Electronic and Steric Effects in the Dienone–Phenol Rearrangement of 2-Hydroxy- and 2-Alkoxycyclohexa-2,5-dien-1-ones

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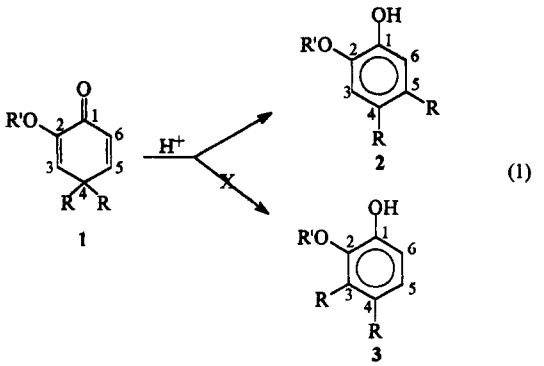
A series of 4,4,6-trisubstituted-2-hydroxy- and -2-alkoxycyclohexa-2,5-dien-1-ones (**7** and **8**) were prepared, where the substituent at C-6 was H, CH_3, Ph, *tert*-butyl, or OEt. In the acid-catalyzed dienone–phenol rearrangement of **7** and **8**, the C-4 substituent migrates regioselectively to C-5, completely shunning the enol double bond, even though the substituents at C-6 are substantially larger than the OH or OMe groups situated at C-2. The C-5 regioselectivity in hydroxy dienones **7a–f** and **8a,b**, as well as the decreased rate of reaction in the case of dienone **7g**, can be simply rationalized by considering the relative electron density at C-3 vs C-5 in the protonated form of **7** or **8**. Our results clearly indicate that the regioselectivity of the dienone–phenol rearrangement in these enolic systems is completely controlled by the electronic factors, which far outweigh any steric considerations.

Introduction

Ever since its first report over 60 years ago,[1] the acid-catalyzed "dienone–phenol rearrangement"[2] has been extensively studied and reviewed.[3] Relatively speaking, the corresponding rearrangement of 4,4-disubstituted-2-hydroxy- and -2-alkoxycyclohexa-2,5-dien-1-ones (**1** in eq 1; R′ = H and R, respectively) has received only limited attention.[4] In these α-keto enols and enol ethers, the C-4 substituent migrates almost exclusively to C-5;[5] migration to C-3 is observed only when C-5 is already substituted. It is not clear, however, whether this overwhelming preference for C-5 results from steric or electronic considerations.



(1)

Our recent studies on the base-catalyzed autoxidation (BCA) of 2-cyclohexen-1-ones in aprotic media[6,7] have allowed us facile access to 4,4,6-trisubstituted-2-hydroxy- and -2-alkoxycyclohexa-2,5-dien-1-ones (**7** and **8**, respectively, in eq 2).[6e] In these systems, the preferred C-5 migration should find itself in conflict with steric hindrance imposed by the C-6 substituent. These systems should, therefore, allow us to evaluate the relative importance of steric and electronic factors in controlling the acid-catalyzed dienone–phenol rearrangement of α-keto enols and enol ethers.

Results and Discussion

For the purpose of this study, dienones **7a**, **7c–g**, and **8a** were synthesized as previously described.[6e] Equation

• Abstract published in *Advance ACS Abstracts*, March 1, 1994.

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(5) We have been able to find only one exception to this "C-5 migration rule" in the rearrangement of 2-hydroxy-2,5-cyclohexadienones to catechols.[5a] Battersby and co-workers[5b,5c] report an example of a C-3 migration in the related dienol–benzene rearrangement, but indicate that prior allylic isomerization is likely to be involved.[5c] (a) Jackson, A. H.; Martin, J. A. *J. Chem. Soc.* **1966** (C), 2222–2229. (b) Battersby, A. R.; Brown, T. H. *Proc. Chem. Soc.* **1964**, 85–86. (c) Battersby, A. R.; Brocksom, T. J.; Ramage, R. *J. Chem. Soc. Chem. Commun.* **1969**, 464–465.

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(7) An extensive review of the oxygenation (including free radical autoxidation, BCA, singlet oxygenation and O_2^- mediated oxidations) of enones and related enols and enolates has recently appeared; see Frimer, A. A. In *The Chemistry of Enones*—Part 2; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 781–921.

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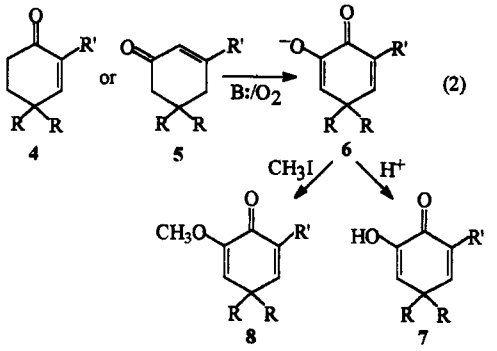
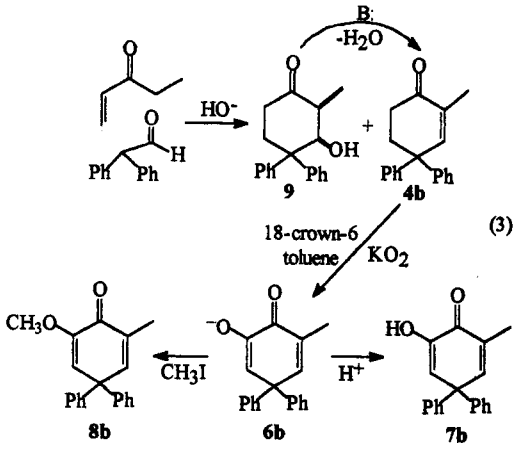


a: R=Ph; R'=H
b: R=Ph; R'=CH_3
c: R=CH_3; R'=H
d: R=R'=CH_3
e: R=CH_3; R'=Ph
f: R=CH_3; R'=t-Bu
g: R=CH_3; R'=OEt

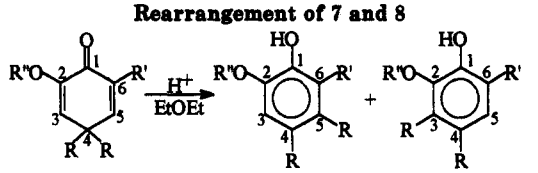
3 outlines the synthetic route to analogs **7b** and **8b**. The condensation of ethyl vinyl ketone with diphenylacetaldehyde, according to the procedure of Newman,[8] yielded a 3:2 mixture of the β-hydroxy ketone **9** and it's dehydration product enone **4b**.[9] [We note in passing that the small ^1H NMR coupling constant for the H-2 and H-3 hydrogens ($J_{2ax,3eq}$ = 2.5 Hz) of β-hydroxy ketone **9** indicates that the C-2 methyl and C-3 hydroxyl group are cis to each other]. It was unnecessary to separate this mixture since both components undergo superoxide-mediated BCA yielding enolate **6b**. Either **7b** or **8b** could be conveniently obtained



in high yield (95%) from this enolate, depending on whether an aqueous or methyl iodide workup of the BCA reaction is used.

As shown in Table 1, 2-hydroxy dienones **7** and methoxy analogs **8** undergo facile acid-catalyzed dienone–phenol rearrangement. With the exception of **7g**, only a single product was formed in each case and, based on their spectral data, these were identified as catechols **10** or guiaicols **11**, as follows. Phenols **10c**,[10] **10d**,[4n,11] **10e**,[12] and **11a**[4m] are known. All the products show a 1H aromatic

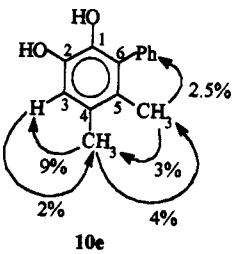
Table 1. Product Yields in the Dienone–Phenol Rearrangement of 7 and 8



substrate	rxn conditions	time	product (% yield)[c]
7a (R = Ph; R' = H)	*a*	16 h	**10a** (90)
8a (R = Ph; R' = H)	*a*	16 h	**11a** (63)
7b (R = Ph; R' = CH_3)	*a*	29 h	**10b** (92)
8b (R = Ph; R' = CH_3)	*a*	29 h	**11b** (62)
7c (R = CH_3; R' = H)	*a*	16 h	**10c** (65)
7d (R = R' = CH_3)	*a*	16 h	**10d** (95)
7e (R = CH_3; R' = Ph)	*a*	7 d	**10e** (81)
7f (R = CH_3; R' = t-Bu)	*b*	1 h	**10c** (95)[d]
7g (R = CH_3; R' = OEt)	*b*	6 h	**10g** (13), **12g** (87)[e]

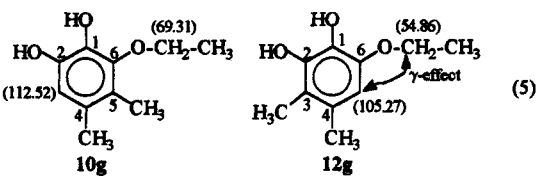
[a] Concentrated HCl (30% by volume) in ether. [b] Concentrated H_2SO_4 (15% by volume) in ether. HCl did not effect rearrangement. [c] Unoptimized isolated yields. The products isolated are the only ones observed by NMR in the crude product mixture. [d] After 0.3 h, **7f** (88%), **10c** (12%). [e] 76% Conversion.

singlet shifted upfield of benzene; this corresponds well to H-3 in **10** and **11** which is expected to be shifted upfield from benzene by the *o*-hydroxy or -alkoxy group.[13] The number of ^{13}C absorptions observed for symmetrical compounds **10a** (seven) and **10c** (four) is substantially lower than could possibly be expected for the unsymmetrical isomers **12a** and **12c**. **10e** was conclusively identified via NOE experiments, whose results are graphically outlined below (eq 4).



(4)

In the case of **7g**, two products, assigned the structures **10g** and **12g**, were obtained in a ratio of 13:87, respectively. This assignment is consistent with the γ-effect observed between C-5 and the ethoxy methylene carbon in the major isomer **12g**, which results in a substantial upfield shift of both these carbons (see eq 5). This phenomenon has been well documented in substituted phenols and anisoles.[14]



(5)

(8) (a) Newman, M. S. *An Advanced Organic Laboratory Course*; Macmillan: New York, 1972; p 181. (b) Zimmerman, H. E.; Keese, R.; Nasulski, J.; Swenton, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 4895–4904; at 4902.

(9) Enone **4b** is known, but no synthetic or spectral data has been reported: Lee, H. S.; Namgung, K. S.; Sung, J. K.; Chae, W. K. *Bull. Korean Chem. Soc.* **1991**, *12*, 247–249.

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(11) Joe, Y. A., Goo, Y. M.; Lee, Y. Y. *Bull. Korean Chem. Soc.* **1991**, *12*, 253–254.

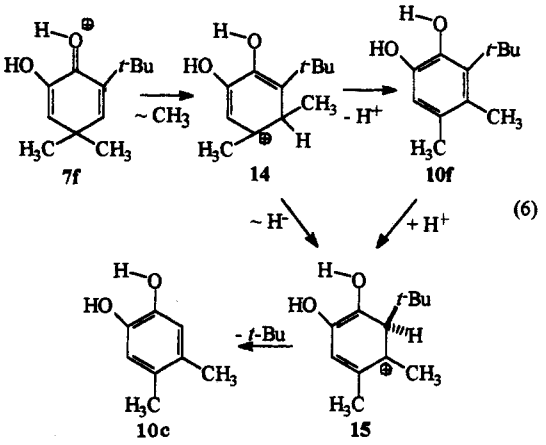
(12) (a) Bruce, J. M.; Suteliffe, K. K. *J. Chem. Soc.* **1956**, 3824–3829. (b) The 60-MHz NMR spectrum for the veratrole (dimethoxy) analog has been reported: Allen, G.; Bruce, J. M. *J. Chem. Soc.* **1963**, 1757–1759.

(13) (a) Thus, H-5 (*ortho* to the methyl) and H-6 (*ortho* to the hydroxy) of 4-methylcatechol absorb ca. 7.2 and 6.85 ppm, respectively.[13b-d] (b) Mohindra Chawla, H.; Sharma, S. K.; Chakrabarty, K.; Bhanumati, S. *Tetrahedron* **1988**, 1227–1234. (c) Cambie, R. C.; Janssen, S. J.; Rutledge, P. S.; Woodgate, P. D. *J. Org. Chem.* **1991**, *420*, 387–418. (d) Richards, T. I.; Layden, K.; Warminski, E. E.; Milburn, P. J.; Haslam, E. *J. Chem. Soc. Perkin Trans. 1* **1987**, 2765–2773.

(14) Gottlieb, H. E., Ph.D. Dissertation, Indiana University, Bloomington, IN, 1975.

Having identified the products, we turn to the regioselectivity of this reaction. We note that, as before,[4] the C-4 substituent in these 2-hydroxy-2,5-cyclohexadienone systems migrates regioselectively to C-5, completely shunning the enol double bond. But what is truly noteworthy is that this C-5 migration occurs despite substituents at C-6 which are substantially larger[15] than the OH or OMe groups situated at C-2. Indeed, when the C-6 substituent is the bulky phenyl group (**7e**), the rate of reaction slows from a single day to a week; yet, only C-5 migration is observed. Only in the case of **7g**, where *both* C-2 and C-6 bear oxy groups, is migration to an enol double bond observed. However, in the latter case, the system is very deactivated and only the more acidic conditions (15% concd H_2SO_4) succeeded in effecting rearrangement.

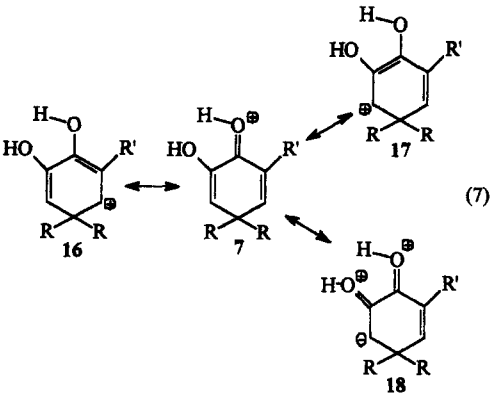
This aforementioned exclusive C-5 migration is, in fact, related to the surprising result observed when the C-6 substituent is the extremely bulky *tert*-butyl group (**7f**). Here, no reaction occurs unless stronger acid (15% concd H_2SO_4) is utilized, and, under such conditions, the *tert*-butyl group is eliminated with the concomitant formation of **10c**. (No intermediate products are detected during the course of the reaction.) Such de-*tert*-butylation has already been observed by Miller[16] in his studies on the dienone–phenol rearrangement of 2,6-di-*tert*-butylcyclohexadienones. According to the mechanism proposed by these workers (eq 6), initial C-5 migration of the C_4-methyl



(6)

group of **7f** yields **10f**. However, the steric crowding between the *o*-*tert*-butyl and *m*-methyl groups, both lying in the plane of the ring, induces rapid reprotonation of **10f** at the *ortho* position to give carbonium ion **15**, thereby moving the *tert*-butyl group out of plane. Subsequent, de-*tert*-butylation yields the observed **10c**. (It is also possible that the initially formed carbonium ion **14** undergoes hydride rearrangement directly to isomer **15**.)

The C-5 regioselectivity in hydroxy dienones **7a–f** and **8a,b** as well as the decreased rate of reaction in the case of dienone **7g** can be simply rationalized by considering the electron density at C-3 vs C-5 in the protonated form of **7** or **8** (see eq 7).[4k] It should be clear that while the protonated carbonyl induces a partial positive charge at both carbons, represented by resonance structures **16** and



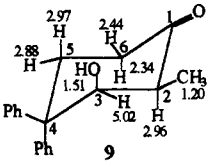
(7)

17, the overall charge at C-5 is neutralized to a large extent by the electron donation of the enolic moiety, as shown in structure **18**. These resonance effects upon electron density are already evident in the ^{13}C NMR spectrum of the unprotonated hydroxy dienones **7**.[6e] Thus, while C-5 resonates downfield at ca. 155 ppm, C-3 absorbs at ca. 125 ppm, slightly *upfield* of benzene (128.5 ppm). Since it is the positive character of C-3 or C-5 that induces this rearrangement, it is their relative sizes that control the overall regioselectivity. Our results clearly indicate that the regioselectivity of the dienone–phenol rearrangement in these enolic systems is completely controlled by the electronic factors, which far outweigh any steric considerations.

Experimental Section

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained on a Bruker AM 300 Fourier transform spectrometer. Assignments (see supplementary material) were facilitated by correlating proton and carbon chemical shifts through analysis of residual couplings in off-resonance decoupled spectra. In all cases, TMS served as the internal standard. EI and CI mass spectra were run on a Finnigan-4000 GC/MS machine, except where exact mass data is given. In the latter instance, the EI data reported is based on the high-resolution mass spectra (HRMS), performed by the Mass Spectroscopy Center at the Technion, Haifa. UV-visible spectra were taken with a Varian DMS-100 spectrometer. Analytical thin-layer chromatography (TLC) was performed using Riedel-De Haen silica gel microcards. Preparative runs (PTLC) were carried out on Merck silica gel F_{254} precoated plates, and the products were extracted from the silica by stirring overnight in a solution of 10% CH_3OH in $CHCl_3$. The retention times (R_f) given are for the analytical runs. Dienones **7a, 7c–f**, and **8a** were synthesized as previously described.[6e] The preparation of **7g** was modified as described below.

2-Methyl-4,4-diphenylcyclohex-2-en-1-one (4b) and 3-Hydroxy-2-methyl-4,4-diphenylcyclohexane (9). The condensation of ethyl vinyl ketone (Aldrich) with diphenylacetaldehyde (Aldrich), according to the procedure of Newman,[8] gave a 70% yield of a 3:2 mixture of the β-hydroxy ketone **9** and it's dehydration product enone **4b**.[9] The reaction mixture was suitable for the preparation of **7b** and **8b**, as described below. For the purpose of analysis, however, the products were separated by silica column chromatography. Eluting with 5% ethyl acetate in hexane a small amount of benzophenone came off followed by **4b**. In order to obtain the more polar but only weakly fluorescent **9**, the solvent ratio was then gradually increased to 1:1. The ^1H NMR data suggests the following structure for **9**:



(15) The relative steric size of a substituent can be evaluated by placing it on a cyclohexane ring and measuring the free-energy differences ($-\Delta G°$) between equatorial and axial substitution. Based on this, the decreasing order of steric size (and the corresponding approximate $-\Delta G°$ values in kcal/mol) for the substituents involved in the present study are: OMe (0.75) > OH (0.95) > Me (1.74) > Ph (2.9) > t-Bu (>4). See March, J. *Advanced Organic Chemistry—Reactions, Mechanisms and Structure*, 3rd ed.; McGraw-Hill: New York, 1985; Table 2, p 126 and references cited therein.

4b: mp (acetone/hexane) 117–118 °C; R_f (15% acetone in hexane) 0.28; ^{1}H NMR ($CDCl_3$) δ 7.38–7.20 (m, 10H), 7.06 (dd, J = 1.5 and 0.5 Hz, 1H), 2.68 (dt, J = 7 and 0.5 Hz; additional AA'XX' splitting, 2H), 2.40 (t, J = 7 Hz; additional AA'XX' splitting, 2H), 1.92 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 199.14, 151.47, 146.06, 135.04, 128.48, 127.69, 126.68, 49.58, 35.98, 34.91; UV ($CHCl_3$) λ_{max} (ϵ_{max}) = 237.2 (3740) nm; HRMS calcd ($C_{19}H_{18}O$, M^+) 262.1357, obsd 262.1355. Anal. Calcd ($C_{19}H_{18}O$): C, 86.98%; H, 6.91%. Found: C, 87.02%; H, 7.01%.

9: mp (acetone/hexane) 180–181 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 and 7.35 (m, 4H), 7.37 and 7.28 (m, 4H), 7.23, 7.16 (m, 2H), 5.02 (ddd, J = 2.5, 2.3 and 2.2 Hz, 1H), 2.97 (ddd, J = 13.7, 13.4, and 4.5 Hz, 1H), 2.96 (dddq, J = 6.9, 2.5, 1.7, and 1.0 Hz, 1H), 2.88 (dddd, J = 13.7, 5.7, 3.0, and 2.2 Hz, 1H), 2.44 (ddd, J = 14.5, 4.5, and 3.0 Hz, 1H), 2.34 (dddd, J = 14.5, 13.4, 5.7, and 1.0 Hz, 1H), 1.51 (dd, J = 2.3 and 1.7 Hz, 1H), 1.20 (d, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 210.55, 145.03, 143.54, 129.06, 128.83, 126.72, 126.65, 126.65, 126.54, 79.78, 51.04, 45.88, 38.12, 29.17, 11.31; MS (CI, ammonia) 298 (MNH_4^+, 100%), 281 (MH^+, 5.13%). Anal. Calcd ($C_{19}H_{20}O_2$): C, 81.39%; H, 7.19%. Found: C, 81.17%; H, 7.28%.

2-Hydroxy-6-methyl-4,4-diphenylcyclohexane (7b) and 2-Methoxy-6-methyl-4,4-diphenylcyclohexane (8b). The title compounds were prepared in 90–95% yield via the superoxide-mediated base-catalyzed autoxidation of the above **4b**/**9** reaction mixture, under the same reaction and workup conditions as described previously for the preparation of **7a** and **8a**, respectively, from **4a**.[6e] The products were purified by recrystallization, though analytical samples were first chromatographed by PTLC.

7b: mp (benzene/petroleum ether or acetone/hexane) 152–153 °C; R_f (15% acetone in hexane) 0.15; ^{1}H NMR ($CDCl_3$) δ 7.40–7.10 (m, 10H), 6.49 (d, J = 3 Hz, 1H), 6.42 (s, 1H), 2.02 (d, J = 3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 182.50, 152.21, 145.17, 143.09, 131.34, 128.78, 127.80, 127.46, 122.79, 53.51, 15.74; FTIR (KBr) 1639.9 (s, CO) cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ_{max}) = 243.0 (8,730), 237.7 (8,840) nm. Anal. Calcd ($C_{19}H_{16}O_2$): C, 82.58%; H, 5.84%. Found: C, 82.34%; H, 5.92%.

8b: mp (benzene/petroleum ether or acetone/hexane) 167–168 °C; R_f (15% acetone in hexane) 0.22; ^{1}H NMR ($CDCl_3$) δ 7.38–7.20 (m, 10H), 7.06 (dd, J = 3 and 1.5 Hz, 1H), 6.33 (d, J = 3 Hz, 1H), 3.71 (s, 3H), 2.00 (d, J = 1.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 181.59, 149.56, 149.24, 143.64, 133.27, 128.77, 127.73, 127.38, 121.19, 55.10, 53.36, 16.17; FTIR (KBr) 1656.6 (s, CO) cm^{-1}; UV ($CHCl_3$) λ_{max} (ϵ_{max}) = 249.0 (12,560), 239.8 (12,440) nm; HRMS calcd ($C_{20}H_{18}O_2$, M^+, 100%) 290.1289, obsd 290.1298. Anal. Calcd ($C_{20}H_{18}O_2$): C, 82.73%; H, 6.24%. Found: C, 82.59%; H, 6.25%.

2-Hydroxy-6-ethoxy-4,4-dimethylcyclohexane (7g). Enol **7g** was prepared from enone **5g** via the KOH-mediated base-catalyzed autoxidation as previously described[6e] with the following modifications. The reactants ratio (ratio of substrate:crown:KOH) was 1:4:8. The reaction vessel, containing all the reaction components except for the KOH, was flushed with argon for 0.5 h. KOH was then added against argon, the reaction vessel was topped with a drying tube, and the reaction was allowed to stir overnight at room temperature. The slow diffusion of molecular oxygen into the reaction vessel that results raises the conversion to almost 100% and improves the yield to over 90%, with no observable lactol formation.

General Rearrangement Procedure for 7a–f and 8a,b. A 10-mL round-bottom flask was fitted with a magnetic stirrer and charged with hydroxy dienone **7** or **8** (0.7 mmol), ether (5 mL), and concd HCl (2 mL) or H_2SO_4 (1 mL). The reaction mixture was stirred for the time shown in Table 1, neutralized with a saturated $NaHCO_3$ solution, washed with water, and finally dried over $MgSO_4$. Analytical samples were purified twice by PTLC followed by recrystallization from acetone/hexane to give white crystals. Samples must be dried thoroughly just prior to elemental analysis. As a general rule the rearranged phenols **10** and **11** have longer TLC retention times than do the corresponding dienones **7** and **8**, with the notable exception of **10b** which actually runs above **7b**. The catechols **10** and guiaicols **11** autoxidize slowly and were, therefore stored in the freezer under nitrogen. Compounds **11a**,[4m] **10c**,[10] **10d**,[4n,11] and **10e**[12] are known; nevertheless, the 300-MHz NMR data is given for the known compounds **11a** and **10e**[12] because the earlier 60-MHz data is incomplete, inaccurate, or lacking.

10a: mp (acetone/hexane) 142–143 °C; R_f (35% acetone in hexane) 0.33; ^{1}H NMR ($CDCl_3$) δ 7.24–7.13 (m, 6H), 7.13–7.08 (m, 4H), 6.95 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 142.73, 141.01, 133.78, 129.86, 127.76, 126.19, 117.56; UV ($CHCl_3$) λ_{max} (ϵ_{max}) = 255.4 (10080) nm; HRMS calcd ($C_{18}H_{14}O_2$, M^+, 100%) 262.0994, obsd 262.1029. Anal. Calcd ($C_{18}H_{14}O_2$): C, 82.42%; H, 5.37%. Found: C, 82.24%; H, 5.41%.

11a: mp (acetone/hexane) 149–150 °C (lit.[4m] 148–152 °C); ^{1}H NMR ($CDCl_3$) δ 7.03 (s, 1H), 7.15 (m, 10H), 6.92 (s, 1H), 5.64 (s, 1H), 3.95 (s, 3H) [lit.[4m] (CCl_4) 7.13, 6.95, 6.82 and 3.98]; ^{13}C NMR ($CDCl_3$) δ 145.72, 144.81, 141.56, 141.07, 133.81, 132.61, 129.93, 129.90, 127.81, 127.73, 126.14, 116.60, 113.00, 56.11; MS (CI, 70 ev) 277 (MH^+, 100%).

10b: mp (acetone/hexane) 147–148 °C; R_f (25% acetone in hexane) 0.24; ^{1}H NMR ($CDCl_3$) δ 7.23–6.95 (m, 10H), 6.81 (s, 1H), 5.28 (bs, 2H), 2.07 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 141.77, 141.69, 141.40, 139.98, 134.22, 134.03, 130.96, 129.82,, 127.59, 127.36, 126.17, 125.78, 123.12, 114.24, 13.65; UV ($CHCl_3$) λ_{max} (ϵ_{max}) = 242.7 (12,880) nm; HRMS calcd ($C_{19}H_{16}O_2$, M^+, 100%) 276.1150, obsd 276.1158. Anal. Calcd ($C_{19}H_{16}O_2$): C, 82.58%; H, 5.83%. Found: C, 82.41%; H, 5.84%.

11b: mp (acetone/hexane) 125–126 °C; R_f (15% acetone in hexane) 0.23; ^{1}H NMR ($CDCl_3$) δ 7.23–6.98 (m, 10H), 6.80 (s, 1H), 5.81 (s, 1H), 3.95 (s, 3H), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 145.05, 143.00, 142.28, 140.06, 134.31, 133.00, 130.99 129.95, 127.48, 127.58, 126.14 125.77, 122.65, 109.08, 56.05, 13.55; UV ($CHCl_3$) λ_{max} (ϵ_{max}) = 247.4 (16200) nm; HRMS calcd ($C_{20}H_{18}O_2$, M^+, 100%) 290.1307, obsd 290.1316. Anal. Calcd ($C_{20}H_{18}O_2$): C, 82.73%; H, 6.24%. Found: C, 82.71%; H, 6.28%.

10e: mp (benzene) 169–170 °C (lit.[12] 171.5–172.5 °C); R_f (15% acetone in hexane) 0.10; ^{1}H NMR[12b] ($CDCl_3$) δ 7.58–7.38 (m, 3H), 7.32–7.24 (m, 2H), 6.73 (s, 1H), 2.23 (s, 1H), 1.89 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 141.47, 137.95, 136.06, 130.21, 129.30, 128.95, 128.54, 128.01, 125.99, 115.96, 19.89, 16.36; HRMS calcd ($C_{14}H_{14}O_2$, M^+, 100%) 214.0994, obsd 214.1008. Anal. Calcd ($C_{14}H_{14}O_2$): C, 78.47%; H, 6.58%. Found: C, 78.18%; H, 6.51%.

Rearrangement of 7g. The rearrangement was carried out as described above for compounds **7a–f**. The reaction did not go to completion (50–76% conversion), however, and attempts to increase the sulfuric acid concentration and/or the reaction time resulted in extensive charring and a sharp reduction in yield. Following the standard workup, the products were separated on a silica column eluting with 25% ethyl acetate in hexane. The major product, identified as **12g**, eluted first and was obtained relatively pure. The minor product **10g**, on the other hand, came off the column together with the starting material **7g**. Since the spectral data of **7g** have been fully characterized,[6e] the NMR data for **10g** could be readily extracted from this mixture. A small sample containing only **10g** and **12g** had essentially the mass spectral data (EI and CI, parent peak 100%) as the latter product alone.

10g: ^{1}H NMR ($CDCl_3$) δ 6.53 (s, 1H), 3.93 (q, J = 7 Hz, 2H), 2.14 (s, 3H), 2.09 (s, 3H), 1.40 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 144.73, 141.76, 134.37, 128.65, 120.80, 112.52, 69.31, 19.49, 15.73, 12.15).

12g: mp (petroleum ether) 43–44 °C; R_f (25% acetone in hexane) 0.37; ^{1}H NMR ($CDCl_3$) δ 6.3 (s, 1H), 5.39 (s, 1H), 5.31 (s, 1H), 4.06 (q, J = 7 Hz, 2H), 2.18 (s, 3H), 2.10 (s, 3H), 1.40 (t, J = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 143.32, 142.11, 130.36, 127.87, 115.77, 105.27, 54.86, 19.73, 15.01, 11.12; HRMS calcd ($C_{10}H_{14}O_3$, M^+, 100%) 182.0943, obsd 182.0947.

Supplementary Material Available: The ^{13}C NMR spectra of **10g** (mixture with **7g**) and **12g** and the complete ^{1}H and ^{13}C NMR peak assignments for the compounds described in the Experimental Section (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(16) (a) Miller, B. *J. Am. Chem. Soc.* **1965**, *87*, 5106–5111 and references cited therein. (b) *Ibid.* 5111–5120.