New method for the synthesis of (3*R*,7*R*)-hexahydrofarnesyl bromide based on the microwave-activated regioselective enolization of homochiral phytone

*M. I. Mallyabaeva, A. Yu. Spivak, T. V. Tyumkina, O. V. Knyshenko, and V. N. Odinokov**

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141 prosp. Oktyabrya, 450075 Ufa, Russian Federation.
Fax: +7 (347) 231 2750. E-mail: ink@anrb.ru

Short and efficient synthesis of (3*R*,7*R*)-hexahydrofarnesyl bromide ((3*R*,7*R*)-1-bromo-3,7,11-trimethyldodecane), the terpenoid synthon for the natural α-tocopherol, has been elaborated based on the microwave-activated regioselective enolization of homochiral phytone.

Key words: (2*R*,4′*R*,8′*R*)-α-tocopherol, (6*R*,10*R*)-phytone, microwave irradiation, enolization, (3*R*,7*R*)-hexahydrofarnesyl bromide, ozonolysis, terpenoids.

Natural α-tocopherol ((2*R*,4′*R*,8′*R*)-6-hydroxy-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)chromane) is the most studied principal component of vitamin E. It is the most important lipid-soluble anti-oxidant, which prevents peroxidation of lipids and other free radical reactions in biological membranes.[1,2] Its use as the medicine, prophylactic substance, and food supplement significantly reduces the risk to develop the cardio-vascular, neurodegenerate, atherosclerotic, and oncological diseases and other pathological processes caused by the oxidative stress.[3,4] In addition, (2*R*,4′*R*,8′*R*)-α-tocopherol participates in transmission of signals between cells, decreases activity of proteinkinase C, inhibits proliferation of the smooth muscle cells, and governs the expression of α-tropomiosine gene.[4] Recent investigations showed[5] that the specific liver transport protein (α-TTP) recognizes only the natural α-tocopherol out of all the coming in tocopherols and provides its transportation to plasma.

Because of the great practical significance of natural α-tocopherol, various methods for its synthesis are under investigation. A methodology based on the combination of chiral chromane fragments with non-racemic isoprenoid synthons (for alternative method see, for example, Refs 6 and 7) seems to be the most attractive. (3*R*,7*R*)-Hexahydrofarnesyl bromide is known the best among the latter.[8,9] It can be obtained from hexahydrofarnesol, which is synthesized following the complicated multi-step schemes with the use of microbiological methods,[10—13] enzymatic biochemical transformations,[8,14] or asymmetric metal complex catalysis.[15—17]

In the present work, we proposed an original method for the transformation of available homochiral phytone (**1**), obtained by ozonolysis of chlorophyll[18] (Scheme 1), to (3*R*,7*R*)-hexahydrofarnesyl bromide (**6**).

Results and Discussion

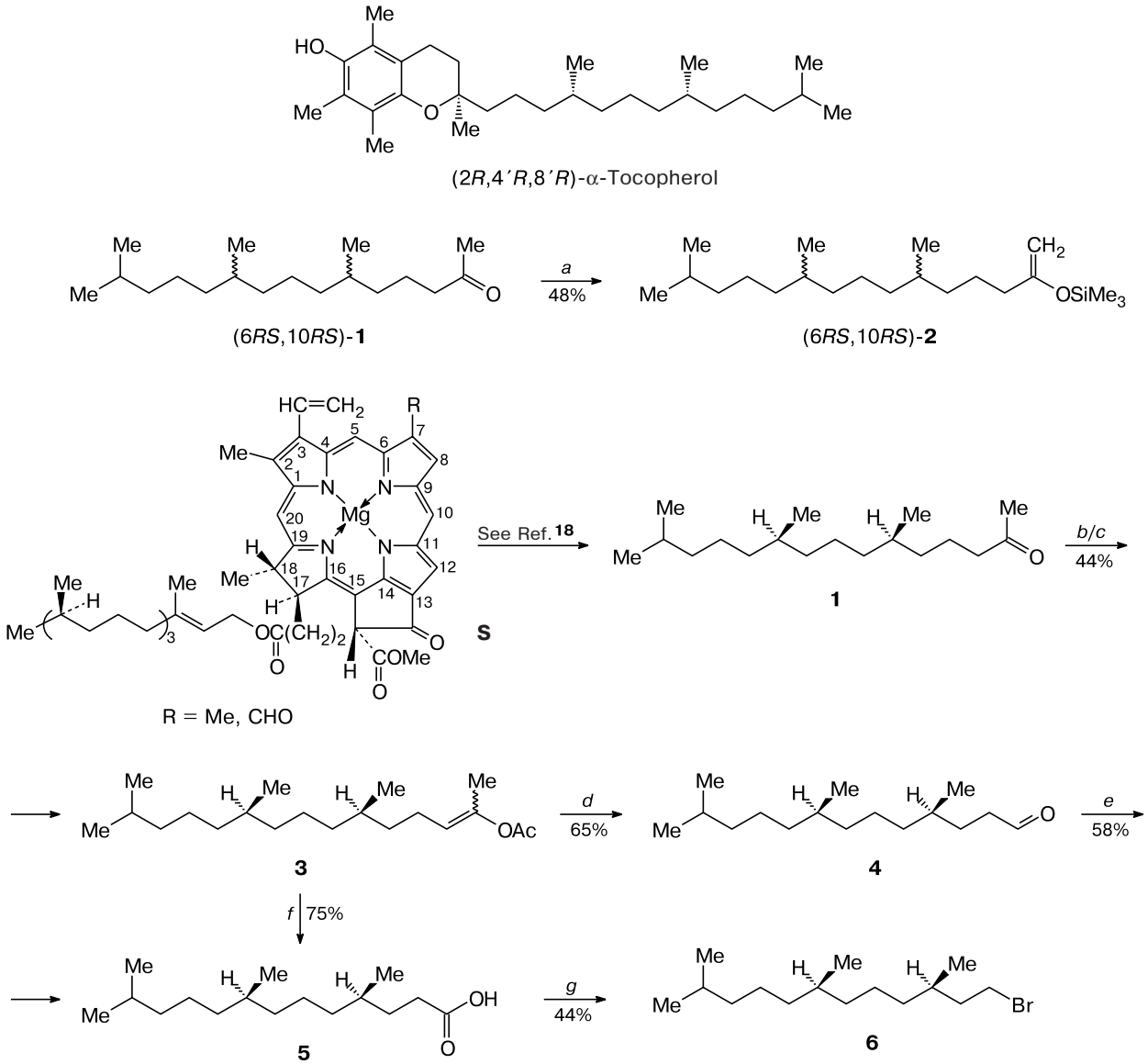
The major problem in the transformation of phytone **1** to C_{15}-bromide **6** consists in the shortening of the starting C_{18}-isoprenoid chain by three C atoms (see Scheme 1). The pathway based on the enolization of ketone **1** to $\Delta^{2,3}$-enol ether, its ozonolytic oxidation to C_{16}-acid **5**, and involvement of the latter into the Hunsdiecker reaction seems to be the most rational. It should be noted that the direction of enolization of phytone **1** has not been previously studied.

Preliminary experiments showed that phytone (6*RS*,10*RS*)-**1** did not afford the desired $\Delta^{2,3}$-silyl ether under conditions for the synthesis of silyl enol ethers from methyl ketones under prolonged reflux with $TMSCl/NEt_3$ in DMF (thermodinamic control of the reaction[19]). As it was to be expected, $\Delta^{1,2}$-ether **2** was the only product under conditions of the kinetic control (the reaction of ketone **1** with LDA and TMSCl at −78 °C) (see Scheme 1). Under reflux of ketone **1** with $Ac_2O/AcOK$,[20] Ac_2O/NEt_3,[20] or $Ac_2O/TMSCl/NaI$,[21] acetate of the corresponding enol was not formed. The desired $\Delta^{2,3}$-enol acetates **3** (a mixture of *E*- and *Z*-isomers) were successfully obtained by the reflux (7 h) of ketone **1** with acetic anhydride in the presence of $TsOH \cdot H_2O$,[22] here, the other $\Delta^{1,2}$-isomer was not formed. In this case, the conversion of ketone **1** was 49%.

Lately, a large number of successful applications of microwave irradiation technology in organic and organo-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2360—2363, December, 2007.

Scheme 1



Reagents and conditions: *a*. 1) Lithium diisopropylamide (LDA), −78 °C, 10 min; 2) TMSCl, −78 °C→20 °C, 1 h; *b*. Ac_2O, $TsOH \cdot H_2O$, microwave irradiation 750 W, 10 min; *c*. Ac_2O, $TsOH \cdot H_2O$, 150 °C, 7 h; *d*. O_3 (1 equiv.)/$Ba(OH)_2$, Me_2CO; *e*. CrO_3/H_2SO_4, Me_2CO; *f*. O_3 (2 equiv.)/$Ba(OH)_2$, Me_2CO; *g*. 1) $KOH/AgNO_3$; 2) Br_2/CCl_4.

metallic synthesis has appeared, allowing one to significantly increase the reaction rates and, in a number of cases, the selectively of the reactions.[23—25] Microwave irradiation was used in the selective synthesis of enol acetates from steroid ketones upon treatment with acetic anhydride.[26] In our case, the use of microwave irradiation allowed us to considerably decrease the reaction time with complete retention of its regioselectivity. Conversion of the starting ketone **1** to the mixture of $\Delta^{2,3}$-enol acetates **3** after irradiation for 10 min (power 750 W) was 57%, however, an increase in the irradiation time did not lead to an increase in the conversion. Enol acetates **3** can be easily separated from the unreacted phytone **1** by column chromatography on silica gel, and the recovered phytone **1** can be repeatedly involved into the enolization reaction. In the ^1H NMR spectrum of the mixture of enol acetates **3**, a triplet for the vinyl proton H(3) in *cis*-position to the acetate group (*Z*-isomer) resonates downfield (δ 5.10, J = 7.7 Hz) as compared with the signal of the corresponding proton in *trans*-position (*E*-isomer) (δ 4.98, J = 7.3 Hz).[22,27,28] From the relative integral intensities of these signals it follows that *E*- and *Z*-isomers are formed in the ratio ~2 : 1 (the GLC data show the same ratio of isomers). In the ^{13}C NMR spectra of enol acetates **3**,

signals of C(2) and C(3) atoms of *Z*-isomer are observed somewhat downfield shifted (Δδ ~0.5 ppm) as compared with the corresponding signals of *E*-isomer.

Aldehyde **4** was obtained by the ozonolysis of a mixture of enol acetates **3** in acetone in the presence of $Ba(OH)_2$ (see Ref. 29), which was further oxidized by the Jones reagent to acid **5**. When enol acetates **3** are treated with excess ozone, they are converted to acid **5** in a single step. The Hunsdiecker reaction was used for the transformation of C_{16}-acid **5** to the target C_{15}-bromide. The reaction of acid **5** with Br_2 in CCl_4 in the presence of HgO gave bromide **6** in 35% yield (after chromatographic purification), while silver salt of acid **5** afforded the target bromide **6** in 44% yield (see Scheme 1).

In the ^{13}C NMR spectrum, a single set of signals of C atoms corresponding to the structure of obtained bromide **6** confirms its configurational homogeneity. In the ^1H NMR spectrum of (*R*,*R*)-bromide **6**, a signal for the protons of the CH_2Br group (δ 3.36—3.52) has a complex structure, which, apparently, is caused by the geminal and vicinal spin-spin interaction of the diastereotopic protons of the CH_2CH_2Br fragment (ABXY spin system). In this case, a complicated multiplicity of the signal, apparently, can be explained not only by the protons being diastereotopic, but also by the restriction of rotation around the C(1)—C(2) bond because of the steric 1,3-interaction of the bromine atom and the Me group at C(3).[30,31]

In conclusion, on the basis of available from chlorophyll chiral compound, (6*R*,10*R*)-phytone **1**, a short stereoselective synthesis of (3*R*,7*R*)-hexahydrofarnesyl bromide **6**, a key compound in the synthesis of (2*R*,4′*R*,8′*R*)-α-tocopherol, has been elaborated. The use of microwave irradiation in the key step of enolization—acetylation of phytone **1** allowed us to significantly decrease the reaction time and regioselectively obtain the target $\Delta^{2,3}$-enol acetates **3**.

Experimental

IR spectra were recorded on a Specord IR-75 spectrometer (for neat samples). ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (^1H, 300.13 MHz; ^{13}C, 75.47 MHz; $CDCl_3$ was used as the solvent). Chemical shifts are given in δ scale relatively to Me_4Si (internal standard). GLC analysis was performed on a Chrom-5 chromatograph (2400×4 mm column, Chromaton N-AW-DMCS and SE-30 (5%) were used as the stationary phases, thermostate temperature programming was 50→300 °C (8 deg min^{-1}), helium was used as the carrier gas). Specific angles of rotation were determined on a Perkin—Elmer-141 polarimeter. Specific rotation is given in deg mL g^{-1} dm^{-1}, solution concentration in g (100 mL)$^{-1}$. A Samsung G2739NR consumer microwave oven (power 750 W) was used in the enolization reaction of phytone. Ozonolysis was carried out with the use of TL-2 ozonator (NPP "Tekhozon", Dzerzhinsk, with O_3 productivity of 30 mmol h^{-1}). Silufol UV-254 plates were used for TLC, visualization was made with 4-methoxybenzaldehyde, for acid **5**, with phosphomolibdic acid. Silica gel L (160—250 μm, KSKG, GOST 3956-76) was used for column chromatography. (6*R*,10*R*)-Phytone **1** ($[\alpha]_D^{20}$ +1.1 (*c* 1.78, $CHCl_3$) was synthesized according to the method described earlier[18]. (6*RS*,10*RS*)-Phytone was obtained by ozonolysis of (7*RS*,11*RS*)-isophytol (Fluka) by the known method.[29]

(6*RS*,10*RS*)-6,10,14-Trimethyl-2-trimethylsilyloxypentadec-1-ene (2). A solution of (6*RS*,10*RS*)-phytone (0.2 g, 0.75 mmol) in anhydrous THF (0.4 mL) was added for 1 min to a solution of lithium diisopropylamide in *n*-hexane (prepared *in situ* by the addition of 2.3 *M* solution of Bu^nLi in *n*-hexane (0.5 mL, 1.15 mmol) to Pr^i_2NH (0.2 mL, 1.43 mmol) in anhydrous THF (1 mL) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C, then, trimethylsilyl chloride (0.2 mL, 1.56 mmol) was added dropwise to it for 30 min, after that, the mixture was heated to 20 °C and stirred for another 1 h. The solvent was evaporated *in vacuo*, *n*-hexane (5 mL) was added to the residue, LiCl was filtered off, the filtrate was concentrated to obtain trimethylsilyl ether **2** (0.12 g, 48%). Found (%): C, 73.91; H, 13.14. $C_{21}H_{44}OSi$. Calculated (%): C, 74.04; H, 13.02. IR, ν/cm^{-1}: 1665 (C=C); 1250 ($SiMe_3$). ^1H NMR, δ: 0.20 (s, 9 H, $SiMe_3$); 0.72—0.90 (m, 12 H, MeC(6), MeC(10), 2 MeC(14)); 1.00—1.55 (m, 19 H, H(4)—H(14)); 2.00 (t, 2 H, H(3), *J* = 7.7 Hz); 4.10 (s, 2 H, H(1)). ^{13}C NMR, δ: 0.1 ($SiMe_3$); 19.66, 19.72 (MeC(6), MeC(C(10)); 22.61, 22.69 (2 MeC(14)); 24.29, 24.45, 24.79 (C(4), C(8), C(12)); 27.95 (C(14)); 32.63, 32.76 (C(6), C(10)); 36.76, 37.27, 37.37 (C(3), C(5), C(7), C(9), C(11)); 39.36 (C(13)); 89.74 (C(1)); 159.58 (C(2)).

(6*R*,10*R*)-2-Acetoxy-6,10,14-trimethylpentadec-2-enes (3), a mixture of *E*- and *Z*-isomers. ***A.*** A mixture of phytone **1** (0.3 g, 1.1 mmol), Ac_2O (0.45 g, 4.4 mmol), and $TsOH \cdot H_2O$ (0.004 g, 0.02 mmol, 1.8 mol.%) in thermoproof chemical glass was subjected to microwave irradiation (750 W) for 10 min. The reaction mixture was diluted with EtOAc (10 mL), sequentially washed with saturated aqueous $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated *in vacuo*. According to the GLC data, the residue (0.28 g) consisted of 57% of a mixture of *E*/*Z*-enol acetates **3** (retention time *E*- and *Z*-isomers was 26.01 and 26.55 min, respectively) and 43% of the starting phytone **1** (retention time was 24.58 min). Column chromatography on SiO_2 (4.5 g, CH_2Cl_2 as the eluent) gave phytone **1** (0.09 g) and a mixture of isomeric enol acetates **3** (0.15 g, 44%), $[\alpha]_D^{20}$ +6.0 (*c* 4.78, $CHCl_3$). Found (%): C, 77.29; H, 12.41. $C_{20}H_{38}O_2$. Calculated (%): C, 77.36; H, 12.33. IR, ν/cm^{-1}: 1750 (OC=O); 1650 (C=C). ^1H NMR, δ: 0.75—0.90 (m, 12 H, MeC(6), MeC(10), 2 MeC(14)); 1.00—1.60 (m, 17 H, H(5)—H(14)); 1.87 (s, 3 H, H(1)); 1.92 (m, 2 H, H(4)); 2.10 (s, 1 H, MeCO *Z*-isomer); 2.15 (s, 2 H, MeCO *E*-isomer); 4.98 (t, ~0.7 H, H(3) *E*-isomer, *J* = 7.3 Hz); 5.10 (t, ~0.3 H, H(3) *Z*-isomer, *J* = 7.7 Hz). ^{13}C NMR, δ: 18.99, 19.20 (MeC(6), MeC(10)); 22.08, 22.17, 22.44 (C(1), 2 MeC(14)); 23.85, 24.26 (C(8), C(12)); 27.44 (C(14)); 29.16 (Me(OAc)); 31.82, 32.26 (C(6), C(10)); 35.70, 36.68, 36.76, 36.91 (C(4), C(5), C(7), C(9), C(11)); 38.85 (C(13)); 117.26 (C(3) *E*-isomer); 117.81 (C(3) *Z*-isomer); 144.59 (C(2) *E*-isomer); 145.02 (C(2) *Z*-isomer); 169.85 (C=O *E*-isomer); 169.60 (C=O *Z*-isomer).

B. A mixture of phytone **1** (0.3 g, 1.1 mmol), Ac_2O (0.45 g, 4.4 mmol), and $TsOH \cdot H_2O$ (0.004 g, 0.02 mmol, 1.8 mol.%) was stirred at 150 °C for 7 h. After treatment similar to that described in method ***A***, a mixture of enol acetates **3** was obtained (0.13 g, 38%).

(4*R*,8*R*)-4,8,12-Trimethyltridecanal (4). An ozone—oxygen mixture was bubbled through a mixture of enol acetates **3** (0.14 g, 0.45 mmol), $Ba(OH)_2$ (0.12 g, 0.7 mmol), and acetone (8 mL) for 1 min at 30 L h^{-1} (0.5 mmol of O_3) followed by the bubbling of Ar. Then, the reaction mixture was filtered, the filtrate was concentrated *in vacuo* to obtain mobile yellow oil (0.09 g). Column chromatography on SiO_2 (3 g, gradient 0→20% EtOAc in hexane as the eluent) gave aldehyde **4** (0.07 g, 65%), identical to the sample described in Ref. 32 in its IR, ^1H and ^{13}C NMR spectra; $[\alpha]_D^{22}$ +6.5 (*c* 6.0, $CHCl_3$).

(4*R*,8*R*)-4,8,12-Trimethyltridecanoic acid (5). ***A.*** The Jones reagent (1 mL, 14 mmol) (prepared from CrO_3 (1.33 g), H_2O (3.8 mL), and H_2SO_4 (1.2 mL)) was added dropwise to a vigorously stirred and cooled with ice solution of aldehyde **4** (0.29 g, 1.2 mmol) in acetone (2 mL). The reaction mixture was stirred at ~20 °C for 2 h, extracted with Et_2O (3×20 mL). The etheral extract was treated with 1 *M* NaOH (3×20 mL), the aqueous layer was separated, acidified with concentrated HCl to pH ~6 and extracted with Et_2O (3×20 mL). The extract was washed with brine, dried with $MgSO_4$, and concentrated to obtain acid **5** (0.18 g, 58%) as viscous colorless oil, which was identical to the sample described in Ref. 32 in its IR, ^1H and ^{13}C NMR spectra; $[\alpha]_D^{18}$ +2.8 (*c* 19.0, $CHCl_3$).

B. An ozone—oxygen mixture was bubbled through a mixture of enol acetate **3** (0.14 g, 0.45 mmol), $Ba(OH)_2$ (0.12 g, 0.7 mmol), and acetone (8 mL) for 2 min at 30 L h^{-1} (1.0 mmol of O_3) followed by the bubbling of Ar. Then, the reaction mixture was filtered, the filtrate was concentrated *in vacuo* to obtain mobile yellow oil (0.12 g), which was dissolved in EtOAc (5 mL), treated with 1 *M* NaOH (3×20 mL), the aqueous layer was separated, acidified with concentrated HCl to pH ~6 and extracted with Et_2O (3×20 mL). The extract was washed with brine, dried with $MgSO_4$, and concentrated *in vacuo* to obtain acid **5** (0.09 g, 75%), identical to the sample obtained in method *A* in its IR, ^1H and ^{13}C NMR spectra.

(3*R*,7*R*)-1-Bromo-3,7,11-trimethyldodecane (6). A solution of $AgNO_3$ (0.34 g, 2.2 mmol) in H_2O (4 mL) was added to a stirred solution of acid **5** (0.5 g, 2.0 mmol) and KOH (11 g, 1.9 mmol) in H_2O (5 mL), a precipitate of silver salt was filtered off, washed with MeOH (5 mL) on the filter and kept at 90—100 °C *in vacuo* (~5 Torr) for 16 h. Bromine (0.25 g, 1.56 mmol) was added dropwise to a stirred suspension of silver salt (0.35 g, 2.0 mmol) in CCl_4 (5 mL), the reaction mixture was refluxed for 1 h, the precipitate (AgBr) was filtered off, and washed with CCl_4. The combined filtrates were washed with 10% aq. $NaHCO_3$, dried with $MgSO_4$, and concentrated. The residue was subjected to column chromatography on SiO_2 (20 g, hexane—EtOAc, 3 : 1 as the eluent) to obtain bromide **6** (0.25 g, 44%) as yellow oil (R_f 0.8, *n*-hexane—EtOAc, 3 : 1), $[\alpha]_D^{20}$ −3.1 (*c* 2.15, $CHCl_3$) (*cf.* Ref. 9: $[\alpha]_D^{20}$ −3.8 (octane)). ^1H NMR, δ: 0.84—0.99 (m, 12 H, MeC(3), MeC(7), 2 MeC(11)); 1.10—1.40 (m, 14 H, H(4)—H(11)); 1.50—1.75 (m, 3 H, H(2), H(3)); 3.36—3.52 (m, 2 H, H(1)). ^{13}C NMR, δ: 19.00, 19.72 (MeC(3), MeC(7)); 22.60, 22.69 (2 MeC(11)); 24.23, 24.78 (C(5), C(9)); 27.97 (C(11)); 31.72 (C(3)); 31.92 (C(1)); 32.77 (C(7)); 36.85, 37.24, 37.29 (C(4), C(6), (C8)); 39.37 (C(10)); 40.08 (C(2)).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 07-03-00438) and by the Presidium of the Russian Academy of Sciences (Program for Fundamental Research P-08 "Development of Methodology of Organic Synthesis and Creation of Compounds with Valuable Applied Properties").

References

1. G. W. Burton and K. U. Ingold, *Acc. Chem. Res.*, 1986, **19**, 194.
2. M. G. Traber, *Free Radic. Biol. Med.*, 1994, **16**, 229.
3. R. Brigelius-Flohe, F. J. Kelly, J. T. Salonen, J. Neuzil, J. M. Zingg, and A. Azzi, *Am. J. Clin. Nutr.*, 2002, **76**, 703.
4. R. Brigelius-Flohe and M. G. Traber, *FASEB*, 1999, **13**, 1145.
5. A. Hosomi, M. Arita, Y. Sato, C. Kiyose, T. Ueda, O. Igarashi, H. Arai, and K. Inoue, *FEBS Lett.*, 1997, **409**, 105.
6. E. Mizuguchi, M. Takemoto, and K. Achiwa, *Tetrahedron Asymmetry*, 1993, **4**, 1961.
7. E. Mizuguchi and K. Achiwa, *Tetrahedron Asymmetry*, 1993, **4**, 2303.
8. M. Nozawa, K. Takahashi, K. Kato, and H. Akita, *Chem. Pharm. Bull.*, 2000, **48**, 272.
9. H. Mayer, P. Schudel, R. Rüegg, and O. Isler, *Helv. Chim. Acta*, 1963, **46**, 650.
10. C. Fugnati and P. Grasselli, *J. Chem. Soc., Chem. Commun.*, 1979, 995.
11. M. Schmid and R. Barner, *Helv. Chim. Acta*, 1979, **62**, 464.
12. N. Cohen, W. F. Eichel, R. J. Lopresti, C. Neukom, and G. Saucy, *J. Org. Chem.*, 1976, **41**, 3505.
13. C. Fugnati, *Pure Appl. Chem.*, 1990, **62**, 1449.
14. C. Y. Chen, S. Nagumo, and H. Akita, *Chem. Pharm. Bull.*, 1996, **44**, 2153.
15. K. Tani, T. Yamagata, S. Otsuka, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, and R. Noyori, *J. Chem. Soc., Chem. Commun.*, 1982, 600.
16. S. Takano, T. Sugihara, and K. Ogasawara, *Synlett*, 1991, 279.
17. R. Schmid, S. Antoulas, A. Rüttimann, M. Schmid, M. Vecchi, and H. Weiser, *Helv. Chim. Acta*, 1990, **73**, 1276.
18. V. N. Odinokov, M. I. Mallyabaeva, A. Yu. Spivak, G. A. Emel´yanova, and U. M. Dzhemilev, *Dokl. Akad. Nauk*, 2001, **380**, 201 [*Dokl. Chem.*, 2001, **380**, 255 (Engl. Transl.)].
19. I. Fleming and I. Paterson, *Synthesis*, 1979, 736.
20. V. N. Odinokov, V. R. Akhmetova, Kh. D. Khasanov, A. A. Abduvakhabov, L. M. Khalilov, B. A. Cheskis, A. M. Moiseenkov, and G. A. Tolstikov, *Zh. Org. Khim.*, 1992, **28**, 1339 [*Russ. J. Org. Chem.*, 1992, **28** (Engl. Transl.)].
21. P. K. Chowdhury, R. P. Sharma, and J. N. Barua, *Tetrahedron Lett.*, 1983, **24**, 3383.
22. P. C. Krueger and M. E. Kenney, *J. Org. Chem.*, 1963, **28**, 3379.
23. S. Caddick, *Tetrahedron*, 1995, **51**, 10403.
24. M. Larhed, C. Moberg, and A. Hallberg, *Acc. Chem. Res.*, 2002, **35**, 717.
25. N. N. Romanova, A. G. Gravis, and N. V. Zyk, *Usp. Khim.*, 2005, **74**, 1059 [*Russ. Chem. Rev.*, 2005, **74** (Engl. Transl.)].
26. P. Marwah, A. Marwah, and H. A. Lardy, *Tetrahedron*, 2003, **59**, 2273.
27. A. Suzuki, K. Ohmori, and M. Itoh, *Tetrahedron*, 1969, **25**, 3707.

28. A. Yu. Spivak, O. V. Knyshenko, M. I. Mallyabaeva, and V. N. Odinokov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 299 [*Russ. Chem. Bull., Int. Ed*., 2006, **55**, 306].
29. I. E. Pokrovskaya, A. E. Menyailo, M. V. Pospelov, A. K. Ryzhankova, A. G. Shil´nikova, G. N. Dudnik, and L. S. Mishina, *Neftekhimiya*, 1970, **10**, 554 [*Petroleum Chem.*, 1970, **10** (Engl. Transl.)].
30. A. A. Petrov, *Stereokhimiya nasyshchennykh uglevodorodov* [*Stereochemistry of Saturated Hydrocarbons*], Nauka, Moscow, 1981, 254 (in Russian).
31. A. N. Vereshchagin, V. E. Kataev, A. A. Bredikhin, A. P. Timosheva, G. I. Kovylyaeva, and E. Kh. Kazakova, *Konformatsionnyi analiz uglevodorodov i ikh proizvodnykh* [*Conformational Analysis of Hydrocarbons and Their Derivatives*], Nauka, Moscow, 1990, 293 pp. (in Russian).
32. V. N. Odinokov, A. Yu. Spivak, M. I. Mallyabaeva, O. V. Knyshenko, and U. M. Dzhemilev, *Dokl. Akad. Nauk*, 2005, **403**, 631 [*Dokl. Chem*., 2005, **403**, 144 (Engl. Transl.)].

Received June 15, 2007;
in revised form October 22, 2007