15: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.14 (d, J = 6.0 Hz, 1 H), 7.02 (d, J = 6.0 Hz, 1 H), 3.62 (dt, J = 7.5, 2.9 Hz, 1 H), 3.44 (m, 1 H), 3.04 (ddd, J = 9.4, 7.5, 3.1 Hz, 1 H), 2.84 (t, J = 5.1 Hz, 1 H), 2.23 (m, 1 H), 0.89 (dd, J = 9.4, 2.7 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 165.3, 147.2, 139.2, 135.4, 120.4, 44.7, 39.5, 31.4, 28.6, 19.8; MS, m/z (M$^+$) calcd 177.0345, obsd 177.0329.

16: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (d, J = 5.6 Hz, 1 H), 7.01 (d, J = 5.6 Hz, 1 H), 3.46 (dt, J = 7.8, 2.6 Hz, 1 H), 3.30 (m, 1 H), 3.00 (ddd, J = 9.5, 7.8, 3.2 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 171.1, 145.7, 138.9, 134.1, 121.1, 44.9, 43.5, 28.3, 26.0, 20.5; MS, m/z (M$^+$) calcd 177.0345, obsd 177.0344.

Photoisomerization of 4-Methoxy-5,8-dihydro-5,8-methanoquinoline (9b). A solution of **9b** (70 mg) and aceto-phenone (50 μL) in dry benzene (30 mL) was irradiated in the usual manner for 1 h. The two photoproducts (ratio 25:75) were obtained in 89% combined yield by MPLC on silica gel (elution with ethyl acetate and peak shaving).

17: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.17 (d, J = 5.9 Hz, 1 H), 6.57 (d, J = 5.9 Hz, 1 H), 3.82 (s, 3 H), 3.54 (dt, J = 6.9, 2.9 Hz, 1 H), 3.30 (m, 1 H), 2.93 (ddd, J = 9.1, 8.0, 3.0 Hz, 1 H), 2.67 (t, J = 5.3 1 H), 2.08 (m, 1 H), 0.79 (dd, J = 9.1, 2.7 Hz, 1 H); [13]C

NMR (75 MHz, CDCl$_3$, ppm) 165.3, 158.5, 148.1, 104.2, 55.2, 44.8, 37.6, 30.9, 28.9, 19.6; MS, m/z (M$^+$) calcd 173.0845, obsd 173.0842.

18: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.08 (d, J = 5.9 Hz, 1 H), 6.60 (d, J = 5.9 Hz, 1 H), 3.90 (s, 3 H), 3.38 (dt, J = 7.8, 2.7 Hz, 1 H), 3.17 (m, 1 H), 2.92 (ddd, J = 9.2, 7.8, 3.2 Hz, 1 H), 2.64 (t, J = 5.2 Hz, 1 H), 2.08 (m, 1 H), 0.82 (dd, J = 9.2, 2.8 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 171.5, 162.2, 147.2, 121.9, 104.7 (2C), 55.2, 44.8, 42.9, 28.6, 23.9, 20.0; MS, m/z (M$^+$) calcd 173.0845, obsd 173.0835.

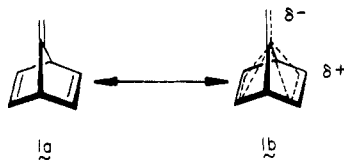# Synthesis of the Parent 1,7-Cyclohexenonorbornadiene and Its Quadricyclane Valence Tautomer

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Cyclopentadiene is transformed in five steps into 1,7-cyclohexenonorbornadiene (**10**). Sensitized irradiation of this triene led to quadricyclane formation (**11**). The ^{1}H and ^{13}C NMR spectra of these hydrocarbons are compared to each other and to those of simpler, nonannulated analogues. The level of homoconjugation in **10** is high, indicating at best a modest strain increase relative to the parent triene. This conclusion is supported by photoelectron spectroscopic measurements and MMP2 calculations. Both **10** and **11** undergo polymerization during attempts at oxidation. The precursor disulfone **9** can, however, be oxidized and monodesulfonylated effectively.

That the arrangement of double bonds peculiar to me-thylenenorbornadiene (**1a**) lends itself to substantial ho-moconjugative interaction as in **1b** was first recognized 15 years ago.[1] The intense ground-state electronic delocal-

ization is perhaps best revealed by ^{13}C NMR spectroscopy. In **1**, C-7 resonates at 177.1 ppm, a record downfield shift for an olefinic carbon atom.[2] More recent spectroscopic studies of 7-alkylidenenorbornadienes show that the extent of homoconjugation is closely linked to the size of the coefficient at C-7, a parameter that can be modified by the number and nature of substituents at C-8.[3,4] The rela-

tionship between semicyclic π-bond polarization and Δδ (^{13}C) is not linear, although the difference in total atomic charge does make a major contribution.[4] Photoelectron spectroscopy constitutes an alternative technique for as-saying the same electronic effects.

The considerable attention paid in the last few years to carbocyclic frameworks typified by **2**,[5] **3**,[6] and **4**[7] prompted us to develop a protocol for the conversion of the 7-oxa-norbornyl ester **5** to the 1,7-cyclohexenonorbornadiene **6** for the purpose of determining the effect of annulation on orbital overlap.[8] Since this approach to **6** necessarily places a substituent R on the cyclohexene subunit, an alternative route was sought to make possible direct access

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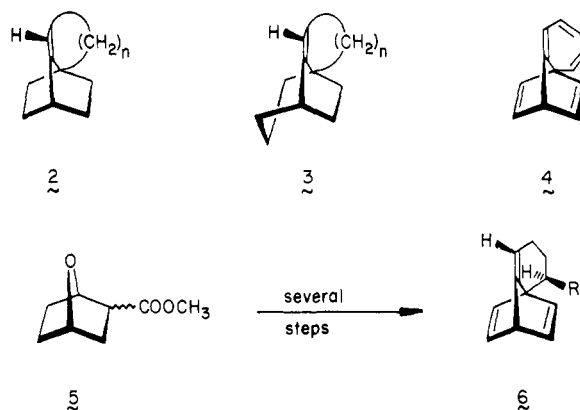
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Figure 1. He I_α photoelectron spectrum of 10 (courtesy of R. Gleiter).

to the parent system. Here, we report the first synthesis of 10 and its quadricyclane counterpart 11.

In a modification of the Sugimura procedure,[9] cyclopentadiene was condensed with ethyl 4-bromobutyrate in the presence of 2 equiv of sodium hydride. The sequential S_N2 displacement and acylation occur efficiently (97%) to provide 7 as a thermolabile, air-sensitive yellow oil. Direct 1,2-reduction of the carbonyl group in 7 was achieved with cerium trichloride doped sodium borohydride[10] in methanol at 0 °C. Without isolation, the dienol was dehydrated with potassium hydroxide in a two-phase (ether–water) solvent system. The resulting fulvene 8 (60% overall yield) proved to be a fluorescent orange oil not unlike its monosubstituted congeners obtained earlier.[8]
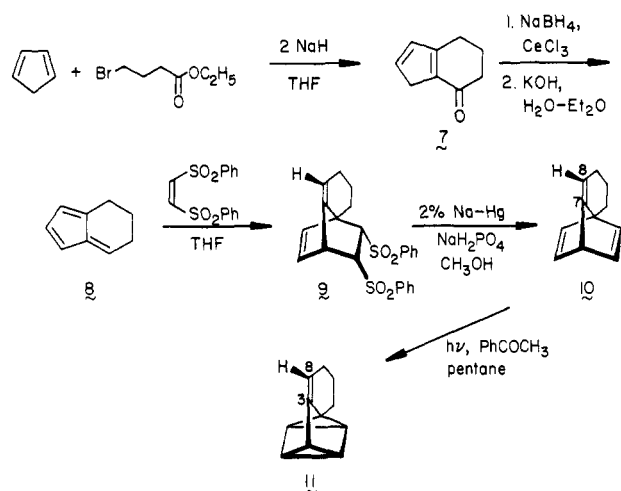
When degassed, anhydrous tetrahydrofuran solutions of 8 and (Z)-1,2-bis(phenylsulfonyl)ethylene[11] were heated at 50 °C under argon for 12 h, a 60% yield of adduct 9 was obtained by direct crystallization. The heating was made necessary by the low reactivity of the dienophile at room temperature. In line with expectation, the efficiency of the Diels–Alder cycloaddition could be measurably improved to 84% by effecting the condensation at 900 000 psi and 25 °C for 24 h.[12] The endo orientation of the sulfone substituents in 9 was readily apparent from the chemical shifts of its α-sulfonyl protons (δ 4.25–4.07 in $CDCl_3$). A contrasting example is found in 12 where the shielding now provided by the central double bond is reflected in the upfield location of the pair of hydrogens
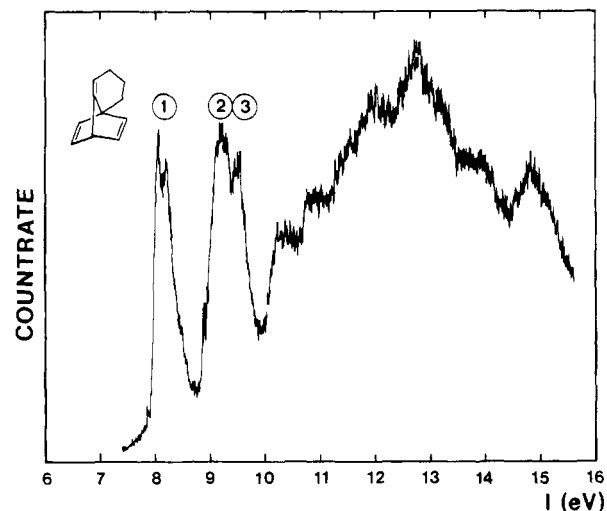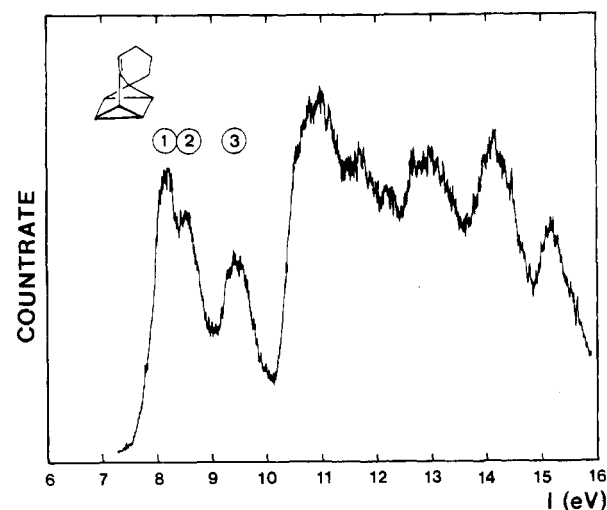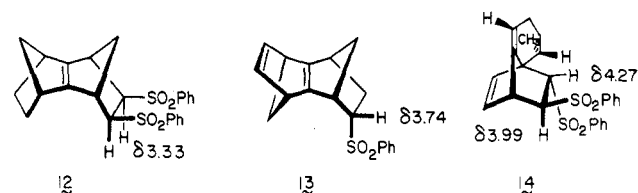
Figure 2. He I_α photoelectron spectrum of 11 (courtesy of R. Gleiter).

geminal to its exo phenylsulfonyl groups.[12] In 13, the downfield shift is not as pronounced as it is in 9, although the trend is unmistakable. The chemical shifts in 9 are also consistent with the closest known model system 14,[8] despite the presence of eclipsing sulfone groups.

Reduction of disulfone 9 with 2% sodium amalgam[13] in methanol buffered with sodium dihydrogen phosphate[14] gave 10 in good yield. The ^1H and ^{13}C NMR spectra of this triene are consistent with its C_s symmetry. Furthermore, the appearance of C-7 at 170.86 ppm supports the contention that homoconjugative interaction is fully op-

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erational in its individual π segments (compare 171.3 ppm for **6**, R = CH$_3$). Since this chemical shift lies intermediate between the values for **1** (177.1 ppm) and its 8,8-dimethyl congener (165.7 ppm), the carbocyclic framework associated with **10** appears to be no more strained than normal.

Acetophenone-sensitized irradiation[14] of **10** in pentane solution gave rise to **11**. The changes in ^{13}C chemical shifts of C-3 (147.58 ppm) and C-8 (114.26 ppm) are particularly useful for analysis of the dropoff in homoconjugation. The $\Delta\delta$ of only 33.3 in **11** pales in significance when compared to the very large difference (81.8) observed for **10**.

The photoelectron spectra of **10** and **11** (Figures 1 and 2) have been recorded.[15] Concerning the three most prominent bands for **10**, the first two (8.07 and 9.24 eV) arise from ionization from within the norbornadiene subunit, while the third at 9.55 eV stems from the exomethylene double bond, in complete agreement with expectation.[4] In the case of **11**, the energy of the double bond is found at 9.4 eV. The other two peaks (8.2 and 8.6 eV) arise because of ionization from the Walsh orbitals of the nortricyclane framework.

The functionalization of **10** and **11** was next given consideration. Expectedly, all attempts to effect allylic oxidation of either hydrocarbon were plagued with complications arising from polymerization and/or rearrangement. In contrast, treatment of **9** with the chromium trioxide-dipyridine complex[16] in dichloromethane did afford enone **15**, although in low yield. Exposure of **15** to varied concentrations of buffered sodium amalgam gave no evidence for delivering **16**. Polymerization occurred under all of the conditions examined.
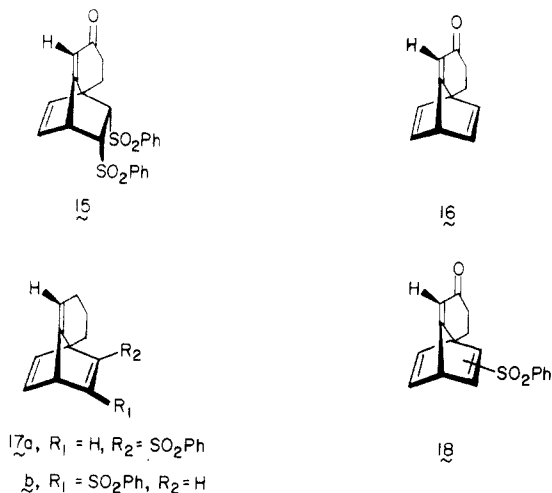
The partial desulfonylation of **9** could be readily accomplished by the action of aqueous potassium hydroxide in tetrahydrofuran solvent. The isomeric sulfones **17a** and **17b** were produced in a 1:1 ratio. No conditions were found to achieve the comparable conversion of **15** to **18**.

The few steps needed to transform cyclopentadiene into **11** now make readily available a quadricyclane having two quite different cyclopropane ring substitution patterns.[17] The annulated ring in both **11** and the related 7-methylenenorbornadiene (**10**) can be utilized to probe possible steric effects on cycloaddition reactions involving electron-deficient olefinic partners.[11,18] A particularly
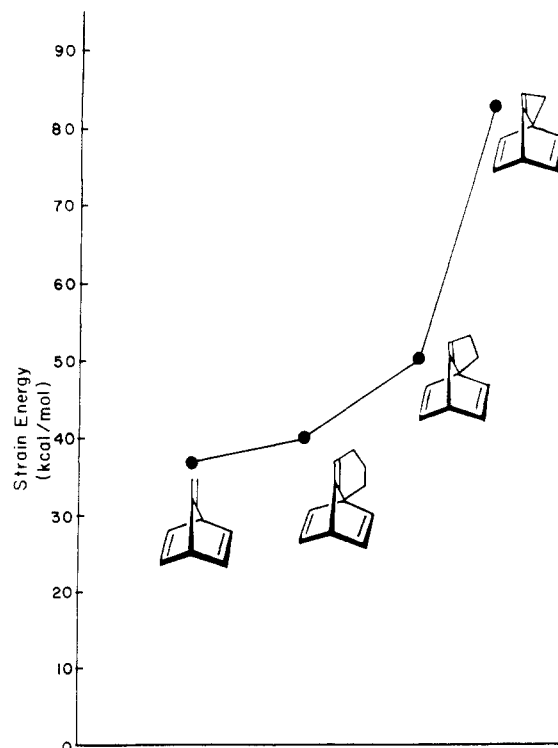

Figure 3. Relative strain energies of the 1,7-annulated 7-methylenenorbornadienes (MMP2 calculations, courtesy of M.-A. Poupart).

interesting extension of this chemistry would involve the known 1,2-dihydropentalene[19] as starting material. Successful completion of the same set of reactions would deliver the more strained (see Figure 3) 1,7-cyclopenteno derivatives, where at least a modicum of structural deformation might be made apparent. The data reported from Figure 3 stem from calculations based on the MMP2 force field program developed by Allinger.[20]

Experimental Section

Dienone 7. To a cold (0 °C), mechanically stirred slurry of sodium hydride (32 g, 0.8 mol) in deoxygenated, anhydrous tetrahydrofuran (500 mL) was added dropwise during 30–45 in cold (−78 °C), freshly distilled cyclopentadiene (26.4 g, 0.4 mol). The reaction mixture was stirred at 0 °C for 1 h, cooled to −78 °C, and slowly treated with ethyl 4-bromobutyrate (78 g, 0.4 mol). After 1 h of vigorous stirring at −78 °C, the reaction mixture was allowed to warm to room temperature over a period of 6 h, quenched with cold aqueous ammonium chloride solution (500

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mL), and extracted with ether. The combined ethereal extracts were dried, stirred over charcoal for 5 min, filtered through a pad of Celite, and concentrated in vacuo without applying heat. There was obtained 52 g (97%) of dienone **7** as a thermolabile, air-sensitive yellow oil: IR (neat, cm^{-1}), 1640; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.73 (d, J = 5.2 Hz, 1 H), 6.47 (d, J = 5.2 Hz, 1 H), 3.20 (m, 2 H), 2.57 (m, 2 H), 2.37 (t, J = 6.6 Hz, 2 H), 2.06 (m, 2 H). This material was directly used in the next step.

5,6-Dihydro-4*H*-indene (8). Dienone **7** (52 g, 0.39 mol) was dissolved in anhydrous methanol (1600 mL) and cerium trichloride heptahydrate (149 g, 0.4 mol) was added. The resulting mixture was stirred at room temperature for 0.5 h, cooled to 0 °C, and treated with sodium borohydride (15 g, 0.4 mol) in one portion. Following the brisk evolution of hydrogen, stirring was continued at 0 °C for 1 h. Cold aqueous ammonium chloride solution (500 mL) was added, and the product was extracted into ether. The combined ethereal extracts were dried, filtered, and partially concentrated to give 250–300 mL of a pale yellow solution containing the thermally unstable dienol. This solution was diluted with ether (300 mL), cooled to 0 °C, and treated with cold aqueous 3 N potassium hydroxide solution (500 mL). The resulting mixture was stirred vigorously under an argon atmosphere for 1 h at 0 °C and 12 h at room temperature. The layers were separated, and the ethereal phase was washed with water (3 × 100 mL), dried, and concentrated. Distillation of the residue under an inert atmosphere gave 28.4 g (60% overall) of **8** as an orange-colored fluorescent oil: bp 40 °C (1.0 mm); IR (neat, cm^{-1}) 3080, 3065, 3025, 2925, 2860, 2820, 1645, 1580, 1490, 1445, 1430, 1420, 1340, 1335, 1325, 1315, 952, 885, 810, 735, 675; ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.79 (m, 1 H), 6.52 (m, 1 H), 6.17 (m, 1 H), 6.12 (m, 1 H), 2.70 (m, 2 H), 2.49 (m, 2 H), 1.93 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 144.65, 137.83, 133.01, 131.83, 122.68, 118.91, 26.58, 25.08, 24.20; MS, m/z (M$^+$) calcd 118.0783, obsd 118.0781.

Cycloaddition of 8 with (*Z*)-1,2-Bis(phenylsulfonyl)-ethylene. A. At 50 °C in Tetrahydrofuran Solution. A mixture of **8** (26 g, 0.22 mol) and (*Z*)-1,2-bis(phenylsulfonyl)-ethylene (77 g, 0.25 mol) in anhydrous, degassed tetrahydrofuran solution (250 mL) was stirred at 50 °C under an argon atmosphere for 12 h and cooled to room temperature. The cycloadduct **9**, which crystallized from solution, was filtered, washed with a minimum amount of tetrahydrofuran, and dried under vacuum: yield, 56.2 g (60%). Although this compound could be used directly in the next step, it was purified in a small amount by medium-pressure liquid chromatography on silica gel (elution with 50% ethyl acetate in petroleum ether) and isolated as a white crystalline solid: mp 180–182 °C dec; IR (CH$_2$Cl$_2$, cm^{-1}) 1360–1290, 1180–1120; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.04 (d, J = 7.3 Hz, 2 H), 7.94 (d, J = 7.3 Hz, 2 H), 7.75–7.45 (m, 6 H), 6.66 (m, 1 H), 6.54 (d, J = 5.7 Hz, 1 H), 4.94 (t, J = 3.9 Hz, 1 H), 4.25–4.07 (m, 2 H), 3.23 (m, 1 H), 2.09–1.59 (m, 4 H), 1.40 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 163.52, 148.00, 142.24, 141.44, 138.80, 134.68, 133.45, 128.98, 128.86, 128.73, 128.46, 107.52, 74.86, 72.58, 55.79, 48.73, 26.91, 22.65, 20.52; MS (CI), m/z (M$^{\cdot}$ + H) calcd 427, obsd 427.

Anal. Calcd. for C$_{23}$H$_{22}$S$_2$O$_4$: C, 64.77; H, 5.20. Found: C, 64.51; H, 5.30.

B. At 90 000 psi. A mixture of **8** (0.57 g, 4.8 mmol) and (*Z*)-1,2-bis(phenylsulfonyl)ethylene (1.6 g, 5.2 mmol) in tetrahydrofuran (2 mL) was subjected to 90 000 psi of pressure for 24 h. The reaction mixture was concentrated and purified by medium-pressure liquid chromatography to give 1.7 g (84%) of pure cycloadduct **9**.

Tricyclo[6.2.2.0^{1,6}]undeca-5,8,10-triene (10). Cycloadduct **9** (4.0 g, 9.4 mmol) and sodium dihydrogen phosphate (24.0 g, 174 mmol) were taken into anhydrous methanol and purged with nitrogen for 15 min. With stirring, sodium amalgam (2%, from 1.73 g of Na and 84.3 g of Hg) was added in portions during 1 h. After all the amalgam had been added, the reaction mixture was vigorously stirred at 25 °C for 12 h and then filtered through Celite. The filtrate was diluted with pentane (500 mL), washed with water (5 × 100 mL), dried, and filtered through a small pad of silica gel. Evaporation of the pentane followed by vacuum distillation afforded 1.1 g (81%) of triene **10** as a colorless oil: bp

82 °C (0.5 mm); IR (neat, cm^{-1}) 3110, 3080, 3050, 2990, 2850, 2830, 1700, 1520, 1440, 1330, 950, 860, 830, 800, 730, 710, 680, 620; UV (cyclohexane) λ_{max} (nm) 202 (ϵ_{max} 11 400); ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.91 (m, 2 H), 6.71 (d, J = 5.3 Hz, 2 H), 4.34 (t, J = 3.9 Hz, 1 H), 3.87 (m, 1 H), 2.14 (m, 2 H), 1.76 (m, 2 H), 1.62 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 170.86, 147.07, 143.88, 89.08, 57.48, 52.21, 26.09, 21.64, 21.14; MS, m/z (M$^+$) calcd 144.0939, obsd 144.0943.

Photosensitized Irradition of 10. Triene **10** (1.0 g, 6.94 mmol) and acetophenone (20 mg) were dissolved in anhydrous, deoxygenated pentane (1000 mL) and irradiated with a 450-W Hanovia lamp under an argon atmosphere for 4 h. The reaction mixture was filtered through Celite, concentrated, and purified by medium-pressure liquid chromatography on silica gel (elution with 100% petroleum ether). There was isolated 110 mg (11%) of quadricyclane **11** as a colorless oil: IR (neat, cm^{-1}) 3060, 3000, 2920, 2850, 2830, 1690, 1440, 1220, 935, 875, 825, 815, 805, 760; UV (cyclohexane) λ_{max} (nm) 212 (ϵ_{max} 7075); ^{1}H NMr (300 MHz, CDCl$_3$) δ 5.93 (t, J = 3.9 Hz, 1 H), 2.38 (m, 2 H), 1.95–1.55 (m, 9 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 147.58, 114.26, 30.52, 25.08, 24.94, 24.16, 23.60, 23.46, 19.87; MS, m/z (M$^+$) calcd 144.0939, obsd 144.0939.

Allylic Oxidation of 9. The CrO$_3$·2py complex was prepared from anhydrous chromium trioxide (10 g, 100 mmol) and pyridine (15.8 g, 200 mmol) in dichloromethane (100 mL) according to the reported procedure.[16] Cycloadduct **9** (2.13 g, 5 mmol) dissolved in dichloromethane (10 mL) was added to the vigorously stirred reaction mixture. Stirring was continued at 25 °C for 24 h prior to dilution with dichloromethane (200 mL). The dichloromethane solution was filtered through Celite, flashgrade silica gel (25 g) was added, and solvent was removed on a rotary evaporator. The dried adsorbent was packed onto the top of a column and elution was effected first with 100% petroleum ether (500 mL) and then with 100% ethyl acetate (500 mL). Evaporation of the ethyl acetate solution afforded a beige colored solid, which was further purified by medium-pressure liquid chromatography on silica gel (elution with 80% ethyl acetate in petroleum ether). There was isolated 0.33 g (15%) of **15** as a white cyrstalline solid: mp 201–202 °C dec (from ethyl acetate–petroleum ether); IR (CH$_2$Cl$_2$, cm^{-1}) 1675; ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.05 (d, J = 7.3 Hz, 2 H), 7.94 (d, J = 7.3 Hz, 2 H), 7.73–7.55 (m, 6 H), 6.77–6.66 (m, 2 H), 5.30 (s, 1 H), 4.33–4.13 (m, 2 H), 3.43 (m, 1 H), 2.60–2.22 (m, 4 H); ^{13}C NMR (75 MHz, CD$_3$CN, ppm) 196.65, 167.75, 141.90, 141.01, 136.77, 133.78, 133.69, 133.66, 129.16, 128.89, 128.05, 128.00, 109.90, 70.12, 69.94, 54.47, 47.68, 33.99, 23.21; MS (CI), m/z (M$^+$) calcd 440, obsd 440.

Anal. Calcd for C$_{23}$H$_{20}$S$_2$O$_5$: C, 62.72; H, 4.58. Found: C, 62.72; H, 4.61.

Base-Promoted Elimination within 9. Cycloadduct **9** (1.0 g, 2.34 mmol) was dissolved in tetrahydrofuran (10 mL) and aqueous potassium hydroxide (2.8 g in 10 mL of water) was introduced. The reaction mixture was stirred overnight under nitrogen, diluted with water (100 mL), and extracted with dichloromethane (4 × 50 mL). The combined dichloromethane extracts were dried and concentrated. The residue was subjected to medium-pressure liquid chromatography on silica gel (elution with 20% ethyl acetate in petroleum ether) to afford 0.55 g (83%) of 1:1 mixture of vinyl sulfones **17a** and **17b**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.90–7.72 (m, 4 H), 7.70–7.45 (m, 8 H), 6.70 (m, 1 H), 6.66 (m, 1 H), 6.51 (d, J = 5.1 Hz, 1 H), 6.45 (d, J = 5.1 Hz, 1 H), 4.52 (t, J = 4.0 Hz, 1 H), 4.45 (t, J = 4.0 Hz, 1 H), 4.01 (m, 1 H), 3.95 (m, 1 H), 2.40 (m, 1 H), 2.25–2.05 (m, 2 H), 1.85–1.30 (m, 10 H); ^{13}C NMR (75 MHz, CDCl$_3$, ppm) 166.95, 166.89, 157.41, 157.20, 155.69, 155.07, 146.93, 144.97, 142.94, 141.65, 139.27, 139.01, 133.11, 133.07, 128.98, 128.85, 127.79, 127.58, 94.33, 93.89, 59.77, 58.35, 52.39, 52.23, 25.30, 23.56, 21.25, 21.01, 20.93, 20.70; MS, m/z (M$^+$) calcd 284.0870, obsd 284.0871.