

SHORT
COMMUNICATIONS

Mesogenic Triad with a Benzoyl Group*

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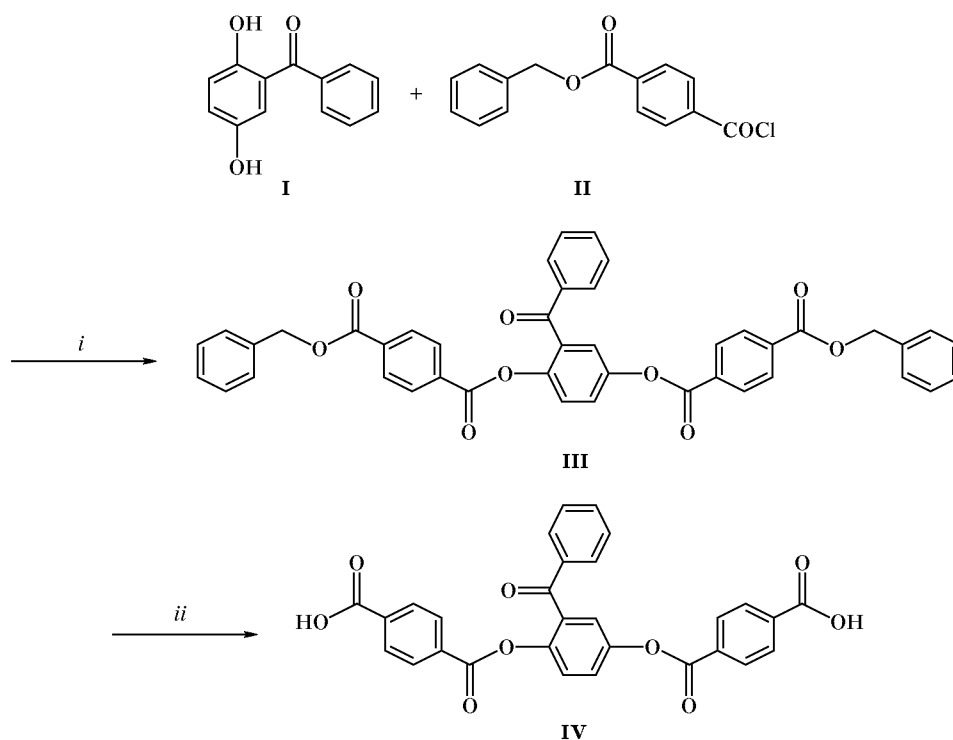
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The reaction of 2,5-dihydroxybenzophenone (**I**) with benzyl 4-chloroformylbenzoate (**II**) in aqueous-organic medium in the presence of a phase-transfer catalyst leads to formation of 2,5-bis(4-benzyloxycarbonylbenzoyloxy)benzophenone (**III**). Debenzylation

of ester **III** [1] gives 2,5-bis(4-carboxybenzoyloxy)benzophenone (**IV**) (Scheme 1). Compound **IV** is a rigid mesogenic triad possessing a photo- and chemically active moiety, a carbonyl group. Compound **I** was synthesized by Friedel-Crafts benzoyla-

Scheme 1.



i: Bu₄NBr or BuMe₃NCl, 4% NaOH, H₂O-CH₂Cl₂; *ii*: HBr (AcOH, CF₃COOH) [1].

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tion of 1,4-dimethoxybenzene, followed by successive dealkylation first with AlCl_3 to 2-hydroxy-5-methoxybenzophenone and then with HI in Ac_2O [2]. Benzyl 4-chloroformylbenzoate was prepared by the procedure described in [3].

2,5-Bis(4-benzyloxycarbonylbzoyloxy)benzophenone (III). A solution of 5.60 g (20.4 mmol) of compound **II** in 60 ml of CH_2Cl_2 was added dropwise to a solution of 2.75 g (12.8 mmol) of 2,5-dihydroxybenzophenone in 60 ml of 4% aqueous sodium hydroxide containing 0.28 g of tetrabutylammonium bromide. The mixture was stirred for 30 min at room temperature in an inert atmosphere. The organic phase was separated, the solvent was removed, and the residue (6.3 g of compound **III**) was twice recrystallized from isopropyl alcohol. Yield 3.14 g (45%), mp 118–120°C. R_f 0.79 (Silufol UV-254, solvent CH_2Cl_2 , eluent alcohol–benzene, 1:10). IR spectrum (KBr), ν , cm^{-1} : 2920 (CH_2), 1755 (C=O, ester), 1680 (C=O, ketone). Found, %: C 74.17; H 4.07. $\text{C}_{43}\text{H}_{30}\text{O}_9$. Calculated, %: C 74.77; H 4.38.

2,5-Bis(4-carboxybenzoyloxy)benzophenone (IV). Compound **III**, 2.82 g (4.08 mmol), was dissolved in 39 ml of CF_3COOH , and 3.1 ml of a 36% solution of HBr in CH_3COOH was added dropwise. The mixture was stirred for 24 h at room temperature,

and the precipitate (1.76 g) of compound **IV** was filtered off. An additional portion of the product, 0.22 g, was isolated from the filtrate by precipitation with acetone. The two portions were combined and washed with acetone. Yield 1.96 g (94%), mp 305–307°C. R_f 0.45 (Silufol UV-254, solvent DMF, eluent benzene–ethyl acetate, 1:1). IR spectrum (KBr), ν , cm^{-1} : 1755 (C=O, ester), 1720 (C=O, acid), 1680 (C=O, ketone). ^{13}C NMR spectrum ($\text{DMF}-d_7$), δ_{C} , ppm: 194.2 (C=O); 167.9, 167.6 (COOH); 165.3, 165.0 (OCO).

The IR spectra were recorded on a Bruker IFS-88 spectrometer. The ^{13}C NMR spectrum was obtained on a Bruker AM-500 instrument at 125 MHz. Elemental analysis was performed on a Perkin–Elmer automatic analyzer.

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