Reaction of thioacetic acid with ethenyl- and ethynyl chlorides

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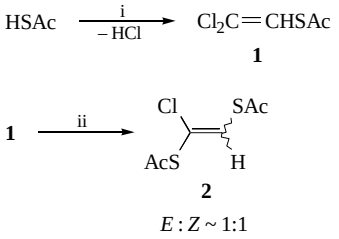
Thioacetic acid (TAA) has been subjected to dichlorovinylation with trichloroethene (TCE) under free-radical conditions to form 1-acetylthio-2,2-dichloroethene **1** (yield 70%) which reacts with TAA at room temperature under phase-transfer catalysis conditions to afford a mixture of *E*- and *Z*-isomers of 1,2-bis(acetylthio)-2-chloroethene **2** (total yield 71%); ethylthio(chloro)ethyne with sodium thioacetate gives acetylthio(ethylthio)ethyne **3**.

Functional ethylenes and acetylenes containing a readily hydrolysable acetylthio group at the multiple bond are highly reactive synthons and intermediates for fine organic synthesis as well as potential monomers for the preparation of polyethenyl- and polyethynylthiols: redox and complexing polymers which can be used in advanced technologies, in particular, as cathode materials for lithium batteries.[1–3] At the same time, the number of such compounds currently known is rather limited, and the methods for their synthesis are, as a rule, multi-stage and time-consuming processes.[4,5]

In the present work we studied some new convenient approaches to the synthesis of acetylthioethenes and -ethynes by the reaction of TAA with available chloroethenes and -acetylenes.[6]

The literature contains no data on the reaction of TAA with TCE, although the latter is known to dichlorovinylate aliphatic and aromatic thiols under radical conditions[7] as well as in the presence of a superbasic KOH/DMSO medium.[8]

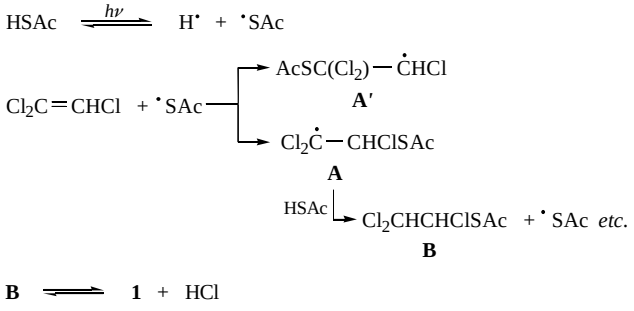
Our studies demonstrate that UV irradiation of a heated (80–85 °C) mixture of TAA in excess TCE leads to 1-acetylthio-2,2-dichloroethene **1** in 70% yield (Scheme 1, i).



Scheme 1 *Reagents and conditions*: i, TCE (2 mol), reflux, UV irradiation, 10 h, 70% yield of **1**; ii, 50% aq. KOH, TAA, $PhCH_2N^+Et_3Cl^-$ (cat.), toluene, 20–22 °C, 2 h, 71% yield of **2**.

The reaction (Scheme 1, i) seems to occur as an addition–elimination process, where the addition is of a chain radical nature, while the elimination follows an ionic monomolecular mechanism (E1):

The HCl elimination from the adduct **B** seems to be reversible, which is typical of E1 reactions, and is facilitated by nitrogen blowing through the reaction mixture and completed by distillation *in vacuo*.



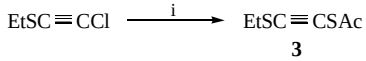
Scheme 2

The observed regioselectivity of the process corresponds to the expected greater steric hindrance of acetylthiyl radical attack at TCE from two chlorine atoms (repulsion of the lone electron pairs of the sulfur and the chlorine atoms), as well as to the greater stability of the radical **A** compared with that of the alternative radical **A′**, due to the participation of the electron shells of two chlorine atoms in the spin density distribution.

Treatment of ethene **1**[†] with an equimolar amount of TAA in a superbasic aqueous–organic emulsion in the presence of phase-transfer catalyst gave 1,2-bis(acetylthio)-2-chloroethene **2**,[‡] in an approximately 1:1 mixture of *E*- and *Z*-isomers (^{1}H NMR) (Scheme 1, ii).

Our numerous attempts to carry out dehydrochlorination of chloroethene **2** with the aim of preparing bis(acetylthio)ethyne failed. Under phase-transfer conditions only black polymeric products were isolated from the reaction mixture irrespective of the organic phase type (toluene, diethyl ether) and dehydrochlorinating agent (KOH, NaOH, K_2CO_3). The reaction of ethylthio(chloro)ethyne with sodium thioacetate in ether at 20 °C leads to acetylthio(ethylthio)ethyne **3** in 20% yield (not optimized).[§]

An attempt to perform this process in a superbasic KOH/DMSO suspension successfully employed previously for thiylation of organylthio(chloro)ethynes with thiols[9] failed: polymeric products were mainly formed in this case along with a small quantity of acetylthioethyne.[¶]



Scheme 3 *Reagents and conditions*: i, AcSNa, Et_2O, room temperature, 3 h, 20% yield of **3**.

[†] IR spectra were recorded on a Specord IR-75 spectrometer in a microlayer. ^{1}H NMR spectra were recorded on a Jeol FX-90 Q instrument (90 MHz) in $CDCl_3$, with HMDS as an internal standard. Commercial grade TCE was purified by distillation. Ethylthiochloroacetylene was prepared by a procedure described in ref. 6. All the operations were performed in an argon atmosphere.

For **1**: bp 45–50 °C (3 mmHg), n_D^{20} 1.5274. ^{1}H NMR δ: 2.41 (s, 3H, Me), 6.97 (s, 1H, =CH). IR (ν/cm^{-1}): 600, 642 (C–S), 784 (C–Cl), 810, 900, 956, 1110, 1342, 1410 (Me, =C–H), 1580 (C=C), 1700 (C=O), 2850, 2910, 2990, 3030 (=C–H, C–H). Found (%): C 28.97; H 2.16; Cl 40.02; S 19.81. Calc. for $C_4H_4Cl_2OS$ (%): C 28.07; H 2.33; Cl 40.52; S 18.71.

[‡] For **2**: a viscous liquid, n_D^{20} 1.5192, which decomposes on heating (35–50 °C) during distillation in a vacuum, was prepared. ^{1}H NMR δ: 2.09 (s, 3H, Me), 2.43 (s, 3H, Me), 6.47 (s, 1H, =CH), 6.70 (s, 1H, =CH). IR (ν/cm^{-1}): 655, 680 (C–S), 765 (C–Cl), 815, 860, 945, 978, 1140, 1370, 1425 (Me, =C–H), 1590 (C=C), 1720 (C=O), 2850, 2920, 2955, 3050 (=C–H, C–H). Found (%): C 33.61; H 3.31; Cl 17.84; S 31.36. Calc. for $C_6H_7ClO_2S_2$ (%): C 34.20; H 3.32; Cl 16.86; S 30.40.

[§] For **3**: bp 85–90 °C (5 mmHg), n_D^{20} 1.5382. ^{1}H NMR δ: 1.13 (t, 3H, Me), 2.21 (s, 3H, MeCO), 2.51 (q, 2H, CH_2). IR (ν/cm^{-1}): 810, 830, 900, 950, 1100 (C–H), 1350, 1430, 1460 (Me), 1700 (C=O), 2130 (C≡C), 2870, 2910, 2970 (C–H). Found (%): C 44.80; H 5.40; S 39.55. Calculated for $C_6H_8S_2O$ (%): C 44.98; C 5.03; S 40.02.

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¶ *Reaction of ethylthio(chloro)ethyne with TAA in a KOH/DMSO suspension*. To a KOH (1.39 g, 25 mmol) suspension in 25 ml of DMSO, 1.26 g (16.5 mmol) of TAA and 2 g (16.5 mmol) of ethylthio(chloro)-ethyne were successively added, dropwise with stirring. The reaction mixture was stirred for another 1 h and filtered. All the above procedures were performed at room temperature. The filtrate was poured into 70 ml of cold water with ice. The precipitated oil-like product of brown color was separated. The aqueous layer was extracted with diethyl ether, the extract was combined with the above oil-like product, dried over Na_2SO_4, passed through an Al_2O_3 packed column, the solvent was filtered off and the residue was dried under a vacuum. The product obtained (0.8 g) was a viscous brown oil. ^{1}H NMR δ: 1.18, 1.26 (m, Me), 2.61 (s, 3H, MeCO) 2.71 (m, 2H, SCH_2). IR (ν/cm^{-1}): 800, 880, 960, 1100, 1180 (C–H), 1250, 1314, 1380, 1442 (Me), 1710 (C=O), 2130 (C≡C), 2860, 2914, 2964 (C–H). Found (%): C 41.66, H 5.53, S 40.69. Calc. for $C_6H_8S_2O$ (%): C 44.98, H 5.03, S 40.02. The product resinified and decomposed during distillation in a vacuum (40–50 °C) in the presence of hydroquinone under argon.

When carried out in a KOH/DMSO suspension at 13–15 °C, the reaction of ethylthio(chloro)ethyne with TAA led to an analogous result.

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