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Calcium carbide as a convenient acetylene source in the synthesis of unsaturated sulfides, promising functionalized monomers

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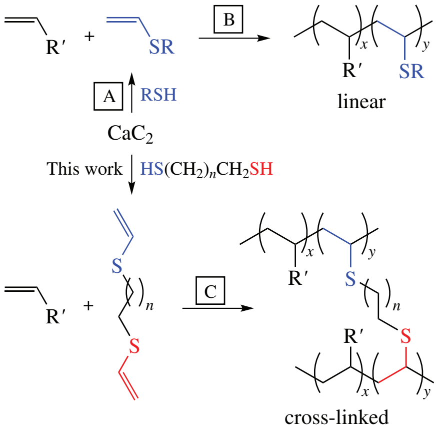
Calcium carbide was studied as a useful solid-state reagent to incorporate acetylene unit into synthetic procedures. Atom-economic thiol-yne click reaction was successfully performed with single and double additions. Heterocyclic thiols and aliphatic dithiols reacted with acetylene generated *in situ* from calcium carbide to afford corresponding vinyl sulfides and bis(thiovinyl)ethers in good to high yields.

Acetylene is an outstanding building block in modern organic chemistry with a variety of transformations already known, including direct access to build molecular complexity with atomic precision.[1] Nevertheless, in spite of outstanding chemical potential, application of gaseous acetylene in everyday laboratory practice is not an easy option since it requires a special dedicated equipment and safety precautions.

Recently, we have shown that calcium carbide can be utilized as a good acetylene source to access aliphatic and aromatic vinyl sulfides[2] (Scheme 1, A). These compounds are demanded in organic synthesis as reagents in cycloaddition,[3] Heck reaction,[4] hydrosilylation,[5] diimide reduction[6] and asymmetric oxidation.[7] For practical applications, vinyl thioethers are promising monomers to produce functionalized polymers (Scheme 1, B). An advantage of S-containing polymers concerns high refractive index and applications in optoelectronics.[8] Vinyl sulfides containing a single sulfur atom allow one to obtain linear polymers and copolymers (Scheme 1, B). The use of heterocyclic thiols (when R is hetaryl) should provide a good option to construct highly functionalized materials.



Scheme 1

Valuable opportunity may be opened by application of bis-vinyl derivatives containing two sulfur atoms. Employment of these monomers in the field of materials science facilitates formation of cross-linked copolymers (Scheme 1, C).

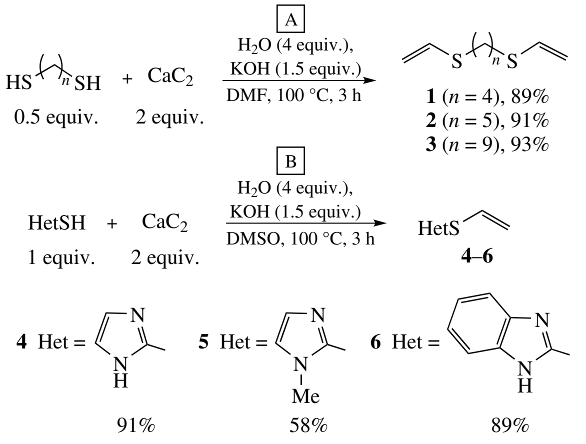
On the moment a plethora of protocols for the synthesis of vinyl sulfides were reported,[9] whereas preparation of bis(thiovinyl)ethers is significantly less developed.[9,10] Synthetic approaches to heterocyclic containing thiovinyl ethers are also rather limited.[9]

In the present work, we demonstrate that vinyl monomers containing heterocyclic moiety as well as bis(thiovinyl) derivatives can be prepared by reaction of the corresponding thiols or dithiols with calcium carbide. The reaction proceeds under mild conditions and does not require a special laboratory set-up. Usage of calcium carbide instead of gaseous acetylene simplifies the procedure and avoids the need of dedicated high-pressure equipment. Equally important, calcium carbide is an inexpensive starting material convenient for storing, weighing and handling.

Optimization has shown that the reaction proceeded smoothly in DMF or DMSO in the presence of a strong base and controlled amount of water. Important solvent parameters include solvation of calcium carbide, solubility of acetylene, optimal reaction temperature and miscibility with water. In the case of heterocyclic substrates DMSO is superior to DMF for the better solubility of the reaction components. The amount of added water was an important option for successful transformation. In the studied reactions an optimal reagents ratios of $CaC_2 : H_2O : \text{thiol} = 2:4:1$ and $CaC_2 : H_2O : \text{dithiol} = 4:8:1$ were found.[†]

Thiol-yne click reaction proceeded sequentially in the case of dithiols (Scheme 2, A). With stoichiometric amount of calcium carbide a mixture of products was formed, including mono-vinylated thiols, bisvinylated ethers and disulfides. Application of an excess of calcium carbide increased the selectivity and provided formation of only one product. Both thiol atoms were clicked to acetylene unit *via* the atom-economic hydrothiolation reaction. Products **1–3** with varying chain length (n = 4, 5 and 9) were obtained in high isolated yields of 89–93% (Scheme 2, A).[‡]

[†] *Synthesis of vinyl sulfides.* Potassium hydroxide (1.5 mmol), thiol (1 mmol)/dithiol (0.5 mmol), and water (4 mmol) were added to a reaction tube (8 ml, Duran glass) with 1 ml of DMSO (DMF in the case of dithiols; DMSO and DMF were stored under molecular sieves). Freshly powdered calcium carbide (2 mmol) was added; the tube was sealed and placed in 100 °C bath with vigorous stirring for 3 h. After heating the mixture was diluted with 10% aqueous solution of KOH (10 ml), extracted with diethyl ether (4×10 ml), organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated *in vacuo* to yield a crude product. The temperature during solvent evaporation should be controlled to avoid product loss due to the volatility of some vinyl sulfides. The crude material was further purified by column chromatography on silica gel (hexane and diethyl ether/hexane). For further purification, if required, the products can be distilled *in vacuo*.



Scheme 2

The presence of nitrogen atoms is required for several materials science applications. To explore the possibility of preparing N-functionalized monomers we have subjected imidazole and benzimidazole thiols to the S-vinylation (Scheme 2, B) and obtained the target sulfides **4–6** in good (58%) to high (89–91%) yields.[‡]

To summarize, we have developed an efficient procedure for the preparation of bis(thiovinyl) derivatives and nitrogen functionalized vinyl sulfides starting from inexpensive calcium carbide and thiols under simple experimental conditions.

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[‡] Elemental analysis was carried out using a Euro EA3028-HT apparatus. HRMS were recorded on a Bruker maXis Q-TOF instrument.

1,4-Bis(vinylthio)butane **1**. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.78 (m, 4H), 2.72 (m, 4H), 5.11 (d, 2H, *J* 16.7 Hz), 5.20 (d, 2H, *J* 10.3 Hz), 6.35 (dd, 1H, *J* 16.7 Hz, *J* 10.3 Hz). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 28.2, 31.0, 111.0, 132.3. MS, *m/z* (%): 115 (33), 86 (100), 85 (29), 73 (78), 55 (36), 45 (51). Found (%): C, 54.89; H, 8.06. Calc. for $C_8H_{14}S_2$ (%): C, 55.12; H, 8.09.

1,5-Bis(vinylthio)pentane **2**. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.53 (m, 2H), 1.68 (q, 4H, *J* 7.4 Hz), 2.70 (t, 4H, *J* 7.3 Hz), 5.10 (d, 2H, *J* 16.7 Hz), 5.19 (d, 2H, *J* 10.2 Hz), 6.35 (dd, 2H, *J* 16.7 Hz, *J* 10.2 Hz). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 28.1, 28.8, 31.3, 110.8, 132.5. MS, *m/z* (%): 87 (40), 86 (100), 73 (59), 69 (55), 67 (28), 45 (50), 41 (63). Found (%): C, 57.27; H, 8.50. Calc. for $C_9H_{16}S_2$ (%): C, 57.39; H, 8.56.

1,9-Bis(vinylthio)nonane **3**. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.30 (br. m, 6H), 1.39 (br. m, 4H), 1.64 (q, 4H, *J* 7.4–7.6 Hz), 2.69 (t, 4H, *J* 7.3 Hz), 5.10 (d, 2H, *J* 16.7 Hz), 5.18 (d, 2H, *J* 10.2 Hz), 6.36 (dd, 2H, *J* 16.7 Hz, *J* 10.2 Hz). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 29.0, 29.1, 29.3, 29.5, 31.5, 110.5, 132.7. MS, *m/z* (%): 101 (43), 87 (100), 81 (55), 85 (59), 73 (59), 69 (50), 55 (98). Found (%): C, 63.55; H, 9.84. Calc. for $C_{13}H_{24}S_2$ (%): C, 63.87; H, 9.90.

2-(Vinylthio)imidazole **4**. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.31 (d, 1H, *J* 16.7 Hz), 5.37 (d, 1H, *J* 9.6 Hz), 6.54 (dd, 1H, *J* 16.7 Hz, *J* 9.6 Hz), 7.16 (br. s, 2H). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 116.2, 124.7 (br. s), 129.7, 137.3. MS, *m/z* (%): 126 (42), 125 (100), 100 (37), 73 (24), 72 (65), 71 (25), 45 (39), 41 (39), 40 (21). Found (%): C, 47.45; H, 4.75; N, 22.15. Calc. for $C_5H_6N_2S$ (%): C, 47.59; H, 4.79; N, 22.20.

2-Vinylthio-1-methylimidazole **5**. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 3.66 (s, 3H), 5.14 (d, 1H, *J* 16.6 Hz), 5.34 (d, 1H, *J* 9.6 Hz), 6.47 (dd, 1H, *J* 16.6 Hz, *J* 9.6 Hz), 7.02 (s, 1H), 7.12 (s, 1H). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 34.6, 115.0, 123.4, 129.6, 130.2, 138.2. MS, *m/z* (%): 140 (42), 139 (100), 114 (19), 81 (25), 72 (39), 54 (15), 42 (40). MS [ESI-(+MS)], *m/z*: 141.0483 [M+H]$^+$ (calc. for $C_6H_8N_2S$, *m/z*: 141.0481).

2-(Vinylthio)benzimidazole **6**. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 5.38 (dd, 1H, *J* 9.2 Hz, *J* 1.2 Hz), 5.68 (dd, 1H, *J* 16.2 Hz, *J* 1.2 Hz), 7.22–7.29 (m, 3H), 7.46 (dd, 1H, *J* 16.2 Hz, *J* 9.2 Hz), 7.50–7.55 (m, 1H). ^{13}C NMR (100.6 MHz, CDCl$_3$) δ: 107.2, 110.4, 110.9, 123.4, 124.1, 129.8, 131.0, 168.3. MS, *m/z* (%): 176 (52), 175 (100), 150 (23), 122 (19), 118 (22), 91 (17), 90 (16), 63 (21). Found (%): C, 61.16; H, 4.54; N, 15.77. Calc. for $C_9H_8N_2S$ (%): C, 61.34; H, 4.58; N, 15.90.