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LETTERS TO THE EDITOR

Features of Claisen Condensation of Dimethyl Perfluorododecanedicarboxylate

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We have reported earlier [1] that dialkyl perfluoroadipinates and perfluoropimelates react with methyl ketones to form as a main product the corresponding diketoesters rather than tetraketones. Moreover, when acetone was used in the reaction as methyl ketone we failed to isolate diketoester.

We studied the reaction of dimethyl perfluorododecacarboxylate with alkyl ketones. It was found that under the conditions described in [2] tetraketones were not isolated. To obtain tetraketones **I–III,** the reaction of dimethyl perfluorododecanedicarboxylate with the corresponding alkyl ketone was carried out in tetrahydrofuran using sodium hydride in the presence of dibenzo-24-crown-8-ether.

$$\mathrm{MeOC(O)(CF_2)_{10}\text{–}COOMe + 2\,RC(O)R^1H}$$
$$\mathrm{\rightarrow [RC(O)R^1C(O)]_2CF_2)_{10}},$$

$\mathrm{R = Ar, R^1 = CH_2}$ (**I**), $\mathrm{CHC_2H_5}$ (**II**); $\mathrm{R = CH_3, R^1 = CHC_2H_5}$ (**III**).

Tetraketones were obtained in 63–69% yield. The yield of tetraketones depends not only on the reaction conditions, but also on the nature of substituents in the starting alkyl ketone.

General procedure for the synthesis. To a THF solution of sodium hydride perfluorododecacarboxylate under inert atmosphere while stirring at 10°C was dosed dimethyl perfluorododecanedicarboxylate and then a mixture of dibenzo-24-crown-8-ether and alkyl ketone. After the reaction completion, 10% solution of sulfuric acid was added. The organic layer was separated and concentrated. The product was crystallized from a suitable solvent. Reaction progress was monitored by means of TLC using Silufol UV-254 plates, eluting with pentane–acetone–toluene–chloroform (8:4:1:1) mixture.

1,16-Diphenyl-3-(decaperfluoromethylene)hexadecan-1,3,11,16-tetrone was obtained from 1.2 g (0.05 mol) of NaH in THF, 30.9 g (0.05 mol) of dimethyl perfluorododecacarboxylate, 6 g (0.10 mol) of acetophenone and 0.15 g (0.33×10^{-3} mol) of dibenzo-24-crown-8-ether. Yield 25.0 g (63%), mp 274–275°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1636(C=O···H), 1730 (RC=O), 1804 ($\mathrm{R_FC{=}O}$), 3402–3450 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 4.42 s (2H, $\mathrm{CH_2}$), 6.71 s (1H, CH), 7.41–7.89 m (5H, $\mathrm{C_6H_5}$), 11.27 s (1H, OH).

3,16-Diisopropyl-4-(decaperfluoromethylene)octadecan-2,4,15,17-tetrone was obtained from 1.2 g (0.05 mol) of NaH in THF, 30.9 g (0.05 mol) of dimethyl perfluorododecacarboxylate, 5 g (0.10 mol) of methyl isobutyl ketone and 0.15 g (0.33×10^{-3} mol) of dibenzo-24-crown-8-ether. Yield 25.2 g (67%), mp 174–175°C. IR specrum, ν, $\mathrm{cm^{-1}}$: 1636 (C=O···H), 1726 (RC=O), 1822 ($\mathrm{R_FC{=}O}$), 3412–3490 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.84–0.85 m (3H, $\mathrm{CH_3}$), 2.30 s (3H, $\mathrm{CH_3C{=}O}$), 2.35 s (1H, CH), 3.58 m (1H, CH–C=O), 12.12 s (1H, OH).

2,15-Diethyl-1,16-diphenyl-3-(decaperfluoromethylene)octadecan-2,4,15,17-tetrone was obtained from 1.2 g (0.05 mol) of NaH in THF, 30.9 g (0.05 mol) of dimethyl perfluorododecacarboxylate, 7.4 g (0.10 mol) of phenyl propyl ketone and 0.15 g (0.33×10^{-3} mol) of dibenzo-24-crown-8-ether. Yield 29.3 g (69%), mp 262–263°C. IR spectrum, ν, $\mathrm{cm^{-1}}$: 1634 (C=O···H), 1726 (RC=O), 1804 ($\mathrm{R_FC{=}O}$), 3432–3570 (OH). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.28 t (3H, $\mathrm{CH_3}$), 2.04 m (2H, $\mathrm{CH_2}$), 4.46 q (1H, CH), 6.93–6.96 m (5H, $\mathrm{C_6H_5}$), 11.75 s (1H, OH).

The IR spectra were obtained on a Specord M-82 spectrometer in the range of 400–3600 cm^{-1} from suspensions in mineral oil. The ^{1}H NMR spectra were recorded on a Varian Mercury spectrometer (300 MHz) relative to internal HMDS using DMSO-d_6 as a solvent.

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