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STUDIES OF ELECTRON-DEPLETED THIOCARBONYL COMPOUNDS—IV[a]

REACTIONS OF TRITHIOCARBONATE S,S-DIOXIDES WITH 1,3-DIENES AND WITH TETRAMETHYLALLENE

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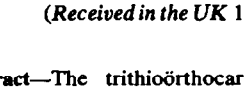
Abstract—The trithioörthocarboxylate S,S-dioxides **B**, a new class of compounds, can be conveniently prepared from trithiocarbonate S,S-dioxides **1** either by Diels–Alder reaction with suitable 1,3-dienes or by ene reaction with tetramethylallene. The monocyclic Diels–Alder adducts **4** readily lose sulfinic acid to yield the 2H-thiopyrans **5**, while treatment of **4** with catalytic amounts of acid results in rearrangement to the isomeric Δ^2-dihydrothiopyrans **6**.

INTRODUCTION

The trithiocarbonate S,S - dioxides **1** which we prepared recently[1] contain an electron - depleted thiocarbonyl group and should thus be potent dienophiles[2] and enophiles.[3] The work to be presented here fully substantiates this expectation.



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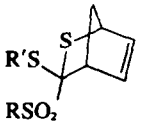
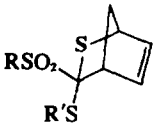
RESULTS AND DISCUSSION

At room temperature, a methylene chloride solution of **1a** (R = *p* - tolyl, R' = phenyl) or **1b** (R = R' = *p* - chlorophenyl) reacts with cyclopentadiene immediately as judged by the discharge of the bright red color of **1**. NMR analysis of the crude products (crude yield ≈ 100%) revealed that *endo* - 2 and *exo* - 2 had been formed in the approximate ratio of 3:1



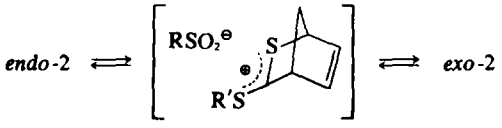
endo-2



exo-2

Upon chromatography on silica gel (methylene chloride or benzene as eluent) *endo* - 2 quantitatively rearranges to *exo*-2. It thus appears that *endo* - 2 is the kinetically favored product while *exo* - 2 is the thermodynamically more stable isomer (the bulky sulfonyl group occupies here the less hindered *exo* position).

We propose that the mechanism of the isomerization hinges upon the ion pair **3** and not upon a retro-Diels–Alder reaction since the cation of **3** should be considerably resonance stabilized.[4] Furthermore, the red color of **1** is not observed in the column.



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The stereochemical assignments for both **2a** and **2b** rest upon the analysis of the Eu (dpm)$_3$ - induced shifts in the NMR spectra of *endo* - **2b** and *exo* - **2b** (Table 1). It is known that sulfide sulfur does not complex with Eu (dpm)$_3$[5] while sulfone oxygen does form weak complexes with Eu (dpm)$_3$.[6] Thus the signals of protons in the proximity of the sulfonyl group will be shifted downfield to a larger extent upon addition of Eu (dpm)$_3$ than those of protons remote from the sulfonyl group. While H_b, H_c, and H_d were assigned on the basis of the observed contact shifts the remaining signals reveal their origin by their chemical shifts and the observed splittings.

There is a close parallel between the findings reported here and the reactivities of cyanodithioformates[7] and other electron - depleted thiocarbonyl compounds[8] towards cyclopentadiene.

The Diels–Alder adducts **4** from **1** and 1,3 - butadiene or 2,3 - dimethyl - 1,3 - butadiene (obtained either from the neat reactants or in solution) readily lose sulfinic acid to yield the 2H - thiopyrans

[a] Part 1: N. H. Nilsson, C. Jacobsen, O. N. Sørensen, N. K. Haunsøe and A. Senning, *Chem Ber.* **105**, 2854 (1972). Parts 2 and 3: in preparation.

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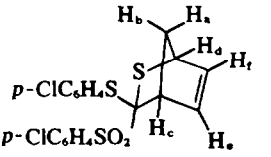
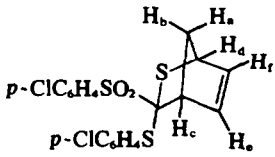
Table 1. NMR spectra of *endo*-**2b** and *exo*-**2b** ($CDCl_3$, TMS, in δ units)



endo-**2b**



exo-**2b**

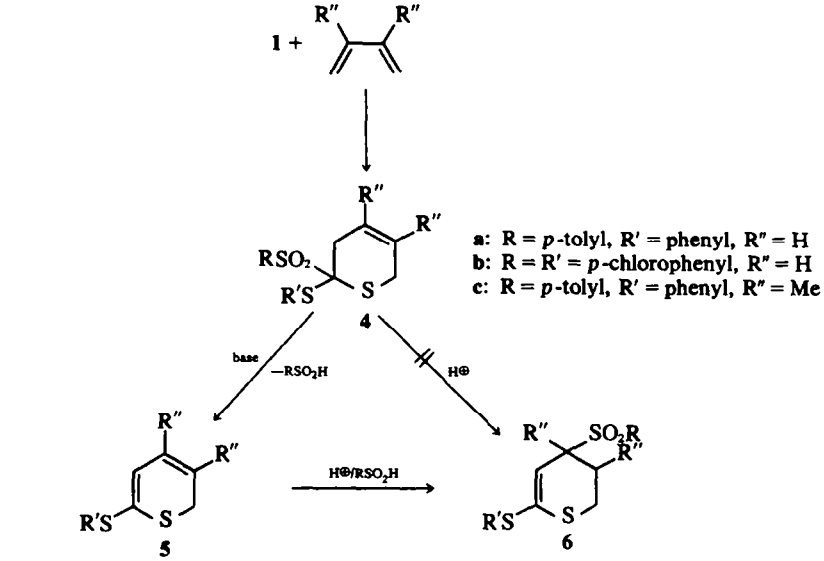
	A	B	Δ ppm		A	B	Δ ppm
H_a	1·87	1·92	0·05	H_a	1·80	1·88	0·08
H_b	2·55	2·60	0·05	H_b	2·62	2·95	0·33
H_c	3·73	3·97	0·24	H_c	4·07	4·39	0·32
H_d	4·37	4·42	0·05	H_d	4·28	4·39	0·11
H_e	6·14	6·35	0·21	H_e	6·33	6·41	0·08
H_f	6·40	6·41	0·01	H_f	6·51	6·58	0·07

A: 0·00 moles of Eu(dpm)$_3$ per mole. B: 0·61 moles of Eu (dpm)$_3$ per mole.

The acid - catalyzed isomerization of **4b** to **6b** could be effected *in situ* by adding a catalytic amount of *p* - toluenesulfonic acid to the methylene chloride solution of **4b** before the 1,3 - butadiene was passed through. Without added catalyst, the conversion of **5b** to **6b** is somewhat erratic, possibly because it requires self - catalysis *via* disproportionation of the sulfinic acid to (*inter alia*) sulfonic acid.

While the intermediacy of **5b** in the isomerization of **4b** to **6b** was self - evident when the reaction was followed by NMR, it remained to be seen whether, at least in the case of the isomerization of **4a** (where no intermediate **5a** could be detected), an acid-catalyzed isomerization **4** → **6** independent of **5** was possible.

Addition of *p* - chlorobenzenesulfinic acid to isolated **5a** produced **6c** in high yield. Treatment of a concentrated carbon disulfide solution of **4a** with an equimolar amount of *p* - chlorobenzenesulfinic acid dissolved in trifluoroacetic acid resulted in the



a: R = *p*-tolyl, R' = phenyl, R'' = H
b: R = R' = *p*-chlorophenyl, R'' = H
c: R = *p*-tolyl, R' = phenyl, R'' = Me

a: R' = phenyl, R'' = H
b: R' = *p*-chlorophenyl, R'' = H
c: R' = phenyl, R'' = Me

a: R = *p*-tolyl, R' = phenyl, R'' = H
b: R = R' = *p*-chlorophenyl, R'' = H
c: R = *p*-chlorophenyl, R' = phenyl, R'' = H

5[9,10] which are oxygen - sensitive (unless stabilized by the presence of sulfinic acid) and have to be handled under nitrogen. Only the Δ^3 - dihydrothiopyran **4a** was sufficiently stable to allow its characterization by NMR and IR in freshly prepared carbon disulfide solution. After addition of pyridine - d_5 to this solution of **4a**, a rapid conversion of **4a** to **5a** could be monitored by NMR. On the other hand, addition of trifluoroacetic acid to the carbon disulfide solution of **4a** led to the formation of **6a** in quantitative yield (as judged by NMR).

formation of **6a** and **6c** in the ratio 1·0:0·9. Tripling the amount of *p* - chlorobenzenesulfinic acid changed this ratio to 1·0:2·0. We consider these findings as compelling evidence to the effect that the isomerization of **4** to **6** is essentially intermolecular and proceeds *via* the allylic cation formed by protonation of **5**. From this allylic cation, the thermodynamically most stable product, *i.e.* the ketene S,S - acetal **6**, is formed. Contrary to **4**, **6** does not split off sulfinic acid when treated with pyridine.

As opposed to **1** and cyanodithioformates[9]

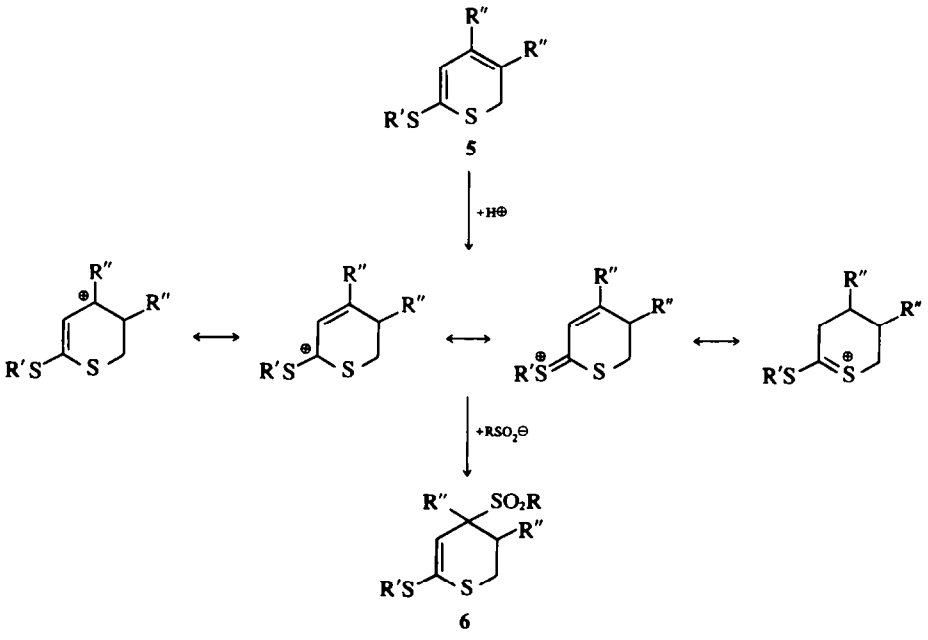
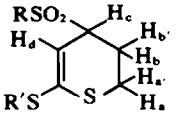


Table 2. NMR parameters of 4 - arysulfonyl - 2 - arylthio - Δ^2 - dihydrothiopyrans, **6** [For unresolved multiplets only the center frequency is given] (Chemical shifts in δ [ppm]; TMS as internal standard)



Compound	R	R'	Solvent*	H_a, $H_{a'}$	H_b, $H_{b'}$	H_c	H_d†	p-CH_3	Aromatic protons
6a	p-$CH_3C_6H_4$	C_6H_5	CS_2	2·87m	2·22m	3·72q	5·90d	2·40s	7·1–7·7(9H)
6b	p-ClC_6H_4	p-ClC_6H_4	$(CD_3)_2SO$	3·00m	2·15m	4·48q	6·00d		7·43d(4H) J < 1Hz 7·84d(4H) J ~ 1Hz
6c	p-ClC_6H_4	C_6H_5	$CDCl_3$	2·97m	2·33m	3·93q	5·98d		7·3–7·9(9H)

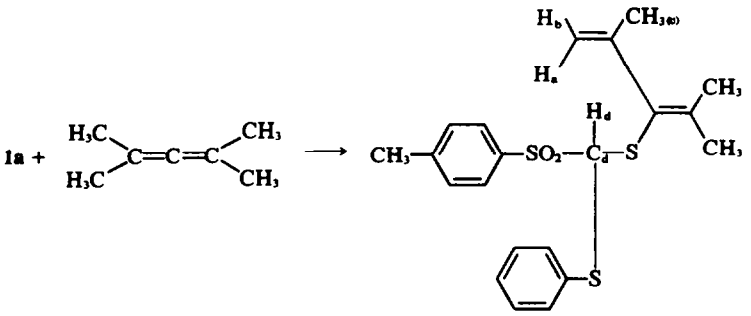
*Concentration: 100 mg/500 μl.

†J_{cd} = 4·5 Hz. Irradiation of H_d changed H_c (formally the X-part of an ABX-system into an unresolved triplet; similar irradiation of H_b, $H_{b'}$ changed H_c into a doublet (J_{cd} = 4·5 Hz).

chlorodithioformates do not appear to react with 1,3 - butadiene. This lack of reactivity might be attributed to the mesomeric effect of the free electron pairs on the chlorine atom, a feature which is absent in **1** and the cyanodithioformates.

The enophilic properties of **1** could be demonstrated by reacting **1a** with the electron - rich olefin tetramethylallene. At room temperature, a quantitative yield of **7a** was observed. In the structure proof of **7a**, the isomeric thiol structure had to be ruled out. Thus, **7a** does not decolorize iodine solution and the NMR signal at δ = 5·08 ppm [$(CD_3)_2$ SO] assigned to H_d does not disappear after equilibration with deuterium oxide. Moreover, a ^{13}CNMR single - frequency off - resonance decoupling experiment demonstrated that the thiocarbonyl carbon atom of **1a** became tertiary in **7a**.

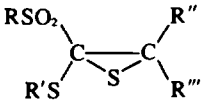
Thus, by irradiation with a R_p. perturbing field at 511 Hz (the resonance frequency of H_d in $CDCl_3$ at 100 MHz field strength), The signal of C_d at 1913·6 Hz in the ^{13}C spectrum of **7a** was completely decoupled. When the irradiation frequency was



7a

moved 40 Hz downfield from H_d, the signal of C_d was split into a doublet. This unambiguously proves the tertiary character of C_d.

The corresponding ene reaction between thiobenzophenones and tetramethylallene was recently described by Gotthardt.[11]



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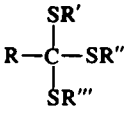
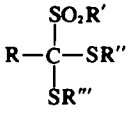
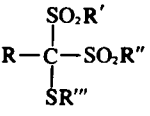


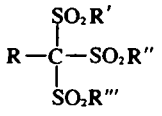
A



B



C



D

With the synthesis of **2**, **4a**, and **7a** we have obtained (together with the thiiranes **8** which can be obtained from **1** and diazoalkanes[12]) the first example of the trithioörthocarboxylate S,S-dioxides **B**, a new class of compounds which closes the systematic gap between the trithioörthocarboxylates[13] **A** on one side and their S,S,S',S' - tetroxides[13] **B** and S,S,S',S',S'',S'' - hexoxides[13] **C** on the other.

EXPERIMENTAL

All m.ps and b.ps are uncorrected, the former were determined on a Büchi m. p. apparatus (Dr. Tottoli). UV spectra were taken on a Bausch and Lomb Spectronic 505. IR spectra were recorded on a Beckman IR - 18A. Mass spectra were taken on a CEC mass spectrometer MS 21–104. NMR spectra were obtained with a Varian A-60 spectrometer. The homonuclear proton double resonance experiments were performed on a Varian XL–100–15 spectrometer operating at 100·1 MHz. The proton decoupled ^{13}C spectra of **7a** were recorded on XL–100–15 (25·16 MHz) operating in the F. T. mode (Varian 620 L computer, 16 K) using a sweep width of 5000 Hz (acquisition time 0·8 sec; pulse width 75 μsec). An internal ^2H field frequency lock was achieved by using deterochloroform as solvent. In all NMR experiments TMS was used as internal standard. All reactions were followed by TLC. Merck Silica Gel 60 was used throughout in the column chromatography.

*exo - 3 - (p - Tolylsulfonyl) - 3 - (phenylthio) - 2 - thiabicyclo [2.2.1]heptene - 5, exo - **2a***

Cyclopentadiene was distilled into a soln of **1a** (5·30 g 17·2 mmoles)[1] in 100 ml CH_2Cl_2 until the red color disappeared. After evaporation of the solvent *in vacuo*, the mixture was chromatographed over a column of silica gel with benzene as eluent. After evaporation of the solvent, *exo* - **2a** (5·10 g; 80%) crystallized from the oily residue (after addition of 15 ml ether), m.p. 104–105°, dec. (Found: C, 60·98; H, 4·87; S, 25·26. $C_{19}H_{18}O_2S_3$ requires: C, 60·96; H. 4·85; S, 25·64%); NMR ($CDCl_3$) (for the numbering, see Table 1): δ1·70 (1H, m, H_a), 2·66 (1H, d, H_b), 2·48 (3H, s, *p* - CH_3), 4·09 (1H, m, H_c), 4·20 (1H, m, H_d), 6·17–6·55 (2H, m, H_e, H_f), 7·20–8·10 (9H, arom. H).

*endo - and exo - 3 - (p - Chlorophenylsulfonyl) - 3 - (p - chlorophenylthio) - 2 - thiabicyclo [2.2.1.] heptene - 5, endo - **2b**, exo - **2b***

Cyclopentadiene was distilled into a solution of 1·0 g **1b*** in 10 ml of benzene until the red color of **1b** disappeared. After evaporation of the solvent, an oil resulted from which a mixture of *endo* - **2b** and *exo* - **2b** crystallized after addition of 10 ml of ether at room temp. *Endo* - **2b** was isolated from this mixture by repeated crystallization. This was done by dissolving the crystals in the minimum amount of CH_2Cl_2 at room temp and addition of 3 volumes of ether, m.p. 99–101°, dec. (Found: C, 50·39; H, 3·44; Cl, 16·67; S, 22·22. $C_{19}H_{14}Cl_2O_2S_3$ requires: C, 50·34; H, 3·29; Cl, 16·51; S, 22·40%), NMR ($CDCl_3$): see Table 1.

The combined mother liquors from the crystallizations were concentrated and the residue was chromatographed over a short column of silica gel with CH_2Cl_2 as eluent. After concentration of the solution, a light-brown oil was obtained from which *exo* - **2b** was obtained after two crystallizations as described for *endo* - **2b**, m. p. 110–111°, dec. (Found: C, 50·21; H, 3·30; Cl, 16·70; S, 22·19. $C_{19}H_{14}Cl_2O_2S_3$ requires: C, 50·34; H, 3·29; Cl, 16·51; S, 22·40%); NMR ($CDCl_3$): see Table 1.

*1b was prepared according to Ref 1 in 33% yield m.p. 128° (cyclohexane).

6 - (p - *Tolylsulfonyl*) - 6 - (*phenylthio*) - Δ^3 - *dihydro* - *thiopyran*, **4a**

Through a soln of **1a** (154 mg; 0·5 mmoles) in 10 ml CH_2Cl_2 cooled to −20° was passed a gentle stream of 1,3 - butadiene until the color of **1a** faded (≈ 2 min). The soln was kept another 5 min at 10°. After evaporation of the solvent *in vacuo* at 10°, crude **4a**, 180 mg (≈ 100%), was obtained as a heavy syrup. Attempts to crystallize **4a** at low temperature were unsuccessful. Crude **4a** was under similar conditions prepared in CS_2, **4a** was unstable in $CHCl_3$, CCl_4 and benzene (conversion to **5a**); IR (CS_2): ν_{SO_2} 1148, 1290, 1305, 1325 cm^{-1}; UV (CH_2Cl_2): λ_{max} 236 nm (log $\epsilon \approx 4$); NMR (CS_2): δ 2·30 (2H, m, H-5$_a$, H-5$_e$), 2·40 (3H, s, *p* - CH_3), 3·22 (2H, m, H-2$_a$, H-2$_e$), 5·64 (2H, m, H-3, H-4), 7·0–7·9 (9H, m, arom. H).

6 - (*Phenylthio*) - 2H - *thiopyran*, **5a**

A gentle stream of butadiene was passed through a soln of 3·08 g (10 mmoles) of **1a** in 25 ml of $CHCl_3$ until the color of **1a** disappeared. After boiling for 2 min in a N_2 atmosphere, the soln was extracted with dil K_2CO_3 aq, dried with K_2CO_3 in a N_2 atmosphere, and evaporated. the residue was rapidly chromatographed on a short column of silica gel with benzene as eluent. After evaporation of the solvent, **5a** was isolated from the residue by molecular distillation under N_2 at 80–90°/0·2 mm, yield 1·23 g (60%). (Found: C, 64·08; H, 4·91; S, 30·86. $C_{11}H_{10}S_2$ requires: C, 64·07; H, 4·89; S, 31·04%); NMR ($CDCl_3$): δ 3·28 (2H, m, H-2), 5·40–5·80 (1H, m, H-3), 5·90–6·25 (1H, m, H-4), 6·47 (1H, d, H-5), 7·20–7·60 (5H, m, arom. H).

6 - (p - *Chlorophenylthio*) - 2H - *thiopyran* **5b**

Compound **5b** was obtained from 2·0 g **1b** by the same procedure as described for **5a**. **5b** was purified by two sublimations under N_2 at 55°/0·1 mm, m.p. 61–62°, yield 0·91 g (67%). (Found: C, 54·67; H, 3·75; S, 26·44. $C_{11}H_9ClS_2$ requires: C, 54·87; H, 3·77; S, 26·64%), UV (C_6H_{12}): λ_{max} 335 nm (log ϵ 3·71), MS: $M^{\oplus}$ at *m/e* 240; base peak at *m/e* 97 (thiopyrylium cation), NMR ($CDCl_3$): δ 3·25 (2H, m, H-2), 5·40–5·80 (1H, m, H-3), 5·90–6·25 (1H, m, H-4), 6·48 (1H, d, H-5), 7·15–7·55 (4H, m, arom. H).

6 - (*Phenylthio*) - 3,4 - *dimethyl* - 2H - *thiopyran*, **5c**

Compound **5c** was obtained from 3·08 g **1a** as described for **5a**. **5c** was purified by 3 low temp (−45°) crystallizations from light petroleum, m.p. 51–53°, yield 0·80 g (40%). (Found: C, 66·48; H, 5·95; S, 27·10. $C_{13}H_{14}S_2$ requires: C, 66·65; H, 6·02; S, 27·32%), NMR ($CDCl_3$): δ 1·80 (3H, s, CH_3), 1·89 (3H, s, CH_3), 3·33 (2H, s, H-2), 6·48 (1H, s, H-5), 7·20–7·60 (5H, m, arom. H).

4 - (p - *Tolylsulfonyl*) - 2 - (*phenylthio*) - Δ^2 - *dihydrothiopyran*, **6a**

Method A. Through a soln of **1a** (3·08 g; 10 mmoles) and 1 ml trifluoroacetic acid in 25 ml CS_2 at room temp was passed a gentle stream of 1,3 - butadiene until the color of **1a** disappeared (≈ 3 min). The solvent was evaporated *in vacuo*. The residue was extracted with 25 ml light petroleum (b.p. 50–60°) and stirred with 50 ml abs EtOH during 3 h. The ppt was filtered off, dissolved in abs EtOH and again precipitated by cooling the soln in a CO_2/acetone bath, yield 1·30 g (36%), m.p. 74–75°. (Found: C, 59·66; H, 5·01; S, 26·31. $C_{18}H_{18}O_2S_3$ requires: C, 59·66; H, 5·01; S, 26·50%); IR (Nujol): ν_{SO_2} 1140, 1290, 1303, 1315; UV ($CHCl_3$): λ_{max} 264 nm (log ϵ 4·09).

Method B. To a slurry of **1a** (1·54 g; 5 mmoles) in 150 ml ether was passed 1,3 - butadiene until the color changed. The solvent was evaporated and the residue dissolved in 25 ml abs EtOH. After addition of 25 mg *p* - toluenesulfonic acid, the soln was boiled 1 h. Then the solvent was evaporated and the residue chromatographed on silica gel (eluent 50% ether, 50% light petroleum, b.p. 50–60°); yield of **6a**: 555 mg (30%).

4 - (p - *Chlorophenylsulfonyl*) - 2 - (p - *chlorophenylthio*) - Δ^2 - *dihydrothiopyran*, **6b**

Method A. Through a soln of **1b** (1·81 g; 5 mmoles) and 100 mg *p* - toluenesulfonic acid in 30 ml CH_2Cl_2 was passed a slow stream of 1,3 - butadiene at 21–29° until the color changed (3 min). The solvent was evaporated *in vacuo* and the residue was treated with 30 ml of light petroleum, b.p. 50–60°, which was discarded. The semisolid residue was stirred with abs EtOH at 0° for 2 h. After filtration, **6b**, 151 g (72%), was obtained, m.p. 140–141° (from acetonitrile). (Found: C, 49·01); H, 3·38; Cl, 16·86; S, 22·75. $C_{17}H_{14}Cl_2O_2S_3$ requires: C, 48·93; H, 3·38; Cl, 16·99; S, 23·05%); IR (Nujol or KBr): ν_{SO_2} 1143, 1148, 1296, 1306, 1318 cm^{-1}; UV (C_2H_5OH): λ_{max} 261 nm (log ϵ 4·18).

Method B. Without added catalyst, but otherwise under the same conditions, **5b**, 180 mg (15%), R_f 0·78, and **6b**, 920 mg (44%), R_f 0·33, were isolated after chromatography on silica gel (eluent CH_2Cl_2). Probably some conversion of **5b** and sulfinic acid to **6b** took place on the column.

Method C. Through a soln of **1b** (0·91 g; 2·5 mmoles) in 30 ml CH_2Cl_2 was passed 1,3 - butadiene until the color faded. The solvent was evaporated and the residue dissolved in 20 ml abs EtOH. To this soln was added 1·76 g (10 mmoles) *p* - chlorobenzenesulfinic acid (dried *in vacuo*) at room temp. No formation of **6b** was observed. Then the soln was heated to boiling for a short moment, cooled, and the EtOH evaporated *in vacuo*. After chromatography on silica gel (eluent CH_2Cl_2), **6b**, 640 mg (60%), was isolated. (S - *p* - Chlorophenyl - *p* - chlorobenzenethiosulfonate was detected as by -product).

Method D. Through a slurry of **1b** (3·63 g; 10 mmoles) in 150 ml dry ether was passed 1,3 - butadiene until the color changed. The ether was evaporated *in vacuo*. The residue (4·17 g) was boiled in 100 ml cyclohexane diluted with 25 ml ether (to dissolve the precipitated *p* - chlorobenzenesulfinic acid) for 5 min. After standing over night at room temp, precipitated **6b**, 850 mg (41%), was filtered off.

4 - (*p* - *Chlorophenylsulfonyl*) - 2 - (*phenylthio*) - Δ^2 - *dihydrothiopyran*, **6c**

To a soln of **5a** (400 mg; 1·95 mmoles) in 40 ml CS_2/$CHCl_3$ 1:1 was added 342 mg (2 mmoles) *p* - chlorobenzenesulfinic acid (prepared by acidifying a sodium *p* - chlorobenzenesulfinate soln with conc H_2SO_4, taking the sulfinic acid up in ether and drying this soln with 4 Å molecular sieves; after filtration, the sulfinic acid was precipitated with light petroleum, b.p. 35–40°, and dried *in vacuo* (0·01 mm Hg) with P_2O_5 at room temp for 2 h) at room temp together with ½ ml trifluoroacetic acid. After ½ h, **5a** had disappeared (TLC!) and the solvent was evaporated *in vacuo*. Treatment of the residue with 40 ml light petroleum, b.p. 50–60°, and cooling this soln in a CO_2/acetone bath afforded **6c**, 667 mg (89%), m.p. 120–121°. (Found: C, 53·32; H, 4·24; S, 24·77. $C_{17}H_{15}Cl$ requires: C, 53·31; H, 3·95; S, 25·12%); IR (KBr): ν_{SO_2} 1141, 1145, 1295, 1305, 1318 cm^{-1}; UV ($CHCl_3$): λ_{max} 262 nm (log ϵ 4·08).

Cross-over experiments. To a soln of **4a** (0·5 mmoles) in 1 ml CS_2, cooled to −30°, was added 88·3 mg (0·5 mmoles) of *p* - chlorobenzenesulfinic acid dissolved in 1 ml trifluoroacetic acid. The soln was kept for further ½ h at room temp and was then chromatographed on a 12 × 3 cm column packed with silica gel (eluent CH_2Cl_2), yield: 134 mg of a mixture of **6a** and **6c** in the ratio of 1·0:0·9 which was determined by intergration of the H_d signals in a $CDCl_3$ soln. (**6a**, $\delta_{H_d} = 6{\cdot}08$ ppm; **6c**, $\delta_{H_d} = 5{\cdot}98$ ppm).

In a similar experiment (same amounts of **4a**, reaction conditions, and work-up procedure) using the triple amount of *p* - chlorobenzenesulfinic acid) a 100 mg yield of **6a** and **6c** was obtained in the ratio of **6a**:**6c** 1·0:2·0.

NMR experiments A To 5 mmoles **4a**, dissolved in 500 μl CS_2 was added 25 μl CF_3COOH. A spectrum run within ½ h showed a complete conversion to **6a**. *B*: to 5 mmoles **4a**, dissolved in 500 μl CS_2, was similarly added 25 μl pyridine-d_5. A spectrum run within ½ h showed the characteristic pattern of **5a**. C: After addition of 50 μl pyridine - d_5 to a mixture of **6a** and **6c** in deuterochloroform, a spectrum recorded 1½ h later showed no conversion **6** → **5**. *D*: Attempts to prepare **4b** under similar conditions as **4a** were unsuccessful as judged by the NMR spectra of freshly prepared solutions.

2,4 - *Dimethyl* - 3 - [(p - *tolylsulfonyl* - *phenylthio*) - *methylthio*] - 1,3 - *pentadiene*, **7a**

To a soln of tetramethylallene (1·92 g; 20 mmoles) in 75 ml dry benzene **1a** (6·16 g; 20 mmoles) was added in portions during 5 min at room temp (slight increase in temp during the reaction). The reaction was complete after 20 min. The benzene was evaporated *in vacuo*, crude yield: 8·08 g (100%). NMR of the crude product showed only signals belonging to **7a**. For analysis the product was chromatographed on 100 g silica gel (eluent 30% ether, 70% light petroleum, b.p. 50–60°). The solvent was evaporated (finally at 0·01 mm Hg, 150°). **7a** was obtained as a nearly colorless heavy syrup. (Found: C, 62·29; H, 6·03; S, 23·29. $C_{21}H_{24}O_2S_3$ requires: C, 62·37; H, 5·98; S, 23·74%); IR (CCl_4): ν_{CH} 2840, 2900, 2960 cm^{-1}; ν_{SO_2} 1150, 1300 cm^{-1}; ^1H NMR (CCl_4) (δ in ppm, J in Hz): δ 1·50 (3H, dd, H_c, J_{bc} 1·5, J_{ac} 1·0); 1·73 (3H, s, CH_3); 1·94 (3H, s, CH_3); 2·43 (3H, s, *p* - CH_3); 4·65 (1H, dd, H_a, J_{ab} 2·7, J_{ac} 1·0); 4·87 (1H, s, H_d); 5·01 (1H, dd, H_b, J_{ab} 2·7, J_{bc} 1·5); 7·2–8·0 (9H, m, aromatic protons). The assignment of H_a and H_b was based on the observed allylic coupling constants. ^{13}C NMR ($CDCl_3$): The number of signals, their intensities, and positions were in accordance with the proposed structure of **7a**, but no attempts were made to accomplish a complete assignment of the spectrum.

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