A Simple, One-Pot Synthesis of 1-Alkylthio- or 1-Arylthio-3-buten-1-ynes

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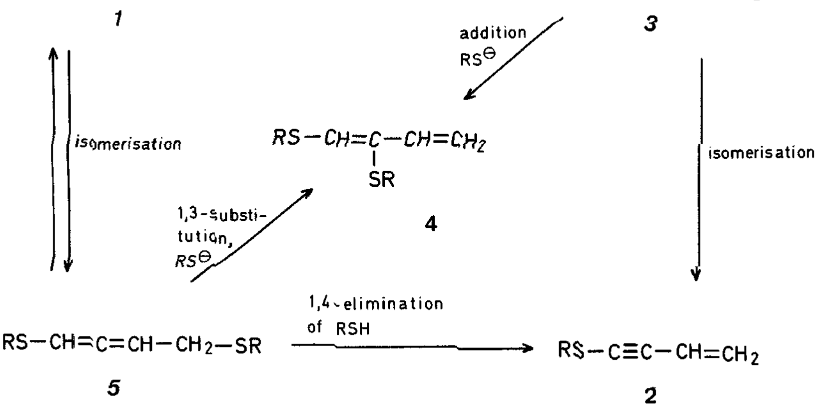
In a previous study[1] of the behaviour of bis-sulfides of the type **1** towards sodium ethoxide in liquid ammonia it was found that these compounds undergo elimination of thiol with formation of 1-alkylthio-3-buten-1-ynes (**2**). The yields of these compounds were generally poor due to the formation of 1,2-bis[alkylthio]-1,3-butadienes (**4**).

$\mathrm{RS{-}CH_2{-}C{\equiv}C{-}CH_2{-}SR}$ **1** $\qquad$ $\mathrm{RS{-}C{\equiv}C{-}CH{=}CH_2}$ **2**

These products were thought to result from re-addition of thiolate, split off in the primary elimination, to intermediary cumulenic sulfides. It is however, also possible that the 1,3-dienes arise from 1,3-substitution of thiolate to intermediary allenic bis-sulfides **5**.



We hoped that by using a suitable stronger base a faster elimination and a faster isomerisation of the intermediary cumulenic sulfide could be brought about, thus repressing the isomerisation to the allenic bis-sulfide and/or the addition of RS$^{\ominus}$ to the cumulenic sulfide. As we found earlier that sodamide caused almost complete destruction of cumulenic sulfides **3** as well as of the desired enynyl sulfides **2**, a base of intermediate strength was tried. We found that in the presence of at least one equivalent of potassium *t*-butoxide a clean conversion into the butenynyl sulfides took place.

Table. Preparation of Enynyl Sulfides **2**

R	Yield [%]	b.p./torr (Lit. b.p./torr)	n_D^{20} (Lit. n_D)	Molecular formula
CH_3	85	34°/12 (42.5°/20)[4]	1.5544 (1.5561)[4]	C_5H_6S (98.1)
C_2H_5	87	50°/15 (51°/18)[1]	1.5415 (1.5415)[1]	C_6H_8S (112.1)
i-C_3H_7	91	57°/15 (53°/13)[1]	1.5272 (1.5283)[1]	$C_7H_{10}S$ (126.2)
t-C_4H_9	90	60°/15 (55.5°/12)[1]	1.5185 (1.5192)[1]	$C_8H_{12}S$ (140.2)
C_6H_5	88	65°/0.01 (94.5°/5)[4]	1.6247 (1.6260)[4]	$C_{10}H_8S$ (160.2)

Combining the elimination with the formation of bis-sulfides **1** from thiolates and the easily accessible 1,4-dichloro-2-butyne[2] (**6**) a convenient one-pot procedure for 1-alkylthio- or arylthio-3-buten-1-ynes **2** resulted, giving overall yields of 85–91%.

$$\underset{\mathbf{6}}{\mathrm{Cl{-}CH_2{-}C{\equiv}C{-}CH_2{-}Cl}} \xrightarrow{\text{2 RSNa / liq. NH}_3}$$

$$\underset{\mathbf{1}}{\mathrm{RS{-}CH_2{-}C{\equiv}C{-}CH_2{-}SR}} \xrightarrow{\text{KOC}_4\text{H}_9\text{-}t\text{ / liq. NH}_3}$$

$$\mathrm{RS^{\ominus}} + \underset{\mathbf{2}}{\mathrm{RS{-}C{\equiv}C{-}CH{=}CH_2}}$$

If desired the bis-sulfides **1** can also be prepared in alcohol[3] and, after isolation, be treated with potassium *t*-butoxide in tetrahydrofuran, which gives the same end products in excellent yields.

Preparation of Enynyl Sulfides 2; General Procedure:

A solution of sodium thiolate (1.1 mol) is prepared by drop-wise addition of the respective thiol (R—SH, R = C_2H_5, i-C_3H_7, or t-C_4H_9; 1.1 mol) to a solution of sodium (1.1 mol) in liquid ammonia (~2000 ml) until the blue colour disappears. (In the case of R = CH_3, dimethyl disulfide is used instead of methanethiol: in the case of R = C_6H_5, sodium is added in pieces to thiophenol (1.1 mol) in liquid ammonia). To the well-stirred solution of the sodium thiolate (1.1 mol) in liquid ammonia (1800 ml) in a 3-litre, round-bottom, three-neck flask is added 1,4-dichloro-2-butyne (0.50 mol) in dry ether (50 ml) during 15 min. 10 min later finely powdered potassium *t*-butoxide (0.6 mol; uncomplexed base from Dynamit-Nobel) is added within 2 min. After 10 min stirring, the solution is poured on to crushed ice and extracted three times with pentane or ether. The combined extracts are dried with magnesium sulfate, the solvent is evaporated under reduced pressure or distilled off at atmospheric pressure and the residue is distilled to give the product (see Table).

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