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Abstract

Full Text

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SYNTHESIS OF 1,14-TETRADECANEDICARBOXYLIC AND 1,15-PENTADECANEDICARBOXYLIC ACIDS

The most rational methods for the synthesis of high-molecular-weight α,ω-dicarboxylic acids are the electrolysis of salts of half-esters of dicarboxylic acids ([1])

$$2\mathrm{ROOC(CH_2)_nCOO^-} \xrightarrow{-2e} \mathrm{ROOC(CH_2)_{2n}COOR} + 2\mathrm{CO_2}$$

and the reductive dimerization of α, α, α, ω-tetrachloroalkanes ([2])

$$\mathrm{Cl(CH_2)_nCCl_3} \xrightarrow{\mathrm{H_2}} \mathrm{(Cl(CH_2)_nCCl{=})_2} \xrightarrow{\mathrm{NaCN}} \mathrm{(NC(CH_2)_nCCl{=})_2} \rightarrow$$

$$\rightarrow \mathrm{(HOOC(CH_2)_nCCl{=})_2} \rightarrow \mathrm{HOOC(CH_2)_{2n+2}COOH}$$

Karash et al. ([3]) showed that irradiation with ultraviolet light of a mixture of cyclohexanone and octene-1 gives 2-octylcyclohexanone in 20-30% yield.

As a result of a detailed study of the reactions of free-radical addition of acids and alcohols to α-olefins, we found the optimal conditions for obtaining adducts in high yields ([4]). Taking these conditions into account, in the present study we carried out the addition reactions of cyclopentanone and cyclohexanone to undecylenic acid in the presence of tert-butyl peroxide. The reactions were conducted at a molar ratio ketone : undecylenic acid : peroxide = 3 : 0.3 : 0.06, with cyclopentanone at 130-132°, and with cyclohexanone at 151-153°. The acid and peroxide were added dropwise to the ketone over the course of 6-6.5 hr. The yield of the 1 : 1 adduct with cyclopentanone was 69.5%, and with cyclohexanone 50%. 11-(2′-Ketocyclopentyl)undecanoic acid was oxidized to 5-ketotetradecanedicarboxylic-1,14 acid, and the latter was reduced with hydrazine hydrate to 1,14-tetradecanedicarboxylic acid.

$$\text{cyclopentanone} + \mathrm{CH_2{=}CH(CH_2)_8COOH} \rightarrow \text{2-}(\mathrm{(CH_2)_{10}COOH})\text{cyclopentanone}$$
$$\rightarrow \mathrm{HOOC(CH_2)_3CO(CH_2)_{10}COOH} \rightarrow \mathrm{HOOC(CH_2)_{14}COOH}$$

Similarly, 1,15-pentadecanedicarboxylic acid was obtained from 11-(2′-ketocyclohexyl)undecanoic acid.

Experimental Part

11-(2′-Ketocyclopentyl)undecanoic acid. To 200 g (2.4 mol) of cyclopentanone at 130–132° over 6.5 hr was added a solution of 55.3 g (0.3 mol) of undecylenic acid and 8.8 g (0.06 mol) of peroxide in 52.3 g (0.6 mol) of cyclopentanone. The reaction mixture was heated for another 2 hr, after which distillation from it yielded 5 g of unreacted ···

into the reaction of undecylenic acid, 56 g of 11-(2′-ketocyclopentyl)undecanoic acid, residue 16 g. The yield of 11-(2′-ketocyclopentyl)undecanoic acid, calculated on the undecylenic acid taken, was 69.5%, b.p. 213–220° (2 mm), m.p. 51.6–52° (from acetone).

Found, %:	C 71.46; 71.36; H 10.50; 10.30
$C_{16}H_{28}O_3$. Calculated, %:	C 71.60; H 10.51

Semicarbazone, m.p. 166.5–167.5° (from alcohol)

Found, %:	C 62.56; 62.69; H 9.51; 9.57
$C_{17}H_{31}O_3N_3$. Calculated, %:	C 62.74; H 9.60

5-Ketotetradecanedicarboxylic-1,14 acid. The oxidation was carried out under the conditions developed by V. V. Korshak and co-workers (5). To a solution of 50 g of sulfuric acid in 85 ml of water at 55° and with vigorous stirring, 55 g (0.205 mole) of molten 11-(2′-ketocyclopentyl)undecanoic acid was added, and then, at the same temperature (cooling), over 20 min, a solution of 31 g of chromic anhydride and 50 g of sulfuric acid in 50 ml of water was added. Stirring of the reaction mixture at 55° was continued for another 3 h. Then the solid mass on a Büchner funnel was separated from the liquid, dissolved in acetone, the acetone solution was filtered, and the filtrate was evaporated. The acid that precipitated was separated from the mother liquor, again dissolved in acetone, the acetone solution was decanted, filtered, and evaporated. The obtained 5-ketotetradecanedicarboxylic-1,14 acid was recrystallized from benzene. Yield 74% (45.6 g), m.p. 123.5–123.8°.

Found, %:	C 63.76; 63.49; H 9.38; 9.35
$C_{16}H_{28}O_5$. Calculated, %:	C 63.97; H 9.40

Semicarbazone; melts with decomposition at 134°

Found, %:	C 56.14; H 8.81
$C_{17}H_{31}O_5N_3$. Calculated, %:	C 57.12; H 8.74

1,14-Tetradecanedicarboxylic acid. To a solution of 8.5 g of NaOH and 8.5 ml of hydrazine hydrate in 75 ml of diethylene glycol, 7.5 g (0.025 mole) of 5-ketotetradecanedicarboxylic-1,14 acid was added. The mixture was heated for 2 h at 142°, after which the excess hydrazine hydrate and water were distilled off and heating was continued for another 4 h at 210°. To the cooled reaction mixture were added 50 ml of water and hydrochloric acid until a weakly acidic medium was obtained. By filtration the liquid phase was separated from the formed 1,14-tetradecanedicarboxylic acid; its yield after recrystallization was 88% (6.3 g), m.p. 126° (from acetone).

Found, %:	C 66.98; 66.81; H 10.56; 10.48
$C_{16}H_{30}O_4$. Calculated, %:	C 67.10; H 10.56

Literature data (6): m.p. 124–124.2°.

11-(2′-Ketocyclohexyl)undecanoic acid. To 240 g (2.44 moles) of cyclohexanone at 151–153°, over 6 h, a solution of 55.3 g (0.3 mole) of undecylenic acid and 8.8 g (0.06 mole) of peroxide in 55 g (0.56 mole) of cyclohexanone was added, after which the reaction mixture was heated for another 2 h at the same temperature. From the reaction mixture, by vacuum distillation, 18.5 g of unreacted undecylenic acid, 42.7 g of keto acid, and 13 g of residue were isolated. The yield of 11-(2′-ketocyclohexyl)undecanoic acid, calculated on the undecylenic acid taken, was 50%, and on that which entered into the reaction, 75%, m.p. 64° (from acetone).

Found, %:	C 72.11; 79.09; H 10.71; 10.60
$C_{17}H_{30}O_3$. Calculated, %:	C 72.30; H 10.70

Semicarbazone, m.p. 135–136° (from alcohol)

$C_{18}H_{33}O_3N_3$.	Found, %:	C 63.72; 63.85; H 10.03; 10.06
	Calculated, %:	C 63.68; H 9.80

6-Ketopentadecanedicarboxylic-1,15 acid. Oxidation of 11-(2′-ketocyclohexyl)undecanoic acid (carried out at 65°) and isolation from the reaction mixture of the resulting 6-ketopentadecanedicarboxylic-1,15 acid were performed by the same method as that used in obtaining 5-ketotetradecanedicarboxylic-1,14 acid. The yield of 6-ketopentadecanedicarboxylic-1,15 acid was 78%, m.p. 109.5–110.5° (from benzene).

$C_{17}H_{30}O_5$.	Found, %:	C 65.19; 65.12; H 9.78; 9.68
	Calculated, %:	C 64.94; H 9.62

Semicarbazone, m.p. 161–161.3° (from alcohol).

$C_{19}H_{33}O_5N_3$.	Found, %:	C 58.16; 58.20; H 9.08; 9.03
	Calculated, %:	C 58.20; H 8.96

1,15-Pentadecanedicarboxylic acid. To a solution of 6.6 g of NaOH and 7 ml of hydrazine hydrate in 60 ml of ethylene glycol was added 6.3 g (0.02 mole) of 6-ketopentadecanedicarboxylic-1,15 acid. Thereafter the procedure was analogous to the synthesis of 1,14-tetradecanedicarboxylic acid.

There were obtained 5.6 g (yield 93%) of 1,15-pentadecanedicarboxylic acid with m.p. 119° (from acetone).

$C_{17}H_{32}O_4$.	Found, %:	C 67.53; 67.66; H 10.63; 10.72
	Calculated, %:	C 67.96; H 10.74

Literature data ([6]): m.p. 118°.

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CITED LITERATURE

[1] G. E. Svadkovskaya, S. A. Voitkevich, *Usp. khim.*, **29**, 364 (1960).
[2] A. N. Nesmeyanov, L. I. Zakharkin, T. A. Kost, Publishing House of the Academy of Sciences of the USSR, OKhN, 1955, 657.
[3] M. S. Kharasch, J. Kuderna, W. Nudenberg, *J. Org. Chem.*, **18**, 1225 (1953).
[4] A. D. Petrov, G. I. Nikishin, Yu. N. Ogibin, *DAN*, **131**, No. 3 (1960); Author's Certificate 133059 (1960).
[5] V. V. Korshak; S. L. Sosin, E. M. Morozova, *ZhOKh*, **30**, 907 (1960).
[6] P. Chuit, *Helv. chim. Acta*, **9**, 274 (1926).

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