LIV.— β -Methyl- Δ^{α} -dodecadiene and β -Methyl- $\Delta^{\alpha\gamma}$ -decadiene.

By VICTOR JOHN HARDING, GERTRUDE MAUD WALSH, and
CHARLES WEIZMANN.

THE compounds described in this communication were prepared with a view to their possible technical importance, and although some of the substances possess some value as perfumes, their pro-

duction by the methods described here render them too costly to permit of their technical application. β -Methyl- $\Delta^{\alpha\lambda}$ -dodecadiene and β -methyl- $\Delta^{\alpha\gamma}$ -decadiene were prepared by the withdrawal of water from the corresponding tertiary alcohols, it being assumed that they possess the constitution indicated:

(I.)

(II.)

(III.)

(IV.)

The tertiary alcohols were obtained by the action of the Grignard reagent on methyl undecenoate and methyl nonenoate respectively. The removal of water from (I) was easily effected by means of phthalic anhydride, but the second alcohol (III), on treatment with any acid dehydrating agent, gave polymerised products of high boiling point, and anhydrous baryta had no action. By allowing the Grignard mixture to remain for twenty-four hours, however, water was eliminated, and the hydrocarbons were obtained, although in extremely poor yield. Another interesting compound, namely, *methyl θ -aldehydo-n-nonoate*, $\text{CHO}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{Me}$, was obtained by the action of ozone on methyl undecenoate.

EXPERIMENTAL.

$\alpha\alpha$ -Dimethyl- Δ^{α} -undecenyl Alcohol, $\text{CH}_3\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CMe}_2\cdot\text{OH}$.

Fifty grams of magnesium methyl iodide were prepared in ethereal solution in the usual manner, and to the solution were added 30 grams of methyl undecenoate, also in ethereal solution, the flask being kept cold by a stream of water. The product was decomposed by water and hydrochloric acid, the ethereal layer separated, washed with water, and ether removed by distillation. The residual oil was then boiled for ten minutes with alcoholic potassium hydroxide to destroy any unchanged ester, and poured into water. The alcohol, which separated as an oil, was extracted with ether, dried over anhydrous magnesium sulphate,* and distilled. It is a colourless oil, with a characteristic and rather unpleasant odour, and boils at $130^\circ/10$ mm.:

0.1432 gave 0.4134 CO_2 and 0.1718 H_2O . $\text{C}=78.7$; $\text{H}=13.3$.

$\text{C}_{13}\text{H}_{26}\text{O}$ requires $\text{C}=78.8$; $\text{H}=13.1$ per cent.

Determination of the refractive power gave: $t=22.2^\circ$; $D_4^{22.2}$ 0.84217; M_d 62.54; M_β 63.68; M_γ 64.24; $M_\gamma - M_\alpha = 1.7$;

$$\left(M = \frac{\mu^2 - 1}{\mu^2 + 2} \cdot \frac{P}{a}\right).$$

* For drying alcohols in ethereal solution it has been found that anhydrous magnesium sulphate is much preferable to the more commonly used sodium sulphate.

450 β -METHYL- $\Delta^{\alpha\lambda}$ -DODECADIENE AND β -METHYL- $\Delta^{\alpha\gamma}$ -DECADIENE.

β -Methyl- $\Delta^{\alpha\lambda}$ -dodecadiene, $\text{CH}_3\cdot\text{CH}\cdot[\text{CH}_2]_8\cdot\text{CMe}\cdot\text{CH}_2$.

This hydrocarbon is easily and quantitatively prepared from the above-mentioned alcohol by boiling it with the theoretical quantity of phthalic anhydride for four hours. The mixture is then poured into a dilute solution of sodium carbonate, the hydrocarbon extracted by means of ether, and distilled, when it passed over at $150\text{--}155^\circ/67\text{ mm.}$ On redistillation over metallic sodium, the hydrocarbon boiled at $152^\circ/67\text{ mm.}$:

0.1267 gave 0.3999 CO_2 and 0.1518 H_2O . $\text{C}=86.1$; $\text{H}=13.3$.

$\text{C}_{13}\text{H}_{24}$ requires $\text{C}=86.6$; $\text{H}=13.3$ per cent.

β -Methyl- $\Delta^{\alpha\lambda}$ -dodecadiene is a colourless oil with a faint, lemon-like odour.

aa-Dimethyl- Δ^{β} -nonenyl Alcohol, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}_2\cdot\text{OH}$, and

β -Methyl- $\Delta^{\alpha\gamma}$ -decadiene, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2$.

Both these substances can be prepared by the interaction of magnesium methyl iodide and methyl Δ^{α} -nonenoate (compare Harding and Weizmann, *Trans.*, 1910, **97**, 299). To prepare the alcohol, methyl Δ^{α} -nonenoate is added to the theoretical amount of magnesium methyl iodide in ethereal solution. After two hours, the product is worked up in the usual way. The yield is about 30 per cent. of the theoretical. The alcohol boils at $88\text{--}90^\circ/10\text{ mm.}$, and possesses an odour resembling that of *n*-nonaldehyde:

0.1325 gave 0.3778 CO_2 and 0.1514 H_2O . $\text{C}=77.7$; $\text{H}=12.7$.

$\text{C}_{11}\text{H}_{22}\text{O}$ requires $\text{C}=77.6$; $\text{H}=12.9$ per cent.

Determination of refractive power gave: $t=17.7^\circ$; $D_4^{17.7}$ 0.8265; M_d 54.38; M_g 55.46; M_γ 55.92; $M_\gamma - M_d = 1.54$.

The compound can be boiled unchanged over anhydrous baryta, but when treated with dehydrating agents, such as phthalic anhydride, zinc chloride, or potassium hydrogen sulphate, polymerised products of high boiling point are obtained.

β -Methyl- $\Delta^{\alpha\gamma}$ -decadiene is obtained if the mixture of methyl Δ^{α} -nonenoate and magnesium methyl iodide is allowed to remain for twenty-four hours. The yield is, however, extremely poor. The hydrocarbon is purified by repeated distillation over sodium, and boils at 184° :

0.1834 gave 0.5802 CO_2 and 0.2091 H_2O . $\text{C}=86.2$; $\text{H}=12.7$.

$\text{C}_{11}\text{H}_{20}$ requires $\text{C}=86.8$; $\text{H}=13.1$ per cent.

By the interaction of magnesium methyl iodide and methyl crotonate under similar conditions, a small quantity of ethyl alcohol was obtained, and a second fraction, distilling at $122\text{--}124^\circ$, con-

sisted of methylethylisopropylcarbinol. (Found, $C=72.5$; $H=14.4$. Calc., $C=72.4$; $H=13.8$ per cent.)

Determination of the refractive power in ethyl-alcoholic solution gave $t=20.4^\circ$; $D_4^{20.4} 0.8101$; M_a of solute $=36.41$.

Methyl θ -Aldehydo-n-nonoate, $CO_2Me \cdot [CH_2]_8 \cdot CHO$.

This aldehyde was prepared by passing a current of ozonised oxygen through a solution of methyl undecenoate in chloroform, covered by a layer of water, until the ozone ceased to be absorbed. The chloroform solution was then shaken with a solution of sodium hydrogen sulphite, and the sodium hydrogen sulphite compound, which separated out after some time, collected, washed with ether, and freed from the remainder of the adhering oil by porous porcelain. The colourless, lustrous solid was then distilled in a current of steam from very dilute sodium carbonate solution, and the small amount of oil which passed over was converted into the *semicarbazone*, which crystallised from alcohol in small needles, melting at $94-96^\circ$:

0.1309 gave 0.2735 CO_2 and 0.1066 H_2O . $C=57.0$; $H=9.0$.

$C_{13}H_{25}O_3N_3$ requires $C=57.6$; $H=9.2$ per cent.

The aldehydo-acid, which possesses a very agreeable, fruity odour, was liberated from its semicarbazone by warm dilute hydrochloric acid.

THE UNIVERSITY,
MANCHESTER.