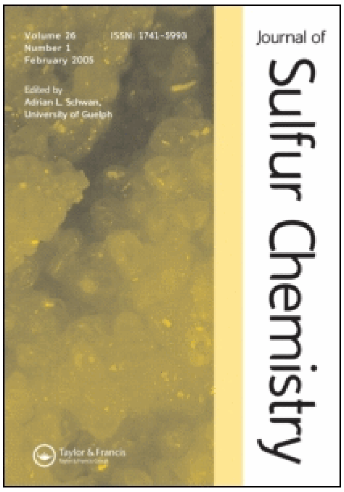

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RESEARCH ARTICLE

An expedient synthesis of methyl vinyl sulfide from dimethyl disulfide and acetylene

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Dimethyl disulfide reacts with acetylene under atmospheric pressure in basic reductive systems MOH (M=Na, K)$-N_2H_4 \cdot H_2O-N$-methylpyrrolidone and $Na_2S{\cdot}9H_2O-N_2H_4{\cdot}H_2O-N$-methylpyrrolidone to form methyl vinyl sulfide in up to 79% yield.

Keywords: Methyl vinyl sulfide; Dimethyl disulfide; Acetylene; Superbases

1. Introduction

Vinyl sulfides are of considerable importance as versatile synthetic intermediates for organic synthesis and as precursors of aldehydes and ketones [1]. Vinyl sulfide derivatives have been utilized as proteolytic enzyme inhibitors [2] and as synthons in the synthesis of polydentate hemilabile S,P-ligands [3, 4], spirocyclic systems [5] and other organic compounds [6–8].

Most known syntheses of alkyl vinyl sulfides are based on reactions of acetylene with thiols, which are usually carried out either as a classic version (100–160 °C; pressure of acetylene up to 35 atm; alkali metal hydroxides, alcoholates or thiolates as catalysts) [9, 10], or in a non-hydroxylic polar solvent (HMPA; DMSO; 20–80 °C; atmospheric or elevated pressure) [11, 12], or in hydrocarbons with KOR and crown ethers as phase-transfer catalysts [13, 14]. At the same time, direct vinylation of methanethiol (which has a bad stench and is volatile and, hence, inconvenient to handle) with acetylene has not been described so far, although there was a single example of the preparation of methyl vinyl sulfide in high yield by heating (95–100 °C) methylisothiuronium bromide in the NaOH–water system under an acetylene pressure of 30 atm [15].

Dimethyl sulfoxide can also be used for methanethiolation of acetylene. The reaction proceeds at 140–150 °C under elevated pressure of acetylene in the presence of water and a base,

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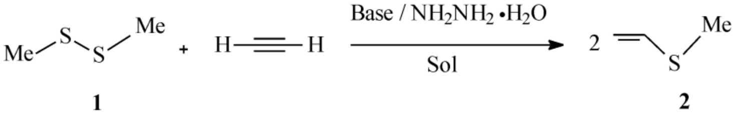
giving methyl vinyl sulfide in low yield [16, 17]. A better and more efficient method for the synthesis of methyl vinyl sulfide is the interaction of acetylene with sodium sulfide and a methylating agent (methyl iodide or DMSO) [18–20].

Reactions of dialkyl disulfides with alkynes in the presence of bases have, for a long time, been studied as an alternative route to vinyl sulfides and 1,2-bis(alkylthio)ethenes [17, 21–23] and as a stereospecific preparation of *Z*-isomers of the latter. By the use of this method, methyl vinyl sulfide in a mixture with 1,2-bis(methylthio)ethene was obtained in 9% yield on heating (160–180 °C) dimethyl disulfide in the presence of KOH under elevated pressure of acetylene [21]. Recently, expensive metal complex catalysts have been proposed for the synthesis of *Z*- or *E*-isomers of 1,2-bis(alkylthio)ethenes through the reactions of dialkyl disulfides with acetylenes [24, 25].

Herein we describe a convenient and efficient route to methyl vinyl sulfide based on the one-pot reduction–vinylation reaction of dimethyl disulfide under atmospheric pressure. Dimethyl disulfide is industrially available from sulfur-rich natural gas and as a side-product of pulp manufacture, but as yet has little large-scale utilization.

2. Results and discussion

Dimethyl disulfide **1** has been found to react with acetylene under atmospheric pressure in superbase reductive systems of the type alkali metal hydroxide (or sulfide) – hydrazine hydrate – polar non-hydroxylic solvent to afford methyl vinyl sulfide in up to 79% yield (scheme 1).



Base: NaOH, KOH, $Na_2S \cdot 9\ H_2O$

Sol: NMP, DMSO, DMF, 1,4-dioxane

SCHEME 1

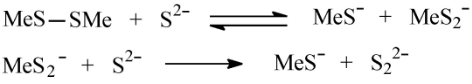
The reaction proceeds upon initial heating (45–98 °C) of dimethyl disulfide in hydrazine hydrate in the presence of an alkali metal hydroxide or sulfide (molar ratio **1**: Base = 1 : 2–3), followed by introduction of a polar non-hydroxylic solvent into the reaction mixture and passing in acetylene at the same temperature for 3 h. The procedure allows one to avoid the necessity of isolating volatile intermediate methanethiol (scheme 2).

$$\mathbf{1} \xrightarrow[-\,N_2]{\substack{1)\ MOH\ (or\ 2\ Na_2S\cdot 9\ H_2O)/N_2H_4\cdot H_2O \\ 2)\ HC\equiv CH,\ Sol}} \mathbf{2}$$

SCHEME 2

To optimize the reaction conditions, the following parameters were varied: amount and nature of the reductive system, nature of the polar non-hydroxylic solvent, temperature, and reaction time.

The best result was achieved when the disulfide **1** was initially treated with 2 equiv. of Na_2S and 1 equiv. of hydrazine hydrate at 96–98 °C. Under such conditions, the reductive cleavage of dimethyl disulfide is complete in 1–1.5 h (the evolution of nitrogen stops). The subsequent addition of NMP to the reaction mixture and the passage of acetylene at 45–50 °C for 3 h result in a 75–79% yield of **2** (the yield was calculated on the disulfide **1** charged, implying that 1 mole of **1** gives 2 moles of **2**) (table, entries 1, 2). To achieve the same yield of the vinyl sulfide **2** in the presence of MOH, one needs to use 6–10 equiv. of hydrazine hydrate (with other conditions being the same) (table, entries 3–5, *cf.* entries 6, 7). This fact agrees well with the known data on a more facile cleavage of the S−S bond under the action of sulfide anions than in the presence of hydroxide anions [26, 27].



SCHEME 3

No divinyl sulfide formation, expected from the reaction of sulfide anions (S^{2-}, NaS^-) with acetylene, was observed in all the cases, probably due to the fact that this reaction normally occurs at a higher temperature (80–100 °C) [1, 23, 28, 29]. The nature of the alkali metal hydroxide has almost no effect on the rate of either process stage (table, entries 3, 4).

An attempt to enhance the reaction efficiency by increasing the molar excess of base turned out to be ineffectual: the same yield (77%) of **2** was attained in both cases (table, entry 8, *cf.* entry 3).

Hydrazine hydrate in this process facilitates the reductive cleavage of the disulfide bond [30, 31]. If the reaction is carried out without $N_2H_4{\cdot}H_2O$, the yield of **2** is drastically decreased

Table 1. Reaction of dimethyl disulfide with acetylene under atmospheric pressure.[a] The effect of conditions.

Entry	**1** (mmol)	Base (mmol)	Reductant (mmol)	Sol (ml)	Yield of **2** (%)
1	40.0	$Na_2S{\cdot}9H_2O$, 80	$N_2H_4{\cdot}H_2O$, 40	NMP, 75	79
2	20.0	$Na_2S{\cdot}9H_2O$, 40	$N_2H_4{\cdot}H_2O$, 20	NMP, 50	75
3	21.5	NaOH, 44	$N_2H_4{\cdot}H_2O$, 120	NMP, 20	75
4	21.5	KOH, 44	$N_2H_4{\cdot}H_2O$, 120	NMP, 40	77
5	21.5	KOH, 44	$N_2H_4{\cdot}H_2O$, 200	NMP, 40	79
6	21.5	NaOH, 44	$N_2H_4{\cdot}H_2O$, 20	NMP, 20	28
7	12.0	NaOH, 36	$N_2H_4{\cdot}H_2O$, 24	NMP, 20	37
8	21.5	KOH, 60	$N_2H_4{\cdot}H_2O$, 120	NMP, 20	77
9	20.0	$Na_2S{\cdot}9H_2O$, 60	not used	NMP, 50	44
10	40.0	NaOH, 120	not used	NMP, 60	29
11	21.5	$Na_2S{\cdot}9H_2O$, 40	Zn, 20	NMP, 50	30
12	21.5	$Na_2S{\cdot}9H_2O$, 40	Na_2SO_3, 10	NMP, 50	39
13	21.5	$Na_2S{\cdot}9H_2O$, 40	$FeSO_4$, 10	NMP, 50	14
14	21.5	$Na_2S{\cdot}9H_2O$, 40	$Na_2S_2O_3$, 20	NMP, 50	9
15	21.5	$Na_2S{\cdot}9H_2O$, 30	not used	DMSO, 20	28
16	21.5	KOH, 44	$N_2H_4{\cdot}H_2O$, 120	DMF, 40	43
17[b]	21.5	NaOH, 44	$N_2H_4{\cdot}H_2O$, 200	1,4-Dioxane, 40	60[c]
18	21.5	NaOH, 44	$N_2H_4{\cdot}H_2O$, 120	not used	24

[a] Acetylene was fed (flow rate ~1–2 l/h) for 3 h at 45–50 °C after preliminary heating of the reaction mixture (dimethyl disulfide/Base/$N_2H_4{\cdot}H_2O$) at 96–98 °C for 1–1.5 h (entries 1–8, 16–18), 4 h (entries 9, 10), 3 h (entries 11–14).

[b] The vinylation was carried out at 80 °C.

[c] GLC-based yield.

(table, entries 9, 10). The use of other reducing agents, such as Zn, Na_2SO_3, $FeSO_4$ and $Na_2S_2O_3$, is of no benefit since the yield of **2** in all cases did not exceed 39% (table, entries 11–14).

The second step of the process, *i.e.* the reaction of acetylene with intermediate methanethiolate, is highly solvent-dependent. Replacement of NMP by DMSO or DMF results in a decreased yield of **2** to 28–43% (table, entries 15, 16). In the case of DMF, the reaction is accompanied by partial solvolysis. The use of 1,4-dioxane as solvent requires a higher reaction temperature (80 °C) and results in a 60% yield of **2** (table, entry 17). However, owing to the close boiling points of 1,4-dioxane and the product sulfide **2**, their separation is difficult. Carrying out the process without an organic solvent gave a low yield (24%) of **2** (table, entry 18).

Optimization of each process stage requires the following conditions: the reductive cleavage of **1** proceeds rapidly at 96–98 °C, whereas the vinylation step is best carried out at a lower temperature (45–50 °C) to slow down the NMP solvolysis, which results in the corresponding salt of γ-aminobutyric acid. Further decrease of the reaction temperature is not beneficial: carrying out the vinylation stage at room temperature decreases the yield of methyl vinyl sulfide to 37%.

Thus, a novel expedient method for the preparation of methyl vinyl sulfide in high yield, based on the reaction of dimethyl disulfide, a component of sulfur-rich natural gas and a side product of the pulp industry, with acetylene in the systems $MOH–N_2H_4{\cdot}H_2O–NMP$ (M = Na, K) and $Na_2S{\cdot}9H_2O–N_2H_4{\cdot}H_2O–NMP$ under atmospheric pressure has been developed. The method may be useful both in chemical laboratories and for industrial scale-up.

3. Experimental

IR spectra were recorded on a Bruker IFS-25 spectrometer. ^1H NMR spectra were taken on a Bruker DPX-400 (400 MHz) instrument for solutions in $CDCl_3$ with HMDS as internal standard. GLC analyses were performed on an Chrom-4 machine, equipped with a heat conducting detector, 2400 × 3.5 mm column, liquid phase: poly(ethylene glycol) 20000, 1%; solid phase: NaCl, 0.16–0.25 mm.

3.1 *Reductive vinylation of 1 with acetylene in the system $Na_2S{\cdot}9H_2O–N_2H_4{\cdot}H_2O–NMP$*

Into a three-necked flask equipped with a stirrer, a tube for an acetylene feed, and a condenser, connected with a cooling vessel for trapping volatile reaction products, was placed 19.2 g (80 mmol) of $Na_2S{\cdot}9H_2O$, which was then heated (50–60 °C) until complete melting; then 3.76 g (40 mmol) of **1** was added. The two-phase mixture was vigorously stirred at 96–98 °C for 0.5 h. Then 2.0 g (40 mmol) of $N_2H_4{\cdot}H_2O$ was added and the mixture was stirred at the same temperature for another 0.5 h until the N_2 evolution ceased. By that time the reaction mixture had become completely homogeneous. The mixture was cooled to 45–50 °C, 75 ml of NMP was added, and acetylene was fed in at a rate of ~1.5 l/h for 3 h. Then the formed sulfide **2** was distilled off together with water at 15–20 mmHg. Upon separation, the organic layer was dried over K_2CO_3 and distilled to afford **2** (4.68 g, purity 99.6%, 79% yield, bp 63 °C; lit. [20] bp 64 °C).

3.2 *Reductive vinylation of 1 with acetylene in the system $MOH–N_2H_4{\cdot}H_2O–NMP$*

Into a flask, equipped as above, were placed 1.76 g (44 mmol) of NaOH and 6.0 g (120 mmol) of $N_2H_4{\cdot}H_2O$ and the mixture was magnetically stirred and heated until complete dissolution of the alkali. Then 2.0 g (21.5 mmol) of **1** was added and the mixture was vigorously stirred at 96–98 °C for ~1 h until N_2 evolution ceased. The homogeneous reaction mixture was cooled to 45–50 °C, 20 ml of NMP was added, and acetylene was fed in at a rate of ~1.2 l/h for 3 h. After completion of the reaction the trap contained 0.35 g of **2**. The reaction mixture representing a biphase aqueous-organic system was separated. The aqueous layer was extracted with diethyl ether, and the extract was washed with water, dried (K_2CO_3), and analysed by GLC (yield 0.19 g of **2**). The organic layer (after drying over K_2CO_3) was distilled under atmospheric pressure. A fraction with boiling point below 80 °C, containing 1.82 g of **2** (GLC), was collected. In total, 2.36 g (32 mmol) **2** was obtained (75% yield). Pure **2** (99.8%, GLC) was isolated by re-distillation under atmospheric pressure.

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