Azafulvenes 8.[1] Cycloaddition Reaction of 8-Azaheptafulvene to Sulfene

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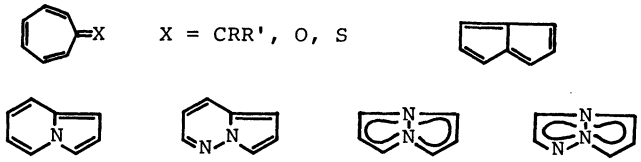
Peri- and stereoselective cycloadducts were obtained from the reactions of 8-aryl-8-azaheptafulvenes with some sulfenes. 8-Aryl-8-azaheptafulvenes reacted with phenylsulfene to give *cis* [8+2] cycloadducts as the sole products which would have resulted either from the endo approach or *via* the endo intermediate of the two reagents. On the other hand, with benzoylsulfene *trans* [8+2] cycloadducts were isolated. The formation of the latter products was rationalized by considering epimerization of the initially formed *cis* adducts. The *cis* [8+2] cycloadducts to vinylsulfene did not give the *trans* isomers but the hydrogen migrated derivatives under the influence of bases. The mechanism of the above reactions is also discussed.

Thermal [8+2] cycloaddition reaction is, as well known, allowed to proceed in a concerted manner.[2] Nevertheless, this type of reaction concerned with a straight polyene has not been reported hitherto because a [4+2] cycloaddition reaction, which is also thermally allowed and known as the Diels-Alder reaction, would compete with an [8+2] cycloaddition reaction and defeat it. Not a [4+2] but an [8+2] cycloaddition, however, is possible to go on well when both the ends of a conjugate system with eight electrons are sterically fixed at the place where a convenient formation of new bonds is possible to occur. A cross-conjugated or peripherally conjugated 8 pi electrons system serves such an example. Thus, heptafulvene,[3] tropone,[4] tropothione,[5] and pentalene[6] have afforded the corresponding [8+2] cycloadducts. In addition, and 8 pi conjugate system along the perimeter (except for one pair of n-electrons on the condensed nitrogen atom) of indolizine[7] and mesoionic polyazapentalene[8] has combined with electron-deficient olefins and acetylenes to give the tricyclic [8+2] cycloadducts.



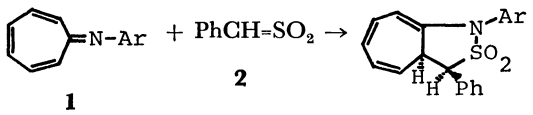
The reactions of 8-azaheptafulvene[9] with isocyanate, isothiocyanate, and ketone showed not only the high reactivity but also the excellent periselectivity of 8-azaheptafulvene toward these heterocumulenes.[10,11] In all of above reactions, 8-azaheptafulvane exclusively behaved only as an 8 pi addend to give the corresponding [8+2] cycloadducts in high yields.

Now, we would like to describe the cycloaddition reaction of 8-aryl-8-azaheptafulvene to some sulfenes. As for tropone, Ciabatonni and his coworker[12] have communicated the reactions with methanesulfonyl or mesylmethanesulfonyl chloride in the presence of triethylamine, both of which yielded the same product that was identified to be the [8+2] cycloadduct of tropone to mesylsulfene. They postulated a stepwise mechanism *via* dipolar intermediate for its formation. Stereoselective [8+2] cycloaddition reactions of tropone to asymmetrically substituted sulfenes have also been reported by Truce and Lin.[13]

Results and Discussion

The reaction of 8-(*p*-methoxyphenyl)-8-azaheptafulvene (**1a**) with phenylsulfene (**2**), generated *in situ* from the corresponding azaheptafulvenium salt and sulfonyl chloride, respectively, afforded the 1 : 1 adduct **3a**. The similarity in the PMR spectrum of **3a** to that of the [8+2] cycloadducts of 8-azaheptafulvenes to some heterocumulenes,[10,11] particularly in spectral patterns for the protons on the seven-membered ring, indicates **3a** to be the [8+2] cycloadduct of **1a** to **2**. Double resonance experiments provided the confirmable assignment for each proton and evidence for the structure of **3a**. The coupling constant between the two methine hydrogens at the 3- and 3a-position was measured to be 8.4 Hz. No difference in the PMR spectra before and after purification shows that the product **3a** is not the mixture of *cis* and *trans* isomer but either of them.

Similarly 8-(*p*-methylphenyl)- (**1b**) and 8-(*p*-chlorophenyl)-8-azaheptafulvene (**1c**) gave the corresponding [8+2] cycloadducts **3b** and **3c** with the same stereochemistry as **3a**.



a: Ar=*p*-$CH_3OC_6H_4$
b: Ar=*p*-$CH_3C_6H_4$
c: Ar=*p*-ClC_6H_4

a: Ar=*p*-$CH_3OC_6H_4$
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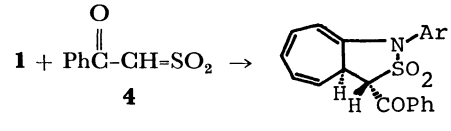
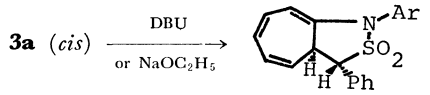


a: Ar=*p*-$CH_3OC_6H_4$
c: Ar=*p*-ClC_6H_4

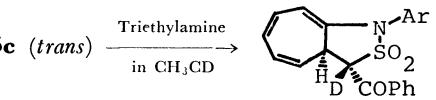
The reactions of benzoylsulfene (**4**) with **1a** and **1c** gave the 1 : 1 adducts **5a** and **5c**, respectively. In these reactions it had been expected that the [8+4] cycloadducts would be formed besides the [8+2] cycloadducts.[10] Contrary to our expectation, the former products could not be even detected by spectroscopy. The IR spectrum of **5a** revealed the carbonyl stretching vibrations at 1685 cm^{-1} and the absorption bands at

1330 and 1160 cm^{-1} characteristic of sulfonyl group. The coupling constant of 4.2 Hz between the two methine hydrogens at the 3- and 3a-position in **5c** indicates that the structure of **5c** may differ from that of **3** in stereochemistry. It is very difficult to estimate the stereochemistry of the cyclic compound which involves sulfonyl group as one member only on the basis of the coupling constant between the two vicinal hydrogens. Therefore the epimerization reactions of both cycloadducts **3** and **5** were investigated using some bases in order to confirm the above anticipation.

The compound **3a** was recovered unchanged on being refluxed in benzene with triethylamine. But **3a** was converted into the isomer **6** when refluxed either with a catalytic amount of sodium ethoxide in ethanol or 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in benzene. The spectral data of **6** are very similar to those of the starting **3a**. The methine proton at the 3-position was observed as doublet with a coupling constant of 7.6 Hz. The above results show that the sole product **3a** from **1a** with **2** was a thermodynamically less stable *cis* isomer which underwent the epimerization into a more stable *trans* isomer **6** *via* the carboanionic intermediate.



6 (*trans*)



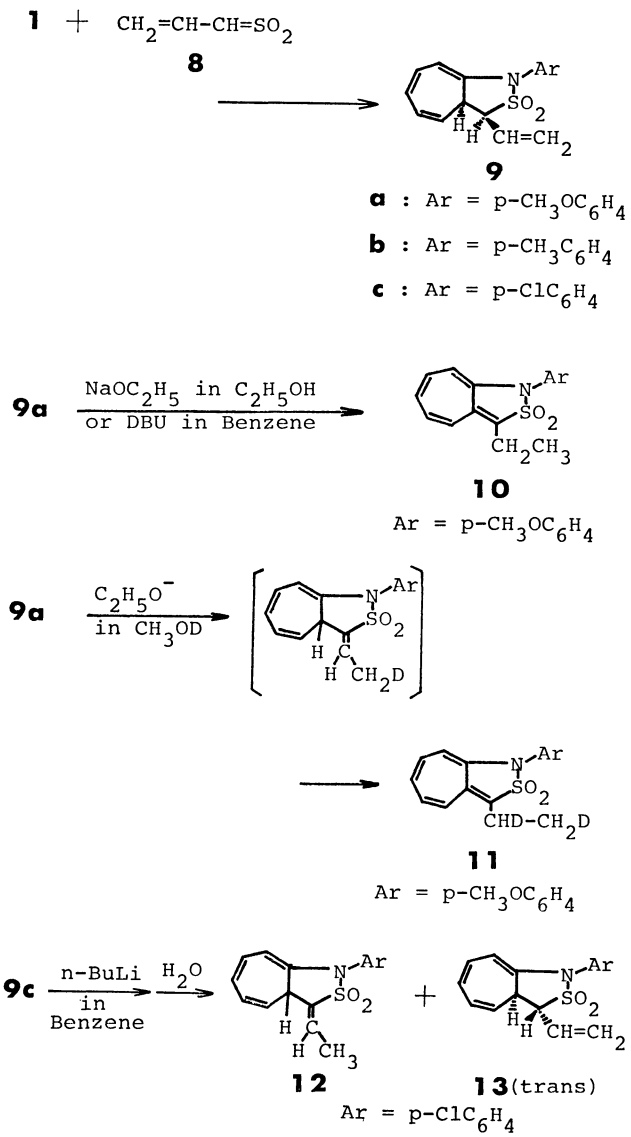
7 (*trans*)

Ar=*p*-ClC_6H_4

On the other hand, the [8+2] cycloadduct **5c** to **4** did not change its stereochemistry even if it was treated with DBU in benzene. An inversion should take place more easily at the 3-position in **5c** than the corresponding position in **3a** because the former contains a more acidic hydrogen atom at 3-position and possibly forms itself into an enolic form. Unchangeableness of **5c** on the treatment with DBU indicates that **5c** is a thermodynamically stable *trans* isomer.

The formation of monodeuterio derivative **7**, which was also a *trans* isomer, from the reaction of **5c** with triethylamine in methanol-*d* at room temperature led us to presume that the reaction of 8-aryl-8-azaheptafulvene (**1**) with **4** would have given the *cis* [8+2] cycloadduct as an initial product and been followed by the epimerization into the isolated *trans* product **5**. The reaction in which the diluted solution of triethylamine in dichloromethane was slowly added to the mixture of **1c** and benzoylmethanesulfonyl chloride in the same solvent at −50 °C, or in which **1c** was trated with the previously generated **4** in dichloromethane at −50 °C failed to form the *cis* [8+2] cycloadduct.

Vinylsulfene (**8**) reacted with **1** affording the 1 : 1 adduct **9** which was also found to be the [8+2] cycloadduct on the basis of the spectral data as well as the chemical conversion. The IR spectrum of **9a** showed the out of plane bending vibration bands at 960 cm^{-1}. The existence of a vinyl group was also confirmed from the PMR spectrum which exhibited the two terminal protons of vinyl group at 5.71 and 5.74 ppm (J_{cis}= 10.0 and J_{trans}=17.8 Hz), and whose spectral patterns were very similar to those of **3** and **5**. The coupling constant between the 3- and 3a-H (8.6 Hz) could not determine whether **9** was the *cis* or *trans* [8+2] cycloadduct.



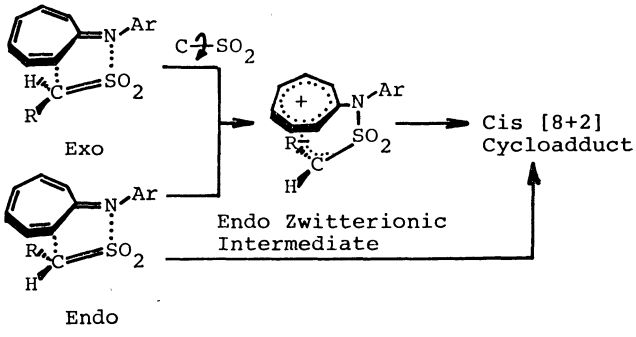
The compound **9a** was recovered unchanged when refluxed with triethylamine in benzene, whereas its treatment with sodium ethoxide in ethanol gave the isomeric **10**. By means of PMR spectroscopy, this product **10** was assigned to the isomer which was derived not from the inversion at carbon atom of the 3-position in **9a** but through the migration of vinyl double bond to a position of conjugation with the seven-membered ring. The mechanism for the double bond migration was confirmed by use of methanol-*d* in the above reaction.

The formation of **10** seemed to be caused by the fact that the allyl anionic intermediate from **9a** by deprotonation readily incorporated a proton from the solvent. Therefore, **9a** was reacted with DBU in dry benzene

at room temperature, but unexpectedly gave the same product **10**. These above results could not determine the stereochemistry of the [8+2] cycloadducts of **1** to **8**.

On the other hand, the reaction of **9c** with butyllithium in dry benzene under nitrogen gave an unseparable mixture of two products **12** and **13** whose structures were decided on the basis of the PMR spectrum of the mixture. The PMR spectrum showed the doublet (1.90, $C\underline{H}_3CH$=), quartet (6.82, $CH_3C\underline{H}$=), and multiplet (3.30 ppm, 3a-H) for the major product **12**, and the complex signals (5.45—5.87, $C\underline{H}_2$=CH– and 4-H), triplet (4.14, 3-H, J_{3-3a}=3.0 Hz), and multiplet (2.89 ppm, 3a-H) for the minor one **13**. The former corresponds to an intermediate involved in the course of isomerization of **9a** to **11**. The latter was assigned to be a thermodynamically stable *trans* [8+2] cycloadduct, whose formation indicated that the reaction of **1** with **8** had afforded the *cis* [8+2] cycloadduct as a sole product. The assignment of stereochemistry of **9** is compatible with the fact that although the treatment with DBU and butyllithium allowed the isomerization into **10**, **12**, and **13**, triethylamine did not change the stereochemistry of **9**.

As mentioned above, the reactions of **1** with **2**, **4**, and **8** gave the corresponding *cis* [8+2] cycloadducts as the isolated and initially formed products. Two mechanisms are possible for these reactions as depicted below: a concerted mechanism and stepwise one. The *cis* [8+2] cycloadduct would have been formed *via* endo approach between the two reagents in a concerted manner or *via* endo zwitterionic intermediate in a stepwise manner. As for the latter mechanism, it has been reported[13] that the reactions of tropone with some sulfenes might proceed stepwise *via* endo zwitterionic intermediates in which Coulombic attractions between the tropylium cation and the negatively charged group would facilitate the formation of thermodynamically unstable *cis* [8+2] cycloadducts.



The similar stepwise reactions of **1** with isocyanates and isothiocyanates have given the [8+2] cycloadducts in general cases but the [8+4] cycloadducts in some cases.[10] Furthermore only the *trans* [8+2] cycloadducts have been obtained from the reactions of **1** with phenylketene.[11]

The [8+4] cycloadducts to benzoyl- or vinylsulfene and the *trans* [8+2] cycloadduct to phenylsulfene should be formed when the reaction of **1** with sulfene proceeds in a stepwise mechanism. The above reactions will have taken place, but not conclusively, in a concerted manner *via* the endo approach between 8-azaheptafulvenes and sulfenes. Further investigation has to be made for the clarification of the reaction mechanism.

Experimental

General. Melting and boiling points are all uncorrected. IR spectra were taken in KBr disks with a Japan Spectroscopic Co. IRA-1 spectrometer. PMR spectra were obtained at 100 MHz using a JEOL JNM-MH-100 spectrometer with tetramethylsilane as an internal standard. Mass spectra were determined with a JEOL JMS-D 100 mass spectrometer equipped with a direct inlet and at an ionization energy of 70 eV.

Materials. (8-*p*-Methoxy-, 8-*p*-methyl-, and 8-*p*-chlorophenyl)-8-azaheptafulvenium fluoroborate were prepared from tropylium fluoroborate and the corresponding anilines according to the method mentioned in the literature.[9] Phenylmethane-: mp 92—93 °C (lit,[14] mp 92—93 °C), benzoylmethane-: mp 87—88 °C (lit,[15] mp 87.5—88.2 °C) and 2-propenesulfonyl chloride: bp 76 °C/15 mmHg (lit,[16] bp 74—75 °C/15 mmHg) were synthesized from the reactions between the corresponding sodium sulfonates and phosphorus pentachloride. Triethylamine and dichloromethane were purified by simple distillation and dried with potassium hydroxide and calcium chloride, respectively.

*1-p-Methoxyphenyl-3-phenyl-3,3a-dihydro-1H-cyclohept[c]isothiazole 2,2-Dioxide (**3a**).* To a solution of 8-*p*-methoxyphenyl-8-azaheptafulvenium fluoroborate (0.30 g) and phenylmethanesulfonyl chloride (0.20 g) in dry dichloromethane (10 ml) was added dropwise a solution of triethyl amine (0.25 g) in dry dichloromethane (3 ml) at −50 °C. The reaction mixture was strired at the same temperature for 1 h and at room temperature overnight, and then evaporated *in vacuo* to dryness. The residue was extracted with hot benzene and the extract was evaporated again to give an oily product. The crude, but almost pure, product was filtered through a short column packed with alumina using benzene as eluent, giving pale yellow prisms of **3a** (0.37 g, 99%) which were purified by recrystallization from methanol; mp 123—124 °C. IR(KBr, cm^{-1}): 1615 (C=C), 1325 and 1140 (SO_2); PMR ($CDCl_3$, δ ppm): 3.34 (m, 1H, 3a-H), 3.77 (s, 3H, OCH_3), 4.97 (d, 1H, J_{3-3a}=8.4 Hz, 3-H), 5.11(dd, 1H, J_{4-3a}=4.5 and J_{4-5}=9.0 Hz, 4-H), 5.29 (br. d, 1H, J_{8-7}= 6.5 Hz, 8-H), 6.02—6.54 (m, 3H, 5-, 6-, and 7-H) and 6.86—7.58 (m, 9H, aromatic protons); MS (*m/e*, relative intensity) : 365 (M^+ 94), 301 (M^+-SO_2, 46), 300 (301$^+$—H, base peak), and 211 (M^+—phenylsulfene, 89).

Found: C, 68.78; H, 5.10; N, 3.64%. Calcd for $C_{21}H_{19}NO_3S$: C, 69.02; H, 5.24; N, 3.83 %.

*1-p-Methylphenyl-3-phenyl-3,3a-dihydro-1H-cyclohept[c]isothiazole 2,2-Dioxide (**3b**).* The reaction of 8-*p*-methylphenyl-8-azaheptafulvenium fluoroborate (0.57 g), phenylmethanesulfonyl chloride (0.40 g) and triethylamine (0.50 g), in a similar way described above, gave colorless prisms of **3b** (0.56 g, 80 %) which were purified by recrystallization from methanol; mp 136—138 °C. IR (KBr, cm^{-1}): 1620 (C=C), 1330 and 1145 (SO_2); PMR ($CDCl_3$, δ ppm): 2.34 (s, 3H, CH_3), 3.33 (m, 1H, 3a-H), 4.96 (d, 1H, J_{3-3a}=8.4 Hz, 3-H), 5.05 (dd, 1H, J_{4-3a}=5.0 and J_{4-5}=9.0 Hz, 4-H), 5.29 (br. d, 1H, J_{8-7}=5.5 Hz, 8-H), 6.01—6.50 (m, 3H, 5-, 6-, and 7-H) and 7.12—7.60 (m, 9H, aromatic protons); MS (*m/e*, relative intensity): 349 (M^+, 57), 285 (M^+-SO_2, 63), 284 (285$^+$—H, base peak) and 195 (M^+—phenylsulfene, 75).

Found: C, 71.73; H, 5.37; N, 3.84%. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01%.

1-p-Chlorophenyl-3-phenyl-3,3a-dihydro-1H-cyclohept[c]*isothiazole 2,2-Dioxide (**3c**).* In a similar way as that of **3a**, the reaction of 8-*p*-chlorophenyl-8-azaheptafulvenium fluoroborate (0.61 g), phenylmethanesulfonyl chloride (0.40 g) and triethylamine (0.50 g) gave colorless prisms of **3c** (0.50 g, 69%) which were purified by recrystallization from methanol; mp 135.5—137 °C. IR (KBr, cm^{-1}): 1615 (C=C), 1330 and 1140 (SO_2); PMR ($CDCl_3$, δ ppm): 3.35 (m, 1H, 3a-H), 5.00 (d, 1H, J_{3-3a}=8.4 Hz, 3-H), 5.08 (dd, 1H, J_{4-3a}=5.0 and J_{4-5}=9.5 Hz, 4-H), 5.31 (br. d, 1H, J_{8-7}=5.5 Hz, 8-H), 6.08—6.60 (m, 3H, 5-, 6-, and 7-H) and 7.19—7.67 (m, 9H, aromatic protons); MS (*m/e*, relative intensity): 369, 371 (M^+, 43, 15), 305, 307 (M^+-SO_2, 73, 24), 304, 306 (305^+-H, base peak, 307^+-H, 32) and 215, 217 (M^+—phenylsulfene, 71, 24).

Found: C, 65.03; H, 4.32; N, 3.79%. Calcd for $C_{20}H_{16}NO_2SCl$: C, 64.95; H, 4.36; N, 3.79%.

3-Benzoyl-1-p-methoxyphenyl-3,3a-dihydro-1H-cyclohept[c]*isothiazole 2,2-Dioxide (**5a**).* To a solution of 8-*p*-methoxyphenyl-8-azaheptafulvenium fluoroborate (0.30 g) and benzoylemthanesulfonyl chloride (0.22 g) in dry dichloromethane (10 ml) was added drowpise a solution of triethylamine (0.20 g) in dry dichloromethane (3 ml) at −50 °C. The reaction mixture was stirred at the same temperature for 1 h and at room temperature overnight, and then evaporated *in vacuo* to dryness. The residue was extracted with hot benzene and the benzene solution was evaporated to give pale yellow prisms of **5a** (0.35 g, 89 %) which were purified by recrystallization from 2-propanol using charcoal; mp 171—173 °C. IR (KBr, cm^{-1}): 1685 (C=O), 1620 (C=C), 1330 and 1160 (SO_2); PMR ($CDCl_3$, δ ppm): 3.66 (m, 1H, 3a-H), 3.77 (s, 3H, OCH_3), 5.16 (dd, 1H, 4-H), 5.21 (br. d, 1H, J_{8-7}=5.5 Hz, 8-H), 5.39 (d, 1H, J_{3-3a}=4.2 Hz, 3-H), 6.06—6.60 (m, 3H, 5-, 6- and 7-H), 6.87, 7.22 (each d, 4H, *p*-methoxyphenyl protons) and 7.52, 8.09 (m, 5H, benzoyl protons); Mass (*m/e*, relative intensity): 393 (M^+, 4), 208 ($M^+-CH_3OPhNSO_2$, 45) and 207 (208^+-H, base peak).

Found: C, 67.25; H, 4.89; N, 3.77%. Calcd for $C_{22}H_{19}NO_4S$: C, 67.16; H, 4.87; N, 3.56 %.

3-Benzoyl-1-p-chlorophenyl-3,3a-dihydro-1H-cyclohept[c]*isothiazole 2,2-Dioxide (**5c**).* In a similar way described above, the reaction of 8-*p*-chlorophenyl-8-azaheptafulvenium fluoroborate (0.30 g), benzoylmethanesulfonyl chloride (0.22 g) and triethylamine (0.20 g) gave colorless needles of **5c** (0.30 g, 78 %) which were purified by recrystallization from methanol; mp 161—162 °C. IR (KBr, cm^{-1}): 1685 (C=O), 1625 (C=C), 1330 and 1160 (SO_2); PMR ($CDCl_3$, δ ppm): 3.68 (m, 1H, 3a-H), 5.20 (dd, 1H, 4-H), 5.32 (br d, 1H, J_{8-7}=5.5 Hz, 8-H), 5.46 (d, 1H, J_{3-3a}=4.2 Hz, 3-H), 6.18—6.66(m, 3H, 5-, 6-, and 7-H), 7.23—7.66 (m, 7H, aromatic protons) and 8.13 (br d, 2H, *o*-protons of benzoyl); MS (*m/e*, relative intensity): 397, 399 (M^+, 2), 208 ($M^+-ClPhNSO_2$, 48) and 207 (208^+-H, base peak).

Found: C, 63.46; H, 4.02; N, 3.80%. Calcd for $C_{21}H_{16}NO_3SCl$: C, 63.39; H, 4.05; N, 3.52%.

*Epimerization of **3a**.* One drop of 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) was added to a solution of **3a** (0.10 g) in dry benzene (5 ml) and the mixture was refluxed for 1 h. Evaporation of benzene *in vacuo* gave pale yellow prisms of **5** (0.08 g, 80 %) which were purified by recrystallization from methanol mp 162—163 °C. IR (KBr, cm^{-1}): 1610 (C=C), 1320 and 1130 (SO_2); PMR ($CDCl_3$, δ ppm): 3.33 (m, 1H, 3a-H), 3.84 (s, 3H, OCH_3), 4.77 (d, 1H, J_{3-3a}= 7.6 Hz, 3-H), 5.25 (dd, 1H, 4-H), 5.35 (br. d, 1H, J_{8-7}=6.0 Hz, 8-H), 6.18—6.49 (m, 3H, 5-, 6-, and 7-H) and 6.89—7.61 (m, 9H, aromatic protons); Mass (*m/e*, relative intensity): 365 (M^+, 43), 301 (M^+-SO_2), 300 (301^+-H, 81) and 211 (M^+—phenyl sulfene, base peak).

The *trans* isomer **5** was also obtained from the following reaction: a solution of **3a** (0.32 g) and sodium ethoxide (0.01 g) in 10 ml of ethanol was refluxed for 1 h and evaporated *in vacuo* to dryness. The residue was dissolved in water and extracted with benzene. The extract was dried over magnesium sulfate and evaporated *in vacuo* to give **5** (0.18 g, 56 %).

*Deuteration of **5c**.* A mixture of **5c** (0.10 g), triethylamine (2 drops), and methanol-*d* (CH_3OD, 98 %, 0.5 g) in benzene (2 ml) was stirred at room temperature overnight and then evaporated *in vacuo* to give colorless crystals of **7** (0.098 g, 98 %) which were purified by recrystallization from methanol. In the PMR spectrum ($CDCl_3$) of **7**, the doublet of 3-H in **5c** which had been observed at 4.97 ppm completely disappeared.

1-p-Methoxyphenyl-3-vinyl-3,3a-dihydro-1H-cyclohept[c]*isothiazole 2,2-Dioxide (**9a**).* To a solution of 8-methoxyphenyl-8-azaheptafulvenium fluoroborate (0.60 g) and 2-propenesulfonyl chloride (0.30 g) in dry dichloromethane (10 ml) was added drowpise a solution of triethylamine (0.50 g) at −50 °C. The reaction mixture was stirred at room temperature overnight and evaporated *in vacuo* to dryness. The residue was extracted with hot benzene and the extract was evaporated again to give an oily product. The crude, but almost pure, product was filtered through a short column packed with alumina using benzene as eluent, giving pale yellow needles of **9a** (0.63 g, 100 %) which were purified by recrystallization from 2-propanol; mp 113.5—115 °C. IR (KBr, cm^{-1}): 1620 (C=C), 1320, 1140 (SO_2) and 960 (CH=CH_2); PMR ($CDCl_3$, δ ppm): 2.92 (m, 1H, 3a-H), 3.83 (s, 3H, OCH_3), 4.40 (t, 1H, $J_{3-3a}=J_{3-4}$=8.6 Hz, 3-H), 5.20 (br. d, 1H, J_{8-7}=5.5 Hz, 8-H), 5.47 (dd, 1H, J_{4-3a}=5.2 and J_{4-5}=8.5 Hz, 4-H), 5.71 (br. d, 1H, J_{trans}=17.8 Hz, =CH_2), 5.74 (br. d, 1H, J_{cis}=10.0 Hz, =CH_2), 6.10—6.55 (m, 4H, 5-, 6-, 7-H and -CH=) and 6.97, 7.30 (each d, 4H, aromatic protons); MS (*m/e*, relative intensity): 315 (M^+, 81), 251 (M^+-SO_2, 42), 250 (251^+-H, 76) and 211 (M^+—vinylsulfene, base peak).

Found: C, 64.65; H, 5.35; N, 4.24%. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44%.

1-p-Methylphenyl-3-vinyl-3,3a-dihydro-1H-cyclohept[c]*isothiazole 2,2-Dioxide (**9b**).* The reaction of 8-*p*-methylphenyl-8-azaheptafulvenium fluoroborate (0.57 g), 2-propenesulfony chloride (0.35 g) and triethylamine (0.50 g), in a similar way described above, gave pale yellow plates of **9b** (0.35 g, 58 %) which were purified by recrystallization from cyclohexane; mp 97.5—100 °C. IR (KBr, cm^{-1}): 1620 (C=C), 1325, 1150 (SO_2) and 940 (CH=CH_2); PMR ($CDCl_3$, δ ppm): 2.34 (s, 3H, CH_3), 2.93 (m, 1H, 3a-H), 4.33 (t, 1H, $J_{3-3a}=J_{3-4}$=8.6 Hz, 3-H), 5.14 (br. d, 1H, J_{8-7}=5.5 Hz, 8-H), 5.38 (dd, 1H, J_{4-3a}=5.0 and J_{4-5}= 9.0 Hz, 4-H), 5.58 (br. d, 1H, J_{trans}=16.0 Hz, =CH_2) 5.61 (br d, 1H, J_{cis}=10.0 Hz, =CH_2), 5.95—6.38 (m, 4H, 5-, 6-, 7-H, and -CH=) and 7.13 (s, 5H, aromatic protons); MS (*m/e*, relative intensity): 299 (M^+, 57), 235 (M^+-SO_2, 44), 234 (235^+-H, 71) and 195 (M^+—vinylsulfene, base peak).

Found: C, 68.22; H, 5.63; N, 4.55%. Calcd for $C_{17}H_{17}NO_2S$: C, 68.20; H, 5.72; N, 4.68%.

1-p-Chlorophenyl-3-vinyl-3,3a-dihydro-1H-cyclohept[c]*isothiazole 2,2-Dioxide (**9c**).* In a similar way as that of **9a**, the reaction of 8-*p*-chlorophenyl-8-azaheptafulvenium fluorobotate (0.61 g), 2-propenesulfonyl chloride (0.28 g) and triethylamine (0.40 g) afforded colorless prisms of **9c** (0.41 g, 64 %) which were purified by recrystallization from 2-propanol; mp 112.5—113 °C. IR (KBr, cm^{-1}): 1620 (C=C), 1330, 1140 (SO_2) and 960 (CH=CH_2); PMR ($CDCl_3$, δ

ppm): 2.93 (m, 1H, 3a-H), 4.46 (t, 1H, $J_{3-3a}=J_{3-4}=8.6$ Hz, 3-H), 5.31 (br. d, 1H, $J_{8-7}=5.0$ Hz, 8-H), 5.51 (dd, 1H, $J_{4-3a}=5.5$ and $J_{4-5}=9.5$ Hz, 4-H), 5.72 (br. d, 1H, $J_{trans}=17.0$ Hz, $=CH_2$), 5.77 (br. d, 1H, $J_{cis}=10.0$ Hz, $=CH_2$), 6.06—6.64 (m, 4H, 5-, 6-, 7-H, and $-CH=$) and 7.34, 7.48 (each d, 4H, aromatic protons); MS (*m/e*, relative intensity): 319, 321 (M^+, 52, 18), 355, 357 (M^+-SO_2, 36, 13), 354, 356 (355^+-H, 83, 357^+-H, 29) and 215, 217 (M^+-vinylsulfene, base peak, 30).

Found: C, 60.01; H, 4.57; N, 4.29%. Calcd for $C_{16}H_{14}NO_2SCl$: C, 60.09; H, 4.41; N, 4.38%.

*3-Ethyl-1-*p*-methoxypehenyl-1*H*-cyclohept*[c]*isothiazol 2,2-Dioxide (**10**).* A solution of **9a** (0.20 g) and sodium ethoxide (0.04 g) in dry ethanol (10 ml) was refluxed for 1 h. The residue obtained by evaporation of the soluvent *in vacuo* was dissolved in water and the aquious solution was extracted with benzene. The extract was dried over magnesium sulfate and evaporated to give orange prisms of **10** (0.18 g, 90 %) which were recrystallized from 2-propanol; mp 152—153 °C. IR (KBr, cm^{-1}): 1590 (C=C), 1290 and 1150 (SO_2); PMR ($CDCl_3$, δ ppm): 1.38 (t, 3H, $C\underline{H}_3CH_2$), 2.80 (q, 2H, $CH_3-C\underline{H}_2$), 3.93 (s, 3H, OCH_3), 5.78 (br. d, 1H, $J_{4-5}=8.0$ Hz, 4-H), 6.30—6.84 (m, 4H, 5-, 6-, 7-, and 8-H) and 7.10, 7.48 (each d, 4H, aromatic protons): MS (*m/e*, relative intesity): 315 (M^+, base peak).

Found: C, 64.48; H, 5.26; N, 4.42%. Calcd for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44%.

This compound **10** was also obtained by the following procedure: a mixture of **9a** (0.11 g) and DBU (1 drop) in dry benzene (5 ml) was refluxed for 1 h and the solvent was evaporated *in vacuo* to give **10** (0.083 g, 75%).

3-(Ethyl-1,2-d_2*)-1-*p*-methoxyphenyl-1*H*-cyclohept*[c]*isothioazole 2,2-Dioxide (**11**).* A solution of **9a** (0.20 g) and sodium ethoxide (0.04 g) in emthanol-*d* (CH_3OD, 98%, 1.0 g) and dry benzene (1 ml) was refluxed for 1 h. The same work-up as described above gave orange prisms of **11** (0.10 g, 50%) which were recrystallized from 2-propanol; mp 151—152 °C. PMR ($CDCl_3$, δ ppm): 1.39 (m, 2H, $C\underline{H}_2DCHD$), 2.83 (m, 1H, $CH_2DC\underline{H}D$) and the other signals which were at the same positions as those of **10**; MS (*m/e*, relative intensity): 317 (M^+, base peak).

*The Reaction of **9c** with Butyllithium.* To a solution of **9c** (0.10 g) in dry benzene (10 ml) was added butyllithium (15% in hexane, 1.0 ml) at 0 °C under nitrogen. The solution was stirred for 15 min at the same temperature and poured into water. The organic compound was collected with benzene, dried over magnesium sulfate, and then the solution was evaporated *in vacuo*. The residue was filtered through a short column packed with alumina using benzene as eluent to give an yellow oil (**12** and **13**).

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