Transformation of homoallylic alcohol oxides into 3-hydroxytetrahydrofurans in aqueous $HClO_4$

M. V. Chirskaya,[a] A. A. Vasil´ev,[b]★ S. V. Shorshnev,[a] and S. I. Sviridov[a]

[a]ChemBridge Corporation,
1 ul. Malaya Pirogovskaya, 119435 Moscow, Russian Federation
[b]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5328. E-mail: vasiliev@ioc.ac.ru

Hydrolysis of allyl carbinol oxides in aqueous $HClO_4$ gave the corresponding 1,2,4-triols. On heating in the same reaction medium, they underwent cyclization into 3-hydroxytetrahydrofurans. The method is restricted to substrates that can generate stable carbocations *via* elimination of the hydroxy group from position 4 in intermediate 1,2,4-triols.

Key words: tetrahydrofuran-3-ols, allyl carbinols, epoxides, triols, heterocyclization.

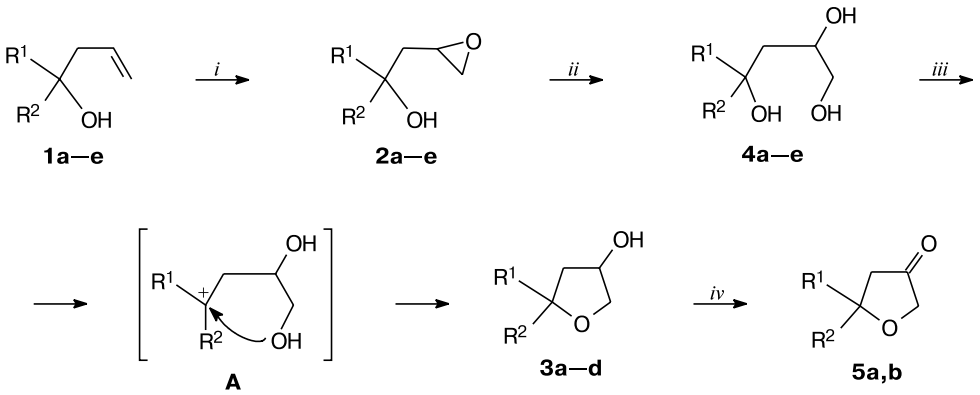
The tetrahydrofuran fragment is found in some natural[1] and pharmacologically active compounds.[2] Among a variety of routes to tetrahydrofurans, cyclization of olefinic alcohols[3] in the presence of electrophilic (including oxidizing) reagents is of particular importance. Cyclization of alk-4-en-1-ols (homoallyl carbinols) usually presents no problem, while reactions of alk-3-en-1-ols (allyl carbinols) leading to 3-substituted tetrahydrofurans should proceed through the generation of primary carbocations and therefore are kinetically unfavorable. To make the reaction follow a desired pathway, the cyclization of allyl carbinols is usually carried out indirectly (most often, by two-step methods). Recently, we have proposed a simple and convenient route to 3-bromotetrahydrofurans *via* bromination of allyl carbinols followed by cyclization of the resulting 1,2-dibromoalkan-4-ols with K_2CO_3 in methanol.[4] A simple method for the synthesis of 3-hydroxytetrahydrofurans by isomerization of allyl carbinol oxides in the presence of magnesium halides in ether has been reported.[5] Direct oxidative cyclization of allyl carbinols with H_2O_2—titanium silicate[6] or $NaIO_4$—$NaHSO_3$ (the latter cyclization occurs through the formation of 1-iodoalkane-2,4-diols)[7] affords 3-hydroxytetrahydrofurans in acceptable yields. Related modern approaches[8] are effective but involve expensive reagents and complex synthetic procedures. Under certain conditions, the cyclization of allyl carbinols or their oxides can lead to oxetane derivatives.[9] Iodocyclization of crotyl alcohol and higher alk-2-enyl carbinols proceeds through the generation of a secondary carbocation and thus is not difficult.[9c,10]

Here we present a simple method of transforming some allyl carbinols **1** through their oxides **2** into 3-hydroxytetrahydrofurans **3** (Scheme 1) in aqueous perchloric acid medium. When stirred at room temperature in water containing 1.5—2% $HClO_4$, compounds **2** underwent opening of the epoxide ring to give water-soluble triols **4** (triol **4a** was isolated and identified from the ^{1}H NMR spectrum). Subsequent heating of the reaction mixture resulted into intramolecular dehydration accompanied by the formation of 3-hydroxytetrahydrofurans **3** in 49—85% yields. In the case of unsymmetrical compounds ($R^1 \neq R^2$), mixtures of two diastereomers were obtained (*e.g.*, (3*R**,5*R**)- and (3*R**,5*S**)-**3a,b**). The structures of these products were additionally confirmed by oxidation of the diastereomeric mixtures of alcohols **3a,b** into the corresponding individual ketones **5a,b** (in the alternative formation of 2-hydroxymethyloxetane derivatives with the primary alcohol group, this oxidation would give diastereomeric mixtures of aldehydes well identifiable from ^{1}H NMR spectra).

Individual diastereomers (3*R**,5*R**)- and (3*R**,5*S**)-**3a** have been obtained earlier by a stereoselective synthesis (see Refs 8b, 11). This allowed us to assign the characteristic signals in the ^{1}H NMR spectrum of their mixture. To determine the configurations of tetrahydrofuranols **3b** and **3b´**, these isomers were separated by column chromatography and studied by a NOESY experiment in DMSO-d_6. The NOESY spectrum of diastereomer (3*R**,5*R**)-**3b** shows cross peaks between the methyl protons (δ 1.38, s) and the H(3) proton (δ 4.43, m), while for diastereomer (3*R**,5*S**)-**3b**, these cross peaks were absent. However, its

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1252—1255, July, 2006.
1066-5285/06/5507-1300

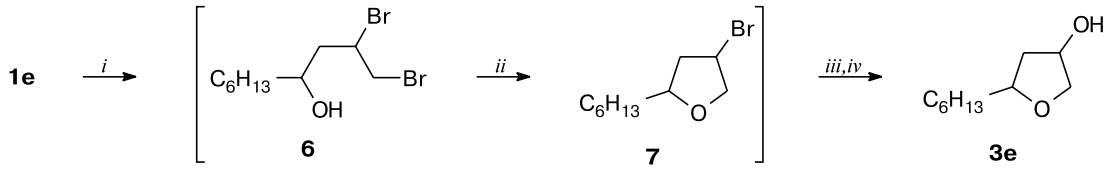
Scheme 1



R^1 = Ph, R^2 = H (**1a—5a**), Me (**1b—5b**); $R^1 + R^2 = (CH_2)_5$ (**1c—4c**); $R^1 = R^2$ = Et (**1d—4d**); $R^1 = C_6H_{13}$, R^2 = H (**1e—4e**)

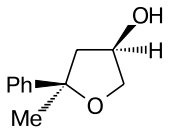
Reagents and conditions: *i*, MCPBA, $CHCl_3$, reflux, 2 h; *ii*, $HClO_4$—H_2O, 20 °C; *iii*, $HClO_4$—H_2O, 100 °C; *iv*, PCC, CH_2Cl_2.

Scheme 2

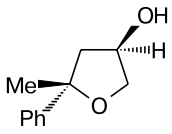


Reagents and conditions: *i*, Br_2, CH_2Cl_2; *ii*, K_2CO_3 (4 equiv.), MeOH, 20 °C; *iii*, AcOK, DMSO, 70 °C; *iv*, K_2CO_3 (cat.), MeOH, 20 °C.

spectrum contains a cross peak between the methyl (δ 1.51, s) and OH protons (δ 4.94, d).



(3*R**,5*R**)-**3b**



(3*R**,5*S**)-**3b**

Apparently, the reaction involves generation of carbocation **A**. Indeed, 3-hydroxytetrahydrofurans **3** were obtained only from the substrates that form stable benzylic (**4a,b**) or tertiary carbocations (**4c,d**). In the case of epoxy alcohol **2e**, whose corresponding diol **4e** forms an unstabilized secondary carbocation, the reaction afforded no desired tetrahydrofuran derivative. The reaction products isolated in low yields differed in spectroscopic characteristics from authentic compound **3e** prepared in an independent way (Scheme 2). To obtain this compound, we used at the key step earlier[4] developed dehydrobromination of 1,2-dibromoalkan-4-ols (in our case, alcohol **6**) with K_2CO_3 in methanol leading to 3-bromotetrahydrofuran derivative **7**. The Br atom was replaced by a hydroxy group in a standard way with potassium acetate in DMSO followed by methanolysis of intermediate furan-3-yl acetate.

It should be noted that previous methods for the transformation of 1,2,4-triols into 3-hydroxytetrahydrofurans involved *p*-toluenesulfonic acid,[12] anhydrous cupric sulfate,[11b] *p*-toluenesulfonyl chloride in pyridine,[13] and a special combination of protective groups.[14] The closest analog to our approach is distillation of triols from aqueous H_2SO_4,[15] which usually provides moderate yields and is restricted to low-molecular-weight substrates that are well steam-distilled. Although our method is not versatile, it is simple and affords tetrahydrofuran derivatives in preparative yields.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 400 Avance instrument (400.13 (^1H) and 100.62 MHz (^{13}C)) in $CDCl_3$ or DMSO-d_6 with reference to signals for a deuterated solvent (^{13}C) or its residual protons (^1H). The ratios of the diastereomeric products were determined from the integral intensities of the characteristic signals in the ^1H NMR spectra. GLC analysis was carried out on a Chrom-5 chromatograph (column 2400×3 mm, 5% SE-30 on Chromaton

N-AW-DMCS, injector and flame ionization detector temperature 260 °C, heating from 130 to 200 °C at a rate of 5 deg min^{-1}). Elemental analysis was performed at an analytical laboratory of the A. N. Nesmeyanov Institute of Organoelement Compounds. TLC analysis was carried out on Kieselgel 60 F_{254} plates (Merck, Cat. No. 1.05554) in 5% (or 10%) MeOH—CH_2Cl_2. Column chromatography was carried out on silica gel L (100/160). The starting allyl carbinols **1a—e** were prepared from appropriate carbonyl compounds and allylmagnesium bromide according to the literature procedures.[16]

Epoxy alcohols 2. A mixture of allyl carbinol **1** (20 mmol) and 70% 3-chloroperoxybenzoic acid (Acros; 6.9 g, 25 mmol) in chloroform (50 mL) was refluxed with stirring for 2—3 h until the starting compound **1** was completely consumed (TLC monitoring). The mixture was cooled and the precipitate of 3-chlorobenzoic acid was filtered off. The filtrate was washed successively with solutions of $Na_2S_2O_3$, NaOH, and NaCl, dried with Na_2SO_4, and concentrated *in vacuo* to give sufficiently pure epoxides **2**. They were used at the next step without additional purification. The physicochemical characteristics of compounds **2a—d** were in agreement with the literature data.[9a,b,17,18]

1,2-Epoxydecan-4-ols (2e), a 1 : 1 mixture of the diastereomers. An analytically pure sample was obtained by column chromatography in AcOEt—hexane with a concentration gradient of AcOEt from 5 to 50%. Found (%): C, 69.52; H, 11.78. $C_{10}H_{20}O_2$. Calculated (%): C, 69.72; H, 11.70. ^{1}H NMR ($CDCl_3$), δ: 0.88 (t, 3 H, J = 6.8 Hz); 1.23—1.54 (m, 10 H); 1.61 (ddd, 0.5 H, J = 14.4 Hz, J = 6.4 Hz, J = 3.4 Hz); 1.78—1.88 (m, 1.5 H); 1.96 (br.s, 1 H); 2.50 (dd, 0.5 H, J = 4.9 Hz, J = 2.7 Hz); 2.61 (dd, 0.5 H, J = 4.9 Hz, J = 2.9 Hz); 2.78 (dd, 0.5 H, J = 4.9 Hz, J = 3.9 Hz); 2.82 (dd, 0.5 H, J = 4.9 Hz, J = 4.2 Hz); 3.08 and 3.14 (both m, 0.5 H each); 3.81 and 3.88 (both m, 0.5 H each). ^{13}C NMR ($CDCl_3$), δ: 13.9; 22.4; 25.3 and 25.4; 29.1; 31.7; 37.3 and 37.5; 39.3 and 39.7; 46.4 and 46.8; 50.0 and 50.3; 69.0 and 70.0.

3-Hydroxytetrahydrofurans 3 (general procedure). A mixture of epoxy alcohol (16 mmol), water (25 mL), and 50% $HClO_4$ (0.8 mL) was stirred at 20 °C for 3—4 h and then refluxed with stirring for 3 h. The mixture was cooled and neutralized with $NaHCO_3$. The product was extracted with $CHCl_3$ and the extract was dried with Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography in MeOH—CH_2Cl_2 with a concentration gradient of MeOH from 0 to 3% to give compounds **3a—d**.

3-Hydroxy-5-phenyltetrahydrofuran (3a). The yield from the two-step process was 70—75%, a 3 : 2 mixture of the (3*R**,5*S**)- and (3*R**,5*R**)-isomers, a yellowish oil. (3*R**,5*S**)-Isomer: ^{1}H NMR ($CDCl_3$), δ: 1.94 (m, 1 H); 2.14 (br.s, 1 H); 2.34, 3.89 (both m, 1 H each); 4.23 (dd, 1 H, J = 10.1 Hz, J = 4.4 Hz); 4.61 (m, 1 H); 5.17 (dd, 1 H, J = 10.1 Hz, J = 5.9 Hz) (*cf.* Ref. 11). (3*R**,5*R**)-Isomer: ^{1}H NMR ($CDCl_3$), δ: 1.96 (m, 1 H); 2.14 (br.s, 1 H); 2.67 (ddd, 1 H, J = 14.3 Hz, J = 7.5 Hz, J = 6.9 Hz); 3.90 (m, 1 H); 4.05 (d, 1 H, J = 10.0 Hz); 4.57 (m, 1 H); 4.91 (t, 1 H, J = 7.5 Hz) (*cf.* Ref. 8b).

3-Hydroxy-5-methyl-5-phenyltetrahydrofuran (3b). The yield from the two-step process was 65—85%, a ~5 : 4 mixture of the (3*R**,5*R**)- and (3*R**,5*S**)-isomers, a yellowish oil. Found (%): C, 74.37; H, 8.01. $C_{11}H_{14}O_2$. Calculated (%): C, 74.13; H, 7.92. The mixture was separated by column chromatography in MeOH—CH_2Cl_2 with a concentration gradient of MeOH from 0 to 3%.

(3*R**,5*R**)-Isomer, R_f 0.63 (10% MeOH—CH_2Cl_2). ^{1}H NMR (DMSO-d_6), δ: 1.38 (s, 3 H); 2.01 (dd, 1 H, J = 12.9 Hz, J = 4.4 Hz); 2.32 (dd, 1 H, J = 12.9 Hz, J = 7.0 Hz); 3.56 (dd, 1 H, J = 8.9 Hz, J = 4.4 Hz); 4.01 (dd, 1 H, J = 8.9 Hz, J = 5.6 Hz); 4.43 (m, 1 H); 4.72 (d, 1 H, J = 4.0 Hz); 7.18 (t, 1 H, J = 7.3 Hz); 7.30 (t, 2 H, J = 7.9 Hz); 7.40 (d, 2 H, J = 8.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 30.1, 48.6, 71.0, 73.8, 83.5, 124.6, 126.0, 127.9, 148.8.

(3*R**,5*S**)-Isomer, R_f 0.54 (10% MeOH—CH_2Cl_2). ^{1}H NMR (DMSO-d_6), δ: 1.51 (s, 3 H); 2.03 (dd, 1 H, J = 12.9 Hz, J = 3.7 Hz); 2.28 (dd, 1 H, J = 12.9 Hz, J = 6.5 Hz); 3.72 (dd, 1 H, J = 9.2 Hz, J = 3.1 Hz); 3.82 (dd, 1 H, J = 9.2 Hz, J = 5.2 Hz); 4.23 (m, 1 H); 4.94 (d, J = 3.7 Hz); 7.19 (t, 1 H, J = 7.0 Hz); 7.30 (t, 2 H, J = 7.9 Hz); 7.35 (d, 2 H, J = 7.0 Hz). ^{13}C NMR (DMSO-d_6), δ: 30.4, 48.5, 71.1, 74.4, 83.8, 124.3, 126.2, 128.1, 148.6.

1-Oxaspiro[4.5]decan-3-ol (3c). The yield from the two-step process was 70—75%. ^{1}H NMR ($CDCl_3$), δ: 1.28—1.54 (m, 6 H); 1.60—1.72 (m, 4 H); 1.75 (ddd, 1 H, J = 13.5 Hz, J = 2.4 Hz, J = 1.2 Hz); 1.91 (br.s, 1 H); 1.94 (dd, 1 H, J = 13.5 Hz, J = 6.6 Hz); 3.77 (ddd, 1 H, J = 9.9 Hz, J = 2.4 Hz, J = 1.2 Hz); 3.89 (dd, J = 9.9 Hz, J = 4.4 Hz); 4.44 (m, 1 H). ^{13}C NMR ($CDCl_3$), δ: 23.5, 23.7, 25.3, 37.1, 38.0, 45.9, 72.7, 73.4, 82.7. The spectroscopic characteristics are close to the literature data.[8a]

5,5-Diethyl-3-hydroxytetrahydrofuran (3d). The yield from the two-step process was 49%, a colorless oil. Found (%): C, 66.39; H, 11.07. $C_8H_{16}O_2$. Calculated (%): C, 66.63; H, 11.18. ^{1}H NMR (DMSO-d_6), δ: 0.76 (t, 3 H, J = 7.5 Hz); 0.80 (t, 3 H, J = 7.4 Hz); 1.29—1.48 (m, 2 H); 1.46—1.77 (m, 3 H); 1.83 (dd, 1 H, J = 12.9 Hz, J = 7.1 Hz); 3.46 (dd, 1 H, J = 9.0 Hz, J = 4.1 Hz); 3.75 (dd, 1 H, J = 9.0 Hz, J = 5.3 Hz); 4.27 (m, 1 H); 4.75 (br.s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 8.3, 8.6, 29.8, 30.2, 43.4, 71.0, 73.5, 84.9.

5-Hexyl-3-hydroxytetrahydrofuran (3e) (parallel synthesis). A solution of bromine (2.2 mmol) in CH_2Cl_2 (4 mL) was added at 0—5 °C to a stirred solution of dec-1-en-4-ol (**1e**) (0.312 g, 2 mmol) in CH_2Cl_2 (6 mL). An aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$ was added and the mixture was stirred for 15—20 min. The organic layer was separated and the product from the aqueous layer was extracted with CH_2Cl_2. The extracts were dried with Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in MeOH (5 mL) and freshly powdered K_2CO_3 (1.104 g, 8 mmol) was added with stirring. The mixture was stirred at 20 °C for 4 h and then the greater part of the solvent was removed *in vacuo*. The residue was diluted with water and organic material was extracted with ether. The extracts were dried with $CaCl_2$ and concentrated *in vacuo*. The residue was dissolved in DMSO (4 mL) and potassium acetate (0.784 g, 8 mmol) was added. The mixture was stirred at 70—80 °C for 6 h (GLC monitoring) and diluted with water (16 mL). The product was extracted with ether and the extracts were washed with a solution of NaCl, dried with $CaCl_2$, and concentrated *in vacuo*. The residue was dissolved in MeOH (3 mL) and K_2CO_3 (100 mg) was added. The mixture was stirred at 20 °C for 6 h. The greater part of the solvent was removed *in vacuo*. Benzene (10 mL) and silica gel (2 mL) were added to the residue. The mixture was evaporated to dryness. The dry friable residue was placed on the top of a chromatographic column packed with silica gel and chromatographed in AcOEt—hexane with a concentration gradient of AcOEt from 0 to 40%. Concentration of the corresponding fractions gave 3 : 2 mixtures of diastereomers **3e** as

colorless oils. The yield was 0.213 g (62% with respect to **1e**). Found (%): C, 70.00; H, 11.70. $C_{10}H_{20}O_2$. Calculated (%): C, 69.72; H, 11.70.

Major diastereomer. ^{1}H NMR ($CDCl_3$), δ: 0.85 (t, 3 H, J = 6.9 Hz); 1.20—1.74 (m, 11 H); 2.30 (quint, 1 H, J = 6.6 Hz); 2.43 (br.s, 1 H); 3.65 (m, 1 H); 3.71—3.82 (m, 2 H); 4.40 (m, 1 H). ^{13}C NMR ($CDCl_3$), δ: 14.0, 22.5, 26.2, 29.2, 31.7, 36.1, 41.4, 72.3, 75.2, 79.2.

Minor diastereomer. ^{1}H NMR ($CDCl_3$), δ: 0.85 (t, 3 H, J = 6.9 Hz); 1.20—1.74 (m, 11 H); 1.95 (dd, 1 H, J = 13.2 Hz, J = 5.6 Hz); 2.43 (br.s, 1 H); 3.64 (dd, 1 H, J = 9.8 Hz, J = 4.4 Hz); 3.96 (dd, 1 H, J = 9.8 Hz, J = 4.7 Hz); 4.07, 4.44 (both m, 1 H each). ^{13}C NMR ($CDCl_3$), δ: 14.0, 22.5, 26.1, 29.3, 31.7, 35.4, 41.6, 72.4, 75.1, 78.1.

4-Phenylbutane-1,2,4-triol (4a). An aqueous 50% solution of $HClO_4$ (0.45 mL) was added to a solution of epoxy alcohol **2a** (0.255 g) in THF (1.25 mL) and water (2.5 mL). The mixture was stirred at 20 °C for 18—20 h and neutralized with $NaHCO_3$. Impurities were extracted with CH_2Cl_2 and the aqueous layer was largely concentrated *in vacuo*. The residue was mixed with MeOH (5 mL) and $CHCl_3$ (5 mL) was added. The inorganic precipitate was filtered off and the filtrate was concentrated *in vacuo*. A viscous oily residue mainly consisted of a 3 : 2 mixture of the diastereomers of triol **4a**. ^{1}H NMR (DMSO-d_6), δ: 1.43 (m, 0.6 H); 1.62—1.71 (m, 1.4 H); 3.19—3.40 (m, 2.4 H); 3.69 (m, 0.6 H); 4.50 (m, 1.6 H); 4.60 (br.s, 0.4 H); 4.68—4.78 (m, 1 H); 5.13 (br.s, 0.6 H); 5.21 (br.s, 0.4 H); 7.21 (m, 1 H); 7.26—7.38 (m, 4 H) (*cf.* Ref. 19).

5-Phenyltetrahydrofuran-3-one (5a). Pyridinium chlorochromate (604 mg, 2.8 mmol) was added to a solution of a diastereomeric mixture of 3-hydroxy-5-phenyltetrahydrofuran (**3a**) (328 mg, 2 mmol) in CH_2Cl_2 (20 mL). The mixture was stirred at 20 °C for 2—3 h (TLC monitoring), diluted with ether (40 mL), and allowed to stand for 30 min. The mixture was filtered through a column of neutral alumina and then the sorbent was washed with ether—CH_2Cl_2 (1 : 1). The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography in AcOEt—hexane with a concentration gradient of AcOEt from 0 to 10%. The yield of ketone **5a** was 195 mg (60%). ^{1}H NMR (DMSO-d_6), δ: 2.51 (dd, 1 H, J = 17.8 Hz, J = 9.9 Hz); 2.88 (dd, 1 H, J = 17.8 Hz, J = 6.0 Hz); 3.98, 4.18 (both d, 1 H each, J = 16.7 Hz); 5.27 (dd, 1 H, J = 9.9 Hz, J = 6.0 Hz); 7.33 (t, 1 H, J = 7.0 Hz); 7.39 (t, 2 H, J = 7.0 Hz); 7.43 (d, 2 H, J = 7.3 Hz) (*cf.* Ref. 8c).

5-Methyl-5-phenyltetrahydrofuran-3-one (5b) was obtained analogously. The yield was 73%, m.p. 51—52 °C. Found (%): C, 75.29; H, 7.02. $C_{11}H_{12}O_2$. Calculated (%): C, 74.98; H, 6.86. ^{1}H NMR ($CDCl_3$), δ: 1.68 (s, 3 H); 2.70, 2.92 (both d, 1 H each, J = 17.6 Hz); 3.97, 4.14 (both d, 1 H each, J = 17.1 Hz); 7.28 (t, 1 H, J = 6.9 Hz); 7.34—7.42 (m, 4 H). ^{13}C NMR ($CDCl_3$), δ: 30.1, 49.9, 70.3, 83.7, 124.7, 127.4, 128.6, 144.5, 214.6.

References

1. A. A. Semenov, *Ocherk khimii prirodnykh soedinenii* [*An Outline of the Chemistry of Natural Compounds*], Nauka, Novosibirsk, 2000, 298 pp. (in Russian).
2. M. D. Mashkovskii, *Lekarstvennye sredstva* [*Drugs*], OOO "Izdatel´stvo Novaya Volna", Moscow, 2001, **1**, **2** (in Russian).
3. R. C. Larock, *Comprehensive Organic Transformations. A Guide to Functional Group Preparations*, Wiley, Inc., 1999, p. 905.
4. M. V. Chirskaya, A. A. Vasil´ev, N. L. Sergovskaya, S. V. Shorshnev, and S. I. Sviridov, *Tetrahedron Lett.*, 2004, **45**, 8811.
5. M. Karikomi, S. Watanabe, Y. Kimura, and T. Uyehara, *Tetrahedron Lett.*, 2002, **43**, 1495.
6. A. Bhaumik and T. Tatsumi, *Chem. Commun.*, 1998, 463.
7. Y. Okimoto, D. Kikuchi, S. Sakaguchi, and Y. Ishii, *Tetrahedron Lett.*, 2000, **41**, 10223.
8. (a) N. A. Petasis and S.-P. Lu, *J. Am. Chem. Soc.*, 1995, **117**, 6294; (b) O. Andrey, L. Ducry, Y. Landais, D. Planchenault, and V. Weber, *Tetrahedron*, 1997, **53**, 4339; (c) M. A. Ciufolini, M. V. Deaton, S. Zhu, and M. Chen, *Tetrahedron*, 1997, **53**, 16299; (d) F. Lacrampe, F. Leost, and A. Doutheau, *Tetrahedron Lett.*, 2000, **41**, 4773.
9. (a) A. Murai, M. Ono, and T. Masamune, *Bull. Chem. Soc. Jpn*, 1977, **50**, 1226; (b) J.-P. Bats, J. Moulines, P. Picard, and D. Leclercq, *Tetrahedron*, 1982, **38**, 2139; (c) R. D. Evans, J. W. Magee, and J. H. Schauble, *Synthesis*, 1988, 862.
10. (a) B. H. Lipshutz and J. C. Barton, *J. Am. Chem. Soc.*, 1992, **114**, 1084; (b) E. D. Mihelech and G. A. Hite, *J. Am. Chem. Soc.*, 1992, **114**, 7318; (c) S. B. Bedford, K. E. Bell, G. Fenton, C. J. Hayes, D. W. Knight, and D. Shaw, *Tetrahedron Lett.*, 1992, **33**, 6511; (d) J. M. Barks and D. W. Knight, *Tetrahedron Lett.*, 1994, **35**, 7259.
11. M. Tiecco, L. Testaferri, L. Bagnoli, R. Terlizzi, A. Temperini, F. Marini, C. Santi, and C. Scarponi, *Tetrahedron: Asymmetry*, 2004, **15**, 1949.
12. (a) R. F. Curtis, C. H. Hassal, and J. Weatherston, *J. Chem. Soc.*, 1962, 4225; (b) Y. Kashman, I. Neeman, and A. Lifshitz, *Tetrahedron*, 1969, **25**, 4617; (c) K. W. Gopinath and P. K. Mahanta, *Tetrahedron*, 1976, **32**, 737.
13. P. Picard and J. Moulines, *Bull. Soc. Chim. Fr.*, 1974, 2889.
14. Y. Ishibashi, S. Nishiyama, Y. Shizuri, and S. Yamamura, *Tetrahedron Lett.*, 1992, **33**, 521.
15. (a) D. Wagner, V. L´vov, and A. Bening, *Zh. Russ. Fiz.-Khim. O-va.*, 1904, **36**, 539; (b) W. Reppe, *Justus Liebigs Ann. Chem.*, 1955, **596**, 113.
16. (a) S. Ranganathan, R. Kumar, and V. Maniktala, *Tetrahedron*, 1984, **40**, 1167; (b) M. P. Dreyfuss, *J. Org. Chem.*, 1963, **28**, 3269; (c) R. Kieffer, *Bull. Soc. Chim. Fr.*, 1967, 3026; (d) G. A. Tolstikov, A. Yu. Spivak, S. I. Lomakina, and A. V. Kuchin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1109 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1012 (Engl.Transl.)].
17. F.-X. Felpin and J. Lebreton, *J. Org. Chem.*, 2002, **60**, 7353.
18. V. I. Pansevich-Kolyada, V. A. Ablova, and L. A. Kureichik, *Zh. Obshch. Khim.*, 1955, **25**, 2448 [*J. Gen. Chem. USSR*, 1955, **25** (Engl.Transl.)].
19. (a) C. Ticozzi and A. Zanarotti, *Tetrahedron Lett.*, 1994, **40**, 7421; (b) A. Bachki, F. Foubelo, and M. Yus, *Tetrahedron: Asymmetry*, 1996, **7**, 2997.

Received March 25, 2006;
in revised form July 26, 2006