Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

The Chemistry of Chlorodithioformates

Ibrahim El-sayed[abc]; Mohamed F. Abdel-megeed[bd]; Salah M. Yassin[ac]; Alexander Senning[ae]
[a] Kemisk Institut, Aarhus Universitet, Århus C, Denmark [b] Chemistry Department, Faculty of Science, Menoufia University, Shebin, Egypt [c] Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt [d] Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt [e] Department of Chemistry and Chemical Engineering, The Engineering Academy of Denmark, Lyngby, Denmark

To cite this Article El-sayed, Ibrahim , Abdel-megeed, Mohamed F. , Yassin, Salah M. and Senning, Alexander(1995) 'The Chemistry of Chlorodithioformates', Journal of Sulfur Chemistry, 16: 2, 235 — 291
To link to this Article: DOI: 10.1080/01961779508048740
URL: http://dx.doi.org/10.1080/01961779508048740

Sulfur Reports, Volume 16, pp. 235–297
Reprints available directly from the publisher
Photocopying permitted by license only

THE CHEMISTRY OF CHLORODITHIOFORMATES

IBRAHIM EL-SAYED,[a,b,1] MOHAMED F. ABDEL-MEGEED,[b,2] SALAH M. YASSIN,[b,1] and ALEXANDER SENNING[a,3]*

[a]*Kemisk Institut, Aarhus Universitet, DK-8000 Århus C, Denmark*

[b]*Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt*

(Received June 30, 1994)

This review is the first exhaustive account of the preparation and synthetic application of chlorodithioformates, based on a CAS Online search. 106 compounds are presented and 187 literature references included.

Key words: Carbon disulfide, chlorodithioformates, thiols, thiophosgene, trithiocarbonates.

CONTENTS

1. INTRODUCTION

The existing secondary literature on chlorodithioformates **1** is fragmented and sketchy and therefore the present authors wish to present a comprehensive and coherent picture of this chemistry drawing on a personal file compiled in support of ongoing research in their laboratories.

The parent compound chlorodithioformic acid has been assigned a CAS registry number, i.e. [16890-84-9], but without being actually mentioned in the corresponding abstracted paper.[4]

The standard preparation of **1** from thiophosgene and a thiol is limited by the availability of the corresponding thiols. In cases where the corresponding thiol is unstable more elaborate methods may become necessary such as the insertion of carbon monosulfide into sulfur-chlorine bonds.

The reactions of **1** fall roughly into two categories, the substitution of the chlorine atom (via an addition-elimination mechanism), and additions (including cycloadditions) to the thiocarbonyl group.

2. THE SYNTHESIS OF CHLORODITHIOFORMATES

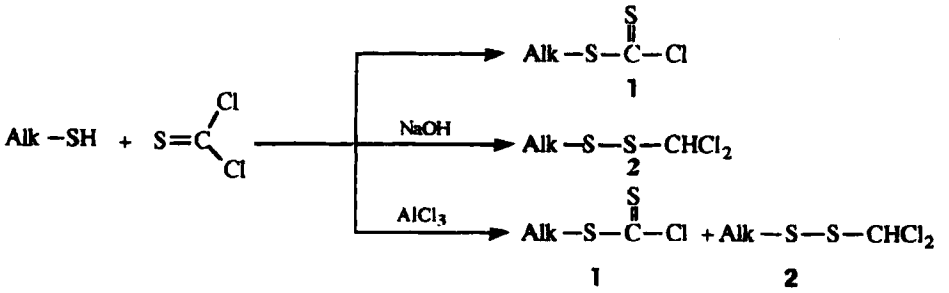
The synthesis of chlorodithioformates has been carried out chiefly from alkane- or arenethiols and thiophosgene along with other methods described below.

2.1. *From Alkanethiols and Thiophosgene*

The preparation of chlorodithioformates **1** from aliphatic thiols and thiophosgene is a well-established method. The reaction of various alkanethiols with thiophosgene under different reaction conditions has been studied extensively.[5–25] The reaction under acidic conditions with[6,7] or without[5,7–14] added Lewis acid catalyst afforded the chlorodithioformates **1** according to Scheme 1, in no case have products corresponding to thiophilic attack at the thiono sulfur been reported.

TABLE 1 The preparation of aliphatic chlorodithioformates **1**

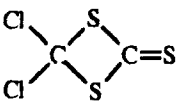
1	R	Bp. (°C/torr)	Yield (%)	Ref.
a	CH_3	156–159/760	66	5, 6–14, 19, 25
b	C_2H_5	56–62/10	80	6–12, 16, 25
c	$CH_3(CH_2)_2$	74–75/12–13	75	5, 6, 16
d	$(CH_3)_2CH$	40/14	47	5, 7, 12, 14, 16
e	$CH_3(CH_2)_3$	96–98/10	81	5, 7, 13, 16
f	$CH_3(CH_2)_5$	85–88/0.6	31	25
g	$C_6H_5CH_2$	104–106/0.4	60	5, 13
h	$CH_3(CH_2)_{11}$	176–178/1.5	—	18
i	$C_2H_5OCOCH_2$	—	—	19
j	$CH_3OCO(CH_2)_2$	—	79	20
k	$(CH_3)_2N(CH_2)_2$	—		21
p	CCl_3	98–100/14	75	52



SCHEME 1

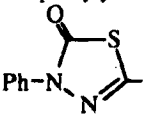
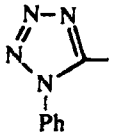
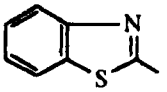
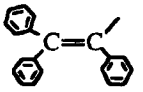
Thus, reaction of ethanethiol and 2-propanethiol with thiophosgene in the presence of aqueous sodium hydroxide affords the corresponding dichloromethyl alkyl disulfides **2**.[6,24] On the other hand reaction of 2-propanethiol with thiophosgene in the presence of aluminum chloride gives a mixture of dichloromethyl isopropyl disulfide **2** and isopropyl chlorodithioformate **1d** according to Scheme 1.[6]

The preparation of sterically hindered *t*-alkyl chlorodithioformates failed when the method suggested by Arndt *et al.* was followed.[7] In an attempt to prepare *t*-butyl and 1-adamantyl chlorodithioformate eqivalent amounts of 2-methyl-2-propanethiol and 1-adamantanethiol, respectively, were allowed to react with thiophosgene in the presence of a catalytic amount of aluminum chloride or of aqueous sodium hydroxide. Instead of the expected chlorodithioformates an 80% yield of dichloromethyl *t*-butyl disulfide and dichloromethyl 1-adamantyl disulfide, respectively, was obtained together with small amounts of 4,4-dichloro-2-thioxo-1,3-dithietane **3**.[6,22,24]



3

TABLE 2 The preparation of aryl chlorodithioformates **4**

4	R	B.p. (°C/torr) M.p. (°C)	Yield (%)	References
a	C_6H_5	135/15	80	5, 12, 15, 26, 27, 41
b	$4\text{-}CH_3C_6H_4$	102–104/11	62	5, 12
c	$2\text{-}CH_3C_6H_4$	93/0.5	74	5, 12
d	$4\text{-}ClC_6H_4$	100–102/0.3	85	40
e	$3\text{-}ClC_6H_4$	90–93/(0.2	78	40
f	$2\text{-}ClC_6H_4$	91–92/0.3	76	40
g	$4\text{-}O_2NC_6H_4$	47	47	13, 40
h	$3\text{-}O_2NC_6H_4$	—	—	40
i	C_6F_5	108–110/20	65	29–31
j	C_6Cl_5	120–122	91	30, 32
k	$2,4,5\text{-}Cl_3C_6H_2$	32–35	65	30
l	1-naphthyl	89–91	67	33, 34
m	2-naphthyl	86.5–87.5	61	30, 35
n	2-thienyl	93/1	75	35
o	mesityl	88–89	63	35
p	2-biphenylyl	164–165/0.3	79	38
q		42–43	—	36
r		—	28	39
s		63–64	67	190
t		134–135	71	190

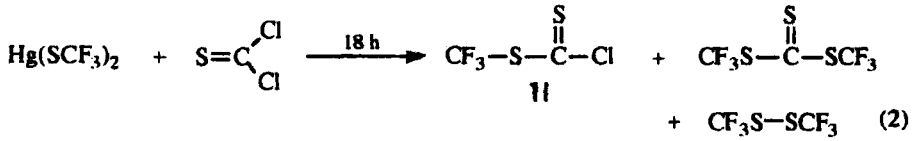
2.2. *From Arenethiols and Thiophosgene*

The treatment of arenethiols with thiophosgene in the presence of base gives the corresponding aryl chlorodithioformates **4** according to (1)[5,8,12,13,15,17,26,26,28–36]

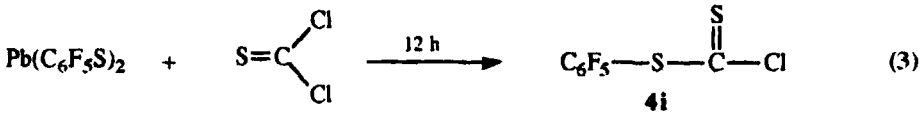
(1)

2.3. *By Reaction Between Thiophosgene and Thiolate Anions*

Haas *et al.* have reported that the reaction between thiophosgene and mercury(II) trifluoromethanethiolate affords trifluoromethyl chlorodithioformate according to (2).[41]

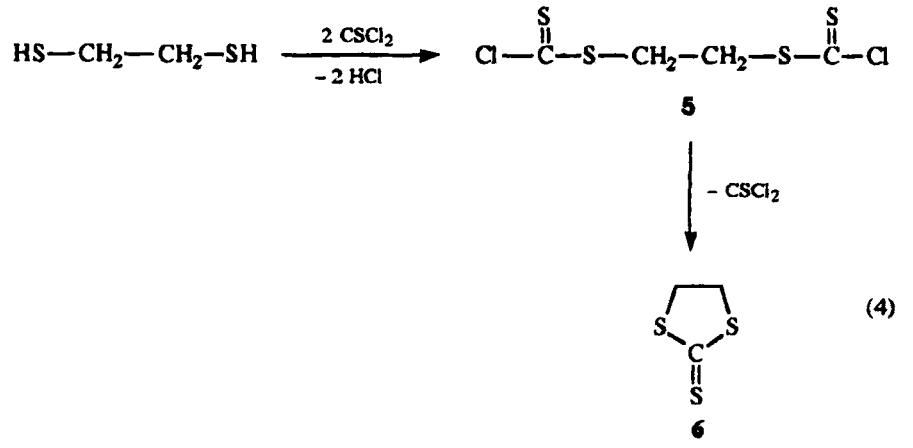


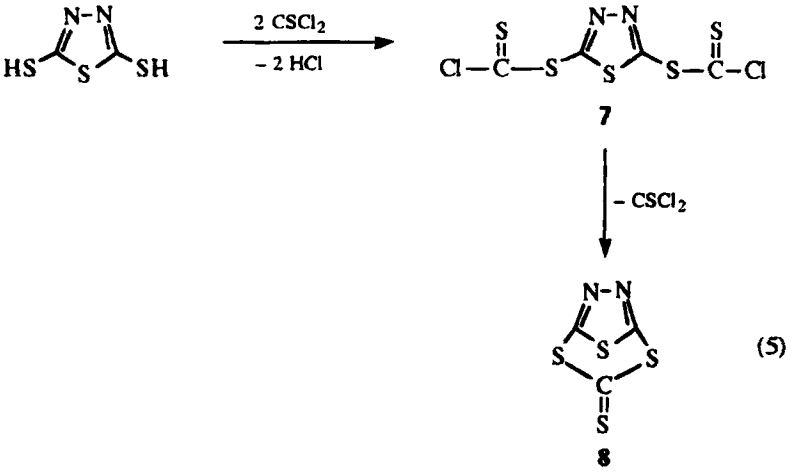
Similarly, the reaction between thiophosgene and the lead(II) salt of pentafluorothiophenol affords pentafluorophenyl chlorodithioformate **4i** according to (3).[28]



2.4. *Synthesis of Bis(chlorodithioformates) by Reaction of Dithiols with Thiophosgene*

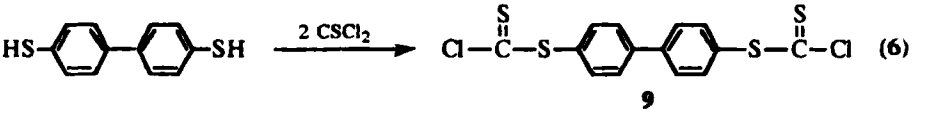
The possible synthesis of bis(chlorodithioformates) by reaction between dithiols and thiophosgene under a variety of conditions has been investigated. Reaction between 1,2-ethanedithiol and thiophosgene yielded the corresponding labile bis(chlorodithioformates) **5** which formed 1,3-dithiolane-2-thione **6**[63] by spontaneous decomposition. The primary product formed from 2,5-dimercaptothiadiazole and thiophosgene was **7** which in turn gave **8** by loss of thiophosgene according to (4) and (5), respectively.[43]





(5)

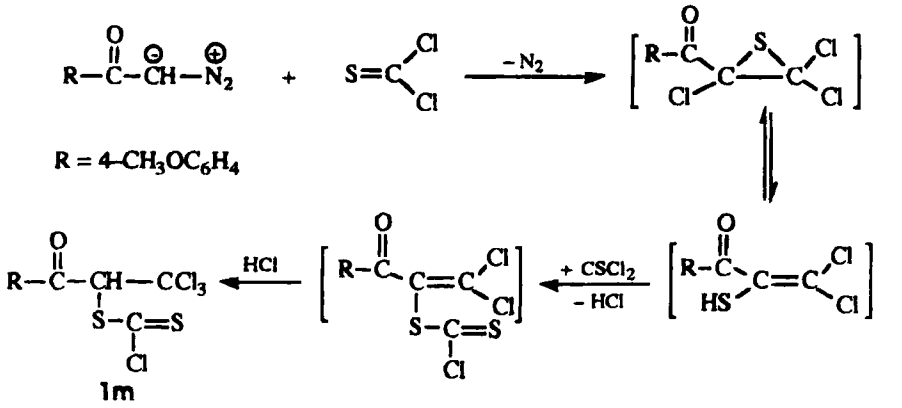
4,4′-Biphenyldithiol reacts with thiophosgene in the presence of base to afford 4,4′-bis[chlorothiocarbonylthio]biphenyl **9** in 95% yield according to (6).[43]



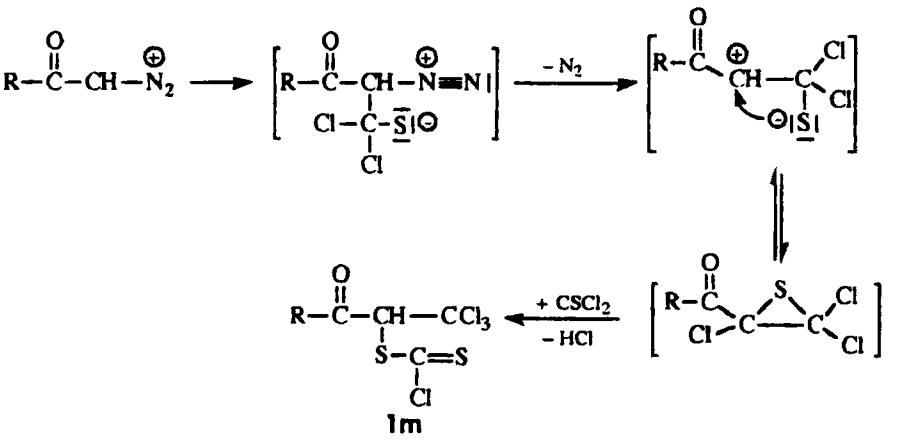
(6)

2.5. *By Reaction of Thiophosgene with Diazo Compounds*

From the reaction of thiophosgene with 4-methoxy-α-diazoacetophenone in benzene Ried and Beck obtained 1,1,1-trichloro-2-chlorothiocarbonylthio-2-(4-methoxybenzoyl)ethane **1m** according to Scheme 2.[44,45]



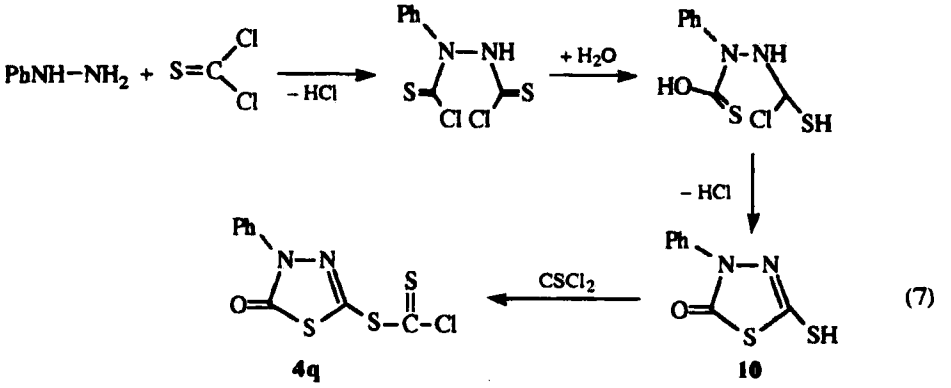
Mechanism:



SCHEME 2

2.6. *By Reaction of Thiophosgene with Hydrazine Derivatives*

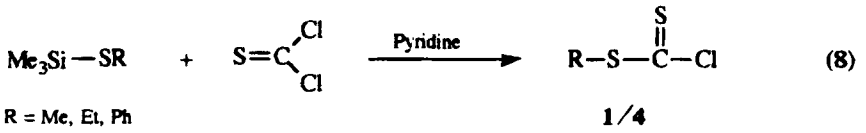
In the reaction of thiophosgene with phenylhydrazine several products are formed among which **4q** has been isolated and characterized.[36] A mechanism involving 5-mercapto-1,3,4-thiadiazol-2(3*H*)-one **10** as intermediate has been proposed according to (7). The initial steps probably involve attack of thiophosgene on both nitrogen atoms of phenylhydrazine. The bis(thioacid chloride) formed undergoes rapid hydrolysis in aqueous medium and the resulting intermediate can eliminate hydrogen chloride to give the 5-mercapto-1,3,4-thiadiazolinone **10**. Further attack by thiophosgene gives the corresponding chlorodithioformate **4q**.



(7)

2.7. *By Exchange Reaction Between Thiophosgene and Organothiosilanes*

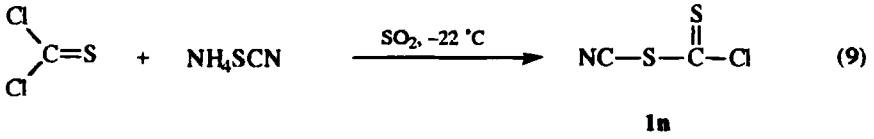
The synthesis of organosulfur compounds from silicon containing reagents has been reported.[41] Thiophosgene undergoes exchange reactions with organothiosilanes in the presence of a catalytic base. Alkyl and aryl chlorodithioformates have been obtained in good yields according to (8).



(8)

2.8. *By Reaction Between Thiophosgene and Ammonium Thiocyanate*

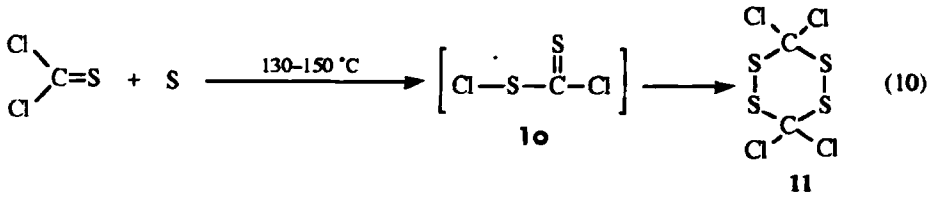
Treatment of thiophosgene in SO_2(l) with ammonium thiocyanate gave the corresponding thiocarbonyl chloride thiocyanate **1n** according to (9).[46]



(9)

2.9. *By Reaction Between Thiophosgene and Sulfur*

Heating of a mixture of thiophosgene and sulfur in a sealed tube at 130–150 °C causes addition of sulfur to thiophosgene and gives chlorothiocarbonyl sulfenyl chloride **1o** which dimerizes to afford the 1,2,4,5-tetrathiane **1l** according to (10).[8,45,47,48]



(10)

2.10. *By Insertion of Carbon Monosulfide into Sulfur-Chlorine Bonds*

2.10.1. *Sulfenyl Chlorides.* Carbon monosulfide reacts readily with alkanesulfenyl chlorides to afford the corresponding chlorodithioformates **1** according to (18).[49–59]

(11)

1

1	Alk
p	CCl_3
q	CH_3CO
r	PhCO
s	Cl_3CSCl_2
t	morpholino

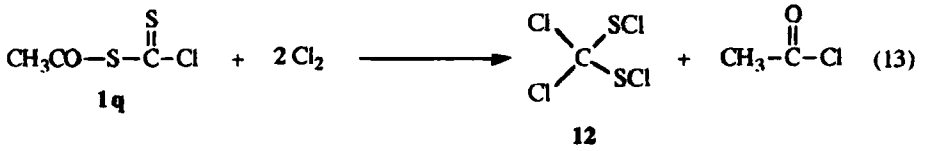
Arenesulfenyl chlorides likewise react with carbon monosulfide to afford the corresponding aryl chlorodithioformates **4** according to (12).

(12)

4

4	Ar
a	C_6H_5
b	4-$CH_3C_6H_4$
c	4-ClC_6H_4

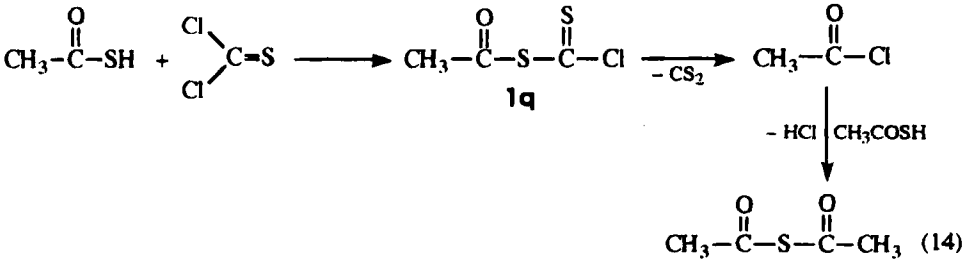
The morpholino derivative could only be obtained in low yield and was only stable for a few days.[49,50] The chlorodithioformate **1** with R = CH_3CO and PhCO would be most desirable precursors, e.g. for an alternative synthesis of the versatile synthon dichloromethanedisulfenyl dichloride **12** according to (13).[53]



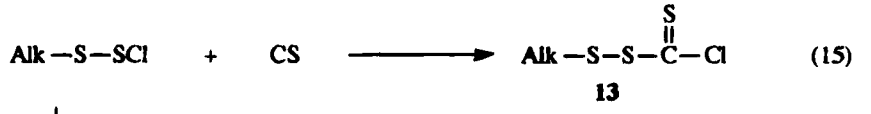
(13)

1q **12**

The most direct route to **1** (R = CH_3CO) is treatment of thiophosgene with thioacetic acid to give the corresponding chlorodithioformate which decomposes to carbon disulfide and the corresponding acyl chloride according to (14).



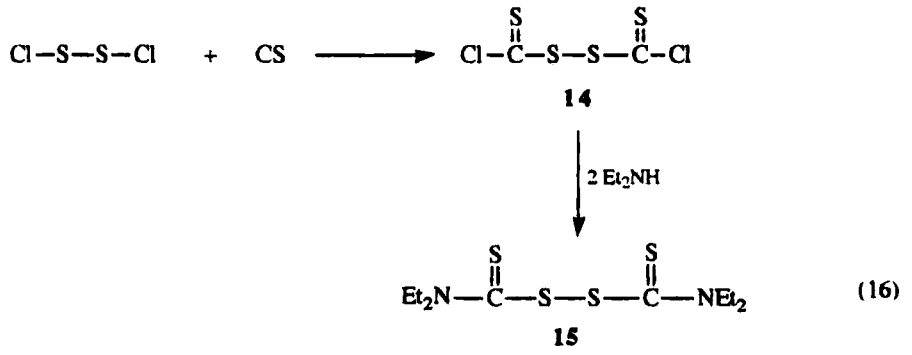
2.10.2. *Thiosulfenyl Chlorides.* The corresponding insertion of carbon monosulfide into thiosulfenyl chlorides constitutes a general route to compounds **13** containing the previously inaccessible functional group ClC(=S)SS; four examples are known all of which were prepared according to (15) in good yield; the versatility of this new class of compounds as synthetic intermediates has been demonstrated.[59,60]



16	Alk
a	CH_3CO
b	ClCO
c	CCl_3
d	C_2Cl_5

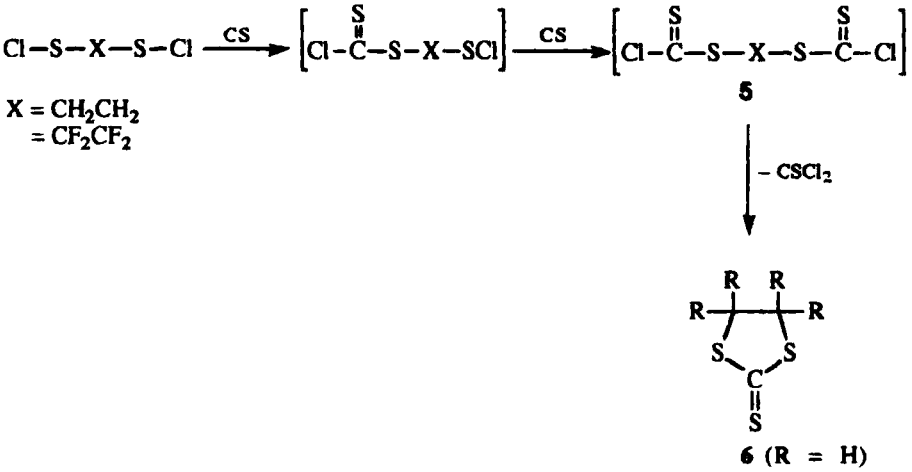
2.11. *Synthesis of Bis(chlorodithioformates) by Insertion of Carbon Monosulfide into Sulfur-Chlorine Bonds*

Treatment of disulfur dichloride with carbon monosulfide in cold toluene solution gave the corresponding unstable diinsertion product dithiobis(thiocarbonyl chloride) **14**[51] which was trapped with diethylamine in carbon tetrachloride solution to give the known *N,N,N′,N′*-tetraethylthiuram disulfide **15** according to (16).



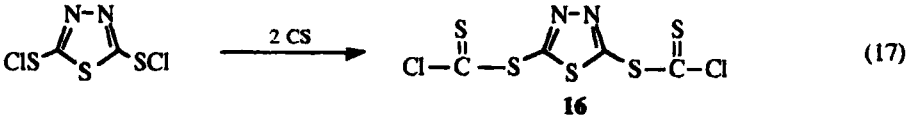
(16)

In general bis(sulfenyl chlorides) diinsert carbon monosulfide to form labile bis(chlorodithioformates) **5** according to Scheme 3.[57,58] In the case of **5** ($X = CF_2CF_2$) no formation of 4,4,5,5-tetrafluoro-1,3-dithiolane-2-thione **6** was observed which might be due to inherent instability caused by its near eclipsed C-F bonds.[57] The diinsertion product **5** was characterized by alternating chlorination and carbon monosulfide treatment.



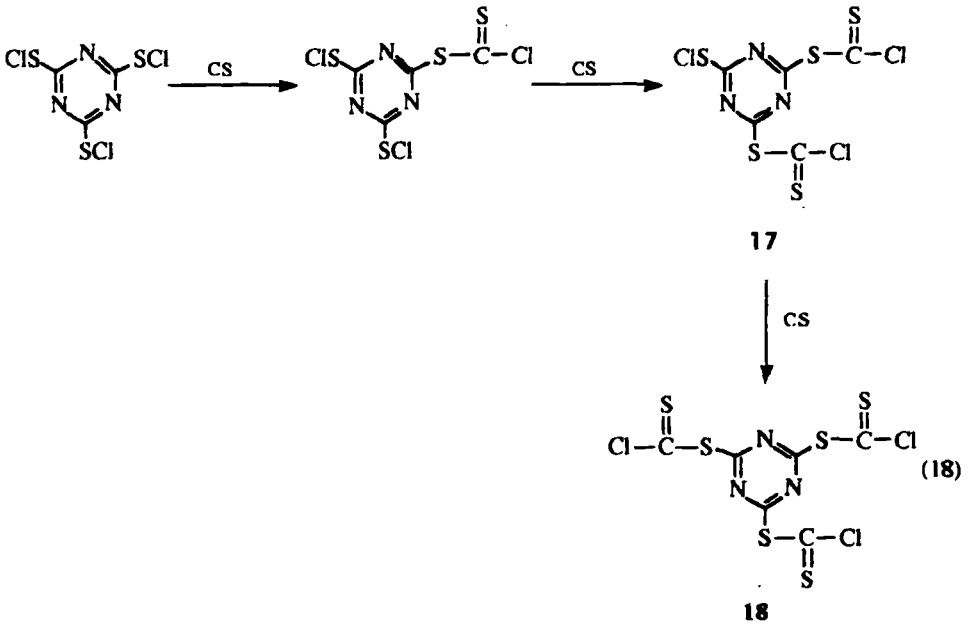
SCHEME 3

1,3,4-Thiadiazole-2,5-disulfenyl dichloride[61] reacts with excess carbon monosulfide to give the diinsertion product **16** according to (17).[58,59] Compound **16** is a crystalline solid which could be fully characterized.



(17)

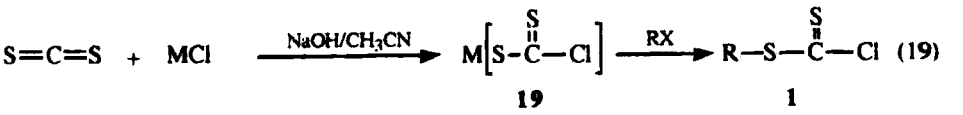
On the other hand treatment of 1,3,5-triazine-2,4,6-trisulfenyl trichloride[62] with excess carbon monosulfide led to a product mixture with properties compatible with the presence of at least two of the three possible insertion products according to (18).[58,59]



(18)

2.12. *By Reaction of Carbon Disulfide with Alkali Metal Chlorides*

Alkali metal chlorides have been claimed to react with carbon disulfide in acetonitrile in the presence of solid sodium hydroxide as a catalyst to form the corresponding unstable yellow alkali metal chlorodithioformates **19**. Alkylation of **19** with haloalkanes has been claimed to give the corresponding alkyl chlorodithioformates **1** according to (19).[64] The experimental details of this work are self-contradictory and, moreover, the claimed nucleophilicity of chloride ions in the solid state and the claimed isolability of **19** are contrary to contemporary chemical thought.

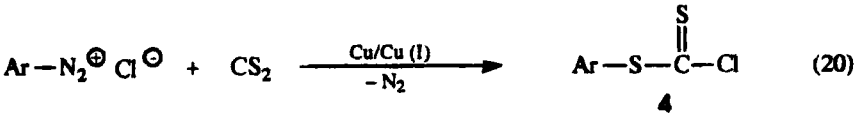


(R = Et , X = I)

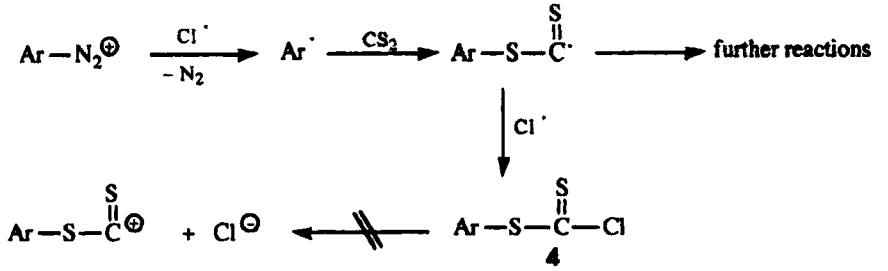
10	M
a	Na
b	K
c	Rb
d	Cs

2.13. *By Reaction of Carbon Disulfide with Aryldiazonium Chlorides*

Aryldiazonium chlorides react with carbon disulfide in the presence of Cu/Cu(I) to give aryl chlorodithioformates **4** according to (20).[40,65,66] The reaction proceeds by a radical mechanism according to Scheme 4.



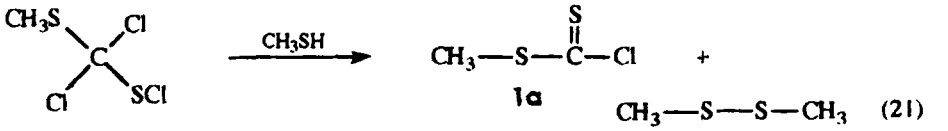
Mechanism:



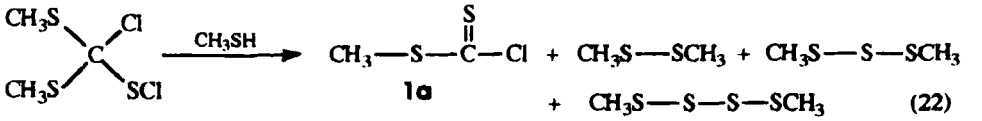
SCHEME 4

2.14. *By Reaction of Sulfenyl Chlorides with Thiols*

(Methylthio)dichloromethanesulfenyl chloride reacts with methanethiol to afford methyl chlorodithioformate **1a** according to (15).[66–68]

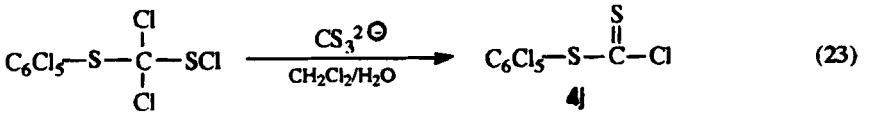


Similarly, bis(methylthio)chloromethanesulfenyl chloride reacts with methanethiol to afford methyl chlorodithioformate **1a** according to (22).[67-69]



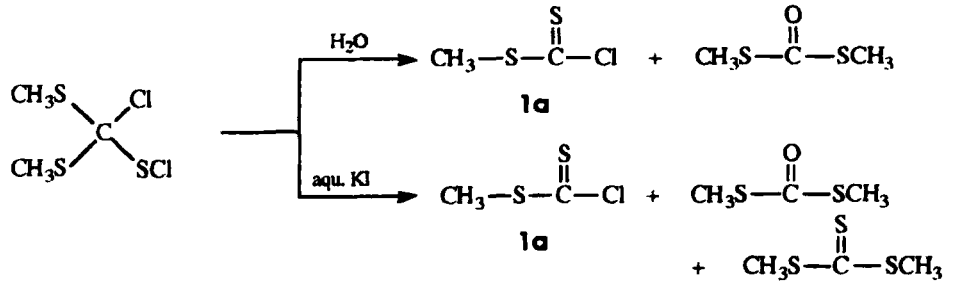
2.15. *By Reaction of Sulfenyl Chlorides with Trithiocarbonate Ions*

The reaction of the sulfenyl chloride shown below with sodium trithiocarbonate gave the chlorodithioformate **4j**. Dechlorination of the sulfenyl chloride by the trithiocarbonate dianion CS_3^{2-} explains the formation of **4j** according to (23).[31]



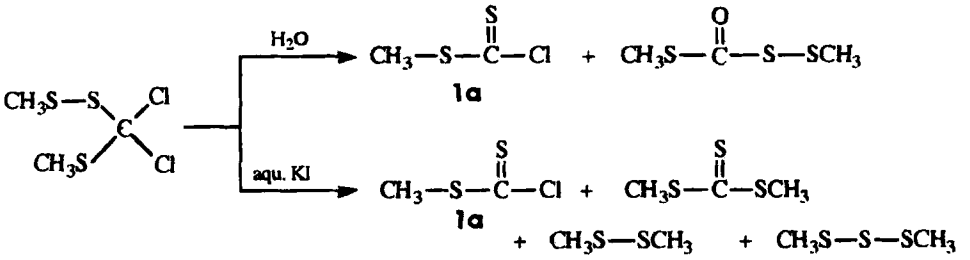
2.16. *By Reaction of α-Chloro α-Thio Alkanesulfenyl Chlorides with Aqueous Iodide Ions*

The reaction of bis(methylthio)chloromethanesulfenyl chloride with water and aqueous potassium iodide affords methyl chlorodithioformate **1a** according to Scheme 5.[67]



SCHEME 5

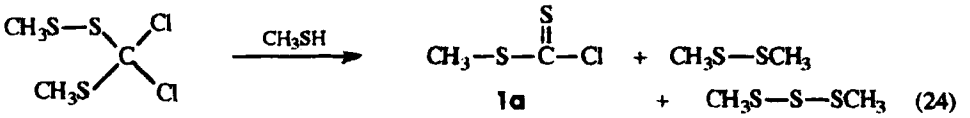
On the other hand (methylthio)dichloromethyl methyl disulfane reacts with water and aqueous potassium iodide to afford methyl chlorodithioformate **1a** according to Scheme 6.[67]



SCHEME 6

2.17. *By Reaction of α-Chloro α-Thio Disulfanes with Thiols*

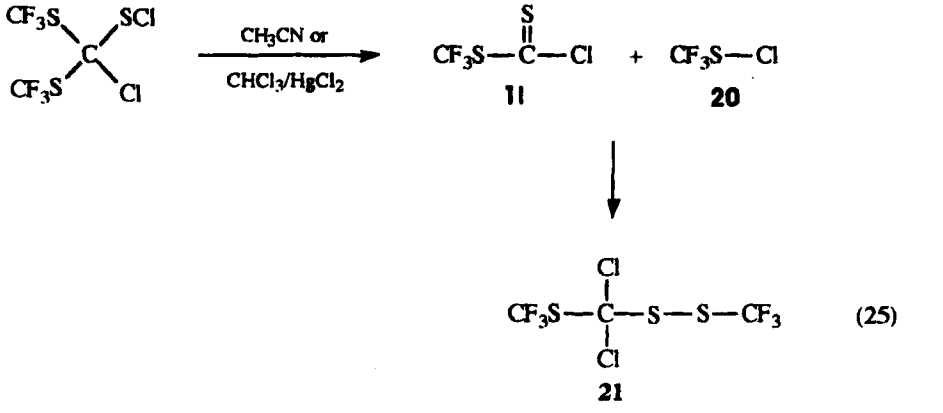
(Methylthio)dichloromethyl methyl disulfane reacts with methanethiol to afford the corresponding methyl chlorodithioformate **1a** according to (24).[67]



(24)

2.18. *By Decomposition of α-Organylthio Alkanesulfenyl Chlorides*

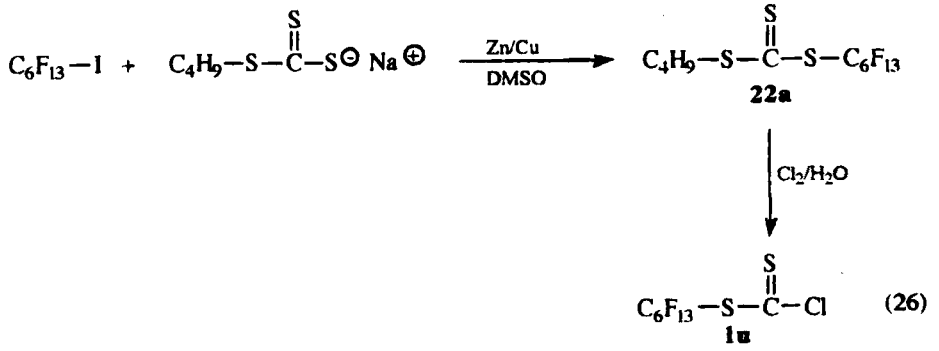
Decomposition of the sulfenyl chloride shown below takes place upon standing at room temperature for some days or with chloroform and $HgCl_2$ as a catalyst with formation of trifluoromethyl chlorodithioformate **11**.[31] Addition of the sulfenyl chloride **20** to **11** in acetonitrile gives the corresponding (trifluoromethylthio)dichloromethyl trifluoromethyl disulfane **21** according to (25).



(25)

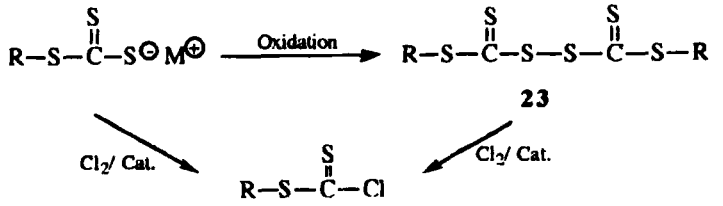
2.19. *By Chlorination of Perfluoroalkyl Trithiocarbonates*

The chlorination of *n*-butyl perfluorohexyl trithiocarbonate (prepared from perfluorohexyl iodide and sodium *n*-butyl trithiocarbonate in DMSO in the presence of a dispersion of the Zn/Cu couple) afforded perfluorohexyl chlorodithioformate **1u** according to (26).[70,71]



2.20. *By Chlorination of Thioxanthates*

Alkyl, cycloalkyl, aralkyl and aryl chlorodithioformates have been prepared[25] from the corresponding thioxanthates[65] by direct chlorination or by oxidation to bis(alkylthiothiocarbonyl) disulfides **23**, followed by chlorination *in situ* according to Scheme (7). Thus, chlorine was passed through a suspension of potassium ethyl trithiocarbonate in carbon tetrachloride containing iodine to give 80% ethyl chlorodithioformate **1b**; similarly prepared were **1** (R = Bu, hexyl) according to Scheme 7.

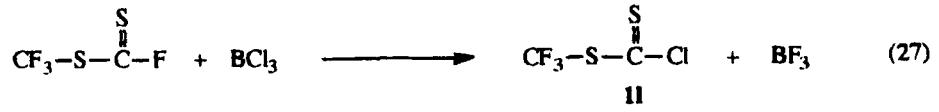


R = Et, Bu, or hexyl
M = Metal, NH_4^+, or NR_4^+
Cat. = Catalyst

SCHEME 7

2.21. *By Exchange Reaction Between Fluorodithioformates and Boron Trichloride*

Haas *et al.* have reported the preparation of trifluoromethyl chlorodithioformate **1l** by exchange reaction between trifluoromethyl flurorodithioformate and boron trichloride according to (27).[72]

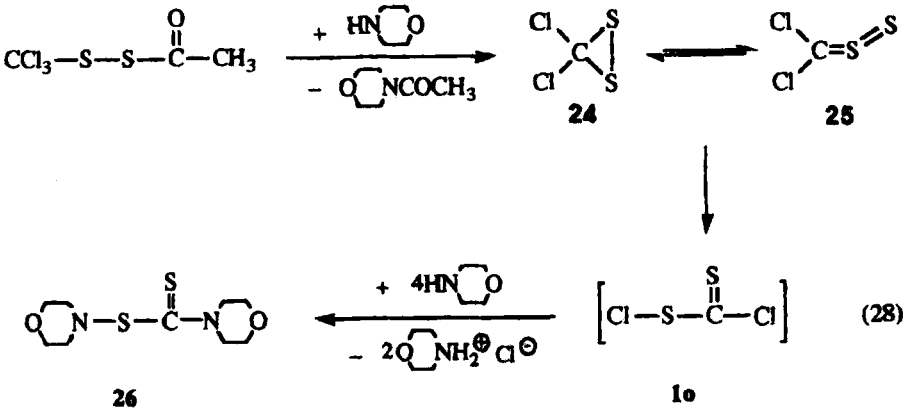


(27)

11

2.22. *By Rearrangement of Dithiiranes*

The deacylation of the thioester shown below can be accomplished with primary and secondary, but not with tertiary amines. Treatment of the thioester with morpholine led, via the corresponding dithiirane/thiosulfine, to the formation of chlorothiocarbonyl sulfenyl chloride **1o** which was trapped with excess morpholine to afford the known sulfenamide **26** in 22% yield according to (28). Literature data[47,48,73–75] suggest that both the dithiirane **24** and the thiosulfine **25** can be utilized as reactive intermediates for preparative purposes.



(28)

24 **25** **26** **1o**

3. SPECTROSCOPIC PROPERTIES OF CHLORODITHIOFORMATES

3.1. *Ultraviolet and Visible Spectra*

The traditional spectroscopic method for the characterization of the thiocarbonyl group in chlorodithioformates is UV/VIS spectroscopy. The reason for this was the relatively early availability of the method along with the fact that chlorodithioformates are colored compounds. The range of the colors goes from yellow to orange. There is general agreement that the color is due to excitation of the n-π^* transition[76,77] and this assignment is supported by computations,[77–80] the solvent effect[81] and by the intensity of this symmetry-forbidden transition. A simple additive increment system for the description of the position of the

TABLE 3 Ultraviolet-visible spectra for some alkyl and aryl chlorodithioformates

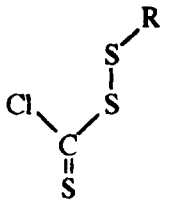
No.	Solvent	n-π* [nm]	log ε	π-π* [nm]	log ε	Ref.
1a	Cyclohexane	337	1.40	302	4.11	16
1b	$CHCl_3$	—	1.4	243	4.15	16
1c	$CHCl_3$	309	5.85	243	4.32	16
1d	$CHCl_3$	308	4.98	243	4.16	16
1e	$CHCl_3$	308	5.10	243	4.10	16
1m	Cyclohexane	468	1.03	—	—	16
4a	Cyclohexane	458	1.52	306	3.94	40
4b	Cyclohexane	454	1.52	307	4.23	40
4c	Cyclohexane	454	1.25	308	3.97	40
4d	Cyclohexane	451	1.42	307	3.97	40
4e	Cyclohexane	452	1.38	306	3.96	40
4f	Cyclohexane	450	1.31	303	4.06	40

long-wavelength band of thiocarbonyl compounds agrees very well with experimental data and quantum chemical calculations for a representative number of molecules.[4]

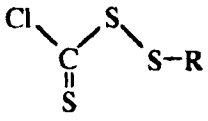
The n-π* transitions for aliphatic chlorodithioformates lie at relatively short wavelengths with intense absorption maxima outside the visible range. The thiocarbonyl group in aliphatic chlorodithioformates shows at least one band in the UV range at 243 nm (for R = C_2H_5) and at 243 and 309 nm (for R = C_3H_7, C_4H_9).[16] The high intensities indicate symmetry-allowed transitions. On the other hand aryl chlorodithioformates show two intense absorption maxima, one in the visible range at about 453 nm and the other in the UV at about 306 nm.

3.2. *IR Spectra*

IR spectra give useful qualitative information diagnostic of the thiocarbonyl group in the chlorodithioformates, The alkyl chlorodithioformates exhibit characteristic absorptions around 1120 and 1100 cm^{-1}.[16] The C=S stretching vibration of the thiocarbonyl group in aryl chlorodithioformates also gives rise to characteristic absorptions at about 1120 and 1100 cm^{-1}.[30,82] The IR spectra of chlorodithioformates show an interesting feature. Thiocarbonyl groups usually have a single absorption in the region 1000–1300 cm^{-1}, but the chlorotrithioperformates **13** display a splitting of this absorption.[60] This splitting is likely due to the existence of the rotamers **13A** and **13B**.



13A



13B

A similar behavior of certain thiocarbonyl compounds has previously been described in the literature.[82]

TABLE 4 The characteristic IR bands of representative examples of chlorodithioformates

No.	$\nu_{C=S}$ (cm^{-1})	Ref.	No.	$\nu_{C=S}$ (cm^{-1})	Ref.
1a	1104–1105	16	**4f**	1110	40
1b	1030, 1150–1250	16	**4j**	1110, 1120	30
1c	1030, 1150–1250	16	**4i**	1100, 1121	29, 30
1d	1030, 1150–1250	16	**4k**	1085, 1115	30
1j	1090	20	**4l**	1095, 1120	33, 34
1l	1138, 1185	42	**7**	1120	58, 59
1p	1123	50	**9**	1120	43
1u	1185	40	**13a**	1110, 1120	60
4a	1120	40	**13b**	1090, 1120	60
4b	1115	40	**13c**	1090, 1130	60
4c	1120	40	**13d**	1090, 1120	60
4d	1115	40	**14**	1120	61
4e	1115	40			

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 shielding influence of the chlorine atom.[81,83,84] Thus, the ^{13}C NMR signals of the thiocarbonyl carbons in alkyl and substituted alkyl chlorodithioformates lie between 189.40 (for **14**) and 203 (for **1t**) ppm.[16,50] The ^{13}C NMR signals of the thiocarbonyl carbons of chlorotrithioperformates lie between 190.44 (for **13b**) and 195.81 (for **13d**) ppm.[60] On the other hand the ^{13}C NMR signals of the thiocarbonyl carbons in aryl chlorodithioformates lie between 180.50 (for **18**) and 197.66 (for **4b**) ppm as shown in Table 5.[50]

TABLE 5 Chemical shift δ (ppm) of thiocarbonyl carbons in alkyl, substituted alkyl and aryl chlorodithioformates and in alkyl trithioperformates

No.	$\delta_{C=S}$ (ppm)	Ref.	No.	$\delta_{C=S}$ (ppm)	Ref.
1a	198.10	50	**4j**	189.50	30
1b	196.05	16	**4k**	192.10	30
1c	196.63	16	**4l**	195.60	33, 34
1d	196.54	16	**4q**	189.80	36
1e	196.00	16	**4s**	189.80	36
1l	180.10	42	**5**	196.68	58, 59
1n	178.70	46	**7**	188.70	58, 59
1p	183.05	50	**9**	196.65	43
1s	183.24	50	**13a**	193.62	60
1t	203.00	50	**13b**	190.44	60
4a	197.28	50	**13c**	193.94	60
4b	197.66	50	**13d**	195.81	60
4d	196.33	50	**14**	189.40	51
4g	194.65	29	**16**	188.70	58, 59
4i	190.10	30	**18**	180.50	58, 59

TABLE 6 Dipole moment in Debye (in benzene solution) for some representative examples of aryl chlorodithioformates

No.	Dipole moment in Debye (in benzene solution)
6a	2.68
6b	2.94
6c	2.79
6d	1.57
6f	3.45

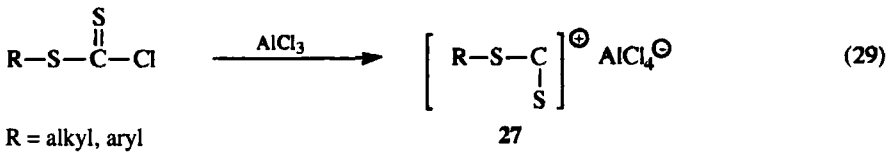
3.4. *Molecular Characteristics of the Thiocarbonyl Group of Chlorodithioformates*

The dipole moments of a few types of aryl chlorodithioformates have been reported as shown in Table 6.[40] The dipole moment of a thiocarbonyl compound is consistently lower than that of the corresponding carbonyl derivative confirming the lesser polarity of the thiocarbonyl group.[85]

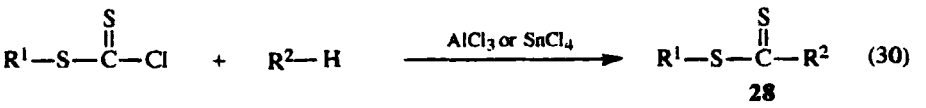
4. THE CHEMICAL PROPERTIES OF CHLORODITHIOFORMATES

4.1. *Reactions at Carbon Centers*

4.1.1. *Friedel-Crafts thioacylation with chlorodithioformates.* The Friedel-Crafts reaction is useful for the synthesis of a variety of dithioesters. The reaction occurs according to (29) in a normal way via the Friedel-Crafts complex **27** as an intermediate which attacks the aromatic system.[82,86–105]



In a number of Friedel-Crafts reactions chlorodithioformates have been used as starting materials for the synthesis of dithioesters. Thus, thioacylation of benzene and of activated arenes with alkyl or aryl chlorodithioformates under Friedel-Crafts conditions results in the formation of **28** according to (30).



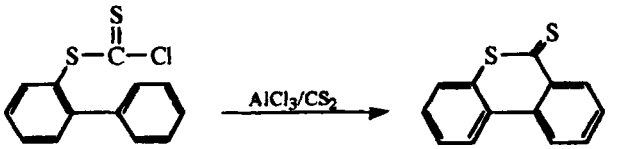
28 (30)

R^1 = alkyl, aryl

R^2 = aryl, 2-furyl, 2-thienyl

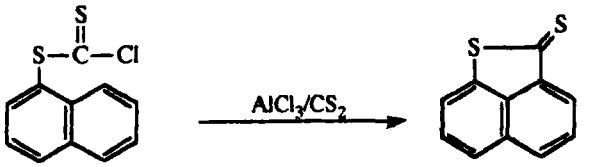
The following examples illustrate the scope of the reaction.

2-Biphenylyl chlorodithioformate reacts with aluminum chloride to afford 6-thioxo-*6H*-dibenzo[*b,d*]thiopyran **29a** in 85% yield according to (31).[37,38]



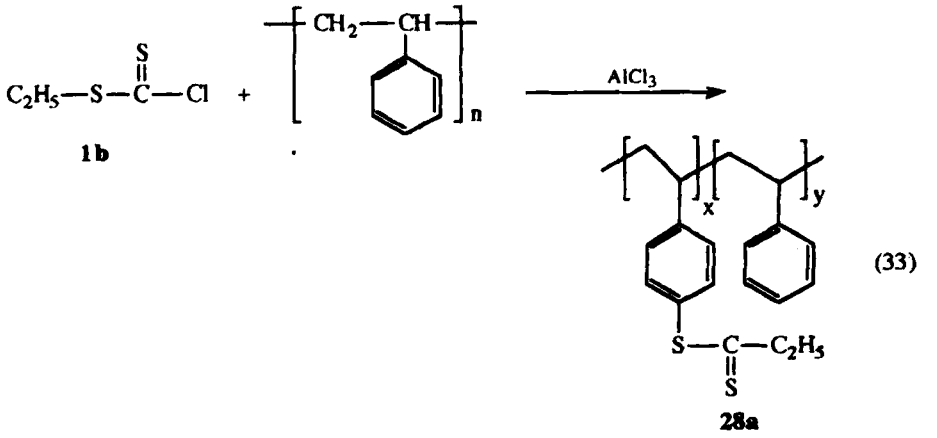
4p **29a** (31)

1-Naphthyl chlorodithioformate reacts with aluminum chloride to give naphtho[1,8-*b,c*]thiophene-2-thione **29b** according to (32).[33,34]



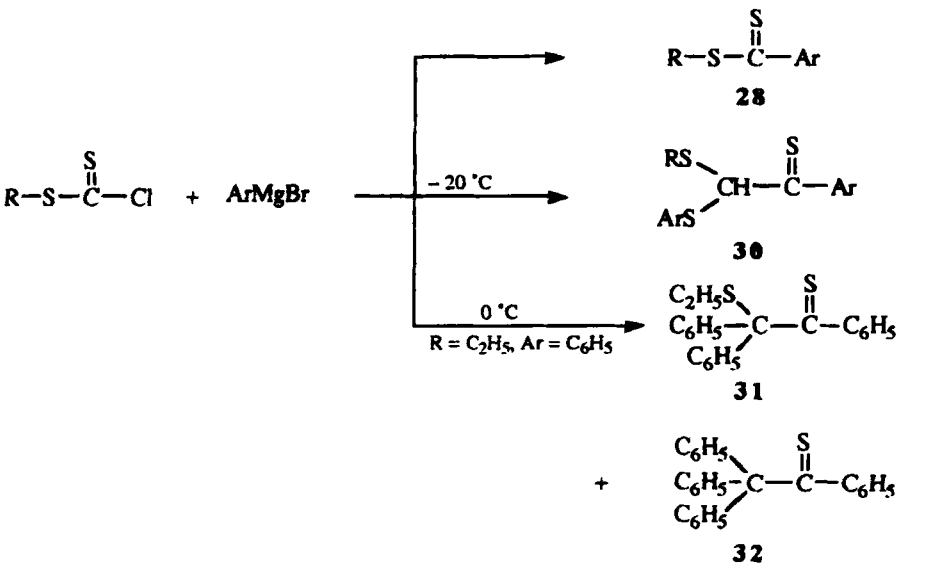
4e **29b** (32)

Dithioester groups have been introduced in linear or cross-linked polystyrenes by Friedel-Crafts reaction with ethyl chlorodithioformate to afford the dithiocarbonate **28a** according to (33).[90]



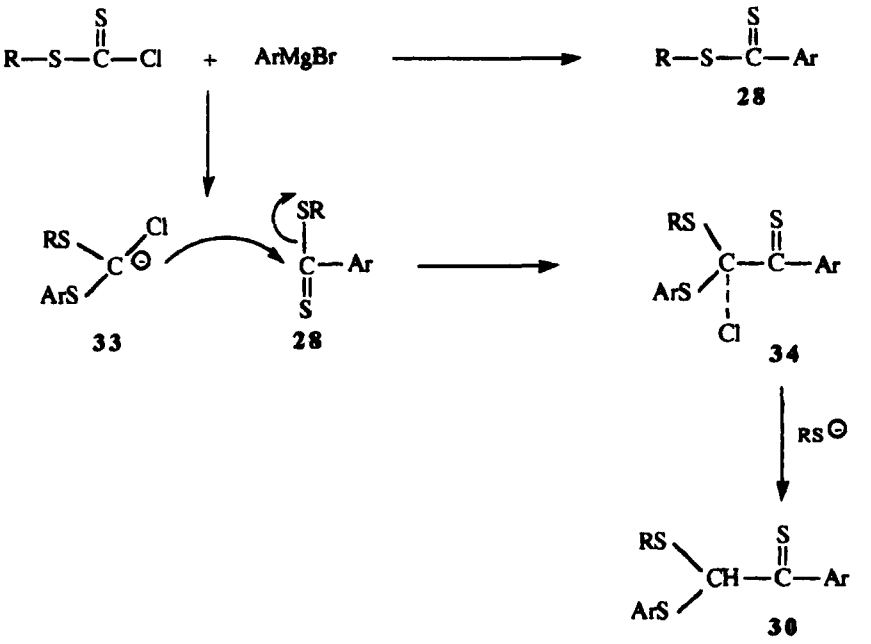
(33)

4.1.2. *Reactions of chlorodithioformates with Grignard reagents.* Alkyl and aryl chlorodithioformates have been treated with arylmagnesium bromides to give substituted thioketones according to Scheme 8.[95] The Grignard reagent attacks the carbon as well as the sulfur atom of the thiocarbonyl group to give the dithioester **28** and the anion **33**, respectively. Then the anion can be thioacylated by the dithioester to form the α-chloro thioketone **35** which can be reduced by the thiolate ions formed during the thioacylation to give the thioketone **30** according to Scheme 9.



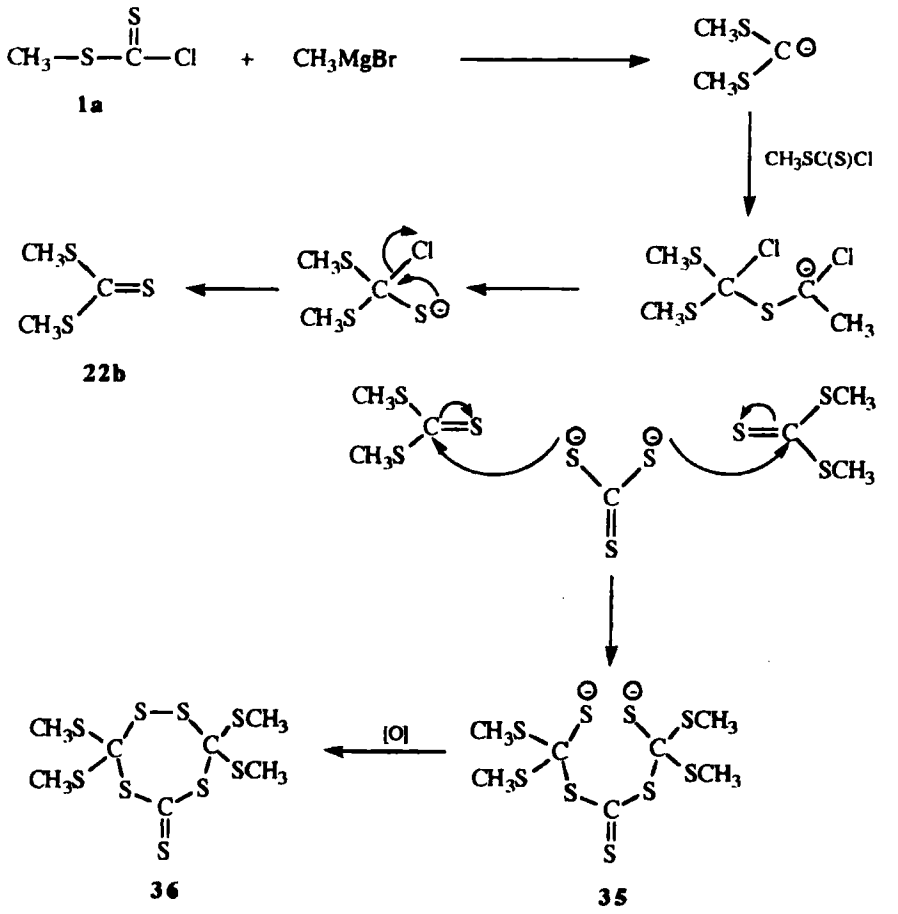
SCHEME 8

Mechanism:



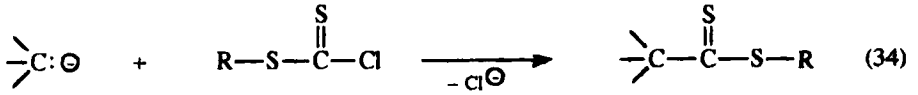
SCHEME 9

The reaction between methyl chlorodithioformate and methylmagnesium iodide at −40 °C gives dimethyl trithiocarbonate **22b** and 3,3,7,7-tetrakis(methylthio)-1,2,4,6-tetrathiepane-5-thione **36**.[95] When the reaction takes place at 0 °C other products are isolated in small yields as shown in Scheme 10. The formation of the tetrathiepane **36** can be explained by assuming the formation of trithiocarbonate dianion which attacks two molecules of dimethyl trithiocarbonate to form the dianion **35**. Subsequent oxidation of **35** affords the cyclic compound **36** according to Scheme 10.



SCHEME 10

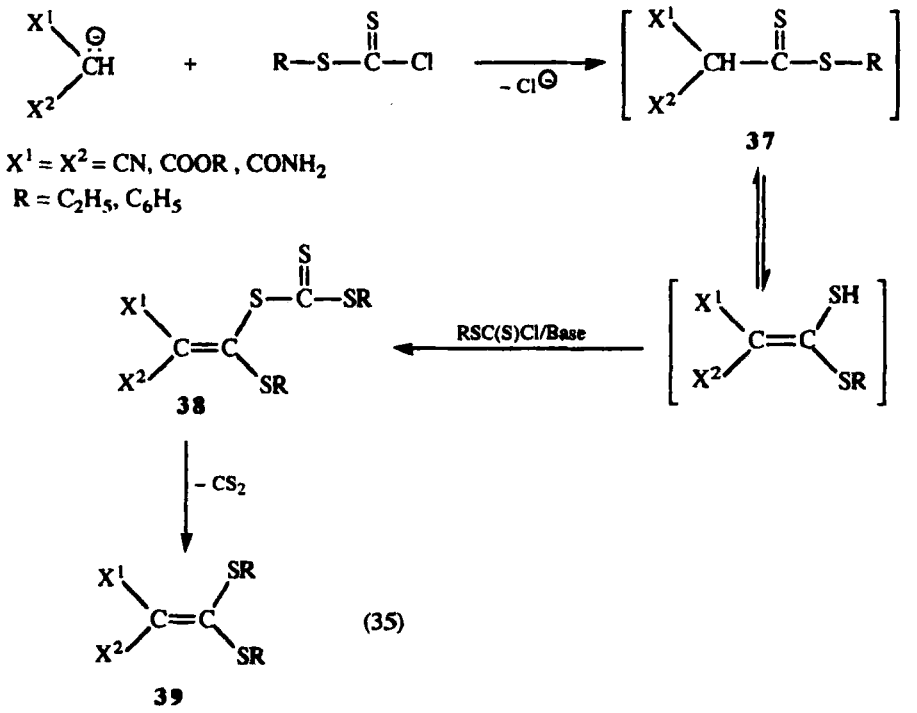
4.1.3. *Reactions of chlorodithioformates with carbanions.* Reactive chlorodithioformates react with carbanions or potential carbanions such as organometallic compounds, CH-acids, enamines and enol ethers with introduction of the group -C(S)SR into the substrate according to (34).[97–106]



(34)

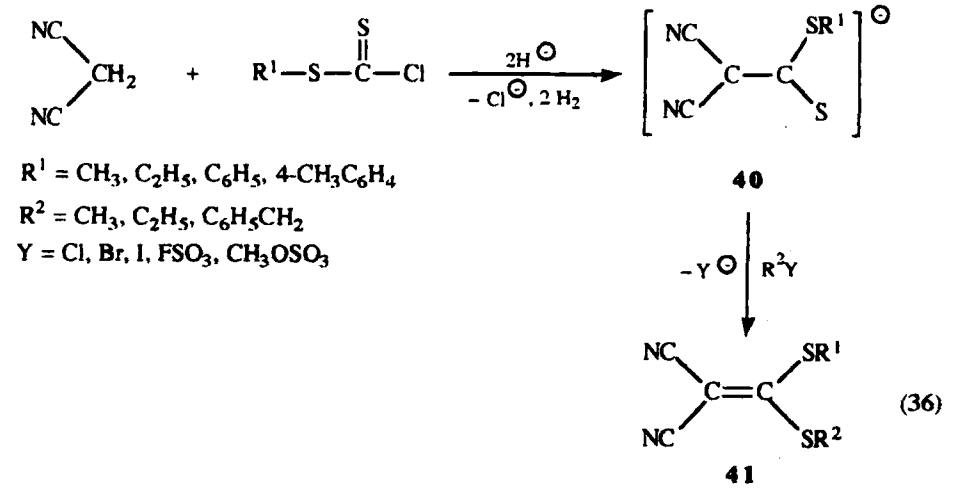
The reaction of chlorodithioformates with metal salts of CH-acidic compounds has been studied repeatedly in the case of cyanoacetic acid esters were the acylation does not stop at the dithioester **37**. Since the intermediate enethiolate is more nucleophilic than

the carbanion the ketene dithioacetals **39** result via the trithiocarbonic acid derivatives **38** according to (35).[99-100]



(35)

A number of unsymmetrical ketene *S,S*-acetals **41** have been synthesized via thioacylation of malononitrile with chlorodithioformates in the presence of two equivalents of sodium hydride and alkylation of the intermediate **40** according to (36).[100]



$R^1 = CH_3, C_2H_5, C_6H_5, 4\text{-}CH_3C_6H_4$

$R^2 = CH_3, C_2H_5, C_6H_5CH_2$

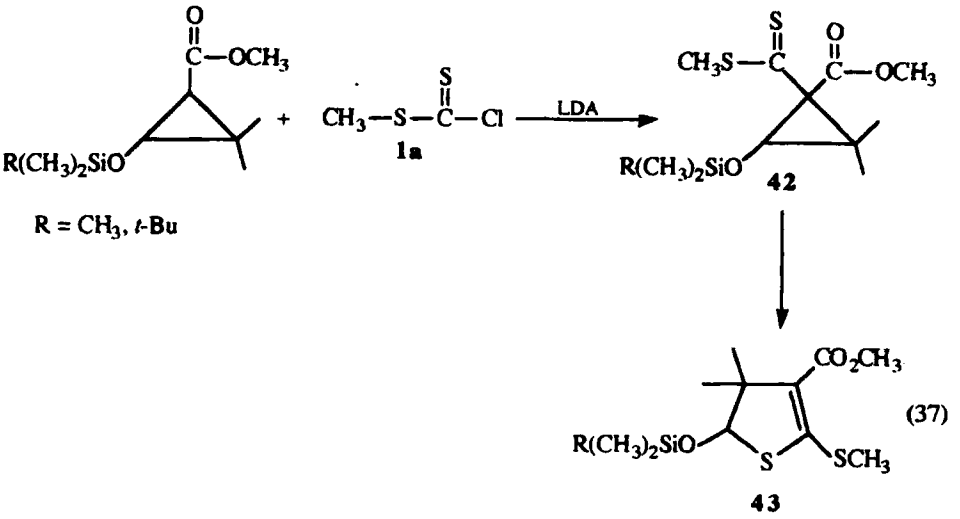
$Y = Cl, Br, I, FSO_3, CH_3OSO_3$

40

41

(36)

Reaction of methyl 2-(trialkylsilyloxy)cyclopropanecarboxylates with methyl chlorodithioformate affords 2-(trialkylsilyloxy)-3,3-dimethyl-1-[(methylthio)thiocarbonyl]-cyclopropanecarboxylic acid methyl esters **42** which can be converted to methyl 3-dihydrothiophene-3-carboxylates **43** through ring enlargement by [1,3] and [1,2] sigmatropic rearrangements according to (37).[101]



$R = CH_3, t\text{-}Bu$

1a

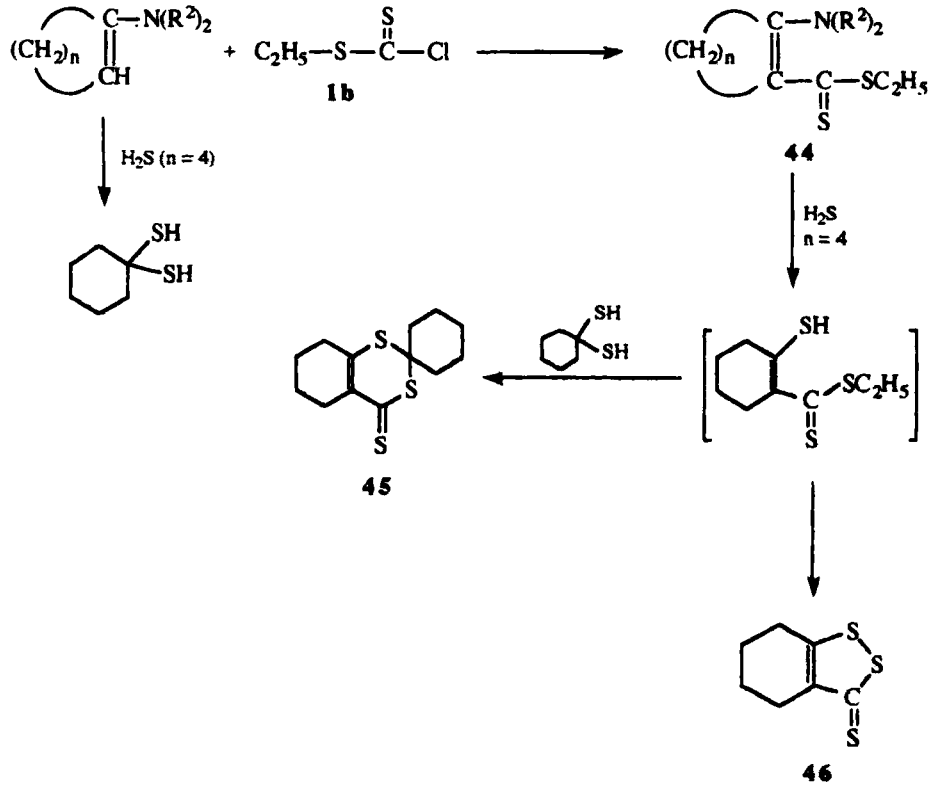
42

43

(37)

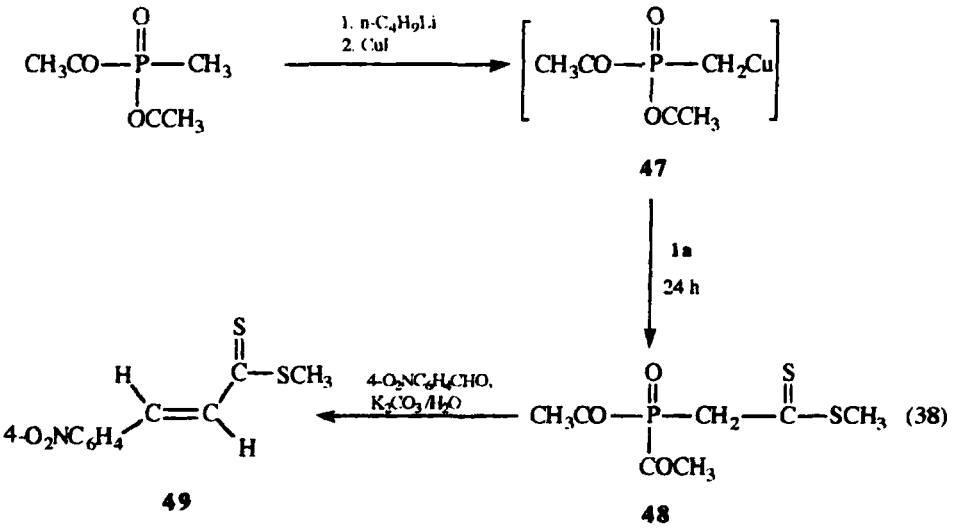
4.1.4. *Reactions of chlorodithioformates with enamines.* Enamines can be thiocarboxylated. Thus, the reaction of 1-morpholinocyclohexene with chlorodithioformates yields

the dithioesters **44** which can be isolated as their hydrochlorides.[97] Their sulfhydrolysis in benzene does not yield the corresponding mercapto dithioesters, but spiro[*4H*-1,3-benzodithiin-2,1′-cyclohexane]-4-thione **45**. The 3-thioxo-1,2-dithiole **46** is formed as a by-product (cf. Scheme 11).

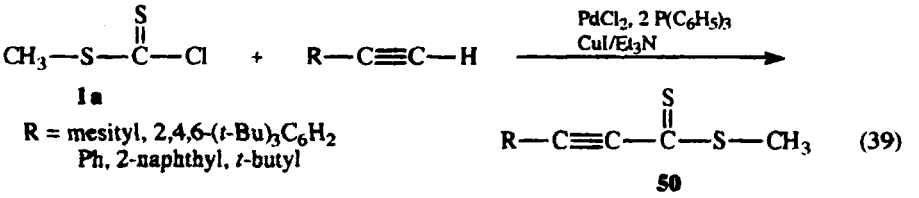


SCHEME 11

4.1.5. *Reactions of chlorodithioformates with the copper derivative of methanephosphonic acid dimethyl ester.* The copper(I) derivative **47** of methanephosphonic acid dimethyl ester is easily thioacylated with chlorodithioformates to afford *S*-alkyl (dimethoxyphosphinyl)-dithioacetates such as **48**.[102] The dithioesters react with aldehydes in a Horner-Emmons reaction to give alkyl 2-alkenedithioates **49** according to (38).



4.1.6. *Reactions of chlorodithioformates with alkynes.* The α,β-acetylenic dithioesters **50** have been prepared according to (39) by palladium(II) catalyzed condensation of alkynes with chlorodithioformates.[103,104] The dithioesters are readily attacked by nucleophiles such as secondary amines and thiols and by alkylating agents, the thiocarbonyl groups of **50** exhibit dienophilic properties.



4.2. *Reaction with Nitrogen Nucleophiles*

Reactions of chlorodithioformates with nitrogen-containing substrates form the major part of chlorodithioformate chemistry as shown below.

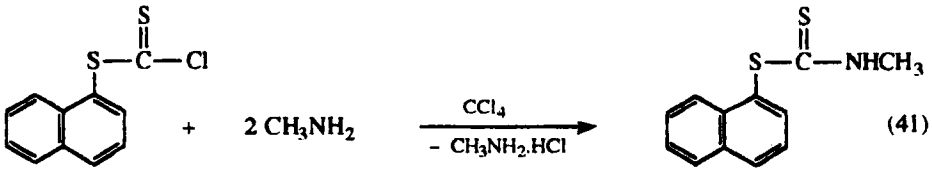
4.2.1. *Reactions with primary amines.* Chlorodithioformates react with ammonia, primary aliphatic, primary aromatic and hydroxylamines to afford the corresponding dithiocarbamates **51** according to (40) as often biologically active compounds.[105–110]

(40)

51

The following interesting new example may illustrate the scope of the reaction:

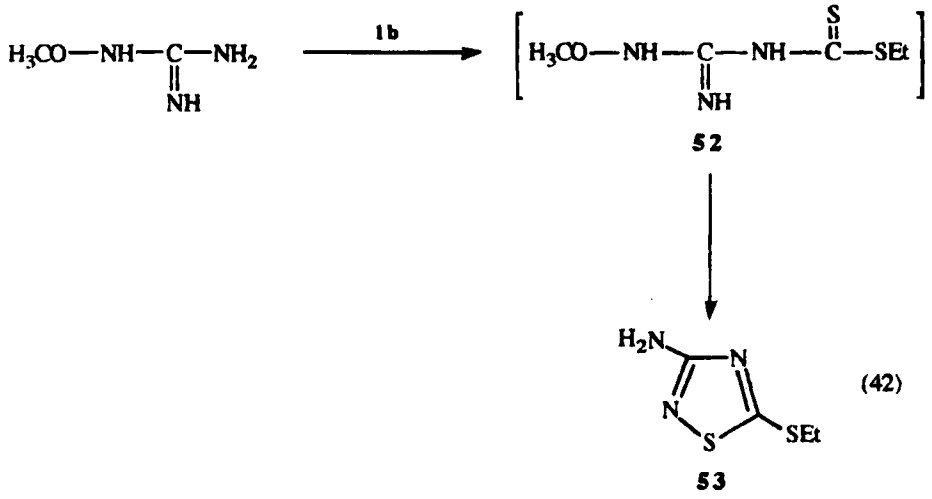
The reaction of methylamine with 1-naphthyl chlorodithioformate leads to 1-naphthyl *N*-methyldithiocarbamate **51a** according to (41) which is a better inhibitor of eel acetylcholine esterase than the corresponding thionocarbamate.[33]



(41)

4e **51a**

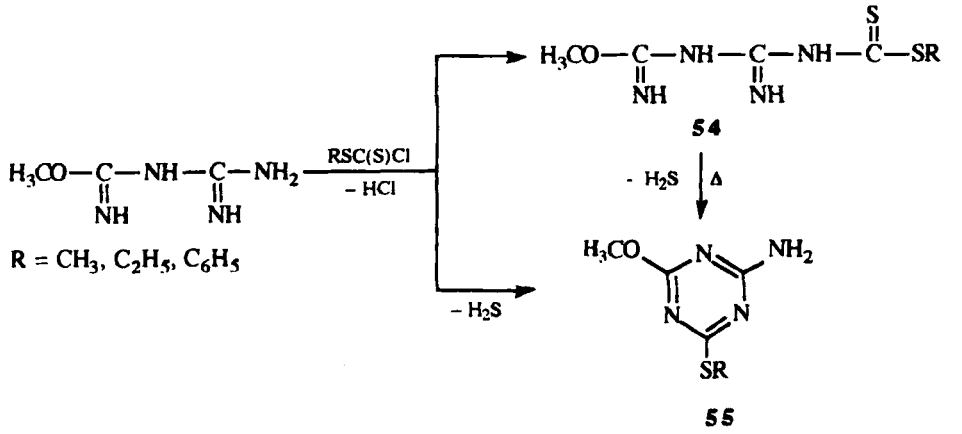
4.2.2. *Reaction with functionalized primary amines.* Chlorodithioformates react in a more complex manner with primary amines containing a second reactive group such as NH. Thus, reaction of ethyl chlorodithioformate with *N*-methoxyguanidine yields the intermediate **52** which cyclises to 3-amino-5-ethylthio-1,2,4-thiadiazole **53** according to (42).[108]



(42)

52 **53**

The reaction of chlorodithioformates with *N*-(methoxycarbimidoyl)guanidine affords the corresponding *N*-(methoxycarbimidoyl)guanidine-*N*-dithiocarboxylic acid ester **54** along with 2-amino-4-methoxy-6-alkyl(aryl)thio-1,3,5-triazine **55** according to Scheme (12).[109,110]

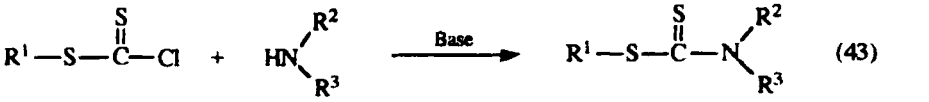


54

55

SCHEME 12

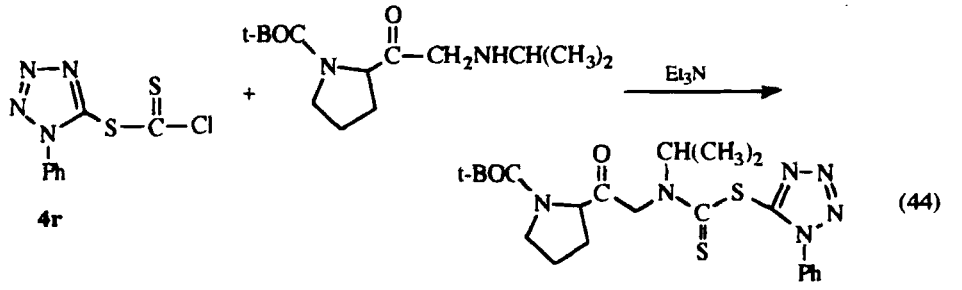
4.2.3. *Reactions with secondary amines.* Chlorodithioformates react with secondary aliphatic, aromatic, heterocyclic and hydroxylamines to form the corresponding dithiocarbamates **56** according to (43).[107,111-124]



(43)

56

4.2.3.1. *With acyclic secondary amines.* Reaction of 1-phenyl-5-tetrazolyl chlorodithioformate **6r** with (1-Boc-L-prolyl)methyl-isopropylamine in the presence of a base affords 1-phenyl-5-tetrazolyl *N*-(1-Boc-L-prolyl)methyl-*N*-isopropyldithiocarbamate **56a** according to (44) which was found to possess a temporary inhibiting effect on PP elastase, but not on trypsin or chymotrypsin.[111]

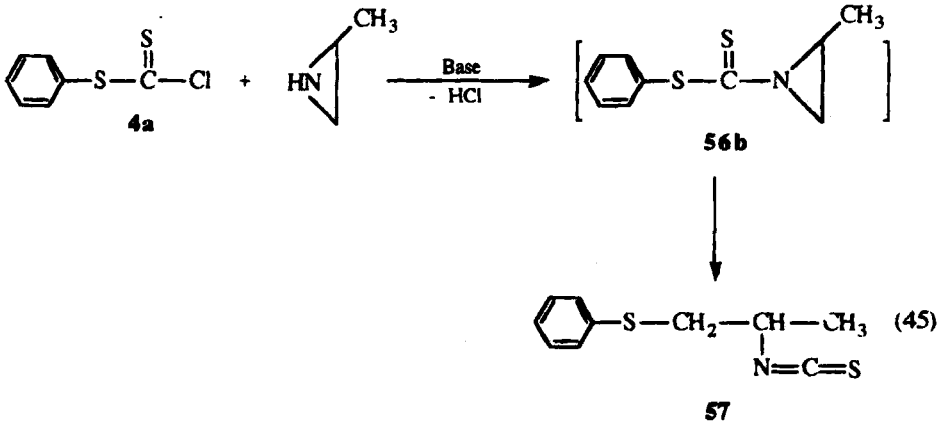


4r

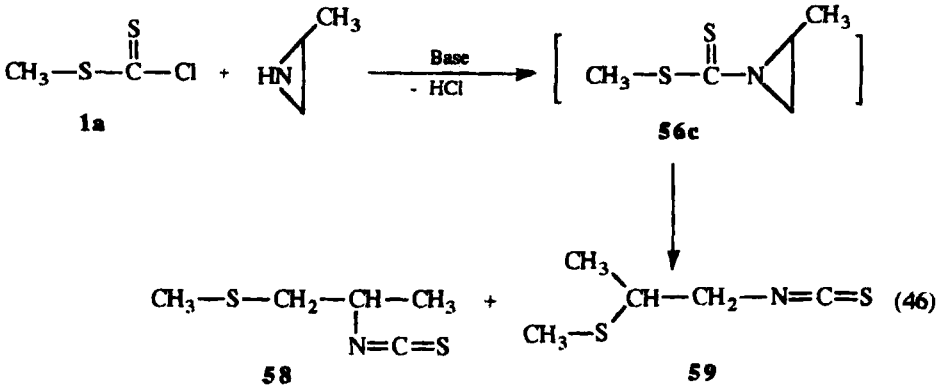
(44)

56a

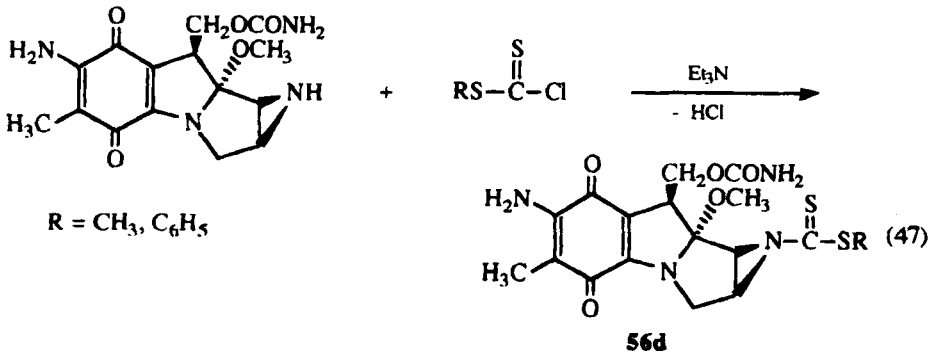
4.2.3.2. *With aziridines.* Reactions of chlorodithioformates with aziridine derivatives have been reported.[114,115] Phenyl chlorodithioformate reacts with 2-methylaziridine to form the corresponding dithiocarbamate **56b** which rearranges to 2-isothiocyanato-1-(phenylthio)propane **32** under a variety of reaction conditions according to (45).



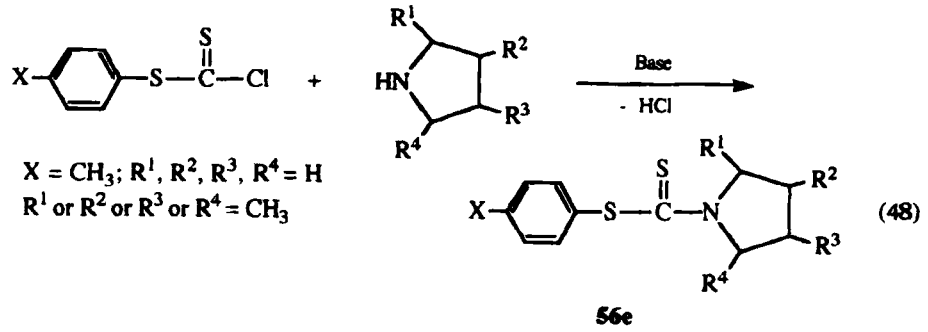
The reaction of methyl chlorodithioformate with 2-methylaziridine affords **56c** which rearranges to the corresponding isothiocyanates **58** and **59** according to (46).[114,115]

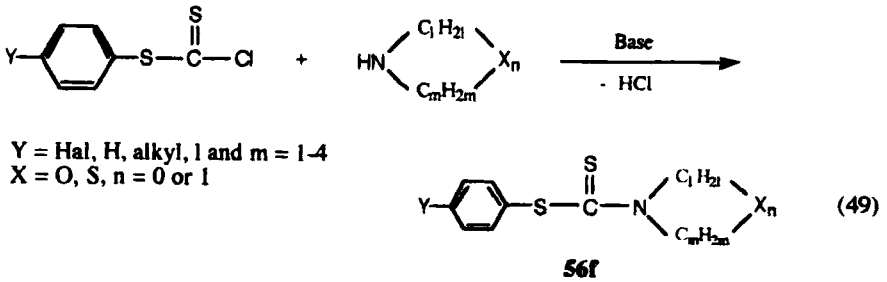


Mitomycin C reacts with chlorodithioformates to form the corresponding dithiocarbamates **56d** according to (47).[114,115] These dithiocarbamates have been tested for antineoplastic activity *in vivo* test.

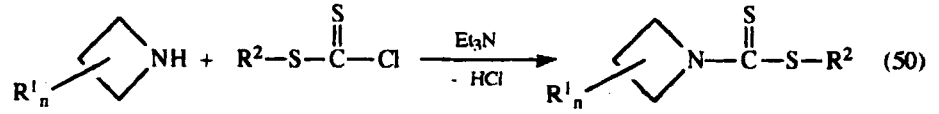


4.2.3.3. *With pyrrolidines.* The reaction of aryl chlorodithioformates with saturated nitrogen heterocycles in the presence of a base affords the corresponding dithiocarbamate **56f** and **56g** according to (49) and (50), respectively, which have been claimed as paddy field herbicides.[113,116,117]





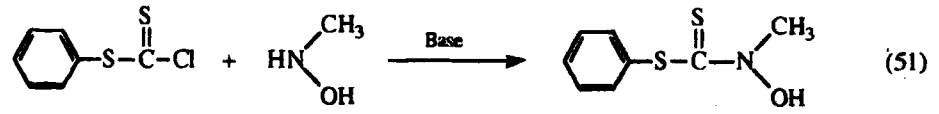
4.2.3.4. *With azetidines.* Reaction of chlorodithioformates with di- or trimethylazetidine in the presence of a base according to (36) affords the corresponding 1-azetidine-carbodithioates **56e** which have been suggested as selective herbicides, especially for cereal cultures.[118]



(50)

56g

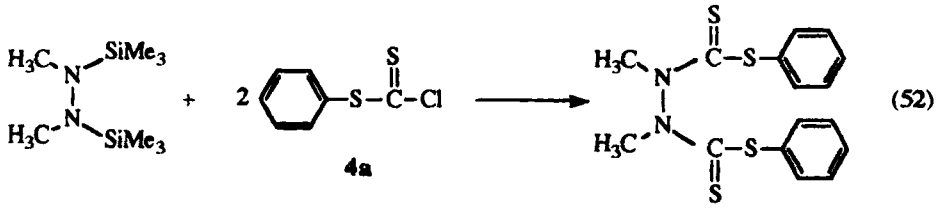
4.2.3.5. *With hydroxylamines.* Reaction of phenyl chlorodithioformate with *N*-methyhyldroxylamine affords the crystalline thiohydroxamic acid **56h** according to (51).[119,120]



(51)

4a **56h**

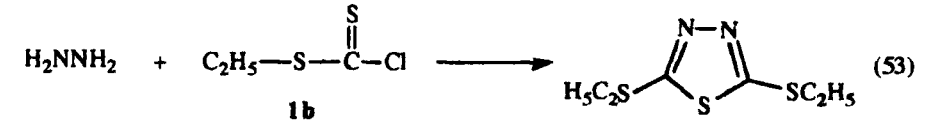
4.2.4. *Reactions with silylated secondary amines.* Senning *et al.* have prepared *N,N'*-bis(phenylthiothioformyl)-*N,N'*-dimethylhydrazine **60** by treating the corresponding silylated amine with phenyl chlorodithioformate according to (52).[121,122]



(52)

4a **60**

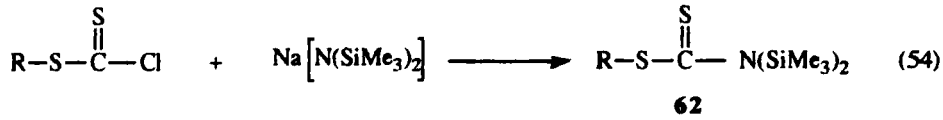
4.2.5. *Reactions with hydrazine.* Ethyl chlorodithioformate reacts with hydrazinium salts in water to give exclusively 2,5-bis(ethylthio)-1,3,4-thiadiazole **61** according to (53).[123]



(53)

1b **61**

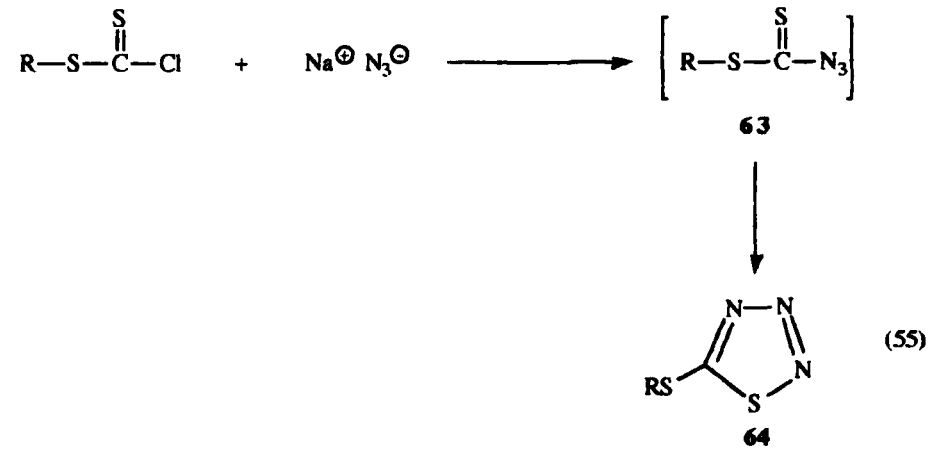
4.2.6. *Reactions with sodium bis(trimethylsilyl)amide.* The reaction of chlorodithioformates with sodium bis(trimethylsilyl)amide affords *N,N*-bis(trimethylsilyl) dithiocarbamic acid *S*-esters **62** according to (54).[124]



(54)

62

4.2.7. *Reaction with azide ions.* Reaction of chlorodithioformates with sodium azide in 70% aqueous acetone gives 5-substituted 1,2,3,4-thiatriazoles **64** which are isolated in quantitative yield as crystalline solids according to (55).[125–128]

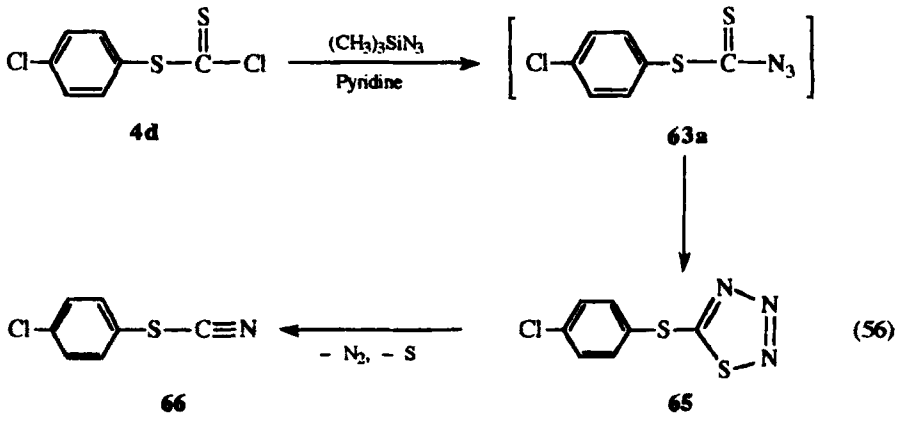


(55)

63

64

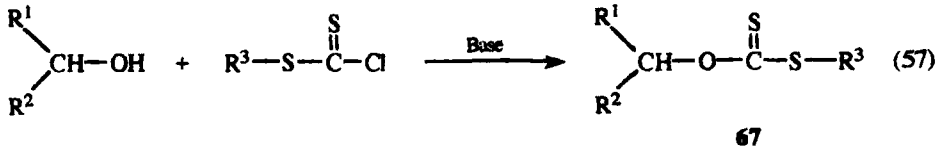
4.2.8. *Reactions with silyl azides.* 4-Chlorophenyl chlorodithioformate **4d** reacts with trimethylsilyl azide in the presence of base to afford 5-(4-chlorophenyl)-1,2,3,4-thiatriazole **65** according to (56).[129] Upon heating 4-chlorophenyl thiocyanate **66** is formed according to (56).[130]



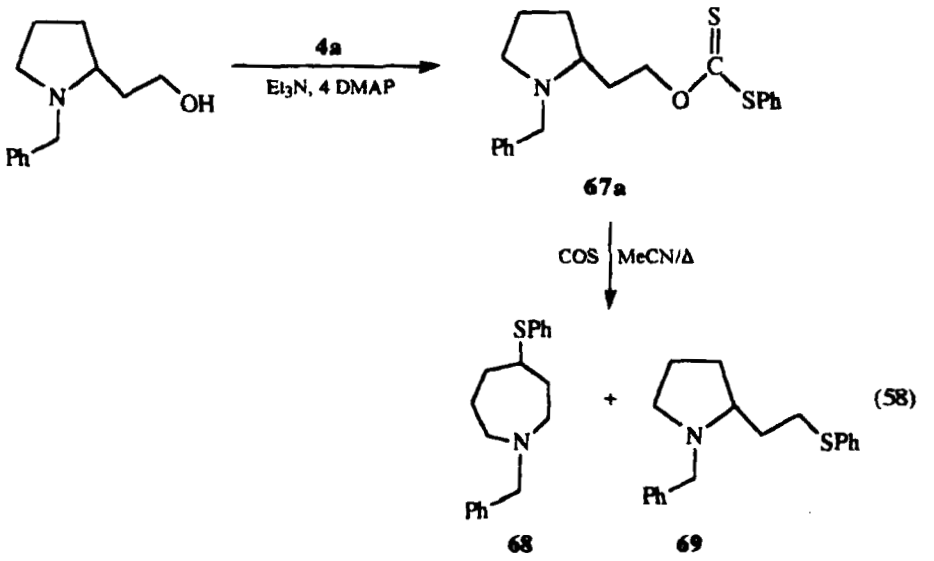
4.3. *Reaction at an Oxygen Center*

Chlorodithioformates react with alcohols and phenols to form the corresponding dithiocarbonates in good yields. Use of alkali metal alkoxides and phenoxides gives a better yield. The following examples may illustrate the scope of the reaction.

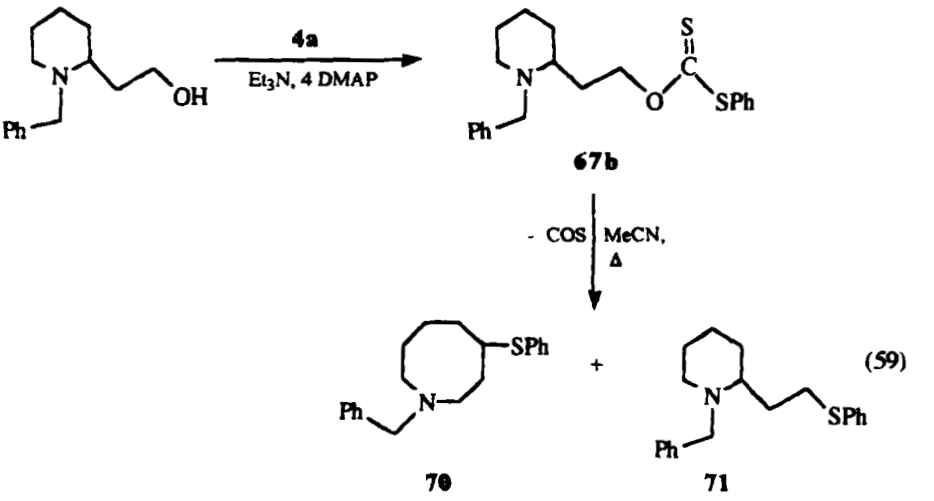
4.3.1. *Reactions with alcohols.* Chlorodithioformates react with primary and secondary alcohols to afford the corresponding dithiocarbonates **67** in good yields according to (57).[131-134]



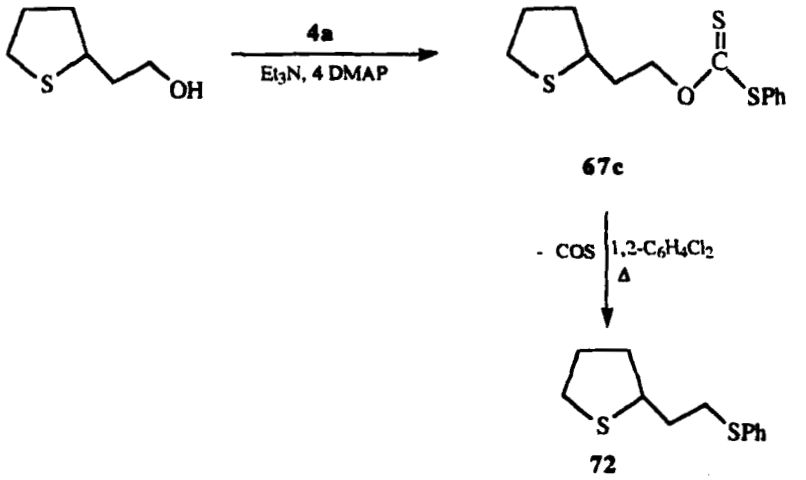
Reaction of 1-benzyl-2-(2-hydroxyethyl)pyrrolidine with phenyl chlorodithioformate **4a** in the presence of a base in acetonitrile at 0 °C affords *O*-2-(1-benzyl-2-pyrrolidinyl)ethyl *S*-phenyl dithiocarbonate **67a** which upon reflux in acetonitrile decomposes according to (58)[132] to form the phenylthiohexahydroazepine **68** and the phenylthioethylpyrrolidine **69** in a ratio of 1:2.



The reaction of 1-benzyl-2-(2-hydroxyethyl)piperidine with phenyl chlorodithioformate **4a** in the presence of a base in acetonitrile at 0 °C affords *O*-2-(1-benzyl-2-piperidyl)ethyl *S*-phenyl dithiocarbonate **67b** which upon reflux in acetonitrile decomposes to form 1-benzyl-4-phenylthiooctahydroazocine **70** and 1-benzyl-2-(2-phenylthioethyl)piperidine **71** according to (59).[132]

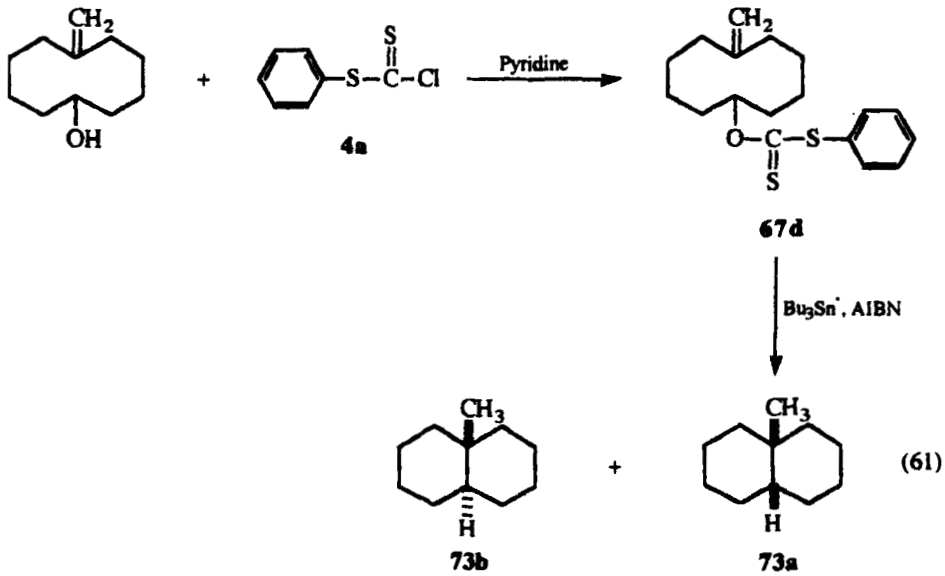


Pyrolysis of *S*-phenyl *O*-2-(2-tetrahydrothienyl)ethyl dithiocarbonate **67c** in *o*-dichlorobenzene provided only the carbonyl sulfide elimination product 2-(2-phenylthioethyl)tetrahydrothiophene **72** according to (60).[132]



(60)

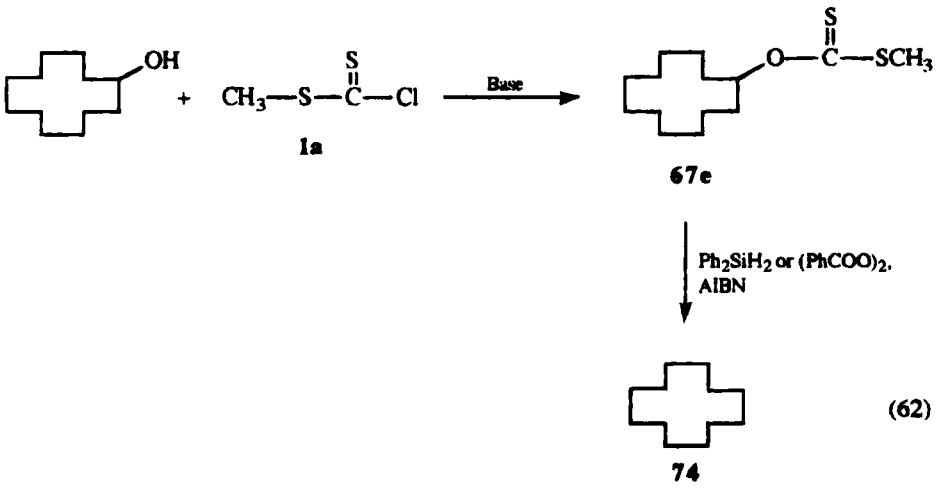
The reaction of phenyl chlorodithioformate **4a** with 6-methylenecyclodecanol in the presence of a base affords *O*-(6-methylenecyclodecyl) *S*-phenyl dithiocarbonate **67d**. Treatment of the dithiocarbonate with tributylstannane and azobisisobutyronitrile as initiator affords a mixture of the *cis* and the *trans* isomer of 9-methyldecahydronaphthalene **73a** and **73b**, respectively, according to (61).[131]



(61)

Methyl chlorodithioformate **1a** reacts with secondary alcohols to afford the corresponding dithiocarbonates **67e** and **67f** which are easily deoxygenated in 58–100% yield by

radical deoxygenation with diphenylsilane and 2,2′-azobisisobutyronitrile or benzoyl peroxide in boiling toluene to **74** and **75** according to (62) and (63), respectively.[133]

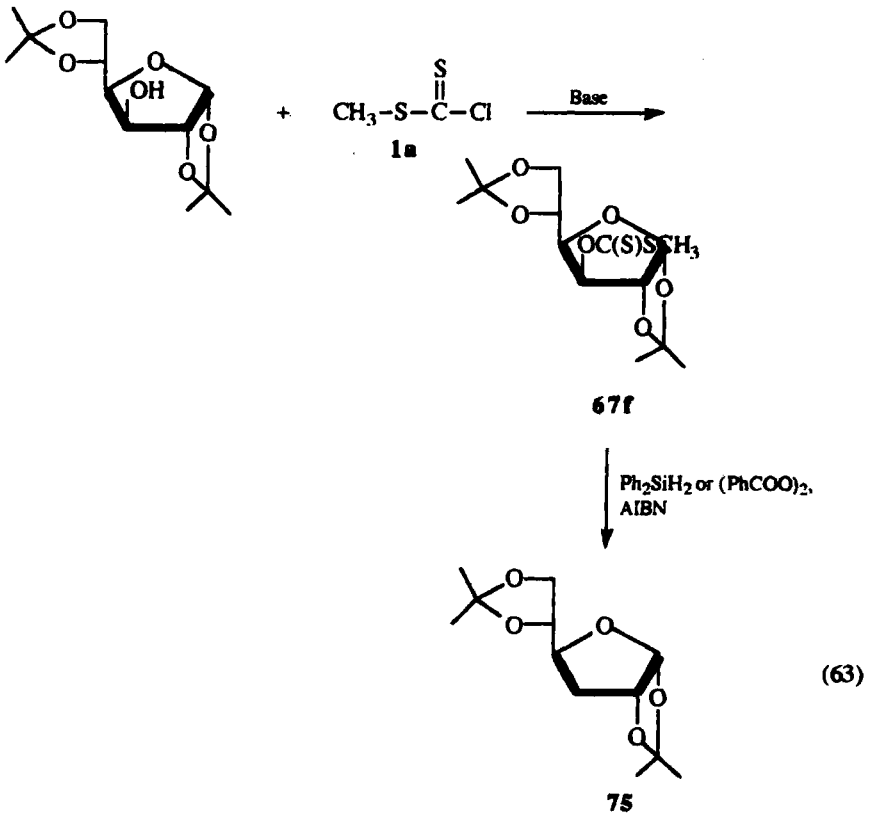


1a

67e

74

(62)



1a

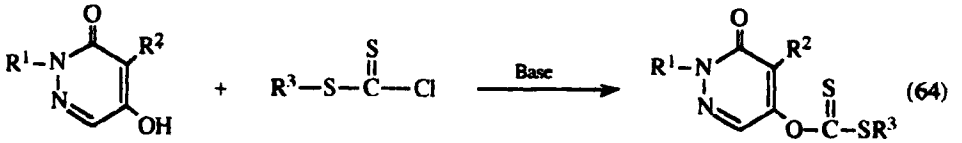
67f

75

(63)

4.3.2. *Reaction with phenols.* Phenols react with chlorodithioformates in the presence of a base to afford the corresponding dithiocarbonates which have been claimed as bactericides and herbicides.[134,135]

The reaction of chlorodithioformates with the potassium salts of 2-alkyl-4-halo-5-hydroxy-3-(2*H*)pyridazinones in acetonitrile affords, according to (64), 2-alkyl-4-halo-5-(alkoxydithiocarbonyl)-3-(2*H*-pyridazinones **76** useful as herbicide safeners.[134]

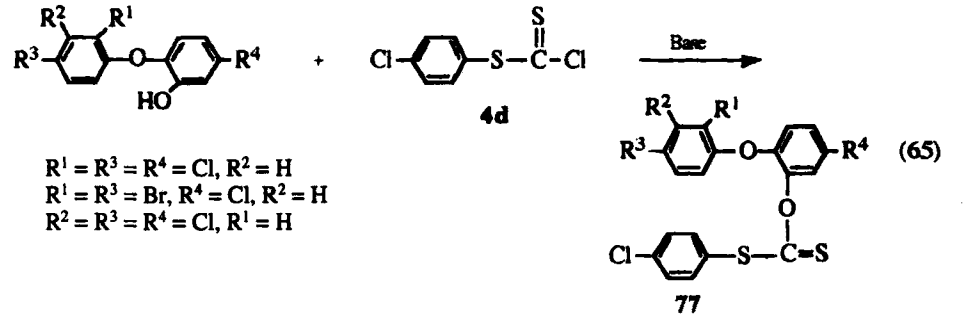


R^1 = alkyl, alkoxyalkyl, cyanoalkyl and aryl

R^1 = Hal, R^3 = alkyl, aryl

76

Reaction of substituted 2-hydroxydiphenyl ethers with 4-chlorophenyl chlorodithioformate **4d** affords the corresponding dithiocarbonates **77** according to (65), useful as bactericides.[135]



4d

$R^1 = R^3 = R^4 = Cl$, $R^2 = H$
$R^1 = R^3 = Br$, $R^4 = Cl$, $R^2 = H$
$R^2 = R^3 = R^4 = Cl$, $R^1 = H$

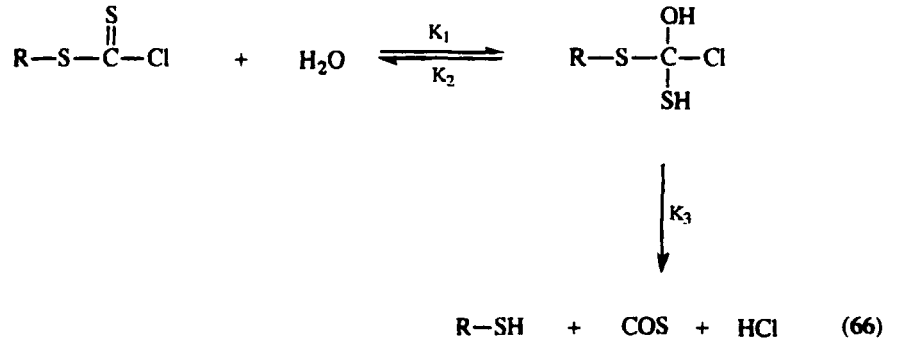
77

4.3.3. *Hydrolysis in 70% aqueous acetone.* Chlorodithioformates hydrolyze by an S_N1 mechanism. First-order rate constants of hydrolysis in 70% aqueous acetone at 278.10 K have been reported (cf. Table 7).[14,141]

TABLE 7 First-order rate constants of hydrolyses in 70% aqueous acetone at 278.10 K

Compound	R	K [s^{-1}]
1a	CH_3	$1.264 \cdot 10^{-4}$
1b	C_2H_5	$7.955 \cdot 10^{-4}$
1d	$(CH_3)_2CH$	$4.217 \cdot 10^{-3}$
4a	C_6H_5	$2.477 \cdot 10^{-5}$

The initial products of the hydrolysis of methyl chlorodithioformate are hydrochloric acid, carbonyl sulfide and methanethiol according to (66).



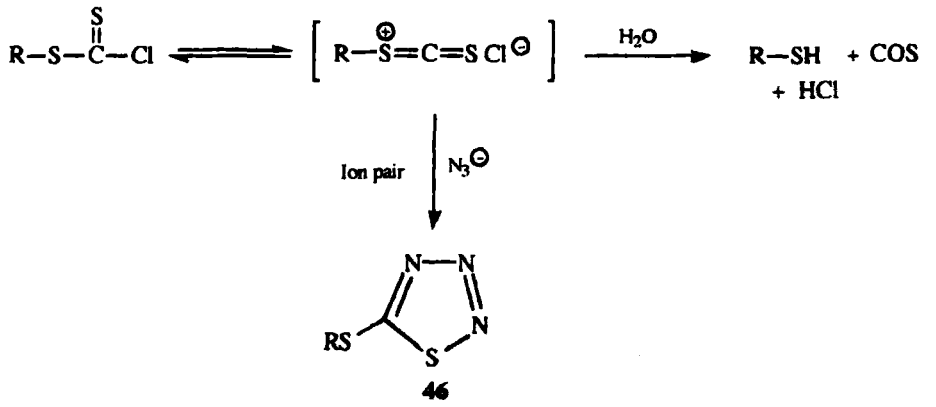
(66)

The latter product reacts with methyl chlorodithioformate **1a** to yield dimethyl trithiocarbonate. The activation energy and entropy for the hydrolysis of the methyl ester are $\Delta H^* = 84.43\ KJ \cdot mol^{-1}$, $\Delta S^* = -15.5\ J \cdot mol^{-1} \cdot deg^{-1}$

Although chlorodithioformates hydrolyse by the S_N1 mechanism in aqueous acetone the corresponding reaction of chlorodithioformates with azide ions in the same medium is largely a bimolecular process[136,137] (cf. Scheme 13). This bimolecular azide attack is supported by the first-order dependence of the rate on nucleophile concentration.

The second-order rate constants have been determined in 70% aqueous acetone at 277.94 K.[138] The activation energy and entropy for the azide reactions can be compared to those for the solvolysis of methyl chlorodithioformate **1a** in 70% aqueous acetone.[138–141] The large effects of azide ions on the rate of the reaction are due to the lower activation enthalpies. These differences provide further support for different paths for solvolysis and bimolecular azide attack.

$\Delta H^* = 20.18\ Kcal \cdot mol^{-1}$, $\Delta S^* = -3.70\ cal \cdot mol^{-1} \cdot deg^{-1}$

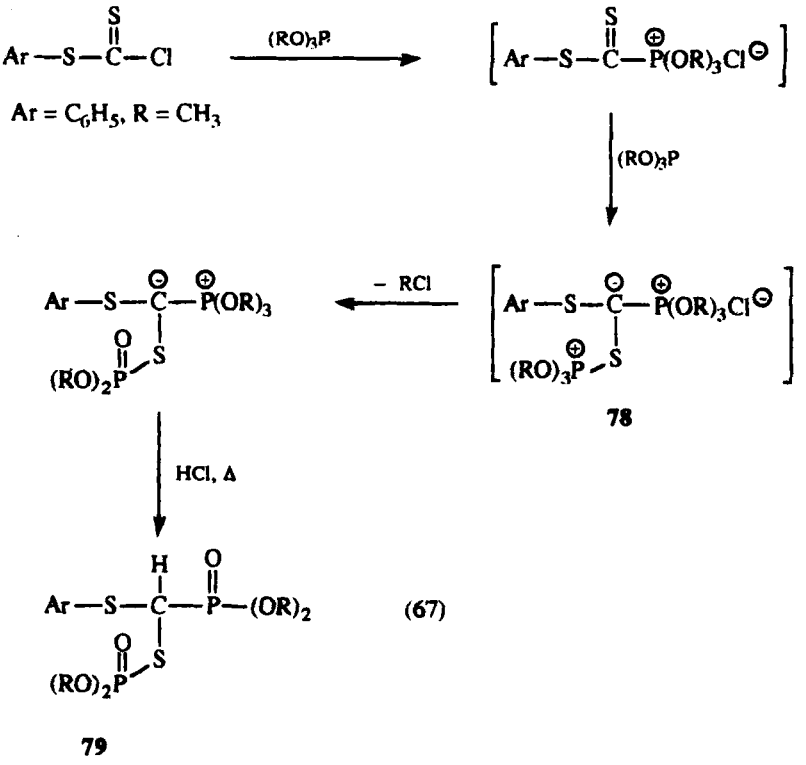


46

SCHEME 13

4.4. *Reactions with Phosphorus Nucleophiles*

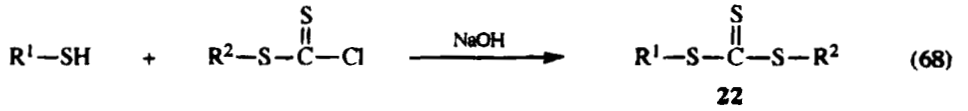
4.4.1 *Asbuzov type reactions.* The reaction of trialkyl phosphites with aryl chlorodithioformates **4** according to (67) leads to the stable ylides **78**. Nucleophilic attack of chloride ion on the alkoxy substituents at phosphorus, protonation, and dealkylation occur only at the trialkoxy-phosphonium moiety α to the sulfur atom. Electronegative substituents on the phosphorus atom facilitate these elimination reactions.[142,143]



(67)

4.5. *Reactions with Sulfur Nucleophiles*

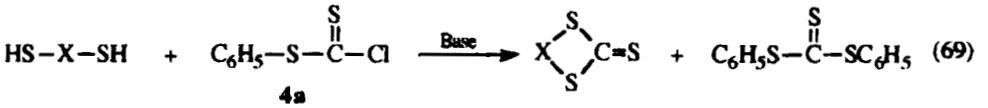
4.5.1. *Reactions with thiols.* Treatment of alkane- or arenethiols with chlorodithioformates in the presence of a base gives the corresponding trithiocarbonates **22**.[12,144–147] Because of the interest in organic trithiocarbonates as biological toxicants and also as oil additives a large number of compounds of this class have been synthesized, including symmetrical and unsymmetrical diaryl, aralkyl, and aralkyl alkyl trithiocarbonates.[12] Various synthetic routes involve the reaction of an arene- or alkanethiol in the presence of a base with an alkyl and aryl chlorodithioformate according to (68).



(68)

22

Similarly the reaction of chlorodithioformates with dithiols affords cyclic trithiocarbonates **22c** according to (69).[43]



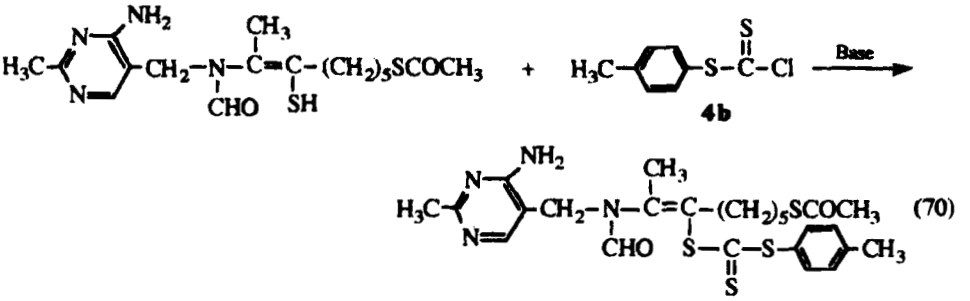
(69)

4a

22c

X = $(CH_2)_2$,

The synthesis of thiamine derivatives by thioacylation with chlorodithioformates has been reported.[148,149] Treatment of 5-{[(7-acetylthio-2-mercapto-1-methyl-1-heptenyl)-formylamino]methyl}-4-amino-2-methylpyrimidine hydrochloride with 4-methylphenyl chlorodithioformate **4b** affords the trithiocarbonate **22d** according to (70), useful as analgesic, antiinflammatory, vitamin B antagonist, hypotensive and coccidiostat.

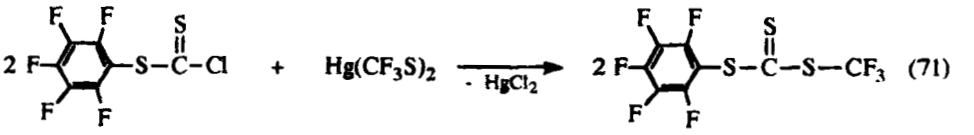


(70)

4b

22d

4.5.2. *Reactions with mercury(II) thiolates.* Pentafluorophenyl chlorodithioformate **4i** reacts with the mercury(II) salt of trifluoromethanethiol to afford *S*-pentafluorophenyl *S*-trifluoromethyl trithiocarbonate **22e** according to (71).[29]

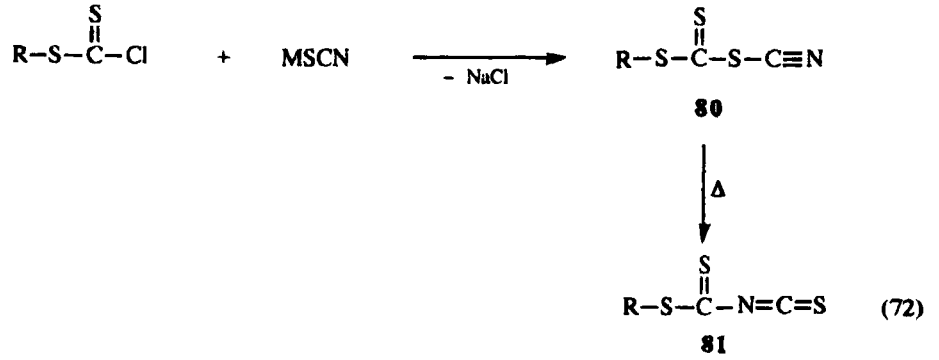


(71)

4i

22e

4.5.3. *Reactions with thiocyanate ions.* Chlorodithioformates react with alkali metal thiocyanates to yield yellow to orange colored alkylthio- and arylthiothiocarbonyl thiocyanates **80**.[13] Best yields were obtained upon treatment of the chlorodithioformates with potassium thiocyanate in the presence of 18-crown-6 as a phase transfer catalyst.[150] The thiocyanates rearrange thermally to the isomeric isothiocyanates **81** according to (72).

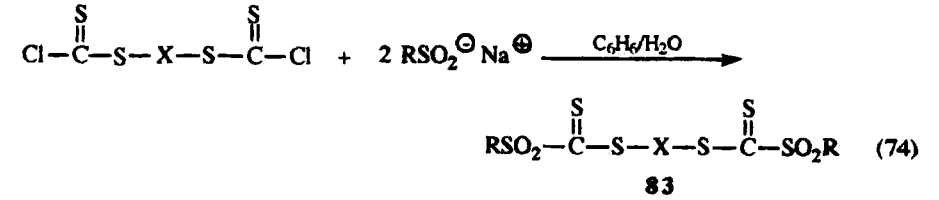


(72)

4.5.4. *Reactions with sulfinate ions.* Senning *et al.* have prepared *C*-sulfonyldithioformates **82** and bis(*C*-sulfonyldithioformates) **83** by thioacylation of metal sulfinates with chlorodithioformates 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 (73).[151-161,188,189]

(73)

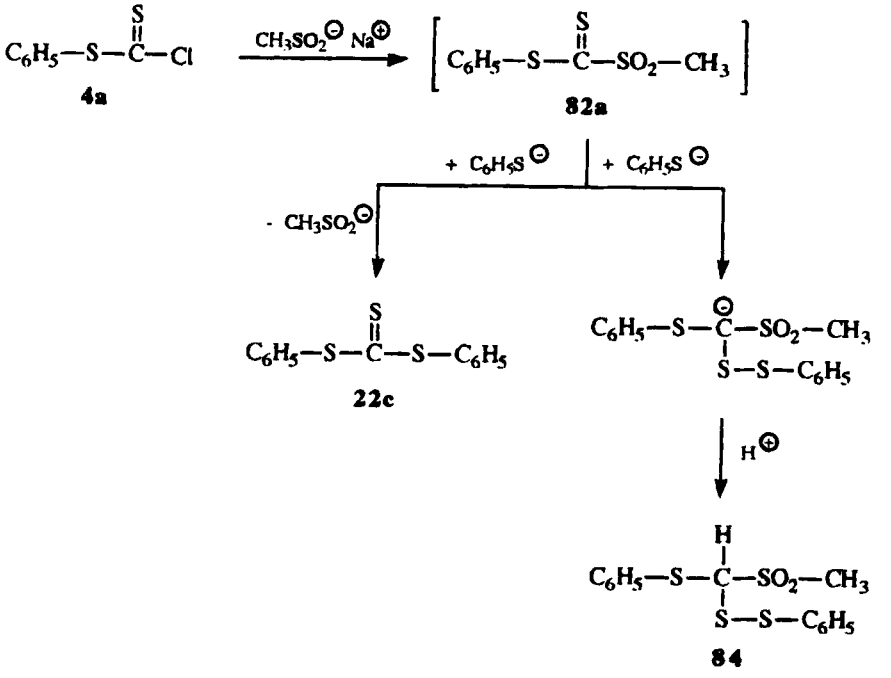
Bis(chlorodithioformates) react with two moles of metal sulfinate to afford the corresponding bis(*C*-sulfonyldithioformates) **83** according to (74).[43]



(74)

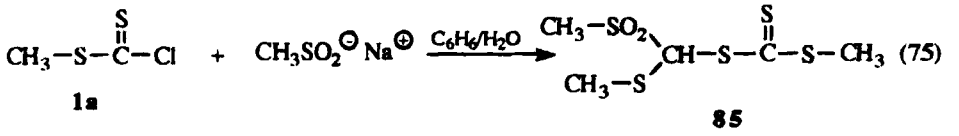
X = 4,4'-biphenylylene, $(CH_2)_2$; R = 4-$CH_3C_6H_4$, 4-ClC_6H_4

Reaction of phenyl chlorodithioformate **4a** with sodium methanesulfinate affords diphenyl trithiocarbonate **22c** and a small amount of the disulfide **84** according to Scheme 14.[151,152]



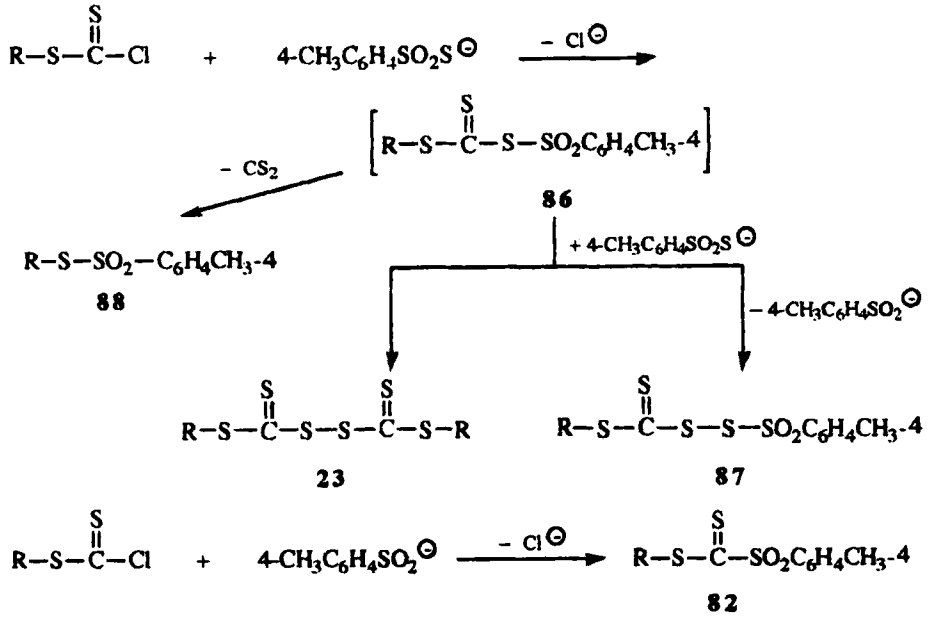
SCHEME 14

Methyl chlorodithioformate **1a** reacts with sodium methanesulfinate to form methyl (methylsulfonyl)(methylthio)methyl trithiocarbonate **85** according to (60) instead of the expected **82**.[151]



(75)

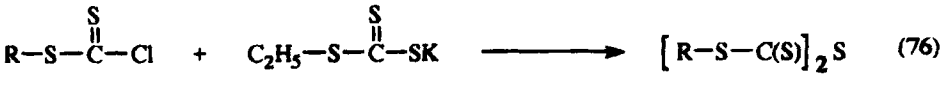
4.5.5. *Reactions with thiosulfonate ions.* Alkyl (aryl) chlorodithioformates react with potassium *p-to*luenethiosulfonate to give alkylthio(arylthio)thiocarbonyl *p*-tolylsulfonyl disulfides **67**, *C*-sulfonyldithioformates **82** and hexathioperoxydicarbonates **23** according to Scheme 15.[155,157]



R = alkyl, aralkyl, aryl

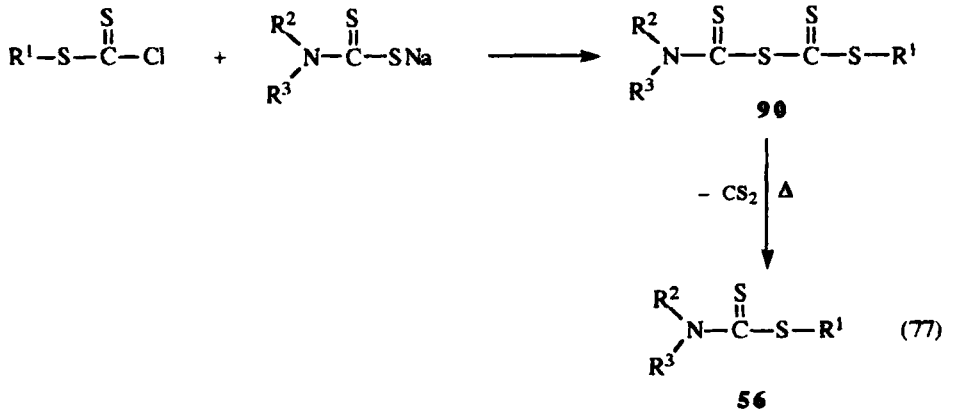
SCHEME 15

4.5.6. *Reactions with thioxanthate ions.* Bis(alkylthio-thiocarbonyl) sulfides **89** have been prepared by reaction of potassium ethylthioxanthate with chlorodithioformates according to (76).[162]



(76)

4.5.7. *Reactions with N,N-disubstituted dithiocarbamate ions.* Aryl chlorodithioformates react with sodium or ammonium salts of *N,N*-disubstituted dithiocarbamic acids to afford *N,N*-disubstituted aryl thiocarbamoyl trithiocarbonates **90** which decompose, when kept at temperatures higher than their melting points, to *N,N*-disubstituted aryldithiocarbamates **56** and carbon disulfide according to (77).[32]



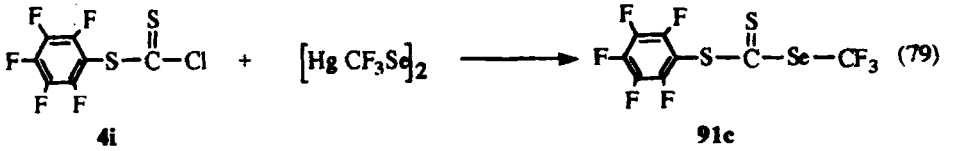
(77)

4.6. *Reactions with Selenium Nucleophiles*

4.6.1. *Reactions with selenols and with selenolate ions.* Treatment of an alkaneselenol or the mercury(II) salt of trifluoromethaneselenol with alkyl chlorodithioformates or pentafluorophenyl chlorodithioformate affords *S,Se*-dialkyl dithioselenocarbonates **91** and *S*-pentafluorophenyl *Se*-trifluoromethyl dithioselenocarbonate **91c**, respectively, according to (78) and (79).[29,163]

(78)

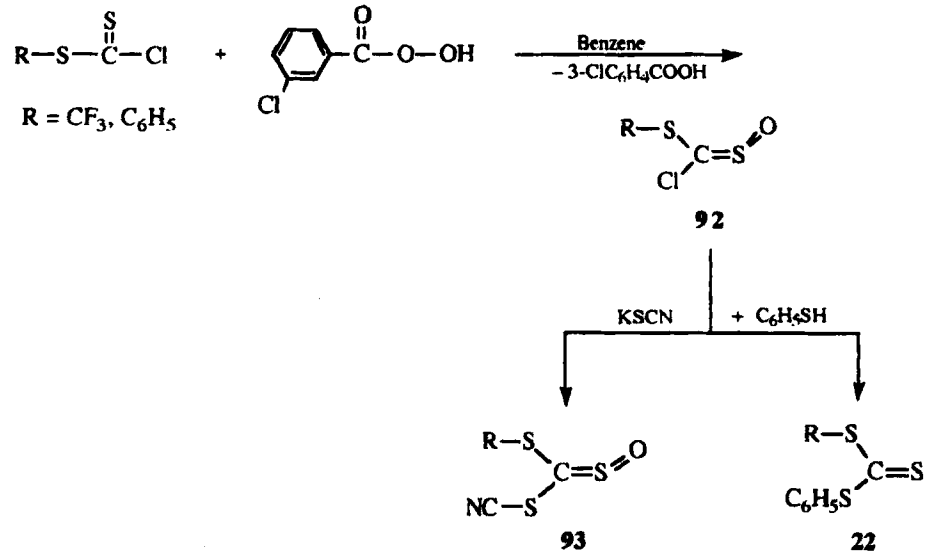
$R^1 = R^1 = C_2H_5, C_3H_7, R^1 = C_2H_5, R^2 = C_3H_7$



(79)

4.7. *Oxidation Reactions*

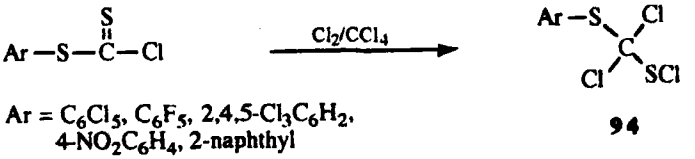
Chlorodithioformates react with *m*-chloroperbenzoic acid to give the corresponding *S*-oxides (sulfines) **101**.[164,165] These sulfines could be distilled at reduced pressure. Some further reactions of **101** are also indicated in Scheme 16.



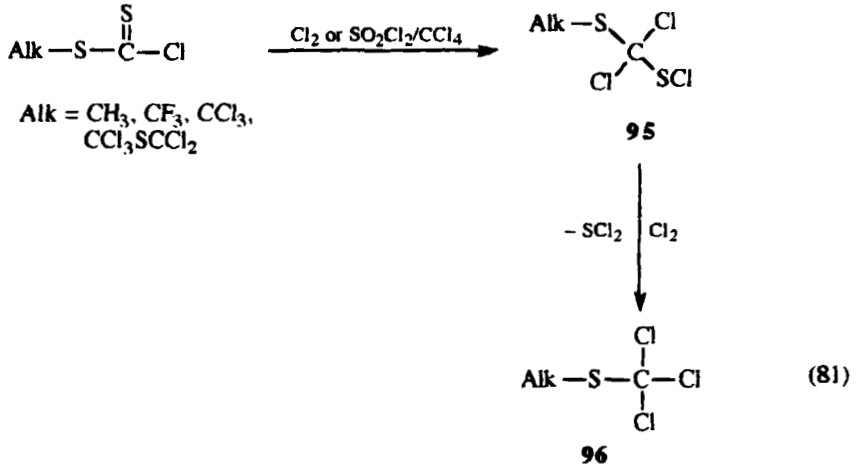
SCHEME 16

4.8. *Addition Reactions at the Thiocarbonyl Group of Chlorodithioformates*

4.8.1. *Addition of chlorine.* The reaction of aryl chlorodithioformates with chlorine at room temperature yields the corresponding (arylthio)dichloromethanesulfenyl chlorides **94** according to (80).[30,166] Under similar conditions phenyl and *p*-tolyl chlorodithioformate fail to give well-defined products.[30] Alkyl chlorodithioformates react with sulfuryl chloride at low temperature to afford the corresponding trichloromethyl alkyl sulfides **96** via the unisolated intermediate sulfenyl chloride **95** according to (81).[52,58–60,166–169]

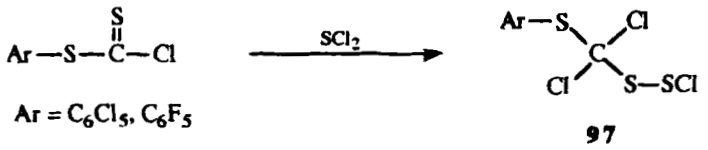


(80)



(81)

4.8.2. *Addition of sulfur dichloride.* The addition of sulfur dichloride to aryl chlorodithioformates leads to stable α-chloro thiosulfenyl chlorides **97** according to (82).[30,166]

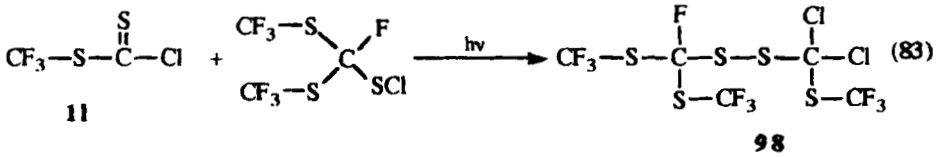


(82)

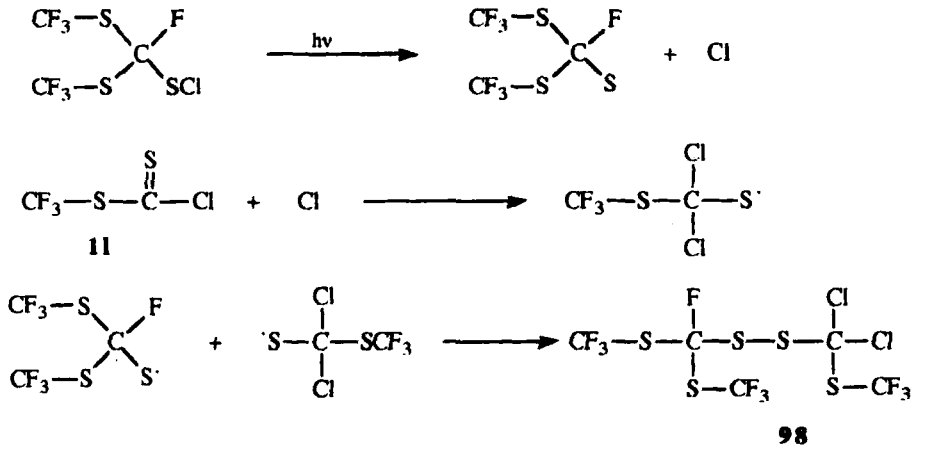
4.8.3. *Addition of sulfenyl chlorides.*

4.8.3.1 *Thermal additions.* The addition of methanesulfenyl chloride to methyl chlorodithioformate **1a** affords the disulfane **21** according to (25).[31,165,170]

4.8.3.2. *Photochemical additions.* Under the influence of UV irradition trifluoromethyl chlorodithioformate **11** adds to fluorobis(trifluoromethylthio)methanesulfenyl chloride to afford dichloro(trifluoromethylthio)methyl fluorobis(trifluoromethylthio)methyl disulfide **98** according to (83).[170]



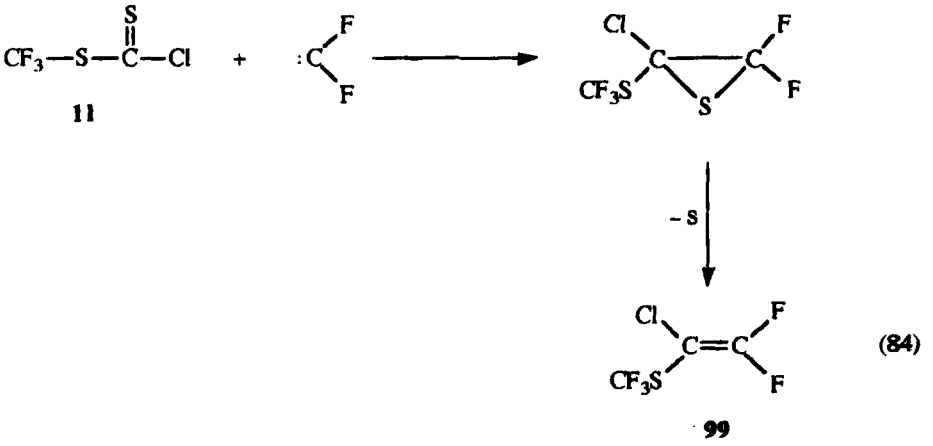
(83)



SCHEME 17

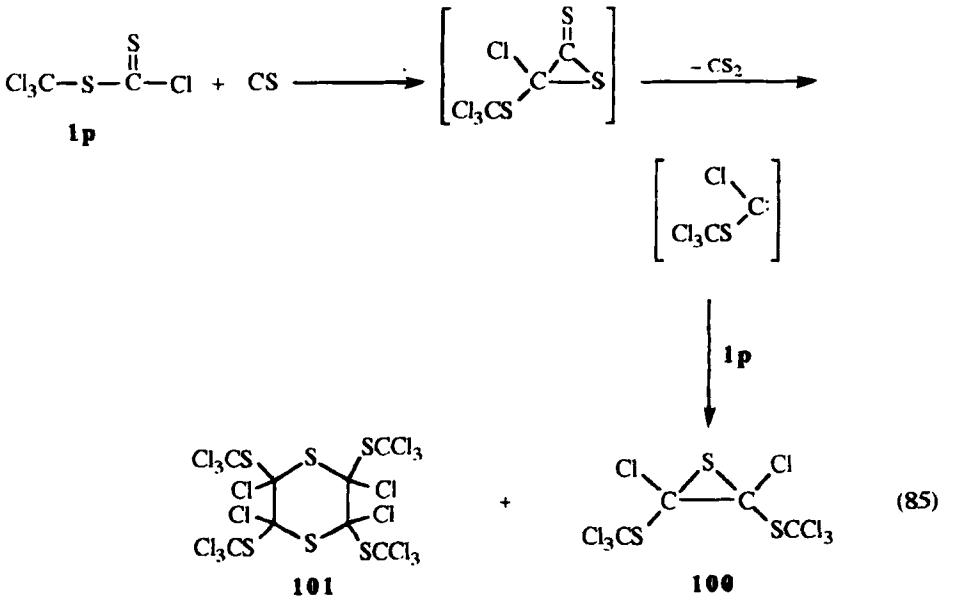
4.9. *Cycloaddition Reactions at the Thiocarbonyl Group of Chlorodithioformates*

4.9.1. *Reactions with carbenes.* Difluorocarbene reacts with trifluoromethyl chlorodithioformate **11** to afford 1-chloro-2,2-difluoro-1-(trifluoromethylthio)ethene **99** according to (84).[171]



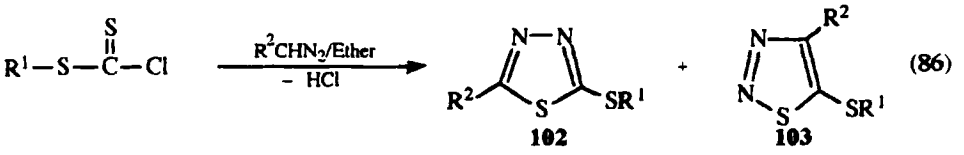
(84)

4.9.2. *Reactions with carbon monosulfide.* The reaction between carbon monosulfide and trichloromethyl chlorodithioformate **1p** has been reported by Senning *et al.* to afford both thiirane **100** and 1,4-dithiane **101** according to (85).[51,52]



(85)

4.9.3. *Reactions with diazo compounds.* The reactions of chlorodithioformates with diazomethane and aroyldiazomethanes have been studied extensively by different workers.[61,172-182] Diazomethane reacts with ethyl chlorodithioformate **1b** to afford a mixture of **2**-(ethylthio)-1,3,4-thiadiazole **102a** and 5-(ethylthio)-1,2,3-thiadiazole **103a** according to (86);[163,175-180] elimination of hydrogen chloride from the primary products leads to the aromatization of the ring system. Propanoic acid 3-(chlorothioxo-methylthio)methyl ester condenses with diazoalkanes at 0 °C to give a 1:2 mixture of the 1,2,3- and the 1,3,4-thiadiazole **102c** and **103c**, respectively, according to (86).[61,178]

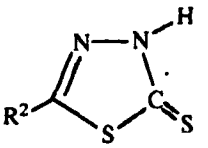


(86)

a: $R^1 = C_2H_5$, $R^2 = H$ b: $R^1 = C_2H_5$, $R^2 = CH_3$

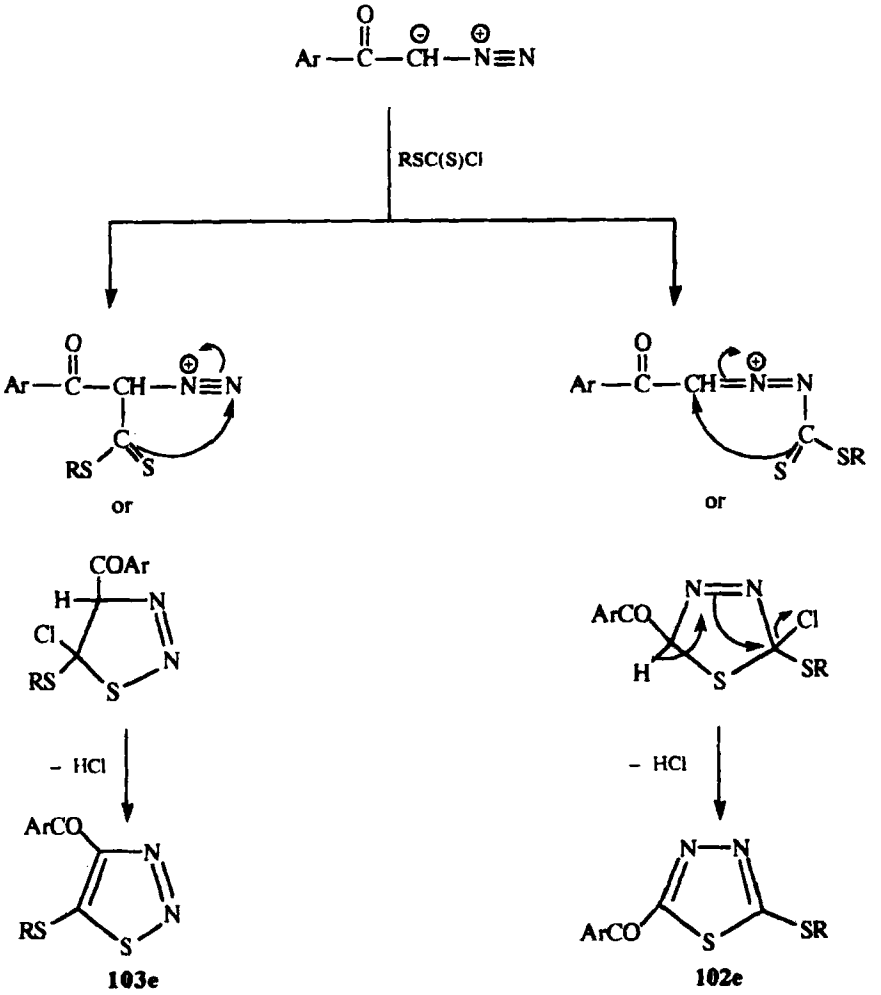
c: $R^1 = CH_2CH_2CO_2CH_3$, $R^2 = H$ d: $R^1 = CH_2CH_2CO_2CH_3$, $R^2 = CH_3$

The formation of the 1,3,4-thiadiazoles **102c** was confirmed by conversion to 1,3,4-thiadiazoline-5-thione **104** by treatment of **102c** with potassium ethoxide, followed by hydrolysis with 10% hydrochloric acid.[178]



104

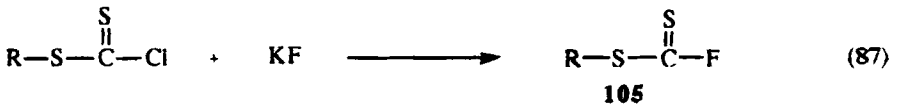
The reaction of chlorodithioformates with α-diazo carbonyl compounds has been reported by Demaree *et al.*[178] Ethyl chlorodithioformate **1b** reacts with α-diazo carbonyl compounds to give exclusively the 1,3,4-thiadiazoles **102e** in the presence of triethylamine and the 1,2,3-thiadiazoles **103e** only when bis(α-diazoacyl)mercury derivatives were used. The mechanism of the formation of **102e** and **103e** has been interpreted as shown in Scheme 18.



SCHEME 18

4.10. *Reactions with Inorganic Compounds*

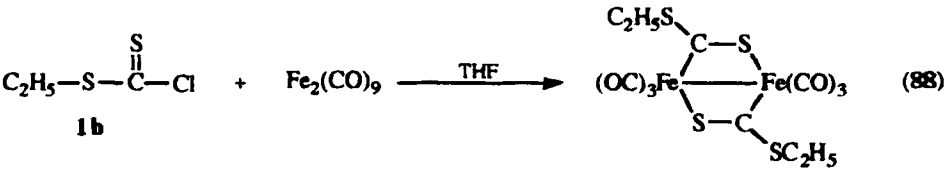
4.10.1. *Reactions with fluoride ions.* Alkyl chlorodithioformates react with potassium fluoride in chloroform or acetonitrile in the presence of kryptofix 222 or 18-crown-6 as phase transfer catalyst to afford fluorodithioformates **105** according to (87).[72,183]



(87)

105

4.10.2. *Reactions with metal carbonyls.* With diironenneacarbonyl and ethyl chlorodithioformate **1b** the remarkable formation of a symmetric complex **106** according to (88) has been observed.[184] Also, the reaction of ethyl chlorodithioformate **1b** with a number of neutral and ionic iron carbonyl compounds in tetrahydrofuran yields a variety of unusual products. The reactivity of ethyl chlorodithioformate **1b** seems to be much greater than that of *N,N*-dimethylthiocarbamoyl chloride.



(88)

1b **106**

REFERENCES AND NOTES

1. Permanent address: Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Kom, Egypt.
2. Permanent address: Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt.
3. Present address: Department of Chemistry and Chemical Engineering, The Engineering Academy of Denmark, Building 376, DK-2800 Lyngby, Denmark.
4. J. Fabian, H. Viola, and R. Mayer, Tetrahedron **23**, 4323 (1967).
5. U. Kraatz, *Houben-Weyl*, **E4**, 414 (1983).
6. N. H. Nilsson, *J. Chem. Soc., Perkin Trans. 1*, 1308 (1974).
7. F. Arndt, E. Milde, and G. Eckert, *Ber.* **56**, 1976 (1923).
8. P. Klason, *Ber.* **20**, 2376 (1887).
9. J. V. Braun, *Ber.* **35**, 3377 (1902).
10. H. Rivier and P. Richard, *Helv. Chim. Acta*, **8**, 499 (1925).
11. K. A. Jensen, *J. Prakt. Chem.* **148**, 101 (1937).
12. H. C. Godet and R. E. Wann, *J. Org. Chem.* **26**, 4047 (1961).
13. J. Goerdeler and H. Hohage, *Chem. Ber.* **106**, 1487 (1973).
14. D. M. McKinnon and A. Queen, *Can. J. Chem.* **50**, 1401 (1972).
15. M. Bögemann, S. Petersen, O. E. Schultz and H. Söll, *Houben-Weyl* **9**, 808 (1955).

16. B. Sturm and G. Gattow, *Z. Anorg. Allg. Chem.* **508**, 136 (1984).
17. J. Houben and K. M. L. Schultze, *Ber.* **44**, 3226 (1911).
18. L. C. F. Blackman and M. J. S. Dewar, *J. Chem. Soc.* 162 (1957).
19. E. L. Engelhard, W. C. Iumma, Jr., and W. Saari, **Ger. Offen. 2,433,397** (1975); *Chem. Abstr.* **82**, 156377g (1981).
20. P. Demaree, M. Doria and J. Muchowski, *J. Heterocycl. Chem.* **15**, 1295 (1978).
21. F. Ishii, T. Uchida, A. Miura and M. Tsuruta (Konica Co.), **Jpn. Kokai Tokkyo Koho 01,206,338 [89,206,338]** (1989); *Chem. Abstr.* **112**, 45610w (1990).
22. J. Goerdeler, H. Hohage and I. Zeid, *Chem. Ber.* **109**, 3108 (1976).
23. G. H. Birum, **U. S. Pat. 3,116,335** (1963); *Chem. Abstr.* **60**, 10549d (1964).
24. I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin and A. Senning, unpublished results.
25. H. Viola and R. Mayer, **Ger. (East) 82,464** (1971); *Chem. Abstr.* **77**, 4957e (1972).
26. M. H. River, *Bull. Soc. Chim. Fr.* [4] **1**, 733 (1907).
27. F. Duus, *Compr. Org. Chem.* **3**, 434 (1979).
28. R. M. Hart and M. A. Whitehead, *Can. J. Chem.* **49**, 2508 (1971).
29. A. Hass and K. W. Kampf, *Tetrahedron* **40**, 4963 (1984).
30. H. C. Hanse, B. Jensen and A. Senning, *Sulfur Lett.* **3**, 61 (1985).
31. H. C. Hansen, A. Senning and R. G. Hazell, *Tetrahedron*, **41**, 5145 (1985).
32. A. Kaji, *Bull. Chem. Soc. Jpn.* **34**, 1147 (1961).
33. B. Lindgren, G. Lindgren, E. Artursson, G. Puu, J. Fredriksson and M. Andersson, *J. Enzym. Inhib.* **1**, 1 (1985).
34. J. Nakayama, S. Dan and M. Hoshino, *J. Chem. Soc., Perkin Trans. 1*, 413 (1981).
35. A. Tangerman and B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 2*, 916 (1975).
36. U. Anthoni, B. M. Dahl, H. Eggert, C. Larsen and P. H. Nielsen, *Acta Chem. Scand.* **B30**, 71 (1979).
37. J. L. Charlton, M. S. Loosmore and D. M. McKinnon, *Can. J. Chem.* **52**, 3021 (1974).
38. L. Benati and P. C. Montevecchi, *J. Org. Chem.* **41**, 2640 (1976).
39. G. A. Digenis, B. J. Agha and K. Tsuji, **U.S. US 4,643,991** (1987); *Chem. Abstr.* **106**, 214398s (1987).
40. H. Viola and R. Mayer, *Z. Chem.* **19**, 289 (1979).
41. M. D. Mizhiritskii and V. O. Reikshfeld, *Zh. Obshch. Khim.* **56**, 1547 (1986); *J. Gen. Chem.* **56**, 1373 (1987).
42. A. Haas in *Gmelins Handbook of Inorganic Chemistry, Perfluorohalogen Compounds* **9**, 28 (1971) and references cited therein.
43. H. C. Hansen, Cand. Scient. Thesis, Aarhus University, 1980.
44. W. Ried and B. M. Beck, *Justus Liebigs Ann. Chem.* **673**, 124 (1964).
45. S. Sharma, *Sulfur Rep.* **5**, 1 (1986).
46. R. Bunnenberg and J. C. Jochims, *Chem. Ber.* **114**, 1132 (1981).
47. A. Senning in R. Kh. Freidlina and A. E. Skorova (Eds.), *IUPAC Organic Sulfur Chemistry*, Pergamon Press, Oxford, New York, p. 151 (1981).
48. E. Kühle, *Angew. Chem. Int. Ed. Engl.* **12**, 630 (1973).
49. E. K. Moltzen, K. J. Klabunde and A. Senning, *Chem. Rev.* **88**, 391 (1988).
50. E. K. Moltzen, Cand. Scient. Thesis, Aarhus University, 1985.
51. K. J. Klabunde, M. P. Kramer, A. Senning, and E. K. Moltzen, *J. Am. Chem. Soc.* **106**, 263 (1984).
52. E. K. Moltzen, A. Senning, M. P. Kramer, and K. J. Klabunde, *J. Org. Chem.* **49**, 3854 (1984).
53. E. K. Moltzen and A. Senning, *Sulfur Lett.* **4**, 97 (1986).
54. E. K. Moltzen, B. Jensen and A. Senning, *Sulfur Lett.* **4**, 203 (1986).
55. M. P. Kramer, Ph. D. Thesis, Kansas State University, 1985.
56. E. K. Moltzen, M. P. Kramer, A. Senning and K. J. Klabunde, *J. Org. Chem.* **52**, 1156 (1987).
57. K. J. Klabunde, E. K. Moltzen and K. Voska, *Phosphorus, Sulfur, Silicon* **43**, 47 (1989).
58. J. Nielsen and A. Senning, *Sulfur Lett.* **12**, 143 (1991).
59. J. Nielsen, Cand. Scient. Thesis, Aarhus University, 1990.
60. E. K. Moltzen, B. Jensen, and A. Senning, *Act. Chem. Scand.* **B40**, 609 (1986).
61. S. J. Brois and A. Gutierrez (Exxon Research and Engineering Co.), **U. S. 4,239,636** (1980); *Chem. Abstr.* **94**, 194802 (1981).
62. M. B. Berenbaum and R. H. Gobran (Thiokol Chemical Corp.), **U.S. 3,128,271** (1964); *Chem. Abstr.* **61**, 2038 (1964).
63. [822-38-8]; Aldrich Catalog no. E2,775-0.
64. B. Sturm and G. Gattow, *Z. Anorg. Allg. Chem.* **502**, 7 (1983).
65. A. D. Dunn and W. D. Rudorf, *Carbon Disulfide in Organic Chemistry*, Ellis-Horwood Ltd, Chichester, 1989, p. 341.
66. L. Benati and P. C. Montevecchi, *J. Org. Chem.* **42**, 2025 (1977); eidem, *ibid.* **41**, 2639 (1976).

67. A. W. Mott and G. Barany, *Sulfur Lett.* **2**, 241 (1984).
68. G. Barany, *Tetrahedron Lett.* **24**, 5683 (1983).
69. G. Barany, A. L. Schroll, A. W. Mott and D. A. Halsrud, *J. Org. Chem.* **48**, 4750 (1983).
70. A. Commeyrase, H. Blancou, and P. Moreau, **Ger. Offen, 2,708,751** (1977); *Chem. Abstr.* **87**, 183970e (1977).
71. H. Blancou and A. Commeyras, *J. Fluorine Chem.* **20**, 267 (1982).
72. A. Haas and M. Yazdanbakshch, *Chem. Ber.* **109**, 1976 (1976).
73. A. Senning, *Angew. Chem.* **91**, 1006 (1979).
74. A. Senning, H. C. Hansen, M. F. Abdel-Megeed, W. Mazurkiewicz and B. Jensen, *Tetrahedron*, **42**, 739 (1986).
75. A. Ishii, T. Akazawa, M.-X. Ding, T. Honjo, J. Nakayama and M. Hoshino, *J. Am. Chem. Soc.* **115**, 4914 (1993).
76. E. Schaumann, *Tetrahedron* **44**, 1827 (1988).
77. J. Fabian, *Z. Phys. Chem. (Leipzig)* **250**, 377 (1972).
78. H. Bock, K. Wittel and A. Haas, *Z. Anorg. Allg. Chem.* **408**, 107 (1974).
79. B. Solouki, P. Rosmus and H. Bock, *J. Am. Chem. Soc.*, **98**, 6054 (1976).
80. H. Bock, T. Hirabayashi and S. Mohmand, *Chem. Ber.* **115**, 492 (1982).
81. A. Ohno, K. Nakamura, Y. Nakazima and S. Oka, *Bull. Chem. Soc. Jpn.*, **48**, 2403 (1975).
82. S. Scheithauer, and R. Mayer, *Thio- and Dithiocarboxylic Acids and Their Derivatives*, in: A. Senning (Ed.) *Topics in Sulfur Chemistry*, Vol. 4, Georg Thieme Verlag, Stuttgart, 1979, pp. 192ff. and references cited therein.
83. W. Gombler, *Z. Naturforsch., B: Anorg. Chem.* **36B**, 1561 (1981).
84. R. M. Hart and M. A. Whitehead, *Can. J. Chem.* **49**, 2508 (1971).
85. C. G. Andrieu, P. Metzner, D. Debruyne, D. M. Bertin and H. Lumbroso, *J. Mol. Struct.*, **39**, 263 (1977).
86. H. Viola, S. Scheithauer and R. Mayer, *Chem. Ber.* **101**, 3517 (1968).
87. J. Voss in S. Patai (Ed.), *The Chemistry of Acid Derivativs*, Suppl. B, Part 2, John Wiley & Sons, Chichester, 1979, p. 1021.
88. R. Mayer and S. Scheithauer, *Houben-Weyl* **E5**, 891 (1985).
89. S. R. Ramadas, P. S. Srinivasan, J. Ramachandran and V. V. S. K. Sastry, *Synthesis*, 605 (1983).
90. R. Haraoubia, J.-C. Gressier and G. Levesque, *Makromol. Chem.* **183**, 2367 (1982).
91. A. Haas and W. Wanzk, *Chem. Ber.* **120**, 429 (1987).
92. C. Bruckner and H.-U. Reissig, *Justus Liebigs Ann. Chem.* 465 (1988).
93. K. Hartke and W. Hoederath, *Sulfur Lett.* **1**, 191 (1983).
94. K. Hartke and L. Peshkar, *Arch. Pharm. (Weinheim)* **301**, 601 (1968); eidem, *Pharm. Zentralhalle* **107**, 348 (1968); K. Hartke and L. Seib, *Pharmazie* **25**, 517 (1970); K. Hartke and F. Meissner, *Tetrahedron* **28**, 875 (1972).
95. F. C. V. Larsson and S.-O. Lawesson, *Recl. Trav. Chim. Pays-Bas* **94**, 1 (1975).
96. Y. Aufauvre, M. Verny and R. Vessiere, *Bull. Soc. Chim. Fr.* 1373 (1973).
97. H. Viola, Dissertation, Technical University, Dresden, 1969.
98. H. Viola and R. Mayer, *Z. Chem.* **16**, 355 (1976).
99. N. H. Nilsson, A. Senning, S. Karlsson and J. Sandström, *Synthesis*, 314 (1972).
100. N. H. Nilsson, *Tetrahedron* **30**, 3181 (1974).
101. B. Christiane and H. U. Reibig *Justus Liebigs Ann. Chem.*, 465 (1988).
102. K. Hartke, O. Kunze and W. Hoederath, *Synthesis*, 960 (1985).
103. K. Hartke, H.-D. Gerber and U. Roesrath, *Tetrahedron Lett.* **30**, 1073 (1989).
104. K. Hartke, H.-D. Gerber and U. Roesrath, *Justus Liebigs Ann. Chem.*, 903 (1991).
105. D. G. Crosby and C. Niemann, *J. Amer. Chem. Soc.* **76**, 4458 (1954).
106. A. Rieche, G. Hilgetag, D. Martin and I. Kreyzi, *Arch. Pharm. (Weinheim)* **296**, 310 (1963).
107. W. Walter and K.-D. Bode, *Angew. Chem.* **79**, 285 (1967).
108. S. Lotz and G. Gattow, *Z. Anorg. Allg. Chem.* **581**, 99 (1990).
109. S. Lotz and G. Gattow, *Z. Anorg. Allg. Chem.* **585**, 151 (1990).
110. S. Lotz and G. Gattow, *Z. Anorg. Allg. Chem.* **585**, 142 (1990).
111. G. A. Digenis, J. B. Agha and K. Tsuji, **U.S. US 4,643,991** (1984); *Chem. Abstr.* **106**, 214398s (1987).
112. L. Carlsen and H. Egsgaard, *Chem. Ber.* **120**, 987 (1987).
113. T. Takematsu, M. Konnai, T. Nishida, T. Hosogai, M. Mizano and M. I. Shiguro, **Jpn. Kokai Tokkyo Koho 79,145,654** (1979); *Chem. Abstr.* **92**, 198267h (1980).
114. D. A. Tomalia, D. P. Sheetz and G. E. Ham, *J. Org. Chem.* **35**, 47 (1970).
115. P. L. Fishbein and H. Kohn, *J. Med. Chem.* **30**, 1967 (1987).
116. T. Takematsu, M. Konnai, T. Nishida, T. Hosogai, M. Mizuno and M. Ishiguro, **Jpn. Kokai Tokkyo**

Koho 79,145,215 (1979); *Chem. Abstr.* **92**, 141806d (1980).
117. T. Takematsu, M. Konnai, T. Nishida, T. Hosogai, M. Mizano and M. Ishiguro **Jpn. Kokai Tokkyo Koho 79,145,214** (1979); *Chem. Abstr.* **92**, 141805c (1980).
118. A. Fischer, H. Hansen and W. Rucher, **Ger. Offen 2,312,045** (1974); *Chem. Abstr.* **82**, 4108g (1975).
119. C. W. Voigt and G. Gattow, *Z. Anorg. Allg. Chem.* **438**, 195 (1978).
120. D. H. R. Barton, D. Crich and P. Potier, *Tetrahedron Lett.* **26**, 5943 (1985).
121. S. J. i Skorini, Cand. Scient. Thesis, Aarhus University, 1979, p. 32.
122. S. J. i Skorini and A. Senning *Tetrahedron* **36**, 539 (1980).
123. G. Gattow and S. Lotz, *Z. Anorg. Allg. Chem.* **533**, 99 (1986).
124. G. Schubert and G. Gattow, *Z. Anorg. Allg. Chem.* **579**, 129 (1989).
125. E. Lieber, C. N. Pillai, J. Ramachandran and R. D. Hites, *J. Org. Chem.* **22**, 1750 (1957).
126. E. Lieber, I. Oftendahl and C. N. R. Rao, *J. Org. Chem.* **28**, 194 (1963).
127. D. M. McKinnon and A. Queen, *Can. J. Chem.* **50**, 1401 (1972).
128. A. Queen and T. C. Matts, *Tetrahedron Lett.*, 1503 (1975).
129. H.-R. Kricheldorf, *Synthesis*, 561 (1974).
130. A. Hantzsch and B. Hirsch, *Ber.* **29**, 947 (1896).
131. A.-L. J. Beckwith, V. W. Bowry and C. H. Schiesser, *Tetrahedron* **47**, 121 (1991).
132. S. Sakanone, S. Hawusawa, N. Yamazaki, R. Yoneda and T. Kurihara, *Chem. Pharm. Bull.* **38**, 2981 (1990).
133. D. H. R. Barton, D. O. Jang and J. Cs. Jaszberenyi, *Synlett*, 435 (1991).
134. W. Lüders, G. Salbeck, J. Bauer and H. Bieringer, **Ger. Offen. DE 3,818,848** (1989); *Chem. Abstr.* **112**, 235333f (1990).
135. W. Traber and A. Weiss, **Swiss 544,745** (1974); *Chem. Abstr.* **80**, 82424e (1974).
136. E. Lieber, C. N. Rao, T. S. Chao and C. W. W. Hoffman, *Anal. Chem.* **2**, 916 (1957).
137. R. A. Sneen and H. W. Robbins, *J. Am. Chem. Soc.* **91**, 3100 (1969).
138. R. A. Sneen and A. W. Larsen, *J. Am. Chem. Soc.* **91**, 6031 (1969).
139. G. Kohnstam, *Adv. Phys. Org. Chem.* **5**, 121 (1967).
140. A. Queen, *Can. J. Chem.* **45**, 1619 (1967).
141. A. Queen, D.-M. McKinnon and A. W. Bell, *Can. J. Chem.* **54**, 1976.
142. S. Masson and A. Sene, *Phosphorus Sulfur* **40**, 1 (1988).
143. G. H. Birum, **U.S. 3,089,891** (1963); *Chem. Abstr.* **63**, 5678h (1966).
144. J. T. Bashour, **U. S. 2,676,129** (1954); *Chem. Abstr.* **48**, 8472i (1954).
145. J. T. Bashour, **U. S. 2,731,487** (1956); *Chem. Abstr.* **50**, 15583h (1956).
146. H. J. Renner, G. Schneider and J. Weissflog, **Ger. (East) 15,431** (1958); *Chem. Abstr.* **54**, 2650f (1960).
147. E. S. Blake, **U. S. Patent 2,396,487** (1946); *Chem. Abstr.* **40**, 2974 (1946).
148. M. E. Brokke and D. G. Stoffey, **U.S. 3,247,052** (1966); *Chem. Abstr.* **69**, 1598t (1968).
149. A. Takamizawa and K. Hirai, **Jpn. 72,43,951** (1972); *Chem. Abstr.* **78**, 97702b (1973).
150. B. Sturm and G. Gattow, *Z. Anorg. Allg. Chem.* **512**, 231 (1984).
151. N. H. Nilsson and A. Senning, *Chem. Ber.* **107**, 2345 (1974).
152. N. H. Nilsson, C. Jacobsen and A. Senning, *Chem. Commun.*, 314 (1971).
153. J. Drabowicz, P. Kielbasinski and M. Mikolajzyk in S. Patai (Ed.), *The Chemistry of Sulfenic Acids, Esters and Their Derivatives*, John Wiley and Sons Ltd., Chichester, 1990, p. 376.
154. H. C. Hansen and A. Senning, *J. Chem. Soc., Chem. Commun.*, 692 (1980).
155. H. C. Hansen and A. Senning, *J. Chem. Soc., Chem. Commun.*, 1135 (1979).
156. A. Senning, H. C. Hansen and S. J. i Skorini, *Phosphorus Sulfur* **5**, 359 (1979).
157. S. Holm, J. A. Boerma, N. H. Nilsson and A. Senning, *Chem. Ber.* **109**, 1069 (1976).
158. J. A. Boerma, N. H. Nilsson and A. Senning, *Tetrahedron* **30**, 2735 (1974).
159. S. Holm and A. Senning, *Tetrahedron Lett.* 2389 (1973).
160. N. H. Nilsson and A. Senning, *Organic Sulfur Chemistry*, C. J. M. Stirling (Ed.), Butterworths London, 1975, p. 414.
161. N. H. Nilsson, C. Jacobsen and A. Senning, *Chem. Commun.*, 658 (1970).
162. D. Twiss, *J. Am. Chem. Soc.* **49**, 490 (1927).
163. B. Sturm and G. Gattow, *Z. Anorg. Allg. Chem.* **514**, 129 (1984).
164. G. Didderich and A. Haas, *Chem. Ber.* **109**, 3432 (1976).
165. B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.* **5**, 89 (1970).
166. H. C. Hansen and A. Senning, *Org. Prep. Proced. Int.* **17**, 275 (1985).
167. H. Böhme, M. Brinkmann and H.-P. Steudel, *Justus Liebigs Ann. Chem.*, 244 (1981).
168. G. Barany and A. W. Mott, *J. Org. Chem.* **49**, 1043 (1984).
169. I. W. J. Still, G. Kutney and D. McLean, *J. Org. Chem.* **47**, 555 (1982).
170. A. Haas and K. W. Kampf, *Tetrahedron* **40**, 4963 (1984).

171. G. Didderich, A. Haas and M. Yazdanbakhsch, *Chem. Ber.* **110**, 616 (1977).
172. P. Demaree, M. C. Doria and J. M. Muchowski, *Can. J. Chem.* **55**, 243 (1977).
173. J. M. Beiner, D. Lecadet, D. Paquer, A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 1979 (1973).
174. B. J. Millard and D. L. Pain, *J. Chem. Soc. C*, 2042 (1970).
175. K. P. Zeller, H. Meier and E. Müller, *Tetrahedron* **28**, 1353 (1972).
176. B. R. Baker, M. V. Quarry, S. Bernstein, S. R. Safir and Y. Subarow, *J. Org. Chem.* **12**, 167 (1947).
177. J. Goerdeler, J. Ohm and O. Tegtmeyer, *Chem. Ber.* **89**, 1534 (1956).
178. P. Demaree, M. Doria and J. M. Muchowski, *J. Heterocycl. Chem.* **15**, 1295 (1978).
179. D. E. Horning and J. M. Muchowski, *Can. J. Chem.* **51**, 2349 (1973).
180. G. Lacasse and J. M. Muchowski, *ibid.*, **51**, 2353 (1973).
181. J. A. Marshall and J. J. Partridge, *J. Org. Chem.* **33**, 4090 (1968).
182. L. F. Audrieth, J. R. Johnson, A. W. Brown and C. W. Mason, *J. Am. Chem. Soc.* **52**, 1928 (1930).
183. B. Sturm and G. Gattow, *Z. Anorg. Allg. Chem.* **509**, 67 (1984).
184. W. K. Dean, *J. Organometal. Chem.* **135**, 195 (1977).
185. N. H. Nilsson and A. Senning, *Org. Prep. Proced. Int.* **12**, 229 (1980).
186. Y. Inagaki and R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi* **36**, 1 (1978); *Chem. Abstr.* **89**, 41580v (1978).
187. G. Gattow, *Sulfur Rep.* **14**, 1 (1993).
188. A. Senning, *Sulfur Lett.* **12**, 235 (1991).
189. I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin and A. Senning, *Sulfur Lett.* **15**, 1 (1992).
190. I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin and A. Senning, *Phosphorus, Sulfur, Silicon Relat. Elem.* **86**, 239 (1994).