The MCPBA-oxidation of 8*H*-Cyclohepta[*b*]thiophen-8-ones to Their 1,1-Dioxides and Further Ring-contracted Benzo[*b*]thiophene Derivatives

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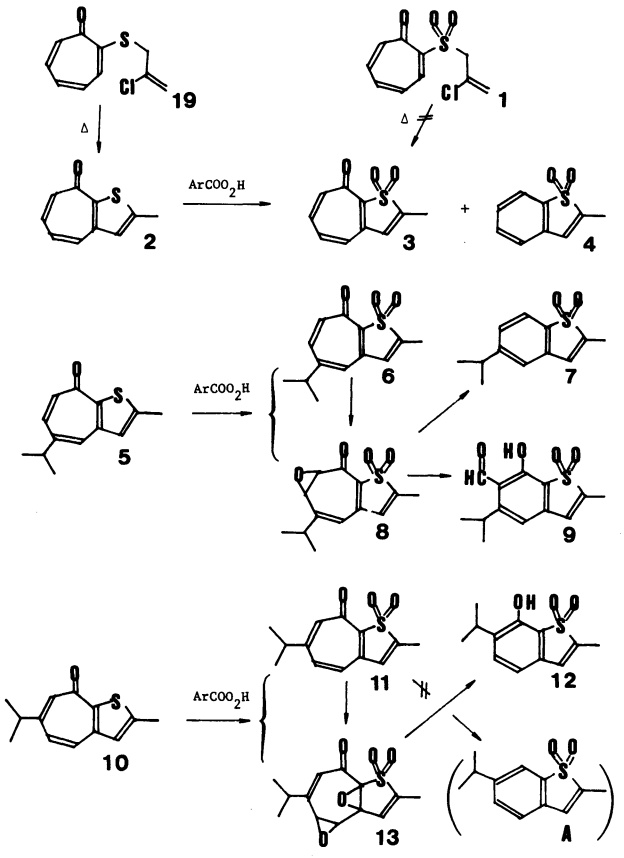
Upon MCPBA-oxidation, several 8*H*-cyclohepta[*b*]thiophen-8-ones yielded the 8*H*-cyclohepta[*b*]thiophen-8-one 1,1-dioxides and their epoxides. The latters were shown to be convertible to several ring-contracted derivatives, the benzo[*b*]thiophene 1,1-dioxides and/or their corresponding phenol and salicylaldehyde derivatives.

Recently, we have reported[1,2] a series of thermal rearrangement of functionalized 2-(allylthio)tropone derivatives. In connection with this, the thermolysis of the sulfonyl derivatives, *i.e.*, 2-(allylsulfonyl)tropones, should be of interest concerning potential precursors for α-keto sulfene intermediates. However, the sulfones have been shown to be stable around 110 °C, where the corresponding sulfinyl derivatives are reactive. Herein we wish to describe an unprecedent oxidative ring contraction to a variety of benzenoid derivatives from the isopropyltropone derivatives in the preparation of the 8*H*-cyclohepta[*b*]thiophen-8-one 1,1-dioxides.

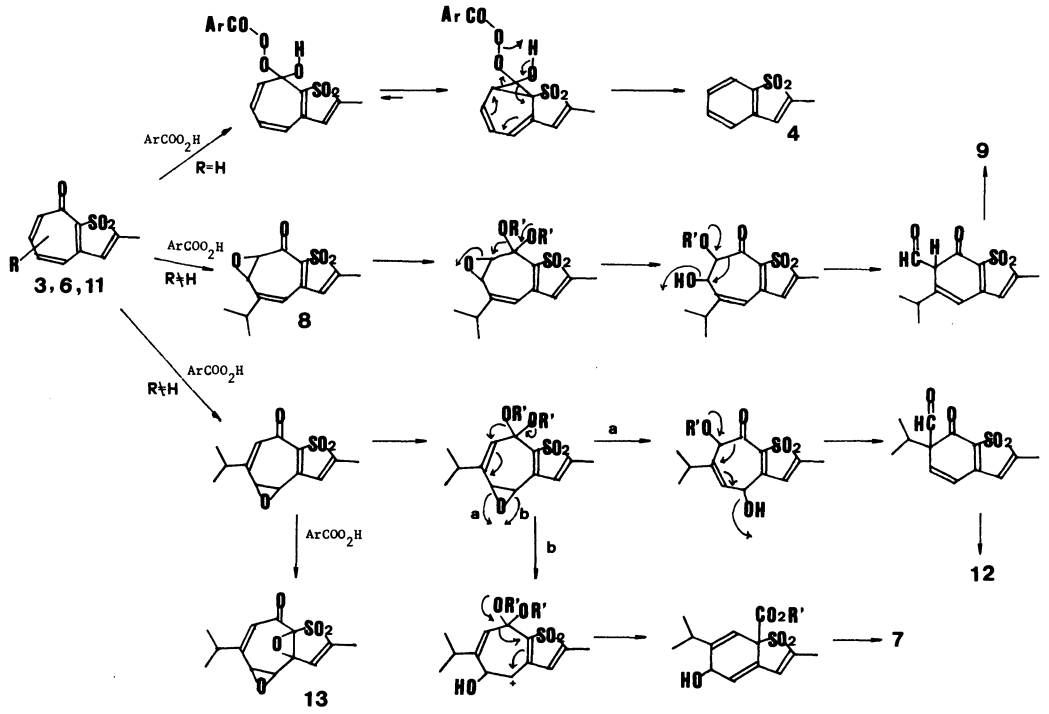
In a hope to obtain thienotropone dioxide *via* a "*sulfono*"-Claisen rearrangement, 2-(2-chloro-2-propenylsulfonyl)tropone (**1**) was heated at 110 °C for 10 min, but no reaction occurred at all. However above 180 °C, a decomposition of the material gradually took place although no definite product could be isolated. Obviously, an alternative route must be the *m*-chloroperbenzoic acid (MCPBA)-oxidation of 2-methyl-8*H*-cyclohepta[*b*]thiophen-8-one (**2**).[1] In fact, oxidation in chloroform yielded two products (**3** and **4**); the NMR spectrum of the major product (**3**) indicated the retention of the seven-membered ring, and the IR spectrum showed absorptions due to the newly formed sulfonyl group. Therefore, it must be the expected product. However, the minor product (**4**), analyzing for $C_9H_8O_2S$ on the basis of the mass spectrum, was 2-methylbenzo[*b*]thiophene 1,1-dioxide, and the ^{1}H-[3] and ^{13}C-NMR[4] were in good agreement with the data already reported. A further MCPBA-oxidation of **3** under similar conditions gave **4**. This unexpected occurrence of a novel ring contraction prompted us to investigate the reaction in more detail.



Scheme 1.

Accordingly, the oxidation of 5-isopropyl derivative (**5**)[1] was investigated. The four products identified were the corresponding isopropyl derivatives (**6** and **7**) of **3** and **4** together with two new products (**8** and **9**), which were isolated by preparative thin-layer chromatography (PTLC). One (**8**) of the minor products was assumed to be a further epoxidation product of **6** on the basis of its spontaneous conversion to **7** and **9**. Its extreme instability is not surprising because of a thiophene 1,1-dioxide structure. Nevertheless, the NMR spectrum of **8** showed a pair of *AB*-type signals at δ=3.71 and 4.08, of which the former was further spin-coupled to the other methine proton at δ=6.12, and showed a magnetically nonequvalent pair of doublet methyls, indicating a presence of sp^3-carbons in the vicinity of the isopropyl group. No other characterization was successful due to its rapid decomposition to **7** and **9**. The further MCPBA oxidation of **6** indicated a formation of **8** in substantial amount. Therefore, its structure is shown to be 6,7-epoxy-5-isopropyl-2-methyl-6,7-dihydro-8*H*-cyclohepta[*b*]thiophen-8-one 1,1-dioxide.

Another product, **9**, was 6-formyl-7-hydroxy-5-isopropyl-2-methylbenzo[*b*]thiophene 1,1-dioxide; the NMR spectrum exhibits only one phenyl proton as a singlet, and the isopropyl and thiophene 1,1-dioxide moieties still remained. In addition, there are characteristic signals at δ=10.36 and 12.58 ascribable to the



Scheme 2.

salicylaldehyde function. Since the chemical shift of the C-4 proton of the phenyl ring, δ=6.80, was higher than that of **7**, $\Delta\delta$=0.30, this should eliminate an alternative, 6-hydroxy-7-formyl structure.

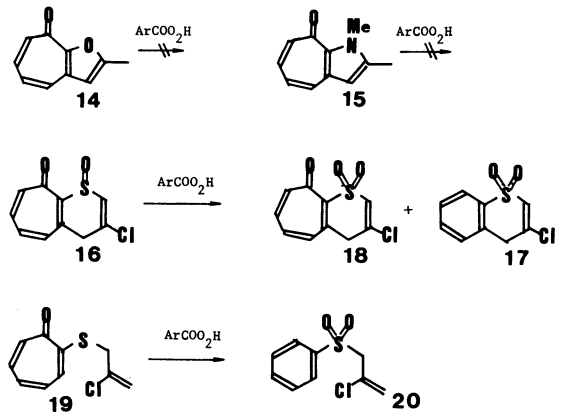
On the other hand, the 6-isopropyl derivative (**10**)[1] gave the corresponding dioxide, 6-isopropyl-2-methyl-8*H*-cyclohepta[*b*]thiophen-8-one 1,1-dioxide (**11**), in good yield, but the ring-contracted 6-isopropyl-2-methylbenzo[*b*]thiophene 1,1-dioxide (**A**) was undetectable. Instead of this, a phenol (**12**) and an epoxide, 3a,8a:4,5-diepoxy-6-isopropyl-2-methyl-3a,4,5,8a-tetrahydro-8*H*-cyclohepta[*b*]thiophen-8-one 1,1-dioxide (**13**),[5] were obtained. The ^{1}H-NMR spectrum of **13** also showed the *AB*-signals due to epoxy methine protons and a nonequivalent pair of methyl doublets. The ^{13}C-NMR spectrum showed only five sp^2-carbons, and the mass spectrum indicated its composition to be $C_{13}H_{14}O_5S$. Moreover, **13**, unlike **8**, was relatively stable under the reaction conditions. Therefore, **13** could be formulated as shown.

The remaining product, **12**, was also identified from the NMR analysis to be 7-hydroxy-6-isopropyl-2-methylbenzo[*b*]thiophene 1,1-dioxide. Unlike **9**, **12** possesses the isopropyl group at C-6, and the α-formylcyclohexadienone as an intermediate could not be enolized to yield the salicylaldehyde derivative. Therefore, a mechanism for this eliminative rearrangement could be proposed as shown in Scheme 2.

It is not surprising that the substituent on the tropone ring determined the site of the reaction, and the subtle difference of such chemical properties leads to entirely different results. Another interesting feature is that, from the same type of precursors (the epoxycycloheptadienones), the formation of aromatic compounds at a different oxidation level, *i.e.*, benzene, phenol, and salicylaldehyde derivatives, occurred. Moreover, there must be two different mechanisms operative for the benzene formation; one is, operative in the parent tropone derivatives, the oxidative decarbonylation *via* the 7-acyldioxy-7-hydroxytropylidenes,[6] and the other is hydrolytic ring contraction of the epoxycycloheptadienones as verified in cases of the isopropyl derivatives.

To gain insight into the scope and limitations of this reaction, we have examined other heterocylic troponoids. 2-Methyl-8*H*-cyclohepta[*b*]furan-8-one (**14**)[7] resulted in a recovery of the starting **14**. On the other hand, the oxidation of 1,2-dimethyl-8*H*-cyclohepta[*b*]pyrrol-8-one (**15**)[8] should be of interest since it should at first be oxidized to an *N*-oxide, which resembles sulfonyl derivatives in respect to having a positive, formal charge on the C-2 substituent. An extensive decomposition occurred under thse conditions, and only a small amount of **15** was recovered. However, 3-chlorocyclohepta[*b*]thiopyran-9(4*H*)-one 1-oxide (**16**)[2] afforded 3-chloro-4*H*-benzo-[*b*]thiopyran 1,1-dioxide (**17**) and 3-chlorocyclohepta-[*b*]thiopyran-9(4*H*)-one 1,1-dioxide (**18**). From this, it seems to be characteristic for 2-sulfonyltropones. Indeed, when 2-(2-chloro-2-propenylthio) tropone (**19**) was oxidized with an excess of MCPBA, (2-chloro-2-propenylsulfonyl) benzene (**20**) was obtained as the by-product of **1** after a prolonged period.

Several examples on the ring contractions of troponoids or tropylidenes to benzene derivatives have been reported in the literature. Beside the well-known rearrangement of 2-halogeno- and 2-alkoxytropones to benzoic acid derivatives on base-treatment,[9] Mukai *et al.* have reported a thermolysis of tropone (**B**) to benzene (**C**) above 600 °C,[10] and Volpin *et al.*[11] have



Scheme 3.

observed the formation of **C** in the hydrogen peroxide oxidation of the tropylium salt; probably, this would be a cheletropic fragmentation of tropyl hydroperoxide *via* the valence isomer, 7-hydroperoxybicyclo[4.1.0]-hepta-2,4-diene. A similar mode to this ring contraction to condensed benzenoid was also found in the MCPBA-oxidation of condensed polycyclic tropylium salt as well as the parent tropylium tetrafluoroborate.[12] However, no precedence has been known for the oxidative formation of benzenes from the tropones. In the concomitant formation of **C** and **B** from tropylidene during the sensitized photooxygenation, an intermediacy of **B** for **C** has been disproven by us.[13] Therefore, the present oxidation is the first example of that reaction.

Experimental

The mps were measured by a Yanagimoto Micro mp apparatus and not corrected. The elemental analyses were performed by Miss M. Yamaguchi and Miss S. Hirashima of this Institute. The high-resolution mass spactra were obtained with a JEOL OSlG Model spectrometer. The NMR spectra were taken with a JEOL FX 100 Model spectrometer in $CDCl_3$ solutions otherwise specified under the Fourier transform mode, and the chemical shifts expressed were δ unit from the internal Me_4Si. The IR spectra were measured either as KBr disk or CCl_4 solution with a Jasco IR 101 Model spectrophotometer.

Preparation of 2-(2-Chloro-2-propenylsulfonyl) tropone (1). A $CHCl_3$ solution (3 cm³) of **19** (204 mg), prepared from 2-mercaptotropone and 2,3-dichloropropene,[1] was treated with MCPBA (534 mg) at 20 °C for 20 h. The mixture was then washed with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The organic extracts were fractionated with silica-gel column to isolate **1**, 204 mg (87%), pale yellow needles, mp 79—80 °C [Found: C, 48.95; H, 3.48%. Calcd for $C_{10}H_9O_3SCl$: C, 49.08; H, 3.71%. δ=4.55 (2H, s), 5.48 (2H, s), 7.0—7.4 (4H, m), and 8.16 (1H, dd, J=8, 2 Hz). δ(C)= 63.3, 122.0, 128.9, 131.7, 136.1, 139.9, 140.8, 144.1, 146.2, and 182.3. ν: 1630, 1520, 1310, 1140, 900, and 790 cm⁻¹].

Attempted Thermolysis of 1. a) An *N,N*-dimethylformamide (DMF) solution (0.5 cm³) of **1** (30 mg) was heated in a sealed NMR tube at 110 °C for 1 h. No appreciable change was detected.

b) A DMF solution (0.4 cm³) of **1** (25 mg) was heated in a sealed NMR tube at 180 °C for 10 min. The NMR spectroscopy revealed an extensive decomposition to intractable material.

MCPBA-oxidation of 2-Methyl-8H-cyclohepta[b]thiophen-8-one (2).[1] A $CHCl_3$ solution (3 cm³) of **2** (128 mg) was mixed with MCPBA (394 mg, 2.5 mol equiv) and kept at 15—25 °C for 48 h. The mixture was then washed with aqueous $NaHSO_3$ and $NaHCO_3$, and extracted with $CHCl_3$. PTLC of the extracts on silica gel gave **3**, 66 mg (44%), yellow needles, mp 192—193 °C [Found: C, 57.38; H, 3.95%. Calcd for $C_{10}H_8O_3S$: C, 57.68; H, 3.87%. δ=2.27 (3H, d, J=2 Hz), 6.62 (1H, q, J=2 Hz), and 6.9—7.4 (4H, m). δ(C)=9.5, 124.6, 132.2, 135.7, 140.0, 140.1, 140.9, 146.5(2C), and 177.3. *m/z*, 208 (M^+). ν: 1620, 1580, 1520, 1460, 1300, 1240, 1140, 860, and 800 cm⁻¹], **4**, colorless needles, mp 105—106 °C, 10 mg (8%) [δ=2.20 (3H, d, J=2 Hz), 6.74 (1H, q of quint, J=2, 1 Hz), and 7.2—7.7 (4H, m), δ(C)=9.1, 121.4, 124.2, 125.8, 129.2 131.6, 133.5, 136.4, and 140.9. ν: 1445, 1285, 1140, and 750 cm⁻¹].

Further Oxidation of 3 to 4. A $CDCl_3$ solution (0.3 cm³) of **3** (16 mg) and MCPBA (34 mg, 2.1 mol equiv) was kept at 15—25 °C for 72 h. The NMR spectroscopy indicated the partial formation of **4**, 33%.

MCPBA-oxidation of 5-Isopropyl-2-methyl-8H-cyclohepta[b]-thiophen-8-one (5) to 6, 7, 8, and 9. A $CHCl_3$ solution (3 cm³) of **5** (200 mg) was mixed with MCPBA (497 mg, 2.5 mol equiv) and kept at 15—20 °C for 72 h with stirring. After filtration of the resultant MCBA, the filtrate was chromatographed on a silica-gel column to give colorless needles, mp 53—54 °C, **7**, 3 mg (1.5%) [Found: M^+, 222.0712. Calcd for $C_{12}H_{14}O_2S$: M^+, 222.0715. δ=1.25 (6H, d, J=7 Hz), 2.21 (3H, d, J=2 Hz), 2.94 (1H, sept, J=7 Hz), 6.71 (1H, m), 7.10 (1H, d, J=1.5 Hz), 7.26 (1H, dd, J=8, 1.5 Hz), and 7.60 (1H, d, J=8 Hz). δ=9.2, 23.7 (2C), 34.5, 121.6, 122.6, 126.1, 127.4, 141.2, and 155.5. ν: 2975, 1295, 1145, and 825 cm⁻¹], and yellow needles, mp 196—197 °C, **6**, 124 mg (54%) [Found: C, 62.54; H, 5.68%. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64%. δ=1.26 (6H, d, J=7 Hz), 2.28 (3H, d, J=2 Hz), 2.87 (1H, sept, J=7 Hz), 6.64 (1H, quint, J=2 Hz), 6.86 (1H, dd, J=2, 1.5 Hz), 7.08 (1H, dd, J=12, 1.5 Hz), and 7.22 (1H, dd, J= 12, 2 Hz). δ(C)=9.4, 22.5 (2C), 39.0, 125.7, 128.0, 137.7, 138.5, 140.8, 145.7, 146.2, 162.9, and 176.8. *m/z*, 250 (M^+). ν: 2980, 1620, 1560, 1300, 1140, and 870 cm⁻¹].

The combined filtrates were further purified by PTLC to give minor products, an unstable yellow oil, **8**, 13.6 mg (5.6%) [δ=1.27 (3H, d, J=7 Hz), 1.28 (3H, d, J=7 Hz), 2.22 (3H, d, J=2 Hz), 2.84 (1H, sept, J=7 Hz), 3.71 (1H, dd, J=4, 2 Hz), 4.08 (1H, d, J=4 Hz), 6.12 (1H, dd, J=2, 1 Hz), and 6.38 (1H, q, J=2 Hz)], and pale yellow needles, **9**, mp 166—167 °C, 9.7 mg (4%) [Found: M^+, 266.0591. Calcd for $C_{13}H_{14}O_4S$: M^+, 266.0608. δ=1.35 (6H, d, J=7 Hz), 2.24 (3H, d, J=2 Hz), 3.68 (1H, sept, J=7 Hz), 6.69 (1H, q, J=7 Hz), 6.80 (1H, s), 10.38 (1H, s), and 12.58 (1H, s). δ(C)=9.5, 22.4 (2C), 24.0, 113.0, 118.2, 124.5, 140.5, 146.6, 157.9, 161.4, and 216.7. ν: 2975, 1650, 1300, 1140, and 905 cm⁻¹].

Further MCPBA-oxidation of 6. A $CHCl_3$ solution (5 cm³) of **6** (29 mg) was mixed with MCPBA (64 mg) and was kept at 15—25 °C for 72 h. The NMR spectral analysis of the mixture indicated the formation of **8**, 35%.

Spontaneous Conversion of 8 to 7, and 9. A neat liquid of **8** (10.7 mg) was kept in a glass vessel at 15—25 °C for 20 h. The resultant crystals thus formed were collected by filtration to give **9**, 4.2 mg (39%), and liquid chromatographic analysis of the filtrate, *ca.* 6 mg, indicated the composition of **7** and **9** as 53:47.

MCPBA-oxidation of 6-Isopropyl-2-methyl-8H-cyclohepta[b]-thiophen-8-one (10) to 11, 12, and 13. A $CHCl_3$ solution (3 cm³) of **10** (206 mg) was mixed with MCPBA (523 mg, 2.5 mol eq) and kept at 15—20 °C for 72 h. After removal of MCBA by filtration, the filtrate was chromatographed on a silica-gel column to give yellow needles, **11**, mp 179—180 °C, 141 mg (60%) [Found: C, 62.10; H, 5.64%. δ=1.24 (6H, d, J= 7 Hz), 2.26 (3H, d, J=2 Hz), 2.78 (1H, sept, J=7 Hz), 6.68

(1H, q, J=2 Hz), 7.02 (1H, dd, J=11, 1 Hz), 7.12 (1H, dd, J=1.5, 1 Hz), and 7.22 (1H, dd, J=11, 1.5 Hz). δ(C)=9.5, 22.5 (2C), 38.7, 124.8, 131.0, 139.9, 140.2, 142.7 (2C), 146.2, 156.9, and 177.1. *m/z*, 250 (M^+). ν: 2970, 1615, 1580, 1305, 1140, and 880 cm^{-1}].

From more polar fractions, the minor products, yellow needles, **13**, mp 133—134 °C, 3 mg (1.2%) [Found: M^+, 282.0555. Calcd for $C_{13}H_{14}O_5S$: M^+, 282.0562, δ=1.20 (3H, d, J=7 Hz), 1.21 (3H, d, J=7 Hz), 2.09 (3H, d, J=2 Hz), 2.63 (1H, sept, J=7 Hz), 3.42 (1H, dd, J=4, 1 Hz), 3.90 (1H, d, J=4 Hz), 6.04 (1H, t, J=1 Hz), and 6.61 (1H, q, J=2 Hz). δ(C)=9.7, 20.9, 21.1, 37.5, 54.8, 55.1, 65.2, 124.9, 127.3, 147.1, 157.3, and 185.6. δ(C)C_6D_6=9.1, 20.5, 20.7, 36.8, 54.3 (2C or 3C), 63.8, 126.0, 147.6, 155.9, and 185.7. ν: 2980, 1165, 1325, 1295, and 1150 cm^{-1}], and colorless needles, **12**, mp 119—120 °C, 2.2 mg (1%) [Found: M^+, 238.0671. Calcd for $C_{12}H_{14}O_3S$: M^+, 238.0690. δ=1.24 (6H, d, J=7 Hz), 2.17 (3H, d, J=2 Hz), 3.22 (1H, sept, J=7 Hz), 6.67 (1H, q, J=7 Hz), 6.76 (1H, d, J=8 Hz), and 7.27 (1H, d, J=8 Hz). δ(C)=9.0, 22.6, 26.9, 116.9, 126.5, 130.5, 131.9, 133.2, 139.1, 140.2, and 149.5. ν: 3420, 2960, 1470, 1290, 1140, and 880 cm^{-1}], were isolated by further PTLC.

Further MCPBA-oxidation of 11. A $CHCl_3$ solution (5 cm^3) of **11** (132 mg) was mixed with MCPBA (287 mg) and was kept at 15—25 °C for 72 h. The HPLC analysis of the mixture revealed a formation of **12**, 21%, and **13**, 4%, together with the recovered **11**, 63%.

Attempted MCPBA-oxidation of 2-Methyl-8H-cyclohepta[b]furan-8-one (14). A $CDCl_3$ solution (2 cm^3) of **14** (52 mg) was mixed with MCPBA (147 mg, 2.0 mol equiv) and kept at 15—25 °C for 48 h. The NMR spectroscopy revealed no appreciable change.

Attempted MCPBA-oxidation of 1,2-Dimethyl-8H-cyclohepta-[b]pyrrol-8-one (15). A $CHCl_3$ solution (1 cm^3) of **15** (60 mg) and MCPBA (160 mg, 2.1 mol equiv) was kept at 15—25 °C for 24 h in an NMR tube. The ^{1}H-NMR spectrum of the mixture was complicated; the strongest signals were those of the starting compound, **15**. No further work was attempted.

MCPBA-oxidation of 3-Chloro-9-oxo-4H,9H-cyclohepta[b]-thiopyrane-1-oxide (16). A $CHCl_3$ solution (4 cm^3) of **16** (163 mg) and MCPBA (342 mg, 2.2 mol equiv) was kept at 15—20 °C for 72 h. The mixture was fractionated on a silica-gel column to give **17**, 8 mg (10%), colorless needles, mp 106—107 °C [Found: C, 50.43; H, 3.52%. Calcd for $C_9H_7O_2SCl$: C, 50.35; H, 3.29%. δ=4.53 (2H, d, J=2 Hz), 7.13 (1H, m), and 7.2—7.7 (4H, m). δ(C)=34.8, 121.7, 125.4, 129.0, 130.3, 130.5, 134.0, 137.3, and 140.6. *m/z*, 214 (M^+). ν: 1450, 1295, 1150, and 770 cm^{-1}], **18**, pale yellow fine needles, mp 130—132 °C (decomp), 39 mg (46%) [Found: C, 49.59; H, 2.98%. Calcd for $C_{10}H_7O_3SCl$: C, 49.49; H, 2.91%. $\delta^{(CD_3)_2CO}$=4.70 (2H, d, J=2 Hz), 7.0—7.6 (4H, m), and 7.36 (1H, t, J=2 Hz). δ(C)=34.8, 126.8, 131.9, 135.9, 138.7, 140.2, 146.0, 146.9, and 177.3. *m/z*, 242 and 244 (M^+). ν: 3100, 1615, 1580, 1310, 1140, and 800 cm^{-1}], and the recovered **16**, 85 mg (52%). On contact of **18** with water hydrolytic decomposition to an unidentifiable compound occurred.

Prolonged MCPBA-oxidation of 2-(2-Chloro-2-propenylsulfonyl)tropone (1). A $CHCl_3$ solution (2 cm^3) of **1** (106 mg) was kept at 15—20 °C for 95 h. The mixture was then washed with aqueous Na_2CO_3, and extracted with $CHCl_3$. The extracts were fractionated by PTLC to colorless needles, **20**, mp 45—46 °C, 9 mg (19%) [Found: C, 49.87; H, 4.15%. Calcd for $C_9H_9O_2SCl$: C, 49.88; H, 4.19%. δ=4.05 (2H, s), 5.34 (1H, d, J=1 Hz), 5.49(1H, d, J=1 Hz), and 7.4—8.0 (4H, m). δ(C)=64.6, 121.8, 128.5, 128.7, 129.1, 134.1, and 137.7. *m/z*, 216 and 218 (M^+)], and the recovered **1**, 50 mg (47%).

Alternative Preparation of 20. An EtOH solution (5 cm^3) of benzenethiol (119 mg) was mixed with 2,3-dichloropropene (106 mg) and refluxed for 2 h. The mixture containing **20** thus formed was then evaporated, dissolved in $CHCl_3$ (5 cm^3), and kept at 15—25 °C for 24 h with MCPBA (550 mg, 2.5 mol equiv). The colorless needles (20.7 mg, 97%) were identical with **20** in respects of mp, mass, and NMR spectra.

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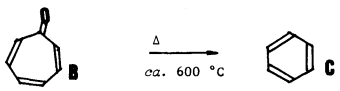

Scheme 4.

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