PREPARATION OF α-ALKYL-GLYCEROLS

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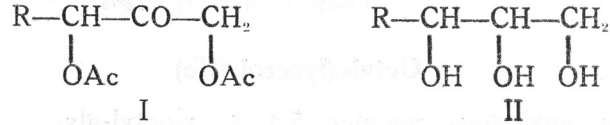
Only a certain number of homologues of the normal α-alkyl-glycerols such as α-methyl-[1]) and α-ethyl-glycerol[2]) are known at present. The first is obtained by boiling 2,3-dibromobutanol-1 with water and the second by the oxidation of ethyl-vinyl-carbinol with potassium permanganate. We show on two examples the preparation of α-alkyl-glycerols by reducing the easily obtainable 1,3-diacetoxy-n-alkanones-2[3]) with lithium aluminium hydride. By using this method we obtained from 1,3-diacetoxy-n-heptanone-2 (Ia) α-butyl-glycerol (IIa) and from 1,3-diacetoxy-n-undecanone-2 (Ib), α-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.



I II

a) R = — C_4H_9
b) R = — C_8H_{17}

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

EXPERIMENTAL

α-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. $LiAlH_4$ 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. Prošteník, 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 N_2 (21°, 756 mm)
$C_{28}H_{31}O_6N_3$ (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 acetanhydride 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 CO_2, 10,85 mg H_2O
$C_{13}H_{22}O_6$ (274, 31) Calcd. C 56,92, H 8,08%
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. $LiAlH_4$ in 125 ccm abs. ether. The colourless destillate 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 CO_2, 6,12 mg H_2O
$C_{11}H_{24}O_3$ (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 CO_2, 5,82 mg H_2O
5,790 mg subst.: 0,382 ccm N_2 (21°, 756 mm)
$C_{32}H_{39}O_6N_3$ (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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[Received, August 2, 1950]

IZVOD

Priredba α-alkil-glicerola

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Dosada slabo poznati α-alkil-gliceroli mogu se prirediti redukcijom lagano pristupačnih 1,3-diacetoksi-n-alkanona-2[3]) sa litijevim aluminijevim hidridom. 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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Primljeno 2. kolovoza 1950.