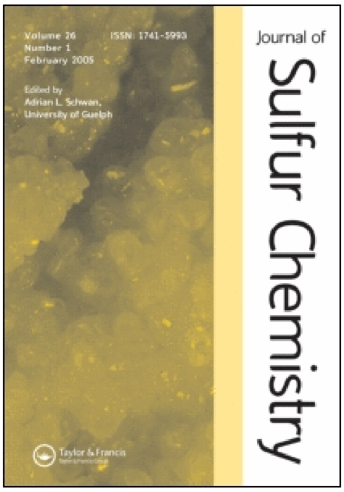

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Salah M. Yassin[a]
[a] Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

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THE CHEMISTRY OF C-SULFONYLDITHIOFORMATES

SALAH M. YASSIN
Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt

This review is the first exhaustive account of the preparation and synthetic application of *C*-sulfonyldithioformates, based on a CAS Online search.

Key words: Chlorodithioformates, sulfinates, *C*-sulfonyldithioformates.

CONTENTS

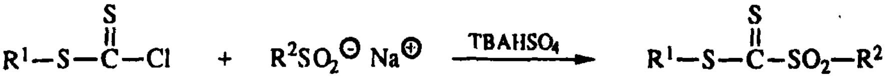
1. INTRODUCTION

The *C*-sulfonyldithioformates can be regarded as push-pull (capto-dative) substituted thioformaldehyde. They possess excellent stability to storage in the crystalline state and are at the same time highly reactive towards a variety of reagent such as electrophiles, nucleophiles, and many π-electron systems. Combined with their easy accessibility this makes them excellent intermediates for a multitude of organic syntheses.

2. THE SYNTHESIS OF *C*-SULFONYLDITHIOFORMATES

2.1. *By Reactions of Chlorodithioformates with Sulfinate Ions*

Senning *et al.* have prepared *C*-sulfonyldithioformates **3** and bis(*C*-sulfonyldithioformates) **5** by thioacylation of metal sulfinates with chlorodithioformates[13] in a two-phase reaction between aqueous sulfinate anions and the chlorodithioformates dissolved in benzene with tetrabutylammonium hydrogen sulfate as a phase transfer catalyst or by treatment of anhydrous sodium sulfinates, suspended in dry *N,N*-dimethylformamide, with chlorodithioformates according to (1).[1-16]

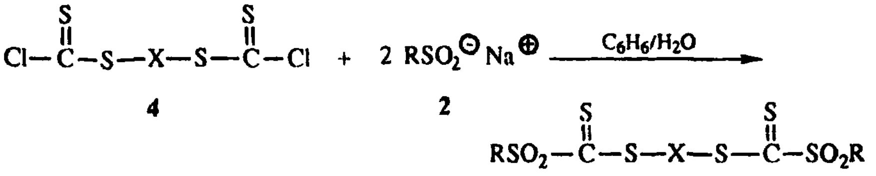


$$R^1{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}Cl \quad + \quad R^2SO_2^{\ominus}\,Na^{\oplus} \xrightarrow{TBAHSO_4} R^1{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SO_2{-}R^2 \qquad (1)$$

1 **2** **3**

2.2. *By Reactions of Bis(Chlorodithioformates) with Sulfinate Ions*

Bis(chlorodithioformates) react with two moles of metal sulfinate to afford the corresponding bis(*C*-sulfonyldithioformates) **5** according to (2).[16]

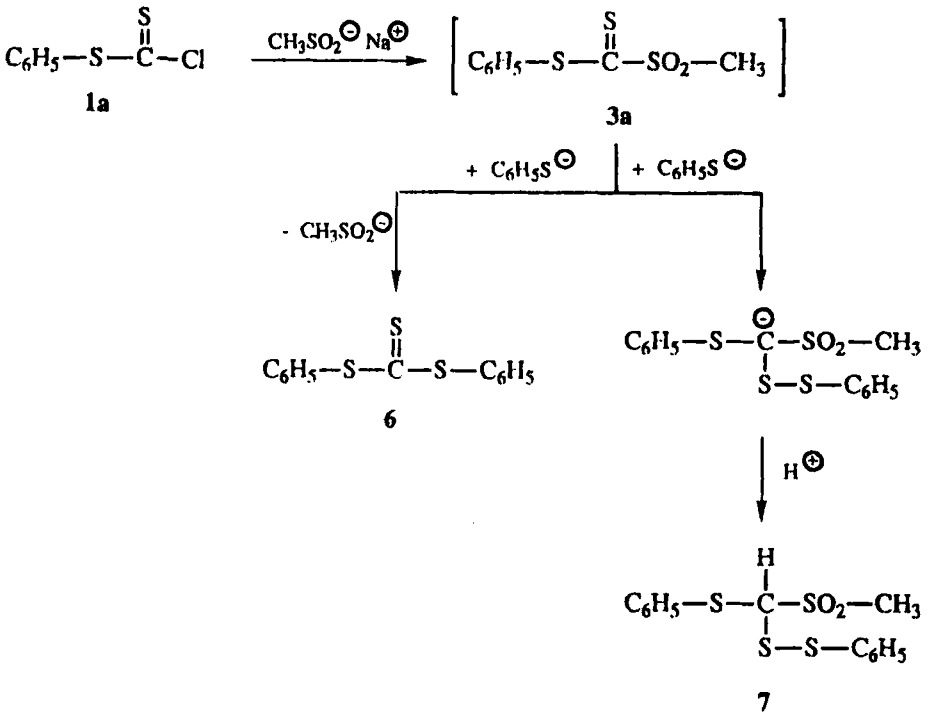


$$Cl{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S{-}X{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}Cl \quad + \quad 2\ RSO_2^{\ominus}\,Na^{\oplus} \xrightarrow{C_6H_6/H_2O} RSO_2{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S{-}X{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}SO_2R \qquad (2)$$

4 **2** **5**

X = 4,4'-biphenylylene, $(CH_2)_2$; R = $4\text{-}CH_3C_6H_4$, $4\text{-}ClC_6H_4$

Reaction of phenyl chlorodithioformate **1a** with sodium methanesulfinate affords diphenyl trithiocarbonate **6** and a small amount of the disulfide **7** according to Scheme 1.[2]

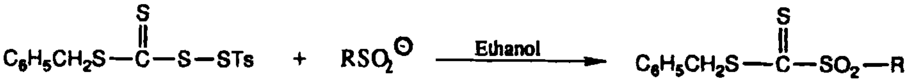


SCHEME 1

Methyl chlorodithioformate **1b** reacts with sodium methanesulfinate to form methyl (methylsulfonyl)(methylthio)methyl trithiocarbonate **8** according to (3) instead of the expected **3b.**[1]

2.3. *By Reaction of Benzylthio-thiocarbonyl* p*-tolylsulfonyl Disulfide with Sulfinates*

Benzylthio-thiocarbonyl *p*-tolylsulfonyl disulfide **9** reacts with sodium sulfinates in ethanol to afford the corresponding *C*-sulfonyldithioformates **3** according to (3).[5]



$$\underset{\mathbf{9}}{C_6H_5CH_2S-\overset{\overset{\displaystyle S}{\|}}{C}-S-STs} + RSO_2^{\ominus} \xrightarrow{\text{Ethanol}} \underset{\mathbf{3}}{C_6H_5CH_2S-\overset{\overset{\displaystyle S}{\|}}{C}-SO_2-R} \quad (3)$$

3. SPECTROSCOPIC PROPERTIES OF C-SULFONYLDITHIOFORMATES

3.1. *Ultraviolet and Visible Spectra*

The traditional spectroscopic method for the characterization of the thiocarbonyl group in *C*-sulfonyldithioformates is UV/VIS spectroscopy. The reason for this was the relatively

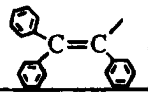
TABLE 1 Ultraviolet-visible spectra for some *C*-sulfonyldithioformates **3**

Cpd.	R^1	R^2	Solvent	λ_{max} (nm) $C{=}S\ \pi\text{-}\pi^*$	log ε	Ref.
3o	C_6H_5	C_6H_5	Ethanol	338	3.91	1, 16
3p	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	Chloroform	340	3.76	1, 16
3n	$(CH_3)_2CH$	$4\text{-}ClC_6H_4$	Ethanol	336	3.96	1, 16
3r	C_6H_5	CH_3	CCl_4	333	3.84	1, 16
3s	CH_3	1-adamantyl	Ethanol	333	3.97	1, 16
3t	CH_3	C_6H_5	Ethanol	332	3.95	1, 16
3u	CH_3CH_2	$4\text{-}CH_3C_6H_4$	Chloroform	334	3.88	1, 16
3v	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	Ethanol	338	3.66	1, 16
3w	C_6H_5	$4\text{-}CH_3C_6H_4$	Ethanol	338	3.78	1, 16
3x	CH_3	$4\text{-}CH_3C_6H_4$	Ethanol	331	3.94	1, 16

Cpd.	R^1	R^2	Solvent	λ_{max} (nm) $C{=}S\ \pi\text{-}\pi^*$	log ε	$\lambda_{max.}$ (nm) $C{=}S\ n\text{-}\pi^*$	log ε	Ref.
3s	CH_3	1-adamantyl	C_6H_{12}	328	3.96	516 537	1.58 1.62	1, 16
			CCl_4	330	3.89	516 535	1.63 1.66	
			$(CH_3)_2CO$	332	3.94	515 533	1.59 1.59	
			CH_3CN	332	3.96	517 528	1.67 1.67	
3w	C_6H_5	$4\text{-}CH_3C_6H_4$	C_6H_{12}	335	3.78	530	1.57	1, 16
			CCl_4	336	3.83	530	1.62	
			$(CH_3)_2CO$	336	3.74	528	1.66	
			CH_3CN	333	3.73	524	1.57	

early availability of the method along with the fact that *C*-sulfonyldithioformates are colored compounds. The range of the colors goes from red to violet due to excitation of the n-π* transition of the thiocarbonyl group.[1,16] The *C*-sulfonyldithioformates **3** show two intense absorption maxima, one in the visible range at about 533 nm (cf. Table 2) and the other in the UV range at about 332 nm (cf. Table 1).[1,16]

TABLE 2 The Spectral Properties of *C*-Sulfonyldithioformates **3**

Cpd	R^1	R^2	^{13}C NMR ($CDCl_3$) $\delta_{C=S}$ (ppm)	IR (KBr) (cm^{-1})		Ref.
				$\nu_{C=S}$	ν_{SO_2}	
3a	C_6H_5	1-adamantyl	220.31	1115	1140, 1300	18
3b	C_6Cl_5	1-adamantyl	213.77	1127	1146, 1340	18
3c	4-ClC_6H_4	4-$CH_3C_6H_4$	223.92	1125	1155, 1320	18
3d	4-ClC_6H_4	1-adamantyl	220.23	1120	1144, 1308	18
3e	4-$CH_3C_6H_4$	C_6H_5	224.07	1120	1155, 1320	18
3f		4-$CH_3C_6H_4$	218.58	1080	1110, 1235	18
3g	4-$O_2NC_6H_4$	4-$CH_3C_6H_4$	222.74	1120	1157, 1355	18
3h	C_6Cl_5	4-ClC_6H_4	216.32	1123	1160, 1340	18
3i	C_6Cl_5	C_6H_5	216.90	1123	1157, 1345	18
3j	2,4,5-$Cl_3C_6H_2$	4-$CH_3C_6H_4$	220.18	1122	1158, 1336	18
3k	C_6H_5	4-ClC_6H_4	222.99	1123	1160, 1336	18
3l	C_6Cl_5	4-$CH_3C_6H_4$	217.40	1130	1160, 1340	18
3m	CH_3	4-$CH_3C_6H_4$	224.88	1120	1160, 1330	18

3.2. *IR Spectra*

IR spectra give useful qualitative information diagnostic of the thiocarbonyl group in the *C*-sulfonyldithioformates **3a-e** and **3g-q** which exhibit characteristic $\nu_{C=S}$ absorption around 1120 cm^{-1} while the *C*-sulfonyldithioformate **3f** exhibits characteristic $V_{C=S}$ absorption at 1080 cm^{-1} (cf. Table 2). The *C*-sulfonyldithioformates **3a-q** exhibit characteristic ν_{SO_2} absorptions around 1145 and 1330 cm^{-1}[11,16,17] (cf. Table 2).

TABLE 2 *Continued*

Cpd.	R^1	R^2	^{13}C NMR ($CDCl_3$) $\delta_{C=S}$ (ppm)	IR (KBr) (cm^{-1})		Ref.
				$\nu_{C=S}$	ν_{SO_2}	
3n	$(CH_3)_2CH$	$4\text{-}ClC_6H_4$	221.18	1122	1163, 1328	18
3o	C_6H_5	C_6H_5	223.47	1120	1155, 1327	18
3p	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	222.79	1123	1155, 1319	18
3q	C_6H_5	$4\text{-}CH_3C_6H_4$	224.01	1120	1152, 1325	18

3.3. ^{13}C *NMR Spectra*

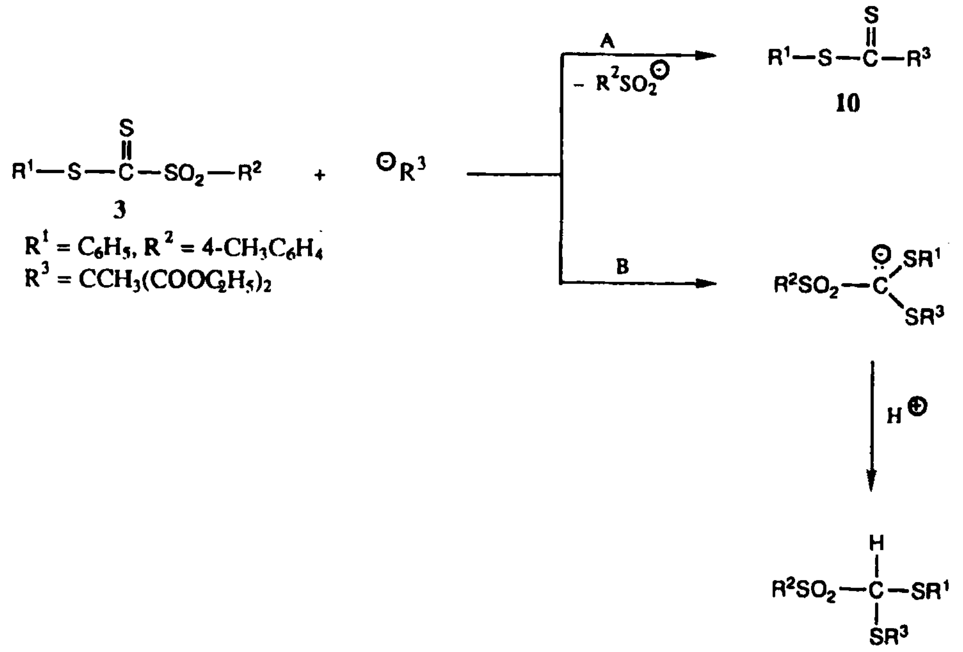
^{13}C NMR spectroscopy allows direct insight into the nature of the thiocarbonyl carbon. The influence of substituents is quite pronounced for the chemical shifts of the thiocarbonyl carbon along with the deshielding influence of the strongly electron-withdrawing sulfonyl group. Thus, the ^{13}C NMR signals of the thiocarbonyl carbons in the *C*-sulfonyldithioformates 3 lie between 214 ppm (for **3b**) to 225 ppm for (**3m**) (cf. Table 2) and shows the deshielding effect of the strongly electron-withdrawing sulfonyl group.[17,18] An interesting detail among the substituent effects seen is the more strongly electron-withdrawing character of the 4-chlorophenyl group for (**3c**) compared to that of the pentachlorophenyl group for (**3l**).[18] In the latter case steric hindrance involving the 2- and 6-chlorine atoms twists the pentachlorophenyl group strongly out of the S_2CS plane, thus reducing the inductive and resonance interaction between the substituent and the thiocarbonyl carbon atom.

3.4. *The Mass Spectra*

The mass spectra of *C*-sulfonyldithioformates **3a-g**, **3j**, **3k** and **3m-q** give the molecular ion peaks as the first fragment, molecular ion minus sulfur peaks for **3h** and **3l** and the molecular ion minus carbon disulfide peak for **3i**. The next fragmentation pattern includes the loss of arylsulfonyl, arylsulfinyl, arylthio, aryloxy, and aralkyl dithiocarbonyl as common fragments. The ion compositions for the *C*-sulfonyldithioformates **3a-q** are in agreement with the expected isotopic patterns.

4. THE CHEMICAL PROPERTIES OF *C*-SULFONYLDITHIOFORMATES

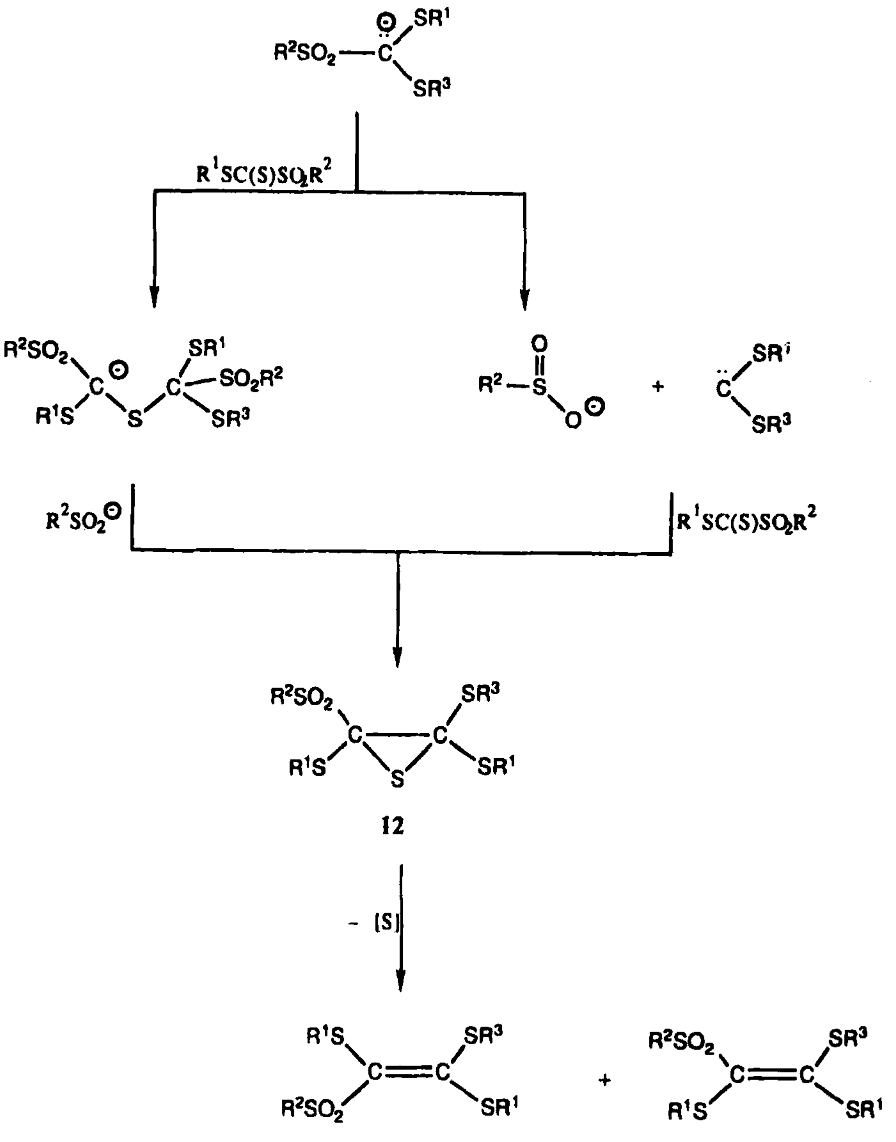
4.1. *Thiophilic Additions*



SCHEME 2

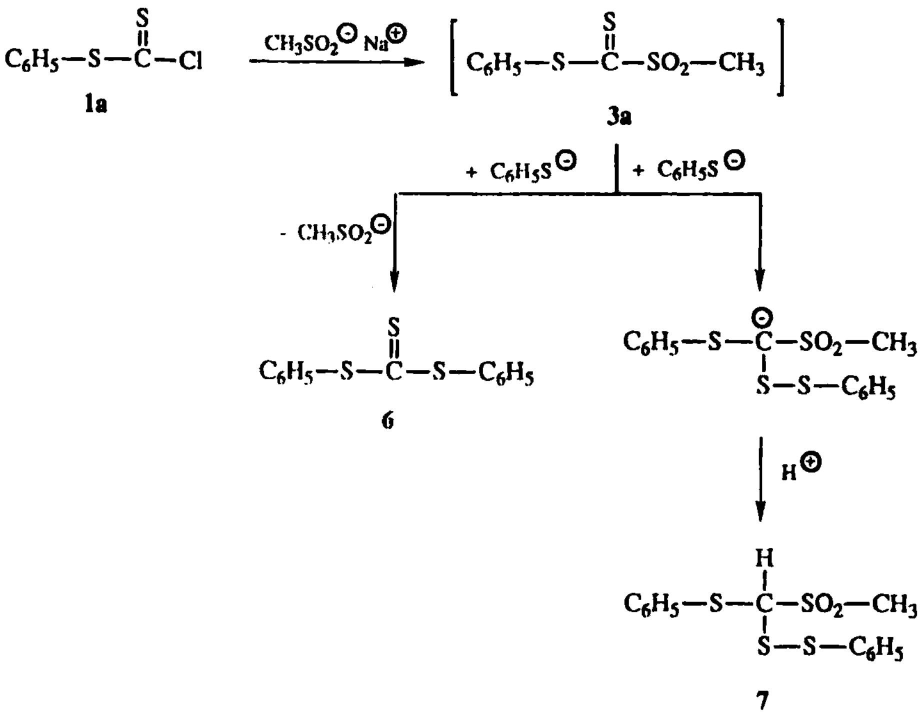
Sodium diethyl methylmalonate is thioacylated by *C*-sulfonyldithioformates **3** to yield **10**.[1,5,16] Here the carbanion is thioacylated (pathway A), while the less bulky phenyllithium attacks **3** in a thiophilic manner at the thiono sulfur to yield *S′*,*S″*-diphenyl *S*-*p*-tolyl trithioorthoformate *S*,*S*-dioxide sulfonyldithioformate **11** according to pathway B.

On the other hand the inverse addition of Grignard solutions to **3** produces the 1-sulfonyl-1,2,2-trithioethylenes **13** according to Scheme 3.[1,5,16]



SCHEME 3

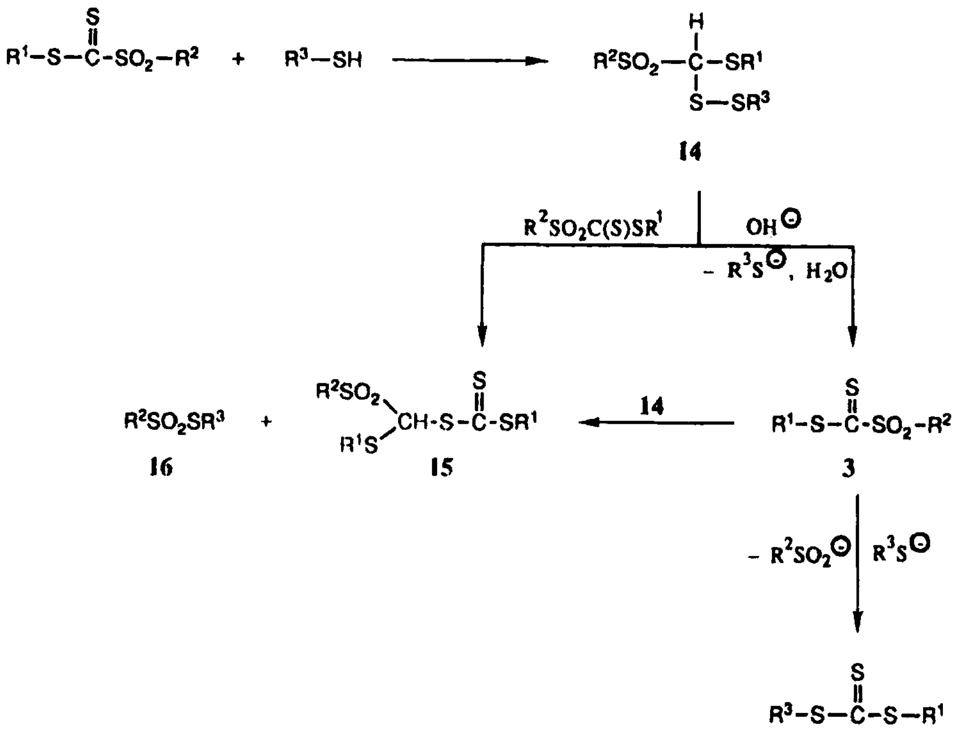
Similarly phenyl *C*-methylsulfonyldithioformate **3a** behaves as a thioacylating agent towards nucleophiles to afford phenyl (phenylthio)(methylsulfonyl)methyl disulfide **7** and diphenyl trithiocarbonate **6** according to Scheme 4.[2,16] The benzenethiolate ion is probably derived from partial hydrolysis of the corresponding chlorodithioformates.



SCHEME 4

4.2. *Reactions with Thiols*

Reduction of *C*-sulfonyldithioformates **3** with thiophenols was found to proceed via the disulfide **14** which in the presence of a catalytic amount of base is thioacylated by **3** to yield **15** and the thiosulfonate **16**. On the other hand, addition of one equivalent of base of **3** yields the trithiocarbonate **17**.[1,16]



SCHEME 5

4.3. *Reaction with Amines*

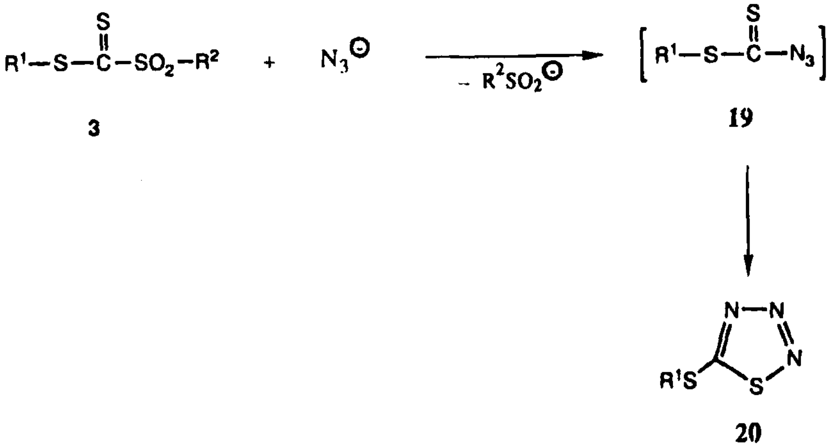
C-Sulfonyldithioformates **3** react with amines to afford the corresponding dithiocarbamates **18** according to (4).[2,4]

(4)

3 **18**

4.4. *Reactions with Azides*

Attack of azide ion on *C*-sulfonyldithioformates **3** leads to 5-alkylthio- or 5-arylthio-1,2,3,4-thiatriazoles **20** according to (5).[2,4]

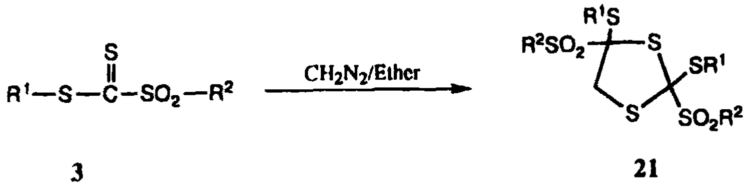


(5)

4.5. *Cycloadditions*

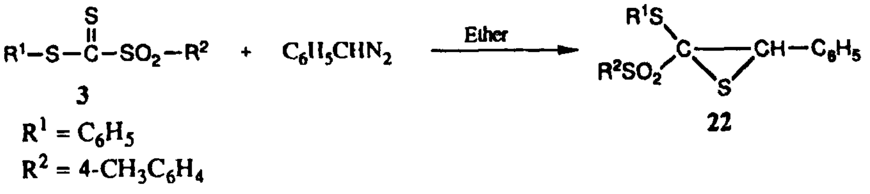
4.5.1. *Dipolar cycloadditions*

4.5.1.1. ***Reactions with diazoalkanes.*** *C*-Sulfonyldithioformates **3** in ethereal solution react immediately with diazomethane to afford the dithiolanes **21** according to (6).[9,16]

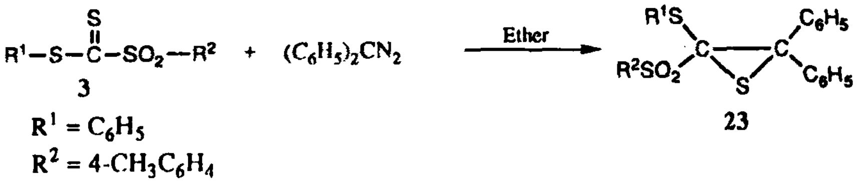


(6)

The reaction of **3** with phenyldiazomethane and diphenyldiazomethane afford thiiranes **22** and **23**, respectively, according to (7) and (8).[9,16]

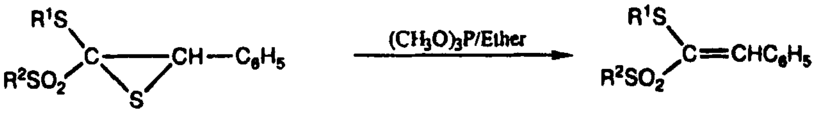


(7)

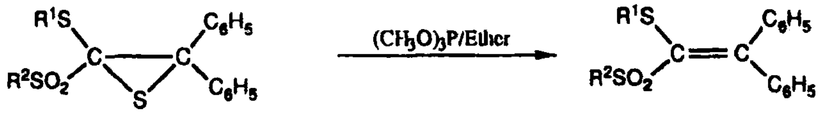


(8)

Both thiiranes **22** and **23** can be converted to the corresponding alkenes **24** and **25** in quantitative yield by treatment with trimethyl phosphite in ether according to (9)[9] and (10), respectively. Compounds **22** and **24** can exist as either *E* or *Z* isomers. The identity of the isolated products as *E*- or *Z*-isomers was not established.

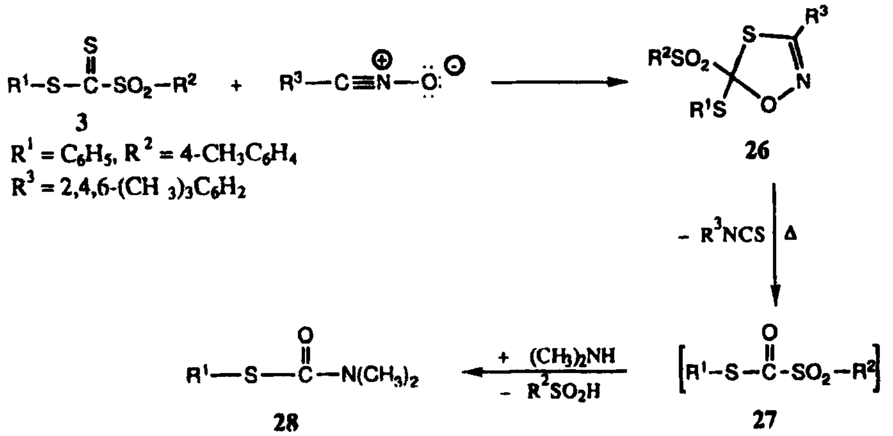


22 **24** (9)



23 **25** (10)

4.5.1.2. *Reaction with nitrile oxides.* *C*-Sulfonyldithioformates **3** readily undergo 1,3-dipolar cycloadditions. Since **3** possess electron-withdrawing substituents they act as dipolarophiles to afford the corresponding 1,4,2-oxathiazoles **26** which upon pyrolysis are cleaved to the *S,S'*-dithiocarbonate *S,S*-dioxides **27** and isothiocyanates according to (11).[7]



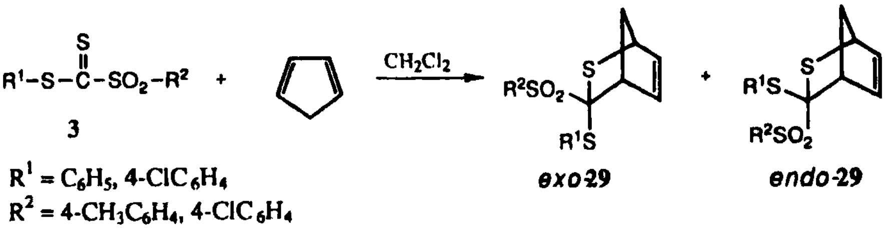
$R^1 = C_6H_5$, $R^2 = 4\text{-}CH_3C_6H_4$

$R^3 = 2,4,6\text{-}(CH_3)_3C_6H_2$

3 **26** **27** **28** (11)

4.5.2. *Diels-Alder reactions.* *C*-Sulfonyldithioformates **3** undergo Diels-Alder reaction with suitable 1,3-dienes since **3** contain an electron-depleted thiocarbonyl group and should thus be potent dienophiles[8,20] and enophiles.[21] The following two examples may serve as illustrations.

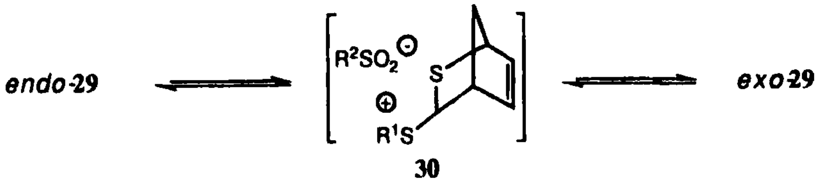
4.5.2.1. *Reactions with cyclopentadiene.* At room temperature **3** react readily with cyclopentadiene to afford *endo*-**29** and *exo*-**29** in the approximate ratio of 3:1 according to (12).[8,16]



(12)

$R^1 = C_6H_5$, 4-ClC_6H_4
R^2 = 4-$CH_3C_6H_4$, 4-ClC_6H_4

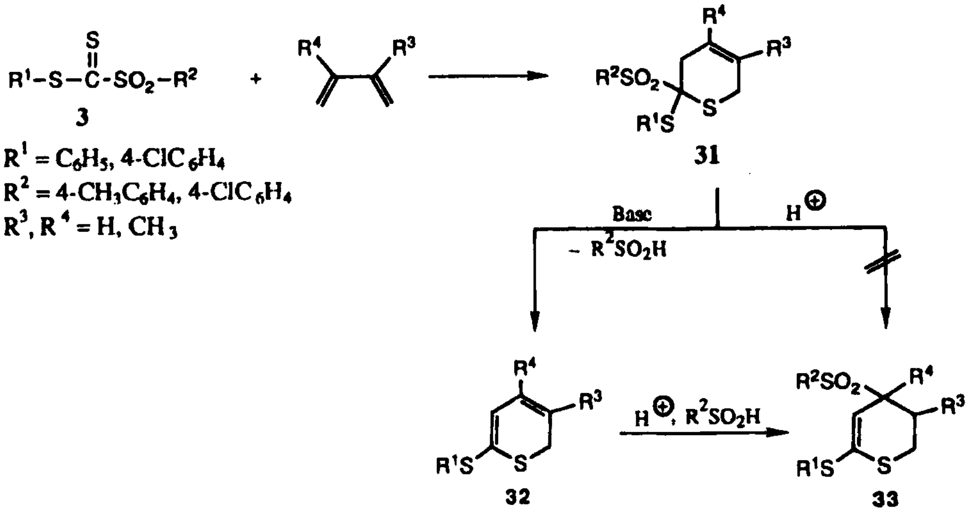
It has been reported that *endo*-**29** quantitatively rearranges to *exo*-**29** according to (13).[8,16] It thus appears that *endo*-**29** is the kinetically favored product while *exo*-**29** is the thermodynamically stable isomer. The mechanism of the isomerization hinges upon the ion pair **30** and not upon a retro-Diels-Alder reaction. The cation of **30** should be considerably resonance stabilized.



30

(13)

4.5.2.2. *Reactions with 1,3-butadiene.* The monocyclic Diels-Alder adducts **31** from **3** and 1,3-butadiene or 2,3-dimethyl-1,3-butadiene readily lose sulfinic acid to yield the 2*H*-thiopyrans **32**,[8,22,23] while treatment of **32** with catalytic amounts of acid results in rearrangement to the isomeric Δ^2-dihydrothiopyrans **33** according to Scheme 6.[8,16]

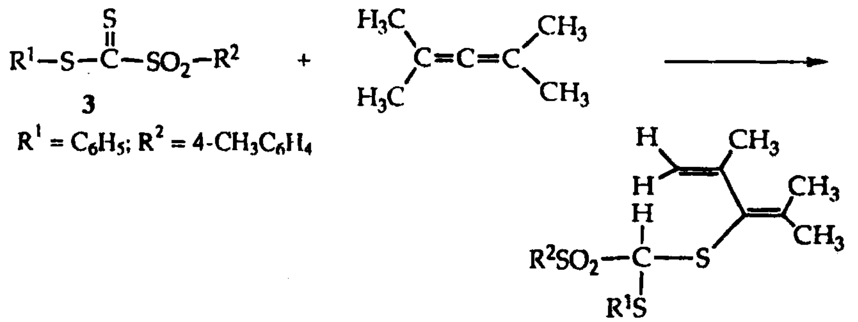


$R^1 = C_6H_5$, 4-ClC_6H_4
R^2 = 4-$CH_3C_6H_4$, 4-ClC_6H_4
$R^3, R^4 = H, CH_3$

SCHEME 6

4.6. *Reactions with Alkenes*

The enophilic properties of **3** could be demonstrated by reaction with the electron-rich olefin tetramethylallene to afford **34** in quantitative yield according to (14).[8,16,21] In the structure proof of **34**, the isomeric thiol structure had to be ruled out.



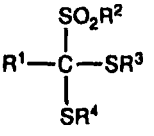
34

(14)

The trithioorthoformate *S,S*-dioxides **35**[8,16] and the thiiranes **36**[9] can be formed with **29**, **31** and **34** either by Diels-Alder reaction with suitable 1,3-dienes or by ene reaction with tetramethylallene.

4.7. *Addition Reactions*

C-Sulfonyldithioformates **82** react with excess chlorine at room temperature according to (15)[7,15] to form the corresponding α-chloromethanesulfenyl chlorides **37**.



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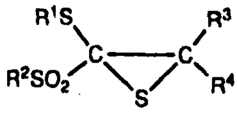

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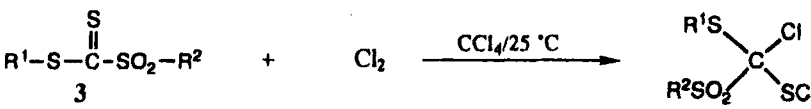
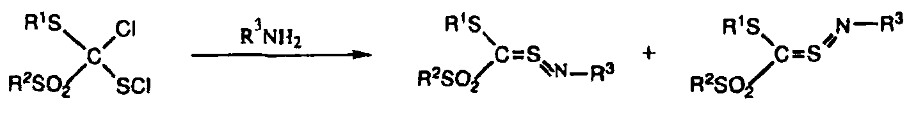


37

(15)

The latter react with excess *t*-alkylamines according to (16) to form *C*-sulfonyldithioformate thiocarbonyl *S*-[*N*-(*t*-alkyl)imides] **38**.[7,15]



37 Z-38 E-38 (16)

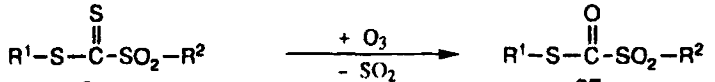
4.8. *Reaction with Tetrasulfur Tetranitride*

C-Sulfonyldithioformates **3** react with tetrasulfur tetranitride **39** to form the corresponding bis-methyleneamino sulfides **40**, a subtype of **3** according to (17).[25]

3 39 40 (17)

4.9. *Oxidation Reactions*

C-Sulfonyldithioformates readily react with ozone to afford the corresponding *S,S'*-dithiocarbonate *S,S*-dioxides **27** according to (18).[1,16]



$$\underset{\mathbf{3}}{R^1\text{-}S\text{-}\overset{\overset{S}{\|}}{C}\text{-}SO_2\text{-}R^2} \xrightarrow[-\ SO_2]{+\ O_3} \underset{\mathbf{27}}{R^1\text{-}S\text{-}\overset{\overset{O}{\|}}{C}\text{-}SO_2\text{-}R^2} \qquad (18)$$

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