91. *Further Observations on the Optically Active αγ-Dimethylallyl Alcohols.*

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Hills, Kenyon, and Phillips (J., 1936, 576), described the erratic mutarotation of (+)-αγ-dimethylallyl alcohol and the preparation of an unusual *lævo*-alcohol,* from the lævo-chloride. These peculiarities are not shown by other substituted allyl alcohols. On the other hand, the general conclusion that these alcohols and their derivatives can undergo anionotropic rearrangement, which is accompanied by partial racemisation, does not explain the peculiarities of αγ-dimethylallyl alcohol.

Re-examination of the (+)alcohol indicates that during the mutarotation a lævorotatory substance is formed which is also present in the alcohol obtained from the *lævo*-chloride. The nature of this substance has not been elucidated, but it would appear to form only a small proportion of the alcohols in which it occurs.

(+)-αγ-Dimethylallyl alcohol yields, with a variety of reagents, *lævo*-αγ-dimethylallyl chloride (2-chloro-Δ$^{\gamma}$-pentene; Hills, Kenyon, and Phillips, *loc. cit.*; Levene and Haller, *J. Biol. Chem.*, 1929, **81**, 703), with α^{20}_{5461} ranging from $-1°$ to $-19°$ (*l*, 1). The chloride racemises on standing, as it does in benzene or acetone solution in presence of stannic or mercuric chloride (Böhme, *Ber.*, 1938, **71**, 2372), presumably on account of the lability of the chlorine atom.

Solvolytic reactions (see following table) of the chloride with methyl and *n*-butyl alcohol give extensively racemised products. This is to be expected, since these reactions are initiated by ionisation of the chloride (compare the reactions of α- and γ-methylallyl chlorides with ethyl alcohol; Hughes, *Trans. Faraday Soc.*, 1941, **37**, 627). Replacement reactions of the chloride with solid potassium or silver acetate also result in much racemisation, possibly due to the heterogeneous reaction conditions (see Cowdrey, Hughes, Ingold, Masterman, and Scott, J., 1937, 1252).

The homogeneous reaction with sodium methoxide also gives a highly racemised product. Bergmann (*Helv. Chim. Acta*, 1937, **20**, 590) observed complete racemisation in the reaction of *lævo*-αγ-dimethylallyl chloride with the sodium derivatives of benzhydrol (in ethyl ether) and of ethyl malonate (in ethyl alcohol). These racemisations suggest that even the homogeneous replacement reactions are controlled by the unimolecular (ionisation) mechanism; this conclusion is not improbable, in view of the ease with which αγ-disubstituted allyl derivatives react by this mechanism (Balfe, Hills, Kenyon, Phillips, and Platt, J., 1942, 556). On the other hand, the bimolecular mechanism predominates in the reactions of monoalkyl-substituted allyl chlorides with sodium ethoxide, since Hughes (*loc. cit.*) found that no rearrangement occurred during the interaction of α- and γ-methylallyl chlorides with sodium ethoxide in ethyl alcohol (confirmed by Roberts, Young, and Winstein, *J. Amer. Chem. Soc.*, 1942, **64**, 2157).

Reactions of αγ-dimethylallyl chloride.

α^{20}_{5461} (*l*, 1).*	Reactant.	Product.	Optical purity of product, %.	α^{20}_{5461} (*l*, 1).*	Reactant.	Product.	Optical purity of product, %.
$-7.1°$	MeOH	Methyl ether	1·3	$-11.2°$	AgOAc	Acetate	2·1
-2.9	*n*-BuOH	*n*-Butyl ether	1·6	$+6.8$	NaOMe	Methyl ether	3·5
-1.1	KOAc	Acetate	0·3				

* Maximum recorded, 19°.

The hydrolysis of αγ-dimethylallyl chloride by water is kinetically unimolecular (Arcus and Smith, J., 1939, 1748) and would therefore be expected to be accompanied by much racemisation, as are the hydrolyses of γ-methyl-α-propylallyl chloride (Arcus and Kenyon, J., 1938, 1912) and of γ-methyl-α-ethylallyl chloride (Airs, Balfe, and Kenyon, J., 1942, 18). The *lævo*-chloride prepared from the (+) alcohol yields on hydrolysis a *lævo*-alcohol similar in magnitude of rotatory power to the (+)alcohol. This result is unexpected, because optically active halides on hydrolysis usually yield alcohols of the same sign of rotation as that of the parent alcohol.

By methods which produce optically active derivatives from (+)- or (−)-αγ-dimethylallyl alcohol, this *laevo*-alcohol yields a hydrogen phthalate and a methyldibromo-*n*-propylcarbinol, both optically inactive. It, therefore, does not contain the normal form of (−)-αγ-dimethylallyl alcohol. Certain optically active derivatives can, however, be prepared from the *lævo*-alcohol; the acetate has $\alpha^{18}_{5461} - 0.66°$ (*l*, 1) and the reduction product (methyl-*n*-propylcarbinol) has $\alpha^{18}_{5461} + 0.3°$ (*l*, 1); these values are about 2% of those of the corresponding derivatives from (+)-αγ-dimethylallyl alcohol.

These observations are best explained by assuming that the major product of the hydrolysis of the *lævo*-chloride is *dl*-dimethylallyl alcohol, but that it contains some source of optical activity. The occurrence or absence of optical activity in derivatives prepared from this alcohol could then be accounted for by different rates of reaction of the *dl*-alcohol and the optically active substance, or removal of this substance during purification of the derivatives. Our investigations have not revealed the nature of the optically active substance.

During the preparation and hydrolysis of γ-methyl-α-ethyl- and -α-*n*-propyl-allyl chlorides (Airs, Balfe,

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* We use (+) and (−) to refer to the sign of rotatory power of optically pure substances, and *dextro-* and *lævo*- for substances of unspecified optical purity. We define as (+), the αγ-dimethylallyl alcohol which, when freshly prepared from the (+)hydrogen phthalate by hydrolysis with 5N-sodium hydroxide, is dextrorotatory (homogeneous) in the visible spectrum at 20°. The alcohol which Levene and Haller (*loc. cit.*) described as *l*-, because it gave a lævorotatory solution in ethyl ether, is the (+)alcohol, as is shown by the results of Hills, Kenyon, and Phillips (*loc. cit.*).

and Kenyon; Arcus and Kenyon, *locc. cit.*), rearrangement and racemisation occur, without the optical peculiarities observed with αγ-dimethylallyl chloride.

As the following evidence suggests, it appears that a lævorotatory substance is also formed during the mutarotation of (+)-αγ-dimethylallyl alcohol : (i) the mutarotation, though erratic, leads to a fall in rotatory power, with eventual change in sign ((Hills, Kenyon, and Phillips, *loc. cit.*); (ii) a specimen of the alcohol, having $\alpha_{5461}^{20°} + 0.70°$, $\alpha_{5461}^{70°} - 2.66°$, after 48 hours at 70° had $\alpha_{5461}^{70°} - 3.22°$ and, after cooling, $\alpha_{5461}^{20°} + 0.47°$ (*l*, 1); (iii) the alcohol recovered from the interaction of (+)-αγ-dimethylallyl alcohol (1 mol.) and phenyl carbimide (0.5 mol.) is lævorotatory, but from (+)alcohol which has become lævorotatory during muta-rotation the recovered alcohol is also lævorotatory. The last experiment suggests that the *lævo*-substance is present even in the alcohol which we define as (+). This was usually purified by redistillation to b. p. 120—122° and prepared from phthalate which had been several times recrystallised in the form of its brucine salt, and in some cases had also been recrystallised after removal of the brucine. Distillation of the alcohol freshly prepared from the phthalate yields a small fraction of lower b. p. (119—121°) and lower dextrorotation ($\alpha_{5461}^{20°} + 0.18°$, $\alpha_{4358}^{20°} + 1.58°$) than the main fraction (b. p. 121—122°; $\alpha_{5461}^{20°} + 0.60°$, $\alpha_{4358}^{20°} + 2.25°$, *l*, 1), so the lævorotatory substance may have a lower b. p. than αγ-dimethylallyl alcohol (both fractions undergo the characteristic mutarotation). The presence of a lævorotatory substance would be a cause of the anomalous rotatory dispersion (Hills, Kenyon, and Phillips, *loc. cit.*; Levene, and Rothen, *J. Chem. Physics*, 1937, **5**, 980), though this is equally well explained by the unsaturation of the alcohol. On standing, peroxides and acids are formed in the alcohol, but our evidence indicates that the formation of these is not the cause of the mutarotation. Although the boiling range of the crude alcohol suggests the presence of some αγ-dimethylallyl ether (b. p. 156—157°), the above observations were made with alcohol which had been redistilled to a b. p. within 120—122°.

The hydrogen phthalate prepared from the alcohol at various stages of its mutarotation diminishes (by not more than 10%) in rotatory power, but this change is much less marked than that of the parent alcohol, and the sign of rotation of the phthalate is always the same, even when that of the alcohol from which it is prepared has reversed. The very low rotatory power of the alcohol would, of course, be sensitive to the presence of traces of other optically active substances.

Since αγ-dimethylallyl alcohol is the only α-methyl-substituted allyl alcohol which we have examined, we have considered whether its peculiarities may be due to the formation of methylallylcarbinol, through electron release from the α-methyl group (Baker and Nathan, J., 1935, 1844; Hughes, Ingold, and Taher, J., 1940, 949). The properties of the carbinol would agree with this suggestion : it has b. p. 115—116° (Stöhr, *Ber.*, 1939, **72**, 1138), $\alpha_{5893}^{20°} - 4.4$ (*l*, 1), and its hydrogen phthalate has $[\alpha]_{5893} - 7.8°$ in ethyl ether; the last two values are calculated from those given for the *lævo*-carbinol by Levene and Haller (*loc. cit.*), using the ratio between the rotatory power of its reduction product and that of optically pure methyl-*n*-propylcarbinol (Pickard and Kenyon, J., 1911, **99**, 49). However, we have not been able to isolate the α-naphthylurethane of methylallylcarbinol from that of the alcohol obtained from αγ-dimethylallyl chloride or of αγ-dimethylallyl alcohol which has been kept for a long time.

The mutarotation of other substituted allyl alcohols may often involve some racemisation occurring as a concomitant of anionotropic rearrangement. This has been shown to be the cause of the partial racemisation of γ-methyl-α-ethylallyl alcohol (Airs, Balfe, and Kenyon, *loc. cit.*) and may therefore be taken to apply to that of αγ-diethylallyl alcohol (Platt, J., 1941, 316). Owing to the same cause, γ-phenyl-α-methyl-allyl alcohol loses some 10% of its rotatory power during 2 years, as does α-phenyl-γ-methylallyl alcohol (Kenyon, Partridge and Phillips, J., 1937, 207). Similarly, the rotation of a specimen of *lævo*-α-phenylallyl alcohol (Duveen and Kenyon, J., 1939, 1697) changed from $\alpha_{5461}^{20°} - 23.1°$ to $\alpha_{5461}^{20°} - 18.8°$ (*l*, 2) in 4 years; hydrogen phthalates prepared from the alcohol before and after mutarotation had $[\alpha]_{5893} + 37.8°$ and 27.0° (in carbon disulphide). Only in one other case have we observed reversal of sign during mutarotation. A specimen of *lævo*-γ-methyl-α-*n*-propylallyl alcohol (Arcus and Kenyon, J., 1938, 312), during 4 years at room temperature, changed from $\alpha_{5461}^{17°} - 5.44°$ to $\alpha_{5461}^{20°} + 5.40°$ (*l*, 2); hydrogen phthalates from the alcohol before and after mutarotation had $[\alpha]_{5461} - 6.8°$ and $- 2.9°$, respectively, in ethyl alcohol. This change, which merits further investigation, may be due to rearrangement to α-methyl-γ-*n*-propylallyl alcohol (the rotatory power of which is unknown), accompanied by some racemisation.

The above six examples are in harmony with the suggestion that mutarotation of the unsymmetrically substituted allyl alcohols is due to anionotropic rearrangement with concomitant racemisation. This does not explain the mutarotation of αγ-dimethylallyl alcohol. On account of its symmetrical substitution, change in sign of rotation during rearrangement of the (+)alcohol would be due to formation of *lævo*-dimethylallyl alcohol, and a rearranged alcohol should give a *lævo*-phthalate, which is contrary to our observations.

EXPERIMENTAL.

dl-, (+)-, and (−)-αγ-Dimethylallyl alcohols were prepared as described by Hills, Kenyon, and Phillips (*loc. cit.*). *Preparation of αγ-Dimethylallyl Chloride.*—(i) *By means of thionyl chloride.* (+)-αγ-Dimethylallyl alcohol (16 g.) was added slowly to thionyl chloride (22 g.) at 0°. After warming to room temperature, the product was dissolved in ether, washed with water, and the ether removed after drying. The residual αγ-dimethylallyl chloride had b. p. 101°, $n_{5893}^{12°}$ 1.4352 (Found : C, 56.9; H, 8.6; Cl, 33.3. Calc. for C_5H_9Cl : C, 57.4; H, 8.6; Cl, 34.0%). From (−)alcohol with $\alpha_{5893}^{14°} - 0.99°$, $\alpha_{5461}^{14°} - 1.40°$, $\alpha_{4358}^{14°} - 3.78°$ (*l*, 2), the chloride had $\alpha_{5893} + 0.21°$, $\alpha_{5461} + 0.29°$ (*l*, 2), and gave on hydrolysis an alcohol with $\alpha_{5893}^{20°} + 0.12°$, $\alpha_{5461}^{20°} + 0.19°$ (*l*, 0.25). A similar experiment, in which the (−)alcohol (25 g.)

was first dissolved in a mixture of dry ether (100 c.c.) and pyridine (26·5 g.), gave 14 g. of chloride, b. p. 22°/14 mm., $a_{5893}^{20°} + 31·3°$, $a_{5461}^{20°} + 38·4°$, $a_{4358}^{20°} + 74·0°$ (l, 2).

(ii) *By means of phosphorus trichloride and pyridine.* This is the better method. A mixture of the alcohol (32·6 g.) and pyridine (6·8 g.) was run slowly into redistilled phosphorus trichloride (20 g.) at 0°. After warming to room temperature, the upper layer was separated and distilled, yielding 23 g. of chloride, b. p. 20°/12 mm. From *dextro*-alcohol, $a_{5893}^{16°} + 1·12°$, $a_{5461}^{16°} + 1·63°$, $a_{4358}^{16°} + 4·94°$ (l, 2), the chloride had $a_{5893}^{17°} - 8·92°$, $a_{5461}^{17°} - 10·74°$ (l, 2). From *dextro*-alcohol, $a_{5893}^{21°} + 0·52°$, $a_{5461}^{21°} 0·84°$, $a_{5461}^{21°} + 1·18°$, $a_{4358}^{21°} + 4·30°$ (l, 2), the chloride had $a_{5893}^{18°} - 4·61°$, $a_{5780}^{18°} - 4·87°$, $a_{5461}^{18°} - 5·59°$, $a_{4358}^{18°} - 10·65$ (l, 0·5). From *lævo*-alcohol, $a_{5461}^{19°} - 0·70°$ (l, 0·5), a chloride was obtained with $a_{5893}^{18°} + 12·09°$, $a_{5461}^{18°} + 14·75°$, $a_{4358}^{18°} + 28·1°$ (l, 2). In the absence of pyridine, reaction with phosphorus trichloride yields a racemic chloride. The chloride is a pungent liquid which evolves hydrogen chloride, particularly on heating, and the decrease in its rotatory power with increasing temperature is probably due to decomposition.

Reactions of αγ-Dimethylallyl Chloride.—(i) *With methyl alcohol.* The chloride (4·5 g.), $a_{5461}^{16°} - 15·14°$ (l, 2), prepared from (+)alcohol, was shaken intermittently during 24 hours with dry methyl alcohol (20 c.c.) and calcium carbonate (2·3 g.). The mixture was then gently warmed, treated with anhydrous calcium chloride to remove excess of methyl alcohol, and then extracted with ether. From the dried ethereal extract, methyl αγ-dimethylallyl ether (2·5 g.) was obtained; b. p. 89—89·5°, $n_{5893}^{14·5°}$ 1·4031, $a_{5893}^{18°} - 0·33°$, $a_{5780}°-0·36°$, $a_{5461}^{18°} - 0·38°$, $a_{4358}^{18°} - 0·50°$ (l, 0·5).

(ii) *With n-butyl alcohol.* The chloride (4 g.), $a_{5461} + 1·47°$ (l, 0·5), was warmed for 3 hours on the steam-bath with *n*-butyl alcohol (15 c.c.) and calcium carbonate (2 g.). The cooled product was diluted with ether and filtered; from the dried filtrate *n*-butyl αγ-dimethylallyl ether was obtained, b. p. 150—151°, $n_{5893}^{18°}$ 1·4100, $a_{5461}^{17°} + 0·24°$ (l, 0·5).

(iii) *With potassium acetate.* The chloride (5 g.), $a_{5461}^{20°} - 0·54°$ (l, 0·5), was warmed on the steam-bath with potassium acetate (8 g.) which had been moistened with water. Calcium carbonate was added and the mixture extracted with ether. The dried, filtered extract was distilled. Redistillation of the fraction, b. p. 120—140°, gave αγ-dimethylallyl acetate (2 g.), b. p. 135—136°, $n_{5893}^{15°}$ 1·4200, $a_{5461}^{15°} + 0·10°$, $a_{5893}^{15°} + 0·08°$ (l, 0·5). The chloride did not react with dry potassium acetate, in the absence of solvent or with acetone or benzene as diluents.

(iv) *With silver acetate.* The chloride (4 g.), $a_{5893}^{18°} - 4·61°$, $a_{5461}^{18°} - 5·59°$, $a_{4358}^{18°} - 10·65°$ (l, 0·5), was triturated with 17 g. of silver acetate at 0°; a vigorous reaction occurred. The mixture was diluted with ether, filtered, dried (calcium chloride), and distilled. The αγ-dimethylallyl acetate produced had, after redistillation, b. p. 37—40°/15 mm., $n_{5893}^{19°}$ 1·4112, $a_{5893}^{18°} - 0·28°$, $a_{5780}^{18°} - 0·30°$, $a_{5461}^{18°} - 0·35°$, $a_{4358}^{18°} - 0·66°$ (l, 0·25).

(v) *With sodium methoxide.* *lævo*-αγ-Dimethylallyl alcohol (16·3 g.), $a_{5461}^{20°} - 0·51°$ (l, 1), prepared from phthalate of $[a]_{5461} - 20·4°$ in chloroform, was converted (pyridine-phosphorus trichloride) into the chloride (11 g.; $a_{5461}^{22°} + 6·76°$, l, 1); this (5 g.) was warmed for 5 mins. with sodium methoxide (2·5 mols.) in methyl alcohol (50 c.c.), the solution diluted with water, and extracted with ether. From the dried ethereal extract, methyl αγ-dimethylallyl ether (2 g.) was obtained, b. p. 90—91°/760 mm., $n_{5893}^{21°}$ 1·4243, $a_{5461}^{21°} + 0·50°$ (l, 0·25).

Hydrolysis of αγ-Dimethylallyl Chloride.—This was conducted with an aqueous suspension of calcium carbonate (Hills, Kenyon, and Phillips, *loc. cit.*). (i) Chloride of $a_{4358}^{18°} + 28·1°$ (l, 2) (see above) gave alcohol of b. p. 120°, $n_{5893}^{18°}$ 1·4288, $a_{5893}^{17°} + 1·50°$, $a_{5461}^{17°} + 1·66°$, $a_{4358}^{17°} + 2·90°$ (l, 2) (Found : C, 69·4; H, 11·6. Calc. for $C_5H_{10}O$: C, 69·8; H, 11·6%). Other results are summarised below :

αγ-Dimethylallyl alcohol.		αγ-Dimethylallyl chloride.		Alcohol obtained from the chloride.	
$a_{5461}^{t°}$; l, 1.	t.	$a_{5461}^{t°}$; l, 1.	t.	$a_{5461}^{t°}$; l, 1.	t.
−0·15°	22°	+0·64°	22°	+0·14°	22°
−0·13	20	+0·44	20	+0·18	21
−0·21	22	+6·40	20	+0·54	18
−0·13	20	+3·91	12	+0·73	15
−0·35	20	+4·66	19	+0·74	17
−0·35	20	+7·37	18	+0·90	18

(ii) A specimen of the (+)alcohol (originally $a_{5461}^{22°} + 0·10°$; l, 0·25), which after mutarotation for 20 months had $a_{5461}^{9°} - 1·05°$ (l, 1), gave a chloride of $a_{5461}^{19°} - 1·02°$ (l, 1) from which, on hydrolysis, alcohol of $a_{5461}^{19°} - 0·08°$ (l, 1) was obtained.

The alcohols obtained from αγ-dimethylallyl chloride did not change in rotatory power when kept for many months, and their rotatory power is not very sensitive to temperature; *e.g.*, a specimen had $a_{5461}^{12°} + 1·45°$, $a_{5461}^{24°} + 1·56°$, whereas (+)-αγ-dimethylallyl alcohol has $a_{5461}^{12°} + 2·00°$, $a_{5461}^{24°} + 0·65°$ (l, 2). The rotatory powers of the two alcohols are affected in the opposite sense by temperature.

Derivatives of the Alcohol obtained by Hydrolysis of αγ-Dimethylallyl Chloride.—(i) *Hydrogen phthalate.* A number of preparations were made (*e.g.*, from the alcohols in the last double column of foregoing table) by the usual method, with phthalic anhydride and pyridine (Hills, Kenyon, and Phillips, *loc. cit.*). The phthalate did not crystallise well. Some preparations were extracted with carbon disulphide [in which the (+)- and (−)-phthalates are more soluble than the *dl*-]; others were dissolved in ethyl alcohol or in chloroform. All the solutions were optically inactive in the visible spectrum.

(ii) *p-Nitrobenzoate.* This (4·3 g.) was obtained from the alcohol (1·7 g.), $a_{5461} + 1·46°$ (l, 2), by Einhorn's method. The crude ester (m. p. 52—54°) was optically inactive in ethyl alcohol (*c*, 10·0; *l*, 2); after recrystallisation from aqueous alcohol it had m. p. 56°, alone or mixed with authentic *dl*-αγ-dimethylallyl *p*-nitrobenzoate.

(iii) *Acetate.* The alcohol (3 g.), $a_{5893}^{20°} + 1·20°$, $a_{5461}^{20°} + 1·49°$, $a_{4358}^{20°} + 2·55°$ (l, 2), was mixed with pyridine (3·5 g.) and acetic anhydride (4·2 g.). The rotatory power of the solution ($a_{5461} + 0·60°$; l, 2) did not change during 2 days; the mixture was then warmed for 2 hours on the steam-bath, dissolved in ether, and the solution washed, dried, and distilled. On redistillation, the acetate had b. p. 136—137°, $n_{5893}^{19°}$ 1·4179, $a_{5893}^{18°} + 0·29°$, $a_{5780}^{18°} + 0·31°$, $a_{5461}^{18°} + 0·33°$, $a_{4358}^{18°} + 0·55°$ (l, 0·5).

(iv) *Benzoate.* Prepared by Einhorn's method from alcohol (3 g.) with $a_{5893}^{20°} + 1·20°$, $a_{5780}^{20°} + 1·34°$, $a_{5461}^{20°} + 1·49°$, $a_{4358}^{20°} + 2·55°$ (l, 2), 5·5 g. of *dl*-benzoate were obtained after redistillation; b. p. 140°/21 mm., $n_{5893}^{23°}$ 1·5075. From alcohol with $a_{5893}^{21°} + 0·05°$, $a_{5461}^{21°} + 0·09°$, $a_{4358}^{21°} + 0·16°$ (l, 0·5), the benzoate had b. p. 124°/13 mm., $a_{5893}^{16°} - 0·04°$, $a_{5461}^{16°} - 0·06°$, $a_{4358}^{16°} - 0·17°$ (l, 0·5). From alcohol with $a_{5893}^{19°} - 0·16°$, $a_{5461}^{19°} - 0·11°$ (l, 0·5), the benzoate had b. p. 126°/14 mm., $n_{5893}^{16°}$ 1·5084, $a_{5893}^{16°} + 0·10°$, $a_{5461}^{16°} + 0·14°$, $a_{4358}^{16°} + 0·42°$ (l, 0·5). The same specimen of alcohol gave an optically inactive hydrogen phthalate.

(v) *Reduction to methyl-n-propylcarbinol.* The alcohol ($a_{5893}^{17°} + 1·50°$, $a_{5461}^{17°} + 1·66°$, $a_{4358}^{17°} + 2·9°$; l, 2) absorbed the theoretical amount of hydrogen within 5 mins. in presence of Adams's platinum oxide catalyst. The resulting methyl-*n*-propylcarbinol had b. p. 118°, $n_{5893}^{17·5°}$ 1·4061, $a_{5893}^{18°} - 0·15°$ (l, 0·5). Pickard and Kenyon (J., 1911, **99**, 49) give $a_{5893}^{20°} + 11·10°$ (l, 1) for the optically pure carbinol.

Partially Racemised Derivatives prepared from the (+)Alcohol which has undergone Mutarotation.—(i) *Hydrogen phthalate.* See Hills, Kenyon, and Phillips (*loc. cit.*).

(ii) *Benzoate.* A specimen of the (+)alcohol, with $\alpha_{5461}^{14^\circ} + 1\cdot76^\circ$ (*l*, 2) when freshly prepared, had $\alpha_{5461}^{21^\circ} - 7\cdot03^\circ$ (*l*, 2) after 18 months. It was then converted into the benzoate (Einhorn's method), which had b. p. 137—138°/18 mm., $n_{5893}^{23^\circ}$ 1·5078, $\alpha_{5893}^{24^\circ} + 7\cdot38^\circ$, $\alpha_{5780}^{24^\circ} + 7\cdot97^\circ$, $\alpha_{5461}^{24^\circ} + 9\cdot41^\circ$, $\alpha_{4358}^{24^\circ} + 21\cdot00^\circ$ (*l*, 0·5).

(iii) *Methyl-n-propylcarbinol.* $\alpha\gamma$-Dimethylallyl alcohol having $\alpha_{5461}^{20^\circ} - 0\cdot16^\circ$ (*l*, 2) 15 months after its preparation from the (+)phthalate was reduced in the presence of platinum oxide to methyl-*n*-propylcarbinol, b. p. 117—118°, $n_{5893}^{14\cdot5^\circ}$ 1·4077, $\alpha_{5893}^{17^\circ} + 5\cdot02^\circ$, $\alpha_{5780}^{17^\circ} + 5\cdot22^\circ$, $\alpha_{5461}^{17^\circ}$ 5·89°, $\alpha_{4358}^{17^\circ} + 9\cdot7^\circ$ (*l*, 0·5).

$\alpha\gamma$-*Dimethylallyl phenylurethane* was prepared by mixing the alcohol (2 mols.) and phenylcarbimide (1 mol.) and after 5 days at room temperature removing the excess of alcohol by distillation under reduced pressure (b. p. 35°/12 mm.), the alcohol then being redistilled at atmospheric pressure; the residual urethane either crystallised (in a mass of fine, oblong needles, very soluble in light petroleum) or was isolated by distillation. (i) From the (−)alcohol with $\alpha_{5893}^{19^\circ} - 0\cdot05^\circ$, $\alpha_{5461}^{19^\circ} - 0\cdot10^\circ$, $\alpha_{4358}^{19^\circ} - 0\cdot56^\circ$ (*l*, 0·5), the recovered alcohol had b. p. 120—122°, $n_{5893}^{18\cdot5^\circ}$ 1·4309, $\alpha_{5893}^{19^\circ} + 0\cdot04^\circ$, $\alpha_{5461}^{19^\circ} + 0\cdot16^\circ$, $\alpha_{4358}^{19^\circ} + 0\cdot35^\circ$ (*l*, 0·5).

(ii) From the (+)alcohol, which 7 weeks after its separation from the phthalate had $\alpha_{5461}^{17^\circ} + 1\cdot46^\circ$ (*l*, 2), the recovered alcohol had $\alpha_{5461}^{13^\circ} + 1\cdot84^\circ$ (*l*, 2) which, by calculation from figures given by Hills, Kenyon, and Phillips (*loc. cit.*), corresponds to $\alpha_{5461}^{17^\circ} + 1\cdot41^\circ$. After redistillation the alcohol had b. p. 119·5—120°, $\alpha_{5893}^{18^\circ} + 0\cdot57^\circ$, $\alpha_{5461}^{18^\circ} + 1\cdot00^\circ$, $\alpha_{4358}^{18^\circ} + 4\cdot00^\circ$ (*l*, 2), and 118 days after redistillation, $\alpha_{5893}^{21^\circ} - 0\cdot78^\circ$, $\alpha_{5461}^{21^\circ} - 0\cdot63^\circ$, $\alpha_{4358}^{21^\circ} + 0\cdot80^\circ$ (*l*, 2). The urethane crystallised, m. p. 32°, $[\alpha]_{5893}^{20^\circ} - 72\cdot6^\circ$, $[\alpha]_{5461}^{20^\circ} - 76\cdot5^\circ$, $[\alpha]_{5780}^{29^\circ} - 87\cdot9^\circ$, $[\alpha]_{4358}^{20^\circ} - 162\cdot5^\circ$ in carbon disulphide (*l*, 2) (*c*, 5·28) (Found : N, 6·8. $C_{12}H_{15}O_2N$ requires N, 6·8%).

(iii) From *lævo*-$\alpha\gamma$-dimethylallyl alcohol (obtained from hydrogen phthalate of $[\alpha]_{5461}^{20^\circ} - 15\cdot7^\circ$ in chloroform). The original alcohol had $\alpha_{5893}^{20^\circ} - 0\cdot20^\circ$, $\alpha_{5461}^{20^\circ} - 0\cdot38^\circ$, $\alpha_{4358}^{20^\circ} - 1\cdot63^\circ$ (*l*, 2) and the recovered alcohol had $n_{5893}^{20^\circ}$ 1·4279, $\alpha_{5893}^{20^\circ} + 0\cdot05^\circ$, $\alpha_{5461}^{20^\circ} + 0\cdot08^\circ$, $\alpha_{4358}^{20^\circ} + 0\cdot22^\circ$ (*l*, 0·5); it gave a hydrogen phthalate with $[\alpha]_{5893}^{20^\circ} - 12\cdot6^\circ$, $[\alpha]_{5461}^{20^\circ} - 16\cdot8^\circ$, $[\alpha]_{4358}^{20^\circ} - 39\cdot7^\circ$ in chloroform. The urethane crystallised with difficulty; it had $n_{5780}^{20^\circ}$ 1·5422 (supercooled), $[\alpha]_{5893}^{20^\circ} + 2\cdot5^\circ$, $[\alpha]_{5461}^{20^\circ} + 3\cdot2^\circ$, $[\alpha]_{4358}^{20^\circ} + 11\cdot4^\circ$ (*l*, 0·5; *c*, 10·4 in ethyl alcohol) (Found : N, 6·6%).

(iv) (+)Alcohol, which originally had $\alpha_{5893}^{20^\circ} + 0\cdot23^\circ$, $\alpha_{5461}^{20^\circ} + 0\cdot46^\circ$, $\alpha_{4358}^{20^\circ} + 1\cdot82^\circ$ (*l*, 1), had after 201 days $\alpha_{5893}^{17^\circ} - 0\cdot43^\circ$, $\alpha_{5461}^{17^\circ} - 0\cdot38^\circ$, $\alpha_{4358}^{17^\circ} + 0\cdot49^\circ$ (*l*, 2) and was then converted into the urethane. The residual alcohol had $\alpha_{5893}^{20^\circ} - 0\cdot42^\circ$, $\alpha_{5461}^{20^\circ} - 0\cdot36^\circ$, $\alpha_{4358}^{20^\circ} - 0\cdot25^\circ$, (*l*, 0·25) and gave a hydrogen phthalate with $[\alpha]_{5893}^{20^\circ} + 18\cdot5^\circ$, $[\alpha]_{5461}^{20^\circ} + 24\cdot5^\circ$, $[\alpha]_{4358}^{20^\circ} + 52\cdot5^\circ$ (*l*, 2; *c*, 4·15 in chloroform). The urethane (b. p. 174°/18 mm.) had $\alpha_{5893}^{20^\circ} - 6\cdot02^\circ$, $\alpha_{5461}^{20^\circ} - 7\cdot40^\circ$ (*l*, 0·5; homogeneous) and $[\alpha]_{5893}^{20^\circ} - 3\cdot3^\circ$, $[\alpha]_{5461}^{20^\circ} - 4\cdot3^\circ$ (*l*, 0·5; *c*, 10 in ethyl alcohol) (Found : C, 70·9; H, 7·7. $C_{12}H_{15}O_2N$ requires C, 70·0; H, 7·5%).

Presence of Peroxides in Old Samples of the Alcohol.—A year after preparation from the phthalate, samples of $\alpha\gamma$-dimethylallyl alcohol gave positive reactions for peroxides by the method of Kharasch and Mayo (*J. Amer. Chem. Soc.*, 1933, **55**, 2468), but addition of 0·2% of the pro-oxygen benzoyl peroxide, or the anti-oxygen diphenylamine, did not affect the rate of mutarotation of the (+)alcohol.

Attempts to Isolate an Optically Active Acid Fraction from $\alpha\gamma$-Dimethylallyl Alcohol.—A number of specimens of the alcohol which had undergone mutarotation were dissolved in ethyl ether and washed with aqueous alkalis; the washings were in all cases optically inactive.

α-Naphthylurethane of $\alpha\gamma$-Dimethylallyl Alcohol.—Levene and Haller (*loc. cit.*) obtained the urethane prepared from the *dextro*-alcohol in two fractions, m. p. 109—113° and 130° severally; the latter had the higher rotatory power. We find the *dl*-urethane from alcohol freshly prepared from the hydrogen phthalate to have m. p. 105°.

α-Naphthylurethane of dl-Methylallylcarbinol.—The urethane obtained by combination of the carbimide (2 g.) and the alcohol (1 g.) at room temperature was extracted with hot *cyclo*hexane. The extract deposited two types of crystal, bulky clusters of soft needles, m. p. 46—47°, and hard glassy tablets, m. p. 62° (Found : N, 5·4. Calc. for $C_{10}H_{17}O_2N$: N, 5·5%). These could be separated by the readier solubility of the former in hot light petroleum, but recrystallisation of either form from petroleum gave a mixture of both. It would appear, therefore, that they are isomorphous forms of the same compound. Levene and Haller (*J. Biol. Chem.*, 1929, **81**, 425) give 47—49° as the m. p. of the urethane prepared from *lævo*-carbinol.

Attempts to Fractionate the α-Naphthylurethane of $\alpha\gamma$-Dimethylallyl Alcohol.—A specimen of the *dl*-alcohol which had been stored for 18 months was taken to represent alcohol which had undergone mutarotation. It gave a urethane of m. p. 105° after recrystallisation, and no fraction of lower m. p. could be isolated from the mother-liquors.

α-Naphthylurethane of the Alcohol prepared by Hydrolysis of dl-$\alpha\gamma$-Dimethylallyl Chloride.—The alcohol (14·3 g., b. p. 118—120°) readily combined with α-naphthylcarbimide (29 g.). The resultant solid was extracted several times with boiling ether (200 c.c.), and the extract evaporated to about 50 c.c., yielding $\alpha\gamma$-dimethylallyl naphthylurethane (13·5 g.), m. p. 98—101° raised to m. p. and mixed m. p. 105° by one recrystallisation. The filtrate from the crude urethane was evaporated to dryness, the crystalline residue extracted with boiling light petroleum (40 c.c.), and the extract allowed to evaporate at room temperature until its volume was about 5 c.c.; the crystalline crop of rosettes of short needles had m. p. 98—100°. The filtrate was allowed to evaporate down to about 1 c.c., and the crystalline crop of needles showed no signs of softening until 92° and had m. p. 92—97°.

Fractional Distillation of the Alcohol obtained from $\alpha\gamma$-Dimethylallyl Chloride.—Alcohol obtained from *dl*-chloride by the above method was separated by slow distillation into the following fractions : b. p. 80—115° (1 c.c.); 118—122° (14 c.c.); 124—129° (1 c.c.); 130—160° (0·5 c.c.).

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