogeneous state).

| | | <i>$\alpha\gamma$-Dimethylallyl alcohol.</i> | | | | | | | | |
|-------------------------------|----------------|---|--------|--------|--------|--------|--------|--------|--------|--------|
| | | 20°. | 30°. | 40°. | 50°. | 60°. | 70°. | 80°. | 90°. | 100°. |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 0.8354 | 0.8270 | 0.8189 | 0.8106 | 0.8023 | 0.7941 | 0.7859 | 0.7776 | 0.7694 |
| | λ 5893 | +0.50° | -0.14° | -0.78° | -1.41° | -2.05° | -2.65° | -3.21° | -3.71° | -4.03° |
| | λ 5461 | +0.84 | +0.10 | -0.61 | -1.86 | -2.12 | -2.77 | -3.41 | -4.04 | -4.61 |
| | λ 4358 | +3.04 | +1.35 | -0.12 | -1.33 | -2.37 | -3.40 | -4.20 | -5.46 | -6.37 |
| | | <i>(-)-$\alpha\gamma$-Dimethylallyl formate.</i> | | | | | | | | |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 0.8790 | 0.8693 | 0.8597 | 0.8500 | 0.8403 | 0.8305 | 0.8208 | 0.8110 | 0.8012 |
| | λ 5893 | -61.0 | -59.8 | -59.3 | -58.9 | -58.8 | -58.5 | -58.3 | -58.0 | — |
| | λ 5461 | 72.8 | 72.5 | 72.1 | 71.9 | 71.5 | 71.1 | 70.8 | 70.4 | 69.9 |
| | λ 4358 | 129.0 | 128.3 | 127.9 | 127.3 | 126.9 | 126.2 | 125.4 | 125.0 | 124.9 |
| | | <i>(-)-$\alpha\gamma$-Dimethylallyl acetate.</i> | | | | | | | | |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 0.8980 | 0.8882 | 0.8788 | 0.8689 | 0.8591 | 0.8493 | 0.8395 | 0.8297 | 0.8199 |
| | λ 5893 | 65.2 | 64.4 | 63.8 | 63.4 | 62.8 | 62.2 | 62.0 | — | — |
| | λ 5461 | 76.1 | 75.3 | 74.5 | 73.7 | 73.2 | 72.9 | 72.5 | 72.0 | 71.2 |
| | λ 4358 | 136.3 | 135.1 | 134.1 | 133.2 | 132.0 | 131.1 | 129.9 | 128.9 | 127.8 |
| | | <i>(+)-$\alpha\gamma$-Dimethylallyl benzoate.</i> | | | | | | | | |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 1.0149 | 1.0067 | 0.9984 | 0.9904 | 0.9820 | 0.9738 | 0.9656 | 0.9574 | 0.9492 |
| | λ 5893 | +20.6° | +20.7° | +20.8° | +20.9° | +21.0° | +21.1° | +21.2° | +21.3° | +21.4° |
| | λ 5461 | 26.5 | 26.4 | 26.2 | 26.2 | 26.3 | 26.1 | 25.9 | 25.9 | 25.8 |
| | λ 4358 | 57.3 | 57.0 | 56.5 | 56.2 | 55.9 | 55.5 | 55.2 | 54.8 | 54.6 |
| | | <i>(+)-$\alpha\gamma$-Dimethylallyl o-nitrobenzoate.</i> | | | | | | | | |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 1.1424 | 1.1339 | 1.1254 | 1.1172 | 1.1087 | 1.1003 | 1.0913 | 1.0831 | 1.0743 |
| | λ 5893 | +22.4 | +21.7 | +21.1 | +20.3 | +19.65 | +19.0 | +18.3 | +17.6 | +16.9 |
| | λ 5461 | 29.9 | 27.8 | 26.9 | 26.0 | 25.05 | 24.2 | 23.1 | 22.3 | 21.4 |
| | λ 4358 | 77.1 | 74.2 | 71.5 | 69.0 | 66.6 | 64.2 | 62.5 | 60.8 | 59.2 |
| | | <i>(+)-$\alpha\gamma$-Dimethylallyl m-nitrobenzoate.</i> | | | | | | | | |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 1.1693 | 1.1609 | 1.1520 | 1.1432 | 1.1344 | 1.1259 | 1.1169 | 1.1082 | 1.0995 |
| | λ 5893 | +21.9 | +21.4 | +21.0 | +20.8 | +20.6 | +20.2 | +20.1 | +20.0 | +20.0 |
| | λ 5461 | 27.0 | 26.5 | 26.0 | 25.6 | 25.4 | 24.9 | 24.7 | 24.4 | 24.2 |
| | λ 4358 | 56.2 | 55.0 | 54.2 | 53.4 | 52.6 | 51.8 | 51.3 | 50.6 | 50.0 |
| | | <i>(-)-Benzyl $\alpha\gamma$-dimethylallyl ether.</i> | | | | | | | | |
| $[\alpha]_{\lambda}^{\theta}$ | d_4^c | 0.9740 | 0.9656 | 0.9574 | 0.9490 | 0.9403 | 0.9317 | 0.9230 | 0.9143 | 0.9057 |
| | λ 5893 | -38.4° | -38.0° | -37.5° | -36.9° | -36.2° | -35.6° | -35.1° | -34.6° | -34.0° |
| | λ 5461 | 45.6 | 44.9 | 44.3 | 43.6 | 43.0 | 42.3 | 41.7 | 40.9 | 40.2 |
| | λ 4358 | 74.9 | 78.5 | 72.3 | 71.0 | 69.8 | 68.5 | 67.1 | 65.7 | 64.2 |

The rotatory power of the (+)-alcohol is very sensitive to the influence of solvents (Table IV). These rotatory powers, when plotted, give two distinct characteristic diagrams: those determined in water, ethyl alcohol, and carbon disulphide form one group, and those

in ether, benzene, pyridine, and chloroform another. No permanent mutarotation occurs in the solutions: the (+)-alcohol can be recovered from them without serious alteration in rotatory power.

TABLE IV.

Specific Rotatory Powers of (+)- $\alpha\gamma$ -Dimethylallyl Alcohol and its p-Nitrobenzoate in Various Solvents.

| Solvent. | (+) - $\alpha\gamma$ -Dimethylallyl alcohol. | | | | (+) - $\alpha\gamma$ -Dimethylallyl p-nitrobenzoate. | | | |
|---------------------------------|--|---------------------------|---------------------------|---------------------------|--|---------------------------|---------------------------|---------------------------|
| | <i>c.</i> | $[\alpha]_{5893}^{\circ}$ | $[\alpha]_{5461}^{\circ}$ | $[\alpha]_{4358}^{\circ}$ | <i>c.</i> | $[\alpha]_{5893}^{\circ}$ | $[\alpha]_{5461}^{\circ}$ | $[\alpha]_{4358}^{\circ}$ |
| H ₂ O | 1.5 | - 3.3° | - 4.3° | - 8.3° | - | - | - | - |
| EtOH | 5.0 | - 0.6 | - 0.1 | + 1.6 | - | - | - | - |
| CS ₂ | 5.0 | + 1.2 | + 3.0 | + 8.4 | 5 | + 12.1° | + 14.3° | + 45.7° |
| Et ₂ O | 5.0 | - 5.8 | - 7.0 | - 9.4 | 5 | + 45.9 | + 57.3 | - |
| C ₆ H ₆ | 5.0 | - 4.0 | - 4.1 | - | 5 | + 37.6 | + 47.5 | + 115.0 |
| C ₆ H ₅ N | 5.0 | + 7.4 | + 8.9 | + 21.8 | 5 | + 35.5 | + 44.0 | - |
| CHCl ₃ | 10.0 | - 15.1 | - 17.5 | - 28.9 | 5 | + 45.0 | + 54.8 | + 127.3 |
| | 5.0 | - 15.4 | - 18.0 | - 32.6 | | | | |

In sharp contrast to the parent (+)-alcohol, its esters with formic, acetic, benzoic, and *o*-, *m*-, and *p*-nitrobenzoic acids (like its hydrogen phthalic ester) are normal. Their rotatory powers are little influenced by temperature, they remain unchanged over long periods, and their dispersion is simple, since straight lines are obtained when $1/\alpha$ is plotted against λ^2 . Similarly, benzyl $\alpha\gamma$ -dimethylallyl ether, prepared by the interaction of benzyl chloride and the potassio-derivative of the (+)-alcohol, also retains its rotatory power unchanged and exhibits simple rotatory dispersion.

The determined parachors of a number of specimens of (+)-, (-)-, and *dl*- $\alpha\gamma$ -dimethylallyl alcohols, prepared by the methods enumerated in Table V, are much smaller than those calculated from the atomic and structural parachors of either Sugden ("The Parachor and Valency," p. 38) or Mumford and (J.W.C.) Phillips, J., 1929, 2113. The differences between the observed and the calculated parachors are unlikely to be due to the presence of unforeseen impurities in these alcohols, since the (+)-alcohol has been converted into derivatives having parachors (Table VI) which are either very close to the values calculated for the open-chain, double-bond formulæ or deviate therefrom only slightly, the largest deviations being for the benzoate and the nitrobenzoates, all of which are somewhat unstable at their boiling points and are therefore difficult to obtain pure.

The parachors of allyl alcohol and some monosubstituted allyl alcohols have been determined (Table VII): allyl alcohol has a normal parachor, but those of α - and γ -substituted alcohols are low.

TABLE V.

Observed Parachors of $\alpha\gamma$ -Dimethylallyl Alcohols.

| Calc. for CH ₃ :CH:CH(OH):CH ₃ : | | | | Cyclic form, %. | |
|---|------------------------------|--------------------|-------|-----------------|-----------|
| | { Sugden | 238.2 | | S. | M. and P. |
| | { Mumford and Phillips | 233.6 | | | |
| | <i>t.</i> | [<i>P</i>], obs. | | | |
| <i>dl</i> -Alcohol, from Grignard reaction | 17—30° | 226.7 | 99.5 | 82.0 | |
| <i>dl</i> -Alcohol, by hydrolysis of (+)-hydrogen phthalic ester with dil. H ₂ SO ₄ | 21—31 | 230.5 | 64.0 | 2.0 | |
| <i>dl</i> -Alcohol, by hydrolysis of (+)-hydrogen phthalic ester with NaOAc soltn. | 20—33 | 233.0 | 58.0 | — | |
| (+)-Alcohol, by hydrolysis of (+)-hydrogen phthalic ester with NaOH soltn. | 20—25 | 228.3 | 83.5 | 49.0 | |
| (-)-Alcohol, by hydrolysis of (-)-hydrogen phthalic ester with NaOH soltn. | 18—29 | 230.4 | 65.0 | 4.0 | |
| (+)- and (-)-Alcohols, by hydrolysis of (+)- and (-)- $\alpha\gamma$ -dimethylallyl chlorides | (a) } (b) } (c) } | 229.2 | 80.0 | 29.5 | |
| | | 227.4 | 90.0 | 68.0 | |
| | | 226.0 | 100.0 | 87.0 | |

The high parachor contribution of a double bond, 23.2 units (Sugden) or 19.0 units (Mumford and Phillips), suggests that the low observed parachors of the substituted allyl

TABLE VI.

Observed Parachors of Derivatives of (-)- $\alpha\gamma$ -Dimethylallyl Alcohol.

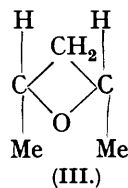
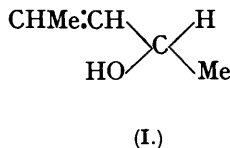
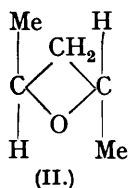
| Derivative. | [P], obs. | [P], calc. | | Derivative. | [P], obs. | [P], calc. | |
|-------------------------|-----------|------------|---------|-----------------------------|-----------|------------|---------|
| | | S. | M. & P. | | | S. | M. & P. |
| Formate | 281.6 | 283.0 | 282.2 | Methyl ether | 277.2 | 277.2 | 276.0 |
| Acetate | 321.2 | 322.0 | 322.1 | <i>n</i> -Butyl ether | 393.8 | 396.2 | 396.0 |
| Benzoate | 450.5 | 455.9 | 455.8 | Benzyl ether | 446.1 | 450.1 | 450.6 |
| <i>o</i> -Nitrobenzoate | 506—509 | 514.5 | 513.9 | Chloride | 257.4 | 255.4 | 255.6 |
| <i>m</i> -Nitrobenzoate | 496.3 | 514.5 | 513.9 | | | | |

TABLE VII.

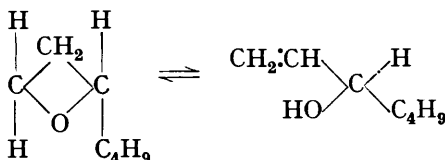
Observed Parachors of Allyl and Monosubstituted Allyl Alcohols.

| Alcohol. | [P], obs. | Calc. (for open chain). | | Cyclic form, %. | |
|---------------------------------------|-----------|-------------------------|---------|-----------------|---------|
| | | S. | M. & P. | S. | M. & P. |
| Allyl | 159.0 | 160.1 | 153.6 | — | — |
| α -Ethylallyl | 228.1 | 238.2 | 230.6 | 78 | 49 |
| α - <i>n</i> -Butylallyl | 305.9 | 316.2 | 310.6 | 85 | 100 |
| γ -Phenylallyl | 324.4 | 331.2 | 328.2 | 65 | 43 |

alcohols are due to isomerism during which their double bonds are lost. On this assumption, $\alpha\gamma$ -dimethylallyl alcohol (I), for example, might exist as an equilibrium mixture of labile open-chain and cyclic isomerides, two forms (II and III) of the latter being possible owing to *cis-trans*-isomerism. This hypothesis was adopted when we first described some



of the properties of $\alpha\gamma$ -dimethylallyl alcohol (*Chem. and Ind.*, 1933, 52, 660). Such isomerism might explain the anomalous rotatory dispersion of the alcohol, because (II) contains an additional centre of asymmetry and the alcohol would therefore contain two optically active alcohols, possibly of opposite rotations and with different dispersive powers. It might also account for the simple rotatory dispersion of *d*- α -*n*-butylallyl alcohol (Kenyon and Snellgrove, J., 1925, 127, 1169), since this alcohol could give rise to only one cyclic isomeride without an additional centre of asymmetry :



Furthermore, isomerism of this type would be restricted to compounds containing a hydroxyl group, and hence the apparent homogeneity of the esters and ethers of $\alpha\gamma$ -dimethylallyl alcohol could be explained. This hypothesis would not, however, explain all our observations. For instance, the (+)-alcohol can be isolated from the optically pure hydrogen phthalic ester with a parachor of 228.3, indicating that it either contains 83.5% or 49% of the cyclic isomerides according as Sugden's or Mumford and Phillips's values are used for atomic and structural parachors. The (+)-alcohol would thus contain a certain proportion of isomeride (III), which, being internally compensated, would give rise to an optically inactive ester when re-esterified with phthalic anhydride. This should cause the (+)-alcohol to yield an optically impure hydrogen phthalic ester of low rotatory power. Experimentally, however, a freshly isolated alcohol with a parachor of 228.3 yielded a hydrogen phthalic ester possessing a rotatory power only 2° lower than that of the optically

pure ester. Similarly, the observed parachors of the α -substituted allyl alcohols suggest that these compounds contain a relatively large proportion of the cyclic isomerides, and these might be expected to yield a mixture of the α - and the γ -substituted allyl esters when re-esterified with acid anhydrides. Kenyon and Snellgrove (*loc. cit.*), however, recovered optically pure α -*n*-butylallyl alcohol from its formic ester which had been prepared by the use of the mixed anhydride of formic and acetic acids.

It might be argued that such evidence does not dispose of the hypothesis, since preferential esterification may cause the alcohols to yield only one hydrogen phthalic or formic ester; *e.g.*, the isomerisation of $\alpha\gamma$ -dimethylallyl alcohol may occur so as to favour the formation of isomeride (II), which would yield an optically pure hydrogen phthalic ester. Alternatively, for stereochemical reasons, preferential esterification of isomeride (II) may occur. Similarly, in the case of unsymmetrical alcohols, such as *d*- α -*n*-butylallyl alcohol, the cyclic form may react with acid anhydrides to produce exclusively either α - or β -substituted esters. In agreement with this view, Baudrenghien (*Bull. Soc. chim. Belg.*, 1922, **31**, 160) showed that α -methylallyl alcohol gave solely α -methylallyl acetate; further, although the parachor of α -phenylallyl alcohol (cinnamyl alcohol) suggests that it possibly contains a considerable proportion of a cyclic isomeride, it yields pure cinnamyl acetate when boiled with acetic anhydride (Burton and Ingold, *loc. cit.*).

Other observations have been made which are difficult to reconcile with the hypothesis of cyclic isomerisation. For example, when reduced, (–)- α -*n*-butylallyl alcohol yields optically pure (+)-ethyl-*n*-butylcarbinol (Levene and Haller, *J. Biol. Chem.*, 1929, **83**, 579; Johnson and Kenyon, *J.*, 1932, 722), and we have found that (+)- $\alpha\gamma$ -dimethylallyl alcohol on reduction yields optically pure methyl-*n*-propylcarbinol (Pickard and Kenyon, *J.*, 1911, **99**, 65). Even more difficult to explain is the unique form of (–)- $\alpha\gamma$ -dimethylallyl alcohol produced by hydroxylation of (–)- $\alpha\gamma$ -dimethylallyl chloride obtained by the action of phosphorus trichloride on the (+)-alcohol in the presence of pyridine. The most remarkable property of this (–)-alcohol is that, although it reacts quantitatively with phthalic anhydride in cold pyridine solution, the resulting hydrogen phthalic ester is optically inactive whereas, under similar conditions, the (+)-alcohol yields a hydrogen phthalic ester with $[\alpha]_{5461} + 28.5^\circ$.

Many of the observations recorded above can be explained on the assumption that (+)- $\alpha\gamma$ -dimethylallyl alcohol isomerises very slowly to a *trans*-cyclic isomeride of relatively high lævorotation. At present this simple interpretation cannot be accepted for two reasons. First, on this hypothesis the (+)-alcohol would contain only a small proportion of cyclic isomerides, and therefore some other explanation must be found for the large anomaly in the parachor of the (+)-alcohol; this is not easy to find, since the anomaly is not likely to be due to association—the probable cause of smaller anomalies in the parachors of the lower saturated alcohols (Sugden, *loc. cit.*)—because allyl alcohol possesses a normal parachor. Secondly, this interpretation does not throw any light on the constitution of the novel (–)-alcohol obtained by hydrolysis of (–)- $\alpha\gamma$ -dimethylallyl chloride. This (–)-alcohol is produced from the (+)-alcohol by the aid of two consecutive reactions, both of which are most likely attended by Walden inversions. It therefore probably has the same configuration as the parent (+)-alcohol. Hence, unless it is assumed that there is more than one lævorotatory isomeric form of the (+)-alcohol, the lævorotatory alcohol produced by mutarotation has the same constitution as the lævorotatory alcohol obtained from (–)- $\alpha\gamma$ -dimethylallyl chloride. If this be so, then the alcohol produced when the (+)-alcohol undergoes mutarotation cannot be the *trans*-cyclic isomeride, since this would be expected to yield an optically active hydrogen phthalic ester, whereas the lævorotatory alcohol obtained from the chloride yields an optically inactive hydrogen phthalic ester.

It is evident, therefore, that the nature of the isomerism undergone by (+)- $\alpha\gamma$ -dimethylallyl alcohol will be known with greater certainty when the constitution of the (–)-alcohol obtained by hydrolysis of the chloride has been elucidated.

EXPERIMENTAL.

dl- $\alpha\gamma$ -Dimethylallyl alcohol was prepared (62% yield) by the interaction of crotonaldehyde (0.9 mol.) and methylmagnesium bromide (1 mol.), and dried over potassium carbonate. The

crude *dl*-alcohol, b. p. 120—125°, had $[P]$ 226.7; by distillation through a short column it was separated into three fractions: (i) b. p. 121—121.4°, $[P]$ 229.3; (ii) b. p. 121.5—123°; (iii) b. p. 123—124.8°, $[P]$ 229.8. No sharp end-points could be obtained when attempts were made to determine the iodine value of $\alpha\gamma$ -dimethylallyl alcohol by Wijs's method.

dl- $\alpha\gamma$ -Dimethylallyl Hydrogen Phthalate.—The *dl*-alcohol (1 mol.), phthalic anhydride (1 mol.), and pyridine (1.1 mols.) were heated on a steam-bath for an hour. The cold homogeneous reaction mixture, when poured into dilute hydrochloric acid and ice, yielded the acid ester as an oil, which solidified (m. p. 88—89°, yield 90%); it separates from methylene chloride in small irregular crystals or from ether-light petroleum in rosettes of small needles, m. p. 90—90.5°.

The Optically Active Dimethylallyl Hydrogen Phthalates.—Brucine (800 g.) was dissolved in a warm solution of the *dl*-hydrogen phthalic ester (468 g.) in a mixture of chloroform (800 c.c.) and acetone (1600 c.c.). The crystals of *lB,dA* salt which separated on cooling were obtained optically pure after two recrystallisations from acetone-chloroform. The brucine salt of the racemate tends to separate when acetone alone (Levene and Haller, *loc. cit.*) is used. By working up the mother-liquors, a total yield of 575 g. of the optically pure salt was obtained. *l*-Brucine (+)- $\alpha\gamma$ -dimethylallyl phthalate has m. p. 169—169.5° and $[\alpha]_{5461} - 15.2$ (*c*, 5.6; *l*, in 2) ethyl alcohol; Levene and Haller (*loc. cit.*) record $[\alpha]_{5893} - 13.7^\circ$ at the same concentration. (+)- $\alpha\gamma$ -Dimethylallyl hydrogen phthalate, obtained by the decomposition of the brucine salt, has m. p. 82—84°, $[\alpha]_{5893} + 38.75^\circ$ in ether (*c*, 10.0; *l*, 2); Levene and Haller (*loc. cit.*) record $[\alpha]_{5893} + 30.8^\circ$ (*c*, 26.0; *l*, 1) in the same solvent.

The (−)-salt separated as rosettes of fine crystalline rods when the acetone-chloroform filtrates from the less soluble brucine salt were evaporated to small bulk and set aside for several days. After four crystallisations from acetone, it was obtained optically pure, m. p. 157—159°, $[\alpha]_{5461} - 8.2^\circ$ (*c*, 5.0; *l*, 2) in ethyl alcohol. When decomposed it gave (−)- $\alpha\gamma$ -dimethylallyl hydrogen phthalate, m. p. 82—84°, $[\alpha]_{5893} - 24.1^\circ$, $[\alpha]_{5461} - 29.4^\circ$, $[\alpha]_{4359} - 60.7^\circ$ (*c*, 5.0; *l*, 2) in chloroform solution. A mixture of the (+)- and the (−)-acid phthalic ester softened slightly at 82—84° and melted at 89—90°. The optically active acid esters are more soluble than the *dl*-acid ester; a warm solution of *l* + *dl*-ester ($[\alpha]_{5461} - 13^\circ$ in chloroform) in methylene chloride deposited the *dl*-ester when cooled; *l* + *dl*-ester with $[\alpha]_{5461} - 27^\circ$ was obtained from the filtrate.

Hydrolysis of the Optically Active $\alpha\gamma$ -Dimethylallyl Hydrogen Phthalates.—(i) *Hydrolysis of sodium (−)- $\alpha\gamma$ -dimethylallyl phthalate by aqueous sodium acetate.* A current of steam was passed through an aqueous solution of the (−)-acid ester (11.7 g., 1 mol.; $[\alpha]_{5461} - 13.4^\circ$), sodium carbonate (0.5 mol.), and sodium acetate (1 mol.). The $\alpha\gamma$ -dimethylallyl alcohol extracted from the steam-distillate was optically inactive both in the homogeneous state and in chloroform solution. Between 20° and 33° its parachor was 233.0.

(ii) *By methyl-alcoholic potassium acetate.* A solution of the (+)-acid ester (47 g.; $[\alpha]_{5461} + 30.2^\circ$ in chloroform solution) and freshly fused potassium acetate (20 g.) in dry methyl alcohol (100 c.c.) was heated under reflux for 70 hours. The cooled mixture was poured into water and extracted with ether; by washing the ethereal layer with sodium carbonate, unchanged (+)-acid ester (11.3 g.) was recovered. On distillation, the dried ethereal extract gave (+)- $\alpha\gamma$ -dimethylallyl alcohol, b. p. 119—121° (7.3 g.), $\alpha_{5461}^{18^\circ} + 0.27^\circ$, $\alpha_{4359}^{18^\circ} + 0.64^\circ$, (*l*, 0.25); $[\alpha]_{5461} - 8.0^\circ$, $[\alpha]_{4359} - 12.6^\circ$ (*l*, 2; *c*, 5.25); $[\alpha]_{5461} - 8.9^\circ$, $[\alpha]_{4359} - 13.3^\circ$ (*l*, 2; *c*, 2.625) in ether. The acid phthalic ester prepared from this alcohol by the method described above had $[\alpha]_{5461} + 27.6^\circ$ (*l*, 2; *c*, 5.0) in chloroform solution.

(iii) *By aqueous sodium hydroxide.* The (+)- $\alpha\gamma$ -dimethylallyl alcohol obtained by heating the (+)-acid ester with 5*N*-sodium hydroxide (2.5 mols.) on a steam-bath for 15 mins. had b. p. 119—120°, $\alpha_{5461}^{13^\circ} + 1.14^\circ$ (*l*, 1); $[\alpha]_{5893} - 5.8^\circ$ in ether (*c*, 5; *l*, 2); Levene and Haller (*loc. cit.*) record $[\alpha]_{5893} - 6.1^\circ$ (*c*, 12.1; *l*, 1). It had $[P]$ 228.3 between 20° and 25°; a second specimen of the alcohol isolated by similar methods had $[P]$ 229.9 between 22° and 45°.

*Reduction of (+)- $\alpha\gamma$ -Dimethylallyl Alcohol to (+)-Methyl-*n*-propylcarbinol.*—(+)- $\alpha\gamma$ -Dimethylallyl alcohol, from (+)-acid phthalic ester, was reduced in ethereal solution in the presence of platinum oxide to (+)- $\alpha\gamma$ -dimethyl-*n*-propyl alcohol (methyl-*n*-propylcarbinol), b. p. 118—119°, $\alpha_{5893}^{17^\circ} + 2.71^\circ$ (*l*, 0.25) [Levene and Haller, *J. Biol. Chem.*, 1929, 83, 579, carried out this reduction by using colloidal palladium and obtained $\alpha_{5893}^{24^\circ} + 7.95^\circ$ (*l*, 1)]. This was converted into its hydrogen phthalic ester, m. p. 34°, $[\alpha]_{5893} + 35.9^\circ$ (*c*, 5.31; *l*, 2) in chloroform solution. By the resolution of the *dl*-ester with brucine, Pickard and Kenyon (*J.*, 1911, 99, 63) obtained this (+)-ester with m. p. 34°, $[\alpha]_{5893} + 36.9^\circ$ in chloroform (*c*, 5.0; *l*, 2).

(−)- $\alpha\gamma$ -Dimethylallyl formate, prepared by heating the (+)-alcohol (5 g.) for $\frac{1}{2}$ hour with the mixed anhydride of formic and acetic acids (9 g.), had b. p. 122—123°, $n_D^{19^\circ} 1.4163$, $d_4^{19^\circ} 0.9139$

(Found : C, 62.5; H, 8.6. $C_8H_{10}O_2$ requires C, 63.1; H, 8.8%). The *acetate*, prepared by gently heating the (+)-alcohol with acetic anhydride and pyridine for an hour, had b. p. 136—137°, n_D^{19} 1.4179, n_D^{26} 1.4143, d_4^{25} 0.8931 (Found : C, 65.0; H, 9.5. $C_7H_{12}O_2$ requires C, 65.6; H, 9.4%).

(+)- α -Dimethylallyl benzoate, prepared by the action of benzoyl chloride on a solution of the (+)-alcohol in pyridine, had b. p. 126°/13 mm., d_4^{25} 1.0108, n_D^{19} 1.5117 (Found : C, 75.1; H, 7.3. $C_{12}H_{14}O_2$ requires C, 75.8; H, 7.4%).

(+)- α -Dimethylallyl *o*-nitrobenzoate, prepared by means of *o*-nitrobenzoyl chloride, had b. p. 124—125°/ < 0.1 mm., d_4^{25} 1.1382, n_D^{19} 1.5226 (Found : C, 61.0; H, 5.5. $C_{12}H_{13}O_4N$ requires C, 61.3; H, 5.5%). The *m*- and the *p*-isomeride, similarly prepared, had respectively b. p. 126—127°/ < 0.1 mm., d_4^{25} 1.1641, n_D^{19} 1.5327 (Found : N, 6.2. $C_{12}H_{13}O_4N$ requires N, 6.0%), and m. p. 48°, needles from light petroleum (Found : N, 6.1%).

(-)-Methyl α -Dimethylallyl Ether.—Potassium (3.9 g.) was dissolved in a solution of the (+)-alcohol in ether (50 c.c.), and methyl iodide (14.2 g.) added. After 12 hours, the ethereal solution was washed with water, dried (calcium chloride), and distilled; redistillation of the fraction, b. p. 83—95°, afforded the required *ether*, b. p. 90°, n_D^{18} 1.4045, d_4^{15} 0.7729, α_{5461}^{20} - 14.07°, α_{4359}^{20} - 23.53° (*l*, 0.25), $[P]$ 276.4 (Calc. : 277.2) (Found : C, 71.6; H, 11.8. $C_6H_{12}O$ requires C, 72.0; H, 12.0%).

The *n*-butyl ether, similarly prepared by use of *n*-butyl bromide, had b. p. 149—150°, $d_4^{25.6}$ 0.7864, n_D^{18} 1.4192, α_{5461}^{20} - 7.60°, α_{4359}^{20} - 12.5° (*l*, 0.25) (Found : C, 76.4; H, 12.3. $C_9H_{18}O$ requires C, 76.1; H, 12.7%), and the *benzyl ether* (benzyl chloride and 4 hours' refluxing) had b. p. 107°/11 mm., d_4^{25} 0.9698, n_D^{19} 1.4993, α_{5461}^{19} - 11.82° (*l*, 0.25) (Found : C, 81.4; H, 9.1. $C_{12}H_{16}O$ requires C, 81.8; H, 9.1%).

Conversion of (-)- α -Dimethylallyl Alcohol into (-)-Methyl α -Dimethylallyl Ether by the Action of Methyl Alcohol and Sulphuric Acid.—A mixture of the (-)-alcohol (5 g.; α_{5461}^{20} - 0.52°, *l*, 2), methyl alcohol (50 c.c.), and sulphuric acid (2 c.c.) was kept for 24 hours and then poured into ether; the ethereal solution was washed with sodium carbonate, dried with calcium chloride, and distilled, yielding (-)-methyl α -dimethylallyl ether, b. p. 90—91°, n_D^{16} 1.4050, α_{5461}^{20} - 0.25 (*l*, 0.25), $[P]$ 276.9.

Conversion of (-)- α -Dimethylallyl Alcohol into dl-n-Butyl α -Dimethylallyl Ether by the Action of n-Butyl Alcohol and Sulphuric Acid.—By the method described in the preceding paragraph, but by using *n*-butyl alcohol, there was obtained *dl-n*-butyl α -dimethylallyl ether, b. p. 150—151°, $n_D^{15.5}$ 1.4188, $[P]$ 394.3.

Conversion of (-)- α -Dimethylallyl Chloride into (-)- α -Dimethylallyl Alcohol.—(-)- α -Dimethylallyl chloride, prepared from the (+)-alcohol, obtained from the (+)-hydrogen phthalic ester with $[\alpha]_{5461} + 30.2^\circ$ in chloroform, had b. p. 20°/13 mm., α_{5893}^{16} - 12.46°, α_{5780}^{16} - 13.02°, α_{5461}^{16} - 15.14°, α_{4358}^{16} - 28.8° (*l*, 2) (Found : C, 57.8. Calc. : C, 57.4%). This chloride (10.5 g.) was shaken for 1 hour with a suspension of calcium carbonate (5.3 g.) in water (80 c.c.). The (-)-alcohol, extracted with ether and dried with potassium carbonate, had b. p. 33°/10 mm. and α_{5893}^{10} - 1.28°, α_{5780}^{10} - 1.32°, α_{5461}^{10} - 1.48°, α_{4358}^{10} - 2.45° (*l*, 2), n_D^{19} 1.4288 (Found : C, 69.4; H, 11.5. Calc. : C, 69.8; H, 11.6%). It (0.4 g.) was left over-night with a suspension of phthalic anhydride (0.7 g.) in pyridine (1 c.c.), and the resulting solution decomposed with cold dilute hydrochloric acid. The liberated acid phthalic ester (0.8 g.), m. p. 89—90°, was optically inactive in chloroform solution (*c*, 3.5; *l*, 2). A parallel esterification of the (+)-alcohol yielded a hydrogen phthalic ester with $[\alpha]_{5461} + 28.5^\circ$ in chloroform solution.

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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