volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-4177.

Photochemistry of Thianaphthene 1,1-Dioxide. Addition of Alkenes

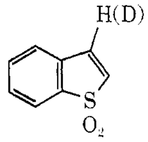
DAVID N. HARPP* AND CYRIL HEITNER[1]

Department of Chemistry, McGill University, Montreal, Canada

Received February 27, 1973

The photocycloaddition of thianaphthene 1,1-dioxide to various unsymmetrically substituted olefins gives products with orientational and stereochemical specificity. The mechanism appears to involve a resonance stabilized 1,4-diradical intermediate.

Photochemically induced cycloaddition reactions of mixed alkene partners have received considerable attention as routes to theoretically interesting compounds and natural products as well as for their mechanistic properties.[2] While a number of alkene systems have been examined, there is little known concerning the role that α heteroatoms may have on the coupling mode. Accordingly, we have studied the addition of several alkene derivatives to thianaphthene 1,1-dioxide (**1**, benzo[*b*]thiophene 1,1-dioxide).[3]



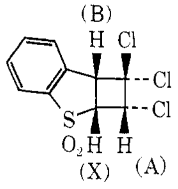
1a, H
b, D

Results and Discussion

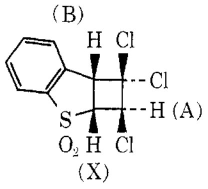
Reaction solutions were irradiated with light of wavelength 300 nm and greater; thianaphthene 1,1-dioxide (**1a**) absorbs 99% of the emitted radiation while the olefins absorb no more than 1%.

Cycloaddition to Trichloroethene.—Thianaphthene 1,1-dioxide (**1a**) was dissolved in trichloroethene, purged with dry nitrogen, and irradiated for 3 hr. Fractional crystallization from benzene gave adduct **2a** (52%) and the two photodimers of **1a** (48%).[3a]

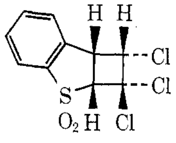
Analysis of the mass spectrum (*m/e* 296, parent) and ir [$\bar{\nu}$ at 1320 and 1160 (SO_2) and 670 cm^{-1} (CCl)] indicated a 1:1 adduct with the possible structures I–IV. Photoadducts with trans stereochemistry at the junction of the five- and four-membered ring are unlikely, particularly considering the two-step process proposed by Corey.[4] Isomerization of a possible trans ring juncture cannot be performed because of rapid hydrohalide elimination from the substrate (*vide infra*).



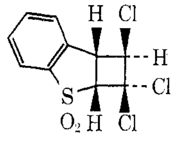
I



II



III



IV

The structure and stereochemistry of **2** were determined by a comparison analysis of cycloadducts **2a** and **2b**. Adduct **2b** was formed by using 3-deuteriothianaphthene 1,1-dioxide (**1b**). Resonances appearing in the nmr spectrum of **2b** were τ 2.18 (4 H, aromatic), 5.18 (1 H, d, J_{AX} = 8.0 Hz, CH), and 5.69 (1 H, d, J_{AX} = 8.0 Hz, CH). This spectrum is consistent with structure I or II. If structure III or IV were correct, the coupling between the chloro proton (A) and the SO_2 proton (X) would be expected to be of the order of 0–2.5 Hz instead of 8.0 Hz (cross-ring coupling constants higher than 2.5 Hz have been recorded only for rigid bicyclobutane derivatives[5]). The nmr spectrum of compound **2a** consists of a multiplet at τ 2.18 (4 H, m, aromatic) and an ABX multiplet in which the AB portion is centered at τ 5.18 (2 H) and the X part at τ 5.69 (1 H). Examination of the ABX signals revealed J_{AB} = 1.5 Hz (cross-ring coupling) and $J_{AX} + J_{BX}$ = 15.5 Hz. Because the AB section (expanded scale) of the spectrum has only six recognizable peaks, it was not possible to determine values for D^+, D^-, and $^1/_2(J_{AX} + J_{BX})$;[6] hence J_{AB} and $J_{AX} - J_{BX}$ could not be calculated. However, from ($J_{AX} + J_{BX}$) and J_{AX} = 8 Hz (determined from nmr spectrum of deuterated adduct **2b**), a value of J_{BX} (7.5 Hz) was determined. The X section of the ABX spectrum contained four peaks; thus J_{AX} and J_{BX} have the same sign.[5]

The nmr data obtained for compound **2a** are consistent with structure I rather than II. It has been observed[7] for vicinal protons that $J_{cis}/J_{trans} > 1$. Hence, J_{BX} = 7.5 Hz for the vicinal cis benzylic and sulfonyl protons and J_{AX} = 8.0 Hz, $J_{BX(cis)}/J_{AX} < 1$, supports cis stereochmistry for protons A and X.

---

[1] NRCC Bursary Holder, 1968–1970.

[2] For leading references see P. de Mayo, *Accounts Chem. Res.*, **4**, 41 (1971); P. G. Bauslaugh, *Syntheses*, **2**, 287 (1970).

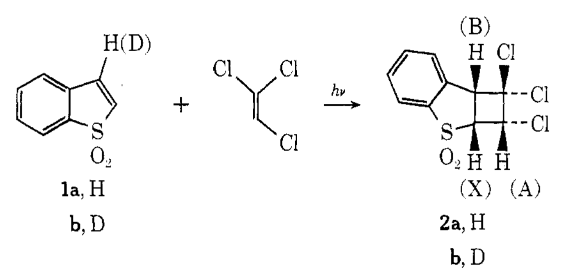
[3] For previous papers on the photochemistry of **1** see (a) D. N. Harpp and C. Heitner, *J. Org. Chem.*, **35**, 3256 (1970); (b) D. N. Harpp and C. Heitner, *J. Amer. Chem. Soc.*, **94**, 8179 (1972).

[4] E. J. Corey, J. D. Bass, R. La Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

[5] R. M. Dodson and A. G. Zielske, *J. Org. Chem.*, **32**, 28 (1967).

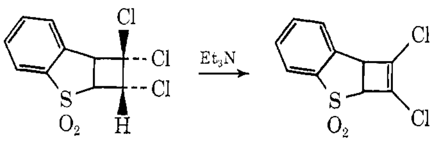
[6] C. N. Banwell, "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press, New York, N. Y., 1967, p 85.

[7] I. Fleming and D. H. Williams, *Tetrahedron*, **23**, 2747 (1967).



Since cross-ring coupling constants for protons with 1,3 cis stereochemistry range from 0.9 to 2.5 Hz for cyclobutane compounds and cross-coupling constants for protons with trans stereochemistry are 0.5 Hz,[6] the value for J_{AB} of 1.5 Hz provides further evidence that protons A, B, and X have cis stereochemistry.

The elemental analysis for compound **2a** was not completely satisfactory. This is most likely due to slow decomposition (dehydrohalogenation) on standing. Characterization of a stable derivative was therefore necessary. Dehydrohalogenation of **2a** in refluxing triethylamine gave dihalide **3**: nmr (C_6D_6) τ 2.60–3.35 (4 H, m, aromatic), 6.35 (2 H, AB q, $\Delta\nu = 20.1$, $J_{AB} = 4.0$ Hz, CH); ir $\bar{\nu}$ 1680 (C–C), 1320 and 1150 (SO_2), 650 cm^{-1} (CCl). The above data are consistent with the loss of HCl to give cyclobutene derivative **3**.



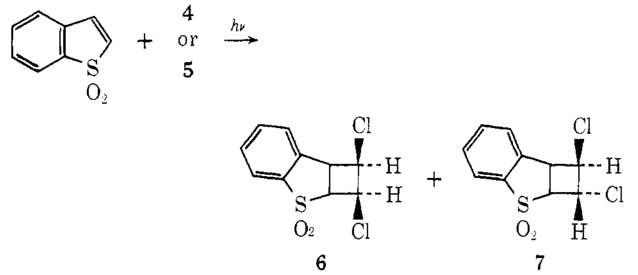
2a **3**

Purging the trichloroethene solution of **1a** with O_2 completely inhibited cycloaddition, indicating a triplet excited state as intermediate.

Cycloaddition to *cis*- and *trans*-Dichloroethene.—Thianaphthene 1,1-dioxide (**1a**) was dissolved in *cis*-(**4**) or *trans*-dichloroethene (**5**) and irradiated. The solvent was then evaporated and the reaction mixture was crystallized (ethanol, *cis*-dichloroethene adduct; benzene, trans adduct). Examination of the crude reaction mixture by vpc, nmr, and ir techniques revealed the same two products for each reaction.

The crystals obtained from photoaddition of dioxide **1a** to *cis*-dichloroethene (**4**) were separated on a silica gel column. The first fraction was pure **6** [nmr τ 2.3 (4 H, aromatic), 5.0 (m), 5.5 (m)]; the second fraction contained a mixture of **6** and **7** and was crystallized from CCl_4 to give pure **7** [nmr τ 2.3 (4 H, aromatic), 5.1–5.9 (m)].

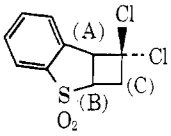
Consideration of the spectral data has led to structure assignments for **6** and **7** as shown below. It has been observed that halogen atoms shield protons that are cis to them.[6] The lower field signals appear to move into the envelope while peaks have been shifted to high field out of the envelope (in comparing cis with trans). Hence, a tentative structure as illustrated by **6** and **7** can be proposed without defining the relative stereochemistry of the ring junction protons.



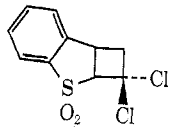
	%6	%7
4 (cis)	53	47
5 (trans)	23	77

By comparing the integration for the nmr signal that is unique to each of **6** and **7** in the reaction mixtures, ratios of **6**:**7** = 53:47 and 23:77 were estimated for cycloadditions of **1a** to *cis*- and *trans*-1,2-dichloroethylene, respectively. It is of interest to note that, in these cycloaddition reactions, only two of the four possible products were observed. The photocycloaddition of *cis*- and *trans*-1,2-dichloroethylene to thianaphthene and cyclopentenone gave four products.[8,9]

Cycloaddition to 1,1-Dichloroethene (8).—Thianaphthene 1,1-dioxide (**1a**) and 1,1-dichloroethene (**8**) were irradiated in benzene. Work-up and recrystallization from ethanol gave 77% of **9a** as the only product. Spectroscopic evidence [nmr τ 2.2 (4 H, aromatic), 5.20 (1 H, m), 5.73 (1 H, m), 6.25–7.0 (2 H, m)] indicates that the compound is a 1:1 adduct between thianaphthene 1,1-dioxide and 1,1-dichloroethane as represented by either structure V or VI.



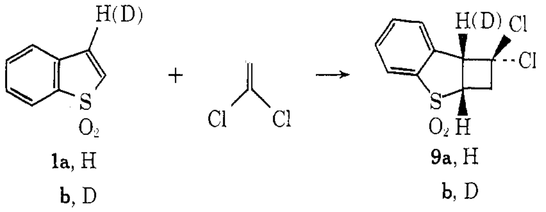
V



VI

Irradiation of the resonance at τ 6.25–7.0 (proton C) causes the peaks at τ 5.20 (proton A) to collapse to a doublet (J = 8.0 Hz). This same signal (τ 5.20) collapsed to a doublet (J = 2.5 Hz) and the multiplet at τ 6.25–7.01 into a distorted quartet when the resonance at τ 5.73 (proton B) was irradiated. This indicates that proton A is strongly coupled to proton B while B is similarly coupled to C; proton A is weakly coupled to proton C. The assignments for A, B, and C will then lead to the elucidation of the structure of adduct **9a**. Final evidence for this assignment is derived from the product of the irradiation of 3-deuteriothianaphthene 1,1-dioxide (**1b**) in 1,1-dichloroethene. Photolysis of **1b** in the presence of **8** under the same conditions as for **1a** gave compound **9b** (melting point identical with that of **9a**).

Examination of the nmr spectrum revealed that the



---

[8] D. C. Neckers, J. H. Dopper, and H. Wynberg, *J. Org. Chem.*, **35**, 1582 (1970). Although this paper by Neckers produced more cycloaddition products than the present study in the reactions of methyl-substituted benzo[*b*]thiophenes with *cis*- and *trans*-1,2-dichloroethene, in the one comparable case to our work (2,3-dimethylbenzo[*b*]thiophene) the cis/trans ratio of products was very similar (cis olefin 51:48 *vs.* 53:47; trans olefin 72:28 *vs.* 77:23.

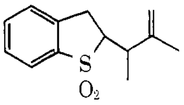
[9] W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, **92**, 1399 (1970). de Mayo has recently reported four.[9b] (b) R. O. Loutfy and P. de Mayo, *Can. J. Chem.* **50**, 3465 (1972).

resonance at τ 5.73 (B) had collapsed to a triplet (J = 8.0 Hz). In addition, the signal at τ 6.25–7.0 (C) appeared as a pair of doublets (τ 6.53, J = 8.0 Hz, and τ 6.61, J = 8.0 Hz). Thus, A is the benzylic proton and B is the sulfonyl proton; the above results are consistent with **9a** having structure V.

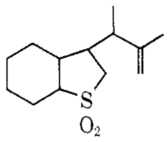
Cycloaddition of Thianaphthene 1,1-Dioxide (1a) to Tetrachloroethene.—Thianaphthene 1,1-dioxide was irradiated in the presence of tetrachloroethene; the only materials recovered after all of compound **1a** was consumed were the two photodimers of **1a.**[3a]

Cycloaddition of Thianaphthene 1,1-Dioxide (1a) to 2-Methyl-2-butene (10).—Compound **1a** was irradiated in the presence of 2-methyl-2-butene in benzene for 1 hr. Analysis of the reaction mixture by vpc and tlc indicated that two products formed. The components of the reaction mixture were separated by preparative tlc developed by cyclohexane–ethyl acetate (4:1).

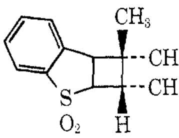
The first fraction, after recrystallization from ethanol, showed nmr τ 2.4 (m, aromatic), 5.0 (s, 2 H, $=CH_2$), 6.3-7.2 (m, 4 H), 8.2 (s, 3 H, CH_3), 8.4 (d, 3 H, $CHCH_3$), and m/e 236 (molecular ion). The above data are consistent with a 1:1 adduct of compound **1a** and 2-methyl-2-butene of structure VII or VIII. The second fraction, **12a**, showed nmr τ 2.5 (m, 4 H), 6.4 (m, 2 H), 7.7 (m, 1 H), 8.8 (d, 3 H), 9.3 (s, 3 H), and m/e 236 (molecular ion). The structures that are consistent with the spectral properties listed above are 1:1 adducts IX–XII shown below.



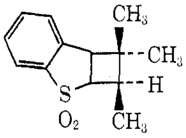
VII



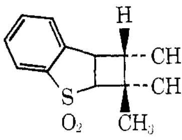
VIII



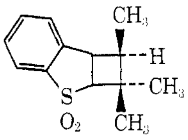
IX



X



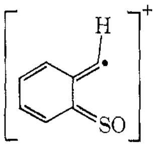
XI



XII

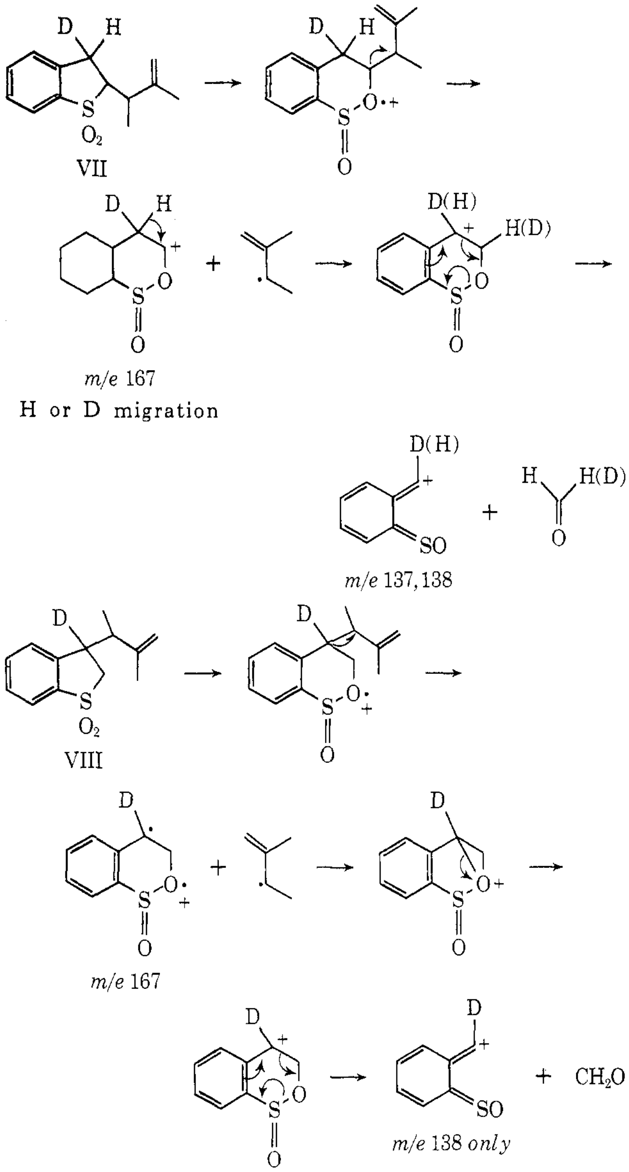
In order to facilitate mass spectra and nmr interpretations, 3-deuteriothianapthene 1,1-dioxide (**1b**) was used as a substrate for the previous photochemical reaction. The two 3-deuterio products (**11b** and **12b**) were separated as before.

One of the consistently prominent peaks in the mass spectra of thianaphthene 1,1-dioxide (**1a**) and its derivatives, photodimers, and adducts **2a**, **6**, **7**, **9a**, **11a**, and **12a** occurs at m/e 137.006 (C_7H_5SO). This peak can be envisioned to arise from either VII or VIII *via* ions with m/e 167 as illustrated in Scheme I. Compound **11b** (deuterium in the benzylic position) has a mass spectrum in which peaks at m/e 137 and 138 are prominent. This observation is consistent with **11a** having structure VII. If compound **11a** had structure VIII, one would expect to find only a very small peak for m/e 137 in the mass spectra of the 3-deuterio derivative (**11b**).

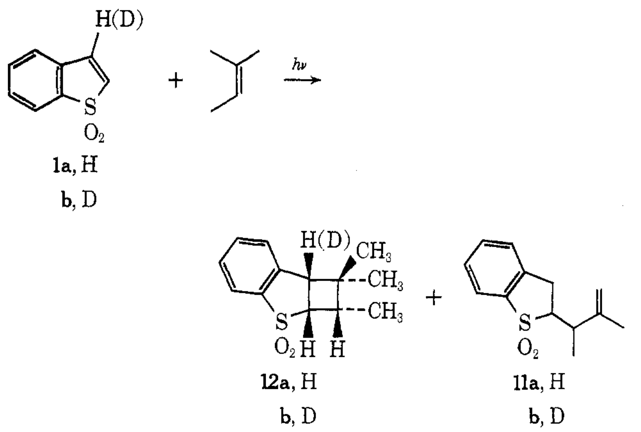


≡ C_7H_5SO

SCHEME I



The nmr of compound **12b** (the 3-deuterio derivative of compound **12a**) was identical with that of compound **12a** except that the resonance at τ 6.20–6.56 collapsed to a doublet at τ 6.35 (J = 9.0 Hz). This means that the α sulfonyl proton is vicinal to the α methyl proton, since the broad quintet at τ 7.58 did not collapse to a first-order quartet. The vicinal coupling constant (9.0 Hz) is consistent with all methine protons being cis (if one assumes that protons at the junction of five- and four-membered rings formed by a two-step process are cis). Therefore, the data given are consistent with compound **12a** having structure IX. The reaction to produce compounds **11a** and **12a** is summarized below.

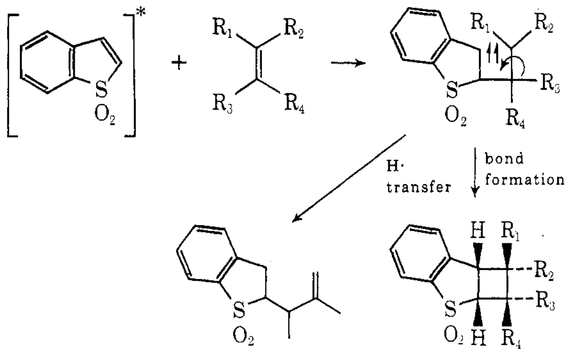


1a, H
b, D

12a, H
b, D

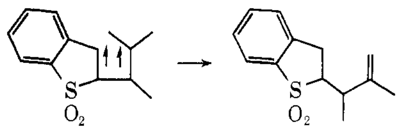
11a, H
b, D

The results obtained for the photocycloaddition of thianaphthene 1,1-dioxide (**1a**) to olefins are consistent with a resonance-stabilized 1,4-diradical intermediate. The initial addition appears to involve bond formation between the 2 position of compound **1a** and the least substituted carbon atom of the olefins (analogous to free-radical attack on an alkene).[10] The resulting intermediate thus is the most stabilized diradical (benzylic and tertiary). The hypothesis is borne out by the fact that photocycloaddition of **1a** to trichloroethane and 2-methyl-2-butene gives only one cyclobutane derivative. If attack occurred from the 3 position to the highly substituted carbon atom of the olefin (carbon atom with two chlorine or two methyl groups), then rotation around the C–C bond of the substrate moiety would cause two stereoisomers to form. The occurrence of this type of rotation during photocycloaddition was found in the case of *cis*- and *trans*-1,2-dichloroethene, where cycloaddition to both the cis and trans isomers resulted in a mixture of two adducts identical in structure except for the stereochemistry of the chlorine atoms. The products of cycloaddition of dioxide **1a** to 1,1-dichloroethene is also consistent with a free-radical attack by the 2 position of the excited state of **1a** on the least substituted carbon atom.[10]



The fact that tetrachloroethene does not add to the excited state of **1a** can be attributed to steric hindrance by the four chlorine atoms to attack on the π bond. This results in photodimerization being much faster than mixed cycloaddition.

The isolation of compound **11a** from the photocycloaddition of dioxide **1a** to 2-methyl-2-butene provides evidence for the existence of 1,4-diradical intermediate **13**. Compound **11a** was likely formed by a hydrogen abstraction from the methyl group of the 2-methyl-2-butene moiety by the benzylic position.[11]



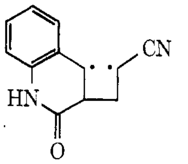
13 **11a**

Thianaphthene 1,1-dioxide (**1a**) reacts under similar conditions as cyclic enones[4,10,12] and indenes[13,14] to give comparable compounds. The photocycloaddition of cyclic enones to unsymmetrical olefins gives two cyclic products with each possible orientation in which one orientation predominates,[4,12] while indene,[14] 1,1-dimethylindene,[13] carbostryil,[15] and thianaphthene 1,1-dioxide (**1a**) give one product. These results can be explained by invoking resonance-stabilized diradical intermediates for those olefins that are fused and conjugated to aromatic systems. Such intermediates are not involved in the case of cyclic enones.

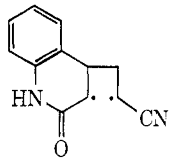
It has been suggested that most of the products formed by cycloaddition of cyclic α,β-unsaturated ketones to unsymmetrical olefins can be rationalized by a two-stage mechanism.[4,12] While controversy exists concerning aspects of this proposal,[9a,b] it generally accounts for the orientational selectivity of cycloadditions of unsymmetrical alkenes and the lack of stereospecificity of addition of cis and trans alkenes. This mechanism, however, does not account for the orientation of the cycloadducts of carbostyril,[15] indene,[13] and 1,1-dimethylindene to acrylonitrile.[13]

Acrylonitrile adds to an opposite orientation to that predicted by Corey's mechanism.[4] It has been well established that a change in polarity occurs in an $n-\pi^*$ transition (for cyclic enones) while no such change has been observed for $\pi-\pi^*$ transition (carbostyril, indene, 1,1-dimethylindene).[16]

These latter results can be well explained by considering the stabilization of the resulting 1,4-diradical intermediate. The 1,4 diradical **14** with a resonance-stabilized benzylic free radical would be expected to be more stable than diradical **15** (with a less stabilized



14



15

---

[10] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Reinhart and Winston, New York, N. Y., 1959, p 732.

[11] A referee has noted that the likely involvement of diradical **13** rather than alternative intermediates may possibly be indicative of the tendency of the sulfone group to destabilize adjacent radical centers.

[12] O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Amer. Chem. Soc.*, **90**, 1657 (1968); T. S. Cantrell, W. S. Haller, and J. C. Williams, *J. Org. Chem.*, **34**, 509 (1969).

[13] J. J. McCullough and C. W. Huang, *Can. J. Chem.*, **47**, 757 (1969).

[14] W. Metzner, *Tetrahedron Lett.*, 1321 (1968).

[15] G. R. Evanega and D. L. Fabing, *J. Org. Chem.*, **35**, 1757 (1970).

[16] G. Porter, "Reactivity of the Photoexcited Molecule," Proceedings of the Thirteenth Conference on Chemistry, Interscience, New York, N. Y., 1967, p 79.

free radical). This hypothesis also accounts for the observations of Corey.[4]

Experimental Section

Apparatus.—Infrared spectra of KBr pellets were measured with a Perkin-Elmer 337 spectrometer, nmr spectra were obtained from a Varian Associates T-60 instrument, and mass spectra were recorded on an AEI MS 902 spectrometer. Melting points were taken on a Gallenkamp apparatus and are not corrected. The vpc data were obtained on a Hewlett-Packard F & M series 5670 research chromatograph. A Hanovia medium-pressure mercury vapor lamp (type L, 450 W) in a Pyrex water-cooled immersion apparatus, surrounded by the reaction mixture, was used for all photocycloadditions. With the exception of the reaction with 2-methyl-2-butene (34%) an excellent material balance was obtained (77–100%) for each reaction.

Thianaphthene 1,1-Dioxide (1a).—This compound was prepared and purified as previously described.[3a]

3-Bromothianaphthene.—This material was synthesized according to the method of von Komppa.[17]

3-Deuteriothianaphthene.—This compound was synthesized by slowly adding 2.0 g of D_2O to thianaphthene-3-magnesium bromide. The latter was formed by adding 6.4 g (0.032 mol) of 3-bromothianaphthane in 20 ml of tetrahydrofuran to 0.76 g (0.32 mol) of magnesium turnings in 20 ml of tetrahydrofuran. Normal work-up and fractional distillation at 78–80° (2 mm) gave 2.5 g (0.018 mol, 62% yield) of 3-deuteriothianaphthene (80% deuterated as determined by mass spectra).

3-Deuteriothianaphthene 1,1-Dioxide (1b).—This compound was prepared in the same way as compound **1a** (mp 142–142.5°; mp of **1a** 142–142.5°).

Photocycloaddition of Thianaphthene 1,1-Dioxide (1a) to Trichloroethene.—Thianaphthene 1,1-dioxide (3.5 g, 0.021 mol) was dissolved in 500 ml of reagent-grade trichloroethene (distilled at 86–86.5°), and the solution was purged with dry nitrogen for 45 min and irradiated for 3 hr. After the solution was evaporated and the resultant oil was refluxed in CCl_4, 5.1 g of a white solid containing three compounds (tlc on silica gel developed by $CHCl_3$ and glpc on 6 ft × 0.125 in., 10% Apiezon L column of reaction mixture) was obtained. Fractional crystallization in 50 ml of benzene gave 1.7 g (0.005 mol, 48% yield) of the photodimers of **1a** and 3.4 g (0.013 mol, 52% yield) of compound **2a**: mp 142–144°; ir $\bar{\nu}$ 1320 and 1160 (SO_2), 670 cm^{-1} (CCl); nmr ($CDCl_3$) τ 218 (4 H, multiplet, aromatic), 5.18 (2 H, AB part of ABX spectrum, CH), 5.69 (1 H, X part of ABX spectrum, CH); mass spectrum *m/e* 296 (molecular ion).

Anal. Calcd for $C_{10}H_7SO_2Cl_3$: C, 40.33; H, 2.43; S, 10.76; Cl, 35.80. Found: C, 41.01; H, 2.42; S, 10.93; Cl, 34.60.

Dehydrochlorination of Adduct 2a.—Compound **2a** (3.0 g, 0.009 mol) was dissolved in 50 ml of triethylamine (reagent grade) and refluxed for 20 hr. Evaporation of solvent and recrystallization from ethanol–activated charcoal gave **3** (2.0 g, 0.008 mol, 89% yield): mp 169–170°; nmr (C_6D_6) τ 2.60–3.35 (4 H, aromatic), 6.35 (2 H, AB q, $\Delta\nu = 20.1$, $J_{AB'} = 4.0$ Hz, CH); ir $\bar{\nu}$ 1680 (C=C), 1320 and 1150 (SO_2), 650 cm^{-1} (CCl).

Anal. Calcd for $C_{10}H_6SO_2Cl_2$: C, 45.98; H, 2.30; S, 12.25; Cl, 27.20. Found: C, 45.97; H, 2.34; S, 12.24; Cl, 27.21.

Photocycloaddition of 3-Deuteriothianaphthene 1,1-Dioxide (1b) to Trichloroethane.—A 150-ml trichloroethene solution of 3-deuteriothianaphthene 1,1-dioxide (**1b**, 0.5 g, 0.003 mol) was irradiated for 30 min. The product was isolated and purified as above and resulted in compound **2b** (0.5 g, 0.0014 mol, 47%): mp 142–144°; nmr ($CDCl_3$) τ 2.18 (4 H, m, aromatic), 5.18 (1 H, $J = 8.0$ Hz, CH), 5.70 (1 H, $J = 8.0$ Hz, CH); mass spectrum *m/e* 297 (molecular ion).

Photocycloaddition of Thianaphthene 1,1-Dioxide (1a) to *cis*-1,2-Dichloroethene.—Thianaphthene 1,1-dioxide (**1a**, 1.75 g, 0.0105 mol) was dissolved in 350 ml of *cis*-1,2-dichloroethene (reagent grade) and irradiated for 9 hr under nitrogen atmosphere. Dichloroethene was removed by distillation and ethanol was added to the oily residue, resulting in white crystals (2.0 g). The unreacted starting material (0.7 g) was separated from the products by filtering from boiling water. The resulting solid (1.3 g, 0.005 mol, 79% yield based on unreacted starting material) was examined by vpc (6 ft × 0.125 in., 10% Apiezon L on Chromosorb W) and was found to contain two compounds, **6** and **7**. This mixture was chromatographed over silica gel by $CHCl_3$ and partial separation was obtained. The first fraction contained 0.2 g (13% yield based on the amount of compound **1a** consumed) of compound **6**: mp 144.5–146.5°; ir $\bar{\nu}$ 1320 and 1170 (SO_2), 665 cm^{-1} (CCl); nmr ($CDCl_3$) τ 2.00–2.50 (4 H, aromatic), 4.94–5.15 (1 H, m, CH), 5.33–5.60 (3 H, CH).

Anal. Calcd for $C_{10}H_8SO_2Cl_2$: C, 45.63; H, 3.04; S, 12.17; Cl, 27.00. Found: C, 45.61; H, 3.09; S, 12.26. Found: C, 45.95; H, 3.20; S, 12.23; Cl, 26.26.

The ratio of compounds **6** and **7** in the original mixture was estimated by comparing the integration of the resonances at τ 4.94–5.15 for **6** with that at τ 5.80–6.00 for **7**, found 53:47.

Photocycloaddition of Thianaphthene 1,1-Dioxide (1a) to *trans*-1,2-Dichloroethene.—A solution of thianaphthene 1,1-dioxide (0.134 g, 0.8 mmol) in 150 ml of *trans*-1,2-dichloroethene was irradiated for 45 min. Distillation of the dichloroethene and crystallization in ethanol–hexane (4:1) gave 0.185 g (87% yield) of compounds **6** and **7**. Fractional crystallization in ethanol gave 40 mg (29% yield) of compound **7** (mp 170–171°, mixture melting point with **7** from photoaddition of *cis*-1,2-dichloroethene was not depressed). The ratio of compound **6** and **7** by vpc analysis was found to be 23:77.

Photocycloaddition of Thianaphthene 1,1-Dioxide (1a) to 1,1-Dichloroethene.—Thianaphthene 1,1-dioxide (0.5 g, 0.003 mol) and 1,1-dichloroethene (12 g, 0.12 mol) in 150 ml of benzene were irradiated for 3 hr. The polymeric material that had formed was filtered, an additional 12 g of 1,1-dichloroethene was added, and the irradiation was continued for 3 hr. At this point glpc analysis (6 ft × 0.125 in., 10% UC-W98 on Diatoport S) indicated complete reaction and together with tlc (silica gel developed by $CHCl_3$) indicated only one product. Recrystallization in ethanol gave compound **9a** (mp 139.5–140.5°, 0.6 g, 0.0023 mol, 77% yield): ir $\bar{\nu}$ 1310 and 1160 (SO_2) and 615 cm^{-1} (CCl); nmr ($CDCl_3$) τ 2.10–2.50 (4 H, m, aromatic), 5.20 (1 H, $J_{2,3} = 8.0$, $J_{3,5} = 2.5$ Hz, CH), 5.73 (1 H, $J = 8.0$ Hz, CH), 6.25–7.00 (2 H, CH_2); mass spectrum *m/e* 262 (molecular ion).

Anal. Calcd for $C_{10}H_8SO_2Cl_2$: C, 45.63; H, 3.04; S, 12.17; Cl, 27.00. Found: C, 45.87; H, 3.05; S, 12.42; Cl, 26.18. Exact mass measurement of the molecular ion (calcd for $C_{10}H_8$-$2O_2Cl_2$, 261.9622), 261.9631.

Photocycloaddition of 3-Deuteriothianaphthene 1,1-Dioxide (1b) to 1,1-Dichloroethene.—Thianaphthene 1,1-dioxide (1.7 g, 0.01 mol) and tetrachloroethene (108 g, 0.8 mol) in 170 ml of benzene was irradiated until all of the starting material was consumed (6 hr). Evaporation of the benzene and tetrachloroethylene gave white crystals which tlc (silica gel developed by acetone) and glpc (6 ft × 0.125 in., 10% Apiezon L on Chromosorb W) revealed to be the photodimers of **1a** (1.7 g, 100% yield). No mixed cycloadduct was observed.

Photocycloaddition of Thianaphthene 1,1-Dioxide to 2-Methyl-2-butene.—Compound **1a** (0.35 g, 2.1 mmol) and 2-methyl-2-butene (14 g, 0.2 mol) were irradiated in benzene for 1 hr under nitrogen atmosphere. Evaporation of the solvent left 0.49 g of an oily material (theoretical yield for 100% cycloaddition is 0.46 g). Examination of the reaction mixture by tlc [silica gel developed by cyclohexane–ethyl acetate (4:1)] and glpc (6 ft × 0.125 in., 10% UX-W98 silicone rubber on Diatoport S) showed that two products were formed. The reaction mixture was then chromatographed on preparative tlc plates (0.75 mm thick) of silica gel with cyclohexane–ethyl acetate (4:1) (development was repeated until separation occurred). Fraction 1 (recrystallization with ethanol) gave **11a** (39 mg, 0.089 mmol, 9% yield, mp 145–145.5°): ir $\bar{\nu}$ 1670 (C=C), 1305 and 1152 cm^{-1} (SO_2); nmr ($CDCl_3$) τ 2.18–2.58 (4 H, aromatic), 5.08 (2 H, broad, vinylidene), 6.40–7.20 (3 H, CH_2 and CH), 8.23 (3 H, $J = 1.0$ Hz, CH_3), 8.55 (3 H, $J = 6.0$ Hz, CH_3); mass spectrum *m/e* 236 (molecular ion).

Anal. Calcd for $C_{13}H_{16}SO_2$: C, 66.10; H, 6.78; S, 13.56. Found: C, 65.84; H, 6.83; S, 13.36.

Fraction 2 (recrystallization from ethanol) gave compound **12a** (115 mg, 0.5 mmol, 25%, mp 131.5–132°): ir $\bar{\nu}$ 1470 cm^{-1} (CCH_3); nmr τ 2.11–2.75 (4 H, aromatic), 6.20–6.56 (2 H, m, CH), 7.58 (1 H, $J = 7.0$ Hz, CH), 8.70 (3 H, s, CH_3), 8.88 (3 H, $J = 7.0$ Hz, CH_3), 9.20 (3 H, CH_3); mass spectrum *m/e* 236 (molecular ion).

Anal. Calcd for $C_{13}H_{16}SO_2$: C, 66.10; H, 6.78; S, 13.56. Found: C, 66.03; H, 6.97; S, 13.41.

Photocycloaddition of 3-Deuteriothianaphthene 1,1-Dioxide (1b) to 2 Methyl-2-butene.—This experiment was executed in exactly the same way as was the cycloaddition of compound **1a**

---

(17) G. von Komppa, *J. Prakt. Chem.*, **622**, 319 (1929).

to 2-methyl-2-butene. The resulting products were compound **11b** (mp 145–145.5°), mass spectrum m/e 237 (molecular ion), and **12b** (mp 131.5–132°): nmr ($CDCl_3$) τ 2.11–2.75 (4 H, aromatic), 6.35 (1 H, J = 9.0 Hz, CH), 7.58 (1 H, J = 7.0 Hz, CH), 8.70 (3 H, CH_3), 8.88 (3 H, J = 7.0 Hz, CH_3), 9.20 (3 H, CH_3); mass spectrum m/e 237 (molecular ion).

Acknowledgment.—We are grateful to Dr. John G. Gleason for spin-decoupling experiments and to the National Research Council of Canada for financial support.

Registry No.—**1a**, 825-44-5; **1b**, 41674-77-5; **2a**, 41674-78-6; **2b**, 41674-79-7; **3**, 41674-80-0; **4**, 156-59-2; **5**, 156-60-5; **6–7**, 41674-81-1; **8**, 75-35-4; **9a**, 41674-82-2; **11a**, 41674-83-3; **11b**, 41674-84-4; **12a**, 41674-85-5; **12b**, 41674-86-6; 3-deuteriothianaphthene, 15816-45-2; 3-bromothianaphthene, 7342-82-7; trichloroethylene, 79-01-6; 2-methyl-2-butene, 513-35-9.

Directed Metalation Reactions. V.[1] Metalation and Rearrangement in Substituted 2-Thiophenesulfonamides

D. W. SLOCUM* AND P. L. GIERER

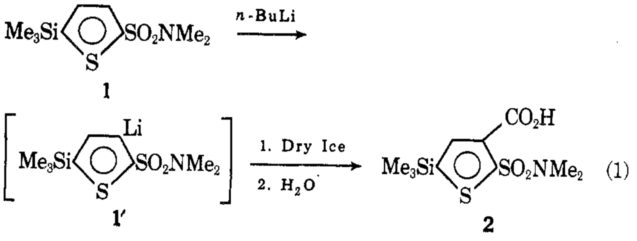
Neckers Laboratory, Southern Illinois University, Carbondale, Illinois 62901

Received May 10, 1973

Metalation of several 2-N,N-dialkylthiophenesulfonamides with n-butyllithium has revealed some diverse behavior. Whereas metalation of 5-trimethylsilyl-N,N-dimethyl-2-thiophenesulfonamide (**1**) gave 3 metalation only, metalation of the diethyl analog (**4**) produced 3 metalation accompanied by loss of the trimethylsilyl group when the lithio intermediate **4′** was condensed with Dry Ice. When other reagents were condensed with **4′**, loss of the trimethylsilyl group was not observed and 3-substituted derivatives of **4** were produced. Moreover, when dimethylsulfonamide **1** was treated with n-butyllithium–TMEDA complex, a rearrangement ensued which produced 2-trimethylsilyl-4-N,N-dimethylthienylamine (**3**).

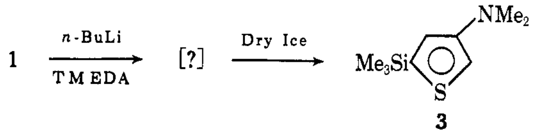
Ortho metalation of both N-methyl- and N-phenylbenzenesulfonamide has been demonstrated.[2a] Similarly, N,N-dimethylbenzenesulfonamide was found[2b] to undergo metalation ortho to the sulfonamide group and to give good yields of various condensation products. Such studies involving the metalation of thiophenesulfonamides have not been reported in the literature. However, it has been shown by Stoyanovitch and Fedorov[3] that *tert*-butyl 2-thienyl sulfone was dimetalated in the 3 and 5 positions with excess n-butyllithium. Similar results were anticipated in the metalation of the thiophenesulfonamides, but, as described below, other processes intervened at times.

Initial attempts to effect metalation of N,N-dimethyl-2-thiophenesulfonamide in the 3 or 3,5 positions were unsuccessful, metalation occurring only at the 5 position. This observation prompted the introduction of a blocking group into the 5 position of the thiophenesulfonamide with the result that 5-trimethylsilyl-N,N-dimethyl-2-thiophenesulfonamide (**1**) was prepared. Metalation of **1** with n-butyllithium followed by condensation of the lithio intermediate (**1′**) with Dry Ice afforded a 10% yield of 5-trimethylsilyl-3-carboxyl-N,N-dimethyl-2-thiophenesulfonamide (**2**) (eq 1) and 75% recovery of starting material. An ir spectrum of **2** exhibited bands between 3000 and 2450 and at 1710 cm^{-1} characteristic of a carboxyl group. In addition, its nmr spectrum showed a singlet at 7.66 ppm for the lone remaining thiophene ring proton and singlet peaks for the methyl groups attached to the sulfonamide group and silicon atom at 2.94 and 0.37 ppm, respectively. The site of metalation is postulated as being the 3 position, in analogy to the results for N,N-dimethylbenzenesulfonamide[2] and also as a result of a deuterium labeling experiment. When lithio intermediate **1′** was quenched with D_2O, a deuterated disubstituted thiophene resulted which exhibited attenuation of the more downfield signal, the signal which was assigned to the 3-position proton since it was adjacent to the highly deshielding sulfonamide group. A similar deshielding has been observed for SO_2R derivatives of cymantrene and ferrocene.[4]



(1)

In order to possibly increase the yield of condensation product, sulfonamide **1** was metalated with n-butyllithium–N,N,N',N'-tetramethylethylenediamine (TMEDA) at −30° and condensed with Dry Ice. No carboxylic acid condensation product was isolated but rather a rearranged aminothiophene identified as 2-trimethylsilyl-N,N-dimethyl-4-thienylamine (**3**) was obtained in 39% yield (eq 2). Attempts to eliminate Dry Ice from the reaction with substitution of ice water led to much lower yields of amine **3**. The structure of amine **3** was deduced from examination of its ir and nmr spectra. Its ir spectrum exhibited two bands at 2800 and 1250 cm^{-1} characteristic of tertiary aryl amines,[5] whereas the intense sulfonamide bands at 1350 and



(2)

---

[1] For paper IV in this series, *cf.* D. W. Slocum and B. P. Koonsvitsky, *J. Org. Chem.*, **38**, 1675 (1973).

[2] (a) H. Watanabe, R. L. Gay, and C. R. Hauser, *J. Org. Chem.*, **33**, 900 (1968); (b) H. Watanabe, R. A. Schwarz, C. R. Hauser, J. Lewis, and D. W. Slocum, *Can. J. Chem.*, **47**, 1543 (1969).

[3] F. M. Stoyanovitch and B. P. Fedorov, *Khim. Geterotsikl. Soedin.*, **5**, 823 (1967); *Chem. Abstr.*, **69**, 7119 (1968).

[4] (a) D. W. Slocum and C. R. Ernst, *Organometal. Chem. Rev., Sect. A*, **6**, 283 (1970); (b) D. W. Slocum and C. R. Ernst, *Advan. Organometal. Chem.*, **10**, 79–114 (1972).

[5] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, pp 38 and 40.