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THE CHEMISTRY OF GEMINAL DISULFENYL DICHLORIDES

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The chemistry of geminal disulfenyl dichlorides $R^1R^2C(SCl)_2$ is reviewed based on CAS and Beilstein Online substructure and supplementary searches.

Keywords: Active methylene compounds; chlorination; geminal disulfenyl dichlorides; 1,3λ⁴,5,2,4-trithiadiazines

CONTENTS

1. INTRODUCTION

The existing literature on geminal disulfenyl dichlorides **1** is very sketchy and fragmented and to date no coherent picture of the chemistry of these compounds seems to have emerged. It is therefore intended here to present a full bibliography as well as a comprehensive appraisal of the known chemistry of **1**.

Geminal disulfenyl dichlorides **1** constitute a distinctive subclass of sulfenyl chlorides with potential for the construction of heterocycles and polymers. Sulfenyl chlorides are a well known type of compounds whose synthesis and reactivity are well documented in the literature. Major reviews can be found in handbooks like Patai[1] and Houben-Weyl.[2] The more general methods for the preparation of sulfenyl chlorides include chlorination of sulfides, thiols, and thiocarbonyl compounds, reaction between SCl_2 and CH-acidic (mainly mono- or dicarbonyl) compounds, and addition of SCl_2 to double and triple bonds. Alkanesulfenyl chlorides are colored liquids (yellow to red), the lower alkanesulfenyl chlorides being rather unstable. Arenesulfenyl chlorides are mostly colored liquids or solids (orange to yellow).

Synthetic methods appropriate for **1** are found among the general methods for the preparation of sulfenyl chlorides mentioned above.

The reactions of **1** can be categorized as substitution reactions, additions to double bonds, and redox reactions.

2. THE SYNTHESIS OF GEMINAL DISULFENYL DICHLORIDES

The synthesis of **1** has mainly been carried out by treatment of active methylene compounds **2** with SCl_2 or by chlorination of suitable starting materials such as sulfides. A complete overview over these methods is given below.

In a substructure search for **1** with CAS and Beilstein Online five journal articles[3,4,6–8] and one patent[5] covering a total of eight **1** were found. A manual search uncovered one additional **1** mentioned in one relevant docu-

TABLE I Geminal disulfenyl dichlorides $R^1R^2C(SCl)_2$ **1**, registry numbers and references

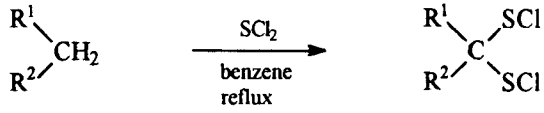
Cmpd.	*R^1, R^2*	*CAS Reg. No.*	*Ref.*
1a	$R^1 = R^2 = PhNHCO$	128174-86-7	[3,4]
1b	$R^1 = R^2 = 2\text{-}CH_3C_6H_4NHCO$	*	[3]
1c	$R^1 = R^2 = EtOCO$	128174-88-9	[4]
1d	$R^1 = PhNHCO$ $R^2 = EtOCO$	128174-87-8	[4]
1e	$R^1 = MeOCO$ $R^2 = t\text{-}BuOCO$	128174-89-0	[4]
1f	$R^1 = R^2 = Cl$	17494-65-4	[4-7]
1g	$R^1 = R^2 = H$	114079-01-5	[4,8]
1h	$R^1 + R^2 = CH_2(CH_2CH_2)_2$	*	[4]
1i	$R^1 = R^2 = Me$	*	[9]

*These compounds have no CAS registry numbers

ment.[9] These nine compounds and the corresponding literature references are collected in Table I together with their respective CAS registry numbers.

2.1. From Active Methylene Compounds

The first synthesis of **1** was carried out in 1926 by Naik *et al.*[3] These authors treated the active methylene compounds **2a** and **2b** with SCl_2 in refluxing benzene and isolated 2,2-bis(chlorosulfanyl)-*N*,*N*′-diphenylpropanediamide **1a** and 2,2-bis(chlorosulfanyl)-*N*,*N*′-bis(2-methylphenyl)-propanediamide **1b**, respectively, as stable crystalline products. Com-pounds **1a** and **1b** were only characterized by elemental analysis. This rudimentary work was partly repeated and expanded by Rees *et al.* who confirmed the structure of **1a** with spectroscopic data and by derivatization. The range of **1** was then expanded to include substitution with electron-withdrawing groups other than amide groups such as ester groups by treatment of the corresponding **2** with SCl_2 in refluxing benzene according to Eq. (1).[4]



(1)

2a: $R^1 = R^2 = PhNHCO$
2b: $R^1 = R^2 = 2\text{-}CH_3C_6H_4NHCO$
2c: $R^1 = R^2 = EtOCO$
2d: $R^1 = PhNHCO$; $R^2 = EtOCO$
2e: $R^1 = MeOCO$; $R^2 = t\text{-}BuOCO$

1a, 1b, 1c, 1d, 1e

Compounds **1c, 1d**, and **1e** were obtained as crude oils. Their structures were established by means of spectroscopy and derivatization with bis(trimethylsilyl)sulfur diimide **3** (see 4.1.1.). The experimental data concerning the preparation of **1a, 1c, 1d**, and **1e** are shown in Table II.

The exact reaction conditions are very important. When **2c** was treated with SCl_2 at r.t. without solvent a mixture of diethyl 2-chloropropanedioate **4** and diethyl 2-chloro-2-(chlorosulfanyl)propanedioate **5** were obtained after vacuum distillation without any trace of **1c**.[10] As a general rule **1** derived from **2** are very easily prepared and remarkably stable to storage.

2.2. From Carbon Disulfide

The addition of chlorine to the C=S bond of thiocarbonyl compounds is well known and has been thoroughly reviewed.[11] Such a reaction has been used for the preparation of dichloromethanedisulfenyl dichloride **1f** according to Eq. (2).[4,5]

$$CS_2 \xrightarrow{Cl_2} ClS{-}CCl_2{-}SCl \qquad (2)$$

1f

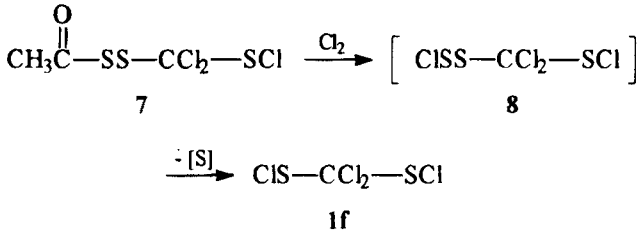
Compound **1f** was prepared by coirradiation of CS_2 and chlorine at −15 to −5 °C in a photochemical reactor where careful monitoring was needed to prevent chlorinolysis of **1f**. Even so, trichloromethanesulfenyl chloride **6** is always formed as an inconvenient by-product and can only be removed from **1f** by high vacuum distillation resulting in considerably loss of **1f**. In addition to its spectroscopic characterization the structure of **1f** was confirmed by derivatization with **3** (cf. 4.1.1.).[4] Compound **1f** has also been detected as a minor component of commercial trichloromethanesulfenyl chloride **6** prepared by non-photolytic chlorination of CS_2.[7]

TABLE II Geminal disulfenyl dichlorides $R^1R^2C(SCl)_2$ **1**, reaction times and yields

Compd.	*R^1, R^2*	*reaction time*	*yield (%)*	*Ref.*
1a	$R^1 = R^2$ = PhNHCO	3.5 h	34	[4]
1c	$R^1 = R^2$ = EtOCO	36 h	99	[4]
1d	R^1 = PhNHCO R^2 = EtOCO	1 h	97	[4]
1e	R^1 = MeOCO R^2 = *t*-BuOCO	36 h	55	[4]

2.3. From Thiocarboxylic Acid S-Esters

Another approach to the synthesis of **1f** is the chlorination of 7 with chlorine at –10 °C according to Eq. (3). After vacuum distillation **1f** is obtained in 56% yield without **6** as by-product.[6]

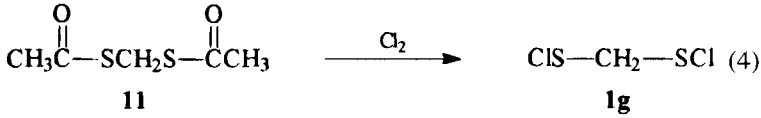


(3)

It is reasonable to assume that **1f** is obtained from **7** by asymmetric cleavage of the disulfide bond, followed by spontaneous loss of sulfur from the unstable intermediate **8**. It was possible to isolate elemental sulfur from the reaction mixture. This can be regarded as proof that **1f** is not formed by symmetric cleavage of the disulfide bond. Furthermore, no acetylsulfenyl chloride, MeCOSCl, **9**, the expected coproduct of a symmetric S-S cleavage, could be found in the reaction mixture. This further supports the postulate that **8** is an unstable intermediate of this reaction.[6] The asymmetric cleavage of acetyl disulfides is a known phenomenon first reported by Böhme.[12]

The structure of **1f** could be ascertained by spectroscopy and by derivatization with morpholinium *p*-toluenesulfinate **10** (cf. 4.1.2.).

Cleavage of an Ac-S bond by chlorine has also been used in the preparation of other **1**. By treatment of *S,S*-methylene bis(thioacetate) **11** with two equivalents of chlorine at –18 °C methanedisulfenyl dichloride **1g** could be prepared according to Eq. (4).[8]



(4)

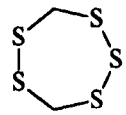
S-[(Chloromethyl)sulfanylmethyl] thioacetate, $MeCOSCH_2SCl$, **12** was obtained as a by-product due to incomplete chlorination of **9**. Neither **1g** nor **12** were isolated, but instead derivatized with cyclohexene **13** (cf. 4.2.) immediately after preparation. By characterization of the derivatives thus prepared the presence of **1g** and **12** after the chlorination of **11** could be confirmed.

2.4. From Oligosulfides

A number of **1** have been prepared by chlorination of appropriate oligosulfides.

2.4.1. From 1,2,3,5,6-pentathiepanes

Chlorinolysis of lenthionine **14** at 0 °C gave methanedisulfenyl dichloride **1g** according to Eq. (5).[4]



14

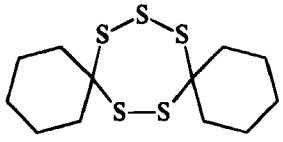
$$\xrightarrow{Cl_2} \quad ClS{-}CH_2{-}SCl \quad (5)$$

1g

The labile **1g** was not isolated, but immediately derivatized with **3** (cf. 4.1.1.). The derivative was isolated and characterized to prove the presence of **1g**.

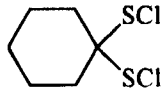
A second compound could be isolated and identified by conversion to a derivative of (chlorodisulfanyl)methanesulfenyl chloride, $ClSSCH_2SCl$, **15**. Compound **15** obviously forms from **14** after incomplete S-S bond cleavage by chlorine.

1,1-Cyclohexanedisulfenyl dichloride **1h** is obtained by chlorinolysis of 7,8,15,16,17-pentathiaspiro[5.2.5.3]heptadecane **16** at –5 °C according to Eq. (6).[4]



16

$$\xrightarrow{Cl_2}$$



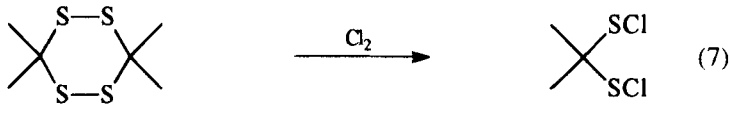
(6)

1h

The presence of **1h** was confirmed by derivatization with triethyl phosphite **18** (cf. 4.1.3.).

2.4.2. From 1,2,4,5-tetrathianes

Treatment of 3,3,6,6-tetramethyl-1,2,4,5-tetrathiane **17** with chlorine at –70 °C results in cleavage of the two disulfide bonds. Thus, 2,2-propanedisulfenyl dichloride **1i** is obtained according to Eq. (7).[9]

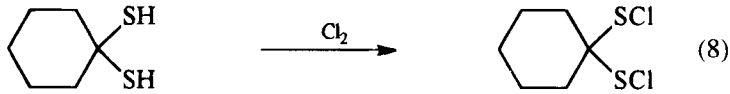


17 1i (7)

Compound **1i** was subsequently derivatized with **18** (cf. 4.1.3.) in lieu of isolation and characterization.

2.5. From Geminal Dithiols

The chlorination of thiols is a well known method for the preparation of sulfenyl chlorides in general. Subject to the availability of geminal dithiols it is also applicable to **1**. Compound **1h** has been obtained by chlorination of 1,1-cyclohexanedithiol **19** with sulfuryl chloride at r.t. according to Eq. (8).[4]

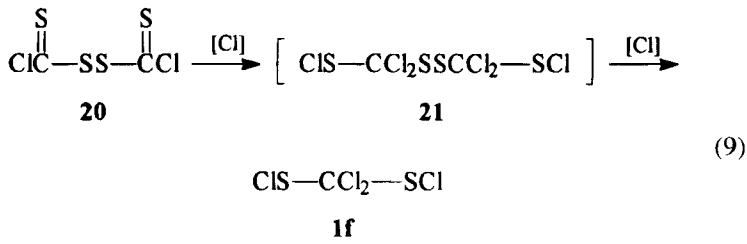


19 1h (8)

The presence of **1h** was demonstrated by derivatization with **3** (cf. 4.1.1.).

2.6. From Chlorodithioformates

Treatment of **20** with chlorine at 0 °C gave **1f** according to Eq. (9).[6]



20 21 1f (9)

Since thiocarbonyl groups are more susceptible to chlorination than S-S bonds[11] the reaction sequence in Eq. (9) is likely to take place via the reactive intermediate **21**. All attempts to chlorinate **20** with chlorine or sulfuryl chloride in various solvents and at various temperatures resulted in a mix-

ture of **1f** and trichloromethanethiosulfenyl chloride **22** as shown both by spectroscopy and by derivatization with **10** (cf. 4.1.2.). A possible pathway to **22** is unsymmetrical cleavage of the disulfide group in the intermediate **21**, but a more likely route is a chlorotropic rearrangement of **1f** to **22**. Such rearrangements of sulfanyl substituted alkanesulfenyl chlorides and of α-sulfanyl-α-sulfonylalkanesulfenyl chlorides ($[R^1SO_2][R^2S]CR^3SCl$) are well documented.[13–16] The occurrence of this mixture of **1f** and **22** is most inconvenient; separation by distillation is impossible due to the very close boiling points of the two isomeric compounds.

3. SPECTROSCOPIC PROPERTIES OF GEMINAL DISULFENYL DICHLORIDES

The spectroscopic data for **1** are very limited and only two papers contain state-of-the-art spectroscopic data.[4,6] In both cases the compounds in question are substituted with electron-withdrawing groups. Simple aliphatic compounds of type **1** have always been used immediately after preparation for "one-pot" reactions and no attempts to isolate these compounds have been described. All available IR, ^1H NMR, ^{13}C NMR, and MS data for **1** are presented in Table III.

TABLE III Spectroscopic data for **1**

Cmpd.	*IR (cm^{-1})*	*^1H NMR, δ*	*^{13}C NMR, δ*	*MS (m/z)*	*Ref.*
1a	(Nujol) 3285, 1647, 1598, 1537, 1510, 1446, 1235, 742	[$(CD_3)_2CO$] 7.1–7.9 (10 H, br m), 10.5 (2 H, br s)	–	–	[4]
1c	($CHCl_3$) 2985, 1736, 1269, 1028, 521	($CDCl_3$) 1.3 (6 H, t), 4.4 (4 H, q)	($CDCl_3$) 13.89, 64.41, 79.65, 163.76	292 (M^+), 260, 84, 29	[4,17]
1d	– (3 H, t), 4.3 (2 H, q), 7.1 7.8 (5 H, m), 8.8 (1 H, br s)	($CDCl_3$) 1.3 –	– 303, 271, 78	339 (M^+),	[4]
1e	– (9 H, s), 3.9 (3 H, s)	($CDCl_3$) 1.5	– 259, 227, 57	306 (M^+),	[4]
1f	(NaCl) 825, 800, 780, 725	–	($CDCl_3$) 99.79	216 (M^+), 181, 146, 114	[6]

4. THE CHEMICAL PROPERTIES OF GEMINAL DISULFENYL DICHLORIDES

The reactions of **1** can be categorized in three groups. Substitution reactions with nucleophiles, additions to double bonds, and redox reactions.

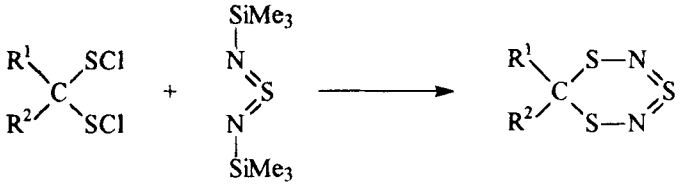
4.1. Reactions with Nucleophiles

The electrophilic sulfenyl chloride groups of **1** can take part in substitution reactions with nitrogen, sulfur, and phosphorus nucleophiles.

4.1.1. Reactions with nitrogen nucleophiles

The interest of Rees *et al.*[4] for **1** originates from their work with 1,3λ^4,5,2,4-trithiadiazines **23**. Originally they used tetrasulfur tetranitride and diazoalkanes to prepare **23**, but the scope of these reactions was limited to the formation of alkyl and aryl substituted **23**.[18] They sought a more rational route to this ring system, which was also compatible with functional groups on the ring carbon of **23**. A very attractive route to be considered was the reaction of a 1,3-bis-nucleophilic NSN component with a 1,3-bis-electrophilic SCS component. The choice fell on bis(trimethylsilyl)sulfur diimide **3** as the former component and on **1** as the latter precursor.

Several **1**, both containing electron-withdrawing substituents and alkyl substituents, were treated with **3** to yield **23** according to Eq. (10).[4]



(10)

1a, 1c, 1d, 1e, 1f, 1g, 1h **3** **23a, 23b, 23c, 23d, 23e, 23f, 23g**

The high-dilution technique was employed to minimize polymerization, the best yields being obtained with slow simultaneous addition of **1** and **3**. In Table IV the varying yields of **23** indicate that **1** containing electron-withdrawing groups seem to be more reactive towards **3** than unsubstituted aliphatic **1** with the exception of **23d**. This result needs further elaboration

TABLE IV Yields of 1,3λ⁴,5,2,4-trithiadiazines **23**

Cmpd.	*R^1, R^2*	*yield (%)*	*Ref.*
23a	$R^1 = R^2 =$ PhNHCO	52*	[4]
23b	$R^1 = R^2 =$ EtOCO	49*	[4]
23c	$R^1 =$ PhNHCO $R^2 =$ EtOCO	46*	[4]
23d	$R^1 =$ MeOCO $R^2 = t$-BuOCO	13*	[4]
23e	$R^1 = R^2 =$ Cl	56*	[4]
23f	$R^1 = R^2 =$ H	12**	[4]
23g	$R^1 = R^2 = CH_2(CH_2CH_2)$	22**	[4]

*Yield of the last reaction step
**Total yield of the reaction sequence

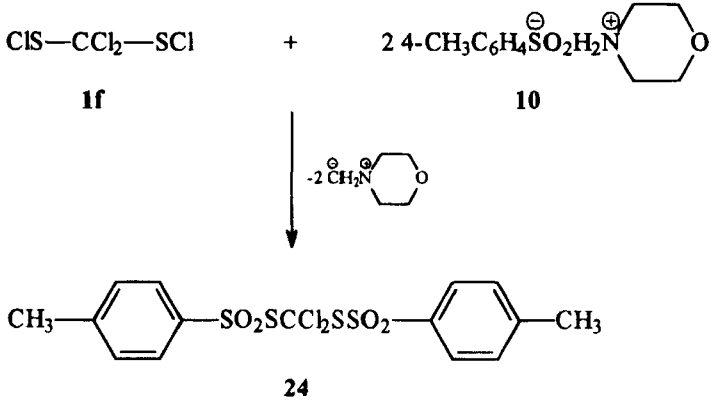
since **1g** and **1h** were not isolated, but treated *in situ* with **3**. Therefore, in these two cases only the total yield of the complete reaction sequence is known.

The isolation and identification of **23f** and **23g** were used as evidence for the presence of the not directly observed **1g** and **1h**.

It can be concluded that **1** are good synthetic precursors for **23**, particularly for **23** with electron-withdrawing substituents on the ring carbon atom.

4.1.2. Reactions with sulfur nucleophiles

In the synthesis of **1f** from **20** compound **22** was generated as an inconvenient by-product which could not be removed from **1f**. Beyond the characterization of this mixture by spectroscopy it was also derivatized with morpholinium *p*-toluenesulfinate **10**. The disubstituted product S,S-(dichloromethylene) bis(*p*-toluenesulfonothioate) **24** was obtained after treatment of **1f** with **10** at 0 °C according to Eq. (11).[6]

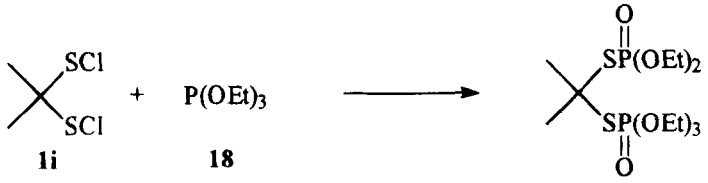


(11)

S-(Trichloromethyl) *p*-toluenesulfonodithioperoxoate, 4-$MeC_6H_4SO_2SCCl_3$, **25** was also isolated from the reaction mixture, thereby confirming the presence of **22** as a by-product of the chlorination of **20**.

4.1.3. Reactions with phosphorus nucleophiles

The derivative **26** was obtained after treatment of **1i** with triethyl phosphite **18** according to Eq. (12).[9]

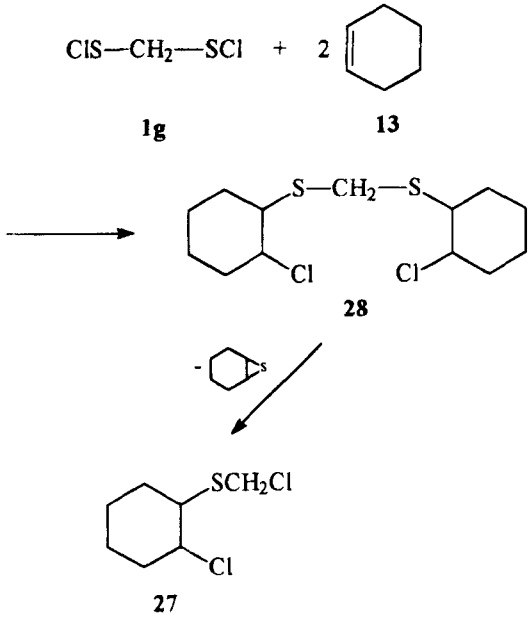


1i **18** **26** (12)

The authors present no physical nor spectroscopic evidence to confirm their result, therefore this claim must be regarded with caution.

4.2. Reactions with Alkenes

The reaction of **1** with an alkene has been reported. Crude **1g** was treated with cyclohexene **13** at –20 °C according to Eq. (13).[8]



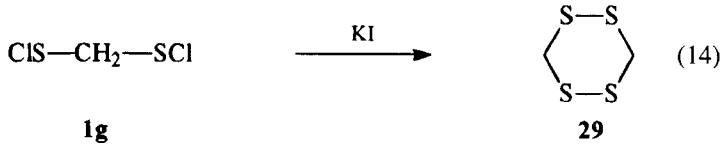
1g **13** **28** **27** (13)

2-Chloro-1-(chloromethylsulfanyl)cyclohexane **27** was isolated by vacuum distillation. A possible pathway to **27** is via formation of the intermediate **28** formed by addition of **1g** to two equivalents of cyclohexene. The intermediate **28** loses 7-thiabicyclo[4.1.0]heptane, thereby yielding **27**. Whether this loss of 7-thiabicyclo[4.1.0]heptane from **28** occurs spontaneously or is induced by the distillation could not be determined.

4.3. Redox Reactions

When **1g** was treated with aqueous KI as a reducing agent different products were obtained. There was found a correlation between the type of product and the ratio of **1g** to **12** after the preparation of **1g** from **11**.

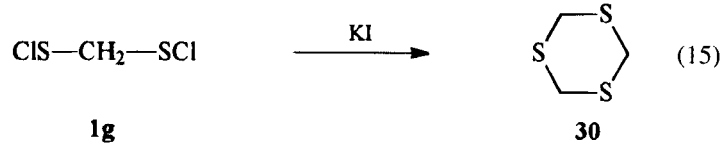
When **11** was treated with one equivalent of chlorine, **1g** was obtained as minor product compared to **12**. Subsequent treatment of the reaction mixture with aqueous KI led to 1,2,4,5-tetrathiane **29** according to Eq. (14).[8]



(14)

1g **29**

Compound **1g** was obtained as the main product when **11** was treated with two equivalents of chlorine. Treatment of the crude reaction product with KI gave 1,3,5-trithiane **30** according to Eq. (15).[8]



(15)

1g **30**

The authors provide no explanation of these observations. Strong dependence of the outcome on the relative concentrations of **1g** and KI must be one of the factors responsible.

5. CONCLUSION

The known chemistry of **1** is still too rudimentary to allow the routine preparation of a large variety of **1** and their routine utilization for synthetic

purposes such as polymerizations and cyclizations. Even for some of the known compounds such as **1f** the known methods of preparation are too cumbersome to allow extensive investigations of their synthetic potential.

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