Russian Journal of General Chemistry, Vol. 72, No. 3, 2002, pp. 418–425. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 3, 2002, pp. 450–457.

Organylthiochloroacetylenes: V.[1] Dimerization of Alkylthiochloroacetylenes in the Presence of Sodium Sulfite

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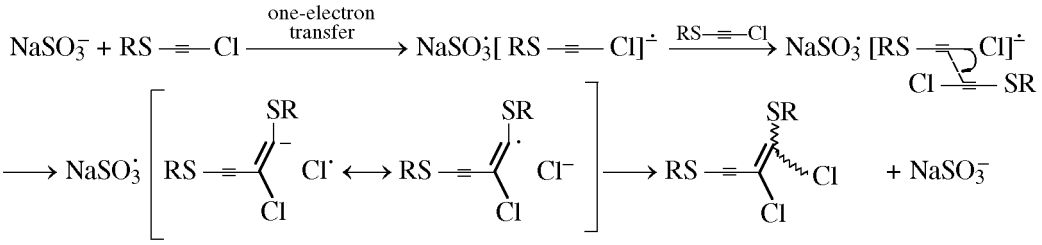
Received December 29, 2000

Abstract — Alkylthiochloroacetylenes dimerize at room temperature in the system sodium sulfite–polar nonhydroxyl solvent (DMSO, DMF, HMPA) to form in 40–63% yields (*Z*)-1,4-bis(alkylthio)-1,2-dichloro-1-buten-3-ynes which are promising polyfunctional monomers and building blocks for fine organic synthesis. The structure of the resulting dimers was established by means of IR and ^{1}H and ^{13}C NMR spectroscopy, X-ray fluorescent analysis, and dielcometry and confirmed by mass spectrometry and elemental analysis.

Haloacetylenes are highly reactive compounds which react with various nucleophiles to give chlorine substitution products and adducts by the triple bond [1–10]. At the same time, to our best knowledge, there have been only two works concerning dimerization of haloacetylenes [11, 12]. As found in [11], under conditions of electrophilic catalysis aryliodoacetylenes dimerize in the presence of iodopyridinium fluoroborate to form 1,3-diaryl-4,4-iodobutenynes; however, the structure of these products has not been proved unambiguously.

We reported recently the unexpected reaction of alkylthioacetylenes in the presence of the system sodium sulfite–DMSO, leading to dimers which were assigned the structure of 1,4-bis(alkylthio)-1,2-dichloro-1-buten-3-ynes [12]. It was also conjectured that the dimerization proceeds by the scheme of catalytic vicarious nucleophilic substitution involving the stage of one-electron transfer (Scheme 1). The radical-ion character of the reaction was evidenced, among other things, by the fact that mixing the above reagents was accompanied by development of an intense reddish brown color, whereas the resulting compounds were isolated as fluid light yellow liquids.

Scheme 1.



R = Alk.

The aim of the present study was to examine the synthetic potential of the dimerization of alkylthiochloroacetylenes, to assess the steric structure of the resulting dimers, and to obtain additional information on the ways of their formation.

Alkylthiochloroacetylenes **Ia**–**Ic** dimerize at room temperature in the presence of sodium sulfite not only in DMSO, but also in other polar nonhydroxyl sol-

[1] For communication IV, see. [1].

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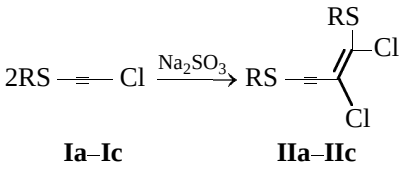
vents, such as DMF and HMPA, to give (*Z*)-1,4-bis-(alkylthio)-1,2-dichloro-1-buten-3-ynes **IIa**–**IIc**. The structure of the products was established by means of IR and ^{1}H and ^{13}C NMR spectroscopy, X-ray fluorescent analysis, dielcometry, mass spectrometry, and elemental analysis.

Scheme 2.

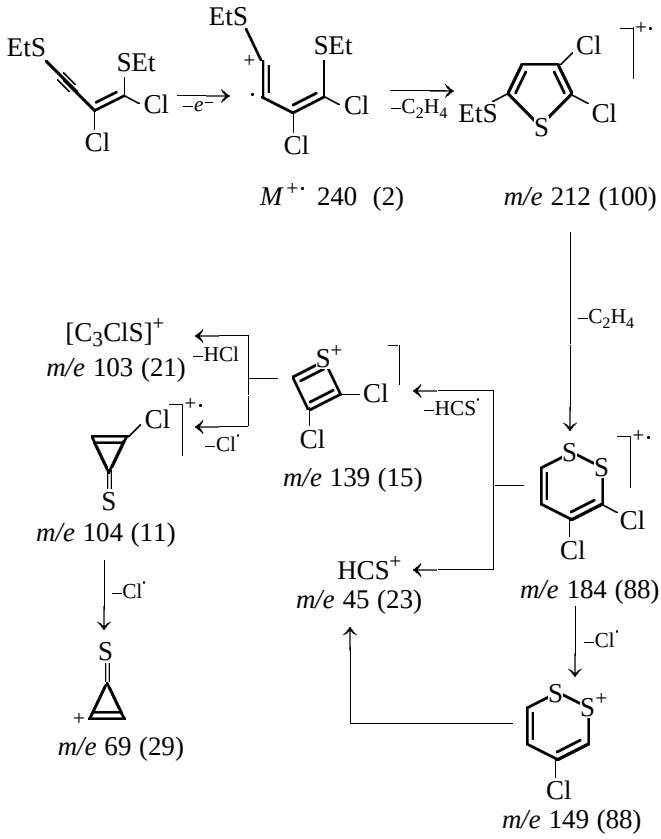


Ia–**Ic** **IIa**–**IIc**

R = Et (**Ia, IIa**), *n*-Pr (**Ib, IIb**), *i*-Bu (**Ic, IIc**).

The IR spectra of compounds **IIa**–**IIc** contain a weak absorption band at 1524–1540 cm^{-1} and a strong absorption band at 2142–2150 cm^{-1}, which belong to stretching vibrations of the C=C and C≡C bonds, respectively. In the IR spectra of the starting alkylthiochloroacetylenes, the ν(C≡C) band is in a shorter wave region (2150–2170 cm^{-1}) and its intensity is by far lower. The ^{1}H NMR spectra of compounds **IIa**–**IIc** show signals of two magnetically nonequivalent alkylthio groups, while the ^{13}C NMR spectra, along with signals of the two alkylthio groups, two pairs of signals in the ranges characteristic of C_{sp^2} and C_{sp} atoms, respectively [13, 14]. The parameters of the ^{1}H NMR and IR spectra are in agreement with published data for analogous compounds, 1,4-bis(alkylthio)-1,2-dichloro-1-buten-3-ynes (Alk = *n*-C_6H_{13}, *n*-C_8H_{17}, *t*-Bu), obtained by reactions of polychlorobutenes with alkali metal thiolates [15–17].

Scheme 3.



The mass spectral behavior of 1,4-bis(alkylthio)-1,2-dichloro-1-buten-3-ynes **IIa** and **IIc** is also consistent with their structure (Schemes 3 and 4). The fragmentation pathway of the molecular ions of the compounds studies can be controlled both by the thioether and vinylacetylene groups. The molecular

Scheme 4.

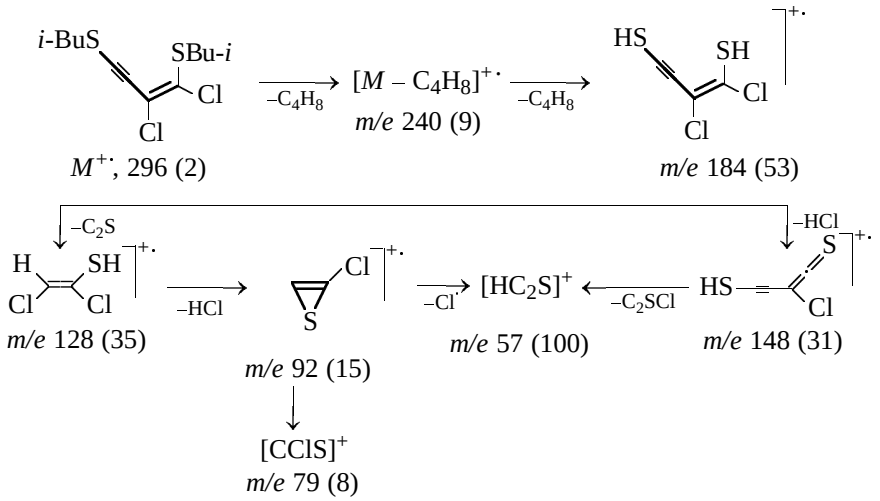


Table 1. Principal characteristic ions[a], *m/e* (I_{rel}, %) in the mass spectra of compounds **IIa** and **IIc**, taken at 60 V

Ion[b]	**IIa**	**IIc**
$M^{+\cdot}$	240 (2)	296 (2)
$[M - C_nH_{2n}]^{+\cdot}$	212 (100)	240 (9)
$[M - 2\ C_nH_{2n}]^{+\cdot}$	184 (88)	184 (53)
$[M - 2\ C_nH_{2n} - Cl]^{+\cdot}$	149 (88)	
$[M - 2\ C_nH_{2n} - HCl]^{+\cdot}$		148 (31)

[a] Based on ^{35}Cl. The ratios of isotope peak intensities agree with calculation. [b] n = 2 (**IIa**) and 4 (**IIc**).

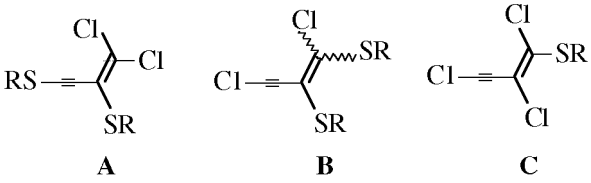
ions of thioethers and vinylacetylenes are characteristically very stable. Alkyl substitution in vinylacetylene lowers the stability of the molecular ion, and, as the length of the alkyl chain grows, the intensity of the $M^{+\cdot}$ peak drops down to 1% [18]. Compounds **IIa** and **IIc** give weak molecular ion peaks (Table 1). The common fragmentation pathaway involves sequential loss of two molecules of the corresponding olefin from $M^{+\cdot}$. The fragmentation scheme, structure, *m/e* values, and relative intensities of ions for compound **IIa** are presented in Scheme 3. The base peak in the mass spectrum of compound **IIa** is formed by the odd-electron ion $[M - C_2H_4]^{+\cdot}$ (*m/e* 212), and the second in intensity is an $[M - 2\ C_2H_4]^{+\cdot}$ ion peak (*m/e* 184). The high intensity of the peak at *m/e* 212 is presumably due to formation of a stable unsaturated heterocycle, 2,3-dichloro-5-(ethylthio)thiophene, as a result of skeletal rearrangement of $M^{+\cdot}$, typical of alkynes under electron impact [19, 20]. Loss of a second olefin molecule from the alkyl substutent in the *m/e* 212 ion is accompanied by enlargement of the thiophene ring to give a stable radical cation of 3,4-dichloro-1,2-dithiyne, *m/e* 184. The observation of a peak of an *m/e* 139 ion containing two chlorine atoms, as well as of *m/e* 69 and 45 ion peaks provide further evidence for the proposed fragmentation scheme.

Replacement of the ethyl radical in dimer **IIc** by *iso*-butyl results in appearance in the spectrum of strong peaks of hydrocarbon ions. This can probably be connected with the fact that the positive charge in the molecular ion of compound **IIc** is mainly localized on the *iso*-butyl radical, thus causing an alternative fragmentation pathway. The intensity of the $[M-C_nH_{2n}]^{+\cdot}$ ion peak in the mass spectrum of compound **IIc** is lower than in the spectrum of dimer **II**, being as low as 9% (Table 1). The intensity ratios of the $M^{+\cdot}/[M - C_nH_{2n}]^{+\cdot}$ ion peaks for compounds **IIa** and **IIc** are 0.02 and 0.2, respectively, i.e. they differ by an order of magnitude. The main contribution to the total ion current is made by the hydrocarbon ions $[Bu]^+$, *m/e* 57 (100), $[C_3H_5]^+$, *m/e* 41 (65), and $[Et]^+$, *m/e* 29 (55). The *m/e* 184 odd-electron ion of compound **IIc** splits off an HCl molecule rather than a chlorine ion; the mass spectrum also contains no *m/e* 139, 69, and 45 ion peaks typical of compound **IIa** and shows *m/e* 128, 92, and 79 ion peaks. The intensity ratios of the $[M - C_nH_{2n}]^{+\cdot}/[M - 2\ C_nH_{2n}]^{+\cdot}$ ion peaks are 1.1 and 0.2, respectively. The above findings point to another structure of the *m/e* 184 ion of compound **IIc** compared with compound **IIa**. The fragmentation pathway of compound **IIc**, the structure of fragment ions and their *m/e* values and relative intensities are given in Scheme 4.

Thus, the common direction in the mass-spectral fragmentation of dimers **IIa** and **IIc** is sequential loss by their molecular ions of two molecules of the corresponding olefin.

However, the parameters of the IR, ^1H and ^{13}C NMR spectra, and mass spectra of the dimers formed by the reaction under study (Scheme 2) gave no unequivocal evidence for the structure of the products, since they are consistent not only with the proposed structure **II**, but also with structures **A**–**C** (Scheme 5).

Scheme 5.



A **B** **C**

At the same time, the X-ray fluorescent spectra rule out structures **B** and **C**. Thus, the observation in the spectrum of dimer **IIa** of a broadened S$K\alpha$ line strongly proposes the presence in this compound of two different sulfide atoms [21] linked to C_{sp^2} and C_{sp} atoms. Below are given the shifts of the sulfur $K\alpha$ lines ($\Delta SK\alpha$, relative to S_8) and their half-widths ($W_{H/2}$, confidence level 95%).

Compound	S_8	Dimer **IIa**
$\Delta SK\alpha$, eV	0.00	–0.05 (1)
$W_{H/2}$, eV	2.36 (1)	2.39 (2)

Moreover, formation of structures **B** and **C** is inconsistent with the chemistry of both organylthiochloroacetylenes and organylethynyl sulfides, since in the literature there are no examples of easy transfer of the alkylthio group with S–C_{sp} bond cleavage, especially in as mild conditions as in the case of the reaction under study. At the same time, the chlorine atom in chloroacetylenes is rather active and can

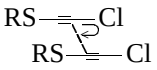
Table 2. Synthesis of 1,4-bis(alkylthio)-1,2-dichloro-1-buten-3-ynes **IIa**–**IIc** by dimerization of alkylthiochloroacetylenes **Ia**–**Ic** in the system Na_2SO_3–organic solvent[a]

No.	RSC≡CCl		Amount of Na_2SO_3 (mmol)	Solvent (ml)	Dimer **II**	Yield of compound **II**, %
	R	mmol				
1	*n*-Pr	6.50	6.50	DMSO (10)	**IIb**	60
2	*n*-Pr	5.50	5.50	HMPA (10)	**IIb**	27
3	*n*-Pr	5.50	5.50	DMF (10)	**IIb**	30
4	Et	5.50	5.50	Dioxane (10)	[b]	[b]
5	Et	21.60	21.60	DMSO (20)	**IIa**	63
6	*i*-Bu	13.50	13.50	DMSO (20)	**IIc**	40
7	*n*-Pr	6.40	12.80	DMSO (20)	**IIb**	61
8	*n*-Pr	14.90	7.45	DMSO (20)	**IIb**	60
9	*n*-Pr	10.00	1.00	DMSO (10)	**IIb**	61
10	Et	5.50	[c]	DMSO (10)	[d]	[d]

[a] Reaction temperature 20–22°C, reaction time 24 h. [b] No reaction occurs, the starting acetylene **Ia** is practically fully recovered from the reaction mixture. [c] Was not used. [d] Instead of the expected dimer **IIa**, products of polymerization of ethylthiochloroacetylene are formed.

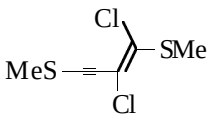
easily be substituted by various nucleophiles [6, 9, 10].

Dimer **B** is also unlikely to be formed because of the presence in its molecule of bulky geminal substituents (alkylthio and chloroethynyl groups). Apparently, the same is true of isomer **A** which can only be formed via a strained transition state **D** with eclipsed alkylthio groups and chlorine atoms.

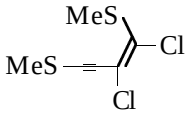


D

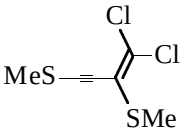
The regio- and stereoselectivity of the dimerization reaction also follow from dielcometric data and the nonemiprically (HF/6-31G*) calculated dipole moments of (*Z*)- and (*E*)-1,4-bis(methylthio)-1,2-dichloro-1-buten-3-ynes (**IIIa** and **IIIb**, μ 1.56 and 2.43 D), 2,4-bis(methylthio)-1,1-dichloro-1-buten-3-yne (**IV**, μ 3.07 D), (*Z*)- and (*E*)-1,2-bis(methylthio)-1,4-dichloro-1-buten-3-ynes (**Va** and **Vb**, μ 2.40 and 2.11 D), and 4,4-bis(methylthio)-1,3-dichloro-1-buten-3-yne (**VI**, μ 3.03 D), modeling dimers **II** and **A**–**C**.



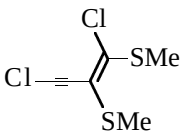
IIIa



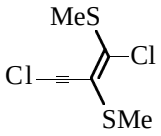
IIIb



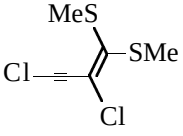
IV



Va



Vb

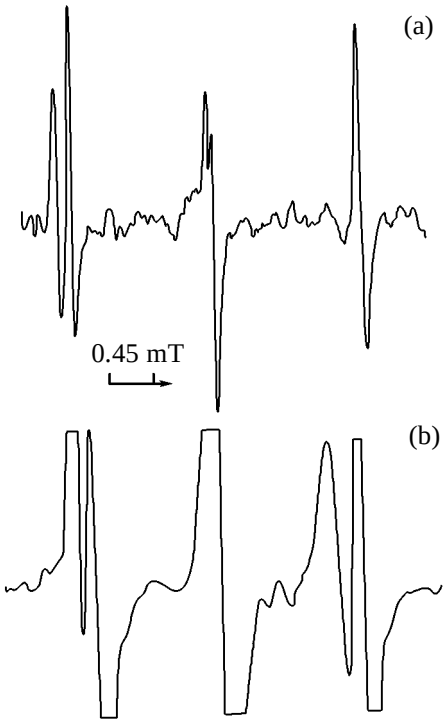


VI

To illustrate, the experimental dipole moment (μ 2.53 D) of dimer **IIa** most closely fits the dipole moment (μ 2.43 D) calculated for (*Z*)-1,4-bis(methylthio)-1,2-dichloro-1-buten-3-yne (**IIIb**). Consequently, the above results indicate that the dimers formed by the reaction (Scheme 2) have the structure of the *Z* isomers of 1,4-bis(alkylthio)-1,2-dichloro-1-buten-3-ynes (**II**).

Examining the preparative possibilities of the reaction we showed that the highest yield of dimers **II** is attained in the system Na_2SO_3–DMSO (Table 2). Changing DMSO to HMPA or DMF results, all other conditions being the same, in a markedly decreased yield (from 60 to 27–30%) of the product (Table 2, run nos. 1–3). In dioxane, the reaction failed to occur (Table 2, run no. 4). Alkylthiochloroacetylenes with normal alkyl radicals (Et, *n*-Pr) dimerize more effectively than *iso*-butylthiochloroacetylene (Table 2, run nos. 1, 5, and 6).

It is to be noted that the yield of butenynes **II** is practically the same both with excess sodium sulfite and in the presence of catalytic amounts of the salt (10 wt%) (Table 2, run nos. 1 and 7–9), which means that the effect of the latter is catalytic in nature. Moreover, the reaction (Scheme 2) gives viscous dark brown undistillable substances whose elemental composition is close to that of the starting chloroacetylenes **I**. The ^{1}H NMR spectra of these by-products show unresolved multiplets in the region characteristic of



ESR spectra of the reaction mixture obtained under the conditions of dimerization of chloro(ethylthio)acetylene (**Ia**) in the system Na_2SO_3–DMSO in the presence of a spin trap (*t*-BuNO). Amplitude modulation, mT: (a) 0.0125 and (b) 0.125.

alkylthio groups. The ^{13}C NMR spectra contain, along with aliphatic carbon signals, signals in the region characteristic of C_{sp^2} atoms, and the IR spectrum displays a broad absorption band in the region 1530–1680 cm^{-1} characteristic of polyacetylenes and lacks bands due to C≡C stretching vibrations [22]. These viscous undistillable producte are presumably formed by polymerization of the starting acetylenes **I**.

In the absence of sodium sulfite, no dimerization reaction takes place (Table 2, run no. 10). Nevertheless, under these conditions we were able to isolate the product of polymerization of the starting acetylene **Ia**.

The IR spectrum of this polymer showed no absorption bands of the triple bond, and its ^1H NMR spectrum contained unresolved multiplets in the region characteristic of alkylthio groups. On keeping chloro(ethylthio)acetylene in the resonator of an ESR spectrometer, we observed, already within 0.5 h, a weak asymmetric signal (*g* 2.0049) whose intensity grew for some hours. We failed to obtain a well-resolved signal, while it is evident that it consisted of several components. After 20 h, the spectrum was a superposition of two signals with much different widths and close *g* factors (ΔH_1 0.44 mT, *g* 2.0057 and ΔH_2 0.055 mT, *g* 2.0043). One more day after, the broad signal disappeared, and the spectrum contained a single symmetic signal of the Lorentz shape with ΔH_2 0.055 mT and *g* 2.0043. The observed signals, by analogy with polyacetylene [23, 24], can be assigned to polyalkylthiochloroacetylene. The parameters of the signals agree with published evidence for the soliton nature of paramagnetic centers. The observation of two signals of different width may imply formation, in the course of polymerization of alkylthiochloroacetylenes, of thermodynamically stable molecules of *trans* and *cis* configuration. The *cis* form first prevails but then gradually transforms into the *trans* form which gives the observed single symmetrical signal of the Lorentz shape in the ESR spectrum.

The ESR spectrum of the reaction mixture obtained under the conditions of dimerization of acetylene **Ia** in the system Na_2SO_3–DMSO (Table 2, run no. 5) contains a weak signal (*g* 2.0052). Analysis of published data allows us to assign this signal to the radical anion $SO_3^{\cdot}$. Specifically, the direct registration in the ESR spectrum of a weak singlet of the radical anion $SO_3^{\cdot}$ with the same *g* factor of 2.0052 in the oxidation of sodium sulfite with peroxidase has been reported [25]. Moreover, as shown in [25, 26], this radical anion is captured by nitroso compounds, e.g. nitrosobenzene or 2-methyl-2-nitrosopropane (*t*-BuNO).

Addition of *t*-BuNO into the reaction mixture obtained under the conditions of run no. 5 (Table 2) resulted in appearance in the ESR spectrum of this mixture of three signals (see picture). One of them belongs to the radical *t*-$Bu_2NO^{\cdot}$ (a_N 1.555 mT, *g* 2.0060). The second signal is a nitrogen triplet with a_N 1.400 mT and *g* 2.0057 (these characteristics are very close to those for the spin adduct of 2-methyl-2-nitrosopropane and the radical anion $SO_3^{\cdot}$, given in [26]). The third signal (a_N 1.310 mT, *g* 2.0062) evidently belongs to the spin adduct of *t*-BuNO with radicals formed from the starting acetylene. In fact, in the ESR spectrum of a mixture of acetylene **Ia**, DMSO, and *t*-BuNO we observed the same signal.

The higher effectiveness of the dimerization reaction in DMSO as compared with the other solvents (Table 2) is in line with the reported ability of DMSO to initiate radical anion reactions [27].

Thus, the above evidence is not in conflict with the earlier proposed scheme of dimerization of alkylthiochloroacetylenes in the system Na_2SO_3–DMSO, which involves the stage of one-electron transfer (Scheme 1).

The detection of the radical anion $SO_3^{\cdot}$ in the course of the reaction under study can be explained by a secondary process involving escape from the solvent cage of $NaSO_3^{\cdot}$ and its subsequent decay.

$$NaSO_3^{\cdot} \longrightarrow SO_3^{\cdot-} + Na^+.$$

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 spectrometer in microlayers. The ^1H and ^{13}C NMR spectra were taken on Jeol FX-90Q (90 MHz) and Bruker DPX-400 (400 MHz) spectrometers in $CDCl_3$, internal reference HMDS.

The mass spectra were run on an LKB-2091 GC–MS system (ionizing voltage 60 V) with both chromatographic and direct sample inlet (ion source temperature 240°C); glass capillary column, length 30 m, stationary phase SE-54, injection temperature 270°C, temperature programming at a rate of 16 deg/min from 50 to 250°C.

The dielectric constants of benzene solutions of compound **IIa** were measured on an Epsilon dielcometer (Angarsk; Experimental Design Office of Automation Joint-Stock Company). The dipole moments were calculated by the second Debye method using the Higasi extrapolation formula [28]. The semiempirical calculations of the dipole moments were made by the PM3 method. The nonempirical (HF/6-31G*) calculations of the dipole moments of the model compounds were performed using the GAUSSIAN 98 program package [29].

The ESR spectra were taken on a Radiopan SE/X-2547 (Poland) radiospectrometer equipped with a magnetometer in special cells under argon. The sensitivity of the instrument was 5×10^{11} spin/mT, resolution ≤ 0.006 mT.

Alkylthiochloroacetylenes were prepared by the procedure described in [30].

The reaction mixtures and the obtained compounds were analyzed by TLC on alumina in hexane, developer I_2.

1,4-Bis(ethylthio)-1,2-dichloro-1-buten-3-yne (IIa) (Table 2, run no. 5). To a suspension of 2.72 g of sodium sulfite in 20 ml of DMSO, 2.60 g of acetylene **I** was added dropwise at 20–22°C for 10 min with stirring. The reaction mixture was stirred for 24 h at 20–22°C and then poured into 10 ml of cold water and extracted with diethyl ether (3×15 ml). The ether extract was washed with water (2×5 ml) and dried with $MgSO_4$. The ether was removed in a vacuum to obtain 2.30 g of crude product. Distillation gave 1.64 g (63% per taken acetylene) of compound **II** as a light yellow liquid, bp 42–44°C (3 mm), n_D^{20} 1.5341. IR spectrum (microlayer), cm^{-1}: 2970, 2928, 2814 [ν(C–C)], 2142 [ν(C≡C)], 1528 [ν(C=C)], 1442, 1414, 1370, 1314 [δ(C–H)], 1256, 1170, 1128, 1056 [ν(C–C), δ(H–C–H), δ(C–C–S)], 942, 900, 800 [ν(C–S)], 770 [ν(C–Cl)], 628 [ν(C–S)]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.37 d. t (6H, CH_3), 2.59 m (4H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.97, 28.15 (SC_2H_5), 15.81, 29.49 (SC_2H_5), 59.84, 69.84 (C_{sp}), 114.24, 127.95 (C_{sp^2}). Found, %: C 40.00; H 3.98; Cl 29.06; S 26.54. $C_8H_{10}Cl_2S_2$. Calculated, %: C 39.84; H 4.18; Cl 29.40; S 26.59.

The residue (0.65 g) after distillation of compound **IIa** was a dark brown viscous material which could not be distilled in vacuo (3–5 mm) even at 150–200°C. It was insoluble in water but soluble in organic solvents. IR spectrum (microlayer), cm^{-1}: 2976, 2914, 2860 [ν(C–H)], 1680–1535 [ν(C=C)], 1500, 1446, 1380, 1314 [δ(C–H)], 1246, 1056, 980 [ν(C–C), δ(H–C–H), δ(C–C–S)], 946, 890 [ν(C–S)], 800, 750 [ν(C–Cl)], 552 [ν(C–S)]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.01–1.40 m (CH_3), 2.40–2.80 m (CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.88, 14.07, 14.26, 14.44, 14.77, 14.91, 26.67, 27.20 (C, AlkS), 119.43, 120.70, 129.51 (C_{sp^2}). Found, %: C 40.20; H 3.99; Cl 28.48; S 27.80.

The check run was carried out by the same procedure. It was shown (Table 2, run no. 10) that in the absence of sodium sulfite no dimer **IIa** is formed from acetylene **Ia** in DMSO at room temperature for 24 h. Under these conditions we isolated the product of polymerization of the starting acetylene **Ia**. IR spectrum (microlayer), cm^{-1}: 2948, 2910, 2890, 2850 [ν(C–C)], 1640 br [ν(C=C)], 1448, 1360 [δ(C–H)], 1298, 1260, 1112, 1080, 892, 884 [ν(C–C), δ(H–C–H), δ(C–C–S)], 628 [ν(C–Cl)]. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.01–1.50 m (CH_3), 2.40–2.78 m (CH_2S).

1,4-Bis(propylthio)-1,2-dichloro-1-buten-3-yne (IIb) (Table 2, run no. 1). To a suspension of 0.82 g of sodium sulfite in 10 ml of DMSO, 0.87 g of acetylene **Ib** was added dropwise for 10 min at room temperature with stirring. The reaction mixture was stirred for 24 h at 20–22°C and then poured into 10 ml of cold water and extracted with diethyl ether (3×15 ml). The ether extract was washed with water (2×5 ml) and dried with $MgSO_4$. The ether was removed in vacuo to obtain 0.74 g of crude product. Distillation gave 0.52 g (60%) of compound **IIb** as a light yellow liquid, bp 52–54°C (3 mm), n_D^{20} 1.5368. IR spectrum (microlayer), cm^{-1}: 2970, 2928, 2884 [ν(C–H)], 2142 [ν(C≡C)], 1524 [ν(C=C)], 1450, 1414, 1370, 1328 [δ(C–H)], 1294, 1228, 1156, 1142,

1056, 942 [ν(C–C), δ(H–C–H), δ(C–C–S)], 900, 894, 828 [ν(C–S)], 728 [ν(C–Cl)], 700 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 d. t (6H, CH_3), 1.74 m (4H, CH_2), 2.58 m (4H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.79, 22.74, 36.20 (SC_3H_7), 13.05, 23.13, 37.04 (SC_3H_7), 59.93, 66.96 (C_{sp}), 122.04, 134.59 (C_{sp^2}). Found, %: C 44.50; H 5.57; Cl 26.07; S 23.92. $C_{10}H_{14}Cl_2S_2$. Calculated, %: C 44.61; H 5.24; Cl 26.33; S 23.82.

The residue (0.2 g) after distillation of compound **IIb** was a dark brown material insoluble in water and soluble in organic solvents. IR spectrum (microlayer), cm^{-1}: 2980, 2920, 2852 [ν(C–H)], 1650–1510 [ν(C=C)], 1448, 1380, 1320 [δ(C–H)], 1236, 1036, 990 [ν(C–C), δ(H–C–H), δ(C–C–S)], 956, 890 [ν(C–S)], 790, 750 [ν(C–Cl)], 652 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.10–1.65 m (CH_3), 1.70–1.95 m (CH_2), 2.60–3.00 m (CH_2S). Found, %: C 43.60; H 6.57; Cl 24.07; S 25.92.

Dimerization of acetylene **Ib** in the system Na_2SO_3–DMSO at various proportions of the acetylene and the salt (Table 2, run nos. 1, 7–9), as well as in DMF, HMPA, and dioxane at equimolar proportions of chloroacetylene **Ib** and sodium sulfite (Table 2, run nos. 2–4) was carried out by the same procedure.

1,4-Bis(*iso*-butylthio)-1,2-dichloro-1-buten-3-yne (IIc) (Table 2, run no. 6). To a suspension of 1.70 g of sodium sulfite in 20 ml of DMSO, 2.00 g of acetylene **Ic** was added dropwise for 10 min at room temperature with stirring. The reaction mixture was stirred for 24 h at 20–22°C and then poured into 10 ml of cold water and extracted with diethyl ether (3 × 15 ml). The ether extract was washed with water (2 × 5 ml) and dried with $MgSO_4$. The ether was removed in vacuo to obtain 1.86 g of crude product. Distillation gave 0.80 g (40%) of compound **IIc** as a light yellow liquid, bp 58–60°C (5 mm). IR spectrum (microlayer), cm^{-1}: 2956, 2914, 2870 [ν(C–H)], 2150 [ν(C≡C)], 1540 [ν(C=C)], 1456, 1384, 1370, 1314 [δ(CH)], 1248, 1214, 1170, 1084, 942 [ν(C–C), δ(H–C–H), δ(C–C–S)], 900, 814, 800 [ν(C–S)], 730 [ν(C–Cl)], 628 [ν(C–S)]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 m (12H, CH_3), 1.95 m (2H, CH), 2.61 m (4H, CH_2S). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.42, 21.67, 28.55, 29.39 (SC_4H_9-*i*), 21.51, 21.74, 28.71, 29.76 (SC_4H_9-*i*), 60.45, 68.34 (C_{sp}), 121.77, 136.78 (C_{sp^2}). Found, %: C 47.90; H 6.00; Cl 24.07; S 21.92. $C_{12}H_{18}Cl_2S_2$. Calculated, %: C 48.48; H 6.10; Cl 23.85; S 21.57.

The residue (1.0 g) after distillation of compound **IIc** was a viscous dark brown material insoluble in water and soluble in organic solvents.

ACKNOWLEDGMENTS

The authors are grateful to V.A. Lopyrev for providing the software and to G.V. Dolgushin for carrying out nonempirical calculations of the dipole moments of the model compounds.

This study was financially supported by the Russian Foundation for Basic Research (project no. 99-03-32939).

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