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Letter

Carboxylate-Catalyzed *C*-Silylation of Terminal Alkynes

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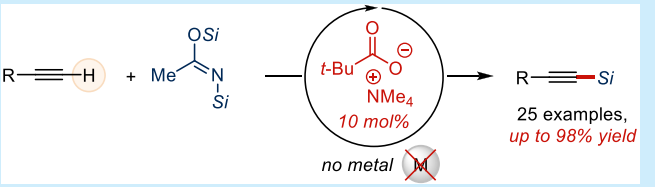
ABSTRACT: A carboxylate-catalyzed, metal-free *C*-silylation protocol for terminal alkynes is reported using a quaternary ammonium pivalate as the catalyst and commercially available *N*,*O*-bis(silyl)acetamides as silylating agents. The reaction proceeds under mild conditions, tolerates a range of functionalities, and enables concomitant *O*- or *N*-silylation of acidic OH or NH groups. A Hammett ρ value of +1.4 ± 0.1 obtained for *para*-substituted 2-arylalkynes is consistent with the proposed catalytic cycle involving a turnover-determining deprotonation step.

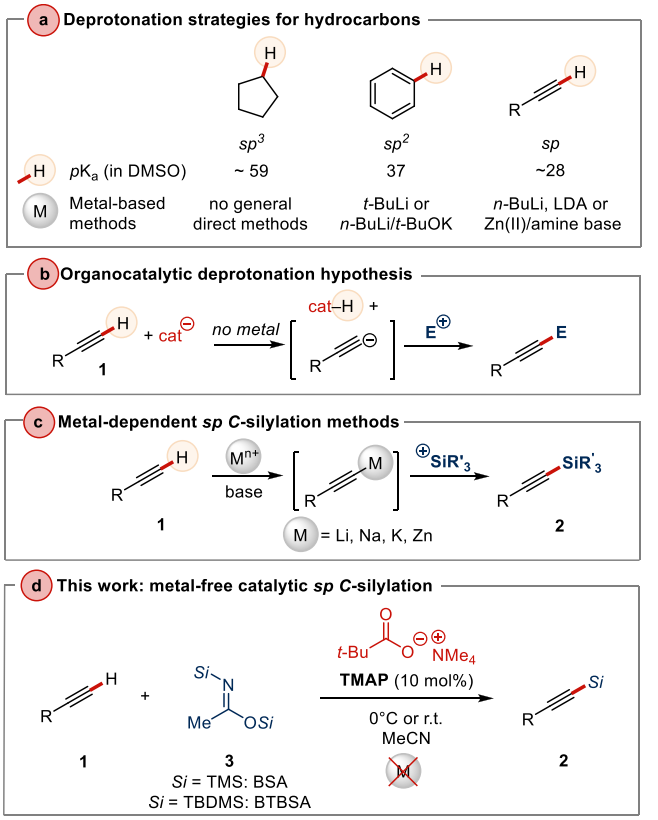


Metal-free deprotonation of hydrocarbons is challenging due to the high pK_a values of most hydrocarbons,[1] and typical methods to generate carbanions with strong organometallic bases result in the formation of another organometallic species. For example, aromatic hydrocarbons can be deprotonated only by strong bases (e.g., Schlosser reagent)[2−4] unless they are activated by a directing group.[5−7] With a pK_a of ca. 28 (in DMSO), terminal alkynes might be an exception to this rule, but in practice even they require the use of strong organometallic bases and/or more electropositive, π-coordinating metals such as Zn.[8,9] Catalytic deprotonation reactions of alkynes without metals are presumed to be highly challenging,[10] although reactions with aldehydes and ketones (Favorskii reaction) have been realized with strong metal-free bases such as quaternary ammonium hydroxides.[11−13]

We have previously shown that metal-free catalytic enoyl isomerization[14] and silylative aldol reactions[15] are possible with simple carboxylate salt catalysts, without the need of metal or strong (and potentially nucleophilic) hydroxide bases. In the aldol reaction, the combination of tetramethylammonium pivalate (TMAP) and the neutral silylating agent *N*,*O*-bis(trimethylsilyl)acetamide (BSA) was required for rapid turnover rates. Herein we show that catalytic deprotonation of terminal alkynes with concomitant *C*-silylation can be achieved under very mild conditions using a metal-free carboxylate catalyst (Scheme 1) and silylamides as the silyl source.

Silylated terminal alkynes are versatile precursors of alkynyl nucleophiles in synthetic organic chemistry,[16−18] and the silyl group also plays a role of a protecting group. Typical approaches to the synthesis of *C*-silylated alkynes include deprotonation of terminal alkynes with stoichiometric amount of organolithium compounds (e.g., *n*-BuLi) and the use of halosilanes as the silylating agent.[19] An alternative silylation method with stoichiometric Lewis acid ($ZnCl_2$) has been reported using silylamines,[20] and the more reactive $Zn(OTf)_2$ has been used as a Lewis acid in stoichiometric and catalytic variants employing halosilanes[21] and silyl triflates,[22] respec-

Scheme 1. Deprotonation of Hydrocarbons: The Concept of Metal-Free Deprotonation−Silylation Sequence



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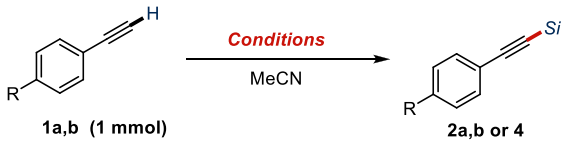
tively. More recent catalytic versions of TMS protection employing the Ruppert–Prakash reagent ($TMSCF_3$)[23] and bis(trimethylsilyl)acetylene as the electrophilic TMS donor[24] with strong bases, NaH and KHMDS, have also been reported recently. Catalytic decarboxylations of silyl alkynoates have been reported as an alternative pathway to silylalkynes.[25,26] Silyl hydrides can also be used as silylating agents with alkali-metal hydroxides or transition metals as catalysts.[27−30]

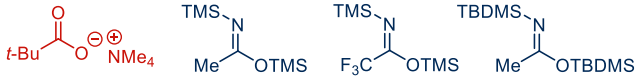
We initiated our study by using phenylacetylene (**1a**) and *p*-CF_3-phenylacetylene (**1b**) as model substrates and exposing these alkynes to a catalytic amount of TMAP and 1.5 equiv of BSA. To our delight, both substrates were converted to the desired TMS–acetylenes (R = H, **2a** or R = CF_3, **2b**) in high yields (Table 1, entries 1 and 2). With **1b**, the reaction proceeded at −10 °C in nearly quantitative yield (94% **2b** was obtained). Deviations in catalyst loading or the quantity of BSA did not lead to any improvement (Table 1, entries 3−5), but in the absence of the catalyst (TMAP), no **2a** was detected (Table 1, entry 6). Interestingly, replacing the silylating agent with BSTFA gave no reaction (Table 1, entry 7), but the bulkier *tert*-butyldimethylsilylating agent BTBSA afforded the corresponding TBDMS-protected alkyne **4** in 65% yield.

Table 1. Optimization of the TMAP-Catalyzed Silylation of Alkynes[a]



1a,b (1 mmol) 2a,b or 4

Entry	Conditions	Yield, %
1	**1a** (R = H), TMAP (0.1 equiv.), BSA (1.5 equiv.), r.t., 5 h	85
2	**1b** (R = CF_3), TMAP (0.1 equiv.), BSA (1.5 equiv.), -10 °C, 1 h	94
	Deviations from above	
3	R = CF_3, TMAP (0.05 equiv.), BSA (1.5 equiv.), r.t., 5 h	50[a]
4	R = H, TMAP (0.1 equiv.), BSA (1.3 equiv.), r.t., 5 h	82[a]
5	R = CF_3, TMAP (0.1 equiv.), BSA (1.5 equiv.), r.t., 5 h	90[a]
6	R = H, TMAP (0.1 equiv.), BSTFA (1.5 equiv.), r.t., 5 h	n.d.[b]
7	R = H, TMAP (0 equiv.), BSA (1.5 equiv.), r.t., 24 h	n.d.[b]
8	R = H, TMAP (0.1 equiv.), BTBSA (1.5 equiv.), r.t., 5 h	65



TMAP BSA BSTFA BTBSA

[a]Conversion based on ^{1}H NMR analysis of the crude reaction mixture. [b]Run as an ^{1}H NMR experiment in MeCN-d_3.

The utility of the carboxylate–BSA silylating protocol was then explored with a range of substrates. Substituted phenylacetylenes **1a–i** gave the TMS-protected alkynes **2a–i** in excellent, even nearly quantitative yields with both electron-donating and electron-withdrawing groups (EWGs). Typically, the reactions proceeded to quantitative conversions, as judged by ^{1}H NMR and/or TLC analysis of the crude reaction mixture. In general, EWG-substituted substrates **1b**, **1f**, and **1i** gave better yields when the reaction was conducted at −10 or 0 °C. Double silylation of **1u** was also readily achieved using 3 equiv of BSA, giving **2u** in 98% yield. Heterocyclic and other aromatic terminal alkynes **1j–m** also gave high yields of TMS-protected alkynes **2j–m**. The reaction also tolerated enynes and propargylic substrates bearing different functionalities and protecting groups (**1n–q**). With **1o**, a gram-scale experiment demonstrated that the process is scalable (91% yield of **2o** at 10 mmol scale vs 97% at 1 mmol scale).

The process also tolerates aliphatic alkynes **1r–t**, but with these, the reaction is more sluggish. With these substrates, reactions typically reached ca. 90% conversion, requiring additional purification. The desired TMS-protected alkynes **2r–t** can nevertheless be obtained in moderate isolated yields (52–70%) after purification.

The current catalytic BSA–TMAP system can also readily protect other hydroxy and amine groups in situ. To demonstrate the applicability of the silylation protocol with a complex substrate, we carried out a reaction with ethynylestradiol **1v** using an excess of BSA (7 equiv). The triply silylated product **2v**, with the TMS-protected phenol, tertiary alcohol, and terminal alkyne, was obtained in 84% yield (based on 90% sample purity). The triple silylation was unambiguously confirmed by scXRD (see the Supporting Information (SI); CCDC 2313380).

In addition, double *N*,*C*-silylation of Boc-propargylamine **1w** could be achieved in 95% yield. Recently, interest in N–H silylation protocols has been growing,[31−34] although *N*-silylated compounds, especially those bearing an *N*-TMS group, are known to be relatively unstable.[35,36] Indeed, spontaneous hydrolysis of the *N*-TMS group of **2w** during storage (4 °C) led to slow crystallization of the *C*-silylated carbamate **2x** (see Scheme 2). The scXRD structure of **2x** also confirmed the position of the *C*-silyl group (Scheme 2).

Limitations of the present catalytic *C*-silylation method include the following examples (see Scheme 3). *N*-Tosyl-protected *N*-methylpropargylamine (**1y**) underwent partial isomerization to provide a poorly separable mixture of allene **5** and the desired TMS-protected alkyne **2y**. Attempts to perform double silylation for primary hydroxy group and terminal alkyne (**1z**, derived from 5-(hydroxymethyl)furfural) gave a mixture of mono- (**5z′**) and bis-silylated (**5z**) products in a 25:75 ratio, respectively, in a total yield of 50%. Finally, we noted that the phthalimide protecting group is not tolerated under the reaction conditions, and only decomposition of starting material **1aa** or **1ab** was observed.

Since control experiments without the TMAP catalyst (Table 1, entry 7) or with the alternative CF_3-substituted silylating agent BSTFA (Table 1, entry 6) resulted in no reaction, the catalytic cycle appears to require both species. We propose a probase mechanism involving an initial silyl transfer from BSA to the pivalate anion of TMAP,[15] leading to formation of anionic species **I** (Scheme 4)[37−40] with subsequent deprotonation of the alkyne (Scheme 4). This mechanism is supported by the inertness of BSTFA, which should give rise to a weaker base. Furthermore, this mechanistic scenario also corroborated by the Hammett plot with different aryl-conjugated alkynes (**2a**, **2c–g**), which resulted in a ρ value of +1.4 ± 0.1 (see the SI). This value

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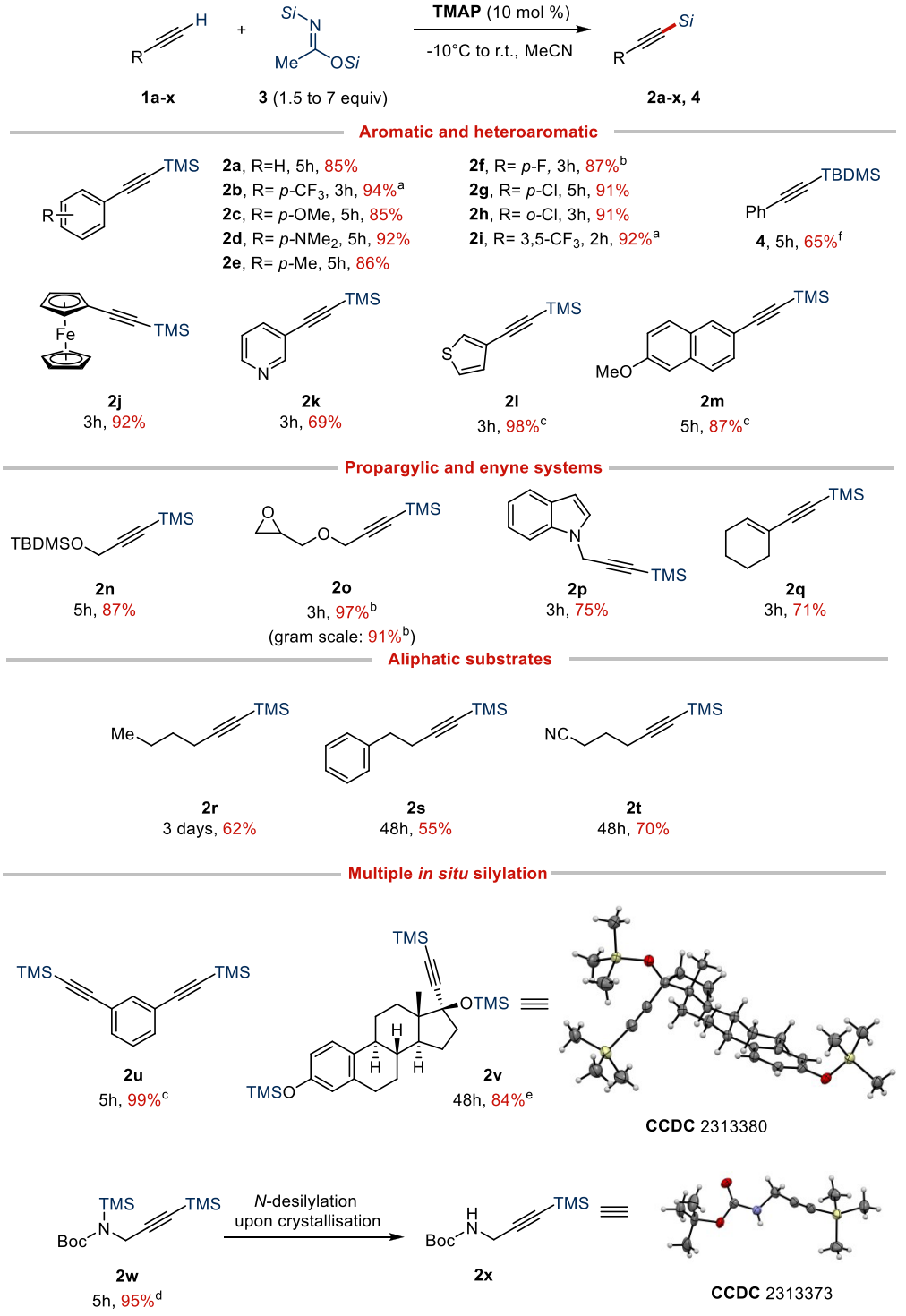
Scheme 2. Scope of the Carboxylate-Catalyzed Silylation of Alkynes[a]



[a]Reactions were carried out at r.t. with 1.5 equiv of BSA, unless otherwise noted: (a) run at −10 °C; (b) run at 0 °C; (c) 3 equiv of BSA was used; (d) 5 equiv of BSA was used; (e) 7 equiv of BSA and MeCN/THF (1:1 v/v) were used; (f) 1.5 equiv of BTBSA was used. See the Supporting Information for details.

is consistent with the formation of carbanionic-like species in the turnover-determining deprotonation step and agrees with our initial mechanistic blueprint for the reaction.[41−43,20] In the proposed catalytic cycle, the alkyne anion−Me_4N^+ ion pair **II** (Scheme 4)[10−12] is silylated by BSA, generating the probase and completing the cycle. In the kinetic experiments with phenylacetylenes, 1 mol % TMAP catalyst was sufficient to give reasonable rates in ^{1}H NMR studies (see the SI), but in preparative experiments, we found that using 10 mol % TMAP was a safer option to cover a broad range of substrates.

In conclusion, we report a new carboxylate-catalyzed, metal-free protocol for the silylation of terminal alkynes. A bench-stable, inexpensive catalyst (TMAP) and commercially available noncorrosive silylating agent (BSA or BTBSA) can

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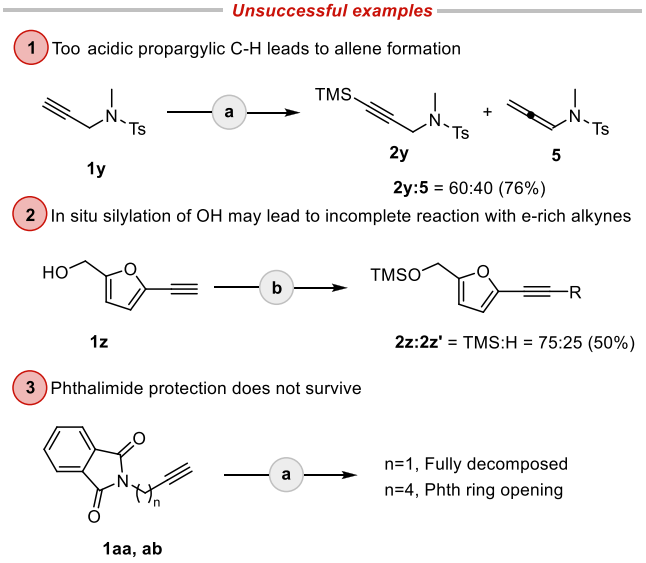
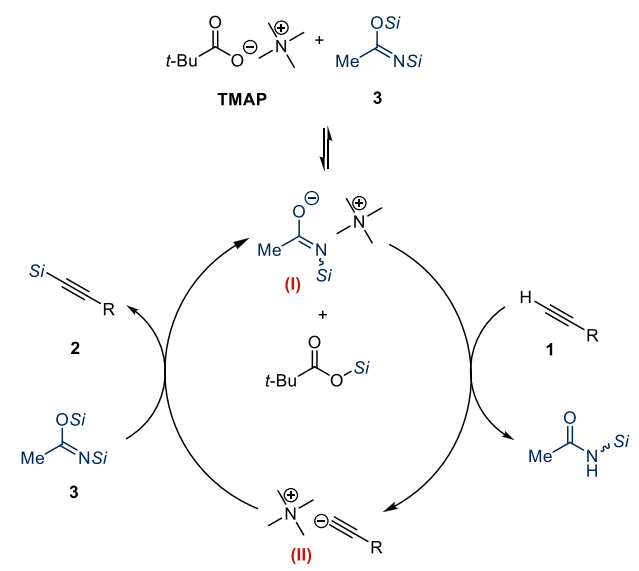
Scheme 3. Unsuccessful Examples[a]



[a]Reaction conditions: (a) TMAP (10 mol %), BSA (1.5 equiv), MeCN, 0 °C to r.t.; (b) TMAP (10 mol %), BSA (5 equiv), MeCN, 0 °C to r.t. Product ratios were determined by ^{1}H NMR analysis.

Scheme 4. Plausible Reaction Mechanism



be employed. The protocol tolerates a range of substrates, and unprotected OH and NH groups are typically silylated as well under the reaction conditions.[44]

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c04213.

Experimental procedures, details of kinetics experiments, and crystallographic data (PDF)

Copies of NMR spectra (PDF)

FAIR data, including the primary NMR FID files, for compounds **2a**−**2x** and **4** (ZIP)

Accession Codes

CCDC 2313373 and 2313380 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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