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Abstract

Full Text

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ANIONOTROPIC REARRANGEMENT OF 2,6-DIMETHYLOCTA-2,4,7-TRIEN-6-OL

An interesting feature of polyene alcohols is that, under the action of dilute acids, they very readily undergo an anionotropic rearrangement with migration of the hydroxyl group and an increase in the number of conjugated bonds ([1]). The study of this rearrangement is of interest from the standpoint of the possibility of obtaining primary polyene alcohols, especially of the isoprenoid type.

We investigated the anionotropic rearrangement of 2,6-dimethylocta-2,4,7-trien-6-ol (III), which, in the structure of its carbon chain, is an analogue of linalool with one additional double bond.

By the action of lithium acetylide in liquid ammonia solution on 2-methylhepta-2,4-dien-6-one (I), the previously undescribed 2,6-dimethylocta-2,4-dien-7-yn-6-ol (II) was obtained in good yield.

Upon absorption of 1 mole of hydrogen in the presence of a Pd catalyst, carbinol III was converted into 2,6-dimethylocta-2,4,7-trien-6-ol (III), a liquid with a pleasant floral odor.

$$\mathrm{I} \xrightarrow[\text{liq. } \mathrm{NH_3}]{\mathrm{LiC{\equiv}CH}} \mathrm{II} \xrightarrow{\mathrm{H_2/Pd}} \mathrm{III}$$

For the anionotropic rearrangement of carbinol III, two directions are possible: either rearrangement toward formation of the primary alcohol (dehydrogeraniol IV) with the shift of one double bond, or toward formation of the tertiary alcohol V, with simultaneous shift of two double bonds.

$$\mathrm{III} \longrightarrow \begin{cases} \mathrm{IV\ (CH_2OH)} \\ \mathrm{V\ (HO)} \end{cases} \qquad \mathrm{V} \xrightarrow{\mathrm{H_2/Pt}} \mathrm{VI}$$

We established that, upon treatment of carbinol III with 0.05% sulfuric acid for 1.5 hr at room temperature, only the tertiary alcohol V is formed, while the primary alcohol IV is not formed.

To prove this direction of the reaction, the V obtained was subjected to exhaustive hydrogenation to 2,6-dimethyloctan-2-ol (VI), and then the same alcohol VI was obtained by the following reactions:

$$\text{II} \xrightarrow{1\%\,H_2SO_4} \text{VII} \xrightarrow{H_2/Pd} \text{V} \xrightarrow{H_2/Pt} \text{VI}$$

2,6-Dimethylocta-2,4-dien-7-yn-6-ol (II), for which an anionotropic rearrangement is possible only toward formation of the tertiary alcohol, under the action of 1% sulfuric acid is isomerized into 2,6-dimethylocta-3,5-dien-7-yn-2-ol (VII). The latter, upon partial hydrogenation in the presence of a Pd catalyst, is converted into V, and upon complete hydrogenation in the presence of a Pt catalyst, into VI. The saturated alcohols VI obtained by both methods give 3,5-dinitrobenzoates (molecular-

compounds with α-naphthylamine), melting at one and the same temperature (100-101°) and giving no depression on mixed melting.

The methylheptadienone I required for the synthesis of carbinol II was obtained by us in two ways:

1. By pyrolysis of the acetoacetate of dimethylethynylcarbinol (2,3):

$$\begin{matrix}(CH_3)_2{-}C{-}C{\equiv}CH \\ |\quad\quad\quad\quad \\ OCOCH_2COCH_3\end{matrix} \xrightarrow[175-185^\circ]{-CO_2} (CH_3)_2C{=}CH{-}CH{=}CHCOCH_3$$

IX I (yield 49%)

2. By condensation of dimethylacrolein with acetone under the influence of aluminum isopropoxide and tert-amylate (yield 68-72%), and also of caustic soda (yield 47.5%).

$$(CH_3)_2C{=}CHCHO \xrightarrow[(RO)_3Al \text{ or } NaOH]{CH_3COCH_3} (CH_3)_2C{=}CH{-}CH{=}CHCOCH_3$$

I

Experimental Part

Synthesis of 2-methylhepta-2,4-dien-6-one (I) from dimethylethynylcarbinol (VIII)

a) **Acetoacetate of dimethylethynylcarbinol (IX).** To a mixture of 120 g of dimethylethynylcarbinol (VIII) and 10 drops of triethylamine heated to 85°, with stirring over 1.5 hr, 112 g of diketene was added (b.p. 51-52°/50 mm; n_D^{20} 1.4350). The reaction mass was stirred for 15 min at 85-95° and subjected to vacuum distillation. 191 g (92%, calculated on diketene) of the acetoacetate of dimethylethynylcarbinol (IX) was obtained, b.p. 90-92°/10 mm (2).

b) **Pyrolysis of the acetoacetate of dimethylethynylcarbinol (IX).** A mixture of 90 g of IX and 100 ml of dry vaseline oil was heated at 175–185° for 5 hr. Continuous evolution of carbon dioxide was observed.

At the end of the experiment the temperature began gradually to fall as a result of accumulation of a low-boiling liquid, and the evolution of carbon dioxide slowed greatly. Under a vacuum of 15 mm, 12 g of liquid was distilled off, b.p. 30–38°; n_D^{20} 1.4405. The residue was heated for 30 min at 190–210° until gas evolution ceased, and the product was distilled off in vacuum. 29 g of (I) was obtained, b.p. 77–79°/7 mm; n_D^{20} 1.5327 (4). $\lambda_{\max}^{*}$ (in isooctane) 275 mμ. Yield 49%.

The 2,4-dinitrophenylhydrazone of dienone I melts at 209–210° (from a mixture of ethyl alcohol with ethyl acetate). $\lambda_{\max}$ (in isooctane) 372 mμ.

The semicarbazone of dienone I has m.p. 174–175° (from ethyl alcohol). $\lambda_{\max}$ (in methanol) 295 mμ ($\lg \varepsilon$ 4.746).

Condensation of dimethylacrolein with acetone

a) To a suspension of 8 g of finely powdered caustic soda in 650 ml of dry acetone, over several minutes with cooling by tap water, 78.7 g of dimethylacrolein was added (b.p. 133–135°; n_D^{20} 1.4525); warming to 40° was observed. The mixture was stirred for 10 min, then the separated alkaline solution was removed, and the acetone solution was neutralized with solid carbon dioxide, dried, and distilled. The crude ketone I obtained, b.p. 50–60°/1 mm, was steam-distilled and then again distilled in vacuum. 55 g of dienone I was obtained, b.p. 56–59°/1 mm; n_D^{20} 1.5310. Yield 47.5%.

b) A mixture of 10.7 g of dimethylacrolein, 260 ml of acetone, 500 ml of benzene, and 87 g of a 35% benzene solution of aluminum tert-amylate

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* The ultraviolet spectra were recorded in the optical laboratory of Moscow State University.

was heated under reflux in a stream of nitrogen for 40 h. Then, with stirring, 200 ml of 10% sulfuric acid was added to the mixture cooled to 0°. The product was extracted with ether, washed with a 5% sodium bicarbonate solution and with water, dried over magnesium sulfate, and distilled. 11.4 g (yield 72%) of methylheptadienone I was obtained, b.p. 57–59°/1 mm; n_D^{20} 1.5301. When aluminum isopropylate was used, the yield of methylheptadienone was 68%.

Condensation of acetylene with 2-methylhepta-2,4-dien-6-one

2,6-Dimethylocta-2,4-dien-7-yn-6-ol (II). The reaction was carried out in a three-necked flask of 3 l capacity, equipped with a mechanical stirrer, gas-inlet

tubes for acetylene and ammonia, a thermometer, a dropping funnel, and a drying tube with alkali.

Into the flask, 1200 ml of dry liquid ammonia was condensed while cooling with a mixture of solid carbon dioxide and acetone. Then a vigorous stream of purified acetylene was passed through the ammonia, and after 25 min, 6.5 g of finely cut lithium was introduced into the stirred liquid over 15 min. After 40 min, the initially black reaction mass became milky in color, indicating complete conversion of the lithium into acetylide. The stream of acetylene was considerably reduced, and to the lithium acetylide, with stirring at a temperature of −70°, 57.3 g (0.46 mole) of methylheptadienone I in 250 ml of absolute ether was added over 2.5 h. The reaction mass was then stirred for 3 h at −70° and left under cooling overnight. The next day the cooling was removed and the ammonia was allowed to evaporate. At a temperature of −5°, 300 ml of ether, 300 ml of water, and 60 g of ammonium chloride were added. The ether layer was separated, washed with water, dried over magnesium sulfate, and distilled. 55.7 g of carbinol II was obtained, b.p. 52–61° at 0.1 mm. After purification of carbinol II from an admixture of methylheptadienone with the aid of semicarbazide, 35 g of 2,6-dimethylocta-2,4-dien-7-yn-6-ol (II) was isolated, b.p. 60–62° at 0.05 mm; n_D^{20} 1.5120; d_4^{20} 0.9055; MR found 50.07; calcd. 46.91. λ_{max} (in isooctane) 239 mμ (lg ε 4.416), 274 mμ (lg ε 3.740). Yield 51%.

Found* %: C 80.10; 80.17; H 9.62; 9.58
$C_{10}H_{14}O$. Calculated %: C 79.95; H 9.39

2,6-Dimethylocta-2,4,7-trien-6-ol (III). 7.5 g (0.05 mole) of 2,6-dimethylocta-2,4-dien-7-yn-6-ol (II) was hydrogenated in 30 ml of absolute ethyl alcohol in the presence of a Pd catalyst. In 1 h the calculated amount (0.05 mole) of hydrogen was absorbed (1240 ml; 18°/749 mm), and the hydrogenation was stopped. After distillation, 6.9 g of 2,6-dimethylocta-2,4,7-trien-6-ol (III) was obtained as a colorless liquid with a pleasant floral odor, b.p. 47–48°/0.04 mm; n_D^{20} 1.5039; d_4^{20} 0.8804; MR found 51.14; calcd. 48.50. λ_{max} (in methanol) 273 mμ (lg ε 4.079), 280 mμ (lg ε 3.340).

Found* %: C 78.05; 77.95; H 10.57; 10.60
$C_{10}H_{16}O$. Calculated %: C 78.85; H 10.58

2,6-Dimethylocta-3,5,7-trien-2-ol (V). A mixture of 4.2 g of 2,6-dimethylocta-2,4,7-trien-6-ol (III), 60 ml of 0.05% sulfuric acid, and 0.01 g of hydroquinone was shaken for 90 min at room temperature. The product was extracted with ether, washed with a 5% sodium bicarbonate solution and with water, dried, and distilled. 3.0 g (yield 72%) of 2,6-dimethylocta-3,5,7-trien-2-ol (V) was obtained, b.p. 53–55°/0.02 mm; n_D^{20} 1.5311; d_4^{20} 0.8945; MR found 52.61; calcd. 48.50. λ_{max} (in isooctane) 268 mμ (lg ε 4.528), 279 mμ (lg ε 4.428).

	Found %: C 77.56; 77.70; H 10.52; 10.62
$C_{10}H_{16}O$.	Calculated %: C 78.85; H 10.58

* The analysis was carried out immediately after distillation of carbinol II.

1.52 g (0.01 mole) of carbinol (V) was subjected to exhaustive hydrogenation in 8 ml of abs. ethyl alcohol in the presence of a Pt catalyst. 0.0294 mole of hydrogen was absorbed (660 ml, 18°; 753 mm). After distillation, 1.3 g of 2,6-dimethyloctan-2-ol (VI) was obtained, b.p. 82–83°/10 mm; n_D^{20} 1.4352; d_4^{20} 0.8335; MR found 49.72; calc. 49.90. λ_{max} (in isooctane) 265 mμ.

Found %:	C 75.77; 75.63; H 13.74; 13.63
$C_{10}H_{22}O$. Calculated %:	C 75.86; H 14.00

The molecular compound of the 3,5-dinitrobenzoate of alcohol (VI) with α-naphthylamine has m.p. 100–101° (from ethyl alcohol).

Found %:	N 8.84; 8.62
$C_{27}H_{33}O_6N_3$. Calculated %:	N 8.47

2,6-Dimethylocta-3,5-dien-7-yn-2-ol (VII). A mixture of 8 g of 2,6-dimethylocta-2,4-dien-7-yn-6-ol (II), 54 ml of ether, 535 ml of 1% sulfuric acid, and 0.01 g of hydroquinone was stirred in a nitrogen atmosphere for 5 h at room temperature. The product was extracted with ether, washed with sodium bicarbonate solution and water, dried, and distilled.

6.3 g (yield 79%) of 2,6-dimethylocta-3,5-dien-7-yn-2-ol (VII) was obtained, b.p. 59–62°/0.05 mm; n_D^{20} 1.5300; d_4^{20} 0.9097. MR found 50.97; calc. 46.91. λ_{max} (in isooctane) 262 mμ ($\lg \varepsilon$ 4.506).

Found %:	C 79.14; 79.01; H 9.00; 9.17
$C_{10}H_{14}O$. Calculated %:	C 79.95; H 9.39

Hydrogenation of 2,6-dimethylocta-3,5-dien-7-yn-2-ol (VII)

2,6-Dimethylocta-3,5,7-trien-2-ol (V) and 2,6-dimethyloctan-2-ol (VI). 5.1 g (0.034 mole) of 2,6-dimethyloctadien-3,5-yn-7-ol-2 (VII) was hydrogenated in 15 ml of abs. ethyl alcohol in the presence of a Pd catalyst. In 2 h, the calculated amount (0.034 mole) of hydrogen was absorbed (860 ml; 18°/739 mm), and the hydrogenation was stopped. After distillation, 4.1 g of 2,6-dimethylocta-3,5,7-trien-2-ol (V) was obtained, b.p. 55–56° at 0.02 mm; n_D^{20} 1.5320; d_4^{20} 0.8976; MR found 51.98; calc. 48.50. λ_{max} (in isooctane) 267 mμ ($\lg \varepsilon$ 4.399), 289 mμ ($\lg \varepsilon$ 4.103).

Found %:	C 78.19; 78.24; H 10.57; 10.63
$C_{10}H_{16}O$. Calculated %:	C 78.91; H 10.59

3.1 g (0.02 mole) of 2,6-dimethylocta-3,5,7-trien-2-ol* (V) was subjected to exhaustive hydrogenation in 12 ml of abs. ethyl alcohol in the presence of a Pt catalyst. 1480 ml of hydrogen was absorbed (18°/739 mm), which corresponds to 2.9 mole of hydrogen per 1 mole of substance. After distillation, 2.9 g of dimethyloctan-2-ol (VI) was obtained, b.p. 81–83°/10 mm; n_D^{20} 1.4352; d_4^{20} 0.8333. The molecular compound of the 3,5-dinitrobenzoate of alcohol VI with α-naphthylamine has m.p. 100–101° (from ethyl alcohol) and gives no depression on mixed melting with the 3,5-dinitrobenzoate of alcohol VI described above.

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* The low percentage of carbon in this and other alcohols with several double bonds (see below) is explained by the great sensitivity of these compounds to atmospheric oxygen.

Note: Figure translations are in progress. See original paper for figures.