

# The Preparation of Caged Keto Sulfides. An Analysis of S-C<sub>CO</sub> Interaction in Certain Tetrahydro-1,4-thiapyrones Possessing Rigid Boat Conformations<sup>1,2</sup>

Leo A. Paquette<sup>3</sup> and Lawrence D. Wise

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received July 17, 1967

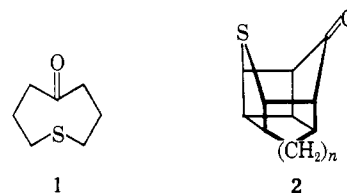
**Abstract:** In order to gain further insight into the structural requirements of S-C<sub>CO</sub> transannular interactions, certain caged keto sulfides were prepared. Diels-Alder addition of 1 equiv of a 1,3-diene to 1,4-thiapyrone 1,1-dioxide, followed by photochemical cyclization of the adduct, resulted in the formation of caged keto sulfones in good yield. Lithium aluminum hydride reduction of these substances gave variable results; in two instances, *endo*-hydroxy sulfides were obtained. Mild oxidation of the alcohol group (DMSO-DCC) led to the formation of ketones without concomitant oxidation of the divalent sulfur to sulfoxide and sulfone. The mass spectra of the various caged keto sulfones and keto sulfides are recorded. Dipole moment, infrared, and ultraviolet studies of the latter compounds have been undertaken. The electric moments denote that the rigid keto sulfides exist in pronounced boat conformations. The infrared data have been found to be anomalous; the conclusion is reached that it does not constitute a technique sufficiently sensitive to provide reliable quantitative data on the extent of S-C<sub>CO</sub> electronic interactions. In contrast, excitation of these molecules with ultraviolet light in solvents of differing polarity provides an excellent method for distinguishing interacted from noninteracted sulfur carbonyl combinations.

Past studies on the capability of properly constructed medium-sized heterocyclic ketones to display interaction between donor (heteroatom) and acceptor (carbonyl) functional groups have led to a partial understanding of the steric, electronic, and structural requirements for this phenomenon. Although considerable information concerning the limitations of N-C<sub>CO</sub> interaction is available,<sup>4</sup> the detection of S-C<sub>CO</sub> interaction is limited to a single representative example<sup>5</sup> and transannular participation of the O-C<sub>CO</sub> variety has been observed only recently.<sup>6,7</sup>

One of the more challenging questions in this area concerns the accurate determination of the heteroatom-carbonyl interaction as a function of the interatomic distance between the two centers involved. Access to quantitative data of this type seemed desirable for several reasons: (i) to achieve a more fundamental understanding of the nature of such electronic interaction, (ii) to provide a more accurate guide by which prediction of related interactions could be made, and (iii) to permit, in retrospect, conclusions regarding the flexibility of systems which display such phenomena at least under certain conditions.

The conformational mobility associated with mesocyclic<sup>8</sup> ring systems obviously does not allow a reasonable assessment of this significant factor. For example, the previous examination of the dipole moment and spectra of **1** has led to an interpretation in terms of a mixture of interacted and noninteracted conformations under the various conditions employed. The present

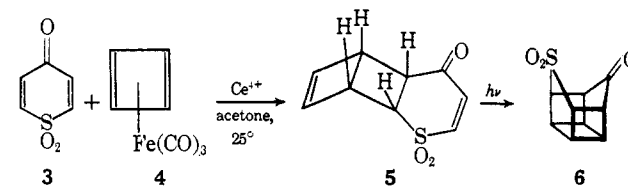
study was designed to examine the nature of S-C<sub>CO</sub> interactions in a series of tetrahydro-1,4-thiapyrones constructed in such a manner that the six-membered thiaketones were locked into their respective boat conformations, *i.e.*, **2**. Further, because of the capability



to alter systematically the value of *n* in the carbon superstructure of **2**, the sulfur atom and the carbonyl group can be rigidly held at differing atomic distances, the magnitudes of which can be estimated with some degree of accuracy.

## Synthetic Considerations

**Formation of the Cage Keto Sulfones.** The synthesis of the desired keto sulfides began with the addition of 1 equiv of an appropriate conjugated cyclic diene to 1,4-thiapyrone 1,1-dioxide (**3**). Thus, exposure of **3** to an acetone solution of cyclobutadiene, generated *in situ* from its iron tricarbonyl complex (**4**) according to the method of Pettit, *et al.*,<sup>9</sup> led in near-quantitative yield to a pale yellow crystalline solid (**5**). The nmr spectrum of **5** displays absorptions at  $\delta$  7.38 (multiplet, area 1), 6.32 (complex multiplet, area 3), and *ca.* 3.90



(9) (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965); (b) G. F. Burt and R. Pettit, *Chem. Commun.*, 517 (1965); (c) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 623 (1966); (d) J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1328 (1966); (e) J. C. Barborak and R. Pettit, *ibid.*, **89**, 3080 (1967).

(1) Unsaturated Heterocyclic Systems. XXXIV. For paper XXXIII in this series, refer to L. A. Paquette, T. J. Barton, and E. B. Whipple, *J. Am. Chem. Soc.*, **89**, 5481 (1967).

(2) Supported in large part by the National Science Foundation, Grant GP5977, to whom we are grateful for financial support.

(3) Fellow of the Alfred P. Sloan Foundation, 1965-1967.

(4) For a review of this subject, see N. J. Leonard, *Record Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **17**, 243 (1956).

(5) N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Am. Chem. Soc.*, **82**, 4075 (1960).

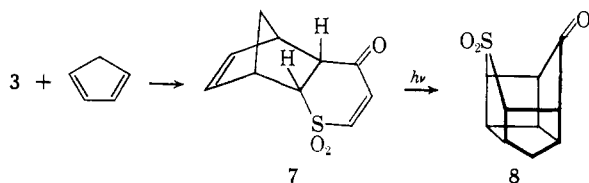
(6) L. A. Paquette and R. W. Begland, *ibid.*, **87**, 3784 (1965).

(7) R. W. Begland and P. C. Storm, submitted for publication.

(8) This term is employed herein to designate "medium size."<sup>6</sup>

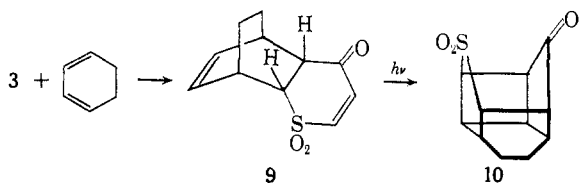
(broad complex multiplet, area 4). Infrared and ultraviolet spectra are likewise in agreement with this structural assignment (see Experimental Section). The *endo* configuration of **5** was assigned on the basis of earlier precedent<sup>9c,d</sup> and because of its photochemical behavior. When a solution of **5** in ethyl acetate was irradiated in Pyrex with a medium-pressure mercury arc for 3 hr, the colorless photoisomer **6** was obtained in 40% yield. The structure **6** follows from its infrared (saturated carbonyl band at 1750 cm<sup>-1</sup>), ultraviolet (end absorption only), nmr (no absorption due to olefinic protons), and mass spectra (see below).

Treatment of **3** with 1 equiv of cyclopentadiene in benzene solution at 60° for 30 min led in quantitative yield to *endo* adduct **7**.<sup>10</sup> Irradiation of **7** under near-identical conditions was found to give rise to photoisomer **8**.<sup>11</sup> Convincing proof of the structure of **8** was



derived not only from the compatible spectral data, but also from the observation that **8** could be sublimed readily despite the fact that its melting point was well above 300°. Such physical properties are generally associated with cage-type molecules.

In similar fashion, the interaction of 1,3-cyclohexadiene with **3** gave **9** which in turn was converted photochemically into the desired **10**. This keto sulfone also



displayed high crystallinity, ease of sublimation, and only complex high-field nmr absorption.

**The Question of Sulfone Reduction.** To date, the most well-established method for the conversion of sulfones to sulfides involves the use of lithium aluminum hydride. However, this process is by no means general; whereas four-<sup>12</sup> and five-membered ring sulfones have been found to be readily reducible under most conditions, acyclic sulfones and larger cyclic sulfones are generally known to be resistant to such reduction.<sup>13</sup> The strain operative on the sulfonyl group therefore appears to be a factor involved in its propensity for hydride reduction.

Examination of molecular models of keto sulfones **6**, **8**, and **10** reveals that, as the number of methylene units in the bridge (*i.e.*, the value of *n* in structure **2** (as

(10) Of some relevance to this stereochemical assignment is the fact that the *endo* nature of the cyclopentadiene-1,4-benzoquinone adduct has recently been confirmed: D. F. O'Brien and J. W. Gates, Jr., *J. Org. Chem.*, **30**, 2593 (1965).

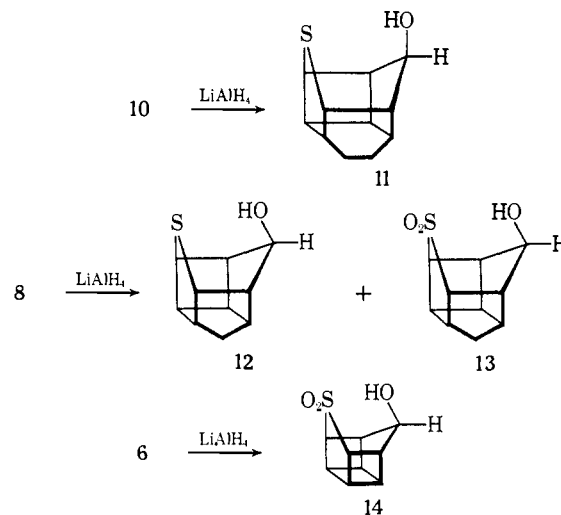
(11) Similar photochemical cyclizations have previously been reported in the case of certain 1,4-benzoquinone Diels-Alder adducts; see, for example, R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind. (London)*, 1003 (1958); D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 5202 (1964).

(12) See, for example, L. A. Paquette, *J. Org. Chem.*, **30**, 629 (1965).

(13) F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, **73**, 2251 (1951).

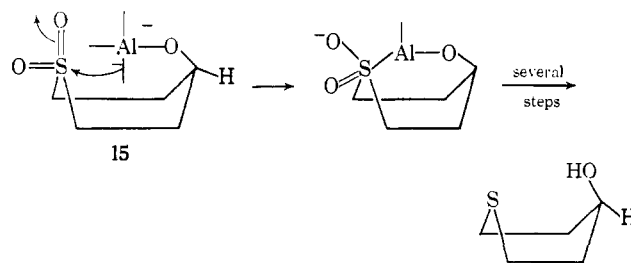
the sulfone)) increases from 0 in the case of **6** to 2 in the case of **10**, a significant enhancement in nonbonded interactions at the sulfonyl group is engendered because of greater steric compression between the 1,4 substituents in the heterocyclic ring of **10**. Extrapolation of this line of reasoning regarding the ease of reduction of sulfone groups would therefore suggest that the reactivity order of these keto sulfones toward lithium aluminum hydride should be **10** > **8** > **6** despite the fact that the size of the hetero ring remains constant (six-membered) throughout the series (Scheme I).

Scheme I



Such conclusions have been borne out and a very clear-cut pattern of reactivity has emerged. Whereas **10** is reduced cleanly to hydroxy sulfide **11** in 70% yield, the cage keto sulfone **8** has been invariably observed to give rise to a mixture of **12** and **13** under an assortment of reaction parameters. That **13** may be the precursor of **12** is suggested by the fact that it can in turn be converted into this hydroxy sulfide. A striking feature of this reduction process was the fact that **6** could not be reduced beyond the hydroxy sulfone stage (*i.e.*, **14**), even under strenuous conditions.

Although the demonstrated behavior of the keto sulfones can be explained in terms of strain effects, we would like to call attention to a possible alternate mechanism of reduction. Thus, it is also conceivable that the sulfone group may be subject to preliminary intramolecular chemical attack of the type outlined.



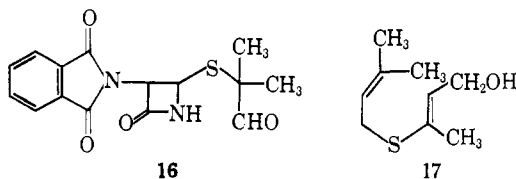
Once the stable nature of the sulfone moiety is altered by interaction with the aluminum atom in this fashion, rapid conversion to the divalent sulfur species can be expected. Because the centers undergoing the reaction depicted in **15** are significantly more compressed in **10** than in **6** (in fact, interaction may be precluded in this latter example because of the distances involved), ease

of sulfone reduction is experienced in the first case. However, since data on the mechanism by which hydride converts sulfones into sulfides is entirely lacking, this rationale must be considered speculative until new evidence is brought to bear on the question.

The stereochemistry of the hydroxyl group in the resulting alcohols need now be considered. *A priori*, it would seem most plausible that the principle of steric approach control<sup>14</sup> would be operative in these examples. That attack of hydride reagent did occur from the less hindered side of the carbonyl group to provide *endo* axial alcohols was ascertained on the basis of physical evidence. First, it was noted early that hydroxy sulfides **11** and **12** were eluted readily from a variety of chromatographic substrates. In fact, both substances could be eluted with hexane although for preparative purposes it was found more expeditious to admix approximately 20% ether (by volume) to the solvent system. Such behavior is congruent with molecules containing a hindered hydroxyl group as the only polar functionality. Secondly, and perhaps more significantly, compounds **11–14** were seen to display strong intramolecular hydrogen bonding (see Experimental Section). The participation of a sulfide function in  $>S \cdots HO-$  bonding is believed to be very sensitive to structural factors<sup>15</sup> and as a result has been found only in a relatively small number of situations. However, in each of the present examples this phenomenon is quite apparent and is a further reflection of the proximity of the interacting functions.<sup>16</sup>

In order to guarantee that an unexpected rearrangement had not occurred during the reduction process, hydroxy sulfone **13** was oxidized with chromic acid. The derived ketone **8** was isolated in quantitative yield.

**The Problem of Selective Oxidation.** Our inability to convert **14** into its hydroxy sulfide precluded further studies with this particular cage structure. With regard to the remaining two systems, however, the final aspect of the synthetic scheme was to consist in the selective oxidation of the hydroxyl group in the presence of the highly susceptible sulfide linkage. To our knowledge, two reagents had previously been utilized for similar purposes. Sheehan and Brandt<sup>17</sup> reported that aldehyde **16** could be oxidized with Jones' reagent in purified acetone to the corresponding carboxylic acid in 83% yield without converting the thioether to the sulfoxide or sulfone. Also, the thia alcohol **17** has been transformed by Huisman and co-workers<sup>18</sup>



(14) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956); W. G. Dauben, E. J. Blanz, Jr., J. Jin, and R. A. Micheli, *ibid.*, **78**, 3752 (1956).

(15) M. P. Mertes, *J. Org. Chem.*, **26**, 5236 (1961); H. H. Szmant and J. J. Rigau, *ibid.*, **31**, 2288 (1966); and pertinent references cited in these papers.

(16) Worthy of note is the fact that the  $\epsilon_{\max}$  of the hydroxyl absorbance band in hydroxy sulfides **11** and **12** was approximately one-half the intensity of the same band in the hydroxy sulfones **13** and **14**.

(17) J. C. Sheehan and K. G. Brandt, *J. Am. Chem. Soc.*, **87**, 5468 (1965).

(18) J. L. Baas, A. Davies-Fidder, and H. O. Huisman, *Tetrahedron*, **22**, 259 (1966).

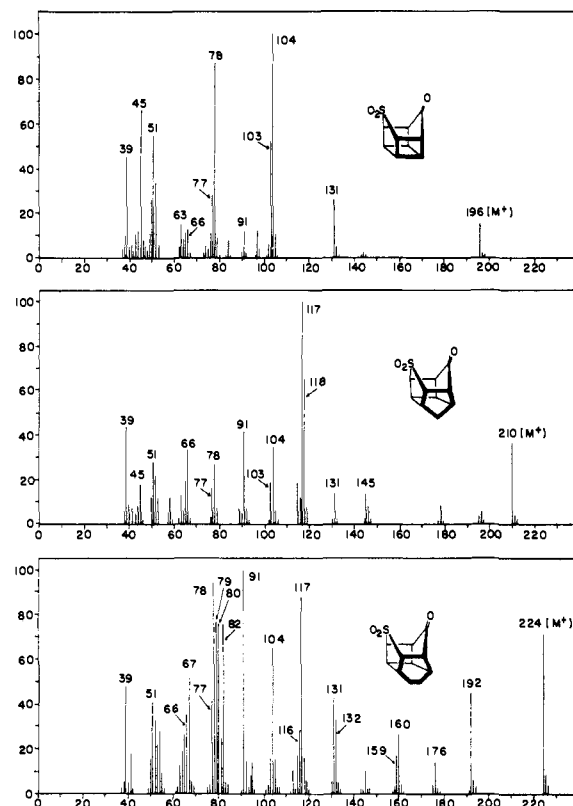
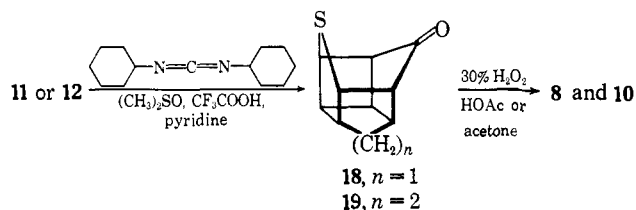


Figure 1. Mass spectra of keto sulfones **6**, **8**, and **10**.

into the related thiocarboxaldehyde in 70% yield with the chromium trioxide–pyridine complex.

In our hands, exposure of **11** or **12** to these, and several similar, oxidizing agents did not afford the desired keto sulfides. In contrast, **18** and **19** were obtained in excellent yield when the alcohols were subjected to the mild (room temperature, essentially neutral conditions



using pyridinium trifluoroacetate as the proton source) yet efficient oxidizing capability of the dicyclohexylcarbodiimide–dimethyl sulfoxide reagent.<sup>19</sup> The spectral characteristics of the two ketones are discussed later in this paper. For the purpose of final structural confirmation, **18** and **19** were individually oxidized with 2 moles of hydrogen peroxide in acetone or acetic acid to keto sulfones **8** and **10**, respectively.

**Mass Spectra.** Owing to the considerable recent interest which has been accorded caged hydrocarbons in general and because of the inherent novelty of these sulfur-containing caged molecules, it was deemed of interest to examine the major fragmentation patterns of these compounds. The mass spectrum of **6** (Figure 1) appears to arise predominantly from initial expulsion of both carbon monoxide and sulfur dioxide. The

(19) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661 (1965); K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 3670 (1965).

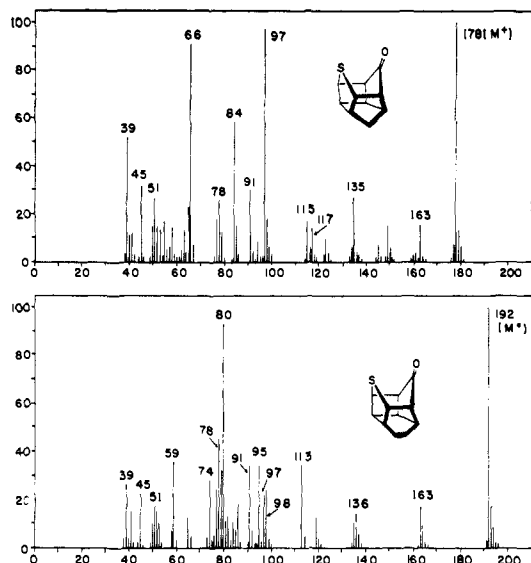


Figure 2. Mass spectra of keto sulfides **18** and **19**.

resulting base peak ( $m/e$  104,  $C_8H_8^+$ ) undergoes further fragmentation in a manner duplicating almost exactly that reported for cubane.<sup>20</sup> The facile loss of CO represents a further example of the preferred reaction pathway for strained cyclic ketones when under electron impact.<sup>21</sup> In view of this fact, the concomitant  $SO_2$  expulsion is not unexpected, especially in view of the driving force provided by the relief of strain.

The fragmentation schemes of **8** and **10** (Figure 1) generally parallel the pattern displayed by keto sulfone **6**. Several slight deviations are noted in the case of **10**, however, presumably because of the increase in carbon content. It is also interesting to note that a gradual increase in the relative intensities of the respective molecular ions is encountered in the order  $6 < 8 < 10$  (Figure 1).

The predominant mode of fragmentation of pentacyclodecane derivatives is known to be rupture of the cage into two similar fragments.<sup>21b</sup> Such is not the case with the caged keto sulfones. A further measure of support for this conclusion has been derived from the mass spectra of 1,4-thiapyrone and its tetrahydro derivative which reflect very few, if any, similarities to those of the title compounds.<sup>22</sup>

Because it is now well established that aliphatic sulfides follow a fragmentation route wherein carbon-heteroatom bond rupture with charge retention on the heteroatom is very pronounced,<sup>23</sup> the mass spectra of **18** and **19** were expected to differ considerably from their sulfone counterparts and this was found to be the situation (Figure 2). For example, the most abundant species in the case of **18** was the molecular ion (100%). An  $M - 15$  species is present in the spectrum, which ion very likely is the source of the  $m/e$  135 peak [ $C_8H_7S^+$  ( $163 - CO$ ) and/or  $C_7H_5OS^+$  ( $163 - C_2H_4$ )]. In addition

to the fragments which result from cleavage and rearrangement of the hydrocarbon moiety, there is seen an intense (97%)  $C_8H_5S^+$  peak ( $m/e$  97). Because this ion and the  $C_8H_6S^+$  (18%) species are characteristic of the fragmentation pattern of 2- and 3-methylthiophenes,<sup>24</sup> it appears that the divalent sulfur atom controls the cleavage of **18** in a manner which leads to an aromatic thiophene.

A noticeable change is seen in the spectrum of **19**. Although the most abundant species remains the molecular ion, the influence of the sulfur atom is apparently not exerted in a parallel direction. Thus, the appearance of an intense peak for the  $C_8H_8^+$  ion (93%) suggests that in this instance considerable fragmentation along the horizontal plane is occurring.

Obviously, before a thorough understanding of the ability of heteroatoms to control and direct the mass spectrometric fragmentation of strained cage molecules is available, a great variety of related structures require examination.

## Discussion

As a prelude to the spectral studies on thia ketones **18** and **19**, attention was initially directed to an estimation of the interatomic distances between the sulfur and carbonyl groups in these two molecules. Although values of this type are obtainable from various molecular models, the data were not considered overly reliable because the compounded bond compressions present in the caged molecules are not duplicated in the models. Alternatively, the solution dipole moments of **18** and **19** were considered a more accurate measure of the angles between the dipole vectors. Calculations for 1-thia-cyclooctan-5-one (**1**) have demonstrated that as the ring system becomes increasingly folded the magnitude of the electric moment increases noticeably.<sup>5</sup>

The observed dipole moments of **18** and **19** are 4.086 and 4.231 D., respectively.<sup>25</sup> These values, larger than those of any similar molecules, are not surprising in view of the rigidity imparted to the boat conformation by the cage structure in each case. The most significant fact to be culled from these measurements, however, is that the heterocyclic ring of **19** is more folded than that of **18**. This conclusion is entirely consistent with the unique chemical and physical characteristics of the series derived from 1,3-cyclohexadiene.

**Infrared Studies.** The solvent dependence of the infrared carbonyl maxima of **18**, **19**, and four related model compounds has been measured. The experimental results, determined with 2.5% solutions, are listed in Table I. The nature of the medium was varied from nonpolar (cyclohexane and  $CCl_4$ ) to moderately hydrogen bonding ( $CH_2Cl_2$ ,  $CHCl_3$ ). As expected, frequency shifts to lower wave numbers were observed with increasing solvent polarity, but to varying extents in each case. Visual inspection of the carbonyl infrared bands of the four model compounds indicated no significant alteration in the symmetry and shape of the peaks. The carbonyl maxima for caged ketones **18** and **19** are illustrated in Figure 3; although the carbonyl band of **18** similarly exhibits relatively sharp

(24) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of the Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp 232, 233.

(25) We are gratefully indebted to Professor Norman L. Allinger for the dipole moment determinations.


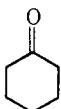
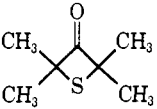
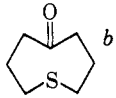
(20) B. D. Kybett, S. Carroll, P. Natalis, D. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, **88**, 626 (1966).

(21) (a) N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D. Angelo, *ibid.*, **87**, 4097 (1965); (b) W. L. Dilling and M. L. Dilling, *Tetrahedron*, **21**, 1225 (1967).

(22) L. D. Wise, unpublished observations.

(23) (a) S. Sample and C. Djerassi, *J. Am. Chem. Soc.*, **88**, 1937 (1966); (b) A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *ibid.*, **87**, 2920 (1965); (c) D. C. DeJongh, *ibid.*, **86**, 3149, 4027 (1964); (d) E. J. Levy and W. A. Stahl, *Anal. Chem.*, **33**, 707 (1961).

Table I. Ketone Carbonyl Infrared Spectral Data<sup>a</sup>

Compound	Values of $\nu_{\max}$ and $10^3(\Delta\nu/\nu)$				
	C <sub>6</sub> H <sub>12</sub>	CCl <sub>4</sub>	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
<b>18</b>	1759	1754	1745	1745	1742
		0.284	0.796	0.796	0.966
<b>19</b>	1759	1756	1752	1752	1751
		0.171	0.398	0.398	0.455
				1743	1739
				0.909	1.14
	1718.5	1716	1713	1712.5	1712
		0.145	0.320	0.349	0.379
	1724	1719	1709	1708	1705
		0.290	0.870	0.928	1.10
	1772	1768.5	1766	1765	1765
		0.198	0.339	0.395	0.395
	1713	1704	1701	1698	1695
		0.525	0.701	0.876	1.05
		1690	1691	1689	1686
			1.30	1.42	1.60

<sup>a</sup> Values of C=O stretching maxima (in cm<sup>-1</sup>) observed with 2.5% solutions. <sup>b</sup>  $\nu$  values are taken from ref 5; however, the  $\Delta\nu/\nu$  values have been revised to conform strictly to the methodology devised by L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

symmetry in all solvents, the behavior of the carbonyl band of **19** differs markedly. Thus, this band is gradually altered with increasing polarity and is finally split (reproducibly) into a pronounced doublet in chloroform solution. The unprecedented nature of this change may find its origin in strong S-C=O interaction, although the possible intervention of Fermi resonance cannot be ruled out.

the relative frequency shifts ( $\Delta\nu/\nu$ ) for a given compound in various solvents are plotted against the relative quantities of a standard substance, straight lines generally result. In the present instance, cyclohexanone was employed as the standard and  $\Delta\nu$  was measured from the values of  $\nu$  in cyclohexane since gas-phase measurements were not available.<sup>27</sup> The results are plotted in

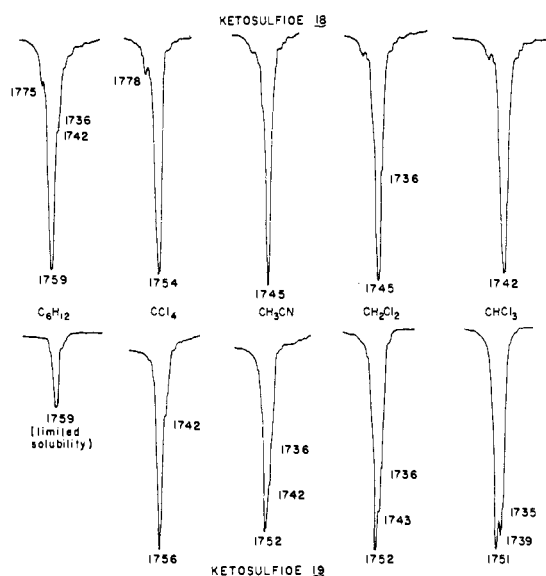


Figure 3. Solvent dependence of infrared carbonyl maxima of **18** and **19** (2.5% solutions).

In order to elaborate further upon the differing sensitivities of the carbonyl stretching vibrations of the six ketones to solvent effects, the data of Table I were analyzed according to the method of Bellamy.<sup>26</sup> When

(26) L. J. Bellamy, H. E. Hallam, and R. L. Williams, *Trans. Faraday Soc.*, **54**, 1120 (1958); L. J. Bellamy and R. L. Williams, *ibid.*, **55**, 14 (1959).

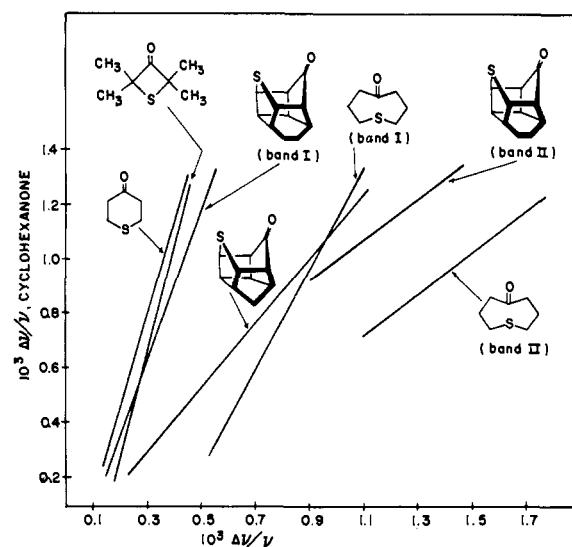
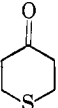
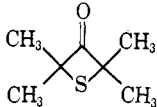
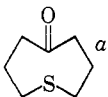


Figure 4. Analysis of infrared data according to the method of Bellamy. Slope of  $(\Delta\nu/\nu)$  vs.  $(\Delta\nu/\nu)$ (cyclohexanone) for: tetrahydro-1,4-thiapyrone, 3.40; 2,2,4,4-tetramethyl-3-thietanone, 3.80; 1-thiacyclooctan-5-one (band I), 1.84; (band II), 0.754; cage keto sulfide **18**, 1.18; cage keto sulfide **19** (band I), 2.78; (band II), 0.750.

Figure 4. Straight lines were obtained in all cases, indicating normal response of each carbonyl group to environmental changes. The points for caged keto

(27) This modification has seen previous utility.<sup>5</sup> As before, this change is not expected to effect the validity of the treatment.

Table II. Ultraviolet Spectra of Various Thiaketones

Compound	Solvent <sup>b</sup>	Z	$\lambda_{\max}$ ( $\epsilon$ ), m $\mu$	$E_T$ , kcal/mole
<b>18</b>	Cyclohexane	60.1	238 (233)	120.14
	Acetonitrile	71.3	240 (204)	119.12
	Methanol	83.6	248 (194)	115.28
	Ethanol	79.6	245 (178)	116.69
	Water	94.6	252 (170)	113.45
<b>19</b>	Cyclohexane	60.1	239 (453)	119.62
	Acetonitrile	71.3	243 (333)	117.65
	Methanol	83.6	245 (306)	116.69
	Ethanol	79.6	246 (286)	116.22
	70% ethanol-water	86.4	248 (290)	115.28
	Cyclohexane	60.1	233 (513)	122.70
	Acetonitrile	71.3	233 (505)	122.70
	Methanol	83.6	230 (246)	124.30
	Ethanol	79.6	234 (363)	122.18
	Cyclohexane	60.1	253 (314)	113.00
	Acetonitrile	71.3	254 (264)	112.56
	Methanol	83.6	254 (267)	112.56
	Ethanol	79.6	255 (273)	112.12
	70% ethanol-water	86.4	257 (244)	111.25
	Cyclohexane	60.1	226 (2445)	126.51
	Acetonitrile	71.3	229 (2690)	124.85
	Methanol	83.6	236 (variable)	121.14
	Ethanol	79.6	238 (2565)	120.14
	Water	94.6	242 (2775)	118.13

<sup>a</sup> Data culled from ref 5. <sup>b</sup> The values in methanol were seen to be somewhat variable presumably caused by small changes in water content when the different solutions were exposed to the atmosphere.

sulfide **19** and 1-thiacyclooctan-5-one have been divided into two groups (called bands I and II, respectively) both of which form linear segments. The slopes of the lines for tetrahydro-1,4-thiapyrone, 2,2,4,4-tetramethyl-3-thietanone, 1-thiacyclooctan-5-one (band I), and **19** (band I) are seen to be roughly of the same order of magnitude. In contrast, the observed shifts for **18** and the second bands of **19** and 1-thiacyclooctan-5-one are relatively larger. Since the slopes of the lines obtained presumably represent the varying degrees of polarization of the C=O bond in the various solutes relative to cyclo-

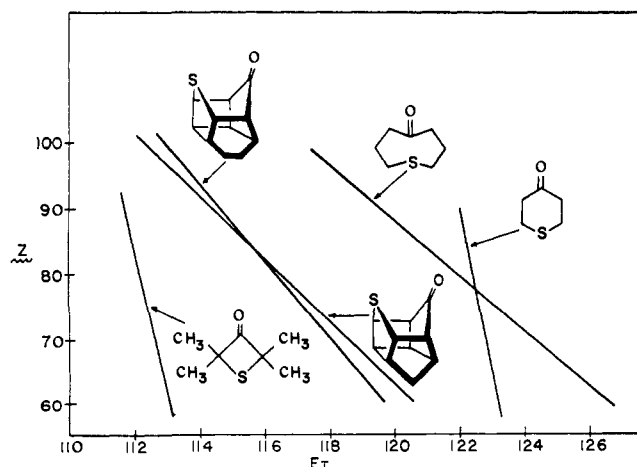


Figure 5. Electronic transition energies for various thiaketones in solvents of different Z values.

hexanone, the values appear to be anomalous in the case of **18** and **19**. On the basis of previous argumentation, keto sulfide **19** was expected to possess the greatest extent of polar S-C<sub>CO</sub> interaction, a conclusion reached on the basis of proximity effects operative in the

pronounced boat conformation. The above results demonstrate that alternative factors which could contribute to polarized molecular deformation modes need also to be considered. Thus, it is well recognized that the position and shape of carbonyl stretching vibrations depend on several factors such as electronic distribution about the C=O bond, mass effects of substituents, conjugation, strain effects, dipole-dipole interactions, and vibrational coupling. Especially significant in the present examples is the fact that in complex molecules such as **18** and **19** the band position may truly be due to cumulative effects of several of these factors. Unfortunately, techniques for accurately evaluating these additional parameters are presently not available. We have therefore concluded that infrared studies of the type herein described do not constitute a technique sufficiently sensitive to provide reliable quantitative data on the extent of S-C<sub>CO</sub> electronic interactions.

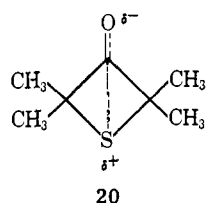
**Ultraviolet Studies.** The ultraviolet absorption maxima of **18**, **19**, tetrahydro-1,4-thiapyrone, and 2,2,4,4-tetramethyl-3-thietanone in solvents of varying polarity are summarized in Table II. Values for the previously studied<sup>5</sup> 1-thiacyclooctan-5-one have also been included for purposes of comparison. The transition energies were calculated on the basis of the Kosower Z parameter, a spectroscopic solvent polarity index,<sup>28</sup> by means of the relationship

$$E_T \text{ (kcal/mole)} = \frac{2.859 \times 10^4}{m\mu}$$

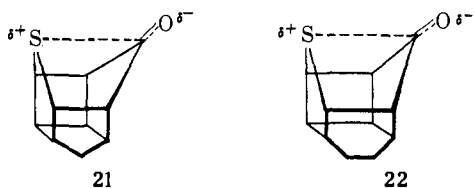
Plots of  $E_T$  vs. Z are given in Figure 5. On a qualitative basis alone, the slopes of the lines for **18**, **19**, and 1-thiacyclooctan-5-one are seen to reflect a marked dependence on solvent polarity, a feature not shared by tetrahydro-1,4-thiapyrone or the 3-thietanone derivative. The red shift observed in the first three examples is in

(28) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253, 3261, 3267 (1958).

agreement with the concept that greater dipolar character obtains in the excited state than in the ground state and suggests effective electron transfer from divalent sulfur to the proximate carbonyl group in each instance. Such interaction appears absent or at best extremely weak in the remaining two cases; such data point to the existence in the tetrahydro-1,4-thiapyrone system of an intrinsic difference directly associated with the preferred conformation of this heterocyclic ring system. The inability of the 3-thietanone system to manifest transannular interaction is not surprising in view of the exceptional strain incorporated in the extreme canonical form **20**.



Thus, these spectral parameters suggest the intervention of interacted forms **21** and **22** for **18** and **19**, respectively. It should be noted that **21** and **22** are structures which encompass high degrees of strain; in this regard, we have not yet found it possible to prepare crystalline perchlorate salts corresponding in structure to **21** and **22**.



The factor(s) responsible for the deviation in the  $\epsilon_{\max}$  values of 1-thiacyclooctan-5-one relative to **18** and **19** are not entirely obvious; however, the apparent discrepancy in extinction coefficient may be attributable to a dependence on the geometry of S-C=O orbital interaction permissible in the various systems. On the one hand, the mesocyclic ketone with its conformational mobility is in a position to achieve the most favorable orbital interaction available, whereas the molecular constraint in **18** and **19** severely restricts any opportunity for appreciable bond movement. Additional supporting evidence for this theory is lacking, however, and the suggestion must be considered tentative at this time.

### Experimental Section<sup>29</sup>

**Cyclobutadieneiron Tricarbonyl.**<sup>30</sup> To a mechanically stirred solution of 41.5 g (0.34 mole) of *cis*-1,2-dichlorocyclobutene<sup>31</sup> in 500 ml of hexane was added in portions 275 g (0.76 mole) of diiron enneacarbonyl over an 8-hr period. During the course of the reaction, the temperature of the mixture was maintained at

(29) Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with Beckman IR-9 and Perkin-Elmer Model 237 spectrometers fitted with sodium chloride prisms. Ultraviolet spectra were recorded with a Cary Model 14 spectrometer. The nmr spectra were determined with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing energy of 70 eV.

(30) The authors are grateful to Professor R. Pettit for supplying them with details of his procedure prior to publication.

(31) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marica, G. Mateescu, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 372 (1964).

approximately 50°. After 3 additional hr of stirring at 50°, the completion of the reaction was confirmed by the absence of the dichlorocyclobutene in the reaction mixture (vpc analysis). The resulting mixture was filtered and the solvent was evaporated *in vacuo*. Distillation of the dark residue under reduced pressure gave a fore-run which was mainly iron pentacarbonyl. The product was collected as a yellow-green oil, 33.4 g (51% yield), bp 45–47° (3 mm), which solidified in the refrigerator.

**7-Thiatricyclo[4.4.0.0<sup>2,5</sup>]deca-3,8-dien-10-one 7,7-Dioxide (5).** To a solution of 2.00 g (13.9 mmoles) of 1,4-thiapyrone-1,1-dioxide<sup>32</sup> and 2.92 g (15.3 mmoles) of cyclobutadieneiron tricarbonyl in 500 ml of acetone at room temperature was added over a 4-min period 30 g of powdered ceric ammonium nitrate. Vigorous stirring was allowed to continue 1 additional min after which the reaction mixture was poured into 500 ml of salt solution. The solution was well extracted with ether and the combined organic extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded 2.70 g (98%) of yellow crystals, mp 160–165°. Several recrystallizations of this solid from benzene-acetone-hexane gave pure **5**: mp 171–172°;  $\nu_{\max}^{\text{CHCl}_3}$  1680 (>C=O), 1630 (>C=C<), 1300, and 1120 cm<sup>-1</sup> (>SO<sub>2</sub>);  $\lambda_{\max}^{\text{EtOH}}$  220 m $\mu$  ( $\epsilon$  7750).

*Anal.* Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>S: C, 55.09; H, 4.11; S, 16.34. Found: C, 55.05; H, 4.16; S, 16.24.

**7-Thiapentacyclo[4.4.0.0<sup>2,5</sup>.0<sup>3,9</sup>.0<sup>4,8</sup>]decan-10-one 7,7-Dioxide (6).** A solution of 0.50 g (2.55 mmoles) of **5** in 250 ml of ethyl acetate was irradiated in Pyrex with a Hanovia 200-w medium-pressure arc for 3 hr. Evaporation of the solvent afforded an oily residue which was taken up in hot Methyl Cellosolve and cooled. There was obtained 200 mg (40%) of white needles, mp > 300°. Three recrystallizations from this solvent gave an analytical sample of **6**: mp > 300°;  $\nu_{\max}^{\text{CHCl}_3}$  1750 (>C=O), 1310, and 1120 cm<sup>-1</sup> (>SO<sub>2</sub>); the ultraviolet spectrum showed only end absorption.

*Anal.* Calcd for C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>S: C, 55.09; H, 4.11; S, 16.34. Found: C, 55.04; H, 4.11; S, 16.06.

**endo-7-Thiapentacyclo[4.4.0.0<sup>2,5</sup>.0<sup>3,9</sup>.0<sup>4,8</sup>]decan-10-ol 7,7-Dioxide (14).** A solution of 2.00 g (10.2 mmoles) of **6** in 25 ml of tetrahydrofuran was treated with 2.00 g (52.6 mmoles) of lithium aluminum hydride. The rapidly stirred mixture was refluxed under anhydrous conditions for 18 hr, after which time the mixture was cooled and worked up under the usual alkaline conditions (see **8**). Evaporation of the solvent *in vacuo* afforded 1.45 g (88.0%) of white solid, mp > 300°. Several recrystallizations from chloroform-ether gave pure **14**: mp > 300°;  $\nu_{\max}^{\text{CHCl}_3}$  3460 (-OH), 1320, and 1120 cm<sup>-1</sup> (>SO<sub>2</sub>).

*Anal.* Calcd for C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>S: C, 54.53; H, 5.08; S, 16.18. Found: C, 54.53; H, 5.07; S, 16.03.

Attempts to reduce the remaining sulfone function by prolonged exposure of **6** to lithium aluminum hydride at elevated temperatures led solely to the successful recovery of **14**.

**4a,5,8,8a-Tetrahydro-5,8-methano-4H-1-benzothioipyran-4-one 1,1-Dioxide (7).** A solution of 10.00 g (0.0694 mole) of 1,4-thiapyrone 1,1-dioxide and 4.60 g (0.0694 mole) of freshly distilled cyclopentadiene in 500 ml of benzene was warmed to 60° for 0.5 hr in a sealed glass pressure bottle. The mixture was cooled and the solvent was evaporated *in vacuo* to give 14.60 g (100%) of **7** as white needles, mp 154–157°. Three recrystallizations of this material from benzene-hexane afforded an analytical sample: mp 158–160°;  $\nu_{\max}^{\text{CHCl}_3}$  1670 (>C=O), 1610 (>C=C<), 1320, and 1130 cm<sup>-1</sup> (>SO<sub>2</sub>);  $\lambda_{\max}^{\text{EtOH}}$  218 m $\mu$  ( $\epsilon$  6190);  $\delta_{\text{TMS}}^{\text{CDCl}_3}$  ca. 1.55 (multiplet, 2 H, protons), 3.41–4.20 (complex pattern, 4 H, methine protons), 6.05–7.05 (multiplets, vinyl protons).

*Anal.* Calcd for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>S: C, 57.12; H, 4.79; S, 15.25. Found: C, 57.27; H, 4.89; S, 15.31.

**Octahydro-1,3,5-ethanlylidene-2-thiacyclobuta[cd]pentalen-7-one 2,2-Dioxide (8).** A solution of 10.0 g (0.047 mole) of **7** in 300 ml of ethyl acetate was irradiated in quartz optics with a Hanovia 200-w medium-pressure mercury arc for 6 hr. Concentration of the solvent afforded a brownish solid which was filtered and dried to give 8.50 g (85.0%) of a white powder, mp > 300°. The product was sublimed and the sublimate was recrystallized from Methyl Cellosolve to analytical purity: mp > 300°;  $\nu_{\max}^{\text{CHCl}_3}$  1760 (>C=O), 1320 and 1140 cm<sup>-1</sup> (>SO<sub>2</sub>); the ultraviolet spectrum displayed only end absorption.

*Anal.* Calcd for C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>S: C, 57.12; H, 4.79; S, 15.25. Found: C, 56.92; H, 4.78; S, 15.22.

**Lithium Aluminum Hydride Reduction of 8.** A solution of 4.00 g (19.0 mmoles) of **8** and 4.00 g (0.105 mole) of lithium aluminum

(32) E. Fehnel and M. Cormack, *J. Am. Chem. Soc.*, **70**, 1813 (1948).

hydride in 125 ml of purified dioxane was refluxed with stirring for 24 hr. The mixture was worked up by the careful addition of 4 ml of water, 4 ml of 30% sodium hydroxide solution, and 12 ml of water. The resulting solid was filtered and washed well with methylene chloride. The filtrate and washings were combined and evaporated to dryness. The resulting off-white semisolid was chromatographed on silica gel. Elution with hexane-ether (5:1) afforded 1.65 g (48.1%) of *endo*-octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*ca*]pentalen-7-ol (**12**), mp 240–250°. Two recrystallizations of this material from hexane followed by sublimation yielded an analytical sample: mp 267–268°;  $\nu_{\max}^{\text{CHCl}_3}$  3420  $\text{cm}^{-1}$  (–OH).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_2\text{S}$ : C, 66.62; H, 6.71; S, 17.79. Found: C, 66.64; H, 6.65; S, 17.65.

Elution with ether-hexane (1:1) yielded 850 mg (21.1%) of *endo*-octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*ca*]pentalen-7-ol 2,2-dioxide (**13**), mp >300°. Two recrystallizations of this material from benzene-hexane and subsequent triple sublimation afforded an analytical sample: mp >320°;  $\nu_{\max}^{\text{CHCl}_3}$  3420 (–OH), 1330, and 1130  $\text{cm}^{-1}$  (> $\text{SO}_2$ ).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{S}$ : C, 56.58; H, 5.70; S, 15.12. Found: C, 56.47; H, 5.74; S, 15.06.

**Lithium Aluminum Hydride Reduction of 13.** A solution of 8.00 g (0.0376 mole) of **13** in 250 ml of anhydrous tetrahydrofuran was treated with 6.00 g (0.158 mole) of lithium aluminum hydride. The suspension was stirred under reflux for 3 days after which time it was cooled and worked up under the usual alkaline conditions. Chromatography of the oily residue on silica gel (elution with hexane-ether 5:1) afforded 2.75 g (40.6%) of **12**, mp 264–267°, identical with the previous sample by all the usual criteria. Elution with ether led to the recovery of 2.55 g (31.9%) of starting material, mp >300°.

**Chromic Acid Oxidation of 13.** To a solution of 600 mg (2.83 mmoles) of **13** in 6 ml of methylene chloride and 4 ml of water cooled to 0° was added dropwise a solution of 600 mg (6.00 mmoles) of chromium trioxide in 1.6 ml of concentrated sulfuric acid and 4.5 ml of water over a 30-min period. After the resulting mixture was stirred for an additional 3.5 hr at 0°, the layers were separated and the aqueous phase was extracted repeatedly with methylene chloride. The combined organic extracts were washed with dilute sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The solvent was evaporated *in vacuo* to give 600 mg (100%) of **8**: mp >300°;  $\nu_{\max}^{\text{CHCl}_3}$  1760  $\text{cm}^{-1}$  (C=O). This sample proved to be identical with an authentic sample of **8** in all respects.

**Octahydro-1,3,5-ethanylylidene-2-thiacyclobuta[*ca*]pentalen-7-one (18).** To a solution of 400 mg (2.22 mmoles) of **12** in 5 ml of benzene and 5 ml of dimethyl sulfoxide were added 1.85 g (9.0 mmoles) of *N,N*-dicyclohexylcarbodiimide, 0.24 ml of pyridine, and 0.12 ml of trifluoroacetic acid. The mixture was stirred at room temperature for 48 hr after which 20 ml of benzene was added. The resulting suspension was filtered and the filtrate was washed well with water to remove the dimethyl sulfoxide. The organic solution was dried and evaporated. Chromatography of the residue on Florisil (elution with hexane-ether 5:1) afforded 396 mg (100%) of white crystals, mp 247–250°. Several recrystallizations from hexane afforded pure **18**: mp 248–250°;  $\nu_{\max}^{\text{CHCl}_3}$  1750  $\text{cm}^{-1}$  (C=O).

*Anal.* Calcd for  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{S}$ : C, 67.38; H, 5.65; S, 17.99. Found: C, 67.18; H, 5.74; S, 18.25.

**Oxidation of 18.** To a solution of 100 mg (0.562 mmole) of **18** in 3 ml of glacial acetic acid was added 122 mg (1.12 mmoles) of

30% hydrogen peroxide. The mixture was allowed to stir overnight at room temperature during which time a white solid was deposited. Filtration of the precipitate afforded 57 mg (51.4%) of **8**, mp >300°, identical in all respects with an authentic sample.

**4a,5,8,8a-Tetrahydro-5,8-ethano-4H-1-benzothiopyran-4-one 1,1-Dioxide (9).** A solution of 4.00 g (0.0278 mole) of 1,4-thiapyrone 1,1-dioxide and 2.24 g (0.0280 mole) of 1,3-cyclohexadiene in 50 ml of benzene was heated at 60° for 24 hr in a sealed glass pressure bottle. The mixture was concentrated under reduced pressure and the precipitate was filtered and dried to give 5.95 g (95.4%) of white solid: mp 111–113°;  $\nu_{\max}^{\text{CHCl}_3}$  1625 (>C=O), 1600 (>C=C<), 1320, 1140, and 1120  $\text{cm}^{-1}$  (> $\text{SO}_2$ ). Attempts to purify this adduct by recrystallization led to the formation of the retro Diels-Alder products. Therefore, crude **9** was used without further purification.

**Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*ca*][2]benzothio-phen-7-one 1,1-Dioxide (10).** A solution of 2.00 g (8.9 mmoles) of **9** in 300 ml of ethyl acetate was irradiated in quartz optics with a Hanovia 200-w medium-pressure mercury arc for 6 hr. Concentration of the solvent afforded 1.85 g (92.5%) of brownish solid. Sublimation of this material, followed by three recrystallizations from Methyl Cellosolve, afforded pure **10** as long colorless needles: mp 328–330°;  $\nu_{\max}^{\text{CHCl}_3}$  1750 (>C=O), 1310, 1140, and 1110  $\text{cm}^{-1}$  (> $\text{SO}_2$ ); the ultraviolet spectrum displayed only end absorption.

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_4\text{S}$ : C, 58.90; H, 5.40; S, 14.30. Found: C, 58.75; H, 5.40; S, 14.37.

**Lithium Aluminum Hydride Reduction of 10.** A stirred mixture of 500 mg (2.60 mmoles) of **10** and 500 mg (13.1 mmoles) of lithium aluminum hydride in 25 ml of anhydrous tetrahydrofuran was refluxed with stirring for 48 hr. The mixture was cooled and treated dropwise in turn with 0.5 ml of water, 0.5 ml of 20% sodium hydroxide solution, and 1.5 ml of water. The resulting white solid was filtered and washed well with methylene chloride. The combined filtrates were evaporated to dryness and the resulting oily semisolid was chromatographed on Florisil. Elution with hexane-ether (5:1) led to the isolation of 400 mg (79.3%) of white solid, mp 203–207°. Pure **11** was obtained by further recrystallization from hexane: mp 207–208°;  $\nu_{\max}^{\text{CHCl}_3}$  3360  $\text{cm}^{-1}$  (–OH).

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}$ : C, 68.00; H, 7.26; S, 16.50. Found: C, 67.93; H, 7.25; S, 16.18.

**Octahydro-6,2,5-ethanylylidene-2H-cyclobuta[*ca*][2]benzothio-phen-7-one (19).** To a solution of 800 mg (4.10 mmoles) of **11** in 5 ml of benzene and 5 ml of dimethyl sulfoxide were added 1.85 g (9.0 mmoles) of *N,N*-dicyclohexylcarbodiimide, 0.12 ml of trifluoroacetic acid, and 0.25 ml of pyridine. The mixture was stirred at room temperature for 3 days after which time 20 ml of benzene was added. The suspension was filtered and the filtrate was washed well with water to remove the dimethyl sulfoxide. Drying and evaporation of the organic phase afforded a noncrystalline residue which was chromatographed on silica gel. Elution with hexane-ether (3:1) afforded 500 mg (63%) of white solid, mp 258–259°. Several recrystallizations from benzene-hexane gave analytically pure **19**: mp 258–259°;  $\nu_{\max}^{\text{CHCl}_3}$  1750  $\text{cm}^{-1}$  (>C=O).

*Anal.* Calcd for  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{S}$ : C, 68.71; H, 6.29; S, 16.68. Found: C, 68.84; H, 6.29; S, 16.58.

**Oxidation of 19.** A solution of 200 mg (1.04 mmoles) of **19** in 10 ml of acetone was treated with 240 mg (2.08 mmoles) of 30% hydrogen peroxide and refluxed overnight. The resulting precipitate was filtered and dried to give 130 mg (56.0%) of **10**, mp >300°, identical in all respects with an authentic sample.