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Aryl Ketone Catalyzed Radical Allylation of C(sp^3)−H Bonds under Photoirradiation

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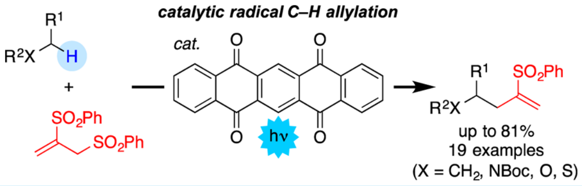
Supporting Information

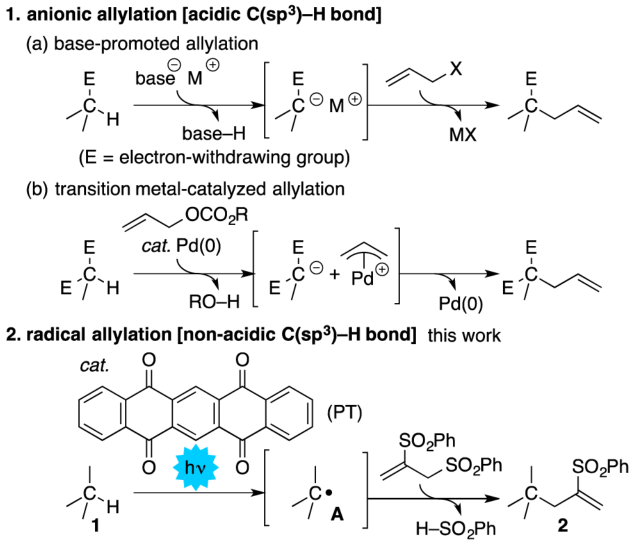
ABSTRACT: The catalytic introduction of an allyl group at nonacidic C(sp^3)−H bonds was achieved under photoirradiation, in which 1,2-bis(phenylsulfonyl)-2-propene acts as an allyl source and 5,7,12,14-pentacenetetrone (PT) works as a C−H bond-cleaving catalyst. A variety of substances, including alkanes, carbamates, ethers, sulfides, and alcohols, were chemoselectively allylated in a single step under neutral conditions. The present transformation is catalyzed solely by an organic molecule, PT, and proceeds smoothly even under visible light irradiation (425 nm) in the case of alkanes as a starting substance.



The allyl group is one of the most important carbon units in organic chemistry because of its synthetic versatility.[1] For instance, the allyl group provides multiple opportunities for further bond-forming transformations since the olefinic moiety can be easily converted to electrophilic functional groups, such as aldehydes and epoxides, by oxidative manipulations. The synthetic utility of the allyl group has been further accentuated by the emergence of metathesis, the formation of a new olefinic product by the recombination of two olefins.[2] For this reason, intensive investigations have been carried out on allylation reactions from a wide array of aspects, such as the development of new allylating agents, stererochemical control of allylation, and catalytic allylation as well as their mechanistic investigations. Among the substitutive introductions of the allyl group at C(sp^3)−H bonds, the majority of methods involve anionic allylation after generation of a carbanion by making use of the acidic nature of C−H bonds adjacent to electron-withdrawing groups (E, Scheme 1-1). LDA and LHMDS are representative bases for deprotonation to generate the carbanion (Scheme 1-1a),[3] and an allyl carbonate−Pd(0) catalyst is a standard combination for allylation of active methine/methylene moieties (Scheme 1-1b).[4] Despite numerous examples for allylation of acidic C(sp^3)−H bonds, the methods for substitutive introduction of an allyl group at nonacidic C(sp^3)−H bonds are still underdeveloped.[5,6]

We therefore investigated allylation of unreactive C(sp^3)−H bonds by applying a photochemical C−H functionalization strategy (Scheme 1-2).[7,8] The keys to realizing such a transformation are to find a suitable aryl ketone as a precursor for an oxyl radical species to cleave the C−H bonds, and the design of an allyl source to trap the in situ generated carbon radical **A**. We herein report the photoinduced catalytic allylation of nonacidic C(sp^3)−H bonds, in which 1,2-bis(phenylsulfonyl)-2-propene acts as the allyl source and 5,7,12,14-pentacenetetrone (PT) works as the C−H bond-cleaving catalyst. The characteristic features of the present transformation are that the reaction is catalyzed solely by the organic molecule, PT, and the allylation of alkanes smoothly proceeds even under irradiation of visible light at 425 nm wavelength.

Scheme 1. Strategies for Substitutive Allylation of C(sp^3)−H Bonds



At the outset of our investigation, we screened aryl ketones that are potentially effective for C−H bond cleavage of cyclooctane with employment of 1,2-bis(phenylsulfonyl)-2-propene as the allyl source[9,10] (Table 1). The reaction was catalyzed by benzophenone (Ph_2CO, 10 mol %), and the allylation product **2a** was obtained in 52% yield (entry 1). This is a rare example of a photoinduced substitutive C−H function-

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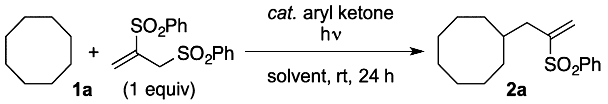
Table 1. Optimization of Reaction Conditions[a]

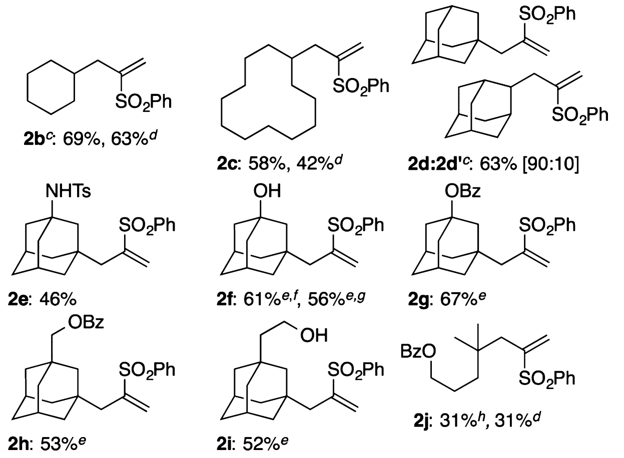


entry	aryl ketone	mol %	hν, nm	solvent	yield, %[b,c]
1	Ph_2CO	10	365	MeCN	52[d]
2	4-BzPy	10	365	MeCN	30[d]
3	2-ClAQ	10	365	MeCN	61
4	PT	10	365	MeCN	58[d]
5	PT	10	425	MeCN	55
6	PT	10	455	MeCN	34[d]
7	PT	10	425	CH_2Cl_2	59
8	PT	5	425	CH_2Cl_2	55
9[e]	PT	5	425	CH_2Cl_2	60
10[e]	PT	5	365	CH_2Cl_2	63
11[e]	PT	1	425	CH_2Cl_2	38

[a] Conditions: cyclooctane **1a** (10 equiv), allyl source (1 equiv), aryl ketone (1−10 mol %), solvent (0.05 M), photoirradiation using an LED lamp at rt for 24 h. [b] Isolated yields unless otherwise noted. [c] Recovery of the allyl source was observed in general. [d] Yield based on ^{1}H NMR analysis of the crude mixture. [e] The reaction was conducted with addition of K_2CO_3 (1.1 equiv).

alization that was efficiently promoted even with a catalytic amount of aryl ketone.[7i,8c,d,g] The use of 4-benzoylpyridine (4-BzPy)[7h,i,11] reduced the product yield (30%, entry 2), and that of quinone-based ketones, 2-chloroanthraquinone (2-ClAQ)[7j] and PT, improved the yield (61% and 58% yield, entries 3 and 4). The application of PT enabled the use of visible light at 425 nm wavelength, and **2a** was formed in practically the same yield as observed by the reaction under 365 nm light irradiation (entry 5).[12] The use of 455 nm light, however, appeared to retard the reaction progress (entry 6). A halogenated solvent, CH_2Cl_2, slightly improved the solubility of PT (entry 7), and its amount could be reduced (5 mol %, entry 8).[13] Further investigations revealed that the addition of K_2CO_3 slightly increased the yield of **2a** (60%, entry 9).[14] The irradiation of 365 nm light again gave almost the same yield of **2a** under the optimized conditions (63%, entry 10), whereas the reaction with 1 mol % PT decreased the product yield (38%, entry 11).

Scheme 2. Allylation of Alkanes[a,b]

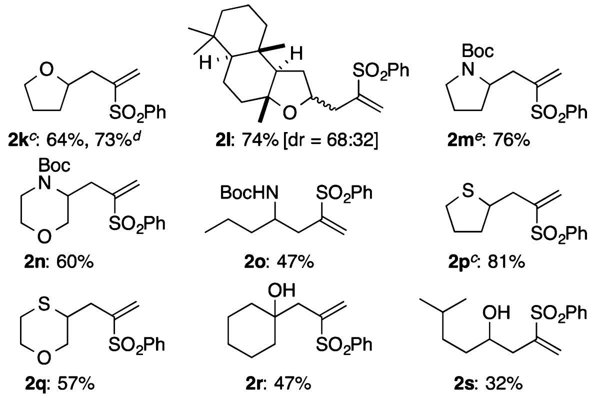


[a] Conditions: alkane **1** (5 equiv), allyl source (1 equiv), PT (5 mol %), K_2CO_3 (1.1 equiv), CH_2Cl_2 (0.05 M), photoirradiation using a 425 nm LED lamp at rt for 24 h unless otherwise noted. [b] Isolated yield. [c] The alkanes **1b** and **1d** (10 equiv) were used. [d] Isolated yield of reaction using a 365 nm LED lamp. [e] Minute amounts of the methylene adducts were observed (<4%). [f] The reaction was conducted without addition of K_2CO_3. [g] The reaction was conducted using **1f** (1 equiv) and the allyl source (1.2 equiv). [h] Yield based on ^{1}H NMR analysis of the crude mixture.

We then explored the applicability of the catalytic allylation of nonacidic C−H bonds by treating various alkanes **1b**−**j** with the allyl source (1 equiv) in the presence of 5 mol % PT and 1.1 equiv of K_2CO_3 under photoirradiation in CH_2Cl_2 (Scheme 2). The reactions of cyclohexane **1b** and cyclododecane **1c** using 425 nm light afforded the corresponding products **2b** and **2c** in 69% and 58% yield, respectively. Irradiation of 365 nm light promoted the allylation as well for these cycloalkanes (63% and 42% yield, respectively). The reaction of adamantane **1d** predominantly provided the 1-allyladamantane **2d** along with a minute amount of 2-allyladamantane **2d′**.[15] This result clarified that the reactivity of the methine C−H bond is higher than that of the methylene one. The reaction of functionalized adamantanes **1e** and **1f**, with tosylamide and hydroxy groups, proceeded selectively at the methine carbon to furnish the respective adducts **2e** and **2f**. It is noteworthy that allylation at the amide and hydroxy functional groups was not detected at all under the present conditions. The benzoylated adamantanol **1g** and the adamantanemethanol derivative **1h** furnished the expected allylation products **2g** and **2h**. The allylation of adamantaneethanol **1i** took place at the adamantane core as well. The acyclic compound **1j** was chemoselectively allylated at the methine C−H bond to furnish the product **2j** in 31% yield. Although the yield of **2j** remained moderate, an alternative method for one-step conversion of **1j** to **2j** is not readily available at the moment.

We next examined the catalytic allylation of heteroatom-containing substances **1k**−**s** (Scheme 3). The reaction of tetrahydrofuran (THF) **1k** revealed that the allyl group was chemoselectively introduced to the C-center adjacent to the O-atom to form the product **2k** in 64% yield with 365 nm light and 73% yield with 425 nm light. The allylation of ambroxide **1l** proceeded with the same chemoselectivity without touching potentially reactive methine C−H bonds. In the case of allylation

Scheme 3. Allylation of Heteroatom-Containing Substances[a,b]

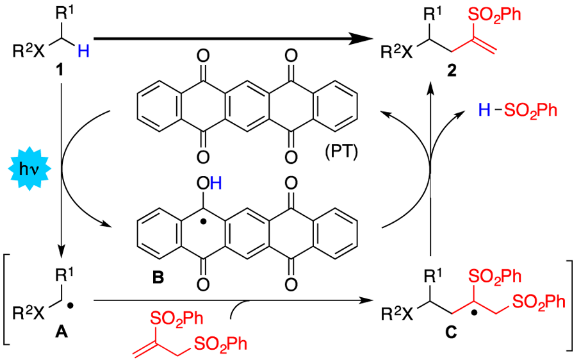


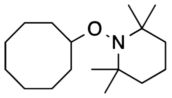
[a] Conditions: starting substance **1** (5 equiv), allyl source (1 equiv), PT (5 mol %), K_2CO_3 (1.1 equiv), CH_2Cl_2 (0.05 M), photoirradiation using a 365 nm LED lamp at rt for 24 h unless otherwise noted. [b] Isolated yield. [c] The heterocycle **1k** or **1p** (10 equiv) was used. [d] Irradiated using a 425 nm LED lamp. [e] The reaction using a 425 nm LED lamp gave <26% yield based on ^{1}H NMR analysis of the crude mixture.

of *N*-Boc pyrrolidine **1m**, the irradiation of 365 nm light (76%) was more effective than that of 425 nm light (<26% yield determined by NMR analysis). The allylation of the morpholine derivative **1n** clarified that the C−H bond proximal to the *N*-Boc group has higher reactivity than that next to the O-atom (**2n**). The acyclic starting material **1o** derived from butylamine furnished the expected adduct **2o** as well. The cyclic sulfides, such as tetrahydrothiophene **1p** and thioxane **1q**, were allylated at the C−H bond adjacent to the S-atom to produce the corresponding adducts **2p** (81%) and **2q** (57%). The allylation of cyclohexanol **1r** took place at the hydroxylated C-center to give the tertiary homoallyl alcohol **2r**. The construction of a tetrasubstituted C-center via selective allylation at the most sterically congested methine C−H bond is of note. The allyl group was similarly introduced to the primary alcohol **1s** to provide the secondary alcohol **2s**. This result illustrates that the reacting C−H bond can be controlled by the proper choice of alcohol protecting group (see Scheme 2, **1j** → **2j**).

Having succeeded in the photoinduced catalytic substitutive introduction of an allyl group to a variety of substances, we turned our attention to obtaining mechanistic information on the present transformation. We conducted the allylation of cyclooctane **1a** in the presence of TEMPO (see Supporting Information for details). The analysis of the crude mixture revealed the formation of the TEMPO adduct **3a** along with a trace amount of the allylated product **2a** and recovery of the allyl source. This result strongly indicated the generation of carbon radical **A** during the course of the reaction (Schemes 1 and 4).

Scheme 4. Proposed Mechanism for the Photoinduced Catalytic Radical Allylation of Nonacidic C(sp^3)−H Bonds





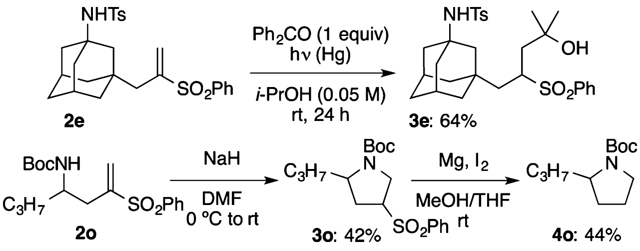
3a

We then measured the kinetic isotope effect by treating a mixture of cyclohexane **1b** and its deuterated analogue **1b-*d*** with the allyl source under the standard conditions (see Supporting Information for details). The value of the kinetic isotope effect (KIE) was determined to be 3.6, indicating that C(sp^3)−H bond cleavage is involved in the rate-determining step.

Taking all this information into account, we propose a reaction mechanism as illustrated in Scheme 4. The photoexcited aryl ketone, PT, having biradical reactivity, abstracts a hydrogen from the starting substance **1** to generate the carbon radical intermediate **A** and the semiquinone-type radical **B**.[16,17] The generation of the carbon radical **A** was strongly supported by the TEMPO trap (**3a**), and this step was suggested to be the rate-determining step based on the KIE experiment. The derived radical **A** then adds to the electron-deficient vinyl sulfone moiety of the allyl source to furnish the radical **C**.[7e,j] Subsequent elimination of the sulfonyl radical furnishes the allylated product **2**, and the released sulfonyl radical most probably accepts the hydrogen from **B** to regenerate PT,[18] completing the catalytic cycle for the present substitutive allylation of nonacidic C−H bonds.

To highlight the superiority of the present one-step allylation of nonacidic C(sp^3)−H bonds for rapid assembly of several molecules and for construction of a cyclic molecular framework, we performed the following two transformations (Scheme 5).

Scheme 5. Transformations of Allylated Products



The first one is the reaction of the allylated adduct **2e** with isopropyl alcohol by the photoinduced Michael-type radical addition (**3e**).[7e,j,8h,19] Thus, two different molecules could be successfully linked with 1,2-bis(phenylsulfonyl)-2-propene as a tethering precursor utilizing the two different types of photoinduced C−H functionalization reactions. The second one is the preparation of azacycles **3o** and **4o**[20] from acyclic homoallylamine **2o**. The pyrrolidine core could be constructed in merely two steps from *N*-Boc butylamide **1o** as a starting substance.

In conclusion, we have developed the photoinduced catalytic allylation of nonacidic C(sp^3)−H bonds of a variety of substances, including alkanes, carbamates, ethers, sulfides, and alcohols, in a chemoselective manner. The reaction is proposed to proceed through a radical mechanism, in which the homolytic cleavage of nonacidic C(sp^3)−H bonds is effected solely by photoexcited 5,7,12,14-pentacenetetrone (PT), and the allyl group is delivered from 1,2-bis(phenylsulfonyl)-2-propene. In this study, we showed for the first time that (1) the organic molecule, PT, acts as an excellent C−H bond cleaving agent; (2) the direct allylation of nonacidic C(sp^3)−H bonds can be efficiently catalyzed by PT; and (3) PT allows the use of visible light (425 nm) for the functionalization of alkanes. The newly developed radical allylation of nonacidic C(sp^3)−H bonds complements conventional methods for anionic introduction of an allyl group at acidic C(sp^3)−H bonds under basic conditions. In addition, the present C−H allylation provides rapid access to structurally complex substances by taking advantage of the electrophilic nature of the installed vinyl sulfone moiety for further transformations. The protocol developed in this study, therefore, should serve as a unique tool for carbon chain extension stemming from nonacidic C(sp^3)−H bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03586.

Additional experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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