The Reaction of Sulfur Dichloride with *o*-Divinylbenzene

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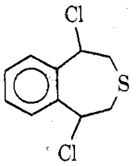
Several investigations on the addition of sulfenyl chlorides to alkyl-substituted terminal olefins have concluded that steric factors control the direction of ring opening of the cyclic thiiranium cation by chloride, thus resulting in anti-Markovnikov products.[2-5] However, the product ratio can be drastically changed by the presence of a phenyl group. For example, styrene, which is capable of forming a benzyl cation, affords Markovnikov addition products with greater than 98% selectivity.[6,7] We have investigated the reaction of *o*-divinylbenzene with sulfur dichloride[8] in anticipation of forming the cyclic dichlorosulfide (**1**). The dehydrohalogenation of **1** was viewed as a likely route to the unknown benzo[*d*]thiepin, a molecule for which extensive MO calculations have recently been reported.[9]



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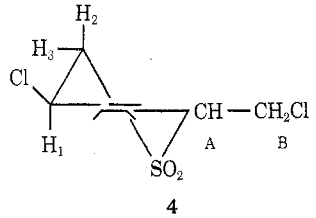
Under high dilution conditions, simultaneous addition of sulfur dichloride and *o*-divinylbenzene (**2**) affords a 98% yield of an unstable product whose complex, unsymmetrical nmr spectrum (see Experimental Section) strongly suggests a mixture of cis and trans isomers of 3,4-dihydro-1-chloromethyl-4-chloro-1*H*-2-benzothiopyran (**3**) (Scheme I). Oxidation of **3** with *m*-chloroperbenzoic acid yielded the sulfone (**4**) in 90% yield as a mixture of cis and trans isomers from which a single isomer (**4a**, mp 98–100°) could be isolated by fractional recrystallization. The structure of **4a** was deduced from nmr analysis (*vide infra*).



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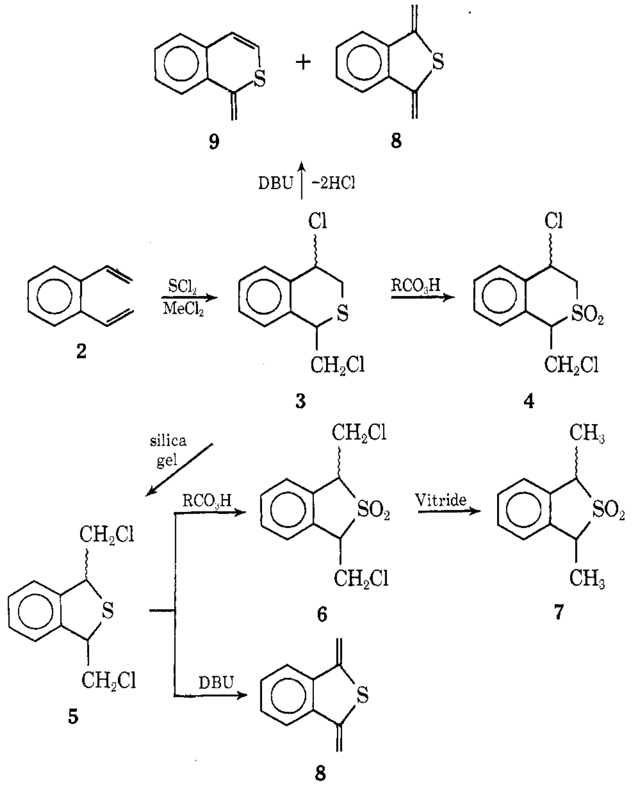
SCHEME I



The nmr spectrum of **4a** shows a clean doublet for H_B at δ 3.82 and a triplet for H_A centered at 5.61 (J_{AB} = 6.0 Hz). Irradiation at δ 5.61 collapses the doublet to a singlet at δ 3.82. H_1 appears as a doublet of doublets centered at δ 4.85 which collapses to a doublet with irradiation at H_2 or H_3. H_2 and H_3 appear as two overlapping doublets of doublets which simplify to two doublets centered at δ 4.40 and 4.15 with irradiation at H_1 ($J_{1,2}$ = 6.6, $J_{1,3}$ = 4.0, and $J_{2,3}$ = 11.5 Hz).

Upon standing at room temperature **3** rearranges to a mixture of **3** and an isomer (**5**). Complete destruction of **3** can be affected by percolation of a solution of **3** through a silica gel column, a procedure which yields **5** (cis–trans isomer mixture) as the sole isolable product. The nmr spectrum [two doublets at δ 3.82 and 3.84 (4 H), two triplets at 4.60 and 4.80 (2 H) (J = 6 Hz)] does not by itself allow conclusive differentiation between **5** and **1**.

Structure **1** was ruled out through peracid oxidation of **5** to sulfone **6** (85% yield), followed by reductive dechlorination (Vitride) to **7**. The nmr spectrum of **7** showed two methyl doublets [δ 1.61 and 1.59 (J = 7 Hz)] thereby eliminating structure **1** from consideration and establishing the dihydrobenzo[*c*]thiophene system (**5**) as the rearrangement product from **3**.

Additional evidence for the proposed structures is found in the DBU dehydrochlorination of a mixture of cis and trans isomers of **5** to cleanly provide only one unsaturated product, **8**. While the extreme instability of neat **8** precluded isolation, the nmr spectrum [δ 5.24 (d, 2 H); (5.78, (d, 2 H, J_{gem} = ~1 Hz); (7.50 (m, 4 H)] was

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[1] Gulf Oil Predoctoral Fellow, 1971–1972.

[2] F. Lautenschlager, *J. Org. Chem.*, **33**, 2620 (1968).

[3] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **88**, 2866 (1966).

[4] G. M. Beverly and D. R. Hogg, *Chem. Commun.*, 138 (1966).

[5] We adopt the usual convention of "Markovnikov" indicating addition of the chlorine on a secondary or tertiary carbon atom and "anti-Markovnikov" addition of the chlorine on the terminal carbon.

[6] W. H. Mueller and P. E. Butler, *J. Amer. Chem. Soc.*, **90**, 2075 (1968).

[7] For a review of thiiranium ions, see W. H. Mueller, *Angew. Chem., Int. Ed. Engl.*, **8**, 482 (1969).

[8] For reviews of diolefin–sulfur dichloride additions, see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, p 1121, and Vol. 2, 1969, p 391.

[9] M. J. S. Dewar and N. Trinajstic, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

unambiguous. Similar treatment of **3** with DBU afforded **9** along with **8**, the latter presumably arising from partial isomerization of **3** to **5** under the reaction conditions.

The isomerization of **3** to **5** has precedence in the literature from alkyl-substituted, linear diolefins which rearrange through thiiranium ions with the ring-size preference 5 > 6 > 7.[10] The finding that the six-membered-ring sulfide (**3**) is the initially observed product, therefore, does not rule out the possibility that **1** is the initial product. Indeed our results do not deny the possibility of initial formation of **1**, rearrangement to **3**, and a slower rearrangement to **5**. However, attempts to observe **1** under quite mild conditions have been uniformly unsuccessful.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. Proton nmr spectra were determined on a Varian Model A-60 or a Hitachi R20-B spectrometer for decoupling studies using TMS as an internal standard. Mass spectra were obtained on an Atlas CH-4 spectrometer. All melting points are uncorrected. Elemental analyses were performed by Ilse Beetz, Kronach, West Germany. Commercial sulfur dichloride (Matheson Coleman and Bell) was purified as previously described.[11] *o*-Divinylbenzene was prepared by the method of Hauser[12] and purified by distillation at 56–58° (8 Torr).

Addition of Sulfur Dichloride to *o*-Divinylbenzene. 3,4-Dihydro-1-chloromethyl-4-chloro-1*H*-2-benzothiopyran (**3**).—Solutions of *o*-divinylbenzene (6.90 g, 53 mmol) and freshly distilled sulfur dichloride (5.46 g, 53 mmol) in 125 ml of dry methylene chloride were simultaneously added to 125 ml of stirred methylene chloride. The addition was completed after 1 hr and the solvent was removed *in vacuo* to afford 12.0 g (98.2%) of yellow oil (**3**), which was allowed to stand at room temperature. The nmr spectrum then revealed that rearrangement to a mixture of **3** and **5** had occurred, thus necessitating the immediate use of **3** in subsequent experiments: ir (film) 1490, 1445, 1300, 1255, 1025, 770, 740 cm^{-1}; nmr ($DCCl_3$) δ 7.20 (m, 4 H), 5.24–5.68 (m, 1 H), 2.80–4.22 (m, 5 H); mass spectrum *m/e* 232 (M^+), 234 (70% of M^+).

Oxidation of 3 with *m*-Chloroperbenzoic Acid. 3,4-Dihydro-1-chloromethyl-4-chloro-1*H*-2-benzothiopyran 2,2-Dioxide (**4**).—To a solution of **3** (2.17 g, 9.3 mmol) in 5 ml of chloroform was added dropwise 3.77 g (18.6 mmol) of 85% *m*-chloroperbenzoic acid in 50 ml of chloroform over a period of 5 min. After 1 hr, *m*-chlorobenzoic acid was removed by filtration and the filtrates were washed with 10% sodium sulfite until neutral to KI solution. Excess acid was removed by extraction with 5% sodium bicarbonate and the chloroform layer was dried over $MgSO_4$. Removal of solvent *in vacuo* afforded 2.0 g (81.9%) of *cis*- and *trans*-**4** as a colorless oil which solidified upon standing. Repeated recrystallization from chloroform–ether yielded a white solid, mp 98–100°, as one pure isomer (**4a**): ir (KBr) 1140, 1330 cm^{-1}; nmr ($DCCl_3$) δ 3.82 (d, 2 H), 5.61 (t, 1 H), 4.85 (q, 1 H), 4.19–4.34 (2 d, 2 H), 7.50 (s, 4 H); mass spectrum *m/e* (rel intensity) 264 (45, M^+), 266 [31, ($M + 2^+$)], 228 (80, M − HCl), 200 (63, M − $HClSO_2$), 165 (100, M − $C_2H_5Cl_2SO_2$).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2S$: C, 45.30; H, 3.80; Cl, 26.74; S, 12.09. Found: C, 45.45; H, 3.99; Cl, 26.75; S, 11.93.

Rearrangement of 3 to 1,3-Dihydro-1,3-bis(chloromethyl)-benzo[*c*]thiophene (**5**).—Compound **3** (2.3 g) was chromatographed on a 3 × 40 cm column of silica gel with elution by 3 l. of hexane. Concentration *in vacuo* left 1.47 g (63%) of a red liquid. A small fraction was distilled at 80° (0.1 Torr) to afford a colorless liquid for an analytical sample. Both the crude and purified samples had the same isomer ratio and were in all respects identical by nmr. (The ratio of isomers was approximately 70:30 by nmr, but severe overlap reduces the confidence level of this number.) The purified product darkens rather rapidly and must be stored under nitrogen at 0° in solution. The same conversion was found to occur on neutral alumina. An nmr spectrum of chromatographed material shows no evidence of **3**; ir (thin film), 450, 700, 750, 1435, 1455, 1480 cm^{-1}; nmr ($DCCl_3$) δ 3.82 and 3.84 (2 d, 4 H), 4.60 and 4.80 (2 t, 2 H, J = 6 Hz), 7.20 (symmetrical m, 4 H); mass spectrum *m/e* (rel intensity) 232 (6, M^+), 234 [4, ($M + 2^+$)], 183 (100, M − CH_2Cl), 134 (39, M − $C_2H_4Cl_2$).

Anal. Calcd for $C_{10}H_{10}Cl_2S$: C, 51.55; H, 4.32; Cl, 30.41; S, 13.75. Found: C, 51.74; H, 4.45; Cl, 30.32; S, 13.56.

Oxidation of 5 with *m*-Chloroperbenzoic Acid. 1,3-Dihydro-1,3-bis(chloromethyl)benzo[*c*]thiophene 2,2-Dioxide (**6**).—The procedure employed was identical with the oxidation of **3** (*vide supra*). From 0.410 g of **5** was obtained 0.390 g (85%) of yellow oil which was readily crystallized from methylene chloride–ether as a pale yellow solid: mp 117–119°; ir (KBr) 1490, 1330, 1150, 1120, 730, 540 cm^{-1}; nmr ($DCCl_3$), two doublets centered at δ 4.07 and 4.10 (4 H), a triplet at δ 4.60 (2 H), a singlet at 7.49 (4 H); mass spectrum *m/e* (rel intensity) 264 (35, M^+), 266 [24, ($M + 2^+$)], 200 (100, M − SO_2^+).

Anal. Calcd for $C_{10}H_{10}Cl_2O_2S$: C, 45.30; H, 3.80; Cl, 26.74; S, 12.09. Found: C, 45.46 H, 3.93; Cl, 26.71; S, 12.04.

Reduction of 6 with Vitride. 1,3-Dihydro-1,3-dimethylbenzo[*c*]thiophene 2,2-Dioxide (**7**).—To a solution of **6** (0.584 g, 2.2 mmol) in 50 ml of sodium-dried benzene was added 0.80 cc (2.8 mmol) of a 70% benzene solution of Vitride [$NaAlH_2(OCH_2CH_2OCH_3)_2$, Eastman Kodak] *via* syringe and the solution was refluxed for 12 hr. The reaction was cooled to 0° and neutralized with 20% H_2SO_4.

The benzene layer was separated, washed with 10 ml of H_2O, dried over K_2CO_3, and concentrated to 0.480 g of yellow oil: ir (film) 770, 1140, 1320 cm^{-1}; nmr ($DCCl_3$) δ 4.22 (q, 2 H), 1.61 and 1.59 (2 d, 6 H, J = 7 Hz), 7.3 (s, 4 H); mass spectrum *m/e* (rel intensity) 196 (14, M^+), 132 (100, M − SO_2); high resolution mass spectrum 196.057587 (observed), 196.055796 (calculated), 0.001791 (Δ).

Dehydrochlorination of 5 with DBU. 1,3-Bis(methylene)-benzo[*c*]thiophene (**8**).—To a solution of 0.870 g (3.73 mmol) of **5** in 30 ml of acetonitrile was added 1.07 g (7.04 mmol) of 1,5-diazobicyclo[5.4.0]undec-5-ene (DBU) in 3 ml of acetonitrile and this solution was stirred for 5 min. The reaction mixture was concentrated to ~2 ml, 20 ml of chloroform was added, and residual acetonitrile and DBU salts were removed by washing with water. The chloroform layer was dried over anhydrous potassium carbonate and concentrated under a nitrogen atmosphere. The structure assignment was based on the nmr spectrum since the instability of **8** precluded its purification despite numerous attempts. Oxidation of **8** with *m*-chloroperbenzoic acid in an attempt to obtain a stable sulfone derivative failed to afford an isolable product. The olefinic protons appeared as sharp peaks at δ 5.24 and 5.78 (each slightly split by geminal coupling, J = 1 Hz) and the aromatic protons as a symmetrical multiplet at 7.50.

Dehydrochlorination of 3 with DBU. 1-Methylene-2-benzothiopyran (**9**).—The procedure was the same as described above for the reaction of **5** with DBU. The isomeric diolefin **9** was also unstable to isolation, and its structure was based on the appearance of four olefinic peaks at δ 5.15, 5.50, 6.42, and 6.48. The two olefinic peaks of **8** were also observable.

Registry No.—**2**, 91-14-5; *cis*-**3**, 36736-00-2; *trans*-**3**, 36736-01-3; *cis*-**4**, 36736-02-4; *trans*-**4**, 36736-03-5; *cis*-**5**, 36736-04-6; *trans*-**5**, 36736-05-7; *cis*-**6**, 36736-06-8; *trans*-**6**, 36736-07-9; *cis*-**7**, 36736-08-0; *trans*-**7**, 36736-09-1; **8**, 36740-03-1; **9**, 36740-04-2; sulfur dichloride, 10545-99-0.

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[11] T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970).

[12] C. F. Hauser, *ibid.*, **28**, 372 (1963).