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Alkylation of Nonacidic C(sp^3)−H Bonds by Photoinduced Catalytic Michael-Type Radical Addition

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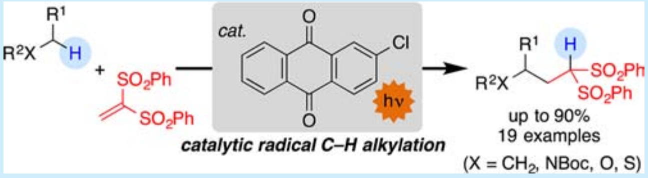
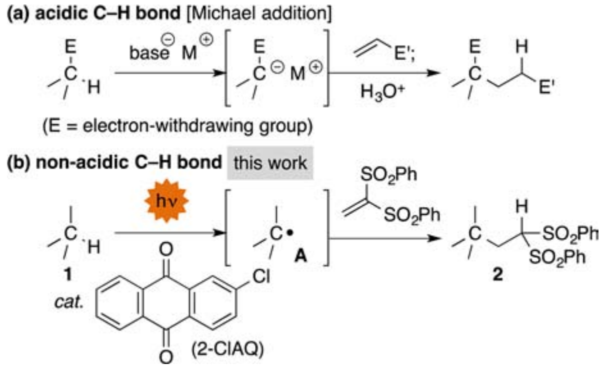
Supporting Information

ABSTRACT: Photoinduced catalytic Michael-type radical addition was achieved via olefin insertion into a nonacidic C(sp^3)−H bond, utilizing 2-chloroanthraquinone as a C−H bond-cleaving catalyst and 1,1-bis(phenylsulfonyl)ethylene as an olefinic substrate. The present radical protocol allows carbon chain extension stemming from nonacidic C−H bonds, which complements alkylation at acidic C−H bonds under ionic conditions and installs the active methine site that acts as a versatile synthetic handle for further transformations.



Alkylation of a carbon center adjacent to an electron-withdrawing group via ionic activation, by taking advantage of the acidic nature of the α-proton, is one of the standard strategies for carbon chain extension to increase the structural complexity of organic substances.[1] The Michael reaction is a typical example of such a transformation, in which the reaction proceeds through a sequence of nucleophile activation by deprotonation with a base, conjugate addition of the derived carbanion to an electron-deficient olefin, and protonation to furnish the alkylated product (Scheme 1a).[2] This is an established protocol for alkylation through formal insertion of an olefin into a C−H bond, although the applicability of the Michael reaction is principally limited to compounds possessing acidic α-protons (acidic C−H bonds).[3] In contrast, no general protocol is available for alkylation stemming from nonacidic C−H bonds (Scheme 1b).[4] Such C−H bonds are ubiquitous in carbon frameworks of organic compounds; however, they remain intact under ionic conditions due to their extremely low acidic nature. Accordingly, nonacidic C−H bonds are conventionally considered as unreactive components, and selective functionalization of these bonds is not an easy task, even with the latest synthetic technologies.

Scheme 1. Carbon Chain Extension by Olefin Insertion into C(sp^3)−H Bonds



We have been developing methods to realize direct functionalization of nonacidic C(sp^3)−H bonds.[5,6] During the course of our studies, we disclosed that the generation of carbon radical **A** is feasible by the homolysis of C−H bonds with the employment of photoexcited aryl ketones. We thus expected that the combination of homolytic C−H bond cleavage and radical addition to an electron-deficient olefin should provide a Michael-type addition for nonacidic C−H bonds of representative substances such as alkanes, ethers, carbamates, and sulfides.[7−9] Here, we report a catalytic radical alkylation via olefin insertion into nonacidic C(sp^3)−H bonds utilizing 2-chloroanthraquinone (2-ClAQ) as a catalyst and 1,1-bis(phenylsulfonyl)ethylene as an olefin under photoirradiation conditions (Scheme 1b). The present radical protocol achieves carbon chain extension stemming from nonacidic C−H bonds, which complements alkylation at acidic C−H bonds under ionic conditions and installs the active methine site that acts as a versatile handle for further transformations.

Optimization of the reaction conditions was conducted using cyclooctane **1a** as a starting substance (Table 1). Among the aryl ketones examined, 2-ClAQ[10−12] afforded a higher yield of the expected adduct **2a** (54%, entry 1) than did benzophenone (40%, entry 2) or 4-benzoylpyridine[5h,i,13] (42%, entry 3). It is important to note that the present transformation could be promoted merely by a catalytic amount of 2-ClAQ (0.1 equiv). An LED lamp of monochromic light at 365 nm was essential as the light source, whereas use of a Hg lamp was detrimental to the product yield (entry 1 vs entry 4).[14,15] The employment of a stoichiometric amount of 2-ClAQ improved the yield of **2a** to 78%; however, the low solubility of 2-ClAQ in a wide range of

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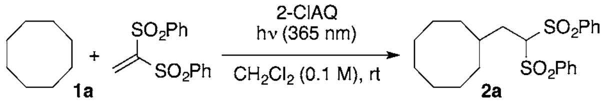
Table 1. Optimization of Reaction Conditions



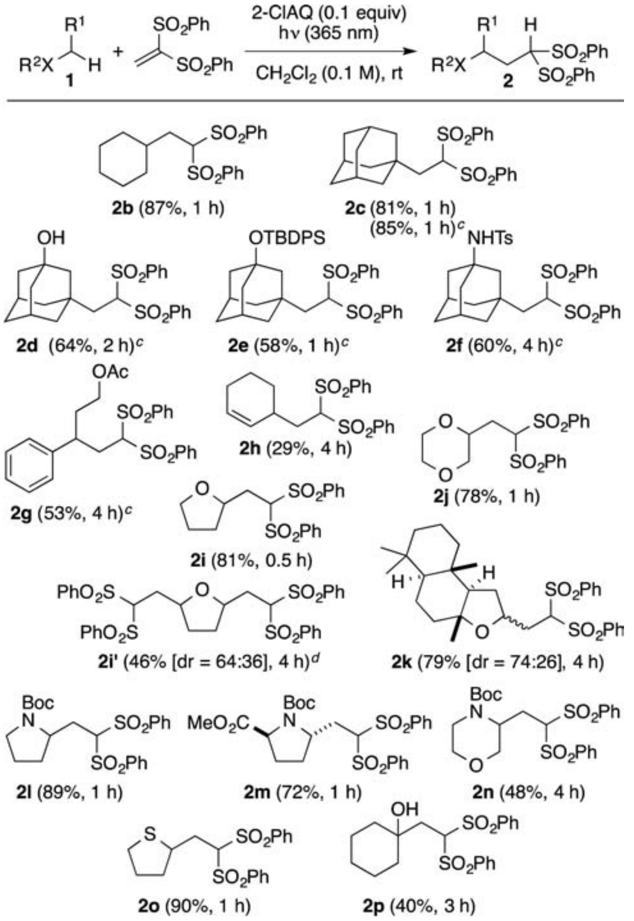
entry	2-ClAQ	1a (equiv)	time (h)	yield (%)[b]
1	0.1	5	1	54[c]
2	0.1[d]	5	1	40
3	0.1[e]	5	1	42
4[f]	0.1	5	1	7[g]
5[h]	1	5	1	78[c]
6[h]	1	2	1	71
7[h]	1	1.2	2	48

[a] Conditions: cyclooctane **1a** (1 mmol, 5 equiv), olefin (0.2 mmol, 1 equiv), 2-ClAQ (0.02 mmol, 0.1 equiv), CH$_2$Cl$_2$ (2 mL, 0.1 M), photoirradiation under an Ar atmosphere using an LED lamp (365 nm) at rt unless otherwise noted. [b] Yield determined by NMR analysis. [c] Yield of isolated product. [d] Benzophenone was employed instead of 2-ClAQ. [e] 4-Benzoylpyridine was employed instead of 2-ClAQ. [f] A Hg lamp was used instead of an LED lamp. [g] Recovery of the olefin was observed in ca. 47% yield. [h] The reaction was conducted using 1 equiv of 2-ClAQ in 0.04 M solution.

organic solvents caused problems during product isolation (entry 5). Reduction of the cyclooctane loading resulted in a decrease in the product yield (entries 6 and 7). Considering the observations above, we conducted the reaction between starting substance (5 equiv) and olefin (1 equiv) in the presence of a catalytic amount of 2-ClAQ (0.1 equiv) under photoirradiation using an LED lamp (365 nm) as the standard set of conditions in subsequent experiments.[16]

With the standard reaction conditions in hand, we investigated the generality of the photoinduced catalytic radical alkylation of nonacidic C(sp^3)−H bonds found in a variety of carbon frameworks (Scheme 2). The reaction of cyclohexane **1b** furnished a high yield of the alkylated product **2b**. Alkylation of adamantane **1c** proceeded selectively at the methine carbon to give **2c** in 81% yield under the standard conditions (**1c**/olefin = 5:1). This reaction proceeded with the same efficiency using **1c** as the limiting reagent (**1c**/olefin = 1:1.2). Prevention of further C−H alkylation by forming a quaternary carbon center and the high reactivity of the methine C−H bond of adamantane might be the reasons for the success. Functionalized adamantanes **1d**−**f** were all suitable substances, providing the respective adducts **2d**−**f** in around 60% yields. These results showed that the present transformation is compatible with not only silyloxy groups but also protic hydroxy and amide groups. The alkylation also took place at benzylic (**1g**) and allylic positions (**1h**). The yield of allylic alkylation was only 29%, yet it is worth mentioning that the alkylation product can be prepared in a single step from commercially available cyclohexene **1h**. We then explored the reactivity of C(sp^3)−H bonds substituted with heteroatoms. Alkylation of THF **1i**, 1,4-dioxane **1j**, and ambroxide **1k** proceeded chemoselectively at the ethereal C−H bonds, furnishing the respective monoalkylated products **2i**−**k** in around 80% yields. Stepwise alkylation of the THF adduct **2i** took place regioselectively at the ethereal methylene carbon to furnish the dialkylated product **2i′** in 46% yield. For nitrogen-containing heterocycles **1l**−**n**, chemoselective alkylation occurred at the C−H bond proximal to the nitrogen atom. In the case of proline derivative **1m**, the more electron-rich methylene was regioselectively alkylated and *trans*-adduct **2m** was stereoselectively formed. From the morpholine product **2n**, the C−H bond of the nitrogen side was found to be more reactive than that on the oxygen side. Alkylation of cyclic sulfide **1o** took place at the methylene adjacent to the sulfur atom, and adduct **2o** was formed in high yield. The reaction of cyclohexanol **1p** gave rise to the tertiary alcohol **2p** with formation of a tetrasubstituted carbon center.

Scheme 2. Photoinduced Catalytic Alkylation[a]

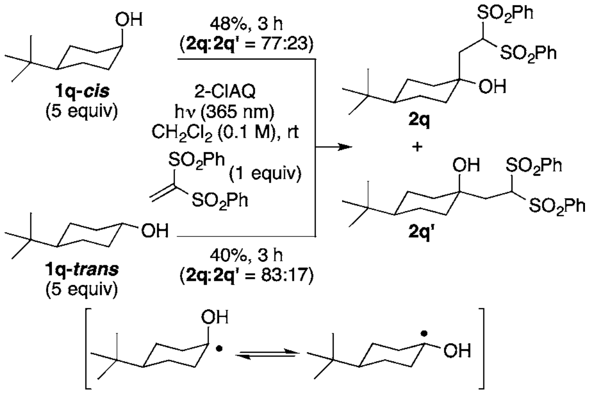


[a] Conditions as described in entry 1 of Table 1, unless otherwise noted. [b] Yield of isolated product. [c] Reaction using **1** (1 equiv) and olefin (1.2 equiv). [d] Reaction using alkylated THF **2i** (1 equiv) and olefin (1.2 equiv).

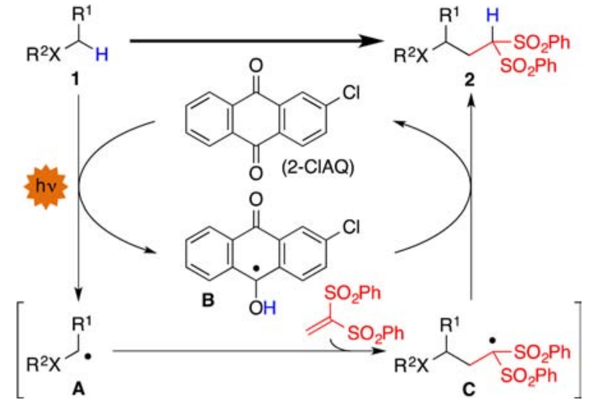
With the success of the alcohol alkylation, we examined the reaction employing *cis*- and *trans*-isomers of 4-*tert*-butylcyclohexanol, **1q**-***cis*** and **1q**-***trans*** (Scheme 3). Both isomers exhibited similar reactivity and gave the expected adducts **2q** and **2q′** in approximately the same combined yield and diastereoselectivity. These results support an intervention of carbon radical intermediates during the reaction course.

A proposed reaction mechanism for the present alkylation of nonacidic C(sp^3)−H is illustrated in Scheme 4. The reaction starts with hydrogen abstraction of the starting substance **1** by photoexcited 2-ClAQ, forming the carbon radical **A** and semianthraquinone radical **B**.[17] This hydrogen abstraction step is suggested to be the rate-determining step based on the observed kinetic isotope effect (KIE).[18] The stereochemical interconversion of *cis*- and *trans*-substituted cyclohexanol derivatives, **1q**-***cis*** and **1q**-***trans***, as described in Scheme 3, supports the intervention of the carbon radical species **A**. The conjugate addition of the derived radical **A** to 1,1-bis-

Scheme 3. Alkylation of 4-(*tert*-Butyl)cyclohexanols



Scheme 4. Proposed Reaction Mechanism for Photoinduced Catalytic Alkylation via Olefin Insertion into Nonacidic $C(sp^3)-H$ Bonds

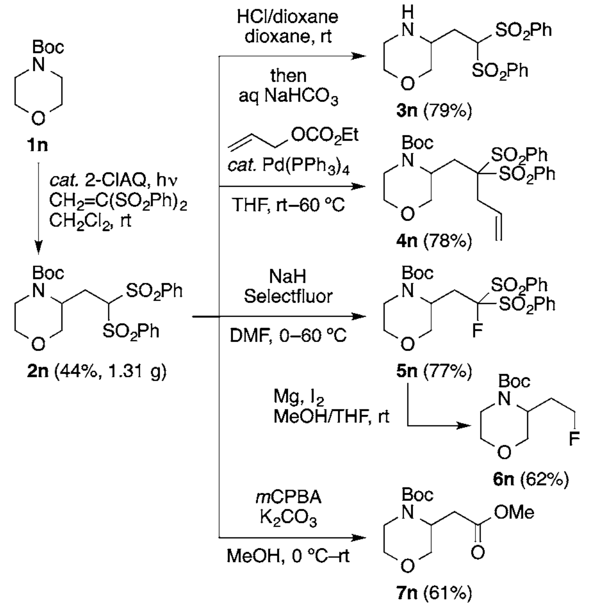


(phenylsulfonyl)ethylene, a highly electron-deficient olefin, takes place smoothly to provide radical **C**. The hydrogen should be delivered from the semianthraquinone radical **B** to **C** to regenerate 2-ClAQ.[19]

To probe the robustness and reliability of the present method, we conducted a gram-scale reaction of *N*-Boc-morpholine **1n** (Scheme 5). Alkylated product **2n** was obtained in 44% yield (1.31 g), essentially the same yield as observed in Scheme 2. The installed alkyl chain can be an excellent handle for further transformations. Indeed, we demonstrated several reactions to highlight the synthetic utility of derived compound **2n**. Deprotection of the Boc group was achieved with acid treatment (**3n**).[20] The palladium-catalyzed allylation (**4n**)[21] and fluorination under basic conditions (**5n**)[22] completed modifications at the active methine moiety. Removal of the sulfonyl group readily occurred under reductive conditions (**6n**).[22b,23] Oxidation with *m*CPBA in MeOH converted the active methine moiety to the ester functional group (**7n**).[24]

In conclusion, we have developed a catalytic radical alkylation of nonacidic $C(sp^3)-H$ bonds via Michael-type addition, utilizing 2-ClAQ as a catalyst and 1,1-bis(phenylsulfonyl)ethylene as an olefin under photoirradiation conditions. This radical C−H alkylation method complements conventional Michael addition for carbon chain extension at acidic $C(sp^3)-H$ bonds under ionic conditions. In addition, the present transformation is inherently atom-economical because alkylated products are formed via olefin insertion into C−H bonds. The newly developed protocol is applicable to a wide variety of nonacidic C−H bonds of alkanes, ethers, carbamates, sulfides, and alcohols as well as those at benzylic and allylic positions. The installed two-carbon unit, the bis(phenylsulfonyl)ethylene chain, is a versatile synthetic handle. The active methine site can be easily allylated, fluorinated, and converted to an ester, and the phenylsulfonyl group can be readily removed under reductive conditions. Accordingly, the radical alkylation method developed in this study should serve as a unique tool for carbon chain extension stemming from nonacidic C−H bonds.

Scheme 5. Gram-Scale Preparation of Alkylated Morpholine Derivative 2n and Its Derivatizations



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02391.

Additional experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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(14) The reaction did not proceed at all without addition of 2-ClAQ, and the starting olefin was recovered quantitatively.

(15) We confirmed that the photoirradiation was essential for the alkylation to proceed, as it ceased when the light source was turned off. See the Supporting Information for details.

(16) The reaction of cyclooctane and vinyl phenyl sulfone under the optimized conditions gave only a low yield of the alkylated product, probably due to the high tendency of olefin polymerization.

(17) We cannot exclude the possibility of the photoexcitation of the other carbonyl group. For the chemistry on semiquinone radicals, see: (a) Bruce, J. M. *Q. Rev., Chem. Soc.* **1967**, *21*, 405. (b) Alberti, A.; Hudson, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, *2*, 1098.

(18) We measured the KIE to be 2.8 by treating a mixture of cyclohexane **1b** and its deuterated analogue **1b-*d*** with the olefin under the standard reaction conditions. See the Supporting Information for details.

(19) The computational calculation implied that radical chain reaction is less probable in this transformation. The in situ generated carbon radical **C** probably abstracts hydrogen from the semianthraquinone radical **B** and not from starting substance **1**. Deuteration at the disulfonylated methine position was confirmed in the KIE experiment. See the Supporting Information for details.

(20) For unambiguous structure confirmation, amine **3n** was obtained with base treatment of its HCl salt (**3n**·HCl) formed right after the Boc deprotection. See the Supporting Information for details.

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