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An Efficient and Safe Method for the Preparation of Alkyl Vinyl Sulfides

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Alkyl vinyl sulfides RSCH=CH2 (**1**) (R = alkyl) are interesting synthons in organic chemistry due to their high reactivity [1]. RSH reacts with acetylene to give **1**; i) in the presence of free-radical initiators [2], ii) with bases as catalyst according to Reppe at temperatures up to 150–160 °C and pressures (C_2H_2/N_2) up to 2 MPa [3] and iii) in superbasic systems like KOH/DMSO at 10–100 °C under normal pressure and 1 MPa C_2H_2, respectively [4]. $RSCH_2CH_2SR$ is formed as a side product in the cases i) and ii). Extensive safety measures are required due to the danger of explosion at higher acetylene pressure. The addition of NaSR/KSR to activated alkynes like $PhC\equiv CH$ and $R'C\equiv CSR''$ in the presence of phase-transfer catalysts was described in [5].

We found that KOR in hydrocarbons with crown ethers as phase-transfer catalysts are highly active catalytic systems for vinyl ether syntheses from alcohols and acetylene. The reactions proceed smoothly already at 70 °C and normal pressure [6]. Here an analogous synthesis of vinyl thioethers is presented.

Mercaptans and acetylene react with KSR/18-crown-6 as catalyst system in aromatic solvents at 70-80 °C and normal pressure to give vinyl thioethers (eq 1).

$$HC\equiv CH + RSH \xrightarrow{KSR/18\text{-}cr\text{-}6} RSCH{=}CH_2 \qquad (1)$$

R = Bu, Et, *i*-Pr

Side products were not detected. Only in the case of complete consumption of the mercaptan and in the absence of other protic substrates, the reaction mixture turns to a dark color and potassium acetylide and resin-like products (obviously oligomers/polymers of acetylene) are formed. Small amounts of alcohols and water are tolerated without appreciable reduction of the catalytic activity. This is an important difference to the analogous vinyl ether syntheses in which alcohols strongly reduce the catalytic activity already at a ratio alcohol/catalyst ≥ 1/1 [7]. This different reactivity is due to the lower degree of solvation of KSR by protic substrates in comparison with KOR.

There are three different ways to conduct the reaction:

Homogenous catalysis:

Complexes [K(18-cr-6)SR] (**2**) are quite soluble in aromatic solvents at elevated temperatures. Thus, the vinylation of mercaptans can be conducted in a homogenously catalyzed reaction, e.g. a reaction rate of about 20 mol $BuSCH{=}CH_2$/(mol **2** × h) at 70 °C was obtained in the formation of *n*-butyl vinyl sulfide with **2** (R = Bu) as catalyst.

Solid-liquid phase-transfer catalysis:

The same complexes **2** are formed by using KSR as starting compounds and crown ethers as phase-transfer catalysts. BuSH and acetylene react with KSBu as solid phase at 70 °C to give 20 and 6 mol $BuSCH{=}CH_2$/(mol 18-cr-6 × h) in toluene and *n*-butyl mercaptan, respectively. The reaction rate amounts to 13 mol $BuSCH{=}CH_2$/(mol 18-cr-6 × h) with KOH as solid phase in toluene at 70 °C.

Here and in the homogenously catalyzed reactions, an excess of (higher-boiling) mercaptans does not reduce the catalytic activity appreciably. But if there is an excess of lower-boiling mercaptans, then the vinyl thioether formation proceeds much more slowly because the high partial pressure of low-boiling mercaptans reduces the partial pressure of acetylene and the solubility of acetylene in the reaction mixture.

Liquid-liquid phase-transfer catalysis:

Lower-boiling mercaptans are vinylated best by bubbling a gas mixture of acetylene and mercaptan through a mixture of concentrated aqueous potassium hydroxide solution (50–70 %) and an aromatic hydrocarbon in which 18-crown-6 is dissolved. An excess of RSH does not disturb unless the KOH is completely converted to KSR. In that case the supply of mercaptan has to be stopped until the reaction rate increases indicating that the RSH dissolved in the organic phase is consumed. In this way, e.g. a reaction rate of 2-3 mol $EtSCH{=}CH_2$/(mol 18-cr-6 × h) can be obtained.

As expected [8], the vinylation reaction described is stereospecific and follows the trans-addition rule. Thus, n-butyl mercaptan reacts with phenyl acetylene to give exclusively (Z)-2-(n-butylthio)vinylbenzene (3) besides 1.5% 1-(n-butylthio)vinylbenzene. Alkynes with a terminal triple *bond react analogously to acetylene itself, but with a lower reaction rate. Kinetic investigations prove that the addition of the non-dissociated complex 2 to acetylene is the rate-determining step of the vinylation reaction [9].*

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Experimental

All reactions and manipulations were carried out under purified argon using Schlenk techniques. Acetylene was purified by passage through concentrated sulfuric acid, charcoal and molecular sieves 5Å and 3Å. Toluene and mesitylene were distilled under argon from sodium benzophenone ketyl. The mercaptans were dried over calcium chloride and distilled under argon. GC and GC/MS analyses were performed on a CP9000 (Chrompack), on a GCHF18.3-4 (Chromatron) and on a chromatograph 5890 (series II) combined with a mass spectrometer 5972 (Hewlett Packard), respectively. The NMR spectra were recorded on a Unity 500 (Varian) and a HX90R (Bruker) in $CDCl_3$. Ethyl and *n*-butyl vinyl sulfide were identified with authentic samples obtained according to [4].

[K(18-cr-6)SR] (**2**, *R = Bu*)

A solution of 18-cr-6 (29.8 g, 0.11 mol) in toluene (100 ml) was added to a suspension of KSBu (12.8 g, 0.10 mol) in toluene (150 ml). After heating (90 °C, 8 h) and stirring (25 °C, 15 h), the crystals of **2** were filtered off, washed with pentane (3 x 20 ml) and dried in vacuo (yield: 38.2 g, 97 %).

n-Butyl vinyl sulfide (**1**, R = Bu).

In toluene as the solvent: The experimental apparatus is shown in Fig. 1. The reaction vessel (5) was flushed with argon, filled with KSBu (2.57 g, 20.0 mmol) and with a solution of the crown ether 18-cr-6 (2.64 g, 10,0 mmol) in toluene (60 ml) via the dropping funnel (7). At 70 °C BuSH (9.0 g, 0.10 mol) was added and acetylene (ca. 5 l/h) was passed directly through the vigorously stirred reaction mixture. From time to time new portions of BuSH were added. The reaction mixture was washed (20 ml 40% KOH; 3 x 50 ml water), dried (Na_2SO_4) and fractionated (20 cm Vigreux column), affording *n*-butyl vinyl sulfide in nearly quantitative yield; b.p. 141 °C (lit. b.p. 141 °C [3, 10]).

MS: *m/z*(%) 116 (55) [M^+], 101 (17) [$M\text{-}CH_3$], 87 (5) [$M\text{-}C_2H_5$], 73 (24) [$M\text{-}C_3H_7$], 60 (100) [$CH_2{=}CHSH$], 59 (46) [$CH_2{=}CHS$].

In BuSH as the solvent: The reactor was loaded with KSBu (2.57 g, 20.0 mmol), 18-cr-6 (2.64 g, 10.0 mmol) and BuSH (45.1 g, 0.5 mol). At 70 °C acetylene (1.5 l/h) was passed through the vigorously stirred reaction mixture. Within 8 h, the BuSH was converted completely to *n*-butyl vinyl sulfide. The work-up procedure is analogous to that described above.

Ethyl and *isopropyl vinyl sulfide* (**1**, *R = Et, i-Pr*)

The reactor was filled with a solution of crown ether 18-cr-6 (2.20 g, 8.3 mmol) in p-xylene (60 ml) and a solution of KOH (3.0 g) in water (1.5 ml). Acetylene (0.8 ... 1.5 l/h) was loaded

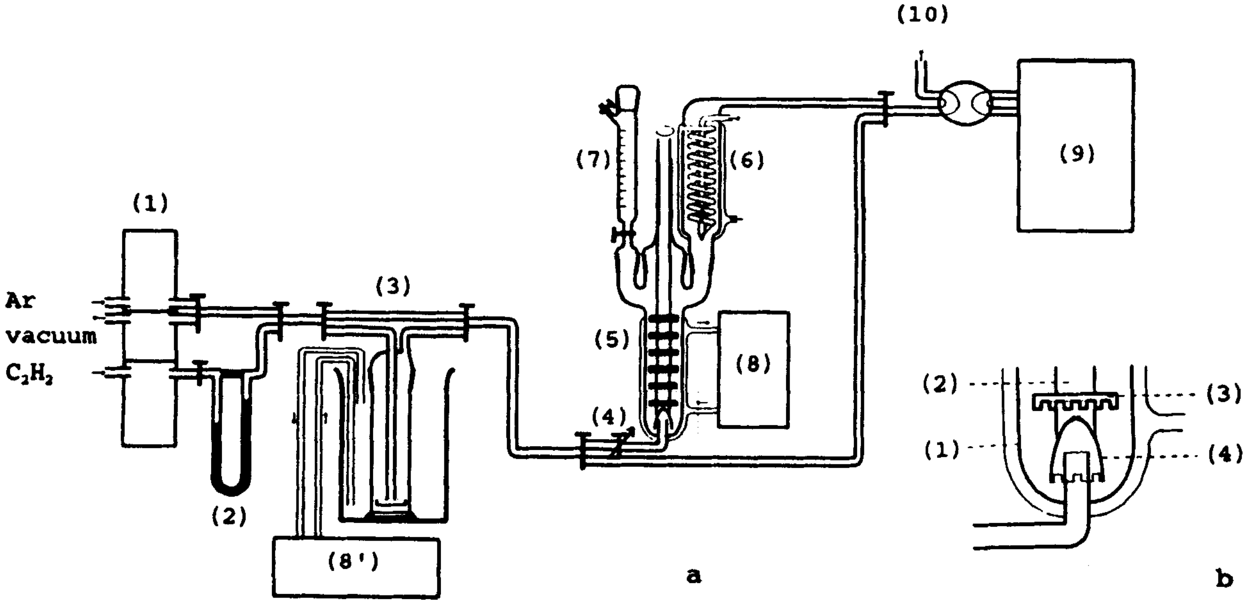

Fig. 1 (a) Experimental apparatus for vinylation of mercaptans: (1) Gas supplying unit for acetylene and argon. (2) Flowmeter for acetylene. (3) Bubbler filled with RSH. (4) Regulating valve. (5) Reactor (100 ml) equipped with a stirrer. (6) Reflux condenser. (7) Dropping funnel for filling the reactor. (8, 8') Thermostat. (9) Gas chromatograph to control the composition of the exit gas. (10) Absorption unit/fume hood.

(b) Detail of reactor: (1) Tube with regulating valve. (2) Stirrer, equipped with (3) teflon disks like a gear (for intensive mixing). (4) Cap preventing the strike back of the reaction mixture into the tube (1).

with EtSH in the bubbler (3) at 10 ...0 °C (320...210 mbar EtSH) and passed through the vigorously stirred reaction mixture at 70 °C. Within 1 h, 2.2 g ethyl vinyl sulfide were formed. The organic phase was separated, washed (3 x 50 ml water), dried (Na_2SO_4) and fractionated (20 cm Vigreux column), affording ethyl vinyl sulfide in a nearly quantitative yield; b.p. 91 °C (lit. b.p. 92 °C [11]).
MS: *m/z(%)* 88 (40) [M^+], 73 (20) [M-CH_3], 60 (90) [CH_2=CHSH], 59 (72) [CH_2=CHS], 27 (100) [CH_2=CH].

Isopropyl vinyl sulfide (1, R = i-Pr) was analogously prepared (solvent: mesitylene: T = 80 °C; p(*i*-PrSH) = 240 mbar). The fraction boiling between 90 and 140 °C was fractionated (20 cm Vigreux column; reflux ratio 1/10) once more; b.p. 107 °C (lit. b.p. 105-108 °C [12]). Yield: 90–95% (gc); 68% (isol.).
MS: *m/z(%)* 102 (52) [M^+], 87 (5) [M-CH_3], 60 (100) [CH_2=CHSH], 59 (50) [CH_2=CHS]. ^{1}H-NMR: δ (ppm): 1.29 (d, CH_3), 5.23 (sept, CH), 6.36 (dd, S-CH=), 5.19 (d, =CH_{tr}H) [$^3J(H,H)_{tr}$ 16.71, $^3J(H,H)_{cis}$ 10.20 Hz], 5.21 (d, =CH_{cis}H) . ^{13}C-NMR: δ (ppm): 23.2 (CH_3), 35.8 (CH), 131.7 (S-CH=), 112.7 (=CH_2).

(Z)-2-(n-Butylthio)vinylbenzene (**3**)

Phenyl acetylene (25.5 g, 0.25 mol) was added within 2.5 h at 70–80 °C to a stirred solution of BuSH (23.4 g, 0.26 mol), crown ether 18-cr-6 (1.06 g, 4.0 mmol) and KOH (0.6g, 10.7 mmol). The reaction mixture was washed (2 × 20 ml 10% NaOH; 2 × 20 ml 5% KCl; 3 × 20 ml water), dried (Na_2SO_4) and fractionated (20 cm Vigreux column); b.p. (1.5 mbar) 115–118 °C (lit. b.p. (1 mm) 114–115 °C [10]). Yield: 41.4 g (87% related to phenyl acetylene).
MS: *m/z(%)* 192 (82) [M^+], 136 (61) [PhCH=CHSH], 135 (100) [PhCH=CHS]. ^{1}H-NMR: δ (ppm): 0.86 (t, CH3), 1.37 (se, CH_2), 1.60 (qu, CH_2), 2.69 (t, CH_2), 6.17 (d, S-CH=) [$^3J(H,H)$ 10.89 Hz], 6.36 (d, =CH-C_i), 7.45 (d, C_oH), 7.29 (t, C_mH), 7.13 (t, C_pH). ^{13}C-NMR: δ (ppm): 13.5 (CH_3), 21.5 (CH_2), 35.4 (CH_2), 32.1 (CH_2), 128.0 (S-CH=), 125.2 (=CH-C_i), 137.4 (C_i), 128.7 (C_o), 128.2 (C_m), 126.5 (C_p).

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