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Copper-Catalyzed C(sp)−C(sp^3) Coupling of Terminal Alkynes with Alkylsilyl Peroxides via a Radical Mechanism

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Supporting Information

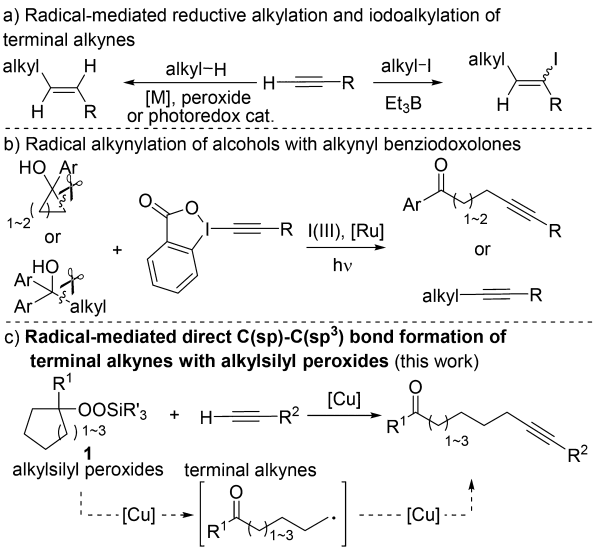
ABSTRACT: A copper-catalyzed C(sp)−C(sp^3) coupling reaction between terminal alkynes and alkylsilyl peroxides is reported. In the presence of a copper catalyst and 4-dimethylaminopyridine, the reaction smoothly affords a variety of internal alkynes by coupling alkylsilyl peroxides and terminal alkynes. Mechanistic studies suggest that the reaction proceeds via a radical mechanism, whereby the alkyl radicals are generated from the alkylsilyl peroxides. The present transformation represents a rare example of a radical-mediated C(sp)−C(sp^3) coupling reaction of terminal alkynes.

Alkynes are structurally important in natural products, biologically active molecules, and functional materials, and they also represent versatile synthetic intermediates.[1] Therefore, considerable research efforts have been devoted in recent decades to the development of novel synthetic methods to generate substituted alkynes.[2] The Sonogashira coupling of terminal alkynes and aryl/vinyl halides or triflates is one of the most reliable ways for the formation of C(sp)−C(sp^2) bonds for the synthesis of internal alkynes.[3] On the other hand, the Sonogashira coupling of terminal alkynes with alkyl halides, i.e., the formation of C(sp)−C(sp^3) bonds, still remains a challenging topic in current organic synthesis.[4] Thus, the development of alternative approaches to the formation of C(sp)−C(sp^3) bonds involving terminal alkynes is a very promising research target.

Recently, radical alkynylations using electrophilic alkyne reagents such as alkynyl sulfones or alkynyl benziodoxolones have emerged as a particularly useful approach for the formation of C(sp)−C(sp^3) bonds.[5−7] Given the recent focus on atom-economic and sustainable chemistry, the direct use of terminal alkynes for the synthesis of internal alkynes should be preferable from a practical perspective. However, examples for the direct C(sp)−C(sp^3) coupling between terminal alkynes and alkyl radicals to obtain internal alkynes remain elusive, as the reaction between terminal alkynes and alkyl radicals usually leads to the difunctionalization or reductive alkylation of alkynes, resulting in the formation of internal alkenes (Scheme 1a).[8−10] Therefore, the development of novel radical strategies for the direct formation of C(sp)−C(sp^3) bonds for the synthesis of internal alkynes from terminal alkynes is highly desirable.

The β-fragmentation reaction of alkoxy radicals has been recently recognized as a useful strategy for the generation of alkyl radicals and successfully been applied in a variety of radical reactions.[11] In 2016, Chen and co-workers reported the visible-light-induced radical alkynylation of strained cycloalkanols (i.e., cyclobutanol and cyclopropanol) and linear alcohols with alkynyl benziodoxolones via β-fragmentation of alkoxy radicals (Scheme 1b).[6h] While this approach allows the synthesis of versatile internal alkynes under mild reaction conditions, the reaction still requires alkynyl benziodoxolone reagents. In this context, we report herein the copper-catalyzed direct C(sp)−C(sp^3) coupling reaction of terminal alkynes with alkylsilyl peroxides via a radical mechanism (Scheme 1c). This approach enables the generation of alkyl radicals by β-fragmentation of less strained cyclic and linear alkoxy radicals, thus resulting in the formation of a variety of internal alkynes.

Scheme 1. Reactions of Alkynes and Their Derivatives with Alkyl Radicals



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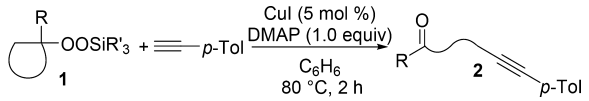
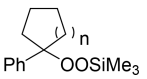
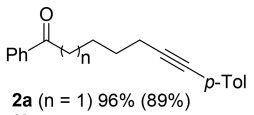
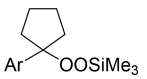
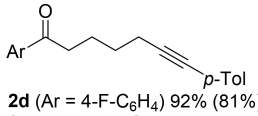
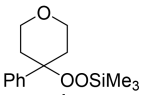
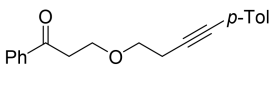
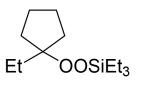
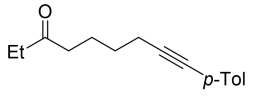
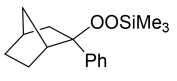
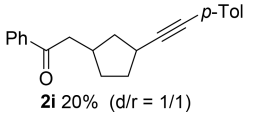
As part of our efforts on the development of radical-mediated reactions, we have recently reported a novel approach to the generation of alkyl radicals using alkylsilyl peroxides (**1**), i.e., the copper-catalyzed selective mono-*N*-alkylation of primary amides and arylamines.[12] These peroxides are readily prepared by the reactions of corresponding alcohols with hydrogen peroxide in the presence of sulfonic acid, followed by the protection with trialkylsilyl groups. They also easily generate a variety of alkyl radicals via β-fragmentation of alkoxy radicals under mild conditions depending on their structure. To demonstrate the further utility of **1**, we became interested in the development of a direct C(sp)−C(sp^3) coupling reaction between terminal alkynes and alkylsilyl peroxides.

Initially, we examined the reaction between 1-ethynyl-4-methylbenzene and cyclic alkylsilyl peroxide **1a** as an alkyl radical source, which afforded δ-alkynyl ketone **2a** (for optimization details, see Supporting Information). After extensive screening of conditions, we finally discovered that the reaction of the alkyne with **1a** (1.4 equiv) in the presence of CuI (5 mol %) and 4-dimetylaminopyridine (DMAP) (1.0 equiv) at 80 °C furnished **2a** in excellent yield (Table 1, entry 1). With the optimized conditions in hand, we subsequently examined the scope of this reaction with respect to the alkylsilyl peroxides (**1**). The use of six- (**1b**) and seven-membered cyclic peroxides (**1c**) furnished the corresponding products (**2b** and **2c**) in moderate to good yields (entries 2 and 3). Different substituents on the aryl moiety of the peroxides (**1d**−**f**) were well tolerated, affording the respective products (**2d**−**f**) in high yield (entries 4−6). The reaction with **1g**, which bears an ether moiety, afforded **2g** in moderate yield (entry 7). When ethyl-substituted cyclopentyl peroxide **1h** was used, the ring opening of the cyclopentyl moiety occurred selectively to furnish δ-alkynyl ketone **2h** in good yield (entry 8). In the case of bicyclic peroxide **1i**, which is a norcamphor derivative, **2i** was obtained as a diastereomeric mixture via the selective cleavage of the C(1)−C(2) bond of the norbornane moiety (entry 9). Acyclic alkylsilyl peroxides **3a** and **3b** were also applicable to introduce cyclohexyl or tetrahydropyranyl moieties, affording **4a** and **4b** in good yield (Scheme 2).

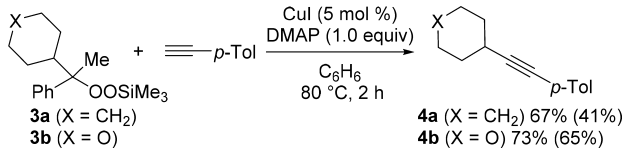
Table 1. Alkynylation Reaction Using Cyclic Alkylsilyl Peroxides 1 with 1-Ethynyl-4-methylbenzene[a,b]



entry	1	2
		
1	**1a** (n = 1)	**2a** (n = 1) 96% (89%)
2	**1b** (n = 2)	**2b** (n = 2) 39%
3	**1c** (n = 3)	**2c** (n = 3) 68% (59%)
		
4	**1d** (Ar = 4-F-C_6H_4)	**2d** (Ar = 4-F-C_6H_4) 92% (81%)
5	**1e** (Ar = 4-Me-C_6H_4)	**2e** (Ar = 4-Me-C_6H_4) 99% (92%)
6	**1f** (Ar = 4-CF_3-C_6H_4)	**2f** (Ar = 4-CF_3-C_6H_4) 81% (72%)
7	 **1g**	 **2g** 42% (37%)
8[c]	 **1h**	 **2h** 70% (59%)
9	 **1i**	 **2i** 20% (d/r = 1/1)

[a]Unless otherwise specified, reactions were carried out in the presence of **1** (1.4 equiv), alkyne (0.2 mmol), CuI (5 mol %), and DMAP (1.0 equiv) in benzene (0.2 M) at 80 °C under an atmosphere of argon. [b]The yield was determined by ^{1}H NMR spectroscopy using CH_3NO_2 as an internal standard; the isolated yield is given in parentheses. [c]Temp = 50 °C.

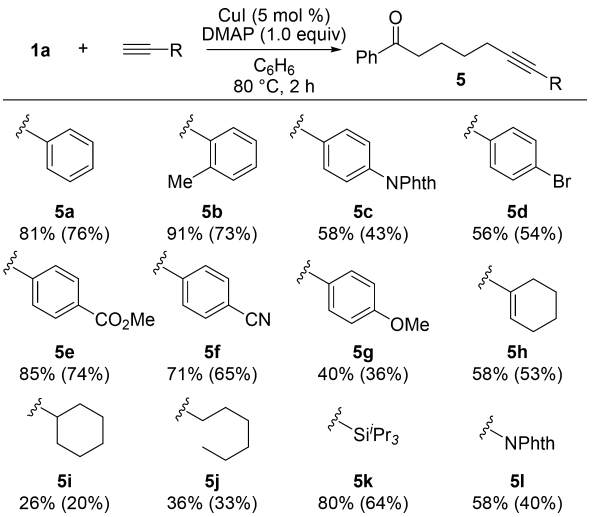
Scheme 2. Alkynylation Using Acyclic Alkylsilyl Peroxides 3[a]



[a]The yield was determined by ^{1}H NMR spectroscopy using CH_3NO_2 as an internal standard; the isolated yield is given in parentheses.

Subsequently, the suitability of different alkynes for this transformation was examined (Scheme 3). The reaction of phenylacetylene with **1a** proceeded smoothly to afford **5a** in high yield. A methyl substituent at the *ortho* position of the aryl moiety did not affect the reaction, and **5b** was obtained in excellent yield. A variety of aryl groups containing electron-withdrawing or -donating substituents successfully furnished the corresponding products (**5c**−**g**) in moderate to good yields. The use of an alkenyl-substituted alkyne also afforded the corresponding product (**5h**) in 53% yield. In the case of alkyl-substituted alkynes, the desired products (**5i** and **5j**) were obtained in low yield. The reactions using silyl or phthalimide (Phth) substituents on the alkyne provided the corresponding alkynes (**5k** and **5l**) in moderate yield.

Scheme 3. Scope of Alkynes[a]



[a]The yield was determined by ^{1}H NMR spectroscopy using CH_3NO_2 as an internal standard; the isolated yield is given in parentheses.

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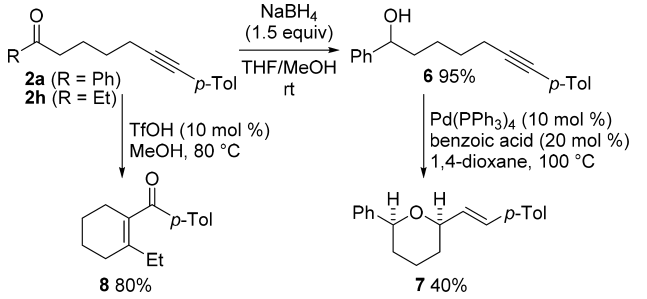
The synthetic utility of the δ-alkynyl ketones thus obtained is illustrated in Scheme 4. δ-Alkynyl ketone **2a** (R = Ph) was

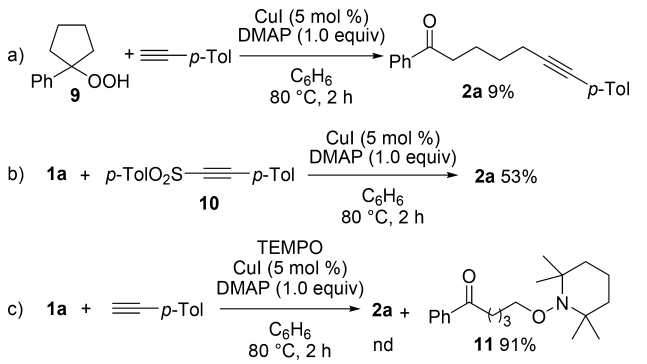
Scheme 4. Subsequent Transformations of Products



converted into the corresponding alcohol (**6**) by treatment with sodium borohydrate, followed by palladium-catalyzed intramolecular cyclization to give a 2,6-disubstituted tetrahydropyran (**7**).[14] Additionally, **2h** (R = Et) was readily converted into α−β-unsaturated ketone **8** in 80% yield upon carrying out an acid-catalyzed intramolecular cyclization.[15]

In order to better understand the underlying reaction mechanism, a series of control experiments were carried out. Initially, in order to rule out the potential involvement of alkyl hydroperoxides formed from the alkylsilyl peroxides as a possible source of alkyl radicals, the same reaction was carried out using 1-ethynyl-4-methylbenzene and hydroperoxide **9** instead of **1a**.[16] The reaction with hydroperoxide **9** provided a complex mixture, including a small amount of **2a** (Scheme 5a). This result revealed

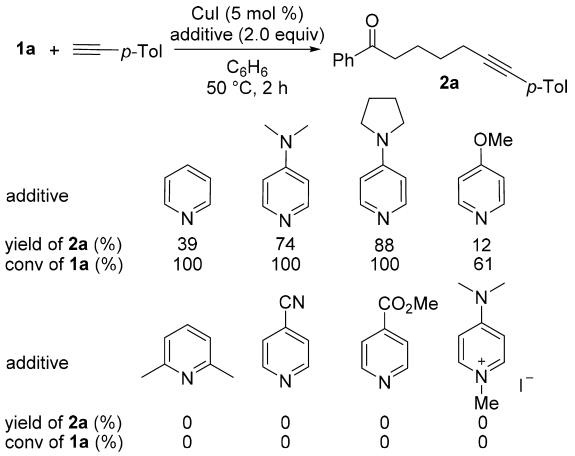
Scheme 5. Control Experiments



the importance of the silyl group for the efficient cleavage of the O−O bond to generate the alkoxy radicals. Next, we carried out radical-trapping experiments. A reaction using alkynyl sulfone **10** instead of a terminal alkyne as the alkyl radical acceptor provided **2a** in 53% yield (Scheme 5b).[5,17] The addition of the radical scavenger 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) radical under standard conditions inhibited the reaction, thus affording radical adduct **11** (Scheme 5c). These results suggest that the reaction probably involves a free-radical mechanism involving alkyl radicals.

Upon screening several pyridines, we tentatively concluded that DMAP should work as a base as well as a ligand for the copper catalyst, promoting the degradation of the peroxides (Scheme 6).[18] While pyridine and electron-rich pyridines such as DMAP, 4-(pyrrolidin-1-yl)pyridine, or 4-methoxypyridine facilitated the decomposition of the peroxide and thus the formation of **2a**, the addition of bulky or electron-deficient pyridines such as

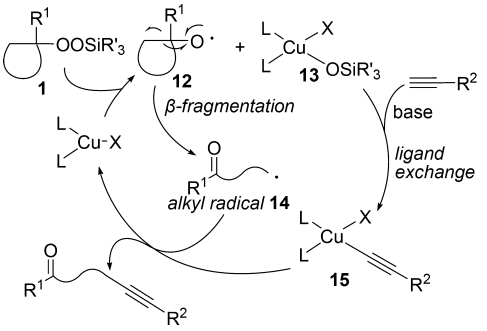
Scheme 6. Effect of Different Pyridines on the Copper-Catalyzed C(sp)−C(sp^3) Coupling between Terminal Alkynes and Alkylsilyl Peroxides



2,6-lutidine, 4-cyanopyridine, or methyl isonicotinate was not effective. The use of an *N*-methyl DMAP salt was also not successful. These observations suggest that electronic and steric effects of the pyridine nitrogen atom significantly affect the decomposition of the peroxide.

Scheme 7 shows our proposed catalytic cycle for the C(sp)−C(sp^3) coupling of terminal alkynes and alkylsilyl peroxides.

Scheme 7. Plausible Reaction Mechanism



Alkylsilyl peroxides **1** should decompose in the presence of nitrogen-coordinated copper species, which would lead to the generation of alkoxy radicals (**12**) and copper−silanoxide complexes (**13**).[19] A subsequent β-fragmentation of **12** would generate the corresponding alkyl radicals **14**. After a ligand exchange on the copper center between an alkyne and a silanoxide, the coupling of the alkyl radicals and copper−alkynyl complexes (**15**) could finally afford the desired products.

In conclusion, a copper-catalyzed C(sp)−C(sp^3) coupling reaction between terminal alkynes and alkylsilyl peroxides has been developed. We discovered that the use of 4-dimethylaminopyridine (DMAP) is critical for the efficient formation of a C−C bond between the terminal alkynes and alkyl radicals. The reaction provides access to versatile internal alkynes by coupling terminal alkynes and alkylsilyl peroxides, and it offers a synthetic approach to internal alkynes that complements Sonogashira-type reactions. Further investigation into the applications of such alkylsilyl peroxides and the details of the reaction mechanism is currently in progress in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00173.

Experimental procedures and characterization data for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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