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The reaction of alkynes with dimethyl sulfoxide, halogenated hydrocarbons and sulfur trioxide

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1,2-Disubstituted alkynes are converted in CCl_4 or $CHCl_3$ with dimethyl sulfoxide in the presence of sulfur trioxide into the corresponding (*E*, *Z*)-1-chloro-2-methylthio-ethenes. The reaction of 1,2-diphenylethyne with $CHBr_3$, DMSO, and dioxane sulfotrioxide gives (*E*, *Z*)-1,2-dimethylthio-1,2-diphenylethene.

Keywords: alkynes; dimethyl sulfoxide; halogenmethanes; sulfur trioxide; multicomponent reactions

1. Introduction

We have recently developed several new useful methods for functionalization of acetylenes by reagents on the basis of sulfuric trioxide. Phenylacetylene in the reaction with a complex of SO_3 and dioxane gives an unsaturated δ-sultone, 4,6-diphenyl-[1,2]-oxathiin-2,2-dioxide (*1, 2*), whereas the treatment of terminal acetylenes with the same complex and nitrates results in the formation of isoxazoles (*3, 4*). 1,2-disubstituted acetylenes are oxidized with the complex of sulphuric anhydride and dioxane into 1,2-diketones (*5*).

In a previous communication, we also reported the unexpected formation of (*E*)-1-chloro-2-methylthio-1,2-diphenylethene **2a** by treatment of 1,2-diphenylethyne **1a** with a mixture of dimethyl sulfoxide, CCl_4, and SO_3 (*6*). The reaction is carried out at 70°C to give compound **2a** as the major product (up to 68% yield) and benzil **4a** as a by-product (26% yield). Here we report a further study of this new transformation of acetylenes.

2. Results and discussion

A further investigation revealed an essential influence of the ratio of DMSO and CCl_4 in the reaction mixture on the yield of addition and oxidation products. An increase in the amount of

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†X-ray diffraction analysis

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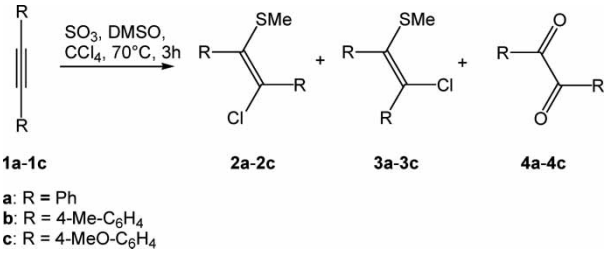

Figure 1. The reaction of diarylacetylenes with DMSO, CCl_4, and SO_3.

Table 1. The reaction of alkynes with dimethyl sulfoxide, halogenated hydrocarbons, and SO_3.[a]

Entry	Substrate	Halogenmethane	DMSO/ halogenmethane ratio (mol/mol)	Products	Yield (%)
1	**1a**	CCl_4	6:1	**2a** + **3a** (95:5)[b] **4a**	52 23
2	**1a**	CCl_4	1:1	**2a** + **3a** (95:5)[b] **4a**	68 26
3	**1a**	CCl_4	1:7	**2a** + **3a** (95:5)[b] **4a**	77 <5
4	**1b**	CCl_4	1:7	**2b** + **3b** (72:28)[b] **4b**	78 <5
5	**1c**	CCl_4	1:7	**2c** + **3c** (62:38)[b] **4c**	84 <5
6	**5**	CCl_4	1:7	**6a/b/c** (6:84:10)[c]	64
7[d]	**1a**	$CHCl_3$	1:9	**2a** + **3a** (64:36)[b] **4a**	90 7
8[e]	**1a**	$CHCl_3$	1:9	**2a** + **3a** (34:66)[b] **4a**	87 5
9[f]	**1a**	$CHBr_3$	1:5	**7** + **8** (42:58)[b] **4a**	40 34

[a] Alkynes **1a–1c**, **5** 1 mmol, SO_3 3 mmol, DMSO 14 mmol, CCl_4 or $CHCl_3$ 10 ml, reaction time 3 h, reaction temperature 70°C,
[b] ^{1}H NMR data,
[c] A mixture of three stereo and regio isomers 6:84:10 (GC MS),
[d] Reaction temperature 61°C,
[e] The reaction in a sealed tube at 70°C,
[f] Dioxane sulfotrioxide 6 mmol, $CHBr_3$ 17.691 g, reaction temperature 110°C.

DMSO relating to carbon tetrachloride results in an augmentation of the oxidation product **4a**. On the contrary, the formation of addition product **2a** is favored at excess of CCl_4 and the oxidation into **4a** is diminished (Figure 1, Table 1).

The reaction of 1,2-*bis*-(*p*−tolyl)ethyne **1b** and 1,2-*bis*-(4-methoxyphenyl)ethyne **1c** with DMSO and CCl_4 in the presence of SO_3 gives mixtures of (*E*)- and (*Z*)−isomers, 72:28 (**2b**:**3b**) and 62:38 (**2c**:**3c**), respectively, whereas 1,2-diphenylethyne **1a** gives almost pure (*E*)-isomer **2a** as a product of the addition (**2a**:**3a** = 95:5).

In previous reactions, compounds **2a** and **3a** were prepared in a ratio of 1:4 by the reaction of excess MeSCl with (*E*)-stilbene (77% yield) (*7*). Compound **2a** was also prepared (*7*) by the reaction of 1,2-diphenylethyne with MeSCl and boron trifluoride etherate (70% yield).

As the signal of the methyl group of (*E*)-isomer **2a** on the ^{1}H NMR spectrum is shifted into a strong field rather than the signal of (*Z*)-isomer **3a** (1.85 and 1.94 ppm, respectively) and inversely the signals of the aromatic protones of **2a** are located in a weak field rather than the aromatic

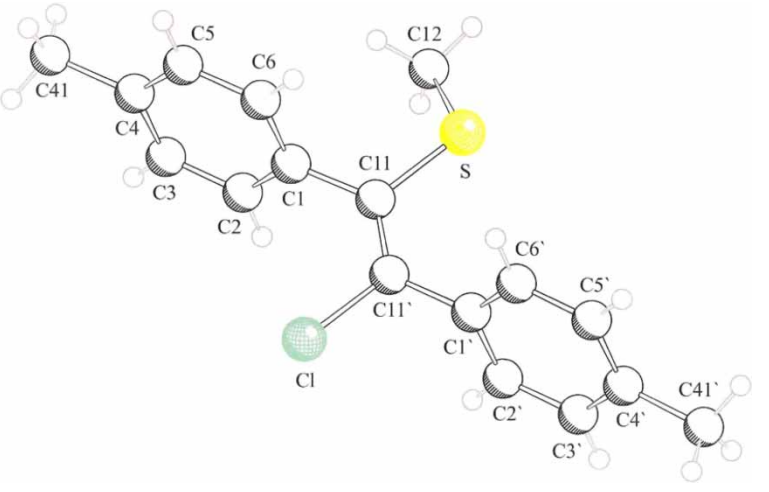

Figure 2. X-ray crystal structure of ***2b***.

Table 2. Determinations for the crystal structure of (*E*)-1,2-*bis*-(p-tolyl)-1-methylthio-2- chloroethene **2b**.

Parameter	Value
Chemical formula	$C_{17}H_{17}ClS$
Formula weight ($gmol^{-1}$)	288.82
Crystal system	Orthorhombic
Unit-cell dimensions:	
a (Å)	5.515 (1)
b (Å)	7.860 (1)
c (Å)	34.792 (3)
α (°)	90
β (°)	90
γ (°)	90
Unit-cell volume ($Å^3$)	1508.2 (4)
T (°C)	−75 (2)
Space group symbol	P 21 21 21
No. of formula units in unit cell, *Z*	4
Linear absorption coefficient, μ (mm^{-1})	0.376
Number of independent reflections	2955
R_{int}	0.030
R	0.0353
R_W^2	0.0825

signals of **3a** (7.37–7.65 and 7.11–7.28, respectively) (*7*), it is most reasonable to assume that the corresponding signals of (*E*)-isomers **2b** and **2c** and (*Z*)-isomers **3b** and **3c** have similar relative shifts. This interpretation is also confirmed by X-ray crystallographic analysis of the product **2b**[1] (Figure 2, Table 2).

Although the mechanism of the reaction of DMSO and CCl_4 with alkynes in the presence of SO_3 is not completely solved, we assume that this transformation is also of a free-radical nature (Figure 3). It is well known that in a Pummerer-type reaction, DMSO can decompose into CH_3SH and CH_2O in the presence of electrophiles (*8, 9*). Furthermore, thiols are capable of transforming into disulfides (*10, 11*), and many reactions involving thiols and disulfides proceed via a free-radical mechanism (*12–15*). The addition of sulfonyl chlorides to acetylenes is also known to be a free-radical reaction. It was found to be stereoselective and dependent on the polarity of the solvent as well as the presence of additional chloride ions (*16*).

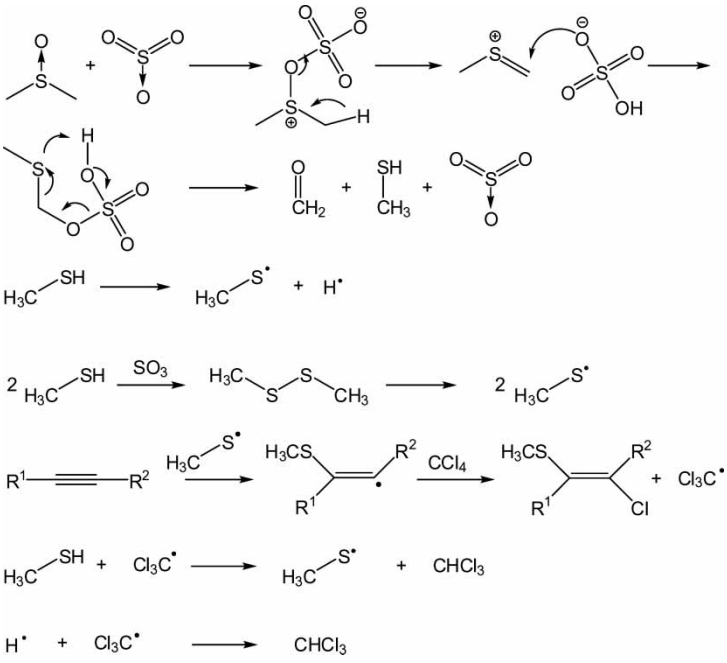

Figure 3. The hypothetic mechanism of the reaction of alkynes with DMSO, halogenated hydrocarbons, and SO_3.

We have observed the formation of formaldehyde and *S*-methyl methanethiosulfonate, which was detected using the GC MS analysis of crude reaction mixtures (M^+ 126). This compound is known to be the oxidation product of dimethyl disulfide (*17, 18*).

The formation of 1-chloro-2-methylthiostilbenes seems to proceed via the addition of the CH_3S radical to the triple bond followed by chlorine abstraction from CCl_4 to give the appropriate intermediate free vinyl radical. The last step of this hypothetic mechanism is comparable to a chain rupture, a common reaction of telomerization of alkenes in the presence of halogenated hydrocarbons.

We have also found that (*E*)-stilbene is stable under the reaction conditions, whereas an increase in the temperature up to 100°C leads to benzil **4a** (yield 51%). Consequently, the formation of compound **2a** is not of electrophilic nature.

According to the calculations of the DFT B3LYP/6-311G* method, the thermodynamic stabilities of isomers **2a** and **3a** are almost identical in the gas phase and in polar medium (PCM model), (Figure 4). The anti attack of the free radical Ph(SMe)C = CPh should be favored over a *syn* attack (Figure 5). Therefore, it is reasonable to suggest that steric factors are of critical importance in this reaction.

Similarly, alkylthiohalogenation is also possible for arylalkylsubstituted acetylenes. The reaction of 1-*n*-pentyl-2-phenylethyne **5** with DMSO, CCl_4, and SO_3 gives a mixture of three

3a **2a**

Figure 4. Transformation of (*E*)- and (*Z*)- isomers according to the calculation by B3LYP/6-311G* method: $\Delta H = -0.08$ kcal/mol (gas phase); $\Delta G = 0.19$ kcal/mol (gas phase); $\Delta G = 1.89$ kcal/mol (H_2O).

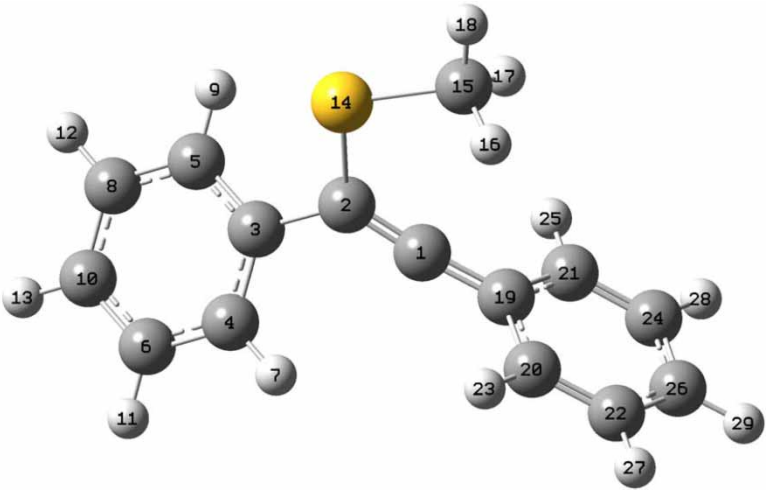

Figure 5. Configuration of the free radical Ph(SMe)C=CPh according to the calculation by B3LYP/6-311G* method.

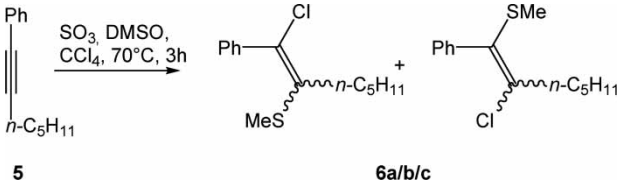

Figure 6. The reaction of 1-*n*-pentyl-2-phenylacetylene **5** with DMSO, CCl_4, and SO_3.

regio- and stereo-isomers **6a**, **6b**, and **6c** in the ratio of 6:84:10 (GC-MS control) and 64% overall yield (Figure 6). The major product is obtained from the mixture in 49% yield as a pure compound.

Apparently, similar transformations are also characteristic for other halogenated hydrocarbons. Thus, the refluxing of 1,2-diphenylethyne **1a** with dimethyl sulfoxide and SO_3 at atmospheric pressure in $CHCl_3$ (absence of CCl_4) results in products **2a** and **3a** as a 64:36 mixture (87% overall yield). However, in a sealed tube, at 70°C, this reaction gives an opposite ratio of (*E*)- and (*Z*)-isomers **2a** and **3a** (34:66, respectively) in 90% overall yield (Table 1).

The reaction of 1,2-diphenylethyne **1a** with DMSO, dioxane sulfotrioxide, and $CHBr_3$ in the absence of CCl_4 gives halogen-free products – 1,2-dimethylthio-1,2-diphenylethene as a 42:58 mixture of (*E*)- and (*Z*)-isomers **7** and **8** (NMR integration) respectively, in 40% overall yield (Figure 7, Table 1). The ^{1}H NMR spectrum revealed two groups of signals in the aromatic

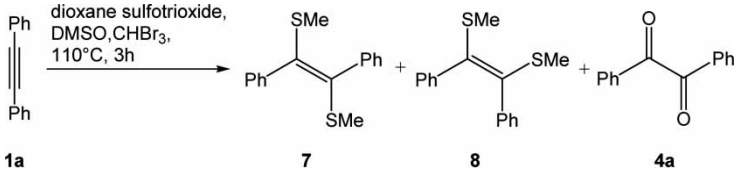

Figure 7. The reaction of diphenylacetylene **1a** with DMSO, $CHBr_3$ and dioxane sulfotrioxide.

(7.38–7.48 and 7.08–7.18 ppm) and aliphatic (1.78 and 1.98 ppm) region; chemical shifts and intensities are identical in every respect with the literature data (*19*). Probably, brominated intermediates such as **2a** and **3a** are substituted with the SMe group due to higher temperature and higher reactivity than equal chlorinated compounds.

Compounds **7** and **8** are minor products from electrolysis of a solution of dithiobenzoic acid methyl ester, with *bis*-(methylthio)-phenylmethane as the major product (*20*). It is interesting to note that by electrolysis predominant yields of the (*Z*)-isomer **8** are obtained. Compound **8** is also known as a ligand in complexes with Ni, Pd, and Pt (*19*).

Use of SO_3 causes decomposition of bromoform; therefore, dioxane sulfotrioxide was used instead. Products **7** and **8** are not obtained by treatment of **1a** with DMSO and SO_3 in the absence of $CHBr_3$.

In conclusion, 1,2-disubstituted alkynes are converted into the corresponding 1-chloro-2-methylthio-ethenes in favor of (*E*)-isomers via a free-radical reaction with CCl_4 and dimethyl sulfoxide in the presence of sulfur trioxide. The reaction of 1,2-diphenylethyne with $CHBr_3$, DMSO, and dioxane sulfotrioxide affords 1,2-dimethylthio-1,2-diphenylethene in an *E*/*Z* ratio of 42:58.

3. Experimental section

3.1. *General procedures*

Starting acetylenes are synthesized according to the literature known method (*21*). Sulfur trioxide was distilled from a solution of SO_3 in sulphuric acid (20–60% oleum) into a receiver containing carbon tetrachloride. The concentration was calculated by weight and volume increase of the solution. The SO_3-dioxane complex was obtained according to the literature known method (*22*). All commercially available compounds were used as received unless stated otherwise. Flash chromatography: Merck silica gel 60 (40–63 μm). Thin layer chromatography: Merck silica gel 60 F254 plates with UV detecting of the spots. Melting points: Kleinfeld Labortechnik Electrothermal IA 9100 apparatus. ^{1}H- and ^{13}C-NMR: Bruker AC-300 (^{1}H: 300 MHz, ^{13}C: 75.4 MHz, $CDCl_3$, δ, ppm, calibrated to the residual resonance of the solvent, s = singulet, d = doublet, t = triplet, m = multiplet). FT-IR spectra: Nicolet 205 and Nicolet Avatar 360 spectrometer (ν, cm^{-1}, s = strong, m = middle, w = weak, br = broad). Mass spectra: Hewlett Packard 5890 GC coupled with a Hewlett Packard 5972 detector (70 eV, m/z, (%)). Elemental analysis: Carlo Erba Instruments EA 1108 and Hekatech EA 3000. X-ray: NONIUS Kappa CCD.

3.2. *Reaction of alkynes with DMSO, SO_3, and CCl_4 (or $CHCl_3$)*

To a stirred solution of 1 mmol of alkyne **1a-c** or **5** and 1.094 g (14 mmol) DMSO in 9 ml of CCl_4, a solution of 0.240 g (3 mmol) of SO_3 in 1 ml of CCl_4 was added dropwise at room temperature. The exothermic reaction is started, and the reaction mixture was stirred and warmed on an oil bath at 70°C for 3 h. After cooling to room temperature, the resulting mixture was diluted with 50 ml of water and extracted with CH_2Cl_2 (2×30 ml). The combined extracts were washed with 50 ml of water and dried with $MgSO_4$. The solvent was removed *in vacuo*, and the resulting yellow oil was purified by flash chromatography (silica gel, pentane/EtOAc 10:1) with TLC control.

This procedure was also applied to the reaction with $CHCl_3$ in the absence of CCl_4.

3.2.1. *(E)-1,2-diphenyl-1-methylthio-2-chloroethene* ***2a***

$R_f = 0.25$ (pentane). mp 73–74°C (methanol), lit. mp 74°C (*7*). IR: 637 m, 695 s, 735 s, 760 m, 800 w, 858 m, 955 w, 982 w, 1030 w, 1075 w, 1202 w, 1240 w, 1315 w, 1431 m, 1443 m, 1488 m, 1596 w, 1811 br w, 2923 w, 2989 w, 3024 w, 3054 w. NMR ^{1}H: 1.85 (s, 3H, CH_3), 7.37–7.54 (m, 8H, H aromat.), 7.60–7.65 (m, 2H, H aromat.). NMR ^{13}C: 16.67 (SCH_3), 126.43 (C-Cl), 127.89 (CH), 127.99 (CH), 128.23 (CH), 128.58 (CH), 129.15 (CH), 129.41 (CH), 134.96 (CSMe), 137.38 (C), 138.59 (C). GC MS: 260 $[M]^+$ (100), 245 $[M\text{-}CH_3]^+$ (12), 225 $[M\text{-}Cl]^+$ (8), 210 $[M\text{-}Cl\text{-}CH_3]^+$ (66), 192 (3), 178 $[M\text{-}Cl\text{-}SCH_3]^+$ (28). Anal. calcd for $C_{15}H_{13}ClS$: C 69.08, H 5.02, S 12.30. Found: C 69.21, H 4.98, S 12.51.

3.2.2. *(Z)-1,2-diphenyl-1-methylthio-2-chloroethene* ***3a***

Isolated as a mixture with (*E*)-isomer **2a**. Selected data for the (*Z*)-isomer **3a**: NMR ^{1}H: 1.94 (s, 3H, CH_3), 7.11–7.28 (m, 10H, H aromat.).

3.2.3. *(E)-1,2-bis-(p-tolyl)-1-methylthio-2-chloroethene* ***2b***

$R_f = 0.44$ (pentane), mp 93–95°C (pentane). IR: 641 m, 693 s, 742 s, 781 s, 816 m, 834 m, 862 s, 949 br w, 980 m, 1019 m, 1036 w, 1107 m, 1177 m, 1315 w, 1432 br m, 1509 m, 1606 br w, 1904 br w, 2851 br w, 2922 m, 3023 w. NMR ^{1}H: 1.76 (s, 3H, CH_3), 2.35 (s, 6H, $2CH_3$), 7.19 (m, 4H, H aromat.), 7.31 (d, $J = 8$ Hz, 2H, H aromat.), 7.42 (d, $J = 8$ Hz, 2H, H aromat.). NMR ^{13}C: 16.77 (SCH_3), 21.29 (CH_3), 21.34 (CH_3), 126.38 (=C-Cl), 128.72 (CH), 128.97 (CH), 129.11 (CH), 129.41 (CH), 134.53 (C), 134.60 (CSMe), 135.93 (C), 137.70 (C), 138.56 (C). GC MS: 288 $[M]^+$ (100), 273 $[M\text{-}CH_3]^+$ (5), 253 $[M\text{-}Cl]^+$ (5), 238 $[M\text{-}Cl\text{-}CH_3]^+$ (100), 206 $[M\text{-}Cl\text{-}SCH_3]^+$ (40), 189 (15), 178 $[M\text{-}Cl\text{-}SCH_3]^+$ (10), 165 (8), 152 (4). Anal. calcd for $C_{17}H_{17}ClS$: C 70.69, H 5.93, S 11.10. Found: C 70.78, H 6.03, S 11.28.

3.2.4. *(Z)-1,2-bis-(p-tolyl)-1-methylthio-2-chloroethene* ***3b***

Isolated as a mixture with (*E*)-isomer **2b**. Selected data for the (*Z*)-isomer **3b**: $R_f = 0.44$ (pentane). NMR ^{1}H: 1.84 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 6.95 (m, 2H, H aromat.), 7.08 (m, 6H, H aromat.). NMR ^{13}C: 15.66 (SCH_3), 21.08 (CH_3), 21.17 (CH_3), 125.88 (=C-Cl), 128.34 (CH), 129.04 (CH), 129.33 (CH), 130.06 (CH), 133.25 (C), 134.53 (=CSMe), 136.64 (C), 137.13 (C), 137.40 (C). GC MS: 288 $[M]^+$ (100), 273 $[M\text{-}CH_3]^+$ (5), 253 $[M\text{-}Cl]^+$ (5), 238 $[M\text{-}Cl\text{-}CH_3]^+$ (100), 206 $[M\text{-}Cl\text{-}SCH_3]^+$ (40), 189 (15), 178 $[M\text{-}Cl\text{-}SCH_3]^+$ (10), 165 (8), 152 (4).

3.2.5. *(E)-1,2-bis-(4-methoxyphenyl)-1-methylthio-2-chloroethene* ***2c***

$R_f = 0.46$ (pentane/EtOAc 5:1), mp 102–104°C (pentane). IR: 637 m, 699 s, 746 s, 789 s, 824 s, 844 s, 866 m, 982 m, 1027 s, 1105 m, 1171 s, 1242 s, 1293 s, 1453 s, 1509 s, 1573 m, 1604 s, 1656 w, 2038 w, 2836 w, 2921 br w, 2990 br w. NMR ^{1}H: 1.81 (s, 3H, SCH_3), 3.84 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.95–7.01 (m, 4H, H aromat.), 7.43 (d, $J = 6.7$ Hz, 2H, H aromat.), 7.54 (d, $J = 6.7$ Hz, 2H, H aromat.). NMR ^{13}C: 16.89 (SCH_3), 55.24 (OCH_3), 55.28 (OCH_3), 113.36 (CH), 113.63 (CH), 126.17 (=C-Cl), 129.85 (CH), 130.72 (CH), 130.92 (CH), 131.24 (CH), 134.05 (=CSMe), 159.09 (C), 159.59 (C). GC MS: 320 $[M]^+$ (100), 305 $[M\text{-}CH_3]^+$ (5), 285 $[M\text{-}Cl]^+$ (4), 270 $[M\text{-}Cl\text{-}CH_3]^+$ (92), 255 $[M\text{-}Cl\text{-}2CH_3]^+$ (38), 238 $[M\text{-}Cl\text{-}SCH_3]^+$ (50), 223

$[M\text{-}Cl\text{-}CH_3\text{-}SCH_3]^+$ (33). Anal. calcd for $C_{17}H_{17}ClO_2S$: C 63.64, H 5.34, S 9.99. Found: C 63.78, H 5.40, S 9.96.

3.2.6. *(Z)-1,2-bis- (4-methoxyphenyl)-1-methylthio-2-chloroethene* ***3c***

Isolated as a mixture with (*E*)-isomer **2c**. Selected data for the (*Z*)-isomer **3c**: $R_f = 0.37$ (pentane/EtOAc 5:1). IR: 750 w, 804 m, 833 m, 866 w, 1032 s, 1108 w, 1173 s, 1246 s, 1293 m, 1462 m, 1508 s, 1605 s, 2836 w, 2925 br w, 3002 br w. NMR ^{1}H: 1.93 (s, 3H, SCH_3), 3.74 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.65 (d, $J = 6.8$ Hz, 2H, H aromat.), 6.78 (d, $J = 6.7$ Hz, 2H, H aromat.), 7.06–7.11 (m, 4H, H aromat.). NMR ^{13}C: 15.75 (SCH_3), 55.11 (OCH_3), 55.14 (OCH_3), 113.09 (CH), 113.78 (CH), 125.84 (C-Cl), 128.61 (CH), 130.83 (CH), 131.24 (CH), 131.49 (CH), 135.86 (CSMe), 158.54 (C), 158.85 (C). GC MS: 320 $[M]^+$ (100), 305 $[M\text{-}CH_3]^+$ (5), 285 $[M\text{-}Cl]^+$ (4), 270 $[M\text{-}Cl\text{-}CH_3]^+$ (92), 255 $[M\text{-}Cl\text{-}2CH_3]^+$ (38), 238 $[M\text{-}Cl\text{-}SCH_3]^+$ (50), 223 $[M\text{-}Cl\text{-}CH_3\text{-}SCH_3]^+$ (33). Anal. calcd for $C_{17}H_{17}ClO_2S$: C 63.64, H 5.34, S 9.99. Found: C 63.87, H 5.38, S 10.07.

3.2.7. *Methylthio-chloro-1-n-pentyl-2-phenylethenes* ***6a–6c***

Isomer **6a**: pale yellow oil, yield 6%, $R_f = 0.67$ (pentane). NMR ^{1}H: 0.94–1.00 (m, 3H, CH_3), 1.38–1.45 (m, 4H, $2CH_2$), 1.69 (t, $J = 7.4$ Hz, 2H, CH_2), 1.88 (s, 3H, SCH_3), 2.85 (t, $J = 7.4$ Hz, 2H, CH_2), 7.29–7.43 (m, 5H, H aromat.). NMR ^{13}C: 14.03 (CH_3), 16.34 (SCH_3), 22.50 (CH_2), 27.29 (CH_2), 30.92 (CH_2), 37.10 (CH_2), 127.55 (CH), 128.11 (CH), 129.61 (CH), 132.20 (=CCl), 132.97 (C), 137.87 (=CSMe). GC MS: 254 $[M]^+$ (80), 163 (86), 149 (55), 129 (42), 115 (100).

Isomer **6b**: pale yellow oil, yield 49%, $R_f = 0.55$ (pentane). NMR ^{1}H: 0.95–1.00 (m, 3H, CH_3), 1.41–1.47 (m, 4H, $2CH_2$), 1.70 (t, $J = 7.4$ Hz, 2H, CH_2), 2.13 (s, 3H, SCH_3), 2.65 (t, $J = 7.8$ Hz, 2H, CH_2), 7.34–7.44 (m, 5H, H aromat.). NMR ^{13}C: 14.06 (CH_3), 16.31 (SCH_3), 22.55 (CH_2), 27.41 (CH_2), 31.47 (CH_2), 33.16 (CH_2), 127.36 (=CCl), 128.01 (CH), 128.32 (CH), 129.26 (CH), 134.72 (C), 139.12 (=CSMe). GC MS: 254 $[M]^+$ (85), 163 (90), 149 (63), 129 (52), 115 (100).

Isomer **6c**: Isolated as a mixture with **6b**. Selected data for **6c**: GC MS: 254 $[M]^+$ (84), 163 (85), 149 (55), 129 (40), 115 (100).

3.3. *Reaction of 1,2-diphenylethyne 1a with DMSO, $CHBr_3$, and SO_3*

To a mixture of 17.691 g (70 mmol) of $CHBr_3$ and 1.094 g (14 mmol) of DMSO, 1.010 g (6 mmol) of dioxane sulfotrioxide was added at room temperature. The suspension was stirred for 5 min at room temperature, and 0.178 g (1 mmol) of 1,2-diphenylethyne **1a** was added. The reaction mixture was stirred at 110°C for 3 h, cooled to room temperature, diluted with 50 ml of water, and extracted with CH_2Cl_2 (2 × 50 ml). The combined extracts were washed with 50 ml of water and dried with $MgSO_4$. The solvent and residue of $CHBr_3$ were removed *in vacuo*, and the crude product mixture was separated and purified by flash chromatography (silica gel, pentane/EtOAc 10:1) under TLC control.

3.3.1. *(E)- and (Z)-1,2-dimethylthio-1,2-diphenylethenes* ***7*** *and* ***8***

Yield 0.110 g (40%). White solid. $R_f = 0.31$ (pentane/EtOAc 20:1). IR: 626 m, 694 s, 735 s, 765 m, 862 m, 955 m, 992 m, 1030 m, 1072 m, 1175 w, 1277 m, 1314 m, 1417 m, 1429 m 1440 m, 1487 m, 1561 m, 1573 w, 1597 m, 1953 br w, 2920 m, 2988 w, 3075 br w. NMR ^{1}H: 1.78 (s, 6H, $2SCH_3$ from the (*E*)-isomer), 1.98 (s, 6H, $2SCH_3$ from the (*Z*)-isomer), 7.08–7.18 (m,

10H, H aromat. from the (*Z*)-isomer), 7.38–7.41 (m, 2H, H aromat. from the (*E*)-isomer), 7.44–7.48 (m, 8H, H aromat. from the (*E*)-isomer). NMR ^{13}C: 16.01 (SCH_3), 16.71 (SCH_3), 126.75 (CH), 127.73 (CH), 128.24 (CH), 129.66 (CH), 130.29 (CH), 134.42 (C), 134.66 (C), 137.91 (C), 138.40 (C). GC MS: 272 $[M]^+$ (74), 210 $[M\text{-}SCH_3\text{-}CH_3]^+$ (100), 178 $[M\text{-}2SCH_3]^+$ (25), 165 $[M\text{-}C_6H_5\text{-}2CH_3]^+$ (14). Anal. calcd for $C_{16}H_{16}S_2$: C 70.54, H 5.92, S 23.54. Found: C 70.34, H 5.92, S 23.68.

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Note

1. Crystallographic data for the structure **2b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 664634.

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