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Regio- and stereoselective *tert*-butylthiolation of internal alkynes with thioethers initiated and maintained by silylium-ion catalysis

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A two-component protocol for the regio- and *trans*-selective addition of aryl tertiary alkyl (especially *tert*-butyl) thioethers across internal C≡C triple bonds is reported. This carbothiolation is initiated by the catalytic formation of a silylated sulfonium ion as a tertiary carbenium ion (*tert*-butyl cation) source. Competing loss of a proton by β-elimination of that carbenium-ion intermediate and as such a potential hydrothiolation pathway are efficiently suppressed by the substoichiometric addition of an arylsilane as a “proton-into-silylium ion” generator. Through this, the silylium-ion activation is restored, thereby maintaining the carbothiolation pathway. The method enables the synthesis of sterically crowded, fully substituted aryl vinyl sulfides as well as the sulfoxides and sulfones.

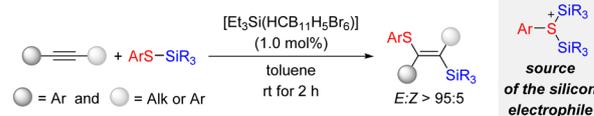
Introduction

Alkenes are widely used in the synthesis of complex organic molecules and are themselves commonly found in natural products and bioactive compounds.¹ Despite their ubiquity, the formation of alkenes is non-trivial with the necessity of considering both stereo- and (depending on the method) regioselectivity factors. This is particularly true for the delicate challenging synthesis of highly substituted alkenes, this being C=C double bonds with three or even four carbon substituents.^{2,3} One possible approach to the synthesis of sterically encumbered alkenes is the selective difunctionalization of alkynes.^{4,5} A wide range of functional groups and carbon substituents have been added across C≡C triple bonds by either three- or two-component reaction systems.^{6–12} Three-component reactions involve the use of a separate nucleophile and electrophile component for sequential addition to the alkyne unit.^{13,14} From an atom-economy perspective the more attractive option however is a two-component reaction in which both units for the addition to the alkyne come from a single reactant.^{4,15} A carbon substituent that has proven particularly challenging to install is a quaternary carbon atom emerging from a tertiary reactant. Although a number of examples have been published where addition of a tertiary carbon center to a terminal alkyne is achieved,^{16–22} examples involving the addition to an internal alkyne are more limited and usually involve activation of the reactants.^{23–27}

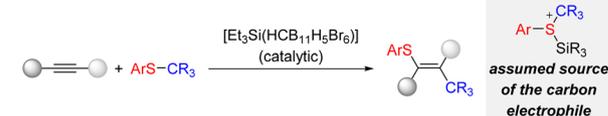
Our group recently showed that S–Si bonds can be selectively added across an internal triple bond in a silylium-ion²⁸ promoted reaction (Scheme 1A).¹⁵ This two-component

difunctionalization provided a reliable access to fully substituted double bonds with two synthetic handles for further functional-group manipulation. Given the intermediacy of various cationic species, we asked ourselves whether that strategy would allow for the release and transfer of tertiary carbenium ions from thioethers (Scheme 1B). This would correspond to an intermolecular carbothiolation of alkynes. We are only aware of a single related example where Nakamura and co-workers disclosed an intramolecular gold-catalyzed carbothiolation by starting from an allylated thiophenyl derivative (Scheme 1C).²⁹ Since then, a number of metal-catalyzed carbothiolation reactions of alkynes have been developed^{29–36} but, to

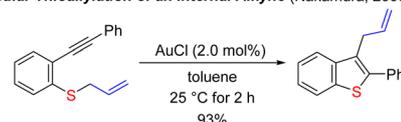
A Intermolecular Thiosilylation of Internal Alkynes (2024)



B Intermolecular Thioalkylation of Internal Alkynes (this work)



C Intramolecular Thioallylation of an Internal Alkyne (Nakamura, 2006)



Scheme 1 Silylium-ion-promoted thiosilylation and thioalkylation (carbothiolation) of internal alkynes.

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the best of our knowledge, none of these involved simple tertiary alkyl groups.

Results and discussion

We began our optimization using *tert*-butyl(phenyl)sulfane (**1a**) and *but-1-yn-1-yl*benzene (**2a**) as model compounds (Table 1 and for full details see Tables S1–S5 in the SI). Beginning with the reaction conditions from the aforementioned thiosilylation,¹⁵ the desired carbothiolation product **3aa** was obtained as a single stereoisomer in toluene with 1.0 mol% of [Me₃-Si(HCB₁₁H₅Br₆)] in a 28% yield along with 18% yield of the hydrothiolation byproduct **4aa** (entry 1). A survey of solvents revealed that (deuterated) benzene is an optimal choice, providing **3aa** in a 43% yield with 17% of **4aa** (entry 2). The reaction time could be reduced from 16 to 6 h with the yield maintained (entry 3). The equivalents of the starting material used played a significant role: Increasing the amount of the alkyne to two equivalents improved the yield of **3aa** to 63% with 13% of **4aa** (entry 4). This was likely due to the increased concentration of the alkyne accelerating the rate of the bimolecular process. If the volume of solvent used was increased, the overall yield reduced further pointing towards the importance of substrate concentration in this reaction (see Table S3 in the SI). A number of different initiators were then tested and, for example, the trityl salt [Ph₃C][HCB₁₁H₅Br₆] failed to initiate the reaction (entry 5) but the silylium salt [Et₃Si(HCB₁₁H₅Br₆)] improved the yield to 75% **3aa** with 14% of **4aa** (entry 6). We presumed that the hydrothiolation product **4aa** was being generated by a proton released from the tertiary carbenium ion by β -elimination. We therefore added an arylsilane in order to trap this proton by proton-into-silylium ion interconversion.^{37–41} Ph₄Si as an additive was almost completely insoluble, hence not bringing about any improvement (entry 7). Using 0.50 equiv. of

Ph₃SiH, it was possible to reduce the amount of **4aa** to 5% while maintaining a 73% yield of the desired product **3aa** (entry 8). Use of 1.0 equiv. of the alkyne led to a reduction in the yield of **3aa** to 51% (entry 9).

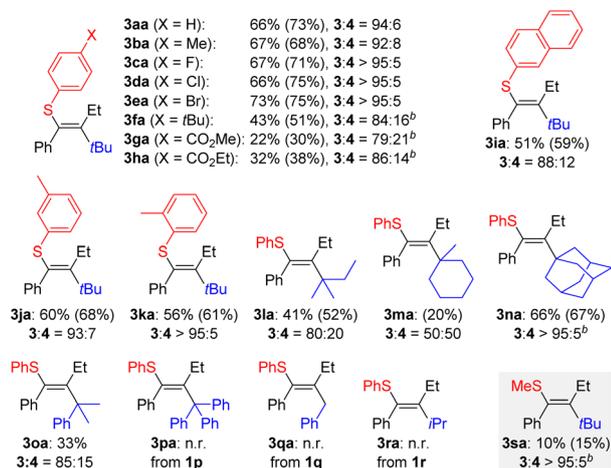
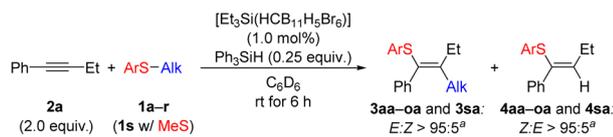
With the optimized conditions in hand, we turned to the substrate scope of the reaction. In many cases, separation of the product from unreacted Ph₃SiH proved difficult, so the amount used was reduced from 0.50 to 0.25 equiv. We began gauging the substrate scope by varying the aryl ring on the thioether reagent **1** (Scheme 2). Methyl and halogen groups were well tolerated at the *para* position of the aryl group with only a small impact on the yield observed for **3ba–ea**. When a bulkier group such as *tert*-butyl as in **1f** was present, the activity of the reaction reduced significantly but a yield of 43% for **3fa** could be obtained when the reaction temperature was increased to 60 °C. Although the yields remained low even at increased temperatures, products **3ga** and **3ha** bearing an ester group could also be obtained. The configuration of the double bond was assigned for **3ha** by an nOe measurement (see Fig. S2 in the SI). A more sterically bulky β -naphthyl group in **1i** resulted in a moderate yield for **3ia**. Likewise, **1j** and **1k** with *meta*- and *ortho*-tolyl groups led to yields for **3ja** and **3ka** in the same range. Variation of the tertiary alkyl group was next looked at. When the *tert*-butyl group was replaced by a *tert*-amyl residue, a yield of 41% was obtained for **3la** along with a substantial amount of the hydrothiolation product **4la**. The hydrothiolation pathway became even more pronounced when a cyclic tertiary carbenium ion was present, resulting in a 1 : 1 ratio of **3ma** and **4ma**. An adamantyl worked equally well as a *tert*-butyl group, leading to the formation of **3na** in 66% yield with hardly any hydrothiolation byproduct. Any benzylic carbocation was either transferred sluggishly (**1o** \rightarrow **3oa**) or did not react as planned (trityl as in **1p** and benzyl as in **1q**). A secondary alkyl group as potentially released from isopropyl-substituted thioether **1r** did

Table 1 Optimization of the *trans*-selective alkyne carbothiolation^{a,b}

Entry	Initiator	Solvent	2a (equiv.)	Additive	Yield of 3aa (%) ^c	Yield of 4aa (%) ^c	Ratio of 3aa : 4aa ^d
1 ^e	[Me ₃ Si(HCB ₁₁ H ₅ Br ₆)]	Toluene	1.0		28	18	61 : 39
2 ^e	[Me ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	1.0		43	17	72 : 28
3	[Me ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	1.0		46	18	72 : 28
4	[Me ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	2.0		63	13	83 : 17
5	[Ph ₃ C][HCB ₁₁ H ₅ Br ₆]	C ₆ D ₆	2.0		n.r.	n.r.	
6	[Et ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	2.0		75	14	84 : 16
7	[Et ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	2.0	Ph ₄ Si	36	9	80 : 20
8	[Et ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	2.0	Ph ₃ SiH	73	5	94 : 6
9	[Et ₃ Si(HCB ₁₁ H ₅ Br ₆)]	C ₆ D ₆	1.0	Ph ₃ SiH	51	7	88 : 12

^a All reactions were performed on a 0.20 mmol scale in a glovebox under an argon atmosphere in 0.5 mL of the indicated solvent. ^b *E* : *Z* ratios estimated by ¹H NMR spectroscopy of the crude reaction mixture. ^c Yield determined by ¹H NMR spectroscopy of the crude reaction mixture using CH₂Br₂ as an internal standard. ^d **3aa** : **4aa** ratios determined by ¹H NMR spectroscopy of the crude reaction mixture. ^e Reaction time 16 h. n.r. = no reaction.



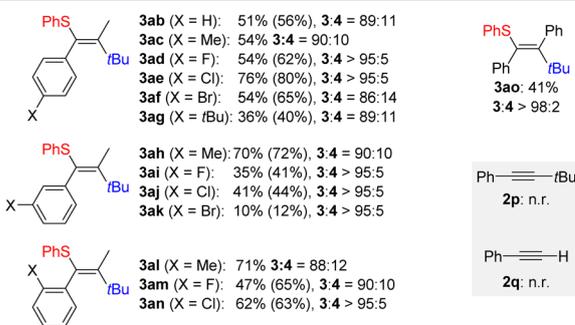
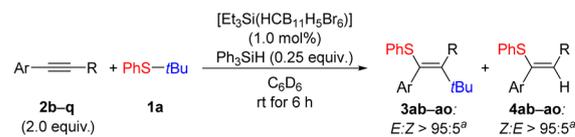


Scheme 2 Substrate scope I: variation of the thioether. All reactions were performed using the indicated thioether **1** (0.20 mmol), the alkyne **2a** (0.40 mmol, 2.0 equiv.), Ph₃SiH (0.050 mmol, 0.25 equiv.), and the initiator [Et₃Si(HCB₁₁H₅Br₆)] (2.0 μmol, 1.0 mol%) in a glovebox under an argon atmosphere in C₆D₆ (0.5 mL) at rt. Isolated yields refer to analytically pure material (combined **3** and **4**) after flash chromatography on silica gel; yields in parentheses determined by ¹H NMR spectroscopy of the crude reaction mixture using CH₂Br₂ as an internal standard. ^a E : Z ratios estimated by ¹H NMR spectroscopy of the crude reaction mixture. ^b Reaction performed at 60 °C.

not engage in the reaction. A dialkyl thioether such as **1s** furnished the carbothiolation product **3sa** only in poor yield (gray box).

Following this, the aryl-substituted alkyne used was varied systematically (Scheme 3). Aliphatic alkynes were not compatible with this reaction with the aryl ring necessary for reaction initiation. Substitution at the *para* position of the aryl substituent in alkyne **2** was tolerated with moderate to good yields for **3ab–af**. The exception to this was again a *tert*-butyl group which led to a reduction in yield to 36% for **3ag**. Substitution at the *meta* position proved to be more challenging although a good yield was obtained for the tolyl-substituted derivative **3ah**. The three halogenated products **3ai–ak** were all obtained in low yields. In turn, substitution at the *ortho* position had little effect on the overall yield of the product **3al–an**. It was possible to utilize diphenylacetylene (**2o**) in the reaction, and a moderate yield of 41% was found for the carbothiolation product **3ao**. Conversely, no reaction occurred with an alkyne bearing a *tert*-butyl group as in **2p** or with a terminal alkyne as for phenylacetylene (**2q**), respectively (gray box).

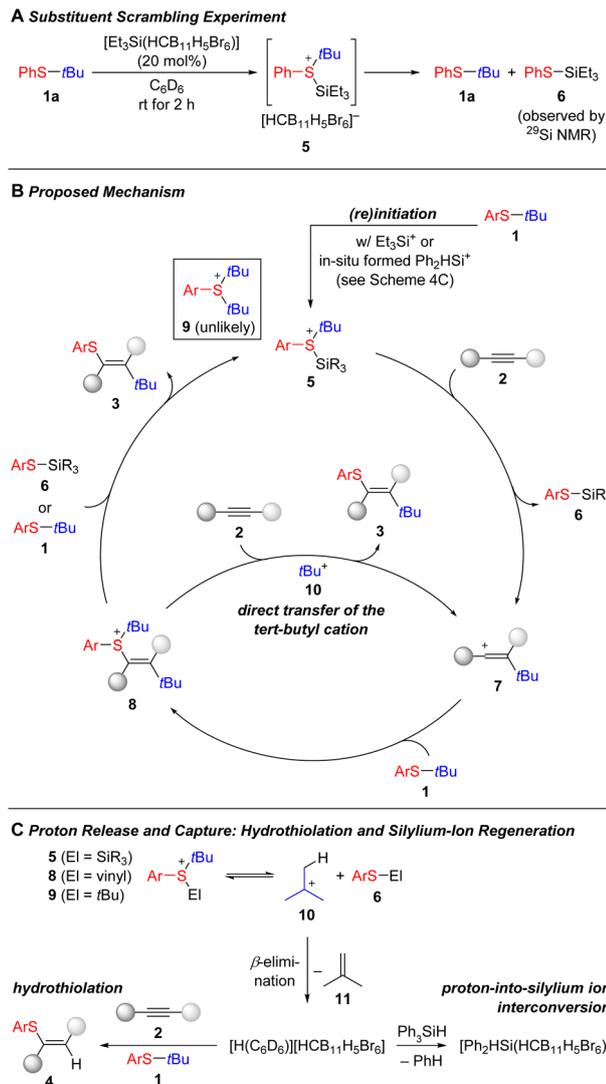
We believe that the mechanism of this carbothiolation reaction exhibits similarities to that of the silylium-ion-promoted thiosilylation of alkynes (see Scheme 1A).¹⁵ Interaction of the initiator [Et₃Si(HCB₁₁H₅Br₆)] with the aryl *tert*-butyl thioether was verified by a substituent exchange experiment



Scheme 3 Substrate scope II: variation of the internal alkyne. All reactions were performed using the thioether **1a** (0.20 mmol), the indicated alkyne **2** (0.40 mmol, 2.0 equiv.), Ph₃SiH (0.050 mmol, 0.25 equiv.), and the initiator [Et₃Si(HCB₁₁H₅Br₆)] (2.0 μmol, 1.0 mol%) in a glovebox under an argon atmosphere in C₆D₆ (0.5 mL) at rt. Isolated yields refer to analytically pure material (combined **3** and **4**) after flash chromatography on silica gel; yields in parentheses determined by ¹H NMR spectroscopy of the crude reaction mixture using CH₂Br₂ as an internal standard. ^a E : Z ratios estimated by ¹H NMR spectroscopy of the crude reaction mixture.

(Scheme 4A). When thioether **1a** was reacted with 20 mol% of the counteranion-stabilized silylium ion, the formation of the thiosilane **6** was detected by ²⁹Si NMR spectroscopy, thereby suggesting the intermediacy of the silylsulfonium ion **5**. Intermediate **5** is the starting point of the catalytic cycle (Scheme 4B). It transfers the *tert*-butyl cation onto the alkyne **2** to form the vinyl cation **7**,^{42–48} which in turn reacts with excess thioether **1** to yield another sulfonium-ion intermediate **8**. Although it is obvious that this sulfonium ion will release the *tert*-butyl cation to eventually liberate the carbothiolation product **3**, its actual fate remains unclear. The role of sulfides **1** and **6** as carbenium-ion shuttles is a possibility but *tert*-butyl-substituted **1** to form bis-*tert*-butylated arylsulfonium ion **9** is unlikely for steric considerations and thiosilane **6** is only available at low concentration. Hence, we assume that the *tert*-butyl group is directly transferred from intermediate **8** to alkyne **2** thereby closing the catalytic cycle. The observation of the hydrothiolation product **4** lends further evidence for this pathway (Scheme 4C). Dissociation of any of the sulfonium ions **5**, **8**, or **9** gives access to a free *tert*-butyl cation **10**, that suffers β-elimination by loss of a proton to give isobutene **11**. That proton can be accepted by the alkyne **2** (or thioether **1** and silylated thioether **6**) opening the door to the hydrothiolation channel. To suppress this side reaction, we decided to exploit the ability of [H(C₆D₆)] [HCB₁₁H₅Br₆] to convert arylsilanes into counteranion-stabilized silylium ions by dearylation.^{37–41} That proton-into-silylium ion interconversion not only sequesters the strong Brønsted acid but also makes available [Ph₂HSi(HCB₁₁H₅Br₆)] (from Ph₃SiH) for further sulfonium-formation. The arylsilane additive thereby enhances the overall performance of

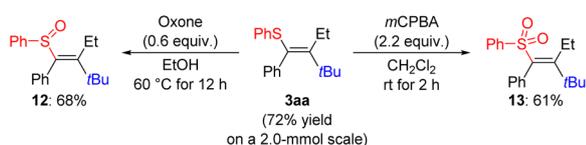




Scheme 4 Discussion of the mechanism. The $[\text{HCB}_{11}\text{H}_5\text{Br}_6]^-$ counterion is omitted for clarity in the catalytic cycle.

the catalysis.^{37,49} We also examined whether the carbothiolation is reversible but a scrambling experiment between product **3aa** (Ar = Ph) and thioether **1b** (Ar = 4-Tolyl) under the standard reaction conditions showed no exchange; the vinyl sulfide **3aa** was recovered exclusively and a small amount of degradation was seen for **1b**.

To explore the utility of this reaction, we performed the model reaction on a 2.0-mmol scale, furnishing the vinyl sulfide



Scheme 5 Oxidation of the fully substituted vinyl sulfide. Yields are isolated and refer to analytically pure material after flash chromatography on silica gel.

3aa in a slightly improved isolated yield of 72% (Scheme 5). In an effort to prime the carbon–sulfur bond in **3aa** for further functional-group manipulation, we oxidized sulfur atom to the sulfoxide **12** with oxone in ethanol,⁵⁰ and to the sulfone **13** with *m*CPBA.¹⁵ At this stage, attempts to engage any of these three vinyl components in a transition-metal-catalyzed cross-coupling have been unsuccessful in our hands.^{51–53}

Conclusions

We have here disclosed a new method for the regio- and *trans*-selective carbothiolation (thioalkylation) of internal alkynes that specifically enables the installation of a *tert*-butyl group at an alkene. A *tert*-butyl-substituted arylsulfide serves as the *tert*-butyl electrophile and at the same time as the sulfur nucleophile. This is made possible by initiation of the reaction with a counteranion-stabilized silylium ion to form a sulfonium ion as the actual carbenium-ion carrier. The reaction displays a good substrate scope with functional-group tolerance similar to that typically seen in other catalyses under superacidic conditions.

Author contributions

D. M. M., H. F. T. K. and M. O. conceptualized this work. D. M. M. performed and analyzed the experiments. H. F. T. K. and M. O. supervised the research and acquired funding. All authors contributed to the writing and editing of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article has been included as part of the supplementary information (SI). Supplementary information: reaction optimizations, experimental procedures, full characterization data and copies of NMR spectra. See DOI: <https://doi.org/10.1039/d5sc09722c>.

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