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Cycloaddition Reactions of Diarylthiirene 1,1-Dioxides with Enamines[1]

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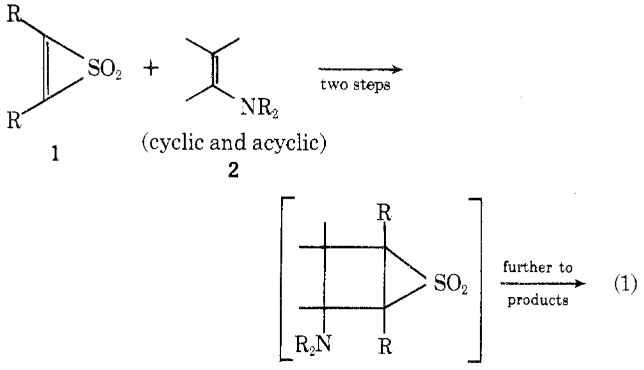
Reaction of 2,3-diphenylthiirene 1,1-dioxide (**5**) with enamines provided novel acyclic and cyclic systems. Products of carbon–carbon and carbon–sulfur bond cleavage in the intermediate episulfone **3** are described (eq 1). In some instances, medium- and large-sized sulfur-containing heterocycles are obtained in good yield. Other cases provided thiophene 1,1-dioxides which undergo a unique disproportionation reaction. Some of the medium-sized rings were heat labile and underwent transannular reactions on purification. Nuclear magnetic resonance decoupling experiments and employment of nmr complexing agents for the structural determination of these materials are described. Mechanistic interpretations are provided for all the results. The reaction is thought to be a thermal [2 + 2] cycloaddition with formation of **3** in a stepwise fashion. Subsequent scission of the cyclobutane portion of **3** could occur by a $[_{\sigma}2_{s} + {}_{\sigma}2_{a}]$ or stepwise process using the nonbonded pair of electrons of nitrogen. Products of loss of sulfur dioxide are more prevalent when **5** was substituted with a chloro group (**42**). Diarylthiirene 1,1-dioxides appear to have less conjugative stabilization than **4** and lack any aromatic character.

Knowledge of the synthesis and chemistry of thiirene 1,1-dioxides **1**[2–5] and the cycloaddition of α,β-unsaturated sulfones with electron-rich olefins **2**[6,7] indicated that employment of **1** in place of these sulfones might afford facile incorporation of its components, thus providing a unique method for the synthesis of novel acyclic and cyclic systems. The transformation would test the extent of nonbenzenoid aromatic character or the conjugative stabilization offered by the SO_2 group of **1** and would indicate the relative energetics involved with the cleavage of σ bonds within the expected intermediate **3** (eq 1).[8]



1

(cyclic and acyclic)
2

3

(1)

Diphenylcyclopropenone (**4**) and **1** have been compared with respect to their reaction with base and it was found that **1** reacted approximately 5000 times faster than **4**; marked conjugative stabilization of **4** and slight conjugative stabilization of **1** were cited as the apparent explanation.[9] More recently, the reaction of enamines with **4** has received different interpretations[10] from the previously published results;[11] the present investigation compares those findings with these utilizing **1**.

Another goal was to demonstrate the synthetic potential for the reaction of **1** and **2** which could prove to be just as dramatic as realized in the treatment of the latter with dimethylacetylene dicarboxylate.[12–14] It would provide with cyclic **2** a facile entry into medium-sized ring sulfur containing heterocycles and thus would join the other methods described for the synthesis of analogous heterocyclic systems.[10f,15]

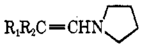
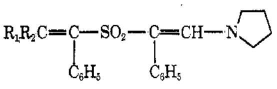
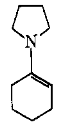
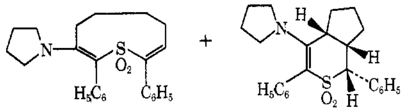
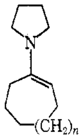
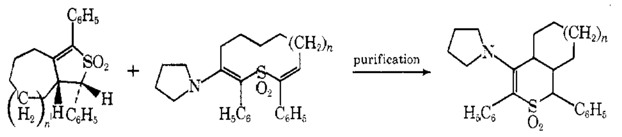
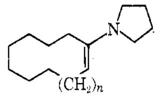
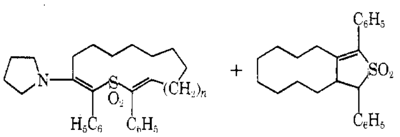
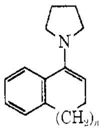
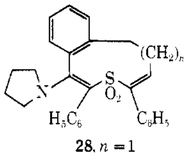
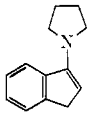
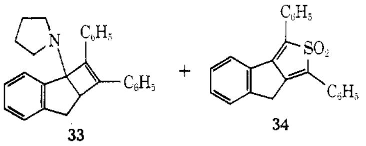
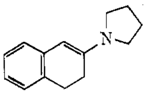
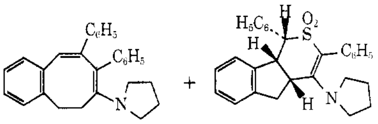
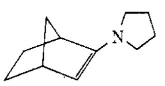
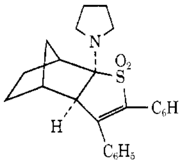
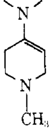
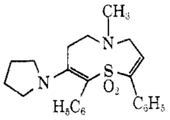
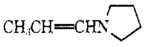
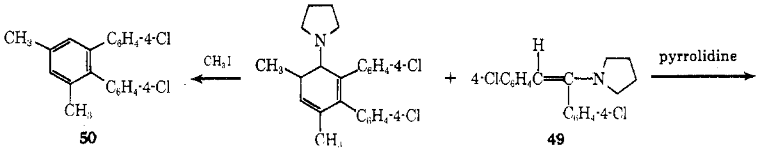
Results

An exothermic reaction between 2,3-diphenylthiirene 1,1-dioxide (**5**) and 1-(1-propenyl)pyrrolidine (**6a**) afforded vinylogous sulfonamide **7a** (Table I, eq a). The same transformation when controlled by intermittent cooling at 20° gave no physical evidence for an intermediate and the same product was obtained. Enamine **6b** and **6c** and **5** required external heating for transformation to **7b** and **7c**, respectively (Table I, eq a). The acyclic products were characterized unambiguously on the basis of spectral data and on comparisons with similar materials from the literature.[16] When enamine **6b** was modified from pyrrolidino to its piperidino, morpholino, and dimethylamino analogs, the usual decrease in enamine reactivity was observed[17] and no vinylogous sulfonamides were observed. Prolonged refluxing of reactants in benzene yielded diphenylacetylene, the sulfur dioxide extrusion product of **5**.

The reaction of **5** and 1-(1-cyclohexen-1-yl)pyrrolidine (**8**) was spontaneous on mixing in benzene and afforded a substance with a found empirical formula for a 1:1 adduct, $C_{24}H_{27}NO_2S$. Thin-layer chromatography indicated the presence of two components (*ca.* 80:20). The material was characterized before recrystallization since all suitable solvents of purification yielded a pure sample of the minor component. This new substance had the same empirical formula but possessed different physical and spectral properties. The major product has been assigned as nine-membered ring **9** and its isomer obtained on recrystallization as vinylogous sulfonamide **10** (Table I, eq b).

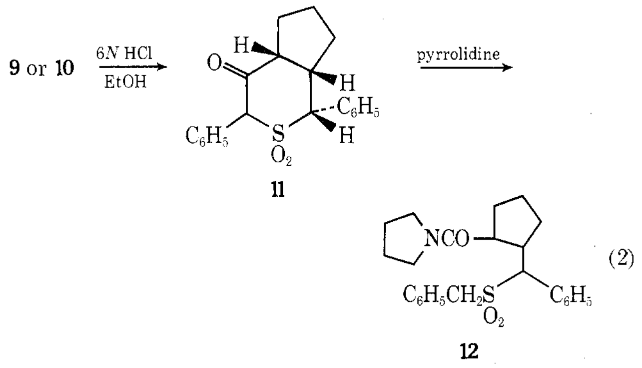
The structural assignment for **9** followed from its characteristic infrared absorption at 1520 cm^{-1} and its ultraviolet

Table I
Reactions of 2,3-Diphenyl (5) and 2,3-Bis(4-chlorophenyl)thiirene 1,1-Dioxide (42)

Enamine	Products	
 6a, $R_1 = CH_3$; $R_2 = H$ b, $R_1 = R_2 = CH_3$ c, $R_1 = C_6H_5$; $R_2 = H$	 7a–c 43b[b]	(a)
 8	 ethanol, reflux 9 44[a,b] 10 45[b,c]	(b)
 13, $n = 1$ 14, $n = 2$	 purification 15, $n = 1$ 16, $n = 2$ 17,[a] $n = 1$ 18,[a] $n = 2$ 19, $n = 1$ 20, $n = 2$	(c)
 21, $n = 1$ 24, $n = 2$ 25, $n = 3$	 22,[a] $n = 1$ 26,[a] $n = 2$ 27,[a] $n = 3$ 23	(d)
 29, $n = 1$ 30, $n = 2$	 28, $n = 1$ 31, $n = 2$ 46[b], $n = 1$	(e)
 32	 33 34	(f)
 35	 36 47[b] 37	(g)
 38	 39	(h)
 40	 41[a]	(i)
 6a	 pyrrolidine → 42 50 48 49	(j)

[a] One of three possible structural assignments. [b] 4-ClC$_6$H$_4$ in place of C$_6$H$_5$. [c] 4-ClC$_6$H$_4$ is in the equatorial position since the coupling constant for the two adjacent protons is 13-Hz diaxial interaction.

absorption at 326 $m\mu$. Employment of deuterated Eu(fod)$_3$ in its nmr spectrum furnished indirect evidence for the presence of a vinyl proton (Experimental Section). The configuration of the double bonds is unknown although the cis–cis appears to be in a relative sense the isomer with the least amount of transannular nonbonded interactions on inspection of Dreiding models. Evidence for the structural assignment for **10** was derived from its infrared and ultraviolet absorptions of 1550 cm^{-1} and 294 $m\mu$, respectively.[16] Decoupling of the nmr spectrum demonstrated that the α-sulfonyl and methine protons were coupled to each other. Both **9** and **10** hydrolyze to sulfone **11** which affords a ring cleavage product (**12**) on treatment with pyrrolidine (eq 2).[18]



The course of reaction changed dramatically when the ring size of the enamine was increased. Treatment of **5** with 1-(1-cyclohepten-1-yl)- and 1-(1-cycloocten-1-yl)pyrrolidine, **13** and **14**, respectively, afforded dihydrothiophene 1,1-dioxides **15** and **16** as major products. In addition, 10-membered ring **17** and 11-membered ring **18** were observed and vinylogous sulfonamides **19** and **20** were isolated on purification (Table I, eq c).

The infrared spectra of **17** and **18** with their characteristic absorptions at 1520–1530 cm^{-1} and those for **19** and **20** at 1555–1560 cm^{-1} compared well with those obtained with **9** and **10**. The major products **15** and **16** were established on the basis of their spectral properties and through an awareness of what happens in the analogous diphenylcyclopropenone case (see Discussion).

Employment of 1-(1-cyclodecen-1-yl)pyrrolidine (**21**) with **5** afforded a 50:50 mixture of 13-membered ring **22** (stable to purification) and bicyclic dihydrothiophene 1,1-dioxide **23** (Table I, eq d). This reaction seems to be the point at which the formation of the large ring begins to become the major product again, for utilization of enamine **24** and **25** afforded in good yield the 14-membered and 15-membered rings, **26** and **27**, respectively (Table I, eq d).

Only one product, nine-membered ring **28**, was obtained on treatment of **5** with 1-(3,4-dihydro-1-naphthyl)pyrrolidine (**29**) (Table I, eq e). The structure of **28** followed from its infrared and ultraviolet spectra which compared with those of the above large rings (1524 cm^{-1} and 314 $m\mu$, respectively). Nuclear magnetic resonance decoupling experiments and employment of deuterated Eu(fod)$_3$ provided the best evidence for the presence of the vinyl proton (Experimental Section). Assignment of all cis double bonds was based on the assumption that a trans double bond would yield a very strained system. The homologous enamine **30** afforded a ten-membered ring (**31**) (Table I, eq e). No dihydrothiophene 1,1-dioxide corresponding to **15** was isolated.

Reducing the ring size of **29**, that is, employment of 1-inden-3-ylpyrrolidine (**32**), gave a unique result. Instead of the expected eight-membered ring, olefin **33** and thiophene 1,1-dioxide **34** were isolated (Table I, eq f). The structures of these materials were established on the basis of their spectral properties (Experimental Section) and on mechanistic interpretation considered later (see Discussion).

A novel product was obtained when 1-(3,4-dihydro-2-naphthyl)pyrrolidine (**35**) was treated with **5**; dienamine **36** was isolated as the major and vinylogous sulfonamide **37** as the minor product (Table I, eq g). Decoupling of the nmr spectrum of **37** established the position of all of its protons (Experimental Section). The infrared and ultraviolet spectra for **36** when compared with similar materials in the literature[19] provided particularly striking evidence for its structural assignment (Experimental Section).

The course of reaction again changed when 1-(bicyclo[2.2.1]hept-2-en-2-yl)pyrrolidine (**38**) was employed; the sole isolated product was aminosulfone **39** (Table I, eq h). Evidence for the structure of **39** was established on the basis of its analytical spectra and mechanistic considerations to be discussed later. Although exo and endo ring fusion are both possible, **39** was assigned as the indicated exo fused ring according to literature precedence.[20] Direct proof for such an assignment would follow from the singlet nature of the endo hydrogen in the nmr spectrum since it would not be expected to couple with the bridgehead hydrogen. However, the region of the spectrum where this hydrogen would appear is masked by the rest of the hydrogens of the molecule.

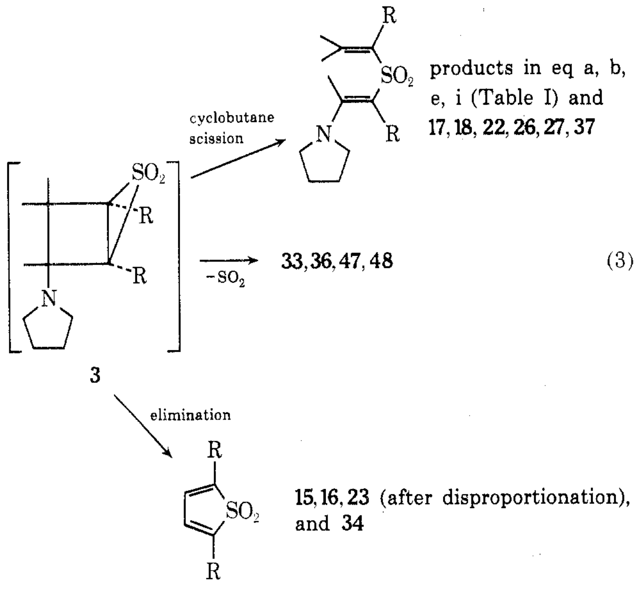
The synthetic value of this transformation is further emphasized by the employment of heterocyclic enamine **40** whereupon nine-membered ring **41** was obtained (Table I, eq i).

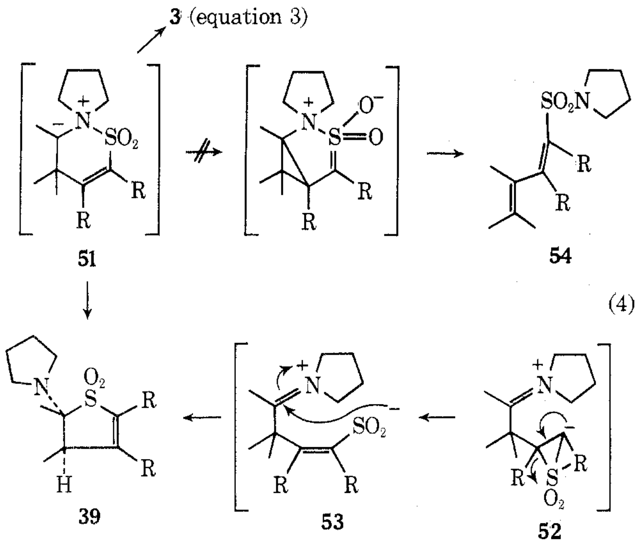
The effect of aromatic substitution in the thiirene 1,1-dioxide was investigated to see if the course of reaction would change. Synthesis of 2,3-bis(4-chlorophenyl)thirene 1,1-dioxide (**42**) was achieved in the usual manner[2] and reactions with several of the above enamines gave the analogous chloro-substituted products (Table I). One unique difference was the sole formation of **47** in twice the yield on comparison with the preparation of **36** (Table I, eq g). Another was the isolation of **48** and **49** on utilization of enamine **6a**; no product corresponding to **7a** was observed (Table I, eq i). Evidence for **48** lies in its analytical spectra and its degradation to a fully aromatic system, terphenyl **50**, on treatment with methyl iodide. Enamine **49** is an artifact since independently **42** yields the same material with pyrrolidine (Table I, eq j).

Discussion

The reaction of an enamine with a thiirene 1,1-dioxide can be considered as a thermal $[2 + 2]$ cycloaddition which, according to orbital symmetry theory, is not a concerted process.[21] The transformation is represented in sequence 1 and intermediate **3** accounts directly or indirectly for all of the observed products, except for **39** (eq 3).

The transformation can be interpreted in another way. Participation of the nonbonded lone pair of electrons of the enamine nitrogen allows for a concerted $[4n + 2]$ cycloaddition.[21] The first step in the mechanism is postulated as attack by the enamine on nitrogen[22] at the sulfonyl group of **1**[23] with subsequent addition to the β carbon of the vinylammonium ion; zwitterion **51** would result. This intermediate is similar to the one invoked for the corresponding reaction with diphenylcyclopropenone.[10] Bond reorganization could then afford all the described products (including **39**) (eq 4). However, such an interpretation seems unnecessary even though it accounts for **39** since this material could arise from an initial Michael addition of **38** and **5** (Table I, eq h) with subsequent bond reorganizations as shown with zwitterionic intermediates **52** and **53** (eq 4). In

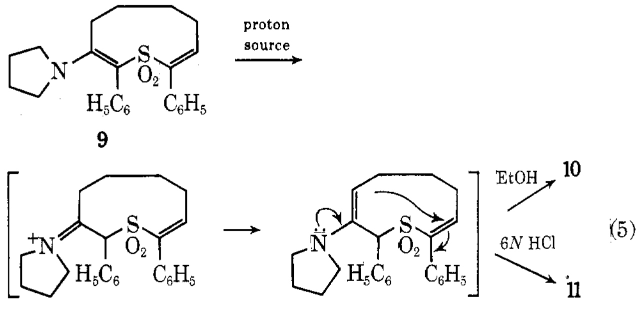




addition, no products were observed related to **54**,[24] one of the major structural types found in the analogous diphenylcyclopropenone case.[10]

Upon inspection of the results, loss of pyrrolidine and cyclobutane ring scission are processes where the C–C bond of the thiirane 1,1-dioxide part of **3** is cleaved. This bond has been shown through theoretical and experimental studies to be the weakest one.[8] Only **33** and **48** (as shown below) can be explained by a concerted extrusion of sulfur dioxide.[21,25] The driving force for relief of strain in the cyclobutane portion could account for the rarity of this pathway.

The concerted scission of a cyclobutane is a [$_\sigma 2_s + {}_\sigma 2_a$] process which would yield the cis–cis structure,[21] but in the case of **3**, participation of the nonbonded pair of electrons of nitrogen after initial cleavage of the episulfone portion could account for the result.[8] In addition, it is unwise to assign the geometry of a molecule on the basis of Woodward–Hoffmann predictions since the steric interactions in the kinetic product might cause inversions to the more stable thermodynamic one. With these restrictions in mind, inspection of Dreiding models for materials like **9** predicts the cis–cis conformer to be favored and the best one to account for the facile transannular reaction encountered on purification (Table I, eq b) or acidic hydrolysis (eq 2). The possible mechanism for this is shown in eq 5.



Loss of pyrrolidine from **3** results in the formation of a thiophene 1,1-dioxide which in the transformation with **32** (Table I, eq f) was isolated (**34**). In the other instances (Table I, eq c and d) a disproportionation reaction would account for the products. Such an oxidation–reduction reaction is well documented in the enamine literature[26] and has been observed in analogous cyclopropenone investigations.[11]

Apparently the transannular nonbonded interactions for an eight-membered ring are severe ones, since employment of enamine **32** (Table I, eq f) afforded products of other pathways. Cyclobutene **33** showed no tendency to undergo a concerted conrotatory ring opening to a cycloheptatriene.[21] Such an event would yield an undesired trans double bond. The material was not heated at a sufficient temperature (*i.e.*, 400°) to undergo the disrotatory process observed for an analogous material in the literature.[27]

It is unlikely that **36** and **47** are derived from initial loss of sulfur dioxide based on the above discussion, for such an occurrence followed by a concerted opening of the derived cyclobutene would afford a trans double bond in a cyclooctatriene. The temperature of the transformation seems too low to allow the corresponding disrotatory mode of ring opening (eq 6). If the lone pair of electrons on nitrogen aids the opening, then such a process should also apply for the former case (enamine **32**). The driving force for this transformation (Table I, eq g) is apparently the formation of a benzylic carbanion (intermediate **55**) which could undergo bond neutralization as shown (eq 6). The same stabilization is not present in the corresponding intermediate **56** from employment of enamine **29** (or **32**). In addition, **28**, and **37** are stable to extended reflux in benzene.

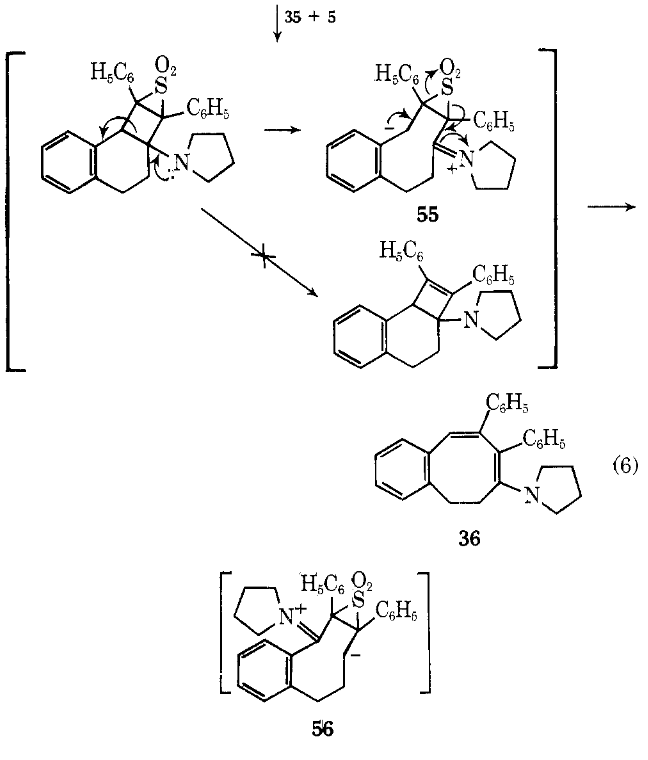
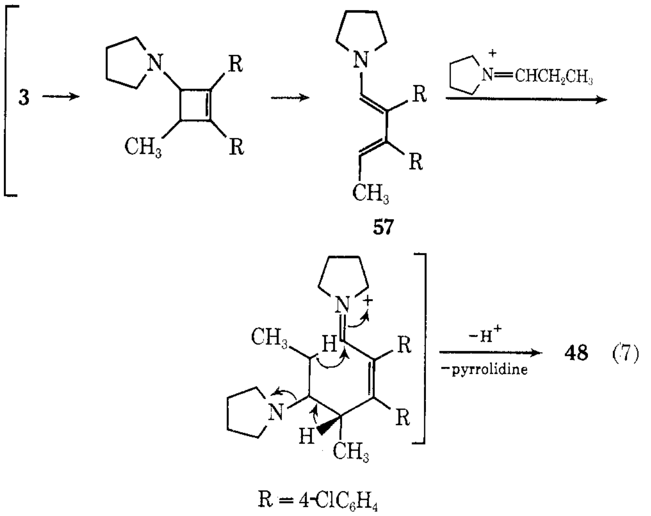


Table II
Experimental Conditions for the Reactions of 2,3-Diphenylthiirene 1,1-Dioxide (5)

Product(s)	**5** (g, mol)	Enamine (g, mol)	Benzene, ml	Temp, °C	Time, min
7a	3.0, 0.012	**6a**[e] (2.0, 0.018)	30	80[b]	15
7b	5.0, 0.02	**6b**[e] (3.5, 0.028)	15	80[b]	120
7c	3.0, 0.012	**6c**[f] (3.0, 0.017)	15	65[a]	120
9, 10[d]	17.0, 0.07	**8**[g] (12.0, 0.08)	300	40[b]	15
15, 17, 19[d]	2.3, 0.01	**13**[g] (1.8, 0.01)	30	40[b]	10
16, 18, 20[d]	6.0, 0.025	**14**[g] (4.5, 0.025)	60	60[b]	10
22, 23	3.5, 0.015	**21** (3.3, 0.016)	30	30[b]–65[a]	120
26	3.5, 0.015	**24** (3.5, 0.016)	30	30[b]–65[a]	120
27	3.0, 0.012	**25**[h] (3.2, 0.014)	30	30[b]–60[a]	120
28	6.0, 0.025	**29**[i] (5.5, 0.028)	45	80[a]	90
31	3.0, 0.012	**30**[j] (3.0, 0.014)	30	60[a]	120
33, 34	5.0, 0.02`	**32**[k] (4.0, 0.022)	30	60[b]	5
36, 37	4.0, 0.017	**35**[22] (3.5, 0.017)	30	70[a]	180
39	6.0, 0.025	**38**[l] (4.8, 0.003)	50	65[b]–70[a]	120
41	6.0, 0.025	**40**[m] (4.2, 0.025)	30	15[c]	120

[a] Reaction mixture was externally heated. [b] Reaction mixture was exothermic to this temperature. [c] Reaction mixture was externally cooled. [d] Material obtained from purification of one of the other products from the reaction. In each case, see specific experiment. [e] G. Opitz, H. Hellmann, and H. W. Schubert, *Justus Liebigs Ann. Chem.*, **623,** 112 (1959). [f] J. N. Wells and F. S. Abbott, *J. Med. Chem.*, **9,** 489 (1966). [g] M. E. Kuehne, *J. Amer. Chem. Soc.*, **81,** 5400 (1959). [h] K. C. Brannock, R. D. Burpitt, V. W. Goodlett, and J. G. Thweatt, *J. Org. Chem.*, **28,** 1464 (1963). [i] G. Bianchi and E. Frati, *Gazz. Chim. Ital.*, **96,** 559 (1966). [j] L. H. Hellberg, R. J. Milligan, and R. N. Wilke, *J. Chem. Soc. C*, 35 (1970). [k] E. D. Bergmann and E. Hoffmann, *J. Org. Chem.*, **26,** 3555 (1961). [l] J. F. Stephen and E. Marcus, *J. Org. Chem.*, **34,** 2535 (1969). [m] S. Donishefsky and R. Cavanaugh, *J. Org. Chem.* **33,** 2959 (1968).

The electronic influences operative in 2,3-bis(4-chlorophenyl)thiirene 1,1-dioxide (**42**) allow the loss of sulfur dioxide to compete to a greater extent.[28] Not only is the yield of **47** much greater, the products obtained with **6a** (Table I, eq j) lack the sulfonyl group. Formation of **48** is best envisioned as a loss of sulfur dioxide from intermediate **3** and ring opening of the intermediate cyclobutene. The intermediate butadiene **57** could add in a typical enamine fashion to the protonated form of **6a** with subsequent loss of a proton and pyrrolidine from that intermediate to afford **48** (eq 7).[29] The materials **48** and **49** are not formed by reaction of enamine **6a** or pyrrolidine with bis(4-chlorophenyl)acetylene for such transformations were shown to afford starting materials.



From comparisons of Tables II and III (Experimental Section) with the data furnished in ref 10 and 11,[30] it becomes apparent that the reaction of enamines with diarylthiirene 1,1-dioxides (**1**) is qualitatively a much faster one than with diphenylcyclopropenone. Perhaps this is further evidence for the slight conjugative stabilization and lack of aromatic character of **1**.[4,8c]

The synthetic utility of this transformation for 9-, 10- (in the case of **31**), 14-, and 15-membered sulfur-containing heterocycles has been demonstrated. In the other ring cases, the course of reaction is dependent on competing steric and electronic factors.

Experimental Section

General Comments. Melting points were determined on a Thomas Hoover capillary apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 21 or 521 grating spectrophotometer and performed in Nujol (abbreviation: en, enamine); ultraviolet spectra were recorded on a Cary 14 and performed in methanol. The nuclear magnetic resonance spectra were determined in deuterated chloroform unless otherwise stated and performed on a Varian A-60, XL-100, or HA-100 instrument. Absorptions are quoted in δ values against tetramethylsilane as internal standard (abbreviations: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; cp, complex pattern; p, proton, Ar, aryl; pyrr, pyrrolidino group). Mass spectra were obtained on an AEI MS-902 spectrometer (70 cV). Elemental analyses were done on a Perkin-Elmer 240.

Starting Materials. Most of the starting materials were prepared according to the literature (see Table II for references). The following are unknown (except for **42**) and synthesized as indicated.

1-(1-Cyclodecen-1-yl)pyrrolidine (21) was obtained in 49.0% yield (3.3 g) by refluxing a solution of 5.0 g (0.03 mol) of cyclodecanone, 6.0 g (0.08 mol) of pyrrolidine, 0.2 g of *p*-toluenesulfonic acid, and 75 ml of toluene for 24 hr using a Dean-Stark trap for water separation. Concentration of the solution *in vacuo* and distillation afforded **21:** bp 90° (0.25 mm); nmr δ (60 MHz) 4.05 (t, 1, J = 10 Hz, vinyl p).

1-(1-Cycloundecen-1-yl)pyrrolidine (24) was obtained in 53.0% yield (3.5 g) by refluxing a solution of 5.0 g (0.03 mol) of cycloundecanone, 6.0 g (0.08 mol) of pyrrolidine, 0.3 g of *p*-toluenesulfonic acid, and 75 ml of toluene for 48 hr as above: bp 99–100° (0.25 mm); nmr δ (60 MHz) 3.95 (t, 1, J = 10 Hz, vinyl p).

α,α′-Sulfonylbis(α-bromo-4-chloro)toluene was prepared by method B in ref 5: mp 195–200° (47.8% yield).

Anal. Calcd for $C_{14}H_{10}Br_2Cl_2O_2S$: C, 35.47; H, 2.13. Found: C, 35.03; H, 2.57.

2,3-Bis(4-chlorophenyl)thiirene 1,1-Dioxide (42). A stirred solution of 312 g (0.66 mol) of the above material in 1800 ml of toluene was treated at the initial reflux temperature but with the heat source removed with 480 ml of triethylamine in 5 min. The mixture was cooled immediately in an ice bath. The solid was filtered and stirred with 2000 ml of water, filtered, and the operation repeated with 2000 ml of aqueous hydrochloric acid solution (3 *N*). The solid was suspended in ethanol, filtered, and air dried to afford **42** in 16.6% yield (51.8 g): mp 174–177° (same mp as the derived acetylene);[31] ir 1590 (double bond), 1260, 1155, and 1090

Table III
Experimental Conditions for the Reactions of 2,3-Bis(4-chlorophenyl)thiirene 1,1-Dioxide (42)

Product(s)	**40**; g, mol	Enamine (g, mol)	Benzene, ml	Temp, °C	Time, min
43[b]	3.0, 0.01	**6b** (2.5, 0.02)	30	70[a]	120
44, 45[c]	15.3, 0.05	**8** (8.0, 0.05)	150	35[b]–50[a]	120
46	5.0, 0.016	**29** (3.5, 0.017)	30	65[a]	180
47	6.75, 0.022	**35** (4.0, 0.02)	30	70[a]	180
48, 49	3.0, 0.01	**6a** (2.2, 0.02)	30	30[b]–65[a]	120

[a] Reaction mixture was externally heated. [b] Reaction mixture was exothermic to this temperature. [c] This material was obtained from purification of **42** (see experimental procedure).

cm^{-1} (all SO_2); uv max 226 (20,200), 234 sh (16,600), 271 sh (13,100), 288 (16,800), 306 (21,400), 318 (20,700), and 334 mμ (14,900); nmr δ (DMSO-d_6) (60 MHz) 7.50–8.00 (cp due to decomposition to the acetylene, Ar); mass spectra M$^+$ 311 (20 eV).

Anal. Calcd for $C_{14}H_8Cl_2O_2S$: C, 54.04; H, 2.59. Found: C, 53.80; H, 2.59.

The above toluene filtrate was concentrated to dryness *in vacuo* and the residue was stirred with water and filtered. The remaining solid was refluxed in 400 ml of benzene for 10 min and filtered hot. Cooling the benzene solution afforded 11.7 g of bis(4-chlorophenyl)acetylene, mp 174–177°.

General Procedure for the Reaction of Thiirene 1,1-Dioxides 5 and 42 with Enamines. Tables II and III describe the amounts of reactants, the experimental conditions, and the products of the reaction of **5** and **42** with the designated enamines. Unless otherwise stated, the following procedure is typical of that employed for these materials. A stirred mixture of **5** or **42** and two-thirds the quoted amount of anhydrous benzene was treated dropwise under nitrogen with a solution of the enamine in the remaining specified benzene. In some cases the reaction was exothermic (footnote *b* in Tables II and III) and was maintained at the indicated temperature for the specified time by regulating the addition of the benzene–enamine solution. In the instances where the reaction was not exothermic (footnote *a* in Tables II and III), the addition of the benzene–enamine solution was very rapid and the reaction mixture was externally heated at the reported temperature and time specified. In all cases, the reaction was allowed to cool to ambient temperature and left overnight. Some of the products crystallized directly from the reaction mixture while others were obtained upon concentration of the mixture *in vacuo* and trituration with ethanol–ether.

1-{2-Phenyl-2-[(1-phenyl-1-propenyl)sulfonyl]ethenyl}pyrrolidine (7a) was isolated in 20.6% yield (0.9 g); mp 161–163°. Analytical sample prepared from ethanol showed: mp 165–166.5°; ir 1610 (en), 1282 and 1120 (both SO_2), strong bands at 768, 705, and 650 cm^{-1}; uv max 286 mμ (17,000); nmr δ (60 MHz) 1.40–1.80 [cp with superimposed d (approximately 1.53, J = 7.0 Hz), 7, CH_2, pyrr and CH_3CH=], 2.63–3.05 (cp, 4, CH_2NCH_2), 6.64 (q, J = 7.0 Hz, 1, CH_3CH=), 7.07 (br s, 1, >NCH=), and 7.24 and 7.30 (s, 10, Ar); mass M$^+$ 353.

Anal. Calcd for $C_{21}H_{23}NO_2S$: C, 71.35; H, 6.56; N, 3.96. Found: C, 71.09; H, 6.57; N, 3.92.

1-{2-[(2-Methyl-1-phenyl-1-propenyl)sulfonyl]-2-phenylethenyl}pyrrolidine (7b) was isolated in 31.3% yield (2.3 g), mp 120–122°. Analytical sample obtained from ethanol showed: mp 121–122°; ir 1602 (en), 1287 and 1118 (both SO_2), strong bands at 700, 665, and 650 cm^{-1}; uv max 286 mμ (18,700); nmr δ (60 MHz) 1.40–1.92 (cp with two superimposed s at 1.48 and 1.85, 10, CH_2, pyrr and $(CH_3)_2C$=), 2.68–3.10 (cp, 4, CH_2NCH_2), and 6.84–7.50 (cp with superimposed s at 7.29, 11, vinyl and Ar); mass M$^+$ 367.

Anal. Calcd for $C_{22}H_{25}NO_2S$: C, 71.78; H, 6.85; N, 3.81. Found: C, 72.15; H, 6.73; N, 3.80.

1-{2-[(1,2-Diphenylethenyl)sulfonyl]-2-phenylethenyl}pyrrolidine (7c) was obtained in 73.8% yield (3.8 g), mp 142–145°. Analytical sample from ethanol showed: mp 150–151°; ir 1605 (en), 1280 and 1115 (both SO_2), medium to strong bands at 990, 945, 755, 697, 688, 660, and 662 cm^{-1}; uv max 256 (18,800) and 308 mμ (18,500); nmr δ (60 MHz) 1.45–1.78 and 2.65–3.00 (cp, 4 each, pyrr p), and 6.68–7.45 (m with two superimposed singlets at 7.00 and 7.32, 17, vinyl and Ar); mass M$^+$ 415.

Anal. Calcd for $C_{26}H_{25}NO_2S$: C, 75.15; H, 6.06; N, 3.37. Found: C, 74.90; H, 5.96; N, 3.42.

Formation of 9 and 10. Reaction of 1-(1-Cyclohexenyl)pyrrolidine (8) with 5. 2,9-Diphenyl-3-(1-pyrrolidinyl)-4,5,6,7-tetrahydrothionin 1,1-dioxide (9) was obtained by direct crystallization analytically pure after washing with ether in 86.5% yield (23.9 g), mp 135–137° dec (the melting point of **9** is lower and over a wider range if the temperature of the experiment is not carefully controlled at 70°; thin-layer analysis in these instances indicates the presence of **10**): ir 1520 (en), 1277 and 1124 (both SO_2), medium to strong bands at 1022, 932, 758, 704, 690, and 656 cm^{-1}; uv max 234 (16,900), 260 (11,400), and 326 mμ (8760); nmr δ (100 MHz) 1.40–1.90 (m, 12, CH_2 of nine-membered and pyrr rings), 2.70–3.20 (m, 4, CH_2NCH_2), and 6.90–7.60 (cp, 11, vinyl and Ar). The spectrum of this material as noted is very broad owing to the many signals concentrated over a small chemical-shift range. It was virtually impossible to identify any long range or the vicinal coupling of the vinyl proton. However, utilization of deuterated Eu(fod)$_3$ afforded complexation and a shift to lower field of the aromatic and the vinyl protons (dd), but temperature effects did not allow for accurate integration. This experiment is complimentary to the detailed description of the complexation in the spectrum for **28**. Mass spectrum was M$^+$ 393.

Anal. Calcd for $C_{24}H_{27}NO_2S$: C, 73.24; H, 6.92; N, 3.55. Found: C, 73.47; H, 6.81; N, 3.68.

1,4a,5,6,7,7a-Hexahydro-1,3-diphenyl-4-(1-pyrrolidinyl)cyclopenta[*c*]thiopyran 2,2-dioxide (10) was afforded by recrystallization of **9** (1.0 g) from ethanol in 45.0% yield (0.45 g): mp 243–244° dec; ir 1550 (en), 1270 and 1115 (both SO_2), medium to strong bands at 890 and 696 cm^{-1}; uv max 219 (20,000), 262 (11,000), and 294 mμ (8430); nmr δ (100 MHz) 1.50–1.80 (cp, 10, CH_2 of fused five-membered and pyrr rings), 2.80–3.30 (cp, 6, angular methines and CH_2NCH_2), 4.5 (d, 1, α-sulfonyl p, J = 6.00 Hz (equatorial–axial), 7.15–7.45 and 7.50–7.70 (two cp, 8 and 2, Ar); a decoupling experiment located the group coupled to the α-sulfonyl proton at 3.0 ppm; mass M$^+$ 393.

Anal. Calcd for $C_{24}H_{27}NO_2S$: C, 73.24; H, 6.92; N, 3.55. Found: C, 73.00; H, 6.97; N, 3.57.

Acidic Hydrolysis of 9 and 10 to 1,4a,5,6,7,7a-Hexahydro-1,3-diphenylcyclopenta[*c*]thiopyran-4(3*H*)-one 2,2-Dioxide (11). A stirred slurry of 2.7 g (0.0069 mol) of **9** and 25 ml of 95% ethanol was treated over 5 min with 6 ml of 6 *N* aqueous hydrochloric acid solution. A solution was obtained in 10 min and the stirred reaction mixture was heated at reflux for 2.5 hr and left at ambient temperature overnight. Filtration of the precipitate and washing of the solid with ether gave **11** in 98% yield (2.3 g), mp 235–237°. Analytical sample from ethyl acetate showed: mp 249–250°; ir 1727 (C=O), 1320, 1310, 1295, 1142, 1122, and 1082 cm^{-1} (all SO_2); uv max 219 (23,500) and 258 mμ (850); nmr δ (DMSO-d_6) (60 MHz) 1.17–2.8 (two multiplets, 6, methylene p), 3.30 (m, 2, methine p), 5.32 [d, J = 5.0 Hz (equatorial–axial), 1, SO_2 CHC_6H_5], 5.98 (s, 1, $SO_2C(-C_6H_5)HCO$), and 7.40 (br s, 10, Ar); mass M$^+$ 340.

Anal. Calcd for $C_{20}H_{20}O_3S$: C, 70.55; H, 5.92. Found: C, 70.60; H, 5.90.

A stirred solution of 0.5 g (0.0013 mol) of **10**, 5 ml of 95% ethanol, and 5 ml of saturated ethanolic hydrochloric acid solution was refluxed for 1.5 hr and left at ambient temperature overnight. Concentration of the reaction mixture and recrystallization of the resultant solid from ethanol gave **11** in 46.5% yield (0.2 g), mp 235–237°. The material possessed identical physical properties when compared with the above data.

Reaction of 11 and Pyrrolidine to 2-[α-(Benzylsulfonyl)benzyl]cyclopentanecarbonyl Piperidide (12). A mixture of 1.5 g (0.004 mol) of **11**, 2.0 g (0.03 mol) of pyrrolidine, and 150 ml of dry benzene was contained in a 300-ml round-bottomed flask topped by a 12-in. column containing glass helices and equipped with a Dean-Stark trap. The mixture was refluxed for 2 hr whereupon a solution was obtained and reflux was maintained overnight. Concentration *in vacuo* gave an 83.3% yield of **12** (1.5 g), mp 178–180°. An analytical sample was obtained from acetone: mp 183–184°; ir 1625 (amide), 1310, 1290, and 1125 (all SO_2), medium bands at 700 and 690 cm^{-1}; nmr δ (60 MHz) 1.25–2.10 (m, 10, CH_2 of the rings), 2.20–3.30 (two m, 6, CH_2NCH_2 and methines of five-membered ring), 3.75–4.15 (cp with superimposed s at 3.84, 3, $\mathit{CH}SO_2\mathit{CH}_2$), and 7.27 and 7.37 (two s, 10, Ar); mass M^+ 411.

Anal. Calcd for $C_{24}H_{29}NO_3S$: C, 70.05; H, 7.10; N, 3.40. Found: C, 70.34; H, 7.07; N, 3.16.

Formation of 15, 17, and 19. Reaction of 1-(1-Cycloheptenyl)pyrrolidine (13) with 5. 5,6,7,8-Tetrahydro-2,10-diphenyl-3-(1-pyrrolidinyl)-4*H*-thiecin 1,1-dioxide (17) was isolated by direct crystallization and obtained analytically pure after washing with ether in 5.0% yield (0.2 g): mp 121–123° dec; ir 1521 (en), 1267, 1240, 1134, 1106 (all SO_2), and medium peaks at 740 and 680 cm^{-1}; mass M^+ 407. (Attempts to obtain nmr and uv data in deuterated chloroform and methanol, respectively, afforded spectra characteristic of **19.** However, one experiment performed in a uv tube with acetonitrile as solvent gave a spectrum with a uv max of 327 mμ.) Only this experiment afforded pure **17.** In all other attempts, **17** was isolated along with **15** and attempted purification *via* chromatography on alumina or fractional crystallization gave **19.**

Anal. Calcd for $C_{25}H_{29}NO_2S$: C, 73.67; H, 7.17; N, 3.44. Found: C, 73.30; H, 7.05; N, 3.63.

Recrystallization of **17** from ethanol afforded **4a,5,6,7,8,8a-hexahydro-1,3-diphenyl-4-(1-pyrrolidinyl)-1*H*-2-benzothiopyran 2,2-dioxide (19)** in 45.0% yield, mp 259–260° dec; ir 1560 (en), 1268 and 1108 (both SO_2), medium to strong bands at 920, 730, and 698 cm^{-1}; uv max 219 (22,100), 262 (11,600), and 295 mμ (7360); mass M^+ 407. (Poor solubility in organic solvents prevented the determination of the 60-MHz nmr spectrum.)

Anal. Calcd for $C_{25}H_{29}NO_2S$: C, 73.67; H, 7.17; N, 3.44. Found: C, 73.39; H, 7.17; N, 3.47.

Diluting the filtrate from the isolation of **17** with ether and cooling overnight at 0° gave **3a,4,5,6,7,8-hexahydro-1,3-diphenyl-3*H*-cyclohepta[*c*]thiophene 2,2-dioxide (15)** in 74.0% yield (2.5 g). An analytical sample was obtained (ethanol): mp 125–127°; ir 1284 and 1120 (both SO_2), and strong bands at 752 and 690 cm^{-1}; uv max 240 mμ (9100) and end absorption; nmr δ (60 MHz) 1.00–2.80 (two m, 10, methylene p), 3.40 (m, 1, methine p), 4.60 (d, 1, α-sulfonyl p, J = 7.0 Hz, equatorial–axial coupling), and 7.38 and 7.45 (two s, 10, Ar); mass M^+ 338.

Anal. Calcd for $C_{21}H_{22}O_2S$: C, 74.52; H, 6.55; S, 9.48. Found: C, 74.36; H, 6.36; S, 9.35.

Formation of 16, 18, and 20. Reaction of 1-(1-Cyclooctenyl)pyrrolidine 14 with 5. 1,4,5,6,7,8,9,9a-Octahydro-1,3-diphenylcycloocta[*c*]thiophene 2,2-dioxide (16) was isolated in 82.8% yield (7.3 g), mp 144–146°. Analytical sample obtained from ethanol showed: mp 158–160° slight dec; ir 1295 and 1129 (both SO_2), and strong band at 695 cm^{-1}; uv max 240 mμ sh (8920) and end absorption; nmr δ (60 MHz) 1.17–2.75 (two m, 12, methylene p), 3.22 (m, 1, methine p), 4.62 [d, 1, α-sulfonyl p, J = 7.0 Hz (equatorial–axial)], and 7.46 (s, 10, Ar); mass M^+ 352.

Anal. Calcd for $C_{22}H_{24}O_2S$: C, 74.96; H, 6.86; S, 9.10. Found: C, 74.77; H, 6.73; S, 9.04.

Examination of the infrared spectrum of crude **16** (mp 144–146°) showed absorption at 1530 cm^{-1} for **2,11-diphenyl-3-(1-pyrrolidinyl)thiacycloundeca-2,10-diene 1,1-dioxide (18).** Chromatography of residues from combined filtrates on 100 g of Woelm neutral alumina (activity 1) gave on elution with 1000 ml of petroleum ether (30–60°), 1000 ml of 50:50 petroleum ether–ethyl ether, and 500 ml of ethyl ether, 0.4 g of **16,** mp 132–135°. Further elution with 500 ml of ethyl ether gave 0.05 g of **1,4a,5,6,7,8,9,9a-octahydro-1,3-diphenyl-4-(1-pyrrolidinyl)cyclohepta[*c*]thiopyran 2,2-dioxide (20):** mp 200–201°; ir 1555 (en), 1270 and 1115 (both SO_2), medium to strong bands at 868, 766, 700, and 670 cm^{-1}; uv max 215 sh (17,500), 256 (9110), and 295 mμ (7790); mass M^+ 421.

Anal. Calcd for $C_{26}H_{31}NO_2S$: mass spectrum molecular weight ion 421.208. Found: 421.208.

Formation of 22 and Evidence for 23. Reaction of 1-(1-Cyclodecenyl)pyrrolidine (21) with 5. The generalized procedure yielded 2.1 g of a brown solid, mp 86–100°; the thin layer indicated two major compounds; ir 1520 (en), 1280, and 1112 cm^{-1} (SO_2, most intense bands of spectrum); uv max 306 mμ (7170); uv min 272 mμ (4710); nmr δ same as spectrum reported below with a superimposed doublet at 4.65 (J = 7.0 Hz, 1, α-sulfonyl p) (*ca.* 25% of expected intensity). Recrystallization from the common organic solvents gave oils. Chromatography on Woelm neutral alumina (activity 1) afforded 0.7 g (9.3% yield) of a colorless material (elution with 75:25 hexane–ether, 1000 ml, and with 5:50 hexane–ether, 1000 ml), mp 145–147°. Analytical sample of **2,13-diphenyl-3-(1-pyrrolidinyl)thiacyclotrideca-2,12-diene 1,1-dioxide (22)** from acetonitrile had: mp 153–154°; ir 1535 (en), 1286 and 1117 (both SO_2), strong to medium bands at 938, 717, 698, 670, and 645 cm^{-1}; uv max 224 sh (14,900), 268 sh (6380), and 308 mμ (12,800); nmr δ (60 MHz) 1.30–2.30 (two m, 20, CH_2 of 13-membered and pyrr rings), 2.60–3.10 (m, 4, $\mathit{CH}_2N\mathit{CH}_2$), and 6.50–7.40 (cp, 11, vinyl and Ar); mass M^+ 449.

Anal. Calcd for $C_{28}H_{35}NO_2S$: C, 74.80; H, 7.85; N, 3.12. Found: C, 74.71; H, 7.95; N, 3.05.

Even though **23** was not isolated, the evidence described in the first part of this experiment is conclusive for its presence.

2,14-Diphenyl-3-(1-pyrrolidinyl)thiacyclotetradeca-2,13 diene 1,1-dioxide (26) was isolated in 59.6% yield (4.0 g), mp 144–145°. Analytical sample from acetonitrile had: mp 145–147°; ir 1522 (en), 1279 and 1120 (both SO_2), strong band at 697 cm^{-1}; uv max 224 sh (15,900) and 303 mμ (13,300); nmr δ (60 MHz) 1.25–2.20 (two m, 22, CH_2 of 14-membered and pyrr rings), 2.60–3.10 (m, 4, $\mathit{CH}_2N\mathit{CH}_2$), and 6.60–7.30 (cp, 11, vinyl and Ar); mass M^+ 463.

Anal. Calcd for $C_{29}H_{37}NO_2S$: C, 75.13; H, 8.05; N, 3.02. Found: C, 75.38; H, 7.95; N, 3.31.

2,15-Diphenyl-3-(1-pyrrolidinyl)thiacyclopentadeca-2,14-diene 1,1-dioxide (27) was obtained in 61.5% yield (3.5 g), mp 151–152°. Analytical sample prepared from acetonitrile had: mp 155–156°; ir 1525 (en), 1275 and 1117 (both SO_2), and strong band at 692 cm^{-1}; uv max 220 sh (16,600) and 301 mμ (10,900); nmr δ (60 MHz) 1.20–2.20 (two m, 24, CH_2 of 15-membered and pyrr rings), 2.60–3.00 (m, 4, $\mathit{CH}_2N\mathit{CH}_2$), and 6.80–7.50 (cp, 11, vinyl and Ar); mass M^+ 477.

Anal. Calcd for $C_{30}H_{39}NO_2S$: C, 75.43; H, 8.23; N, 2.93. Found: C, 75.80; H, 8.07; N, 2.56.

Combined residues from filtrates chromatographed on 50 g of Woelm neutral alumina (activity 1). Elution with 800 ml of 50:50 petroleum ether–ethyl ether and 1000 ml of ethyl ether afforded 0.8 g of **27,** mp 148–150° (total yield, 4.3 g; 75.5%). Elution of the column was continued with 500 ml of chloroform; no further materials were isolated.

6,7-Dihydro-2,4-diphenyl-1-(1-pyrrolidinyl)-3-benzothionine 3,3-dioxide (28) was afforded by direct crystallization in 65.8% yield (7.2 g), mp 218–219° dec. Analytical sample of light yellow crystals from ethanol had mp 228–229° dec; ir 1510 (en), 1270 and 1110 (both SO_2), strong bands at 747 and 690 cm^{-1}; uv max 239 (23,700) and 314 mμ (6030); nmr δ (100 MHz) 1.30–1.75 (m, 4, CH_2, pyrr), 2.00–3.00 (cp, 8, CH_2 of nine-membered ring and $\mathit{CH}_2N\mathit{CH}_2$), and 6.50–7.70 (cp, 15, vinyl and Ar); mass M^+ 441.

Anal. Calcd for $C_{28}H_{27}NO_2S$: C, 76.15; H, 6.16; N, 3.17. Found: C, 76.42; H, 6.33; N, 3.21.

Direct evidence for the presence of the vinyl proton in this nmr (100 MHz) was obtained using deuterated Eu(fod)$_3$. The aliphatic region was little affected; aromatic region: 6.7–7.10, 7.20–7.45, and 7.55–7.75 (three complex patterns, 6, 4, and 1, respectively, Ar), 8.05 (dd, 1, J = 11.0 and 4.0 Hz, vinyl p), and 8.30 (dd, 1, J = 2.0 Hz, Ar). Irradiation at 2.33 ppm causes collapse of the 8.05-ppm signal to a singlet with residual long-range coupling.

7,8-Dihydro-2,4-diphenyl-1-(1-pyrrolidinyl)-6*H*-3-benzothiecin 3,3-dioxide (31) was obtained in 52.5% yield (3.0 g) by direct crystallization, mp 227–229°. Analytical sample of light yellow crystals from ethanol had: mp 254–256°; ir 1518 (en), 1290 and 1121 (both SO_2), medium to strong bands at 1075, 810, 766, 758, 748, 700, 690, and 640 cm^{-1}; uv max 249 (16,500), 277 sh (7090), 287 sh (5030), 295 (5140), and 334 mμ (8290); nmr δ (100 MHz) 1.40–1.80 (m, 4, CH_2, pyrr), 2.10–2.85 (cp, 10, remaining CH_2), 6.18 [poorly resolved t (merged dd), 1, J = 8.0 Hz, vinyl p], 7.10 and 7.40 (m and s, respectively, 14, Ar). Irradiation of the sample in the nmr determination at 2.25 ppm caused collapse of the 6.18-ppm signal to a singlet; mass M^+ 455.

Anal. Calcd for $C_{29}H_{29}NO_2S$: C, 76.46; H, 6.40; N, 3.08. Found: C, 76.85; H, 6.30; N, 2.83.

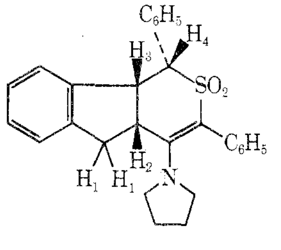
Formation of 33 and 34. Reaction of 1-Inden-3-ylpyrrolidine (32) with 5. 1-(7,7a-Dihydro-1,2-diphenylcyclobut[*a*]inden-2a-yl)pyrrolidine (33) was obtained in 55.0% yield (4.0 g), mp 168–170° dec, by triturating with ethanol (ether complexes the work-up). Analytical sample from ethanol had: mp 178–179° dec; ir 1255 (medium), 1135 (medium doublet), 760 (strong), 730 (strong), 683 cm^{-1} (strong); uv max 224 (23,000), 271 sh (10,000), 277 sh (11,600), and 294 mμ (12,700); nmr δ (60 MHz) 1.60–1.90 and 2.40–2.85 (cp, 4 each, pyrr), 2.90–3.10 (complex ABX pattern with the wings of the AB q not visible, 2, J = 4.6 and 7.0 Hz, CH_2CH), 3.94 (dd, 1, J = 4.5 and 7.0 Hz, $CH_2\mathit{CH}$), and 7.00–7.80 (cp, 14, Ar); mass M^+ 363.

Anal. Calcd for $C_{27}H_{25}N$: C, 89.31; H, 6.93; N, 3.85. Found: C, 89.38; H, 6.78; N, 3.95.

Combined filtrates on concentration and trituration with ethanol gave **1,3-diphenyl-8*H*-indeno[1,2-*c*]thiophene 2,2-dioxide (34)**: 0.7 g, (9.5% yield), mp 189–191° dec. Analytical sample from ethanol had mp 243–244° dec; ir 1275 and 1130 (both SO_2) and medium bands at 750, 725, 695, and 680 cm^{-1}; uv max 222 (20,100), 250 (20,600), 270 (20,500), 304 (8450), and 394 $m\mu$ (8290); nmr δ (60 MHz) 4.20 (s, 2, benzyl p) and 7.25–7.90 (cp, 14, Ar); mass M^+ 356.

Anal. Calcd for $C_{23}H_{16}O_2S$: C, 77.51; H, 4.53; S, 8.98. Found: C, 77.15; H, 4.49; S, 9.04.

Formation of 36 and 37. Reaction of 1-(3,4-Dihydro-2-naphthyl)pyrrolidine (35) with 5. 1,4a,5,9b-Tetrahydro-1,3-diphenyl-4-(1-pyrrolidinyl)indene[1,2-*c*]thiapyran 2,2-dioxide (37) was obtained by trituration with ether in 6.9% yield (0.5 g), mp 204–205° dec. Analytical sample by washing with acetone (or from tetrahydrofuran) had: mp 228–229° dec; ir 1548 (en), 1282 and 1118 (both SO_2), medium to strong bands at 770, 748, 722, 718, 703, and 660 cm^{-1}; uv max 266 (14,000), 273 (13,300), and 295 $m\mu$ (10,200); nmr δ (100 MHz) 1.60–1.90 (m, 4, CH_2, pyrr), 2.90–3.20 (m, 4, CH_2NCH_2), 3.29 (d, 2, $J_{1,2}$ = 10.0 Hz, 2 H_1), 3.80 (q, 1, $J_{1,2}$ = 10.0, $J_{2,3}$ = 8.0 Hz, H_2), 4.42 (t, 1, $J_{2,3}$ = $J_{3,4}$ = 8.0 Hz, H_3), 4.65 (d, 1, $J_{3,4}$ = 8.0 Hz, H_4), 6.57 (d, 1, J = 7.0 Hz, Ar), and 6.80–7.50 (cp, 13, Ar). Irradiation of the sample in the nmr determination at the designated position caused the following changes (position of irradiation [changes]): 3.25 (H_1) [H_2 becomes a d, $J_{2,3}$ = 8.0 Hz]; 3.80 (H_2) [H_1 becomes a s; H_3 and H_4 become an AB q, J = 10.0 and 13.0 Hz]; 4.40 (H_3) [H_2 becomes a t, J = 10.0 Hz, H_4 not determined]; mass M^+ 441.



Anal. Calcd for $C_{28}H_{27}NO_2S$: C, 76.15; H, 6.16; N, 3.17. Found: C, 76.46; H, 6.09; N, 3.12.

1-(5,6-Dihydro-8,9-diphenyl-7-benzocyclooctenyl)pyrrolidine (36) was afforded by the concentration of the filtrates and trituration with ethanol–ether in 25.8% yield (1.6 g), mp 118–120°. Analytical sample of golden yellow crystals from ether–hexane had: mp 127–129°; ir 1588 and 1558 (en), 756 and 690 cm^{-1} doublet (strong olefin bands); uv max 271 (41,900), 292 (19,700), 304 (18,800), 316 sh (15,400), and 340 $m\mu$ sh (7240); nmr δ (100 MHz) 1.20–1.80 (m, 4, CH_2, pyrr), remaining aliphatic p at 1.95–2.55 (nine-line cp, 2), 2.55–3.00 (cp, 4), and 3.10–3.40 (cp, 2), and 6.65–7.70 (cp, 15, vinyl and Ar); mass M^+ 377.

Anal. Calcd for $C_{28}H_{27}N$: C, 89.08; H, 7.21; N, 3.71. Found: C, 89.40; H, 7.30; N, 3.87.

***cis-exo*-3a,4,5,6,7,7a-Hexahydro-2,3-diphenyl-7a-(1-pyrrolidinyl)-4,7-methanobenzo[*b*]thiophene 1,1-dioxide (39)** was obtained in 58.0% yield (5.5 g), mp 129–131°. Analytical sample prepared from ethyl acetate–hexane had: mp 132–134°; ir 1635, 1600 and 1575 (double bonds), 1270 and 1120 (both SO_2), and strong bands at 800, 770, 755, 722, and 700 cm^{-1}; uv max 224 (21,600) and 256 $m\mu$ sh (10,810); nmr δ (60 MHz) 1.00–2.30 (m, 11, methylene and one bridgehead p), 2.80–3.60 (m, 6, CH_2NCH_2, bridgehead p nearest the SO_2 group, according to Dreiding models, and $CHC(C_6H_5){=\!=}CC_6H_5$), and 7.00–7.60 (merging singlets centered at 7.28, 10, Ar); mass M^+ 405.

Anal. Calcd for $C_{25}H_{27}NO_2S$: C, 74.05; H, 6.71; N, 3.45. Found: C, 74.05; H, 6.96; N, 3.59.

4,5,6,7-Tetrahydro-5-methyl-2,9-diphenyl-8-(1-pyrrolidinyl)-1,5-thiazonine 1,1-dioxide (41) was obtained by direct crystallization in 37.2% yield (3.8 g), mp 142–144°. Analytical sample by washing with cold ether (0°) and ethanol (material decomposed on attempted recrystallization from benzene, methylene chloride, ethanol, and ethyl acetate) had: mp 146–148°; ir 1512 (en), 1270 (doublet) and 1113 (both SO_2), and strong band at 700 cm^{-1}; uv max 232 (14,600), 260 (10,700), and 332 $m\mu$ (6280); nmr δ (60 MHz) 1.7 (m, 4, CH_2, pyrr), 2.25–3.90 (cp with superimposed s at 2.5, 13, CH_2NCH_2 and remaining CH_2 and CH_3), and 7.00–7.80 (cp with two s at 7.18 and 7.46, 11, vinyl and Ar); mass M^+ 408.

Anal. Calcd for $C_{24}H_{28}N_2O_2S$: C, 70.55; H, 6.91; N, 6.86. Found: C, 70.86; H, 6.76; N, 6.71.

Methiodide from methanol had mp 201–203°.

Anal. Calcd for $C_{25}H_{31}INO_2S$: C, 54.50; H, 5.68; N, 4.97. Found: C, 54.45; H, 5.68; N, 5.10.

1-{2-[(1-(4-Chlorophenyl)-2-methyl-1-propenyl)sulfonyl]-2-(4-chlorophenyl)ethenyl}pyrrolidine (43b) was isolated in 63.6% yield (2.8 g), mp 144–146° [bis(4-chlorophenyl)acetylene is the major impurity, ~10%]. Analytical sample obtained by chromatography on Woelm neutral alumina (eluting with ether) and subsequent recrystallization from ethanol had mp 171–172°; ir 1615 (en), 1280, 1120, and 1090 (all SO_2), weak to medium bands at 1015, 989, 956, 920, 860, 812, 714, and 668 cm^{-1}; uv max 225 (26,500), 268 sh (16,300), and 288 $m\mu$ (16,900); nmr δ (60 MHz) 1.50–2.00 [cp with two superimposed s at 1.55 and 1.95, 10, CH_2, pyrr and $(CH_3)_2C{=\!=}$], 2.80–3.20 (m, 4, CH_2NCH_2), and 6.90–7.50 [AB q (one-half at 7.00, J = 10.0 Hz) with superimposed s at 7.38 (9, vinyl and Ar, J = 12.0 and 14.0 Hz)]; mass M^+ 435.

Anal. Calcd for $C_{22}H_{23}Cl_2NO_2S$: C, 60.55; H, 5.31; N, 3.21. Found: C, 60.75; H, 5.13; N, 3.21.

Formation of 44 and 45. Reaction of 1-(1-Cyclohexenyl)pyrrolidine (8) with 42. 4,5,6,7-Tetrahydro-2,9-bis(4-chlorophenyl)-3-(1-pyrrolidenyl)thionin 1,1-dioxide (44) was obtained in 88.0% yield (19.5 g), mp 125–130°. Analytical sample afforded by washing with ether had: mp 137–139°; ir 1510 (en), 1272, 1110, 1095, and 1085 (all SO_2), and medium to weak bands at 1010, 920, 818, 735, 720, 710, and 650 cm^{-1}; uv max 236 (21,300), 264 sh (12,400), 306 (6660), and 329 $m\mu$ (8040); nmr δ (100 MHz) 1.40–2.00 (m, 12, CH_2 of nine-membered and pyrr rings), 2.80–3.20 (m, 4, CH_2NCH_2), and 6.90–7.60 (cp, 9, vinyl and Ar); mass M^+ 461.

Anal. Calcd for $C_{24}H_{25}Cl_2NO_2S$: C, 61.79; H, 5.40; N, 3.00. Found: C, 61.87; H, 5.80; N, 2.86.

1,4a,5,6,7,7a-Hexahydro-1,3-bis(4-chlorophenyl)-4-(1-pyrrolidinyl)cyclopenta[*c*]thiopyran 2,2-dioxide (45) was prepared by recrystallization of 44 (1.0 g) from ethanol in 55.0% yield (0.55 g): mp 259–260° dec; ir 1575 (en), 1275, 1120, 1102, and 1090 (all SO_2), medium to weak bands at 1012, 958, 877, 845, 748, 720, and 650 cm^{-1}; uv max 230 (32,900), 265 (11,900), and 303 $m\mu$ (7770); nmr δ (100 MHz) 1.55–1.90 (cp, 10, CH_2 of fused five-membered and pyrr rings), 2.85–3.10 (cp, 6, angular methines and CH_2NCH_2), 4.12 (d, 1, α-sulfonyl p, J = 13.0 Hz, axial–axial coupling), 7.25 and 7.38 (two s, 8, Ar); a decoupling experiment located the group coupled to the α-sulfonyl proton at 3.0 ppm; mass M^+ 461.

Anal. Calcd for $C_{24}H_{25}Cl_2NO_2S$: C, 61.79; H, 5.40; N, 3.00. Found: C, 61.93; H, 5.55; N, 2.97.

6,7-Dihydro-2,4-bis(4-chlorophenyl)-1-(1-pyrrolidinyl)-3-benzothionin 3,3-dioxide (46) was obtained by direct crystallization in 90.3% yield (7.4 g), mp 210–212° dec. Analytical sample of light yellow crystals afforded from ethanol had: mp 222–224° dec; ir 1528 (en), 1279, 1118, 1097, 1089 (all SO_2), medium bands at 1012, 860, 835, 820, 752, and 715 cm^{-1}; uv max 244 (28,700), 300–312 plateau (6120), and 320 sh $m\mu$ (5900); nmr δ DMSO-d_6 (100 MHz) 1.25–1.70 (m, 4, CH_2, pyrr), 1.80–2.90 (m, 8, CH_2 of nine-membered ring and CH_2NCH_2), and 6.20–7.50 [cp with a superimposed AB q (6.34 and 6.87, J = 10.0 Hz), 13, vinyl and Ar]; mass M^+ 509.

Anal. Calcd for $C_{28}H_{25}Cl_2NO_2S$: C, 65.88; H, 4.94; N, 2.74. Found: C, 65.94; H, 4.94; N, 2.48.

1-[5,6-Dihydro-8,9-bis(4-chlorophenyl)benzocycloocten-7-yl]pyrrolidine (47) was obtained by direct crystallization and through trituration of the filtrate residue with ethanol–ether in 56.2 yield (2.0 and 3.0 g, respectively), mp 208–210° dec and 201–203° dec, respectively. Analytical sample of brilliant orange crystals from ether had mp 209–210° dec; ir 1580 and 1545 (dienamine), medium bands at 1080, 1008, and 757 cm^{-1}; uv max 213 (44,700), 274 (63,500), 308 sh (12,800), and 320 $m\mu$ sh (7160); nmr δ (100 MHz) 1.20–1.80 (m, 4, CH_2, pyrr), remaining aliphatic p at 1.95–2.60 (nine-line cp, 2), 2.60–3.00 (cp, 4), and 3.10–3.40 (cp, 2), and 6.70–7.70 (cp, 13, vinyl and Ar); mass M^+ 445.

Anal. Calcd for $C_{28}H_{25}Cl_2N$: C, 75.33; H, 5.65; N, 3.14. Found: C, 75.72; H, 5.88; N, 3.18.

Formation of 48 and 49. Reaction of 1-(1-Propenyl)pyrrolidine (6a) with 2,3-Bis(4-chlorophenyl)thiirene 1,1-Dioxide (42). 1,2-Bis(4-chlorophenyl)-1-(1-pyrrolidinyl)ethylene (49) was afforded in 25.0% yield (0.8 g), mp 118–119°. Recrystallization from ethanol gave an analytical sample: mp 122–123°; ir 1600 and 1580 (en), 1550 (aromatic double bond), and strong bands at 1395, 1345, 1085, 830, and 820 cm^{-1}; uv max 224 sh (16,100), 272 sh (10,900), 287 (16,900), 295 (16,600), 305 (18,900), and 324 $m\mu$ sh (12,900); nmr δ (60 MHz) 1.70–2.05 and 2.83–3.25 (two m, 4 and 4, $(CH_2)_2$ and CH_2NCH_2, respectively, of the pyrrolidino group), 5.25 (s, 1, vinyl p), 6.52 and 6.90 (AB q, 4, J = 10.0 Hz, Ar), and 7.25 (cp, 4, Ar); mass M^+ 317.

Anal. Calcd for $C_{18}H_{17}Cl_2N$: C, 67.93; H, 5.39; N, 4.40. Found: C, 68.26; H, 5.25; N, 4.15.

Column chromatography of the combined residues on Woelm neutral alumina (100 g), elution with 750 ml of hexane, and usual work-up with one recrystallization from ethanol gave analytically pure a 25.0% yield (1.0 g) of **1-[2,3-bis(4-chlorophenyl)-4,6-dimethylcyclohexa-2,4-dienyl]pyrrolidine (48):** mp 87–89°; ir 1580 (stilbene double bond, weak) and strong bands at 1082, 1007, and 812 cm^{-1};[28] uv max 221 mμ sh (19,800);[32] nmr δ (60 MHz) 0.98 (d, 3, $\mathrm{C}H_3\mathrm{CH}$, J = 7.5 Hz), 1.65–1.90 (cp, 7, $\mathrm{HC{=}C\text{-}C}H_3$ and $(CH_2)_2$, pyrr), 2.5–3.1 (m, 5, $\mathrm{C}H_2\mathrm{NC}H_2$ and $\mathrm{CH_3C}H$), 3.98 (d, 1, $\mathrm{C}H\mathrm{N}<$, J = 6.0 Hz), 5.78 (d further split in each portion into a t, 1, $\mathrm{C}H\mathrm{{=}CCH_3}$, J = 5.0 and 1.0 Hz), 6.70–7.35 (cp with superimposed s at 7.10, 8, Ar); a decoupling experiment showed that the proton at 3.98 and 5.78 were not coupled to each other; mass M^+ 3.97.

Anal. Calcd for $C_{24}H_{25}Cl_2N$: C, 72.36; H, 6.33; N, 3.52. Found: C, 72.11; H, 6.31; N, 3.56.

4,4″-Dichloro-3′,5′-dimethyl-1,1′:2′,1″-terphenyl (50). A stirred solution of 0.5 g (0.001 mol) of **48**, 0.5 g (0.003 mol) of methyl iodide, and 10 ml of methanol was heated at reflux for 3.0 hr and remained at ambient temperature overnight. Concentration *in vacuo* gave a slightly yellow solid which on washing with ethanol and filtering gave **50** in 77.0% yield (0.30 g), mp 109–110°. Analytical sample from ethanol had: mp 109–110°; ir 1600 and 1590 (both weak), 1081 (strong), 1010 (medium), 1000 (medium), and 823 cm^{-1} (strong); uv max 224 sh (26,400) and 236 mμ sh (25,200); nmr δ (60 MHz) 2.10 and 2.38 (two s, 6, CH_3) and 6.80–7.35 (cp, 10 Ar); mass M^+ 326.

Anal. Calcd for $C_{20}H_{16}Cl_2$: C, 73.40; H, 4.93. Found: C, 73.26; H, 4.86.

1,2-Bis(4-chlorophenyl)-1-(1-pyrrolidinyl)ethylene (49) was obtained in 85.0% yield (0.85 g) by treating a stirred mixture of **42** (1.0 g, 0.003 mol) and 10 ml of benzene with a solution of 0.5 g (0.007 mol) of pyrrolidine and 5 ml of benzene in one portion at 25° (reaction was evidenced by a rise in temperature to 35° and the formation of a yellow solution); solution heated at 65° for 2 hr, concentrated *in vacuo*, and triturated with cold absolute ethanol (0°) to afford a material (mp 119–120°) identical in all respects with the one isolated above.

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Registry No.—**5**, 5162-99-2; **6a**, 13937-88-7; **6b**, 2403-57-8; **6c**, 6908-73-2; **7a**, 52919-52-5; **7b**, 52919-53-6; **7c**, 52919-54-7; **8**, 1125-99-1; **9**, 52919-55-8; **10**, 52919-56-9; **11**, 52919-57-0; **12**, 52919-58-1; **13**, 14092-11-6; **14**, 942-81-4; **15**, 52919-59-2; **16**, 52919-60-5; **17**, 52919-61-6; **18**, 52964-36-0; **19**, 52919-62-7; **20**, 52919-63-8; **21**, 52919-64-9; **22**, 52919-65-0; **23**, 52919-66-1; **24**, 52919-67-2; **25**, 25769-05-5; **26**, 52919-68-3; **27**, 52919-69-4; **28**, 52919-70-7; **29**, 7007-34-3; **30**, 25579-44-6; **31**, 52919-71-8; **32**, 31554-37-7; **33**, 52919-72-9; **34**, 52919-73-0; **35**, 21403-95-2; **36**, 52919-74-1; **37**, 52919-75-2; **38**, 20238-06-6; **39**, 52949-88-9; **40**, 16675-55-1; **41**, 52919-76-3; **41** methiodide, 52919-77-4; **42**, 30739-21-0; **43b**, 52919-78-5; **44**, 52919-79-6; **45**, 52919-80-9; **46**, 52919-81-0; **47**, 52919-82-1; **48**, 52929-83-2; **49**, 52919-84-3; **50**, 52919-85-4; cyclodecanone, 1502-06-3; pyrrolidine, 123-75-1; cycloundecanone, 878-13-7; α,α'-sulfonylbis(α-bromo-4-chloro)toluene, 52964-37-1; bis(4-chlorophenyl)acetylene, 1820-42-4.

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(32) The ultraviolet spectrum is abnormal due to the lack of coplanarity which is evident on inspection of a Dreiding model.