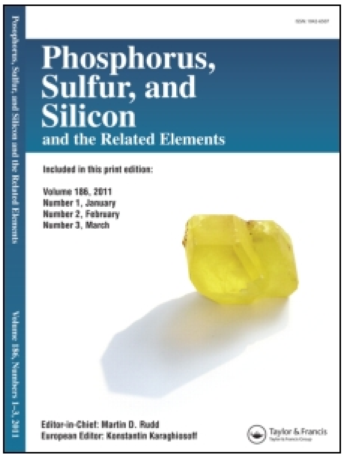

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The Chemistry of Alk-1-yn-1-yl Disulfides—A Review

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The preparation and the properties of the elusive alk-1-yn-1-yl disulfides are reviewed, including the most recent quantum chemical findings with regard to their reactivity.

Keywords Alkynes; alk-1-yn-1-yl disulfides; disulfides; thioketenes

INTRODUCTION

At present, a total of 23 observed or postulated alk-1-yn-1-yl disulfides are on record,[1–10] which can be conveniently divided into three subclasses, the monofunctional **1**, the difunctional **2**, and the lone cyclic disulfide **3**, cf. Table I. It should be noted that compound **1b** is an artifact created by the indiscriminate manipulation of Markush formulas by Chemical Abstracts and does not actually appear in the cited patent,[3] neither explicitly nor by implication.

THE PREPARATION OF ALK-1-YN-1-YL DISULFIDES

The very first alk-1-yn-1-yl disulfide to be mentioned in the literature in 1963 was **2c**, claimed by Schmidt and Potschka[11] to be formed by the reaction sequence (1) and (2). However, our reexamination of this early claim 30 years later showed that the product assumed to possess the structure **2c** was, in fact, a mixture of the dithioles (*Z*)-**4** and (*E*)-**4**,

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

The author is grateful to Professor Emeritus J. Hahn, Department of Inorganic Chemistry, University of Cologne, Germany for providing a reprint of Ref.[7]

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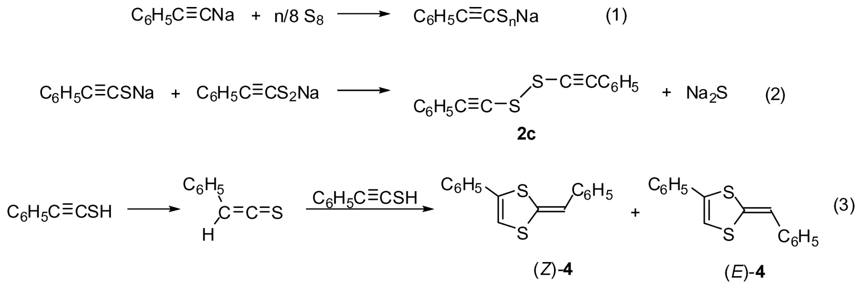
TABLE I Alk-1-yn-1-yl Disulfides

	R^1	R^2	Ref.
	Monofunctional alk-1-yn-1-yl disulfides **1**		
1a	H	H	1,2,9
1b	H	[[5-hydroxy-4-(hydroxymethyl)-6-methylpyridin-3-yl]methyl]	3
1c	Me	Me	4
1d	Me	Me_2N	4
1e	*t*-Bu	Me	4
1f	*t*-Bu	*t*-Bu	4–7
1g	*t*-Bu	Ph_3C	5
1h	*t*-Bu	Ph	5–7
1i	*t*-Bu	Me_2N	4
1j	*t*-Bu	morpholin-4-yl	5
1k	Ph	Me	5
1l	Ph	CCl_3	5
1m	Ph	C_2Cl_3	5
1n	Ph	*t*-Bu	5
1o	Ph	Ph_3C	5
1p	Ph	Ph	5
1q	Ph	morpholin-4-yl	5,8
1r	Ph	Cl	5
1s	HSS	H	1
	Difunctional alk-1-yn-1-yl disulfides **2**		
	$R^1 = R^2$		Ref.
2a	H		9
2b	*t*-Bu		6,7
2c	Ph		5
	Cyclic alk-1-yn-1-yl disulfide		
3	1,2-dithiacyclooct-3-yne		10

Eq. (3), probably caused by inadvertent partial protonation of the key phenylethynethiolate ion (Scheme 1).[5]

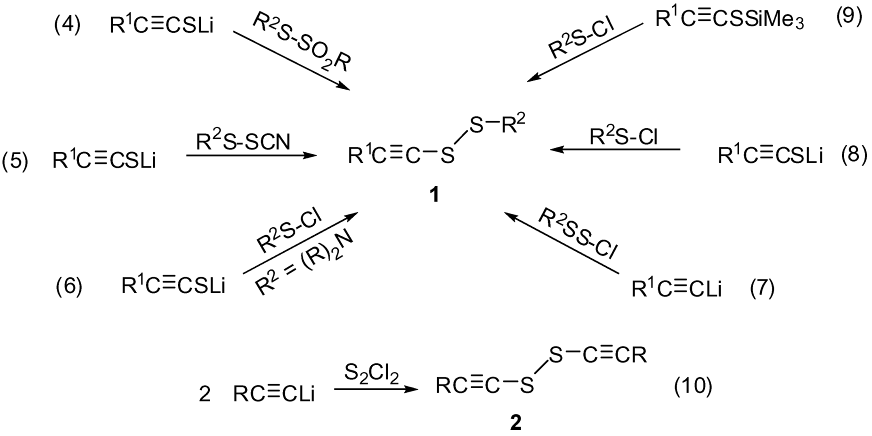
Authentic alk-1-yn-1-yl disulfides **1**, i.e., **1c–f** and **1i**, became first available in 1972 through the work of Meijer et al.[4] Here the key alk-1-yne-1-thiolate ion was *S*-sulfenylated with a thiosulfonate (Eq. 4), a sulfenyl thiocyanate (Eq. 5), or a sulfenyl chloride (Eq. 6). These disulfides could be purified by ultra-low vacuum distillation and were described as reddish liquids. This red hue is most likely due to partial rearrangement to the corresponding thioketenes **5**, vide infra.

In 1992, Hahn and Hosch[7] prepared the rather labile disulfides **1f** and **1h** by treatment of the appropriate lithium alk-1-yn-1-ide with a thiosulfenyl chloride, Eq. (7), an alk-1-yne-1-thiolate with a sulfenyl chloride, Eq. (8), or from a 1-(trimethylsilylthio)alk-1-yne and a sulfenyl



SCHEME 1

chloride, Eq. (9). An equally labile disulfide **2b** was obtained from a lithium alk-1-yn-1-ide and disulfur dichloride, Eq. (10) (Scheme 2).



SCHEME 2

Finally, the disulfides **1f–h** and **1j–q**, some of them reasonably stable, were prepared by Nørkjær and Senning[5] according to methods (7) and (8) while an attempted synthesis of **2c** according to Eq. (10) only led to a rearrangement product, vide infra. The use of disulfide **1q** as an auxiliary in a Japanese patent[8] remains unclear in the absence of appropriate references to its source.

The hypothetical thiosulfenyl chloride **1r** must by necessity be an intermediate in reaction (10) with $R = C_6H_5$, but cannot be observed directly.[5]

Ethynyl hydrogen disulfide (**1a**)[1,2] and 1,2-bis(disulfanyl)ethyne (**1s**)[1] have so far only been dealt with in theoretical work. The likewise hypothetical and without doubt highly labile diethynyl disulfide (**2a**)[9] and 1,2-dithiacyclooct-3-yne (**3**)[9,10] have so far only received attention in computational chemistry, vide infra.

THE PHYSICAL PROPERTIES OF ALK-1-YN-1-YL DISULFIDES

While a number of compounds **1** are stable enough for elemental analysis and conventional spectroscopic characterization, neither most of **2** nor **3** have been amenable to physical characterization. Compounds **1c–f** and **1i** exhibit the expected ^{1}H NMR and IR spectroscopic features.[4] Hahn and Hosch[7] observed **1f**, **1h**, and **2b** by ^{13}C NMR, but only in admixture with their rearrangement products, the corresponding thioketenes **5e**, **5h**, and **7b**, respectively, as well as products of oligomerization and polymerization. In fact, this study aimed at the preparation of such oligomers and polymers. XANES (X-ray absorption near end) spectra of **1f**, **1h**, and **2b** were also obtained, but without an independent check of the identity and integrity of the samples used.[6]

In the study of Nørkjær and Senning,[5] the liquid disulfides **1f**, **1l**, **1n**, and **1p** were found too unstable for elemental analysis, but still amenable to IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The liquid disulfides **1g**, **1h**, **1j**, **1k**, and **1o** gave satisfactory elemental analyses, as well as IR, ^{1}H NMR, and ^{13}C NMR spectra. The only room temperature solid in their series of **1** was **1m** (mp 52.0–52.8°C), likewise with satisfactory elemental analyses and spectral data.

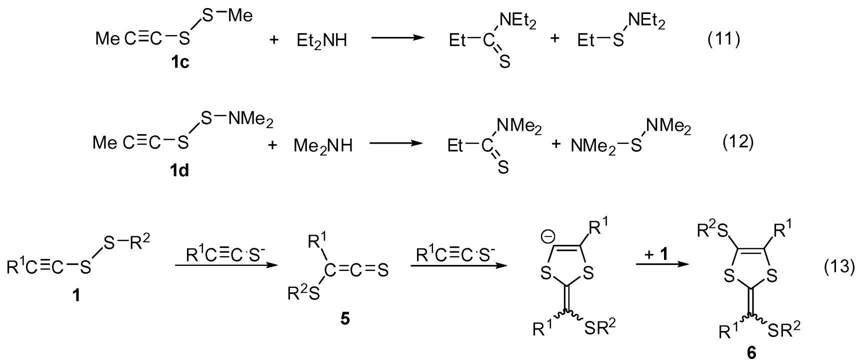
Quantum chemical calculations predict a ΔH_f° value of 67 kcal mol^{-1} for **1a** and of 80 kcal mol^{-1} for **1s**.[1]

An MNDO theoretical study of the geometrical ring strain of nine isomeric dithiacyclooctynes showed that 1,2-dithiacyclooct-3-yne **3** is severely strained (E_g 17.7 kcal mol^{-1}), only surpassed by the isomer 1,4-dithiacyclooct-2-yne (E_g 18.4 kcal mol^{-1}).[10] The rearrangement of **3** to **8** according to Eq. (16), vide infra, would, of course, relieve this ring strain.

The calculated CSSC dihedral angle of **2a** is 83.5°,[9] well within the accepted experimental range for common acyclic disulfides, i.e., 80–100°.[12]

THE CHEMISTRY OF ALK-1-YN-1-YL DISULFIDES

The disulfide **1c** was shown to react with diethylamine according to Eq. (11). The corresponding reaction between **1d** and dimethylamine proceeded according to Eq. (12).[4] Compounds **1** furthermore dimerize, catalyzed by the mesomeric alk-1-yne-1-thiolate ions and via the corresponding thioketene **5**, to the corresponding 2-methylene-1,3-dithioles **6**, Eq. (13) (Scheme 3).[13]



SCHEME 3

For each subclass of alk-1-yn-1-yl disulfides, a rearrangement to the corresponding thioketene, i.e., **5**, **7**, and **8**, respectively, can be considered as a possible reaction mode, cf. Eqs. (14), (15), and (16).

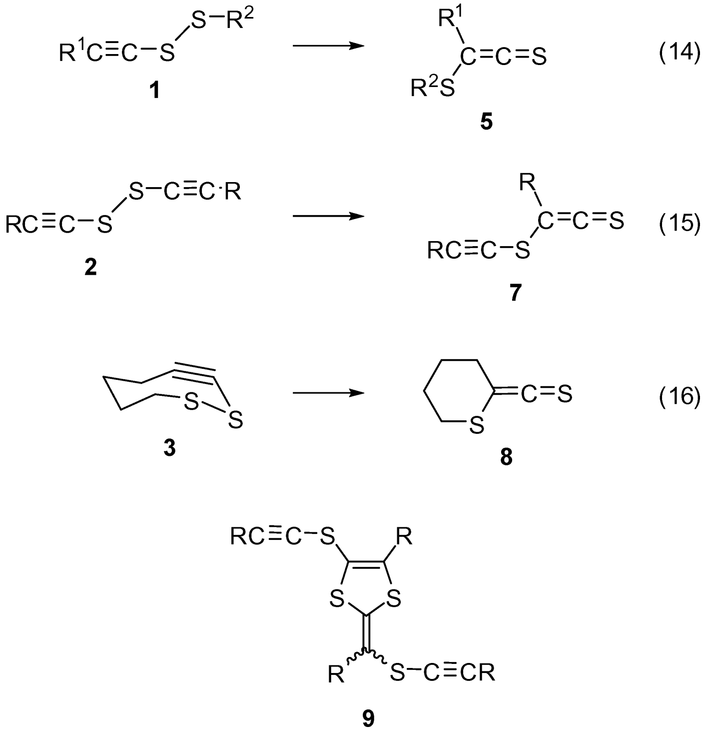
The first explicit mention of such a rearrangement is that by Hahn and Hosch,[7] who obtained the disulfide/thioketene mixtures **1f/5f**, **1h/5h**, and **2b/7b** upon attempted synthesis of the mentioned disulfides, vide supra. These thioketenes further formed oligomers and/or polymers that could be processed to thin films with potential electric conductivity.

Nørkjær and Senning[5] observed five disulfides, i.e., **1f**, **1h**, **1k**, **1l**, and **1n**, to rearrange to the corresponding thio substituted thioketenes **5f**, **5h**, **5k**, **5l**, and **5n**, respectively, Eq. (14). These thioketenes, easy to spot because of their characteristic red color, formed in small to minute yields and could only be characterized spectroscopically.

In the same study, attempts to prepare authentic **2c** led to the isolation and characterization of the 1,3-dithiole derivatives (*E*)-**9c** and (*Z*)-**9c** (R = Ph) as an inseparable mixture. This was taken as evidence that **2c** had indeed been formed as an intermediate that rearranged according to Eq. (15) to form the elusive thioketene **5c** (R = Ph), which subsequently dimerized in an anion-assisted reaction (Scheme 4).[5]

Thioketene chemistry has recently been shortly reviewed by Spanka and Schaumann.[14]

In an ongoing in silico mechanistic study, Shim and Senning[9] examined the theoretically possible pathways for these rearrangements, i.e., 1) a [1,3]-sigmatropic shift, 2) a homolytic cleavage of the sulfur–sulfur bond, followed by recombination, 3) a heterolytic cleavage of the



SCHEME 4

sulfur–sulfur bond, followed by recombination, or, finally, 4) some kind of bimolecular rearrangement. In ab initio calculations, the transition states for the rearrangements of the symmetrical model compounds **2a** and **2c**, as well as **3**, were explored. It was found that the activation energy, enthalpy, and Gibbs energy, $\Delta E_e^{\ddagger}$, $\Delta H^{\ddagger}_{298.15}$, and $\Delta G^{\ddagger}_{298.15}$, for the rearrangement **2a** → **7a** as derived in G3(MP2) calculations amount to 36.1, 34.7, and 35.2 kcal mol^{-1}, respectively. The reaction is exergonic with $\Delta G_{298.15}$ amounting to –13.4 kcal mol^{-1}. The data suggest that the rearrangement **2a** → **7a**, Eq. (15), occurs as a [1,3]-sigmatropic shift.

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