

SHORT
COMMUNICATIONS

Mesogenic V-Like Triad
on the Basis of 3,4-Dihydroxybenzophenone*

E. V. Demina¹, M. N. Bol'shakov², N. V. Klimova¹, L. I. Rudaya¹, T. A. Yurre¹,
V. V. Shamanin², and S. S. Skorokhodov²

¹ St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 198013 Russia
e-mail rudi@mail.avmgroupp.ru

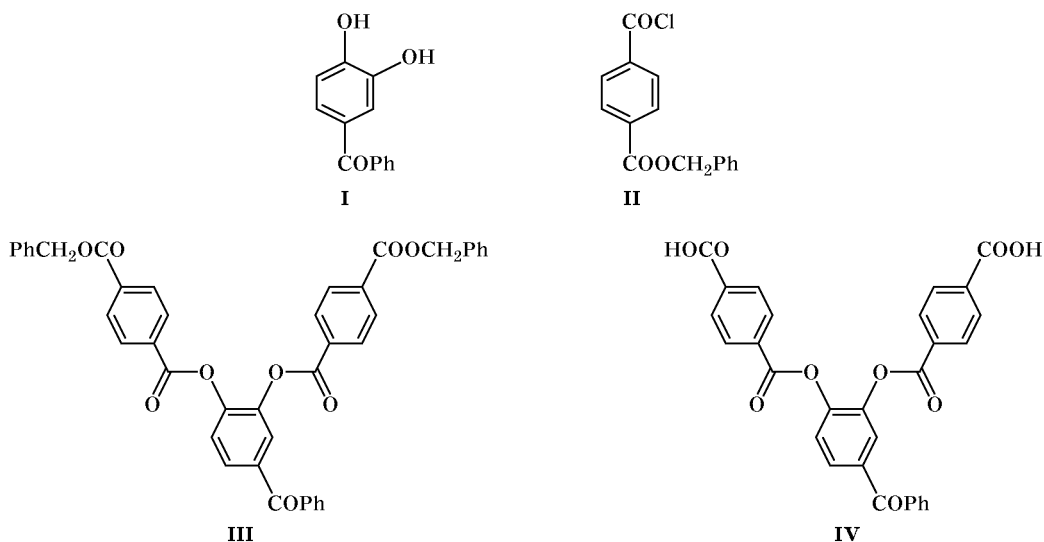
² Institute of High-Molecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

Received July 5, 2002

The reaction of 3,4-dihydroxybenzophenone (**I**) with benzyl 4-chloroformylbenzoate (**II**) in aqueous–organic medium (CH₂Cl₂, 2.3% aqueous NaOH) in the presence of phase-transfer catalyst (Bu₄NBr or Me₃PhCH₂NCl) gave 3,4-bis(4-benzyloxycarbonylbenzoyloxy)benzophenone (**III**). Debenzoylation of **III** in solution (HBr, CH₃COOH, CF₃COOH) by analogy with the procedure reported in [1, 2] afforded 3,4-bis(4-carboxybenzoyloxy)benzophenone (**IV**) which can be regarded as a rigid mesogenic V-like triad having a photoactive and chemically reactive group. Com-

pound **I** was synthesized by benzylation of 1,2-dihydroxybenzene [3], followed by the Fries rearrangement in nitrobenzene in the presence of AlCl₃ [4]. Ester **II** was prepared as described in [5].

3,4-Bis(benzyloxycarbonylbenzoyloxy)benzophenone (III). To a solution of 0.59 g (2.75 mmol) of 3,4-dihydroxybenzophenone in 15 ml of a 2.3% solution of sodium hydroxide, containing 0.06 g of tetrabutylammonium bromide, we added dropwise a solution of 1.5 g (5.46 mmol) of compound **II** in 15 ml of methylene chloride. The mixture was stirred for



* This study was financially supported by the Russian Foundation for Basic Research (project no. 01-03-32292) and by the Program "Higher School Research in the Priority Fields of Science and Technics" (project no. 203.02.06.015).

30 min at room temperature in an inert atmosphere. The aqueous and organic phases were separated, the organic phase was evaporated, the residue (a viscous red-brown material) was dissolved in 40 ml of methylene chloride, and the solution was poured into 95 ml of cold alcohol. The yellowish oily substance was reprecipitated again with alcohol from a solution in CH_2Cl_2 . The fine snow-white precipitate was filtered off and dried at 60°C . Yield 0.88 g (46%), mp 93°C , R_f 0.44 (Silufol UV-254, solvent CH_2Cl_2 , eluent alcohol-benzene, 1:40). IR spectrum (KBr), ν , cm^{-1} : 2940, 3070 (CH_2), 1730 ($\text{C}=\text{O}$, ester), 1660 ($\text{C}=\text{O}$, ketone).

3,4-Bis(4-carboxybenzyloxy)benzophenone (IV). To a solution of 0.76 g (1.40 mmol) of compound **III** in 15 ml of CF_3COOH we added dropwise 2.0 ml of a 36% solution of HBr in CH_3COOH . The mixture was stirred for 24 h at room temperature and poured into 35 ml of cold acetone, and the precipitate of **IV** was filtered off. Yield 0.51 g (91%), mp 179 – 181°C , R_f 0.32 (Silufol UV-254, solvent DMF, eluent benzene-ethyl acetate, 2:1). IR spectrum (KBr), ν , cm^{-1} : 1710 ($\text{C}=\text{O}$, ester), 1720 ($\text{C}=\text{O}$, acid), 1670 ($\text{C}=\text{O}$, ketone). ^{13}C NMR spectrum ($\text{DMF}-d_7$), δ_{C} ,

ppm: 194.4 ($\text{C}=\text{O}$), 162.4 and 162.2 (COOH), 163.6 and 163.3 (OCO). Found, %: C 68.45; H 3.57. $\text{C}_{29}\text{H}_{18}\text{O}_9$. Calculated, %: C 68.24; H 3.55.

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

REFERENCES

1. Galli, G., Chiellini, E., Ober, Ch.K., *et al.*, *Makromol. Chem.*, 1982, vol. 183, no. 11, pp. 2693–2708.
2. Bol'shakov, M.N., Klimova, N.V., Rudaya, L.I., Yurre, T.A., Shamanin, V.V., and Skorokhodov, S.S., *Russ. J. Org. Chem.*, 2002, vol. 38, no. 10, pp. 1540–1541.
3. Dobner, O., *Justus Liebigs Ann. Chem.*, 1881, vol. 210, pp. 246–284.
4. Rosenblatt, D.H., Epstein, J., and Levitch, M., *J. Am. Chem. Soc.*, 1953, vol. 75, pp. 3277–3278.
5. Hasslin, H.-W., Droscher, M., and Wegner, G., *Makromol. Chem.*, 1980, vol. 181, no. 2, pp. 301–323.