Supplemental online material

Lactic acid derivatives with terphenyl molecular core

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Synthesis

Synthetic route for preparation of the studied products, 4-(((1-(hexyloxy)-1-oxopropan-2-yl)oxy)carbonyl)phenyl 3"-chloro-4"-(decyloxy)-[1,1':4',1"-terphenyl]-4-carboxylate designated as **SOSn/6**, is schematically depicted in Scheme 1. Terphenyl carboxylic acids have been prepared using condensation synthetic approach developed earlier [21,22]. The preparation of intermediates **1-4** and details of the synthesis are described below.

3-(4'-Biphenyl-4-yl)-6-decylcyclohex-2-en-1-one **1**

A mixture of 57.8 g (0.20 mol) of 4-(3-dimethylaminopropanoyl)biphenyl hydrochloride (Mannich salt has been prepared in the usual way by refluxing of 4-acetylbiphenyl with dimethylamine hydrochloride and paraformaldehyde in isopropyl alcohol in the presence of hydrochloric acid), 54.0 g (0.20 mol) of ethyl 2-decylacetoacetate (it has been prepared by standard alkylation of Na-acetoacetic ester with 1-bromodecane in ethanol) and 33.6 g (0.60 mol) potassium hydroxide in 400 ml of dioxane was refluxed for 6 h under stirring. After cooling to room temperature, 1000 ml of 5% sulphuric acid solution was added carefully (evolution of carbon dioxide!) and the product was extracted with methylene chloride. The organic layer was washed with water, dried over anhydrous magnesium sulphate and filtered through a layer of aluminium oxide. The residue obtained after the solvent had been removed was crystallized from isopropanol-acetone mixture (v/v 3:1). The yield was 55.8 g (72%); m.p. 79°C. MS m/Z: 388 (M⁺), 261, 220, 168. ¹H NMR (400 MHz, CDCl₃), δ: 0.92 (3H, m), 1.18-1.44 (16H, m), 1.80-1.84 (2H, m), 2.40 (2H, m, CH₂), 2.80-2.86 (3H, m), 6.54 (1H, s, CH=), 7.20-7.34 (7H, m), 7.44-7.47 (2H, d).

3-Chloro-4-decyl-*p*-terphenyl **2**

Phosphorous pentachloride (29.2 g, 0.14 mol) was slowly added to a stirred solution of 3-(4'-biphenyl)-6-decylcyclohex-2-en-1-one (38.8 g, 0.10 mol) in 250 ml of toluene. The reaction

mixture was heated under reflux for 6 h and then poured into a mixture of 5% sodium hydroxide solution with ice. The organic layer was then washed with water, diluted hydrochloric acid and again with water. After toluene had been removed in vacuum, the product was dissolved in hexane and filtered through column with silica gel to remove dark coloured impurities. After removing of solvent, the final product was crystallized from acetone. Yield was 24.7 g (61%): Phase transition temperatures: Cr. 53°C - SmB 69°C - Iso. MS m/Z: 404, 406 (M⁺), 277, 279. ¹H NMR (CDCl₃), δ: 0.90 (3H, m), 1.20-1.44 (14H, m), 1.76-1.80 (2H, m), 2.46(2H, t, CH₂Ph), 7.14-7.22 (3H, m), 7.27-7.34 (4H, m), 7.56 (2H, m), 7.66 (3H, m).

1-Acetyl-3-chloro-4''-decyl-*p*-terphenyl **3**

3-Chloro-4-decyl-*p*-terphenyl was acetylated according standard Friedel-Crafts acylation procedure in methylene chloride. Acetylating complex prepared from acetyl chloride (6.1 g, 0.078 mol) and anhydrous aluminium chloride (9.6 g, 0.072 mol) in 150 ml of dry methylene chloride. The prepared solution was slowly dropped into the stirred solution of 3-chloro-4-decyl-*p*-terphenyl (24.3 g, 0.06 mol) in 150 ml of dry methylene chloride at room temperature. The reaction mixture was stirred for 6 h and then underwent the standard treatment procedure. The obtained crude product was twice crystallized from acetone; yield was 14.7 g (55%); Phase transition temperatures: Cr. 72°C - SmA 158°C - Iso. MS m/Z: 446, 448 (M⁺), 3129, 321. ¹H NMR (400 MHz, CDCl₃), δ: 0.90 (3H, m), 1.22-1.44 (14H, m), 1.74-1.78 (2H, m), 2.48(2H, t, Ph), 2.56 (3H, s), 7.10-7.20 (3H, m), 7.32-7.36 (2H, m), 7.50 (2H, m), 7.60-7.66 (3H, m), 7.82 (2H, d).

3-Chloro-4-decyl-*p*-terphenyl-1''-carboxylic acid **4**

1-Acetyl-3-chloro-4''-decyl-*p*-terphenyl (13.4 g, 0.03 mol) in 100 ml of dioxane was added to the oxidizing agent prepared by dropping of bromine (14.4 g, 0.09 mol) to the solution of sodium hydroxide (12.0 g, 0.30 mol) in 50 ml of water at 0-5°C. The reaction mixture was then slowly heated to 60-62°C under stirring. At this temperature, the white precipitate forms. After 15 min, 5 ml of acetone was added and then the reaction mixture was acidified with hydrochloric acid and additionally stirred for 1 h. The reaction mixture was diluted with cold water and the precipitate was filtered out and then twice washed with water. The final product was crystallized from 2-butanone. The yield was 11.7 g (83%), m.p. >300°C. MS m/Z: 448, 450 (M⁺). ¹H NMR (300 MHz, DMSO), δ: 0.85 (3H, t), 1.20-1.40 (14H, m), 1.60 (CH₂CH₂Ar, q), 7.40 (1H, meta to Cl, d), 7.61 (1H, para to Cl, d), 7.70 (1H, ortho to Cl, s), 7.75 -7.80 (6H, ortho to Ar, m), 8.08 (2H, ortho to COOH, d).