Preparation of $\gamma$-di-tertiary Glycols From the Esters of $\gamma$-keto Carboxylic Acids. II

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Some $\gamma$-di-tertiary glycols have been prepared by the Grignard’s method from the Et esters of $\gamma$-keto carboxylic acids.

In a previous communication\(^1\) we have described the synthesis of some $\gamma$-ditertiary glycols from the esters of $\gamma$-ketocarboxylic acids, prepared by the method of Peters Jr. and R. Fischer\(^4\). III-a was prepared earlier by Blaise and the same way 1.1.4-triphenylheptane-1,4-diol [IV-b] and 5,8-dibutyldodecane-5,8-diol [IV-a]. The compound IV-a has been prepared earlier by Petrov and Sanin\(^3\) from ethyl succinate and n-butyl-magnesium bromide.

As starting material for the preparation of 5,8-dibutyldodecane-5,8-diol we used ethyl 3-ketoheptane-1-carboxylate [III-a], which was synthesized by the method of Chichibabin\(^2\) from $\alpha$-furyl-propylcarbinol [II-a], prepared by method of Peters J. and R. Fischer\(^4\). III-a was prepared earlier by Blaise and Koehler\(^5\) from carboetoxy methane carboxyl chloride and n-amyl-zinc-chloride.

Intending to prepare some ditertiary glycols from the esters of $\gamma$-keto-dodecane-1-carboxylic acid [III-c], we synthesized for that purpose by the Grignard’s method $\alpha$-furyloctylcarbinol [II-c]. The attempt to prepare III-c by cleavage of II-c according to the mentioned method\(^2\) proved to be till now unsuccessful.

The synthesized compounds IV-a and IV-b gave positive Deniges-reaction\(^6\) on tertiary alcohols.

\[\text{HC} - \text{C} - \text{H}\]

\[\text{HC} - \text{C} - \text{CH}\]

\[\text{O} \quad \text{O}\]

\[\text{I.}\]

\[\text{HC} - \text{C} - \text{CH} \quad \text{RMgBr} \quad \text{HC} - \text{C} - \text{CH} - \text{R}\]

\[\text{O} \quad \text{OH} \quad \text{II.}\]

\[\text{HC} - \text{C} - \text{CH} \quad \text{R}_1 \text{MgBr} \quad \text{HC} - \text{C} - \text{CH} \quad \text{R}_1 \text{OH}\]

\[\text{IV.}\]

\[\text{H}_2\text{C} - \text{CH}_2 \quad \text{R}_1 \text{OH}\]

\[\text{III.}\]

\[\text{H}_2\text{C} - \text{CH}_2\]

\[\quad \text{R}_1 \quad \text{OH}\]

\[\text{a) } R = \text{C}_8\text{H}_7; \quad R_1 = \text{C}_4\text{H}_9 \quad \text{b) } R = \text{C}_2\text{H}_5; \quad R_1 = \text{C}_6\text{H}_5\]
x-Furyl-propylcarbinol [II-a]

11.0 g. (0.45 g-atom) of magnesium, 51.0 g. (0.41 mole) of n-propyl bromide and 20.0 g. (0.21 mole) of furfural [I] in 250 ml. of dry ether yielded following a previously described method1 18.0 g. (62%) of α-furyl-propylcarbinol (b. p. 90.5—91.5/15 mm in an atmosphere of carbon dioxide). Peters and Fischer4 recorded 55% yield, b. p. 91—921/12 mm.

Ethyl 3-ketoheptane-1-carboxylate [III-a]

To 16.0 g. (0.11 mole) of α-furyl-propylcarbinol [II-a] in 53 ml. of abs. ethanol was added 1.7 ml. of a 260/o ethanolic solution of hydrochloric acid. The reaction mixture was refluxed for 30 minutes, and the ethanol distilled off on a water bath in an atmosphere of carbon dioxide. The residue was cooled, added to a cool 10/o solution of sodium hydroxide, and the mixture extracted with ether (3 X 50 ml.). The ethereal solution was dried over sodium sulfate, and the mixture evaporated on a water bath in an atmosphere of carbon dioxide. After fractionation in vacuo in an atmosphere of carbon dioxide, 8.5 g. (40%) of colourless liquid of an agreeable aromatic odour was obtained, b. p. 122—124°/12 mm. For the analysis a sample was redistilled and the fraction boiling at 115—116°/4 mm was used. Blaise and Koehler5 recorded b. p. 125°/15 mm.

d^20 : 0.9710 n^20 : 1.4382; calc'd : MR^7 50.2, found : MR 50.4

Anal. 29.530 mg. subst.: 69.820 mg. CO₂, 25.230 mg. H₂O
C₁₀H₁₅O₃ (186.24) calc'd: C 64.49; H 9.74/o
found: C 64.39; H 9.54/o.

3-Ketoheptane-1-carboxylic acid

The ethyl ester II-a was saponified by refluxing it with 50/o aqueous hydrochloric acid for two hours. Thin and colourless glistening plate-like crystals were obtained, m. p. 53°.

5,8-Dibutyldodecane-5,8-diol [IV-a]

To a solution of butyl-magnesium bromide prepared from 4.6 g. (0.19 g-atom) of magnesium and 24.0 g. (0.18 mole) of n-butyl bromide in 200 ml. of dry ether, 8.0 g. (0.04 mole) of ethyl 3-ketoheptane-1-carboxylate was added. Following a procedure reported earlier1 an orange-red semicrystalline solid (15.0 g.) was obtained. Removal of the oily by-product by suction yielded crystalline IV-a (10.5 g., 80%). For the analysis the compound was washed with petroleum ether, and recrystallized from dilute acetic acid. The pure compound consisted of very thin, shiny, transparent leaflets, m. p. 103° (recorded m. p. 103°), which were soluble in acetone, ether, chloroform and benzene, slightly in petroleum ether, and sparingly soluble in dilute ethanol (1 : 1).

Anal. 29.980 mg. subst.: 83.645 mg. CO₂, 35.975 mg. H₂O
C₂₀H₄₂O₂ (314.54) calc'd: C 76.36; H 13.46/o
found: C 76.14; H 13.42/o.

The oily by-product decomposed when distilled in vacuo.

1,1,4-Triphenylheptane-1,4-diol [IV-b]

To a solution of phenyl magnesium bromide prepared from 5.4 g. (0.22 g-atom) of magnesium and 32.0 g. (0.20 mole) of bromobenzene in 100 ml. of dry ether, 5.0 g. (0.03 mole) of ethyl 3-ketohexane-1-carboxylate1 in 50 ml. of dry ether was added. Following a procedure reported earlier1, a semicrystalline solid was obtained. Removal of the oily by-product by trituration with a cooled ether-acetone-petroleum ether-mixture (1:1:1) yielded crystalline IV-b (5.2 g., 50%), which after recrystallization from petroleum ether gave small white silky needles, m. p. 113.5—114°.

The compound was easily soluble in acetone, ether, chloroform and benzene, less readily in petroleum ether and sparingly soluble in dilute ethanol (1 : 1).
Preparation of \( \gamma \)-di-tertiary glycols

Anal. 29.570 mg. subst.: 90.230 mg. CO\(_2\), 20.680 mg. H\(_2\)O
\[ C_{25}H_{2s}O_2 \] (360.47) calc'd: C 83.29; H 7.83\%
found: C 83.27; H 7.83\%.

\( \alpha \)-Furyl-octylcarbinol [II-c]

To a solution of octyl magnesium bromide prepared from 3.15 g. (0.13 g-atom) of magnesium and 24.0 g. (0.13 mole) of n-octyl bromide in 100 ml. of dry ether, a solution of 10.0 g. (0.10 mole) of freshly distilled furfural [I] in 25 ml. of dry ether was added. The reaction was accomplished in the same way as described previously\(^1\). The crude \( \alpha \)-furyloctylcarbinol was distilled twice in vacuo. 9.8 g (41\%) of the pure product was obtained, b. p. 137-138° / 3 mm. The compound was a clear yellowish liquid, with an aromatic, fruitlike odour. By cooling the liquid hardens at 20°, giving a white, waxy, amorphous mass which melts at 90°.

\[ d^20 : 0.9287 \quad n^20_D : 1.4674; \quad \text{calc'd: MR 62.72, found: MR 62.9}. \]

Anal. 30.525 mg. subst.: 82.892 mg. CO\(_2\), 28.044 mg. H\(_2\)O
\[ C_{13}H_{22}O_2 \] (210.31) calc'd: C 74.24; H 10.54\%
found: C 74.10; H 10.28\%.

REFERENCES

IZVOD

Priprava \( \gamma \)-ditercijarnih dialkohola iz estera \( \gamma \)-ketokarbonskih kiselina. II

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Prema modificiranoj metodi\(^2\) Čičibabina\(^2\) pripravljen je iz \( \alpha \)-furil-propilkarbinola [II-a] etilni ester 3-ketoheptankarbonske kiseline-1 [III-a] (40\%) T. k.115-116\°. Iz [III-a] i butilmagnezijevog bromida dobiven je 5,8-dibutilododekandiol-5,8 [IV-a] (80\% sirovog produkta). T. t. 103\° (iz razr. octene kiseline). Etilni ester 3-ketoheksan­karbonske kiseline-1 i fenilmagnezijev bromid daje 1,1,4-trifenilheptandiol-1,4 (50\% sirovog produkta). T. t. 113,5-114\° (iz petroletera).

Iz furfurala [I] i oktilmagnezijevog bromida sintetiziran je \( \alpha \)-furil-oktilkarbinol [II-c] (41\%) T. k.137-89\°. T. t. 9\°, koji za sada nije uspjelo metodom Čičibabina\(^2\) prevesti u ester odnosne \( \gamma \)-ketokarbonske kiseline [III-c].

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