400. *The Resolution of* n-*Propylallylcarbinol.*

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(—)-*n*-Propylallylcarbinol has been prepared, and a comparison made of its rotatory power and dispersion with those of the isomeric (—)-*n*-propylpropenylcarbinol.

In the course of our investigation of the influence of unsaturation on the rotatory power and dispersion of secondary alcohols there have been prepared optically active *n*-propylpropenylcarbinol (I) (Arcus and Kenyon, this vol., p. 312) and propenylallylcarbinol (II) (Duveen and Kenyon, *Bull. Soc. chim.*, 1938, **5**, 704). We now describe the preparation of optically active *n*-propylallylcarbinol (III).

(I.) $CHMe{:}CH{\cdot}CHPr^{\alpha}{\cdot}OH$ $CHMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH_2$ (II.)

(III.) $CH_2{:}CH{\cdot}CH_2{\cdot}CHPr^{\alpha}{\cdot}OH$

Fractional crystallisation of the brucine salt of dl-n-*propylallylcarbinyl hydrogen phthalate* yielded the brucine salt of (—)-*n*-propylallylcarbinyl hydrogen phthalate, from which were obtained successively (—)-*n*-propylallylcarbinyl hydrogen phthalate and (—)-*n*-propylallylcarbinol. The rotatory powers are given in Tables I—III.

Table I.

Specific Rotatory Powers of (—)-n-*Propylallylcarbinyl Hydrogen Phthalate in Various Solvents at Room Temperature* (1, 2).

Solvent.	*c*.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	$\alpha_{4358}/\alpha_{5461}$.
EtOH	5·001	−21·5°	−27·1°	−28·0°	−31·9°	−57·4°	1·80
C_5H_5N	5·004	—	25·8	26·8	30·8	55·2	1·76
C_6H_6	5·007	18·2	24·5	25·6	28·8	52·3	1·79
CS_2	5·003	18·5	21·6	22·9	26·0	45·7	1·76
$CHCl_3$	5·030	18·6	21·5	22·6	25·6	45·1	1·76
H_2O (Na salt)	5·002	—	16·3	16·6	18·8	33·6	1·80

Table II.

Rotatory Powers of (—)-n-*Propylallylcarbinol.*

l.	*t*.	α_{6438}.	α_{5893}.	α_{5780}.	α_{5461}.	α_{5086}.	α_{4800}.	α_{4358}.
2·0	20·5°	−7·21°	−8·62°	−8·92°	−9·96°	−11·45°	−12·77°	−15·07°
2·0	24	—	8·70	9·03	10·07	—	—	15·14

Specific Rotatory Powers of (—)-n-*Propylallylcarbinol at Different Temperatures* (1, 0·5).

t.	$d^{t^\circ}_{4^\circ}$.	α_{5780}.	α_{5461}.	α_{4358}.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	$\alpha_{4358}/\alpha_{5461}$.
14°	0·8450	−2·32°	−2·52°	−3·77°	−5·49°	−5·99°	−8·93°	1·50
20·5	0·8388	2·23	2·49	3·77	5·32	5·94	9·00	1·51
24	0·8366	2·26	2·52	3·79	5·30	6·03	9·06	1·50
29	0·8326	2·39	2·64	3·91	5·74	6·34	9·40	1·48
34·5	0·8280	2·39	2·63	3·94	5·77	6·35	9·52	1·50
41	0·8224	2·39	2·61	3·91	5·81	6·35	9·51	1·50
54·5	0·8114	2·36	2·60	3·91	5·82	6·41	9·64	1·50

TABLE III.

Specific Rotatory Powers of (—)-n-*Propylallylcarbinol in Various Solvents at Room Temperature* (1, 2).

Solvent.	*c.*	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.	$\alpha_{4358}/\alpha_{5461}$.
CS_2	5·3495	—	−13·1°	−13·2°	−14·9°	−24°	1·61
Et_2O	5·1025	−7·8°	8·7	9·3	10·5	16	1·53
C_6H_6	4·9275	—	11·5	12·2	13·5	22·3	1·65
EtOH	5·1780	—	6·85	7·62	8·40	12·5	1·49

Rotatory Dispersion of (—)-n-*Propylallylcarbinol.*—When $1/\alpha$ is plotted against λ^2, a straight line is obtained, which might suggest that the alcohol exhibits simple rotatory dispersion. On the other hand, the rotation data lead to the equation

$$\alpha = -\,3{\cdot}112/(\lambda^2 + 0{\cdot}01693), \text{ whence (for } l, 2\text{) we get :}$$

λ.	$\alpha_{obs.}$.	$\alpha_{calc.}$.	$\alpha_{obs.} - \alpha_{calc.}$.	λ.	$\alpha_{obs.}$.	$\alpha_{calc.}$.	$\alpha_{obs.} - \alpha_{calc.}$.
6348	−7·21°	−7·21°	0	5086	−11·45°	−11·30°	−0·15°
5893	8·62	8·55	−0·07	4800	12·77	12·59	−0·18
5780	8·92	8·87	−0·05	4358	15·07	15·03	−0·04
5461	9·96	9·88	−0·08				

The value of $\lambda_0^2 = -\,0{\cdot}01693$ is "impossible," *i.e.*, λ_0 is imaginary, thus indicating that the dispersion is complex.

The complexity is confirmed by the dispersion ratio having the value *ca.* 1·50, which is lower than the minimum value of 1·65 required for simple rotatory dispersions. The sensitivity of the dispersion ratio to solvent influence (Table III) lends further support to this view.

As compared with (+)-*n*-propylpropenylcarbinol, (—)-*n*-propylallylcarbinol is insensitive to the influence of temperature, thus showing the greater influence of a double bond in the αβ-position to the asymmetric centre as compared with one in the βγ-position. The following comparisons are of interest :

	Rotatory Dispersion.
(+) $CHMe{:}CH{\cdot}CHPr^{\alpha}{\cdot}OH$	complex (Arcus and Kenyon, this vol., p. 312)
(—) $CH_2{:}CH{\cdot}CH_2{\cdot}CHPr{\cdot}OH$	,, (Present paper)
(—) $CH_2{:}CH{\cdot}CHPr{\cdot}OH$	simple (Kenyon and Snellgrove, J., 1925, **127**, 1169)
(+) $CH_2{:}CMe{\cdot}CH_2{\cdot}CHMe{\cdot}OH$	complex (Kenyon and Young, this vol., p. 1452)

EXPERIMENTAL.

dl-n-*Propylallylcarbinol.*—Considerable difficulty was experienced in the preparation of this alcohol. The addition of *n*-butaldehyde (0·9 mol.) to allylmagnesium chloride resulted in very poor yields of the alcohol and the formation of much high-boiling material. Better yields were obtained by the procedure of Kipping and Davies (J., 1911, **99**, 296), an ethereal solution of allyl chloride and *n*-butaldehyde being added very slowly to a well-stirred suspension of magnesium and ether. On one occasion the yield was as high as 65%, but was generally only about half this amount. The crude alcohol, b. p. 58—59°/18 mm., contained a variable amount of *n*-butanol (see below).

dl-n-*Propylallylcarbinyl hydrogen phthalate* was prepared by heating a mixture of the *dl*-alcohol (171 g.), phthalic anhydride (222 g.), and pyridine (120 g.) at 55—60° for 2 hours. Next day the homogeneous mass was mixed with ether and cold dilute aqueous ammonia. The ammoniacal solution was acidified, and the precipitated oil extracted with ether and dried. The hydrogen phthalate (327 g.) was a semi-solid crystalline mass which, after spreading on porous earthenware, was allowed to crystallise slowly from carbon disulphide–light petroleum. After two recrystallisations and the systematic working up of the mother-liquors *dl-n*-propylallylcarbinyl hydrogen phthalate (234 g.) was obtained in crystalline plates, m. p. 39—40° (Found by titration with sodium hydroxide : *M*, 264. $C_{15}H_{18}O_4$ requires *M*, 262).

From the mother-liquors considerable (10—20%) amounts of *n*-butyl hydrogen phthalate were obtained, m. p. 72·5° alone and when mixed with an authentic specimen.

(—)-n-*Propylallylcarbinyl Hydrogen Phthalate.*—Anhydrous brucine (394 g.) was dissolved in a hot solution of the *dl*-hydrogen phthalate (262 g.) in acetone (1½ l.). After removal of the first crop of crystals, which separated overnight, the filtrate was concentrated, and a second crop of crystals obtained. Decomposition with acid of the second filtrate yielded partially active hydrogen phthalate (34 g.) with $[\alpha]_{5893}$ + 11·3° (*l*, 2; *c*, 5·0) in chloroform solution. Some eleven recrystallisations from acetone of the original crop of crystals were necessary before constancy of rotatory power was reached: this gave the brucine salt of (—)-*n*-propylallylcarbinyl hydrogen phthalate (110 g.), needles, m. p. 137—140° (decomp.); $[\alpha]_{5780}$ — 22·0°, $[\alpha]_{5461}$ — 24·9°, $[\alpha]_{4358}$ — 46·7° (*l*, 2; *c*, 5·00) in chloroform solution. By decomposition with dilute acid this salt yielded (—)-*n*-propylallylcarbinyl hydrogen phthalate (43 g.), m. p. 39—40°, which separated from carbon disulphide and light petroleum in crystalline plates, m. p. 39—40°. The rotatory powers of the (—)-hydrogen phthalate—which were unaltered by its recrystallisation—are recorded in Table I. By systematic working up of the mother-liquors further amounts of pure brucine salt were obtained. Crystallisation of *d* + *dl*-hydrogen phthalate from various solvents effected but little alteration in its rotatory power and although this highly optically active material gave a crystalline salt with cinchonidine—the other common alkaloids gave gummy salts—it was far too soluble to be of service.

(—)-n-*Propylallylcarbinol*.—The (—)-hydrogen phthalate (65 g.) was dissolved in a solution of sodium hydroxide (27 g.) in water (60 c.c.), and a current of steam passed. Extraction of the steam distillate yielded the (—)-alcohol (26 g.), b. p. 59—60°/20 mm., $n_D^{18^\circ}$ 1·4345. Rotatory powers are recorded in Tables II and III.

Determinations of density were made in a pyknometer of just over 1 c.c. capacity: $d_{4^\circ}^{17\cdot1^\circ}$ 0·8426, $d_{4^\circ}^{22\cdot1^\circ}$ 0·8384, $d_{4^\circ}^{29\cdot3^\circ}$ 0·8314, $d_{4^\circ}^{35\cdot4^\circ}$ 0·8260.

A portion of the alcohol was reconverted into the hydrogen phthalate; this had $[\alpha]_{5893}$ — 24·8°, $[\alpha]_{54661}$ — 29·2° (*l*, 2; *c*, 5·00) in benzene solution, thus showing that no racemisation occurred during the hydrolysis of (—)-*n*-propylallylcarbinyl hydrogen phthalate.

(—)-n-*Propylallylcarbinyl acetate*, prepared by the action of acetic anhydride on a solution of the (—)-alcohol in pyridine, had b. p. 71°/23 mm., $n_D^{19^\circ}$ 1·4216; α_{5893} — 14·35°, α_{5780} — 14·98°, α_{5461} — 17·08°, α_{4358} — 29·5° (*l*, 0·5; *t*, 19°). Its odour was pleasant but slightly pungent (Found: C, 69·5; H, 10·5. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%).

(—)-n-*Propylallylcarbinyl benzoate* (5 g.), obtained by the addition of benzoyl chloride (4·3 g.) to a solution of the (—)-alcohol (3·4 g.) in pyridine (2·9 g.), had b. p. 147—148°/19 mm., $n_D^{20^\circ}$ 1·5015; α_{5893} — 5·85°, α_{5780} — 6·03°, α_{5461} — 6·76°, α_{4358} — 10·8° (*l*, 0·5; *t*, 18°) (Found: C, 76·6; H, 8·3. $C_{14}H_{18}O_2$ requires C, 77·0; H, 8·3%).

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