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Synthesis and structure of (*R**,*R**)-3,3:6,6-dipropano-3a,6a-diphenyltetrahydrofuro[3,2-*b*]furan-2,5-dione

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Interaction of methyl 1-bromocyclobutanecarboxylate with zinc and 1,2-diphenyl-1,2-ethanedione affords the title compound, whose structure was confirmed by X-ray analysis.

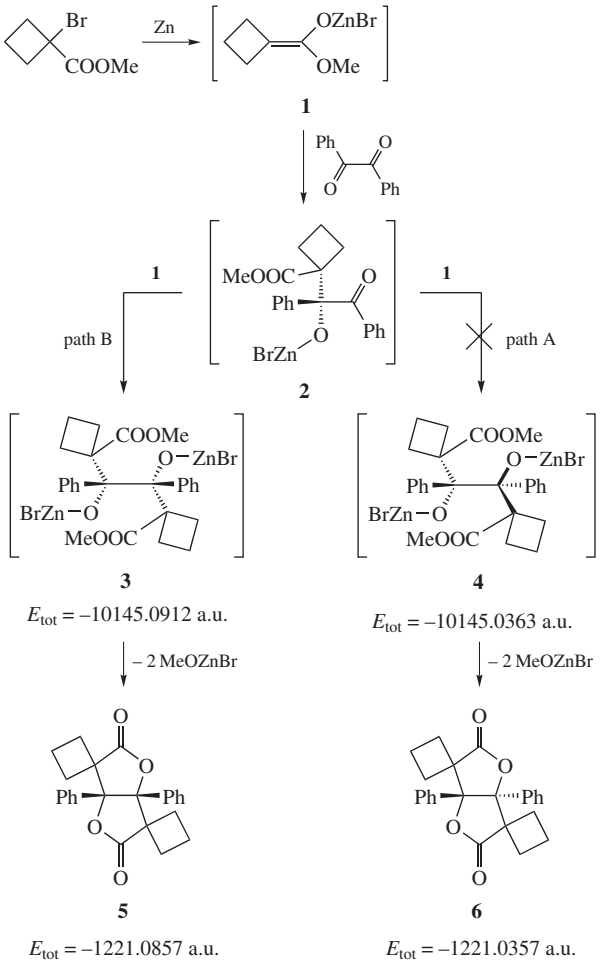
The Reformatsky reagents form with α-dicarbonyl compounds substituted furofurandiones.[1,2] However, reactions of methyl 1-bromocyclopentane- and 1-bromocyclohexanecarboxylates with zinc and 1,2-diphenyl-1,2-ethanedione lead to formation of only one tetrahydrofuran cycle, probably, due to steric hindrances of two large phenyl substituents.[2]

Herein, we report that the interaction between methyl 1-bromocyclobutanecarboxylate, zinc and 1,2-diphenyl-1,2-ethanedione (Scheme 1) gives the corresponding (*R**,*R**)-isomer of 3,3:6,6-dipropano-3a,6a-diphenyltetrahydrofuro[3,2-*b*]furan-2,5-dione **5** in 82% yield.† Apparently, the smaller size of cyclobutane compared to cyclopentane and cyclohexane allows this reaction to proceed in an ordinary manner.

Obviously, the initially formed Reformatsky reagent **1** adds at 1,2-diphenylethane-1,2-dione to afford intermediate **2**, which is further attacked by the second species **1** (Scheme 1). This attack can in principle proceed from the side of phenyl group, bonded with sp^3-hybridized carbon atom (path B), or from opposite side (path A) leading to stereoisomers **5** and **6**. In case of realization of path A the chiral centres in intermediate **4** will have *R**,*S** configuration, and of path B – *R**,*R** configuration in intermediate **3**. The configuration of these chiral centres in intermediates **3** and **4** must retain in products **5** and **6**, respectively. The isomer **5** is featured by space proximity of phenyl rings, while in the isomer **6** their steric disunity may be expected.

To speculate on a preferable stereo outcome of the reaction, we performed calculation of total energies (E_{tot}) of intermediates **3** and **4** and dilactones **5** and **6** by *ab initio* MO method [basis 6-31G(d)]. According to calculations, intermediate **3** has smaller energy in comparison with alternative one **4**. Dilactone **5** formed from intermediate **3** also has smaller value of E_{tot} in comparison with dilactone **6**. Possible reason of increased stability of *R**,*R** isomers may be connected with secondary orbital interaction between two benzene rings.

Since MO calculations are modeling molecule behaviour in gaseous phase, we performed X-ray study of monocrystal of compound **5**.



Scheme 1

† The IR spectrum was measured on a Specord 75 IR instrument in Nujol. The ^{1}H NMR spectrum was recorded at 300 MHz on a Varian Mercury Plus-300 spectrometer in $CDCl_3$ with TMS as an internal standard. *Ab initio* MO calculations of molecules of diastereomers with full geometric parameters optimization were realized by Toshiba Portege 400 PC (GAMESS[3] package).

*(*R**,*R**)-3,3:6,6-Dipropano-3a,6a-diphenyltetrahydrofuro[3,2-*b*]furan-2,5-dione* **5**. The suspension of 1.50 g (0.023 mol) of fine chip zinc, catalytic amount of mercuric chloride, 2.63 g (0.005 mol) of 1,2-diphenyl-1,2-ethanedione, 2.12 g (0.011 mol) of methyl 1-bromocyclobutanecarboxylate, 20 ml of toluene and 20 ml of ethyl acetate was boiled for 2 h with stirring. After cooling, the organic layer was decanted and treated with 5% HCl. The water layer was twice extracted with ethyl acetate. Combined organic layers were dried with anhydrous Na_2SO_4. After removal of the solvent the resulted precipitate was recrystallized from ethyl acetate. Yield, 1.65 g (82%), mp 187–188 °C. IR (ν/cm^{-1}): 1765, 1780 (C=O). ^{1}H NMR, δ: 1.40–2.80 [m, 12H, 2$(CH_2)_3$], 6.70–7.10 (m, 10H, 2Ph). Found (%): C, 77.19; H, 5.78. Calc. for $C_{24}H_{22}O_4$ (%): C, 76.99; H, 5.92.

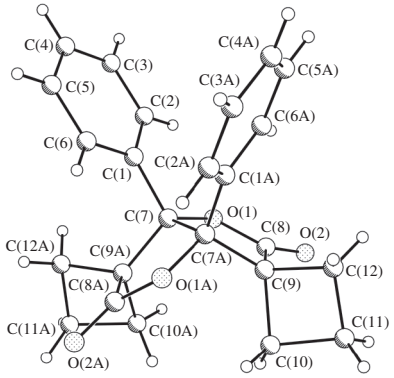


Figure 1 Molecular structure of compound **5**.

‡ *Crystal data for* **5**: $C_{24}H_{22}O_4$, Crystal system orthorhombic, space group *Iba*2, $a = 8.6715(8)$, $b = 12.4462(6)$ and $c = 17.6391(19)$ Å, $V = 1903.7(3)$ Å^3, $Z = 4$, $d_{calc} = 1.306$ g cm^{-3}, $\mu = 0.088$ mm^{-1}, $F(000) = 792$, $2.86° < \theta < 28.28°$. 3263 reflections were collected, from which 1677 are independent (R_{int} = = 0.0301). Analysis was accomplished for a colorless prismatic crystal, 0.47×0.39×0.22 mm in size, on an Xcalibur 3 CCD diffractometer [MoKα-radiation, 295(5) K, ω-scans]. Structure solution and refinement were carried out using SHELX-97 programs package[4] by full-marix least-squares procedure on F^2. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0297$, $wR_2 = 0.0547$, R indices (all data): $R_1 = 0.0557$, $wR_2 = 0.0570$, largest difference peak and hole 0.120 and –0.137 eÅ^{-3}. Non-hydrogen atoms were refined anisotropically, H-atoms were placed in calculated positions and refined isotropically.

CCDC 812945 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2011.

According to X-ray structural data,‡ compound **5** is crystallized in chiral *Iba*2 space group of the orthorhombic crystal system. The enantiomers of this compound are placed in private positions on the axe (Figure 1). Phenyl substituents are attracted together in space: distance C(1)···C(1A) is 2.943(3) Å and C(4)···C(4A) is 5.662(3) Å. It may be assumed that the π–π interaction between phenyl groups exists. The layers of the molecules parallel plane *a*0*b* form molecular packing.

In summary, the easy access to complex spiro cyclobutane derivative **5** may promote the wide use of its analogues in fine synthesis. It is worth noting that this reaction proceeds stereospecifically.

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