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Preparation and Reactions of Dianions from the Cresols

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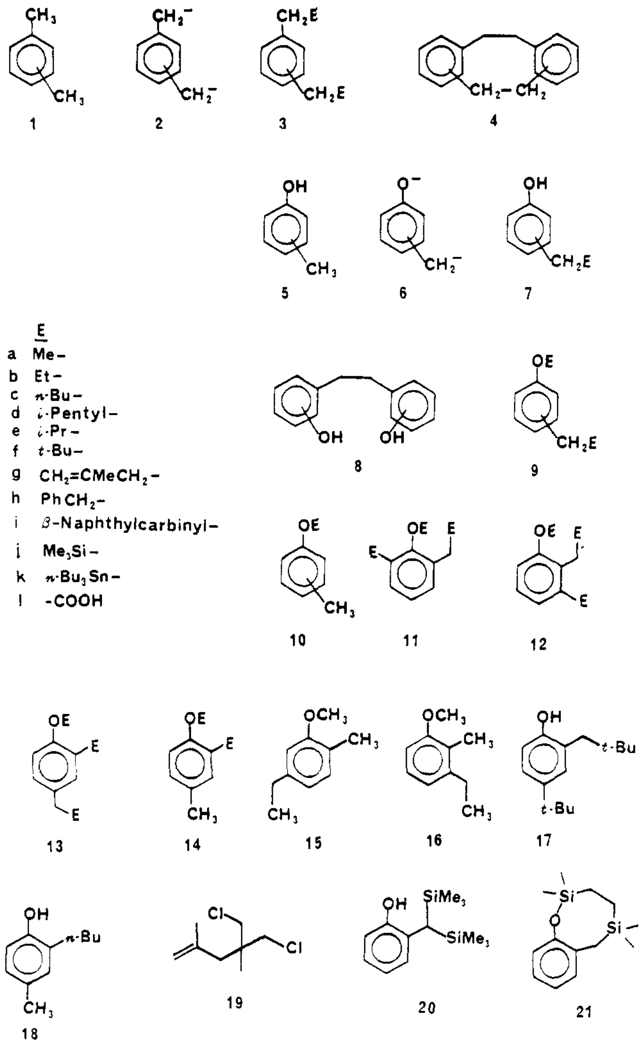
With n-BuLi/KO-t-Bu, protons are removed from the hydroxyl and methyl groups of cresols **5** to give dianions **6** in yields of 85% (ortho), 95% (meta), and 42% (para). These dianions react with alkyl halides, Me_3SiCl, Bu_3SnCl, CO_2, and oxidizing agents at carbon only and with dialkyl sulfates at both carbon and oxygen. Thus phenol derivatives bearing primary alkyl groups can be prepared from the corresponding methylphenols via dianions **6**.

Certain aromatics containing primary alkyl groups are best prepared by two-step one-pot sequences consisting of dimetalating readily available methylated aromatics such as the xylenes **1** in the benzylic positions to give delocalized dianions such as **2** and then adding electrophiles or oxidizing agents to give derivatives such as **3** and **4**, respectively, which cannot readily be prepared by Friedel–Crafts reactions due to carbonium rearrangements and orientation limitations in electrophilic aromatic substitutions.[1] We now report that dimetalation of the cresols **5** with n-BuLi/KO-t-Bu gives the analogous oxygen-containing dianions o- and m-**6** in good yields and p-**6** in fair yield[2] and that these dianions react with a variety of electrophiles at carbon only to give derivatives **7**, with oxidizing agents to give coupled products **8**, and with dialkyl sulfates and excess methyl iodide at both carbon and oxygen to give dialkylated derivatives **9**. Reactions of these types should provide the best routes to many of the natural products which are alkylated phenol derivatives.[3]

Table I gives yields of various products from two-step sequences involving dianions **6** as intermediates. The maximum yield in the meta case (95%, with Me_2SO_4) puts a minimum on the yield of dianion m-**6**. To obtain the yields shown for the ortho derivatives (maximum 85%, with Et_2SO_4), the metalation was run in refluxing heptane for 3 h. The formation of dianion p-**6** from p-cresol was even more difficult (maximum 42%, with Me_3SiCl), and was done by refluxing in heptane for 20 h. This yield order parallels that observed in the formation of the xylylene dianions **2** and can be explained in terms of their differing resonance energies.[4]

The cresol dianions **6** reacted with dimethyl and diethyl sulfates to give primarily products of type **9**. Besides the desired products o-**9**, o-**5** gave **11a** and **11b**, products from the trianion in which the third proton was removed from the ring ortho to the oxygen, along with small amounts of **10a** and **10b** from monoanion; **12b**, a very minor product from a different trianion, was observed in the Et_2SO_4 case. In the m-**5** case, no trianion products were observed. However, p-**5** gave four types of byproducts: **10a** and **10b** from monoanion, **13a** from the trianion where the third proton was removed from the ring ortho to the oxygen, **14a** and **14b** from the dianion where the second proton was removed from the ring ortho to oxygen, and p-**7b** from ethylation of dianion p-**6** at carbon only.

Chart I



	E
a	Me-
b	Et-
c	n-Bu-
d	i-Pentyl-
e	i-Pr-
f	t-Bu-
g	CH_2=CMeCH_2-
h	PhCH_2-
i	β-Naphthylcarbinyl-
j	Me_3Si-
k	n-Bu_3Sn-
l	-COOH

Dianions **6** were each reacted with a variety of alkyl halides, with o-**6** usually giving a lower yield of the desired product from dianion, presumably for steric reasons. Excess MeI gave mostly dialkylation product m-**9a**, but monoalkylation product m-**7a** was made the major product by using only 2 equiv of MeI. Byproducts found included monoanion product **10a** in one case and trianion products **15** and **16** in the other.[5] Primary alkyl bromides reacted very well with dianions **6**; however, the byproducts of metalation of p-**5** to make p-**6** led to byproducts analogous to those found with dialkyl sulfates and, in addition, oxidation product p-**8**. The yields in the reactions of dianions **6** with alkyl halides decrease from primary to secondary to tertiary halides. *tert*-Butyl iodide presumably reacts

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[1] Bates, R.; Ogle, C. *J. Org. Chem.* **1982**, *47*, 3949.

[2] L. Latimer of Eastman Kodak Co. (private communication) has independently prepared these dianions using (1) KH followed by (2) n-BuLi/THF and reacted them successfully with other electrophiles at carbon.

[3] A. S. Kende, F. H. Ebetino, and T. Ohta (*Tetrahedron Lett.* **1985**, *26*, 3063) have dimetalated 3,5-dimethylphenol with Latimer's Bases[2] to give the 5-methyl derivative of dianion m-**6**, which sequentially reacted on carbon and then oxygen with different electrophiles to give a model for fredericamycin.

[4] Bates, R.; Hess, B.; Ogle, C.; Schaad, L. *J. Am. Chem. Soc.* **1981**, *103*, 5052.

[5] Apparently the former dimetalation was incomplete and the latter went slightly too far.

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Table I. Yields (in Parentheses, Estimated from ^{1}H NMR Spectrum of Crude Product Using CH_2Cl_2 as an Internal Standard) of Products 7–23 from Cresols 5

electrophile	from *o*-**5** (%)	from *m*-**5** (%)	from *p*-**5** (%)
Me_2SO_4	*o*-**9a** (82); *o*-**10a** (10); **11a** (8)[a]	*m*-**9a** (95)[a]	*p*-**9a** (25); *p*-**10a** (25); **13a** (25); **14a** (24)[a]
Et_2SO_4	*o*-**9b** (85); *o*-**10b** (8); **11b** (4); **12b** (3)[a]	*m*-**9b** (76); *m*-**10b** (9)[b]	*p*-**9b** (17); *p*-**10b** (13); **14b** (12); *p*-**7b** (11)[a]
MeI		*m*-**7a** (32); *m*-**9a** (59); *m*-**10a** (9)[a]	
MeI		*m*-**7a** (38); *m*-**9a** (3); **15** (5); **16** (1)[c]	
n-BuBr	*o*-**7c** (60); *o*-**8** (12)[b]	*m*-**7c** (72)[b]	*p*-**7c** (36); *p*-**8** (2); *p*-**9c** (3); **14c** (3); **18** (3)[b]
isopentyl bromide		*m*-**7d** (72)[b]	
i-PrBr	*o*-**7e** (40); *o*-**8** (28)[b]	*m*-**7e** (62); *m*-**8** (5)[a]	*p*-**7e** (28); *p*-**8** (7)[b]
t-BuI	*o*-**7f** (12); *o*-**8** (19); **17** (2)[b]	*m*-**7f** (31); *m*-**8** (39)[b]	*p*-**7f** (12); *p*-**8** (20)[b]
t-BuBr		*m*-**7f** (9); *m*-**8** (29)[b]	
I_2	*o*-**8** (15)[a]	*m*-**8** (24)[a]	
1,2-dibromoethane		*m*-**8** (10)[a]	
CuBr		*m*-**8** (19)[a]	
β-methallyl chloride	*o*-**7g** (35); **19** (52)[b]	*m*-**7g** (71)[b]	*p*-**7g** (30); *p*-**8** (4); **19** (46)[b]
benzyl chloride		*m*-**7h** (55)[b]	
β-naphthylcarbinyl bromide		*m*-**7i** (35); *m*-**8** (17)[b]	
Me_3SiCl	*o*-**7j** (40); **20** (13)[b]	*m*-**7j** (88)[b]	*p*-**7j** (42)[a]
1,1,4,4-tetramethyl-1,4-dichlorodisilylethylene	**21** (44)[a]		
Bu_3SnCl		*m*-**7k** (60)[b]	
CO_2		*m*-**7l** (30)[b]	

[a] Direct addition. [b] Inverse addition. [c] Two equivalents of MeI.

through an electron-transfer mechanism. In the case of *m*-**6**, besides producing considerable *m*-**7f**, this reaction produced the highest yield of oxidation product *m*-**8**; *t*-BuBr reacted the same way but the yields were lower.

The oxidation products of dianions **6** are of the one-electron-type **8**[6] rather than of the two-electron-type **4** observed without oxygen;[1] apparently in the oxygen-containing case, the intermediate anion-radical dimerizes and further oxidation does not occur. Attempts to oxidize these dianions with I_2, 1,2-dibromoethane, CuBr, and Br_2[7] did not give as high a yield as did *tert*-butyl iodide.

When β-methallyl chloride was used to react with *o*- and *p*-**6**, additional product **19**, a dimer of β-methallyl chloride formed in the presence of radicals,[8] was observed; presumably **19** results in the present case from a radical process. Bibenzyl and 1,2-di-β-naphthylethane were observed in the reaction of benzyl chloride and β-naphthylcarbinyl bromide with *m*-**6**, respectively, indicating that electron transfer occurs in these cases and suggesting why the yields in these reactions were lower than with β-methallyl chloride.

Me_3SiCl gives high yields of monosilylation products *m*- and *p*-**7j** from dianions *m*- and *p*-**6** (the aqueous acid workup used would cleave silyl groups from oxygen), but a relatively low yield of *o*-**7j** from *o*-**6**, presumably for steric reasons; a surprising byproduct in the ortho case was disilylation product **20**. 1,1,4,4-Tetramethyl-1,4-dichlorodisilylethylene disilylated *o*-**6** in good yield to give **21**; in this case acid was not used in the workup in order to preserve the Si–O bond. Bu_3SnCl reacted well with *m*-**6** and CO_2 somewhat less satisfactorily.

Experimental Section

Proton NMR spectra were obtained at 250 MHz on a Bruker WM-250 spectrometer. Most crude products were vacuum distilled at 80–120 °C at 10–15 mmHg. Separations were done by GC (Varian Aerograph 700) or LC. Pentane, hexane, and heptane used in the reactions were stirred overnight with 100 mL of concentrated H_2SO_4/L, distilled, and stored over KOH. THF was freshly distilled from Na with indicator benzophenone. All operations involving carbanions were carried out under argon.

***o*-Cresol Dianion (*o*-6).** Argon was bubbled through 130 mL of heptane for 15 min. *t*-BuOK (4.48 g, 40 mmol, Aldrich) and 25.8 mL of 1.55 M (40 mmol) *n*-BuLi in hexane (Aldrich) were added. After stirring for 15 min, 1.08 g (10 mmol) *o*-cresol was added to this mixture, turning it bright yellow; refluxing for 3 h turned it brown. After cooling to 0 °C, dianion *o*-**6** was filtered off and washed with 100 mL of pentane. THF (150 mL, dry precooled (0 °C)) was added to dissolve the dianion for reactions.

***m*-Cresol Dianion (*m*-6).** *m*-**6** was made almost the same way as *o*-**6**; however, hexane was used as solvent and it was refluxed for 3 h. The addition of *m*-cresol to *n*-BuLi/KO-*t*-Bu gave a bright yellow color, and after refluxing it turned yellowish brown.

***p*-Cresol Dianion (*p*-6).** *p*-**6** was made the same way as *o*-**6** except refluxing was carried out for 20 h. When *p*-cresol was added the mixture turned orange, and after refluxing the mixture was reddish brown.

Reactions of Dianions with Electrophiles. Two modes of addition were used: direct and inverse. Direct addition was done by adding the electrophile (20–30 mmol dissolved in 25 mL THF) to a suspension of dianion in THF at 25 °C. In inverse addition, the suspension of dianion was transferred via cannula needle into a solution of electrophile dissolved in 100 mL of THF. In both cases, the reaction was stirred for 20 to 30 h. Water (10 mL) was added dropwise, and the solution was acidified by adding 5 M HCl. The water layer was separated and extracted with 3 × 50 mL of chloroform. After drying ($MgSO_4$), the solvent was evaporated from the combined organic layers to leave crude product. Note: An acid was not used in the workup of **23**. In the preparation of *m*-**7l**, the carbanion suspension was poured over excess dry ice. **13a**,[9] *o*-**7c**,[10,11] *m*-**7c**,[10,11] *p*-**7c**,[11] *o*-**7e**,[12] *m*-**7e**,[13] *p*-**7e**,[12] *o*-**8**,[6] *m*-**8**,[14] *p*-**8**,[6] and *m*-**7h**[15] are known compounds. Satisfactory C and H analyses were obtained for all new com-

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(6) B. Cardillo, M. Cornia, and L. Merlini (*Gazz. Chim. Ital.* **1975**, *105*, 1151) prepared *o*-**8**, and J. C. Drummond and L. J. Hughes (United States Patent, US 4110542, Aug. 29, 1978) prepared *o*-**8** and *p*-**8** by routes which were either longer or gave mixtures of isomers.

(7) With Br_2, no oxidation product *m*-**8** was observed, but instead only bromination products (O'Bara, E. J.; Balsley, R. B.; Starer, I. *J. Org. Chem.* **1970**, *35*, 16).

(8) Cristol, S. J.; Daughenbaugh, R. J.; Opitz, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 6347.

(9) Fischer, A.; Henderson, G. N. *Can. J. Chem.* **1981**, *59*, 2314.

(10) Lucatello, F. G.; Smith, G. E. Brit. Pat. GB 1265152, Mar. 1, 1972.

(11) Ivanovskaya, L. Yu.; Gorfinkel, M. I. *Zh. Org. Khim.* **1968**, *4*, 1227.

(12) Iyer, P.; Pillai, C. N. *Indian J. Chem., Sect. B.* **1978**, *16B*, 321.

(13) Inoue, M.; Nakagawa, T.; Enomoto, S. *Yuki Gosei Kagaky Kyokai Shi*, **1970**, *28*, 1127.

(14) Hata, K.; Baba, K.; Kozawa, M. *Chem. Pharm. Bull.* **1979**, *27*, 984.

(15) Malcolmbruce, J.; Creed, D.; Dawes, K. *J. Chem. Soc. C.* **1971**, *22*, 3749.

pounds except for *m*-**7h**, which decomposed before analysis. ^{1}H NMR parameters (CDCl$_3$, Me$_4$Si) of the new compounds are given below.

2-Ethyl-6-methylanisole (11a): δ 7.00 (m, 3 H, J = 7.4 Hz, ArH), 3.74 (s, 3 H, OMe), 2.66 (q, 2 H, J = 7.6 Hz, HCα), 2.30 (s, 3 H, ArCH$_3$), 1.23 (t, 3 H, J = 7.6 Hz, HCβ).

2-Propylethoxybenzene (*o*-9b): δ 7.14 (t, 1 H, J = 7.4 Hz, ArH-5), 7.12 (d, 1 H, J = 7.4 Hz, ArH-3), 6.86 (t, 1 H, J = 7.4 Hz, ArH-4), 6.82 (d, 1 H, J = 7.4 Hz, ArH-6), 4.02 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.59 (t, 2 H, J = 7.4 Hz, HCα), 1.61 (m, 2 H, J = 7.4 Hz, HCβ), 1.41 (t, 3 H, J = 7.0 Hz, OCH$_2$CH$_3$), 0.94 (t, 3 H, J = 7.4 Hz, HCγ).

3-Propylethoxybenzene (*m*-9b): δ 7.18 (t, 1 H, J = 7.4 Hz, ArH-5), 6.75 (d, 1 H, J = 7.4 Hz, ArH-4), 6.73 (s, 1 H, ArH-2), 6.68 (d, 1 H, J = 7.4 Hz, ArH-6), 4.02 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.55 (t, 2 H, J = 7.4 Hz, HCα), 1.62 (sextet, 2 H, J = 7.4 Hz, HCβ), 1.41 (t, 3 H, J = 7.0 Hz, OCH$_2$CH$_3$), 0.94 (t, 3 H, J = 7.4 Hz, HCγ).

4-Propylethoxybenzene (*p*-9b): δ 7.08 ($\sim$d, 2 H, J = 8.6 Hz, ArH-3,5), 6.81 (d, 2 H, J = 8.6 Hz, ArH-2,6), 4.01 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.52 (t, 2 H, J = 7.4 Hz, HCα), 1.60 (sextet, 2 H, J = 7.4 Hz, HCβ), 1.40 (t, 3 H, J = 7.0 Hz, OCH$_2$CH$_3$), 0.92 (t, 3 H, J = 7.4 Hz, HCγ).

2-Propyl-6-ethylethoxybenzene (11b): δ 7.03 (m, 3 H, ArH), 3.83 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.67 (q, 2 H, J = 7.6 Hz, HCα'), 2.60 (t, 2 H; J = 7.4 Hz, HCα), 1.64 ($\sim$sextet, 2 H, J = 7.4 Hz, HCβ), 1.43 (t, 3 H, J = 7.0 Hz, OCH$_2$CH$_3$), 1.23 (t, 3 H, J = 7.6 Hz, HCβ'), 0.98 (t, 3 H, J = 7.4 Hz, HCγ).

2-Propyl-3-ethylethoxybenzene (12b): δ 7.08 (t, 1 H, J = 7.8 Hz, ArH-5), 6.69 (d, 1 H, J = 7.8 Hz, ArH-6), 6.78 (d, 1 H, J = 7.8 Hz, ArH-4), 4.00 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.64 (q, 2 H, J = 7.6 Hz, HCα'), 2.62 (t, 2 H, J = 7.4 Hz, HCα), 1.52 ($\sim$sextet, 2 H, J = 7.4 Hz, HCβ), 1.41 (t, 3 H, J = 7.0, OCH$_2$CH$_3$), 1.20 (t, 3 H, J = 7.6 Hz, HCβ'), 0.98 (t, 3 H, J = 7.4 Hz, HCγ).

2-Ethyl-4-methylethoxybenzene (14b): δ 6.95 (s, 1 H, ArH-3), 6.94 (d, 1 H, J = 7.8 Hz, ArH-5), 6.72 (d, 1 H, J = 7.8 Hz, ArH-6), 4.00 (q, 2 H, J = 7.0 Hz, OCH$_2$CH$_3$), 2.61 (q, 2 H, J = 7.5 Hz, HCα), 2.27 (s, 3 H, HCα'), 1.40 (t, 3 H, J = 7.0 Hz, OCH$_2$CH$_3$), 1.18 (t, 3 H, J = 7.5 Hz, HCβ).

4-Pentylbutoxybenzene (*p*-9c): δ 7.07 (d, 2 H, J = 8.6 Hz, ArH-3,5), 6.81 (d, 2 H, J = 8.6 Hz, ArH-2,6), 3.93 (t, 2 H, J = 6.5 Hz, ORα), 2.53 (t, 2 H, J = 7.6 Hz, HCα), 1.75 ($\sim$pentet, 2 H, J = 6.5 Hz, ORβ), 1.55 ($\sim$m, 2 H, J = 7.6 Hz, HCβ), 1.51 ($\sim$m, 2 H, J = 6.9 Hz, ORγ), 1.31 ($\sim$m, 2 H, J = 7.6 Hz, J = 6.9 Hz, HCγ), 1.14 ($\sim$m, 2 H, J = 6.9 Hz, HCδ), 0.97 (t, 3 H, J = 6.9 Hz, ORδ), 0.88 (t, 3 H, J = 6.9 Hz, HCϵ).

2-Butyl-4-methylphenol (18): δ 6.91 (s, 1 H, ArH-3), 6.89 (d, 1 H, J = 8.0 Hz, ArH-5), 6.68 (d, 1 H, J = 8.0 Hz, ArH-6), 4.55 (s, 1 H, OH), 2.56 (t, 2 H, J = 7.8 Hz, HCα), 2.25 (s, 3 H, HCα'), 1.41 (m, 2 H, J = 7.8 Hz, J = 7.1 Hz, HCβ), 1.14 (m, 2 H, J = 7.1 Hz, HCγ), 0.94 (t, 3 H, J = 7.1 Hz, HCδ).

2-Butyl-4-methylbutoxybenzene (14c): δ 6.94 (s, 1 H, ArH-3), 6.92 (d, 1 H, J = 8.6 Hz, ArH-5), 6.72 (d, 1 H, J = 8.6 Hz; ArH-6), 3.92 (t, 2 H, J = 6.3 Hz, ORα), 2.57 (t, 2 H, J = 7.6 Hz, HCα), 2.26 (s, 3 H, HCα'), 1.76 (m, 2 H, J = 6.3 Hz, J = 7.3 Hz, ORβ), 1.49 (m, 2 H, J = 7.3 Hz, ORγ), 1.36 (m, 2 H, J = 7.6 Hz, HCβ), 1.13 (m, 2 H, J = 7.6 Hz, J = 7.3 Hz, HCγ), 0.97 (t, 3 H, J = 7.3 Hz, ORδ), 0.92 (m, 2 H, J = 7.3 Hz, HCδ).

2-Neopentylphenol (*o*-7f): δ 7.09 (td, 1 H, J = 7.7 Hz, J = 1.7 Hz, ArH-5), 7.06 (dd, 1 H, J = 7.7 Hz, J = 1.7 Hz, ArH-3), 6.86 (td, 1 H, J = 7.7 Hz, J = 1.2 Hz, ArH-4), 6.78 (dd, 1 H, J = 7.7 Hz, J = 1.2 Hz, ArH-6), 4.59 (s, 1 H, OH), 2.52 (s, 2 H, HCα), 0.95 (s, 9 H, HCγ).

2-Neopentyl-3-*tert*-butylphenol (17): δ 6.98 (d, 1 H, J = 7.9 Hz, ArH-3), 6.80 (d, 1 H, J = 1.9 Hz, ArH-6), 6.87 (dd, 1 H, J = 7.9 Hz, J = 1.9 Hz, ArH-4), 4.54 (s, 1 H, OH), 2.48 (s, 2 H, HCα), 1.29 (s, 9 H, HCβ'), 0.95 (s, 9 H, HCγ).

3-Neopentylphenol (*m*-7f): δ 7.13 (t, 1 H, J = 8.0, ArH-5), 6.70 (d, 1 H, J = 8.0 Hz, ArH-4), 6.67 (d, 1 H, J = 8.0 Hz, ArH-6), 6.61 (s, 1 H, ArH-2), 4.75 (s, 1 H, OH), 2.44 (s, 2 H, HCα), 0.90 (s, 9 H, HCγ).

4-Neopentylphenol (*p*-7f): δ 6.92 (d, 2 H, J = 8.1 Hz, ArH-3,5), 6.71 (d, 2 H, J = 8.1 Hz, ArH-2,6), 2.33 (s, 2 H, HCα), 0.82 (s, 9 H, HCγ).

2-(3-Methyl-3-butenyl)phenol (*o*-7g): δ 7.12 (td, 1 H, J = 7.6 Hz, J = 1.5 Hz, ArH-5), 7.07 (dd, 1 H, J = 7.6 Hz, J = 1.5 Hz, ArH-3), 6.87 (td, 1 H, J = 7.6 Hz, J = 1.2 Hz, ArH-4), 6.76 (dd, 1 H, J = 7.6 Hz, J = 1.2 Hz, ArH-6), 4.79 (br s, 1 H, OH), 4.75 (br s, 2 H, HCδ), 2.76 (t, 2 H, J = 8.0 Hz, HCα), 2.32 (t, 2 H, J = 8.0 Hz, HCβ), 1.79 (br s, 3H, HCϵ).

3-(3-Methyl-3-butenyl)phenol (*m*-7g): δ 7.14 (td, 1 H, J = 7.6 Hz, J = 0.8 Hz, ArH-5), 6.77 (d, 1 H, J = 7.6 Hz, ArH-4), 6.68 (s, 1 H, ArH-2), 6.66 (d, 1 H, J = 7.6 Hz, ArH-6), 4.89 (br s, 1 H, OH), 4.74 (br s, 1 H, HCδ_a), 4.71 (br s, 1 H, HCδ_b), 2.70 (t, 2 H, J = 8.1 Hz, HCα), 2.30 (t, 2 H, J = 8.1 Hz, HCβ), 1.76 (br s, 3 H, J = 0.9 Hz, HCϵ).

4-(3-Methyl-3-butenyl)phenol (*p*-7g): δ 7.06 (d, 2 H, J = 8.6 Hz, ArH-3,5), 6.75 (d, 2 H, J = 8.6 Hz, ArH-2,6), 4.73 (br s, 1 H, OH), 4.70 (br s, 2 H, HCδ), 2.68 (t, 2 H, J = 8.1 Hz, HCα), 2.27 (t, 2 H, J = 8.1 Hz, HCβ), 1.76 (s, 3 H, HCϵ).

2-(3-Hydroxy-β-phenethyl)naphthalene (*m*-7i): δ 7.14 (t, 1 H, J = 7.6 Hz, PhH-5′), 6.78 (d, 1 H, J = 7.6 Hz, PhH-6′), 6.66 (s, 1 H, PhH-2′), 6.65 (d, 1 H, J = 7.6 Hz, PhH-4′), 7.77 (m, 2 H, NphH-5,8), 7.76 (d, 1 H, J = 8.4 Hz, NphH-4), 7.60 (s, 1 H, NphH-1), 7.43 (m, 2 H, NphH-6,7), 7.31 (dd, 1 H, J = 8.4 Hz, J = 1.7 Hz, NphH-3), 4.79 (s, 1 H, OH), 3.00 (m, 4 H, J = 11 Hz, J = 2.6 Hz, HCα,β).

2-[(Trimethylsilyl)methyl]phenol (*o*-7j): δ 6.97 (td, 1 H, J = 7.8 Hz, J = 1.8 Hz, ArH-5), 6.96 (d, 1 H, J = 7.3 Hz, ArH-3), 6.82 (td, 1 H, J = 7.3 Hz, J = 1.6 Hz, ArH-6), 6.73 (dd, 1 H, J = 7.8 Hz, J = 1.6 Hz, ArH-6), 4.49 (s, 1 H, OH), 2.06 (s, 2 H, HCα), 0.02 (s, 9 H, HCγ).

3-[(Trimethylsilyl)methyl]phenol (*m*-7j): δ 7.08 (t, 1 H, J = 7.8 Hz, ArH-5), 6.58 (d, 1 H, J = 7.8 Hz, ArH-4), 6.55 (d, 1 H, J = 7.8 Hz, ArH-6), 6.49 (s, 1 H, ArH-2), 4.80 (s, 1 H, OH), 2.04 (s, 2 H, HCα), 0.00 (s, 9 H, HCγ).

4-[(Trimethylsilyl)methyl]phenol (*p*-7j): 6.86 ($\sim$d, 2 H, J = 8.5 Hz, ArH-3,5), 6.70 ($\sim$d, 2 H, J = 8.5 Hz, ArH-2,6), 1.99 (s, 2 H, HCα), –0.02 (s, 9 H, HCγ).

2-[Bis(trimethylsilyl)methyl]phenol (20): δ 6.95 (td, 1 H, J = 7.5 Hz, J = 1.4 Hz, ArH-5), 6.90 (dd, 1 H, J = 7.5 Hz, J = 1.4 Hz, ArH-3), 6.81 (td, 1 H, J = 7.5 Hz, J = 1.4 Hz, ArH-4), 6.72 (dd, 1 H, J = 7.5 Hz, J = 1.4 Hz, ArH-6), 4.49 (s, 1 H, OH), 1.96 (s, 1 H, HCα), 0.04 (s, 18 H, HCγ).

3-[(Tributylstannyl)methyl]phenol (*m*-7k): δ 7.02 (t, 1 H, J = 7.7 Hz, ArH-5), 6.56 (d, 1 H, J = 7.7 Hz, ArH-4), 6.45 (s, 1 H, ArH-2), 6.45 (d, 1 H, J = 7.7 Hz, ArH-6), 4.58 (s, 1 H, OH), 2.25 (s, 2 H, HCα), 1.42 (m, 6 H, J = 6.9 Hz, HCγ), 1.26 (m, 12 H, J = 6.9 Hz, HCδ,ϵ), 0.87 (t, 9 H, J = 6.9 Hz, HCζ).

1,1,4,4-Tetramethyl-6,7-benzo-5-oxa-1,4-disila-6-cyclooctene (21): δ 6.97 (t, 1 H, J = 6.9 Hz, ArH-5), 6.96 (d, 1 H, J = 6.9 Hz, ArH-3), 6.87 (td, 1 H, J = 6.9 Hz, J = 1.4 Hz, ArH-4), 6.74 (dd, 1 H, J = 6.9 Hz, J = 1.4 Hz, ArH-6), 2.10 (s, 2 H, HCα), 0.63 (m, 4 H, HCγ,δ), 0.27 (s, 6 H, HCϵ), –0.03 (s, 6H, HCβ).

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Registry No. *3*-**5**, 95-48-7; *m*-**5**, 108-39-4; *p*-**5**, 106-44-5; *o*-**6**, 101144-86-9; *m*-**6**, 101144-87-0; *p*-**6**, 101144-88-1; *m*-**7a**, 620-17-7; *p*-**7b**, 645-56-7; *o*-**7c**, 136-81-2; *m*-**7c**, 20056-66-0; *p*-**7c**, 14938-35-3; *m*-**7d**, 10414-74-1; *o*-**7e**, 4167-75-3; *m*-**7e**, 30749-25-8; *p*-**7e**, 4167-74-2; *o*-**7f**, 16670-59-0; *m*-**7f**, 101144-99-4; *p*-**7f**, 2316-92-9; *o*-**7g**, 18272-65-6; *m*-**7g**, 82615-37-0; *p*-**7g**, 18272-69-0; *m*-**7h**, 33675-75-1; *m*-**7i**, 101145-00-0; *o*-**7j**, 101145-01-1; *m*-**7j**, 101145-03-3; *p*-**7j**, 101224-30-0; *m*-**7k**, 101145-05-5; *m*-**7l**, 621-37-4; *o*-**8**, 1875-21-4; *p*-**8**, 6052-84-2; *m*-**8**, 70709-67-0; *o*-**9a**, 14804-32-1; *m*-**9a**, 10568-38-4; *p*-**9a**, 1515-95-3; *o*-**9b**, 101144-90-5; *m*-**9b**, 101144-93-8; *p*-**9b**, 101144-94-9; *p*-**9c**, 101144-97-2; *o*-**10a**, 578-58-5; *m*-**10a**, 100-84-5; *p*-**10a**, 104-93-8; *o*-**10b**, 614-71-1; *m*-**10b**, 621-32-9; *p*-**10b**, 622-60-6; **11a**, 101144-89-2; **11b**, 101144-91-6; **12b**, 101144-92-7; **13a**, 21573-35-3; **14a**, 6738-23-4; **14b**, 101144-95-0; **14c**, 30090-82-5; **15**, 79744-81-3; **16**, 101144-96-1; **17**, 101144-98-3; **18**, 6891-45-8; **19**, 38696-17-2; **20**, 101145-02-2; **21**, 101145-04-4; Me$_2$SO$_4$, 77-78-1; Et$_2$SO$_4$, 64-67-5; MeI, 74-88-4; BuBr, 109-65-9; MeCH(Me)(CH$_2$)$_2$Br, 107-82-4; *i*-PrBr, 75-26-3; *t*-BuI, 558-17-8; *t*-BuBr, 507-19-7; I$_2$, 7553-56-2; BrCH$_2$CH$_2$Br, 106-93-4; CuBr, 7787-70-4; H$_2$C=C(Me)CH$_2$Cl, 563-47-3; C$_6$H$_5$CH$_2$Cl, 100-44-7; Me$_3$SiCl, 75-77-4; Me$_2$Si(Cl)C=CSi(Cl)Me$_2$, 18146-12-8; Bu$_3$SnCl, 1461-22-9; CO$_2$, 124-38-9; β-naphthylcarbinyl bromide, 101145-06-6.