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Easy Synthesis of 2,4-Dialkyl Substituted Phenols and Anisoles from *p*-Benzoquinone

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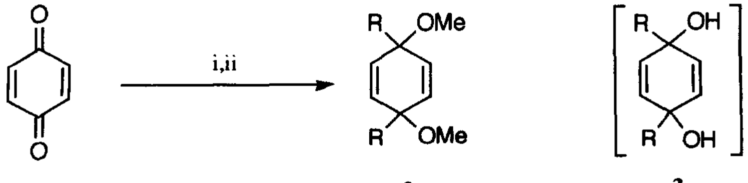
Abstract: *The reaction of* p-*benzoquinone (1) with several organolithium compounds (methyl-, ethyl-,* n-*butyl, phenyllithium) leads directly, after acid hydrolysis, to the corresponding 2,4-dialkylphenols **4a-d**, resulting from a rearrangement/aromatization process of the corresponding intermediate diols **3**. The use of two different alkyllithium reagents leads to the mixed products **4e,f**. Alternatively, the same results are obtained treating the crude isolated diols **3** with a catalytic amount of concentrated sulfuric acid. Applying this last methodology to the diethers **2**, 2,4-dialkylanisoles **8** are obtained. A possible mechanism is proposed.*

Introduction

The most important procedure for the alkylation of phenol is the Friedel-Crafts and related reactions,[1] which usually proceed under mild conditions yielding a mixture of products resulting from a *para* and *ortho* substitution; inconvenients of this reaction are: (a) isomerization of the alkyl rest, and (b) polyalkylations.[2] On the other hand, we have recently reported that *p*-quinone (**1**) can be easily transformed into the corresponding 1,4-dialkyl-1,4-dimethoxycyclohexa-2,5-dienes (**2**) by successive addition of an alkyllithium compound and methylation with methyl iodide (Scheme 1).[3] In this reaction diols **3** are obviously formed prior the final methylation. This paper reports the *in situ* transformation of diols **3** into the corresponding 2,4-dialkylphenols **4** by acid treatment and the obtention of 2,4-dialkylanisoles **8** from the ethers **2** by the same procedure.

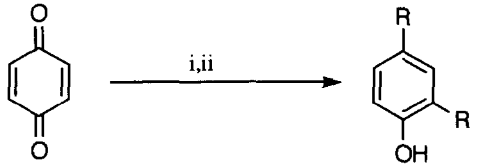


1 **2** **3**

Scheme 1. *Reagents*: i, RLi; ii, NaH, then MeI.

Results and Discussion

The reaction of *p*-benzoquinone **1** with an alkyllithium reagent (1:3 molar ratio) at temperatures ranging between -78 and 20°C led to the corresponding diol of the type **3**,[3] which by treatment with diluted sulfuric acid afforded the 2,4-dialkylphenols **4** (Scheme 2 and Table 1, entries 1-4). If this last hydrolysis was carried out with aqueous ammonium chloride, the corresponding diols **3** can be isolated;[4] the further treatment of these crude diols **3** with a catalytic amount of concentrated sulfuric acid in ether[5a] yielded the same products **4**.

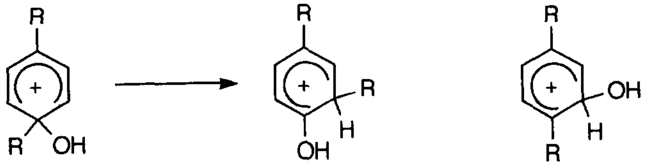


1

4a: R=Me
4b: R=Et
4c: R=*n*-Bu
4d: R=Ph

Scheme 2. *Reagents*: i, RLi; *ii*, H_2SO_4-H_2O.

The probable mechanism for the dienol-benzene rearrangement[6] corresponding to the transformation **3**→**4** should involve a 1,2-migration of an alkyl group from the cation **5** initially formed (resulting from an acid catalyzed dehydration of **3**) to give **6**, which suffers final aromatization. The other alternative possibility through the intermediate **6'**, which would give the corresponding 2,5-disubstituted phenols, does not occur due to its lower stability compared to **6** (see corrections in references 5b and 6).



5 **6** **6'**

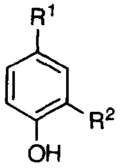
We tried also to prepare "mixed" systems such as **4e,f**. Thus, the successive addition of an alkyllithium reagent R^1Li (R^1=Me) to *p*-quinone (1:1 molar ratio) followed by a second organolithium reagent R^2Li (R^2=*n*-Bu, Ph; 1:2 molar ratio) led to the mixed diols of the type **7**,[4] which by final acid treatment as above afforded the products **4e,f** (Table 1, entries 5 and 6). For R^1=Me, R^2=*n*-Bu, the expected mixture of compounds **4e**/**4e'** (1:1 molar ratio) was obtained. However, when methyl- and phenyl-lithium were successively used, only the phenol **4f** was isolated: in this case, the 1,2-migration prior to the aromatization takes place *via* the more stable intermediate **5f**, in comparison with the other one **5f'**.

Finally, we have also studied the same process starting from compounds **2**[3] in order to prepare the corresponding methyl ethers **8**. When compounds **2** were treated with a catalytic amount of concentrated sulfuric acid in ether the expected products **8** were isolated (Table 1, entries 7-10). In this case the mechanism should be the same as for compounds **4**.

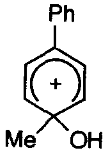
Table 1. Preparation of Compounds **4** and **8**

Entry	Product[a]			
	no.	yield (%)[b]	R_f^c	lit.
1	**4a**	70 (90)	0.22	7
2	**4b**	67 (95)	0.59[d]	8
3	**4c**	63 (98)	0.60[e]	9
4	**4d**	63 (88)	0.40[d]	10
5	**4e/4e'**	40 (94)	0.39[e]/0.33[e]	11
6	**4f**	41 (96)	0.36[d]	12
7	**8a**	97[f]	0.61	5
8	**8b**	95[f]	0.58	13
9	**8c**	97[f]	0.64	4a
10	**8d**	99[f]	0.40	14

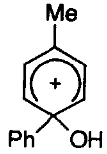
[a] All products **4** and **8** were >95% pure (g.l.c. and 300 MHz ^{1}H n.m.r.). [b] Isolated yield after flash chromatography (silica gel, hexane/ethyl acetate) based on the starting *p*-quinone **1**; in parentheses the corresponding yield based on the crude diols **3** or **7**. [c] Silica gel, hexane/ethyl acetate: 19/1. [d] Silica gel, hexane/ethyl acetate: 4/1. [e] Silica gel, hexane/ethyl acetate: 9/1. [f] Isolated yield based on the starting material **2**.



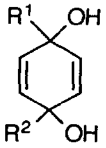
4e: R^1=Me, R^2=*n*-Bu
4e': R^1=*n*-Bu, R^2=Me
4f: R^1=Ph, R^2=Me



5f



5f'



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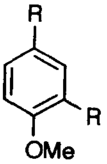

8a: R=Me
8b: R=Et
8c: R=*n*-Bu
8d: R=Ph

From the results described here we conclude that this procedure represents an easy entry for 2,4-dialkyl phenols and anisoles from simple precursors and in a regioselective manner.

Experimental

General.- For general information see reference 3. Retention times (t_r) are given under the conditions indicated therein.

Preparation of Compounds **4** and **8**. *General Procedure.*- To a solution of *p*-benzoquinone (**1**) (0.50 g, 4.6 mmol) in THF (25 ml) was added the corresponding organolithium reagent (13.8 mmol) at -78°C. The resulting solution was stirred for 6 h allowing the temperature to rise to 20°C. The resulting mixture was then hydrolyzed with water (10 ml), acidified with 2 N sulfuric acid, and extracted with ether (3x10 ml). The organic layer was dried over sodium sulfate and evaporated (15 torr) to give the crude products **4a-d**, which were purified by flash chromatography (silica gel, hexane/ethyl acetate). In the case of the mixed products **4e,f**, after the addition of the first alkyllithium reagent (4.6 mmol; 1:1 molar ratio), a second organolithium compound (9.2 mmol; 1:2 molar ratio) was added under the above described conditions, and the reaction mixture was worked up as above to yield the products **4e,f**.
Alternatively, for products **4** or in the case of compounds **8**, the crude diols **3**[4] or the ethers **2**[3] (1 mmol) in ether (2 ml) were treated with concentrated sulfuric acid (0.01 mmol) and stirred for 1 h. Then the mixture was hydrolyzed with water (4 ml) and worked up as above to afford the corresponding products **4** or **8**.

2,4-Dimethylphenol (**4a**):[7] t_r=8.90 min (lit.,[7] m.p. 27-28°C); ν_{max} (film) 3400 (OH), 3020, 1620, 1590 (HC=C), and 1255 cm^{-1} (C-O); δ_H ($CDCl_3$) 2.20, 2.23 (6 H, 2 s, 2xMe), 4.95 (1 H, br s, OH), 6.64, 6.85 (2 H, 2 d, *J*=8.0, 5,6-ArH), and 6.91 (1 H, s, 3-ArH); *m/z* 122 (M^+, 84%), 121 (36), 107 (100), 91 (19), 79 (18), and 77 (35).

2,4-Diethylphenol (**4b**):[8] t_r=11.53 min (lit.,[8] b.p. 112-113°C/10 mmHg); ν_{max} (film) 3400 (OH), 3000, 1600 (HC=C), and 1115 cm^{-1} (C-O); δ_H ($CDCl_3$) 1.20, 1.22 (6 H, 2 t, *J*=7.7, 2xMe), 2.55, 2.61 (4 H, 2 q, *J*=7.7, 2xCH_2), 4.87 (1 H, s, OH), 6.66 (1 H, d, *J*=8.1, 6-ArH), 6.89 (1 H, dd, *J*=8.1, 1.8, 5-ArH), and 6.95 (1 H, s, 3-ArH); δ_C ($CDCl_3$) 14.1, 15.9 (2xMe), 23.0, 28.1 (2xCH_2), 115.0, 126.0, 128.7, 129.7, 136.6, and 151.2 (ArC); *m/z* 151 (M^++1, 3%), 150 (M^+, 29), 135 (100), 121 (26), 107 (14), 91 (37), and 77 (20).

2,4-Dibutylphenol (**4c**):[9] t_r=16.12 min (lit.,[9] b.p. 156-158°C/15 mmHg); ν_{max} (film) 3400 (OH), 3020, 1600 (HC=C), and 1120 cm^{-1} (C-O); δ_H ($CDCl_3$) 0.92, 0.94 (6 H, 2 t, *J*=7.2, 2xMe), 1.30-1.45 (4 H, m, 2xCH_2Me), 1.50-1.64 (4 H, m, 2x CH_2CH_2Me), 2.51, 2.57 (4 H, 2 t, *J*=7.7, 2xCH_2Ar), 4.56 (1 H, s, OH), 6.66, 6.87 (2 H, 2 d, *J*=8.0, 5,6-ArH), and 6.91 (1 H, s, 3-ArH); δ_C ($CDCl_3$) 13.9, 14.0 (2xMe), 22.3, 22.6 (2xCH_2Me), 29.7, 32.1 (2xCH_2CH_2Me), 34.0, 34.8 (2xCH_2Ar), 115.0, 126.7, 128.2, 130.1, 135.1, and 151.3 (ArC); *m/z* 207 (M^++1, 3%), 206 (M^+, 15), 164 (12), 163 (100), 133 (11), 121 (26), 120 (14), 107 (11), 92 (11), 91 (45), 77 (20), 43 (13), and 41 (24).

2,4-Diphenylphenol (**4d**):[10] t_r=22.69 min, m.p. 85-87°C (hexane) (lit.,[10] m.p. 88.5°C); ν_{max} (KBr) 3510, 3400 (OH), 3040, 3020, and 1600 cm^{-1} (HC=C); δ_H ($CDCl_3$) 5.27 (1 H, s, OH), 7.05, 7.31 (2 H, 2 d, *J*=8.7, 5,6-ArH), and 7.41-7.58 (11 H, m, ArH); δ_C ($CDCl_3$) 116.2, 126.8, 127.8, 128.0, 128.4, 128.7, 128.9, 129.1, 129.3, 134.1, 137.0, 140.6, and 152.0 (ArC); *m/z* 247 (M^++1, 18%), 246 (M^+, 100), 245 (13), 215 (10), and 202 (13).

2-Butyl-4-methylphenol (**4e**):[11] t_r=12.69 min (lit.,[11] m.p. 19°C); ν_{max} (film) 3400 (OH), 3010, and 1610 cm^{-1} (HC=C); δ_H ($CDCl_3$) 0.94 (3 H, t, *J*=7.3, *Me*CH_2), 1.35-1.42 (2 H, m, CH_2Me), 1.56-1.61 (2 H, m, CH_2CH_2Me), 2.25 (3 H, s, *Me*Ar), 2.56 (2 H, t, *J*=7.7, CH_2Ar), 4.64 (1 H, s, OH), 6.65, 6.86 (2 H, 2 d, *J*=8.0, 5,6-ArH), and 6.91 (1 H, s, 3-ArH); δ_C ($CDCl_3$) 14.0 (*Me*CH_2), 20.5 (*Me*Ar), 22.6 (CH_2Me), 29.6 (CH_2CH_2Me), 32.1 (CH_2Ar), 115.0, 127.3, 128.3, 129.8, 130.7, and 151.1 (ArC); *m/z* 165 (M^++1, 4%), 164 (M^+, 30), 122 (16), 121 (100), 115 (10), 107 (10), 93 (10), 92 (10), 91 (77), 78 (14), 77 (53), 65 (15), 51

(12), and 41 (21).

4-Butyl-2-methylphenol (**4e'**):[11] t_r=13.08 min (lit.,[11] m.p. 24°C); ν_{max} (film) 3400 (OH), 3010, and 1610 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.91 (3 H, t, *J*=7.3, *Me*CH$_2$), 1.30-1.37 (2 H, m, C*H*$_2$Me), 1.52-1.57 (2 H, m, C*H*$_2$CH$_2$Me), 2.23 (3 H, s, *Me*Ar), 2.50 (2 H, t, *J*=7.7, C*H*$_2$Ar), 4.69 (1 H, s, OH), 6.67, 6.87 (2 H, 2 d, *J*=8.0, 5,6-ArH), and 6.92 (1 H, s, 3-ArH); δ_C (CDCl$_3$) 13.9 (*Me*CH$_2$), 15.7 (*Me*Ar), 22.3 (*C*H$_2$Me), 34.0 (*C*H$_2$CH$_2$Me), 34.7 (*C*H$_2$Ar), 114.7, 123.4, 126.8, 131.0, 135.1, and 151.6 (ArC); *m/z* 165 (M^++1, 2%), 164 (M^+, 13), 121 (100), 91 (35), 77 (31), and 41 (19).

2-Methyl-4-phenylphenol (**4f**):[12] t_r=17.63 min, m.p. 112-113°C (hexane, two recrystallizations) (lit.,[12] m.p. 113-114°C); ν_{max} (KBr) 3300 (OH), 3020 (HC=C), and 1120 cm^{-1} (C-O); δ_H (CDCl$_3$) 2.30 (3 H, s, Me), 4.50 (1 H, s, OH), 6.82 (1 H, d, *J*=8.2, 6-ArH), and 7.28-7.54 (7 H, m, ArH); δ_C 15.9 (Me), 115.2, 124.0, 125.8, 126.6, 126.7, 128.7, 129.8, 133.9, 140.9, and 153.4 (ArC); *m/z* 185 (M^++1, 14%), 184 (M^+, 100), 183 (29), 165 (20), 153 (13), 152 (12), 128 (13), 115 (16), 77 (11), and 51 (10).

2,4-Dimethylanisole (**8a**):[5b,7] t_r=8.20 min (lit.,[7] b.p. 192°C); ν_{max} (film) 3020, 1605, 1580 (HC=C), 1250, 1225, and 1035 cm^{-1} (C-O); δ_H (CDCl$_3$) 2.19, 2.26 (6 H, 2 s, 2x*Me*Ar), 3.80 (3 H, s, OMe), 6.72 (1 H, d, *J*=8.8, 6-ArH), and 6.94 (2 H, br s, 3,5-ArH); *m/z* 137 (M^++1, 7%), 136 (M^+, 85), 135 (12), 121 (100), 105 (15), 93 (11), 91 (68), 78 (14), 77 (65), 65 (16), and 51 (11).

2,4-Diethylanisole (**8b**):[13] t_r=10.69 min; ν_{max} (film) 1600 (HC=C) and 1250 cm^{-1} (C-O); δ_H (CDCl$_3$) 1.19, 1.21 (6 H, 2 t, *J*=7.4, 2x*Me*CH$_2$), 2.58, 2.62 (4 H, 2 q, *J*=7.4, 2xCH$_2$), 3.80 (3 H, s, OMe), 6.76, 6.99 (2 H, 2 d, *J*=8.8, 5,6-ArH), and 7.00 (1 H, s, 3-ArH); δ_C (CDCl$_3$) 14.3, 15.9 (2x*Me*CH$_2$), 23.3, 28.1 (2xCH$_2$), 55.4 (OMe), 110.2, 125.7, 128.6, 132.4, 136.1, and 155.4 (ArC); *m/z* 165 (M^++1, 3%), 164 (M^+, 27), 150 (10), 149 (100), 135 (22), 105 (11), 103 (10), 91 (28), and 77 (15).

2,4-Dibutylanisole (**8c**):[4a] t_r=15.53 min; ν_{max} (film) 1600 (HC=C), 1090, and 1030 cm^{-1} (C-O); δ_H (CDCl$_3$) 0.84, 0.85 (6 H, 2 t, *J*=7.3, 2x*Me*CH$_2$), 1.23-1.32 (4 H, m, 2xC*H*$_2$Me), 1.46-1.50 (4 H, m, C*H*$_2$CH$_2$Me), 2.42-2.53 (4 H, m, 2xC*H*$_2$Ar), 3.70 (3 H, s, OMe), 6.66, 6.88 (2 H, 2 d, *J*=8.7, 5,6-ArH), and 6.86 (1 H, s, 3-ArH); δ_C (CDCl$_3$) 13.9, 14.0 (2x*Me*CH$_2$), 22.4, 22.7 (2x*C*H$_2$Me), 29.9, 32.2 (2x*C*H$_2$CH$_2$Me), 34.0, 34.8 (2x*C*H$_2$Ar), 55.4 (OMe), 110.1, 126.2, 129.9, 131.0, 134.6, and 155.5 (ArC); *m/z* 221 (M^++1, 4%), 220 (M^+, 25), 178 (17), 177 (100), 135 (14), 105 (14), 91 (20), 42 (11), and 41 (20).

2,4-Diphenylanisole (**8d**):[14] t_r=22.75 min, m.p. 95-7°C (hexane) (lit.,[14] m.p. 97.5°C); ν_{max} (film) 3050, 3020, and 1600 cm^{-1} (HC=C); δ_H (CDCl$_3$) 3.85 (3 H, s, Me), 7.06, 7.32 (2 H, 2 d, *J*=8.8, 5,6-ArH), 7.40-7.45, and 7.54-7.60 (11 H, 2 m, ArH); δ_C (CDCl$_3$) 55.7 (Me), 111.5, 126.7, 126.8, 127.0, 127.1, 128.0, 128.7, 129.6, 129.7, 131.0, 133.9, 138.4, 140.7, and 156.0 (ArC); *m/z* 261 (M^++1, 19%), 260 (M^+, 100), 245 (19), 227 (33), 226 (20), 217 (10), 215 (29), 202 (21), 189 (10), 139 (11), 115 (14), and 77 (11).[17]

References and Notes

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3. Alonso, F.; Yus, M. *Tetrahedron* **1991**, *47*, 7471.
4. (a) Alonso, F. Ph. D. Thesis, University of Alicante, 1991. (b) Selected data for **3** or **7**: *cis*-**3a** (R=Me):[15] ν_{max} (film) 3350 (OH), 3020, and 1650 cm^{-1} (HC=C); δ_H (CDCl$_3$) 1.27 (6 H, s, 2xMe), 3.88 (2 H, br s, 2xOH), and 5.75 (4 H, s, olefinic H); δ_C (CDCl$_3$) 28.2 (2xMe), 65.2 (2x*C*Me), and 132.6 (olefinic C); *m/z* 122 (M^+-18, 78%). *cis*-**3b** (R=Et):[4a] ν_{max} (film) 3350 (OH), 3010, and 1650 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.75 (6 H, t, *J*=7.5, 2xMe), 1.59 (4 H, q, *J*=7.5, 2xCH$_2$), 4.14 (2 H, br s, 2xOH), and 5.72 (4 H, s, olefinic H); δ_C (CDCl$_3$) 8.3 (2xMe), 33.2 (2xCH$_2$), 68.5 (2x*C*Me), and 132.9

(olefinic C); *m/z* 168 (M^+, 0.2%). *trans*-**3b** (R=Et):[4a] m.p. 103-105°C (ether); ν_{max} (KBr) 3250 (OH), 3010, and 1660 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.80 (6 H, t, J=7.5, 2xMe), 1.62 (4 H, q, J=7.5, 2xCH$_2$), 1.94 (2 H, br s, 2xOH), and 5.79 (4 H, s, olefinic H); δ_C (CDCl$_3$) 8.6 (2xMe), 32.8 (2xCH$_2$), 68.8 (2xCOH), and 133.2 (olefinic C); *m/z* 150 (M^+-18, 1%). *cis*-**3c** (R=*n*-Bu):[4a] ν_{max} (film) 3350 (OH) and 3010 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.86 (6 H, t, J=7.2, 2xMe), 1.11-1.14 (4 H, m, 2xCH_2Me), 1.25-1.30 (4 H, m, 2xCH_2CH$_2$Me), 1.53-1.58 (4 H, m, 2xCH_2COH), 3.80 (2 H, br s, 2xOH), and 5.72 (4 H, s, olefinic H); δ_C (CDCl$_3$) 13.9 (2xMe), 22.9 (2xCH$_2$Me), 26.3 (2xCH$_2$CH$_2$Me), 40.5 (2xCH$_2$COH), 68.1 (2xCOH), and 133.1 (olefinic C); *m/z* 244 (M^+, 0.1%). *trans*-**3c** (R=*n*-Bu):[4a] m.p. 110-115°C (ether); ν_{max} (KBr) 3350 (OH) and 3010 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.88 (6 H, t, J=7.2, 2xMe), 1.13-1.19 (4 H, m, 2xCH_2Me), 1.27-1.32 (4 H, m, 2xCH_2CH$_2$Me), 1.57-1.62 (4 H, m, 2xCH_2COH), 1.70 (2H, br s, 2xOH), and 5.80 (4 H, s, olefinic H); δ_C (CDCl$_3$) 13.9 (2xMe), 22.8 (2xCH$_2$Me), 26.5 (2xCH$_2$CH$_2$Me), 40.0 (2xCH$_2$COH), 68.4 (2xCOH), and 133.5 (olefinic C); *m/z* 206 (M^+, 18%). *cis/trans*-**3d** (R=Ph):[4a] m.p. 130-132°C (ether); ν_{max} (KBr) 3350 (OH), 3060, 3040, and 3010 cm^{-1} (HC=C); δ_H [(CD$_3$)$_2$CO] 4.47 (2 H, s, 2xOH), 5.95 (4 H, s, olefinic H), and 7.23-7.50 (10 H, m, ArH); δ_C [(CD$_3$)$_2$CO] 69.4 (2xCOH), 132.7 (olefinic C), 126.5, 127.7, 128.9, and 146.5 (ArC); tandem g.l.c./MS *m/z*, *cis* isomer: 247 (M^+-17, 19%), *trans* isomer: 247 (M^+-17, 22%). *cis*-**7e** (R^1=Me, R^2=*n*-Bu):[16] ν_{max} (film) 3350 (OH), and 3010 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.86 (3 H, t, J=7.2, *Me*CH$_2$), 1.06-1.09 (2 H, m, CH_2Me), 1.26 (3 H, s, *Me*COH), 1.29-1.32 (2 H, m, CH_2CH$_2$Me), 1.52-1.57 (2 H, m, CH_2COH), 4.23, 4.30 (2 H, 2 s, 2xOH), 5.64, and 5.80 (4 H, 2 d, J=9.9, olefinic H); δ_C (CDCl$_3$) 13.8 (*Me*CH$_2$), 22.8 (CH$_2$Me), 26.1 (CH$_2$CH$_2$Me), 28.1 (*Me*COH), 40.3 (CH$_2$COH), 65.3, 68.1 (2xCOH), 131.5, and 133.7 (olefinic C); *m/z* 164 (M^+-18, 6%). *trans*-**7e** (R^1=Me, R^2=*n*-Bu):[16] m.p. 115-118°C (ether); ν_{max} (KBr) 3360 (OH), 3020, and 1625 cm^{-1} (HC=C); δ_H (CDCl$_3$) 0.88 (3 H, t, J=7.2, *Me*CH$_2$), 1.16-1.18 (2 H, m, CH_2Me), 1.25-1.32 (2 H, m, CH_2CH$_2$Me), 1.35 (3 H, s, *Me*COH), 1.57-1.60 (2 H, m, CH_2COH), 1.63 (2 H, br s, 2xOH), 5.75, and 5.91 (4 H, 2 d, J=10.1, olefinic H); δ_C (CDCl$_3$) 14.0 (*Me*CH$_2$), 22.9 (CH$_2$Me), 26.6 (CH$_2$CH$_2$Me), 28.2 (*Me*COH), 40.1 (CH$_2$COH), 65.6, 68.3 (2xCOH), 132.4, and 134.4 (olefinic C); *m/z* 134 (M^+-48, 4%). *cis*-**7f** (R^1=Ph, R^2=Me):[4a] m.p. 95-97°C (ether); ν_{max} (KBr) 3320 (OH), 3050, and 3010 cm^{-1} (HC=C); δ_H [(CD$_3$)$_2$CO] 1.33 (3 H, s, Me), 3.83, 4.40 (2 H, 2 s, 2xOH), 5.74, 5.85 (4 H, 2 d, J=10.1, olefinic H), 7.21 (1 H, d, J=7.3, 4-ArH), 7.30 (2 H, t, J=7.5, 2x3-ArH), and 7.43 (2 H, d, J=7.5, 2x2-ArH); δ_C [(CD$_3$)$_2$CO] 29.3 (Me), 65.3, 69.8 (2xCOH), 126.3, 127.4, 128.8, 146.6 (ArC), 132.4, and 133.4 (olefinic C); *m/z* 185 (M^+-17, 14%). *trans*-**7f** (R^1=Ph, R^2=Me):[4a] m.p. 113-115°C (ether); ν_{max} (KBr) 3330 (OH), 3040, and 3010 cm^{-1} (HC=C); δ_H [(CD$_3$)$_2$CO] 1.33 (3 H, s, Me), 4.00, 4.48 (2 H, 2 s, 2xOH), 5.71, 5.87 (4 H, 2 d, J=10.1, olefinic H), 7.19 (1 H, d, J=7.2, 4-ArH), 7.27 (2 H, t, J=7.3, 2x3-ArH), and 7.53 (2 H, d, J=7.1, 2x2-ArH); δ_C [(CD$_3$)$_2$CO] 29.4 (Me), 65.1, 69.9 (2xCOH), 126.7, 127.3, 126.5, 146.6 (ArC), 133.0, 134.1 (olefinic C); *m/z* 202 (M^+, 18%).

5. (a) Alonso, F.; Barba, I.; Yus, M. *Tetrahedron* **1990**, *46*, 2069. (b) In ref 5a we assigned erroneously the structure of 2,5-dimethylanisole for compound **8a**.
6. For examples of a similar rearrangement see, for instance: Dodge, J. A.; Chamberlin, A. R. *Tetrahedron Lett*. **1988**, *29*, 4827, and references cited therein.
7. (a) *Dictionary of Organic Compounds*; Chapman and Hall: New York; Vol. 2, p. 2201. (b) In our previous paper (ref 5) we assigned erroneously the structure of 2,5-dimethylphenol for compound **4a**.
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