PREPARATION OF $\alpha$-ALKYL-GLYCEROLS

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Only a certain number of homologues of the normal $\alpha$-alkyl-glycerols such as $\alpha$-methyl- and $\alpha$-ethyl-glycerol are known at present. The first is obtained by boiling 2,3-dibromobutanol-1 with water and the second by the oxidation of ethylvinyl-carbinol with potassium permanganate. We show on two examples the preparation of $\alpha$-alkyl-glycerols by reducing the easily obtainable 1,3-diacetoxy-n-alkanones with lithium aluminium hydride. By using this method we obtained from 1,3-diacetoxy-n-heptanone-2 ($\alpha$-butyl-glycerol (IIa)) and from 1,3-diacetoxy-n-undecanone-2 ($\alpha$-octyl-glycerol (IIb)) in good yields. The first substance is at room temperature partly crystallized, the second is well crystallized but with a rather varying melting point caused by the presence of two diastereomeric forms. From these hitherto unknown triols trisphenylurethanes and triacetates are prepared.

\begin{align*}
\text{R—CH—CO—CH}_3 & \quad \text{R—CH—CH—CH}_2 \\
\text{OAc} & \quad \text{OAc} \quad \text{OH} \quad \text{OH} \quad \text{OH} \\
\text{I} & \quad \text{II}
\end{align*}

a) $\text{R} = -\text{C}_3\text{H}_7$

b) $\text{R} = -\text{C}_{17}\text{H}_{35}$

It is believed that the method can be used in the preparation of any of the $\alpha$-alkyl-glycerols as 1,3-diacetoxy-n-alkanones-2 are easily obtainable.

EXPERIMENTAL

$\alpha$-Butyl-glycerol (IIa)

6.3 g. of 1,3-diacetoxy-n-heptanone-2 is dissolved in 50 ccm abs. ether and added dropwise to the mixture of 3.13 g. LiAlH₄ in 100 ccm abs. ether while stirring constantly. The mixture is heated 15 minutes in the steam-bath and afterwards 10 ccm water and 100 ccm 10% sulphuric acid is carefully added under violent stirring. The ether layer is separated, dried by sodium sulphate and after the evaporation of ether the substance is

1) Lieben and Zeisel, Monatsh., 1, 832 (1880).
2) Wagner, Ber. 21, 3349 (1888).
3) M. Proštenik, Arhiv kem. 21, 182 (1949).
distilled. 3.45 g. of a colourless, dense oil, with a boiling point about 113—115° in vacuo of 0,03 mm of Hg, was obtained which crystallized partly after standing for several hours.

**Trisphenylurethane of α-butyl-glycerol** is obtained by heating the triol with phenylisocyanate for an hour at 100°. While the mixture was heated it crystallized in the flask. For the analysis the compound was recrystallized four times from benzene and dried in high vacuum at 100°; m. p. 163—164°.

4,795 mg subst.: 0,356 ccm N₂ (21°, 756 mm)

C₃₈H₅₁O₉N₃ (505, 55) Calcd. N 8.31, found. N 8.59%

**Triacetate of α-butyl-glycerol** was prepared in the manner already known using 2 g. of triol, 5 ccm acetonhydride and 5 ccm abs. pyridine. 1.85 g. of a colourless oil with boiling point at 105—107° and in vacuo of 0.03 mm Hg was obtained.

14.95 mg subst.: 31.27 mg CO₂, 10.85 mg H₂O

C₁₈H₂₆O₁₈ (274, 31) Calcd. C 56.92, H 8.09%

Found C 57.08, H 8.12%

**α-Octyl-glycerol (IIb)**

In an analogous manner 5.3 g. α-octyl-glycerol, b. p. 130—140°, in vacuo 0,03 mm Hg, was obtained from 9.75 g. 1,3-diacetoxy-n-undecanone-2 in 50 ccm abs. ether, and 3.9 g. LiAlH₄ in 125 ccm abs. ether. The colourless distillate crystallized immediately; but even after repeated crystallizations from acetone, the melting point still remained variable at 40—70°.

5,840 mg subst.: 13.89 mg CO₂, 6.12 mg H₂O

C₁₁H₂₂O₅ (204, 30) Calcd. C 64.66, H 11.84%

Found C 64.91, H 11.73%

**Trisphenylurethane of α-octyl-glycerol** was recrystallized for analysis four times from benzene and dried in high vacuum during six hours at 100°; m. p. 157—158°.

9.598 mg subst.: 24.18 mg CO₂, 5.82 mg H₂O

5,790 mg subst.: 0,382 ccm N₂ (21°, 756 mm)

C₃₂H₅₉O₉N₃ (561, 66) Calcd. C 68.43, H 7.00, N 7.47%

Found C 68.75, H 6.79, N 7.62%

The analyses were performed by prof. M. Munk-Weinert and prof. L. Filipović.

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IZVOD

Priredba α-alkil-glicerola

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Dosada slabo poznati α-alkil-gliceroli mogu se priređiti redukcijom lagano pristupačnih 1,3-diacetoksi-n-alkanona-29) sa litijevim alum'niijevim h'ı'dridom. Na taj način su dobiveni: α-butil-glicerol t. v.0.03 113—115°, triacetat t. v.0.03 105—107°, trisfeniluretan t. t. 163—164° i α-oktil-glicerol t. v.0.03 130—140°, t. t. 40—70°, trisfeniluretan t. t. 157—158°.

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