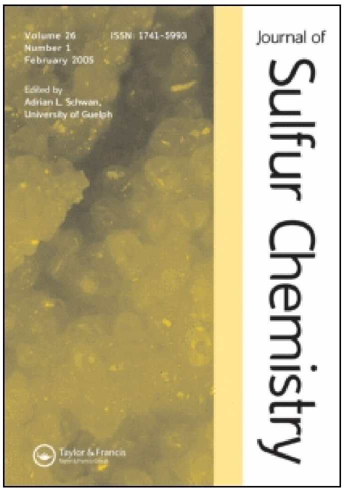

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Sulfinyl, α-Sulfinyl, Sulfonyl, and α-Sulfonyl Radicals

Fillmore Freeman[a]; Monica C. Keindl[a]
[a] Department of Chemistry, University of California, Irvine Irvine, California, USA

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SULFINYL, α-SULFINYL, SULFONYL, AND α-SULFONYL RADICALS

FILLMORE FREEMAN and MONICA C. KEINDL
Department of Chemistry, University of California, Irvine
Irvine, California 92717 USA

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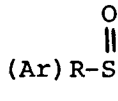
The formation and chemistry of sulfinyl, α-sulfinyl, sulfonyl, and α-sulfonyl radicals in a wide variety of systems are described. The mechanisms for radical formation and for their chemical reactivity are discussed. Molecular orbital calculations and spectral properties of the radicals are also included.

CONTENTS

I. INTRODUCTION

Short-lived, highly reactive, and sometimes elusive sulfur-containing radicals are important intermediates in a wide variety of chemical reactions.[1–7] Organosulfur radicals play important roles in biological chemistry, mechanistic and synthetic chemistry, polymer chemistry, and atmospheric chemistry. Sulfur-containing radicals also play significant roles in the mechanisms of antioxidation and in the action of radioprotective (antiradiation) agents. This review, which covers the chemical literature to 1984, will discuss the properties and chemistry of sulfinyl (**1**), α-sulfinyl (**2**), sulfonyl (**3**), and α-sulfonyl (**4**) radicals.


$(\text{Ar})\text{R-}\overset{\text{O}}{\overset{\|}{\text{S}}}{}^{\bullet}$

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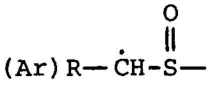
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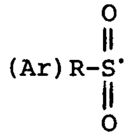
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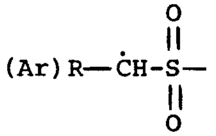
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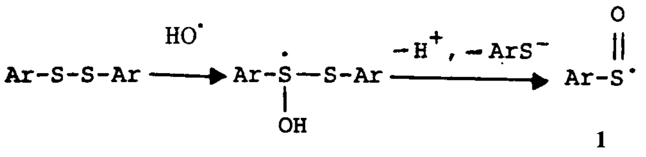
II. SPECTRAL PROPERTIES OF SULFINYL, α-SULFINYL, SULFONYL, AND α-SULFONYL RADICALS

A. Electron Spin Resonance (ESR) Spectroscopy

Electron spin resonance (ESR) spectra of sulfur-containing radicals provide important information about the delocalization of the unpaired electron and the geometry of the species.[8–17] Low q-values (spectroscopic splitting factor) are observed for radicals in which there is some delocalization of the unpaired electron. The hyperfine splitting contant a ($a_{\alpha-\text{H}}$), which reflects the interaction of the unpaired electron with nuclei possessing spin such as ^{1}H, ^{13}C, ^{14}N, ^{33}S, etc., also is a valuable ESR parameter.

1. Sulfinyl and α-Sulfinyl Radicals ESR spectroscopy has been employed to demonstrate that certain alkanesulfinyl radicals (**1**, RSO$^{\bullet}$) play important roles in the oxidation of 1,4-bis-(sulfoxides),[13] disulfides,[10] and thiols[10] under aqueous conditions. However, owing to the absence of ESR signals for simple alkanesulfinyl radicals in aqueous solution and the uncertainties concerning previous radical assignments,[14] Gilbert and coworkers[9] generated a variety of alkane- and arenesulfinyl radicals (**1**) by the reaction between hydroxyl radicals and both disulfides (Eq. 1) and thiols (Eq. 2), and by the photolysis of sulfinyl chlorides (Eq. 3). The ESR spectra of alkanesulfinyl and arenesulfinyl radicals so obtained are shown in Tables I and II, respectively.



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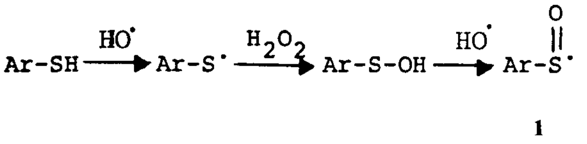

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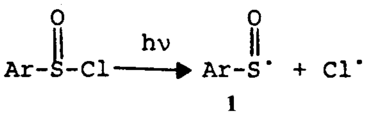


(3)

Table I shows that alkanesulfinyl radicals have g values of *ca.* 2.011 and $a\ (\beta - H)$ values in the range 0.80 to 1.1 mT. The large linewidth for methanesulfinyl radical ($CH_3S\dot{O}$) in solution is notable (ΔH 1.1 mT at −113 °C).[9,14,18] The preferred conformations for the methanesulfinyl radical are structures **5** and **6**. For the radicals $RCH_2SO^{\bullet}$

TABLE I

ESR Spectra of Alkanesulfinyl Radicals ($RSO^{\bullet}$)[a]

R	T/°C	a(H)/mT[b]	g[c]	ΔH/mT
CH_3	−113	1.15 (3 H)	2.0100	1.10
CH_3CH_2	−116	0.91 (2 H)	2.0110	0.10
$CH_3CH_2CH_2$	−105	0.89 (2 H)	2.0111	0.12
$CH_3CH_2CH_2CH_2$	−92	0.91 (2 H)	2.0111	0.12
$(CH_3)_2CH$	−110	1.00 (1 H)	2.0110	0.10
$CH_3CH_2CH(CH_3)$	−112	0.76 (1 H)	2.0110	0.17
	−61	0.86 (1 H)	2.0110	0.10
$(CH_3)_2CHCH_2$	−98	0.79 (2 H)	2.0105	0.10
$(CH_3)_3C$[d]			2.0106	
$HOCH_2CH_2$	−65	0.86 (2 H)	2.0110	0.12

[a] Generated by photolysis of the corresponding alkanesulfinyl chloride in diethyl ether (Reference 9).

[b] ±0.01 mT.

[c] ±0.0001.

[d] Generated by photolysis of di-*tert*-butyl peroxide in a solution of 2-methyl-2-propanesulfenic acid in methylbenzene or 2-methylbutane (Reference 15).

TABLE II

ESR Spectra of Some Arenesulfinyl ($ArSO^{\cdot}$) Radicals[9]

Reactant	Radical	Method of generation[a,b]	Hyperfine splittings (mT)[c,d] a(2-H)	a(3-H)	a(4-H)	$a(H\text{-}CH_3)$	g[e]
$C_6H_5S(O)Cl$	$C_6H_5SO^{\cdot}$	hν, −75 °C	0.240(2)	0.070(2)	0.240		2.0090
$2\text{-}CH_3C_6H_4S(O)Cl$	$2\text{-}CH_3C_6H_4SO^{\cdot}$	hν, −97 °C	0.250(1)[f]	0.075(2)	0.250[f]	0.125[f]	2.0092
$3\text{-}CH_3C_6H_4S(O)Cl$	$3\text{-}CH_3C_6H_4SO^{\cdot}$	hν, −90 °C	0.240(2)	0.075(1)	0.240	0.075	2.0090
$4\text{-}CH_3C_6H_4S(O)Cl$	$4\text{-}CH_3C_6H_4SO^{\cdot}$	hν, −80 °C	0.230(2)	0.075(2)		0.285	2.0089
$4\text{-}ClC_6H_4S(O)Cl$	$4\text{-}ClC_6H_4SO^{\cdot}$	hν, −69 °C	0.250(2)	g			2.0092
$(4\text{-}\overset{+}{N}H_3C_6H_4S)_2$	$4\text{-}\overset{+}{N}H_3C_6H_4SO^{\cdot}$	$^{\cdot}OH$	0.325(2)	h			2.0085
$C_6H_5SSCH_2CH_2OH$	$C_6H_5SO^{\cdot}$	$^{\cdot}OH$	0.26(2)	h	0.26		2.0084
C_6H_5SH	$C_6H_5SO^{\cdot}$	$^{\cdot}OH$	0.26(2)	h	0.26		2.0084
$2\text{-}(HCO_2C_6H_4S)_2$	$2\text{-}HCO_2C_6H_4SO^{\cdot}$	$^{\cdot}OH$	0.26(1)	0.07(2)	0.26		2.0088
$2\text{-}HCO_2C_6H_4SH$	$2\text{-}HCO_2C_6H_4SO^{\cdot}$	$^{\cdot}OH$	0.26(1)	0.07(2)	0.26		2.0088

[a] *hν*; photolysis of the corresponding arenesulfinyl chloride in diethyl ether.

[b] $^{\cdot}OH$ oxidations; aqueous solution, 22–24 °C.

[c] For photolyses, ±0.005 mT; for $HO^{\cdot}$ oxidations, ±0.02 mT.

[d] Linewidth 0.04 mT unless indicated otherwise.

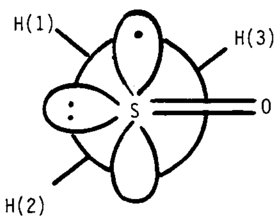
[e] For photolysis, ±0.0001; for $HO^{\cdot}$ oxidations, ±0.0044.

[f] Tentative assignment, see Reference 9.

[g] Further proton splittings not resolved; a(4-Cl) *ca.* 0.045 mT.

[h] Proton splittings not resolved; Δ*H* *ca.* 0.15 mT.

(R = CH_3CH_2, $CH_3CH_2CH_2$, or $(CH_3)_2CHCH_2$) the conformational preferences are structures **7** and **8** or **9** and **10**. Although conformation **11** is favored on steric grounds over conformation **12** for the 2-propanesulfinyl radical ($(CH_3)_2CHSO^{\cdot}$), structures **13** and **14** must also be considered.[9]



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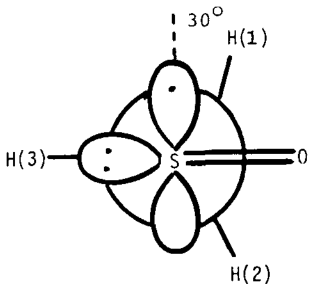

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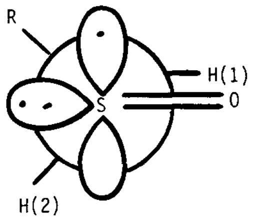

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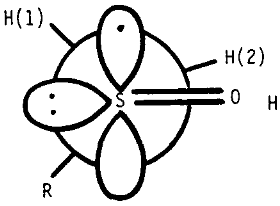

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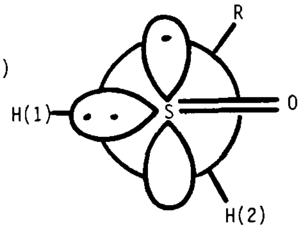

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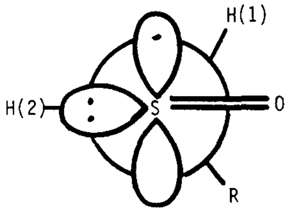

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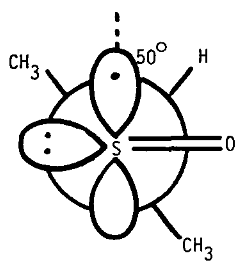

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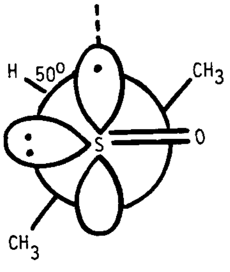

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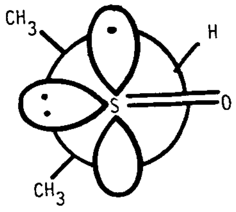

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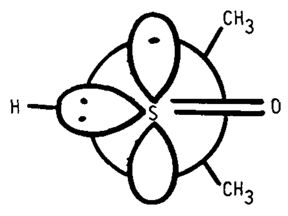


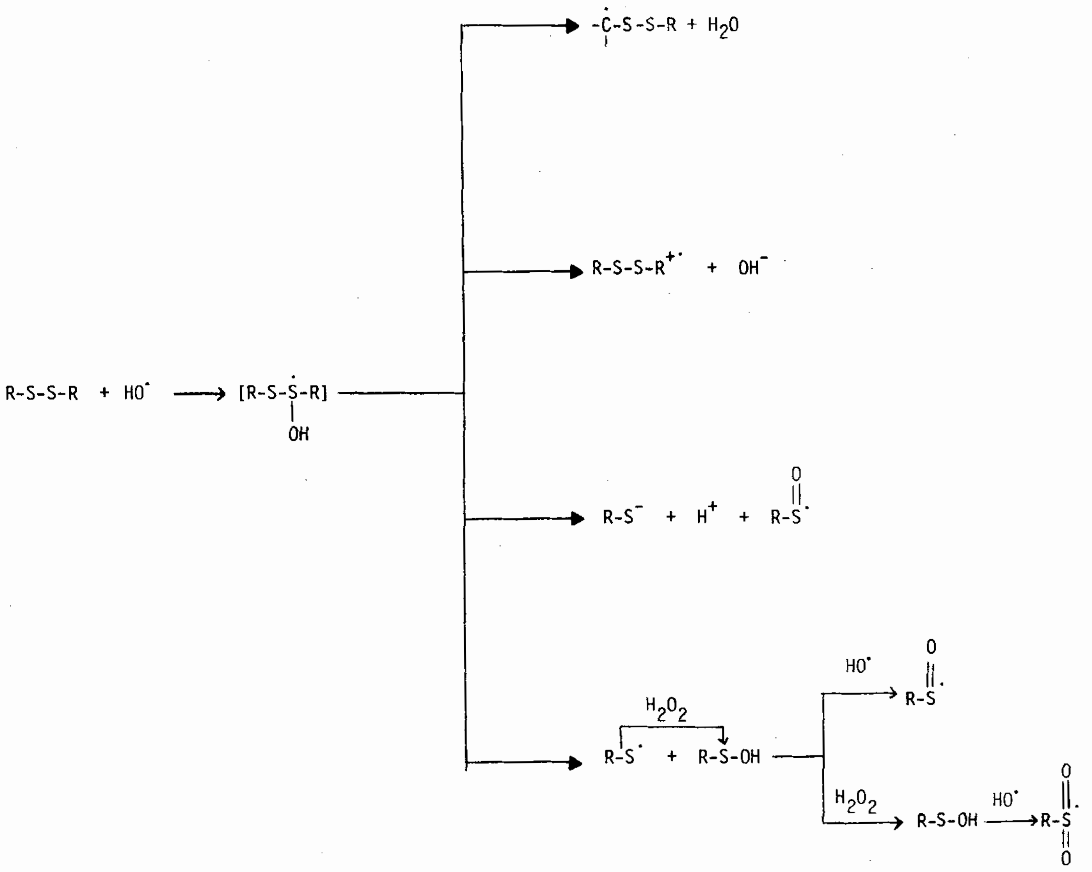
14

ESR spectral studies show that arenesulfinyl radicals are π-type species with extensive delocalization of the unpaired electron onto the aromatic ring.[9]

The ESR parameters of radicals detected during the oxidation of thiols by the titanium(III)–hydrogen peroxide couple at pH 1 to 2 (Scheme I) or by cerium (IV) at pH 1.5 have been recorded.[10]

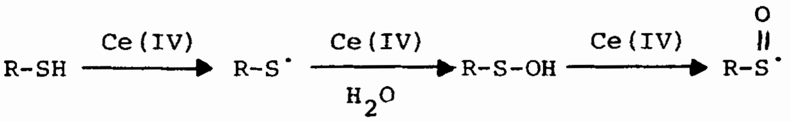
The alkanesulfinyl radicals were characterized by spectra with *g*-factors in the range *ca.* 2.010 to 2.011, proton splittings of *ca.* 1 mT, and broad lines (linewidth *ca.* 0.35 mT) (*cf.* Table I).

SCHEME I



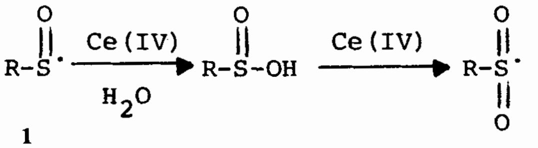
Some of these spectra were previously ascribed to thiyl radicals.[19–27] Although the major reaction of thiols with the hydroxyl radical is formation of thiyl radicals,[28] thiyl radicals are not expected to be detectable by ESR in solution owing to their excessively broad lines.[10]

Important reactions in the cerium(IV) oxidation of thiols in aqueous solution are shown in Eqs. 4 and 5.[10]



$$\mathrm{R{-}SH} \xrightarrow{\mathrm{Ce(IV)}} \mathrm{R{-}S^{\bullet}} \xrightarrow[\mathrm{H_2O}]{\mathrm{Ce(IV)}} \mathrm{R{-}S{-}OH} \xrightarrow{\mathrm{Ce(IV)}} \mathrm{R{-}\overset{\overset{O}{\|}}{S}{}^{\bullet}} \qquad (4)$$

1

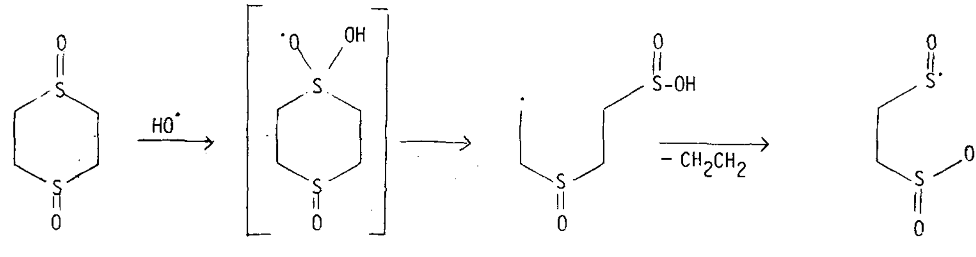


$$\mathrm{R{-}\overset{\overset{O}{\|}}{S}{}^{\bullet}} \xrightarrow[\mathrm{H_2O}]{\mathrm{Ce(IV)}} \mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \xrightarrow{\mathrm{Ce(IV)}} \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{}^{\bullet}} \qquad (5)$$

1 3

Sulfinyl (**1**) and sulfonyl (**3**) radicals are observed in the titanium(III)–hydrogen peroxide couple oxidation of disulfides.[10]

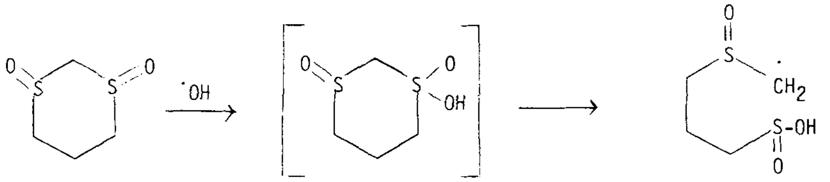
The reaction of 1,4-dithian 1,4-dioxide (**15**) with the titanium (III)–hydrogen peroxide couple gives an ESR spectrum which is consistent with the formation of the sulfinyl radical **18** (*a* (2H) 0.95 mT; *g* 2.0105; Eq. 6).[10,29,30]



(6)

15 **16** **18**

α-Sulfinyl radicals (**2**) generated from the reaction of dialkyl sulfoxides and hydroxyl radicals (Eq. 7; *cf.* Eq. 6), from sulfoxides and hypophosphinate radical anion (Eq. 8), and from sulfoxides and radicals (Eq. 9) have been studied by ESR spectroscopy.[13] Interestingly, in contrast to photolytic[32] and pyrolytic[33] studies on neat dimethyl sulfoxide, methyl radicals do not abstract hydrogen from dimethyl sulfoxide in solution (*cf.* Eq. 9).[31] Moreover, hydroxyl radicals react with dimethyl sulfoxide at sulfur rather than abstract a hydrogen atom from the methyl group (Eq. 10, *cf.* Eqs. 6 and 7).[34]



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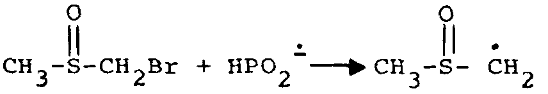
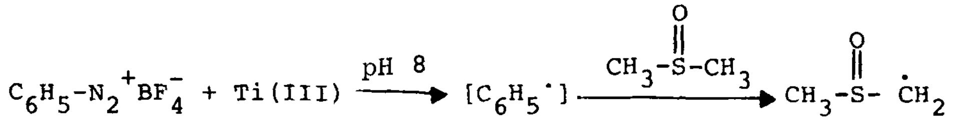
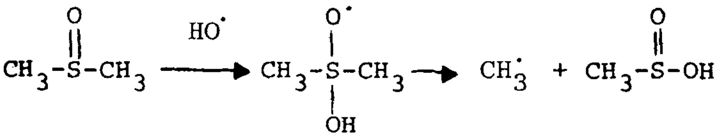


$$CH_3\text{-}\overset{\overset{O}{\|}}{S}\text{-}CH_2Br + HPO_2^{\bullet -} \longrightarrow CH_3\text{-}\overset{\overset{O}{\|}}{S}\text{-}\dot{C}H_2 \qquad (8)$$



$$C_6H_5\text{-}N_2^+BF_4^- + Ti(III) \xrightarrow{pH\ 8} [C_6H_5^{\bullet}] \xrightarrow{CH_3\text{-}\overset{\overset{O}{\|}}{S}\text{-}CH_3} CH_3\text{-}\overset{\overset{O}{\|}}{S}\text{-}\dot{C}H_2 \qquad (9)$$



$$CH_3\text{-}\overset{\overset{O}{\|}}{S}\text{-}CH_3 \xrightarrow{HO^{\bullet}} CH_3\text{-}\underset{\underset{OH}{|}}{\overset{\overset{O^{\bullet}}{|}}{S}}\text{-}CH_3 \longrightarrow CH_3^{\bullet} + CH_3\text{-}\overset{\overset{O}{\|}}{S}\text{-}OH \qquad (10)$$

The *g* values for α-sulfinyl radicals are essentially the *g* values for simple alkyl radicals (Table III).[13,31] α-Sulfinyl radicals have a planar geometry at the tervalent carbon atom

TABLE III.

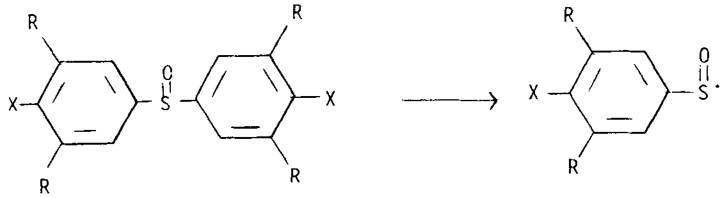
ESR Spectra of Some α-Sulfinyl Radicals[13]

Radical	Origin	g	Hyperfine Splittings/mT
$\dot{C}H_2S(O)CH_3$	a,b	2.0025	2.00 (2 H)
$CH_3\dot{C}HS(O)CH_2CH_3$	c	2.0025	2.02 (1 H) 2.53 (3H)
$\dot{C}H_2S(O)[CH_2]_2SO_2H$	d	2.0025	2.00 (2 H)
$\dot{C}H_2S(O)[CH_2]_3SO_2H$	d	2.0025	2.00 (2 H)
$CH_3\dot{C}HS(O)[CH_2]_2SO_2H$	d	2.0025	2.01 (1 H) 2.52 (3 H)
$(CH_3)_2\dot{C}S(O)[CH_2]_2SO_2H$	d	2.0025	2.33 (6 H)

[a] $(CH_3)_2SO + C_6H_5^{\cdot}$.
[b] $CH_3S(O)CH_2Br + HPO_2^{\cdot -}$.
[c] $(CH_3CH_2)_2SO + C_6H_5^{\cdot}$.
[d] The cyclic 1,3-bissulfoxide + $HO^{\cdot}$.

and the sulfinyl group withdraws six percent of the unpaired spin from the tervalent carbon atom.[13]

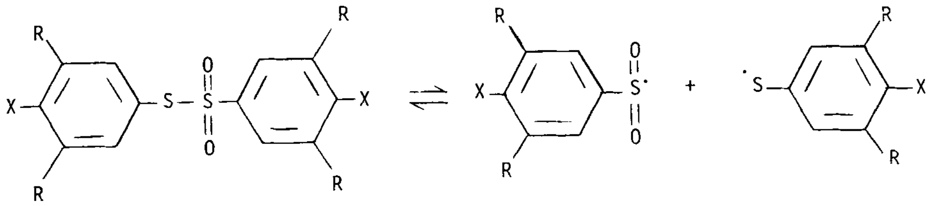
2. *Sulfonyl and α-Sulfonyl Radicals* Evidence has been obtained using ESR spectroscopy for the formation of arenesulfinyl radicals (**21**) during the photolytic and pyrolytic homolysis of diaryl sulfoxides (**19**, Eq. 11)[16,17] and *S*-aryl arenesulfonothioates (**20**, Eqs. 12 and 13),[16,17] possibly via arenesulfonyl (**22**) and arenethiyl (**23**) radicals and *O*-sulfenyl sulfinates (**24**, *vide infra*).[35–44]



(11)

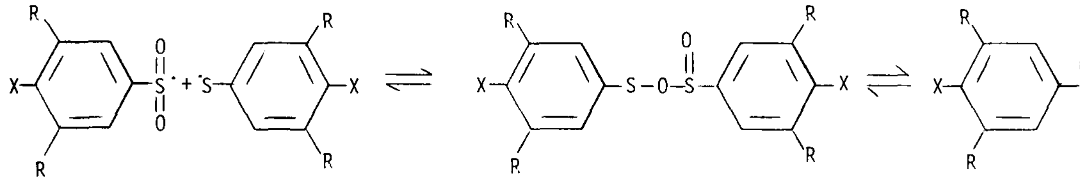
19a R = X = H
19b R = H, X = NO_2
19c R = H, X = Br
19d R = H, X = CH_3
19e R = t-C_4H_9, X = OH

21a R = X = H
21b R = H, X = NO_2
21c R = H, X = Br
21d R = H, X = CH_3
21e R = t-C_4H_9, X = OH



(12)

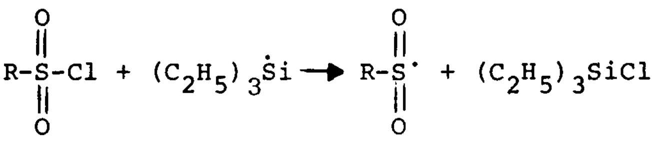
20a–20e **22** **23**



22 **23** **24** **21**

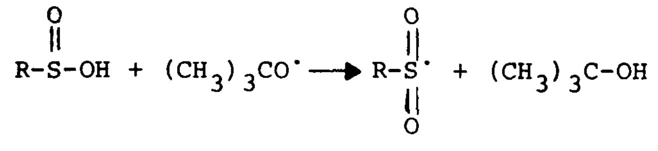
(13)

ESR spectroscopy has been employed to characterize the formation of alkanesulfonyl radicals (**3**) in a variety of systems including photolysis of sulfones,[45,46] chlorine abstraction from alkanesulfonyl chlorides by triethylsilyl radicals (Eq. 14),[47] hydrogen atom abstraction from alkanesulfinic acids with *t*-butoxy radicals (Eq. 15),[47] and hydrogen atom abstraction from dialkyl sulfoxides with hydroxyl radicals.[13,30] Alkanesulfonyl radicals are a σ-type species with a pyramidal radical center at the sulfur atom.[12,47] Table IV shows ESR parameters for a variety of alkanesulfonyl radicals.[12,47]



$$R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-Cl + (C_2H_5)_3\dot{S}i \longrightarrow R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}^{\bullet} + (C_2H_5)_3SiCl \qquad (14)$$

3



$$R-\overset{\overset{O}{\|}}{S}-OH + (CH_3)_3CO^{\bullet} \longrightarrow R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}^{\bullet} + (CH_3)_3C-OH \qquad (15)$$

3

Arenesulfonyl radicals have been generated in a variety of processes, including photolysis and thermolysis of diaryl sulfoxides **19**, Eqs. 11–13)[16,17] and *S*-aryl arenesulfonothioates (**20**, Eqs. 12 and 13),[16,17] cerium(IV) oxidation of arenesulfinic acids (*cf.* Eq. 5),[48] chlorine abstraction from arenesulfonyl chlorides by triethylsilyl radicals (*cf.* Eq. 14),[47] flash photolysis of sulfones,[49] and photolysis of arenesulfonyl halides (Eq. 3).[11,50] Tables V and VI show the ESR spectra of arenesulfonyl radicals (**3**) generated by photolysis of solutions of di-*tert*-butyl peroxide, triethylsilane, and arenesulfonyl chlorides in methylbenzene, 1,3-dimethylbenzene, or cyclopropane-oxirane.[11]

ESR spectral studies show that arenesulfonyl radicals are pyramidal with respect to sulfur and are with regard to spin distribution similar to benzoyl radicals. These data suggest that the unpaired electron is centered mainly on sulfur in a 3p type orbital which is in the plane of the benzene ring (**25**).[47] Radicals without *ortho*-substituents have a (m-H) > a (o-H), a (p-H) and undergo relatively rapid rotation about the carbon-sulfur bond (Eq. 16).[11] For some di-*ortho*-substituted radicals (Eq. 20), rotation about the carbon-sulfur bond is slow at low temperatures.

TABLE IV

ESR Spectra of Alkanesulfonyl Radicals ($RSO_2^{\cdot}$)[9,a]

		Hyperfine splittings[a]			
R	T/°C	a(α-H)	α(β-H)	a(other)	g[c]
CH_3	−50	0.055			2.0049
	−125	0.076[d]			
CH_3CH_2	−50	0.075	0.173		2.0050
	−80	0.090[d]	0.173		
	−120	0.115[d]	0.172		
$CH_3CH_2CH_2$	−40	0.070	0.212	0.070 (3H)	2.0051
	−110	0.122	0.245	0.072 (3H)	
$(CH_3)_2CH$	−60	0.040	0.190		2.0052
$ClCH_2$	−78	0.129			2.0055
	−105	0.144[d]			
	−105[e]	0.100[d]			
	−107[f]	0.190[d]			
$ClCH_2CH_2$[g]	−33	0.065	0.267	0.065 (1Cl)	2.0054
	−80	0.087[d]	0.300[d]	0.055 (1Cl)	
	−105		0.305[d]	0.050 (1Cl)	
$HOCH_2CH_2$	−47	0.130	0.275	0.065 (OH)	2.0052
CF_3CH_2	−23			0.400 (3F)	2.0047
	−94	0.035		0.383 (3F)[d]	
	−115	d		d	

[a] Cyclopropane solvent unless indicated otherwise.

[b] In MT, ±0.005.

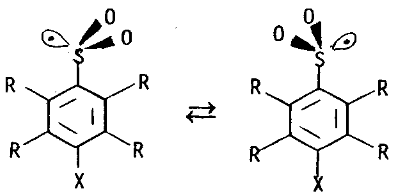
[c] Line broadening observed; see reference 47.

[d] ±0.0001.

[e] Dimethyl ether solvent.

[f] Diethyl ether solvent.

[g] Cyclopropane-oxirane solvent.



(16)

25 R = H, X = F or Cl

26 R = CH_3, X = H

α-Sulfonyl radicals (**4**) have been studied by ESR flow techniques.[13] Dimethyl sulfone (**27**) and sulfolane (**28**) react with phenyl radicals to give the respective α-sulfonyl radicals

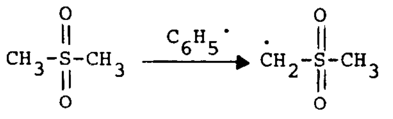
TABLE V

ESR Spectra of Arenesulfonyl Radicals ($ArSO_2^{\bullet}$)[11,a]

Ar	q[b]	Hyperfine splittings (mT)[c]		
		a(*o*-H)	*a*(*m*-H)	*a*(*p*-X)
C_6H_5	2.0045	0.033	0.113	0.052
4-FC_6H_4	2.0044	0.031	0.090	0.175 (${}^{19}F$)
3,5-$(CF_3)_2C_6H_3$	2.0043	0.055		0.055
4-ClC_6H_4	2.0045	0.032	0.096	
	2.0045	0.032	0.096	0.012 (${}^{35}Cl$) 0.010 (${}^{37}Cl$)[d]
4-BrC_6H_4	2.0047	0.031	0.095	
4-$CH_3C_6H_4$	2.0045	0.032	0.118	0.065
4-*t*-$C_4H_9C_6H_4$	2.0045	0.028	0.103	
3-CH_3-4-ClC_6H_3	2.0046	0.030	0.100	
3-CH_3-4-BrC_6H_3	2.0046	0.030	0.100	

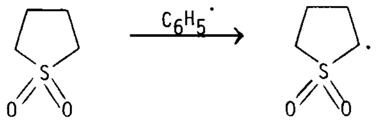
[a] Methylbenzene solvent; −80 °C; proton splitting except where indicated otherwise.
[b] Generally ±0.0001.
[c] Generally ±0.005 mT.
[d] At *ca.* 60 °C.

29 and **30** (Eqs. 17 and 18; *cf.* Eq. 10). The β-sulfonyl radical **31** is the major product from the reaction of sulfolane (**28**) and hydroxyl radicals (Eq. 19; *cf.* Eqs. 6 and 7).[13]



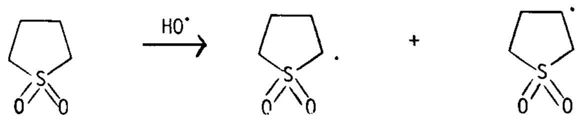
$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-CH_3 \xrightarrow{C_6H_5^{\bullet}} {}^{\bullet}CH_2-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-CH_3 \qquad (17)$$

27 **29**



(18)

28 **30**

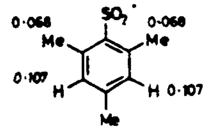
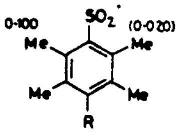
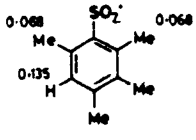
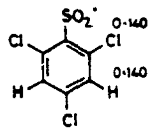
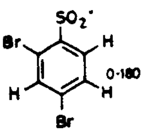
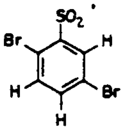
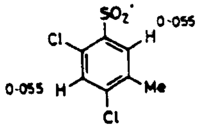
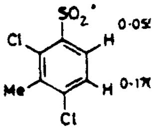
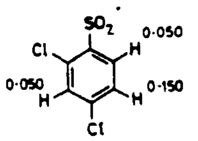
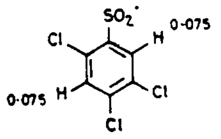
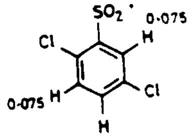
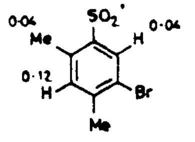


(19)

28 **30** **31**

TABLE VI

ESR Spectra of Some *ortho*-Substituted Arenesulfonyl Radicals (a_H/mT)[11;a]

 g 2.0049	 R=H,CH3[b] g 2.0049	 g 2.0049	 g 2.0054[c]
 g 2.0068	 g 2.0069	 g 2.0051	 g 2.0051
 g 2.0050	 g 2.0050[d]	 g 2.0050	 g 2.0050

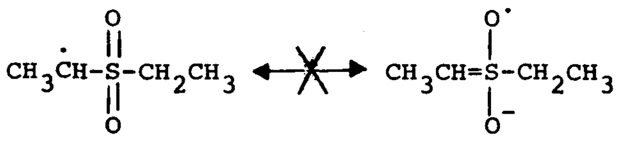
[a] Splittings ±0.005 mT; g-values ±0.0001; data refer to low temperatures (*ca.* −80 °C) and to proton splittings except where stated otherwise.

[b] Line-width alternation detected; at −30 °C, analysis has a(6H) 0.060 mT. The smaller indicated methyl-proton splitting in the low-temperature spectra is not resolved but is calculated from the averaged splitting.

[c] Line-width alternation detected; at −30 °C, a(2H) = a(2Cl) = 0.07 mT.

[d] A chlorine splitting became resolved above −40 °C.

Table VII gives ESR data for some α- and substituted α-sulfonyl radicals. The ratios of $a(\beta\text{-H}):a(\alpha\text{-H})$ of *ca.* 1.2:1 (Tables VII and VIII) for α-sulfonyl radicals are consistent with a planar geometry at the tervalent carbon atom. The value of $\alpha(\beta\text{-H})$ suggests that the sulfonyl group is ineffective in removing spin. Thus, structure **32b** is not a significant contributor to α-sulfonyl radical **32** (Eq. 20).[13] In contrast to these results from α-sulfinyl (**2**) and α-sulfonyl (**4**) radicals, the carbonyl group removes *ca.* 16% of the spin from an

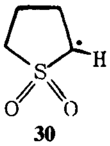
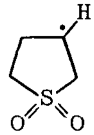
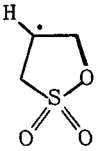
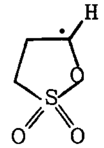


$$CH_3\dot{C}H-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_2CH_3 \quad \not\leftrightarrow \quad CH_3CH=\overset{\overset{O^{\bullet}}{|}}{\underset{\underset{O^-}{|}}{S}}-CH_2CH_3 \qquad (20)$$

32a **32b**

TABLE VII

ESR Spectra of Some Substituted Sulfonyl Radicals[13]

Radical	Origin	g	Hyperfine splittings/mT
$\dot{C}H_2S(O_2)CH_3$	a	2.0025	2.23 (2 H), 0.21 (3 H)
$CH_3\dot{C}HS(O_2)CH_2CH_3$	a,b	2.0025	2.16 (1 H), 2.73 (3 H), 0.21 (2 H)
 30	a,b	2.0025	2.10 (1 H) 3.88 (2 H), 0.18 (2 H)
	b	2.0029	2.21 (1 H), 3.275 (2 H), 3.475 (2 H), 0.08 (2 H)
$\dot{C}H_2CH_2CH_2S(O_2)C_3H_7$-$n$	b	2.0026	2.19 (2 H), 2.68 (2 H), 0.05 (2 H)
	c	2.0028	2.18 (1 H), 3.36 (2 H), 3.52 (2 H)
	c	2.0030	1.60 (1 H), 2.98 (2 H), 0.09 (2 H)
$CH_3\dot{C}HS(O_2)O^-$	d	2.0025	2.17 (1 H), 2.59 (3 H)
$\dot{C}H_2CH_2S(O_2)O^-$	d	2.0027	2.22 (2 H), 1.85 (2 H)

[a] Phenyl radical + sulfone.
[b] Hydroxyl radical + sulfone.
[c] Hydroxyl radical + 1,2-oxathiolan.
[d] Hydroxyl radical + $CH_3CH_2SO_3^-$.

adjacent tervalent carbon atom and the ethylthio group in $CH_3\dot{C}HSCH_2CH_3$ removes *ca.* 22%.[13]

B. Chemically Induced Dynamic Nuclear Polarization (CIDNP)

The observation of enhanced absorption and emission signals arising from chemically induced dynamic nuclear spin polarization (CIDNP) has been used for the detection of paramagnetic species.[53,54] Proper interpretation of CIDNP spectra allows the detection of radical pair processes, the assignment of the multiplicity of these pairs, identity of the pair parameters, and possible calculations of g-factors and the hyperfine fields of the

TABLE VIII

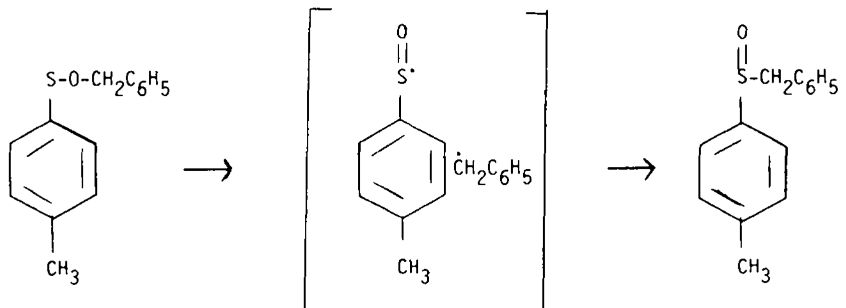
Isotropic ESR Parameters for Some Radicals[a;13]

Radical	g	Hyperfine splittings/mT[b] $a(\alpha\text{-H})$	$a(\beta\text{-H})$	$a(\gamma\text{-H})$
$\dot{C}H_3$[c]	2.0025	2.29		
$\dot{C}H_2SCH_3$[d]	2.0049	1.65		0.36
$\dot{C}H_2S(O)CH_3$	2.0025	2.00		
$\dot{C}H_2S(O)_2CH_3$	2.0025	2.23		0.21
$CH_3\dot{C}H_2$	2.0025	2.22	2.71	
$CH_3\dot{C}HSCH_2CH_3$[d]	2.0044	1.70	2.10	0.15
$CH_3\dot{C}HS(O)CH_2CH_3$	2.0025	2.16	2.73	0.21
$CH_3\dot{C}HS(O)_2O^-$	2.0025	2.17	2.59	

[a] In aqueous solution at 22–24 °C.
[b] α, β, γ refer to protons attached to the tervalent carbon atom and successive atoms.
[c] Beckwith, A.J.L.; Norman, R.O.C. *J. Chem. Soc. B* 1969, 400.
[d] Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. *J. Chem. Soc., Perkin 2* 1973, 1748.

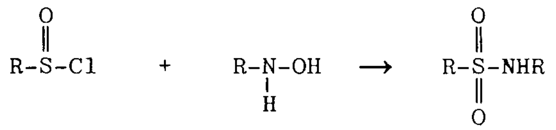
individual radicals.[53] During the diffusion of radicals in solution and the variations of exchange interactions during the pair lifetime, it is not yet possible to predict absolute enhancements of CIDNP spectral intensities.

CIDNP emission signals are observed in the thermal rearrangement of phenylmethyl *p*-toluenesulfenate (**33**) to phenylmethyl *p*-tolyl sulfoxide (**34**) which suggests a radical pair is involved in the process (Eq. 21).[53–55]

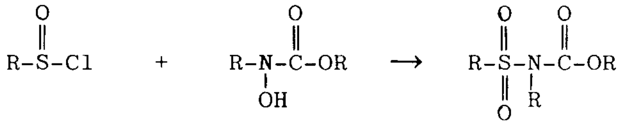


33 **34** (21)

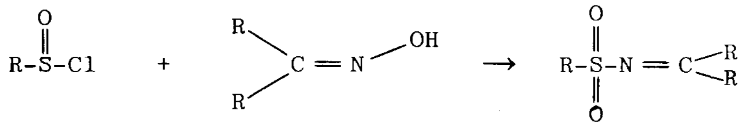
Alkane- and arenesulfinyl chlorides react with several types of *N*-hydroxy compounds, including hydroxylamines,[56] *N*-hydroxycarbamates,[57] *N*-hydroxyureas,[58] *N*-phenylhydroxamic acids,[59] and oximes,[60] via the formation of *O*-sulfinylated intermediates which subsequently undergo thermal rearrangements involving radical cage processes (Eqs. 22–24). The radical process is accompanied by pronounced ^{1}H-CIDNP effects, which may be interpreted using Kaptein's rule.[57,58]



$$R-\overset{O}{\overset{\|}{S}}-Cl + R-\underset{H}{\underset{|}{N}}-OH \longrightarrow R-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-NHR \qquad (22)$$



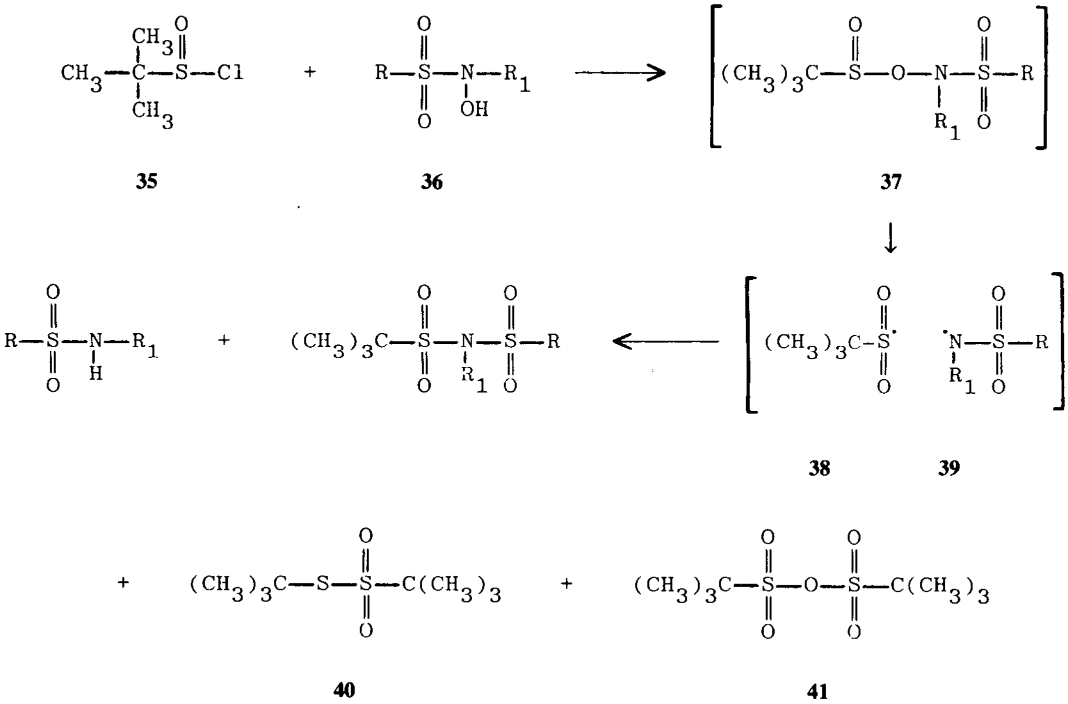
$$R-\overset{O}{\overset{\|}{S}}-Cl + R-\underset{OH}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-OR \longrightarrow R-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-\underset{R}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-OR \qquad (23)$$



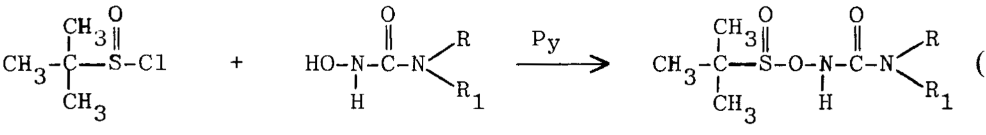
(24)

The reaction of 2-methyl-2-propanesulfinyl chloride (**35**) with *N*-hydroxysulfonamides (**36**) in the presence of 1 equiv of azabenzene (pyridine) gives a transient *N*-[(2-methyl-2-propylsulfinyl)oxy]-sulfonamide intermediate via sulfonoamidyl radicals.[61a] Proton CIDNP and ^{13}C CIDNP effects provide evidence for a homolytic rearrangement of this transient intermediate (Scheme II).

SCHEME II



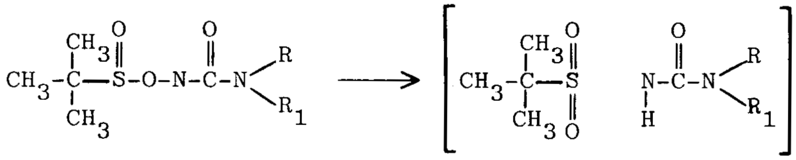
2-Methyl-2-propanesulfinyl chloride (**35**) reacts smoothly with *N*-hydroxyureas (**42**) in propanone at 22–24 °C, in the presence of two equiv of azabenzene, to give radical recombination and escape products.[58] The postulated *O*-(2-methyl-2-propanesulfinyl)-*N*-hydroxyurea intermediate **43** rearranges via a radical cage mechanism to give the corresponding *N*-*tert*-butylsulfonylurea as the recombination product (Eqs. 25, 26; *cf*. Scheme II). Homolytic cleavage of the N—O bond in intermediate **37** is accompanied by pronounced ^{1}H-CIDNP effects.



$$(CH_3)_3C{-}S(O){-}Cl + HO{-}NH{-}C(O){-}NRR_1 \xrightarrow{Py} (CH_3)_3C{-}S(O){-}O{-}NH{-}C(O){-}NRR_1$$

35 **42** **43**

(25)

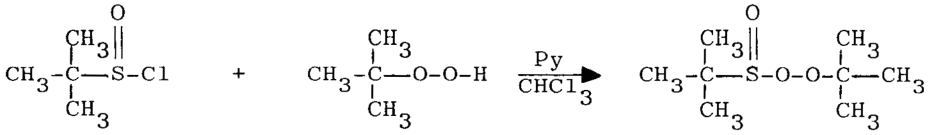


$$(CH_3)_3C{-}S(O){-}O{-}NH{-}C(O){-}NRR_1 \longrightarrow \left[(CH_3)_3C{-}SO_2 \quad NH{-}C(O){-}NRR_1\right]$$

43 **38** **44**

(26)

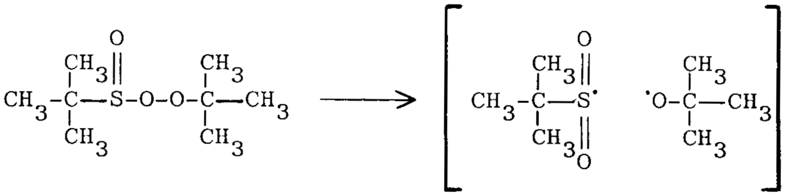
2-Methyl-2-propanesulfinyl chloride (**35**) reacts with *tert*-butyl hydroperoxide in the presence of azabenzene to give a variety of products including *tert*-butylsulfonate (radical recombination), *S*-(2-methyl-2-propyl) 2-methyl-2-propanesulfonothioate (**40**), and 2-methyl-2-propanesulfonic acid anhydride (**41**, Eqs. 27, 28; *cf*. Scheme II)[61b] Proton-CIDNP effects provided strong evidence for homolytic cleavage of the initially formed 2-methyl-2-propyl 2-methyl-2-propaneperoxysulfinate (**45**) via a radical cage process.



$$(CH_3)_3C{-}S(O){-}Cl + (CH_3)_3C{-}O{-}O{-}H \xrightarrow[CHCl_3]{Py} (CH_3)_3C{-}S(O){-}O{-}O{-}C(CH_3)_3$$

35 **45**

(27)

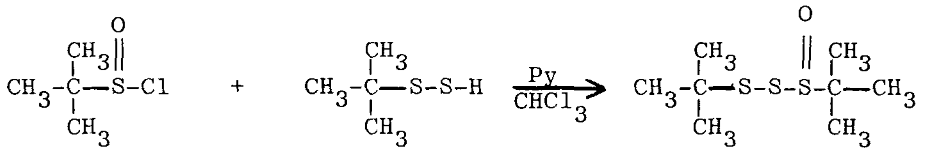


$$(CH_3)_3C{-}S(O){-}O{-}O{-}C(CH_3)_3 \longrightarrow \left[(CH_3)_3C{-}S^{\bullet}O_2 \quad {}^{\bullet}O{-}C(CH_3)_3\right]$$

45 **38** **46**

(28)

2-Methyl-2-propanesulfinyl chloride (**35**) reacts with *tert*-butyl hydrosulfide to give 2-methyl-2-propyl 2-methyl-2-propanesulfinyl disulfide (**47**, 90%).[61b] Thermal decomposition of **47** is slower than peroxysulfinate **45** owing to the higher S(O)—S bond dissociation energy in **47** relative to the low O—O bond dissociation energy in **45**.

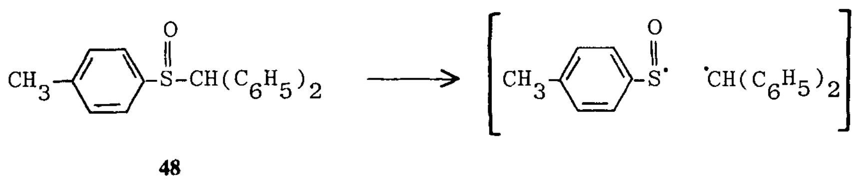


$$(CH_3)_3C{-}S(O){-}Cl + (CH_3)_3C{-}S{-}S{-}H \xrightarrow[CHCl_3]{Py} (CH_3)_3C{-}S{-}S{-}S(O){-}C(CH_3)_3$$

(29)

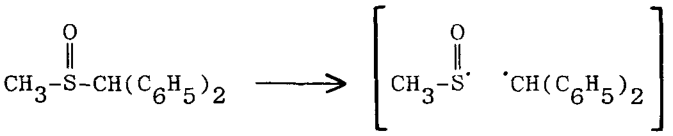
35 **47**

Product analysis, ESR, and CIDNP results showed that the thermal (100–130 °C) decomposition of benzhydryl *p*-tolyl sulfoxide (**48**) and benzhydryl methyl sulfoxide (**49**) gave *p*-toluenesulfinyl and methanesulfinyl radicals, respectively, by cleavage of carbon-sulfur bonds (Eqs. 30, 31; *cf*. Eq. 21).[62]



(30)

48



$$CH_3{-}S(O){-}CH(C_6H_5)_2 \longrightarrow \left[CH_3{-}S^{\bullet}(O) \quad {}^{\bullet}CH(C_6H_5)_2\right]$$

(31)

49

A comparative photo-CIDNP study of triplet benzophenone sensitized C—S photocleavage of sulfoxides reveals significant structural dependence of the cage recombination and escape processes.[43] In the photoreactive *ortho*-substituted methyl phenyl sulfoxides the triplet spin-correlated methyl-arylsulfinyl radical pair ($CH_3^{\bullet}$ + $ArSO^{\bullet}$) is formed by triplet benzophenone sensitization or in some molecules, by direct excitation and intersystem crossing.

C. Absorption Spectra

A pulse radiolysis study of aqueous solutions of some alkanesulfonyl chlorides has been carried out.[63] The optical spectral properties (λ_{max} = 332 nm) of the sulfonyl radicals were obtained along with the rate constants associated with their formation.[63a]

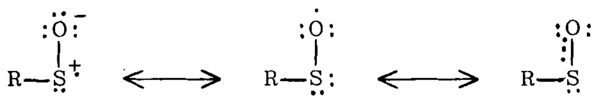
The flash photolysis of some arenesulfonyl iodides and aromatic sulfones showed transient spectra with maxima near 330 nm and continuous bands up to 500 nm, which were attributed to arenesulfonyl radicals.[49] No wavelength shift in the absorption maxima was observed for substituted benzenesulfonyl radicals. The absorption maxima and decay rate constants of arenesulfonyl radicals were compared with those of some isoelectronic radicals (anilino, benzyl, phenoxy, thiophenoxy).[49a]

III. MOLECULAR ORBITAL CALCULATIONS

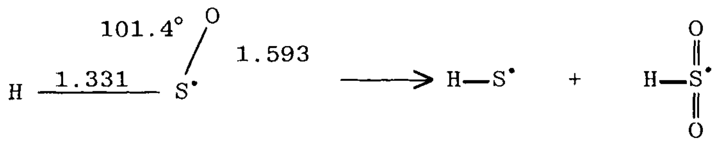
Benson[7] has discussed the thermochemistry and kinetics of sulfur-containing molecules and radicals (Table IX).

A. Sulfinyl Radicals

The structure of the simplest sulfinyl radical (hydrosulfinyl, $H\dot{S}O$) has been examined by ab initio molecular orbital calculations at the HF/3-21G level.[64] Although sulfinyl radicals (**1**) are considered to be relatively stable delocalized and unreactive π type radicals (Eq. 32), ab initio molecular orbital calculations (HF/3-21G) show the disproportionation of hydrosulfinyl radical to thiyl sulfonyl radicals (Eq. 33) to be thermodynamically favorable (13.6 kcal mol^{-1}).



(32)



(33)

The hydrosulfinyl radical, which is the isovalent sulfur analog of the hydroperoxyl radical ($HO_2^{\bullet}$), was observed in the gas phase for the first time in a chemiluminescence

TABLE IX

Bond Dissociation Energies of Some Organosulfur Compounds[7]

Bond	Dissociation energy (kJ/mol)	Bond	Dissociation energy (kJ/mol)
CH_3—SH	384.9	CH_3SO_2—CH_3	284.5
R—SH	384.9	$C_2H_5SO_2$—C_2H_5	284.5
C_6H_5—SH	343.1	$C_6H_5SO_2$—C_6H_5	347.3
CH_3S—SCH_3	309.6	CH_3SO_2—$CH_2C_6H_5$	234.3
RS—SR	309.6	CH_3SO_2—$CH_2CH_2CH_2$	230.1
C_6H_5S—SC_6H_5	230.1	CH_3SO_2—C_6H_5	347.3
C_6H_5S—SCH_3	272	$C_6H_5SO_2$—CH_3	225.9
$CH_3S(O)$—CH_3	(230.1)[a]	ArS(O)—S—Ar	146.4[b]
$C_6H_5S(O)$—C_6H_5	150.6	$C_6H_5S(O)$—$SO_2C_6H_5$	117.2
ArS(O)—$CH_2C_6H_5$	184[b]	$C_6H_5SO_2$—$SO_2C_6H_5$	169.2

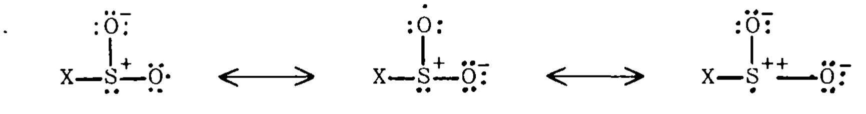
[a] Estimated value.

[b] Reference 3.

spectrum.[65,66] Accurate ground- and excited-state molecular constants have been obtained for the hydrosulfinyl radical using a Doppler-limited single-mode dye laser.[67] Webster and coworkers[68] have obtained the electric dipole moments[69] of the hydrosulfinyl radical which are in close agreement with SCF and CI molecular orbital methods.[64,70,71]

B. Sulfonyl Radicals

Extensive ab initio molecular orbital calculations have been performed on six sulfonyl radicals ($X\dot{S}O_2$, where $X = H, CH_3, NH_2, OH, F$, and Cl).[72] The calculated equilibrium geometries for the six sulfonyl radicals show essentially constant structural parameters of the SO_2 functional group: $r(S{-}O) = 1.47 \pm 0.01$ Å, $< OSO = 123 \pm 2°$, and a nonplanar (pyramidal) arrangement about the sulfur atom with the unpaired electron delocalized over both oxygens and the sulfur. The sulfonyl radical may be represented by the three principal contributors shown in equation 34 (*cf.* Eq. 16). There is restricted rotation about the C—S bond in $CH_3SO_2^{\cdot}$.[12] The total energies (au) for HSO_2 and methanesulfonyl radicals are −541.43082 and −580.02968, respectively.[72]



$$\mathrm{X{-}\overset{:\ddot{O}:^{-}}{\overset{|}{\ddot{S}^{+}}}{-}\ddot{O}\cdot} \longleftrightarrow \mathrm{X{-}\overset{:\dot{O}:}{\overset{|}{\ddot{S}^{+}}}{-}\ddot{O}:^{-}} \longleftrightarrow \mathrm{X{-}\overset{:\ddot{O}:^{-}}{\overset{|}{\dot{S}^{++}}}{-}\ddot{O}:^{-}} \qquad (34)$$

Sulfur-33 splittings show that aminosulfonyl radicals ($RRNSO_2^{\cdot}$) are pyramidal and have more than 50% of the spin density on sulfur.[8b]

The INDO molecular orbital method has been used to calculate possible structures and conformations of alkane-, alkene-, and arenesulfonyl radicals.[11,12]

IV. FORMATION AND CHEMISTRY OF SULFINYL AND α-SULFINYL RADICALS

Sulfinyl radicals have been characterized as relatively delocalized and unreactive π radicals in comparison to σ-type sulfonyl radicals. Kice[3] ascribed the bond-weakening effect of SO on adjacent bonds to the stability of sulfinyl radicals. Benson[7] suggested that the bond weakening effect of SO arises from the low ΔH_f° of the parent molecule owing to the principle of alternating polarity. It was also concluded that arenesulfonyl radicals possess greater resonance stabilization than arenesulfinyl radicals.[7] Interestingly, it is known that resonance stabilized and highly hindered radicals are trapped by spin radical traps with difficulty and that sulfonyl radicals, but not sulfinyl radicals, have been trapped. The facile and rapid reaction of sulfinyl radicals with other sulfinyl radicals may explain the lack of success of the trapping experiments.

A. From Sulfenic Acids and their Derivatives

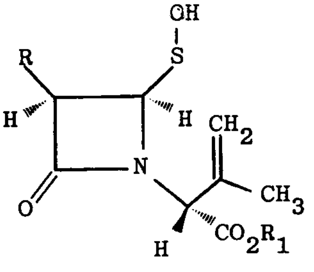
Highly reactive and usually unstable sulfenic acids (RSOH) undergo hydrogen atom transfer to free radicals very rapidly with other radicals (Eqs. 35, 36).[73,74] Block and O'Connor[75] suggested that the marked antioxidant activity of many sulfinothionic acid

S-esters (thiosulfinates) is probably due to the reaction of free radicals with the sulfenic acid generated by thermolysis of the sulfinothioic *S*-ester.

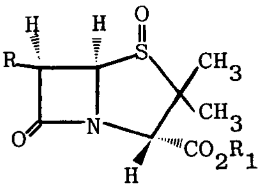
$$\mathrm{R{-}\ddot{\underset{\cdot\cdot}{S}}{-}O{-}H} \; + \; \mathrm{R_1^{\bullet}} \longrightarrow \mathrm{R{-}\ddot{\underset{\cdot\cdot}{S}}{-}\ddot{\underset{\cdot\cdot}{O}}\cdot} \; + \; \mathrm{R_1H} \qquad (35)$$

$$\mathrm{H_2O_2} \; + \; \mathrm{RS^{\bullet}} \longrightarrow \mathrm{R{-}\ddot{\underset{\cdot\cdot}{S}}{-}O{-}H} \; + \; \mathrm{HO^{\bullet}} \longrightarrow \mathrm{R{-}\ddot{\underset{\cdot\cdot}{S}}{-}\ddot{\underset{\cdot\cdot}{O}}\cdot} \; + \; \mathrm{H_2O} \qquad (36)$$

Oxoazetidinesulfenic acids (**50**), which are intermediates in the thermolysis of penicillin sulfoxides **51**, give the corresponding sulfinyl halides (**52**) on treatment with various halogenating agents. In some cases, sulfinyl radicals may be intermediates.[76]



50



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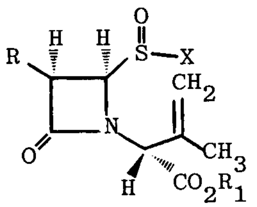
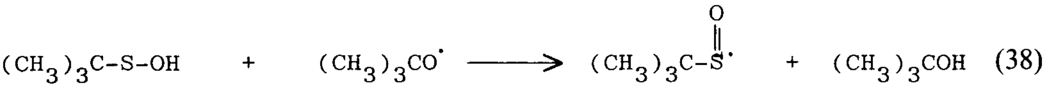


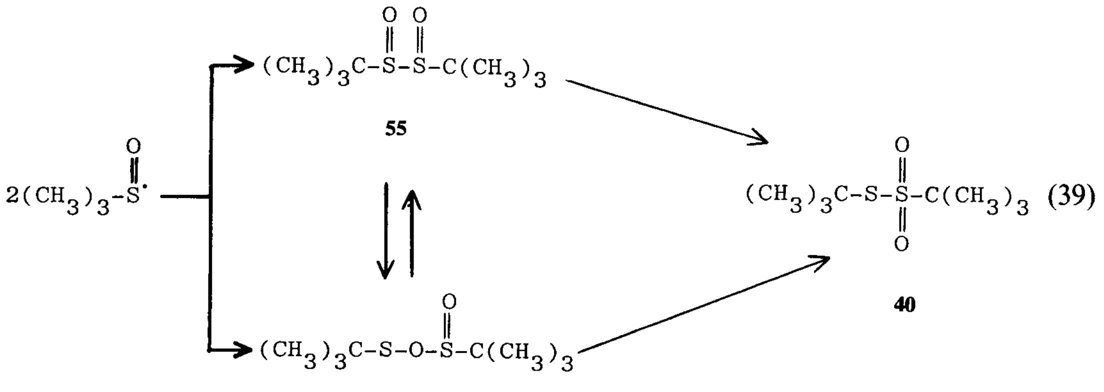
52

S-(2-Methyl-2-propyl) 2-methyl-2-propanesulfonothioate (**40**) is the major product when *tert*-butyl hyponitrite is thermally decomposed in the presence of a solution of 2-methyl-2-propanesulfenic acid (**53**) in methylbenzene (Eqs. 37–39).[15] Thus, it appears that

$$\mathrm{(CH_3)_3CON{=}NOC(CH_3)_3} \longrightarrow \mathrm{2(CH_3)_3CO^{\bullet}} \; + \; \mathrm{N_2} \qquad (37)$$



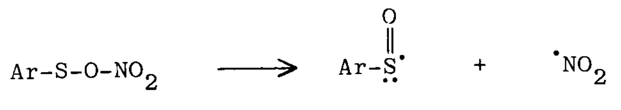
$$\underset{\mathbf{53}}{\mathrm{(CH_3)_3C{-}S{-}OH}} \; + \; \mathrm{(CH_3)_3CO^{\bullet}} \longrightarrow \underset{\mathbf{54}}{\mathrm{(CH_3)_3C{-}\overset{O}{\overset{\|}{S}}{}^{\bullet}}} \; + \; \mathrm{(CH_3)_3COH} \qquad (38)$$



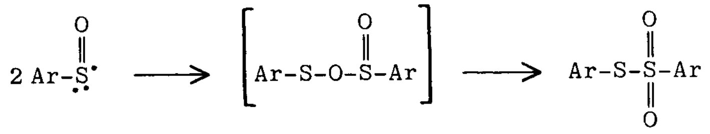
56

the 2-methyl-2-propanesulfinyl radical (**54**), *vic*-disulfoxides (**55**), and/or *O*-sulfenyl sulfinates (**56**) are possible transient intermediates. Thiosulfonate **40** is also the expected product from the photolysis of di-*tert*-butyl peroxide in a solution of 2-methyl-2-propanesulfenic acid (**53**) in methylbenzene or 2-methylbutane.[15]

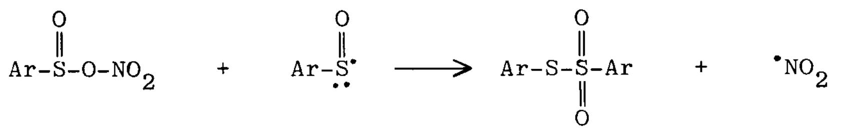
Sulfenyl nitrates, which are prepared by reactions of equivalent quantities of the sulfenyl chlorides and silver nitrate in dry ethanenitrile, are rapidly converted to the corresponding *S*-aryl arenesulfonothioates with certain solvents such as ethanol, 1,2-dichloroethane, dichloromethane, and water.[38,77] The proposed mechanism for the decomposition of sulfenyl nitrate involves initial homolytic cleavage to arenesulfinyl and nitrogen dioxide radicals. Coupling of the arenesulfinyl radicals to give *O*-sulfenyl sulfinates and/or *vic*-disulfoxides followed by rearrangement to *S*-aryl arenesulfonothioates is reasonable (Eqs. 40, 41). The possibility that the arenesulfinyl radical interacts with sulfenyl nitrate, giving *S*-aryl arenesulfonothioate and nitrogen dioxide radical, has not been ruled out (Eq. 42).[38,77] The question as to whether sulfinyl radicals might couple to yield sulfenyl peroxides (**57**) is also of interest (Eq. 43).



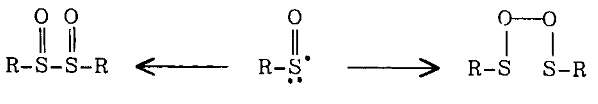
$$\mathrm{Ar{-}S{-}O{-}NO_2} \longrightarrow \mathrm{Ar{-}}\overset{\mathrm{O}}{\overset{\|}{\underset{\cdot\cdot}{\mathrm{S}}}}{}^{\bullet} + {}^{\bullet}\mathrm{NO_2} \qquad (40)$$



$$2\,\mathrm{Ar{-}}\overset{\mathrm{O}}{\overset{\|}{\underset{\cdot\cdot}{\mathrm{S}}}}{}^{\bullet} \longrightarrow \left[\mathrm{Ar{-}S{-}O{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}Ar}\right] \longrightarrow \mathrm{Ar{-}S{-}}\overset{\mathrm{O}}{\overset{\|}{\underset{\overset{\|}{\mathrm{O}}}{\mathrm{S}}}}\mathrm{{-}Ar} \qquad (41)$$



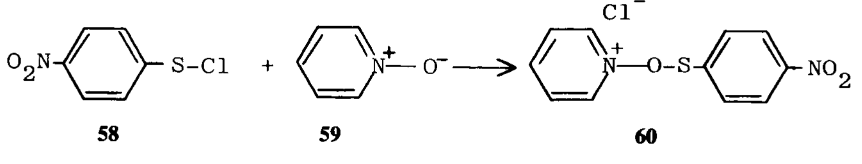
$$\mathrm{Ar{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}O{-}NO_2} + \mathrm{Ar{-}}\overset{\mathrm{O}}{\overset{\|}{\underset{\cdot\cdot}{\mathrm{S}}}}{}^{\bullet} \longrightarrow \mathrm{Ar{-}S{-}}\overset{\mathrm{O}}{\overset{\|}{\underset{\overset{\|}{\mathrm{O}}}{\mathrm{S}}}}\mathrm{{-}Ar} + {}^{\bullet}\mathrm{NO_2} \qquad (42)$$



$$\mathrm{R{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}}\overset{\mathrm{O}}{\overset{\|}{\mathrm{S}}}\mathrm{{-}R} \longleftarrow \underset{\mathbf{1}}{\mathrm{R{-}}\overset{\mathrm{O}}{\overset{\|}{\underset{\cdot\cdot}{\mathrm{S}}}}{}^{\bullet}} \longrightarrow \underset{\mathbf{57}}{\mathrm{R{-}}\overset{\mathrm{O{-}}}{\overset{|}{\mathrm{S}}}\;\overset{\mathrm{O}}{\overset{|}{\mathrm{S}}}\mathrm{{-}R}} \qquad (43)$$

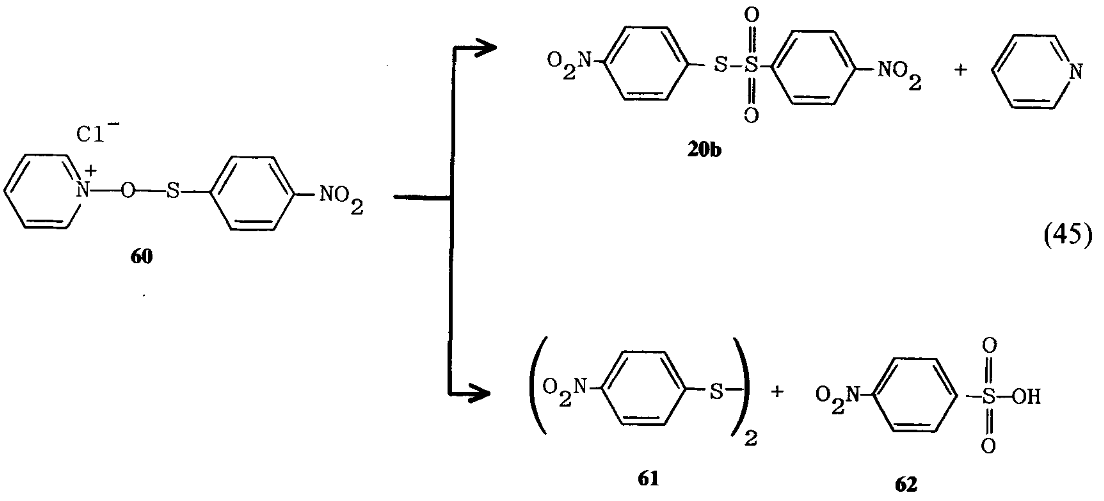
1 **57**

Equivalent amounts of *p*-nitrobenzenesulfenyl chloride (**58**) and azabenzene *N*-oxide (**59**) react to give 1-*p*-nitrobenzenesulfinylpyridinium chloride (**60**) which, on heating, gives azabenzene, 4,4′-dinitrophenyl disulfide (**61**), 4-nitrobenzenesulfonic acid (**62**), and *S*-(4-nitrophenyl) 4-nitrobenzenesulfonothioate (**20b**, Eqs. 44, 45).[77] The lack of hetero-ring substituted products and the ESR signals observed during and shortly after reaction appear to support a mechanism involving the 4-nitrobenzenesulfinyl radical (**63**).



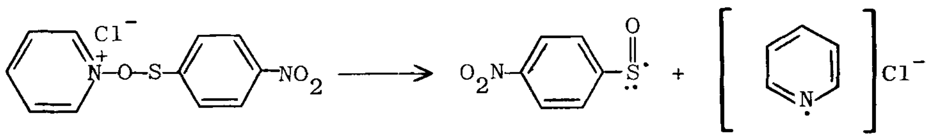
58 **59** **60**

(44)



60 **20b** **61** **62**

(45)



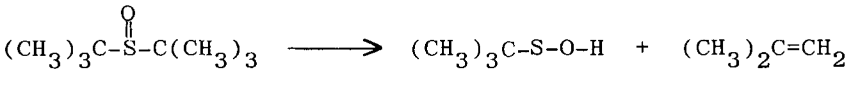
60 **63** **64**

(46)

The enhanced absorption and emission signals (CIDNP) observed during the rearrangement of sulfenate **33** (Eq. 21) and in other sulfenate systems have generated considerable discussion concerning the intermediacy of radicals.[37,55,78–80]

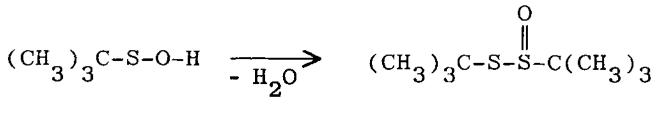
B. From Sulfoxides

1. Thermolysis The thermal decomposition of sulfoxides in solution, which proceeds via a cis β-elimination, leads to sulfenic acids and unsaturated compounds (*cf.* Eqs. 11, 30, 31).[16,17,37,80–88] Sulfenic acids (*vide supra*) can lead to sulfinothioic acid *S*-esters via a cyclodehydration mechanism or to sulfonothioic acid *S*-esters via sulfinyl radicals (Eq. 47, 48; *cf.* Eqs. 38, 39; Scheme III). Sulfenate intermediates also have been proposed in the rearrangement of certain sulfoxides.[37,55,79,80,89]



$$(CH_3)_3C-\overset{O}{\overset{\|}{S}}-C(CH_3)_3 \longrightarrow (CH_3)_3C-S-O-H + (CH_3)_2C=CH_2 \qquad (47)$$

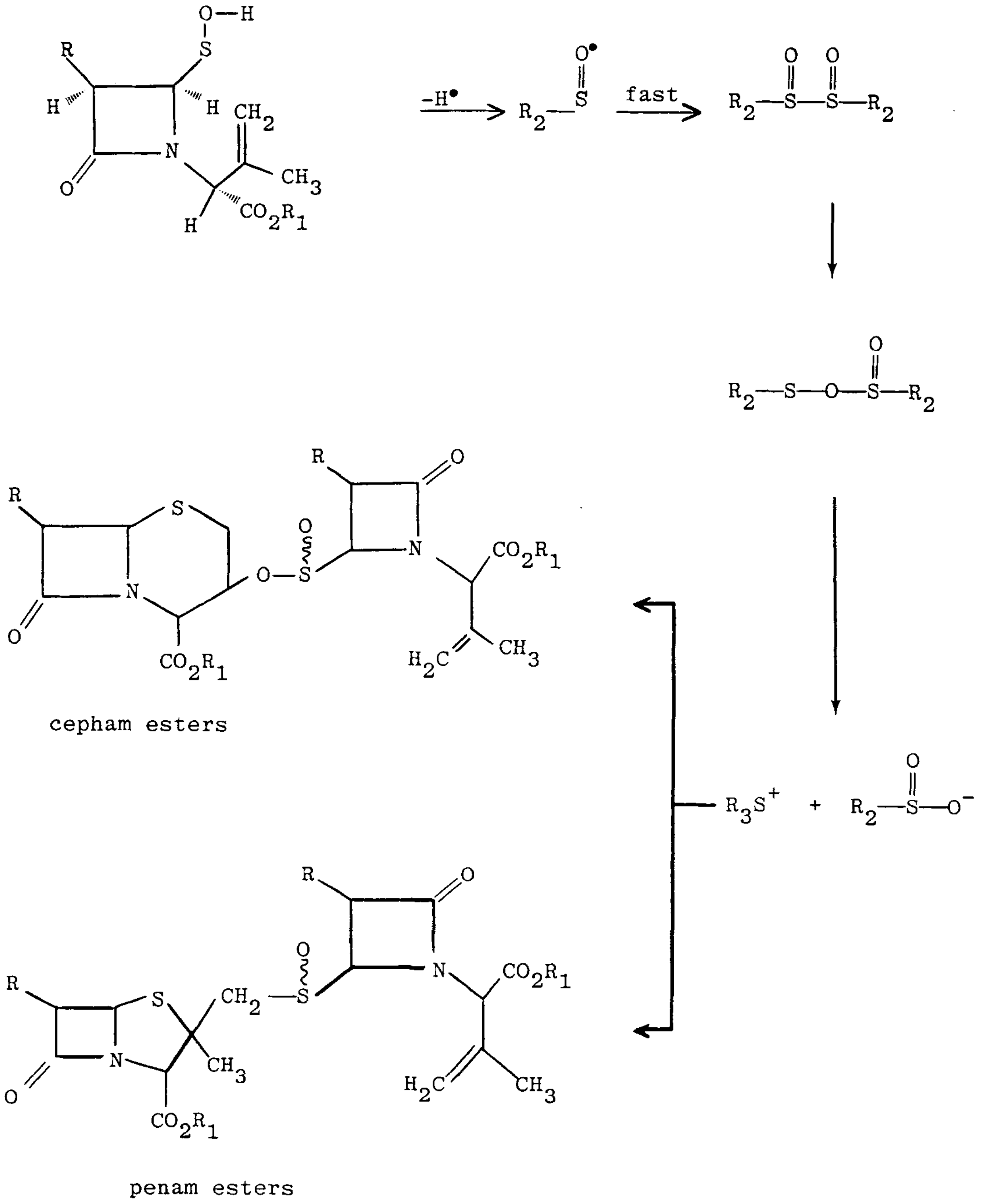
65 **53**



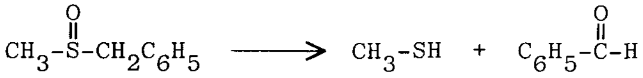
$$(CH_3)_3C-S-O-H \xrightarrow[-\,H_2O]{} (CH_3)_3C-S-\overset{O}{\overset{\|}{S}}-C(CH_3)_3 \qquad (48)$$

53 **66**

SCHEME III

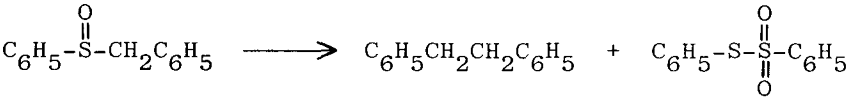


Sulfoxides without a β-hydrogen atom are not thermolyzed to sulfenic acids and unsaturated compounds. Pyrolysis of methyl phenylmethyl sulfoxide (**67**) gives methanethiol and phenylmethanal (Eq. 49).[90] The flash vacuum pyrolysis (FVP) of phenyl phenylmethyl sulfoxide (**68**) at 500 °C gave 1,2-diphenylethane and *S*-phenyl benzenesulfonothioate (**20a**) as principal products (Eq. 50; *cf.* Eqs. 30, 31).[63,84] Phenylsulfinyl (**21a** $C_6H_5\dot{S}O$) and phenylmethyl radicals are formed in pyrolysis of **68** as evidenced by the formation of **20a**. The coupling of sulfinyl radicals, probably through *O*-sulfenyl sulfinates, has been proposed (*cf.* Eqs. 11–13, 39, 41, 43).[1,40–42,73,77,83b] Mislow and coworkers[37] have shown that sulfinyl radicals are involved in the thermal racemization of aryl phenylmethyl sulfoxides.



$$CH_3-\overset{O}{\overset{\|}{S}}-CH_2C_6H_5 \longrightarrow CH_3-SH + C_6H_5-\overset{O}{\overset{\|}{C}}-H \qquad (49)$$

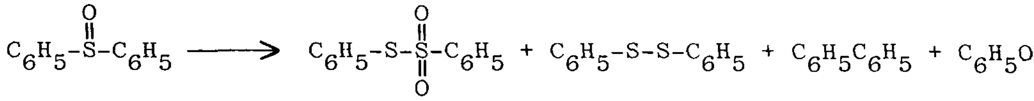
67



$$C_6H_5-\overset{O}{\overset{\|}{S}}-CH_2C_6H_5 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + C_6H_5-S-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-C_6H_5 \qquad (50)$$

68 **20a**

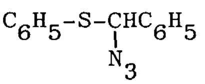
Flash vacuum pyrolysis (FVP) of diphenyl sulfoxide (**19a**) gave thiosulfonate **20a** (40%), diphenyl disulfide (12%), phenylbenzene (6%), benzenol (4%), and diphenyl sulfide (7%) as the major products (Eq. 51).[84]



$$C_6H_5-\overset{O}{\overset{\|}{S}}-C_6H_5 \longrightarrow C_6H_5-S-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-C_6H_5 + C_6H_5-S-S-C_6H_5 + C_6H_5C_6H_5 + C_6H_5OH \qquad (51)$$

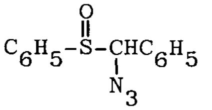
19a **20a**

Thermolysis of α-azidophenylmethyl phenyl sulfide (**69a**), and the corresponding sulfoxides (**69b**) and sulfone (**69c**), proceeds at markedly different rates. Sulfoxide **69b** readily decomposes at 70 °C through a radical pair intermediate ($[C_6H_5—\dot{S}O][C_6H_5—\dot{C}HN_3]$) which gives rise to a CIDNP effect in the reaction products.[84]



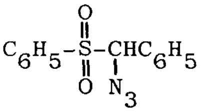
$$C_6H_5-S-\underset{\underset{N_3}{|}}{C}HC_6H_5$$

69a



$$C_6H_5-\overset{O}{\overset{\|}{S}}-\underset{\underset{N_3}{|}}{C}HC_6H_5$$

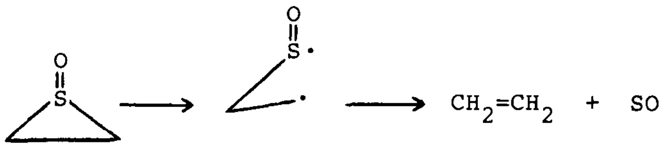
69b



$$C_6H_5-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-\underset{\underset{N_3}{|}}{C}HC_6H_5$$

69c

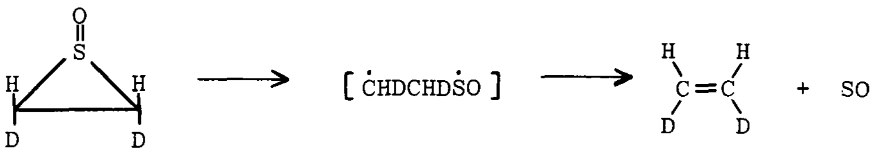
The thermal decomposition of cyclic sulfoxides and sulfones has been reviewed by Block,[2a] by Braslavsky and Heicklen,[91] and by Brown.[92] Thiirane oxide (ethylene episulfoxide, **70**) decomposes slowly into ethene and sulfur monoxide.[93,94] Dienes have been used to trap sulfur monoxide.[93] Whether the nascent sulfur monoxide is an excited singlet ground state or in the triplet ground state has been discussed.[94]



70

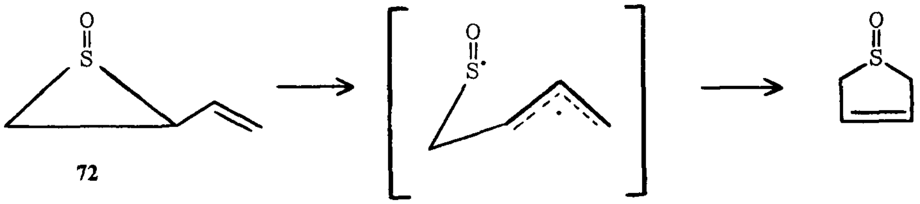
(52)

The pyrolysis of E- and Z-2,3-dideuteriothiirane (**71**) gave deuterated ethenes with 95% retention of stereochemistry which suggests a significant contribution of a concerted process or a stereochemically rather rigid biradical intermediate (Eq. 52).[95,96] Sulfinyl radicals are also thought to be involved in the thermolysis of thiirane oxides **72**, **73**, and **74** (Eqs. 54–56).[97–]



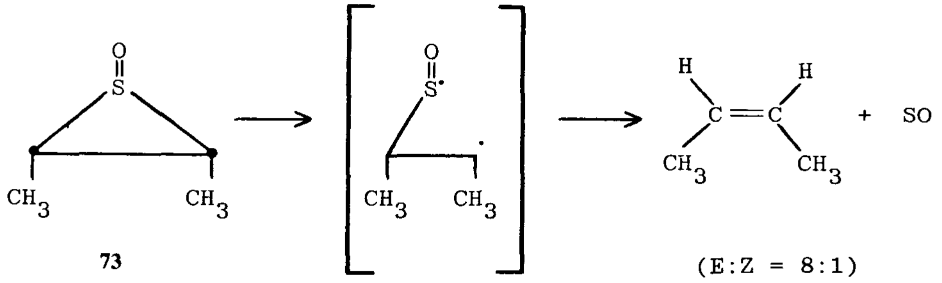
71

(53)



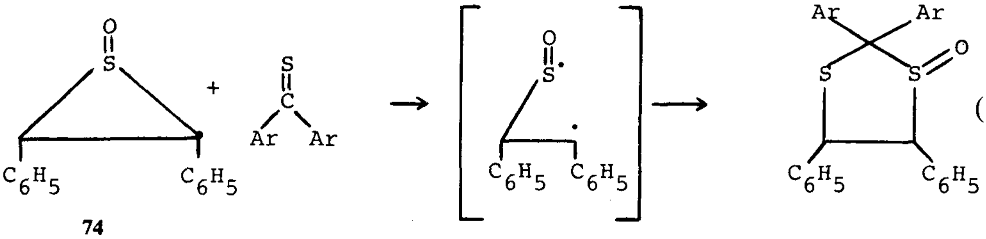
72

(54)



73

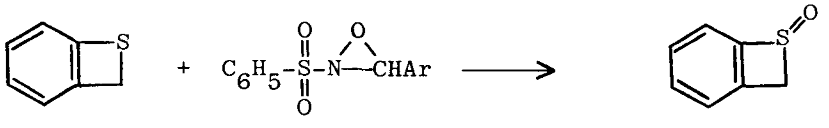
(55)



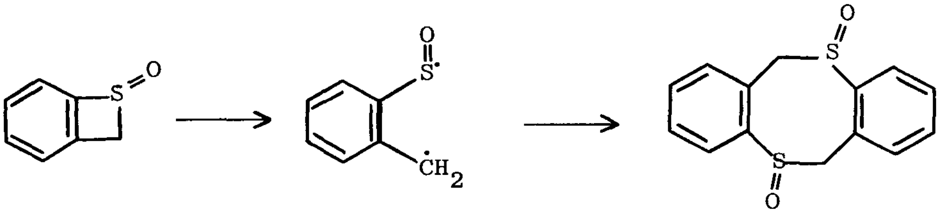
74

(56)

Oxidation of benzo[b]thiete (**75**) by 2-(phenylsulfonyl)-3-*p*-nitrophenyl)oxaziridine gave only dimeric sulfoxide **78** as a 58:42 mixture of diastereomers.[83] The formation of benzothiete *S*-oxide dimer **78** is believed to occur by dimerization of diradical **77** resulting from rupture of the C—S(O) bond in benzo[b]-thiete *S*-oxide (**76**, Eqs. 57, 58).

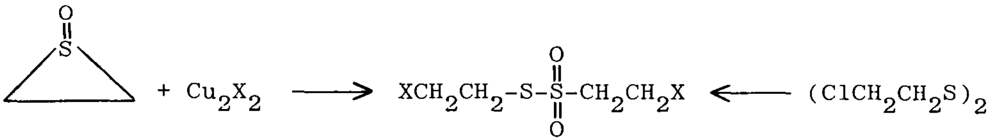


75 **76** (57)



76 **77** **78** (58)

Thiirane oxide (**70**) reacts with cupric chloride in benzene at 22–24 °C to give *S*-(2-chloroethyl) 2-chloroethanesulfonothioate (**79**, 66%).[100] Compound **79** was also prepared from bis(2-chloroethyl) disulfide (**80**). The dibromo analogue of **79** (**81**) was prepared from thiirane oxide (**70**) and cupric bromide. Although the proposed mechanism involves attack of sulfinyl cation at the sulfoxide group, a free radical mechanism involving sulfinyl radical has not been disproved. Support for the ionic mechanism comes from the reaction of thiirane oxide (**70**) and ethanesulfinyl chloride (**82**) which gives *S*-ethyl ethanesulfonothioate (**83**, 20%) and *S*-(2-chloroethyl) ethanesulfonothioate (**84**, 80%).[100]

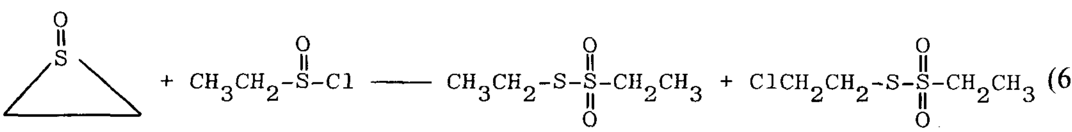


$$+\ \mathrm{Cu_2X_2} \longrightarrow \mathrm{XCH_2CH_2{-}S{-}\overset{O}{\underset{O}{S}}{-}CH_2CH_2X} \longleftarrow \mathrm{(ClCH_2CH_2S)_2} \qquad (59)$$

70 **80**

79 X = Cl

81 X = Br

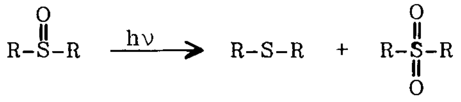


$$+\ \mathrm{CH_3CH_2{-}\overset{O}{S}{-}Cl} \longrightarrow \mathrm{CH_3CH_2{-}S{-}\overset{O}{\underset{O}{S}}{-}CH_2CH_3} + \mathrm{ClCH_2CH_2{-}S{-}\overset{O}{\underset{O}{S}}{-}CH_2CH_3} \qquad (60)$$

70 **82** **83** **84**

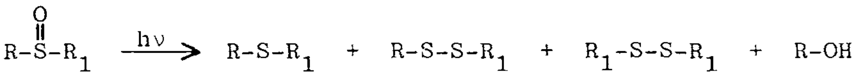
2. *Photolysis* A series of sulfoxides including dialkyl, dialkenyl, and alkyl aryl types were exposed to direct and sensitized photolysis. Only those photosensitizers containing a carbonyl group were effective. Scission of a carbon-sulfur bond of the sulfoxide was

confirmed by products derived from initially formed alkyl radicals and sulfinyl radicals. Products derived from alkoxyl and thiyl radicals indicated formation of sulfenate esters by combination of alkyl radical with oxygen of the sulfinyl radical and subsequent cleavage of the sulfur-oxygen bond. Other reactions may occur in some cases, including deoxygenation, disproportionation, 1,2-elimination, and racemization (Eqs. 61, 62).[88]



$$R{-}\overset{O}{\overset{\|}{S}}{-}R \xrightarrow{h\nu} R{-}S{-}R + R{-}\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}{-}R \qquad (61)$$

85a $R = CH_3$
85b $R = n\text{-}C_3H_7$
85c $R = \text{allyl}$

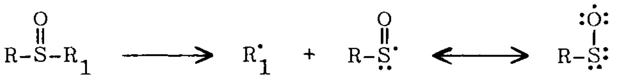


$$R{-}\overset{O}{\overset{\|}{S}}{-}R_1 \xrightarrow{h\nu} R{-}S{-}R_1 + R{-}S{-}S{-}R_1 + R_1{-}S{-}S{-}R_1 + R{-}OH \qquad (62)$$

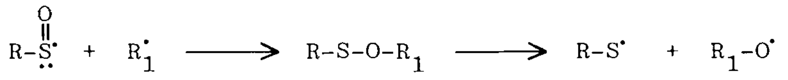
86a $R = R_1 = i\text{-}C_3H_7$
86b $R = R_1 = i\text{-}C_4H_9$
86c $R = R_1 = t\text{-}C_4H_9$
86d $R = t\text{-}C_4H_9,\ R_1 = CH_3$
86e $R = t\text{-}C_4H_9,\ R_1 = C_6H_5$

The formation of products derived from alkoxy radicals requires a carbon-oxygen bond, which suggests intermediacy of a sulfenate ester (Eq. 64, *cf.* Eq. 21).[88] A sulfoxide to sulfenate rearrangement has been postulated for the pyrolysis of sulfoxides (*vide supra*: *cf* Eqs. 21, 31).[80,101]

The formation of disulfides from alkanesulfinyl radicals in this system[88] is in marked contrast to the reaction of sulfinyl radicals to give thiosulfonates (*cf.* Eqs. 40, 41). However, combination of two sulfinyl radicals in the thioperoxy form (**87**; *cf.* Eqs. 32, 63) would give a sulfenyl peroxide (**87**) which could decompose to give oxygen and disulfide (Eqs. 67, 68).[88]



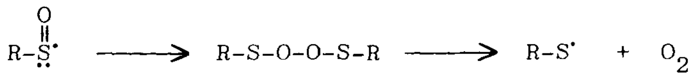
$$R{-}\overset{O}{\overset{\|}{S}}{-}R_1 \longrightarrow R_1^{\bullet} + R{-}\overset{O}{\overset{\|}{\underset{\cdot\cdot}{S}}}{}^{\bullet} \longleftrightarrow R{-}\overset{:\dot{O}:}{\overset{|}{\underset{\cdot\cdot}{S}}}: \qquad (63)$$



$$R{-}\overset{O}{\overset{\|}{\underset{\cdot\cdot}{S}}}{}^{\bullet} + R_1^{\bullet} \longrightarrow R{-}S{-}O{-}R_1 \longrightarrow R{-}S^{\bullet} + R_1{-}O^{\bullet} \qquad (64)$$

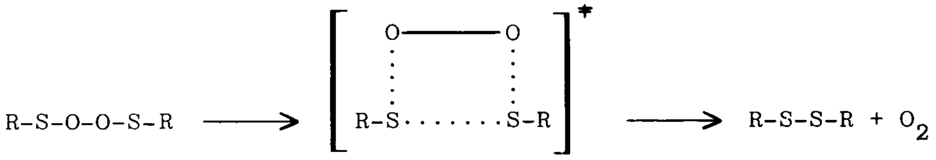
$$2\ R{-}S^{\bullet} \longrightarrow R{-}S{-}S{-}R \qquad (65)$$

$$R_1{-}O^{\bullet} + R'{-}H \longrightarrow R_1{-}OH + R'^{\bullet} \qquad (66)$$



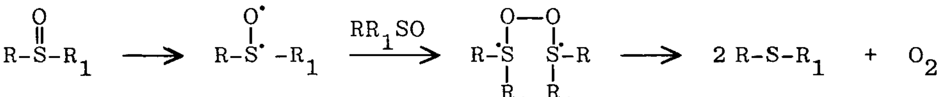
$$R{-}\overset{O}{\overset{\|}{\underset{\cdot\cdot}{S}}}{}^{\bullet} \longrightarrow \underset{\mathbf{87}}{R{-}S{-}O{-}O{-}S{-}R} \longrightarrow R{-}S^{\bullet} + O_2 \qquad (67)$$

87


(68)

87

The product distributions for the photolysis of sulfoxides under a variety of experimental conditions have been compared.[88] Considerable amounts of monosulfides were formed in the sensitized photolysis of unsymmetrical sulfoxides 2-methyl-2-propyl methyl sulfoxide (**86d**); 2-methyl-2-propyl propyl sulfoxide and in the direct photolysis of diallyl sulfoxide (**85c**; Table X). One of several proposed mechanisms involves reaction of an excited triplet state sulfoxide with a ground state sulfoxide to form a triplet peroxide (**88**) which could decompose to the observed sulfide and triplet oxygen (Eq. 69).[88]



$$R{-}\overset{\overset{O}{\|}}{S}{-}R_1 \longrightarrow R{-}\overset{\overset{O^\bullet}{|}}{S^\bullet}{-}R_1 \xrightarrow{RR_1SO} \underset{88}{\begin{matrix}O{-}O\\ R{-}\dot{S}\quad \dot{S}{-}R\\ R_1\quad R_1\end{matrix}} \longrightarrow \underset{89}{2\,R{-}S{-}R_1} + O_2 \qquad (69)$$

TABLE X

Product Distributions for the Benzophenone Sensitized Photolysis of Various Sulfoxides in Benzene and in *iso*-Propylbenzene[88,a]

$R{-}\overset{\overset{O}{\|}}{S}{-}R_1$ R/R_1	Solvent	% Reaction	Mole % products				
			Propanone	ROH	R—S—S—R	R—S—R$_1$	% Sulfur[b]
allyl	A[c,d]	75	—	trace	1.9	4.8	8.6
allyl	B[e]	74	—	0.7	30	8.2	68
t-Bu	A[c]	78	0	5.2	trace	25	25
CH$_3$	B[e]	74	0	2.3	trace	23	23
i-Pr	A[c]	24	5.7	5.3	16	0	26
i-Pr	B[e]	25	trace	trace	trace	0	32
t-Bu	A[c]	40	1.7	16	12	0	40
t-Bu	B[e]	44	0	3.0	40	0	96

[a] Sulfoxide (0.1 M) and benzophenone (0.1 M) photolyzed for 30 min with pyrex filtration.

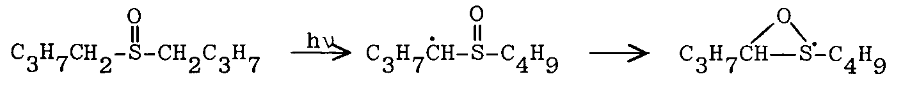
[b] Total sulfur accounted for in the observed products.

[c] Benzene solvent.

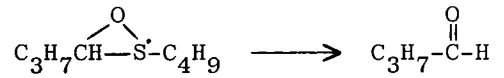
[d] Photolyzed for 60 min.

[e] *iso*-Propylbenzene.

Ultraviolet irradiation of dibutyl sulfoxide (**89**) under argon in a quartz tube gave butanal, dibutyl disulfide, and butanethiol (Eqs. 70, 71).[102] An alternate mechanism involves isomerization to a sulfenate ester followed by radical decomposition.[2b] The irradiation products from diphenylmethyl sulfoxide are similar to those for the photolysis of dibutyl sulfoxide (**89**).[103]

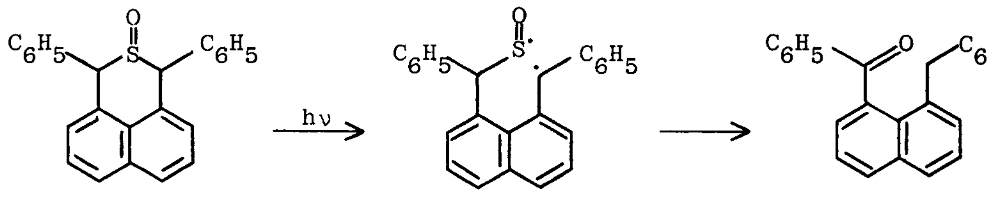


89 **90** **91** (70)



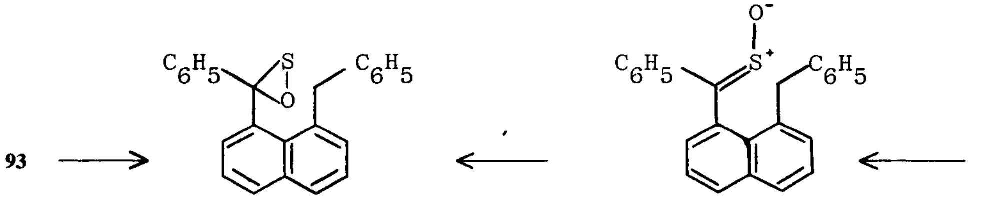
91 (71)

Benzophenone-sensitized photodesulfurization of E- or Z-1,3-dihydro-2-thiophenalene 2-oxide (**92**) in benzene gave 1-benzoyl-8-(phenylmethyl)naphthalene (**94**, 80%) as the sole product (Eq. 72).[104,105] In addition to the sulfinyl radical **93**, the mechanism may involve oxathiirane **95** or sulfine **96**.[106,107]



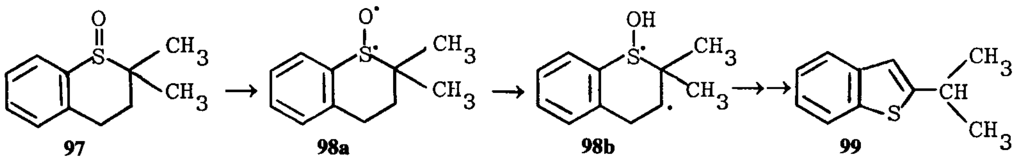
92 **93** **94**

(72)



95 **96** (73)

2,2-Dimethylthiachroman 1-oxide (**97**) on irradiation with a medium pressure Hg lamp gave 2-isopropylbenzothiophene (**99**).[108] A reasonable mechanism involves initial

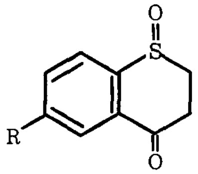


97 **98a** **98b** **99**

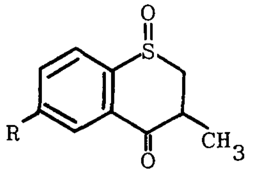
(74)

excitation of the sulfoxide (**97**) to the excited-state species **98a**, followed by intramolecular abstraction of a hydrogen atom to give **98b**, which ultimately leads to **99**.

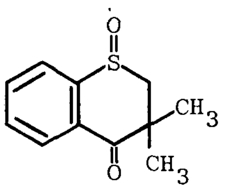
The photochemical behavior of a number of substituted derivatives of thiochroman-4-one 1-oxide (**100**) has been examined.[109] In contrast to the analogous sulfones, these sulfoxides undergo a variety of photochemical rearrangements. At least three distinct pathways have been recognized; a) photochemical deoxygenation; b) rearrangement to cyclic sulfenates; c) β-hydrogen abstraction. Sulfinyl radical and sulfine are intermediates in the irradiation of 3,3-dimethylthiochroman-4-one 1-oxide (**100f**, *cf.* Eq. 74).[109]



100a R = H
100b R = CH_3
100c R = OCH_3



100d R = H
100e R = CH_3

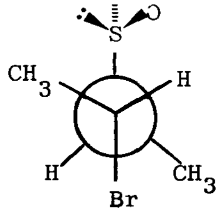


100f

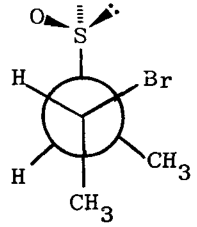
3. *Radical Reactions* The formation of sulfinyl radicals and α-sulfinyl radicals from the reactions of sulfoxides and hydroxyl radicals, hypophosphinate radical anion, or radicals is described above (Eq. 69).[10,13,29–34]

The primary processes in the hydroxyl radical-induced oxidation mechanism of sulfoxides have been investigated by pulse radiolysis in particular, by an improved conductivity detection method with a time resolution of *ca.* 50 ns in aqueous solution.[110] Electrophilic addition of the hydroxyl radical to the sulfoxide group leads to a transient adduct $[RRSO(OH)^{\cdot}]$ which decays unimolecularly into a sulfinic acid (RSO_2H) and a radical ($R^{\cdot}$). Depending on the nature of the sulfoxide, other competing reactions, including hydrogen atom abstraction from longer-chain and branched aliphatic groups and addition of hydroxyl radicals to aromatic systems to form hydroxycyclohexadienyl radicals, may occur.[110]

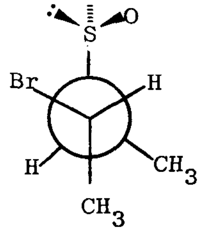
The four diastereomeric 2-bromo-3-phenylsulfinylbutanes (**101a**, **101b**, **101c**, **101d**) react with tributyltin radicals to generate β-phenylsulfinyl *sec*-butyl radicals, which eliminate phenylsulfinyl radicals to form the 2-butenes in a stereoselective manner.[111] This stereoselectivity is the result of rapid loss of phenylsulfinyl radicals before appreciable rotation about the C2-C3 in the β-phenylsulfinyl *sec*-butyl radicals can occur.



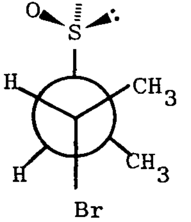
101a



101b



101c



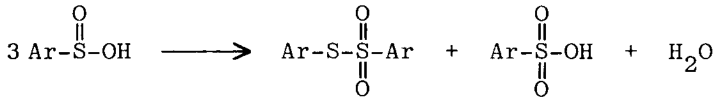
101d

The relative rates of reaction of the diastereromers (**101a**, **101b**, **101c**, **101d**) are consistent with a modest interaction between sulfur and the developing *p*-orbital of the radical.

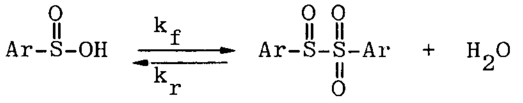
C. From Sulfinic Acids and Their Derivatives

The decomposition of a novel class of compounds, the sulfenyl nitrates ($ArSONO_2$), is described in equations 40–43.[38]

1. Sulfinic Acids Sulfinic acids slowly disproportionate on standing at 22 to 24 °C (Eq. 75). Kice and coworkers[112–114] have elucidated the mechanism for the disproportionation of aromatic sulfinic acids (Eqs. 76–78). The key intermediate in this mechanism is the sulfinyl sulfone (**102**), which can undergo a facile homolysis of the S—S bond to an arenesulfinyl radical and an arenesulfonyl radical.[50,112–114] Head-to-tail recombination of these radicals give sulfenyl sulfonate **103**, which reacts rapidly with an additional molecule of sulfinic acid to afford products. A ρ value of -1.1 was observed for the disproportionation reaction.[112a]

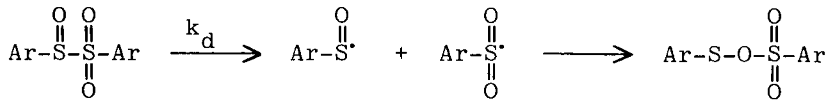


$$3\ \mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}OH} \longrightarrow \mathrm{Ar{-}S{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} + \mathrm{Ar{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}OH} + H_2O \qquad (75)$$



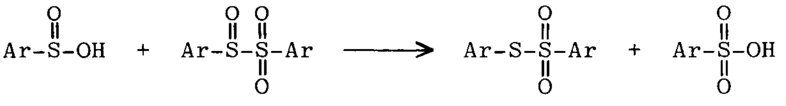
$$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}OH} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} + H_2O \qquad (76)$$

102



$$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} \xrightarrow{k_d} \mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}^{\bullet} + \mathrm{Ar{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}^{\bullet} \longrightarrow \mathrm{Ar{-}S{-}O{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} \qquad (77)$$

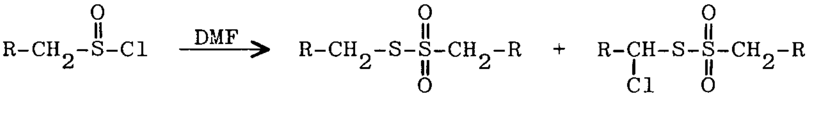
102 **103**



$$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}OH} + \mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} \longrightarrow \mathrm{Ar{-}S{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} + \mathrm{Ar{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}OH} \qquad (78)$$

102

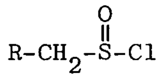
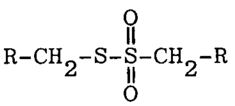
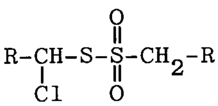
2. Sulfinyl Chlorides The facile reaction of linear alkanesulfinyl chlorides and *N*,*N*-dimethylmethanamide (DMF) gives mixtures of *S*-alkyl alkanesulfonothioates (minor product) and *S*-(1-chloroalkyl) alkanesulfonothioates in excellent to quantitative yields (Eq. 79; Table XI).[115,119] The products are easily separated via flash



$$\mathrm{R{-}CH_2{-}}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}\mathrm{{-}Cl} \xrightarrow{\mathrm{DMF}} \mathrm{R{-}CH_2{-}S{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}CH_2{-}R} + \mathrm{R{-}}\underset{\underset{\mathrm{Cl}}{|}}{\mathrm{CH}}\mathrm{{-}S{-}}\underset{\underset{\mathrm{O}}{\|}}{\overset{\overset{\mathrm{O}}{\|}}{\mathrm{S}}}\mathrm{{-}CH_2{-}R} \qquad (79)$$

TABLE XI

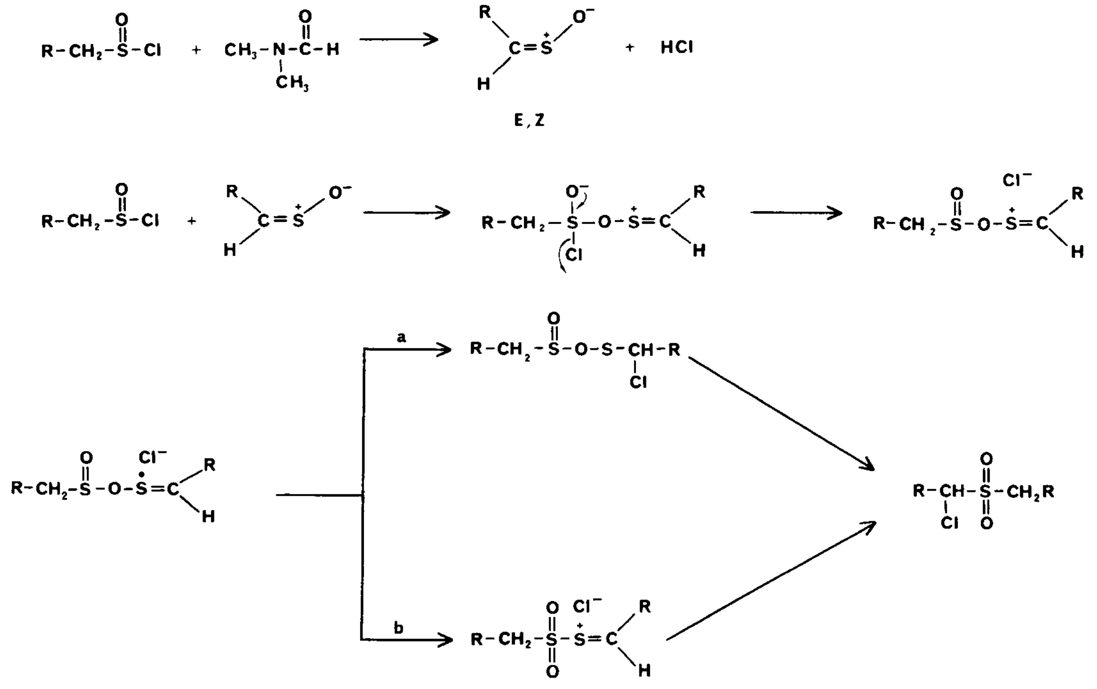
Yields of *S*-Alkyl and *S*-(1-Chloroalkyl) Alkanesulfonothioates from the Reaction of Linear Alkanesulfinyl Chlorides and *N*,*N*-Dimethylmethanamide[115–117]

 $R\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{S}\text{-}Cl$ R	Yield, %  $R\text{-}CH_2\text{-}S\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}CH_2\text{-}R$	  $R\text{-}\underset{\underset{Cl}{\vert}}{CH}\text{-}S\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}CH_2\text{-}R$
H	11	63
CH_3	18	82
C_2H_5	13	87
C_3H_7	15	85
C_4H_9	14	81
C_7H_{15}	15	90

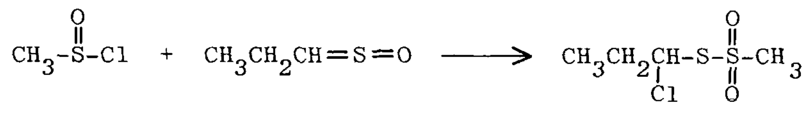
chromatography.[116] Interestingly, addition of 1,4-dihydroxybenzene to the reaction leads to formation of only *S*-(1-chloroalkyl) alkanesulfonothioate.[115,117]

Although detailed kinetic and mechanistic studies are not yet available,[118] a reasonable mechanism for the formation of *S*-(1-chloroalkyl) alkanesulfonothioates is shown in Scheme IV.

SCHEME IV



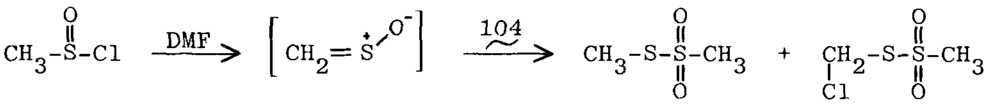
Support for the proposed mechanism comes from the work of Block and Bazzi[119] who obtained *S*-(1-chloropropyl) methanesulfonothioate (**106**, 64%) from the reaction of methanesulfinyl chloride (**104**) and propanethial *S*-oxide (the onion lachrymatory factor, **105**). Thus, the reaction of methanesulfinyl chloride (**104**) and DMF[115–118]



$$\mathrm{CH_3-\overset{O}{\overset{\|}{S}}-Cl} + \mathrm{CH_3CH_2CH{=}S{=}O} \longrightarrow \mathrm{CH_3CH_2\underset{Cl}{CH}-S-\overset{O}{\underset{O}{S}}-CH_3} \qquad (80)$$

104 **105** **106**

to give *S*-methyl and *S*-(1-chloromethyl) methanesulfonothioate (**108** and **109**), provides the first evidence for the formation of methanethial *S*-oxide (**107**) in solution.[115,116]

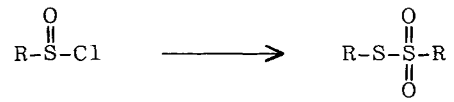


$$\mathrm{CH_3-\overset{O}{\overset{\|}{S}}-Cl} \xrightarrow{\mathrm{DMF}} \left[\mathrm{CH_2{=}\overset{+}{S}{-}O^-}\right] \xrightarrow{104} \mathrm{CH_3-S-\overset{O}{\underset{O}{S}}-CH_3} + \mathrm{\underset{Cl}{CH_2}-S-\overset{O}{\underset{O}{S}}-CH_3} \qquad (81)$$

104 **105** **106** **107**

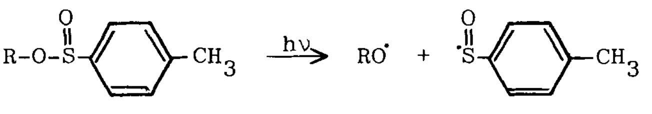
The path to *S*-alkyl alkanesulfonothioates could involve sulfinyl radicals, *vic*-disulfoxides, and/or *O*-sulfenyl sulfinates (Scheme V). The sole formation of *S*-(1-chloroalkyl) alkanesulfonothioates in the presence of 1,4-dihydroxybenzene is consistent with a radical pathway for formation of the *S*-alkyl alkanesulfonothioates.[115,116]

Alkane- and arenesulfinyl chlorides react with zerovalent metals (Ag, Cu, Zn, $Fe(CO)_5$) to give symmetrical sulfonothioic acid *S*-esters in good to excellent yields (Eq. 82, Table XII).[35,50,117,120–129] Although the mechanism of this synthetically useful reaction has not been explored, sulfinyl radicals, *vic*-disulfoxides, and/or *O*-sulfenyl sulfinates may be involved (Scheme VI, VII).[1,120]



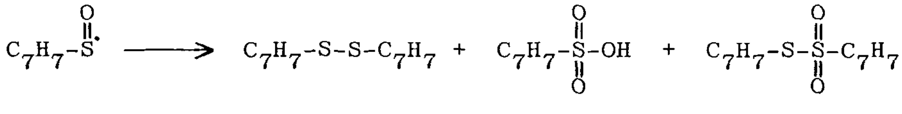
$$\mathrm{R-\overset{O}{\overset{\|}{S}}-Cl} \longrightarrow \mathrm{R-S-\overset{O}{\underset{O}{S}}-R} \qquad (82)$$

3. *Sulfinic Acid O-Esters* Methyl, ethyl, butyl, acetyl, phenylmethyl, and allyl *p*-toluenesulfinates (**108**) were photolyzed in hexane or without solvent.[130] Product



(83)

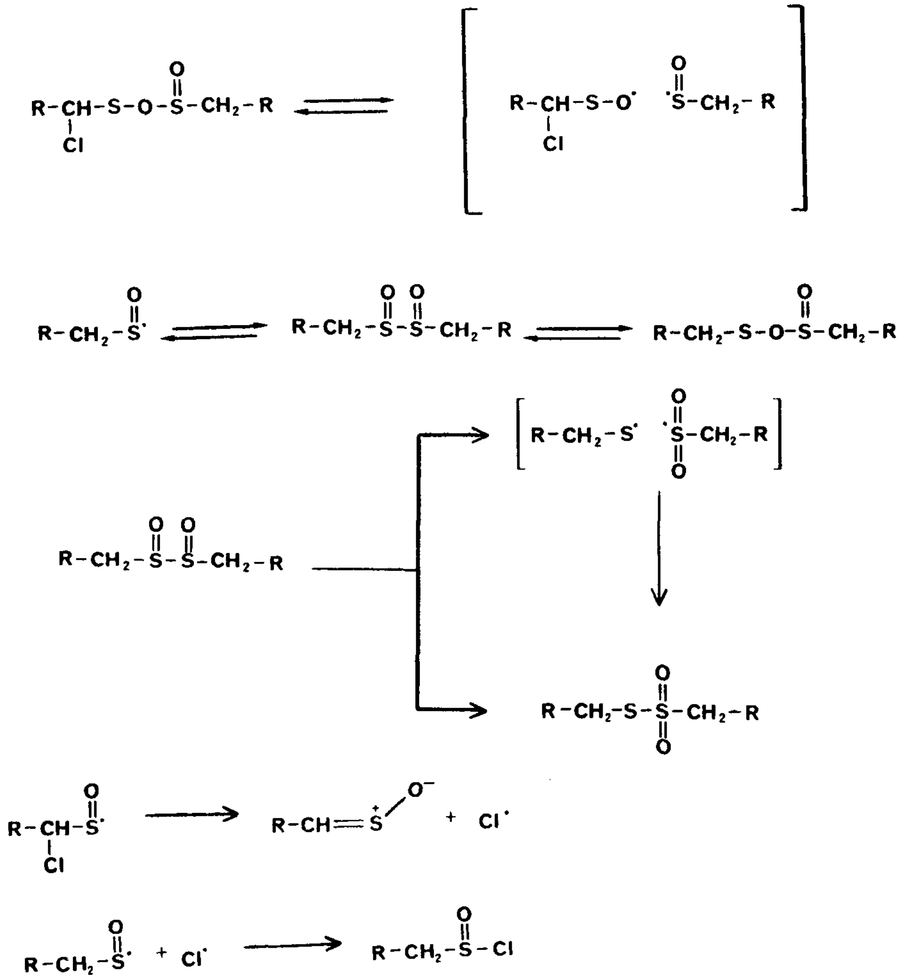
108 **21d**



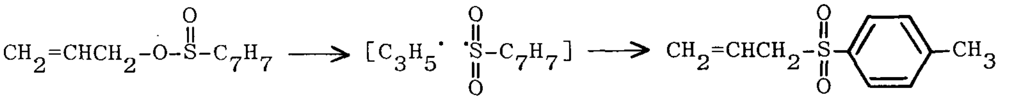
$$\mathrm{C_7H_7-\overset{O}{\overset{\|}{S}}{}^{\bullet}} \longrightarrow \mathrm{C_7H_7-S-S-C_7H_7} + \mathrm{C_7H_7-\overset{O}{\underset{O}{S}}-OH} + \mathrm{C_7H_7-S-\overset{O}{\underset{O}{S}}-C_7H_7} \qquad (84)$$

21d **20d**

SCHEME V



analyses indicated that the photolysis involves fission of the S(O)—O bond to give a sulfinyl radical and an alkoxy radical (Eq. 83). The major products from the photolysis of alkyl *p*-toluenesulfinates **108** were the sulfonic acid, disulfide, and *S*-(4-methylphenyl) 4-methylbenzenesulfonothioate (**20d**), which arose from the 4-methylphenylsulfinyl radical **21d** (Scheme VIII).[50,130]

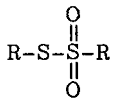

(85)

109 **110**

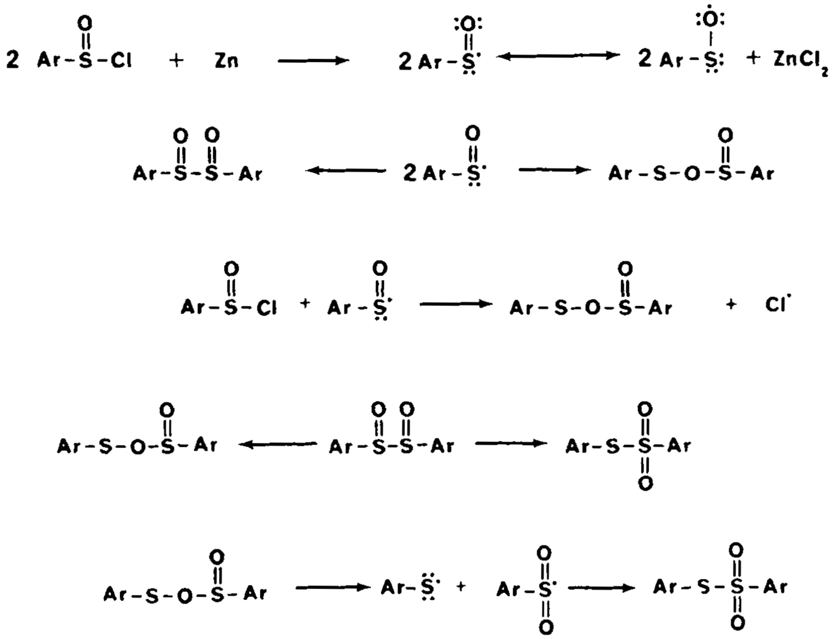
In the case of the allyl ester (**109**), partial isomerization to the corresponding sulfone (**110**) also occurred (Eq. 85).[130–133] Photoracemization was observed during the photolysis of optically active sulfinic acid *O*-esters.[130]

TABLE XII

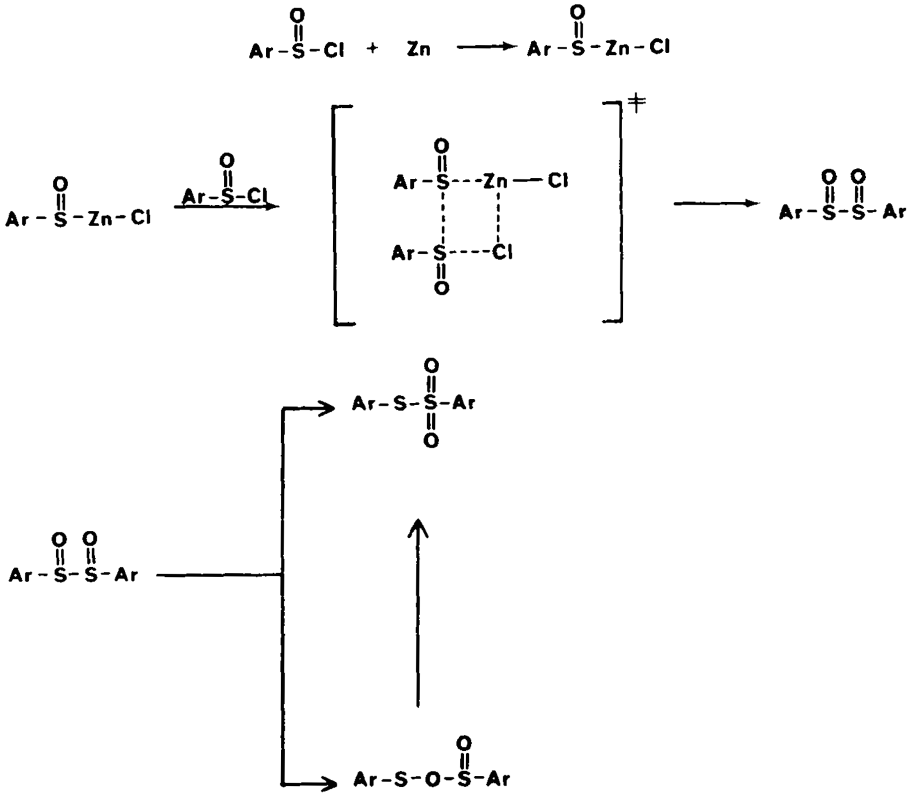
Yields of Symmetrical Sulfonothioic Acid S-Esters from the Reaction of Sulfinyl Chlorides and Zerovalent Metals

 $R{-}S{-}\overset{O}{\underset{O}{S}}{-}R$	Metal	Solvent	Yield, %	Reference
CH_3	Zn	Et_2O	55	120, 122
	Zn	CCl_4	54	120, 122
C_2H_5	Zn	Et_2O	49	120, 122
	Zn	CCl_4	68	120, 122
C_3H_7	Zn	Et_2O	63	120, 122
	Zn	CCl_4	73	120, 122
C_4H_9	Zn	Et_2O	79	120, 122
	Zn	CCl_4	78	120, 122
C_5H_{11}	Zn	Et_2O	72	120, 122
	Zn	CCl_4	78	120, 122
neo-C_5H_{11}	Zn	CCl_4	78	121
	Zn	C_6H_6	79	121
C_6H_{13}	Zn	Et_2O	68	120, 122
	Zn	CCl_4	78	120, 122
C_8H_{17}	Zn	Et_2O	61	120, 122
	Zn	CCl_4	78	120, 122
$C_{12}H_{25}$	Zn	Et_2O	40	120, 122
	Zn	CCl_4	46	120, 122
C_6H_5	Zn	Et_2O	—	35
	Zn	C_6H_6	91	123, 124
4-$CH_3C_6H_4$	Zn	Et_2O	88	123, 124
	Ag	pet. ether	—	127, 128
	Cu	CCl_4	96	50, 129
4-FC_6H_4	Zn	Et_2O	62	123, 124
4-ClC_6H_4	Zn	Et_2O	75	123, 124
	Ag	pet. ether	—	127, 128
4-ClC_6H_4	Zn	Et_2O	80	123, 124
	Ag	pet. ether	—	127, 128
2,2′-dinaphthyl	Zn	Et_2O	77	123, 124
	Ag	pet. ether	—	127

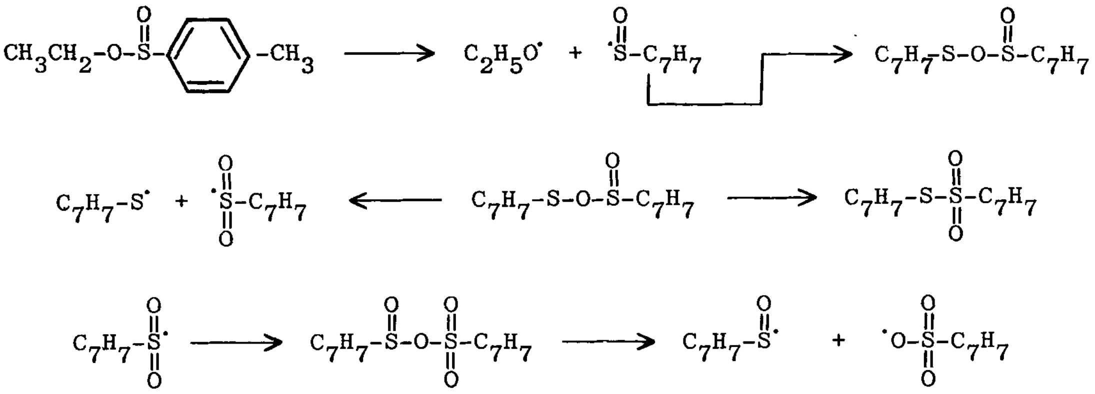
SCHEME VI



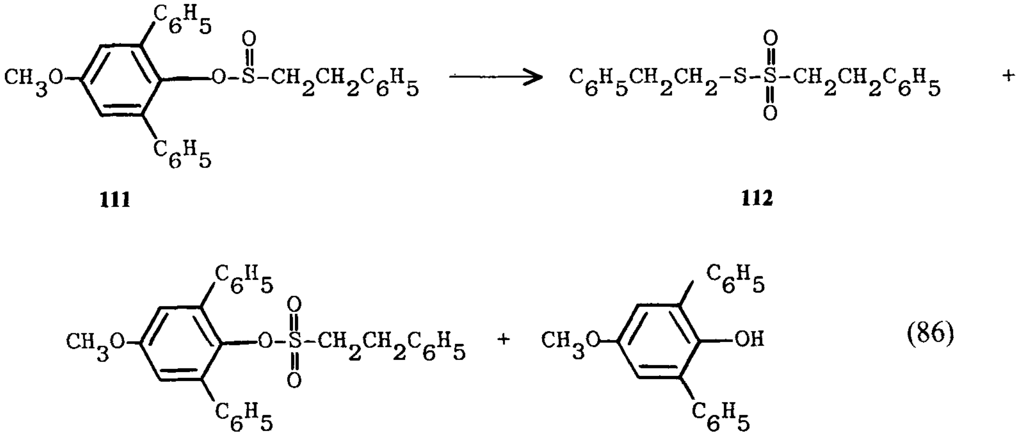
SCHEME VII



SCHEME VIII

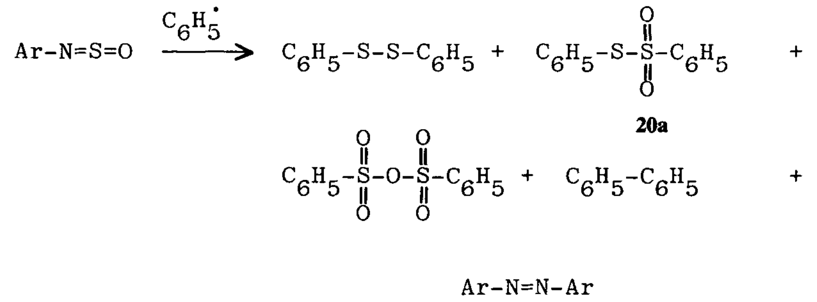


Sulfinyl radicals, *vic*-disulfoxides, and/or *O*-sulfenyl sulfinates may be involved in the pyrolysis of sulfinic acid ester **111** (Eq. 86).[134]



111 **112** **113** **114** (86)

4. *N-Sulfinylanilines and N-Sulfinylarylhydrazines* The reaction of phenyl radicals, from benzoyl peroxide, with *N*-sulfinylanilines (ArNSO) (Eq. 87) may also involve sulfinyl radicals.[135]

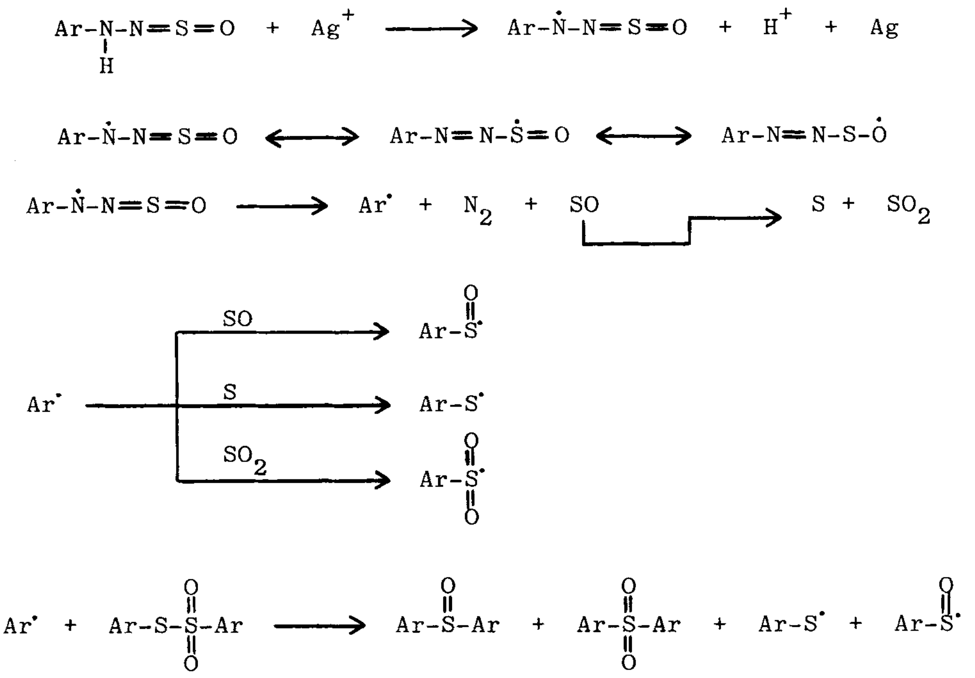


$$\text{Ar-N=S=O} \xrightarrow{C_6H_5^{\bullet}} C_6H_5\text{-S-S-}C_6H_5 + C_6H_5\text{-S-}\overset{O}{\underset{O}{\text{S}}}\text{-}C_6H_5 + C_6H_5\text{-}\overset{O}{\underset{O}{\text{S}}}\text{-O-}\overset{O}{\underset{O}{\text{S}}}\text{-}C_6H_5 + C_6H_5\text{-}C_6H_5 + \text{Ar-N=N-Ar} \quad (87)$$

20a

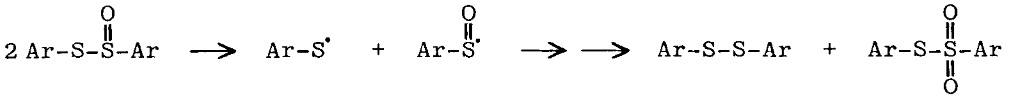
Sulfinyl and sulfonyl radicals may be involved in the reaction of *N*-sulfinylarylhydrazines (ArHNNSO) with sodium *tert*-butoxide[136a] or with silver oxide (Scheme IX; *cf.* Schemes VI and VII).[136b] The products from the silver oxide oxidation include sulfinic acids, disulfides, sulfides, thiosulfonates, sulfoxides, sulfones, thiols, and sulfonic acids.

SCHEME IX



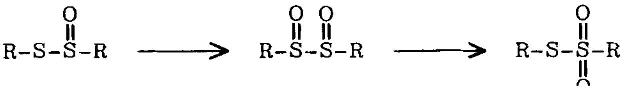
D. From Sulfinothioic Acid S*-Esters*

1. Thermolysis Although it is generally agreed that sulfinothioic acid *S*-esters disproportionate into disulfides and sulfonothioic acid *S*-esters via sulfinyl radicals, *vic*-disulfoxides and/or *O*-sulfenyl sulfinates (Eq. 88),[1,3,36,137–140] the subtle mechanistic nuances of this reaction remain to be elucidated.[1,3,36,137–140]



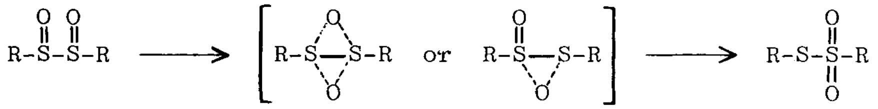
$$2\,\mathrm{Ar{-}S{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{{-}Ar} \longrightarrow \mathrm{Ar{-}S^{\bullet}} + \mathrm{Ar{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}{}^{\bullet} \longrightarrow \longrightarrow \mathrm{Ar{-}S{-}S{-}Ar} + \mathrm{Ar{-}S{-}}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{{-}Ar} \qquad (88)$$

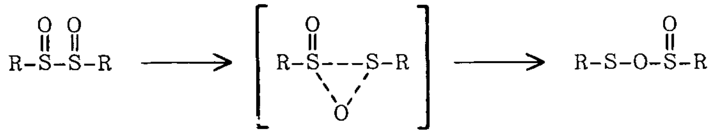
2. Peroxidation Symmetrical alkanesulfinothioic acid *S*-esters react with *m*-chloroperoxybenzoic acid (MCPBA) at low temperatures to give *vic*-disulfoxides (Eq. 89). The major products of the peroxidations are the sulfonothioic acid *S*-esters.

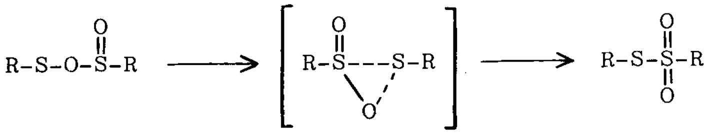


$$\mathrm{R{-}S{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{{-}R} \longrightarrow \mathrm{R{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}\mathrm{{-}R} \longrightarrow \mathrm{R{-}S{-}}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{\mathrm{S}}}\mathrm{{-}R} \qquad (89)$$

The peroxidation of symmetrical or unsymmetrical[39] *S*-aryl arenesulfinothioates, of *S*-alkyl arenesulfinothioates, and of *S*-aryl alkanesulfinothioates, which also probably involves *vic*-disulfoxides, gives complicated product mixtures which include thiosulfonates.[44,141–150] The *vic*-disulfoxides may isomerize to thiosulfonates (Eq. 90) or to *O*-sulfenyl sulfinates (Eq. 91) via nonradical pathways.[1,145] *O*-Sulfenyl sulfinates may also rearrange to thiosulfonates via nonradical pathways (Eq. 92).


(90)

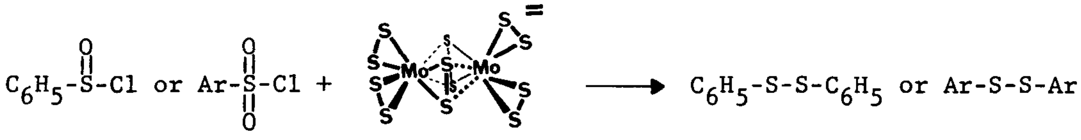

(91)

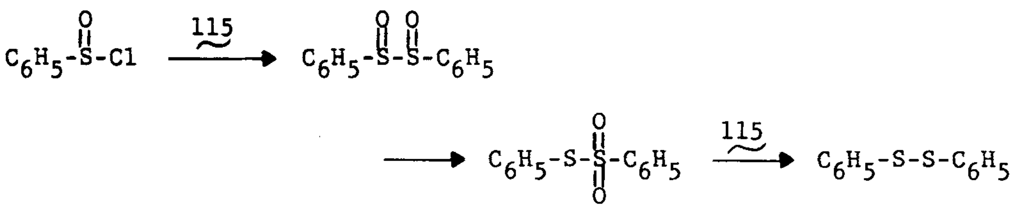

(92)

The initially formed *vic*-disulfoxide may undergo rapid homolysis of the sulfur-sulfur bond to give sulfinyl radicals (Scheme VII). In unsymmetrical *vic*-disulfoxides, recombination of the two different sulfinyl radicals can lead to the formation of four different sulfonothioic acid *S*-esters (Scheme X).[1,150] The *O*-sulfenyl sulfinates may also rearrange to sulfonothioic acid *S*-esters via radical mechanisms (Scheme VII).[1,44,138]

E. Other Systems

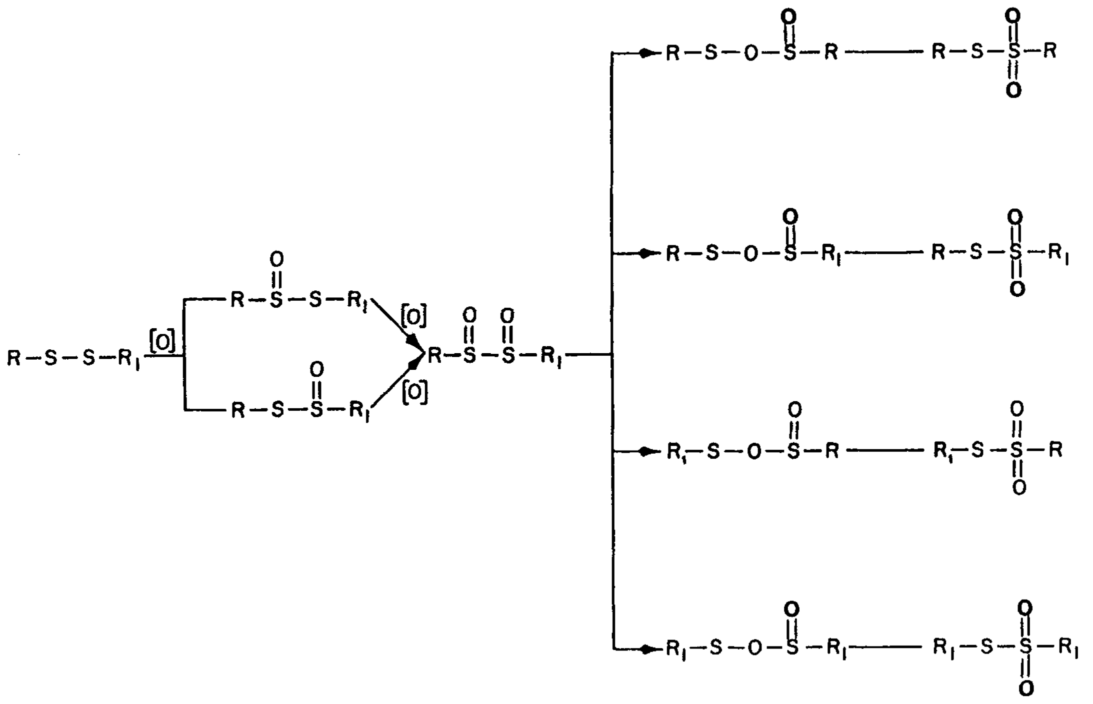
Harpp and MacDonald[151] found that the molybdenum persulfide complex **115** converted benzenesulfinyl chloride or arenesulfonyl chlorides in refluxing ethanenitrile under a nitrogen atmosphere to diphenyl disulfide or diaryl disulfides (Eq. 93). It was suggested that the reaction pathway of benzenesulfinyl chloride involves a *vic*-disulfoxide which


115 (93)


(94)

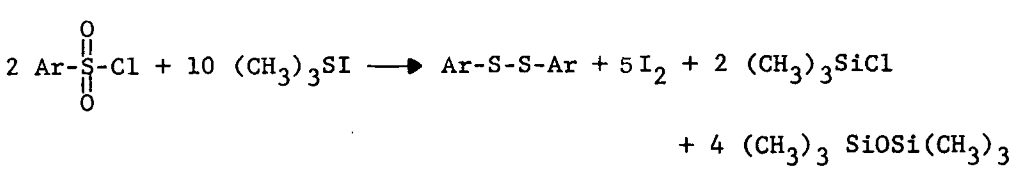
20a

SCHEME X



could isomerize via sulfinyl radicals to *S*-phenyl benzenesulfonothioate (**20a**). Reduction of **20a** by **115** would afford disulfide. Alternatively, the *vic*-disulfoxide could isomerize to *O*-sulfenyl sulfinate which subsequently rearranges to **20a**.

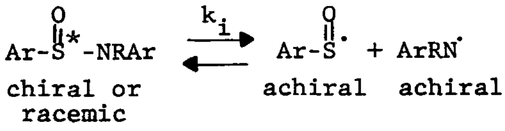
vic-Disulfoxides and *S*-aryl arenesulfonothioates, and perhaps *O*-sulfenyl sulfinates and sulfinyl radicals, are involved in the reduction of sulfonyl halides with iodotrimethylsilane (Eq. 95).[152–154] Mikolajczyk and coworkers[152] were able to detect *S*-aryl arenesulfonothioates as intermediates during the reduction. Presumably, *vic*-disulfoxides (sulfinyl radicals?) are precursors of the thiosulfonates (Scheme XI).



$$2\ \text{Ar-}\overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{O}}{\|}}{\text{S}}}\text{-Cl} + 10\ (\text{CH}_3)_3\text{SI} \longrightarrow \text{Ar-S-S-Ar} + 5\,\text{I}_2 + 2\ (\text{CH}_3)_3\text{SiCl} + 4\ (\text{CH}_3)_3\ \text{SiOSi}(\text{CH}_3)_3 \qquad (95)$$

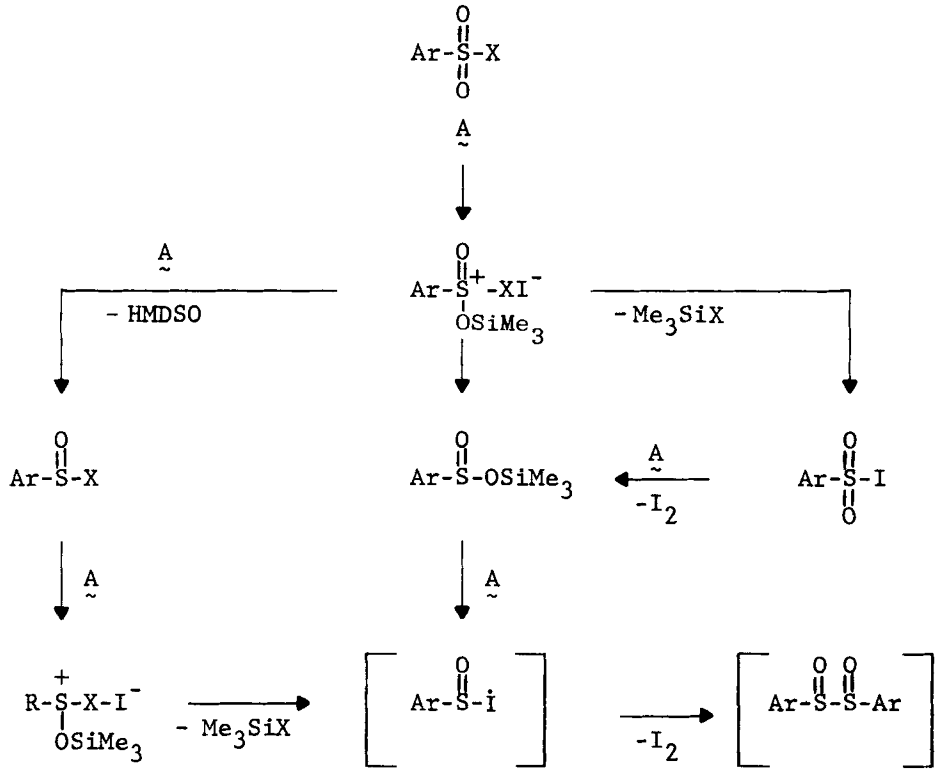
Sulfinyl and sulfonyl radicals are observed in the oxidation of thiols with the Ti(III)-H_2O_2 couple and with Ce(IV), and in the oxidation of disulfides with the former reagent (Eqs. 4, 5).[10]

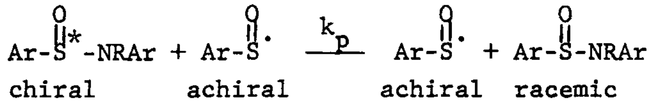
Sulfinyl radicals are involved in the racemization of sulfinamides (Eqs. 96–100).[155]



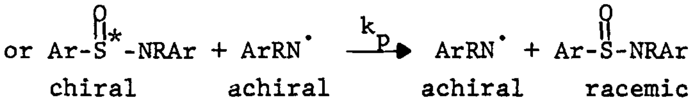
$$\underset{\text{chiral or racemic}}{\text{Ar-}\overset{\overset{\text{O}}{\|}}{\text{S}}{}^{*}\text{-NRAr}} \underset{}{\overset{k_i}{\rightleftarrows}} \underset{\text{achiral}}{\text{Ar-}\overset{\overset{\text{O}}{\|}}{\text{S}}{}^{\bullet}} + \underset{\text{achiral}}{\text{ArRN}^{\bullet}} \qquad (96)$$

SCHEME XI

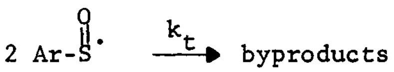




$$\underset{\text{chiral}}{\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{}^{*}{-}NRAr}} + \underset{\text{achiral}}{\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{}^{\bullet}}} \xrightarrow{k_p} \underset{\text{achiral}}{\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{}^{\bullet}}} + \underset{\text{racemic}}{\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{-}NRAr}} \tag{97}$$



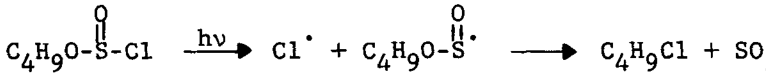
$$\text{or } \underset{\text{chiral}}{\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{}^{*}{-}NRAr}} + \underset{\text{achiral}}{\mathrm{ArRN^{\bullet}}} \xrightarrow{k_p} \underset{\text{achiral}}{\mathrm{ArRN^{\bullet}}} + \underset{\text{racemic}}{\mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{-}NRAr}} \tag{98}$$



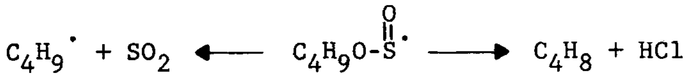
$$2\ \mathrm{Ar{-}\overset{O}{\overset{\|}{S}}{}^{\bullet}} \xrightarrow{k_t} \text{byproducts} \tag{99}$$

$$\text{or} \quad 2\ \mathrm{ArRN^{\bullet}} \xrightarrow{k_t} \text{byproducts} \tag{100}$$

Photolysis of butyl chlorosulfite (**116**) gives products which suggest initial cleavage of the S—Cl bond (Eqs. 101, 102).[130]



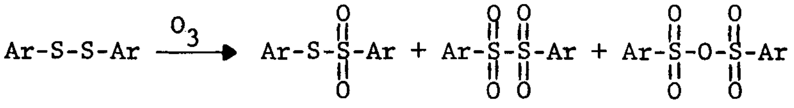
$$\underset{\mathbf{116}}{\mathrm{C_4H_9O{-}\overset{O}{\overset{\|}{S}}{-}Cl}} \xrightarrow{h\nu} \mathrm{Cl^{\bullet}} + \underset{\mathbf{117}}{\mathrm{C_4H_9O{-}\overset{O}{\overset{\|}{S}}{}^{\bullet}}} \longrightarrow \mathrm{C_4H_9Cl + SO_2} \tag{101}$$



$$C_4H_9^{\bullet} + SO_2 \longleftarrow C_4H_9O\text{-}\overset{O}{\overset{\|}{S}}{}^{\bullet} \longrightarrow C_4H_8 + HCl \qquad (102)$$

117

Sulfinyl and sulfonyl radicals may be involved in the ozonolysis of sulfides to sulfones, of disulfides to sulfonic acid anhydrides, *vic*-disulfones, and sulfonothioic acid *S*-esters (Eq. 103), and of tetrasulfides to sulfonic acid anhydrides and sulfur dioxide.[156]



$$\text{Ar-S-S-Ar} \xrightarrow{O_3} \text{Ar-S-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-Ar} + \text{Ar-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-Ar} + \text{Ar-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-O-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-Ar} \qquad (103)$$

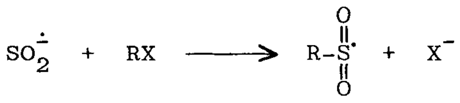
V. FORMATION AND CHEMISTRY OF SULFONYL AND α-SULFONYL RADICALS

Formation of sulfonyl radicals from sulfoxides (Eqs. 11–13),[16,17] sulfonothioic acid *S*-esters,[16,17] sulfinic acids,[48] sulfones,[49] and sulfonyl halides[11,47,50] has been described above. Equations 17 to 19 show formation of α-sulfonyl radicals from sulfones.

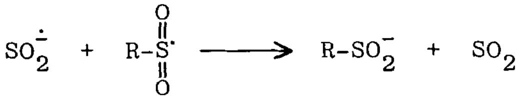
A. From Sulfur Dioxide

A potentially useful sulfone synthesis (57–88 %) is based on the reaction of electrochemically generated sulfur dioxide radical anion with acyl or alkyl halides in ethanenitrile.[156] The blue color of the sulfur dioxide anion may be used as an indicator to follow the progress of the reaction (Eqs. 104–107).

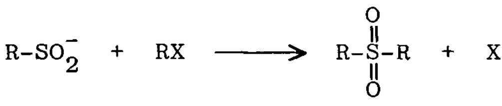
$$O{=}S{=}O + e^- \rightleftarrows SO_2^{\dot{-}} \qquad (104)$$



$$SO_2^{\dot{-}} + RX \longrightarrow \text{R-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}{}^{\bullet} + X^- \qquad (105)$$



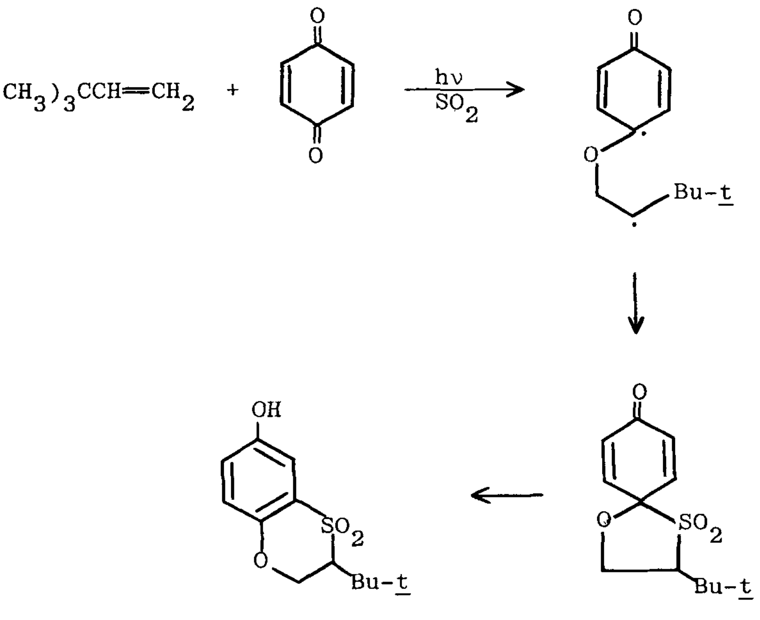
$$SO_2^{\dot{-}} + \text{R-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}{}^{\bullet} \longrightarrow R\text{-}SO_2^- + SO_2 \qquad (106)$$



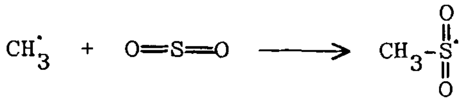
$$R\text{-}SO_2^- + RX \longrightarrow \text{R-}\underset{O}{\underset{\|}{\overset{O}{\overset{\|}{S}}}}\text{-R} + X^- \qquad (107)$$

Sulfur dioxide, which can serve as an efficient biradical trap (Eq. 108),[157] is an important factor in air pollution.

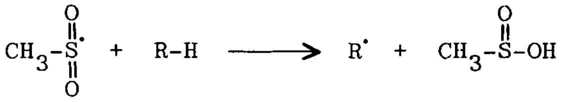
Sulfur dioxide reacts with methyl radicals to generate methanesulfonyl radicsls which can abstract hydrogen atoms from alkanes (Eqs. 109, 110)[158,159] to yield alkanesulfinic acids which may contribute to aerosol formation in polluted atmospheres.[160–166]



(108)



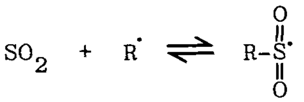
$$CH_3^{\bullet} + O{=}S{=}O \longrightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{}^{\bullet} \qquad (109)$$



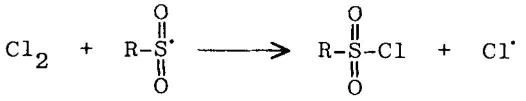
$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{}^{\bullet} + R{-}H \longrightarrow R^{\bullet} + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{S}{-}OH \qquad (110)$$

The Reed reaction (chlorosulfonation)[167] affords alkanesulfonyl chlorides from alkanes, sulfur dioxide, and chlorine (Eqs. 111–113).[168]

$$Cl_2 \longrightarrow 2\,Cl^{\bullet} \xrightarrow{RH} R^{\bullet} + HCl \qquad (111)$$

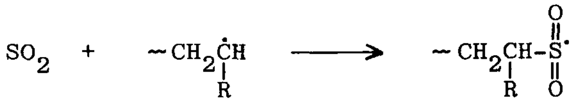


$$SO_2 + R^{\bullet} \rightleftharpoons R{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{}^{\bullet} \qquad (112)$$

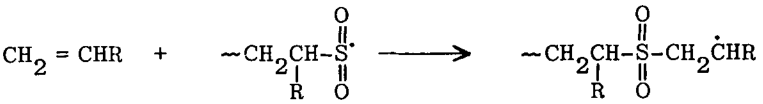


$$Cl_2 + R{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{}^{\bullet} \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}{-}Cl + Cl^{\bullet} \qquad (113)$$

The addition of sulfur dioxide to an alkyl radical is also important in the formation of polysulfones from olefins.[169–171] The addition of sulfur dioxide to the radical (Eq. 114) and addition of the sulfonyl radical to olefin (Eq. 115) may be reversible (*vide infra*).

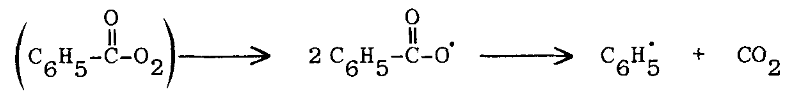


$$SO_2 + \sim CH_2\underset{R}{\underset{|}{\dot{C}H}} \longrightarrow \sim CH_2\underset{R}{\underset{|}{CH}}\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}^{\bullet} \qquad (114)$$

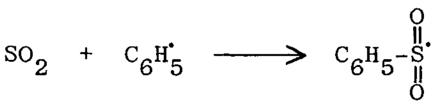


$$CH_2 = CHR + \sim CH_2\underset{R}{\underset{|}{CH}}\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}^{\bullet} \longrightarrow \sim CH_2\underset{R}{\underset{|}{CH}}\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}CH_2\dot{C}HR \qquad (115)$$

Benzenesulfonyl radicals are formed by passing sulfur dioxide through a solution of benzoyl perotide in either benzene or methylbenzene (Eqs. 116, 117).[172]



$$\left(C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}O_2\right) \longrightarrow 2\,C_6H_5\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^{\bullet} \longrightarrow C_6H_5^{\bullet} + CO_2 \qquad (116)$$



$$SO_2 + C_6H_5^{\bullet} \longrightarrow C_6H_5\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}^{\bullet} \qquad (117)$$

Sulfonyl radicals have been observed during the reactions of butanamide, propanamide, 2-methylpropanamide, methacrylamide, valeramide, and stearamide with sulfur dioxide.[173]

Although sulfur dioxide insertion is one of the more common reactions of σ-bonded organometallic complexes, it has been demonstrated that in the case of certain organocobaloximes, organorhodoximes, and possibly in the case of some organoiron complexes under appropriate conditions, the reaction is not a true insertion into the carbon-metal bond.[174] For example, 4-bromobenzyl-bis(dimethylglyoximato)pyridinecobalt(III) (**118**) and benzylbis-(dimethylglyoximato)pyridinerhodium(III) (**119**) separately undergo "insertion" in liquid SO_2 in sealed tubes at 22 to 24 °C to give the corresponding products **120** and **121**, respectively (Eqs. 118, 119). Under identical conditions, an equimolar mixture of **118** and **119** reacts to give *four* products, **120**, **121**, **122**, and **123** (Eq. 120, Scheme XII).[174] Thus, the reaction is an intermolecular process in which the organic and metal fragments of the "insertion" product do not originate from the same molecule of organometallic substrate. The mechanism shown in Scheme XII is not universal in sulfur dioxide insertion reactions, but may also apply to some organoiron complexes under extreme conditions.[174]

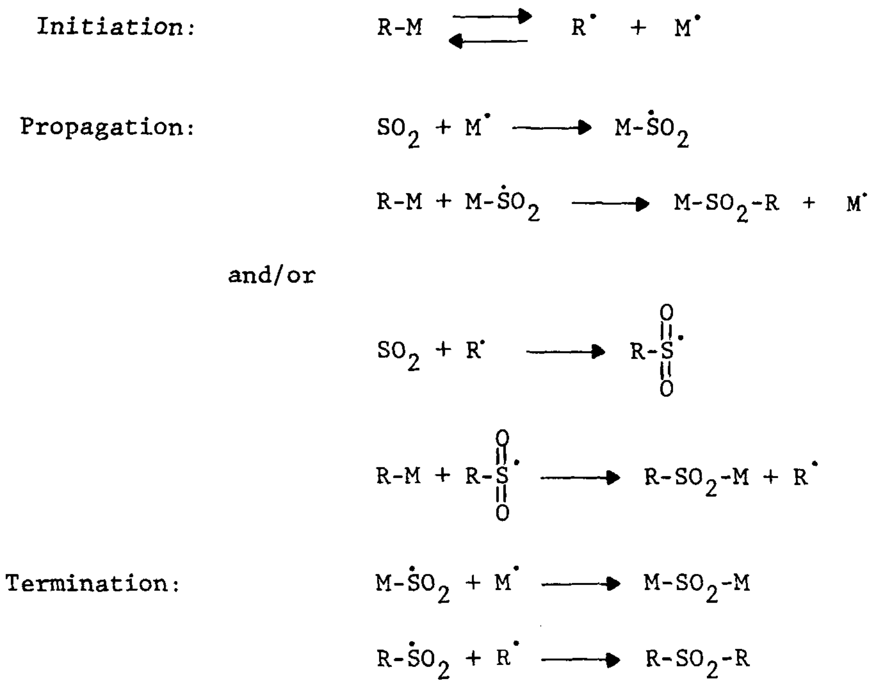
$$BrC_6H_4CH_2Co(dmgH)_2py \xrightarrow{SO_2} BrC_6H_4CH_2SO_2Co(dmgH)_2py \qquad (118)$$

118 **120**

$$C_6H_5CH_2Rh(dmgH)_2py \xrightarrow{SO_2} C_6H_5CH_2SO_2Rh(dmgH)_2py \qquad (119)$$

119 **121**

SCHEME XII



Initiation: $R\text{-}M \rightleftharpoons R^{\bullet} + M^{\bullet}$

Propagation: $SO_2 + M^{\bullet} \longrightarrow M\text{-}\dot{S}O_2$

$R\text{-}M + M\text{-}\dot{S}O_2 \longrightarrow M\text{-}SO_2\text{-}R + M^{\bullet}$

and/or

$SO_2 + R^{\bullet} \longrightarrow R\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{}^{\bullet}$

$R\text{-}M + R\text{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{}^{\bullet} \longrightarrow R\text{-}SO_2\text{-}M + R^{\bullet}$

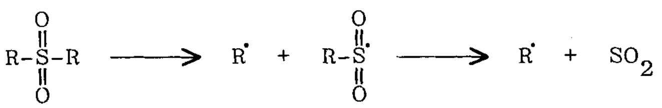
Termination: $M\text{-}\dot{S}O_2 + M^{\bullet} \longrightarrow M\text{-}SO_2\text{-}M$

$R\text{-}\dot{S}O_2 + R^{\bullet} \longrightarrow R\text{-}SO_2\text{-}R$

$$\begin{array}{c}\underset{\mathbf{118}}{BrC_6H_4CH_2Co(dmgH)_2py}\\ + \\ \underset{\mathbf{119}}{C_6H_5CH_2Rh(dmgH)_2py}\end{array} \xrightarrow{SO_2} \mathbf{120} + \mathbf{121} + \underset{\mathbf{122}}{BrC_6H_4CH_2SO_2Rh(dmgH)_2py} + \underset{\mathbf{123}}{C_6H_5CH_2SO_2Co(dmgH)_2py} \qquad (120)$$

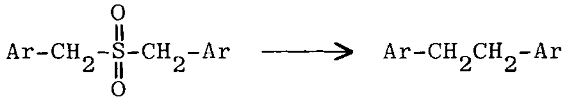
B. From Sulfones

Thermolysis of alkyl sulfones at high temperatures in the gas phase may lead to desulfonylation of the nascent sulfonyl radical since sulfones are thermally very stable compounds.[175–179] Diaryl sulfones are more stable than alkyl aryl sulfones which are more stable than dialkyl sulfones. However, allylic, benzylic, and some cyclic sulfones are more prone to thermolysis. Of course, photolysis provides a relatively mild method for generating sulfonyl radicals from sulfones.[180–183,184c]



$$\mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}R \longrightarrow R^{\bullet} + R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{}^{\bullet} \longrightarrow R^{\bullet} + SO_2} \qquad (121)$$

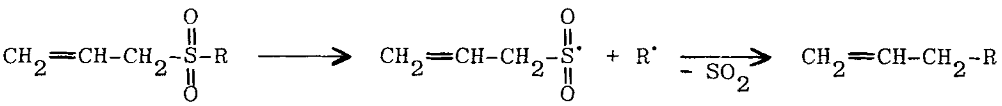
Arylmethyl sulfones (**124**) lose sulfur dioxide on heating at reduced pressure to afford 1,2-diarylethanes, probably via arylmethyl radicals.[184–186]



$$\mathrm{Ar{-}CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}Ar \longrightarrow Ar{-}CH_2CH_2{-}Ar} \qquad (122)$$

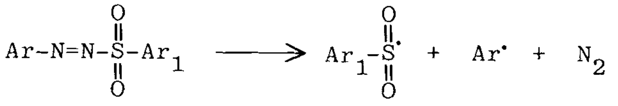
124

Allylic sulfones between 150 and 400 °C decompose with rearrangement and extrusion of sulfur dioxide.[186] At low temperatures a cyclic concerted (cheletropic) mechanism may be operative while at high temperatures sulfonyl and alkyl radicals are thought to be involved (Eq. 123).[2a,186–190]



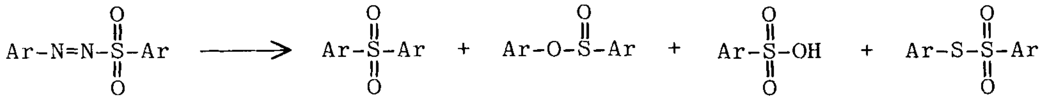
$$\mathrm{CH_2{=}CH{-}CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}R \longrightarrow CH_2{=}CH{-}CH_2{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{}^{\bullet} + R^{\bullet} \xrightarrow[-\,SO_2]{} CH_2{=}CH{-}CH_2{-}R} \qquad (123)$$

Arylazo aryl sulfones (**125**) decompose unimolecularly on heating in neutral or weakly basic media to yield an aryl and sulfonyl radical pair (Eq. 124).[191–197] ^{1}H- and ^{13}C-CIDNP spectra were obtained during the thermal decomposition of several arylazo aryl aryl sulfones in tetrachloroethene or 1,1,2,2-tetrachloroethane.[191] The formation of sulfones and sulfinic esters as recombination products in a solvent cage was established from the signs of polarization (enhanced absorption or emission).



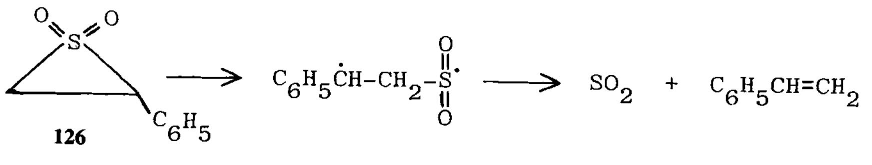
$$\mathrm{Ar{-}N{=}N{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Ar_1 \longrightarrow Ar_1{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{}^{\bullet} + Ar^{\bullet} + N_2} \qquad (124)$$

125



$$\mathrm{Ar{-}N{=}N{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Ar \longrightarrow Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Ar + Ar{-}O{-}\overset{\overset{O}{\|}}{S}{-}Ar + Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}OH + Ar{-}S{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Ar} \qquad (125)$$

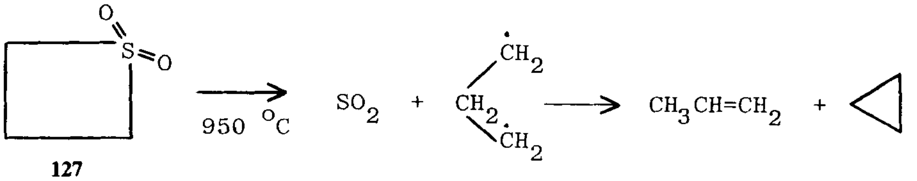
Photolysis or thermolysis of **126** gives phenylethene and sulfur dioxide.[198]



126

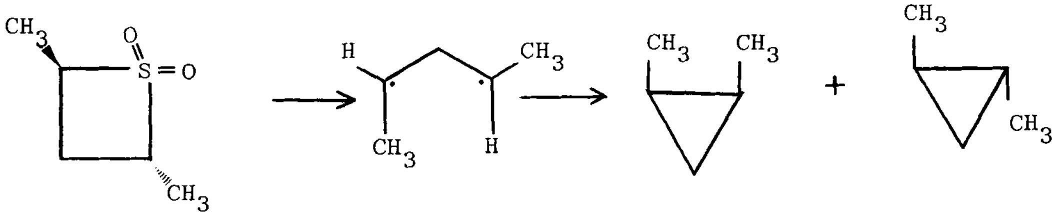
(126)

Flash vacuum pyrolysis (FVP) of thietane 1,1-dioxide (**127**) affords sulfur dioxide and the 1,3-diradical which then forms cyclopropane and propene (Eq. 127).[199] The flow pyrolysis of 2,4-dimethylthietane 1,1-dioxide (**128**) gives E- and Z-dimethylcyclopropanes with some 2-pentenes (Eq. 128).[200a] Both isomers of **128** show net crossover, *i.e.* Z-**128** produce mostly E-1,2-dimethylcyclopropane and E-**128** produce mainly Z-1,2-dimethylcyclopropane. The inversions observed are explicable on the basis of π-cyclopropane character for the diradicals.[200b,200c]



127

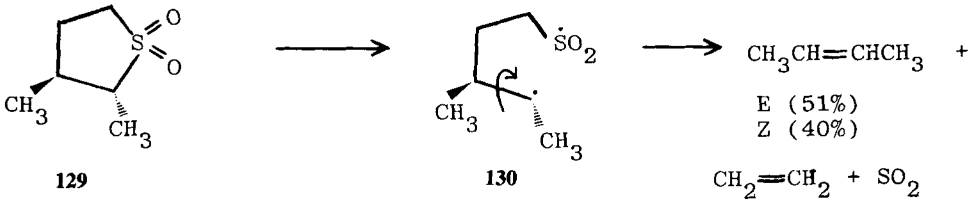
(127)



128

(128)

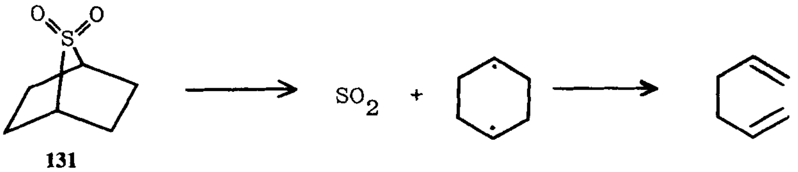
Pyrolysis of tetrahydrothiophene 1,1-dioxides (**129**) gives isomeric alkenes and sulfur dioxide via sulfonyl radicals (Eq. 129).[201,202] The predominant loss of stereochemistry may result from external rotation in diradical **130**.



129 **130**

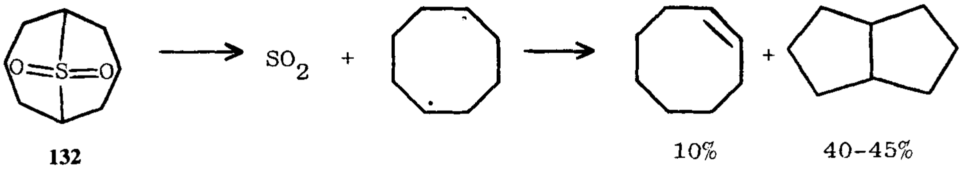
(129)

Flash pyrolysis of bridged cyclic sulfones (*e.g.* **131** and **132**) generates 1,*n*-diradicals which may cyclize to bicyclic products and/or fragment (Eqs. 130, 131).[203]



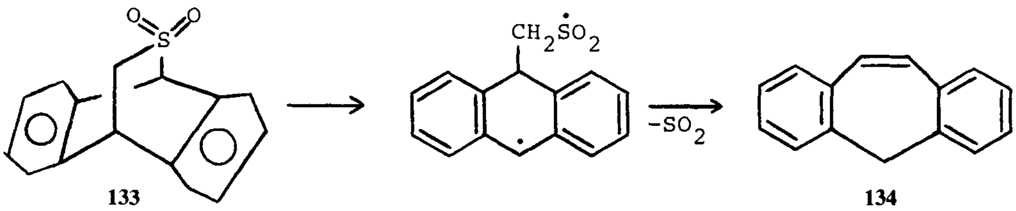
131

(130)



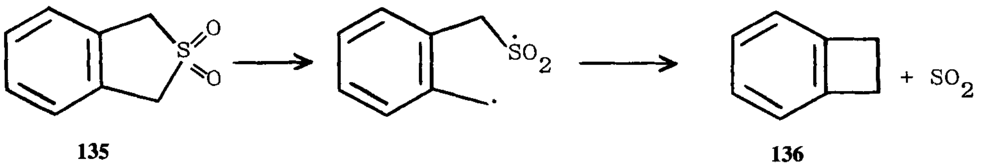
(131)

Thermolysis of bridged sulfone **133** gives 5*H*-dibenzo[*a*,*d*]-cycloheptene (**134**, 89%), probably via an initial diradical (Eq. 132).[204]



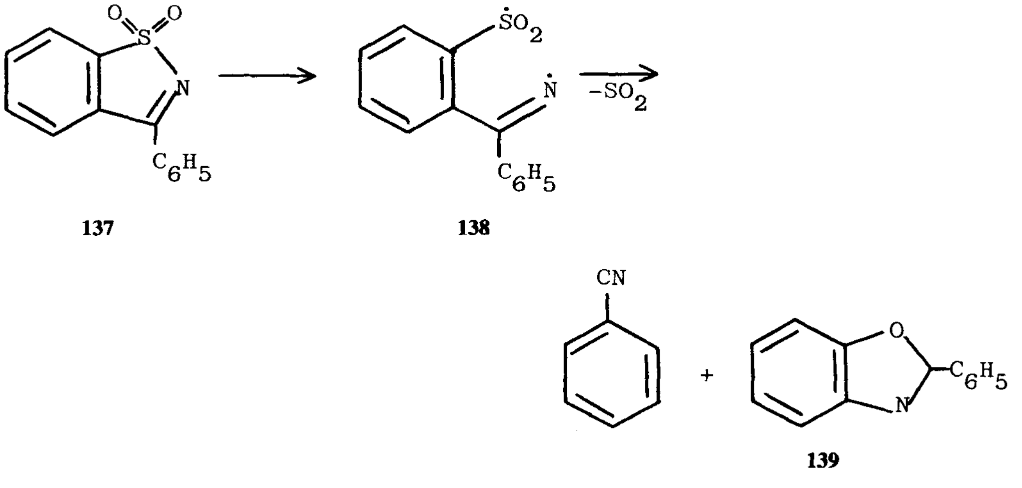
(132)

The pyrolysis of 1,3-dihydroisothianaphthalene 2,2-dioxide (**135**) to the strained hydrocarbon benzocyclobutene (**136**, 63%)[187] may involve sulfonyl radicals (Eq. 133)[205] or a cheletropic elimination leading directly to *o*-quinodimethane and sulfur dioxide.



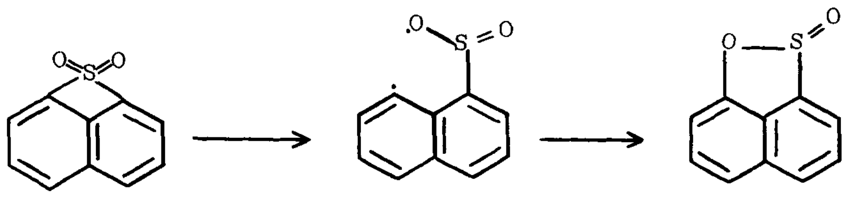
(133)

Pyrolysis of 3-phenyl-1,2-benzisothiazole 1,1-dioxide (**137**) gave cyanobenzene and 2-phenylbenzoxazole (**139**, 32%).[206] Although the mechanism of this interesting transformation is not known, an initially formed diradical (**138**) may be involved (Eq. 134).



(134)

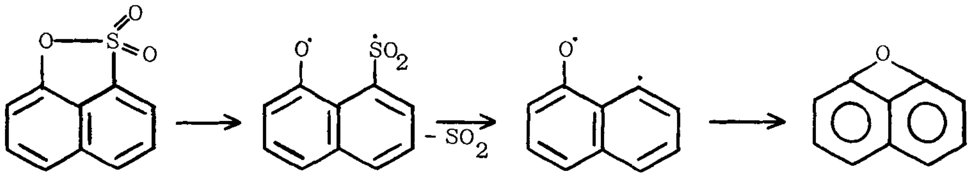
Thermolysis of naphtho[1,8-*b*,c]-thietene 1,1 dioxide (**140**) gives sultine **141** (54%)[207]



140 **141**

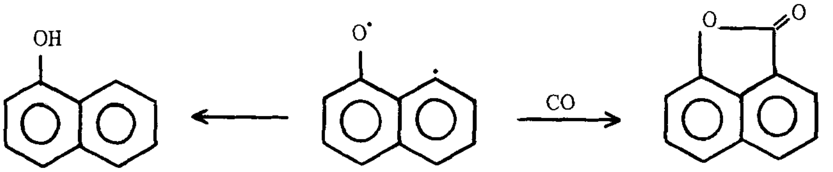
(135)

Napth[1,8-*c*,*d*]-1,2-oxathiole 2,2-dioxide (**142**) gives traces of indene and naphthalene, and naphtho[1,8-*b*,*c*]furan-2-one (**145**).[208,209] A plausible mechanism for this remarkable reaction is shown in equations 136 and 137.



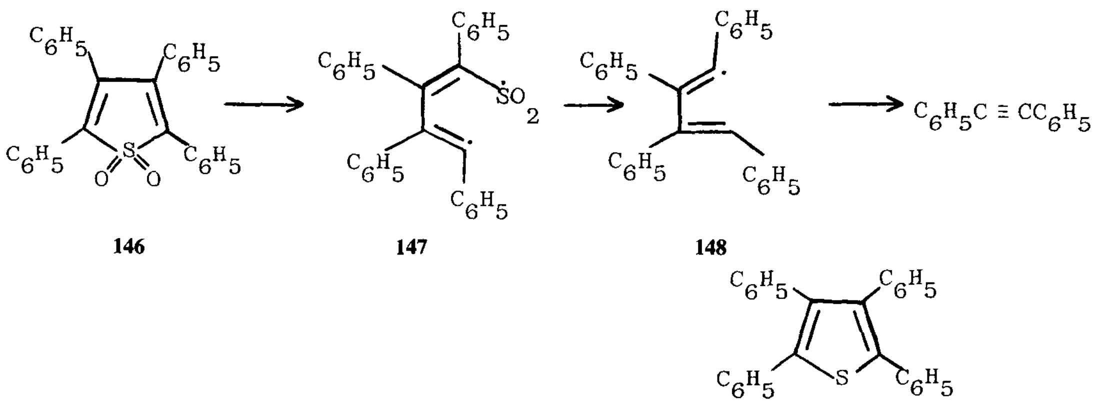
142 **143** **144** **145**

(136)



(137)

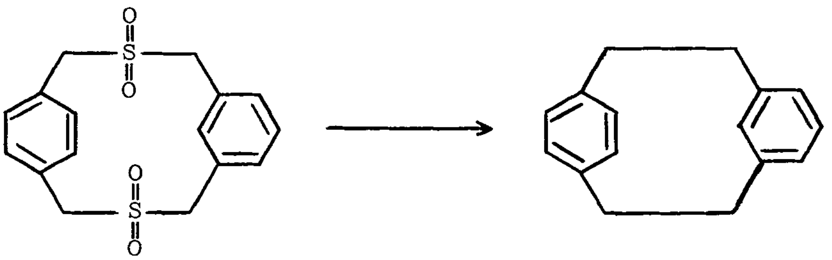
Thermolysis of tetraphenylthiophene 1,1-dioxide (**146**) gives diphenylethyne (81%) and tetraphenylfuran (**149**; 2%).[210]



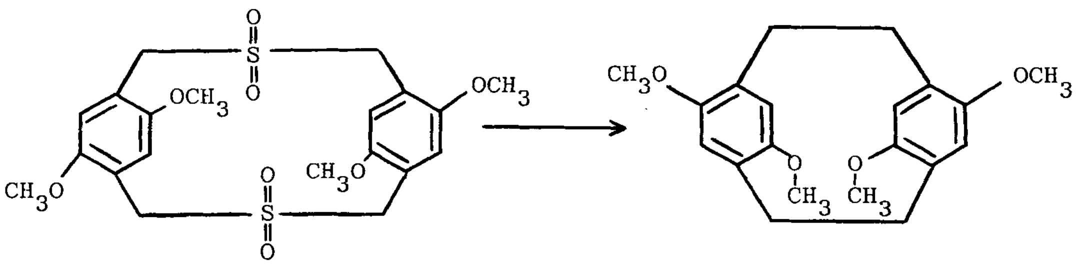
146 **147** **148** **149**

(138)

Photolysis[211] or thermolysis[2a,187–190] of bis-sulfones may afford cyclophanes in comparable yields (Eqs. 139, 140).



(139)



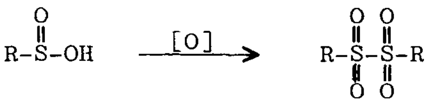
(140)

C. *From Sulfinic Acids and Their Derivatives*

Flash photolysis of aqueous solutions of arenesulfinic acids or sodium arenesulfinates gives a transient absorption with a maximum near 315 nm and a continuous band up to 500 nm.[49] Although no transient absorption at 700 nm due to the hydrated electron could be observed, it is possible that the sulfonyl radical is formed by the photoejection of an electron from the arenesulfinate anion.

Sulfinyl and sulfonyl radicals are intermediates in the disproportionation of sulfinic acids (Eqs. 75–78).[112,113]

The permanganate ion oxidation of sulfinic acids in acid media to *vic*-disulfones (Eq. 141) may involve sulfonyl radicals.[212,213] Cobalt(III) also oxidizes sulfinic acids to *vic*-disulfones, perhaps via sulfonyl radicals or ligand transfer processes at cobalt (Eq. 141).[214]



$$\mathrm{R{-}\overset{\overset{O}{\|}}{S}{-}OH} \xrightarrow{[O]} \mathrm{R{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}R}$$

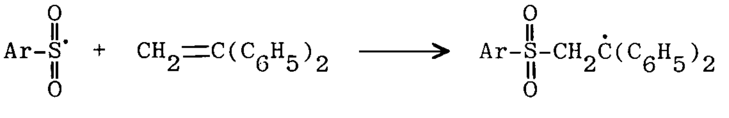
(141)

Sulfinyl and sulfonyl radicals may be intermediates in the reaction of sulfinyl chlorides with DMF (Eq. 79; Scheme V),[115–117] with alkanethial *S*-oxides (Eq. 80),[115–119] or with zerovalent metals (Eq. 82; Schemes VI, VII).[35,50,117,120–129] Sulfinyl chlorides and *N*-hydroxy compounds give sulfonyl radicals (Eqs. 22–28; Scheme II).[56–62]

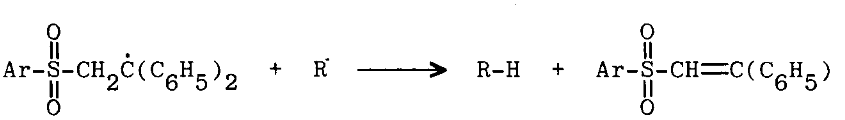
The photolysis of sulfinic acid esters also produce sulfinyl and sulfonyl radicals (Eq. 85; Scheme VIII).[130]

The reaction of phenyl radicals or nitrenes with *N*-sulfinylanilines or *N*-sulfinylarylhydrazines may involve sulfinyl and sulfonyl radicals (Eq. 87).[135,136]

Aromatic sulfinyl sulfones undergo rather facile unimolecular homolytic dissociation of the S—S bond (*cf.* Table IX), the rate being little affected by either solvent or the nature of the aryl group.[113b] Experiments using inhibitor and trapping sulfonyl radicals by added 1,1-diphenylethene (Eqs. 142, 143) showed that the decomposition proceeded as shown in Scheme XIII. Comparison of the rates of homolytic dissociation of aromatic sulfinyl sulfones with the rates for such compounds as disulfides and thiosulfonates shows that the cleavage of S—S bonds in sulfinyl sulfones occurs orders of magnitude more readily than the homolytic scission of the S—S bond in these related compounds.[113b]



$$\mathrm{Ar{-}\overset{O}{\underset{O}{S}}{}^{\bullet} + CH_2{=}C(C_6H_5)_2 \longrightarrow Ar{-}\overset{O}{\underset{O}{S}}{-}CH_2\dot{C}(C_6H_5)_2} \qquad (142)$$

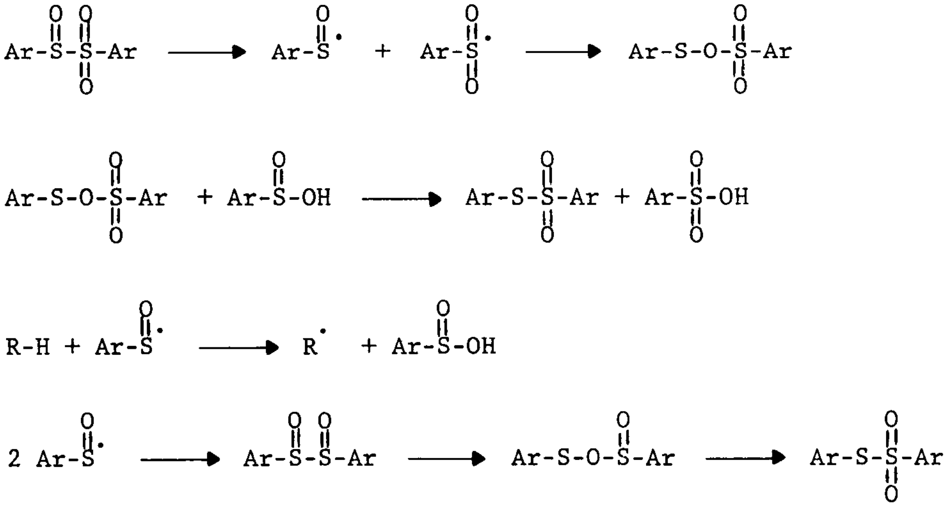


$$\mathrm{Ar{-}\overset{O}{\underset{O}{S}}{-}CH_2\dot{C}(C_6H_5)_2 + R^{\bullet} \longrightarrow R{-}H + Ar{-}\overset{O}{\underset{O}{S}}{-}CH{=}C(C_6H_5)} \qquad (143)$$

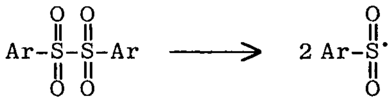
Since no aromatic sulfinyl radical-olefin adducts were observed (*cf.* Eqs. 142, 143) it was tentatively suggested that sulfinyl radicals may be considerably less reactive than aromatic sulfonyl radical toward 1,1-diphenylethene.[7,113b] This particular stability of the sulfinyl radical may account for the ease of homolytic dissociation of organosulfur compounds in which a sulfinyl group is one of the participants in the S—S bond.[7,113b,138] Moreover, the ease with which aryl benzyl sulfoxides undergo homolytic dissociation as compared to aryl benzyl sulfides or sulfones is consistent with the postulate that sulfinyl radicals are more stable and easier to form than thiyl or sulfonyl radicals.[138,215]

vic-Disulfones, which are mixed anhydrides of a sulfinic acid and a sulfonic acid, undergo unimolecular dissociation in diglyme or bromobenzene at 145 to 165 °C to give a complex mixture of products.[216] The large positive entropy of activation (16.6 eu) is

SCHEME XII

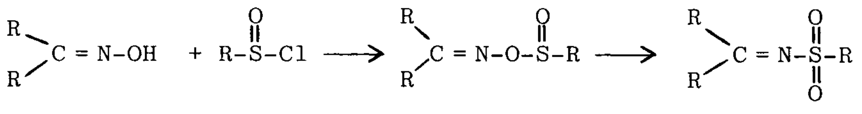


consistent with the rate-determining step being homolytic dissociation of the S—S bond in the *vic*-disulfone (Eq. 144). Although it is not clear how the final products are formed, several reasonable pathways are shown in Scheme XIV.[216]



$$Ar-SO_2-SO_2-Ar \longrightarrow 2\,Ar-SO_2^{\bullet} \qquad (144)$$

The reaction of amidoximes and ketoximes with sulfinyl chlorides at low temperatures produces thermally unstable *O*-sulfonated oximes which rearrange to *N*-sulfonylimines (Eq. 145).[217] This rearrangement has been shown, by means of ESR, ^{13}C-CIDNP, and kinetic studies, to involve homolytic N—O bond cleavage to give iminyl sulfonyl radicals followed by radical recombination with N—S bond formation.

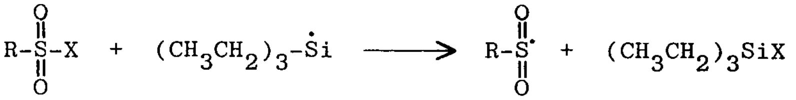


(145)

D. From Derivatives of Sulfonic Acids

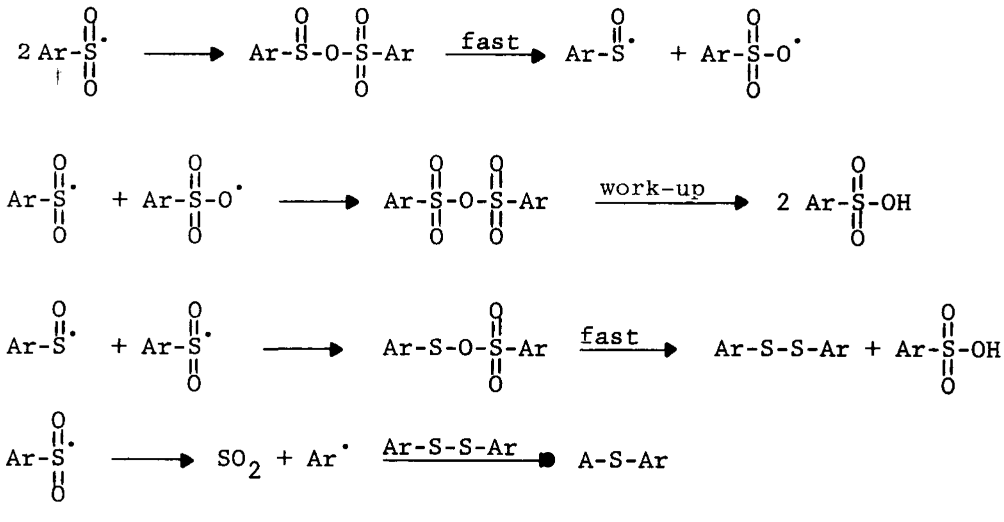
Sulfonyl radicals are generated from sulfonyl halides by photolysis,[11,12,50,182,218–222] by thermolysis,[50,223] and by abstraction of the halogen by some other radical (Eqs. 146,147).[218–222,224–227]

$$(CH_3CH_2)_3SiH + (CH_3)_3C{-}O^{\bullet} \longrightarrow (CH_3CH_2)_3\dot{S}i + (CH_3)_3COH \qquad (146)$$



$$R-SO_2-X + (CH_3CH_2)_3\dot{S}i \longrightarrow R-SO_2^{\bullet} + (CH_3CH_2)_3SiX \qquad (147)$$

SCHEME XIV



The activation energies for the decomposition of alkanesulfonyl radicals have been reported.[158,220a,228] Kinetic studies on the formation and decay of some sulfonyl radicals show that the triethylsilyl radical (*cf.* Eqs. 146,147) abstracts chlorine radicals from methanesulfonyl chloride and benzenesulfonyl chloride at comparable rates.[220a] Similar results were obtained using the corresponding sulfonyl fluorides. Thus, it was concluded that arenesulfonyl radicals are not stabilized appreciably relative to alkanesulfonyl radicals.

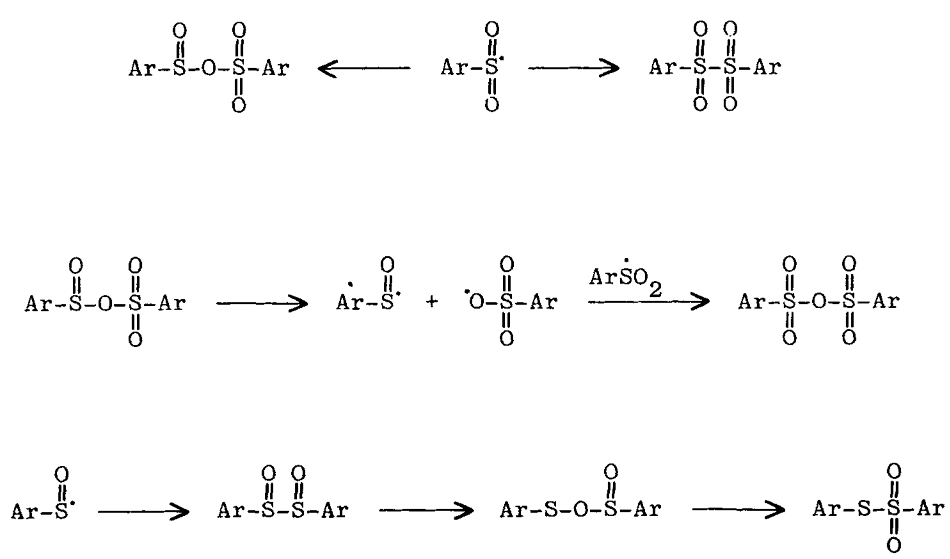
Benzenesulfonyl, phenyl, and thiyl radicals are involved in the thermal reaction of benzenesulfonyl chloride at 500–600 °C, under nitrogen to give sulfuryl chloride, chlorobenzene, thiobenzene, diphenyl sulfide, diphenyl, and dibenzothiophene.[229]

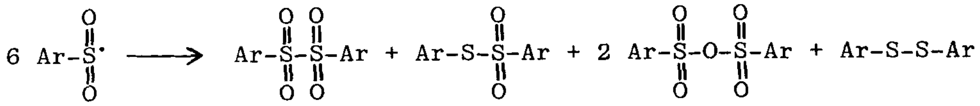
The cathodic cleavage of aromatic sulfonyl chlorides, sulfonic esters, sulfonamides, and sulfones were examined by electro-generated chemiluminescence in the presence of aromatic hydrocarbons at the dropping Ag electrode or at Pt disk electrode in a 1:1 ethanenitrile/methylbenzene mixture or in DMF.[230] The luminescence intensity with the sulfonyl chlorides is much stronger than with the sulfonic esters. The results are discussed in terms of the reduction potentials of intermediate radicals ($Ar\dot{S}O_2$, $ArO^{\cdot}$ ArNR) and with respect to the kinetics of the homogeneous catalysis of cleavage by the hydrocarbon redox system.

The 4-methylbenzenesulfonyl radicals produced by the photolysis or thermolysis of 4-methylbenzenesulfonyl iodide add homolytically to olefins and disproportionate according to equation 148 (Scheme XV, *cf.* Scheme XIII).[50,231–234] The radicals also add to 1,4-benzoquinone (Eq. 149).

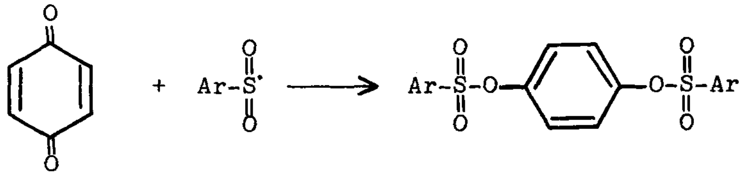
The generation of sulfonyl radicals by halogen abstraction from sulfonyl halides[218–222,224–227] has been performed with phenyl,[234,235] 1-cyano-1-methylethyl,[50,235] and triethylsilyl[236] free radicals (*cf.* 146, 147). The relative reactivities

SCHEME XV





$$6\,\mathrm{Ar{-}SO_2^{\bullet}} \longrightarrow \mathrm{Ar{-}SO_2{-}SO_2{-}Ar} + \mathrm{Ar{-}S{-}SO_2{-}Ar} + 2\,\mathrm{Ar{-}SO_2{-}O{-}SO_2{-}Ar} + \mathrm{Ar{-}S{-}S{-}Ar} \quad (148)$$



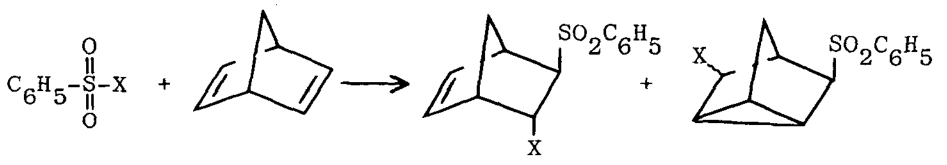
(149)

of halogen abstraction from arenesulfonyl bromides and iodides by benzyl, 1-cyano-1-methylethyl, and phenyl radicals in benzene at 60 °C have been reported.[235] These relative reactivities are almost independent of the nature of the substituents on the benzene ring of arenesulfonyl bromides. Arenesulfonyl iodides are more reactive toward phenyl radicals than bromides which in turn are more reactive then the corresponding chlorides (relative reactivities 602:192:1).

The rates of photochemically promoted additions of 4-methylbenzenesulfonyl iodide to phenylethene and its derivative were measured in benzene solutions containing picric acid to inhibit concurrent polymerization.[50,222,231,232] Electron-attracting substituents in the phenylethenes slow the rate of addition of the 4-methylbenzenesulfonyl radicals to the carbon-carbon double bond (ρ or $\rho^+ = -0.55$).[231]

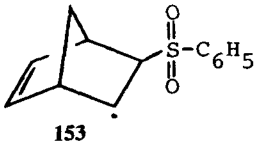
It has been shown that the rates of additions of light-generated sulfonyl radicals to vinyl monomers are independent of the structure of the sulfonyl radical.[237a] Chain-transfer constants (C_{tr}) of arene- and alkanesulfonyl chlorides at 60 °C in phenylethene and methyl methacrylate (MMA) polymerizations have been determined.[236b] A Hammett plot for substituted benzenesulfonyl chlorides gave $\rho = 0.86$, which may be explained by the contribution of a charge-transfer resonance form ($\mathrm{ArSO_2^-Cl^+CH(C_6H_5)CCH_2}$—) in the activated complex.

Benzenesulfonyl halides react with norbornadiene (**150**) to give mixtures of *endo*-3-halo-*exo*-5-norbornen-2-yl phenyl sulfone (**151**) and 5-halo-3-nortricyclyl phenyl sulfone (**152**).[225] The proportion of saturated component (**152**) decreases along the series.



(150)

150 **151** **152**



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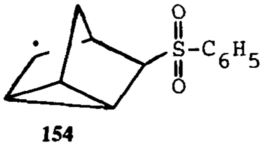

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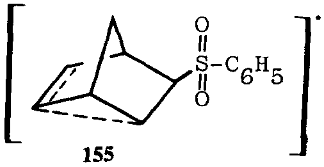
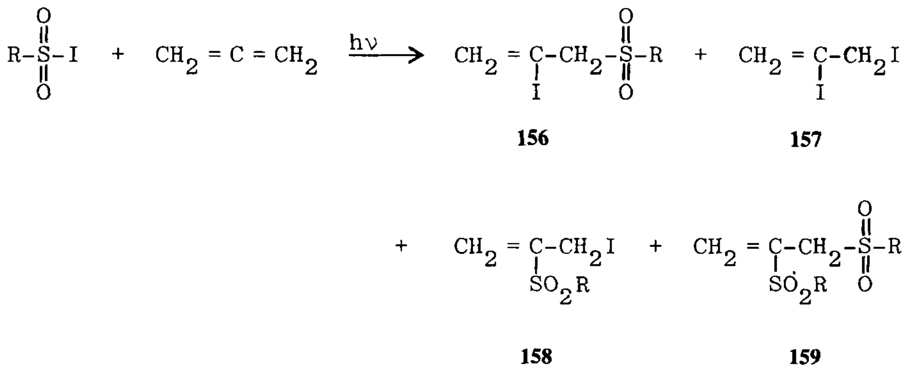


155

(Cl > Br > I). These results and dilution experiments are consistent with two separate intermediates (**153** and **154**) rather than the nonclassical homoallylic radical intermediate (**155**).

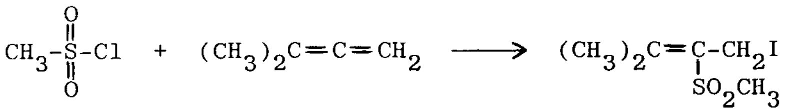
Alkyl- and arylsulfonyl iodides add to both the central and terminal positions of 1,2-propadiene (allene) to give 1:1 adducts (eq 151; Scheme XVI).[238,239] When substituted



$$R-\overset{O}{\underset{O}{S}}-I + CH_2=C=CH_2 \xrightarrow{h\nu} CH_2=\underset{I}{C}-CH_2-\overset{O}{\underset{O}{S}}-R + CH_2=\underset{I}{C}-CH_2I + CH_2=\underset{SO_2R}{C}-CH_2I + CH_2=\underset{SO_2R}{C}-CH_2-\overset{O}{\underset{O}{S}}-R \qquad (151)$$

156 **157** **158** **159**

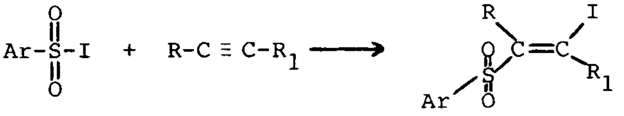
1,2-propadienes such as phenyl-1,2-propadiene or 3-methyl-1,2-butadiene (**160**) were employed, nearly quantitative yields of the 1:1 adducts resulting from attack by an intermediate sulfonyl radical on the central carbon atom of the allenic unit were usually obtained (Eq. 152).[239] The addition of 4-methylbenzenesulfonyl iodide to 2,3-pentadiene behaves in a similar fashion giving a moderate yield of 1:1 adduct resulting from attack on the central carbon atom.[238]



$$CH_3-\overset{O}{\underset{O}{S}}-Cl + (CH_3)_2C=C=CH_2 \longrightarrow (CH_3)_2C=\underset{SO_2CH_3}{C}-CH_2I \qquad (152)$$

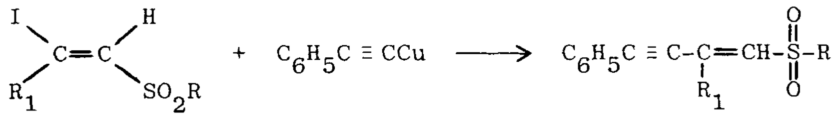
160 **161**

Sulfonyl iodides add readily and stereoselectively to alkynes to form 1:1 adducts (**162**) in good to excellent yields (Eq. 153).[240] The adducts represent convenient precursors to sulfonylalkynes and, on treatment with cuprous phenylacetylide, yield the novel ene-yne sulfones (**163**, Eq. 154). The acetylenic sulfones undergo a smooth thermally induced extrusion of sulfur dioxide in several cases.



(153)

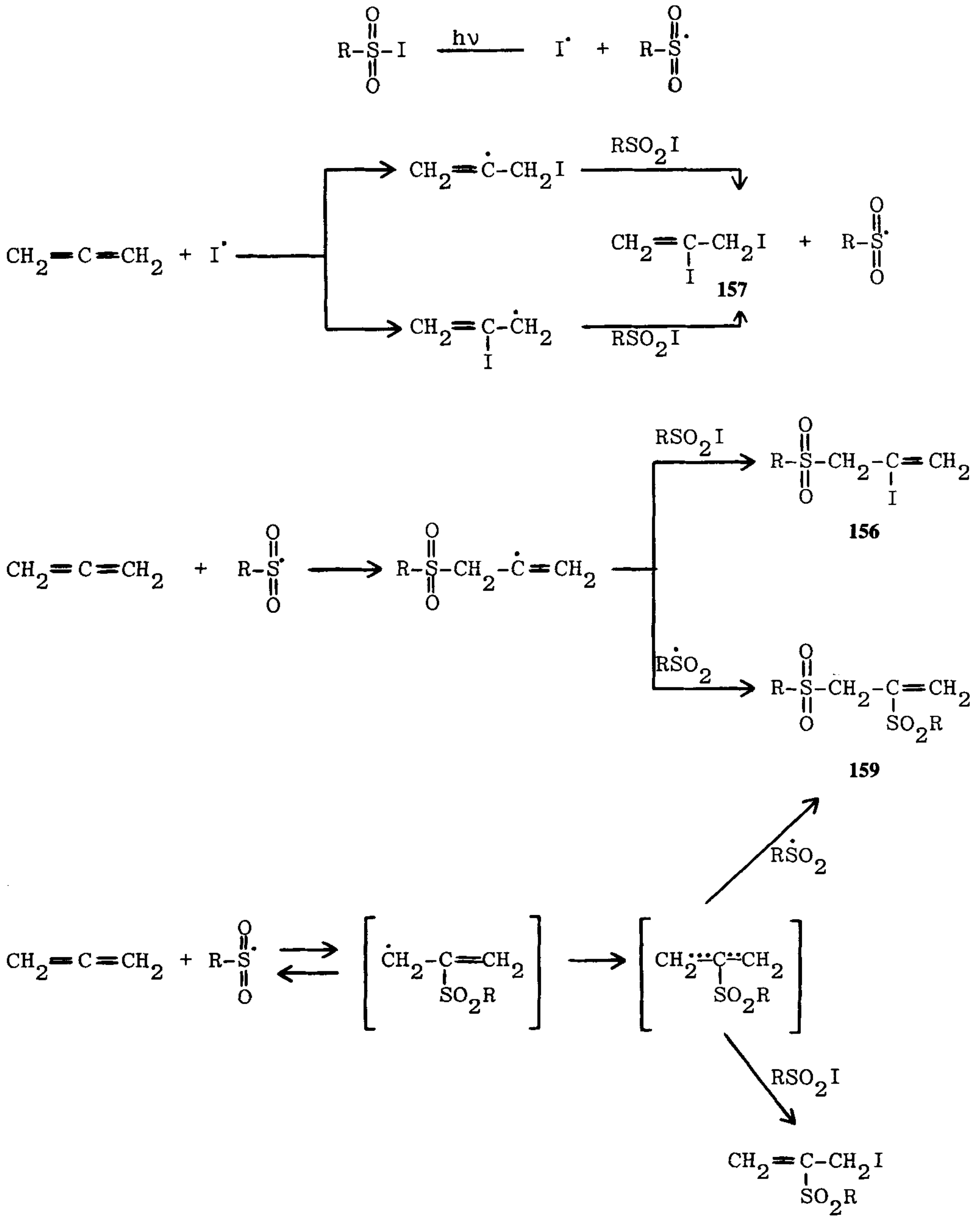
162



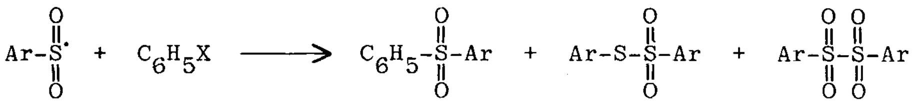
(154)

163

SCHEME XVI

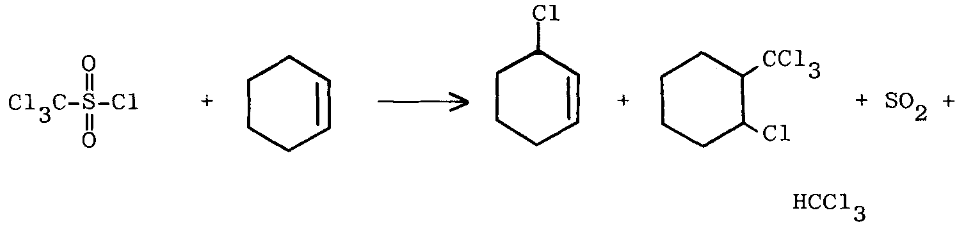


When arylsulfonyl radicals are generated from sulfonyl iodides or sulfones in chloro-, bromo-, and iodobenzene at 150–190 °C, the halogen atom is replaced by the arylsulfonyl group.[233] The relative ease of displacement of Cl : Br : I is 1 : 5.9 : 18.6; fluorobenzene does not react appreciably under these conditions. The reaction is facilitated by electron-releasing substituents on the halobenzene.



$$\mathrm{Ar{-}SO_2^{\bullet}} + \mathrm{C_6H_5X} \longrightarrow \mathrm{C_6H_5{-}SO_2{-}Ar} + \mathrm{Ar{-}S{-}SO_2{-}Ar} + \mathrm{Ar{-}SO_2{-}SO_2{-}Ar} \quad (155)$$

The relative rates of free radical addition with respect to the rate of allylic halogenation of cyclohexene by trichloromethanesulfonyl chloride suggests that trichloromethanesulfonyl radicals are complexed by alkenes (Eq. 156).[241,242] A reaction of the complexed radical with another molecule of the alkene results in the addition of the trichloromethyl moiety to the alkene. Competitive chlorinations of cyclohexane and methylbenzene in the presence of azabenzene showed that only uncomplexed trichloromethanesulfonyl radicals are involved in hydrogen atom abstractions.[241]



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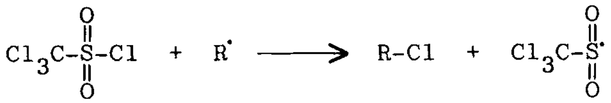
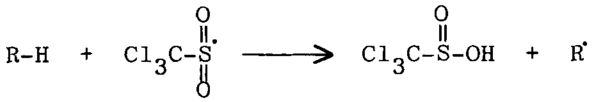
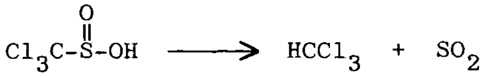


$$\mathrm{Cl_3C{-}SO_2{-}Cl} + \mathrm{R^{\bullet}} \longrightarrow \mathrm{R{-}Cl} + \mathrm{Cl_3C{-}SO_2^{\bullet}} \quad (157)$$

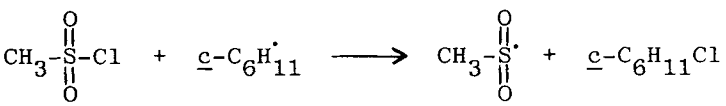


$$\mathrm{R{-}H} + \mathrm{Cl_3C{-}SO_2^{\bullet}} \longrightarrow \mathrm{Cl_3C{-}S(O){-}OH} + \mathrm{R^{\bullet}} \quad (158)$$

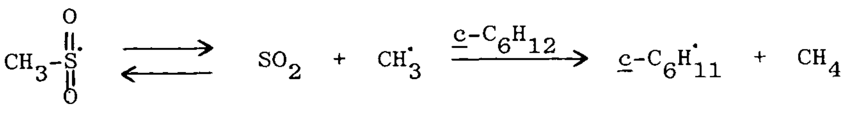


$$\mathrm{Cl_3C{-}S(O){-}OH} \longrightarrow \mathrm{HCCl_3} + \mathrm{SO_2} \quad (159)$$

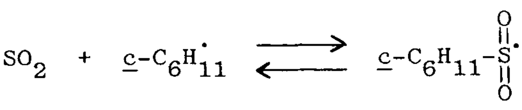
The γ-radiolysis of cyclohexane containing methanesulfonyl chloride between 60 and 150 °C involves methanesulfonyl radicals (Eqs. 160–162).[243] Bond dissociation energies of 14.94 ± 0.92 and 11.91 ± 0.82 kcal/mol were calculated for $D(CH_3\text{-}SO_2)$ and $D(c\text{-}C_6H_{11}\text{-}SO_2)$, respectively.



$$\mathrm{CH_3{-}SO_2{-}Cl} + \underline{c}\mathrm{{-}C_6H_{11}^{\bullet}} \longrightarrow \mathrm{CH_3{-}SO_2^{\bullet}} + \underline{c}\mathrm{{-}C_6H_{11}Cl} \quad (160)$$

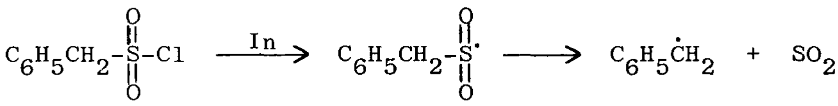


$$\mathrm{CH_3{-}SO_2^{\bullet}} \rightleftarrows \mathrm{SO_2} + \mathrm{CH_3^{\bullet}} \xrightarrow{\underline{c}\mathrm{{-}C_6H_{12}}} \underline{c}\mathrm{{-}C_6H_{11}^{\bullet}} + \mathrm{CH_4} \quad (161)$$

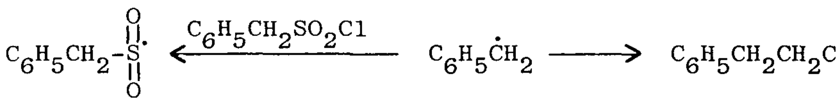


$$\mathrm{SO_2} + \underline{c}\mathrm{{-}C_6H_{11}^{\bullet}} \rightleftarrows \underline{c}\mathrm{{-}C_6H_{11}{-}SO_2^{\bullet}} \quad (162)$$

Phenyl radicals produced in the decomposition of phenylmethanesulfonyl chloride initiated by dicyclohexyl peroxycarbonate either couple to give 1,2-diphenylethane or abstract chlorine from the sulfonyl chloride (Eqs. 163,164).[244] Similar results have been observed with phenylmethanesulfonyl iodide.[239,245]

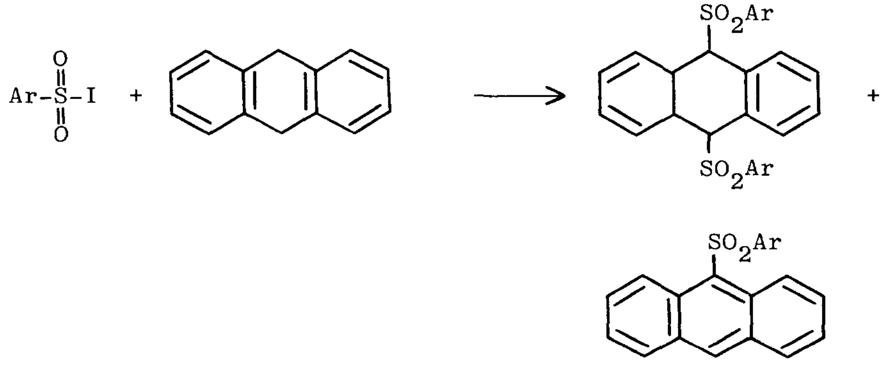


$$C_6H_5CH_2-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-Cl \xrightarrow{In} C_6H_5CH_2-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{}^{\bullet} \longrightarrow C_6H_5\dot{C}H_2 + SO_2 \qquad (163)$$



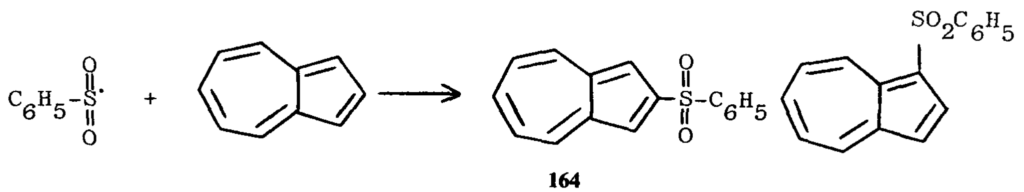
$$C_6H_5CH_2-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{}^{\bullet} \xleftarrow{C_6H_5CH_2SO_2Cl} C_6H_5\dot{C}H_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (164)$$

4-Methylbenzenesulfonyl iodide, in the presence of copper powder, adds 4-methylbenzenesulfonyl radicals to the *meso*-positions of both anthracene and 2,3-benzanthracene: there is no reaction with phenanthrene and 1,2-benzanthrene.[246] Side chain substitution of hydrogen by the sulfonyl radical occurs at a *meso* methyl group with both 9-methyl- and 9,10-dimethylanthracene.



(165)

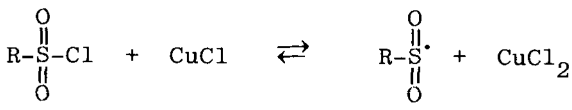
Phenylsulfonyl radicals, prepared by thermolysis of nonionized $Cu(SO_2C_6H_5)_2$ in azabenzene, reacted with azulene to give 2-(phenylsulfonyl)azulene (**164**) along with a smaller amount of 1-(phenylsulfonyl)azulene.[247] The same products were obtained with benzenesulfinic acid.



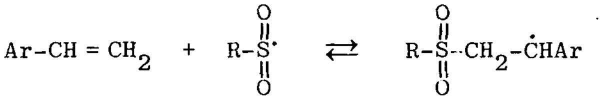
164

(166)

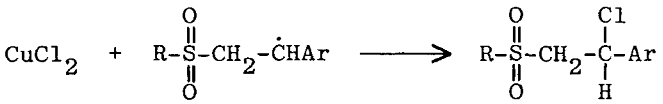
The cupric chloride catalyzed addition of sulfonyl chlorides to alkenes is an important reaction for the synthesis of β-chlorosulfones (Eqs. 167–169).[228,248,249]



$$\mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}Cl} + \mathrm{CuCl} \rightleftarrows \mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{^\bullet}} + \mathrm{CuCl_2} \tag{167}$$



$$\mathrm{Ar{-}CH{=}CH_2} + \mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{^\bullet}} \rightleftarrows \mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CH_2{-}\dot{C}HAr} \tag{168}$$

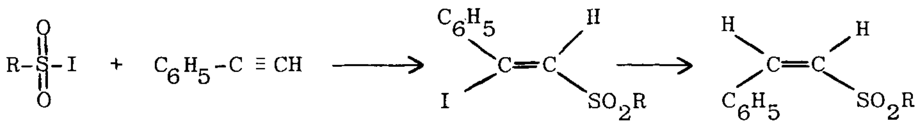


$$\mathrm{CuCl_2} + \mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CH_2{-}\dot{C}HAr} \longrightarrow \mathrm{R{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}CH_2{-}\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}{-}Ar} \tag{169}$$

A kinetic study of the copper chloride-catalyzed addition of benzenesulfonyl chloride to a number of substituted phenylethenes showed that the overall rates were very little affected by the substituents.[248] These data rule out the possibility of a concerted reaction in which the olefin participates in the rate-determining step and confirm a redox chain mechanism (Scheme XVII).

Product analyses and relative rate data indicated that in the cuprous chloride catalyzed addition of alkyl- and arylsulfonyl chlorides to phenylethene, phenylethyne, $CH_3Si(C_2H_5)_2CHCHCH_2$, and $(CH_3)_3SiCCCHCH_2$ the copper is involved in electron transfer to form an organosulfonyl radical and Cl-transfer to form the final product.[250] The former role can be played by several metals in different oxidation states, but the latter role requires metals with low redox potentials.

Alkyl- and arylsulfonyl iodides add to phenylethyne in ethanenitrile containing triethylamine hydrochloride and cuprous chloride at 22–24 °C to 1:1 adducts (**165**), which were deiodinated with zinc in dilute ethanoic acid to give (Z)-sulfones (**166**, eq 170; *cf.* eq 153).[251]



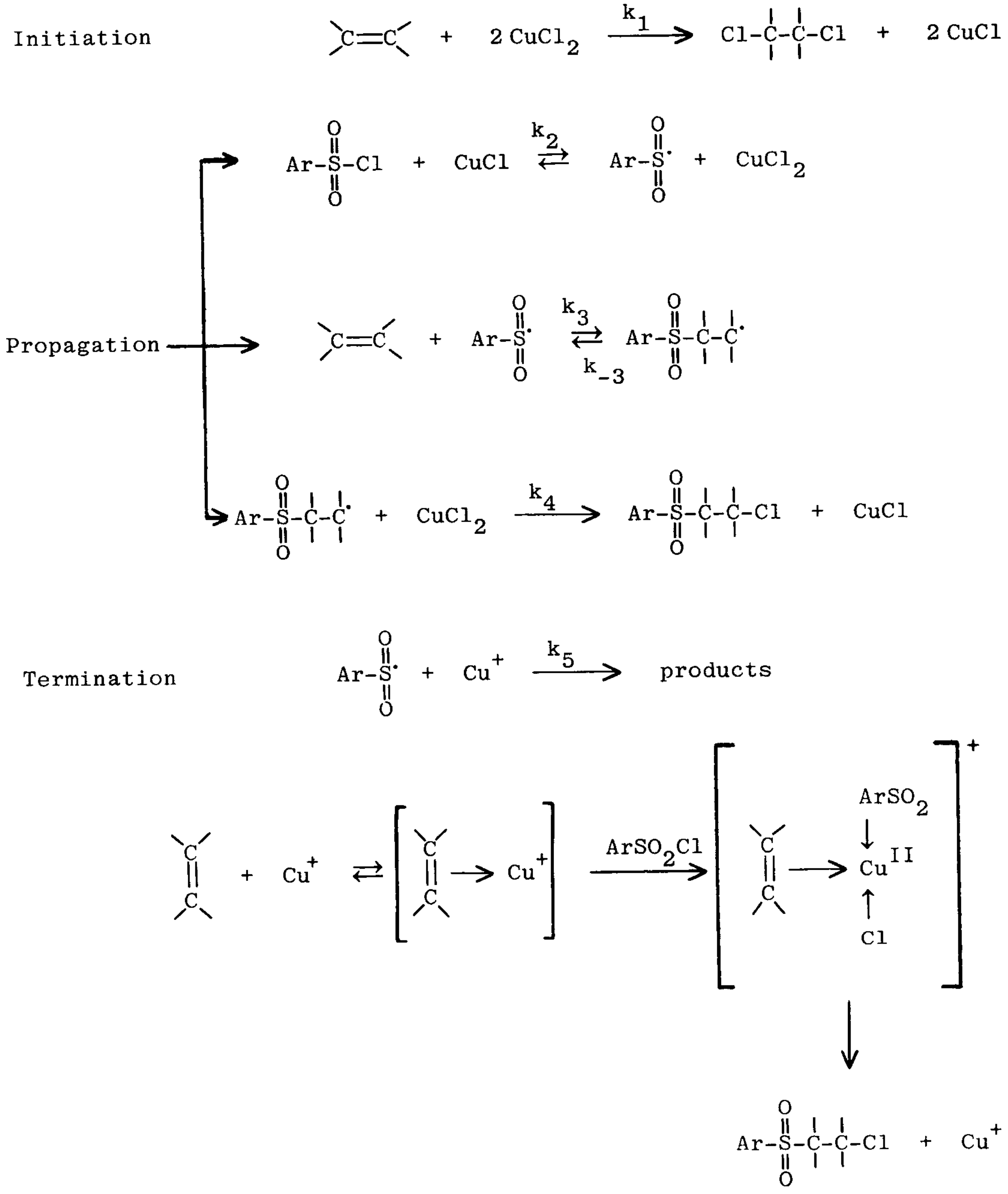
(170)

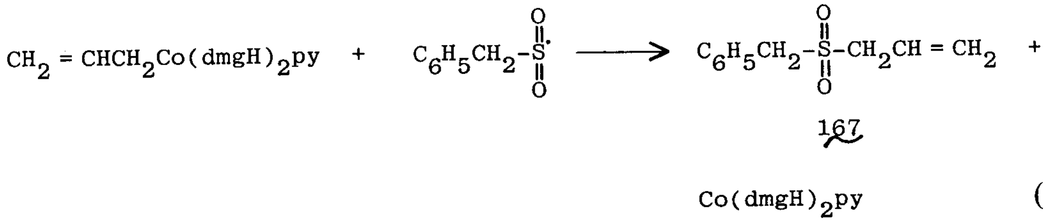
165 **166**

Phenylmethanesulfonyl radicals, generated by chlorine atom abstraction from phenylmethanesulfonyl chloride by cobaloxime(II) (Eq. 171), react with allylcobaloximes to give high yields of phenylmethyl 3-propenyl sulfone (**167**, Eq. 172) and no insertion product **123** (*cf.* Eq. 120).[174]

$$\mathrm{C_6H_5CH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}Cl} + \mathrm{Co^{II}(dmgH)_2py} \longrightarrow \mathrm{C_6H_5CH_2{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{^\bullet}} + \mathrm{ClCo(dmgH)_2py} \tag{171}$$

SCHEME XVII

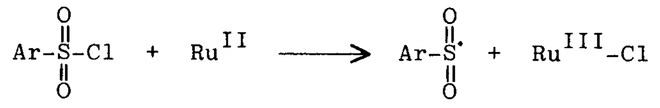




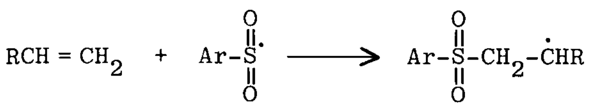
$$CH_2=CHCH_2Co(dmgH)_2py + C_6H_5CH_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\cdot \longrightarrow C_6H_5CH_2-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-CH_2CH=CH_2 + Co(dmgH)_2py \qquad (172)$$

167

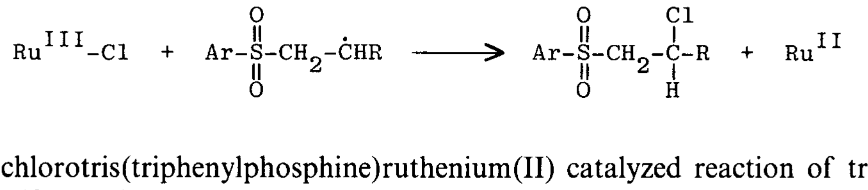
The dichlorotris(triphenylphosphine)ruthenium(II) catalyzed reaction of methanesulfonyl chloride or arenesulfonyl chlorides with 1-alkenes gives 1:1 adducts in high yields.[252] Telomer formation is not observed. A radical-chain mechanism is proposed for this convenient synthesis of *β*-chlorosulfones (Eqs. 173–175, *cf.* Eqs. 108,109,167–169).[252,253]



$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}Cl} + \mathrm{Ru^{II}} \longrightarrow \mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{^\bullet}} + \mathrm{Ru^{III}{-}Cl} \qquad (173)$$

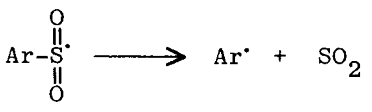


$$\mathrm{RCH=CH_2} + \mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{^\bullet}} \longrightarrow \mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}\dot{C}HR} \qquad (174)$$



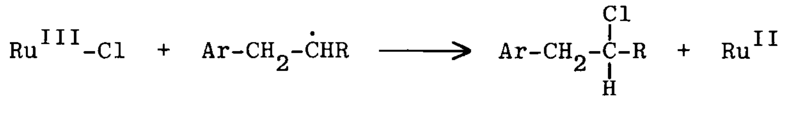
$$\mathrm{Ru^{III}{-}Cl} + \mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}\dot{C}HR} \longrightarrow \mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{-}CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}{-}R} + \mathrm{Ru^{II}} \qquad (175)$$

The dichlorotris(triphenylphosphine)ruthenium(II) catalyzed reaction of trichloromethanesulfonyl chloride with 1-alkenes also gives 1:1 adducts in good yields with extrusion of sulfur dioxide (Eqs. 176–178).[252]



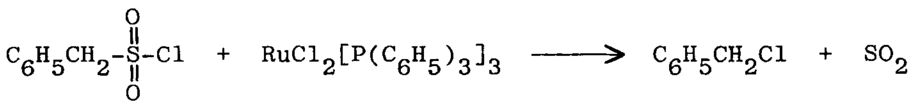
$$\mathrm{Ar{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}{^\bullet}} \longrightarrow \mathrm{Ar^\bullet} + \mathrm{SO_2} \qquad (176)$$

$$\mathrm{RCH=CH_2} + \mathrm{Ar^\bullet} \longrightarrow \mathrm{Ar{-}CH_2{-}\dot{C}HR} \qquad (177)$$



$$\mathrm{Ru^{III}{-}Cl} + \mathrm{Ar{-}CH_2{-}\dot{C}HR} \longrightarrow \mathrm{Ar{-}CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C}}{-}R} + \mathrm{Ru^{II}} \qquad (178)$$

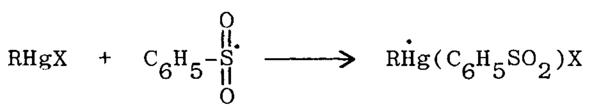
Desulfonylation occurred when arylmethanesulfonyl chlorides were treated with catalytic amounts of the ruthenium(II) catalyst to give chloromethylarenes in high yields. A desulfonylation pathway proceeding by a redox transfer promoted homolytic mechanism in the coordination sphere of the catalyst was proposed.[253] No addition of the sulfonyl chloride to olefin was observed when the reaction was carried out in the presence of an equimolar amount of an olefin. The rate of disappearance of the sulfonyl chloride was accelerated by addition of an olefin. In the presence of large excess of phenylethenes, arylmethanesulfonyl chlorides added to the olefins to give 1:1 adducts competitively with the desulfonylation yielding chloromethylarenes.



$$C_6H_5CH_2-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-Cl + RuCl_2[P(C_6H_5)_3]_3 \longrightarrow C_6H_5CH_2Cl + SO_2$$

(179)

The photostimulated reaction of alkylmercury halides and benzenesulfonyl chlorides yields alkyl halide and no alkyl phenyl sulfone.[254] These products are consistent with a free-radical mechanism (Eqs. 180–182). The reaction does not occur for C_6H_5HgX or (cyclopropyl)HgX, presumably because of the high bond dissociation energies in **168** (Eq. 181).



$$RHgX + C_6H_5-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S^{\bullet}}}}} \longrightarrow R\dot{H}g(C_6H_5SO_2)X$$

168

(180)

$$R\dot{H}g(C_6H_5SO_2)X \longrightarrow R^{\bullet} + C_6H_5SO_2HgX \quad (181)$$

168

$$C_6H_5-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-Cl + R^{\bullet} \longrightarrow R-Cl + C_6H_5-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S^{\bullet}}}}}$$

(182)

With R in RHgX equal $^5\Delta$-hexenyl, the second order rate constant for attack (cyclization) of the $^5\Delta$-hexenyl radical on benzenesulfonyl chloride and 4-$CH_3C_6H_4SO_2SeC_6H_5$ were found to be 3.7×10^4 and 3.0×10^6 1/(mol s), respectively.[254]

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