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Generation of Cation Radicals from Allylic Sulfides and Their Reactions with Silyl Enol Ethers by the Use of Cerium(IV) Ammonium Nitrate

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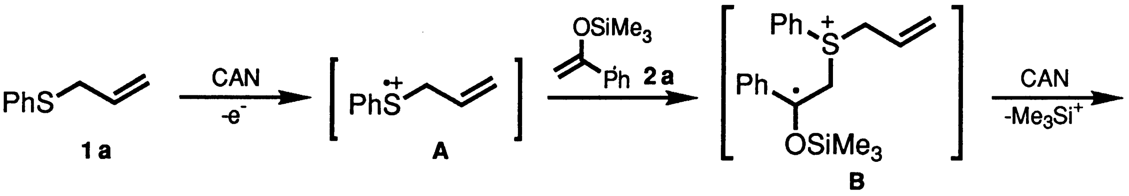
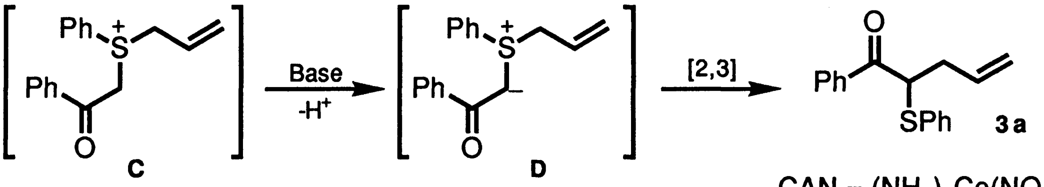
Allyl sulfides react with silyl enol ether, siloxy diene and siloxy enyne by the oxidation with cerium(IV) ammonium nitrate to give α-phenylthio γ,δ-unsaturated ketones through the nucleophilic addition of silyl enol ethers to the sulfur cation radicals and the successive [2,3]-sigmatropic rearrangement.

Characterization and reaction of organosulfur cation radicals have been studied mostly on rather stable heterocyclic cation radicals, that is, those of phenothiazine, thianthrene and phenoxathiin.1) Those sulfur cation radicals react with nucleophiles usually at the sulfur atom;1,2) to our knowledge, the utilization of sulfur cation radicals to construct carbon skeletons has been scarcely performed.3)

Recently, we reported the selective intermolecular addition reactions of the radicals, generated from β-keto carboxylic acids4) and silyl derivatives of *aci*-nitroalkanes,5) with olefinic compounds by the use of Mn(III) 2-pyridinecarboxylate as an oxidant.6) In these reactions, the generated electron-deficient radicals reacted with various electron-rich olefins. As sulfur cation radicals are also electrophilic species, they were expected to react readily with electron-rich olefins. To apply sulfur cation radicals to carbon-carbon bond formation, was examined the reaction between an allylic sulfide **1** and a silyl enol ether **2** by the use of cerium(IV) ammonium nitrate (CAN). The attack of a silyl enol ether to the cation radical **A**, followed by the successive oxidation of the resulting radical intermediate **B**, would form the β-keto sulfonium salt **C**. Then, the sulfonium salt **C** would be converted to the sulfonium ylide **D** by deprotonation with a silyl enol ether and further rearrange to an α-phenylthio γ, δ-unsaturated ketone **3**. Thus, totally 2 molar amounts of CAN and a silyl enol ether to the allylic sulfide would be required to accomplish this reaction.



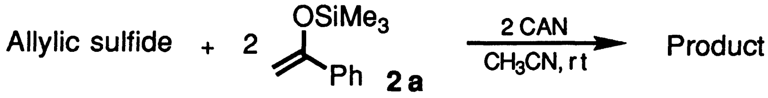


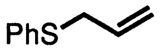
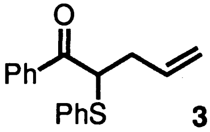
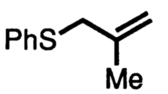
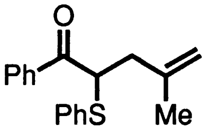
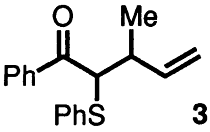
$CAN = (NH_4)_2Ce(NO_3)_6$

In fact, the reaction of allyl phenyl sulfide (**1a**) with 2 molar amounts of α-trimethylsiloxystyrene (**2a**) proceeded immediately by the use of 2 molar amounts of CAN in degassed acetonitrile in the presence of Molecular Sieves 4A at room temperature, affording the expected product **3a** in 75% yield.

Employment of some other one-electron metallic oxidants such as Mn(III), Fe(III), Ag(II), and Cu(II) was not so effective as CAN. And acetonitrile was found to be the suitable solvent, since it has a good solubility of CAN and is not oxidized in the above reaction conditions. Allylic sulfides **1b** and **1c** also reacted smoothly with α-siloxystyrene **2a** and the corresponding α-phenylthio γ,δ-unsaturated ketones **3b** and **3c** were obtained in good yields as shown in the following table.

The typical experimental procedure is as follows: To an acetonitrile (2 ml) suspension of Molecular Sieves 4A (200 mg) and CAN (355 mg, 0.65 mmol) was added an acetonitrile solution (2 ml) of the silyl enol ether **2a** (134 mg, 0.70 mmol) and allyl phenyl sulfide (**1a**, 49 mg, 0.32 mmol) at room temperature and the mixture was stirred for 10 min. By usual work-up and purification by preparative TLC (silica gel), the corresponding product **3a** was isolated (65 mg, 75%).



Allylic sulfide	Product	Yield/%
 **1a**	 **3a**	75
 **1b**	 **3b**	79
 **1c**$^{a)}$	 **3c**$^{b)}$	77

a) A mixture of (*E*)-**1c**, (*Z*)-**1c** and 3-phenylthio-1-butene (76:15: 9) was used.[7]

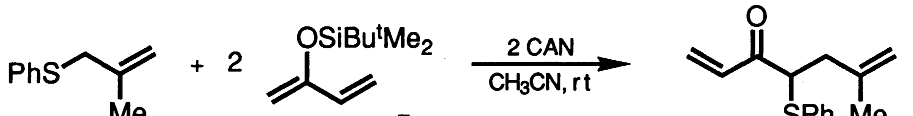
b) The product **3c** was obtained as a diastereo mixture (62:38) and contained a small amount (7%) of 1-phenyl-2-phenylthio-4-hexen-1-one.

Since a stable thianthrene cation radical and its analogue are known to react with ketones to form β-keto sulfonium salts,[2)] preparation of the sulfonium salt **C** was also examined by employing acetophenone instead of α-siloxystyrene. After treatment of a mixture of acetophenone and **1b** with CAN, triethylamine was added to the reaction mixture but the rearranged product **3b** was not obtained at all. Furthermore, **3b** was not produced by treatment of **1b** and acetophenone with CAN in the presence of 1-benzyloxy-1-(*t*-butyldimethylsiloxy)ethene (ketene silyl acetal) as a neutral base.[8)]

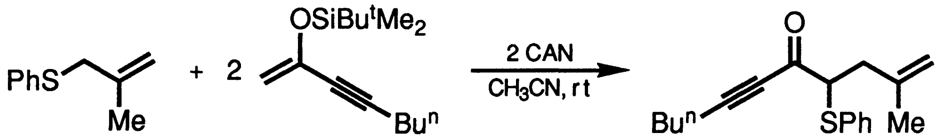
An aliphatic silyl enol ether **2b** also reacted with the allylic sulfide **1b** but the product **4** was obtained in only 19% yield. The lower yield may be due to the poorer reactivity of **2b** to the sulfur cation radical of **1b** because of the less stability of the corresponding radical intermediate like **B**. The competitive nucleophilic attacks by nitrate ion and moisture occurred toward the sulfur cation radical.[9)]

1b **2b** **4** 19%

The siloxy diene **5** and enyne **6**[10)] were, therefore, employed as nucleophiles, expecting that the radical intermediate corresponding to **B** would be stabilized by alkenyl and alkynyl groups. As expected, the reactions proceeded smoothly and the resulting α, β-unsaturated carbonyl compounds **7** and **8** were isolated in good yields.



5 **7** 66%



6 **8** 79%

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