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Carbon-13 Nuclear Magnetic Resonance Studies of Sulfur Heterocycles. Evidence for Intramolecular 1,3 Electronic Interaction in 3,3-Disubstituted 2*H*-Tetrahydrothiapyran-1-*N*-*p*-tosylsulfimides[1]

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Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra of several mono- and disubstituted 2*H*-tetrahydrothiapyrans and dithianes have been recorded and assigned. The compounds studied provide a series which is amenable to correlation by the additivity of substituent effects in ^{13}C NMR spectroscopy. The $\Delta\delta$'s between calculated and observed ^{13}C NMR shifts provided a sensitive probe for substituent–substituent interactions in compounds **6–8, 13,** and **14.** The ^{13}C NMR data obtained suggest an intramolecular 1,3 electronic interaction in 3,3-dimethyl- and 3,3-dialkoxy-1-*N*-*p*-tosylthianes and dithianes (**6–8**) and **13** and **14.** Specifically, the data suggest a weak coulombic attractive interaction between the molecular orbitals of the sulfur with the formal positive charge S^1 and the electrons of the C^2–C^3 bond.

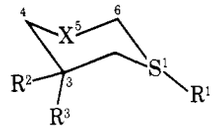
Proton nuclear magnetic resonance (^1H NMR) studies of 2*H*-tetrahydrothiapyran (thiane) and dithiane derivatives have centered primarily on conformational analyses.[2] Recent reports of ^{13}C NMR studies of substituted six-membered-ring hydrocarbons and heterocycles have shown the power of ^{13}C NMR in conformational analysis.[2i,j,3] In many cases, ^{13}C NMR data related to intramolecular 1,3 steric and/or electronic interactions which lead to conformational preferences for six-membered rings have been obtained.[2m] However, definitive elucidation and differentiation of steric and/or electronic interactions based on ^{13}C NMR data have not been possible generally.[4]

Since the chemistry of sulfur compounds is important in many biological and photographic processes, the elucidation of intramolecular interactions and their relation to the physical and chemical properties of thiane derivatives are of interest. Presently, we report a ^{13}C NMR study which provides *direct* ^{13}C NMR spectroscopic evidence for a transannular 1,3 *electronic* interaction in 3,3-disubstituted thiane derivatives.

Results and Discussion

The compounds studied are thiane (**X = CH_2**) derivatives **1–8** and dithiane derivatives (**X = S**) **9–14.**[2,13]

Data for the thiane ring carbon atoms of compounds **1–14** are shown in Table I. Assignments for **1–14** are based on line



X = CH_2		X = S
1	≡ R^1 = electron pair; R^2, R^3 = H	≡ **9**
2	≡ R^1 = *N*-*p*-tosyl; R^2, R^3 = H	≡ **10**
3	≡ R^1 = electron pair; R^2, R^3 = C^7H_3, C^8H_3	≡ **11**
4	≡ R^1 = electron pair; R^2, R^3 = OC^7H_3, OC^8H_3	
5	≡ R^1 = electron pair; R^2, R^3 = $-O-C^7H_2C^8H_2-O-$ (cyclic ketal)	≡ **12**
6	≡ R^1 = *N*-*p*-tosyl; R^2, R^3 = C^7H_3, C^8H_3	≡ **13**
7	≡ R^1 = *N*-*p*-tosyl; R^2, R^3 = OC^7H_3, OC^8H_3	
8	≡ R^1 = *N*-*p*-tosyl; R^2, R^3 = $-O-C^7H_2C^8H_2-O-$ (cyclic ketal)	≡ **14**

intensity, ^{13}C–H coupling constants and the chemical shifts of model compounds. The ^{13}C NMR spectrum of **2** was recorded at −90 °C in CH_2Cl_2.[2c] The high-field signals in the spectrum (−90 °C) of compound **2** have been assigned to those of the axial 1-*N*-*p*-tosyl isomer.[2c] From the relative area of the ^{13}C NMR signals of C^2 in **2** at 41.7 ppm (axial) and 47.9 (equatorial), the axial/equatorial isomer ratio has been determined to be 1.44. This correlates well with the ratio of 1.50 determined from ^1H NMR by Lambert et al.[2c]

Calculated shifts for the ring carbon atoms of compounds

Table I. ^{13}C NMR Chemical Shifts for the Ring Carbon Atoms of Thiane and Dithiane Derivatives[a]

Registry no.	Compd	Chemical shifts[b] C^2	C^3	C^4	C^5	C^6	C^7(a)	C^8(e)
16131-51-0	**1**[h]	29.1	27.8	26.5	27.8	29.1		
13553-73-6	**2** (a)[c]	41.7	16.2	23.2	16.2	41.7		
	2 (e)[c]	47.9	23.7	23.5	23.7	47.9		
57259-83-3	**3**[h]	41.1	29.7	39.3	23.8	28.7	28.3[e]	28.3[e]
63449-32-1	**4**	33.2	96.7	32.6	25.6	28.0	47.5[e]	47.5[e]
177-13-9	**5**	35.5	105.3	35.1	27.1	27.5	64.6[e]	64.6[e]
31815-14-2	**6**[d]	58.2	33.5	36.4	19.3	47.1	25.1[f]	31.4[g]
63449-33-2	**7**[d]	52.2	98.4	30.4	18.5	46.8	47.9[f]	48.2[g]
63449-34-3	**8**[d]	53.7	105.6	33.4	21.4	46.2	65.1[f]	65.2[g]
505-23-7	**9**[h]	28.9	26.3	28.9		30.9		
58484-97-2	**10**	46.4	26.2	26.5		46.5		
60311-39-9	**11**[h]	41.9	26.8	41.9		31.5	27.5[e]	27.5[e]
177-14-0	**12**	36.4	100.4	36.3		30.4	65.1[e]	65.1[e]
63449-35-4	**13**[d]	60.0	37.7	40.1		48.6	24.7[f]	30.8[g]
63449-36-5	**14**[d]	53.2	105.5	33.6		45.1	65.1[e]	65.1[e]

[a] ^{13}C NMR data were recorded at 35 ± 0.1 °C in a 10-mm tube with a Varian CFT-20 spectrometer at 15% (w/v) in Me_2SO-d_6. [b] Chemical shifts are reported as δ in parts per million downfield (+) of tetramethylsilane. [c] These isomers were frozen out in CH_2Cl_2 solution 5% (w/v) at −90 °C in an 8-mm tube (see ref 2c). [d] These compounds have the 1-*N*-*p*-tosyl group in the equatorial position. [e] Averaged signal at 28 °C in $CDCl_3$. [f] Axial group based on shielding effect. [g] This δ is assigned to the equatorial group based on deshielding effect. [h] These data have been reported previously by various authors (see ref 2).

6–8, 13, and **14** were obtained by the additivity of substituents as shown in eq 1–3,[3] where δ is the chemical shift in parts per million (Table I) of the C^n carbon atom of the numbered compound (**1–14**) and a = axial; e = equatorial. This method has been shown to have general success in predicting the ^{13}C NMR shifts of unknown compounds.[5] The $\Delta\delta$ values obtained from these calculated and observed shifts are shown in Table II. The additivity of substituent effects has been used in several instances to predict effectively the chemical shifts of saturated heterocycles.[3] Even with appropriate models, as the number of polar substituents in a molecule is increased, the accuracy of additivity relationships can drop dramatically depending upon substituent–substituent interactions in the unknown compound studied. With appropriate structural models, therefore, large $\Delta\delta$ values between predicted and observed shifts can be interpreted in terms of structural changes which originate directly from substitutent interactions that cannot occur in the models.

Thiane axial:

$$\delta^{C^n}\mathbf{6}(a)(\mathbf{7}(a) \text{ or } \mathbf{8}(a)) = \delta^{C^n}\mathbf{2}(a) - \delta^{C^n}\mathbf{1} + \delta^{C^n}\mathbf{3}(\mathbf{4} \text{ or } \mathbf{5}) \quad (1)$$

Thiane equatorial:

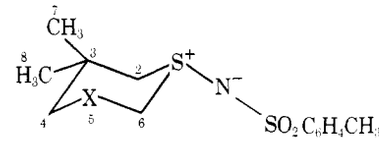
$$\delta^{C^n}\mathbf{6}(e)(\mathbf{7}(e) \text{ or } \mathbf{8}(e)) = \delta^{C^n}\mathbf{2}(e) - \delta^{C^n}\mathbf{1} + \delta^{C^n}\mathbf{3}(\mathbf{4} \text{ or } \mathbf{5}) \quad (2)$$

Dithiane equatorial:

$$\delta^{C^n}\mathbf{13} \text{ (or } \mathbf{14}) = \delta^{C^n}\mathbf{10} - \delta^{C^n}\mathbf{9} + \delta^{C^n}\mathbf{11} \text{ (or } \mathbf{12}) \quad (3)$$

The small average deviations between the predicted and observed ^{13}C NMR shifts for *equatorial* and the large positive average deviations for the *axial* 1-*N*-*p*-tosyl conformation clearly show that this substituent is *equatorial* in thiane compounds **6–8**.[2] The 1-*N*-*p*-tosyl group is known to prefer the *equatorial* conformation in thiane derivatives **3** and **6** and dithiane derivatives **10, 13,** and **14**.[2b,21,3d]

The ^{13}C and ^1H NMR signals of the methyl carbons C^7 and C^8 and of the methyl protons in compounds **3** and **11**, respectively, occur as averaged signals at 28 °C in $CDCl_3$ (see Table I and Experimental Section). Under identical conditions, these methyl carbons and protons in 3,3-dimethyl compounds **6** and **13** are observed as two separate signals. The numerical averages of these two signals for 1-*N*-*p*-tosyl derivatives **6** and **13** are identical to the averaged NMR signals of the methyl groups observed for **3** and **11**, respectively. This

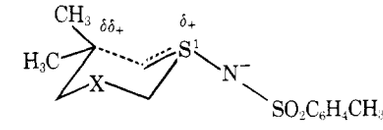


6, X = CH_2; **13**, X = S

shows that there is no observable steric or electronic perturbation of the methyl groups in **6** and **13** resulting from the presence of the 1-*N*-*p*-tosyl moiety. The resolution of separate signals for the two methyl groups in compounds **6** and **13** is related only, therefore, to the predominance of one conformer. Furthermore, that the NMR spectra of compounds **7–8, 13** and **14** are temperature independent is evidence for the exclusive existence of compounds **6** and **13** as the equatorial 1-*N*-*p*-tosyl conformers.

The ^{13}C NMR signals of the exocyclic C^7 and C^8 methoxy and methylene carbons in the thiane compounds **4** and **5** are very weakly shielded ($\Delta\delta^{max}$ <1.0 ppm) relative to those same carbons in 1-*N*-*p*-tosyl derivatives **7** and **8** (Table I). For dithiane **12** the ^{13}C NMR signals of the exocyclic methylene groups are identical to those observed for 1-*N*-*p*-tosyl compound **14** (Table I). The ^1H NMR signals for the pendant groups of dithiane compounds **11–14** are also insensitive to any 1,3 interactions in these compounds.

With the knowledge that the conformation of the 1-*N*-*p*-tosyl group in **6**[21], **7, 8, 13**,[21] and **14** is equatorial, further information related to intramolecular interactions in these molecules can be gleaned from the relative magnitudes of the deviations shown in the *equatorial* columns of Table II. It is evident that large $\Delta\delta$ values are observed for the C^3 and C^5 carbon atoms of **7**, and for the C^3 carbon atoms of **13, 14, 8,** and **6.**



6, X = CH_2; **13**, X = S

Considerable evidence has been reported previously indicating that dithiane compounds analogous to **9–14** exist predominately in the chair conformation.[2b] $\Delta\delta$ values could possibly reflect a difference in conformation of the compounds **6–8, 13,** and **14** from some or all of their model compounds.

Table II. Deviations ($\Delta\delta$ and $\Delta(\Delta\delta)$ values) between Predicted and Observed C^{13} NMR Shifts for Thiane and Dithiane Derivatives[a]

Carbon atom	Compound 6		13		7		14		8	
	$\Delta\delta a^b$	$\Delta\delta e^c$	$\Delta\delta e$	$\Delta(\Delta\delta)e^d$	$\Delta\delta a^b$	$\Delta\delta e^c$	$\Delta\delta e$	$\Delta(\Delta\delta)e$	$\Delta\delta a^b$	$\Delta\delta e$
C^2	*+4.6*	**−1.7**[e]	**+0.6**	**−2.3**	*+6.4*	**+0.2**	**−0.7**	**−0.9**	*+5.6*	**−0.6**
C^3	*+14.8*	**+7.9**	**+12.0**	**+4.1**	*+13.3*	**+5.8**	**+5.2**	**−0.6**	*+11.9*	**+4.4**
C^4	*+0.4*	**+0.1**	**+0.6**	**+0.5**	*+0.9*	**+0.8**	**−0.3**	**−1.1**	*+1.6*	**+1.2**
C^5	*+7.1*	**+0.6**			*+4.5*	**−3.0**			*+5.7*	**−1.6**
C^6	*+5.8*	**−0.4**	**+1.5**	**+1.9**	*+5.9*	**0.0**	**−0.9**	**−0.9**	*+6.5*	**+0.7**

[a] $\Delta\delta = \delta c^n$ observed $- \delta c^n$ calculated; δc^n values calculated were determined from eq 1, 2, or 3. $\Delta\delta$ = ppm and positive (+) number indicates that the observed shift is to lower field of that calculated. For the numbers shown in this table, only those larger than ±2.0 ppm are considered significant. Although no actual estimate of the error for these numbers is available, it is evident that any attempt to interpret $\Delta\delta$ values < ±2.0 in terms of molecular structure would be tenuous and could lead to specious conclusions. [b] See eq 1. [c] See eq 2. [d] $\Delta(\Delta\delta) = \Delta\delta e^n$ dithiane $- \Delta\delta e^n$ thiane. [e] Numbers shown in boldface type are those assigned to the compound. Those in italics are based on the hypothetical axial 1-*N*-*p*-tosyl isomer and are not real (see text).

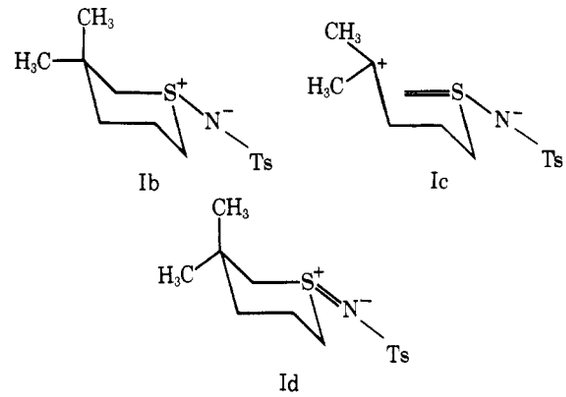
However, the substantial $\Delta\delta$ values for compounds **6, 8, 13,** and **14** are localized at C^3, and those for compound **7** at C^3 and C^5. This indicates that the $\Delta\delta$ values in Table II are very probably related to a specific interaction of the substituents in the chair conformation and not to a change in overall conformation (i.e., chair → boat). The lack of any substantial differences in the ^1H and ^{13}C NMR shifts of the substituent carbons C^7 and C^8 (see Table I) of compounds **6–8, 13,** and **14** relative to the models is a further indication of a localized interaction, since any overall conformational changes would be expected to result in changes in the NMR shifts of these atoms.

Since the 1-*N*-*p*-tosyl group is equatorial in compounds **6** and **13,** any interactions leading to large $\Delta\delta$ values for these compounds would be expected to be predominately electronic and not steric. A steric effect at C^3 would be expected to affect the ^{13}C and ^1H NMR shifts of thianes **6** and **13** to give more shielded signals and hence larger negative $\Delta\delta$ values (in the order $\Delta\delta^{C^7} > \Delta\delta^{C^3} > \Delta\delta^{C^5} > \Delta\delta^{C^2}$) than those found in Table II for the C^7, C^5, and C^2 carbon atoms. Alternatively, the severe 1,3 steric repulsion of the substituents in all of the compounds **6–8, 13,** and **14** with the axial 1-*N*-*p*-tosyl group is implied by the exclusive predominance of the equatorial 1-*N*-*p*-tosyl isomer.

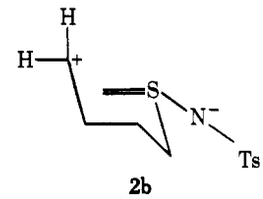
It is evident that the quaternary nature of C^3 in **6** and **13** is important to the interpretation of the substantially deshielded $\Delta\delta$ values of C^3, since the ^{13}C NMR shifts of C^3 and C^5 in the model thiane derivative **2** *equatorial* are shielded by the introduction of the equatorial 1-*N*-*p*-tosyl group. This shielding effect produced by the introduction of the 1-*N*-*p*-tosyl group occurs also in compound **6** at C^5. This is shown by the δ calculated for C^5 using **2** *equatorial* as a model. *The absence of any $\Delta\delta$ for C^5 demonstrates that no interaction or absence of interaction originates at C^5 in* **6** *that does or does not occur in the models.*

It is known that tertiary carbenium ions are thermodynamically much more stable than primary ions.[6] The positively charged carbon in tertiary carbenium ions is deshielded by about 180 ppm relative to the corresponding neutral species, while the α-carbons are deshielded by 20–30 ppm.[6] The enhanced deshielding of C^3 in compounds **6** and **13** of +7.9 and +12.0 ppm, respectively, therefore suggests a weak coulombic attractive interaction between the molecular orbitals of the formal positively charged sulfur S^1 and the electrons of the C^2–C^3 bond. Based on analogy with the chemical-shift data for carbon atoms α to a carbenium carbon,[5] if such an interaction gives rise to a deshielding effect at C^3 of 8–12 ppm the deshielding effect on C^2, C^4, C^7, and C^8 should be negligible. This is in accordance with our findings.

If we consider the three structures of **6** and **13,** *viz.*, Ib–d, we can predict the relative weight that each has in the molecular orbitals of I in light of the NMR data. The magnitude



of the deshielding effect at C^3 is consistent with only a small but measurable contribution from structure Ic. As the weight of the uncharged sulfimide canonical form Id in the molecular orbitals of **6** and **13** increases, the potential for the proposed interaction of S^1 and the C^2–C^3 bond decreases. Alternatively, when the much lower energy of Ic as compared to 2b is con-



2b

sidered, weak hyperconjugative interaction of the C^2–C^3 bond appears to be a plausible explanation for the measurable large positive $\Delta\delta$ values of C^3 in compounds **6** and **13.**

In compounds **7, 8,** and **14,** an additional heteroatom, oxygen, is attached to the C^3 carbon atom. It is evident from Table II that in addition to the deshielding ($\Delta\delta^{C^3}$ = +5.8 ppm) of C^3 in **7** there is a smaller shielding ($\Delta\delta^{C^5}$ = −3.0 ppm) of C^5. The shielding ($\Delta\delta^{C^5}$ = −1.6 ppm) of C^5 in **8,** where the oxygen atoms are held rigidly away from the thiane ring, is substantially diminished.

Based on similar arguments to those presented above for the 3,3-dimethyl compounds **6** and **13,** significant deshielding of C^3 in compounds **7, 8,** and **14** therefore suggests very weak hyperconjugation of the C^2–C^3 bond. That this overall deshielding of C^3 is smaller for compounds **7, 8,** and **14** than that observed for **6** or **13** is consistent with the much lower deshielding of alkoxycarbenium ion carbons relative to their alkyl carbenium ion analogues.

The $\Delta(\Delta\delta)$ values reported in Table II are the $\Delta\delta$ values between the thiane and dithiane derivatives. They reflect the effect of sulfur S^5 upon the chemical shifts of the carbon atoms of the corresponding dithiane.

Table II shows a substantial $\Delta(\Delta\delta)$ of +4.1 ppm for C^3 in thiane **6** relative to dithiane **13**. No significant $\Delta(\Delta\delta)$ values are observed for compounds **8** and **14**. Thus, a significant localized perturbation is produced at C^3 in compound **13** by the sulfur in the 5 position (S^5). This additional deshielding of C^3 in **13** relative to **6** may indicate that S^5 enhances the small changes in bonding at C^3 as discussed above. For compounds **8** and **13**, where oxygen is directly bonded to C^3 and can directly participate in the interactions of C^2–C^3 with S^1, the introduction of S^5 has no marked effect, as would be expected.

Experimental Section

Samples of thiane (**1**) and 1,3-dithiane (**9**) were obtained from Aldrich Chemical Co.; the corresponding *N*-*p*-tosyl sulfimide derivatives **2** and **10** were prepared by published procedures.[2c,3c] Carbon-13 magnetic resonance spectra were obtained on a Varian Associates CFT-20 spectrometer; proton NMR spectra were obtained on a Varian T-60. Reported melting and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

3,3-Dimethylthiapyran-*N*-*p*-tosylsulfimide[8] (6). (A) 2,2-Dimethylpentane-1,5-diol.[9a,b] To a solution (70% in benzene) of Vitride (260 mL, 935 mmol) in 150 mL of sieve-dried tetrahydrofuran (THF) contained in a dried 3-L three-necked, round-bottomed flask equipped with an air-driven stirrer, reflux condenser, nitrogen inlet, and dropping funnel, a solution of 2,2-dimethylglutaric acid[11] (25 g, 156 mmol) in 120 mL of THF was added dropwise over 0.5 h. An exothermic reaction commenced immediately, and a thick precipitate began to separate which then dissolved as the reaction mixture spontaneously attained a slow reflux. Following completion of addition, the reaction mixture was heated for 2 h at reflux and then allowed to cool and to stand at room temperature overnight. The nearly colorless solution was chilled to 0 °C in an ice–salt water bath, and a chilled (5 °C) solution of 125 mL of concentrated sulfuric acid in 400 mL of water was added *very* slowly to control the strongly exothermic reaction. When the addition was complete, 500 mL of ether was added and vigorous stirring was maintained for 2 h. The organic phase was separated and dried over magnesium sulfate, and the solvents were removed in vacuo to give a pale amber syrup (33 g) which was distilled under reduced pressure to give the title compound (13.3 g, 65%), bp (~16 mm) 144–145 °C [lit.[10] bp (~16 mm) 140–142 °C].

(B) **2,2-Dimethyl-1,5-pentyl di-*p*-toluenesulfonate.** A stirred solution of 2,2-dimethylpentane-1,5-diol (3.6 g, 27.2 mmol) in 35 mL of dry pyridine was chilled to 0 °C in an ice–salt water bath, and *p*-toluenesulfonyl chloride (11.4 g, 60 mmol) was added in portions over 20 min so that the internal temperature did not exceed 5 °C. The reaction mixture was stirred at 0–5 °C for 4 h and then stored in a refrigerator overnight. The white crystalline mass was poured onto excess ice, collected, washed thoroughly with cold 5% hydrochloric acid, and air-dried to give a homogeneous creamy white solid, mp 71–73 °C (10.8 g, 90%), which on crystallization from ethanol-2B (1 g/30 mL) afforded white needles, mp 78–79 °C. Anal. Calcd for $C_{21}H_{28}O_6S_2$: C, 57.30; H, 6.37. Found: C, 57.63; H, 6.52.

(C) A mixture of 2,2-dimethyl-1,5-pentyl di-*p*-toluenesulfonate (16.8 g, 38.2 mmol) and freshly ground sodium sulfide nonahydrate (9.2 g, 38.2 mmol) was taken up in 80 mL of *N*,*N*-dimethylformamide at room temperature. A transiently green-beige suspension resulted, and the temperature rose spontaneously ~6 °C. The reaction mixture was heated slowly to reflux. A rich emerald-green solution was attained at 85 °C which slowly changed to amber as reflux was approached. After an additional 4.5 h at reflux, the reaction mixture was cooled and poured into 500 mL of cold water to give a milky suspension from which some amorphous solid separated on standing overnight. The mixture was filtered by suction, and the filtrate was extracted with 3 × 150 mL of ether. The combined organic extracts were washed with 3 × 100 mL of water, dried over magnesium sulfate, and evaporated in vacuo to give a pale yellow syrup (3.6 g, 72%).[12] the crude 3,3-dimethylthiapyran (**3**) (ca. 25 mmol) was taken up in 100 mL of methanol and filtered to remove a small amount of insoluble material. The methanol solution was treated with Chloramine T trihydrate (8.45, 30 mmol) in small portions over 0.5 h. The reaction mixture was allowed to stir for 1 h; the solvent was removed in vacuo, and the residue was taken up in chloroform. Insoluble material was removed by filtration; the filtrate was dried over magnesium sulfate and evaporated to give an amber syrup. Clusters of white needles formed on standing overnight which were triturated with acetone and collected to give the title compound **6** (3.3 g, ca. 44%), mp 175–177 °C (lit.[8] 173–174 °C).

5,5-Dimethyl-1,3-dithiane-1-*N*-*p*-tosylsulfimide (13). (A) 5,5-Dimethyl-1,3-dithiane (11). To a solution of boron trifluoride etherate (5 mL), acetic acid (10 mL), and chloroform (150 mL) in a dry 500-mL three-necked, round-bottomed flask fitted with mechanical stirrer, coil condenser, and nonpressure equalizing dropping funnel, 2,2-dimethyl-1,3-propanedithiol[13] (5.7 g, 42 mmol) and dimethoxymethane (3.5 g, 46 mmol) were added according to the method of Corey and Seebach.[14] Workup following the described procedure afforded crude 5,5-dimethyl-1,3-dithiane as a pale yellow liquid (6.1 g, 98%) which was homogeneous by TLC (silica gel/benzene): NMR ($CDCl_3$) δ 1.15 (s, 6 H), 2.86 (s, 4 H), 3.58 (s, 2 H).

(B) To a stirred methanolic solution (25 mL) of 5,5-dimethyl-1,3-dithiane (1 g, 6.75 mmol), Chloramine T trihydrate (2.3 g, 8.1 mmol) was added in portions over 5 min. A white solid began to separate after 5 min. The reaction mixture was stirred for 1.5 h at ambient temperatures and then poured into 75 mL of water and stirred for 5 min. The homogeneous solid sulfimide **13** was collected and dried (1.9 g, 89%), mp 187–190 °C. An analytical sample was obtained by crystallization from ethanol-2B (1 g/15 mL), mp 188–190 °C. Anal. Calcd for $C_{13}H_{19}NO_2S_3$: C, 49.16; H, 5.99; N, 4.42. Found: C, 49.24; H, 5.94; N, 4.38.

1,4-Dioxaspiro[4.5]-7-thiadecane-7-*N*-*p*-tosylsulfimide (8). A suspension of sodium hydride (57% in mineral oil, 14.5 g, 346 mmol) in 200 mL of dry THF was heated to 65 °C, and 3-thiaheptanedioic acid diethyl ester[15] was added dropwise over 1 h according to the method of Lüttringhaus and Prinzbach.[16] Workup following the described procedure afforded a mixture of the crude thiapyran keto esters (22.3 g, 72%) which on treatment with 10% sulfuric acid for 6 h at reflux, extraction with ether, washing with 5% sodium bicarbonate solution, and drying over magnesium sulfate gave an orange oil (9.8 g, 71%). Purified 3-oxothiapyran (5.2 g, 38%) was obtained by distillation under reduced pressure, bp (~25 mm) 113–115 °C [lit.[17] bp (~18 mm) 101–102 °C]. Ketalization was effected by heating 3-oxothiapyran (5.2 g, 44.7 mmol) in 10 mL of ethylene glycol saturated with hydrogen chloride on the steam bath for 1 h. The cooled reaction mixture was poured into cold 5% sodium hydroxide and extracted with ether. Following removal of solvent in vacuo, the residual amber syrup was heated for 1 h with 30% sodium bisulfite solution. Upon extraction with ether, washing with water, drying over magnesium sulfate, and evaporation of solvent, an amber syrup (5.4 g, 75%) remained which showed no carbonyl absorption in the IR. Distillation under reduced pressure gave 1,4-dioxaspiro[4.5]-7-thiadecane (**5**) (4.5 g, 63%), bp (~17 mm) 126–128 °C, shown to be homogeneous by GLC. A solution of the ketal **5** (2 g, 12.5 mmol) in 30 mL of methanol was treated with Chloramine T trihydrate (3.9 g, 13.8 mmol) in portions over 10 min. The reaction mixture was allowed to stir for 2 h at ambient temperatures and then poured into 150 mL of cold water. The precipitated white solid was collected, washed, and dried to give the title compound **8** (3.4 g, 83%, mp 168–169 °C). Crystallization from ethanol-2B (1 g/25 mL) left the melting point unchanged. Anal. Calcd for $C_{14}H_{19}NO_4S_2$: C, 51.12; H, 5.77; N, 4.26. Found: C, 51.21; H, 5.79; N, 4.20. NMR (Me_2SO-d_6) δ 1.6 (m, 4 H), 2.3 (s, 3 H), 3.1 (m, 4 H), 4.0 (s, 4 H), 7.4 (AB m, 4 H)

1,4-Dioxaspiro[4.5]-7,9-dithiadecane-7-*N*-*p*-tosylsulfimide (14). A solution of 5-oxo-1,3-dithiane dimethylene ketal **12** (1 g, 6.2 mmol) prepared according to the method of Howard and Lindsey[18] was treated with Chloramine T trihydrate (2.1 g, 7.4 mmol) in the manner described for **8** to give the title sulfimide **14** (1.3 g, 62%). Crystallization from ethanol-2B (1 g/40 mL) afforded an analytical sample, mp 185–187 °C. Anal. Calcd for $C_{13}H_{17}NO_4S_3$: C, 45.00; H, 4.89; N, 4.04. Found: C, 45.06; H, 4.99; N, 4.07. NMR (Me_2SO-d_6) δ 2.3 (s, 3 H), 2.9 (m, 2 H), 3.35 (s, 2 H), 4.0 (s, 4 H), 4.3 (s, 2 H), 7.45 (AB m, 4 H)

3,3-Dimethoxythiapyran-1-*N*-*p*-tosylsulfimide (7). A solution of 3-oxothiapyran (3.2 g, 27.5 mmol) in 20 mL of methanol was chilled and saturated with hydrogen chloride over 15 min. After standing at room temperature for 1.5 days, workup as described for **5** gave a brown liquid (2.8 g, 63%) which was distilled under reduced pressure to give 3,3-dimethoxythiapyran **4** (0.95 g, 22%) as a colorless liquid, bp (~8 mm) 93–95 °C. Treatment of the purified sample (0.95 g, 6.5 mmol) in 15 mL of methanol with Chloramine T trihydrate (2.8 g, 10 mmol) gave the title compound **7** (1.5 g, 60%), white solid, mp 126–128 °C. Crystallization from benzene (1 g/20 mL) gave an analytical sample, mp 130–132 °C. Anal. Calcd for $C_{14}H_{21}NO_4S_2$: C, 50.70; H, 6.34; N, 4.23. Found: C, 50.39; H, 6.09; N, 4.62.

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New Effective Desulfurization Reagents

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Hydrocarbons and amines are formed in good yields by treatment of thioketones and thioamides, respectively, with iron pentacarbonyl and potassium hydroxide [i.e., $HFe(CO)_4^-$]. A different, and useful, desulfurization reaction occurred by the use of dicobalt octacarbonyl, the cobalt tetracarbonyl anion, or cyclopentadienyliron dicarbonyl dimer as reagents. Mechanisms are proposed for several of these reactions.

There is considerable current interest in the desulfurization of fuel oil and flue gases. A variety of materials (e.g., butagas)[1] have been employed, with mixed success, as desulfurization reagents. We have initiated a study directed toward the development of new desulfurization reagents, the results of such an investigation being potentially applicable to the fuel oil desulfurization problem. This paper describes the use of several iron and cobalt carbonyls in the desulfurization of thiocarbonyl compounds.[2]

Iron pentacarbonyl reacts with 3 equiv of hydroxide ion to generate the hydridotetracarbonylferrate anion $[HFe(CO)_4^-]$. The latter can effect a variety of interesting transformations including the room temperature reduction of nitroarenes to anilines in high yields.[3] We have now found the hydride to be a convenient desulfurization reagent.

Aliphatic and aromatic thioketones (**1**) react with 4 equiv of $HFe(CO)_4^-$ in hot 1,2-dimethoxyethane (8–12 h) to give the corresponding hydrocarbon, **2**, in 60–81% yield. Thioamides also react with $HFe(CO)_4^-$ affording amines in lower, but reasonable, yields as compared to thioketones. Product yields and melting points or boiling points are listed in Table I.

$$\underset{\mathbf{1}}{R_2CS} + Fe(CO)_5 + KOH \longrightarrow \underset{\mathbf{2}}{R_2CH_2}$$

$$\xrightarrow[\text{or } [C_5H_5Fe(CO)_2]_2]{C_6H_6,\ Co_2(CO)_8,\ \text{or } (Ph_3P)_2N^+Co(CO)_4^-} R_2C{=}CR_2$$

Treatment of 4,4′-dimethoxythiobenzophenone (**1**, R = *p*-$CH_3OC_6H_4$) with $DFe(CO)_4^-$ [from KOD and $Fe(CO)_5$] affords the dideuterio compound, $(p\text{-}CH_3OC_6H_4)_2CD_2$, in 74% yield. Similarly 2,2′-dideuterioadamantane was obtained in 78% yield from adamantanethione.

A different desulfurization reaction takes place when the cobalt tetracarbonyl anion is employed as the reagent. Reaction of bis(triphenylphosphine)iminium tetracarbonylcobaltate $[(Ph_3P)_2N^+Co(CO)_4^-]$[4] with thiobenzophenones in benzene at 90–100 °C (Carius tube) affords tetraarylethylenes (**3**) in 45–70% yields (Table II). Significantly higher yields of **3** (71–83%) could be realized by simply refluxing a mixture of the thione and dicobalt octacarbonyl $[Co_2(CO)_8]$ in benzene for 5 h. Desulfurization was also observed using the cyclopentadienyliron dicarbonyl dimer $[C_5H_5Fe(CO)_2]_2$, but this reagent is less effective than dicobalt octacarbonyl.

Possible pathways for the $HFe(CO)_4^-$ ion reaction are illustrated in Scheme I. Thiophilic addition of the iron hydride to the thione would give **4** which can then undergo a hydride shift to form **5**. The latter is convertible to the hydrocarbon **2**, either by attack of another molecule of $HFe(CO)_4^-$ or by