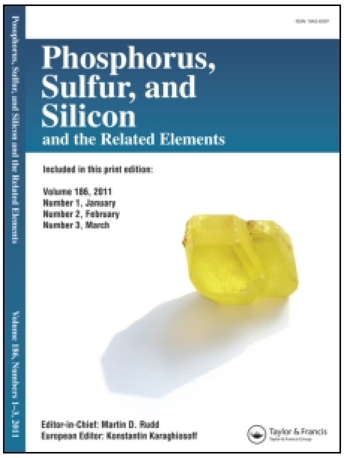

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# DIMERIZATION OF (ALKYLTHIO)CHLOROACETYLENES INITIATED BY SODIUM SULFITE

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(Alkylthio)chloroacetylenes 1 dimerize in the system $Na_2SO_3$ – DMSO to form 1,2-dichloro-1,4-bis(alkylthio)but-1-en-3-ynes 2 in 40–63% yield.

*Keywords:* (Alkylthio)chloroacetylenes; dimerization; sodium sulfite

## INTRODUCTION

Previously we have reported the reactions of (organylthio)chloroacetylenes with *S*-centered nucleophiles (sodium sulfide[1], thiols[2], thioacetic acid[3]), which occur according to addition and/or substitution schemes.

In the present work we have found that (alkylthio)chloroacetylenes[4] **1a-c** unexpectedly undergo dimerization in the presence of sodium sulfite to afford 1,2-dichloro-1,4-bis(alkylthio)but-1-en-3-ynes **2a-c**, which are promising polyfunctional unsaturated building blocks for fine organic synthesis.

There is an example[5] of the $Ipy_2BF_4/HBF_4$-induced catalytic dimerization of iodoarylacetylenes which follows an electrophilic mechanism to afford 1-(4,4-diiodo-3-phenylbut-3-en-1-ynyl)benzenes, the structure of which was confirmed by the data of NMR and IR spectra.

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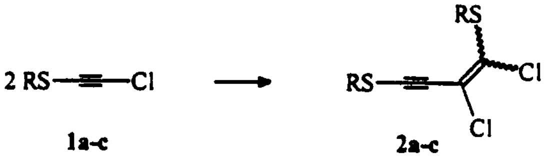
## RESULTS AND DISCUSSION

The dimerization of chloroacetylenes **1a-c** (Scheme 1) occurs in DMSO at 20–22°C and is independent of the ratio of initial reagents: the yield of butenynes **2a-c** is nearly the same with both equimolar and catalytic amounts of sodium sulfite, therefore the action of the latter is of catalytic nature. It should be noted that the reaction mixture acquires red-brown color when the reagents are mixed, while the compounds **2a-c** isolated in pure state represent mobile yellow liquids.

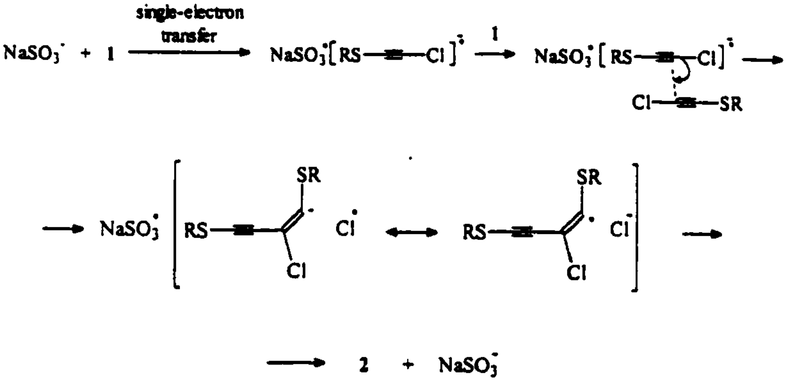


R = Et (**a**), *n*-Pr (**b**), *i*-Bu (**c**)

SCHEME 1

A control experiment, carried out with the initial acetylene under the same conditions without $Na_2SO_3$ has not led to the products **2a-c**.

The formation of dimers **2** catalyzed by sulfite-anion can be explained by a scheme including the single-electron transfer stage (Scheme 2):



SCHEME 2

The key stage of the dimerization is assumed to be the nucleophilic attack of the second molecule of **1** by the anion-radical counterpart of the anion-radical pair. An important feature of this peculiar dimerization that worth attention is a temporary delegation of nucleophilicity from the sulfite anion to the acetylene **1** molecule thus transforming it into an active nucleophilic species. The revealed dimerization of (alkylthio)chloroacetylenes **1** can be attributed to the type of catalytic vicarious nucleophilic addition by analogy with the known reaction of stoichiometric vicarious nucleophilic substitution[6].

The dimerization does not proceed in dioxane, indicating that the ion pair separation, such as it occurs in DMSO, is important. This is in keeping with the Scheme 2, which implies that the reaction requires a "naked" anion for a facile single-electron transfer. The mechanism of (alkylthio)chloroacetylenes dimerization is under investigation.

The structure of dimers **2** was proved by IR, NMR $^1$H, $^{13}$C and mass spectra and is in agreement with the literature data for similar compounds: 1,2-dichloro-1,4-bis(*t*-butylthio)but-1-en-3-yne[7], 1,2-dichloro-1,4-bis(cyclo-hexylthio)but-1-en-3-yne[8], 1,2-dichloro-4-(4-methylphenylthio)but-1-en-3-ynyl-4-methylphenyl sulfide[8], 1,2-dichloro-1,4-bis(octylthio)but-1-en-3-yne[9], and 1,2-dichloro-1,4-bis(hexylthio)but-1-en-3-yne[9].

## EXPERIMENTAL

IR spectra were run on a Specord IR-75 spectrometer in a microlayer. $^1$H and $^{13}$C NMR spectra were recorded on a Jeol FX-90 Q instrument (90 MHz) in $CDCl_3$, HMDS as an internal standard. Mass spectra were obtained on an LKB-2091/152 instrument. The reaction mixture analysis and purity control of the obtained compounds were performed by TLC using plates with $Al_2O_3$ (eluent – octane; developer – $I_2$). (Alkylthio)chloroacetylenes were prepared by a procedure described in[4].

### 1,2-Dichloro-1,4-bis(ethylthio)but-1-en-3-yne (2a)

To a suspension of 2.72 g (21.6 mmol) of sodium sulfite in 20 ml of DMSO, 2.6 g (21.6 mmol) of acetylene **1a** was added by drops upon stirring for 10 min. The mixture was stirred for 24 h more at 20–22°C. The reaction course was monitored using TLC by disappearance of the initial acetylene in the reaction mixture. The mixture was poured into 50 ml of cold water. The aqueous solution was extracted with diethyl ether (3 × 15 ml). The ether extract was washed with water and dried over $MgSO_4$ and purified on a column filled with $Al_2O_3$. Then the ether was removed *in vacuo*. The remaining liquid was distilled *in vacuo* to give 1.64 g (63%) of **2a** – yellow liquid. B.p. 42°C (5 mm Hg), $n_D^{20}$ 1.5341. IR: 2970, 2928, 2814 (ν, C-H), 2142 (ν, C≡C), 1528 (ν, C=C), 1442, 1414, 1370, 1314 (δ, CH), 1256, 1170, 1128, 1056 (ν, C-C; δ, H-C-H; δ, C-C-S), 970, 942, 900, 800 (ν, C-S), 770 (ν, C-Cl), 628 (ν, C-S) $cm^{-1}$. $^1H$ NMR (ppm): δ 1.37 (d.t., 6H, $CH_3$), 2.59 (m, 4H, $CH_2S$). MS, m/z (rel. int., %): $M^+$ 240 (10), 225 (7) $[M\ -CH_3]^+$, 206 (15.5), 183 (53) $[M\ -C_2H_5,\ -C_2H_4]^+$, 167 (53) $[M\ -CSC_2H_5]^+$, 141 (36) $[M\ -2Cl,\ -C_2H_5]^+$, 111 (84) $[M\ -2Cl,\ -C_2H_5,\ -C_2H_6]^+$, 97 (10) $[M\ -2Cl,\ -CSC_2H_5]^+$, 69 (34) $[M\ -2Cl,\ -CSC_2H_5,\ -C_2H_4]^+$, 45 (15) $[CHS]^+$, 28 (72) $[C_2H_4]^+$. Anal. Calcd for $C_8H_{10}Cl_2S_2$: C, 39.84; H, 4.18; Cl, 29.40; S, 26.59. Found: C, 40.00; H, 3.98; Cl, 29.06; S, 25.54 %.

Compounds **2b** and **2c** were prepared analogously from acetylenes **1b**, **1c**, respectively, and sodium sulfite.

### 1,2-Dichloro-1,4-bis(*n*-propylthio)but-1-en-3-yne (2b)

Yield – 60%, b.p. 52–54°C (5 mm Hg), $n_D^{20}$1.5368. IR: 2970, 2928, 2884 (ν, C-H), 2142 (ν, C≡C), 1514 (ν, C=C), 1450, 1414, 1370, 1328 (δ, CH), 1294, 1228, 1156, 1142, 1056 (ν, C-C; δ, H-C-H; δ, C-C-S), 942, 900, 894, 828 (ν, C-S), 728 (ν, C-Cl), 700 (ν, C-S) $cm^{-1}$. $^1H$ NMR (ppm): δ 1.00 (d.t., 6H, $CH_3$), 1.74 (m, 4H, $CH_2$), 2.58 (m, 4H, $CH_2S$). $^{13}C$ NMR (ppm): δ 12.79, 22.74, 36.20 ($SC_3H_7$-*n*), 13.05, 23.13, 37.04 ($SC_3H_7$-*n*), 59.93, 66.96 (≡C), 122.04, 134.59 (=C). Anal. Calcd for $C_{10}H_{14}Cl_2S_2$: C, 44.61; H, 5.24; Cl, 26.33; S, 23.82. Found: C, 44.50; H, 5.57; Cl, 25.07; S, 23.92 %.

### 1,2-Dichloro-1,4-bis(*i*-butylthio)but-1-en-3-yne (2c)

Yield – 40%, b.p. 58–60°C (5 mm Hg). IR: 2956, 2914, 2870 (ν, C-H), 2142 (ν, C≡C), 1540 (ν, C=C), 1456, 1384, 1370, 1314 (δ, CH), 1248, 1214, 1170, 1084 (ν, C-C; δ, H-C-H; δ, C-C-S), 942, 900, 814, 800 (ν, C-S), 730 (v, C-Cl), 628 (v, C-S) cm$^{-1}$. $^1$H NMR (ppm): δ 1.00 (m, 12H, $CH_3$), 1.95 (m, 2H, CH), 2.61 (m, 4H, $CH_2S$). $^{13}$C NMR (ppm): δ 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), 121.77, 126.78 (=C). MS, m/z (rel. int., %): M$^+$ 296 (2), 240 (9) $[M -C_4H_8]^+$, 184 (53) $[M -2C_4H_8]^+$, 148 (31) $[M -C_4H_9SC{\equiv}C, -Cl]^+$, 128 (35) $[M -C_4H_9SC{\equiv}C, -C_4H_7]^+$, 104 (4), 92 (15) $[ClCSCH]^+$, 79 (8) $[ClCS]^+$, 57 (100) $[C_4H_9]^+$, 41 (65) $[C_3H_5]^+$, 29 (55) $[C_2H_5]^+$. Anal. Calcd for $C_{12}H_{18}Cl_2S_2$: C, 48.48; H, 6.10; Cl, 23.85; S, 21.57. Found: C, 47.90; H, 6.00; Cl, 24.07; S, 23.92 %.

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