COMMUNICATIONS

A Convenient Method for the Introduction of a Vinylthio Group

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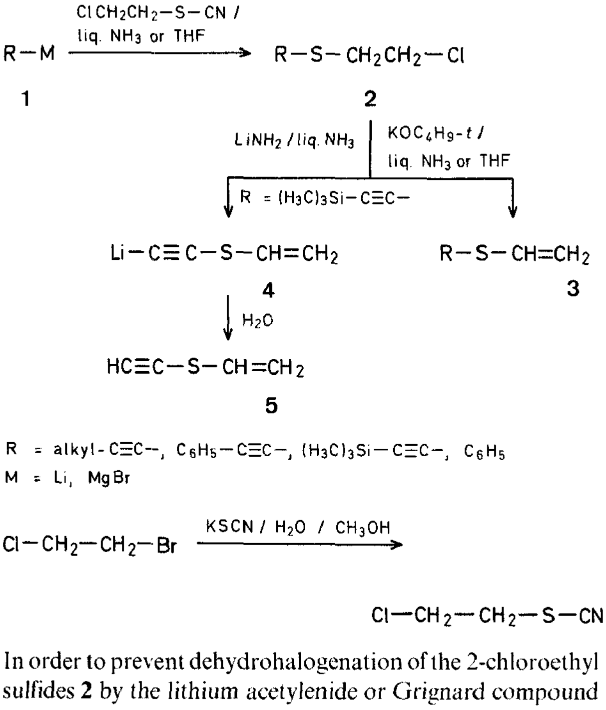
1-Vinylthio-1-alkynes $RC{\equiv}C{-}S{-}CH{=}CH_2$ have been used in the synthesis of a number of new heterocyclic compounds[1]. The synthesis of the starting compounds was described[2] for the first time in 1961. We have developed a more simple method for their preparation, which, in principle, can also be applied for other vinylic sulfides, e.g. phenyl vinyl sulfide (3, $R=C_6H_5$).



R = alkyl-$C{\equiv}C{-}$, $C_6H_5{-}C{\equiv}C{-}$, $(H_3C)_3Si{-}C{\equiv}C{-}$, C_6H_5
M = Li, MgBr

$$Cl{-}CH_2{-}CH_2{-}Br \xrightarrow{KSCN\ /\ H_2O\ /\ CH_3OH} Cl{-}CH_2{-}CH_2{-}S{-}CN$$

In order to prevent dehydrohalogenation of the 2-chloroethyl sulfides 2 by the lithium acetylenide or Grignard compound 1, a process which would lead to wastage of 1, inverse addition was applied, i.e. the solution of 1 was added to 2-chloroethyl thiocyanate. It is not necessary to isolate the intermediary 2-chloroethyl sulfides 2, so that the syntheses of 3 can be carried out as one-pot procedures, giving overall yields of ~ 80 %. For the synthesis of the parent compound 5, however, it was found to be more practical to prepare first the trimethylsilylated compound 2 [$R=(H_3C)_3Si{-}C{\equiv}C$] in tetrahydrofuran and then to bring about elimination of hydrogen chloride and removal of the trimethylsilyl group with lithium amide in liquid ammonia (deprotection with potassium hydroxide or alkoxides would presumably lead to silyl ethers with a volatility comparable with that of 5).

Preparation of 2-Chloroethyl Thiocyanate:

A mixture of potassium thiocyanate (98 g, 1 mol), 1-bromo-2-chloroethane (200 g, 1.4 mol), water (75 ml), and methanol (500 ml) is heated under reflux for ~ 70 h. After addition of water (500 ml) the products are extracted with chloroform. After drying of the extracts with magnesium sulfate, the solvent is removed under a water pump vacuum. Careful distillation of the residue through a 30-cm Widmer column affords the product; yield: 131–149 g (77–88 % based on $Cl{-}CH_2CH_2{-}Br$); b.p. 87–88°/18 torr; n_D^{20}: 1.5150.

Preparation of Phenyl Vinyl Sulfide (3, $R=C_6H_5$):

Phenylmagnesium bromide is made in the usual way from bromobenzene (36 g, 0.23 mol) and magnesium (9.6 g, 0.4 mol) in tetrahydrofuran (250 ml). The obtained solution is added in 10 min to a vigorously stirred solution of 2-chloroethyl thiocyanate (24.2 g, 0.20 mol) in tetrahydrofuran (100 ml), keeping the temperature of the reaction mixture below 40° by occasional cooling; 15 min after this addition potassium *t*-butoxide (45 g, 0.40 mol), dissolved in tetrahydrofuran (75 ml), is added at such a rate that the temperature of the mixture can be easily kept below 55° by cooling. 20 min after this addition, the reaction mixture is hydrolysed by careful addition of a solution of ammonium chloride (50 g) in water (200 ml). The upper layer is separated and combined with the ethereal extract of the aqueous layer. After drying with magnesium sulfate, the solvents are removed under a water pump vacuum. Distillation of the residue gives 3 (see Table for physical constants).

Preparation of Vinylthioalkynes 3 ($R=H_3C{-}C{\equiv}C{-}$, C_6H_5) in Liquid Ammonia:

To a suspension of lithium amide (0.20 mol) in liquid ammonia [prepared from lithium (1.4 g) in liquid ammonia (350 ml)] is added, in 5 min, an ethereal solution of propyne (12 g in

Table. Physical Constants and ^{1}H-N.M.R. Spectral Data[a] of Vinylic Sulfides[b]

R in $R{-}S{-}\overset{(\alpha)}{C}H{=}\overset{(\beta)}{C}\langle^{H(1)}_{H(2)}$	b.p./ torr	n_D^{20}	Lit. b.p./torr	Lit. n_D^{20}	^{1}H-N.M.R. (CCl_4) δ [ppm] H(α)	H(1)	H(2)
C_6H_5	78°/20	1.5872	94–97°/25[3]		6.54 (dd)	5.32 (d)	5.32 (d)
$H{-}C{\equiv}C$	84°/760	1.5063	84°/760[2]	1.5070	6.25 (dd)	5.57 (d)	5.48 (d)
$H_3C{-}C{\equiv}C$	35°/20	1.5220	131°/760[2]	1.5220	6.21 (dd)	5.45 (d)	5.37 (d)
t-$C_4H_9{-}C{\equiv}C$	52°/14	1.4868	—[c]	—	6.22 (dd)	5.47 (d)	5.38 (d)
$C_6H_5{-}C{\equiv}C$	122°/20	1.6309	—[c]		6.31 (dd)	5.63 (d)	5.49 (d)

[a] 20 % Solutions in CCl_4, TMS (δ = 0 ppm) as internal standard; $J_{cis}=10$ Hz; $J_{trans}=16$ Hz.
[b] Yields of all products are around 80 %, based on $Cl{-}CH_2CH_2{-}S{-}C{\equiv}N$.
[c] New compounds, purity according to G.L.C. and ^{1}H-N.M.R. > 97 %.

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50 ml, 0.3 mol), cooled at −60°, or phenylacetylene (20.8 g, 0.20 mol). The obtained grey solutions are poured cautiously into a well-stirred solution of 2-chloroethyl thiocyanate (24.2 g, 0.20 mol) in liquid ammonia (100 ml). Subsequently, finely powdered potassium *t*-butoxide (34 g, 0.30 mol) is introduced in 2 g portions with vigorous stirring. The ammonia is then allowed to evaporate. To the residue is added water (400 ml). The organic product is extracted with small portions of ether. After repeated washing with water, the extracts are dried over magnesium sulfate, and subsequently concentrated under a water pump vacuum. Distillation of the residues through 30 cm Vigreux columns gives the pure products (for physical constants see Table).

Preparation of 3, $R = t\text{-}C_4H_9—C{\equiv}C—$ and 2, $R = (H_3C)_3Si—C{\equiv}C—$ in Tetrahydrofuran:
To a solution of *t*-butylacetylene (16.4 g, 0.20 mol) in tetrahydrofuran (200 ml) is added a solution of butyllithium (0.20 mol) in hexane (~ 140 ml). During this addition the solution of the acetylene is cooled below −10°. The obtained reaction mixture is subsequently poured into a vigorously stirred solution of 2-chloroethyl thiocyanate (24.2 g, 0.20 mol), in tetrahydrofuran (100 ml), keeping the temperature of the reaction mixture between −20 and 0°. Subsequently potassium *t*-butoxide (34 g, 0.30 mol), dissolved in tetrahydrofuran (100 ml), is added with vigorous stirring. During this addition the temperature of the reaction mixture is allowed to rise to 30°. The mixture is then poured into water (500 ml) and the products are extracted with pentane. After several washings with water, the extracts are dried with magnesium sulfate, and subsequently concentrated under a water pump vacuum. Distillation of the residue affords the pure product **3** (for physical constants see Table).

In the case of $R = (H_3C)_3Si—C{\equiv}C—$, the reaction mixture obtained from the reaction of lithium trimethylsilylacetylenide with 2-chloroethyl thiocyanate is poured into water (500 ml). The aqueous layer is extracted with pentane and the combined solutions are washed several times with water. After drying of the solution with magnesium sulfate, the solvents are thoroughly removed by evaporation in vacuo. Distillation gives **2** $[R = (H_3C)_3Si—C{\equiv}C—]$; yield: 85%; b.p. 112°/30 torr; n_D^{20}: 1.5039.

Preparation of Vinylthioacetylene (5):
The *β*-chlorosulfide **2** $[R = (H_3C)_3Si—C{\equiv}C—$; 24 g, 0.15 mol$]$ is added dropwise to a stirred suspension of lithium amide (0.70 mol) in liquid ammonia (1500 ml). When the volume of the reaction mixture has decreased to about 100 ml, high-boiling petrol ether b.p. >170° (200 ml) is added. The reaction flask is cooled in a −50° bath and ice/water (300 ml) is added over a period of 10 min to the vigorously stirred mixture. The cooling bath is then removed and stirring is continued until all solid material has disappeared. The organic layer is separated and the aqueous layer is extracted three times with 40 ml portions of petroleum ether (b.p. 180–210°). The combined solutions are washed with water and dried with magnesium sulfate. The volatile compound is distilled off through a 40 cm Vigreux column until the boiling point has reached 55°/15 torr. During this procedure the receiver is cooled at −70°. The procedure is repeated with the contents of the receiver, now collecting the material passing over below 35°/15 torr. The collected liquid consists of reasonably pure (about 95% according to N.M.R.) $HC{\equiv}C—S—CH{=}CH_2$; yield: 85%. A small amount is distilled at 760 torr in an atmosphere of nitrogen to give a very pure product (for physical data see Table).

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