Formation of a Novel Sulfonated Enedione

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Soft nucleophiles typically add to *p*-benzoquinones at an unsubstituted alkene carbon, yielding a substituted hydroquinone (**1**) as the principal product (Scheme 1).[1,2]

The product of addition to the substituted carbon, an enedione **2**, is typically not isolated, presumably due to the fact that the addition step is reversible. Under thermodynamic control the aromatic addition product **1** naturally dominates the product distribution. Addition of sulfinic acids to benzoquinones is a well known reaction[3] that has been historically useful in the synthesis of sulfonyl substituted hydroquinones and as a preventative of developer stain in photographic systems.[4,5] Due to the electron-withdrawing nature of the sulfone group, sulfonated hydroquinones are less easily oxidized to quinones.[6]

As expected, we observed that addition of *p*-toluenesulfinic acid to norbornene-derived quinone **3** gave the expected hydroquinone **4** in 64% yield (Scheme 2).

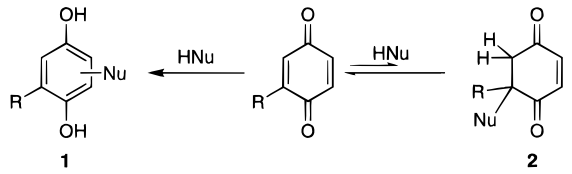
In contrast, when norbornadiene-derived quinone **5** was exposed to the same conditions, two products were isolated. They were separated by flash chromatography and shown to be of the same mass, $m/z = 405$ daltons. The higher R_f species was identified by IR and NMR spectroscopy as the expected tosyl-substituted hydroquinone **6**.

The second product **7** possessed spectroscopic and chemical characteristics inconsistent with a hydroquinone: a strong C=O stretch at 1690 cm^{-1}, the absence of an O−H stretch, and lack of reactivity toward aqueous NaOCl.[7] ^{1}H NMR confirmed that the norbornene double bond and α-carbonyl methine proton in **5** remained intact in **7**. Regeneration of **5** upon treatment of **7** with triethylamine in chloroform confirmed that addition of sulfinate had taken place at the ring fusion, giving one of 4 possible enedione isomers. Assignment of the norbornene ring protons was possible by examination of the 2-D COSY ^{1}H NMR spectrum. The strong differentiation of the two apical protons in **7** compared to **5** suggested that the substitution took place on the *exo* face of **5**. Consistent with this proposal, facile intramolecular [2 + 2] photochemical cycloaddition of **7** occurred in excellent yield to give **8**[8] (Scheme 3).

COSY ^{1}H NMR spectroscopy of **8** indicated 2,6-substitution[9] of the phenyl and tosyl groups in the starting enedione **7**. X-ray crystallographic analysis of **7** provided final confirmation of the structure.

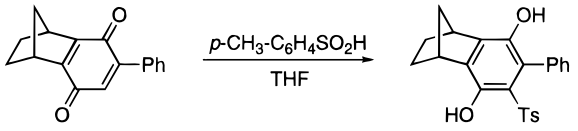
We have found that the conditions of the addition reaction can be varied to favor either **6** or **7**. Reacting sodium *p*-toluenesulfinate heptahydrate in acetic acid resulted in a 2.5:1 ratio of **6** to **7**, with an overall yield of 68%. The yield of **7** can be maximized if the reaction is

Scheme 1

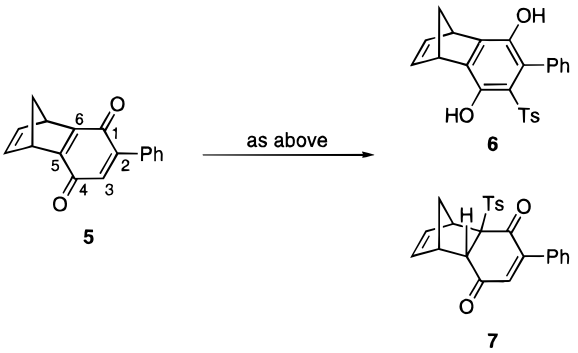


1 **2**

Scheme 2

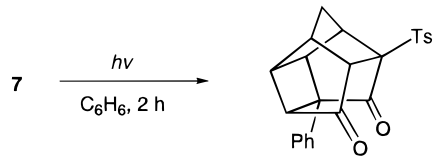


3 **4**



5 **6** **7**

Scheme 3



8(100%)

(1) (a) *Rodd's Chemistry of Carbon Compounds*; Coffey, S., Ed.; Elsevier: Amsterdam, 1974; Vol. 3, pt. B, pp 36−116. (b) *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; Wiley Interscience: New York, 1974; Part 2, pp 880−949.

(2) Redox equilibria may sometimes complicate the reaction, giving the reduced starting quinone, the substituted quinone, and products of multiple substitution/oxidation. Youngblood, M. *J. Org. Chem.* **1986**, *51*, 1981.

(3) (a) Ogata, Y.; Sawaki, Y.; Isono, M. *Tetrahedron* **1969**, *25*, 2715. (b) Ogata, Y.; Sawaki, Y.; Isono, M. *Tetrahedron* **1970**, *26*, 731.

(4) (a) Takahashi, O.; Furutacho, N.; Morigaki, M., Fuji Photo Film Co., Ltd. Eur. Patent Appl. EP 305926, Mar. 8, 1989. (b) Morigaki, M.; Ishikawa, T.; Andoh, K.; Seto, N.; Ueda, S.; Koshimizu, T., Fuji Photo Film Co., Ltd. Eur. Patent Appl. EP 294769, Dec 14, 1988.

(5) In photographic systems sulfinate anion performs the same function as sulfite which has long been used as a preservative of developer solutions and a stain preventative. Sulfite both retards aerial oxidation and adds nucleophilically to quinones to form colorless hydroquinone mono- and disulfonates rather than highly colored products. For a brief discussion of the use of sulfite in developing solutions, see the following reference: *The Theory of the Photographic Process*, 4th ed.; James, T. H., Ed.; Macmillan: New York, London, 1977; pp 309−310.

(6) Brown, E. R.; Finley, K. T.; Reeves, R. L. *J. Org. Chem.* **1971**, *36*, 2849.

(7) NaOCl is a convenient oxidant for hydroquinones: Ishii, F.; Kishi, K. *Synthesis* **1980**, *9*, 706−8.

(8) The [2 + 2] photocyclization reaction of the parent cyclopentadiene−benzoquinone adduct (1,4,4a,8a-tetrahydro-*endo*-1,4-methanonaphthalene-5,8-dione) to pentacyclo[5.4.0.0$^{2,6.03,10.05,9}$]-undecane-8,-11-dione is well known: (a) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3062. (b) Marchand, A.; Allen, R. *J. Org. Chem.* **1974**, *39*, 1596. (c) Galin, F. Z.; Afonichev, D. D.; Lerman, B. M.; Kazakov, V. P.; Tolstikov, G. A. *Zh. Org. Khim.* **1978**, *14*, 2308.

(9) The carbon numbering system of **5** in Scheme 2 is designed to facilitate the following discussion; the standard IUPAC numbering for **5** and related derivatives is used in the Experimental Section.

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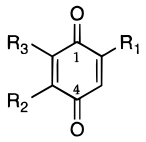
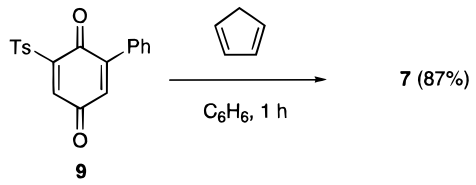
Table 1. AM1 Calculated Heats of Formation of Protonated Quinones (kcal mol^{-1})



quinone	R_1	R_2, R_3	protonated at C-1 CO ΔH_f	protonated at C-4 CO ΔH_f	$\Delta\Delta H_f$
5	Ph	cyclopentene-3,5-diyl	226.95	221.52	5.43
10	Ph	H	177.37	169.09	8.28
11	Me	H	144.05	139.96	4.09

Scheme 4



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carried out in THF with dry *p*-toluenesulfinic acid; under these conditions a 1:7.3 ratio of **6** to **7** is obtained, with an overall yield of 67%. HPLC and ^{1}H NMR analysis confirm that only the enedione diastereomer represented by structure **7** is formed. An alternate synthesis was developed that also serves as an additional proof of the structure of **7**: Diels−Alder reaction of 2-phenyl-6-tosyl-1,4-benzoquinone (**9**) with cyclopentadiene afforded **7** as the sole product in 87% yield (Scheme 4).

We propose that formation of the enedione product **7** is favored due to relief of strain during attack at the ring fused carbon. Presumably this relief of strain renders the nucleophilic addition step less reversible, ultimately enabling isolation of **7**. Wiberg has estimated that norbornadiene undergoes release of 10 kcal mol^{-1} of strain energy upon saturation of one double bond.[10] Furthermore, on the basis of heat of hydrogenation data for the first and second double bonds of norbornadiene[11] it can be shown that norbornene releases 2.2 kcal mol^{-1} less strain energy than norbornadiene upon saturation of a double bond. This difference in the amount of strain energy released may help explain the absence of enedione product in the reaction of quinone **3**.

The formation of a single enedione diastereomer **7** is intriguing and can be rationalized in the following way. Preferential attack of the sulfinate on the exo-face of **5** is expected on steric grounds. A possible explanation for the regiochemical preference for addition at the 6-position rather than at 5-position can be found in the work of Ogata, who demonstrated that addition of sulfinate anion to *p*-benzoquinone in aqueous acid occurs via general acid catalysis.[3a] If the reaction also proceeds under acid catalysis in THF, presumably the most basic quinone oxygen of **5** would be protonated preferentially, thereby activating addition at the ring-fused carbon β to it. The C-4 carbonyl in quinone **5** should be substantially more basic because the incipient oxonium ion is stabilized by the phenyl group in the 2-position. In this scenario preferential protonation of the C-4 carbonyl leads to selective attack at C-6 and thus formation of enedione **7**.[12] AM1 calculations[13] indicate that protonation of the C-4 carbonyl in **5** is favored by 5 kcal mol^{-1} over protonation of the C-1 carbonyl (Table 1).

Preference for C-4 carbonyl protonation is also predicted for monosubstituted quinones 2-phenyl-1,4-benzoquinone (**10**) and 2-methyl-1,4-benzoquinone (**11**). Experimental confirmation of the calculated outcome for the latter two examples is found in the acid-mediated addition of thiourea to monosubstituted quinones.[14] In this case the expected hydroquinone products are obtained with very high levels of 2,6-selectivity.[15] Thus the regioselectivity principle outlined here may find application in other acid-catalyzed nucleophilic additions to quinones.

Experimental Section

General. Melting points were determined in open capillary tubes and are uncorrected. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. ^{1}H NMR signal multiplicities are given as apparent multiplicities from 1-D experiments. Mass spectra were recorded on a double focusing mass spectrometer. HPLC analysis were done on a Waters Millenium Chromatography system using a Whatman ODS reverse phase column. Conditions were isocratic, using 70% methanol with 5 mM tetrabutylammonium phosphate (TBAP) and 30% water with 5mM TBAP adjusted to a pH of 8 with triethylamine. Microanalyses were performed by Galbraith Laboratories. *p*-Toluenesulfinic acid was prepared using the method of Kice and Bowers.[16]

1,2,3,4-Tetrahydro-6-phenyl-1,4-methanonaphthalene-5,8-diol. 1,4-Dihydro-6-phenyl-1,4-methanonaphthalene-5,8-diol[17] (200 g, 0.80 mol) was dissolved in warm 2-propanol (1500 mL) and hydrogenated on a Parr hydrogenator in five portions at 55 psi using 10% Pt on C as catalyst (0.5 g per portion). After the theoretical uptake of hydrogen, the reaction was filtered through Celite and the solvent was removed *in vacuo*. Recrystallization from toluene afforded 1,2,3,4-tetrahydro-6-phenyl-1,4-methanonaphthalene-5,8-diol as a white solid. Yield: 150 g, 74%. An analytical sample was obtained by recrystallization from methylene chloride. Mp: 155−156 °C. ^{1}H NMR (DMSO-d_6): δ 8.55 (1H, s), 7.99 (1H, s), 7.48 (2H, d, J = 7 Hz), 7.36 (2H, t, J = 7 Hz), 7.24 (2H, t, J = 7 Hz), 6.45 (1H, s), 3.71 (1H, s), 3.55 (1H, s), 1.85 (2H, d, J = 8 Hz), 1.58 (1H, d, J = 8 Hz), 1.43 (1H, d, J = 8 Hz), 1.12 (2H, d, J = 8 Hz). ^{13}C NMR (DMSO-d_6): δ 143.52, 139.70, 139.57, 135.59, 133.31, 129.12, 127.74, 127.24, 125.96, 114.90, 48.16, 39.77, 39.57, 26.41, 26.32. IR (KBr): 3400-(br), 2960, 2940, 2860, 1610, 1480, 1440, 1350, 1330, 1300, 1260, 1200, 1160, 1120 cm^{-1}. MS (EI+): 252. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.59; H, 6.38.

1,2,3,4-Tetrahydro-6-phenyl-1,4-methanonaphthalene-5,8-dione (3). 1,2,3,4-Tetrahydro-6-phenyl-1,4-methanonaphthalene-5,8-diol (12.6 g, 0.05 mol) was slurried in methylene chloride (200 mL) and cooled to 5 °C in an ice bath. NaOCl (106 mL, 5.25 wt % solution Chlorox) was slowly added over 10 min, maintaining the temperature below 20 °C. The reaction was allowed to warm to ambient temperature and was complete in 30 min. The organic phase was separated and the aqueous

(10) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85.

(11) Rogers, D. W.; Choi, L. S.; Girellini, R. S.; Holmes, T. J.; Allinger, N. L. *J. Phys. Chem.* **1980**, *84*, 1810.

(12) Nucleophilic attack at the phenyl-substituted quinone carbon (C-2) does not reduce the ring strain of the ring-fused norbornadiene system and would thus remain reversible.

(13) AM1 geometry optimization calculations were carried out on a Silicon Graphics Personal Iris 4D/35 using Spartan 2.0.

(14) Lau, P. T. S.; Kestner, M. *J. Org. Chem.* **1968**, *33*, 4426.

(15) Reported 2,6:2,5 ratios of the hydroquinone addition products: for quinone **10**, 93:7; for quinone **11**, 90:10.

(16) Kice, J.; Bowers, K. *J. Am. Chem. Soc.* **1962**, *84*, 605.

(17) Porter, R. F.; Rees, W. W.; Frauenglass, E; Wilgus, H. S., III; Nawn, G. H.; Chiesa, P. P.; Gates, J. W., Jr. *J. Org. Chem.* **1964**, *29*, 588.

phase washed once with methylene chloride (50 mL). The combined organics were dried over Na_2SO_4 and the solvents removed *in vacuo*. **3** was vacuum dried at 45 °C for 2 h. Yield: 11.93 g, 95%. An analytical sample was prepared by recrystallization from petroleum ether. Mp: 103−104 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (5H, s), 6.65 (1H, s), 3.54 (2H, d, J = 7 Hz), 1.95 (2H, d, J = 9 Hz), 1.69 (1H, d, J = 9 Hz), 1.42 (1H, d, J = 9 Hz), 1.22 (2H, d, J = 7 Hz). ^{13}C NMR ($CDCl_3$): δ 184.64, 183.74 , 151.87, 151.50, 133.23, 132.58, 129.68, 129.31, 128.39, 47.78, 41.02, 40.67, 25.16, 25.12. IR (KBr) 3450, 1640, 1580, 1340, 1260, 1220 cm^{-1}. MS (EI$^+$): 250. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.38; H, 5.38.

1,2,3,4-Tetrahydro-6-phenyl-7-(toluenesulfonyl)-1,4-methanonaphthalene-5,8-diol (4). *p*-Toluenesulfinic acid (1.56 g, 0.01 mol) and 1,2,3,4-tetrahydro-6-phenyl-1,4-methanonaphthalene-5,8-dione, **3**, (1.25 g, 5.0 mmol) were dissolved in tetrahydrofuran (20 mL) and stirred for 5 h at ambient temperature until **3** was completely consumed (TLC 3:1 chloroform:hexanes). The reaction was diluted with methylene chloride (30 mL), and silica gel (10 g) and $MgSO_4$ (10 g) were added. This mixture was filtered, and the solvents were removed *in vacuo*. Recrystallization from 2-propanol (15 mL) afforded **4**. Yield: 1.30 g, 64%. Mp: 157−158 °C. ^{1}H NMR ($CDCl_3$): δ 10.05 (1H, s), 7.2 (8H, complex multiplets), 6.67 (1H, d, J = 8 Hz), 3.76 (1H, s), 3.58 (1H, s), 4.16 (1H, s), 2.37 (3H, s), 1.96 (2H, m), 1.78 (1H, d, J = 6 Hz), 1.53 (1H, dd, J = 6, 2 Hz), 1.27 (2H, complex multiplets). ^{13}C NMR ($CDCl_3$): δ 145.48, 143.83, 142.32, 140.55, 139.31, 137.64, 132.34, 131.80, 131.26, 129.12, 128.58, 128.54, 128.44, 126.88, 124.79, 118.20, 48.94, 40.93, 40.40, 25.91, 25.85, 21.60. IR (KBr) 3500, 3250, 2950, 2875, 1420, 1320, 1290, 1260, 1210, 1150, 1110, 1070 cm^{-1}. MS (EI$^+$) = 406. Anal. Calcd for $C_{24}H_{22}O_4S$: C, 70.91; H, 5.46; S, 7.89. Found: C, 70.51; H, 5.60; S, 7.94.

1,4-Dihydro-6-phenyl-1,4-methanonaphthalene-5,8-dione (5). **5** was prepared by the same method described for **3** from 1,4-dihydro-6-phenyl-1,4-methanonaphthalene-5,8-diol. Yield: 23.3 g, 94%. An analytical sample was prepared by recrystallization from diethyl ether. Mp: 117−118 °C. ^{1}H NMR ($CDCl_3$): δ 7.42 (5H, s), 6.89 (2H, s), 6.64 (1H, s), 4.15 (2H, s), 2.34 (2H, s). ^{13}C NMR ($CDCl_3$): δ 184.15, 183.33, 161.01, 160.57, 145.50, 142.71, 142.51, 133.19, 132.26, 129.68, 129.35, 128.39, 73.79, 48.72, 48.42. IR (KBr) 3450, 1650, 1560, 1330, 1280, 1260 cm^{-1}. MS (EI$^+$): 248. Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.13; H, 4.68.

2-Phenyl-6-(toluenesulfonyl)benzene-1,4-diol. Sodium *p*-toluenesulfinate heptahydrate (6.09 g, 0.02 mol) and phenylbenzoquinone (3.68, 0.02 moles) were reacted in acetic acid (40 mL) for 30 min at 80 °C. Water (80 mL) was added, and the reaction mixture chilled to 5 °C and then filtered. The collected white precipitate was recrystallized from toluene (100 mL) to give 2-phenyl-6-(toluenesulfonyl)benzene-1,4-diol. Yield: 3.58 g, 52%. An analytical sample was prepared by a second recrystallization from toluene. Mp: 180−181 °C. ^{1}H NMR ($CDCl_3$): δ 8.79 (1H, s), 7.78 (2H, d, J = 8 Hz), 7.42 (1H, d, J = 1 Hz), 7.36 (1H, s), 7.26 (2H, d, J = 8 Hz), 7.15 (1H, d, J = 3 Hz), 6.98 (1H, d, J = 3 Hz), 5, (1H, s), 2, (3H, s). ^{13}C NMR (DMSO-d_6): δ 150.48, 144.30, 143.88, 138.38, 136.72, 133.77, 129.74, 129.53, 129.11, 128.29, 127.73, 127.50, 123.36, 113.27, 21.03. MS (EI$^+$): 340. IR (KBr) 3420, 3360, 1600, 1460, 1430, 1250, 1220, 1130, 1080 cm^{-1}. Anal. Calcd for $C_{19}H_{16}O_4S$: C, 67.04; H, 4.74; S, 9.42. Found: C, 66.69; H, 4.75; S, 9.67.

2-Phenyl-6-(toluenesulfonyl)benzene-1,4-dione (9). 2-Phenyl-6-(toluenesulfonyl)benzene-1,4-diol (3.40 g, 0.01 mol) was treated with *o*-chloranil (2.46 g, 0.01 mol) in acetone (30 mL). After 4 h, hexanes (30 mL) were added, and the reaction mixture was chilled to 5 °C. **9** crystallized out of solution and was isolated by filtration as yellow needles. Yield: 1.92 g, 57%. Mp: 160−161 °C. ^{1}H NMR ($CDCl_3$): δ 7.98 (2H, d, J = 8 Hz), 7.66 (1H, d, J = 3 Hz), 7.40 (7H, complex multiplets), 6.90 (1H, d, J = 3 Hz), 2.44 (3H, s). ^{13}C NMR ($CDCl_3$): δ 185.69, 180.75, 146.72, 146.14, 145.97, 136.94, 135.34, 132.88, 131.60, 130.73, 129.94, 129.69, 129.42, 128.66, 21.77. MS (EI$^+$): 338. IR (KBr) 1670, 1650, 1600, 1330, 1300, 1160, 1130 cm^{-1}. Anal. Calcd for $C_{19}H_{14}O_4S$: C, 67.44; H, 4.17; S, 9.47. Found: C, 67.31; H, 4.22; S, 9.77.

1,4-Dihydro-6-phenyl-7-(toluenesulfonyl)-1,4-methanonaphthalene-5,8-diol (6) and 1,4,8a-trihydro-6-phenyl-4a-(toluenesulfonyl)-1,4-methanonaphthalene-5,8-dione (7). *p*-Toluenesulfinic acid (6.248 g, 0.04 mol) and 1,4-dihydro-6-phenyl-1,4-methanonaphthalene-5,8-dione (**5**) (4.965 g, 0.02 mol) were dissolved in 30 mL of tetrahydrofuran and stirred for 5 h at ambient temperature until the quinone was completely consumed (TLC 3:1 chloroform:hexanes). The solvents were removed *in vacuo*. The crude reaction mixture was chromatographed on silica gel using 30% hexanes in methylene chloride as eluent. Hydroquinone **6** was eluted as the first product (15% yield). Enedione **7** was the second product eluted (12% yield).

6 Mp: 173−175 °C. ^{1}H NMR($CDCl_3$): δ 10.00 (1H, s), 7.28. (1H, d, J = 8 Hz), 7.19 (2H, d, J = 5 Hz), 7.09 (2H, d, J = 8 Hz), 6.99 (2H, d, J = 8 Hz), 6.90 (1H, dd, J = 3,5), 6.79 (1H, s), 6.77 (2H, t, J = 3 Hz), 4.33 (1H, s), 4.17 (2H, d, J = 10 Hz), 2.35 (3H, s), 2.30 (2H, s). ^{13}C NMR ($CDCl_3$): δ 146.54, 145.85, 143.90, 143.38, 142.08, 141.55, 141.48, 139.23, 131.82, 131.70, 131.62, 129.13, 128.66, 128.53, 126.90, 125.45, 118.34, 70.44, 47.86, 47.34, 21.60. IR (KBr) 3425, 3280, 2960, 1425, 1335, 1260, 1200, 1120, 1070 cm^{-1}. MS (EI$^+$): 405 (M). An analytical sample was prepared by recrystallization from hexanes. Anal. Calcd for $C_{24}H_{20}O_4S$: C, 71.27; H, 4.98; S, 7.93. Found: C, 71.02; H, 5.04; S, 8.21.

7. Mp: 144−145 °C. ^{1}H NMR(DMSO-d_6): δ 7.72 (1H, d, J = 7 Hz), 7.4 (8H, complex multiplets), 6.88 (1H, s), 6.31 (1H, t, J = 3 Hz), 6.01 (1H, t, J = 3 Hz), 4.12 (1H, d, J = 4 Hz), 3.62 (1H, s), 3.37 (1H, s), 2.45 (3H, s), 2.21 (1H, d, J = 9 Hz), 1.45 (1H, d, J = 9 Hz). ^{13}C NMR (DMSO-d_6): δ 195.4, 191.3, 151.0, 146.0, 139.4, 137.4, 136.2, 132.6, 132.2, 130.4, 130.1, 129.9, 129.0, 128.4, 79.8, 51.9, 51.5, 47.2, 44.9, 21.2. IR (KBr) 3050, 3020, 1670, 1590, 1310, 1280, 1220, 1130 cm^{-1}. MS (EI$^+$): 405 (M). An analytical sample was prepared by recrystallization from 2-propanol. Anal. Calcd for $C_{24}H_{20}O_4S$: C, 71.27; H, 4.98; S, 7.93. Found: C, 71.31; H, 4.97; S, 8.05.

Alternate Synthesis of 7. **9** (1.00 g, 3 mmol) was dissolved in benzene (10 mL). Freshly distilled cyclopentadiene (0.22 g, 3.3 mmol) was added and an immediate color change to pale yellow was observed. The reaction solution was stirred for 1 h, and the solvents were removed *in vacuo*. **7** was recrystallized from 2-propanol (25 mL) and dried for 16 h at 60 °C and 15 mmHg. Yield = 1.04 g, 87%.

Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]-10-phenyl-1-(toluenesulfonyl)undecane-8,11-dione (8). A solution of **7** (0.5 g) in benzene (6 mL) was irradiated with a Hg lamp for 2 h at ambient temperature. The product crystallized out of solution. Quantitative yields can be obtained by removing the solvent *in vacuo*. ^{1}H NMR spectroscopy indicated clean cyclization to **8**. Mp: 196−197 °C. ^{1}H NMR ($CDCl_3$): δ 3.68 (1H, d, J = 9 Hz), 3.58 (1H, m), 3.36 (1H, m), 3.29 (1H, m), 3.18 (1H, m), 2.94 (1H, m), 2.88 (1H, d, J = 12 Hz), 2.43 (3H, s), 2.06 (1H, d, J = 12 Hz). ^{13}C NMR ($CDCl_3$): δ 207.57, 201.43, 145.64, 134.38, 133.51, 130.66, 129.56, 128.67, 128.51, 127.86, 126.87, 80.40, 57.39, 55.68, 51.74, 47.95, 44.65, 43.21, 40.70, 37.05, 21.76. MS (EI$^+$): 404. IR (KBr) 3440, 2980, 1750, 1600, 1320, 1300, 1150, 1080 cm^{-1}. Anal. Calcd for $C_{24}H_{20}O_4S$: C, 71.27; H, 4.98; S, 7.93. Found: C, 71.07; H, 4.98; S, 8.09.

X-ray Analysis. The crystal structure of **7** was determined using Mo Kα radiation and a Nicolet autodiffractometer at 293 ± 1 K. **7** crystallized as triclinic pale yellow parallelepipeds with unit cell dimensions of a = 6.883(1) Å, b = 8.132(2) Å, c = 17.651(4) Å, α = 87.01(3)°, β = 84.34(3)°, γ = 81.74(3)° and space group P-1. Z = 2, density (calcd) = 1.382 mg/cm^3, 4455 independent reflections (R_{int} = 1.79%), final R = 4.61%. Structure solution and refinement was carried out using the Siemens SHELXTL PLUS (PC Version). A molecular thermal ellipsoid plot is included in the supporting information; cell dimensions, atom coordinates, and other crystal data have been deposited with the Cambridge Crystallographic Data Centre.

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Supporting Information Available: The ^{1}H, ^{13}C, and selected COSY spectra of the compounds in the Experimental Section, and a molecular thermal ellipsoid plot of **7** (23 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.

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