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Chlorosulfenylation–Dehydrochlorination Reactions. New and Improved Methodology for the Synthesis of Unsaturated Aryl Sulfides and Aryl Sulfones

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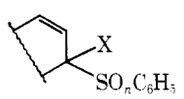
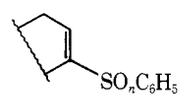
An improved procedure has been developed for the chlorosulfenylation of olefins. The method utilized is based on the quantitative reaction of aryl thiols with *N*-chlorosuccinimide to afford a reagent solution (A) which contains arylsulfenyl chloride as well as the "inert" co-product succinimide. Reaction of this reagent with a representative group of olefins (ethylene, cyclopentene, cyclohexene, cycloheptene, norbornene, butadiene, cyclohexadiene, Δ^2-cholestene, 1,2-dimethylcyclohexene, 1-methylcyclohexene, and 3-sulfolene) generates β-chlorophenyl sulfides in nearly quantitative yield. Aryl-substituted olefins react with reagent A in the presence of sodium carbonate to produce allylic or vinylic sulfides. The β-chloroaryl sulfides produced in the chlorosulfenylation reaction can be dehydrohalogenated with DBU to yield allyl, vinyl, or dienyl sulfides. Alternatively, the β-chloro sulfides can be oxidized to β-chloro sulfones, which may then be dehydrochlorinated with DBU under very mild conditions to afford excellent yields of α,β-unsaturated sulfones.

Unsaturated sulfur systems are valuable weapons in the arsenal of the synthetic organic chemist. Deprotonation reactions, fostered by the propensity of the sulfur moiety to stabilize an adjacent negative charge of allyl sulfides[3,4] (**1a**), allyl sulfoxides[4] (**1b**), and allyl sulfones[5,6] (**1c**), provide thioallylic anions (**2a–c**) of exceptional synthetic utility. A



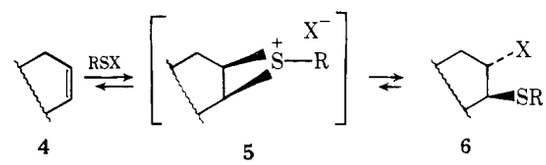
1a, X = H; n = 0
b, X = H; n = 1
c, X = H; n = 2
2a, X = Li; n = 0
b, X = Li; n = 1
c, X = Li; n = 2



3a, n = 0
b, n = 1
c, n = 2

related area of growing interest involves the chemistry of vinyl sulfides[7–9] (**3a**), sulfoxides[8] (**3b**), and sulfones[10] (**3c**). In connection with our synthetic program, we have been investigating methods of producing several of these unsaturated sulfur systems (**1**, **3**) based upon chlorosulfenylation–dehydrochlorination reactions.

The reaction of aryl- and alkylsulfenyl halides with olefins (**4**) to produce *trans*-β-haloaryl (alkyl) sulfides (**6**) is a very well-known process.[11] The reaction proceeds through an episulfonium salt intermediate (**5**)[12] which yields products



4 **5** **6**

R = aryl or alkyl

usually resulting from predominant or exclusive attack of the halide ion at the more positively polarized carbon atom.[11,13–16] The β-halo sulfides so formed have been shown to undergo retrosulfenylation reactions (at elevated temperatures) as well as secondary rearrangements.[16–18] The facility with which these rearrangements occur is directly related to the electron

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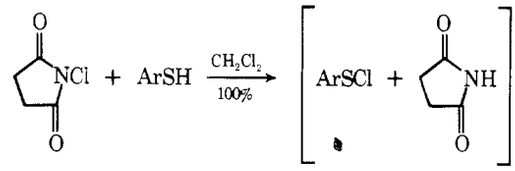
density on sulfur, the β-haloalkyl sulfides being far more labile.[17]

The greater stability of β-haloaryl sulfides, coupled with their higher molecular weight (better crystallinity, lower odor), fostered our decision to limit our initial investigation to the chemistry of arylsulfenyl chlorides. As previously indicated, the reaction of olefins with phenylsulfenyl chloride has been shown to produce 1:1 adducts in excellent yield.[11] A major synthetic disadvantage which accompanies this reaction as traditionally conducted stems from the inconvenience which attends the isolation and purification of the hygroscopic arylsulfenyl halides[11,19] (particularly in multimolar quantities).

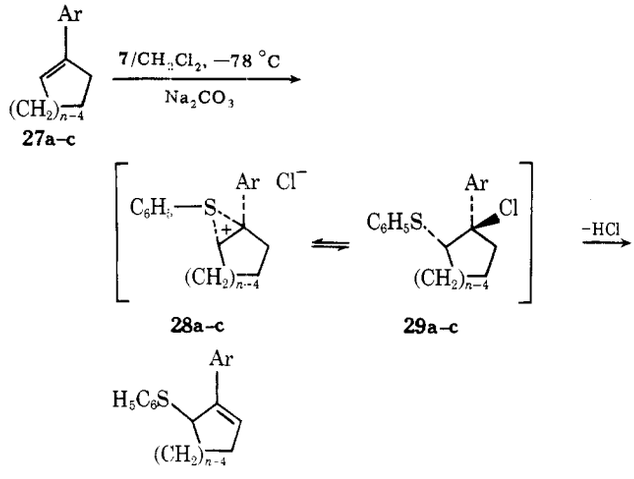
We find that the difficulties associated with manipulations of arylsulfenyl chlorides can be completely avoided simply by generating and subsequently using the reagent in a methylene chloride solution. The reagent **7** is prepared by a modification



7

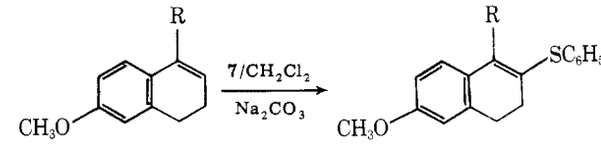
of the method of Harpp[19] via the quantitative reaction of the aryl thiol with a suspension of *N*-chlorosuccinimide in methylene chloride. The chlorosulfenylation reaction is normally conducted by simply adding the olefinic substrate to the reagent solution (−78 °C) and allowing the reaction to warm to room temperature; aryl-substituted olefins are best sulfenylated by the inverse addition mode. The co-product, succinimide, which is produced in the reagent generation step, is conveniently removed (usually by filtration) at the stage of isolation of the β-chlorophenyl sulfide. The β-chlorophenyl sulfides thus prepared are produced in excellent yields and can usually be used in subsequent reactions without any purification (see Table I).

Reaction of phenylsulfenyl chloride with 1-phenylcyclohexene (**27a**) generates adduct **29a** which is too labile to be



conveniently isolated and purified. Therefore, a modified procedure was developed for chlorosulfenylation–dehydrochlorination of aryl-substituted olefins. In these instances, the phenylsulfenyl chloride reagent solution (**7**) is added to a cooled methylene chloride solution of olefins **27a–c** containing excess anhydrous sodium carbonate. This expedient directly affords allylic sulfides **30a–c**.

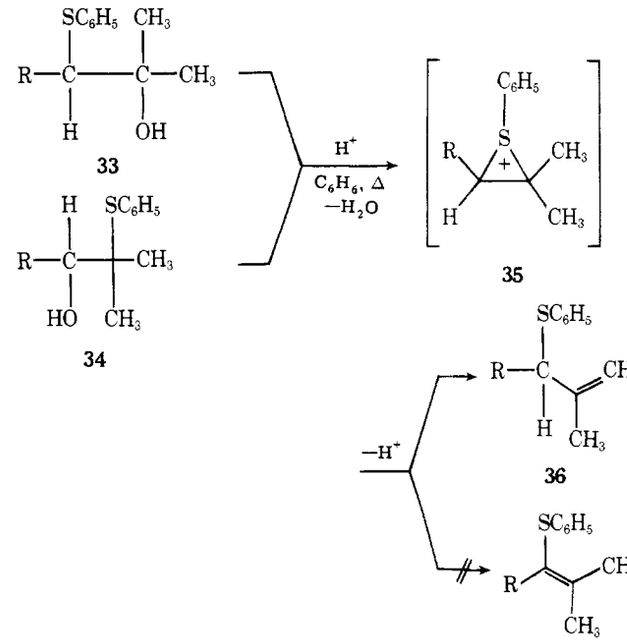
Chlorosulfenylation–dehydrochlorination of dihydronaphthol derivatives **31a,b** under the same reaction conditions produce vinylic sulfides **32a,b**.



31a, R = H
31b, R = CH_3

32a, R = H; 80%
32b, R = CH_3; 99%

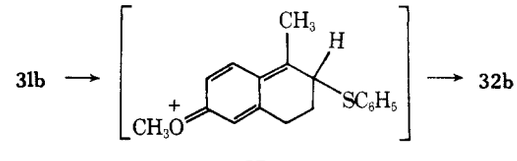
Although a proper mechanistic understanding of the factors which determine the production of allylic vs. vinylic sulfides in these reactions must necessarily await further experimental investigation, several points are worthy of mention. Trost[21] and Warren[22] have shown that dehydration of β-hydroxy sulfides **33**[21] and **34**[22] affords only allylic sulfide **36**, possibly



because the external C–H bonds are more easily able to attain an anti periplanar relationship to the departing C–S bond in episulfonium ion intermediate **35**.[22] Analogous allylic sulfides are formed from β-haloalkyl sulfides.[23]

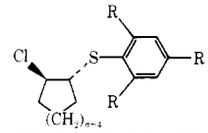
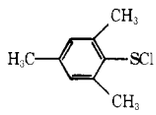
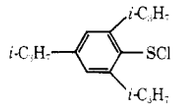
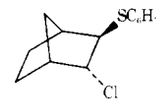
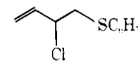
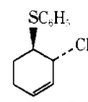
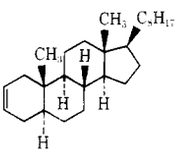
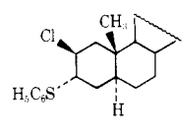
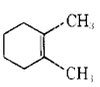
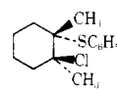
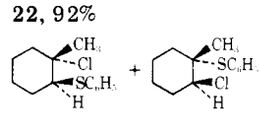
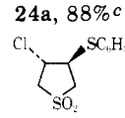
A similar rationale would seem to accommodate the formation of allylic sulfides **30a–c** through the intermediacy of ions **28a–c**. The difficulty of extending this analogy too far is rapidly seen in the case of aryl olefin **31b**. In this instance, the product **32b** is a vinylic sulfide.

It is tempting to invoke oxonium ion **37** as the progenitor of vinyl sulfide **32b**. A highly delocalized ion of this type would not be expected to gain much additional stabilization by formation of an episulfonium ion. Therefore, instead of tending to promote formation of allyl sulfide via an episulfonium ion, the "free" aryl sulfide moiety (of ion **37**) is available for α-CH acidification[24] which assists in formation of the observed vinyl sulfide **32b**. Clearly, the reactions of additional substrates



37

Table I

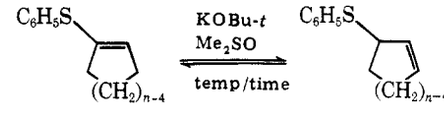
Olefin	Registry no.	In situ arylsulfenyl chloride	Registry no.	β-Chlorosulfide yield[a]	Registry no.
$CH_2{=}CH_2$ **8**	74-85-1	C_6H_5SCl	931-59-9	$ClCH_2CH_2SC_6H_5$ **9**, 98%	5535-49-9
 **10a** (n = 5)	142-29-0	C_6H_5SCl		 **11a** (n = 5; R = H), 99%	64741-03-3
10a (n = 5)			14575-12-3	**12a** (n = 5; R = CH_3), 98%	64741-04-4
10a (n = 5)			64741-02-2	**12b** (n = 5; R = i-C_3H_7), 80% (54%)[b]	64741-05-5
10b (n = 6)	110-83-8	C_6H_5SCl		**11b**[20] (n = 6; R = H), 96%	51704-77-9
10c (n = 7)	628-92-2	C_6H_5SCl		**11c** (n = 7; R = H), 100%	64741-06-6
 **13**	498-66-8	C_6H_5SCl		 **14**,[14] 99%	13204-36-9
 **15**	106-99-0	C_6H_5SCl		 **16**,[16] 100%	16728-08-8
 **17**	592-57-4	C_6H_5SCl		 **18**, 100%	64741-07-7
 **19**	570-73-0	C_6H_5SCl		 **20**,[18] 55%[b]	17150-04-8
 **21**	1674-70-8	C_6H_5SCl		 **22**, 92%	64741-08-8
 **23**	591-49-1	C_6H_5SCl		 **24a**, 88%[c] **24b**, 10%[c]	
 **25**	77-79-2	C_6H_5SCl		 **26**,[29] 81%[b]	15507-87-6

[a] Yield refers to "crude" material of >95% purity. [b] Recrystallized material. [c] Obtained by thermal equilibration of an original 3:1 mixture of **24a/24b**. Registry no: **24a**, 64741-09-9; **24b**, 64741-10-2.

must be examined to test the validity of these hypotheses.[25]

Less activated β-chloroaryl sulfides may also be conveniently dehydrochlorinated by briefly heating with the amidine base 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU).[26,27]

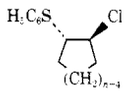
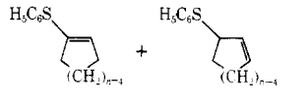
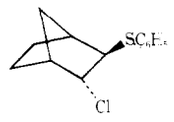
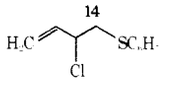
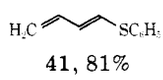
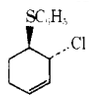
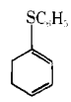
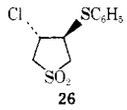
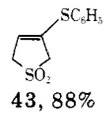
As can be seen in Table II, although the β-chlorocyclohexyl phenyl sulfide (**11b**) yields almost exclusively the allyl sulfide **40b**, the dehydrochlorination reactions of the cyclopentyl and cycloheptyl derivatives are nonspecific, producing about an equal mixture of vinyl (**39a,c**) and allyl sulfides (**40a,c**). The products **39a–c** and **40a–c** were individually resubjected to the conditions of this reaction and were recovered unchanged (see Experimental Section). Furthermore, the equilibrium (**39** ⇄ **40**) was established by potassium *tert*-butoxide/dimethyl sulfoxide[21] treatment of allyl isomers **40a–c**. The finding that



39a–c **40a–c**

a (n = 5) 90%	60 °C/4 h	10%
b (n = 6) 92%	25 °C/20 h	8%
c (n = 7) 92%	60 °C/2 h	8%

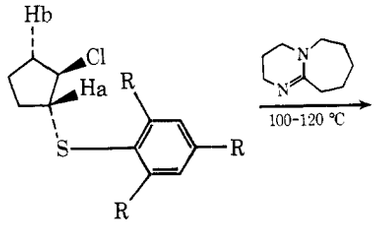
Table II

β-Chloro sulfide	DBU temp/time	Olefin, yield[a]	Registry no.
$ClCH_2CH_2SC_6H_5$ **9**	100 °C/0.25 h	$H_2C{=}CHSC_6H_5$ **38**, 88%	
			
11a (n = 5)	120 °C/3 h	**39a**, 40%[b] **40a**, 40%[b]	
11b (n = 6)	120 °C/9 h	**39b**, 4%[b] **40b**, 77%[b]	
11c (n = 7)	120 °C/9 h	**39c**, 36%[b] **40c**, 24%[b]	
 **14**	170 °C/1 h	No reaction (91%, **14** recovered)	
 **16**	100 °C/0.2 h	 **41**, 81%	53097-28-2
 **18**	100 °C/0.2 h	 **42**, 73%	64691-42-5
 **26**	−40 °C/2 h $CHCl_3$	 **43**, 88%	64741-13-5

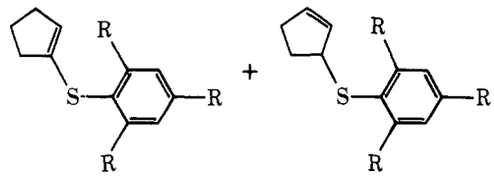
[a] Yield refers to isolated material of >95% purity. [b] Registry no: **39a**, 37053-16-0; **39b**, 4922-47-8; **39c**, 64741-11-3; **40a**, 3467-68-3; **40b**, 3467-73-0; **40c**, 64741-12-4.

the vinyl sulfide predominates at equilibrium is in accord with previous observations by Trost[21] et al. and O'Connor and Lyness.[28]

Having established that the **39/40** product mixture was a kinetic one, we felt that ortho substitution of the aryl sulfide moiety should favor production of the allylic isomer by retarding approach of the DBU to the methine hydrogen H_a relative to the *trans*-β-chloro hydrogen H_b. To this end, we compared the DBU-induced dehydrochlorination reaction of β-chloroaryl sulfides **12a** and **12b** with the parent β-chlo-



11a, R = H
12a, R = CH_3
12b, R = i-C_3H_7



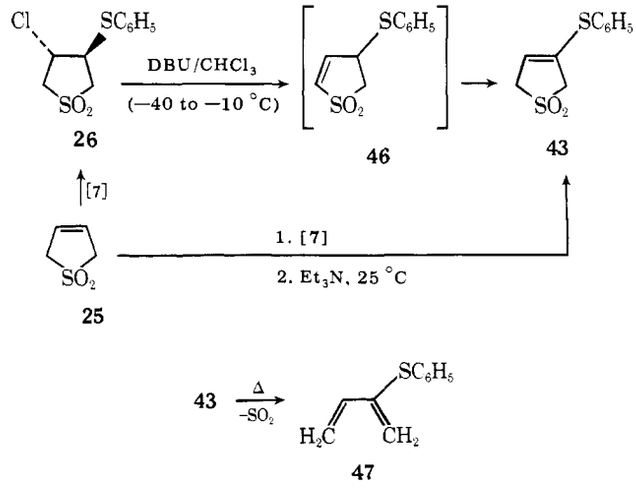
39a, 50%
44a, 20%
44b, 20%

40a, 50%
45a, 80%
45b, 80%

rophenyl sulfide **11a**. While the ratio changes are in the desired direction, at this point the added selectivity is not sufficient to be synthetically useful.

The use of DBU for synthesis of vinyl and dienyl sulfides is especially convenient. The conversion of chloro sulfide **16** to 1-thiophenylbutadiene **41** had been previously achieved by Evans et al. by utilization of potassium *tert*-butoxide as base.[8] Our experience with the *tert*-butoxide reaction indicates that considerable experimental care (freshly prepared *tert*-butoxide) is necessary to consistently achieve satisfactory results. Simple use of commercial DBU for this reaction has been far more rewarding. (See Table II).

A considerable improvement in the ease of synthesis of 3-thiophenyl-3-sulfolene (**43**) has also been achieved. Gundermann and Holtmann have used triethylamine in hot (90 °C) Me_2SO to convert chloride **26** to vinyl sulfide **43**.[29] We find the same transformation can be more cleanly achieved using DBU in chloroform at −40 to −10 °C. The reaction proceeds through the intermediacy of isomer **46** which is further deconjugated to vinyl sulfide **43**.[29] Moreover, we further find that

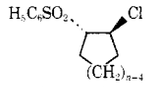
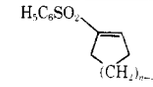
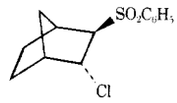
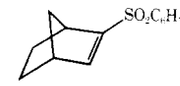
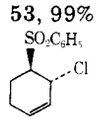
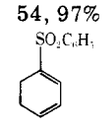
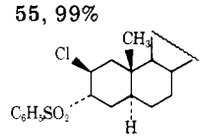
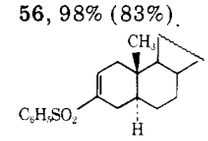
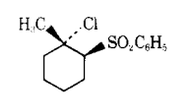
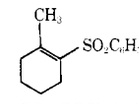


26 **46** **43**

25

47

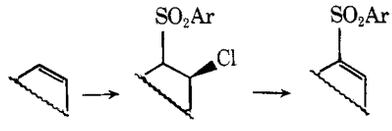
Table III

β-Chloro sulfide	$\xrightarrow{RCO_3H}$ R =	β-Chloro sulfone, yield	Registry no.	$\xrightarrow{DBU}$ solvent/temp/time	α,β-Unsaturated Sulfone, yield (recrystallized yield)	Registry no.
						
11a (n = 5)	3-ClC_6H_4	51a (n = 5), 99%	64741-14-6	CH_2Cl_2/0 °C/0.5 h	52a, 100% (86%)	64740-90-5
11a (n = 5)	CH_3	51a (n = 5), 93%				
11b (n = 6)	3-ClC_6H_4	51b (n = 6), 99%	33995-48-1	CH_2Cl_2/0 °C/0.5 h	52b, 98% (81%)	59059-70-0
11b (n = 6)	CH_3	51b (n = 6), 85%				
11c (n = 7)	3-ClC_6H_4	51c (n = 7), 99%	64740-86-9	CH_2Cl_2/0 °C/0.5 h	52c, 99% (84%)	64740-91-6
11c (n = 7)	CH_3	51c (n = 7), 90%				
14	3-ClC_6H_4			$CHCl_3$/61 °C/0.25 h		
		53, 99%	64740-87-0		54, 97% (68%)	64740-92-7
18	3-ClC_6H_4			CH_2Cl_2/25 °C/0.25 h		
		55, 99%	64740-88-1		56, 98% (83%)	26211-03-0
20	3-ClC_6H_4			CH_2Cl_2/25 °C/1 h		
		57, 96%	17150-06-0		58, (93%)	64740-93-8
24a/24b	3-ClC_6H_5			CH_2Cl_2/40 °C/1.5 h		
		59, 63%[a]	64740-89-2		60, 99% (oil)	64740-94-9

[a] Recrystallized yield, based on amount of 2-chloro-2-methyl-1-cyclohexenylphenyl sulfide in the original 24a/24b mixture.

43 may be synthesized (2.5-mol scale) in a one-pot chlorosulfenylation–dehydrochlorination reaction (using the less expensive triethylamine as the base) in an overall yield of 85% from sulfolene (25). Sulfolene 43 is an excellent source of 2-thiophenylbutadiene 47[29] (and related compounds[30]) via thermolytic SO_2 extrusion reactions.[31]

The conversion of olefins 48 to α,β-unsaturated aryl sulfones 50 has been accomplished in a two-step sequence: (1)



48 49 50

Cu-catalyzed chlorosulfonylation followed by (2) dehydrochlorination of the β-halo sulfone (49) with triethylamine (often at elevated temperature).[32]

In view of several of our eventual applications for natural product synthesis, we felt that a milder and higher overall yield procedure could be developed based on the kinetic work of Goering.[33] He found that β-halophenyl sulfides could be oxidized to sulfones 49 and then subsequently dehydrochlorinated (to 50) with aqueous hydroxide ion by an E1cB mechanism.[33]

We find that simply oxidizing the "crude" β-chloroaryl sulfides from the chlorosulfenylation reaction with m-chloroperoxybenzoic acid provides β-halo sulfones in essentially quantitative yield. [For preparative purposes (>0.4-mol scale), we employ the more economical peracetic acid in the oxidation step]. Dehydrochlorination of these β-halo sulfones with DBU smoothly generates the unsaturated sulfones in outstanding overall yield (see Table III).

Experimental Section

General. Melting points were taken on a Fisher-Johns melting-point apparatus. All melting and boiling points are uncorrected. Infrared spectra were recorded neat or as a melt on a Perkin-Elmer Infracord or 137 spectrophotometer. NMR spectra were determined in chloroform-d_1 solution on a Varian A60A or Perkin-Elmer R-32 spectrometer; chemical shifts are reported in δ with tetramethylsilane as an internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Coupling constants are given in hertz. Mass spectra were recorded on CEC-21-110-B high-resolution mass spectrometer at an ionizing voltage of 70 eV and an ionizing current of 100 μA. Exact mass determinations were obtained on the CEC-21-110-B instrument.

All experiments were carried out under a positive pressure of dry nitrogen. During workup of the reactions, anhydrous magnesium sulfate was used for general solvent drying. Precoated thin-layer Sil G-25 UV_{254} plates were obtained from Brinkman Instruments, Inc.; thick-layer plates were made from silica gel PF-254 containing $CaSO_4$ from EM reagents. Products were recovered from the silica gel by washing with ethyl acetate.

Preparation of Arylsulfenyl Chloride Solutions: Phenylsulfenyl Chloride. The highly unpleasant odor of volatile aryl thiols necessitates that this reaction be conducted in a well-ventillated hood. To a rapidly stirred suspension of 68.1 g (0.510 mol) of N-chlorosuccinimide[34] in 500 mL of dry methylene chloride at room temperature in a 1-L flask equipped with a pressure-equalizing dropping funnel, thermometer, and an efficient water-cooled condenser was added about 5 g of a total 55.1 g (0.500 mol) of thiophenol.[34] Initiation of sulfenyl chloride formation is indicated by the intense orange coloration of the suspension accompanied by gentle boiling of the solvent. Gentle heating on a steam bath for 1 to 2 min may be required to initiate the reaction. Addition of substantially larger quantities of thiophenol prior to initiation will invariably result in an uncontrollably exothermic initiation. Once initiated, the reaction vessel was immersed in an ice bath and the remaining thiophenol added dropwise at a rate sufficient to maintain the solvent at reflux, the addition requiring approximately 15 min. When the addition was complete, the ice bath was immediately removed and the homogeneous orange so-

lution was stirred at room temperature for an additional 30 min. During this time, succinimide precipitated in most runs. The resulting solution contains 0.500 mol of phenylsulfenyl chloride.

Appropriate changes in reagent quantities in the above procedure have allowed convenient preparation of from 30 μmol to 2.5 mol of arylsulfenyl chloride solutions in methylene chloride. Preparation of less than 25 mmol of arylsulfenyl chloride may be accomplished without a dropping funnel, internal thermometer, or reflux condenser via slow syringe addition of thiophenol to a suspension of *N*-chlorosuccinimide in methylene chloride. This procedure has also been used to prepare solutions of 2,4,6-trimethylphenylsulfenyl chloride and 2,4,6-triisopropylphenylsulfenyl chloride from the corresponding thiols.[35]

The subsequently described solutions of arylsulfenyl chlorides are all generated in the manner described above and necessarily contain an equimolar quantity of succinimide, which is removed during reaction workup.

Preparation of 2-Chloroethyl Phenyl Sulfide (9). Ethene (**8**)[36] was bubbled through a solution of 2.00 mmol of phenylsulfenyl chloride at room temperature until the solution was colorless. Concentration in vacuo, stirring for 1 h with 1 mL of carbon tetrachloride, filtration, and concentration of the filtrate in vacuo gave rise to 0.34 g (98%) of **9** as a colorless oil: NMR δ 7.1–7.4 (m, 5 H), 3.4–3.9 (m, 2 H), 2.9–3.3 (m, 2 H). M^+ Calcd for C_8H_9ClS: 172.011. Found: 172.012.

Preparation of *trans*-2-Chloro-1-cyclopentyl Phenyl Sulfide (11a). A solution of 0.600 mol of phenylsulfenyl chloride was cooled to −50 °C and 42.6 g (0.625 mol) of cyclopentene (**10a**)[34] was added rapidly via a dropping funnel. The orange solution was instantly decolorized upon completion of the addition. The temperature rose to 0 °C during the addition, and the cold, colorless solution was filtered to remove the majority of the succinimide as a white solid, which was washed with 50 mL of methylene chloride. Concentration of the combined filtrates in vacuo afforded a light yellow oil to which 200 mL of carbon tetrachloride was added to precipitate the last traces of succinimide. This solution was stirred for 1 h and then filtered, and the filtrate was concentrated in vacuo to yield 126.9 g (99%) of **11a** as an oil: NMR δ 7.1–7.5 (m, 5 H), 4.1–4.4 (m, 1 H), 3.6–4.0 (m, 1 H), 1.4–2.7 (m, 6 H). M^+ Calcd for $C_{11}H_{13}ClS$: 212.043. Found: 212.042.

Preparation of *trans*-2-Chloro-1-cyclopentyl 1-(2,4,6-Trimethyl)phenyl Sulfide (12a). To a solution of 5.0 mmol of 2,4,6-trimethylphenylsulfenyl chloride at −78 °C was added via syringe 0.375 g (5.5 mmol) of cyclopentene (**10a**).[34] The mixture was allowed to warm to room temperature and concentrated in vacuo. The residue was diluted with 5 mL of carbon tetrachloride, stirred for 1 h, and filtered to remove the succinimide as a white solid. Concentration of the filtrate in vacuo afforded 1.25 g (98%) of **12a** as a colorless oil: NMR δ 6.9 (brs, 2 H), 4.1 (m, 1 H), 3.5 (m, 1 H), 1.4–2.8 (m, 6 H), 2.5 (s, 6 H), 2.3 (s, 3 H). M^+ Calcd for $C_{14}H_{19}ClS$: 254.090. Found: 254.089.

Preparation of *trans*-2-Chloro-1-cyclopentyl 1-(2,4,6-Triisopropyl)phenyl Sulfide (12b). To a solution of 5.00 mmol of 2,4,6-triisopropylphenylsulfenyl chloride at −78 °C was added via syringe 0.375 g (5.5 mmol) of cyclopentene (**10a**).[34] The mixture was allowed to warm to room temperature and poured in 100 mL of ether. The organic layer was extracted with 25 mL of water, followed by 25 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded 1.36 g (80%) of a solid which was recrystallized from pentane to yield 0.92 g (54%) of **12b** as a white solid: mp 80.5–82 °C; NMR δ 7.0 (s, 2 H), 4.1 (m, 1 H), 3.9 (m, 2 H), 3.5 (m, 1 H), 2.8 (m, 1 H), 1.5–2.8 (m, 6 H), 1.2 (m, 18 H). M^+ Calcd for $C_{20}H_{31}ClS$: 338.184. Found: 338.185.

Preparation of *trans*-2-Chloro-1-cyclohexyl Phenyl Sulfide (11b).[20] In the procedure for the preparation of **11a**, 51.3 g (0.625 mol) of cyclohexene (**10b**)[34] was used in place of cyclopentene to afford 131.0 g (96%) of **11b** as a light yellow oil: NMR δ 7.2–7.5 (m, 5 H), 3.8–4.2 (m 1 H), 3.1–3.5 (m, 1 H), 1.2–2.6 (m, 8 H). M^+ Calcd for $C_{12}H_{15}ClS$: 226.058. Found: 226.056.

Preparation of *trans*-2-Chloro-1-cycloheptyl Phenyl Sulfide (11c). In the procedure for the preparation of **11a**, 61.8 g (.610 mol) of 95% cycloheptene (**10c**)[34] was substituted for cyclopentene. Workup gave 147.5 g (102%) of **11c** as a crude oil, presumably contaminated with impurities present in the original cycloheptene: NMR δ 7.2–7.5 (m, 5 H), 4.2–4.4 (m, 1 H), 3.5–3.7 (m, 1 H), 1.2–2.3 (m, 10 H). M^+ Calcd for $C_{13}H_{17}ClS$: 240.074. Found: 240.075.

Preparation of *endo*-3-Chloro-*exo*-2-bicyclo[2.2.1]heptyl Phenyl Sulfide (14).[14] To a solution of 0.100 mol of phenylsulfenyl chloride at −78 °C was added via syringe a solution of 9.4 g (0.100 mol) of norbornylene (**13**)[34] in 50 mL of dry methylene chloride. The mixture was allowed to warm to room temperature and concentrated in vacuo. The resulting residue was diluted with 50 mL of carbon tetrachloride, stirred for 1 h, and filtered to remove the succinimide as a white solid. Concentration of the filtrate in vacuo afforded 23.6 g (99%) of **14** as an oil: NMR δ 7.1–7.5 (m, 5 H), 3.9–4.2 (dd, J = 4 and 4 Hz, 1 H), 3.0–3.2 (dd, J = 4 and 3 Hz, 1 H), 2.2–2.3 (m, 2 H), 1.2–2.2 (m, 6 H). M^+ Calcd for $C_{13}H_{15}ClS$: 238.058. Found: 238.058.

Preparation of 2-Chloro-3-buten-1-yl Phenyl Sulfide (16).[16] Freshly distilled 1,3-butadiene (**15**)[37] (5.4 g, 0.100 mol) cooled to −25 °C was added via syringe to a solution of 0.025 mol of phenylsulfenyl chloride at −78 °C. This mixture was allowed to warm to room temperature, concentrated in vacuo, diluted with 12.5 mL of carbon tetrachloride, and stirred for 1 h. Filtration and concentration of the filtrate in vacuo produced 4.95 g (100%) of **16** as an oil: NMR δ 7.1–7.5 (m, 5 H), 5.9 (ddd, J = 8, 8, and 18 Hz, 1 H), 5.2 (dd, J = 2 and 18 Hz, 1 H), 5.2 (dd, J = 2 and 8 Hz, 1 H), 4.4 (ddd, J = 6, 8, and 8 Hz, 1 H), 3.3 (dd, J = 6 and 14 Hz, 1 H), 3.2 (dd, J = 8 and 14 Hz, 1 H). M^+ Calcd for $C_{10}H_{11}ClS$: 198.027. Found: 198.028.

Preparation of *trans*-2-Chloro-3-cyclohexen-1-yl Phenyl Sulfide (18). In the preparation of **16**, 2.20 g (27.5 mmol) of 1,3-cyclohexadiene (**17**)[34] at room temperature was used in place of cold 1,3-butadiene. Workup afforded 5.6 g (100%) of **18**, a colorless oil: NMR δ 7.1–7.5 (m, 5 H), 6.7–6.9 (m, 2 H), 4.4–4.6 (m, 1 H), 3.5–3.8 (m, 1 H), 1.2–2.7 (m, 4 H). M^+ Calcd for $C_{12}H_{13}ClS$: 224.043. Found: 224.044.

Preparation of Δ^2-Cholestene (19). To a solution of 7.77 g (20 mmol) of dihydrocholesterol[38] and 2.78 g (27.5 mmol) of triethylamine[39] in 125 mL of methylene chloride at −20 °C was added dropwise, over a period of 15 min, 2.86 g (25 mmol) of methanesulfonyl chloride.[40] The mixture was allowed to warm to 0 °C and stirred for 1 h and then transferred to a separatory funnel and washed successively with 50 mL of 10% aqueous hydrochloric acid, 50 mL of water, and 50 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded 9.15 g (98%) of crude mesylate which was used without further purification: NMR δ 4.2–4.9 (m, 1 H), 3.0 (s, 3 H), 0.6–2.3 (m, 46 H).

A 7.00-g (15 mmol) portion of the crude mesylate was rapidly added to 4.6 g (30 mmol) of rapidly stirred DBU[34] at 150 °C. The mixture was stirred 0.5 h at this temperature and then cooled to room temperature, and 100 mL of 2% aqueous hydrochloric acid was added. This mixture was extracted with three 100-mL portions of ether and the combined organic layers were washed with 50 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded a colorless oil which was recrystallized from ethanol to yield 4.25 g (77%) of **19** as a white solid: mp 69.5–70.5 °C; NMR δ 5.6 (m, 2 H), 0.6–2.2 (m, 44 H).

Preparation of 3α-Phenylthio-2β-chlorocholestane (20).[18] A 1.48-g (4.00 mmol) portion of Δ^2-cholestene (**19**) was added to 4.0 mmol of phenylsulfenyl chloride solution at −50 °C. The mixture was decolorized over a period of 15 min. After complete decolorization, the solvent was concentrated in vacuo and the residue was stirred with 5.0 mL of carbon tetrachloride. Filtration and concentration of the filtrate in vacuo afforded **20** as a crude oil; recrystallization from acetone afforded 1.13 g (55%) of **20** as a colorless needles: mp 113.5–114.5 °C; NMR δ 7.3–7.5 (m, 5 H), 4.4 (m, 1 H), 3.7 (m, 1 H), 0.6–2.5 (m, 44 H).

Preparation of 2-Chloro-1,2-dimethylcyclohexyl Phenyl Sulfide (22). A solution of 0.83 g (0.75 mmol) of 1,2-dimethylcyclohexene (**21**)[41] in 3 mL of methylene chloride was added all at once to a solution of 0.75 mmol of phenylsulfenyl chloride at −78 °C. The mixture was diluted with 25 mL of ether, washed with 10 mL of water and then 10 mL of saturated aqueous sodium chloride, dried ($MgSO_4$), and concentrated in vacuo to yield 0.175 g (92%) of **22** as an oil: NMR δ 7.1–7.6 (m, 5 H), 1.1–2.5 (m, 8 H), 1.8 (s, 3 H), 1.3 (s, 3 H). M^+ Calcd for $C_{14}H_{19}ClS$: 254.090. Found: 254.090.

Chlorosulfenylation of 1-Methylcyclohexene (23). 1-Methylcyclohexene (**23**),[42] 5.0 g (52 mmol), was added via syringe to a solution of 0.050 mol of phenylsulfenyl chloride such that the temperature did not exceed −70 °C. Addition required about 15 min, after which time, the reaction was warmed to room temperature and concentrated in vacuo, and 25 mL of carbon tetrachloride was added. The mixture was stirred for 1 h and filtered, and the filtrate was concentrated in vacuo to afford 11.80 g (98%) of a product, which was demonstrated by NMR to be a 3:1 mixture of 2-chloro-2-methyl-1-cyclohexyl phenyl sulfide (**24a**) and 2-chloro-1-methyl-1-cyclohexyl phenyl sulfide (**24b**). This mixture was taken up in 50 mL of methylene chloride and heated under reflux for 1.5 h, to yield, after concentration in vacuo, a 90:10 mixture of **24a** and **24b**, respectively. This ratio was unchanged on further heating. The mixture was not separated: NMR δ 7.1–7.6 (m, 5 H), 3.8–4.0 (m, 1 H, due to **24b**), 3.3–3.6 (m, 1 H, due to **24a**), 1.2–1.3

(m, 11 H). M^+ Calcd for $C_{13}H_{17}ClS$: 240.074. Found: None. $M^+ - HCl$ Calcd for $C_{13}H_{16}S$: 204.097. Found: 204.098.

Preparation of *trans*-3-Chloro-4-phenylthiotetrahydrothiophene 1,1-Dioxide (26).[29] A 29.5-g (0.250 mol) portion of 2,5-dihydrothiophene 1,1-dioxide (**25**)[43] was added to a solution of 0.250 mol of phenylsulfenyl chloride at room temperature. This mixture was stirred for 48 h at room temperature then washed with 100 mL of water followed by 100 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded an orange oil which was crystallized from 9:1 (v/v) ether/hexane at 0 °C to yield 53.2 g (81%) of **26** as a white solid: mp 74.5–75.5 °C; NMR δ 7.1–7.6 (m, 5 H), 2.9–4.6 (m, 6 H). M^+ Calcd for $C_{10}H_{11}ClO_2S_2$: 261.989. Found: 261.988.

Preparation of Phenyl 2-Phenyl-2-cyclopenten-1-yl Sulfide (30b). A solution of 0.025 mol of phenyl sulfenyl chloride cooled to −78 °C was added dropwise via syringe over a period of 15 min to a rapidly stirred suspension of 13.25 g (0.125 mol) of anhydrous sodium carbonate in 25 mL of methylene chloride containing 3.61 g (0.025 mol) of 1-phenylcyclopentene (**27b**)[42] which was maintained at about −25 °C. The resulting suspension was then heated under reflux for a period of 24 h to complete the dehydrochlorination. After cooling to room temperature, the mixture was poured into 200 mL of ethyl acetate, and the organic layer was extracted twice with 100-mL portions of water and then with 50 mL of saturated aqueous sodium chloride solution, dried ($MgSO_4$), and concentrated in vacuo to afford 2.5 g (99%) of **30b** as an oil. This oil was recrystallized from ether to yield 5.0 g (79%) of **30b** as light brown cryrstals: mp 80.5–82 °C; NMR δ 7.2–7.7 (m, 10 H), 6.2 (m, 1 H), 4.5–4.7 (m, 1 H), 2.3–2.5 (m, 4 H). M^+ Calcd for $C_{17}H_{16}S$: 252.097. Found: 252.099.

Preparation of Phenyl 2-Phenyl-2-cyclohexen-1-yl Sulfide (30a). In the preparation of **30b,** 3.96 g (0.025 mol) of 1-phenylcyclohexene (**27a**)[34] was substituted for 1-phenylcyclopentene to afford, after recrystallization, 4.2 g (63%) of **30a** as light yellow crystals: mp 46–48 °C; NMR δ 7.2–7.6 (m, 10 H), 6.2 (m, 1 H), 4.3 (m, 1 H), 1.5–2.4 (m, 6 H). M^+ Calcd for $C_{18}H_{18}S$: 266.113. Found: 266.114.

Omission of the 24-h reflux period gave a product which decomposed at room temperature; the NMR showed, in addition to signals due to **30a,** a signal at δ 3.95 (m), which vanished upon the addition of an excess of DBU to the NMR sample with a corresponding increase in the intensity of the signals due to **30a**. The structure was thus assigned as **29a,** containing about 10 mol % **30a**.

Preparation of 1-(3,4-Methylenedioxy-6-[2′-*tert*-butyldimethylsiloxyethyl]phenyl)-5-phenylthio-1-cyclopentene (30c). To a solution of 0.20 mmol of phenylsulfenyl chloride rapidly stirred over 0.21 g (2.0 mmol) of anhydrous sodium carbonate cooled to −78 °C was added in one portion 0.069 g (0.20 mmol) of 1(3,4-methylenedioxy-6-[2′-*tert*-butyldimethylsiloxyethyl]phenyl-1-cyclopentene (**27c**).[44] The colorless suspension was filtered and the filtrate was chromatographed on silica (10% THF/hexane) to yield 0.060 g (66%) of **30c** as a colorless oil: NMR (in ppm relative to CH_3Si of TBDMS group) δ 7.1–7.3 (m, 5 H), 6.65 (s, 2 H), 5.85 (s, 2 H), 5.75 (brs, 1 H), 4.2–4.6 (m, 1 H), 3.7 (t, J = 7 Hz, 2 H), 2–2.9 (m, 6 H), 0.9 (s, 9 H), 0.0 (s, 6 H). M^+ Calcd for $C_{26}H_{34}O_3SSi$: 454.200. Found: 454.200.

Preparation of 6-Methoxy-3,4-dihydronaphthalene (31a).[45] A solution of 17.6 g (0.100 mol) of 6-methoxy-1-tetralone[34] in 300 mL of ether was added dropwise over a period of 0.5 h to a suspension of 3.8 g (.050 mol) of lithium aluminum hydride in 150 mL of ether, the temperature of the reaction mixture being maintained at 5 °C during the entire addition. After stirring an additional 15 min, 3.8 mL of water was added dropwise over a period of 0.5 h, followed by the cautious addition of 3.8 mL of 10% aqueous sodium hydroxide, and, finally, 10.5 mL of water. The mixture was stirred for 10 min and filtered to remove the aluminum salts, and the salts were washed with an additional 50 mL of ether.[46] The combined organic layers were washed with 100 mL of water and then with 100 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded 17.8 g (100%) of 6-methoxy-1,2,3,4-tetrahydro-1- naphthol as a light brown oil: NMR δ 7.3 (ddd, J = 9, 2, and 2 Hz, 1 H), 6.7 (ddd, J = 9, 2, and 2 Hz, 1 H), 6.6 (dd, J = 2 and 2 Hz, 1 H), 4.6 (m, 1 H), 3.75 (s, 3 H), 2.7 (m, 2 H), 1.4–2.2 (m, 5 H). M^+ Calcd for $C_{11}H_{14}O_2$: 178.099. Found: 178.100.

A solution of 16.93 g (0.095 mol) of the crude alcohol and 0.266 g (1.40 mmol) of *p*-toluenesulfonic acid monohydrate[34] in 0.5 L of benzene was heated under reflux for 0.5 h. (Longer reaction times and higher boiling solvents produced low yields of the desired olefin due to dimer formation.)[47] The mixture was cooled to room temperature, washed with 100 mL of water and 100 mL of saturated aqueous sodium chloride, and dried ($MgSO_4$). Concentration in vacuo gave 14.75 g (97%) of **31a** as an orange oil of sufficient purity for the subsequent chlorosulfenylation. Kugelrohr distillation of 0.860 g of this oil at 112 °C (0.6 mm) afforded 0.846 g of **31a** as a colorless oil, for a distilled overall yield of 95% from 6-methoxy-1-tetralone: NMR δ 6.9 (d, J = 9 Hz, 1 H), 6.65 (m, 2 H), 6.4 (m, 1 H), 5.85 (dt, J = 10 and 4 Hz, 1 H), 3.75 (s, 3 H), 2.75 (m, 2 H), 2.0–2.4 (m, 2 H). M^+ Calcd for $C_{11}H_{12}O$: 160.089. Found: 160.089.

Preparation of 6-Methoxy-2-phenylthio-3,4-dihydronaphthalene (32a). A solution of 5.0 mmol of phenylsulfenyl chloride cooled to −78 °C was transferred dropwise, via a cannula, over a period of 1 min to a rapidly stirred suspension of 2.65 g (25 mmol) of anhydrous sodium carbonate in 5 mL of methylene chloride containing 0.80 g (5.0 mmol) of 6-methoxy-3,4-dihydronaphthalene (**31a**) at −78 °C. The colorless mixture was then heated at reflux for a period of 2 h to effect complete dehydrochlorination. The mixture was cooled to room temperature and poured into 100 mL of ether, and the organic layer was washed with 50 mL of water and then with 50 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded 1.33 g (99%) of **32a** as a colorless oil. Crystallization from 50 mL of methanol at 0 °C provided 0.80 g of **32a** as a white solid, mp 51–52 °C; concentration of the filtrate to a volume of 25 mL and cooling to 0 °C afforded a second crop of 0.27 g for a total recrystallized yield of 80%: NMR δ 7.2–7.6 (m, 5 H), 6.5–7.0 (m, 4 H), 3.8 (s, 3 H), 2.85 (t, J = 7 Hz, 2 H), 2.4 (t, J = 7 Hz, 2 H). M^+ Calcd for $C_{17}H_{16}OS$: 268.092. Found: 268.095.

Deletion of the 2-h period at reflux resulted in a product which decomposed at room temperature; the NMR had, in addition to signals due to **32a,** signals at 5.2 (m) and 4.0 (m) which vanished upon addition of excess DBU to the NMR sample and thus were attributed to *trans*-1-chloro-6-methoxy-2-phenylthio-3,4-dihydronaphthalene.

Preparation of 6-Methoxy-1-methyl-2-phenylthio-3,4-dihydronaphthalene (32b). In the preparation of **32b,** 0.87 g (5.0 mmol) of 6-methoxy-1-methyl-3,4-dihydronaphthalene (**31b**)[48] was substituted for 6-methoxy-3,4-dihydronaphthalene, and the reflux period was unnecessary. Workup provided 1.40 g (99%) of **32b** as a brown oil: NMR δ 7.0–7.5 (m, 6 H), 6.5–6.8 (m, 2 H), 3.75 (s, 3 H), 2.1–2.9 (m, 7 H). M^+ Calcd for $C_{18}H_{18}OS$: 282.108. Found: 282.106.

Preparation of Phenyl Vinyl Sulfide (38). To 1.52 g (10.0 mmol) of DBU[34] at 100 °C was added via syringe 0.86 g (5.0 mmol) of 2-chloroethyl phenyl sulfide (**9**). The mixture was stirred for 15 min at 100 °C, then cooled rapidly to room temperature, and diluted with 25 mL of 2% aqueous hydrochloric acid. Extraction with 50 mL of ether, washing of the ether layer with 25 mL of saturated aqueous sodium chloride, drying ($MgSO_4$), and concentration in vacuo afforded a light yellow oil. Kugelrohr distillation at 27 °C (0.5 mm) yielded 0.60 g (88%) of **38:** NMR δ 7.2–7.5 (m, 5 H), 6.5 (ddd, J = 17, 8, and 5 Hz, 1 H), 5.3 (d, J = 17 Hz, 1 H), 5.3 (d, J = 8.5 Hz, 1 H). M^+ Calcd for C_8H_8S: 136.035. Found: 136.036.

Preparation of 1- and 2-Cyclopenten-1-yl Phenyl Sulfides (39a and 40a). A 1.06-g (5.0 mmol) portion of *trans*-2-chloro-1-cyclopentyl sulfide (**11a**) was added via syringe to 1.52 g (10.0 mmol) of DBU[34] at 120 °C. The mixture was stirred for 3 h at 120 °C, cooled to room temperature, diluted with 25 mL of 2% aqueous hydrochloric acid, and extracted with 50 mL of ether, and the organic layer was washed with 25 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo left a light yellow oil which NMR showed to be a 1:1 mixture of **39a** and **40a**. Kugelrohr distillation at 95 °C (0.5 mm) provided 0.80 g (91%) of a colorless oil; this oil was separated by TLC on silica (hexane) to yield 0.35 g (40% overall from the chloride) of **39a** and 0.35 g (40% overall from the chloride) of **40a. 39a:** NMR δ 7.1–7.5 (m, 5 H), 5.7 (t, J = 2, Hz, 1 H), 2.2–2.6 (m, 4 H), 1.7–2.2 (m, 2 H). M^+ Calcd for $C_{11}H_{12}S$: 176.066. Found: 176.065. **40a:** NMR δ 7.1–7.5 (m, 5 H), 5.8 (m, 2 H), 4.1–4.5 (m, 1 H), 1.9–2.5 (m, 4 H). M^+ Calcd for $C_{11}H_{12}S$: 176.066. Found: 176.066.

Preparation of 1- and 2-Cyclohexen-1-yl Phenyl Sulfides (39b and 40b). In the preparation of **39b** and **40b,** 1.13 g (5.0 mmol) of *trans*-2-chloro-1-cyclohexyl phenyl sulfide (**11b**) was substituted for *trans*-2-chloro-1-*trans*-2-chloro-1-cyclopentyl phenyl sulfide and the mixture was heated for 9 h at 120 °C. Kugelrohr distillation at 110 °C (0.2 mm) afforded 0.764 g (81%) of product which NMR showed to be almost exclusively **40**. Thin-layer chromatography on silica (hexane) afforded 0.58 g (62% from the chloride) of **40b** and 0.03 g (3% from the chloride) of **39b. 39b:** NMR δ 7.3 (m, 5 H), 6.0 (m, 1 H), 2.0–2.4 (m, 4 H), 1.5–2.0 (m, 4 H). M^+ Calcd for $C_{12}H_{14}S$: 190.082. Found: 190.079. **40b:** NMR δ 7.1–7.5 (m, 5 H), 5.8 (m, 2 H), 3.7–4.0 (m, 1 H), 1.5–1.2 (m, 6 H). M^+ Calcd for $C_{12}H_{14}S$: 190.082. Found: 190.081.

Preparation of 1- and 2-Cyclohepten-1-yl Phenyl Sulfide (39c and 40c). In the preparation of **39c,** and **40c,** 1.20 g (5.0 mmol) of *trans*-2-chloro-1-cycloheptyl phenyl sulfide (**11c**) was substituted for *trans*-2-chloro-1-cyclopentyl phenyl sulfide, and the mixture was

heated to 120 °C for 9 h. Workup produced 0.72 g (71%) of an oil which by NMR was a 13:7 mixture of **39c** and **40c**, respectively. Kugelrohr distillation at 90 °C (0.15 mm) yielded 0.68 g (66%) of an oil which gave, after thin-layer chromatography, 0.34 g (36% from the chloride) of **39c** and 0.22 g (24% from the chloride) of **40c**. **39c:** NMR δ 7.1–7.3 (m, 5 H), 6.0 (t, J = 6 Hz, 1 H), 2.0–2.4 (m, 4 H), 1.4–1.8 (m, 6 H). M^+ Calcd for $C_{13}H_{16}S$: 204.097. Found: 204.097. **40c:** NMR δ 7.2–7.5 (m, 5 H), 4.8 (m, 2 H), 4.0 (m, 1 H), 1.5–2.4 (m, 8 H). M^+ Calcd for $C_{13}H_{16}S$: 204.097. Found: 204.097.

Equilibration of 1- and 2-Cycloalken-1-yl Phenyl Sulfides. A mixture of 1.76 g (10.0 mmol) of 2-cyclopenten-1-yl phenyl sulfide (**40a**), 0.22 g (2 mmol) of potasssium *tert*-butoxide,[49] and 10 mL of Me_2SO was heated to 60 °C for 4 h, cooled to room temperature, and quenched with 100 mL of 2% aqueous hydrochloric acid. This solution was extracted with 200 mL of ether and the ether layer washed with 100 mL of water followed by 100 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo left 1.72 g (97%) of a light brown oil which was shown by NMR to be a 90:10 mixture of **39a** and **40a**, respectively.

Similar treatment of 1.90 g (10.0 mmol) of 2-cyclohexen-1-yl phenyl sulfide (**40b**) for 20 h at room temperature afforded 1.78 g (94%) of a light brown oil which NMR revealed to be a 92:8 mixture of **39b** and **40b**, respectively.

Equilibration of 2.04 g (10.0 mmol) of 2-cyclohepten-1-yl phenyl sulfide (**40c**) for 2 h at 60 °C led to a recovery of 1.96 g (96%) of a 92:8 mixture of **39c** and **40c**, respectively.

Longer reaction times produced no further change in the ratio of 1- to 2-cycloalken-1-yl phenyl sulfides, and it is thus assumed that these ratios represent the equilibrium value.

Demonstration of the Kinetic Stability of the 1- and 2-Cycloalken-1-yl Phenyl Sulfides. To a solution of 0.304 g (2.0 mmol) of DBU[34] in 5.0 mL of benzene at room temperature was added 83 μL (1.0 mmol) of concentrated hydrochloric acid. Concentration in vacuo produced a 1:1 mixture of DBU and DBU·HCl. This mixture was heated to 125 °C and a quantity (see Table IV) of cycloalkenyl phenyl sulfide was added. After heating for the specified period of time, the mixture was cooled to room temperature and diluted with 10 mL of 2% aqueous hydrochloric acid. Extraction with 25 mL of ether and washing of the organic layer with 10 mL of saturated aqueous sodium chloride furnished, after drying ($MgSO_4$) and concentration in vacuo, a product which by NMR showed no detectable equilibration.

Attempted Dehydrochlorination of *endo*-3-Chloro-*exo*-2-bicyclo[2.2.1]heptyl Phenyl Sulfide (14). To 0.304 g (2.0 mmol) of DBU[34] at 170 °C was added via syringe 0.24 g (1.0 mmol) of *endo*-3-chloro-*exo*-2-bicyclo[2.2.1]heptyl phenyl sulfide (**14**). The mixture was stirred for 1 h at 170 °C and then cooled to room temperature and diluted with 10 mL of 2% aqueous hydrochloric acid. This solution was extracted with 25 mL of ether, and the organic layer was washed with 10 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded 0.22 g (91%) of an oil which NMR showed to be exclusively **14**.

Preparation of *trans*-1,3-Butadien-1-yl Phenyl Sulfide (41).[8] A 1.99-g (10.0 mmol) portion of 2-chloro-3-buten-1-yl phenyl sulfide (**16**) was added via syringe to 3.04 g (20.0 mmol) of DBU[34] at 100 °C. The mixture was stirred for 10 min at 100 °C, cooled to room temperature, and diluted with 50 mL of 2% aqueous hydrochloric acid. Shaking with 50 mL of ether, washing the organic layer with 25 mL of saturated aqueous sodium chloride, drying ($MgSO_4$), and concentration in vacuo produced 1.50 g (92%) of **41** as a light yellow oil. Kugelrohr distillation at 60 °C (0.1 mm) furnished 1.31 g (81%) of **41** as a colorless oil: NMR δ 7.1–7.4 (m, 5 H), 6.0–6.5 (m, 3 H), 4.9–5.5 (m, 2 H); M^+ Calcd for $C_{10}H_{10}S$: 162.050. Found: 162.051.

Preparation of 1,3-Cyclohexadien-1-yl Phenyl Sulfide (42). In the preparation of **41**, 2.24 g (10.0 mmol) of *trans*-2-chloro-3-cyclohexadien-1-yl phenyl sulfide (**18**) was substituted for 2-chloro-3-buten-1-yl sulfide to yield 1.54 g (82%) of crude material which was Kugelrohr distilled at 92 °C (0.7 mm) to yield 1.37 g (73%) of **42** as a colorless oil: NMR δ 7.1–7.5 (m, 5 H), 6.6–6.0 (m, 3 H), 2.1–2.4 (m, 4 H). M^+ Calcd for $C_{12}H_{12}S$: 188.066. Found: 188.063.

Dehydrochlorination of *trans*-2-Chloro-1-cyclopentyl 1-(2,4,6-Trimethyl)phenyl Sulfide (12a). A 0.127-g (0.50 mmol) portion of *trans*-2-chloro-1-cyclopentyl 1-(2,4,6-trimethyl)phenyl sulfide (**12a**) and 0.15 g of DBU[34] were heated to 110–120 °C for 3 h. The mixture was cooled to room temperature, diluted with 50 mL of ether, and washed with 25 mL of 2% aqueous hydrochloric acid. Drying ($MgSO_4$) and concentration in vacuo afforded a dark oil which gave NMR signals at δ 5.8 (m), 5.65 (m) (olefinic protons of **45a**), and 4.95 (br s) (olefinic proton of **44a**) whose intensities indicated an 80:20 mixture of **45a** and **44a**, respectively. About 10 mol % of **12a** was also present in the sample.

Table IV. Kinetic Stability of the 1- and 2-Cycloalken-1-yl Phenyl Sulfides

Sulfide (wt, g; mmol)	Time, h	Product wt, g (% yield)
39a (0.083, 0.47)	3	0.075 (90)
40a (0.176, 1.0)	3	0.130 (74)
39b (0.062, 0.33)	9	0.058 (94)
40b (0.190, 1.0)	9	0.184 (97)
39c (0.063, 0.31)	9	0.045 (71)
40c (0.044, 0.22)	9	0.041 (94)

Dehydrochlorination of *trans*-2-Chloro-1-cyclopentyl 1-(2,4,6-Triisopropyl)phenyl Sulfide (12b). Treatment of 0.17 g (0.5 mmol) of *trans*-2-chloro-1-cyclopentyl 1-(2,4,6-triisopropyl)phenyl sulfide (**12b**) with 0.15 g (1.0 mmol) of DBU[34] for 2.5 h at 110–120 °C and workup identical to that for the dehydrochlorination of **12a** provided an oil whose NMR showed signals at δ 5.8 (m), 5.6 (m) (olefinic protons of **45b**), and 4.9 (br s) (olefinic proton of **44b**); the integrals indicated an 80:20 mixture of **45b** and **44b**, respectively, as well as about 10% recovered starting material **12b**.

Preparation of 3-Phenylthio-2,5-dihydrothiophene 1,1-Dioxide (43).[29] A solution of 12.72 g (48 mmol) of *trans*-3-chloro-4-phenylthio-2,5-dihydrothiophene 1,1-dioxide (**26**) in 250 mL of chloroform was cooled to −40 °C and 7.74 g (51 mmol) of DBU[34] in 5 mL of chloroform was added dropwise over a 5-min period. The resulting solution was stirred for 0.5 h at −40 °C, warmed to −10 °C, and quenched with 50 mL of 10% aqueous hydrochloric acid. The organic layer was then dried ($MgSO_4$) and concentrated in vacuo to afford an oil which was crystallized from ether/hexane to yield 9.7 g (88%) of **43** as white crystals: mp 55.5–56.5 °C; NMR δ 7.2–7.5 (m, 5 H), 5.75 (m, 1 H), 3.75–3.95 (m, 2 H), 3.6–3.75 (m, 2 H). M^+ Calcd for $C_{10}H_{10}O_2S_2$: 226.012. Found: 226.015.

Higher temperatures (75 °C, 1 h, sealed tube) convert **43** cleanly to 3-phenylthio-4,5-dihydrothiophene 1,1-dioxide, a white solid: mp 140.5–141.5 °C; NMR δ 7.5 (m, 5 H), 6.8 (m, 1 H), 3.2–3.6 (m, 2 H), 2.7–3.2 (m, 2 H). M^+ Calcd for $C_{10}H_{10}O_2S_2$: 226.012. Found: 226.012.

One-Pot Preparation of 3-Phenylthio-2,5-dihydrothiophene 1,1-Dioxide (43) from 2,5-Dihydrothiophene 1,1-Dioxide (25).[29] A 295.4-g (2.5 mol) portion of 2,5-dihydrothiophene 1,1-dioxide (**25**)[43] was added to a solution of 2.50 mol of phenylsulfenyl chloride, and the mixture was stirred for 24 h at room temperature. With ice-bath cooling to maintain the temperature below 25 °C, 265.6 g (2.63 mol) of triethylamine[39] was added over a period of 5 min. Intermittant cooling during the next hour was necessary to maintain a temperature of 25 °C, after which time the mixture was allowed to stir for 24 h at room temperature. The resulting brown solution was washed twice with 1-L portions of water, once with 0.5 L of 2% aqueous hydrochloric acid, and once with 0.5 L of saturated aqueous sodium chloride. Concentration in vacuo provided 515 g (91%) of a crude orange oil whose NMR was identical to that of the crystalline sample obtained in the two-step procedure. Crystallization from 2.5 L of ether/hexane provided a first crop of 422 g (75%) of **43** as slightly yellow solid, mp 56.5–57.5 °C. A second, more colored crop of 59 g (NMR identical to colorless crystals of **43**) was collected by concentration of the filtrate in vacuo and cooling to −40 °C. The total recrystallized yield of **43** was, thus, 481 g (85%). Spectral data was identical to that obtained for the two-step procedure.

Preparation of *trans*-2-Chloro-1-cyclopentyl Phenyl Sulfone (51a). Method A. To a solution of 1.06 g (5.0 mmol) of *trans*-2-chloro-1-cyclopentyl phenyl sulfide (**11a**) in 25 mL of methylene chloride immersed in an ice bath at 0 °C was added 2.44 g (12.0 mmol) of 85% *m*-chloroperoxybenzoic acid (MCPBA)[34] at a rate which caused gentle boiling of the solvent. After the addition, the ice bath was removed and the solution was stirred an additional 0.5 h at room temperature. A 10-mL portion of 10% aqueous sodium sulfite was added and the mixture was poured into 50 mL of ether. The organic layer was washed with 25 mL of 10% aqueous sodium carbonate and 25 mL of saturated aqueous sodium chloride, dried ($MgSO_4$), and concentrated in vacuo to yield 1.21 g (99%) of **51a** as a white solid: mp 81–82 °C; NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 4.45–4.7 (m, 1 H), 3.5–3.9 (m, 1 H), 1.7–2.4 (m, 6 H). M^+ Calcd for $C_{11}H_{13}ClO_2S$: 244.032. Found: 244.033.

Preparation of *trans*-2-Chloro-1-cyclopentyl Phenyl Sulfone (51a). Method B. To a solution of 106.2 g (0.500 mol) of *trans*-2-chloro-1-cyclopentyl phenyl sulfide (**11a**) in 180 mL of glacial acetic acid at 20 °C in an ice bath was added dropwise over a 1-h period 171

mL (1.20 mol) of 7 M peracetic acid[50] in acetic acid which had been previously treated with 15 g (0.183 mol) of anhydrous sodium acetate. During the addition, the temperature must be maintained between 20 and 30 °C to assure that the reaction proceeds in a controlled fashion. Failure to do so resulted in low yields and numerous intermittant exotherms. After the addition was completed, the mixture was stirred for 1 h between 20 and 30 °C and then poured into 1 L of ice water. This mixture was stirred until the ice had melted and then filtered to yield a crude white solid. This solid was taken up in 200 mL of methylene chloride and shaken with 100 mL of 10% aqueous sodium sulfite, 200 mL of 10% aqueous sodium carbonate, and finally 50 mL of saturated aqueous sodium chloride. Drying ($MgSO_4$) and concentration in vacuo afforded 113.4 g (93%) of **51a** as a white powder, mp 81–82 °C, whose spectral data were identical with that obtained by method A.

Oxidations by method A or B were conveniently followed by TLC using 10% ethyl acetate in chloroform as eluent, the intermediate sulfoxides showing a substantially higher polarity than the starting sulfide and the sulfone being only slightly more polar than the starting sulfide.

Preparation of *trans*-2-Chloro-1-cyclohexyl Phenyl Sulfone (51b). Oxidation of 1.13 g (5.0 mmol) of *trans*-2-chloro-1-cyclohexyl phenyl sulfide (**11b**) by method A gave 1.28 g (99%) of a colorless oil, **51b:** NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 4.2–4.5 (m, 1 H), 3.1–3.5 (m, 1 H), 1.2–2.5 (m, 8 H). M^+ Calcd for $C_{12}H_{15}ClO_2S$: 258.048. Found: 258.050.

Oxidation of 113.4 g (0.500 mol) of *trans*-2-chloro-1-cyclohexyl phenyl sulfide (**11b**) by method B afforded 110.0 g (85%) of **51b** as a crude white solid, mp 66–70 °C, whose spectral data were identical to that obtained by method A.

Preparation of *trans*-2-Chloro-1-cycloheptyl Phenyl Sulfone (51c). Oxidation of 1.20 g (5.0 mmol) of *trans*-2-chloro-1-cycloheptyl phenyl sulfide (**11c**) by method A yielded 1.34 g (99%) of **51c** as a white solid: mp 67–69 °C; NMR δ 7.8–8.1 (m, 2 H), 7.5–7.8 (m, 3 H), 4.6–4.9 (m, 1 H), 3.4–3.8 (m, 1 H), 1.1–2.5 (m, 10 H). M^+ Calcd for $C_{13}H_{17}ClO_2S$: 272.064. Found: 272.063.

Oxidation of 120.4 g (0.500 mol) of *trans*-2-chloro-1-cycloheptyl phenyl sulfide (**11c**) by method B provided 121.9 g (90%) of white solid **51c** whose spectral data were identical to that obtained by method A.

Preparation of *endo*-3-Chloro-*exo*-2-bicyclo[2.2.1]heptyl Phenyl Sulfone (53). Oxidation of 4.78 g (20 mmol) of *endo*-3-chloro-*exo*-2-bicyclo[2.2.1]heptyl phenyl sulfide (**14**) by method A furnished 5.35 g (99%) of **53** as a white solid: mp 82–84.5 °C; NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 4.4 (dd, J = 5 and 5 Hz, 1 H), 2.9 (dd, J = 5 and 2 Hz, 1 H), 2.8–3.1 (m, 1 H), 2.3–2.7 (m, 1 H), 1.2–2.2 (m, 6 H). M^+ Calcd for $C_{13}H_{15}ClO_2S$: 270.048. Found: 270.053.

Preparation of *trans*-2-Chloro-3-cyclohexen-1-yl Phenyl Sulfone (55). Oxidation of 1.12 g (10.0 mmol) of *trans*-2-chloro-3-cyclohexen-1-yl phenyl sulfide (**18**) by method A furnished 1.275 g (99%) of **55** as an oil which was precipitated as a solid, mp 56–57.5 °C, by adding hexane to a solution of the oil in ether: NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 5.6–6.1 (m, 2 H), 4.8–5.0 (m, 1 H), 3.4–3.7 (m, 1 H), 1.7–2.6 (m, 4 H). M^+ Calcd for $C_{12}H_{13}ClO_2S$: 256.032. Found: None. M^+ − HCl Calcd for $C_{12}H_{12}O_2S$: 220.056. Found: 220.056.

Preparation of 3α-Phenylsulfonyl-2β-chlorocholestane (57).[18] Oxidation of 0.515 g (1.0 mmol) of 3α-phenylthio-2β-chlorocholestane (**20**) by method A afforded 0.526 g (96%) of **57** as a white solid: mp 163–165; NMR δ 7.5–8.0 (m, 5 H), 4.8 (m, 1 H), 3.6 (m, 1 H), 0.7–2.3 (m, 44 H). M^+ Calcd for $C_{33}H_{51}ClO_2S$: 546.330. Found: 546.328.

Preparation of 2-Chloro-2-methyl-1-cyclohexyl Phenyl Sulfone (59). Oxidation of 2.41 g (10.0 mmol) of a 90:10 mixture of **24a** and **24b,** respectively, by method A gave 2.7 g (99%) of a white solid, a 90:10 mixture of **59,** and 2-chloro-1-methyl-1-cyclohexyl phenyl sulfone by NMR. Recrystallization from 60 mL of hexane afforded 1.55 g (63% based on **59** in the mixture) of pure **59:** mp 102.5–105 °C; NMR δ 7.8–8.0 (m, 2 H), 7.5–7.7 (m, 3 H), 3.5 (dd, J = 5 and 7 Hz, 1 H), 1.1–2.4 (m, 8 H), 1.9 (s, 3 H). M^+ Calcd for $C_{13}H_{17}ClO_2S$: 272.064. Found: 272.065.

Preparation of 1-Cyclopenten-1-yl Phenyl Sulfone (52a). To 97.9 g (0.400 mol) of *trans*-2-chloro-1-cyclopentyl phenyl sulfone (**51a**) in 200 mL of methylene chloride at 0 °C in a dry ice/2-propanol bath was added 62.3 g (0.410 mol) of DBU[34] at a rate which maintained the temperature between −5 and 0 °C. The total addition was made over a 0.5-h period. The mixture was allowed to warm to room temperature and poured into 500 mL of ether. The organic phase was extracted with 100 mL of 2% aqueous hydrochloric acid, 100 mL of water, and 100 mL of saturated aqueous sodium chloride, and dried ($MgSO_4$). Concentration in vacuo gave 83.0 g (100%) of crude solid which was recrystallized from 600 ml of 1:1 (v/v) ether/hexane to yield 72.0 g (86%) of a white solid, **52a,** mp 64.5–65 °C. A second crop was obtained by concentration of the filtrate in vacuo and dissolution of the residue in 40 mL of ether. Cooling to −78 °C afforded an additional 4.5 g of white solid for a total recrystallized yield of 92%: NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 6.75 (br s, 1 H), 2.3–2.8 (m, 4 H), 1.7–2.3 (m, 2 H). M^+ Calcd for $C_{11}H_{12}O_2S$: 208.056. Found: 208.058.

Eliminations were conveniently followed by TLC using 4:1 (v/v) ether/hexane as eluent, the vinyl sulfone product being slightly more polar than the starting β-chloro sulfone.

Preparation of 1-Cyclohexen-1-yl Phenyl Sulfone (52b). Substitution of 103.5 g (0.400 mol) of *trans*-2-chloro-1-cyclohexyl phenyl sulfone (**51b**) for *trans*-2-chloro-1-cyclopentyl phenyl sulfone (**51a**) afforded 86.9 g (98%) of a crude oil. Recrystallization from 4 L of hexane gave 64.7 g (73%) of **52b** as a white solid, mp 42.5–43.5 °C; a second crop was obtained by concentration of the filtrate in vacuo, dissolution of the residue in 125 mL of ether, and cooling to −78 °C. This produced an additional 7.7 g of white solid, for a total recrystallized yield of 81%: NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 7.0–7.2 (m, 1 H), 2.0–2.5 (m, 4 H), 1.5–2.0 (m, 4 H). M^+ Calcd for $C_{12}H_{14}O_2S$: 222.071. Found: 222.071.

Preparation of 1-Cyclohepten-1-yl Phenyl Sulfone (52c). Substitution of 109.1 g (0.400 mol) of *trans*-2-chloro-1-cycloheptyl phenyl sulfone (**51d**) for *trans*-2-chloro-1-cyclopentyl phenyl sulfone (**51a**) in the preparation of **52a** resulted in 93.3 g (99%) of a crude brown oil, which was recrystallized from 350 mL of 4:1)v/v) ether/hexane to yield 70 g (84%) of **52c** as a white solid: mp 32–35 °C; NMR δ 7.7–8.0 (m, 2 H), 7.4–7.7 (m, 3 H), 7.3 (t, J = 6 Hz, 1 H), 2.1–2.5 (m, 4 H), 1.2–1.8 (m, 6 H). M^+ Calcd for $C_{13}H_{16}O_2S$: 236.087. Found: 236.087.

Preparation of Bicyclo[2.2.1]hept-2-en-2-yl Phenyl Sulfone (54). To a solution of 6.77 g (25 mmol) of *endo*-3-chloro-*exo*-2-bicyclo[2.2.1]heptyl phenyl sulfone (**53**) in 12.5 mL of chloroform heated under reflux was added via syringe 4.56 g (30 mmol) of DBU.[34] Heating was continued for 15 min, and then the mixture was allowed to cool to room temperature and poured into 50 mL of 2% aqueous hydrochloric acid. Fifty milliliters of ether was added to the acidic solution; the combined organic phase was then washed with 25 mL of saturated aqueous sodium chloride, dried ($MgSO_4$), and concentrated in vacuo to afford 5.68 g (97%) of crude oil. The oil was taken up in 120 mL of ether and cooled to −78 °C to afford 2.6 g (44%) of **54** as a white solid, mp 47.5–48.5 °C. Concentration of the filtrate in vacuo to a total volume of 20 mL and again cooling to −78 °C produced a second crop of 1.4 g (24%), for a total yield of 68%: NMR δ 7.8–8.0 (m, 2 H), 7.5–7.7 (m, 3 H), 6.9 (dm, J = 3 Hz, 1 H), 3.0–3.3 (m, 2 H), 1.0–2.0 (m, 6 H). M^+ Calcd for $C_{13}H_{14}O_2S$: 234.071. Found: 234.074.

Preparation of 1,3-Cyclohexadien-1-yl Phenyl Sulfone (56).[10c] A solution of 2.56 g (10.0 mmol) of *trans*-2-chloro-3-cyclohexen-1-yl phenyl sulfone (**55**) in 50 mL of methylene chloride was cooled to 0 °C in an ice bath and 1.82 g (12.0 mmol) of DBU[39] was added via syringe. When the addition was complete, the cooling bath was removed and the mixture was stirred for 15 min at room temperature. The mixture was poured into 25 mL of 2% aqueous hydrochloric acid and 100 mL of ether was added. The organic layer was washed with 25 mL of saturated aqueous sodium chloride and dried ($MgSO_4$). Concentration in vacuo afforded 2.15 g (98%) of a colorless oil which was recrystallized from 95% ethanol to afford 1.83 g (83%) of **56** as a white solid: mp 92–93 °C; NMR δ 7.8–8.0 (m, 2 H), 7.5–7.8 (m, 3 H), 7.0–7.1 (m, 1 H), 6.0–6.2 (m, 2 H), 2.2–2.4 (m, 4 H). M^+ Calcd for $C_{12}H_{12}O_2S$: 220.056. Found: 226.056.

Preparation of 3-Phenylsulfonyl-Δ²-cholestene (58). To a solution of 0.407 g (0.74 mmol) of 3α-phenylsulfonyl-2β-chlorocholestane (**57**) in 5 mL of methylene chloride was added 0.225 g (1.5 mmol) of DBU,[34] and the mixture was stirred for 1 h at room temperature. The mixture was poured into 25 mL of 2% aqueous hydrochloric acid, and 50 mL of ether was added. The organic layer was washed with 25 mL of saturated aqueous sodium chloride and dried ($MgSO_4$). Concentration in vacuo afforded an oil which was recrystallized from ethanol to yield a first crop of 0.195 g of **58** as white crystals, mp 174–175 °C; a second crop of 0.157 g was collected by cooling the filtrate to 0 °C, for a combined yield of 93%; NMR δ 7.4–8.0 (m, 5 H), 7.0 (m, 1 H), 0.7–2.3 (m, 44 H). M^+ Calcd for $C_{33}H_{50}O_2S$: 510.353. Found: 510. 355.

Preparation of 2-Methyl-1-cyclohexen-1-yl Phenyl Sulfone (60). To a solution of 1.36 g (5.0 mmol) of 2-chloro-2-methyl-1-cyclohexyl phenyl sulfone (**59**) in 25 mL of methylene chloride heated under reflux was added via syringe 1.52 g (10.0 mmol) of DBU.[34] Heating was continued for 1.5 h, and then the mixture was allowed to cool to room temperature and poured into 25 mL of 2% aqueous hydrochloric acid. Fifty milliliters of ether was added, and the solution

was washed with 25 mL of saturated aqueous sodium chloride, dried ($MgSO_4$), and concentrated in vacuo to afford 1.17 g (99%) of **60** as a colorless oil which defied all attempts at recrystallization: NMR δ 7.8–8.0 (m, 2 H), 7.5–7.7 (m, 3 H), 1.9–2.5 (m, 7 H), 1.4–1.8 (m, 4 H). M^+ Calcd for $C_{13}H_{16}O_2S$: 236.087. Found: 236.089.

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Registry No.—**27a,** 771-98-2; **27b,** 825-54-7; **27c,** 64740-95-0; **30a,** 64740-96-1; **30b,** 64740-97-2; **30c,** 64740-98-3; **31a,** 52178-91-3; **31b,** 4242-13-1; **32a,** 64740-99-4; **32b,** 64741-00-0; **38,** 1822-73-7; dihydrocholesterol, 80-97-7; methanesulfonyl chloride, 124-63-0; dihydrocholesterol mesylate, 3381-51-9; 6-methoxy-1-tetralone, 1078-19-9; 6-methoxy-1,2,3,4-tetrahydro-1-naphthol, 1682-32-2; 3-phenylthio-4,5-dihydrothiophene 1,1-dioxide, 20583-25-9; *m*-chloroperoxybenzoic acid, 64741-01-1; peracetic acid, 79-21-0.

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