

Preparation of γ -di-tertiary Glycols From the Esters of γ -keto Carboxylic Acids. II

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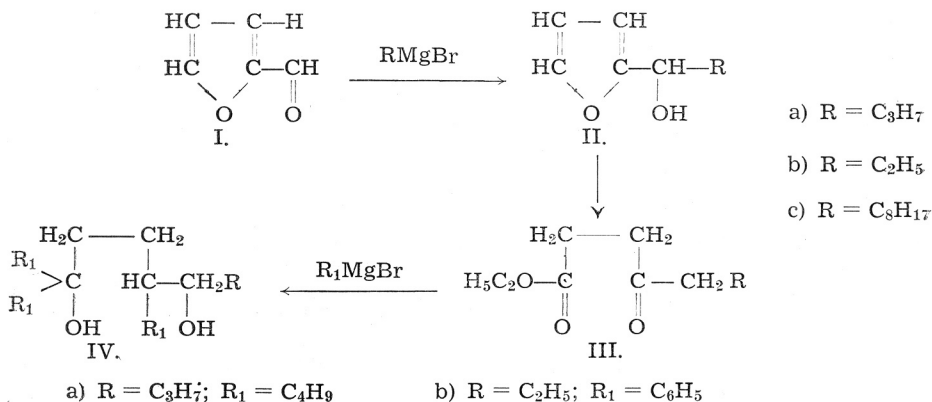
Some γ -di-tertiary glycols have been prepared by the Grignard's method from the Et esters of γ -keto carboxylic acids.

In a previous communication¹ we have described the synthesis of some γ -ditertiary glycols from the esters of γ -ketocarboxylic acids, prepared by the method of Peters Jr. and R. Fischer⁴. 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 Sanin³ 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 Chichibabin² from α -furyl-propylcarbinol [II-a], prepared by method of Peters J. and R. Fischer⁴. III-a was prepared earlier by Blaise and Koehler⁵ from carboetoxymethanecarboxyl chloride and n-amyl-zinc-chloride.

Intending to prepare some ditertiary glycols from the esters of 3-ketododecane-1-carboxylic acid [III-c], we synthesized for that purpose by the Grignard's method α -furyloctylcarbinol [II-c]. The attempt to prepare III-c by cleavage of II-c according to the mentioned method² proved to be till now unsuccessful.

The synthesized compounds IV-a and IV-b gave positive Denigès-reaction⁶ on tertiary alcohols.



EXPERIMENTAL

α-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—01°/15 mm in an atmosphere of carbon dioxide). Peters and Fischer⁴ recorded 55% yield, b. p. 91—92°/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 26% 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 1% solution of sodium hydroxide, and the mixture extracted with ether (3×50 ml.). The ethereal solution was dried over sodium sulfate. The solvent evaporated on a water bath in an atmosphere of carbon dioxide. After fractionation in vacuo in 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_4^{20} : 0.971₀ n_D^{20} : 1.438₂; calc'd : MR⁷ 50.2, found : MR 50.4.

Anal. 29.530 mg. subst.: 69.820 mg. CO₂, 25.230 mg. H₂O
 C₁₀H₁₈O₃ (186.24) calc'd: C 64.49; H 9.74%
 found: C 64.39; H 9.54%

3-Ketoheptane-1-carboxylic acid

The ethyl ester II-a was saponified by refluxing it with 5% aqueous hydrochloric acid for two hours. Thin and colourless glistening plate-like crystals were obtained, m. p. 53°⁸.

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°¹³, 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%
 found: C 76.14; H 13.42%

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).

Anal. 29.570 mg. subst.: 90.230 mg. CO₂, 20.680 mg. H₂O
 C₂₅H₂₈O₂ (360.47) calc'd: C 83.29; H 7.83%
 found: C 83.27; H 7.83%.

α -Furyloctylcarbinol [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 previously¹. The crude α -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 2°, giving a white, waxy, amorphous mass which melts at 9°.

d_4^{20} : 0.9287 n_D^{20} : 1.4678; calc'd: MR 62.72, found: MR 62.9.

Anal. 30.525 mg. subst.: 82.892 mg. CO₂, 28.044 mg. H₂O
 C₁₃H₂₂O₂ (210.31) calc'd: C 74.24; H 10.54%
 found: C 74.10; H 10.28%.

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IZVOD

Priprava γ -ditercijarnih dialkohola iz estera γ -ketokarbonskih kiselina. II

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Prema modificiranoj metodi¹ Čičibabina² pripremljen je iz α -furyl-propilkarbinola [III-a] etilni ester 3-ketoheptankarbonske kiseline-1 [III-a] (40%) T. k. 115–6°. Iz [III-a] i butilmagnezijevog bromida dobiven je 5,8-dibutildodekandiol-5,8 [IV-a] (80% sirovog produkta). T. t. 103° (iz razr. octene kiseline). Etilni ester 3-ketoheksankarbonske kiseline-1¹ 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 α -furyl-oktilkarbinol [II-c] (41%) T. k. 137–8°; T. t. 9°, koji za sada nije uspjelo metodom Čičibabina² prevesti u ester odnosno γ -ketokarbonske kiseline [III-c].

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