Photochemical Generation of Radical Species from α-Stannyl Ethers and Their Reaction with Conjugate Enones

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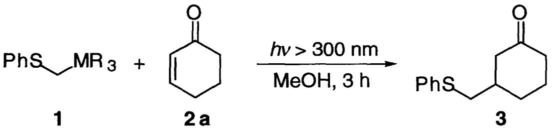
Photochemical reaction of α-stannyl ethers and conjugated enones proceeds in the presence of photosensitizers to give addition products of aryloxymethyl radicals to the enones.

Although application of photoinduced electron transfer reactions to carbon-carbon bond forming reactions has been widely studied,[1] most of them are direct coupling reactions of radical species with electron accepting photosensitizers.[2] Recently, we reported the photo-induced reaction of α-silyl and α-stannyl sulfides with conjugate cyclic enones. The reaction proceeds more efficiently by using the stannyl sulfides as compared with the corresponding silyl compounds.[3] Such a substituent effect is also observed in the formation of radical species from α-stannyl (or silyl) sulfides or amino compounds by the oxidation with metallic compounds and with electrochemical method.[4]

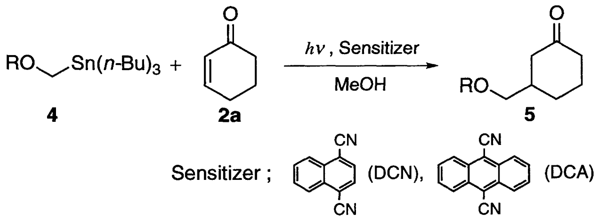


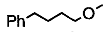
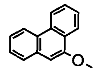
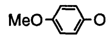
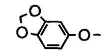
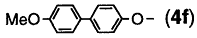
MR 3 = Sn(n-Bu)3 48%
MR 3 = SiMe 3 3%

Since the similar photochemical aryloxymethylation of enones was expected to proceed by employing α-stannyl ethers, we examined the reaction of 2-cyclohexen-1-one (**2a**) and tributyl(phenoxymethyl)stannane (**4a**), which was readily prepared from phenol and tributyl(iodomethyl)stannane.[5] When a methanol solution of **4a** and 5 molar amounts of **2a** was irradiated in the presence of a 0.3 molar amount of 1,4-dicyanonaphthalene (DCN) as a photosensitizer in a Pyrex tube for 20 h with a high pressure mercury lamp through UV cut filter ($h\nu > 320$ nm), 3-(phenoxymethyl)cyclohexan-1-one (**5a**) was obtained in 65% yield. In the absence of the photosensitizer, the reaction didn't proceed and **4a** was recovered.

The use of stannylmethyl ethers having electron-rich aryl group **4d-f** considerably facilitated the aryloxymethylation as compared with the use of the corresponding phenoxy and alkoxy derivatives (**4a,b**), as shown in Table 1. This is mainly due to the efficiency of electron transfer from stannylmethyl ethers to sensitizers. Particularly, the aryloxymethylation product **5e** was obtained in 80% yield with 3,4-methylenedioxyphenoxy derivative **4e**.

Table 1. Reaction of α-stannyl ethers with 2-cyclohexen-1-one



RO-		Sensitizer	Wavelength	Time / h	Yield / %
PhO-	(**4a**)	–	> 320 nm[a]	20	–[c]
	(**4a**)	DCN (30%)	> 320 nm[a]	25	65
	(**4b**)	DCN (10%)	> 320 nm[a]	9	58
	(**4c**)	DCN (10%)	> 340 nm[b]	6	58
	(**4d**)	DCN (30%)	> 320 nm[a]	3	75
	(**4e**)	DCN (10%)	> 320 nm[a]	1	80
	(**4f**)	DCA (30%)	> 340 nm[b]	7	71

[a] Irradiation was carried out using a Riko-Kagaku Sangyo Co. 400 W high pressure mercury lamp and Kenko UV-32 filter.
[b] Irradiation was carried out using a Hamamatsu Photonics Co. 250 W high pressure mercury - xenon lamp and Kenko UV-34 filter in CH_3CN - CH_3OH (2:3) solution.
[c] **4a** was recovered in 93%.

The photochemical reaction of **4e** and various α,β-unsaturated carbonyl compounds was examined in the presence of DCN and the results are summarized in Table 2 (conditions A). In the reaction of cyclopentenone and cyclohexenones (**2b-d**), the aryloxymethylation products were obtained in good yield, whereas cycloheptenone **2f** gave only a small amount of the desired product but mainly a methanol addition product **6** in 63% yield.[6] In the reaction of acyclic enones **2e, g**, the aryloxymethylation products were generated in low yield. The addition reaction of **4e** to maleimide **2i** proceeded smoothly but cyclization occurred successively to yield a cyclized product **8**.

Formation of the methanol adduct of **2f** suggested the generation of strained (*E*)-cycloheptenone by direct irradiation of the enone.[6] Although phenanthrene (PN) was added as a redox cosensitizer to prevent the direct excitation of the enones,[7] no remarkable influence was observed.

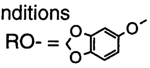
By using 4-(4'-methoxyphenyl)phenyl ether (**4f**), on the whole, the photo-induced aryloxymethylation proceeded more smoothly in the presence of 9,10-dicyanoanthracene (DCA), which was used to prevent the direct excitation of the enones (Table 2 ; conditions B). From the cyclic enones **2b, d, f, h, i**, β-aryloxymethyl ketones **5b, d, f, h, i** were obtained in reasonable yield. Even the aryloxymethylation products of cycloheptenone **2f** and acyclic enones **2e, g** were obtained in moderate yield.

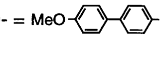
The present photochemical reaction presumably proceeds in the following pathway. The radical ion pair of **4** and DCN is

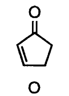
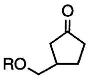
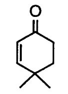
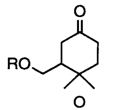
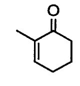
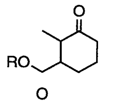
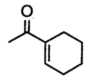
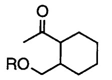
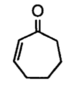
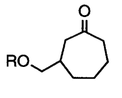
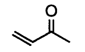
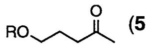
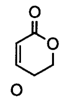
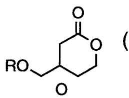
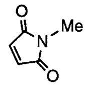
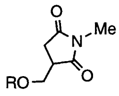
Table 2. Reaction of aryloxymethylstannane (**4**) with enones

$\mathrm{RO\smallsmile Sn}(n\text{-Bu})_3$ + Enone $\xrightarrow{h\nu}$ Product
4 **2** **5**

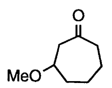
Conditions

A; RO- =  (**4e**), DCN (10%), > 320 nm[a], CH_3OH

B; RO- =  (**4f**), DCA (30%), > 340 nm[b], CH_3CN - CH_3OH (2:3)

Enone		Product		Condition	Time / h	Yield / %
	(**2b**)		(**5b**)	A B	6 7	74 69
	(**2c**)		(**5c**)	A B	7 13	49 21
	(**2d**)		(**5d**)	A B	2 10	81 64
	(**2e**)		(**5e**)	A B	7 10	17 52
	(**2f**)		(**5f**)	A B	7 7	7[c] 55
	(**2g**)		(**5g**)	A B	15 10	22 49[d]
	(**2h**)		(**5h**)	A B	25 11	18[e] 42
	(**2i**)		(**5i**)	A B	4 14	0 (**8**, 67%) 24 (**9**, 18%)

a Irradiation was carried out with a Riko-Kagaku Sangyo Co. 400 W high pressure mercury lamp and Kenko UV-32 filter (Condition A).
b Irradiation was carried out with a Hamamatsu Photonics Co. 250 W high pressure mercury - xenon lamp and Kenko UV-34 filter (Condition B).
c **4e** was recovered in 56% and 3-methoxy-cycloheptanone **6** was obtained in 63% yield.
d The compound **7** was obtained in 19% yield.
e [2+2] cycloadduct of **2h** was observed.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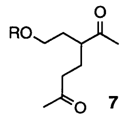
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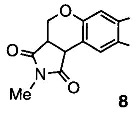
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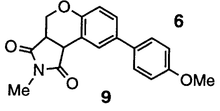
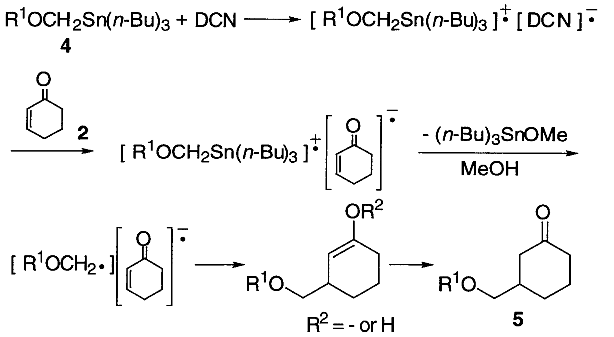
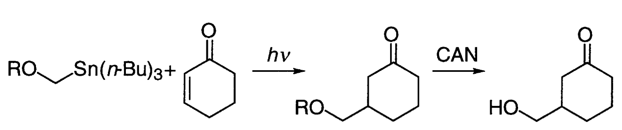

9

formed by photoirradiation. Then, electron transfer occurs between the radical anion of DCN and cyclohexenone, resulting the formation of radical ion pair of $[4]^{+\cdot}$ $[2]^{-\cdot}$.[8] The radical cation $[4]^{+\cdot}$ presumably cleaves into methoxystannane and aryloxymethyl radical, which reacts with $[2]^{-\cdot}$ to give enolate (or enol) of **5**.



The present aryloxymethylation is regarded as hydroxymethylation of enones. In fact, 3-(3,4-methylenedioxyphenoxymethyl)cyclohexan-1-one (**5d**) was converted to 3-(hydroxymethyl)cyclohexanone (**10**) in 88% yield by treatment with cerium(IV) ammonium nitrate (CAN).



4d **2a** **5d** 80% **1 0** 88%

During our study, Steckhan *et al.* have reported the similar aryloxymethylation reaction of electron deficient olefins with α-silyl ethers in the presence of sensitizers.[9] As compared with the silyl compounds, the stannylmethyl ethers are apparently employed more efficiently for aryloxymethylation of enones. The 1,4-addition of alkoxymethyl groups to conjugated enones is usually carried out with organocuprates.[10] The yield of the present photochemical methods is almost the same as those of the organocopper reaction.

References and Notes

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2 P. S. Mariano, "Synthetic Organic Photochemistry," ed by W. M. Horspool, Plenum Press, London (1984).
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4 J. Yoshida, M Itoh, and S. Isoe, *J. Chem. Soc., Chem. Commun.*, **1993**, 547; K. Narasaka and Y. Kohno, *Bull. Chem. Soc. Jpn.*, **66**, 3456 (1993).
5 D. Seyferth and S. B. Andrews, *J. Organomet. Chem.*, **30**, 151 (1971).
6 Noyori and Kato reported the photo-induced polar addition of protic solvents to cycloalkenones via highly strained *trans* isomers.: R. Noyori and M. Kato, *Bull. Chem. Soc. Jpn.*, **47**, 1460 (1974).
7 K. Mizuno, K. Nakanishi, and Y. Otsuji, *Chem. Lett.*, **1988**, 1833, and the references cited therein.
8 One electron transfer is predicted based upon a reduction potential of -1.28 V *vs.* SCE for DCN and that of 2-cyclohexen-1-one, -1.56 V *vs.* SCE. The reduction potentials of sensitizers: H. D. Roth, *Top. Curr. Chem.*, **163**, 131 (1992). The reduction potential of 2-cyclohexene-1-one in polar solvent: E. Brillas and A. Ortiz, *J. Chem. Soc., Faraday Trans. 1*, **82**, 495 (1986), and the references cited therein.
9 G. Gutenberger, E. Steckhan, and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, **37**, 660 (1998).
10 A. D. Borthwick, A. J. Crame, A. M. Exall, and G. G. Weingarten, *Tetrahedron Lett.*, **35**, 7677 (1994); C. R. Johnson and J. R. Medich, *J. Org. Chem.*, **53**, 4131 (1988).