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Dehydrochlorination of 2-Chloroprop-2-en-1-yl Sulfides

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Abstract—Dehydrochlorination of 2-chloroprop-2-en-1-yl sulfides on heating with solid potassium hydroxide afforded the corresponding 1-(organylsulfanyl)propynes in moderate to high yields and minor isomeric allene derivatives, organylsulfanylpropadienes.

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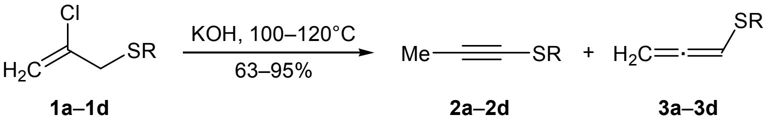
Acetylenic sulfides [1–3] are capable of reacting through both triple bond (electrophilic, nucleophilic, and radical additions) and sulfur atom (oxidation to sulfoxides and sulfones); therefore, they are valuable reagents for the synthesis of various organic and organoelement compounds such as difficultly accessible functionalized benzofurans [4], pyrazoles, thienopyrazoles [5], alkenes [6, 7], dihydrothiophenes [8], and activated acetylenic sulfones [9]. Sulfides containing acetylenic fragments are used as ligands for complexation with metals [10] and are also interesting as models for theoretical studies [11]. Taking the above stated into account, development of efficient methods for the synthesis of alkynyl sulfides is a topical problem.

A classical and quite efficient synthetic approach to acetylenic sulfides is based on dehydrohalogenation of vicinal or geminal dihaloalkyl sulfides, specifically dibromoalkyl sulfides which are prepared in turn by halogenation of the corresponding alkenyl sulfides [1, 3, 12–15]. We previously synthesized a series of 2-chloroprop-2-en-1-yl sulfides using accessible reagents [16, 17], halogen-containing electrophiles, thiourea, and 2,3-dichloropropene; the latter is a waste product in organochlorine industry. In continuation of these studies, in the present work we examined dehydrohalogenation of chloropropenyl sulfides **1a**–**1d** with the goal of developing methods for the synthesis of acetylenic sulfides.

No dehydrochlorination of **1a**–**1d** was observed in the presence of amines or aqueous alkali on heating to 100°C. The reactions of **1a**–**1d** with alkali in high-boiling aprotic solvents (dioxane, DMSO, DMF) resulted in strong tarring, especially at elevated temperature, and we failed to isolate targeted acetylenic derivatives. The reactions of **1a**–**1d** with alcoholic alkali were accompanied by side processes which led to the formation of inseparable mixtures of products, the conversion being complete; acetylenic sulfides were detected among the products by spectral methods.

Variation of the reaction conditions showed that acetylenic sulfides **2a**–**2d** were formed in good yields when sulfides **1a**–**1d** were heated over solid alkali (Scheme 1). This procedure is the least laborious since the products can be isolated directly from the reaction mixture by distillation under atmospheric or reduced pressure, thus avoiding any additional workup. Under the given conditions, compounds **2a**–**2d** were formed as mixtures with minor isomeric allenyl sulfides **3a**–**3d** whose fraction reached 3–5 mol %. Presumably, the isomer ratio **2**/**3** corresponds to thermodynamic equilibrium: this ratio did not change after prolonged

Scheme 1.



R = PhCH$_2$ (**a**), Et (**b**), Pr (**c**), Ph (**d**).

keeping of the isomer mixture over alkali. In no case did we succeed in isolating or detecting spectrally terminal acetylenic sulfides whose formation could also be expected. These isomeric structures are likely to be less thermodynamically stable because of the lack of conjugation between the sulfur atom and acetylenic or allene fragments.

The structure of **2** and **3** was confirmed by spectral methods. Protons of the methyl group on the triple bond resonated in the ^{1}H NMR spectra of **2a**–**2d** as a singlet at 1.86–2.14 ppm, and the triple-bonded carbon atoms gave signals at δ_C 64.5–67.6 and 89.4–95.8 ppm in the ^{13}C NMR spectra. Allenes **3** characteristically showed in the ^{1}H NMR spectra a two-proton multiplet signal at δ 4.91–5.02 ppm (=CH$_2$) and a more downfield signal at δ 5.69–6.00 ppm (=CHS). The ^{13}C NMR spectra of **3a**–**3d** contained signals typical of the allene fragment at δ_C 79.3–80.3, 86.6–87.6, and 206.3–209.9 ppm. The elemental compositions of **2** and **3** were consistent with the assigned structure. Furthermore, compounds **2a**, **2b**, **2d**, **3a**, and **3d** were described previously, and their spectral characteristics were quite consistent with those reported in [18–20].

In summary, we have studied dehydrochlorination of a series of 2-chloroprop-2-en-1-yl sulfides and found conditions for their transformation into 1-(organylsulfanyl)propynes which exist in thermodynamic equilibrium with allene isomers.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-25 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer at 400.13 and 100.62 MHz, respectively, using CDCl$_3$ as solvent and tetramethylsilane as internal standard. The elemental analyses were obtained on a Thermo Scientific Flash 2000 automated CHNS analyzer.

1-(Benzylsulfanyl)propyne (2a) and 1-(benzylsulfanyl)propadiene (3a). Sulfide **1a**, 3.0 g (15.0 mmol), was added to 12.7 g (226 mmol) of potassium hydroxide, and the mixture was heated at a residual pressure of 10 mm while distilling off a fraction with bp 120–122°C. Yield 1.57 g (64%), colorless liquid, ratio **2a**/**3a** 97:3 (according to the ^{1}H NMR data). IR spectrum (film), ν, cm^{-1}: 2203 (C≡C), 1940 (C=C=C). ^{1}H NMR spectrum, δ, ppm: **2a**: 1.86 s (3H, CH$_3$), 3.83 s (2H, CH$_2$S), 7.23 m (5H, C$_6$H$_5$); **3a**: 3.77 s (2H, SCH$_2$), 4.91 d (2H, =C=CH$_2$, ^4J = 6.4 Hz), 5.69 t (1H, =CHS, ^4J = 6.4 Hz), 7.22 m (5H, C$_6$H$_5$). ^{13}C NMR spectrum, δ_C, ppm: **2a**: 5.04 (CH$_3$), 40.11 (SCH$_2$), 67.34 (≡CS), 91.32 (≡**C**CH$_3$), 127.61 (C^p), 128.54 and 129.00 (C^o, C^m), 137.02 (C^i); **3a**: 36.85 (CH$_2$S), 80.19 (H$_2$C=), 86.83 (SCH=), 128.10 (C^p), 128.35 and 128.85 (C^o, C^m), 137.64 (C^i), 206.28 (=C=). Found, %: C 73.97; H 6.42; S 19.60. $C_{10}H_{10}S$. Calculated, %: C 74.02; H 6.22; S 19.76. The spectral data of **2a** and **3a** were in agreement with those reported in [18].

Compounds **2b**–**2d** and **3b**–**3d** were obtained in a similar way.

1-(Ethylsulfanyl)propyne (2b) and 1-(ethylsulfanyl)propadiene (3b) were synthesized by reaction of 1.0 g (7.3 mmol) of **1b** with 6.1 g (110 mmol) of potassium hydroxide. The mixture was heated, and a fraction boiling at 96–98°C under atmospheric pressure was distilled off. Yield 0.46 g (63%), colorless liquid, ratio **2b**/**3b** 96:4 (^{1}H NMR). IR spectrum (film), ν, cm^{-1}: 2200 (C≡C), 1940 (C=C=C). ^{1}H NMR spectrum, δ, ppm: **2b**: 1.34 t (3H, CH$_2$C**H**$_3$), 1.92 s (3H, ≡CCH$_3$), 2.62 (2H, CH$_2$S, *AB*, ^2J = 7.3 Hz); **3b**: 1.26 t (3H, CH$_2$C**H**$_3$), 2.60 d (2H, CH$_2$S), 4.95 d (2H, CH$_2$=, ^4J = 6.4 Hz), 5.72 t (1H, =CHS, ^4J = 6.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: **2b**: 5.00 (CH$_3$), 14.73 (CH$_3$), 29.60 (CH$_2$S), 67.19 (≡CS), 90.14 (≡**C**CH$_3$). Found, %: C 60.05; H 7.99; S 31.93. C_5H_8S. Calculated, %: C 59.94; H 8.05; S 32.01. The spectral data of **2b** were consistent with published data [19].

1-(Propylsulfanyl)propyne (2c) and 1-(propylsulfanyl)propadiene (3c) were synthesized by reaction of 1.0 g (6.6 mmol) of **1c** with 5.6 g (100 mmol) of potassium hydroxide. The mixture was heated, and a fraction boiling at 108°C under atmospheric pressure was distilled off. Yield 0.33 g (43%), colorless liquid, ratio **2c**/**3c** 96:4 (^{1}H NMR). IR spectrum (film), ν, cm^{-1}: 2200 (C≡C), 1940 (C=C=C). ^{1}H NMR spectrum, δ, ppm: **2c**: 0.96 t (3H, CH$_2$C**H**$_3$), 1.69 m (2H, CH$_2$), 1.89 s (3H, CH$_3$), 2.58 t (2H, CH$_2$S); **3c**: 0.92 t (3H, CH$_3$), 1.59 m (2H, CH$_2$), 2.42 t (2H, CH$_2$S), 4.92 d (2H, H$_2$C=, ^4J = 6.4 Hz), 5.70 t (1H, =CHS, ^4J = 6.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: **2c**: 5.03 (CH$_3$), 13.25 (CH$_3$), 22.73 (CH$_2$), 37.39 (CH$_2$S), 67.55 (≡CS), 89.43 (≡**C**CH$_3$); **3c**: 13.28 (CH$_3$), 22.54 (CH$_2$), 34.32 (CH$_2$S), 80.32 (=CH$_2$), 87.56 (=CHS), 205.8 (=C=). Found, %: C 63.05; H 9.07; S 27.85. $C_6H_{10}S$. Calculated, %: C 63.10; H 8.83; S 28.08.

1-(Phenylsulfanyl)propyne (2d) and 1-(phenylsulfanyl)propadiene (3d) were synthesized from 1.5 g (8.1 mmol) of **1d** and 6.8 g (122 mmol) of potassium hydroxide. The mixture was heated under reduced pressure (10 mm), and a fraction boiling at 108°C was distilled off. Yield 1.11 g (92%), colorless liquid, ratio **2d**/**3d** 95:5 (^{1}H NMR). IR spectrum (film), ν, cm^{-1}: 2198 (C≡C), 1941 (C=C=C). ^{1}H NMR spectrum, δ, ppm: **2d**: 2.14 s (3H, CH_3), 7.23 m and 7.76 m (5H, C_6H_5); **3d**: 5.02 d (2H, H_2C=, ^4J = 6.2 Hz), 6.00 t (1H, =CHS, ^4J = 6.2 Hz), 7.23 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: **2d**: 5.77 (CH_3), 64.52 (≡CS), 95.84 (CH_3**C**≡), 126.51 (C^m), 126.73 (C^p), 129.64 (C^o), 134.22 (C^i); **3d**: 79.31 (H_2C=), 86.59 (=CHS), 209.94 (=C=). Found, %: C 73.13; H 5.40; S 21.43. C_9H_8S. Calculated, %: C 72.93; H 5.44; S 21.63. The spectral data of **2d** and **3d** coincided with those given in [20].

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