Generation of Cation Radicals from 2-Tributylstannyl-1,3-dithianes and Their Reaction with Olefins

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Oxidation of 2-tributylstannyl-1,3-dithianes with metallic oxidants generates reactive species such as 1,3-dithian-2-yl radical and/or cation by eliminating the stannyl group. Those intermediates react with olefins to give the intermolecular addition products.

Physicochemical properties of organosulfur cation radicals and their reactions have been studied mostly on rather stable heterocyclic derivatives, for instance, phenothiazines, thianthrenes, and phenoxathiins.[1,2] Since these stable sulfur cation radicals react with nucleophiles usually on the sulfur atom, they have found a limited application to construct carbon skeletons.[3]

Recently we reported the reaction of sulfur cation radicals generated from allylic sulfides with silyl enol ethers. In this reaction, silyl enol ethers initially attack on the sulfur and the carbon-carbon bond formation is accomplished by the successive oxidation and [2,3] rearrangement to give α-phenylthio-β,γ-unsaturated ketones.[4] In order to realize a direct formation of carbon-carbon bond using sulfur cation radicals, we investigated to develop a method for transformation of sulfur cation radicals into carbon radicals and/or cations. One of the successful examples of conversion of hetro atom cation radical to carbon radical was found in the aminomethylation reported by Mariano et al.[5] That is, the cation radicals generated from silylmethylamines are converted into aminomethyl radicals by eliminating the silyl cation. Therefore, the generation of a cation radical from an α-silylated sulfide, such as 2-trimethylsilyl-1,3-dithiane, was investigated with the expectation that trimethylsilyl group would eliminate as a cation from the cation radical of the sulfide.[6] A mixture of 2-trimethylsilyl-1,3-dithiane (1) and α-trimethylsiloxystyrene (2) was treated with ammonium cerium(IV) nitrate (CAN) as an oxidant in acetonitrile, and the desired addition product, 3,3-trimethylenedithio-1-phenyl-1-propanone (3), was obtained in 18% yield (Eq. 1).

$$(1)$$
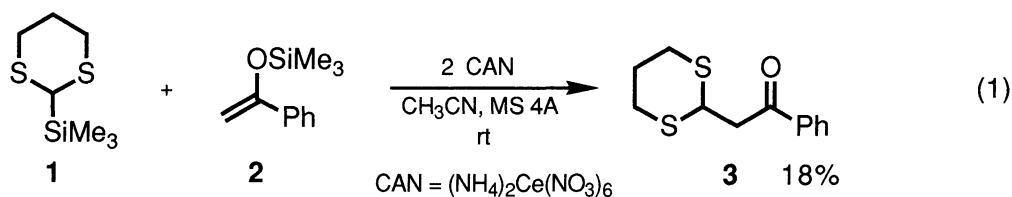
Based on the mechanism of the fragmentation of the silylmethylamine cation radical,[5] the formation of 3 was considered to be as follows: The oxidation of 1 would generate a cation radical 4, which would be converted

into 1,3-dithian-2-yl radical **5** by the elimination of trimethylsilyl cation. Thus, the adduct **3** would be formed via the addition reaction of the radical **5** to the silyl enol ether **2** and the successive oxidation accompanied with the elimination of the silyl group (Scheme 1).
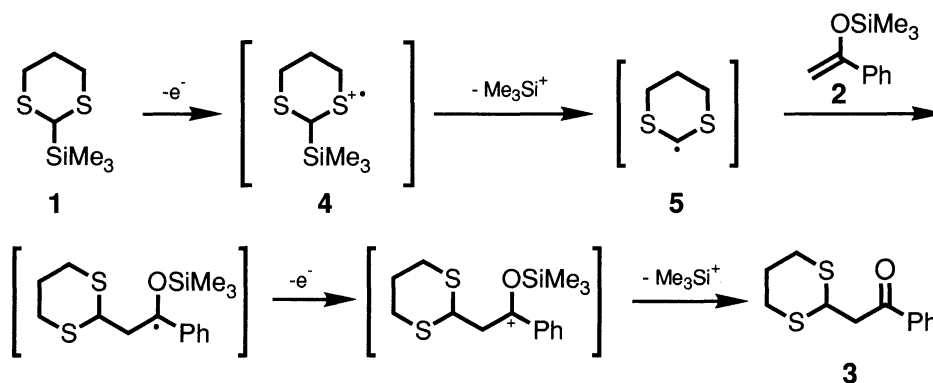
Scheme 1.

The low yield of **3** in the above reaction suggested that the cleavage of the carbon-silicon bond did not proceed smoothly in the cation radical **4** and that the sulfur atom was attacked by nucleophiles such as nitrate anion, a trace amount of water, etc. In search of a suitable substituent that eliminates more easily than trimethylsilyl group, semiempirical molecular orbital calculation of cation radicals of 2-silyl, 2-germyl, and 2-stannyl-1,3-dithianes was performed by PM3 Hamiltonian[7] to compare two-centre energies of their carbon-metal bonds which correspond to bond energies (Table 1).[8]
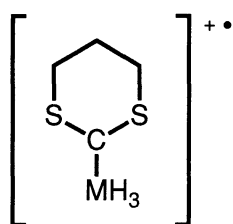

Table 1. MO Calculation of the Cation Radicals

M	Two centre energy (C-M) / eV
Si	-12.5
Ge	-10.8
Sn	-9.3

The calculation shows that the carbon-metal bonds in the cation radicals become weaker from silyl via germyl to stannyl derivatives. Accordingly, 2-tributylstannyl-1,3-dithiane (**6**) was prepared,[9] and reaction of **6** with 2.1 mole equivalents of α-trimethylsiloxystyrene (**2**) was carried out, using 2.1 mole equivalents of CAN[10] in acetonitrile in the presence of Molecular Sieves 4A (MS 4A). Indeed, the product **3** was obtained in good yield (82%). In addition to CAN, ferricenium hexafluorophosphate[11] was employed as an effective oxidant in this reaction (Eq. 2).
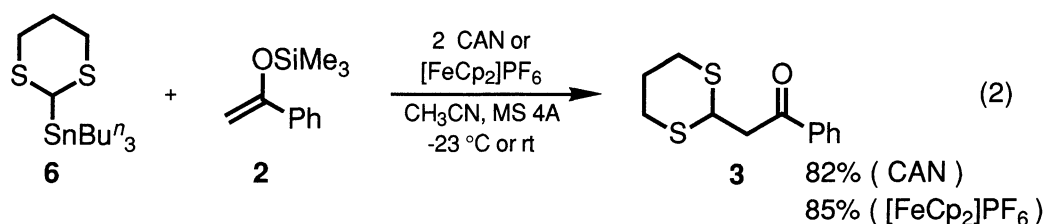
As shown in Table 2, certain 2-stannyl-1,3-dithianes reacted oxidatively with various olefins, giving the corresponding adducts in moderate to good yields. Especially, in the reaction with silyl enol ethers as acceptors, only 2 mole equivalents of them were sufficient to obtain the addition products in good yields. Two possible modes are considered for the cleavage of the carbon-tin bond, that is, the generation of 1,3-dithian-2-yl radical by the elimination of the stannyl cation[5] and/or the generation of 1,3-dithian-2-yl cation with eliminating the stannyl radical. At this stage, however, it is not obvious which intermediate is really generated in the reaction.
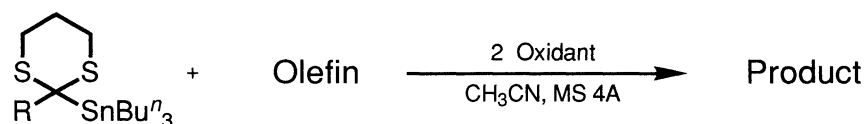

Table 2. The Reaction of 2-Tributylstannyl-1,3-dithiane Derivatives with Olefins

R	Olefin	Conditions[a]	Product	Yield / %
H	$OSiMe_2Bu^t$ Pr^i	A (B)		87 (61)
H	$OSiMe_2Ph$	A		85
H	$OSiMe_2Bu^t$ OEt	B		54
H	Me [b] Ph	B		56
H	Me—Tol [b) c)]	B		52[d]
H	SnPh$_3$	B		67
Me	$OSiMe_3$ Ph	B		64
Ph	$OSiMe_3$ Ph	B		92

a) Conditions: A: 2.1 mole amounts of CAN and olefins were used at -23 °C. B: 2.1 mole amounts of ferricenium hexafluorophosphate and olefins were used at room temperature. b) 10 mole amounts of olefins were used. c) Tol = p-MeC$_6$H$_4$. d) The ratio of (di-substituted olefin) : (tri-substituted olefin) was determined to be 1 : 2 by ^{1}H NMR.

Furthermore, this method was successfully applied to the reaction of phenyl α-tributylstannylbenzyl sulfide (7). Treatment of a mixture of 7 and a silyl enol ether 8 with CAN or ferricenium hexafluorophosphate gave the corresponding addition product 9 in good yields (Eq. 3).
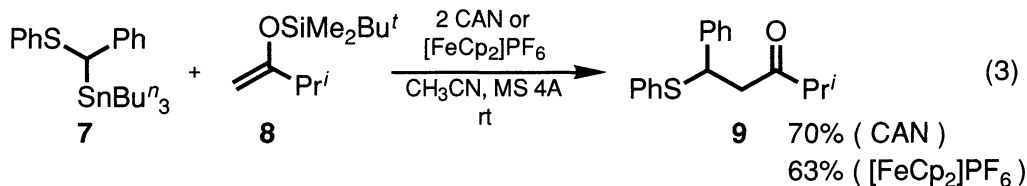
The typical experimental procedure is as follows: To an acetonitrile (2.0 ml) suspension of MS 4A (0.20 g)[12] and CAN (0.27 g, 0.49 mmol) was added an acetonitrile solution (2.0 ml) of the silyl enol ether 2 (0.10 g, 0.52 mmol) and 2-tributylstannyl-1,3-dithiane (4) (95 mg, 0.23 mmol) at -23 °C and the mixture was stirred for 40 min under an argon atmosphere. The reaction was quenched with a saturated aqueous sodium hydrogen carbonate, and the mixture was extracted with dichloromethane. The extract was dried over sodium sulfate. After purification by preparative TLC (silica gel), the corresponding product 6 was isolated (45 mg, 82%).

References

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11) Ferricenium hexafluorophosphate was prepared following the procedure of a literature: D. N. Hendrickson, Y. S. Sohn, and H. B. Gray, Inorg. Chem., 10, 1559 (1971).

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