69. *The Resolution of Propenylethynylcarbinol.*

By J. Kenyon and R. Poplett.

By fractional crystallisation of the cinchonidine salt of its hydrogen phthalic ester, *dl*-propenylethynylcarbinol has been separated into its *d*- and *l*-forms: the (+)carbinol on reduction yielded (−)ethyl-*n*-propylcarbinol.

In view of its high degree of unsaturation, it was considered of interest to attempt the preparation of optically active propenylethynylcarbinol and ascertain whether its rotatory powers and optical rotatory dispersion showed any marked anomalies. Furthermore, since this alcohol undergoes anionic rearrangement in the presence of acid (Jones and McCombie, J., **1943**, **261**, and subsequent papers), it was likely that the optically active material would prove useful in the study of the kinetics of anionotropic rearrangements (this has now proved to be the case; see Braude and Jones, J., **1944**, **436**). *dl*-Propenylethynylcarbinol was prepared and investigated by Jones and McCombie (J., **1942**, **734**), and that used in the present work was very generously placed at our disposal by Dr. E. R. H. Jones.

It is interesting to compare the specific rotatory powers, $[\alpha]_{5893}^{20^\circ}$, of the following four closely related alcohols:

$\mathrm{CHMe{:}CH{\cdot}CH(OH){\cdot}C{\vdots}CH}$	70·6°	$\mathrm{CH_2Me{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_3}$	7·1°
$\mathrm{CHMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH_3}$	13·1	$\mathrm{CH_2Me{\cdot}CH_2{\cdot}CH(OH){\cdot}CH{:}CH_2}$	28·9 *

* Kenyon and Snellgrove (J., 1925, **127**, 1178).

Experimental.

dl-*Propenylethynylcarbinyl Hydrogen Phthalate.*—A mixture of the carbinol (20 g.), phthalic anhydride (30·8 g.), and pyridine (17 g.) was kept at 55—60° for 1 hour and then at room temperature for 2 days. The resulting viscous liquid was diluted with an equal volume of acetone and decomposed with a slight excess of cold dilute hydrochloric acid; the precipitated pasty solid rapidly hardened, and after several hours the resulting crystalline *ester* was collected and dried (48 g., yield 94%), m. p. 85—86°. It separated from ether–light petroleum as hard, transparent prisms, m. p. 86—87° (Found, on titration with 0·1N-NaOH : *M*, 244. $C_{14}H_{12}O_4$ requires *M*, 244).

(+)*Propenylethynylcarbinyl Hydrogen Phthalate.*—A solution of the *dl*-ester (77 g.) and cinchonidine (92·4 g.) in ethyl acetate (400 c.c.), after standing overnight, deposited a mixture of the cinchonidine salts of the dextrorotatory and the lævorotatory hydrogen phthalate (the former in excess). From this mixture, after four extractions with boiling ethyl acetate, the cinchonidine salt of (+)propenylethynylcarbinyl hydrogen phthalate (25 g.) remained as a residue of minute, round crystals, m. p. 155—156° (decomp.). This salt, mixed with acetone, was decomposed with cold dilute hydrochloric acid, and the resulting (+)*propenylethynylcarbinyl hydrogen phthalate* precipitated by the addition of water. It separated from carbon disulphide in hard, irregular crystals, m. p. 56—57° (Found, on titration with 0·1N-NaOH : *M*, 244). Rotatory powers are given in the table below.

(+)*Propenylethynylcarbinol.*—This (+)hydrogen phthalate (24 g.) was heated with 5N-sodium hydroxide (2·5 mols.) on the steam-bath for 10 minutes, and the resulting cooled solution extracted with ether. The ethereal layer was separated, washed with water, dried, and evaporated, and the residue (7·3 g.) distilled. The (+)propenylethynylcarbinol thus obtained had b. p. 157—159°, $n_D^{16\cdot5^\circ}$ 1·4645, $d_{4^\circ}^{14^\circ}$ 0·9125, $d_{4^\circ}^{20^\circ}$ 0·9090, $d_{4^\circ}^{30^\circ}$ 0·9030, $d_{4^\circ}^{40^\circ}$ 0·8970. Rotatory powers are given in the table.

(−)*Propenylethynylcarbinyl Hydrogen Phthalate.*—The mixed filtrates from the first two extractions of the cinchonidine salt of the dextrorotatory hydrogen phthalate were evaporated, and the residue mixed with a little acetone and decomposed with a slight excess of dilute hydrochloric acid. The resulting acid phthalic ester had $[\alpha]_{5893}$ − 24° in ethyl-alcoholic solution. By fractional crystallisation from carbon disulphide, which rapidly separated the less soluble racemic form, the almost optically pure (−)*hydrogen phthalate* was obtained as minute, round crystals, m. p. 62—64°; $[\alpha]_{5893}$ − 41·1° (*c*, 1; *l*, 2) in ethyl-alcoholic solution (Found, by titration : *M*, 245).

Specific rotatory powers of (+)*propenylethynylcarbinyl hydrogen phthalate* (l, 2).

Solvent.	*c*, g. per 100 c.c. soln.	Temp.	$[\alpha]_{6438}$.	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
EtOH	1·568	16°	+38·6°	+47·5°	+47·2°	+60·5°	+110·8°
CS_2	1·024	18	21·6	26·5	27·3	33·1	60·9
$CHCl_3$	1·662	20	21·2	22·0	22·4	26·3	47·5
C_6H_6	2·750	17	12·3	15·1	15·4	17·8	36·0

Observed rotatory powers of (+)propenylethynylcarbinol (*l*, 0·25; *t*, 19·5°) :

λ	6438	5893	5780	5461	4358
α_λ	+13·05°	+16·06°	+16·59°	+19·15°	+34·95°

Reduction of (+)*Propenylethynylcarbinol to* (−)*Ethyl*-n-*propylcarbinol.*—This reduction was kindly carried out for us by Dr. E. R. H. Jones, using palladium–norit catalyst (J., 1942, 734). The resulting saturated carbinol had b. p. 133—134°, $n_D^{22^\circ}$ 1·4140, $\alpha_{5893}^{18^\circ}$ − 1·46° (*l*, 0·25), whence $[\alpha]_{5893}^{18^\circ}$ − 7·13° (Pickard and Kenyon, J., 1913, **103**, 1935) give $n_D^{20^\circ}$ 1·4141).

Ethyl-*n*-propylcarbinol has never been obtained optically pure by the fractional crystallisation of alkaloidal salts of its hydrogen phthalate, but (+)ethyl-*n*-propylcarbinol obtained by the catalytic reduction of (+)-γ-methyl-α-ethylallyl alcohol had $[\alpha]_{5893}^{20^\circ}$ + 7·09° (Airs, Balfe, and Kenyon, J., 1942, 19); it appears very probable, therefore, that these three alcohols—the saturated, the ethylenic, and the acetylenic—are optically pure.

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