

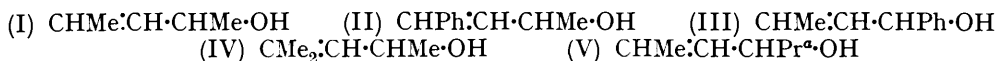
**63. *The Resolution of n-Propylpropenylcarbinol. The Refractivity and Optical Rotatory Dispersion of some Substituted Allyl Alcohols.***

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The resolution of *n*-propylpropenylcarbinol ( $\gamma$ -methyl- $\alpha$ -propylallyl alcohol) into its optically active forms, and the properties of some derivatives of the latter, are described.

Comparison of its molecular refractivity and optical rotatory dispersion is made with those of four other optically active substituted allyl alcohols. It is considered probable that these alcohols have the *trans*-configuration. Evidence is adduced that, although the optical rotatory dispersion of the purely alkyl-substituted allyl alcohols is complex, that of the phenyl-substituted allyl alcohols is simple, and it is suggested that a large proportion of the rotatory power of the latter group of compounds is due to induced dissymmetry of the phenyl radical.

SEVERAL investigations, dealing with the chemical and optical properties of optically active substituted allyl alcohols, which have arisen from the peculiar behaviour of  $\alpha\gamma$ -dimethylallyl alcohol (I) (Hills, Kenyon, and Phillips, J., 1936, 576) have recently appeared [ $\gamma$ -phenyl- $\alpha$ -methylallyl alcohol (II), Kenyon, Partridge, and Phillips, *ibid.*, p. 85;  $\alpha$ -phenyl- $\gamma$ -methylallyl alcohol (III), *idem*, J., 1937, 207;  $\alpha\gamma\gamma$ -trimethylallyl alcohol (IV), Duveen and Kenyon, J., 1936, 1451] and in furtherance of these studies optically active *n*-propylpropenylcarbinol ( $\gamma$ -methyl- $\alpha$ -*n*-propylallyl alcohol) (V) has now been examined.



*dl-n*-Propylpropenylcarbinol has been described by Reif (*Ber.*, 1906, **39**, 1603) and the refractivity of a pure specimen was determined by Auwers and Westermann (*Ber.*, 1921,

54, 2993). A partial resolution of the alcohol by the fractional crystallisation of the brucine salt of its hydrogen phthalic ester was effected by Levene and Marker (*J. Biol. Chem.*, 1934, 106, 173), but the maximum rotatory power obtained was only some 8% of that now reported.

A satisfactory resolution by means of the brucine salt could not be effected, although several procedures were tried. Complete resolution was eventually obtained by fractional crystallisation from dry acetone of the strychnine salt of the hydrogen phthalic ester, followed by fractional crystallisation of the *d* + *dl*- and *l* + *dl*-esters obtained by decomposition of the less soluble and the more soluble fractions, respectively, of the strychnine salt. The *d*- and *l*-hydrogen phthalic esters, when hydrolysed with sodium hydroxide, yielded the corresponding optically active alcohols, the rotatory powers of which under different experimental conditions are recorded in Tables I, II, and III. The acetic and benzoic esters and the methyl ether of the *d*\*-alcohol have been prepared and their rotatory powers are recorded in Tables V—VII.

As experiments are at present in progress on the replacement reactions of this alcohol and its esters whereby a rearrangement to the isomeric  $\alpha$ -methyl- $\gamma$ -*n*-propylallyl alcohol (CHPr<sup>o</sup>:CH-CHMe-OH) and its esters may occur, it was considered expedient to establish the homogeneity of the optically active alcohol and esters, since rearrangement may occur both during the production of the intermediate *dl*-hydrogen phthalic ester (Kenyon, Partridge, and Phillips, *J.*, 1937, 207) and also during the esterification of the alcohol obtained therefrom by hydrolysis. Accordingly these substances were catalytically reduced; the optically active forms then yielded optically inactive di-*n*-propylcarbinol and its esters respectively, indicating the original substances to be free from structural isomerides.

*Optical Rotatory Dispersion of n-Propylpropenylcarbinol and its Derivatives.*—The optical rotatory dispersion of *n*-propylpropenylcarbinol in the homogeneous state at 16° (Table I) may be represented, within the limits of experimental error, by the equation

$$\alpha = 1.027/(\lambda^2 - 0.0723); \lambda_0 = 2690 \text{ \AA.}$$

The simplicity can only be apparent, for the rotatory dispersions of solutions of the alcohol show obvious complexity when  $1/\alpha$  is plotted against  $\lambda^2$  and the solution in benzene shows a reversal of sign of rotation (Table II).

TABLE I.

*Rotatory Powers of (+)n-Propylpropenylcarbinol at 16° (l, 0.5).*

$\lambda$ .	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	$\alpha_{\text{obs.}} - \alpha_{\text{calc.}}$	$\lambda$ .	$\alpha_{\text{obs.}}$	$\alpha_{\text{calc.}}$	$\alpha_{\text{obs.}} - \alpha_{\text{calc.}}$
6438	+2.98°	+3.00°	-0.02°	5086	+5.48°	+5.51°	-0.03°
5893	3.68	3.73	-0.05	4800	6.40	6.49	-0.09
5780	3.96	3.90	+0.06	4678	6.82	7.00	-0.18
5461	4.58	4.54	+0.04	4358	8.76	8.73	+0.03

TABLE II.

*Specific Rotatory Powers of (+)n-Propylpropenylcarbinol in Various Solvents at Room Temperature (l, 2.0).*

Solvent.	<i>t</i> .	<i>c</i> .	$[\alpha]_{6438}$ .	$[\alpha]_{5893}$ .	$[\alpha]_{5461}$ .	$[\alpha]_{4358}$ .
Benzene .....	19°	4.830	-1.86°	-0.21°	+0.72°	+2.69°
Chloroform .....	20	5.245	-7.53	-7.72	-8.30	-13.25
Carbon disulphide .....	21	5.935	+3.37	+6.24	+8.26	+17.6
Pyridine .....	22	4.615	+11.5	+15.8	+19.9	+39.4

Furthermore, the magnitude of the rotatory power of the alcohol in the homogeneous state is much reduced with increase of temperature (Table III) and the dispersion ratio  $\alpha_{4358}/\alpha_{5461}$  increases from 1.92 at 16° to 2.09 at 65° and to 2.24 at 95°, showing the sensitivity to temperature change (and solvent influence) associated with complex rotatory dispersion.

\* In the introductory part of this communication rotatory powers are given for derivatives of the *d*(+)-alcohol, although in some cases the experimental data were determined by using derivatives of opposite configuration.

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No evidence of mutarotation was observed and the alcohol retained its original rotatory power after being kept at 34—39° for 15 days.

TABLE III.

*Rotatory Power of (+)n-Propylpropenylcarbinol at Different Temperatures (l, 0.5).*

<i>t.</i>	$\alpha_{5893}$	$\alpha_{5461}$	$\alpha_{4358}$	<i>t.</i>	$\alpha_{5893}$	$\alpha_{5461}$	$\alpha_{4358}$
16°	+3.68°	+4.58°	+8.76°	65°	+1.88°	+2.35°	+4.90°
26	3.37	4.12	8.05	70	1.69	2.13	4.49
36.5	2.92	3.65	7.23	95	1.01	1.32	2.95
45.5	2.56	3.16	6.35	5 *	4.22	5.13	9.69
54	2.23	2.83	5.66				

\* After cooling.

The rotatory powers of (+)*n*-propylpropenylcarbinyl hydrogen phthalate in various solvents (Table IV) indicate pronounced complex rotatory dispersion when  $1/\alpha$  is plotted against  $\lambda^2$ ; the corresponding benzoic ester in the homogeneous state (Table V) shows a slightly complex rotatory dispersion.

TABLE IV.

*Specific Rotatory Powers of (+)n-Propylpropenylcarbinyl Hydrogen Phthalate in Various Solvents at Room Temperature (l, 2.0).*

Solvent.	<i>t.</i>	<i>c.</i>	$[\alpha]_{6438}$	$[\alpha]_{5893}$	$[\alpha]_{5780}$	$[\alpha]_{5461}$	$[\alpha]_{4358}$
Alcohol .....	16°	4.550	+13.3°	+17.05°	—	+22.85°	+46.4°
Benzene .....	20	4.275	—	+ 6.67	+ 8.31°	+ 9.59	+23.0
Chloroform .....	19	4.815	—	+ 4.26	+ 5.19	+ 6.33	+17.4
Carbon disulphide .....	20	4.38	—	-14.7	-15.2	-16.8	-32.0

TABLE V.

*Rotatory Power of (+)n-Propylpropenylcarbinyl Benzoate (l, 0.5; t, 20°).*

$\lambda$	6438	5893	5780	5461	5086	4800	4678	4358
$\alpha_{obs.}$	+6.47°	+8.50°	+9.19°	+11.16°	+14.00°	+17.39°	+19.05°	+25.76°

The rotatory dispersion of (–)*n*-propylpropenylcarbinyl acetate in the homogeneous state (Table VI) can, however, be accurately represented by the equation

$$\alpha = -6.14/(\lambda^2 - 0.0452); \lambda_0 = 2120 \text{ A.}$$

It appears, therefore, that under these conditions the rotatory power is predominately due to the induced dissymmetry of the  $-C \begin{matrix} \diagup O \\ \diagdown O \end{matrix}$  radical, which has an absorption band at 2100 A. (Lowry, "Optical Rotatory Power," 1935, p. 266).

TABLE VI.

*Rotatory Powers of (–)n-Propylpropenylcarbinyl Acetate in the Homogeneous State at 21° (l, 0.5).*

$\lambda$	$\alpha_{obs.}$	$\alpha_{calc.}$	$\alpha_{obs.} - \alpha_{calc.}$	$\lambda$	$\alpha_{obs.}$	$\alpha_{calc.}$	$\alpha_{obs.} - \alpha_{calc.}$
6438	-16.52°	-16.64°	+0.12°	5086	-28.9°	-28.8°	-0.1°
5893	20.35	20.33	+0.02	4800	33.3	33.2	-0.1
5780	21.25	21.26	+0.01	4678	35.4	35.4	±0.0
5461	24.28	24.30	+0.02	4358	42.4	42.4	±0.0

TABLE VII.

*Rotatory Powers of (–)n-Propylpropenylcarbinyl Methyl Ether at 26° (l, 0.25).*

$\lambda$	$\alpha_{obs.}$	$\alpha_{calc.}$	$\alpha_{obs.} - \alpha_{calc.}$	$\lambda$	$\alpha_{obs.}$	$\alpha_{calc.}$	$\alpha_{obs.} - \alpha_{calc.}$
6438	- 8.14°	- 8.48°	+0.34°	5086	-13.55°	-13.83°	+0.28°
5893	- 9.89	-10.2	+0.31	4800	-15.36	-15.62	+0.26
5780	-10.98	-10.6	-0.38	4678	-16.10	-16.50	+0.40
5461	-12.00	-11.92	-0.08	4358	-19.67	-19.17	-0.50

The rotatory dispersion of (–)*n*-propylpropenylcarbinyl methyl ether (Table VII) can be represented by a single-term Drude equation,  $\alpha = -3.42/(\lambda^2 - 0.0113)$ , but the small value of the dispersion constant,  $\lambda_0^2 = 0.0113$ , raises a suspicion that two terms of opposite sign may be necessary to express the dispersion over a more extended range of observations.

*The Optical Properties of Substituted Allyl Alcohols.*—The investigations recorded in the first paragraph have been directed primarily towards the study of the reactions of optically active substituted allyl alcohols, but many optical data have also been recorded and some relationships are indicated below.

TABLE VIII.  
*Molecular Refractivities.*

Compound.	<i>t.</i>	$n_D^{20}$	$d_4^{20}$	$[R]_D$ obs.	$[R]_D$ calc.
CHMe:CH·CHMe·OH *	18°	1.4282	0.8382	26.44	26.35
CHMe:CH·CHPr <sup>α</sup> ·OH *	14.4	1.4397	0.8422	35.69	35.58
CMe <sub>2</sub> :CH·CHMe·OH	17	1.4297	0.8461	30.51	30.97
CHMe:CH·CHMe·OAc	26	1.4143	0.8931 (at 25°)	35.83	35.71
CHMe:CH·CHPr <sup>α</sup> ·OAc	17	1.4270	0.8815 (at 20°)	45.33	44.95

\* Auwers and Westermann (*loc. cit.*). The calculated values are obtained by means of the constants of Eisenlohr (*Z. physikal. Chem.*, 1911, **75**, 605). In the last two examples, the densities are adjusted to the temperature at which the refractive index is determined (–0.0008 unit for +1°).

The agreement with the values calculated from the open-chain formulæ given above appears satisfactory.

In order to account for various reactions and for values in the observed parachors of  $\alpha\gamma$ -dimethylallyl alcohol it was tentatively suggested that this substance might contain a large proportion of the isomeric inner ether,  $\begin{matrix} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Me} \end{matrix} < \begin{matrix} \text{CH}_2 \\ \diagdown \\ \text{O} \\ \diagup \end{matrix} > \begin{matrix} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H} \end{matrix}$ . A compound of this constitution should have  $[R]_D$  25.21; analogous structures for the other alcohols in Table VIII would have values of  $[R]_D$  lower by 1.14 units than those recorded (the value used for a four-membered ring is +0.48, as determined by Östling; *J.*, 1912, **101**, 457). It now appears that the ethylenic link cannot be absent and accordingly a formulation of these compounds is being developed in which the ethylenic character is distributed between the  $\alpha\beta$ - and the  $\beta\gamma$ -linkage.

*Geometrical Configurations.*—Alcohols (I), (II), (III), and (V) are considered to be *trans*-isomerides on the following evidence; (I), (III), and (V) are prepared by the interaction of the appropriate Grignard reagent and crotonaldehyde. This aldehyde, obtained by the dehydration of aldol, was found by Kaufler (*Monatsh.*, 1929, **53**, 119) to yield on oxidation principally crotonic acid (*trans*-), together with some *isocrotonic* acid; Blacet, Young, and Roof (*J. Amer. Chem. Soc.*, 1937, **59**, 608), however, have concluded that purified commercial crotonaldehyde consists solely of the *trans*-isomeride, since the ultra-violet absorption spectrum remains unaltered after the crotonaldehyde has been submitted to such treatment as would alter the ratio *cis*- to *trans*- if a certain proportion of the former isomeride were originally present. Alcohol (II) is prepared similarly from cinnamaldehyde, which also should possess the *trans*-configuration, since it is converted by aerial oxidation into cinnamic acid (*trans*-). None of the subsequent operations involved in the resolution of the hydrogen phthalic esters appears likely to cause geometrical inversion and no indications that these carbinols are mixtures of geometrical isomerides have appeared. The *d*- and the *l*-form of  $\gamma$ -phenyl- $\alpha$ -methylallyl alcohol are solids which crystallise readily from various solvents, but an exhaustive research failed to effect any separation.

*Rotatory Dispersion.*—The range of wave-lengths for which data are available may in some cases be too restricted for the detection of smaller deviations from simplicity of rotatory dispersion, but where the dispersion ratio  $\alpha_{4358}/\alpha_{5461}$  remains insensitive to variations of temperature and solvent influence it may be concluded that the rotatory dispersion exhibits real simplicity. Alcohol (I) was demonstrated by Hills, Kenyon, and Phillips (*loc. cit.*) to possess a complex rotatory dispersion and this is shown above to apply also to alcohol (V). Alcohol (IV) in the homogeneous state shows a slight complexity of

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rotatory dispersion when  $1/\alpha$  is plotted against  $\lambda^2$ , and the dispersion ratio  $\alpha_{4358}/\alpha_{5461}$  is little influenced by changes of temperature, as the following data show :

$t$ .....	20°	50°	76°
$\alpha_{4358}/\alpha_{5461}$ .....	1.78	1.77	1.75

On the other hand, this dispersion is more susceptible to solvent influence :

Solvent .....	$C_6H_5N$	$CHCl_3$	$Et_2O$
$\alpha_{4358}/\alpha_{5461}$ .....	2.21	1.64	1.90

and in pyridine solution the sign of rotation is reversed.

It thus appears that alcohol (IV) also possesses complex rotatory dispersion.

Unlike the saturated aliphatic secondary alcohols, which uniformly possess simple rotatory dispersions, the alkyl-substituted allyl alcohols hitherto examined all show complexity of rotatory dispersion. The rotatory dispersion of the semi-aromatic alcohol (II) can be represented by a single-term equation (Table IX) :

$$\alpha = 4.425/(\lambda^2 - 0.0876); \lambda_0 = 2960 \text{ \AA.}$$

TABLE IX.

*Rotatory Powers of  $\gamma$ -Phenyl- $\alpha$ -methylallyl Alcohol ( $t$ , 51°; 1, 0.5).*

$\lambda$ .....	5780	5461	4358
$\alpha_{obs.}$ .....	17.96°	21.00°	43.23°
$\alpha_{calc.}$ .....	17.97°	21.01°	43.20°
$\alpha_{obs.} - \alpha_{calc.}$ .....	-0.01°	-0.01°	+0.03°

The dispersion ratio is relatively insensitive to changes in temperature :

$t$ .....	51°	95°
$\alpha_{4358}/\alpha_{5461}$ .....	2.06	2.00

and to the influence of solvents :

Solvent .....	$CS_2$	$C_6H_6$	$COMe_2$	$CHCl_3$
$\alpha_{4358}/\alpha_{5461}$ .....	2.09	1.94	2.06	1.97

The largest deviation from the mean value is found in the benzene solution; the dispersion in this case may be represented, however, by a single-term equation (Table X) :

$$\alpha = 4.97/(\lambda^2 - 0.0742); \lambda_0 = 2730 \text{ \AA.}$$

TABLE X.

*Rotatory Powers of  $\gamma$ -Phenyl- $\alpha$ -methylallyl Alcohol in Benzene Solution ( $c$ , 4.070; 1, 2).*

$\lambda$ .....	5893	5780	5461	4358
$\alpha_{obs.}$ .....	+18.2°	+19.4°	+22.2°	+43.0°
$\alpha_{calc.}$ .....	+18.2°	+19.15°	+22.2°	+43.0°
$\alpha_{obs.} - \alpha_{calc.}$ .....	$\pm 0.0°$	+ 0.25°	$\pm 0.0°$	$\pm 0.0°$

The numerical values of the rotatory powers in other solvents are not very different.

The rotatory dispersion of the isomeric alcohol (III) also can be represented by a single-term equation (Table XI) :

$$\alpha = -7.73/(\lambda^2 - 0.0689); \lambda_0 = 2630 \text{ \AA.}$$

TABLE XI.

*Rotatory Powers of  $\alpha$ -Phenyl- $\gamma$ -methylallyl Alcohol ( $t$ , 20°; 1, 0.5).*

$\lambda$ .....	5780	5461	4358
$\alpha_{obs.}$ .....	-29.16°	-33.59°	-64.0°
$\alpha_{calc.}$ .....	-29.20°	-33.70°	-63.8°
$\alpha_{obs.} - \alpha_{calc.}$ .....	- 0.04°	- 0.11°	+ 0.2°

and the dispersion ratio is insensitive to changes of temperature :

$t$ .....	20°	35°	40.5°	62.5°	71°
$\alpha_{4358}/\alpha_{5461}$ .....	1.905	1.883	1.89	1.91	1.92

No data for its solutions are available, since this alcohol undergoes isomeric change into (II) somewhat readily.

It thus appears that the phenylalkylallyl alcohols exhibit simple rotatory dispersions. The values of  $\lambda_D$  derived from the equations of Tables IX, X, and XI are respectively 2960, 2730, and 2630 Å., and the tentative suggestion may be made that a large proportion of the rotatory power is due to induced dissymmetry of the phenyl group, since Baly and Tryhorn (J., 1915, 107, 1058) found that a large number of benzene derivatives gave absorption bands in the region 2600—2750 Å., and Kuhn (*Trans. Faraday Soc.*, 1930, 26, 307) attributed a large induced dissymmetry to the benzene nucleus in mandelic acid.

Marked mutarotation was observed in alcohol (I), but alcohols (II), (IV), and (V) do not undergo mutarotation, whence it appears that this property may be associated with the symmetrical substitution in  $\alpha\gamma$ -dimethylallyl alcohol. The dispersion ratios at room temperature of the hydrogen phthalic and acetic esters of the various unsaturated alcohols in different solvents are recorded in Table XII.

TABLE XII.

*Values of the Dispersion Ratio,  $\alpha_{4358}/\alpha_{5461}$ , for Derivatives of Alcohols (I)—(V).*

Derivative.	Solvent.	(I).	(II).	(III).	(IV).	(V).
Acetate .....	None	1.79	1.93	3.00	2.00	1.75
Hydrogen phthalate .....	Et <sub>2</sub> O	2.01	—	2.10	—	—
" "	C <sub>6</sub> H <sub>6</sub>	2.11	1.53	—	1.94	2.40
" "	CHCl <sub>3</sub>	2.06	2.41	—	1.86	2.75
" "	CS <sub>2</sub>	1.44	—	—	1.95	1.91
" "	COMe <sub>2</sub>	1.99	1.77	—	—	—
" "	C <sub>6</sub> H <sub>5</sub> Br <sub>2</sub>	2.06	—	—	—	—
" "	EtOH	2.01	—	—	1.90	2.03
" "	CCl <sub>4</sub>	2.27	—	—	—	—
" "	NaOH (aq.)	1.98	—	—	—	—

Since the carboxylic esters of saturated aliphatic secondary alcohols exhibit complex rotatory dispersion, those derived from unsaturated alcohols are unlikely to be less complex. The dispersion ratios are in general greater than the value 1.65 associated with saturated aliphatic compounds and approximate to 2.

## EXPERIMENTAL.

*dl-n*-Propylpropenylcarbinol (b. p. 63—64.5°/14 mm.,  $n_D^{18}$  1.4380) was prepared in 74% yield by the interaction of crotonaldehyde (0.9 mol.) and *n*-propylmagnesium chloride.

*dl-n*-Propylpropenylcarbinyl hydrogen phthalate was prepared by heating the *dl*-alcohol (137 g.) with phthalic anhydride (178 g.) and pyridine (95 g.) at 60—65° for 2 hours. The resultant oil, diluted with acetone, was poured into dilute hydrochloric acid and ice; the acid ester then separated as a solid, m. p. 58—62° (yield, almost theoretical). Purified through its sodium salt and crystallised from carbon disulphide, it formed prisms, m. p. 72.5° (Found, by titration with NaOH: *M*, 260. Calc. for C<sub>15</sub>H<sub>18</sub>O<sub>4</sub>: *M*, 262).

(+)*n*-Propylpropenylcarbinyl Hydrogen Phthalate.—Strychnine (625 g.) was dissolved in a solution of the *dl*-hydrogen phthalic ester (491 g.) in dry chloroform; the solvent was removed, and hot dry acetone (1200 c.c.) added. On cooling, the strychnine salt (800 g.) separated. This was thrice recrystallised by solution in the minimum amount of methyl alcohol and addition of acetone. Further recrystallisation did not increase the optical activity of the salt, which was decomposed to yield a dextrorotatory hydrogen phthalic ester having  $[\alpha]_{5461}^{18} + 19.3^\circ$  in ethyl alcohol. The strychnine salt was readily decomposed by prolonged boiling in acetone solution, and by traces of water in the solvents, and could not be obtained optically pure. After repeated crystallisation from ether—light petroleum (+)*n*-propylpropenylcarbinyl hydrogen phthalate formed needles, m. p. 74°—75°, and attained the constant rotatory power  $[\alpha]_{5461}^{18} + 22.85^\circ$  (*l*, 2.0; *c*, 4.55) in ethyl-alcoholic solution (Found: C, 68.85; H, 6.9. C<sub>15</sub>H<sub>18</sub>O<sub>4</sub> requires C, 68.7; H, 6.9%).

Decomposition of the more soluble fractions of the strychnine salt yielded a hydrogen phthalic ester with  $[\alpha]_{5461}^{18} - 9.5^\circ$  in ethyl-alcoholic solution. By four recrystallisations of its brucine salt from acetone the rotatory power of this hydrogen phthalic ester was raised to a constant value of  $[\alpha]_{5461}^{18} - 16.0^\circ$  in ethyl-alcoholic solution. Finally, by repeated crystallisation

from ether and light petroleum, optically pure (–)*n*-propylpropenylcarbinyl hydrogen phthalate was obtained in needles, m. p. 75°,  $[\alpha]_{5461} - 22.5^\circ$  (*l*, 2.0; *c*, 4.610) in ethyl-alcoholic solution, and  $[\alpha]_{5461}^{45^\circ} + 17.2^\circ$  (*l*, 2.0; *c*, 4.60) in carbon disulphide. In view of the failure of both the strychnine and the brucine salts to effect a complete resolution of this hydrogen phthalic ester, its salts with quinidine and cinchonidine were recrystallised from methyl acetate and acetone respectively: these, however, brought about little, if any, separation.

(+)*n*-Propylpropenylcarbinol.—Steam was passed through a solution of the (+) hydrogen phthalic ester (20 g.) and sodium hydroxide (7 g.) in water (34 c.c.) and from the steam-distillate (+)*n*-propylpropenylcarbinol, b. p. 63.5°/15 mm.,  $n_D^{18} 1.4381$ ,  $d_4^{18} 0.839$ , was obtained. Its rotatory power is recorded in Table I, and the variations with solvent and temperature in Tables II and III. The carbinol (1.1 g.) was reconverted into its hydrogen phthalic ester, which had  $[\alpha]_{5461}^{22^\circ} + 21.1^\circ$  (*l*, 2.0; *c*, 4.855), indicating slight racemisation during hydrolysis.

Reduction of (+)*n*-Propylpropenylcarbinol to Di-*n*-propylcarbinol.—The (+) alcohol ( $\alpha_{5461}^{19^\circ} + 4.02^\circ$ , *l*, 0.5; 2 g.), dissolved in ethyl alcohol (99%; 15 c.c.), was reduced with hydrogen at 2 atms. in the presence of Raney nickel catalyst. The filtered solution was optically inactive to light of  $\lambda_{5461}$  (*l*, 2.0), and yielded optically inactive di-*n*-propylcarbinol, b. p. 66.5°/18 mm.,  $n_D^{20} 1.4216$ , which was converted into its hydrogen phthalic ester, m. p. 60° alone and when mixed with authentic di-*n*-propylcarbinyl hydrogen phthalate.

Absence of Mutarotation in (+)*n*-Propylpropenylcarbinol.—The (+) alcohol ( $\alpha_{5461}^{19^\circ} + 4.11^\circ$ ,  $\alpha_{4358}^{19^\circ} + 7.70^\circ$ , *l*, 0.5) was maintained at 34–39° during 15 days; it was then kept at 20° for 6 hours, and the rotatory power redetermined,  $\alpha_{5461}^{20^\circ} + 4.10^\circ$ ,  $\alpha_{4358}^{20^\circ} + 7.95^\circ$  (*l*, 0.5).

dl-*n*-Propylpropenylcarbinyl acetate, prepared by heating the *dl*-alcohol (6 g.) with acetic anhydride (8 g.) and pyridine (6 g.), had b. p. 63–64.5°/12 mm.,  $n_D^{17} 1.4283$  (Found: C, 69.2; H, 10.3.  $C_9H_{16}O_2$  requires C, 69.2; H, 10.3%). (–)*n*-Propylpropenylcarbinyl acetate, prepared similarly from the (+) alcohol ( $\alpha_{5461}^{19^\circ} + 4.02^\circ$ , *l*, 0.5), had b. p. 74°/16 mm.,  $n_D^{17} 1.4270$ ,  $d_4^{21^\circ} 0.8815$ ,  $\alpha_{5438}^{21^\circ} - 14.96^\circ$ ,  $\alpha_{5893}^{21^\circ} - 18.41^\circ$ ,  $\alpha_{5780}^{21^\circ} - 19.23^\circ$ ,  $\alpha_{5461}^{21^\circ} - 21.98^\circ$ ,  $\alpha_{5086}^{21^\circ} - 26.15^\circ$ ,  $\alpha_{4800}^{21^\circ} - 30.18^\circ$ ,  $\alpha_{4678}^{21^\circ} - 32.00^\circ$ ,  $\alpha_{358}^{21^\circ} - 38.40^\circ$  (*l*, 0.5).

Reduction of the (–) acetate. The (–) acetate ( $\alpha_{5461}^{21^\circ} - 21.98^\circ$ , *l*, 0.5; 3.6 g.) was reduced in ethereal solution by hydrogen at 2 atms. in the presence of platinum oxide. The filtered solution was inactive to light of  $\lambda_{5461}$ , and yielded optically inactive di-*n*-propylcarbinyl acetate, b. p. 69–70°/17 mm.,  $n_D^{19} 1.4105$ .

dl-*n*-Propylpropenylcarbinyl benzoate, prepared by mixing the *dl*-alcohol (5.5 g.) with pyridine (5 g.) and adding benzoyl chloride (8.75 g.), had b. p. 146°/12 mm.,  $n_D^{14} 1.5071$  (Found: C, 76.7; H, 8.4.  $C_{14}H_{18}O_2$  requires C, 76.9; H, 8.3%).

(+)*n*-Propylpropenylcarbinyl benzoate, prepared similarly from the (+) alcohol ( $\alpha_{5461}^{18^\circ} + 4.45^\circ$ ; *l*, 0.5), had b. p. 158°/16 mm.,  $d_4^{18.5^\circ} 0.9908$ ,  $n_D^{20} 1.5046$ ; its rotatory powers are recorded in Table V.

Reduction of the (+) benzoate. The (+) benzoate ( $\alpha_{5461}^{20^\circ} + 11.16^\circ$ , *l*, 0.5; 3.1 g.) was reduced in ethereal solution (20 c.c.) by hydrogen at 2 atms. in the presence of platinum oxide; the filtered solution had  $\alpha_{5461}^{18^\circ} - 0.12^\circ$  (*l*, 2.0), and from it optically inactive di-*n*-propylcarbinyl benzoate, b. p. 148–150°/11 mm.,  $n_D^{20} 1.4883$ , was obtained.

dl-*n*-Propylpropenylcarbinyl Methyl Ether.—Methyl iodide (8 g.) was added to the potassium-derivative obtained by the interaction of potassium (2 g.) and the *dl*-alcohol (5.7 g.) in benzene suspension; the crude methyl ether was freed from unreacted alcohol by heating with phthalic anhydride (6.5 g.) and pyridine (3.5 g.) for 2 hours at 65–70°. After redistillation through a short column, dl-*n*-propylpropenylcarbinyl methyl ether had b. p. 135°/760 mm.,  $n_D^{20.9^\circ} 1.4164$ ,  $d_4^{20.5^\circ} 0.7902$  (Found: C, 75.0; H, 12.8.  $C_8H_{16}O$  requires C, 74.9; H, 12.6%).

(+)*n*-Propylpropenylcarbinyl methyl ether was similarly prepared from the (–) alcohol ( $\alpha_{5461}^{20^\circ} - 2.14^\circ$ ; *l*, 0.5); it had b. p. 135–137°,  $n_D^{20.8^\circ} 1.4169$ ,  $\alpha_{6438}^{25.5^\circ} + 3.73^\circ$ ,  $\alpha_{5893}^{25.5^\circ} + 4.53^\circ$ ,  $\alpha_{5780}^{25.5^\circ} + 5.03^\circ$ ,  $\alpha_{5461}^{25.5^\circ} + 5.50^\circ$ ,  $\alpha_{5086}^{25.5^\circ} + 6.21^\circ$ ,  $\alpha_{4800}^{25.5^\circ} + 7.04^\circ$ ,  $\alpha_{4678}^{25.5^\circ} + 7.38^\circ$ ,  $\alpha_{4358}^{25.5^\circ} + 9.01^\circ$  (*l*, 0.2356).

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