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Reaction of (2*S*,3*S*)-2-Benzyloxybutane-1,2,4-triol with *N*,*N*′-Carbonyldiimidazole

N. K. Selezneva, L. S. Khasanova, V. A. Egorov, F. A. Gimalova, M. Yu. Ovchinnikov, and M. S. Miftakhov

Ufa Institute of Chemistry, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia
e-mail: bioreg@anrb.ru

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Abstract—(2*S*,3*S*)-2-Benzyloxybutane-1,2,4-triol reacted with *N*,*N*′-carbonyldiimidazole to give a mixture of the expected 1,2-carbonate and the corresponding bis-carbonate.

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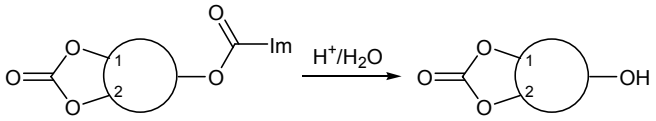
Cyclic carbonates are widely used as protecting and activating groups [1–3]. They are more stable than esters under both acid and base hydrolysis conditions. The 1,2- or 1,3-dihydroxy moiety in triols is usually protected by treatment with an appreciable excess of *N*,*N*′-carbonyldiimidazole.



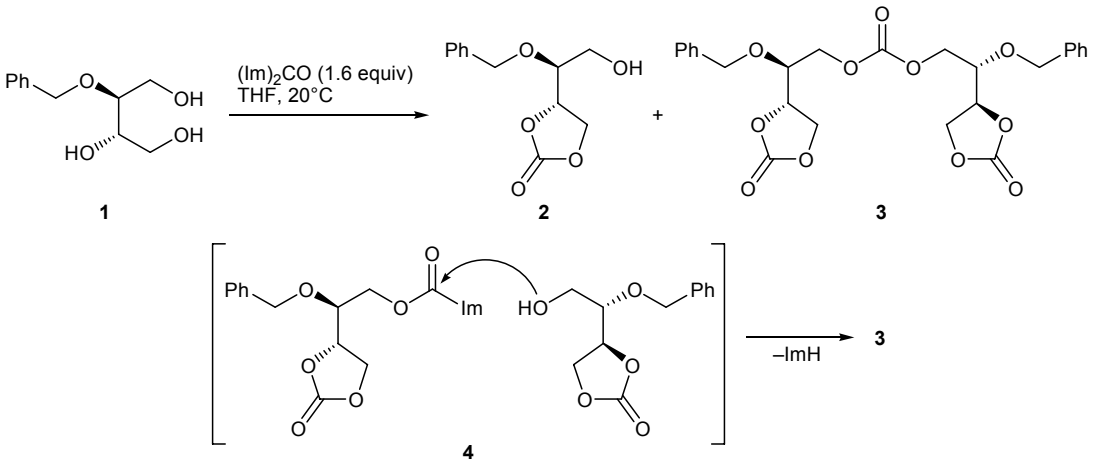
A **B**

Even though the third hydroxy group is acylated with *N*,*N*′-carbonyldiimidazole to form structure **A**, mild aqueous acid treatment of the reaction mixture leads to selective hydrolysis of the latter to hydroxy carbonate **B** [4].

While studying the reaction of (2*S*,3*S*)-2-benzyloxybutane-1,2,4-triol (**1**) with *N*,*N*′-carbonyldiimidazole, we have found that cyclic carbonate **2** generated from triol **1** [5] undergoes intermolecular bis-acylation *in situ*. In the reaction of **1** with a slight excess of *N*,*N*′-carbonyldiimidazole we obtained a mixture of carbonate **2** and bis-carbonate **3** at a ratio of ~3:2.5 in an overall yield of 56% (Scheme 1). The formation of **3** may be rationalized by esterification of a probable intermediate, activated *N*-acyl imidazole **4**, with alcohol **2**.

The following factors were taken into account while assigning the structures of **2** and **3**. It is known

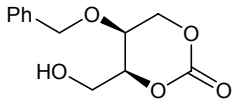
Scheme 1.



1 **2** **3** **4**

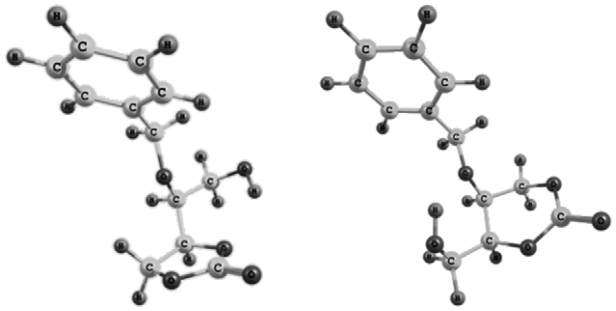
Im = 1*H*-imidazol-1-yl.

that triols preferentially give rise to cyclic 1,2-carbonates [7, 8]. However, insofar as acetyl group [9–12], carbonate [6, 13, 14] and acetal [15] moieties, and other protecting groups in polyols tend to migrate or being involved in rearrangements to thermodynamically more favorable structures, the formation of the corresponding dioxane derivatives like **5** instead of **2** and **3** cannot be ruled out.



5

Furthermore, 1,3-dioxanes are sterically less strained than their five-membered analogs, 1,3-dioxolanes [11]. The ^{1}H and ^{13}C NMR data did not allow us to unambiguously distinguish between structures **2** and **5**. Therefore, we tried to prove the product structure by resorting to quantum chemical calculations and chemical transformations. The results of DFT quantum chemical calculations of the energies of stable conformers of **2** and **5** showed that compound **2** is thermodynamically more favorable (see figure). In addition, the formation of dioxolane derivative **2** was confirmed by its chemical transformations shown in Scheme 2. Protection of the hydroxy group in **2** by treatment with *tert*-butyl(dimethyl)silyl chloride and subsequent base hydrolysis of the carbonate moiety in **9** gave diol **10** whose oxidative cleavage with $Pb(OAc)_4$ afforded aldehyde **8**. Analogous transformations of 1,3-dioxane **5** would lead to 1,3-diol **11** which does not react with lead tetraacetate.



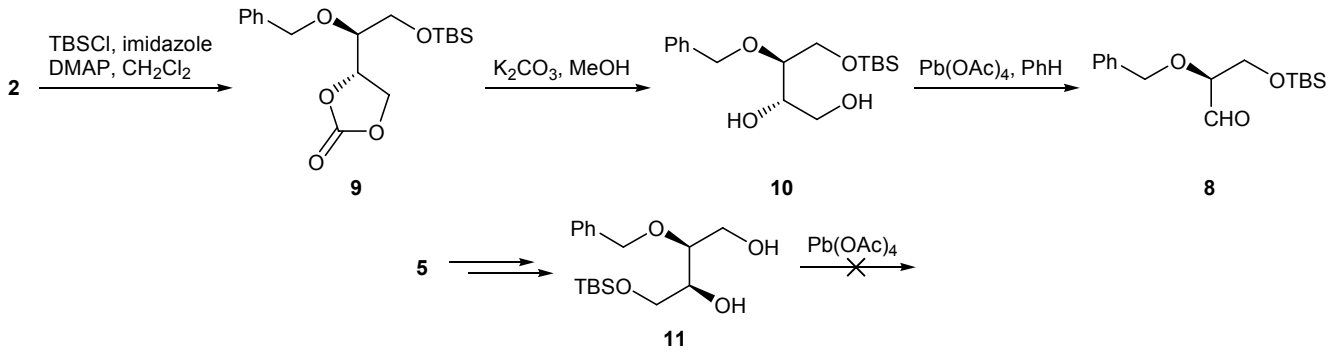
2 **5**

E_{tot}	–842.0558	ΔE_{tot}	22.95	E_{tot}	–842.0471
ΔH	–841.7898	$\Delta\Delta H$	22.31	ΔH	–841.7813
ΔG	–841.8523	$\Delta\Delta G$	22.30	ΔG	–841.8439
	hartree/mol		kJ/mol		hartree/mol

Calculated energies of stable conformers of **2** and **5**.

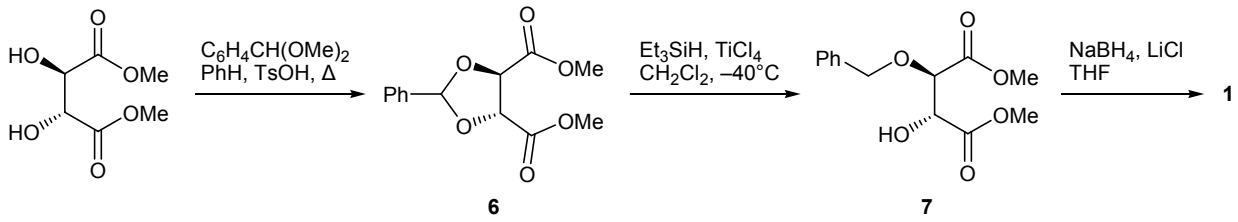
Initial triol **1** was prepared according to a modified procedure from benzylidene acetal **6** [16] via regioselective opening of the dioxolane ring under ionic hydrogenation conditions [17] and reduction of diester **7** with sodium tetrahydrodoborate. Acetal **6** was synthesized from dimethyl L-tartrate and benzaldehyde dimethyl acetal (Scheme 3).

Scheme 2.



TBS is *t*-$BuMe_2Si$, DMAP is 4-dimethylaminopyridine.

Scheme 3.



Thus, the reaction of (2*S*,3*S*)-2-benzyloxybutane-1,2,4-triol (**1**) with *N*,*N*′-carbonyldiimidazole is accompanied by formation of an appreciable amount of biscarbonate **3** in addition to the expected 1,2-carbonate **2**. This should be taken into account while planning syntheses.

EXPERIMENTAL

The IR spectra were recorded from thin films on a Shimadzu IR Prestige-21 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-300 (300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C) and Bruker Avance-500 spectrometers (500.13 MHz for ^{1}H and 125.77 MHz for ^{13}C) using tetramethylsilane as internal standard. The optical rotations were measured on a Perkin Elmer 341 polarimeter. The mass spectra (electron impact, 70 eV) were obtained on a Thermo Finnigan MAT 95XP instrument (ion source temperature 200°C; batch inlet probe temperature programming from 5 to 270°C at a rate of 22 deg/min). The elemental compositions determined using a Euro 2000 CHN analyzer were consistent with the theoretical values. The progress of reactions was monitored by TLC on Sorbfil plates (Russia); spots were detected by treatment with a solution of 4-methoxybenzaldehyde in ethanol acidified with sulfuric acid and subsequent heating to 120–150°C. The products were isolated by column chromatography on silica gel (30–60 g of the sorbent per gram of substrate).

Quantum chemical calculations in terms of the density functional theory [18, 19] were performed with full geometry optimization for the gas phase (298.15 K, 1 atm) using hybrid B3LYP functional [19] including the Becke correlation potential (B3) [20] and Li–Yang–Parr exchange potential [21] in combination with the triple split-valence basis set augmented by polarization *d* and *p* functions and a set of diffuse functions [6–311+G(*d*,*p*)] (Gaussian 09 software package [22]). Localized structures were assigned to minima on the potential energy surfaces by calculating the corresponding Hessian matrices which contained no imaginary frequencies. The quantum chemical data were processed, and the structures were visualized, using ChemCraft [23].

(2*S*,3*S*)-2-Benzyloxybutane-1,3,4-triol (1). A suspension of 0.090 g (2.37 mmol) of sodium tetrahydridoborate and 0.1 g (2.35 mmol) of lithium chloride in 5 mL of anhydrous THF was stirred for 10 min under argon, and 0.3 g (1.12 mmol) of compound **7** was added dropwise. The mixture was stirred for 30 min, 2 mL of anhydrous ethanol was added, the mixture was stirred for 20 h at room temperature, and 1 mL of acetone was added. The mixture was filtered through a thin layer of silica gel, the sorbent was washed with ethanol, the filtrate was evaporated, and the residue was subjected to silica gel column chromatography using chloroform–methanol (10 : 1) as eluent. Yield 0.1 g (44%), white crystals, mp 69–70°C, $[\alpha]_D^{20}$ = +23.1° (*c* = 0.47, $CHCl_3$); published data [5]: $[\alpha]_D^{20}$ = +15.7° (*c* = 1.00, MeOH). ^{1}H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 2.21 br.s (3H, OH), 3.57 d.d (1H, 2-H, *J* = 4.6, 3.7 Hz), 3.68 d.d (1H, OCH_2, *J* = 4.4, 11.6 Hz), 3.74 m (1H, OCH_2), 3.78 m (1H, OCH_2), 3.85 d.d (1H, OCH_2, *J* = 4.6, 10.8 Hz), 3.91 d (1H, 3-H, *J* 4.6 Hz), 4.59 d and 4.72 d (1H each, Ph**C**$\mathbf{H}_2$, *J* = 11.6 Hz), 7.36 m (5H, Ph). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$), δ_C, ppm: 60.87 (OCH_2), 62.98 (OCH_2), 71.64 (C^3), 72.45 (Ph**C**H_2), 79.16 (C^2); 128.02, 128.25, 128.71, 137.61 (Ph).

Reaction of triol 1 with *N*,*N*′-carbonyldiimidazole. *N*,*N*′-Carbonyldiimidazole, 0.35 g (2.16 mmol), was added to a solution of 0.3 g (1.44 mmol) of triol **1** in 5 mL of anhydrous THF. The mixture was stirred for 5 h, an additional 0.03 g of *N*,*N*′-carbonyldiimidazole was added, and the mixture was stirred for 2 h. The solvent was distilled off, the residue was treated with 10 mL of methylene chloride, and the organic phase was washed with 5% aqueous HCl and brine, dried over $MgSO_4$, and evaporated on a rotary evaporator. The residue was subjected to silica gel column chromatography (chloroform–methanol, 20 : 1) to isolate 0.1 g (31%) of **2** and 0.08 g (25%) of **3**.

(4*S*)-4-[(1*S*)-1-Benzyloxy-2-hydroxyethyl]-1,3-dioxolan-2-one (2). $[\alpha]_D^{20}$ = +15.2° (*c* = 1.753, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3055, 2986, 2350, 1815, 1796, 1455, 1422, 1395, 1263, 1169, 1082, 896, 753, 738, 724, 705. ^{1}H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 2.20 br.s (1H, OH), 3.58 d.d (1H, 1′-H, *J* = 4.6, 9.6 Hz), 3.80 d.d (2H, 2′-H, *J* = 4.6, 5.6 Hz), 4.24 d.d (1H, 5-H, *J* = 6.5, 8.4 Hz), 4.44 t (1H, 5-H, *J* = 8.4 Hz), 4.65 d and 4.75 d (1H each, Ph**C**$\mathbf{H}_2$, *J* = 11.9 Hz), 4.88 d.d.d (1H, 4-H, *J* = 4.2, 6.5, 8.4 Hz), 7.36 m (5H, Ph). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$), δ_C, ppm: 60.40 (OCH_2), 66.19 (C^5), 73.01 (Ph**C**H_2), 76.58 ($C^{1'}$), 77.81 (C^4); 127.95, 128.23, 128.63, 137.18 (Ph); 155.12 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 238 (32) $[M]^+$, 207 (75) $[M - CH_2OH]^+$, 194 (65) $[M - CO_2]^+$, 178 (62), 145 (74), 117 (100), 91 (99) $[PhCH_2]^+$.

Bis[(2′*S*,4′*S*)-2-Benzyloxy-2-(2-oxo-1,3-dioxolan-4-yl)ethyl] carbonate (3). White needles, mp 132–

133°C, $[\alpha]_D^{20}$ = +81.0 (*c* = 0.41, $CHCl_3$). IR spectrum, ν, cm^{-1}: 3055, 2987, 2320, 1798, 1795, 1791, 1757, 1477, 1443, 1422, 1395, 1323, 1276, 1260, 1169, 1080, 1012, 896, 759, 731, 724, 710, 701. ^1H NMR spectrum (500.13 MHz, $CDCl_3$), δ, ppm: 3.87 d.t (1H, 2′-H, *J* = 2.6, 5.8 Hz), 4.29 d.d (1H, 1′-H, *J* = 5.5, 8.5 Hz), 4.36 d.d (1H, 5″-H, *J* = 6.1, 11.6 Hz), 4.44 d.d (1H, 5″-H, *J* = 5.3, 11.5 Hz), 4.53 t (1H, 1′-H, *J* = 8.5 Hz), 4.66 d (1H, PhC**H**$_2$, *J* = 11.8 Hz), 4.82 d (1H, PhC**H**$_2$, *J* = 11.7 Hz), 4.96 d.d.d (1H, 4″-H, *J* = 2.6, 8.4, 5.4 Hz), 7.33–7.35 m (10H, Ph). ^{13}C NMR spectrum (125.77 MHz, $CDCl_3$), δ_C, ppm: 65.79 ($C^{5''}$), 66.48 (OCH_2), 73.30 (Ph**C**H_2), 75.62 ($C^{2'}$), 75.75 ($C^{4''}$); 128.25, 128.36, 128.79, 137.69 (Ph); 155.14 (C=O), 154.72 (C^1). Mass spectrum, *m*/*z* (I_{rel}, %): 194 (12), 165 (8), 134 (25), 107 (100), 91 (99).

Dimethyl (4*R*,5*R*)-2-phenyl-1,3-dioxolane-4,5-dicarboxylate (6). Dimethyl L-tartrate, 6.75 g (37.9 mmol), was dissolved in 50 mL of anhydrous benzene, 6.2 mL (41.7 mmol) of benzaldehyde dimethyl acetal and 10 mg of *p*-toluenesulfonic acid were added, and the mixture was heated under reflux with distillation of benzene–methanol azeotrope (bp 57°C) over a period of ~2 h (TLC). The mixture was cooled to room temperature, 0.3 g of potassium carbonate and 10 mL of methylene chloride were added, and the mixture was stirred for 1 h, filtered, and evaporated. The solid residue was recrystallized from methylene chloride–petroleum ether. Yield 5.94 g (59%), colorless crystals, mp 68–69°C; published data [16]: mp 69–71°C. ^1H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 3.82 s and 3.87 s (3H each, OCH_3), 4.92 d (1H, 5-H, *J* = 4.0 Hz), 4.99 d (1H, 4-H, *J* = 4.0 Hz), 6.14 s (1H, 2-H), 7.39−7.40 m (3H) and 7.56−7.59 m (2H) (Ph).

Dimethyl (2*R*,3*R*)-2-benzyloxy-3-hydroxybutanedioate (7). A solution of 1.0 g (3.76 mmol) of compound **6** in 20 mL of anhydrous methylene chloride was cooled to −35 to −40°C, 0.84 mL (5.17 mmol) of triethylsilane was added under argon, and a solution of 0.45 mL (4.16 mmol) of titanium tetrachloride in 3 mL of methylene chloride was added dropwise under stirring. The mixture was stirred at that temperature until the initial compound disappeared (~2 h, TLC), quickly treated with 10 mL of ice water, and allowed to warm up to –5°C. The organic phase was separated, the aqueous layer was extracted with methylene chloride (3×10 mL), and the extracts were combined with the organic phase, washed with brine, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography using ethyl acetate–petroleum ether (1:2) as eluent. Yield 0.92 g (92%), $[\alpha]_D^{20}$ = +93° (*c* = 1.1, $CHCl_3$). ^1H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 3.11 d (1H, OH, *J* = 9.0 Hz), 3.66 s and 3.87 s (3H each, OCH_3), 4.33 d (1H, 2-H, *J* = 1.2 Hz), 4.41 d and 4.89 d (1H each, OCH_2, *J* = 12.0 Hz), 4.59 d.d (1H, 3-H, *J* = 1.2, 9.0 Hz), 7.24–7.28 m (3H) and 7.31–7.37 m (2H) (Ph). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$), δ_C, ppm: 52.48 (OCH_3), 52.69 (OCH_3), 72.33 (C^3), 72.96 (OCH_2), 77.94 (C^2); 128.20, 128.34, 128.46, 136.64 (Ph); 169.79 (C=O), 171.48 (C=O). Found, %: C 58.38; H 5.02. $C_{13}H_{14}O_6$. Calculated, %: C 58.64; H 5.30.

2-Benzyloxy-3-[*tert*-butyl(dimethyl)silyloxy]propanal (8). Lead tetraacetate, 0.065 g (0.144 mmol), was added to a solution of 0.03 g (0.096 mmol) of compound **10** in 5 mL of benzene, and the mixture was stirred at room temperature until compound **10** disappeared (TLC). The mixture was diluted with 10 mL of diethyl ether, washed with 3 mL of brine, dried over $MgSO_4$, and evaporated, and the residue was subjected to silica gel column chromatography using petroleum ether–ethyl acetate (1:4) as eluent. Yield 0.015 g (53%). ^1H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 0.06 s (6H, $SiMe_3$), 0.88 s (9H, *t*-Bu), 3.88 d (1H, 2-H, *J* = 4.6 Hz), 3.93 m (2H, OC^3H_2), 4.71 d.d (2H, PhC**H**$_2$, *J* = 11.9, 17.4 Hz), 7.36 m (5H, Ph), 9.71 s (1H, CHO). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$), δ_C, ppm: 5.97 ($SiMe_2$), 17.95 (**C**Me_3), 25.79 (CH_3), 62.35 (C^3), 72.65 (Ph**C**H_2), 84.13 (C^2); 122.07, 127.97, 128.53, 134.39 (Ph); 202.83 (CHO). Found, %: C 65.58; H 8.82; Si 9.91. $C_{16}H_{26}O_3Si$. Calculated, %: C 65.26; H 8.90; Si 9.54.

(4*S*)-4-{(1*S*)-1-Benzyloxy-2-[*tert*-butyl(dimethyl)silyloxy)]ethyl}-1,3-dioxolan-2-one (9). To a solution of 0.05 g (0.22 mmol) of compound **2** and 0.018 g (0.27 mmol) of imidazole in 5 mL of methylene chloride we added 0.04 g (0.27 mmol) of *tert*-butyl(chloro)(dimethyl)silane and 0.01 g of 4-dimethylaminopyridine. The mixture was stirred for 5 h at room temperature and washed with brine, and the organic phase was separated, dried over $MgSO_4$, and evaporated. The residue was purified by silica gel column chromatography using first benzene and then petroleum ether–ethyl acetate (1:2) as eluent to isolate 0.46 g (75%) of **9**. ^1H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 0.07 s (6H, $SiMe_2$), 0.89 s (9H, *t*-Bu), 3.50 m (1H, 1′-H), 3.74–3.78 m and 3.81–3.83 m (1H each, $OC^{2'}H_2$), 4.24 d.d (1H, 5-H, *J* = 6.3, 8.5 Hz), 4.40 t (1H, 5-H, *J* = 8.5 Hz), 4.60 d and 4.75 d (1H each, PhC**H**$_2$, *J* = 11.9 Hz), 4.85 d.d.d (1H, 4-H, *J* = 3.5, 6.2, 8.5 Hz), 7.34–7.36 m (5H, Ph).

(2*S*,3*S*)-3-Benzyloxy-4-[*tert*-butyl(dimethyl)-silyloxy]butane-1,2-diol (10). Compound **9**, 0.05 g (0.15 mmol), was dissolved in 5 mL of anhydrous methanol, 0.03 g (0.22 mmol) of freshly calcined potassium carbonate was added, and the mixture was stirred until compound **9** disappeared (TLC). The mixture was filtered, the filtrate was evaporated, and the residue was purified by silica gel column chromatography using petroleum ether–ethyl acetate (1:1) as eluent. Yield 0.035 g (75%). ^{1}H NMR spectrum (300.13 MHz, $CDCl_3$), δ, ppm: 0.003 s (6H, $SiMe_2$), 0.82 s (9H, *t*-Bu), 2.59 br.s (2H, OH), 3.45 d.d (1H, 3-H, J = 4.7, 10.1 Hz), 3.59 d.d (2H, OC^4H_2, J = 3.6, 4.8 Hz), 3.72 m (3H, 2-H, OC^1H_2), 4.48 d (1H, Ph**C**$\mathbf{H}_2$, J = 11.5 Hz), 4.68 d (1H, Ph**C**$\mathbf{H}_2$, J = 11.6 Hz), 7.26 m (5H, Ph). ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$), δ_C, ppm: 5.57 ($SiMe_2$), 18.17 (**C**Me_3), 25.79 (CH_3), 62.28 (C^1), 63.62 (C^4), 72.79 (Ph**C**H_2), 71.77 (C^2), 79.49 (C^3); 121.97, 128.14, 128.51, 137.91 (Ph).

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REFERENCES

1. Wuts, P.G.M. and Greene, T.W., *Greene's Protective Groups in Organic Synthesis*, Hoboken, NJ: Wiley, 2007, 4th ed., p. 361.
2. Amaranth, V. and Broom, A.D., *Chem. Rev*., 1977, vol. 77, p. 183.
3. Jarowicki, K. and Kocienski, P., *J. Chem. Soc., Perkin Trans. 1*, 2001, p. 2109.
4. Groneberg, R.D., Miyazaki, T., Stylianides, N.A., Schulze, T.J., Stahl, W., Schreiner, E.P., Suzuki, T., Iwabuchi, Y., Smith, A.L., and Nicolaou, K.C., *J. Am. Chem. Soc*., 1993, vol. 115, p. 7593.
5. Fujita, K., Nakai, H., Kobayashi, S., Inoue, K., Nojima, Sh., and Ohno, M., *Tetrahedron Lett*., 1982, vol. 23, p. 3507.
6. Kang, S.-K., Keun, J.-H., Nam, K.-S., Park, C.-H., and Lee, H.-W., *Synth. Commun*., 1994, vol. 24, p. 305.
7. Kutney, J.P. and Ratcliffe, A.H., *Synth. Commun*., 1975, vol. 5, p. 47.
8. Anderson, B.D., Lambert, W.J., and Couradi, R.A., *J. Pharm. Sci*., 1984, vol. 73, p. 604.
9. Wachen, F. and Hartke, K., *Chem. Ber*., 1975, vol. 108, no. 2, p. 683.
10. Koch, H. and Fischer, F., *Z. Chem*., 1967, vol. 7, no. 1, p. 18.
11. Sands, B.H. and Rowland, A.T., *Steroids*, 1964, vol. 4, no. 2, p. 175.
12. Vostrikov, N.S., Loza, V.V., Selezneva, N.K., and Miftakhov, M.S., *Russ. J. Org. Chem*., 2014, vol. 50, p. 140.
13. Venkatamaran, S., Veronica, N., Wao, Z.X., Hendrick, J.L., and Yang, Y.Y., *Polymer Chem*., 2013, vol. 4, p. 2945.
14. Albanese, D., Landini, D., Penco, M., Tagliable, A., and Carlini, E., *Org. Process Res. Dev*., 2010, vol. 14, p. 705.
15. Shiina, I., Shibata, J., Ibuka, R., Imai, Y., and Mukaiyama, T., *Bull. Chem. Soc. Jpn*., 2001, vol. 74, p. 113.
16. Kocienski, P. and Street, S.D.A., *Synth. Commun*., 1984, vol. 14, p. 1087.
17. Mori, A., Ishihara, K., and Yamamoto, H., *Tetrahedron Lett*., 1986, vol. 27, p. 987.
18. Jensen, F., *Introduction to Computational Chemistry*, Chichester: Wiley, 1999, p. 428.
19. Koch, W. and Holthausen, M.C., *A Chemist's Guide to Density Functional Theory*, Weinheim: Wiley-VCH, 2001, 2nd ed., p. 293.
20. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, no. 7, p. 5648.
21. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. B*., 1988, vol. 37, p. 785.
22. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Martin, R.L., Morokuma, K., Zakrzewski, V.G., Voth, G.A., Salvador, P., Dannenberg, J.J., Dapprich, S., Daniels, A.D., Farkas, Ö., Foresman, J.B., Ortiz, J.V., Cioslowski, J., and Fox, D.J. *Gaussian 09, Revision C.01*, Wallingford CT: Gaussian, 2009. http://www.gaussian.com.
23. http://www.chemcraftprog.com