9.10 μ ($-SO_2-$); $\tau_{TMS}^{CDCl_3}$ 8.11–8.92 (multiplet, 12 H, $-CH_2-$ of piperidino groups), 7.25–8.08 [multiplet, 8 H, $(-CH_2-)_2N-$ of piperidino groups], 6.56 (broad triplet, *J* = 6.0 Hz, H, >CHN<, 6.07 and 5.88 [singlet and doublet (*J* = 3.0 Hz), respectively, 3 H, $-CH_2-SO_2-$ and $C_6H_5-CH-N<$, respectively], 4.93 and 5.13 (doublet of doublets, *J* = 12.0 and 6.0 Hz, 1 H, $>CH-SO_2-$), and 2.75 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{20}H_{30}N_2O_2S$: C, 66.26; H, 8.34; N, 7.73; S, 8.85. Found: C, 66.49; H, 8.46; N, 7.69; S, 8.97.

All filtrates and insoluble residues were combined and chromatographed on neutral alumina. The only material isolated was **37** and the total weight obtained by direct crystallization and chromatography was 15.5 g (61.0%).

Registry No.—**7**, 16808-51-8; **8**, 16808-52-9; **9**, 16808-53-0; **10**, 16808-54-1; **11**, 16808-55-2; **12**, 16808-56-3; **15**, 16808-57-4; **17**, 16808-58-5; **19**, 16793-41-2; **25**, 16793-42-3; **26**, 16793-43-4; **29**, 16791-06-3; **31**, 16790-87-7; **32**, 16790-88-8; **34**, 16790-89-9; **37**, 16790-90-2.

Unsaturated Heterocyclic Systems. XLI. Selected Reactions of 2-Methylenethiete 1,1-Dioxides[1,2]

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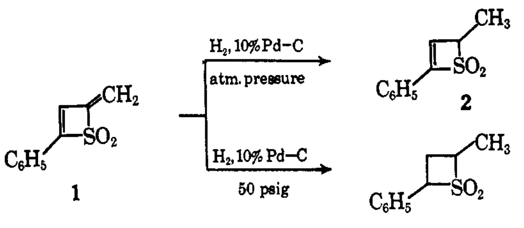
2-Methylene-4-phenyl-2H-thiete 1,1-dioxide (**1**) could be hydrogenated in two distinct stages to a dihydro and tetrahydro derivative, respectively. This strained sulfone (**1**) was also found to undergo ready Michael reaction with dimethylamine. When exposed to 1,3-diphenylisobenzofuran, both **1** and its phenyl congener **7** gave rise to Diels–Alder adducts. In each instance, a single adduct was formed. The stereochemistry of the adducts and the stereospecificity of the processes have been assigned on the basis of spectral data and steric considerations. Irradiation of **1** in diethyl ether leads to the formation of a lone (2 + 2π) dimer. Spectral analysis and dipole moment data establish the structure of the dimer as that of the *trans*-1,2-cyclobutane derivative **14**. The probable mechanistic pathways for the stereoselective photocycloaddition are discussed.

The preceding paper describes the first synthesis of highly unsaturated and reactive methylenethiete dioxides.[1] The "cross conjugation" of the butadiene chromophore with the sulfonyl group in such molecules, when considered together with the relatively high degree of ring strain, makes the system a particularly suitable subject for experimental evaluation of chemical reactivity, bond hybridization, and involvement of d orbitals at the heteroatom. Although the geometrical parameters (*i.e.*, interorbital and internuclear angles) for a molecule such as **1** have not yet been evaluated, a number of modified physical and chemical properties can be expected because of varied hybridization at the vinylic carbon atoms. Although the four carbon centers fall roughly into two sets of similarly hybridized atoms, their relative reactivities were anticipated to differ significantly and to lend to the molecule properties which are not normally seen in unstrained α,β-unsaturated sulfones or thiete dioxides. The present paper describes the chemical properties of **1** and **7**, of which reactions have been selected in an attempt to provide insight into the reactivity differences of the exocyclic and endocyclic double bonds.[4]

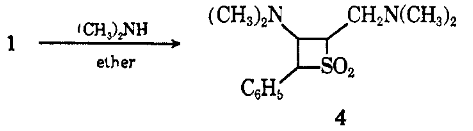
Results and Discussion

When a dilute solution of **1** was hydrogenated at atmospheric pressure over 10% palladium on charcoal, there resulted a rapid uptake of hydrogen which ceased before 1 equiv was consumed. The resulting dihydro derivative was easily identified as 2-methyl-4-phenyl-2H-thiete 1,1-dioxide (**2**) principally on the basis of its nmr spectrum (see Experimental Section). When the pressure of hydrogen was increased to 50 psig and the catalytic hydrogenation allowed to proceed for 58 hr, thietane dioxide **3** was formed in greater than 90% yield (Scheme I).

SCHEME I



Exposure of **1** to a cold ethereal solution of dimethylamine (eq 1) led to the formation of 2-dimethylaminomethyl-3-dimethylamino-4-phenylthietane 1,1-dioxide (**4**), mp 76–78°, isomeric with the sulfone of identical gross structure, mp 91–93°,[5] utilized in the preparation of **1**.[1] The stereochemical relationship of the two isomers could not be established with certainty owing to unresolvable complexities of certain nmr absorptions and the lack of appropriate model compounds.



4 (1)

Reaction of equimolar quantities of **1** and 1,3-diphenylisobenzofuran (**5**) in refluxing benzene solu-

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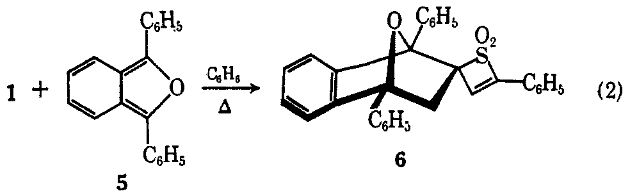
[1] For part XL of this series, see L. A. Paquette, M. Rosen, and H. Stucki, **33**, 3020 (1968).

[2] This work was generously supported by Grant GP-5977 from the National Science Foundation.

[3] Alfred P. Sloan Foundation Research Fellow.

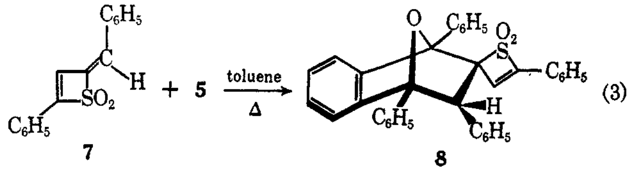
[4] Our intended goal was somewhat beclouded by the fact that, of the two known and available methylenethiete dioxides (**1** and **7**), only **7** possesses two identically substituted (except for the ring) double bonds. However, as will be seen, the chemical behavior of **1** is sufficiently diagnostic of the divergence in reactivity between the two sites of unsaturation to be of interpretive value.

[5] L. A. Paquette and M. Rosen, *J. Amer. Chem. Soc.*, **89**, 4102 (1967).

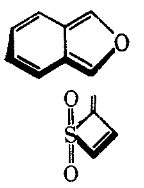


tion (eq 2) for 16 hr afforded in 79% yield a *single* crystalline 1:1 adduct which had been assigned structure **6**. In confirmation of the structural assignment, the nmr spectrum of **6** displayed only an AB quartet (J = 13.0 Hz) at τ 6.67 and 7.17 (methylene protons) and a singlet at 3.38 (styrene proton) in addition to the aromatic proton absorption.

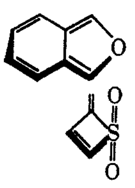
A similar Diels-Alder condensation of **5** with 2-benzylidene-4-phenyl-2H-thiete 1,1-dioxide (**7**) led to the spiro sulfone **8** (eq 3). The *cis* relationship of the endoxy bridge and the sulfonyl group follows from the steric considerations presented below. A decision as to whether the phenyl group is of the *exo* or *endo* configuration was attained from a comparative analysis of the nmr spectra of **8** and **6**. Thus, whereas **6** exhibited a singlet at τ 3.38 for the styryl proton, the spectrum of **8** displays the same proton at 3.94. The magnitude of this upfield shift is most readily understood in terms of diamagnetic shielding experienced by the styryl proton in **8** because of its proximity to the face of the benzene ring in question. It follows therefore that this phenyl substituent occupies the *endo* position and that the structure of methylenethiete dioxide **7** is that in which the benzylidene phenyl group is *trans* to the sulfonyl function.[1]



Diels-Alder additions to methylenethiete dioxides thus clearly prefer involvement of the exocyclic double bond. The formation of lone adducts in these cycloadditions is interesting and suggests steric control in the transition states leading to **6** and **8**. Inspection of diagrams **9** and **10** reveals that in the first transition state the bulky space-filling sulfonyl group is forced to lie in close proximity to the underface of the planar isobenzofuran molecule. Such nonbonded interaction can be expected to raise the energy associated with **9** to the point where transition state **10** becomes the only low energy pass available to the reacting components.



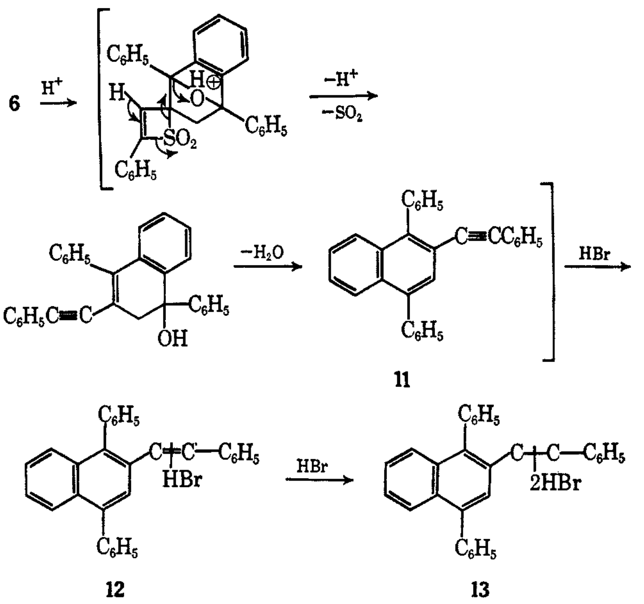
9



10

Endoxy sulfone **6** was reversibly protonated in hot polyphosphoric acid (80% recovery after quenching in water subsequent to 12-hr exposure at 100°). However, when **6** was refluxed in an acetic acid solution of anhydrous hydrogen bromide, there resulted a mixture consisting chiefly of monobromide **12** and traces of dibromide **13**. The gross structural assignment of **12** was substantiated by elemental analysis and spectral data (see Experimental Section); the exact position of attachment of the bromine was not established. On the basis of the above data and precedent concerning the acid-catalyzed dehydrative expulsion of sulfur dioxide from a thietane dioxide,[6] the pathway in Scheme II is proposed. Protonation of **6** at the endoxy bridge can lead with the proper migration of electrons (as shown) to the expulsion of sulfur dioxide. The resulting tertiary carbinol is without doubt rapidly dehydrated to attain the additional resonance energy of the naphthalene ring. Electrophilic addition of hydrogen bromide to the resulting acetylene (**11**) produces the observed products.

Scheme II



Irradiation of a dilute ether solution of **1** with an Hanovia 200 W mercury arc for 5 days gave in 12% yield a *lone* crystalline photodimer (**4**). The dimeric nature of this material was derived from its elemental analysis and mass spectrum. The latter displayed a molecular ion at m/e 384 (18% of base), a peak at m/e 192 (47% of base) corresponding to the molecular ion of the monomer, and peaks at m/e 144 (base) and 128 (86% of base) which result from the loss of sulfur monoxide and oxygen, respectively and consecutively, from the monomer unit. The nmr spectrum of **4** denoted the presence of two vinyl protons, and the ultraviolet absorption curve confirmed the presence of two α-sulfonyl styrene chromophores. These data established the fact that dimerization had occurred exclusively at the exocyclic double bond. On the basis of this analysis, four possible structures for the dimer are theoretically possible: *cis*-1,2 (**14a**), *trans*-1,2 (**14b**), *cis*-1,3 (**14c**), and *trans*-1,3 (**14d**).

The nmr spectrum of **14d** can be expected to display a sharp singlet for the cyclobutane protons since rapid inversion of the puckered cyclobutane ring at room temperature would effectively average the four protons and cause them to be magnetically equivalent. In contrast, the cyclobutane methylene groups of dimer

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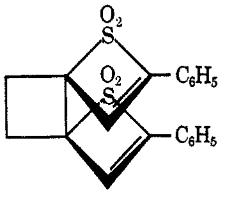
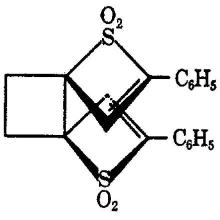
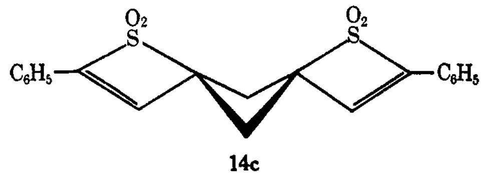
(6) L. A. Paquette and T. R. Phillips, *J. Org. Chem.*, **30**, 3883 (1965).



14a



14b



14c

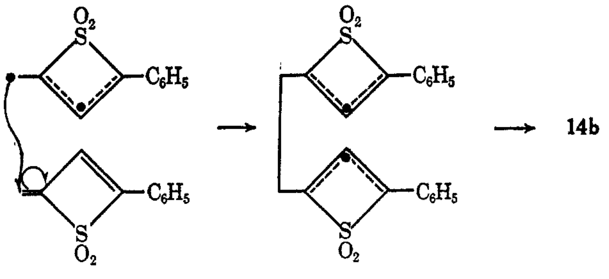
14d

14c would very likely give rise to a symmetrical AB pattern in which the individual peaks would probably be further split by transannular coupling. Precedent for this analysis has been derived from the spectra of the isomeric 1,3-dihalo-1,3-dimethylcyclobutanes.[7] In the *cis*-1,2 structure (**14a**), one hydrogen of each methylene group is seen to be *cis* to a sulfonyl group and therefore subject to its field effect; a significant difference in chemical shift between the two types of protons would very likely result. With regard to the corresponding *trans* compound (**14b**), these effects would be somewhat minimized and large chemical-shift differences would perhaps not be seen. In actuality, the photodimer shows a broad temperature-independent multiplet centered at τ 7.27 ($W_{1/2}$ = 3.7 Hz) for the methylene protons. Although this observation eliminated the 1,1,3,3-tetrasubstituted cyclobutane formulations (**14c** and **d**) from consideration, it remained to differentiate between **14a** and **b**.

The dipole moment of the dimer was 2.7 ± 0.5 D. in benzene solution. Whereas the dipole moments of *cis* isomers **14a** and **14c** can be expected to be very large (8–10 D.),[8] those of *trans* isomers **14b** and **14d** would be expected to have canceling bond moments. Since **14d** had already been eliminated as the correct structure, it became clear that the photodimerization of **1** had given rise exclusively to the *trans*-1,2 dimer (**14b**). The substance possesses a small, but significant, dipole moment since the two hetero rings probably cannot attain the conformation where the two dipoles are completely opposed.

Irradiation of **7** under analogous conditions for varying lengths of time gave no characterized products. The viscous yellow oils which resulted in these attempts contained no sulfonyl absorption in their infrared spectra.

The photodimerization of **1** to **14b** represents yet another example of a symmetry-allowed photochemical 2 + 2 cycloaddition.[9] The question of whether the formation of the cyclobutane ring is concerted or proceeds by means of attack of a photochemically excited ($\pi \rightarrow \pi^*$) molecule of **1** upon a ground-state counterpart (as illustrated) cannot be answered on the basis of the available data. It should be noted, however, that the two odd electrons in **15** enjoy appreciable resonance delocalization. The high degree of stereoselectivity observed in the photodimerization process can be seen to result from minimal steric interference of the two sulfonyl groups in the most favorable transition state.



15

Both **1** and **7** failed to react when refluxed in benzene or toluene with diiron enneacarbonyl. No characterizable products were found on attempted cyclopropanation with trimethylsulfonium bromide and potassium *t*-butoxide in dimethyl sulfoxide solution at room temperature.[10]

Experimental Section[11]

Partial Hydrogenation of 1.—A solution of 0.5 g (2.6 mmol) of **1** in 50 ml of ether containing 300 mg of 10% palladium on carbon was placed in an atmospheric hydrogenation apparatus. The uptake of hydrogen was rapid but ceased before 1 equiv was consumed. The catalyst was removed by filtration, and the filtrate was concentrated to give a colorless solid which possessed an unpleasant odor and contained starting material. Recrystallization of this mixture from ether–petroleum ether afforded 0.25 g (49.5%) of **2-methyl-4-phenyl-2H-thiete 1,1-dioxide** (**2**) as a slightly colored solid, mp 104–107°. An analytical sample of **2** was obtained from ether: mp 111–112°; $\lambda_{max}^{CCl_4}$ 7.62, 8.47, and 8.80 μ (–SO$_2$–); λ_{max}^{EtOH} 255 mμ (ϵ 17,270); $\tau_{TMS}^{CCl_4}$ 8.48 (doublet, J = 7.0 Hz, 3 H, methyl group), 5.25 (broad quartet, J = 7.0 Hz, 1 H, α-sulfonyl proton), 3.10 [singlet (slightly split), J = 2.0 Hz, 1 H, styrene proton], and 2.60 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.83; H, 5.18; S, 16.51. Found: C, 61.95; H, 5.32; S, 16.45.

Complete Hydrogenation of 1.—A solution of 0.2 g (1.05 mmol) of **1** in 30 ml ether containing 100 mg of 10% palladium on charcoal was shaken under 50 psig of hydrogen for 54 hr at room temperature. The catalyst was removed by filtration and the filtrate was concentrated to give 0.2 g (>90%) of a colorless solid, mp 95–97°. Recrystallization from ether-petroleum ether (bp 60–80°) afforded pure 2-methyl-4-phenylthietane 1,1-dioxide (**3**): mp 107–109°; $\lambda_{max}^{CCl_4}$ 7.62, 8.47, and 8.80 μ (–SO$_2$–); $\tau_{max}^{CDCl_3}$ 8.48 (broad doublet, J = 7.0 Hz, 3 H, methyl group), 7.25–7.75 (multiplet, 2 H, ring methylene protons), 5.55–5.95 (multiplet, 1 H, nonbenzylic α-sulfonyl proton), 4.68 (multiplet, 1 H, benzylic α-sulfonyl proton), and 2.60 (singlet, 5 H, phenyl group).

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(7) K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Amer. Chem. Soc.*, **87**, 3151 (1965).

(8) For an excellent discussion of sulfone dipole moments, see C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962, pp 67–73.

(9) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(10) W. E. Truce and V. V. Badiger, *J. Org. Chem.*, **29**, 3277 (1964).

(11) Melting points were determined with a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined with a Cary 14 recording spectrometer. Nuclear magnetic resonance spectra were obtained with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The mass spectrum was measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.18; H, 6.17; S, 16.22.

Reaction of 2-Methylene-4-phenyl-2H-thiete 1,1-Dioxide (1) with Dimethylamine.—Into a cold (−20°) solution of 0.30 g (1.6 mmol) of **1** in 20 ml ether was distilled excess dimethylamine and the resulting brown mixture was left overnight at 0°. Evaporation of the solution and trituration of the residual brown oil with ether afforded on cooling 0.20 g (45.5%) of 2-dimethylaminomethyl-3-dimethylamino-4-phenylthietane 1,1-dioxide (**4**), mp 76–78°. Recrystallization from ether gave pure **4** (unassigned isomer): mp 84–85°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 7.50, 8.55, and 8.67 μ (–SO_2–); $\tau_{\max}^{\mathrm{CDCl_3}}$ 7.83 and 7.60 (two singlets, 6 H each, dimethylamino groups), 6.90 (doublet, J = 6.0 Hz, 2 H, –CH_2NMe_2), 6.43 (doublet, J = 10.0 Hz, 1 H, >$CHNMe_2$), 5.55–5.95 (multiplet, 1 H, nonbenzylic α-sulfonyl proton), 4.82 (doublet, J = 10.0 Hz, 1 H, benzylic proton), and 2.52 (singlet, 5 H, phenyl group).

Anal. Calcd for $C_{14}H_{22}N_2O_2S$: C, 59.54; H, 7.85; N, 9.92. Found: C, 59.63; H, 7.85; N, 9.57.

3,4-Dihydro-1,4,4′-triphenylspiro[1,4-epoxynaphthalene-2(1H),-2′[2H-]thiete] 1′,1′-Dioxide (6).—A solution of 0.7 g (2.6 mmol) of 1,3-diphenylisobenzofuran (**5**)[12] and 0.5 g (2.6 mmol) of **1** in 10 ml of benzene was refluxed for 16 hr under an atmosphere of nitrogen. The resulting brown solution was concentrated to an oil which was chromatographed on neutral alumina. Elution of the column with ether–petroleum ether (1:2) afforded 1.15 g (79.2%) of colorless adduct, mp 210–212° dec. An analytical sample of **6** was obtained from benzene–petroleum ether: mp 207–209°, with prior formation of yellow color at 165°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.67 and 8.69 μ (–SO_2–); $\lambda_{\max}^{\mathrm{EtOH}}$ 262 mμ (ϵ 27,900); $\tau_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 6.67 and 7.17 (AB quartet, J = 13.0 Hz, 2 H, methylene protons), 3.38 (singlet, 1 H, styrene proton), 2.20–3.15 (complex pattern with singlet at 2.68, 17 H, fused aromatic ring protons and phenyl groups), and 1.88 (complex pattern, 2 H, fused aromatic ring protons).

Anal. Calcd for $C_{30}H_{22}O_3S$: C, 77.89; H, 4.80; S, 6.93. Found: C, 78.21; H, 4.92; S, 6.74.

3,4-Dihydro-1,3,4,4′-tetraphenylspiro[1,4-epoxynaphthalene-2(1H),2′[2H-]thiete] 1′,1′-Dioxide (8).—A solution of 1.05 g (3.8 mmol) of 1,3-diphenylisobenzofuran (**5**) and 1.0 g (3.7 mmol) of **7** in 15 ml of toluene was refluxed for one day under an atmosphere of nitrogen. The toluene was removed *in vacuo* and the yellow residue was chromatographed on neutral alumina. Elution of the column with ether–petroleum ether (1:3) gave 0.4 g (20.0%) of yellow adduct, mp 211–213° dec. Recrystallization of this material from benzene–petroleum ether gave colorless crystals of **8**: mp 216°, with prior formation of yellow color at 190°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.66 and 8.69 μ (–SO_2–); $\lambda_{\max}^{\mathrm{EtOH}}$ 263 mμ (ϵ 12,970) and end absorption; $\tau_{\max}^{\mathrm{CDCl_3}}$ 5.40 (multiplet, 1 H, benzylic proton), 3.94 (broad singlet, 1 H, styrene proton), 2.28–3.18 (complex pattern with singlet superimposed at 2.92, 22 H, fused aromatic ring protons and phenyl groups), and 1.68–1.91 (complex pattern, 2 H, fused aromatic ring protons).

Anal. Calcd for $C_{36}H_{26}O_3S$: C, 80.27; H, 4.87; S, 5.95. Found: C, 80.20; H, 4.95; S, 5.94.

Further elution of the column with ether–petroleum ether (1:1) and ether gave 1.5 g of an oily solid. Recrystallization of this material from benzene–petroleum ether afforded 0.45 g of a mixture of **8**, dibenzoyl ethylene, and **7**, mp 162–165°.

Treatment of 6 with Hydrogen Bromide.—A stirred mixture of 0.65 g (1.4 mmol) of **6** and 10 ml of glacial acetic acid containing 0.5 ml of acetic anhydride was treated with gaseous hydrogen bromide for 5 min. The resulting red solution was refluxed for 16 hr whereupon it turned dark brown. The solution was cooled and poured into water, and the organic components were extracted with chloroform. Usual work-up of this solution gave 0.9 g of a brown oil. Chromatography of this material on neutral alumina afforded, on elution with petroleum ether–ether (3:1), 0.5 g (77.0%) of **12**, as a colorless waxy solid, mp *ca.* 73° (prior softening at 63°). Molecular distillation of this material at *ca.* 120° (0.02 mm) and recrystallization from methanol gave pure **12**: mp 68–70°; $\lambda_{\max}^{\mathrm{CCl_4}}$ 14.33 μ (aromatic system); $\lambda_{\max}^{\mathrm{EtOH}}$ 310 (ϵ 20,150), 285 (32,750), and 236 mμ (37,400); $\tau_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 3.16 (singlet, 1 H, vinyl proton), and 2.10–3.05 (complex pattern, 20 H, aromatic protons).

Anal. Calcd for $C_{30}H_{21}Br$: C, 78.09; H, 4.59. Found: C, 77.63; H, 4.21.

Photolysis of 1. *trans*-2,7-Diphenyl-1,6-dithiadispiro[3.0.3.2]-deca-2,7-diene 1,1,6,6-Tetraoxide (14b).—A stirred solution of 5.1 g (0.027 mol) of **1** in 450 ml of ether was irradiated under nitrogen with a Hanovia 200 W mercury arc for 5 days. Work-up gave a black oily solid which was chromatographed on neutral alumina. Elution of the column with ether–petroleum ether (1:1) afforded 0.9 g of starting material and 0.5 g (11.9% based on unrecovered **1**) of photodimer **14b**, mp 231° dec. An analytical sample of **14b** was obtained from acetone: mp 232° dec (sintering at *ca.* 205°); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 7.62 and 8.64 μ (–SO_2–); $\lambda_{\max}^{\mathrm{EtOH}}$ 258 mμ (ϵ 36,900), slight shoulder at 266, and end absorption; $\tau_{\mathrm{TMS}}^{\mathrm{DMSO\text{-}}d_6}$ 7.27 [multiplet, 4 H, $\left(\!-CH_2-\!\right)_2$], 2.47 (singlet, 10 H, phenyl groups), and 2.10 (singlet, 2 H, vinyl protons).

Anal. Calcd for $C_{20}H_{16}O_4S_2$: C, 62.48; H, 4.20; S, 16.68. Found: C, 62.31; H, 4.29; S, 16.65.

Registry No.—**2,** 16791-00-7; **3,** 16791-01-8; **4,** 16791-02-9; **6,** 16791-03-0; **8,** 16791-04-1; **14b,** 16791-05-2.

Acknowledgment.—The authors are especially indebted to Professor N. L. Allinger for the dipole moment data.

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(12) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).