314. *The Resolution of αγγ-Trimethylallyl Alcohol into Optically Active Forms.*

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In view of the interesting behaviour of the optically active forms of αγ-dimethyl- (I) (Hills, Kenyon, and Phillips, this vol., p. 576), γ-phenyl-α-methyl- (II) (Kenyon, Partridge, and Phillips, this vol., p. 85), and α-phenyl-γ-methyl-allyl alcohols (III) (to be communicated shortly), it was considered desirable to examine the properties of a di-γ-substituted allyl alcohol to ascertain whether the absence of hydrogen attached to C_γ would notably modify the abnormal reactivity of the αγ-substituted allyl alcohols and their derivatives.

With this object, αγγ-trimethylallyl alcohol (IV) has been resolved into optically active forms and their behaviour investigated. Fractional crystallisation of the brucine salt of

(I.) $\mathrm{CHMe{:}CH{\cdot}CH(OH)Me}$ $\mathrm{CHMe{:}CH{\cdot}CH(OH)Ph}$ (III.)
(II.) $\mathrm{CHPh{:}CH{\cdot}CH(OH)Me}$ $\mathrm{CMe_2{:}CH{\cdot}CH(OH)Me}$ (IV.)

dl-*αγγ-trimethylallyl hydrogen phthalate* led to the isolation of (+)-αγγ-trimethylallyl hydrogen phthalate, and fractional crystallisation of the strychnine salt yielded the corresponding (—)-acid ester. By hydrolysis with aqueous sodium hydroxide the (+)- and the (—)-hydrogen phthalate yielded the (+)- and the (—)-trimethylallyl alcohol respectively; rotatory powers are recorded in the tables.

That no racemisation occurred during the hydrolysis is shown by reconversion of the (+)-alcohol into its (+)-hydrogen phthalate of undiminished rotatory power, and that optical purity has been reached by the resolution is proved by the reduction of the (+)-alcohol to (+)-methyl*iso*butylcarbinol of correct rotatory power. In marked contrast to the behaviour of the hydrogen phthalic esters of alcohols (I), (II), and (III) and of α-furylmethylcarbinol (Duveen and Kenyon, this vol., p. 621), the acid phthalic ester of αγγ-trimethylallyl alcohol can be heated for many hours with acetic acid (and also with methyl alcohol) without reaction taking place.

There is also a very noticeable difference in behaviour during the saponification by aqueous sodium hydroxide of the hydrogen phthalic esters of these alcohols; compounds (I) and (IV) are obtained optically pure when aqueous sodium hydroxide of various concentrations is used, α-furylmethylcarbinol suffers considerable loss in rotatory power when the concentration of the sodium hydroxide is less than 10*N*, and compounds (II) and (III) are obtained optically pure [or nearly so in the case of (II)] only when alcoholic sodium hydroxide is employed.

The significance of these results will be discussed, along with further work in progress in these laboratories, in a later communication.

Experimental.

αγγ-Trimethyltrimethylene glycol (2-methylpentane-2 : 4-diol), obtained by the reduction of diacetone alcohol in aqueous solution with sodium amalgam, had b. p. 95°/14 mm., $n_{\mathrm{D}}^{16^\circ}$ 1·4297 (Zelinsky and Zelikoff, *Ber.*, 1901, **34**, 2858, give $n_{\mathrm{D}}^{16\cdot7^\circ}$ 1·4298). It is essential that a constant stream of carbon dioxide be passed through the well-stirred mixture, for otherwise a considerable amount of pinacol is formed.

αγγ-Trimethylallyl alcohol. The glycol on distillation in the presence of a trace of iodine yielded a mixture of hexadienes, water, and αγγ-trimethylallyl alcohol. The dried distillate was separated into approximately equal amounts of hexadienes, b. p. 77—79°, and αγγ-trimethylallyl alcohol, b. p. 131—133° (Kyriakides, *J. Amer. Chem. Soc.*, 1919, **36**, 994, who used aniline hydrobromide as dehydrating agent, gives b. p. 125—135°). Its p-*xenylurethane* formed irregular prisms, m. p. 65°, from light petroleum (Found : * N, 4·9. $C_{19}H_{21}O_2N$ requires N, 4·8%).

dl-*αγγ-Trimethylallyl hydrogen phthalate.* The alcohol (100 g.) was added to a cooled suspension of phthalic anhydride (148 g.) in pyridine (90 g.), and the gently warmed mixture kept overnight at room temperature. The acid *ester* (198 g.) separated from ether and light petroleum in irregular prisms, m. p. 81·5° (Found, by titration with sodium hydroxide : *M*, 246. $C_{14}H_{16}O_4$ requires *M*, 248).

(+)-*αγγ-Trimethylallyl hydrogen phthalate.* Dry brucine (290 g.) was added to a solution of the *dl*-hydrogen phthalate (180 g.) in warm acetone (750 c.c.). The brucine salt of (+)-αγγ-trimethylallyl hydrogen phthalate, which separated immediately, had m. p. 144°, and required some 24 l. of boiling acetone for solution. On cooling, there was obtained the optically pure salt, long needles, m. p. 143—144°, and by concentration of the filtrate to 3 l. a further, smaller, crop was obtained, the total weight of pure brucine salt being 208 g.; it had $[\alpha]_{5893}$ − 17·0°, $[\alpha]_{5790}$ − 18·6°, $[\alpha]_{5461}$ − 23·0°, $[\alpha]_{4358}$ − 62·5° (*l*, 2; *c*, 4·570) in chloroform, and when decomposed with dilute hydrochloric acid it yielded (+)-αγγ-trimethylallyl hydrogen phthalate, needles, m. p. 43—44°, from light petroleum, the rotatory powers of which are recorded below. Equally good separation is attained with less volume of solvent by using a mixture of acetone and chloroform.

Specific Rotatory Powers of (+)-*αγγ-Trimethylallyl Hydrogen Phthalate in Various Solvents.*

Solvent.	*l.*	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5790}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
C_5H_5N	2	4·762	+ 5·9°	+ 7·0°	+ 8·3°	+15·0°
Et_2O	2	4·828	10·9	11·2	12·1	22·3
CS_2	2	9·858	11·2	12·5	12·8	19·3
CS_2	2	5·045	12·5	12·9	14·1	27·5
$CHCl_3$	2	5·067	14·5	15·3	16·7	31·0
EtOH	2	4·920	14·8	15·7	17·0	32·4
C_6H_6	2	4·984	18·1	20·0	22·2	43·1

Specific Rotatory Powers of (—)-*αγγ-Trimethylallyl Hydrogen Phthalate.*

CS_2	2	5·007	−12·8	−13·3	−14·2	−27·7

(+)-αγγ-Trimethylallyl alcohol was obtained when the (+)-hydrogen phthalate (139 g.) was dissolved in a slight excess of 5*N*-sodium hydroxide, and the alcohol removed in steam. It (44 g.) had b. p. 43°/17 mm., 129°/760 mm., $n_D^{17°}$ 1·4297, $d_{4°}^{11°}$ 0·8511, $d_{4°}^{20°}$ 0·8436, $d_{4°}^{40°}$ 0·8256, $\alpha_{5893}^{22°}$ + 9·00°, $\alpha_{5790}^{22°}$ + 9·59°, $\alpha_{5461}^{22°}$ + 11·04°, $\alpha_{4358}^{22°}$ + 21·07° (*l*, 2), whence $\alpha_{4358}^{22°}/\alpha_{5461}^{22°}$ = 1·90. These rotatory powers remained unchanged when the alcohol was kept for 8 weeks.

Variation in Rotatory Power of (+)-*αγγ-Trimethylallyl Alcohol with Temperature* (l, 0·5).

t.	α_{5893}.	α_{5790}.	α_{5461}.	α_{4358}.	*t.*	α_{5893}.	α_{5790}.	α_{5461}.	α_{4358}.
20°	+2·11°	+2·23°	+2·58°	+4·60°	50°	+2·45°	+2·52°	+2·90°	+5·13°
31	2·26	2·30	2·65	4·74	72	2·69	2·74	3·15	5·45
39	2·35	2·41	2·77	5·01	76	2·73	2·80	3·20	5·60

Specific Rotatory Powers of (+)-*αγγ-Trimethylallyl Alcohol in Various Solvents at Room Temperature* (l, 2·0).

Solvent.	*c.*	$[\alpha]_{5893}$.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	$[\alpha]_{4358}$.
C_5H_5N	5·15	−4·17°	−4·27°	−5·24°	−11·60°
$CHCl_3$	5·17	+8·02	+8·41	+9·76	+16·00
Et_2O	5·01	+7·89	+8·39	+9·99	+19·01

(+)-αγγ-Trimethylallyl alcohol was reconverted into its hydrogen phthalic ester : this had m. p. 44°, $[\alpha]_{5893}$ + 12·3° (*l*, 2; *c*, 5·019) in carbon disulphide.

(−)-*αγγ-Trimethylallyl hydrogen phthalate.* The more soluble fractions of the brucine salt on decomposition with hydrochloric acid yielded a (−) (+)-*l*+*dl*-αγγ-trimethylallyl hydrogen phthalate, $[\alpha]_{5461}$ − 13·9° (*l*, 2; *c*, 5) in chloroform, which melted with preliminary softening at 43—45°; this (175 g.) on solution in ether and light petroleum gave 36 g. of the *dl*-acid ester, m. p. 81°. Evaporation of the filtrate yielded a highly optically active ester (130 g.), which was dissolved in acetone and then mixed with a warm solution of strychnine (170 g.) in chloroform. The strychnine salt of (−)-αγγ-trimethylallyl hydrogen phthalate, which separated on cooling, was recrystallised from hot chloroform diluted with some 4 vols. of acetone. It (181 g.) formed clusters of needles, m. p. 152° (decomp.), $[\alpha]_{5893}$ − 20·64°, $[\alpha]_{5790}$ − 22·81°, $[\alpha]_{5461}$ − 24·89°, $[\alpha]_{4358}$ − 55·45° (*l*, 2; *c*, 5·085) in chloroform. On decomposition with hydrochloric acid this yielded (−)-αγγ-trimethylallyl hydrogen phthalate (76 g.), needles, m. p. 44°, from light petroleum, which had the rotatory powers recorded on p. 1452.

(−)-αγγ-Trimethylallyl alcohol was obtained by dissolving the (−)-acid ester (58 g.) in a slight excess of 5*N*-sodium hydroxide and then removing the alcohol in steam. It (21 g.) had b. p. 43°/18 mm., 129°/760 mm., $n_D^{17°}$ 1·4298, $\alpha_{5893}^{20°}$ − 2·13°, $\alpha_{5790}^{20°}$ − 2·25°, $\alpha_{5461}^{20°}$ − 2·60°, $\alpha_{4358}^{20°}$ − 4·58° (*l*, 0·5). A mixed solution of the (+)- and the (−)-hydrogen phthalic ester in carbon disulphide deposited glassy prisms of the *dl*-acid ester, m. p. 82°.

(+)-*αγγ-Trimethylallyl acetate*, prepared by gently warming a mixture of the (+)-alcohol (3 g.), pyridine (2·75 g.), and acetic anhydride (4 g.), had b. p. 51°/15 mm., $n_D^{20°}$ 1·4202, $\alpha_{5893}^{22°}$ − 3·91°, $\alpha_{5790}^{22°}$ − 4·06°, $\alpha_{5461}^{22°}$ − 4·72°, $\alpha_{4358}^{22°}$ − 9·45° (*l*, 0·5) (Found : * C, 67·3; H, 9·9. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%). The *dl*-ester, similarly prepared, had b. p. 50°/15 mm., $n_D^{20°}$ 1·4201.

(+)-*αγγ-Trimethylallyl benzoate*, obtained by running benzoyl chloride (7·5 g.) into an ice-cooled mixture of the (+)-alcohol (5 g.) and pyridine (4·5 g.), had b. p. 139°/19 mm., $n_D^{20°}$ 1·5047, $\alpha_{5893}^{20°}$ + 30·11°, $\alpha_{5790}^{20°}$ + 31·32°, $\alpha_{5461}^{20°}$ + 35·71°, $\alpha_{4358}^{20°}$ + 59·12° (*l*, 1·0) (Found : * C, 75·2; H, 7·9. $C_{13}H_{16}O_2$ requires C, 76·5; H, 7·8%). The *dl*-ester had b. p. 138°/19 mm., $n_D^{20°}$ 1·5045.

Reduction of (+)-*αγγ-Trimethylallyl Alcohol to* (+)-*Methyl*iso*butylcarbinol.*—The alcohol (5 g.; $\alpha_D^{20°}$ + 2·11°; *l*, 0·5) was dissolved in 99% ethanol and reduced with hydrogen at 2 atm. by means of Raney's nickel catalyst (*J. Amer. Chem. Soc.*, 1932, **54**, 4116). The calculated volume of hydrogen was absorbed in 3—4 hours, and the resulting (+)-methyl*iso*butylcarbinol (4·5 g.), which had no action on bromine solution, had b. p. 49°/22 mm., 129°/760 mm., $n_D^{19°}$ 1·4102, $[\alpha]_{5893}^{19°}$ + 20·04°, $[\alpha]_{5790}^{19°}$ + 20·84°, $[\alpha]_{5461}^{19°}$ + 23·36°, $[\alpha]_{4358}^{19°}$ + 31·04° (Pickard and Kenyon, J., 1911, **99**, 45, give $n_D^{20°}$ 1·4103, $[\alpha]_{5893}^{21·3°}$ + 20·40°).

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