1-Alkynyl Disulfides: Their Characterization and Their 1-Thiapropargyl–3-Thiaallenyl Rearrangements

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The synthesis of novel 1-alkynyl disulfides **1** is described together with their 1-thiapropargyl–3-thiaallenyl rearrangement and a [1,3]-sigmatropic shift of 1-alkynyl amino disulfides, followed by rearrangement of the aminothio-substituted thioketenes so formed.

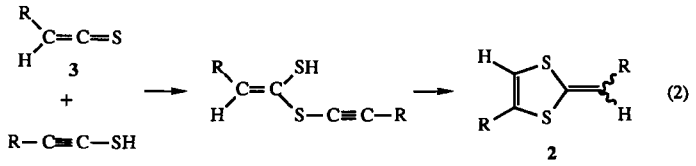
1-Alkynyl Disulfides

While 1-alkynyl sulfides are a well known and well understood class of compounds[1] the corresponding disulfides **1** have only been mentioned rarely[2–4], the very first account[2] even being in error, as shown by us (vide infra). The first account of a 1-alkynyl disulfide was Schmidt and Potschka's report of the synthesis of bis(phenylethynyl) disulfide (**1a**) by oxidation of phenylethynethiolate anion with sulfur according to eq. (1)[2]. Compound **1a** was only characterized by its melting point and elemental analysis. In our present study we repeated their synthesis and found that the product reported as **1a** is in fact 4-phenyl-2-(phenylmethylene)-1,3-dithiole (**2a**) (**2**, R = C_6H_5), formed by addition of 2-phenylethynethiolate anion to phenylthioketene according to eq. (2). Replacement of sulfur by hexacyanoferrate(III) as the oxidant also furnished **2a**. Both stereoisomers could be obtained from this reaction. The (*Z*) stereochemistry of the lower melting **2a** was established by an X-ray crystal structure analysis[5].

$$C_6H_5C{\equiv}CNa + {}^n/_8\,S_8 \rightarrow C_6H_5C{\equiv}CS_nNa \qquad (1a)$$

$$C_6H_5C{\equiv}CSNa + C_6H_5C{\equiv}CS_2Na \rightarrow Na_2S + \underset{\mathbf{1a}}{C_6H_5C{\equiv}C\text{-}S\text{-}S\text{-}C{\equiv}CC_6H_5} \qquad (1b)$$

$$C_6H_5C{\equiv}CNa + C_6H_5C{\equiv}CS_3Na \rightarrow Na_2S + \mathbf{1a} \qquad (1c)$$

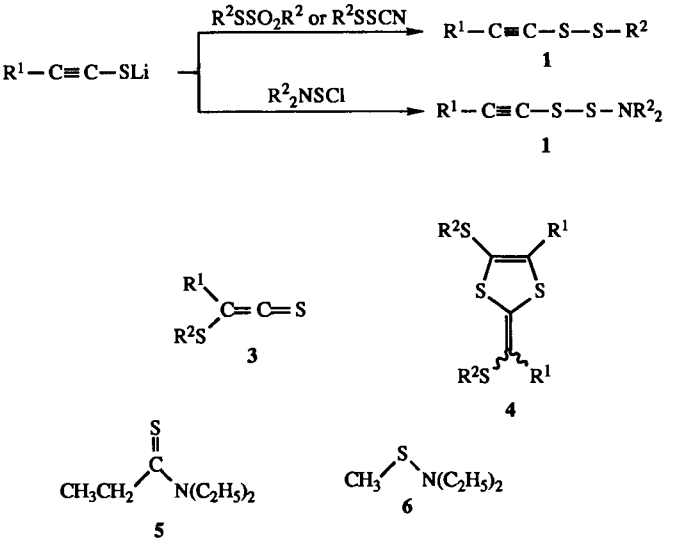


(2)

2

The first authentic 1-alkynyl disulfides were prepared by Brandsma et al.[3] according to Scheme 1. In a side reaction, which was not further investigated, Brandsma et al.[4] observed a product which can be explained either by a 1-thiapropargyl–3-thiaallenyl rearrangement of **1** to the corresponding thioketene **3** which then adds 1-alkynethiolate anion to form, after acidification, the 1,3-dithiafulvene **4**. Alternatively, the thioketene **3** could be formed by *C*-sulfenylation of the ambident 1-alkynethiolate anion.

Scheme 1



Treatment of **1b** (**1**, $R^1 = R^2 = CH_3$) with dimethylamine generated, via the corresponding thioketene **3b** and 1-alkynethiolate anion, the corresponding thioamide **5** and sulfenamide **6**.

Rearrangements of 1-Alkynyl Sulfides

1-Thio-substituted alkynes can be subject to rearrangement to thioketenes either by the [3,3]-sigmatropic (hetero-Cope, thio-Claisen)[6] pathway or by the [1,3]-sigmatropic (1-thiapropargyl–3-thiaallenyl) route.

Known examples of the first type include rearrangements of 1-alkynyl allyl[7,8,9], 1-alkynyl propargyl[10,11], and 1-alkynyl 1-allenyl sulfides[8,12]. Of the second type are the classical spontaneous rearrangement of 1-alkynethiols to

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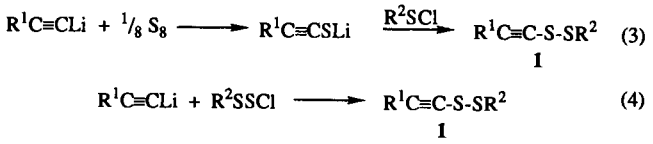
thioketenes[13–20], the rearrangement of e.g. 1-(elementothio)alkynes to elemento-substituted thioketenes[21–23], and the rearrangement of a 1-alkynesulfenyl chloride to a chlorothioketene[24].

Results and Discussion

We were able to prepare new 1-alkynyl disulfides according to two routes, the first according to eq. (3) and the second according to eq. (4). Thio-substituted thioketenes **3** are obtained as rearrangement products of the disulfides **1**.



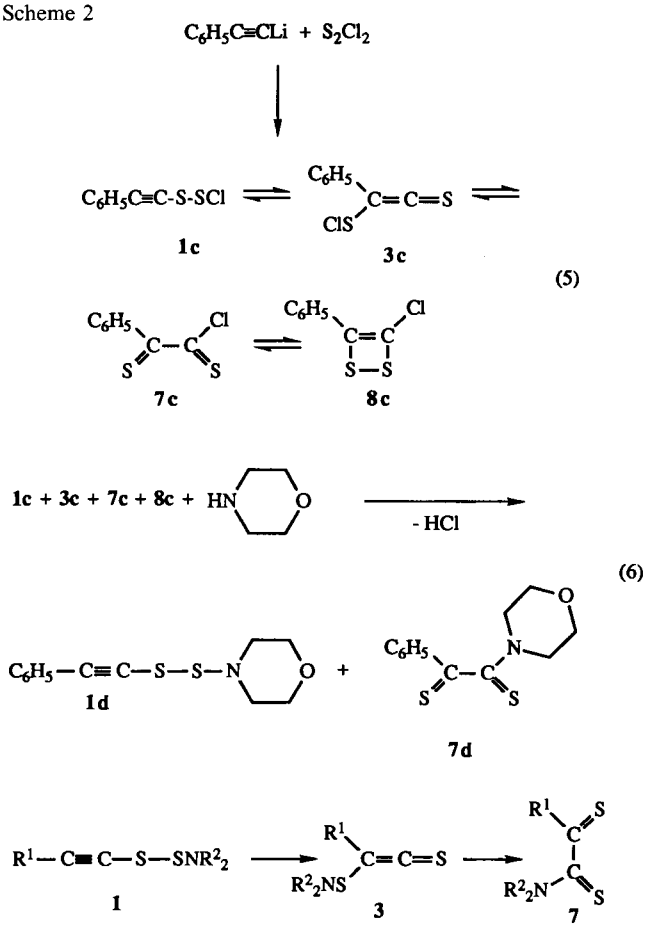
When we kept the equilibrium mixture containing the 1-alkynylchlorodisulfane **1c** in solution at −78°C [eq. (5)] and subsequently treated it with an amine [eq. (6)] we obtained a mixture of the unsymmetric disulfide **1d** and the corresponding rearranged aminothio-substituted thioketene **3d**, the 1,2-dithione **7d** (cf. Scheme 2). The major product was **7d**. The unsymmetric disulfide **1c** was shown by UV experiments to have a half-life of 45 h at room temperature in chloroform solution; thus the bulk of the **7d** isolated is formed from the amine and the potential tautomers **3c**, **7c** and/or **8c** in equilibrium with **1c** rather than by rearrangement of **1d**.

Of the twelve disulfides prepared here (cf. Table 1 and Experimental) five compounds (**1e**, **f**, **i**, **j**, and **m**) rearrange to the corresponding, directly observable thioketenes **3e**, **f**, **i**, **j**, and **m**, one (**1a**) is isolated as a dimer (**9a**), and the remaining six disulfides **1d**, **g**, **h**, **k**, **l**, and **n** appear to possess unlimited shelf life. The rearrangements could not be catalyzed with Lewis acids or bases as suggested by Schaumann[26b]. Two further thioketenes, **3d** (**3**, $R^1 = C_6H_5$, R^2_2N = morpholino) and **3h** [**3**, $R^1 = (CH_3)_3C$, R^2_2N = morpholino)], if formed from the corresponding chlorothio-substituted thioketenes **3** (R^2 = ClS), rearrange by a [1,3]-sigmatropic shift to yield the corresponding α-dithiones **7d** and **7h**, cf. Scheme 2 and Experimental.

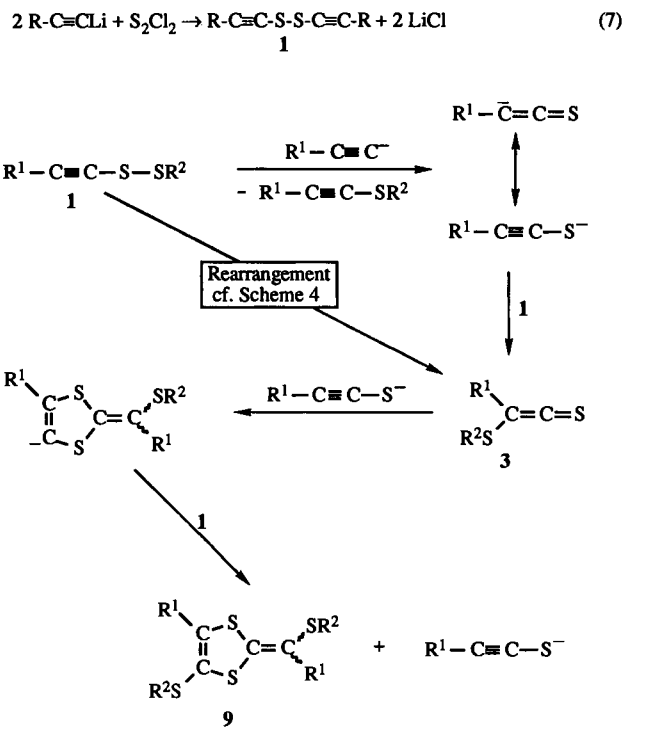
The thioketenes prepared by us (by necessity all containing a thio substituent) are generally stable in solution at room temperature for a few or even for 12 hours (based on IR spectra). The thioketene derived from **1e** seems to be stable in solution for several months. None of the neat acetylenes rearrange to the corresponding thioketenes, but it seems that the rearrangement is induced by adsorption on large surfaces, i.e. on silica gel, used as adsorbent in the column chromatography. Previously eleven thio-substituted thioketenes have been reported[27–36].

Attempted synthesis of **1a** according to eq. (7) leads to the unsymmetric thioketene dimer **9a** (**9**, $R^1 = C_6H_5$, $R^2 = C_6H_5C{\equiv}C$)[37]. The formation of this product can be explained by the general route outlined in Scheme 3, i.e. either by rearrangement (cf. Scheme 4) or via the 1-ethynethiolate anion and the thio-substituted thioketene, eventually yielding the dimer.

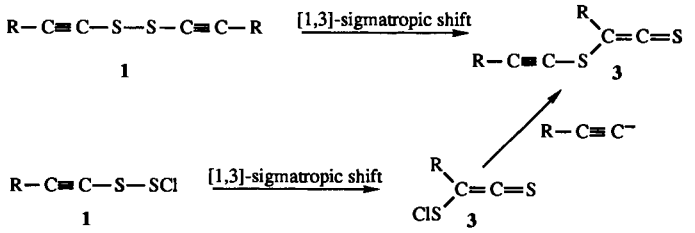
Scheme 2



Scheme 3

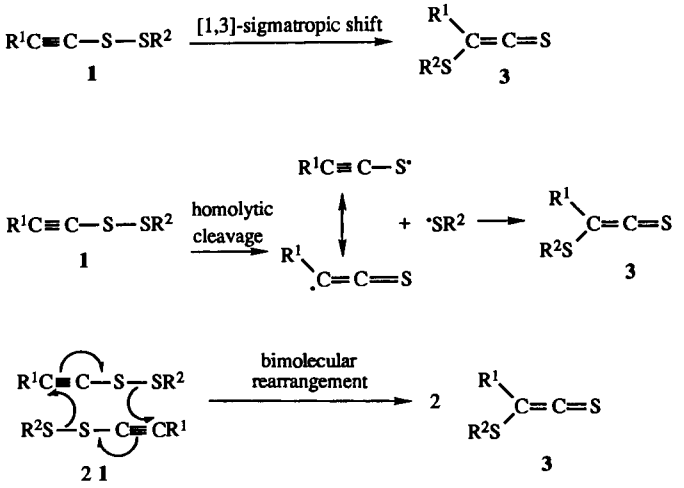


Scheme 4



The proposed mechanism of the shift of the thio group is not necessarily a concerted [1,3]-sigmatropic shift. Other possibilities are 1) homolytic cleavage of the S–S bond, followed by coupling of the solvent-caged radicals; 2) and 3) heterolytic cleavage of the S–S bond to yield ions for either a cationic or an anionic shift; 4) a bimolecular rearrangement (cf. Scheme 5). So far the mechanism in operation has not been elucidated.

Scheme 5



Experimental

All operations were carried out under N_2 in three-necked round-bottom glass flasks fitted with a dropping funnel or syringe inlet and a magnetic stirrer. All solvents were dried. *n*BuLi in pentane was added by means of a syringe. The workup consisted of washing with water, drying, and concentration of the organic phase in vacuo, followed by column chromatography (Merck silica gel 60, 70–230 mesh ASTM). Starting compounds: C_6H_5SSCl[25,38], Cl_3CSSCl[38,47], *t*BuSCl[39], C_6H_5SCl[40], $O(C_2H_4)_2NSCl$[41], MeSCl[42], and C_2Cl_2SCl[43].

1-Alkynyl Dilsulfides **1** *and/or Thioketenes* **3**, *General Method:* The alkyne (0.011 mol) was dissolved in diethyl ether (100 ml), and upon cooling to −78 °C *n*BuLi, dissolved in pentane (5 ml, 2 M), was added and the mixture allowed to warm to room temp.

Route A: The solution of the alkynide anion thus prepared was added slowly at room temp. to the chlorodisulfane (0.010 mol), dissolved in diethyl ether (100 ml).

Route B: The alkynide anion solution was cooled to −78 °C, then elemental sulfur (0.011 mol) was added and this reaction mixture, after warming up to room temp., added to the appropriate sulfenyl chloride (0.010 mol), dissolved in diethyl ether (100 ml). The product was isolated by column chromatography (eluent petroleum ether or diethyl ether/petroleum ether). For compound data see Tables 1–3.

4-Phenyl-2-(phenylmethylene)-1,3-dithioles **2a**: Schmidt and Potschka's synthesis[2] was repeated. For convenience 2-phenylethynyllithium was substituted for the original 2-phenylethynylsodium; this substitution does not appear to have changed the course of the reaction. Workup of the reaction mixture with water and recrystallization of the crude product from diethyl ether gave an

Table 1. Physical and analytical data of **1**

Compound	R^1	R^2	Yield (%)	Route	IR ν(C≡C) [cm^{-1}]	n_D/[°C] or m.p. [°C]	Mol. formula (Mol. weight)		C	H	Cl	N	S
1d	C_6H_5	morpholino	75	B	2162		$C_{12}H_{13}NOS_2$ (251.4)	Calcd.	57.34	5.22			
								Found	57.88	5.35			
1e	*t*Bu	*t*Bu	14	B	2158	1.552/27		[a]					
1f	*t*Bu	C_6H_5	46	A	2159	1.5895/18	$C_{12}H_{14}S_2$ (222.4)	Calcd.	64.82	6.35			[b]
								Found	64.84	6.58			
1g	*t*Bu	$C(C_6H_5)_3$	32	B	2153	[c]	$C_{25}H_{24}S_2 \cdot 0.08\ CHCl_3$ (398.1)[d]	Calcd.	75.61	6.05	2.11		16.08
								Found	75.45	6.26	2.11		16.08
1h	*t*Bu	morpholino	63	B	2161	1.5432/27	$C_{10}H_{17}NOS_2$ (231.4)	Calcd.	51.91	7.41		6.05	[b]
								Found	51.53	7.44		5.75	
1i	C_6H_5	Me	25	B	2162	1.6266/23	$C_9H_8S_2$ (180.3)	Calcd.	59.96	4.47			[b]
								Found	61.36	4.77			
1j	C_6H_5	*t*Bu	60	B	2164	1.6112/25		[a]					
1k	C_6H_5	$C(C_6H_5)_3$	56	B	2162	107–109	$C_{27}H_{20}S_2$ (408.6)	Calcd.	79.37	4.93			15.69
								Found	78.41	5.00			15.40
1l	C_6H_5	C_6H_5	64	B	2157	1.6920/21		[a]					
1m	C_6H_5	CCl_3	33	A	2162			[a]					
1n	C_6H_5	C_2Cl_5	56	B	2161	52.0–52.8	$C_{10}H_5Cl_5S_2$ (366.6)	Calcd.	32.77	1.37	48.36		17.50
								Found	32.77	1.42	47.82		17.50

[a] Elemental analyses could not be obtained due to compound instability. – [b] A satisfactory sulfur analysis could not be obtained; deviation 1–2% absolute. – [c] The compound is a syrup, thus no index of refraction could be obtained. – [d] Residual $CHCl_3$ after conventional drying.

Table 2. ^{1}H- (200 MHz) and ^{13}C-NMR (200 MHz) data of **1**

Compound	^{1}H NMR [δ]	^{13}C NMR [δ]
1d	CH_2 (t, 4H): 3.17 CH_2 (t, 4H): 3.73	S-C≡*C*: 94.10 S-*C*≡C: 82.01 *C*H_2: 55.59, 66.66 Ph: 123.11, 128.41, 128.62, 131.71
1f	Ph (m, 3H): 7.37 Ph (m, 2H): 7.63 CH_3 (s, 9H): 1.23	S-C≡*C*: 107.37 S-*C*≡C: 68.39 *C*H_3: 30.71 Me_3*C*: 29.00 Ph: 128.89, 129.44, 131.15, 136.71
1g	Ph (m, 15H): 7.45 CH_3 (s, 9H): 1.35	S-C≡*C*: 104.17 S-*C*≡C: 72.99 *C*H_3: 30.50 Me_3*C*: 28.46 Ph_3*C*: 68.31 Ph: 127.30, 127.97, 130.38, 143.77
1h	CH_2 (t, 4H): 3.14 CH_2 (t, 4H): 3.74 CH_3 (s, 9H): 1.23	S-C≡*C*: 103.82 S-*C*≡C: 70.74 *C*H_3: 30.69 Me_3*C*: 28.87 *C*H_2: 55.73, 67.00
1i	CH_3 (s, 3H): 2.66 Ph (m, 2H): 7.31 Ph (m, 3H): 7.46	S-C≡*C*: 95.68 S-*C*≡C: 79.18 *C*H_3: 22.18 Ph: 122.74, 128.46, 128.95, 132.10
1j	CH_3 (s, 9H): 1.47 Ph (m, 3H): 7.30 Ph (m, 2H): 7.42	S-C≡*C*: 92.53 S-*C*≡C: 82.32 *C*H_3: 29.89 Me_3*C*: 49.76 Ph: 123.23, 128.65, 128.96, 132.15
1k	Ph (m): 7.36	S-C≡*C*: 94.60 S-*C*≡C: 79.73 Ph_3*C*: 72.98 Ph: 122.82, 127.48, 128.10, 128.37, 128.81, 130.43, 132.06, 143.45
1l	Ph (m): 7.39	S-C≡*C*: 97.13 S-*C*≡C: 77.19 Cl_3*C*: 100.08 Ph: 121.90, 128.56, 129.67, 132.31
1m	Ph (m): 7.38	S-C≡*C*: 97.38 S-*C*≡C: 78.02 Cl_3*C*, *C*Cl_2: 104.56, 104.90 Ph: 121.98, 128.61, 129.70, 132.40

Table 3. Physical data of thioketenes **3**, $R^1R^2C{=}C{=}S$

Compound	R^1	R^2	Yield (%)	IR ν(C=C=S) [cm^{-1}]	^{13}C NMR [δ] C=*C*=S	C=C=*S*
3e	*t*Bu	*t*BuS	≈4	1729	254.11	102.04
3f	*t*Bu	C_6H_5S	≈10	1740	249.63	[a]
3i	C_6H_5	MeS	trace	1698[b]	–	–
3j	C_6H_5	*t*BuS	trace	1725	–	–
3m	C_6H_5	CCl_3S	trace	1690[b]	–	–

[a] The purity was insufficient for the determination of this chemical shift. – [b] This absorption is uncommon for a thioketene.

almost quantitative yield of (*E*)-**2a**. In one instance a small amount of the (*Z*) stereoisomer could be isolated.

Oxidation of the thiolate anion by addition of its diethyl ether solution to a vigorously stirred solution of $K_3[Fe(CN)_6]$ in water gave a quantitative yield of **2a**. The same result was obtained when the aqueous $K_3[Fe(CN)_6]$ solution was saturated with KOH.

(E)-4-Phenyl-2-(phenylmethylene)-1,3-dithiole [(*E*)-**2a**]: M.p. 194–196°C (ref.[44] 194°C). – ^{1}H- and ^{13}C-NMR spectra were in agreement with literature data[45].

(Z)-5-Phenyl-2-(phenylmethylene)-1,3-dithiole [(*Z*)-**2a**]: M.p. 127°C. – ^{1}H- and ^{13}C-NMR spectra were in agreement with literature data[45], a single-crystal X-ray structure analysis was carried out[5].

1,2-Dithiones **7**[46] were obtained according to route B. The tautomeric mixtures **1**/**3**/**7**/**8**, prepared from the appropriate alkyne by deprotonation with butyllithium and subsequent treatment with S_2Cl_2, were quenched with morpholine at –78°C.

1-Morpholino-2-phenyl-1,2-ethanedithione (**7d**): From phenylacetylene; dark green crystals, m.p. <50°C. – IR (cm^{-1}): $\tilde{\nu}$ = 1113 (C=S), 1486 (N–C=S). – UV ($CHCl_3$): λ_{max} = 585.2 nm. – ^{13}C NMR ($CDCl_3$): δ = 128.59, 129.18, 134.42, 140.28 (Ph); 47.84, 51.48 (NCH_2); 66.18, 66.41 (OCH_2); 200.24 (NC=S); 228.37 (MeC=S). – ^{1}H NMR ($CDCl_3$): δ = 3.57 (m, NCH_2, 2H), 3.69 (m, NCH_2, 2H), 3.90 (m, OCH_2, 2H), 4.42 (m, OCH_2, 2H), 7.42 (t, 3-, 5-H, 2H), 7.61 (t, 4-H, 1H), 8.08 (d, 2-, 6-H, 2H).

$C_{10}H_{17}NOS_2$ (231.4)
Calcd. C 51.91 H 7.41 N 6.05 S 27.71
Found C 51.83 H 7.43 N 6.16 S 27.79

3,3-Dimethyl-1-morpholino-1,2-butanedithione (**7h**): From 3,3-dimethyl-1-butyne; red crystals, m.p. 100.3–101.8°C. – IR (cm^{-1}): $\tilde{\nu}$ = 1093 (C=S), 1502 (N–C=S). – UV ($CHCl_3$): λ_{max} = 532.5 nm. – ^{13}C NMR ($CDCl_3$): δ = 32.44 (s, CH_3); 51.31 (s, CMe_3); 47.35, 52.16 (NCH_2); 65.98, 66.54 (OCH_2); 201.50 (NC=S); 258.57 (MeC=S). – ^{1}H NMR ($CDCl_3$): δ = 1.52 (s, CH_3, 9H), 3.52 (m, CH_2, 1H), 3.72 (m, CH_2, 5H), 4.12 (m, CH_2, 1H), 4.45 (m, CH_2, 1H), 3.71 (m,CH_2, 2H), 3.84 (m, CH_2, 2H).

$C_{12}H_{13}NOS_2$ (251.4) Calcd. C 57.34 H 5.21 N 5.57
Found C 57.65 H 5.40 N 5.64

A satisfactory sulfur analysis could not be performed; deviation 1–2% absolute.

4-Phenyl-5-(phenylethynylthio)-2-[phenyl(phenylethynylthio)-methylene]-1,3-dithiole (**9a**) (**9**; R^1 = C_6H_5, R^2 = $C_6H_5C{\equiv}C$): Phenylacetylene (1.12 g, 0.011 mol) was dissolved in diethyl ether (100 ml) and after cooling to –78°C *n*BuLi, dissolved in pentane (5 ml, 2 M), was added and the mixture allowed to warm to room temp. The solution was cooled to –78°C, and disulfur dichloride (0.67 g, 0.005 mol), dissolved in diethyl ether (100 ml), was added slowly. Column chromatography (eluent diethyl ether/petroleum ether, 1:12) yielded the pure compound **9a** (0.37 g, 28%). Both the (*E*) and (*Z*) stereoisomers were present in the product as evident from the ^{13}C-NMR data. M.p. 173.9–175.7°C. – IR (cm^{-1}): $\tilde{\nu}$ = 2165 (C≡C), 1635, 1651 (C=C). – MS (70 eV), *m/z* (%): 532 (77) [M^+], 399 (15) [M^+ – PhC≡CS], 266 (35) [$M^+/2$]. – ^{1}H NMR ($CDCl_3$): δ = 7.44 (Ph, m). – ^{13}C NMR ($CDCl_3$): δ = 94.54, 94.82, 96.35, 96.61 (SC≡*C*); 74.63, 74.75 (SC≡C); 108.48, 108.55, 115.70, 122.36, 122.41, 123.07, 127.78, 127.84, 128.00, 128.12, 128.25, 128.40, 128.44, 128.57, 128.78, 128.86, 128.95, 129.11, 129.34, 129.52, 129.62, 130.90, 131.11, 131.53, 131.58, 131.73, 131.88, 134.58, 136.41, 138.48, 142.08, 142.22.

$C_{32}H_{20}S_4$ (532.8) Calcd. C 72.14 H 3.78 S 24.07
Found C 71.59 H 3.80 S 23.75

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1a: 86197-50-4 / **1d**: 143634-00-8 / **1e**: 42070-56-4 / **1f**: 143634-01-9 / **1g**: 143634-02-0 / **1h**: 143634-03-1 / **1i**: 143634-04-2 / **1j**: 143634-05-3 / **1k**: 143634-06-4 / **1l**: 143634-07-5 / **1m**: 143634-08-6 / **1n**: 143634-09-7 / (*E*)-**2a**: 40753-18-2 / (*Z*)-**2a**: 40753-17-1 / **3e**: 143634-10-0 / **3f**: 143634-11-1 / **3i**: 143634-12-2 / **3j**: 143634-13-3 / **3m**: 143634-14-4 / **7d**: 143634-16-6 / **7h**: 143634-17-7 / (*E*)-**9a**: 143634-18-8 / (*Z*)-**9a**: 143634-19-9 / phenylethyne: 536-74-3 / 3,3-dimethyl-1-butyne: 917-92-0 / chloro phenyl disulfide: 6009-07-0 / 3,3,3-trichloro-1-propyne: 6482-61-7 / sulfur: 7704-34-9 / 1-ethynylmorpholine: 55082-00-3 / 3,3,3-triphenyl-1-propyne: 6104-51-4 / propyne: 74-99-7 / 3,3,4,4,4-pentachloro-1-butyne: 143634-15-5 / (2-phenylethynyl)lithium: 4440-01-1 / sulfur chloride: 10025-67-9