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Author(s)
Ikeno, Taketo; Harada, Manabu; Arai, Noriyoshi; Narasaka, Koichi

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Generation of α-Alkylthio Radicals by Photoinduced One-Electron Oxidation of α-Stannyl Sulfides and Their Use for Carbon-Carbon Bond Formation

Taketo Ikeno, Manabu Harada, Noryoshi Arai, and Koichi Narasaka*
Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113

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Cation radicals, generated from α-stannyl sulfides by the photoinduced single electron transfer, cleave into α-alkylthio radical intermediates with the elimination of the stannyl group. The α-alkylthio radicals thus formed are utilized for carbon-carbon bond forming reactions.

 Though sulfides are easily oxidized to give their cation radicals, these cation radicals have found a limited application to carbon-carbon bond formation due to the localization of cation radical center on the sulfur atom.1 Recently, we have studied on the one-electron oxidation of α-stannyl and α-silyl sulfides with metallic oxidants and it was revealed that cation radicals of α-stannyl sulfides more readily cleave into their carboxications and stannyl radical as compared with the silyl derivatives.2 For example, the oxidation of 2-stannyl-1,3-dithiane 1a with ammonium hexanitratocerate(IV) (CAN) in the presence of electron-rich olefins such as α-siloxystyreren 2 gave the coupling product 3 in 82% yield, while the reaction of the corresponding silyl derivative 1b afforded 3 in much lower yield.

Since α-alkylthio carboxications are formed from α-stannyl sulfides by the oxidation with metallic reagents and are utilized for the C-C bond forming reactions, we have examined the photoinduced one-electron oxidation of α-stannyl sulfides to carry out the C-C bond formation without the metallic oxidants.

A methanol solution of (phenylthiomethyl)tributylstannane (4a) and 5 molar amounts of 2-cyclohexen-1-one (5) in a Pyrex tube was irradiated for 3 h by a high pressure mercury lamp through UV cut filter (hv > 300 nm).3 After the purification by thin layer chromatography (silica gel; hexane : ethyl acetate= 4 : 1), 3-(phenylthiomethyl)cyclohexan-1-one (6) and 1-phenylthiomethyl-2-cyclohexen-1-ol (7) were isolated in 53% total yield as a 48 : 5 mixture. (Methylthiomethyl)tributylstannane (4c) and [bis(methylthio)methyl]tributylstannane (4e) also reacted with 5 and gave the coupling products, but the corresponding silyl derivatives 4b, d, and f gave no or little coupling product even after 20 h photoirradiation.

In the reaction of 4a, 1,2-bis(phenylthio)ethane and thioxanil are obtained in 15% and 9% as side products, which were supposed as the coupling and hydrogen-abstracted products of phenylthiomethyl radical. Thus totally about 80% of the α-alkylthio radical was generated in the reaction. To elucidate the mechanism of the reaction, the photoreaction of 4a and 5 was examined in CH3OD and CD3OD. In CH3OD and CD3OD, the coupling product 6a was deuterated in 77% and 81%, respectively. And the deuterated position was the 2-position of 6a. Based on the observation, the reaction is considered to proceed as follows; the cation radical species of 4a is formed by single electron transfer to 5 and then cleaves into phenylthiomethyl radical, which reacts with the radical anion of 5 to give the anion of 6 which is immediately protonated by methanol.

Table 1. Reaction of α-stannyl and α-silyl sulfides with 2-cyclohexen-1-one

<table>
<thead>
<tr>
<th>R1</th>
<th>R2</th>
<th>MR3</th>
<th>Time / h</th>
<th>Yield of 6 / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph</td>
<td>H</td>
<td>SiMe3</td>
<td>3</td>
<td>48</td>
</tr>
<tr>
<td>Ph</td>
<td>H</td>
<td>SnBu3</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>SiMe3</td>
<td>20</td>
<td>trace</td>
</tr>
<tr>
<td>Me</td>
<td>MeS</td>
<td>SiMe3</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>

In the reaction of (phenylthiomethyl)tributylstannane (4g) and 4,4-dimethyl-2-cyclohexen-1-one (8), a mixture of the
adducts 9 and 10, were isolated in 60% yield in a 1:1 ratio. The
difference of the product distribution in the addition
reactions of 2-cyclohexen-1-one (5) and 4,4-dimethyl-2-cyclo-
hexen-1-one (8) would be due to the steric reason.

\[
\begin{align*}
\text{PhSCH}_2\text{SnMe}_3 & \overset{hv > 300 \text{ nm}, 1.5 \text{ h}, \text{MeOH}}{\longrightarrow} \\
\text{O} & \quad \text{O} & \quad \text{HO} \\
\text{SPh} & + & \text{SPh} \\
\text{8} & \quad \text{9} & \quad \text{10}
\end{align*}
\]

The present radical formation was then applied to intra-
molecular cyclization reactions. 3-Substituted cyclohexenone
derivative 11 which has a (tributylstannyl)methylthio group in
the side chain was directly irradiated (hv > 300 nm) for 3 h in
methanol. The desired spiro compound 12 was, however,
obtained in low yield (23%) along with a methyl sulfide 13
(60%) and a diene 14 (5%). And 11 was directly irradiated
in acetonitrile with 5 molar amounts of water instead of
methanol, the reaction proceeded much slower and the product
12 was little obtained (5%) after 20 h irradiation. On the
contrary, when 11 was irradiated in the presence of a 0.3 molar
amount of 1,4-naphthalenedicarbonitrile (DCN) as a sensitizer
in acetonitrile, the product 12 was produced in 84% yield
without a detectable amount of 13 and 14. Thus, by employing
the DCN-mediated one-electron oxidation, the intramolecular
coupling reaction proceeds smoothly. In acetonitrile with 5
molar amounts of water, photosensitized reaction of 11 with
DCN also gave 12 in 84% yield. This suggests that a trace
amount of water may be proton donor of the reaction.

\[
\begin{align*}
\text{S} & \quad \text{S} & \quad \text{S} \\
\text{11} & \overset{30 \text{ mol\% DCN}, hv > 300 \text{ nm}}{\longrightarrow} & \text{12} & \quad \text{84\%} \\
\text{13} & \quad \text{14}
\end{align*}
\]

The cyclization of the acyclic enone 15 also did not proceed
by the direct irradiation in acetonitrile-methanol, while the
product 16 was obtained in 61% yield by the photoirradiation
in the presence of the sensitizer, DCN.

\[
\begin{align*}
\text{S} & \quad \text{S} \\
\text{15} & \overset{3 \text{ h}, \text{MeCN - MeOH (3 : 1)}}{\longrightarrow} & \text{16} & \quad \text{61\%}
\end{align*}
\]

Concerning α-stannyl and silyl sulfides, Yoshida and Glass
reported that the Sn-C α-orbital interacts with the sulfur π orbital
more than the Si-C α-orbital does, because of the higher energy
level of Sn-C α-orbital than that of Si-C bond. Accordingly,
the cation radical generated on the sulfur atom of α-stannyl
sulfides is delocalized enough into the Sn-C α-orbital to
accelerate the nucleophilic attack on the stannyl group.
The present photoinduced one-electron oxidation of α-
stannyl sulfides generates α-alkythio radical intermediates,
while the oxidation with metallic oxidants gives α-alkythio
carocations as reported before. Each of the reactive species
thus formed reacts with electron-rich and -deficient olefins,
respectively.

References and Notes
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Co. 400W high pressure mercury lamp and Kenko UV-30
filter.
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10. The difference of the cation radical fragmentation between
metallic oxidation and photoinduced electron transfer
oxidation may ascribe to the reaction intermediate. In case
of metallic oxidation, the generated cation radical is naked in
solvent. On the other hand, the cation radical generated by
photoinduced one-electron oxidation is accompanied with
counter anion radical in solvent cage.
11. The similar selective C-Si bond cleavage has been reported
by Mariano et al. in the single electron transfer photoreaction
of (silylmethyl)amines. The photochemical oxidation of
(silylmethyl)amines generates aminomethyl radicals by the
elimination of the silyl group, while iminium cations are
formed from the cation radicals by the oxidation with
metallic oxidants. X. Zhang, Y. S. Jung, P. S. Mariano, M.
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