59. *Optically Active αγ-Diethylallyl Alcohol.*

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αγ-Diethylallyl alcohol has been synthesised and resolved. The properties of the optically active alcohol are compared with those of its lower homologue, αγ-dimethylallyl alcohol.

IN view of the anomalous behaviour of optically active αγ-dimethylallyl alcohol (Hills, Kenyon, and Phillips, J., 1936, 576), it was thought desirable to prepare a second optically active, symmetrically disubstituted αγ-allyl alcohol. The next homologue, *αγ-diethylallyl alcohol,* was accordingly investigated. The *dl*-alcohol, prepared by the usual Grignard method in good yield, was resolved by fractional crystallisation of the strychnine salt of its *hydrogen phthalic ester*, both *d*- and *l*-forms of the hydrogen phthalic ester being obtained. The identity in magnitude of the rotatory powers of the *d*- and *l*-hydrogen phthalic esters and the inability of crystallisation to raise their rotatory powers may be taken as evidence that the optical resolution was complete. The optically pure alcohol was obtained by hydrolysis of the optically pure hydrogen phthalic ester with either concentrated aqueous sodium hydroxide or alcoholic potassium hydroxide; both these reagents bring about very little racemisation, for the optically active alcohol, so obtained, can be reconverted into its hydrogen phthalic ester with but 10% overall loss of rotatory power.

The (+)-hydrogen phthalic esters of αγ-dimethyl- and αγ-diethyl-allyl alcohols are similar in that their specific rotatory powers are essentially unaffected by change of concentration in solvents *except* in carbon disulphide solution (Table I). In this solvent, however, change of the sign of rotation is effected by alteration in the concentration, but the reason for this effect is not apparent.

TABLE I.

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

Solvent.	*c*.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{5086}$.	$[\alpha]_{4358}$.
Et_2O	5·0800	−23·8°	−29·5°	−30·0°	−35·7°	−44·1°	−70·9°
,, ...	2·5400	−24·6	−29·5	−33·8	−36·6	−46·2	−73·9
EtOH	4·8320	−25·6	−27·8	−30·6	−34·7	−43·0	−71·1
C_5H_5N	5·1635	−17·4	−20·4	—	−26·9	−32·9	−60·0
C_6H_6	5·0170	−14·8	−20·3	−22·8	−24·3	−30·2	−52·3
,, ...	2·5085	−16·9	−19·5	−22·9	−23·9	−30·9	−54·0
$CHCl_3$	4·4660	—	−15·1	−17·0	−19·6	—	−38·6
,, ...	2·2452	−10·0 *	−16·0 *	−16·9 *	−18·3 *	−25·1 *	−37·9 *
CS_2	14·1010	− 0·46	− 0·85	—	− 1·13	− 2·02	− 5·85
,, ...	9·4840	+ 0·37	− 0·05	—	− 0·53	− 1·26	− 3·95
,, ...	4·7470	+ 0·42	+ 0·10	—	+ 0·10	+ 0·42	− 2·64
,, ...	2·8012 †	+ 0·8	+ 1·16	—	+ 0·98	—	− 1·51

* Corrected values: experimentally determined with (+)-ester. † *l* = 4.

Optically pure αγ-diethylallyl alcohol has a much larger optical rotatory power than its dimethyl analogue; moreover, the value of the rotation is far less affected by change of temperature (see Table II) than is that of αγ-dimethylallyl alcohol.

Although (+)-αγ-dimethylallyl alcohol undergoes rapid but erratic mutarotation (*loc. cit.*) involving a change in the sign of the rotatory power, yet the rotation of (+)-αγ-diethylallyl alcohol decreases only slowly with time, a 25% loss occurring in 17 months (Table III). It has not been possible to determine whether this loss of rotatory power is due to mutarotation and/or racemisation owing to the slow nature of the change.

TABLE II.

Observed Rotatory Powers and Densities of (+)-*αγ-Diethylallyl Alcohol at Various Temperatures* (1, 0·5).

t.	$d_4^{t°}$.	α_{6438}.	α_{5893}.	α_{5780}.	α_{5461}.	α_{5086}.	α_{4358}.
18·5°	0·8397	—	+5·59°	+5·96°	+6·81°	+8·10°	+12·25°
27	0·8326	+4·40°	5·21	5·65	6·40	7·65	11·95
33·5	0·8270	—	4·95	5·34	6·01	7·10	11·25
71·5	—	2·90	3·42	—	4·06	5·05	7·83
22 *	0·8368	4·85	5·38	5·90	6·60	7·80	12·35

* Recooled.

Since the unsaturated aldehyde used in the synthesis of αγ-diethylallyl alcohol was obtained by a method which may have given rise to a mixture of *cis*- and *trans*-isomers (production of a double bond by elimination of the elements of hydrogen bromide), an attempt was made to separate a solid derivative prepared from the aldehyde into two isomeric forms. Fractional crystallisation of *dl*-αγ-diethylallyl hydrogen phthalate from light petroleum gave, however, no indication of the presence of *cis*- and *trans*-isomers. In addition, Kuhn and Grundmann (*Ber.*, 1937, **70**, 1897) do not record any evidence for the presence of isomeric forms of the aldehyde. Hence it is concluded that the Δ^{α}-pentenal is essentially homogeneous and is probably the *trans*-isomer. Similarly, purified commercial crotonaldehyde, produced by the removal of the elements of water from aldol, is considered by Blacet, Young, and Roof (*J. Amer. Chem. Soc.*, 1937, **59**, 608) to consist solely of the *trans*-isomeride.

TABLE III.

Effect of Time on the Rotatory Powers of (+)-*αγ-Diethylallyl Alcohol* (l, 0·5).

Time, months.	t.	α_{6893}.	α_{5893}.	α_{5780}.	α_{5461}.	α_{5086}.	α_{4358}.	% activity of orig. alcohol at t°.
0	18·5°	—	+5·59°	+5·96°	+6·81°	+8·10°	+12·25°	100
1·6	24	+3·98°	5·23	5·55	6·35	7·63	11·60	98
4	21	—	5·31	—	6·44	—	11·91	97
7	17	4·44	5·43	5·81	6·73	7·92	12·58	97
9	21	—	5·43	5·69	6·46	—	11·86	97
12	21	—	5·08	5·42	6·13	—	10·92	92
17	15	—	4·31	4·50	5·27	—	9·38	75

EXPERIMENTAL.

dl-*αγ-Diethylallyl alcohol* was prepared in 67—74% yields by the interaction of Δ^{α}-pentenal (Kuhn and Grundmann, *loc. cit.*) with ethylmagnesium chloride. It had b. p. 58—64°/13 mm. and 154—156°/760 mm., $n_D^{12°}$ 1·4384 (Found: C, 73·4; H, 12·5. $C_7H_{14}O$ requires C, 73·7; H, 12·4%).

dl-*αγ-Diethylallyl Hydrogen Phthalate.*—The *dl*-alcohol (17 g.) was added to a solution of phthalic anhydride (22·2 g.) in pyridine (15 g.) and heated for 1¾ hours on the water-bath. After the usual working up, there was obtained dl-*αγ-diethylallyl hydrogen phthalate* (30 g., 77% yield), which crystallised from light petroleum (b. p. 40—60°) in rhombs, m. p. 66—68° (Found: C, 68·6; H, 7·0; *M*, by titration with NaOH, 263. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%; *M*, 262).

(+)-*αγ-Diethylallyl Hydrogen Phthalate.*—Strychnine (68 g.) was added to a hot solution of the *dl*-hydrogen phthalate (53 g.) in acetone (1 l.), and a mass of crystals was deposited overnight. These were filtered off, and thrice recrystallised from acetone, affording strychnine αγ-diethylallyl phthalate (43 g.), m. p. 173—178°. This on decomposition gave the (+)-hydrogen phthalate (12 g.), $[\alpha]_{5461}$ + 18·7° (*c*, 4·6175), which on crystallisation from light petroleum was optically pure with m. p. 73—75° and $[\alpha]_{5461}$ + 19·3° (*c*, 4·4905). The rotations of this and the following ester relate to $l = 2$ in chloroform.

(−)-*αγ-Diethylallyl Hydrogen Phthalate.*—Decomposition of the more soluble fractions of the above strychnine salt yielded *l*- + *dl*-hydrogen phthalate (23 g.) with $[\alpha]_{5461}$ − 10·1° (*c*, 4·8050). After two recrystallisations from light petroleum, there was obtained the pure (−)-hydrogen phthalate with $[\alpha]_{5461}$ − 19·1° (*c*, 4·6245) and m. p. 73—75°. Further recrystallisation failed to raise either its m. p. or its rotatory power; their equivalence with those of the (+)-hydrogen phthalate renders it very probable that optical resolution is complete.

Equal amounts of the pure (+)- and (−)-hydrogen phthalic esters were melted together and allowed to resolidify; the resultant solid had m. p. 67—69°, *i.e.*, identical with that of the *dl*-ester.

(+)-*αγ-Diethylallyl Alcohol.*—The (+)-hydrogen phthalate (8·1 g.) was heated on the water-bath for ½ hour with 15 c.c. of 5N-sodium hydroxide. The product, after steam-distillation, was salted out and extracted with ether. The ethereal solution, after drying with potassium carbonate, yielded the (+)-alcohol (3·0 g., 85% yield); b. p. 154—156°, $\alpha_{5893}^{18·5°}$ + 5·59°, $\alpha_{5461}^{18·5°}$ +6·81°, $\alpha_{4358}^{18·5°}$ + 12·25° ($l = 0·5$). Hydrolysis with 5N-alcoholic potash gave a similar result. In each case, reconversion into the (+)-hydrogen phthalate resulted in a 90% retention of optical activity. The effect of time on the rotatory power of the (+)-alcohol is shown in Table III.

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