# Highly efficient atom economical "green chemistry" synthesis of vinyl sulfides from thiols and acetylene in water*

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Potassium thiolates generated by treatment of thiols with aqueous KOH react with acetylene to give the corresponding vinyl sulfides in 90—95% yields.

**Key words:** acetylene, thiols, vinyl sulfides, vinylation, water, "green" chemistry.

In the last decade, the chemistry of vinyl sulfides has been under extensive development.[1—9] Vinyl sulfide fragments are found in natural compounds exhibiting antibiotic, antiinflammatory, anticancer, and antitumor activity[1,2] and are employed in the synthesis of useful compounds such as pesticides and bactericides.[3]

A general atom economical route to vinyl sulfides involves reactions of thiols with alkynes. Vinylation of thiols is mostly catalyzed by bases[3,10] or metal complexes.[7] Special efforts are focused on searching for the conditions that would meet "green chemistry" requirements and, in particular, allow dispensing with toxic organic solvents.[1,7c,8] The synthesis of aryl vinyl sulfides by hydrothiylation of arylalkynes with benzenethiols in the system β-cyclodextrin—acetone—water has been reported.[8] Recently,[1] the system KF—$Al_2O_3$—glycerol has been proposed for the synthesis of 2-organylvinyl sulfides from terminal alkynes and thiols.

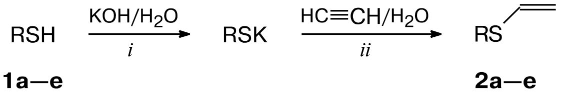
However, data on reactions of thiols with unsubstituted acetylene are scarce, mostly referring to the investigations accomplished in the 20th century.[10—14] For instance, vinyl sulfides can be obtained in 30—50% yields by inefficient and nonselective vinylation of thiols with acetylene under pressure in aqueous KOH[12] or aqueous $Na_2CO_3$[13] at 125—180 °C, with the formation of appreciable amounts of the corresponding 1,2-bis(organylthio)ethanes.

Vinylation[14] in the superbasic systems KOH—DMSO or KOH—hexamethylphosphorous triamide (HMPA) allows the reaction to be effected at 30—50 °C and affords vinyl sulfides in 60—90% yields. However, the use of organic solvents (including toxic and carcinogenic HMPA), with the necessity of recovering them, as well as laborious isolation of vinyl sulfides make this method neither very advantageous nor environmentally acceptable.

Recently,[15] we have proposed a highly efficient approach to the vinylation of thiols with acetylene in an aqueous alkali. In the present work, we present the results of further development of this approach.

We found that both aliphatic and aromatic thiols **1a—e** react with acetylene in aqueous KOH to give the corresponding vinyl sulfides **2a—e**. The reaction occurs under an initial acetylene pressure of 11—14 atm at 100—120 °C within 3—5 h in the presence of a two- and threefold molar excess of KOH with respect to the thiol (Scheme 1). Clearly, it is potassium thiolate rather than free thiol that undergoes vinylation under these conditions. By optimizing the reaction conditions (Table 1), we achieved nearly quantitative yields of vinyl sulfides **2a—e** (90—95%).

**Scheme 1**



R = Pr (**a**), Bu (**b**), $C_5H_{11}$ (**c**), $C_7H_{15}$ (**d**), Ph (**e**)

**Conditions:** *i*. 20—24 °C, 1 h; *ii*. 100—120 °C, 3—5 h.

It follows from Table 1 that benzenethiol is more reactive in the process under study. Apparently, this is due to its higher acidity and, consequently, greater tendency toward the formation of thiolate anions compared to alkanethiols. For instance, benzenethiol (**1e**) is vinylated with acetylene at 100—105 °C over 3 h in a nearly quantitative yield at a twofold molar excess of KOH (the yield of vinyl sulfide **2e** is 93%) (see Table 1, entry *6*). Under similar conditions, butanethiol (**1b**) reacts with acetylene more sluggishly (5 h) to give not only vinyl sulfide **2b** (80% yield) but also 1,2-bis(butylthio)ethane (10% yield) (see Table 1, entry *3*). At the same time, vinylation of alkanethiols **1a—d** at higher temperatures (115—120 °C, 5 h) in

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* Dedicated to Academician of the Russian Academy of Sciences S. M. Aldoshin on the occasion of his 60th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 0439—0441, February, 2013.

**Table 1.** Conditions for the vinylation of potassium thiolates with acetylene in water[a] and the yields of vinyl sulfides **2a—e**

| Entry | Thiol /mol | R | KOH /mol | $T$/°C | Yield (%) |
|---|---|---|---|---|---|
| *1* | **1a** (0.30) | $C_3H_7$ | 0.90 | 115—120 | **2a** (95) |
| *2* | **1b** (0.24) | $C_4H_9$ | 0.72 | 115—120 | **2b** (94) |
| *3*[b] | **1b** (0.24) | $C_4H_9$ | 0.48 | 100—105 | **2b** (80) |
| *4* | **1c** (0.30) | $C_5H_{11}$ | 0.90 | 115—120 | **2c** (90) |
| *5* | **1d** (0.25) | $C_7H_{15}$ | 0.75 | 115—120 | **2d** (95) |
| *6* | **1e** (0.27) | Ph | 0.54 | 100—105 | **2e** (93) |

[a] The vinylation time was 5 (entries *1—5*) and 3 h (entry *6*).

[b] 1,2-Bis(butylthio)ethane is formed as a by-product in 10% yield.

the presence of a threefold molar excess of KOH affords the target alkyl vinyl sulfides **2a—d** in 90—95% yields (see Table 1, entries *1*, *2*, *4*, *5*).

The proposed method has an important technological advantage because virtually pure vinyl sulfides formed as an organic phase can easily be separated from the aqueous basic layer, which then can be reused repeatedly.

To sum up, we developed a highly efficient version of base-catalyzed vinylation of thiols with acetylene in water. This is an atom economical, "green chemistry" synthesis of vinyl sulfides.

## Experimental

Vinylation was carried out with acetylene pumped into a 1-L rotating autoclave to a required pressure.

$^1$H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400.13 MHz) in $CDCl_3$ with $Me_4Si$ as the internal standard. Elemental analysis was carried out on a Flash EA 1112 automatic CHNS-analyzer. The IR spectra of vinyl sulfides **2a—e** were recorded on a Bruker Vertex spectrometer (thin film) and agree with the literature data.[16]

Commercial thiols were used.

**Propyl vinyl sulfide (2a).** Propanethiol (22.64 g, 0.3 mol) and a solution of KOH (50.40 g, 0.9 mol) in water (100 mL) were stirred at ~20 °C for 1 h. The resulting mixture was heated at 115—120 °C for 5 h with acetylene pumped to an initial pressure of 11 atm (residual acetylene pressure 6 atm). The organic layer was separated and distilled *in vacuo*. Yield 29.1 g (95%), b.p. 43 °C (46 Torr) (*cf.* Ref. 12: b.p. 43.5 °C (50 Torr)); $n_D^{20}$ = 1.4741 (*cf.* Ref. 12: $n_D^{20}$ = 1.4734). Found (%): C, 58.95; H, 9.81; S, 31.24. $C_5H_{10}S$. Calculated (%): C, 58.76; H, 9.86; S, 31.38.

**Butyl vinyl sulfide (2b)**. Butanethiol (21.65 g, 0.24 mol) and a solution of KOH (40.32 g, 0.72 mol) in water (100 mL) were stirred at ~20 °C for 1 h. The resulting mixture was heated at 115—120 °C for 5 h with acetylene pumped to an initial pressure of 11 atm (residual acetylene pressure 5 atm). The organic layer was separated and distilled *in vacuo*. Yield 26.2 g (94%), b.p. 55 °C (25 Torr) (*cf.* Ref. 12: b.p. 47.5—48.5 °C (21 Torr)); $n_D^{20}$ = 1.4723 (*cf.* Ref. 12: $n_D^{20}$ = 1.4722). Found (%): C, 61.93; H, 10.52; S, 27.55. $C_6H_{12}S$. Calculated (%): C, 62.00; H, 10.41; S, 27.59.

**Pentyl vinyl sulfide (2c).** Pentanethiol (31.27 g, 0.3 mol) and a solution of KOH (50.40 g, 0.9 mol) in water (100 mL) were stirred at ~20 °C for 1 h. The resulting mixture was heated at 115—120 °C for 5 h with acetylene pumped to an initial pressure of 14 atm (residual acetylene pressure 5 atm). The organic layer was separated and distilled *in vacuo*. Yield 35.2 g (90%), b.p. 56 °C (10 Torr); $n_D^{20}$ = 1.4738. Found (%): C, 64.38; H, 10.98; S, 24.64. $C_7H_{14}S$. Calculated (%): C, 64.55; H, 10.83; S, 24.62. $^1$H NMR, δ: 0.90 (t, 3 H, Me); 1.29—1.42 (m, 4 H, $CH_2$); 1.61—1.68 (m, 2 H, $CH_2$); 2.69 (t, 2 H, $SCH_2$); 5.10 (d, 1 H, $=CH_2$, $^3J_{H,H}$ = 16.3 Hz); 5.18 (d, 1 H, $=CH_2$, $^3J_{H,H}$ = 9.8 Hz); 6.36 (dd, 1 H, =CH, $^3J_{H,H}$ = 16.3 Hz, $^3J_{H,H}$ = 9.8 Hz).

**Heptyl vinyl sulfide (2d).** Heptanethiol (33.07 g, 0.25 mol) and a solution of KOH (42.00 g, 0.75 mol) in water (100 mL) were stirred at ~20 °C for 1 h. The resulting mixture was heated at 115—120 °C for 5 h with acetylene pumped to an initial pressure of 14 atm (residual acetylene pressure 5 atm). The organic layer was separated and distilled *in vacuo*. Yield 37.6 g (95%), b.p. 46 °C (1 Torr) (*cf.* Ref. 17: b.p. 67—68 °C (4 Torr)); $n_D^{20}$ = = 1.4816 (*cf.* Ref. 17: $n_D^{20}$ = 1.4752). Found (%): C, 68.11; H, 11.60; S, 20.29. $C_9H_{18}S$. Calculated (%): C, 68.28; H, 11.46; S, 20.26.

**Phenyl vinyl sulfide (2e).** Benzenethiol (30.00 g, 0.27 mol) and a solution of KOH (30.24 g, 0.54 mol) in water (100 mL) were stirred at ~20 °C for 1 h. The resulting mixture was heated at 100—105 °C for 3 h with acetylene pumped to an initial pressure of 12 atm (residual acetylene pressure 5 atm). The organic layer was separated and distilled *in vacuo*. Yield 34.2 g (93%), b.p. 49 °C (2 Torr) (*cf.* Ref. 12: b.p. 76.5 °C (4 Torr)); $n_D^{20}$ = 1.5891 (*cf.* Ref. 12: $n_D^{20}$ = 1.5888). Found (%): C, 70.69; H, 5.84; S, 23.47. $C_8H_8S$. Calculated (%): C, 70.54; H, 5.92; S, 23.54.

**1,2-Bis(butylthio)ethane.** Butanethiol (21.65 g, 0.24 mol) and a solution of KOH (26.88 g, 0.48 mol) in water (100 mL) were stirred at ~20 °C for 1 h. The resulting mixture was heated at 100—105 °C for 5 h with acetylene pumped to an initial pressure of 12 atm (residual acetylene pressure 6 atm). The organic layer was separated and distilled *in vacuo*. The yield of butyl vinyl sulfide was 22.3 g (80%). The yield of 1,2-bis(butylthio)ethane was 2.5 g (10%), b.p. 92—93 °C (1 Torr) (*cf.* Ref. 18: b.p. 121—124 °C (5 Torr)); $n_D^{20}$ = 1.4992 (*cf.* Ref. 18: $n_D^{20}$ = 1.4967).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 11-03-00334) and the Council on Grants at the President of the Russian Federation (State Support Program for Leading Scientific Schools, Grant NSh-1550-2012.3).

## References

1. E. J. Lenardão, M. S. Silva, R. G. Lara, J. M. Marczewski, M. Sachini, R. G. Jacob, D. Alves, G. Perin, *Arkivoc*, 2011, **ii**, 272.
2. G. Yu. Ishmuratov, M. P. Yakovleva, V. A. Vydrina, O. O. Shakhanova, N. M. Ishmuratova, A. G. Tolstikov, *Makrogeterotsikly*, 2012, **5**, 212 [*Macroheterocycles* (*Engl. Transl.*), 2012, **5**, 212].
3. N. V. Zyk, E. K. Beloglazkina, M. A. Belova, N. S. Dubinina, *Russ. Chem. Rev.* (*Engl. Transl.*), 2003, **72**, 769 [*Usp. Khim.*, 2003, **72**, 864].

4. V. P. Reddy, K. Swapna, A. V. Kumar, K. R. Rao, *Synlett*, 2009, 2783.
5. (a) B. A. Trofimov, N. K. Gusarova, S. F. Malysheva, N. I. Ivanova, B. G. Sukhov, N. A. Belogorlova, V. A. Kuimov, *Synthesis*, 2002, 2207; (b) N. K. Gusarova, N. I. Ivanova, M. V. Bogdanova, L. M. Sinegovskaya, A. V. Gusarov, B. A. Trofimov, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 2005, **180**, 1749.
6. (a) N. K. Gusarova, N. A. Chernysheva, S. N. Arbuzova, M. V. Bogdanova, N. I. Ivanova, A. A. Kudryavtsev, B. A. Trofimov, *Mendeleev Commun.*, 2006, 31; (b) N. K. Gusarova, M. V. Bogdanova, N. I. Ivanova, N. A. Chernysheva, S. V. Yas´ko, V. G. Samoilov, S. M. Markosyan, B. A. Trofimov, *Zh. Obshch. Khim.*, 2006, **76**, 1368 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2006, **76**, 1514]; (c) S. N. Arbuzova, N. K. Gusarova, B. A. Trofimov, *Arkivoc*, 2006, **v**, 12; (d) N. A. Chernysheva, V. L. Mikhailenko, N. K. Gusarova, S. V. Fedorov, B. A. Trofimov, *Zh. Obshch. Khim.*, 2011, **81**, 373 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2011, **81**, 470]; (e) N. K. Gusarova, S. N. Arbuzova, B. A. Trofimov, *Pure Appl. Chem.*, 2012, **84**, 439; (f) A. V. Artem´ev, N. A. Chernysheva, N. K. Gusarova, B. A. Trofimov, *Sulfur Chem.*, 2013, **34**, 474.
7. (a) C. Cao, L. R. Fraser, J. A. Love, *J. Am. Chem. Soc.*, 2005, **127**, 17614; (b) A. Battace, T. Zair, H. Doucet, M. Santelli, *Synthesis*, 2006, 3495; (c) V. P. Ananikov, N. V. Orlov, I. P. Beletskaya, *Organometallics*, 2006, **25**, 1970; (d) D. A. Malyshev, N. M. Scott, N. Marion, E. D. Stevens, V. P. Ananikov, I. P. Beletskaya, S. P. Nolan, *Organometallics*, 2006, **25**, 4462; (e) V. P. Ananikov, N. V. Orlov, S. S. Zalesskiy, I. P. Beletskaya, V. N. Khrustalev, K. Morokuma, D. G. Musaev, *J. Am. Chem. Soc.*, 2012, **134**, 6637.
8. R. Sridhar, K. Surendra, N. S. Krishnaveni, B. Srinivas, K. R. Rao, *Synlett*, 2006, 3495.
9. S. N. Riduan, J. Y. Ying, Y. Zhang, *Org. Lett.*, 2012, **14**, 1761.
10. S. Oae, *Khimiya organicheskikh soedinenii sery* [*The Chemistry of Organosulfur Compounds*], Khimiya, Moscow, 1975, 512 pp. (in Russian; translated from Japanese by Ya. Yu. Bin, B. K. Nefedov and supervised by E. N. Prilezhaeva).
11. M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal, L. G. Stolyarova, *Zh. Obshch. Khim.*, 1960, **30**, 3143 [*J. Gen. Chem. USSR* (*Engl. Transl.*), 1960, **30**].
12. M. F. Shostakovskii, E. N. Prilezhaeva, N. I. Uvarova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1955, **4** [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1955, 906].
13. US Pat. 2910480, 1959; *Chem. Abstrs*, 1960, **54**, 2361.
14. USSR Inventor´s Certificate 287930; *Byull. Izobret.* [*Bulletin of Inventions*], 1970, 36 (in Russian).
15. RF Pat. 2284320; www.findpatent.ru/patent/228/2284320.html.
16. (a) B. A. Trofimov, Yu. L. Frolov, L. M. Sinegovskaya, V. B. Modonov, E. I. Kositsyna, S. V. Amosova, N. K. Gusarova, G. G. Efremova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1977 [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 340]; (b) B. A. Trofimov, N. I. Shergina, Yu. L. Frolov, E. I. Kositsyna, M. Ya. Khil´ko, M. L. Al´pert, N. A. Nedolya, L. M. Sinegovskaya, I. L. Anisimova, I. K. Korobeinicheva, *IK-spektry vinilovykh efirov, sul´fidov, sul´foksidov i KR-spektry arilvinilovykh efirov. Atlas spektrov aromaticheskikh i geterotsiklicheskikh soedinenii* [*IR Spectra of Vinyl Ethers, Sulfides, and Sulfoxides and the Raman Spectra of Aryl Vinyl Ethers. An Atlas of the Spectra of Aromatic and Heterocyclic Compounds*], Novosibirsk Inst. of Organic Chemistry of the Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, 1982, 171 pp. (in Russian).
17. N. P. Petukhova, E. N. Prilezhaeva, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*), 1968, **17** [*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 2314].
18. B. V. Aivazov, S. M. Petrov, V. R. Khairullina, V. G. Yapryntseva, *Fiziko-khimicheskie konstanty seraorganicheskikh soedinenii* [*The Physicochemical Constants of Organosulfur Compounds*], Khimiya, Moscow, 1964, 280 pp. (in Russian).

*Received January 22, 2013;*
*in revised form February 5, 2013*