

274. *Constitution of the Alcohol (δ -Methyl- Δ^{δ} -penten- β -ol) previously resolved and described as $\alpha\gamma\gamma$ -Trimethylallyl Alcohol.*

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The alcohol, the resolution of which was described recently by Duveen and Kenyon (J., 1936, 1451), is shown to be δ -methyl- Δ^{δ} -penten- β -ol and not $\alpha\gamma\gamma$ -trimethylallyl alcohol as was assumed by these authors.

THE resolution of an alcohol to which the constitution $\alpha\gamma\gamma$ -trimethylallyl alcohol was assigned was recorded by Duveen and Kenyon (J., 1936, 1451). The evidence on which the constitution of this alcohol was based is as follows: $\alpha\gamma\gamma$ -trimethyltrimethylene glycol (2-methylpentane-2:4-diol), prepared by reduction of diacetone alcohol, was dehydrated by heating with a trace of iodine, whereby there was obtained a mixture of a hexadiene (b. p. 75—76°) and a hexenol (b. p. 130—131°) in approximately equal proportion.

This hydrocarbon—to which the structure $\text{Me}_2\text{C}:\text{CH}\cdot\text{CH}:\text{CH}_2$ was assigned—is reported as having been obtained by heating the glycol mentioned above with (a) aluminium chloride (Bayer, D.-R.P., 261,642; Friedlaender, XI, 794), (b) aniline hydrobromide (Kyriakides, *J. Amer. Chem. Soc.*, 1914, **36**, 994), or by heating the hexenol [of b. p. 130—131°, obtained by partial dehydration of the glycol and to which the constitution $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{Me}$ was assigned] with aniline hydrobromide (Kyriakides, *loc. cit.*).

In the present investigation *dl*-methyl- β -methylallylcarbinol was prepared by the interaction of β -methylallylmagnesium chloride and acetaldehyde. Fractional crystallisation of the brucine salt of the hydrogen phthalic ester of this alcohol led to the isolation of (+)methyl- β -methylallylcarbinyl hydrogen phthalate, which on hydrolysis yielded (+)methyl- β -methylallylcarbinol.

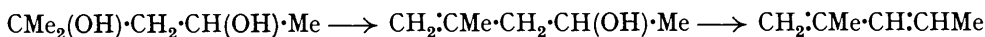
It was soon apparent that there was a remarkable concordance in the m. p.'s and rotatory powers of these compounds and those of the corresponding derivatives described by Duveen and Kenyon (*loc. cit.*). A detailed series of mixed m. p. determinations of the *d*-, *l*-, and *dl*-hydrogen phthalic esters and of the *dl*-*p*-xeny lurethanes left no doubt as to the complete identity of the two alcohols.

A further scrutiny of recent literature revealed that the hydrocarbon obtained by the dehydration of $\alpha\gamma\gamma$ -trimethyltrimethylene glycol is actually $\alpha\gamma$ -dimethylbutadiene (Farmer, Lawrence, and Scott, J., 1930, 511) and not $\alpha\alpha$ -dimethylbutadiene as had been supposed by the earlier workers. This new result throws doubt, as was indeed suggested by Farmer, Lawrence, and Scott, on the structure of the alcohol obtained by partial dehydration of the glycol, a doubt which was strengthened when these workers failed to recognise acetone among its products of oxidation.

We have now found that the unsaturated hydrocarbon obtained by the direct complete dehydration of $\alpha\gamma\gamma$ -trimethyltrimethylene glycol, and also by the further dehydration of the hexenol obtained as a partial dehydration product, combines with maleic anhydride to form 3:5-dimethyl- Δ^4 -tetrahydrophthalic anhydride in excellent yield: it is therefore $\alpha\gamma$ -dimethylbutadiene (Diels and Alder, *Annalen*, 1929, **470**, 98).

This result, taken in conjunction with the synthesis of the unsaturated alcohol described

above, proves quite definitely that the dehydration of $\alpha\gamma\gamma$ -trimethyltrimethylene glycol takes place in the following two stages :



and that the alcohol believed by Duveen and Kenyon to be $\alpha\gamma\gamma$ -trimethylallyl alcohol is actually methyl- β -methylallyl carbinol.

Additional support for this structure of the alcohol has been obtained by ozonolysis, since decomposition of the ozonide gave, not acetone, but pentan- β -ol- δ -one in good yield.

(-)-Methyl- β -methylallylcarbinyl hydrogen phthalate was obtained by Duveen and Kenyon by crystallisation of the strychnine salt of the *l* + *dl*-hydrogen phthalic esters obtained by decomposition of the more soluble fractions of the brucine salts. It has now been found that these brucine salts on crystallisation from methyl alcohol, in place of acetone, readily yield the brucine salt of the optically pure (-)-hydrogen phthalic ester.

EXPERIMENTAL.

dl- δ -Methyl- Δ^{δ} -penten- β -ol was prepared by the slow addition of a solution of β -methylallyl chloride (90 g.) and acetaldehyde (50 g.) in dry ether (150 c.c.) to a stirred suspension of magnesium (24 g.) and ether (250 c.c.); the reaction mixture was then warmed gently for 3 hours to complete the sluggish reaction. The cooled product was decomposed with ice and ammonium chloride, the dried ethereal solution evaporated, and the residue distilled. The crude hexenol (about 20 g.) was collected at 40–50°/18 mm., and a large proportion of high-boiling residue remained. The crude hexenol, which is not economically purified by redistillation, readily yielded *dl*- δ -methyl- Δ^{δ} -penten- β -yl hydrogen phthalate, m. p. 81.5–82°, and *dl*- δ -methyl- Δ^{δ} -penten- β -yl *p*-xenyurethane, m. p. 64–65°; the m. p.'s of these compounds were not depressed when each was mixed with the corresponding compound prepared by Duveen and Kenyon (*loc. cit.*) from $\alpha\gamma\gamma$ -trimethyltrimethylene glycol.

Formation of $\alpha\gamma$ -Dimethylbutadiene from δ -Methyl- Δ^{δ} -penten- β -ol.—The alcohol (4 g.) was heated with a small crystal of iodine, and the products slowly distilled through a short column; the dried distillate (3 c.c.) was redistilled, b. p. 75–77°. This (0.85 g.) combined readily with maleic anhydride (1.0 g.) in benzene solution to yield 3 : 5-dimethyl- Δ^4 -tetrahydrophthalic anhydride (1.3 g.), bulky clusters of fine needles from light petroleum, m. p. 56–57°, alone and when mixed with the same compound prepared from $\alpha\gamma$ -dimethylbutadiene obtained by direct dehydration of $\alpha\gamma\gamma$ -trimethyltrimethylene glycol (Diels and Alder, *loc. cit.*, give m. p. 56–57°).

Oxidation of δ -Methyl- Δ^{δ} -penten- β -ol to Pentan- β -ol- δ -one.—Ozonised oxygen was bubbled through a solution of the *dl*-alcohol (6 g.) in chloroform for several hours, and the solvent allowed to evaporate at room temperature. The residual oily ozonide, after decomposition with water, yielded pentan- β -ol- δ -one (2.3 g.), b. p. 64–65°/18 mm., which was characterised as its (somewhat unstable) phenylhydrazone, brownish prisms, m. p. 102–103° (Claisen, *Annalen*, 1899, 306, 326, gives m. p. 102–103°).

(+) and (-)- δ -Methyl- Δ^{δ} -penten- β -ols.—The brucine salt of the *dl*-hydrogen phthalic ester, after two recrystallisations from acetone, as described by Duveen and Kenyon (*loc. cit.*), yielded on decomposition (+)- δ -methyl- Δ^{δ} -penten- β -yl hydrogen phthalic ester, m. p. and mixed m. p. 42–43°, $[\alpha]_{5461}^{18} + 18.1^{\circ}$ (*l*, 2; *c*, 4.968) in ethyl alcohol. This on hydrolysis gave (+)- δ -methyl- Δ^{δ} -penten- β -ol, b. p. 42°/15 mm., $\alpha_{5461}^{19} + 5.68^{\circ}$ (*l*, 1), $n_D^{20} 1.4339$, $d_4^{20} 0.8435$. The acetone mother-liquors were evaporated to dryness, and the residue recrystallised three times from methyl alcohol; this proved to be the brucine salt of (-)- δ -methyl- Δ^{δ} -penten- β -yl hydrogen phthalate, glassy prisms, m. p. 79–82° (decomp.), $[\alpha]_{5461}^{18} - 18.0^{\circ}$ (*l*, 2; *c*, 5.141) in chloroform solution. This on decomposition yielded the (-)-hydrogen phthalic ester, m. p. and mixed m. p. 42–43°, $[\alpha]_{5461}^{18} - 17.6^{\circ}$ (*l*, 2; *c*, 4.889) in ethyl-alcoholic solution.

The optical properties of δ -methyl- Δ^{δ} -penten- β -ol (believed by them to be $\alpha\gamma\gamma$ -trimethylallyl alcohol) have been briefly discussed by Arcus and Kenyon (this vol., p. 312).

The following additional determinations of rotatory power have been made.

Specific Rotatory Powers of (+)- δ -Methyl- Δ^{δ} -penten- β -ol.

Solvent.	<i>c</i> .	<i>t</i> .	$[\alpha]_{6348}^{\circ}$	$[\alpha]_{5893}^{\circ}$	$[\alpha]_{5780}^{\circ}$	$[\alpha]_{5461}^{\circ}$	$[\alpha]_{5086}^{\circ}$	$[\alpha]_{4800}^{\circ}$	$[\alpha]_{4678}^{\circ}$	$[\alpha]_{4358}^{\circ}$
C ₆ H ₆	5.251	17.5°	+4.2°	+5.1°	+6.6°	+7.3°	+8.1°	+9.3°	+10.1°	+12.5°
CS ₂	5.314	18	4.5	5.9	7.0	7.8	9.3	10.4	11.3	14.8
None	—	19	4.20	5.43	5.77	6.73	8.00	9.70	10.33	12.91

We are indebted to Mr. R. S. AIRS, B.Sc., for the following determinations of the parachor of a freshly distilled specimen of ($-$) δ -methyl- Δ^3 -penten- β -ol, the values marked with an asterisk having been interpolated from a graph.

t	0-0°	10-0°	10-5°	21-2°	28-8°	40-0°	
d_4^{20}	0-8585	0-8523*	0-8518	0-8429	0-8362	0-8269	
t	0-1°	10-0°	12-0°	20-1°	30-7°	40-0°	40-7°
γ , dynes/cm.	27-69	26-93 *	26-82	26-09	24-88	24-13 *	24-04

The values at 10° and 40° give $[P]$ 267-3 and 268-0, respectively, whereas the values calculated from Sugden's constants are 277-2, and from Mumford and Phillips's constants 270-6.

Thanks are expressed to the Government Grants Committee of the Royal Society and to Imperial Chemical Industries, Ltd., for grants.

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[Received, July 4th, 1938.]