Brief Communications

Synthesis and crystal structure of dimethyl 2-benzoyl-2-ethyl-3-phenylcyclopropane-1,1-dicarboxylate

Z. G. Aliev,[a]* *V. V. Shchepin,*[b] *S. B. Lewis,*[c] *R. V. Shchepin,*[b] *and L. O. Atovmyan*[a]

[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 938 2156. E-mail: aliev@icp.ac.ru
[b]*Perm State University,*
15 ul. Bukireva, 614000 Perm, Russian Federation.
Fax: +7 (342 2) 33 3983
[c]*Creghton University,*
2500 California Plaza, Omaha, Nebraska, 68478, USA

The reaction of α,α-dibromobutyrophenone with dimethyl benzylidenemalonate in the presence of zinc gives dimethyl 2-benzoyl-2-ethyl-3-phenylcyclopropane-1,1-dicarboxylate as a single geometrical isomer. Its structure was determined by X-ray diffraction analysis.

Key words: dimethyl 2-benzoyl-2-ethyl-3-phenylcyclopropane-1,1-dicarboxylate, α,α-dibromobutyrophenone, zinc, dimethyl benzylidenemalonate, synthesis, X-ray diffraction analysis.

An approach to the synthesis of cyclopropanes with electron-acceptor acyl and alkoxycarbonyl substituents consists in the addition of organometallic intermediates, resulting from the reactions of α,α-dibromoketones**[1,2]** or alkyl α,α-dihalocarboxylates**[3,4]** with some metals, to activated unsaturated compounds. In certain cases, *e.g.*, in the reaction of α,α-dibromo-α-phenylacetophenone with zinc and olefins, dihydrofuran derivatives were obtained.**[2]**

With the aim of expanding the area of application of this method and of synthesizing dimethyl 2-benzoyl-2-ethyl-3-phenylcyclopropane-1,1-dicarboxylate, we studied the reaction of α,α-dibromobutyrophenone (**1**) with dimethyl benzylidenemalonate (**2**) in the presence of zinc (Scheme 1).

Apparently, dibromide **1** first gives zinc enolate, which reacts with ester **2** to form intermediate **3**. The latter undergoes cyclization into cyclopropane **4**. Its structure was confirmed by data from elemental analysis and IR and NMR spectroscopy (^{1}H and ^{13}C). The ^{1}H NMR spectrum of the reaction product isolated by vacuum distillation contains signals for the protons of the major component and a set of low-intensity signals. Crystallization from hexane gave a single geometrical isomer of cyclopropane **4** in 65% yield.

X-Ray diffraction analysis showed that the major reaction product is isomer **4a**, in which the phenyl and benzoyl substituents are *cis* to each other. The general view of the molecule is displayed in Fig. 1. In the sterically crowded cyclopropane ring, the bond lengths fall in a wide range from 1.504(2) Å for C(6)—C(7) to 1.536(2) Å for C(7)—C(8); the C(6)—C(8) bond length is equal to 1.530(2) Å. The structures of analogous cyclopropane derivatives were analyzed with the use of the data from the Cambridge Structural Database. The analysis reveals a similar scatter in ring bond lengths. Thus, in dimethyl (3*S*)-3-[(4*S*)-2,2-dimethyl-1,3-

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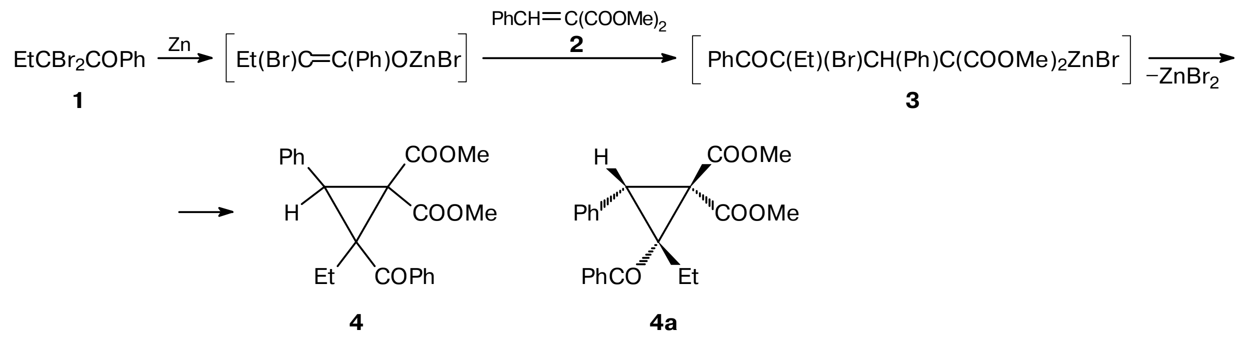
Scheme 1



dioxolan-4-yl]-2,2-dimethylcyclopropane-1,1-dicarboxylate, they lie within 1.491—1.551 Å (see Ref. 5), which is probably due to steric factors. All the other bonds in compound **4a** have standard values and thus need no comments. In the crystal, there are no hydrogen bonds or other shortened intermolecular contacts.

Experimental

IR spectrum was recorded on a UR-20 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on an INOVA-300 Cunmr 1 instrument in $CDCl_3$ with Me_4Si as the internal standard. Mass spectrum was obtained with the Vector/TWO instrument (chemical ionization, isobutene as the reagent gas, ionizing voltage 100 eV).

Dimethyl 2-benzoyl-2-ethyl-3-phenylcyclopropane-1,1-dicarboxylate (4). A solution of a mixture of α,α-dibromobutyrophenone (**1**) (0.05 mol) and dimethyl benzylidenemalonate (**2**) (0.05 mol) in 5 mL of Et_2O and 15 mL of EtOAc was added dropwise with stirring to a suspension of Zn cuttings (10 g) in 5 mL of Et_2O and 15 mL of EtOAc. The reaction mixture was heated until the reaction started, and then heating was stopped. After the reaction was completed, the reaction mixture was heated at ~100 °C for 30 min, cooled, and treated with 5% HCl at ~20 °C (10 min). The organic material was extracted with Et_2O. The extract was dried with Na_2SO_4, and the solvents were removed. The product was distilled *in vacuo* to give a viscous oil, b.p. 235—240 °C (4 Torr). Its ^{1}H NMR spectrum contains signals for the MeO groups at δ 3.30 and 3.81 (major component) and δ 3.33 and 3.67 (relative intensity 10—15%). Crystallization from hexane gave compound **4a** in 65% yield, m.p. 135 °C. Found (%): C, 72.31; H, 6.11. $C_{22}H_{22}O_5$. Calculated (%): C, 72.12; H, 6.05. MS, m/z (I_{rel} (%)): 367 $[M + H]^+$ (100), 335 $[M - MeO]^+$ (48). IR, ν/cm^{-1}: 1720—1740 (COO); 1685 (CO); 1590, 1600 (C=C arom.). ^{1}H NMR ($CDCl_3$), δ: 1.13 (t, 3 H, Me, J = 7 Hz); 1.22, 2.32 (both dq, each 1 H, CH_2, J = 14 Hz, J = 7 Hz); 3.21 (s, 1 H, CH); 3.33, 4.03 (both s, 6 H, OMe); 7.22—7.58, 8.17—8.23 (m, 10 H, Ph, COPh). ^{13}C NMR ($CDCl_3$), δ: 188.60 (CO); 162.13, 163.55 (COO); 131.64, 128.43, 128.06, 125.60, 123.13, 123.01, 123.18, 122.47 (Ph, COPh); 48.51, 47.44 (OMe); 41.81, 41.83 (C(1), C(2)); 34.64 (C(3)); 24.71 (CH_2); 7.08 (Me).

X-Ray diffraction analysis. The crystals of **4a** are monoclinic, a = 12.083(2) Å, b = 20.372(4) Å, c = 8.451(2) Å, β = 110.09(3)°, V = 1953.7(7) Å^3, M = 366.40, d_{calc} = 1.246 g cm^{-3}, Z = 4, space group $P2_1/a$. The unit cell parameters and a set of experimental reflections were measured on a KM-4 automated four-circle diffractometer (KUMA DIFFRACTION) with χ geometry (θ/2θ scan mode, monochromated Cu-Kα radiation, 4.3 < 2θ < 80.3°). The number of independent reflections is 3885. Correction for absorption was not applied (μ = 0.719 mm^{-1}). The structure was solved by the direct method. Hydrogen atoms were located geometrically. The least-squares refinement in the full-matrix anisotropic (isotropic for H atoms) approximation gave the final residual R = 0.046 for 2777 reflections with $I \geq 2\sigma(I)$. All calculations were performed on PC/AT with the SHELX-86[6] and SHELXL-93 programs.[7] The coordinates of atoms are deposited in the Cambridge Structural Database.

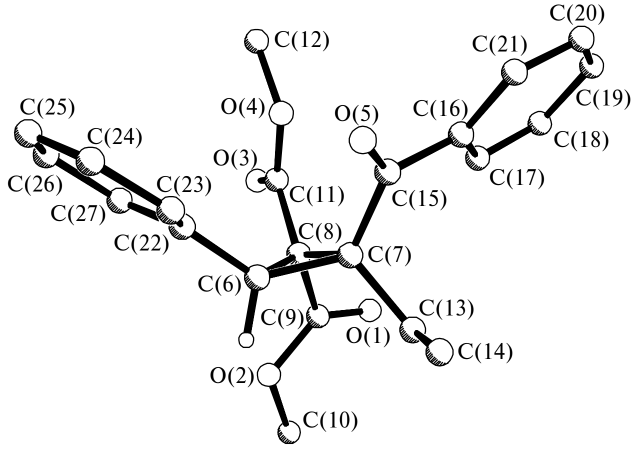


Fig. 1. General view of the molecule **4a**.

References

1. N. Kamubat, T. Fujii, M. Naka, and S. Yamashita, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1005.
2. L. T. Scott and W. D. Cotton, *J. Am. Chem. Soc.*, 1973, **95**, 5416.
3. T. Matsuki, N. X. Hu, Y. Aso, T. Otsubo, and F. Ogura, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2105.
4. J. C. Le Menn and A. T. J. Sarrazin, *Can. J. Chem.*, 1991, **69**, 761.
5. G. Baudox, B. Norbergm, L. Provins, A. Froidbize, A. Krief, and G. Evrazd, *Acta Crystallogr., Sect. C (Cr. Str. Commun.)*, 1998, **54**, 834.
6. G. M. Sheldrick, *SHELX-86, Programme for Crystal Structure Determination*, University of Cambridge, UK, 1986.
7. G. M. Sheldrick, *J. Appl. Cryst.*, 1993, **26**, 593.

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