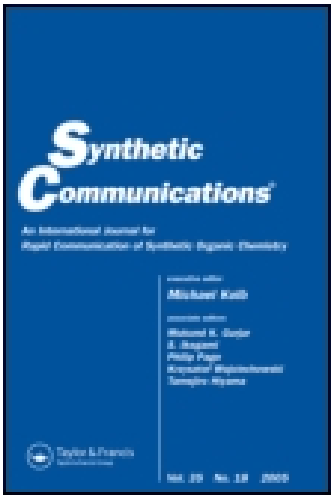

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Efficient One-Pot Preparation of Methylthio Arylbutadiynes by Double Elimination Protocol

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EFFICIENT ONE-POT PREPARATION OF METHYLTHIO ARYLBUTADIYNES BY DOUBLE ELIMINATION PROTOCOL

Qiong Su,[1] Hong Yan,[1] Shi-Chao Gao,[1] De-Xun Xie,[1] Qing-Yun Cai,[1] Guang Shao,[2] Zhi-Hong Peng,[1] and De-Lie An[1]

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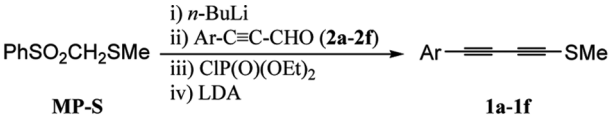
GRAPHICAL ABSTRACT



Ar: **a**. Ph; **b**. 4-$NO_2C_6H_4$; **c**. 4-ClC_6H_4; **d**. 4-$CH_3C_6H_4$; **e**. 4-$MeOC_6H_4$; **f**. 4-IC_6H_4

Abstract *A novel and efficient method for preparation of methylthio arylbutadiynes (Ar-C≡C-C≡C-SCH₃) was described, and a series of compounds have been expediently obtained by the one-pot protocol starting from methylthiomethyl phenyl sulfone (MP-S) and arylpropargyl aldehydes. The mechanism was discussed on the basis of trapping and characterization of key intermediates. The results from experiments indicated that the reaction involved the initial nucleophilic addition of MP-S to arylpropargyl aldehydes to produce an intermediate carrying two leaving groups and subsequent double elimination reactions.*

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Keywords Double elimination; methylthio arylbutadiyne; one-pot preparation

INTRODUCTION

The acetylene family has long been attractive because of its unique structural features as well as optical and electronic properties.[1] The comparable properties of arylbutadiynes are also of current interest and new synthetic methodologies are

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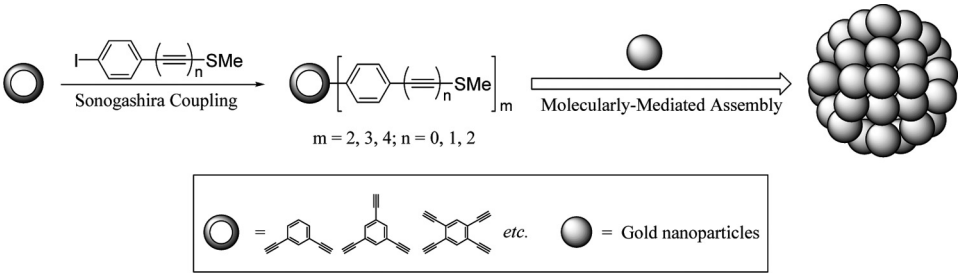


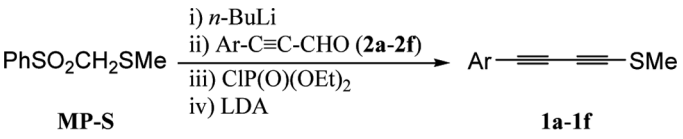
Scheme 1. Constructing of rigid multidentate sulfur-containing molecules and schematic illustration of the molecularly mediated assembly of nanoparticles.

being developed.[2] Multidentate sulfur-containing molecules as interparticle linkages now have generated an increasing interest in the assembly of gold nanoparticles.[3] Although the fundamental understanding of controlling interparticle spatial properties remains very limited so far, from the perspective of morphology control, shape-persistent molecules could serve as an ideal model system for defining interparticle structures because of their good spatial orientation properties. However, compared to extensive studies on the utility of aliphatic derivatives with flexible frameworks, much less attention has been paid to rigid molecular mediators.[4–6] Recently, we have reported the viability of interparticle linkages via coordination of some rigid multimethylthio arylethynyls to gold surfaces.[7–9] These interesting molecules have exhibited some characteristics of controlling sizes of nanoclusters and reversible behavior of assembly/disassembly.

In our studies on assembly of gold nanoparticles mediated by functional materials, various well-defined aryl ethynyls in terms of structural rigidity, size, shape, and number of methylthio group were applied to exploit their unique optical and electrical properties (Scheme 1).[7–9] To compare further the behavior of different rigid molecules in the assembly of gold nanoparticles, we need to develop some efficient methods for the preparation of different terminal building blocks ($Ar\text{-}(C{\equiv}C)_n\text{-}SCH_3$, $n = 0, 1, 2$). Otera et al. developed a convenient methodology for constructing the C≡C bond by the double elimination of β-substituted sulfones,[10] but terminal function groups (-SMe) are not involved in their method. To our knowledge, there have been known several methods of preparing methylthio arylethynes ($Ar\text{-}C{\equiv}C\text{-}SCH_3$),[11] and we also reported a simple and effective method starting from methylthiomethyl phenyl sulfone (MP-S)[12] and aromatic aldehydes by the one-pot protocol.[13] However, no effective method for the preparation of methylthio arylbutadiynes ($Ar\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}SCH_3$) has been reported so far. Herein, we describe a double-elimination-based one-pot strategy for the preparation of methylthio arylbutadiynes **1**.

RESULTS AND DISCUSSION

Arylpropargyl aldehydes **2** as starting materials were prepared from the corresponding substituted iodobenzene and propargyl alcohol by Sonogashira coupling[14] and then oxidation using MnO_2.[15]



Ar: **a**. Ph; **b**. 4-$NO_2C_6H_4$; **c**. 4-ClC_6H_4; **d**. 4-$CH_3C_6H_4$; **e**. 4-$MeOC_6H_4$; **f**. 4-IC_6H_4

Scheme 2. One-pot preparation of methylthio arylbutadiynes **1a**–**1f**.

In fact, the one-pot reaction making use of MP-S could give the desired methylthio arylbutadiynes **1** in good yields (Scheme 2, Table 1). A variety of functionalities, such as methoxy, methyl, chloro, iodo, and nitro groups were well tolerated under the reaction conditions. Compound **1f** is a pivotal building block for constructing multidentate molecules as shown in Scheme 1. This one-pot reaction is quite simple and does not require a tedious separation of the respective intermediates. A typical synthetic procedure was described for compound **1a**. To a tetrahydrofuran (THF) solution of MP-S was added *n*-BuLi (1.0 eq), arylpropargyl aldehyde **2a** (1.0 eq), $ClP(O)(OEt)_2$ (1.2 eq), and lithium diisopropylamide (LDA) (2.5 eq), in order. After the usual workup, the crude mixture was subjected to silica-gel chromatography to give product **1a** in 88% yield. Similarly, the other methylthio arylbutadiynes **1b**–**1f** were prepared from MP-S and the corresponding arylpropargyl aldehydes **2b**–**2f**.

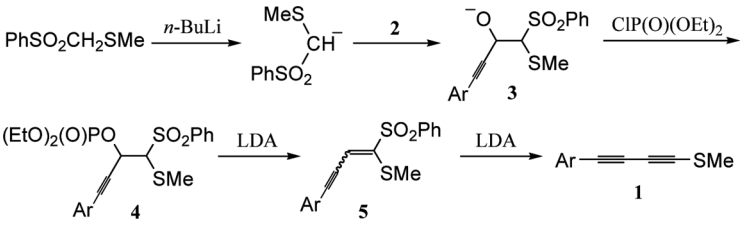
As a plausible mechanism for the formations of **1**, the anion of MP-S reacted with arylpropargyl aldehyde **2** and then $ClP(O)(OEt)_2$, leading first to alkyne phosphate **4** carrying two leaving groups, followed by double elimination of **4** with LDA as a base, to afford methylthio arylbutadiynes **1** (Scheme 3).

To obtain insight into the mechanism of this one-pot reaction, we have tried the isolation of key intermediates (alkyne phosphate **4** and enynic sulfone **5**). Differentiated stepwise procedure was employed to prove the formation of **4** and **5**. However, all attempts to isolate the phosphate **4** [after addition of *n*-BuLi, **2**, and $ClP(O)(OEt)_2$ and quenching with saturated NH_4Cl solution] failed. Although it is not clear whether **4** is unstable or prone to hydrolysis during column chromatography, when acetyl chloride instead of $ClP(O)(OEt)_2$ was exploited to trap the presumptive anion **3**, an analogous compound **6** was obtained (e.g., isolated in 66% yield for **6b**), indirectly indicating the occurance of aldol reaction (Scheme 4).

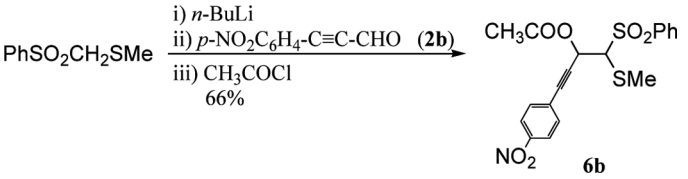
Table 1. One-pot procedure for preparation of compounds **1a**–**1f**

Entry	Ar	Arylpropargyl aldehyde	Product **1** (%)[a]
1	Ph	**2a**	**1a** (88)
2	4-$NO_2C_6H_4$	**2b**	**1b** (76)
3	4-ClC_6H_4	**2c**	**1c** (76)
4	4-$CH_3C_6H_4$	**2d**	**1d** (84)
5	4-$MeOC_6H_4$	**2e**	**1e** (77)
6	4-IC_6H_4	**2f**	**1f** (73)

[a]Yield of the isolated product.



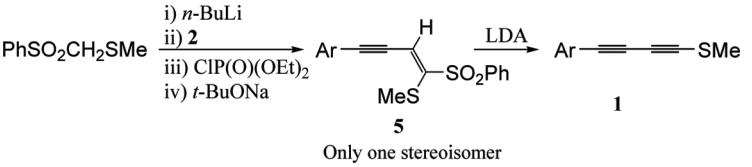
Scheme 3. Plausible reaction mechanism.



Scheme 4. Trapping of the anion **3b**.

Subsequently, when LDA as base was replaced with *t*-BuONa, a controllable elimination process occurred to give the enynic sulfone intermediates **5** (Scheme 5). As expected, all intermediates **5a**–**5f** were isolated. It is worth noting that only one type of geometric isomer for all enynic sulfone intermediates **5a**–**5f** were obtained after the reaction. These isomers were speculated to be *E*-configuration, owing to the strong stereohindrance of the substituted groups on both sides of C=C bond. As an evidence, the structure of **5e** was unambiguously determined by x-ray analysis (Fig. 1). The bond lengths of C(1)–C(2) and C(3)–C(4) show characteristics of C=C and C≡C bonds, respectively. (See the Supplementary Data, available online). Two bulky priority groups ($PhSO_2$- and 4-$MeOC_6H_4C{\equiv}C$-) lie on the opposite sides of C=C bond, indicating clearly *E*-configuration of **5e**.

Furthermore, we have investigated the elimination of enynic sulfone intermediates **5**, which, upon treatment with LDA, occurred smoothly to provide methylthio arylbutadiynes **1** in good yields (Scheme 5, Table 2). Therefore, we can conclude that the formation of **1** involves the double elimination reactions of intermediate **4**.



Scheme 5. Formation of intermediates **5** and preparation of compounds **1** via **5**.

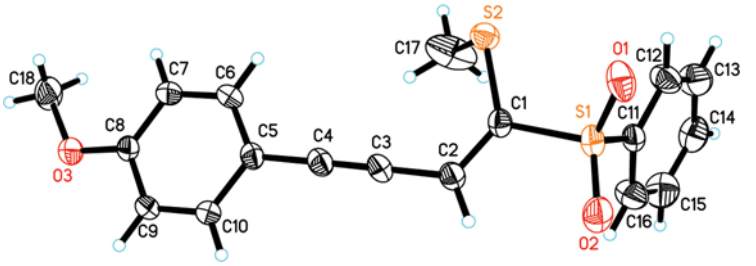


Figure 1. X-ray crystal structure of enynic sulfone intermediate **5e**. (Figure is provided in color online.)

Table 2. Stepwise procedures for preparation of compounds **1a**–**1f**

Entry	Arylpropargyl aldehyde	Intermediate **5** (%[a])	Product **1** (%)[a,b]
1	**2a**	**5a** (72)	**1a** (88)
2	**2b**	**5b** (73)	**1b** (82)
3	**2c**	**5c** (76)	**1c** (91)
4	**2d**	**5d** (85)	**1d** (88)
5	**2e**	**5e** (78)	**1e** (93)
6	**2f**	**5f** (82)	**1f** (89)

[a]Yield of the isolated product.
[b]Yield based on intermediate **5**.

CONCLUSION

In summary, we have developed a convenient one-pot synthetic method of methylthio arylbutadiynes using arylpropargyl aldehydes and MP-S, by which six compounds **1a**–**1f** were obtained in good yields. The mechanism for the formation of **1** was discussed on the basis of trapping and characterization of some important intermediates. Experimental results have indicated that the reaction process involves the initial nucleophilic addition of MP-S to arylpropargyl aldehyde to produce an intermediate **4** carrying two leaving groups, followed by double eliminations using LDA as base to form **1**.

EXPERIMENTAL

All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted. THF was distilled from sodium/benzophenone. LDA was prepared from diisopropylamine and BuLi before use. Silica gel (ZCX-II or SG1115) was used for column chromatography. All melting points were determined with a Taike XT-4 micro-melting-point apparatus and were uncorrected. NMR spectra were recorded on a Varian Inova-400 instrument using tetramethylsilane (TMS) as an internal standard. Mass spectra were measured on Shimazu GC-17A QP-5000 and ThermoFinnigan MAT95XP spectrometers. (IR) spectra were recorded on a Nicolet 6700 Fourier transform (FT)–IR spectrometer. Ultraviolet–visible UV-vis spectra were obtained with a LabTech UV2100 spectrometer.

The crystal used for x-ray diffraction was grown in a solution of chloroform and petroleum ether. X-ray analysis on a single crystal was carried out at 293(2)

K on a Bruker Smart CCD area detector using graphite-monochromated Mo kα radiation (λ = 0.71073 Å). An empirical absorption correction was carried out using SADABS. Stucture solutions and full-matrix least-squares refinements based on F^2 were performed with SHELXS-97 and SHELXL-97 programs, respectively. The nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in geometrical positions and constrained to ride on their parent atoms. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[16] (See the Supplementary data.)

Synthesis of Methylthio (4-Phenyl)butadiyne (1a)

BuLi (2.5 M in hexane, 0.8 mL, 2.0 mmol) was added dropwise to a solution of methylthiomethyl phenyl sulfone (405 mg, 2.0 mmol) in THF (25 mL) at −78 °C, and the mixture was stirred for 10 min. Phenylpropargyl aldehyde **2a** (260 mg, 2.0 mmol) in THF (3 mL) was added dropwise at this temperature. After an additional 10 min, $ClP(O)(OEt)_2$ (414 mg, 2.4 mmol) was added at −78 °C, and the cooler was then removed. The resulting mixture was allowed to warm up to room temperature and stirred for 30 min. The solution was then cooled to −78 °C, and LDA (5.0 mmol) was added. After stirring for 30 min, the reaction was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate (30 mL × 3). The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was subjected to chromatography (SiO_2, hexane) to give **1a** (301 mg, 88%) as orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 7.29–7.35 (m, 3H), 7.47 (dd, J = 8.0 Hz, J = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.93, 74.25, 75.47, 77.79, 79.07, 121.60, 128.33, 129.05, 132.44; MS (EI) m/z (%): 172 (M^+, 82). HRMS (EI) m/z: calcd. for $C_{11}H_8S$ 172.0341; found 172.0347; IR (KBr): υ = 3060, 2927, 2853, 2197, 2105, 1595, 1488, 1441, 1312, 1069, 1023, 976, 754, 688 cm^{-1}; UV-vis (EtOH, 1.0×10^{-4} mol/L): λ_{max} (ε_{max}) = 248 nm (1.8×10^4), 266 nm (9.6×10^3), 280 nm (7.9×10^3), 297 nm (5.6×10^3), 317 nm (4.2×10^3).

Synthesis of (*E*)-1-Methylthio-1-phenylsulphonyl-4-phenyl-1-butene-3-yne (5a)

BuLi (2.5 M in hexane, 0.8 mL, 2.0 mmol) was added dropwise to a solution of methylthiomethyl phenyl sulfone (405 mg, 2.0 mmol) in THF (25 mL) at −78 °C, and the mixture was stirred for 10 min. Phenylpropargyl aldehyde **2a** (260 mg, 2.0 mmol) in THF (3 mL) was added dropwise. After an additional 10 min, $ClP(O)(OEt)_2$ (414 mg, 2.4 mmol) was added at −78 °C, and the cooler was then removed. The resulting mixture was then allowed to warm up to room temperature and stirred for 30 min. The solution was cooled to −78 °C, and *t*-BuONa (384 mg, 4.0 mmol) was added. After stirring for 30 min, the reaction was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate (30 mL × 3). The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was subjected to chromatography (SiO_2, hexane–AcOEt = 10:1) to give **5a** (452 mg, 72%) as pale yellow solid; mp 78–79 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.34–7.43 (m, 3H), 7.48 (s, 1H), 7.51 (d, J = 7.2 Hz, 2H),

7.56 (t, $J = 7.6$ Hz, 2H), 7.65 (t, $J = 7.4$ Hz, 1H), 7.98 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 18.53$, 84.13, 106.50, 121.74, 126.40, 128.57, 128.72, 129.03, 129.94, 132.02, 133.71, 138.48, 147.79; MS (EI) m/z (%): 314 (M^+, 10); HRMS (EI) m/z: calcd. for $C_{17}H_{14}O_2S_2$ 314.0430; found 314.0426. IR (KBr): $\upsilon = 3078$, 3016, 2920, 2870, 2193, 1553, 1445, 1316, 1151, 1087, 912, 759, 717, 688 cm^{-1}.

General Procedure for Synthesis of Compounds 1a–1f from Intermediates 5a–5f

LDA (1.1 mmol) was added dropwise to a solution of **5** (1.0 mmol) in THF (15 mL) at −78 °C. When **5** disappeared (monitored by thin-layer chromatography, TLC), the reaction was quenched with aqueous NH_4Cl solution and extracted with ethyl acetate (30 mL × 3). The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was subjected to chromatography (SiO_2, hexane) to give **1** (Table 2).

Synthesis of (1-(4-Nitro)phenyl)-3-acetyloxyl-4-methylthio-4-phenylsulphonyl Butyne (6b)

BuLi (2.5 M in hexane, 0.8 mL, 2.0 mmol) was added dropwise to a solution of methylthiomethyl phenyl sulfone (405 mg, 2.0 mmol) in THF (25 mL) at −78 °C, and the mixture was stirred for 10 min. (4-Nitrophenyl)propargyl aldehyde **2b** (350 mg, 2.0 mmol) in THF (3 mL) was added dropwise at this temperature. After an additional 10 min, acetyl chloride (188 mg, 2.4 mmol) was added dropwise at −78 °C, and the cooler was then removed. The resulting mixture was allowed to warm up to room temperature and stirred for 30 min. The mixture was then poured into water and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, and filtered. The solvent was evaporated in vacuo, and the residue was subjected to chromatography (SiO_2, hexane–AcOEt = 10:1) to give **6b** (553 mg, 66%) as pale yellow solid; mp 121–122 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.10$ (s, 3H), 2.42 (s, 3H), 4.23 (d, $J = 4.0$ Hz, 1H), 6.23 (d, $J = 4.0$ Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 2H), 7.63 (t, $J = 7.2$ Hz, 1H), 8.05 (d, $J = 7.2$ Hz, 2H), 8.14 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 17.26$, 20.68, 62.69, 73.23, 86.42, 86.77, 123.36, 127.91, 128.84, 130.09, 132.75, 134.36, 136.56, 147.60, 168.94; MS (EI) m/z (%): 419 (M^+, 57). HRMS (EI) m/z: calcd. for $C_{19}H_{17}NO_6S_2$ 419.0485; found 419.0475. IR (KBr): $\upsilon = 3105$, 3066, 2928, 2857, 2230, 1743, 1595, 1518, 1447, 1341, 1224, 1152, 1081, 1022, 856, 778, 750, 688 cm^{-1}.

Supplementary Data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center. CCDC 691648 contains the x-ray data in CIF format for this article. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/products/csd/request/(or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk). Full experimental details, ^{1}H and ^{13}C

NMR spectra, and X-ray crystallography data for **5e** can be found via the Supplementary Content section of this article's WebPage.

ACKNOWLEDGMENTS

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