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STUDIES OF DITHIIRANES AND THIOSULFINES AS REACTIVE INTERMEDIATES

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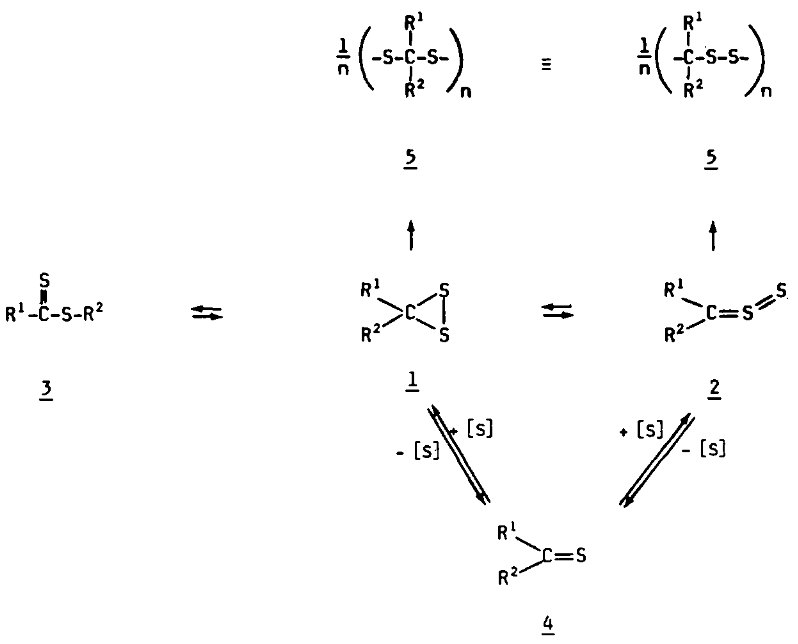
Abstract—Indirect, but compelling evidence for the intermediacy of dithiiranes **1** and thiosulfines **2** has been found by us and is also provided by literature data. The intriguing dithiirane → dithioester rearrangement as well as most of the interrelations and conversions postulated in Scheme 1 have been demonstrated experimentally. In a number of cases acetyl α-chloroalkyl disulfides **16** ($X = Cl$, $Y = COCH_3$) are useful starting materials for the synthesis of thioamides such as **40**.

While the chemistry of some S-coordinated thiocarbonyl derivatives such as thiocarbonyl ylides, thiocarbonyl S-imides, sulfines, and sulfenes (as well as of their cyclic tautomers thiiranes, thiazirines, oxathiiranes, and thiirane 1,1-dioxides) has been relatively well understood for some time the corresponding chemistry of thiosulfines **2** (and dithiiranes **1**), interrelated with the isomeric dithioesters **3** and oligomers **5**, is a more recent development. In the wake of our pilot study of dithiiranes and thiosulfines as reactive intermediates[1,2] additional work has clarified the picture to such an extent that we find it appropriate to sum up our experience in this area and to delineate the state of the art as it presents itself at the end of 1984.§[4–5]

As corroborated by a number of recent independent investigations all extant reports of isolated stable **1/2** are in error and describe in fact dimers, such as 1,2,4,5-tetrathianes **5** ($n = 2$), or oligomers.[2,4,5] A statement in the Houben–Weyl handbook to the effect that tetrathioperoxycarbonic acid has the structure **2** ($R^1 = R^2 = SH$)[6] has no foundation in the cited reference.[7] Alleged $R^1R^1CSe_2$ and $R^1R^1CTe_2$[8] species have also been demonstrated not to be monomeric.



Scheme 1.

Carbon trisulfide **1/2** ($R^1 + R^2 = S$) is an especially simple example of a **1/2** system and deserves to be discussed separately. The species CS_3 has been encountered as a product of the pyrolysis, flash photolysis, and radiolysis, respectively, of CS_2[9,10] and has also been subjected to theoretical treatment[11] as dithiiranethione **1** ($R^1 + R^2 = S$), together with the related C_2 species **6** and **7**.

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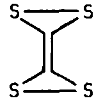
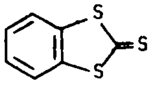
§ The coverage of the literature in this paper is, *inter alia*, based upon a CAS Online substructure search carried out in July 1984.


1 ($R^1 + R^2 = S$) 2 ($R^1 + R^2 = S$)


6


7

The intriguing reaction between benzyne, generated by pyrolysis of phthalic anhydride at 700°, and carbon disulfide yielding **8** and **9** might or might not involve **1/2** ($R^1 + R^2 = S$) as intermediates.[12]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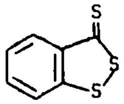
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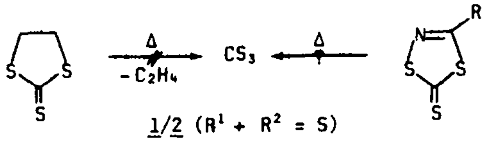
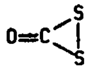
1,3-Dithiolane-2-thione **10**[13] and 1,3,4-dithiazole-2-thiones **11**[14,15] (as well as related heterocycles) are known to react thermally with electrophilic alkynes with formation of the corresponding 1,3-dithiole-2-thiones.

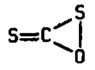


10 11

In the former case, kinetic evidence suggests a concerted reaction between **10** and the alkyne (no intermediate CS_3) while the formation of discrete CS_3 from **11** has not been ruled out.


1 ($R^1 + R^2 = O$)


2 ($R^1 + R^2 = O$)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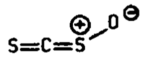
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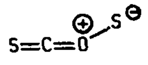
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The five potential tautomers of COS_2[17] which include the dithiirane **1** ($R^1+R^2 = O$) and the thiosulfine **2** ($R^1+R^2 = O$) have been subject to theoretical scrutiny[16] as well as experimental work concerned with laser chemistry,[16] the fate of atmospheric CS_2,[16] and the *in vivo* toxicity of CS_2.[18]

Recent preparative and kinetic work by Oae's group[19] led to the discovery that tertiary amine N-oxides are capable of oxidizing carbon disulfide under mild conditions according to

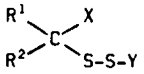
$$CS_2 + R^1R^2R^3NO \longrightarrow COS_2 + R^1R^2R^3N. \quad (1)$$

The likely presence of **1** ($R^1 + R^2 = O$) among the COS_2 tautomers generated was elegantly demonstrated by trapping of disulfane **15** formed by hydrolysis according to

$$\mathbf{1}\ (R^1 + R^2 = O) + H_2O \longrightarrow \underset{\mathbf{15}}{H_2S_2} + CO_2. \quad (2)$$

The radical anion of **1/2** ($R^1 + R^2 = C_6H_5{-}N$) has been generated from the phenylimidogen radical anion and CS_2.[20]

Among generally applicable approaches to the preparative generation of reactive **1/2** intermediates the most straightforward involve 1,3-elimination from suitable precursors **16** or **17**: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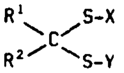
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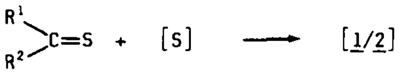
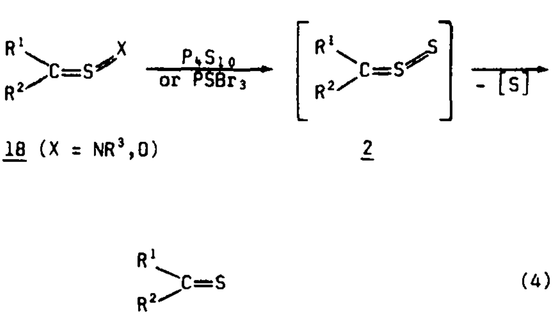
cycloreversions of 5- or 6-membered heterocycles,[2] thiation of thiocarbonyl compounds **4** according to[4]


$$R^1R^2C{=}S + [S] \longrightarrow [1/2] \quad (3)$$
4

and the thiation of heterocumulenes **18**, for instance.[21,22]



18 ($X = NR^3, O$) 2

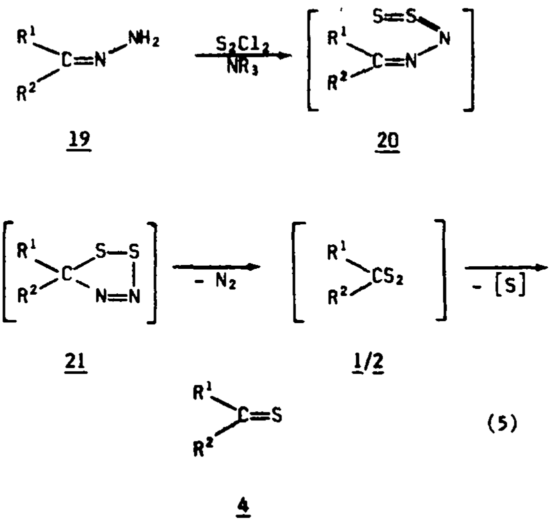
(4)

4

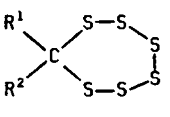
Another synthesis of **4** via a hypothetical **2** intermediate can be effected by treatment of hydrazones **19** with S_2Cl_2.[23–25] In some cases hexathiepanes **22** are also isolated.[23,25]

In a few cases **1/2** intermediates, described as colourless or lightly coloured products which can be kept at low temperatures, but generate the intensely coloured **4** upon warming to room temperature, have been tentatively characterized.[24,25]

It is interesting to note that no 1,2,4-trithiolanes **23** (cf. reaction (6)) have been reported as by-products of these reactions where **2** and **4** are assumed to be present,



(5)



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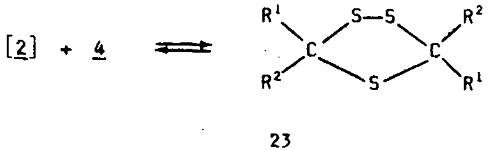
nor is there evidence of the rearrangement in reaction (7).†

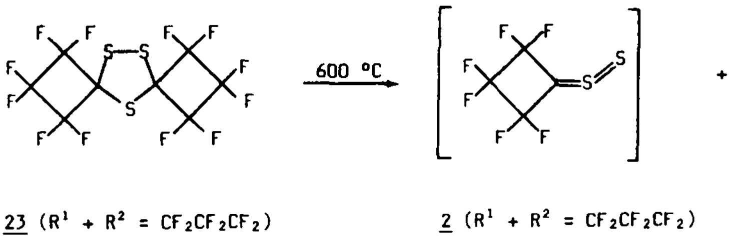


23

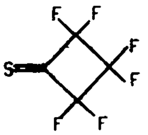
(6)

$$2 \rightarrow 1 \rightarrow 3 \qquad (7)$$

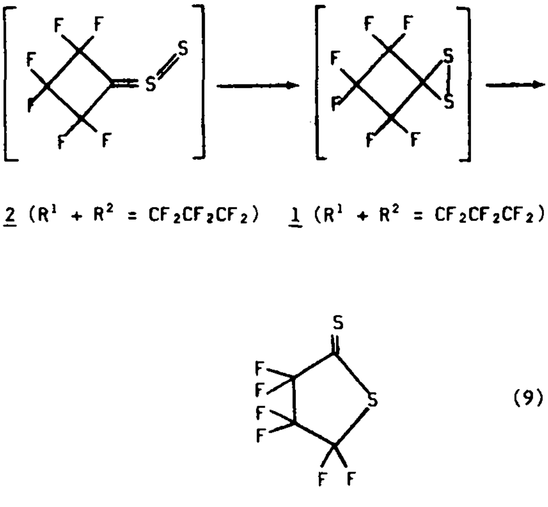
While a number of simple trithiolanes 23 fail to dissociate to 2 and 4 according to reaction (6)[16,27] several cases are on record where 4 form 23 by thiation or unspecific oxidation. Intermediate formation of (*inter alia*) 2 from 23 is evident in the following system.[28]



23 ($R^1 + R^2 = CF_2CF_2CF_2$) 2 ($R^1 + R^2 = CF_2CF_2CF_2$)



(8)



2 ($R^1 + R^2 = CF_2CF_2CF_2$) 1 ($R^1 + R^2 = CF_2CF_2CF_2$)

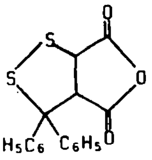
3 ($R^1 + R^2 = CF_2CF_2CF_2$)

(9)

Serendipitous thiation of 4 according to reaction (3)

$$4 \xrightarrow{[S]} [1/2]$$

might well be a key step in the formation of 23 from 1,2,3-thiadiazoles,[29] of 1,2-dithiolane 24 from thiobenzophenone and maleic anhydride,[30] and of a 1,3-dithiole from a cyclic thiourea and diphenylacetylene.[31]



24

A recent report[32] claiming the formation of 1,3-dithiolylium salts from the dication 25 and alkynes does not provide enough experimental detail to prove or disprove the intermediacy of 1/2 ($R^1 + R^2 = Et_2N^+$).

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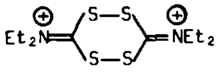
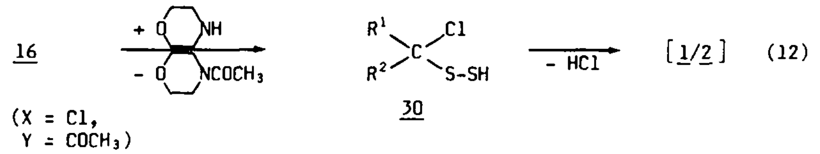
† We have carried out reaction (5) ($R^1 = R^2 = C_6H_5$) in the presence of thiobenzophenone 4 ($R^1 = R^2 = C_6H_5$) and failed to obtain isolable amounts of the notoriously labile 23 ($R^1 = R^2 = R^3 = R^4 = C_6H_5$).[26]



25

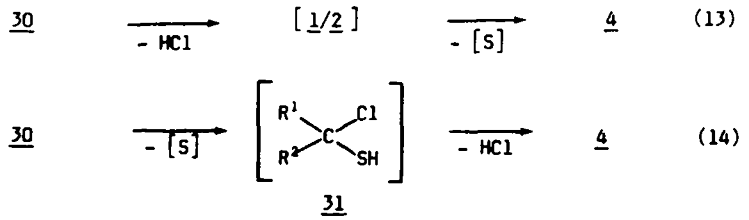
In our experience the appearance of $[R^1R^1CS_2]^+$ peaks in the mass spectra of potential **1/2** precursors such as S-containing heterocycles and acyclic trisulfides has limited prediction value for the course of the pyrolysis of these compounds. Even with sophisticated experimental techniques no **1/2** species could be detected in the mass spectra of such pyrolysates.[27,33]



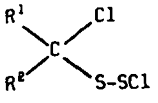
RESULTS AND DISCUSSION

Our efforts to generate and study **1/2** were to a large extent based upon **16** ($X = Cl$, $Y = COCH_3$) as key intermediates, which in turn were prepared from α-chloroalkanesulfenyl chlorides $R^1R^2CClSCl$ **29** and thioacetic acid or from diazoalkanes and acetylchlorodisulfane.

Examples for all theoretical reaction pathways shown in Scheme 1 could be found. However, when final products related to **4** were isolated it was not possible to discern between formation of **4** according to reaction (13) or (14), i.e. the order of the consecutive loss of sulfur and hydrogen chloride, respectively, from **30**.



Attempts to generate **1/2** by 1,3-elimination of chlorine from chloro α-chloroalkyl disulfanes **16** were unsuccessful, but, on the other hand, **1/2** could hardly be expected to survive the reaction conditions chosen by the authors.[34]

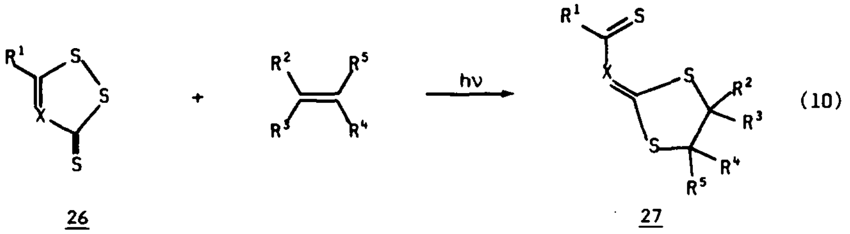


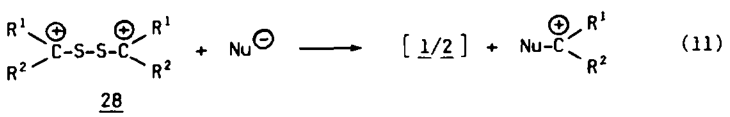
16 (X = Y = Cl)

In addition to the cases mentioned in Ref. 2 the photochemical reaction (10)[35] might well involve **1/2**-type intermediates or related diradicals.

Our first successful attempt to carry out reaction (12) involved **16a** as starting material and was complicated by the dithiirane → dithioester rearrangement **1/2** → **3**.

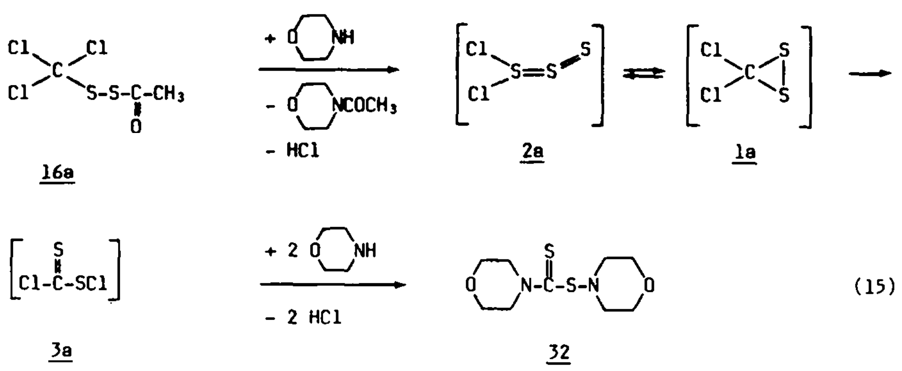
While this experiment was carried out at ambient temperature we later found that reaction (15) takes place below approximately 18°. At higher temperatures the yield of **32** diminishes sharply and varying amounts of oligosulfides **33** (cf. Ref. 37) and S_8 can be isolated besides other, not fully characterized, products.



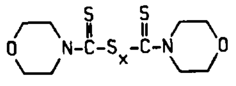


In a study where **4** was isolated after basic hydrolysis of **28** intermediate generation of **1/2** according to reaction (11) was considered in the case of **28** ($R^1 + R^2 = SCH_2CH_2S$), but ruled out because the authors failed to observe any S_8 which they expected if the isolated **4** was formed via **1/2**.[36] However, the authors do not report any experiments in the presence of potential **1/2** scavengers.

Attempts to trap **1a/2a** with a variety of alkynes were unsuccessful nor did experiments aimed at generation of **1a/2a** from **16a** under acidic conditions (for instance for HCl/C_2H_5OH, C_6H_5SH, or $C_6H_5CH_2SH$) meet with success. For instance with thiols **16a** might have been expected to form, *inter alia*, tetrathioperoxy-



(15)



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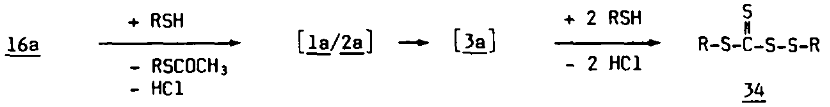
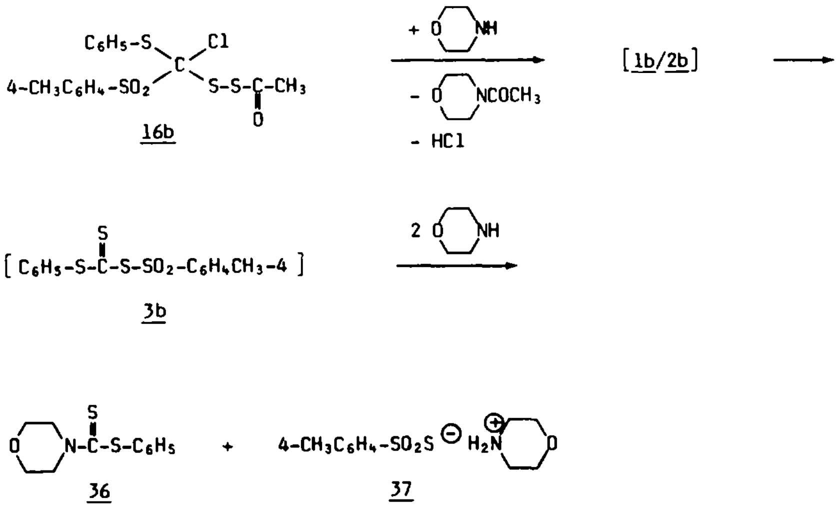
carbonates **34** according to



(16)

In the case of **16b** the same dithiirane → dithioester rearrangement appears to take place in the presence of morpholine. Since the rearranged intermediate **3b** contains a labile anhydrosulfide function[38] the isolable end products are **36** and **37**.[39]



(17)

Here one should take notice of the different migratory aptitudes of R^1 and R^2 in **2b**.

The corresponding reaction of **16c** with morpholine takes a different course. Apparently **2c** is trapped immediately by the nucleophile.

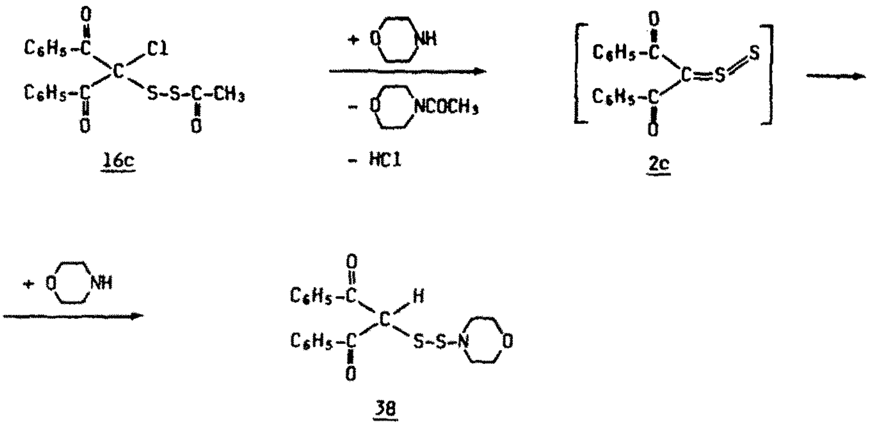
As already encountered in the case of reaction (15), addition of a variety of alkynes failed to trap the hypothetical intermediate **2c** of reaction (18).

When **16d** (generated *in situ* from $(C_6H_5)_2CN_2$ and $CH_3COSSCl$) was treated with morpholine in the usual manner a colourless, highly insoluble product of m.p. 110–112° (forming a blue melt) was obtained, the crude data of which were compatible with the structure **5d** ($n = 2$), i.e. 3,3,6,6-tetraphenyl-1,2,4,5-tetrathiane **39**. However, further work with reaction (19) was abandoned when our efforts to fully characterize **5d** met with limited success.

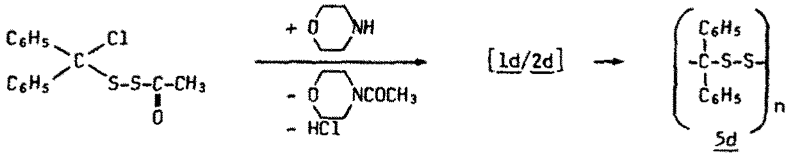
The remaining **16** ($R^2 = X = Cl$) investigated by us was converted by morpholine to products derived from **4**, cf. reactions (13) and (14) discussed above. These results are presented in Tables 1 and 2.

In a number of cases reaction (20) leads to thioamides **40** inaccessible by other methods, cf. Table 2.

In the case of **16h** → **40h** we ruled out the involvement of a preequilibrium (21) (analogous to the reported behaviour of $CClF_2CF_2SSCF_2CClF_2$[40]) by demonstrating the absence of ^1H-NMR signals in the crude reaction mixture assignable to **42**[41] and/or its decomposition products.



(18)



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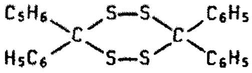

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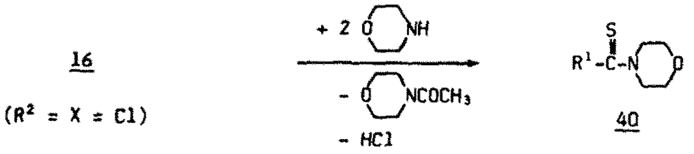
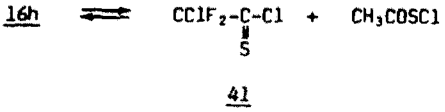
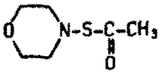


(20)



$$\underline{16h} \rightleftharpoons CClF_2\text{-}C(=S)\text{-}Cl + CH_3COSCl$$

(21)



42

EXPERIMENTAL

All reactions were followed by TLC (Merck Kieselgel 60). The identity of all products was checked by elemental analysis in order to rule out the presence of compounds spectroscopically and chromatographically identical with known compounds, but containing additional S atoms.

The sulfenyl chlorides $R^1R^2CClSCl$ **29a**, **e**, **g** and **h** were commercial products and used as received.

The sulfenyl chlorides $R^1R^2CClSCl$ **29b**,[42] **c**,[43] **f**,[44] **i**,[45] **j**,[46] **k**,[47] and **l**,[47] were prepared according to literature procedures.

Acetyl α-chloroalkyl disulfides **16**

Equimolar amounts of **29** and thioacetic acid were dissolved in CCl_4 and kept at 50–60° until the reaction was complete. The products were isolated by vacuum distillation or by recrystallization. The compounds **16** so obtained are shown in Table 1.

Reactions (15), (17), (18) *and* (20)

Starting material **16** (X = Cl, Y = CH_3CO) (0.1 mol) is dissolved in 100 ml ether or benzene and treated, under

Table 1. Acetyl α-chloroalkyl disulfides **16** ($X = Cl$, $Y = CH_3CO$)*

Compound	R^1	R^2	Mp. (°C)(solvent) bp. (°C)/mmHg	n_D^{20}	Yield (%)	Found/Calculated				Formula (MW)	Ref. and notes
						C	H	Cl	S		
16a	Cl	Cl	109-110/10	1.5680	82	15.75 15.98	1.27 1.34	46.32 47.16		$C_3H_3Cl_3OS_2$ (225.5)	48
16b	C_6H_5S	$4\text{-}CH_3C_6H_4SO_2$	85–87 (ethanol)	-	95	45.93 45.87	3.63 3.61	8.72 8.46	30.14 30.61	$C_{16}H_{15}ClO_3S_4$ (419.0)	-
16c	C_6H_5CO	C_6H_5CO	-	-	-					-	43
16d	C_6H_5	C_6H_5	-	-	-					-	**
16e	$CHCl_2$	Cl	87/0.23	1.5827	63				23.36 23.40	$C_4H_4Cl_2OS$ (274.0)	-
16f	CCl_3	Cl	97/0.30	1.5891	60				20.76 20.79	$C_4H_3Cl_5OS_2$ (308.5)	-
16g	CCl_2F	Cl	106/0.25	1.5560	43				22.44 21.96	$C_4H_3Cl_4FOS_2$ (292.0)	-
16h	$CClF_2$	Cl	70/0.25	1.5212	51				23.63 23.27	$C_4H_3Cl_2F_2OS$ (275.5)	-
16i	C_2H_5OOC	Cl	94-96/0.26	1.5332	61					$C_6H_8Cl_2O_3S_2$ (263.2)	***
16j	C_6H_5NHCO	Cl	85-86 (ether-pet.ether)	-	81			22.59 22.86	20.71 20.67	$C_{10}H_9Cl_2NO_2S_2$ (310.2)	-
16k	C_6Cl_5O	Cl	94-97 (ether-pet.ether)	-	70	24.14 23.74	0.82 0.66	54.33 54.49	13.06 14.08	$C_9H_3Cl_7O_2S_2$ (455.4)	-
16l	C_6Cl_5S	Cl	111-113 (ether)	-	64	22.93 22.93	0.65 0.64			$C_9H_3Cl_7OS_3$ (471.5)	-

* All compounds exhibited satisfactory IR, ^1H NMR, and mass spectra

** Prepared *in situ* from $(C_6H_5)CN_2$ and $CH_3COSSCl$, no spectral or analytical data available

*** 16i was impure as judged by a high sulfur analysis, but did furnish the expected 40i when subjected to reaction (20)(see Table 2)

Table 2. Thioamides **40** obtained according to (20)*

Compound	R^1	Mp. (°C)(solvent) bp. (°C)/mmHg	Lit.mp. (Ref.) bp.		Yield (%)	Found/Calculated				Formula (MW)	
						C	H	Cl	S		
40e	$CHCl_2$	103-111 (**)			42				15.32 14.97	$C_6H_9Cl_2NOS$	(214.1)
40f	CCl_3	90-94 (**)			42				13.13 12.90	$C_6H_8Cl_3NOS$	(248.6)
40g	CCl_2F	99-102 (pentane)			37				13.95 13.82	$C_6H_8Cl_2FNOS$	(232.1)
40h	$CClF_2$	59-61 (**)	61–62	(40)	49				14.80 14.87	$C_6H_8ClF_2NOS$	(215.6)
40i	C_2H_5OOC	120/0.4	150-151/3	(52)	37				15.54 15.77	$C_8H_{13}NO_3S$	(203.3)
40j	C_6H_5NHCO	169-170 (ethanol)	166	(53)	76				12.20 12.81	$C_{12}H_{14}N_2O_2S$	(250.3)
40k	C_6Cl_5O	238-244 (benzene)			71	33.56 33.40	2.10 2.04	44.55 44.82	8.43 8.11	$C_{11}H_8Cl_5NO_2S$	(395.5)
40l	C_6Cl_5S	186 (CCl_4)			83	31.84 31.86		44.06 43.07	15.54 15.58	$C_{11}H_8Cl_5NOS_2$	(411.6)

* All compounds exhibited satisfactory IR, ^1H NMR, ^{13}C NMR, and mass spectra

** Purified by sublimation

stirring, with 0.6 mol of morpholine, dissolved in 50 ml of the same solvent. The rate of the addition is such that no appreciable rise of the temp of the mixture occurs. The mixture is extracted three times with water, dried over $CaCl_2$, and evaporated *in vacuo*. The residue is recrystallized from the appropriate solvent.

Reaction (15). After recrystallization from EtOH **32**, m.p. 137–139° (lit.[49] m.p. 128–134°), is obtained in 22% yield.

Reaction (17). After recrystallization from EtOH **36**, m.p. 141° (lit.[50] m.p. 138–141°), is obtained in 60% yield. In a separate run the mixture was treated with excess MeI at reflux. By preparative TLC (eluent: ether–petroleum ether 1 : 3) *p*-toluenethiosulfonic acid *S*-methyl ester, m.p. 56–58° (lit.[51] m.p. 58°), could be isolated.

Reaction (18). After recrystallization from EtOH **38**, yellow crystals, m.p. 121–122°, are isolated in 25% yield. IR (cm^{-1}, KBr) 1680 s, 1660 s; ^1H-NMR (δ, $CDCl_3$) 2.9 m (4H), 3.6 m (4H), 6.07 s (1H), 7.2–8.2 m (10H); ^{13}C-NMR (δ, $CDCl_3$) 55.4 ($N{-}\underline{C}H_2$), 66.9 ($O{-}\underline{C}H_2$), 68.8 (S—C—H), 128.9, 129.3, 134.0, 135.2 (aromatic), 191.5 (C=O);[54] MS (*m*/*z*, 70 eV) 373 (M), 286 ($M-C_4H_9NO$), 254 ($M-C_4H_9NOS$). (Found: C, 60.42; H, 5.51; N, 3.43; S, 16.67. Calc for $C_{19}H_{19}NO_3S_2$ (373.5): C, 61.10; H, 5.13; N, 3.75; S, 17.17%.)

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