2. log k_0 for **7** decreases with increasing Me_2SO content of the solvent. This is consistent with the large negative log ${}^{W}\gamma_{C^-}^{D}$ values determined from partition experiments with **7**.

3. The solvent effect on log k_0 is about the same for amine and for carboxylate ion reactions, in spite of expectations that log k_0 for the amine reactions should decrease more than for the carboxylate ion reactions, because $\delta_{NH^+} < 0$ (eq 20) but $\delta_{B^-} > 0$ (eq 19). This behavior, which is unique among all systems studied so far, is attributed to the very large Brønsted β values, particularly for the carboxylate ion reaction, which should make δ_{B^-} very small and possibly δ_{NH^+} less negative than in other systems.

Experimental Section

Materials. (α-Cyanodiphenylmethane)bis(tricarbonylchromium(0)) was prepared according to a previously reported method,[37] mp 166 °C (lit. mp 166 °C).[37]

The purification of the amines and carboxylic acids, where needed, has been described previously.[11a] Me_2SO was stored over a 4-Å molecular sieve prior to use.

Kinetic Measurements. The methods used were basically the same as described before.[11a] The reaction was monitored at 414 nm which corresponds to one of three maxima in the spectrum of the carbanion. In some of the experiments where the equilibrium was approached from the carbanion side the carbanion was generated in a multimixing Durrum-Gibson stopped-flow apparatus by reaction of the substrate with 0.002 or 0.01 M KOH. The acidic buffer solution was then added in the same apparatus a few seconds later and the decay of the carbanion monitored in the usual way. This technique was used in those cases where the carbanion solution was unstable which was a most serious problem in 50% Me_2SO.

Solvent Activity Coefficients. The solvent activity coefficients for the transfer of **7** from 50% to 70% Me_2SO (${}^{50}\gamma_{CH}^{70}$) and from 50% to 90% Me_2SO (${}^{50}\gamma_{CH}^{90}$) were determined by measuring partition coefficients for **7** between *n*-heptane and the various Me_2SO–water mixtures. The partition coefficients were measured as described previously;[28] they are defined as ${}^{50}P^{H} = [CH]_H/[CH]_{50}$, ${}^{70}P^{H} = [CH]_H/[CH]_{70}$, and ${}^{90}P^{H} = [CH]_H/[CH]_{90}$, respectively, with $[CH]_H$ being the equilibrium concentration of the carbon acid in *n*-heptane, and $[CH]_{50}$, $[CH]_{70}$, and $[CH]_{90}$ being the equilibrium concentrations of the carbon acid in the respective Me_2SO–water mixtures.

Acknowledgment. This research was supported by Grant CHE-8517370 from the National Science Foundation and by the donors of the Petroleum Research Fund administered by the American Chemical Society. We also thank Dr. S. Top for a sample of (α-cyanodiphenyl)bis(tricarbonylchromium(0)).

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Capacity of Quadricyclane Frameworks Related to *syn*-Sesquinorbornatriene for Excited-State Rearrangement

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Columbus, Ohio 43210. *Received February 3, 1988*

Abstract: By means of a sequence of reactions involving sequential below-plane Diels–Alder cycloaddition to tricyclo[5.2.1.$0^{2,6}$]deca-2,5,8-triene, sensitized irradiation to transform the norbornadiene part structure into a quadricyclane, and introduction of a double bond into the noncyclopropanated bridge, it is possible to arrive efficiently at hexacyclic systems typified by **6**, **12**, and **18**. When the unsaturated center is substituted with an electron-withdrawing group, direct and sensitized irradiation results in quantitative translocation of the two cyclopropane rings. The pair of quadricyclane-containing valence isomers can be thermolyzed to the same *syn*-sesquinorbornatriene, irradiation of which in turn delivers only the photostable quadricyclane derivative. Monodeuteriated compound **18** undergoes excited-state isomerization only when directly irradiated. In contrast, *syn*-sesquinorbornatriene-*1-d* (**20**) engages in ring closure when sensitized (efficient ring closure) or directly irradiated (competitive polymer formation). Mechanistic analyses of this chemical behavior are provided, along with quantitative measurements of selected processes.

The structural uniqueness of the quadricyclane ring system has prompted many researchers to elucidate methods for its construction and to understanding its chemical reactivity. The parent hydrocarbon is available by the direct[2] or preferably sensitized photoisomerization[3] of norbornadiene. Substitution of one of the norbornadiene double bonds by one or two electron-withdrawing groups facilitates the valence isomerization.[4] While it is possible to reverse the light-induced ring closure by heating at 140–190 °C,[5] the cycloreversion occurs rapidly at ambient temperature in the presence of transition metals.[6] As a consequence of this reversible electrocyclization, the norbornadiene–quadricyclane couple has been intensively investigated as a promising tool for solar light energy conservation.[7]

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(1) Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985–1986.

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(3) (a) Hammond, G. S.; Turro, N. J.; Fischer, A. *J. Am. Chem. Soc.* **1961**, *83*, 4674. (b) Hammond, G. S.; Wyatt, P.; DeBoer, C. D.; Turro, N. J. *Ibid.* **1964**, *86*, 2532. (c) Smith, C. D. *Org. Synth.* **1971**, *51*, 133.

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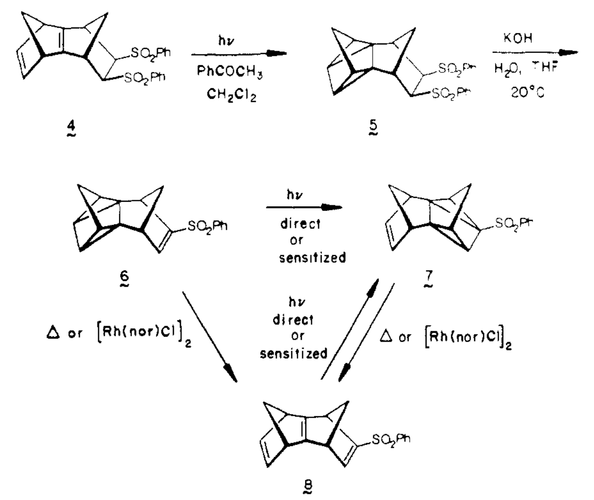
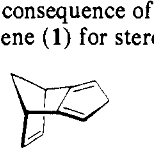
Scheme I



The heightened reactivity of quadricyclane is due to its high strain energy estimated to be 96 kcal/mol.[8] Since the sum of the strain contributed by its cyclopropane and cyclobutane rings amounts only to 83 kcal/mol,[9] an extra strain increment of 13 kcal/mol arises from the manner in which these small rings are mutually fused in close proximity. As a result, the susceptibility of this compact C_7 hydrocarbon to facile electrophilic attack[2,10] and to thermal[11] and photochemical $[2\sigma + 2\sigma + 2\pi]$ cycloaddition[12] is not surprising. The noteworthy exo stereospecificity observed in these reactions has been dealt with in theoretical terms.[13] Finally, while norbornadiene and quadricyclane can be assumed to present a similar steric profile to an attacking reagent, they differ appreciably in having sets of frontier orbitals of inverse symmetry.[14]

In spite of the enormous amount of research activity which quadricyclanes have inspired, no example of a quadricyclane–quadricyclane rearrangement has been reported previously. As a direct consequence of the proclivity of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (**1**) for stereoselective below-plane capture of dienophiles,[15] we have found it possible to prepare molecules capable of undergoing, at least in a stepwise sense, this unprecedented isomerization.[16] The chemical issues considered worthy of investigation were as follows: (i) the feasibility of a synthetic plan capable of providing molecules of general formula **2**; (ii) the response of **2** to thermal and photochemical activation, both sensitized and direct; (iii) the questions of reversible equilibration of **2** with **3** and of possible degenerate behavior (R = D); and (iv) the reactivity of similarly substituted *syn*-sesquinorbornatrienes[17] under comparable reaction conditions. A full account of our findings is provided herein.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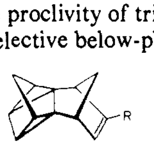
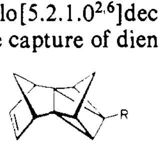


2



3

Results

The Phenylsulfonyl Derivative. Extendability of the Diels–Alder repetoire of **1** to include (*Z*)-1,2-bis(phenylsulfonyl)ethylene[18] led after 2 days in tetrahydrofuran solution at 20 °C (argon atmosphere) to the precipitation of **4** in 82% yield. The relative stereochemistry embodied in **4** has been ascertained by spectral and chemical methods.[17] As a direct consequence of its *syn*-sesquinorbornadiene structure, **4** is particularly susceptible to air oxidation. However, irradiation (450 W Hanovia lamp) of **4** in deoxygenated dichloromethane solution containing acetophenone as sensitizer produced in 57% yield the air-stable, crystalline quadricyclane disulfone **5** (Scheme I).

The stage was now set for introduction of the double bond. After considerable experimentation, it was found that the desired β-elimination of phenylsulfinic acid could be most reproducibly and efficiently achieved by overnight exposure of **5** to potassium hydroxide in aqueous tetrahydrofuran at room temperature. Although the vinyl sulfone moiety in **6** is understandably a good Michael acceptor, the predescribed conditions afforded minimal complications of this type. In fact, the isolated yield of **6** was consistently 80%. The ultraviolet spectrum of **6** recorded in acetonitrile solution is characterized by a single maximum at 238 nm (ϵ 3.0 × 10^4).

The electron-deficient double bond in **6** is rather rigidly fixed in an endo orientation relative to the quadricyclane unit. Figure 1 is an ORTEP drawing showing the structural features of an ordered molecule of **6** as determined crystallographically. There is also a disordered molecule present in the unit cell which affects the hydrocarbon portion of the molecule. The phenylsulfonyl group is not affected by this disorder.[19] Although the bond lengths are not particularly accurate for the disordered position of this ordered molecule, the dihedral angle between the least-squares planes through atoms C3–C6–C2–C7 and C3–C6–C10–C12 is seen to be 154°. The value for that angle through the first plane and C3–C4–C5–C6 is 148°.[20]

Heating of **6** at 140–150 °C in bromobenzene-d_5 solution under anaerobic conditions resulted exclusively in slow conversion to the oxygen-sensitive triene **8**. After 1 week at this temperature, only 50% of **6** had experienced ring opening. No evidence was gained for isomerization to **7** under these somewhat forcing conditions. When **7** became available (see below), this isomeric quadricyclane underwent comparably slow cyclopropane bond cleavage to give **8**. Consequently, some degree of interconversion between **6** and **7** at these elevated temperatures is not likely to have been missed.

Contrastingly, **6** proved to be a highly photoreactive substance. Irradiation (450 W Hanovia lamp) of degassed CH_2Cl_2 solutions of this vinyl sulfone for 3 h resulted in quantitative conversion to **7** [$\lambda_{max}^{CH_3CN}$ 220 sh (ϵ 1.23 × 10^4) and 250 sh nm (3.7 × 10^3)].

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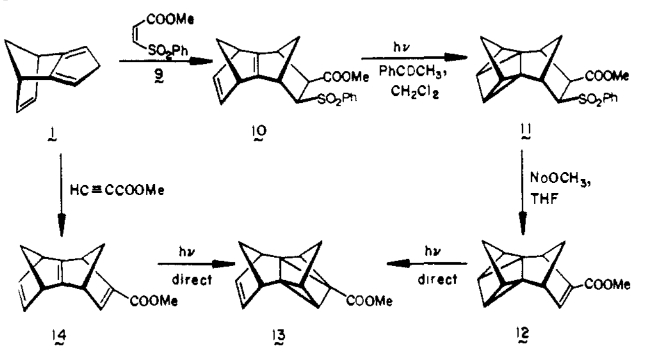
(19) A similar case of enantiomeric disorder has been described for racemic 2-*exo*-norbornanol tosylate [Altona, C.; Sundaralingam, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 1806]. Although the problem can in principle be avoided by selective crystallization of one enantiomer, this has not been attempted.

(20) We thank Dr. J. C. Gallucci for this X-ray crystallographic determination.

Scheme II



The progress of this photoisomerization could be conveniently monitored by ^1H NMR (CD_2Cl_2 as solvent). Particularly diagnostic was the gradual disappearance of the lone vinyl proton absorption of **6** at δ 7.09 (d, $J = 3.3$ Hz) and its supplantation by an AB system at δ 6.18 and 6.12 ($J = 5.6, 2.9$ Hz) due to **7**. An entirely comparable experiment was next carried out in order to assess the response of **6** to a representative triplet sensitizer such as benzophenone ($E_T = 69$ kcal/mol). Under conditions where a large excess of the ketone was present to ensure that the sensitizer absorbed all of the incident 3500 Å light, results identical with the direct irradiation were realized.

As already mentioned, the thermal behavior of **7** is entirely similar to that of **6** in agreement with the orbital-symmetry forbiddenness of the process.[21] The same conversion to triene sulfone **8** could be effected more mildly and in quantitative yield by reaction of **7** with a catalytic quantity of $[Rh(nor)Cl]_2$ in $CDCl_3$ at 50 °C for 3.5 h.

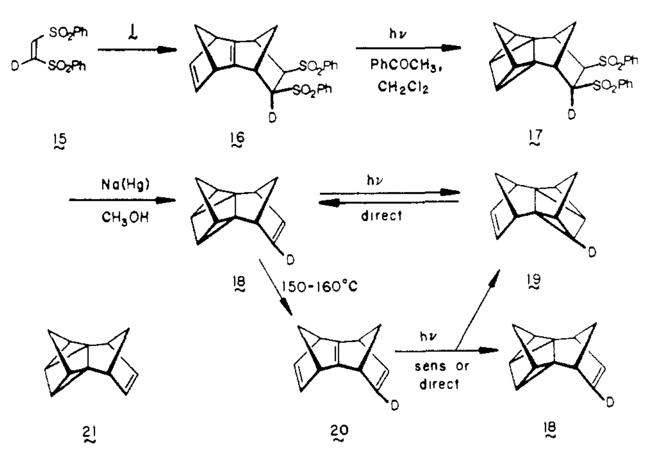
The direct irradiation of **8** was anticipated[4,22] to give rise to **7** rather than **6**. This regioselectivity was indeed found and very cleanly so. Furthermore, in a control experiment involving concurrent photochemical activation of a mixture of **6** and **8**, the latter sulfone proved to be the more reactive (see below). Extensive irradiation of **8** in the presence or absence of benzophenone gave no indication for the formation of **6**. The addition of quenchers such as biphenyl ($E_T = 66$ kcal/mol) and piperylene ($E_T = 59$ kcal/mol) had a notable rate-retarding effect on the conversion of **6** to **7**. Accordingly, the involvement of triplet states in all of these photoconversions goes unquestioned. However, since absolute quantum yields and rates are not available, the extent to which the direct irradiations pass through triplet intermediates cannot be ascertained.

The Consequences of Substitution by Carbomethoxy. In order to expand on the foregoing observations, the carbomethoxy sulfone **9** was prepared[23] and heated overnight at 55–60 °C under argon with **1** in the absence of solvent. Under these conditions, the adduct **10** was obtained smoothly and in quantitative yield (Scheme II). This diene could be transformed into quadricyclane **11** by application of standard sensitized photolysis conditions. Elimination of the phenylsulfonyl group in **11** was realized most efficaciously through the use of sodium methoxide in dry tetrahydrofuran at room temperature.

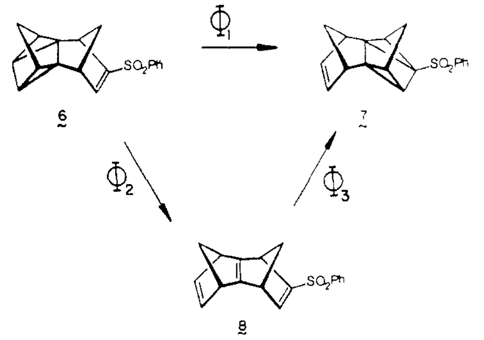
Unsaturated ester **12** exhibits an absorption maximum at 234 nm (ϵ 7.7 $\times 10^3$) in acetonitrile. The direct irradiation of **12** conforms fully with the behavior of **6** and proceeds through **14** to furnish **13** as the ultimate product with remarkable efficiency.

Along different lines, condensation of **1** with methyl propiolate furnished the triene ester **14**.[24] Upon direct irradiation of this highly reactive substance, conversion to **13** was observed. The overall process once again proved to be as clean as that involving **12**. Due to a lack of material, quenching and sensitization experiments were not performed. However, our expectations are that a reactivity pattern comparable to the phenylsulfonyl analogues would emerge.

Scheme III



Scheme IV



The Monodeuteriated Case Study. To arrive suucessfully at the monodeuteriated quadricyclane **18**, it proved possible to adopt the synthetic protocol earlier developed for the unlabeled hydrocarbon.[17a] A central feature of the modification was the inital preparation of isotopically labeled disulfone **15**. Following the logic of kinetic acidity, we found it most expedient to metalate[25,26] (*Z*)-1,2-bis(phenylthio)ethylene[27] and to quench its lithium salt with CH_3OD at −100 °C. Subsequent exposure to hydrogen peroxide in acetic acid gave **15**, the deuterium content in which was typically 20% d_0 and 80% d_1. Diels–Alder addition of this dienophile to **1** gave **16**, which was transformed via **17** to labeled quadricyclane **18** as before (Scheme III).

All attempts to isomerize **18** to **19** photochemically with sensitizers possessing relatively high triplet energies (e.g., benzophenone, acetophenone, and acetone) were to no avail. Quadricyclane itself is known to be responsive to certain sensitizers,[3b] to quench the fluorescence of many aromatic hydrocarbons,[28] and to be reactive in the form of charge-transfer[29] or organometallic complexes.[30] In all of these processes, norbornadiene is produced. However, the excited states of naphthalene and 1,4-dicyanobenzene likewise failed to sensitize any reaction of **18** or **21**. These negative results could signify that steric impedance to exciplex formation is at play here. As a consequence, the ability of the quadricyclane

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(30) Consult, for example: (a) Borsub, N.; Kutal, C. *J. Am. Chem. Soc.* **1984**, *106*, 4826. (b) Grutsch, P. A.; Kutal, C. *Ibid.* **1986**, *108*, 3108.

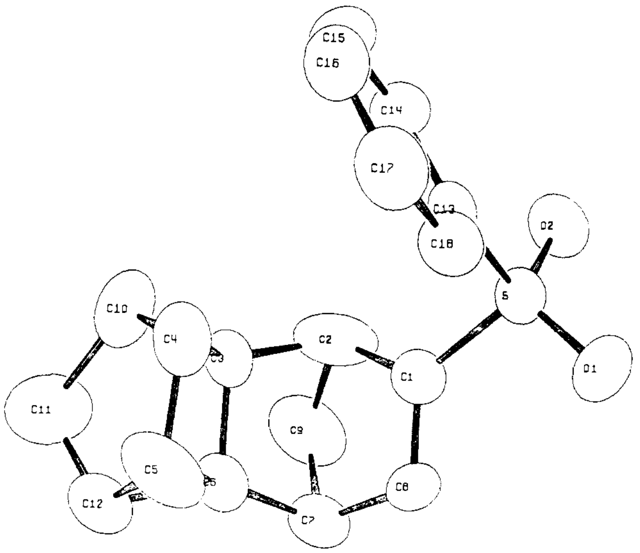


Figure 1. ORTEP drawing of **6**. Hydrogen atoms have been eliminated for clarity, and the non-hydrogen atoms are drawn with 50% probability ellipsoids.

moiety in **18** and **21** to function as an electron donor would be precluded because intermolecular distances are simply too large. We can rule out the possibility that sensitized reversion to *syn*-sesquinorbornatriene does take place and that rapid reconversion to quadricyclane operates subsequently. Such chemistry would require scrambling of the isotopic label in **18** because of concomitant formation of **19**, and this is not seen by ^{1}H NMR at 300 MHz.

On the other hand, direct irradiation of **18** with a 450 W Hanovia lamp through a quartz housing did result in photorearrangement to **19** as revealed by ^{2}H NMR analysis. Under identical conditions, **20** was transformed into a mixture of **18** and **19**. Although polymerization proved to be the dominant process in both cases, no amount of **20** was detected. This was expected, however, since triene **20** happens to be much more reactive than **18** when comparably photoexcited. Obviously, therefore, **20** could, and likely does, mediate the "degenerate" interconversion of **18** with **19**.

Reaction Chronology. Does **6** photoisomerize directly to **7** in a single step, or is this rearrangement mediated by triene **8**? Under ordinary circumstances, there would exist need only to measure Φ_1 and Φ_3 (Scheme IV) for **6** and **8**. However, the marked sensitivity of **8** to atmospheric oxygen has proven extremely troublesome in all of the quantum yield studies attempted. For this reason, recourse had to be made to an alternative protocol for rigorous determination of reaction chronology.

Consideration of standard kinetic expressions revealed that a second option for establishing the order of events rests upon quantitative determination of the [**8**]/[**7**] ratio at 0% conversion. The utilization of ^{1}H NMR techniques is thereby made possible. By this method, ratios determined at various levels of percent conversion should be extrapolatable over the linear portion of a time-dependency plot to the theoretical 0% level. An indirect measure of the ratio of quantum yields Φ_2 and Φ_1 would thereby be achieved.

$$\frac{[{}^{\circledR}8]}{[7]} = \frac{\Phi_2}{\Phi_1} \quad \text{(at 0\% conversion)}$$

Data resulting from two selected experiments involving the photoexcitation of **6** that measure the concentrations of **8** and **7** up to approximately 22% conversion are shown graphically in Figure 2. These and related experiments were performed in sealed NMR tubes on highly purified samples of **6**. Figure 2 shows the striking curvature that sets in rather abruptly upon irradiation of **6**, indicating that **8** not only forms readily under these conditions but is also rapidly consumed as it is being produced. The onset occurs before approximately 3% conversion has taken place, thereby indicating that the reaction proceeds predominantly through triene **8** as intermediate.

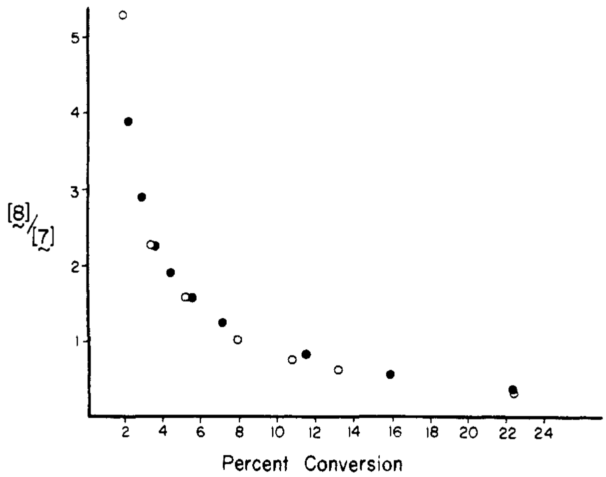
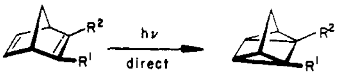


Figure 2. Quantitative analysis (by 300 MHz ^{1}H NMR) of the [**8**]/[**7**] ratio as a function of the percent reaction of **6**.

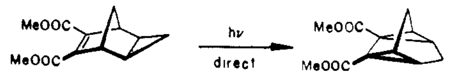
When a comparable analysis of the behavior of ester **12** was subsequently undertaken, efforts at achieving suitable accuracy were seriously thwarted by an unresolved inability to remove trace amounts of **14** from our samples. The complication stems from the high latent chemical reactivity of **12**. For example, epoxidation did serve to consume the triene isomer very rapidly and selectively. Subsequent chromatography, however, invariably promoted small (<1%), although easily detectable isomerization of **12** to **14**. The presence of such trace levels of **14** adequately complicates matters because the [**14**]/[**13**] ratio is also a function of the absolute quantum yield Φ_3. In an experiment in which **12** contaminated with about 0.1% of **14** was irradiated as before in CD_2Cl_2 under argon, the [**14**]/[**13**] ratio at 0% conversion equaled 2.5, equivalent to >70% of the total reaction proceeding through the triene manifold. The presence of **14** at the outset necessarily lowers the actual percentage figure, and the true experimental value is likely comparable to that realized with the sulfone analogue.

Discussion

Our results reveal that the title rearrangement is capable of operation in the absence of a sensitizer in all of the examples studied, irrespective of whether or not the remaining double bond carries a pendant electronegative group. Promotion of excited-state bond reorganizations within norbornadienes has been previously recognized when electron-acceptor substituents are present.[22,31,32] Examples include **22a–c** where ring closure takes place readily on direct irradiation and extend to **23** where involvement of a laterally fused cyclopropane bond is seen.



22a, $R^1 = R^2 = COOH$
b, $R^1 = R^2 = CN$
c, $R^1 = COOCH_3$, $R^2 = H$



23

The population by **6** of its respective S_1 or T_1 energy suufaces allows for conversion to the isomeric quadricyclane **7**. Our results indicate clearly that this rearrangement (and presumably the **12** → **13** conversion as well) is a two-photon process consisting of

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(31) (a) Cristol, S. J.; Snell, R. L. *J. Am. Chem. Soc.* **1958**, *80*, 1950. (b) Edman, J. R. *J. Org. Chem.* **1967**, *32*, 2920. (c) Gorman, A. A.; Sheridan, J. B. *Tetrahedron Lett.* **1969**, 2569.

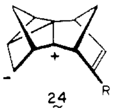
(32) Prinzbach, H.; Eberbach, W.; von Veh, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 436.

(33) Reference deleted in proof.

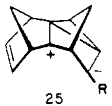
an initial ring opening step to give the monosubstituted *syn*-sesquinorbornatriene and ensuing ring closure in the opposite direction to capture the flanking double bond that carries the functional group. An attractive formulation of the mechanism of direct irradiation involves excitation of **6** to its lowest lying singlet excited state where traversal along the S_1 surface allows for conversion to the respective T_1 state and acquisition of the same nuclear configuration as **8**. Since the quadricyclanes are higher energy isomers of the sesquinorbornatrienes, the **6** → **8** and **12** → **14** processes are exothermic and occur without serious energy impediment.[4e,30b,34]

A rather intriguing aspect of this chemistry is a detailed understanding of the manner in which cascade to the S_0 surface actually occurs. Turro and his co-workers have attempted to deal with the geometries corresponding to the minima on the S_1 and T_1 surfaces for the parent hydrocarbon system and have arrived at a number of important deductions.[34] In the present context, the theoretical framework must make proper allowance for the quite striking preference for formation of quadricyclanes **7** and **13** instead of **6** and **12**. It is not inconceivable that migration along the S_1 surface from left to right features a funnel[35] that provides a ready mechanism for relaxation to the isomeric *syn*-sesquinorbornatriene structures.

The concentrations of trienes **8** and **14** remain very low because they are capable in their own right of reattaining the S_1 or T_1 states under identical conditions. That **8** and **14** are directly transformed into **7** and **13** to the exclusion of the other options signals that the triene approach to the funnel may lie well in the direction of these isomers. As Yamazaki has noted,[4e] the presence of electron-acceptor substituents on the sp^2 centers of norbornadiene decreases both the S_1/ground-state and T_1/ground-state energy gaps. In turn, the strong preference for quadricyclane formation arises because of a shift away from a 1,2-biradicaloid to a 1,3-biradicaloid geometry where ionic contributions are known to play an important role.[34] We see, consequently, that structure **25** enjoys a level of charge stabilization not available to **24**. Decay from the T_1 surface to ground state should therefore occur more readily from **25** and favor regioselective production of those quadricyclane products where the electronegative group is positioned on one of the cyclopropane rings.



24



25

Parallel arguments may be advanced to rationalize the inability of **7** and **13** to convert photochemically to their *syn*-sesquinorbornatriene counterparts. The necessary cycloreversion requires formation of a 1,3-biradical intermediate,[36] and the presence of an electronegative substituent is recognized to curtail strongly the feasibility of such an event,[37] except under unusual circumstances.[7i]

Experimental Section

Sensitized Irradiation of 4. A Pyrex tube was flushed with argon and charged with 70 mL of deoxygenated, argon-saturated dichloromethane, 1.31 g (3.0 mmol) of **4**, and 20 mg of acetophenone. The tube was capped with a rubber septum and shaken until the disulfone was dissolved. This solution was irradiated with a 450 W Hanovia lamp for 3 h during which time a yellow color developed. Evaporation of the solvent furnished a yellow foam, which was taken up in a small amount of acetone. The white crystals that formed were separated by filtration: 750 mg (57%). Disulfone **5** turns brown at 200 °C and melts to a red liquid at 216 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.51 (series of m, 10 H), 4.19 (d, J = 1 Hz, 2 H), 2.93 (br s, 2 H), 2.62 (d, J = 11 Hz, 1 H), 2.16–1.63 (series of m, 4 H), 1.44 (d, J = 4 Hz, 2 H), 1.16 (d, J = 11 Hz, 1 H); ^{13}C NMR (20 MHz, $CDCl_3$) ppm 141.01, 133.52, 128.93, 128.66, 72.18, 42.06, 37.57, 37.08, 34.29, 29.76, 15.38; MS *m/z* ($M^+ - SO_2C_6H_5$) calcd 297.0940, obsd 297.0945.

Quadricyclane 6. A solution of **5** (438 mg, 1.0 mmol) in tetrahydrofuran (30 mL) was treated with potassium hydroxide (560 mg, 10 mmol) in 8 mL of water and stirred vigorously overnight under an argon atmosphere. The reaction mixture was poured into 70 mL in dichloromethane and washed with water (3×) and brine prior to drying. Following solvent evaporation, the solid residue was recrystallized from acetone to give 236 mg (80%) of **6** as white crystals, mp 174 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.49 (series of m, 5 H), 7.10 (d, J = 3.2 Hz, 1 H), 3.19 (br s, 1 H), 3.07 (br s, 1 H), 2.07 ($^{1}/_{2}$ABq, J = 11.3 Hz, 1 H), 1.99 (d, J = 8.7 Hz, 1 H), 1.90 ($^{1}/_{2}$ABq, J = 11.3 Hz, 1 H), 1.67 ($^{1}/_{2}$ABq, J = 4.5 Hz, 1 H), 1.61 ($^{1}/_{2}$ABq, J = 4.5 Hz, 1 H), 1.39 (d, J = 3.9 Hz, 1 H), 1.30 (d, J = 8.7 Hz, 1 H), 0.54 (d, J = 3.8 Hz, 1 H); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.91–7.51 (series of m, 5 H), 7.09 (d, J = 3.3 Hz, 1 H), 3.18 (br s, 1 H), 3.06 (br s, 1 H), 2.09 ($^{1}/_{2}$ABq, J = 11.3 Hz, 1 H), 1.99 ($^{1}/_{2}$ABq, J = 8.7, 7.1 Hz, 1 H), 1.88 ($^{1}/_{2}$ABq, J = 11.3, 1.3 Hz, 1 H), 1.68 (d, J = 4.3 Hz, 1 H), 1.60 (d, J = 4.0 Hz, 1 H), 1.39 (dd, J = 4.5, 1.4 Hz, 1 H), 1.30 ($^{1}/_{2}$ABq, J = 8.7, 1.1 Hz, 1 H), 0.45 (dd, J = 3.0, 1.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) ppm 149.23, 145.84, 140.81, 133.14, 128.98, 128.10, 50.00, 43.26, 43.13, 37.80, 35.07, 34.87, 27.22, 26.93, 15.80, 15.60; MS *m/z* (M^+) calcd 296.0871, obsd 296.0873. Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.66; H, 5.49.

Photoisomerization of 6. A solution of **6** (296 mg, 1.0 mmol) in 8 mL of dichloromethane was placed in a Pyrex tube, degassed during 6 freeze-thaw cycles, and sealed under vacuum. The clear colorless solution was irradiated with a 450 W Hanovia lamp for 3 h. The reaction vessel was cooled in liquid nitrogen, and the seal was broken. Solvent was removed by evaporation to leave **7** as a white solid. The yield is quantitative. The sulfone, which can be recrystallized from dichloromethane/hexane, has a mp of 161 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.47 (series of m, 5 H), 6.18 (br s, 2 H), 3.24 (br s, 1 H), 2.91 (br s, 1 H), 2.61 (br s, 1 H), 2.18 (d, J = 11.8 Hz, 1 H), 2.02–1.91 (series of m, 3 H), 1.87 ($^{1}/_{2}$ABq, J = 8.6 Hz, 1 H), 1.24 ($^{1}/_{2}$ABq, J = 8.6 Hz, 1 H); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.78–7.49 (series of m, 5 H), 6.18 ($^{1}/_{2}$ABq, J = 5.6, 2.9 Hz, 1 H), 6.12 ($^{1}/_{2}$ABq, J = 5.6, 2.9 Hz, 1 H), 3.20 (br s, 1 H), 2.91 (br s, 1 H), 2.58 (br s, 1 H), 2.18 ($^{1}/_{2}$ABq, J = 11.9, 1.2 Hz, 1 H), 2.00–1.92 (m, 3 H), 1.85 ($^{1}/_{2}$ABq, J = 8.6, 1.7 Hz, 1 H), 1.24 ($^{1}/_{2}$ABq, J = 8.6, 0.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 141.68, 136.01, 135.62, 132.63, 128.89, 127.08, 51.65, 48.42, 44.88, 41.64, 40.99, 37.78, 36.19, 35.82, 28.81, 18.33; ^{13}C NMR (75 MHz, CD_2Cl_2) ppm 142.18, 136.21, 136.04, 133.02, 129.31, 127.36, 52.00, 48.76, 45.09, 42.10, 41.44, 38.03, 36.60, 36.20, 29.17, 18.63; MS, *m/z* calcd 296.0871, obsd 296.0871. Anal. Calcd for $C_{18}H_{16}O_2S$: C, 72.94; H, 5.44. Found: C, 72.69; H, 5.50.

Sensitized Irradiation of 6. To a standard 5-mm Pyrex NMR tube was added 11.5 mg of **6** and 20.5 mg of benzophenone. After dissolution of these substances in CD_2Cl_2 (1 mL), the solution was degassed by purging with nitrogen and sealed. The irradiation was performed in a Rayonet reactor equipped with two 3500 Å bulbs at intervals of 30, 70, and 130 s. Each period of irradiation was followed by ^{1}H NMR analysis. Extrapolation of the recorded integrals to 0% conversion indicated the **8**/**7** ratio to equal 4. The ratio (**8**/**7**) = 4 signifies that ≥80% of the reaction proceeds through **8**.

2-(Phenylsulfonyl)-*syn*-sesquinorbornatriene (8). A. Transition-Metal-Catalyzed Isomerization of 6. Chloroform-*d* (1 mL) was subjected to 6 freeze–thaw cycles and transferred via canula to an NMR tube containing **6** (30 mg, 0.1 mmol) and 3 mol% of rhodium norbornadiene chloride dimer under argon. The tube was sealed under vacuum and subsequently heated in an oil bath at 50 °C. The progress of reaction was monitored by 300 MHz ^{1}H NMR. After a total of 3.5 h, no remaining **6** was spectroscopically visible: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85–7.51 (series of m, 5 H), 7.11 (d, J = 3 Hz, 1 H), 6.13 (dd, J = 4.9, 2.9 Hz, 1 H), 5.66 (dd, J = 4.9, 2.9 Hz, 1 H), 3.81 (br s, 1 H), 3.67 (t, J = 1.1 Hz, 1 H), 3.48 (br s, 1 H), 3.3 (br s, 1 H), 2.43 (dt, J = 6.8, 1.7 Hz, 1 H), 2.20–2.13 (m, 2 H), 2.01 (d, J = 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 172.37, 171.00, 155.24, 152.69, 141.36, 139.60, 138.05, 133.21, 128.99, 128.02, 69.80, 64.48, 51.36, 51.05, 49.85 (2C). The air sensitivity of this substance did not permit additional characterization.

B. **Thermal Isomerization of 7.** A solution of **7** (15 mg, 0.05 mmol) in 0.6 mL of bromobenzene-*d*$_5$ contained in a thick-walled NMR tube was degassed by means of 5 freeze–thaw cycles and sealed under vacuum. The tube was subsequently immersed in an oil bath at 140–150 °C, resulting in slow and clean ring opening to **8**. After 1 week, **7** and **8** were

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present in approximately equal amounts as determined by 300 MHz ^{1}H NMR.

Attempted Sensitized Irradiation of 7. A solution of **7** (10 mg) and benzophenone (18.9 mg) in CD$_2$Cl$_2$ (1 mL) was prepared in an NMR tube and deaerated as before. Irradiation in the predescribed manner for 2 h showed no conversion to either **6** or **8** (^{1}H NMR analysis at 300 MHz).

Direct Photoisomerization of 8. The reaction mixture from the thermal isomerization was irradiated with a 250 W Hanovia lamp for 5 h. During this time, the triene vanishes completely. ^{1}H NMR analysis revealed only the presence of **7**.

Sensitized Irradiation of 8. A solution of **8** (10 mg) and benzophenone (20 mg) in CD$_2$Cl$_2$ (1 mL) was deaerated with nitrogen and sealed in an NMR tube as before. Irradiation with a pair of 3500 Å bulbs in a Rayonet reactor for 5 min and NMR analysis at 300 MHz showed no indication for the presence of **6**. Only **7** was formed. Continued irradiation gave identical results.

Methyl (*Z*)-2-(Phenylsulfonyl)acrylate (9). A 500-mL, three-necked flask equipped with an argon inlet, magnetic stirring bar, dropping funnel, and drying tube was flushed with argon and charged with 250 mL of dry methanol and 2.3 g (0.1 mol) of sodium. After the metal reacted (ice bath cooling), thiophenol (11.0 g, 0.1 mol) was introduced with stirring, and the reaction mixture was cooled to 0 °C. Following addition of a solution of methyl propiolate in dry methanol (30 mL) during 20 min, stirring was maintained during warming to room temperature and 60 min thereafter. The contents were poured into 300 mL of ice water, and the product was extracted into dichloromethane, washed with 10% potassium hydroxide solution and water, and dried. Solvent evaporation left a colorless liquid which was carried on directly by dissolution in glacial acetic acid (250 mL).

Hydrogen peroxide (30%, 30 mL) was added, and the reaction mixture was heated at 60–70 °C for 6 h. Additional peroxide (50 mL) was added gradually during the first 4 h of the heating period. The mixture was cooled to 20 °C, poured into water (600 mL), and extracted with dichloromethane. The organic phase was washed sequentially with saturated sodium bisulfite, sodium carbonate, and sodium chloride solutions before drying. Solvent evaporation left an oil that solidified on cooling. The sulfone was recrystallized from chloroform–pentane to give 14.0 g (62%) of **9** as white crystals, mp 65 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.01–7.55 (series of m, 5 H), 6.56 ($^1/_2$ABq, J = 11.5 Hz, 1 H), 6.51 ($^1/_2$ABq, J = 11.5 Hz, 1 H), 3.90 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 164.31, 139.44, 135.68, 134.02, 131.45, 129.30, 128.19, 52.74; MS, *m/z* (M$^+$) calcd 226.0310, obsd 226.0308.

Diels–Alder Addition of 9 to Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (1). A 25-mL Schlenk flask was flushed with argon and charged with 325 mg (2.5 mmol) of **1** and 452 mg (2.0 mmol) of **9**. The reaction vessel was tightly stoppered with a rubber septum, and the contents were thoroughly mixed by shaking. This mixture was heated at 55–60 °C overnight under argon. During this period, the original melt solidified to a white crystalline mass. Excess triene was pumped off by heating at 70 °C and 0.3 Torr for 2 h. The residual solid, which melts at 143 °C and is obtained in quantitative yield, was identified as **10**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.86–7.51 (m, 5 H), 6.53 (dd, J = 5.9, 2.9 Hz, 1 H), 6.40 (dd, J = 4.9, 2.9 Hz, 1 H), 3.69 (s, 3 H), 3.37 (br s, 1 H), 3.23 (br s, 1 H), 3.21 (br s, 1 H), 3.18 (br s, 1 H), 2.63 (dd, J = 9.2, 1.8 Hz, 1 H), 2.52 (dt, J = 9.5, 1.6 Hz, 1 H), 2.14 (dt, J = 6.5, 1.7 Hz, 1 H), 2.04 (dd, J = 9.2, 2.1 Hz, 1 H), 1.96 (d, J = 6.5 Hz, 1 H), 1.63–1.60 (m, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 172.05, 162.79, 159.78, 140.66, 139.74, 138.81, 133.45, 129.08, 128.02, 70.60, 64.53, 52.29, 48.70, 48.24, 46.75, 45.65, 44.92, 42.05; MS, *m/z* (M$^+$) calcd 356.1082, obsd 356.1077.

Photoisomerization of 10. A 712-mg (2.0 mmol) sample of **10** was irradiated in argon-saturated dichloromethane (25 mL) containing acetophenone (40 mg) in the predescribed manner for 6 h. A color change to yellow was again noted. The reaction mixture was concentrated on a rotary evaporator. Solvent residues were removed at 0.3 Torr to give **11** as a pale yellow foam. Recrystallization of this material from acetone furnished 505 mg (71%) of the quadricyclane as white crystals, mp 164 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94–7.53 (series of m, 5 H), 4.02 (dd, J = 9.5, 1.6 Hz, 1 H), 3.75 (s, 3 H), 3.48 (dd, J = 9.5, 1.6 Hz, 1 H), 2.74 (d, J = 11.6 Hz, 2 H), 2.56 (dt, J = 10.4, 1.6 Hz, 1 H), 1.83–1.74 (m, 4 H), 1.52 (dd, J = 4.4, 1.4 Hz, 1 H), 1.42 (dd, J = 4.4, 1.4 Hz, 1 H), 1.19 (dt, J = 10.5, 1.5 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 171.57, 140.57, 133.42, 129.06, 128.23, 71.02, 52.22, 51.30, 41.87, 40.44, 37.72, 37.26, 37.23, 34.20, 29.46, 29.20, 15.36, 15.05; MS, *m/z* (M$^+$) calcd 356.1082, obsd 356.1087. Anal. Calcd for C$_{20}$H$_{20}$O$_4$S: C, 67.39; H, 5.66. Found: C, 67.25; H, 5.67.

Quadricyclane 12. An argon-blanketed solution of **11** (178 mg, 0.50 mmol) in dry tetrahydrofuran (4 mL) was stirred for 4 h at room temperature with sodium methoxide (38 mg, 0.7 mmol). During this time, a precipitate formed. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic phases were washed with water (2×), dried, and evaporated. The residual oil was purified by molecular distillation 40 °C, 0.3 Torr) to give 65 mg (61%) of **12** as an oil which solidified on cooling, mp 42 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.09 (d, J = 3.2 Hz, 1 H), 3.76 (s, 3 H), 3.22 (br s, 1 H), 3.00 (br s, 1 H), 2.17 ($^1/_2$ABq, J = 11.2 Hz, 1 H), 2.01 ($^1/_2$ABq, J = 11.2, 1.3 Hz, 1 H), 1.89 ($^1/_2$ABq, J = 8.6, 1.7 Hz, 1 H), 1.77 (d, J = 4.3 Hz, 1 H), 1.70 (d, J = 4.3 Hz, 1 H), 1.47–1.42 (m, 2 H), 1.28 ($^1/_2$ABq, J = 8.6, 1.2 Hz, 1 H); ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.07 (d, J = 3.1 Hz, 1 H), 3.72 (s, 3 H), 3.19 (br s, 1 H), 2.99 (br s, 1 H), 2.18 ($^1/_2$ABq, J = 11.1 Hz, 1 H), 2.00 ($^1/_2$ABq, J = 11.1 Hz, 1 H), 1.88 ($^1/_2$ABq, J = 8.5, 1.5 Hz, 1 H), 1.41 (d, J = 4.3 Hz, 1 H), 1.71 (d, J = 4.5 Hz, 1 H), 1.46 (d, J = Hz, 1 H), 1.41 (d, J = 4.5 Hz, 1 H), 1.27 ($^1/_2$ABq, J = 8.5, 1.0 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) ppm 165.61, 146.46, 141.05, 51.33, 48.22, 43.08, 41.95, 38.15, 35.38, 34.93, 27.03, 26.86, 15.48, 15.18; MS, *m/z* (M$^+$) calcd 214.0994, obsd 214.1009.

Direct Irradiation of 12. A solution of **12** (21.4 mg, 0.1 mmol) in dichloromethane-d_2 (0.6 mL) contained in a thick-walled NMR tube was degassed by means of 6 freeze–thaw cycles and sealed under vacuum. This clear colorless solution was irradiated with a 450 W Hanovia lamp for 1.5 h and ultimately evaporated to leave **13** in quantitative yield, waxy white solid, mp 50–52 °C: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 6.26 ($^1/_2$ABq, J = 5.6, 3.0 Hz, 1 H), 6.14 ($^1/_2$ABq, J = 5.6, 3.0 Hz, 1 H), 3.57 (s, 3 H), 3.08 (br s, 1 H), 2.89 (br s, 1 H), 2.51 (br s, 1 H), 2.23 ($^1/_2$ABq, J = 11.5, 1.3 Hz, 1 H), 2.14 ($^1/_2$ABq, J = 11.5, 1.3 Hz, 1 H), 1.90 (d, J = 3.9 Hz, 1 H), 1.82 (dt, J = 8.4, 1.7 Hz, 1 H), 1.76 (d, J = 4.5 Hz, 1 H), 1.26 (d, J = 8.1 Hz, 1 H); ^{13}C NMR (75 MHz, CD$_2$Cl$_2$) ppm 173.34, 136.86, 134.93, 51.48, 51.24, 48.87, 41.91, 41.62, 38.91, 38.66, 35.63, 29.31, 27.93, 15.98; MS, *m/z* (M$^+$) calcd 214.0994, obsd 214.0984.

Synthesis and Photoisomerization of 14. Triene **1** (130 mg, 1 mmol) and methyl propiolate (84 mg, 1 mmol) dissolved in dichloromethane (3 mL) were placed in a thick-walled Pyrex tube. The solution was degassed by 5 freeze–thaw cycles, sealed under vacuum, and heated at 50–60 °C for 4 weeks. The progress of reaction was monitored by ^{1}H NMR on a second sample dissolved in CD$_2$Cl$_2$ at approximately the same concentration. At the end of this time, the cycloaddition was essentially complete. For **14**: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 7.24 (d, J = 3.0 Hz, 1 H), 6.33 ($^1/_2$ABq, J = 5.0, 3.4 Hz, 1 H), 6.29 ($^1/_2$ABq, J = 5.0, 3.4 Hz, 1 H), 3.75 (br s, 1 H), 3.64 (s, 3 H), 3.62 (br s, 1 H), 3.51 (t, J = 1.4 Hz, 2 H), 2.32 ($^1/_2$ABq, J = 6.6, 1.7 Hz, 1 H), 2.21 ($^1/_2$ABq, J = 6.2, 1.7 Hz, 1 H), 2.13 ($^1/_2$ABq, J = 6.6 Hz, 1 H), 2.05 ($^1/_2$ABq, J = 6.2, 1.4 Hz, 1 H).

The larger tube was then irradiated for 1 h with a 450 W Hanovia lamp, cooled in liquid nitrogen, and opened. The solution was transferred to a small base-washed flask and concentrated on a rotary evaporator. Volatile residues were removed at 0.3 Torr, and the residue was purified by thin-layer chromatography (silica gel; elution with pentane–dichloromethane (2:1)). There was isolated 156 mg (73%) of **13**, identical in all respects with the material described above.

(*Z*)-1,2-Bis(phenylsulfonyl)ethylene-*1-d* (15). A 250-mL, round-bottomed Schlenk flask containing a magnetic stirring bar was flame dried while being flushed with argon. After the addition of a solution of unpurified (*Z*)-1,2-bis(phenylthio)ethylene (4.88 g, 20 mmol) in anhydrous tetrahydrofuran (100 mL), the reaction mixture was cooled to −100 °C while being stirred and was treated during 15 min with 19 mmol of *tert*-butyllithium in pentane via syringe. After completion of the addition, stirring was maintained for an additional 10 min prior to quenching with 5 mL of methanol-d_1. After warming to room temperature, water and dichloromethane were added, and the organic phase was dried and concentrated.

The combined material from two runs was oxidized with 30% hydrogen peroxide (50 mL) in a solvent system composed of acetic acid (150 mL) and water (80 mL). Recrystallization of the crude product from ethanol gave 6.55 g (53%) of **15**, ^{1}H NMR analysis of which revealed the deuterium content to be 20% d_0 and 80% d_1.

Diels–Alder Cycloaddition of 15 to 1. A Schlenk filtration apparatus was fitted with two 50-mL, one-necked flasks. A magnetic stirring bar was previously placed in that flask destined to be the reaction vessel. The entire apparatus was flushed with argon while being flame dried. Rapidly, the cooled flask was charged with **15** (3.1 g, 10 mmol), dry deoxygenated tetrahydrofuran (20 mL), and triene **1** (1.3 g, 10 mmol). The entire vessel was wrapped in aluminum foil, and the reaction mixture was stirred for 2 days at room temperature under an argon atmosphere. The precipitated product was separated by suction filtration and subsequently dried at 0.3 Torr for 1 h in the Schlenk apparatus. There was obtained 3.73 g (85%) of **16** as white crystals decomposing above 213 °C. The 300 MHz ^{1}H NMR spectrum of **16** was identical with its all-protio counterpart except for the absence of a proton absorption at δ 3.33.

Table I. Quantitative Photochemical Response of **6** during Short Conversion Times

run 1		run 2	
% conversion	[8]/[7]	% conversion	[8]/[7]
1.89	5.52	2.11	3.89
3.45	2.25	2.78	2.86
5.20	1.58	3.60	2.22
7.83	1.01	4.40	1.91
10.69	0.74	5.26	1.58
13.10	0.60	7.06	1.29
22.30	0.30	11.52	0.80
		15.90	0.56
		22.30	0.36

Sensitized Photoisomerization of 16. A solution of **16** (1.32 g, 3.0 mmol) and acetophenone (80 mg) in 70 mL of thoroughly deoxygenated argon-saturated dichloromethane was irradiated in the manner described above. Upon recrystallization of the crude product from acetone, there was isolated 910 mg (69%) of **17** as white crystals decomposing above 215 °C. The 300 MHz ^{1}H NMR spectrum of **17** was identical with that of **7** except for lacking a proton absorption at δ 4.19.

Quadricyclane 18. A three-necked, round-bottomed flask equipped with a magnetic stirring bar was flame dried while being flushed with argon and subsequently charged with 25 mL of dry, deoxygenated, argon-saturated methanol, 1 g of disodium hydrogen phosphate, and 878 mg (2.0 mmol) of **17**. During the next 3 h, 25 g of 1.5% sodium amalgam was introduced in portions, while the mixture was stirred vigorously under argon. Following completion of the addition, stirring was maintained for 3.5 h, the mixture was poured into 80 mL of pentane, and the organic phase was washed with water (3×) and brine prior to drying. After concentration, the colorless oily residue was filtered three times through a small column of deactivated basic alumina (2 g; deactivation: 10 g Al_2O_3/1 g H_2O) with pentane as eluent. Traces of pentane were removed by careful pumping at 0.3 Torr to give **18** as a colorless oil which solidified on cooling over dry ice (185 mg, 59%). The ^{1}H NMR spectrum of this hydrocarbon was identical with that of **21** (see below) except that the absorption at δ 6.21 ppm was reduced to about one-half of the intensity.

Quadricyclane 21. A 100-mL, three-necked flask containing a magnetic stirring bar was flame-dried in a stream of argon and charged with 20 mL of dry methanol, 1.5 g of disodium hydrogen phosphate, 0.6 g (1.36 mmol) of **5**, and 3 g of a total of 20 g of sodium amalgam (1.3% by weight). The remainder of the amalgam was added portionwise during the ensuing 6 h. The reduction was conducted at room temperature with vigorous stirring under argon. Water (20 mL) and dichloromethane (30 mL) were added, and the separated organic phase was washed with water, dried, and evaporated. Purification of the residue was achieved by bulb-to-bulb distillation. There was obtained 76 mg (36%) of **21** as a colorless oil which solidified upon cooling over dry ice: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.21 (br s, 2 H), 2.82 (br s, 2 H), 2.15 ($^1/_2$ABq, J = 11.0 Hz, 1 H), 1.97 ($^1/_2$ABq, J = 11.0, 1.3 Hz, 1 H), 1.74 ($^1/_2$ABq, J = 8.0, 1.7 Hz, 1 H), 1.64 (d, J = 3.9 Hz, 2 H), 1.39 (d, J = 3.9 Hz, 2 H), 1.19 ($^1/_2$ABq, J = 8.0, 1.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) ppm 135.46, 48.81, 41.81, 38.01, 35.98, 26.67, 15.12; MS, m/z (M^+) calcd 156.0939, obsd 156.0935.

Attempted Sensitized Rearrangement of 18. A solution of **18** (20 mg) and benzophenone (3 mg) in 0.7 mL of CD_2Cl_2 was placed in a thick-walled NMR tube, degassed with 5 freeze–thaw cycles, and sealed under vacuum. Irradiation with a 450 W Hanovia lamp for 9 h led to no observable spectral changes except for some decomposition. Similar experiments were conducted with acetone and acetophenone as sensitizers. In these instances, the solvent was CH_2Cl_2, and the course of reaction was monitored by ^{2}H NMR. In neither case was chemical change noted after ca 9 h.

Direct Irradiation of 18. A samaple of **18** containing ca. 10% of the epoxide was placed in a quartz NMR tube, dissolved in CH_2Cl_2, and purged with nitrogen. After sealing the tube, the ^{2}H NMR spectrum was recorded. Irradiation of the tube with a 450 W Hanovia lamp (quartz housing) during 2 h revealed the slow, progressive conversion to **19**.

Thermolysis of 18. A solution of **18** (20 mg) in 0.8 mL of acid-free bromobenzene-d_5 (filtered through basic alumina) was degassed in a thick wall NMR tube by 5 freeze–thaw cycles. After the tube was sealed under vacuum, the solution was heated at 80 °C for 4 h. Since no isomerization was evident (^{1}H NMR analysis), heating was resumed at 100 °C for 17 h. During this period, some conversion to **20** was noted, and this process was enhanced by further heating at 150 °C for 16 h. Even after this time, however, the extent of ring opening was still only 20%, and no rearrangement was detectable by ^{1}H NMR: ^{1}H NMR (300 MHz, C_6D_5Br) δ 6.28 (br s, 3 H), 3.39 (br s, 4 H), 2.17 ($^1/_2$ABq, J = 5.9 Hz, 2 H), 2.06 ($^1/_2$ABq, J = 5.9 Hz, 2 H).

Direct Irradiation of 20. A sample of **20** in deoxygenated CH_2Cl_2 was placed in a quartz NMR tube, deaerated, and sealed. Photolysis with a 450 W Hanovia lamp (quartz housing) for 5 min induced considerable polymerization. However, ^{2}H NMR gave no evidence for residual **20** and indicated that **18** and **19** were both present in small amounts.

Controlled Photochemical Studies. Vinyl sulfone **6** (10.0 mg, 0.03 mmol) was placed in a dry, thick-walled 5-mm NMR tube and dissolved in 0.5 mL of CD_2Cl_2. While at −78 °C, this solution was repeatedly flushed with argon and evacuated to 0.2 Torr. After five of these cycles, the tube was sealed under vacuum. Irradiations were performed in a Rayonet reactor equipped with a bank of 300-nm bulbs. Following short periods of irradiation, ^{1}H NMR spectra were recorded at 300 MHz. Customarily, 32 K data points (1560–2770 scans) were compiled depending on the percent conversion in order to gain a comfortably acceptable signal-to-noise ratio. The results are given in Table I.

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