Stereocontrolled synthesis of (3*Z*,5*E*)-6-aryl-3-methylhexa-3,5-dien-1-ols, intermediates in the synthesis of strobilurin antibiotics

N. Ya. Grigorieva, V. A. Popovsky, A. V. Stepanov, and N. G. Kolotyrkina*

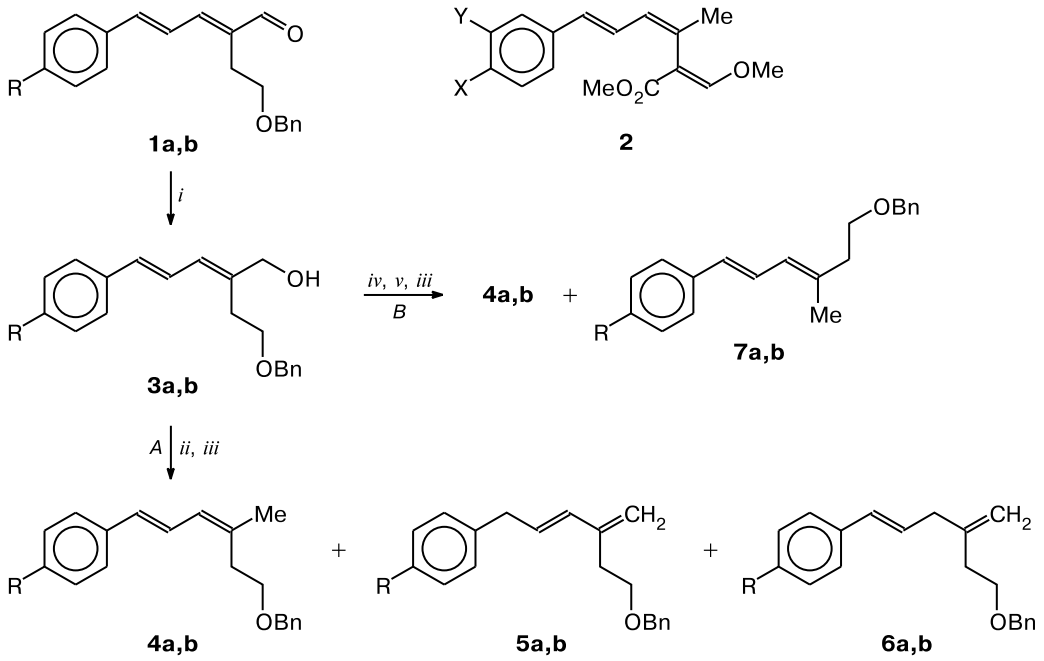
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (499) 135 5328. E-mail: ves@ioc.ac.ru

(2*E*,4*E*)-5-Aryl-2-(2-benzyloxyethyl)penta-2,4-dien-1-als (aryl is phenyl and 4-methoxyphenyl) were reduced with $NaBH_4$ quantitatively and stereospecifically to the corresponding penta-2(*E*),4(*E*)-dien-1-ols. The hydroxymethyl group in the latter was transformed into a methyl one with a stereoselectivity of 92—97%. Debenzylation of the resulting (1*E*,3*Z*)-1-aryl-6-benzyloxy-4-methylhexa-1,3-dienes with $AlCl_3$ in the presence of $PhNMe_2$ afforded the target (3*Z*,5*E*)-6-aryl-3-methylhexa-3,5-dien-1-ols; the configuration of the C=C bonds in the conjugated aryl diene systems was retained at 95%.

Key words: stereocontrolled synthesis, strobilurins, dienols, debenzylation, dehydroxylation.

Recently,[1] we have demonstrated that condensation of cinnamaldehyde and 4-methoxycinnamaldehyde with deprotonated *N*-(*tert*-butyl)-4-benzyloxybutanimine stereoselectively (≥98%) gives (2*E*,4*E*)-dienals **1a** and **1b**, respectively, in high yields (Scheme 1). With the aim of using these compounds[2] for the design of the (1*E*,3*Z*)-1-aryl-4-methylalkadiene system of strobilurin antibiotics of the general formula **2**,[3,4] we studied a transformation of the formyl group of aldehydes **1a,b** into a methyl one through the formation of intermediate dienols **3a,b** and

Scheme 1



R = H (**a**), OMe (**b**)

Reagents and conditions: *i*. $NaBH_4$/EtOH, 3 h, 20 °C; *ii*. Py·SO_3/THF, 2.5 h, 0 °C; *iii*. $LiAlH_4$, 24 h, 20 °C; *iv*. BuLi/C_6H_{14}, 0 °C; *v*. TsCl/HMPA—Et_2O (1 : 3), 0 °C, 2.5 h.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 830—833, April, 2010.

1066-5285/10/5904-0848

benzyloxyalkadienes **4a,b** followed by debenzylation of the latter (see Scheme 1). The present communication is concerned with detailed analysis of the above transformations.

Reduction of dienals **1a,b** with $NaBH_4$ according to a standard procedure gives dienols **3a,b** in quantitative yields. Their structures were confirmed by elemental analysis and physicochemical methods (primarily, ^{1}H NMR spectroscopy). For instance, C—H correlation methods and COSY revealed the following parameters of the H atoms of the diene system in dienol **3a**, δ: 6.33 (d, J = 11.0 Hz); 6.61 (d, J = 15.5 Hz); 7.01 (dd, J_1 = 11.0 Hz, J_2 = 15.5 Hz). Out of the pair of the aforementioned doublets, only the former at δ 6.33 shows NOE (2.2%) with $H_2C(1)$. Therefore, this signal can be assigned to HC(3) and, second, the (*E*)-configuration of the C(2)=C(3) bond can be concluded. This conclusion was confirmed by NOE (3.1%) between the $H_2C(1')$ and $H_2C(4)$ atoms. The latter doublet in the ^{1}H NMR spectrum of dienol **3a** (δ 6.61) was assigned to HC(5). Its coupling constant with HC(4) (J = 15.5 Hz) suggests the (*E*)-configuration of the C(4)=C(5) bond. The (*E*,*E*)-configuration of dienol **3b** was proved in a similar way.

Treatment of dienols **3a,b** with the complex $Py \cdot SO_3$ followed by *in situ* reduction of the resulting sulfates with $LiAlH_4$ (method *A*)[5] gives dienes **4a,b** as major reaction products. Their structures were confirmed by NMR spectroscopy using C—H correlation, COSY, and NOE experiments as described above for compounds **3a,b**.

However, dienes **4a,b** are not the sole reaction products. According to ^{1}H NMR data, the final mixtures contain two by-products. Their total content does not exceed 10% in the reduction of dienol **3a** and is ~25% in the case of compound **3b**. Since the high-resolution mass spectra of the reduction products show only the ions $[M]^+$, $[M + Na]^+$, and $[M + K]^+$, we assume that the by-products are isomeric with compounds **4a** and **4b** regarding the position of the C=C bonds. Based on ^{1}H NMR data, we assigned structures **5a,b** to the major dienes of the mixtures and structures **6a,b** to the minor dienes of the mixtures. Indeed, the ^{1}H NMR spectra of the final mixture in the reduction of dienol **3a** show two minor doublets for the terminal methylidene group at δ 5.04 and 4.93 with an integral intensity ratio of ~2 : 1. In addition, the spectra exhibit a doublet for the CH_2 group between the Ph ring and the C=C bond (δ 3.46)[6] and a signal for the CH_2 group between two C=C bonds (δ 2.98).[6] Their integral intensity ratio is also ~2 : 1. A similar pattern was observed in the ^{1}H NMR spectra of the final mixture upon the reduction of dienol **3b**. Apart from the signals for diene **4b**, the spectra contain two doublets for the $=CH_2$ group at δ 5.0 and 4.90 with an integral intensity ratio of ~3 : 1 and doublets for the groups $ArCH_2C=C$ (δ 3.40) and $C=CCH_2C=C$ (δ 2.96) with an integral intensity ratio of ~3 : 1.

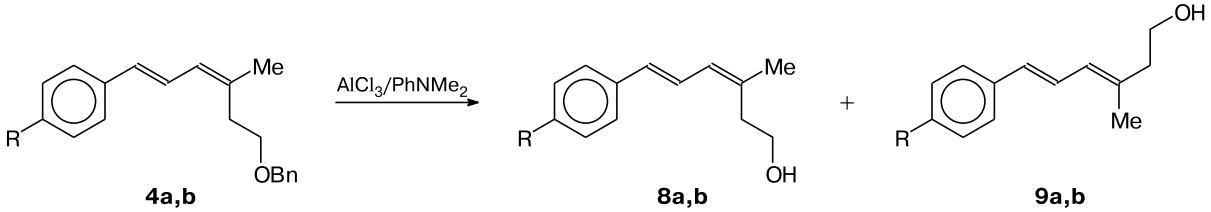
Variation of the conditions of the synthesis of sulfates from dienols **3a,b** and their reduction (reaction temperature, reaction time, and replacement of $LiAlH_4$ by $LiAl(OEt)H_3$ or $[AlH_3]$) did not make the reaction more selective. The content of side dienes in compound **4a** was lowered to ~5—7% by reversing the order of mixing of the reagents (see Experimental).

The high content of impurities in diene **4b** and considerable losses of the target dienes during their purification by column chromatography prompted us to search for an alternative way of converting dienols **3a,b** into compounds **4a,b**. For this purpose, we obtained tosylates from dienols **3a,b** and studied their reduction with $LiAlH_4$ (method *B*). In the case of dienol **3b**, the target diene **4b** contained no impurities **5b** or **6b**. However, the product was contaminated with (*E*)-isomer **7b** (^{1}H NMR): the spectrum showed additional minor signals for the groups $H_2C(2)$ (t, δ 2.45) and HC(4) (d, δ 6.08). By comparing the integral intensities of these signals with the corresponding signals for diene **4b**, we estimated the ratio of **4b** : **7b** at ~95 : 5. Analytically pure diene **4b** was isolated by flash chromatography. The content of (*E*)-isomer **7a** in the transformation **3a**→**4a** according to method *B* was ~20% (^{1}H NMR).

Thus, method *A* is preferred for the reduction of dienol **3a** and method *B*, for the reduction of dienol **3b**.

Debenzylation of benzyloxyalkadienes **4a,b** was *a priori* a difficult problem. Out of a number of methods recommended for deprotection of various benzyl ethers,[7—12] only one[9] provided a satisfactory result: treatment of diene **4a** with $AlCl_3$ in the presence of $PhNMe_2$ afforded a mixture of the target dienol **8a** and its (*E*)-isomer **9a** in a ratio of 9 : 1 (Scheme 2). Similar treatment of diene **4b** gave a mixture of dienols **8b** and **9b** in a ratio of 9.5 : 0.5 (^{1}H NMR). Note that the deprotection of benzyl ethers containing a conjugated aryl diene system of C=C bonds

Scheme 2



4a,b **8a,b** **9a,b**

R = H (**a**), OMe (**b**)

is not described in the references cited above. The target dienols **8a,b** were isolated by flash chromatography and characterized using physicochemical methods, including high-resolution mass spectrometry and ^{1}H NMR spectroscopy (C—H correlation, COSY, and NOE, as described for compound **3a**).

Experimental

UV spectra were recorded on a Specord UV—Vis instrument in ethanol. IR spectra were recorded on a Perkin—Elmer 577 spectrometer in thin films or in solutions in $CHCl_3$ (for alcohols). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$ with reference to the signals of the solvent (δ 7.27 and 77.0, respectively). The signals for the olefinic protons in the ^{1}H NMR spectra were assigned from the NOE experiment. In the ^{13}C NMR spectra of the compounds described, the signals for the C atoms of the benzene rings are omitted. Mass spectra (EI, 70 eV) were measured on a Kratos MS-30 instrument; peaks with I_{rel} >10% are cited only (except for molecular ion peaks). High-resolution mass spectra were measured on a micrOTOF II instrument (Bruker Daltonics) (ESI, *m/z* scan range 50—3000, positive ions (capillary voltage 4500 V)). Samples were syringed as solutions in acetonitrile, flow rate 3 μL min^{-1}, interface temperature 180 °C, nitrogen as a spraying gas (4.0 L min^{-1}). Melting points were determined on a Kofler microscope stage. Column chromatography was performed on Silica gel 60 (0.04—0.06 mm, Fluka). Main solvents were purified as follows: diethyl ether and THF were kept over KOH, distilled successively over metallic Na and $LiAlH_4$, refluxed with sodium benzophenone ketyl until the solvent turned stable blue, and distilled immediately to a reaction vessel; hexane was distilled over metallic Na. A solution of BuLi in hexane was prepared according to a standard procedure. Experiments involving unstable reagents were carried out under argon in glassware kept at 160 °C for 12 h and cooled in an argon flow.

"Routine workup" of organic extracts consisted of washing to pH ~7, drying with Na_2SO_4, and concentration *in vacuo* on a rotary evaporator.

(2*E*,4*E*)-2-(2-Benzyloxyethyl)-5-phenylpenta-2,4-dien-1-ol (3a) was obtained by reduction of compound **1a** (see Ref. 1) with $NaBH_4$ according to a standard procedure. Yield ~100%, b.p. 185 °C ($6\cdot10^{-2}$ Torr (bath)). Found (%): C, 81.55; H, 7.62. $C_{20}H_{22}O_2$. Calculated (%): C, 81.60; H, 7.53. UV, λ_{max}/nm (ε): 211 (22 570), 297 (25 070). IR, ν/cm^{-1}: 3400, 3060, 3028, 2924, 2860, 2244, 1716, 1592, 1492, 1452, 1360, 1204, 1180, 1004, 960, 904, 696, 648. ^{1}H NMR, δ: 2.70 (t, 2 H, $H_2C(1')$, J = 6.2 Hz); 3.67 (t, 2 H, $H_2C(2')$, J = 6.2 Hz); 4.17 (s, 2 H, $H_2C(1)$); 4.57 (s, 2 H, $\underline{H}_2$CPh); 6.33 (d, 1 H, HC(3), J = 11.0 Hz); 6.61 (d, 1 H, HC(5), J = 15.5 Hz); 7.01 (dd, 1 H, HC(4), J_1 = 11.0 Hz, J_2 = 15.5 Hz); 7.22—7.45 (m, 10 H, Ph). ^{13}C NMR, δ: 29.82 (C(1′)); 67.93 (C(1)); 69.56 C(2′); 73.19 ($\underline{C}H_2$Ph); 124.00 (C(4)); 126.34 (C(3)); 133.27 (C(5)); 139.29 (C(2)). MS, *m/z* (I_{rel} (%)): 294 [M]$^+$ (1.5), 186 (10), 157 (10), 155 (24.5), 143 (13), 141 (11), 130 (10.5), 129 (21), 128 (26), 117 (10), 115 (32), 107 (17.5), 105 (11.5), 104 (12.5), 101 (15), 95 (13), 92 (57), 91 (100), 88 (17), 80 (31), 78 (54.5), 77 (30), 76 (40), 69 (24), 67 (43), 65 (78), 63 (14).

(2*E*,4*E*)-2-(2-Benzyloxyethyl)-5-(4-methoxyphenyl)penta-2,4-dien-1-ol (3b) was obtained as described for compound **3a**, yield ~100%, m.p. 59—61 °C (from hexane—ether, 1 : 1). Found (%): C, 77.70; H, 7.57. $C_{21}H_{24}O_3$. Calculated (%): C, 77.75; H, 7.46. UV, λ_{max}/nm (ε): 215 (12 000), 303 (31 500). IR, ν/cm^{-1}: 3425, 3032, 3012, 2840, 1610, 1512, 1456, 1360, 1304, 1252, 1176, 1096, 1036, 964, 892, 852, 820, 700. ^{1}H NMR, δ: 2.68 (t, 2 H, $H_2C(1')$, J = 6.2 Hz); 2.82 (br.s, 1 H, OH); 3.66 (t, 2 H, $H_2C(2')$, J = 6.2 Hz); 3.83 (s, 3 H, MeO); 4.15 (s, 2 H, $H_2C(1)$); 4.56 (s, 2 H, $\underline{H}_2$CPh); 6.29 (d, 1 H, HC(3), J = 10.9 Hz); 6.54 (d, 1 H, HC(5), J = 15.4 Hz); 6.85 (dd, 1 H, HC(4), J_1 = 10.9 Hz, J_2 = 15.4 Hz); 6.88 (d, 2 H, Ar, J = 8.8 Hz); 7.25—7.46 (m, 7 H, Ar). ^{13}C NMR, δ: 29.88 (C(1′)); 55.27 (MeO); 68.10 (C(1)); 69.71 (C(2′)); 73.21 ($\underline{C}H_2$Ph); 122.06 (C(4)); 128.17 (C(3)); 132.93 (C(5)); 138.24 (C(2)). MS, *m/z* (I_{rel} (%)): 324 [M]$^+$ (5), 187 (10), 185 (22), 160 (17.5), 147 (15), 134 (33.5), 121 (68.5), 115 (14), 92 (14), 91 (100), 77 (19), 65 (28), 55 (16), 51 (11), 43 (32.5), 42 (15), 39 (13).

(1*E*,3*Z*)-6-Benzyloxy-4-methyl-1-phenylhexa-1,3-diene (4a). Method *A*. A suspension of Py·SO_3 (1.10 g, 7 mmol) in THF (50 mL) was vigorously stirred at −15 °C while a solution of dienol **3a** (1.30 g, 4.42 mmol) in THF (20 mL) was added for 20 min. The reaction mixture was warmed to 0 °C, stirred at this temperature for 2.5 h, and cooled to −10 °C. A solution of $LiAlH_4$ (26.4 mmol) in THF (22 mL) was added dropwise. Then the mixture was slowly warmed to ~20 °C, stirred at this temperature for 24 h, and recooled to −10 °C. Water (1 mL), 15% NaOH (1 mL), and again water (3 mL) were successively added dropwise. The precipitate that formed was filtered off and thoroughly washed with *tert*-butyl methyl ether (TBME). After routine workup of the combined organic phases, the residue (1.15 g) was chromatographed on SiO_2 (50 g). Gradient elution from hexane to 10% TBME gave diene **4a** (0.58 g, 50%) contaminated with dienes **5a** and **6a** (total content 6%) in a ratio of ~2 : 1 (^{1}H NMR). Analytically pure diene **4a** was isolated by HPLC, R_f 0.48 (10% TBME in hexane). UV, λ_{max}/nm (ε): 211 (18 120), 296 (26 170). IR, ν/cm^{-1}: 3060, 3028, 2960, 2856, 1644, 1596, 1496, 1456, 1364, 1176, 1100, 1028, 960, 748, 696. ^{1}H NMR, δ: 1.90 (s, 3 H, MeC(4)); 2.65 (t, 2 H, $H_2C(5)$, J = 6.2 Hz); 3.62 (t, 2 H, $H_2C(6)$, J = 6.27 Hz); 4.55 (s, 2 H, $\underline{H}_2$CPh); 6.11 (d, 1 H, HC(3), J = 11.0 Hz); 6.48 (d, 1 H, HC(1), J = 15.5 Hz); 7.05 (dd, 1 H, HC(2), J_1 = 11.0 Hz, J_2 = 15.5 Hz); 7.20—7.50 (m, 10 H, Ph). ^{13}C NMR, δ: 24.46 (Me); 33.21 (C(5)); 68.91 (C(6)); 72.96 ($\underline{C}H_2$Ph); 125.29 (C(2)); 126.19 (C(3)); 127.01 (C(1)); 136.71 (C(4)). MS, *m/z* (I_{rel} (%)): 278 [M]$^+$ (14), 187 (13), 169 (10), 157 (47.5), 144 (10), 143 (10), 142 (15), 141 (14), 130 (31.5), 129 (26.5), 115 (19.5), 91 (100), 81 (14), 79 (13), 77 (12.5), 65 (10), 51 (16), 43 (10). High-resolution MS. Found: [M + K]$^+$, 317.1313. $C_{20}H_{22}O$. Calculated: [M + K]$^+$, 317.1302.

Method *B*. Sequential treatment of compound **3a** with BuLi, TsCl, and $LiAlH_4$ as described below for compound **3b** gave a ~4 : 1 mixture of dienes **4a** and **7a** (^{1}H NMR).

(1*E*,3*Z*)-6-Benzyloxy-1-(4-methoxyphenyl)-4-methylhexa-1,3-diene (4b). Method *A*. Treatment of alcohol **3b** with Py·SO_3 followed by *in situ* reduction of the resulting sulfate with $LiAlH_4$ as described above for compound **3a** gave a mixture of dienes **4b**, **5b**, and **6b** in a ratio of 4 : 1.2 : 0.4 (^{1}H NMR). The mixture was not separated by flash chromatography.

Method *B*. A solution of dienol **3b** (0.87 g, 2.7 mmol) in a mixture of Et_2O (17.5 mL) and HMPA (2.6 mL) was vigorously stirred at 0 °C while a solution of BuLi (3.23 mmol) in hexane (1.9 mL) and a solution of TsCl (0.62 g, 3.24 mmol) in HMPA (2.6 mL) were successively added. The reaction mixture was

stirred at 0 °C for 2.5 h and cooled to −15 °C. A solution of $LiAlH_4$ (18.7 mmol) in THF (11 mL) was added dropwise and the mixture was slowly warmed to ~20 °C, stirred at this temperature for 20 h, and subjected to the same workup as for compound **4a** (method *A*) to give an oily mixture (0.9 g) containing dienes **4b** and **7b** in a ratio of ~95 : 5 (^{1}H NMR). Flash chromatography of this mixture on SiO_2 with gradient elution from hexane to 50% benzene gave analytically pure benzyloxyhexadiene **4b** (0.5 g, 50%), b.p. 165 °C (0.1 Torr (bath)). Found (%): C, 81.65; H, 7.60. $C_{21}H_{24}O_2$. Calculated (%): C, 81.78; H, 7.84. UV, λ_{max}/nm (ε): 215 (8600), 303 (22 200). IR, ν/cm^{-1}: 3032, 2984, 2856, 1604, 1512, 1460, 1360, 1300, 1248, 1180, 1100, 1032, 960, 880, 864, 850, 812, 736, 696. ^{1}H NMR, δ: 1.89 (s, 3 H, MeC(4)); 2.63 (t, 2 H, H_2C(5), J = 7.2 Hz); 3.61 (t, 2 H, H_2C(6), J = 7.2 Hz); 3.83 (s, 3 H, MeO); 4.57 (s, 2 H, C$\underline{H}_2$Ph); 6.08 (d, 1 H, HC(3), J = 10.9 Hz); 6.42 (d, 1 H, HC(1), J = 15.5 Hz); 6.87 (d, 2 H, Ar, J = 8.8 Hz); 6.90 (dd, 1 H, HC(2), J_1 = 10.9 Hz, J_2 = 15.5 Hz); 7.20—7.50 (m, 7 H, Ph). ^{13}C NMR, δ: 24.46 (MeC(3)); 33.11 (C(5)); 55.29 (MeO); 68.88 (C(6)); 72.94 ($\underline{C}H_2$Ph); 123.30 (C(2)); 128.36 (C(3)); 130.00 (C(1)); 138.42 (C(4)). MS, m/z (I_{rel} (%)): 308 $[M]^+$ (51), 188 (21), 187 (96), 174 (13), 173 (22), 172 (13), 160 (60), 159 (44), 158 (31), 157 (24), 145 (17), 144 (21), 141 (24), 135 (10), 134 (32), 131 (32), 129 (39), 128 (28), 122 (10), 121 (45), 115 (14), 92 (19), 91(100), 79 (29), 77 (49), 69 (18), 65 (15), 55 (20), 44 (11), 42 (17).

(3*Z*,5*E*)-3-Methyl-6-phenylhexa-3,5-dien-1-ol (8a). A solution of benzyl ether **4a** (0.41 g, 1.51 mmol) in CH_2Cl_2 (1.5 mL) was vigorously stirred at 20 °C while $PhNMe_2$ (0.8 mL, 6.04 mmol) and anhydrous $AlCl_3$ (0.61 g, 4.53 mmol) were successively added. The reaction mixture was stirred for 1 h and then cooled to 0 °C. Dilute HCl (1 : 10, 12 mL) was added dropwise and the resulting layers were separated after 10 min. The product from the aqueous layer was extracted with CH_2Cl_2 (3×7 mL). After routine workup of the combined extracts, the residue (0.42 g) contained a mixture of dienol **8a** and its (*E*,*E*)-isomer **9a** in a ratio of ~9 : 1 (^{1}H NMR). Flash chromatography of this mixture on SiO_2 (25 g) with gradient elution from hexane to 40% TBME gave dienol **8a** (0.12 g). UV, λ_{max}/nm (ε): 235 (15 040), 301 (33 840). IR, ν/cm^{-1}: 3620, 3445, 3036, 3008, 2960, 2928, 2884, 1700, 1640, 1596, 1496, 1448, 1380, 1364, 1232, 1196, 1044, 964, 884, 808, 620. ^{1}H NMR, δ: 1.56 (br.s, 1 H, OH); 1.93 (s, 3 H, MeC(3)); 2.59 (t, 2 H, H_2C(2), J = 6.6 Hz); 3.78 (t, 2 H, H_2C(1), J = 6.6 Hz); 6.20 (d, 1 H, HC(4), J = 10.9 Hz); 6.50 (d, 1 H, HC(6), J = 15.4 Hz); 7.05 (dd, 1 H, HC(5), J_1 = 10.9 Hz, J_2 = 15.4 Hz); 7.08—7.42 (m, 5 H, Ph). ^{13}C NMR, δ: 24.12 (MeC(3)); 35.87 (C(2)); 60.90 (C(1)); 124.93 (C(5)); 126.27 (C(4)); 131.09 (C(6)); 137.78 (C(3)). High-resolution MS. Found: $[M + H]^+$, 189.1255; $[M + Na]^+$, 211.1083; $C_{13}H_{16}ONa$. Calculated: $[M + H]^+$, 189.1274; $[M + Na]^+$, 211.1093.

(3*Z*,5*E*)-6-(4-Methoxyphenyl)-3-methylhexa-3,5-dien-1-ol (8b) was obtained as described above for compound **8a**. Yield 70%, m.p. 55—57 °C (from hexane—ether, 1 : 1). Found (%): C, 77.02; H, 8.10. $C_{14}H_{18}O_2$. Calculated (%): C, 77.03; H, 8.31. UV, λ_{max}/nm (ε): 224 (10 900), 303 (35 000). IR, ν/cm^{-1}: 3640, 3450, 3008, 2960, 2840, 1604, 1512, 1460, 1448, 1384, 1304, 1248, 1176, 1040, 960, 840, 816, 664. ^{1}H NMR, δ: 1.67 (t, 1 H, OH, J = 5.8 Hz); 1.88 (s, 3 H, MeC(3)); 2.56 (t, 2 H, H_2C(2), J = 6.4 Hz); 3.76 (dt, 2 H, H_2C(1), J_1 = 5.8 Hz, J_2 = 6.4 Hz); 3.81 (s, 3 H, MeO); 6.19 (d, 1 H, HC(4), J = 10.9 Hz); 6.44 (d, 1 H, HC(6), J = 15.5 Hz); 6.86 (d, 2 H, Ar, J = 8.7 Hz); 6.91 (dd, 1 H, HC(5), J_1 = 10.9 Hz, J_2 = 15.5 Hz); 7.35 (d, 2 H, Ar, J = 8.7 Hz). ^{13}C NMR, δ: 24.04 (MeC(3)); 35.82 (C(2)); 55.29 (MeO); 60.89 (C(1)); 122.97 (C(5)); 128.79 (C(4)); 130.64 (C(6)), 134.53 (C(3)). MS, m/z (I_{rel} (%)): 219 $[M + 1]^+$ (20), 218 $[M]^+$ (100), 188 (16), 187 (70), 173 (14), 172 (34), 159 (22), 158 (21), 144 (18), 134 (12), 121 (29), 115 (29), 101 (10), 91(13), 78 (15), 76 (11), 59 (41), 56 (11), 45 (10), 43 (26), 42 (19), 41 (11).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 07-03-00454).

References

1. N. Ya. Grigorieva, A. G. Smirnov, V. A. Popovsky, A. V. Stepanov, *Izv. Akad. Nauk, Ser. Khim.*, 2009, 310 [*Russ. Chem. Bull., Int. Ed.*, 2009, **58**, 312].
2. N. Ya. Grigorieva, A. G. Smirnov, V. A. Popovsky, A. V. Stepanov, *Mendeleev Commun.*, 2008, **18**, 84.
3. H. Sauter, W. Steglich, T. Anke, *Angew. Chem.*, *Int. Ed.*, 1999, **38**, 1329.
4. S. Kroiss, W. Steglich, *Tetrahedron*, 2004, **60**, 4921.
5. E. J. Corey, K. Ahiwa, *J. Org. Chem.*, 1969, **34**, 3667.
6. A. J. Gordon, R. A. Ford, *The Chemist´s Companion. Handbook of Practical Data, Techniques and References*, Wiley and Sons, New York—London—Sydney—Toronto, 1972, p. 257.
7. M. E. Jung, M. A. Lyster, *J. Org. Chem.*, 1977, **42**, 3761.
8. D. J. Hart, W.-P. Hong, L.-Y. Hsu, *J. Org. Chem.*, 1987, **52**, 4665.
9. T. Akiyama, H. Hirofuji, S. Ozaki, *Tetrahedron Lett.*, 1991, **32**, 1321.
10. U. Schmidt, R. Meyer, V. Leitenberger, H. Griesser, A. Lieberknecht, *Synthesis*, 1992, 1025.
11. T. Oriyama, M. Kimura, M. Oda, G. Koga, *Synlett.*, 1993, 437.
12. J. S. Debenham, R. Rodebaugh, B. Fraser-Reid, *J. Org. Chem.*, 1997, **62**, 4591.

Received January 22, 2010