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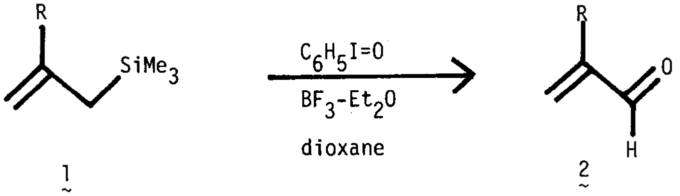
OXIDATION OF 2-SUBSTITUTED ALLYLSILANE TO CONJUGATED ENAL USING HYPERVALENT ORGANOIODINE COMPOUND AND SYNTHESIS OF α-METHYLENE γ- AND δ-LACTONES

Masahito Ochiai and Eiichi Fujita*
Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan
Masao Arimoto and Hideo Yamaguchi
Osaka College of Pharmacy, Matsubara, Osaka-Fu 580, Japan

Summary: 2-Substituted allylsilanes 1 on treatment with iodosobenzene and boron trifluoride etherate in dioxane afforded conjugated enals 2 directly in good yield, from which α-methylene γ- and δ-lactones 7 were synthesized.

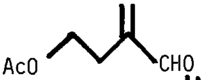
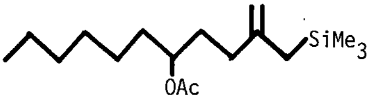
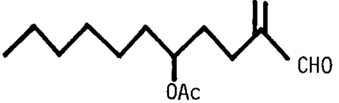
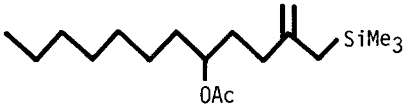
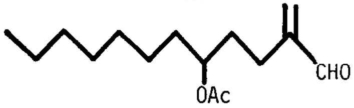
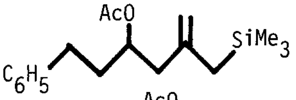
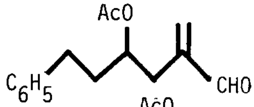
Allylsilanes have been shown to be versatile intermediates in organic synthesis.[1] Their oxidation, however, has been little studied.[2,3] Oxidation of allylsilanes to allyl alcohols with organic peracids does not seem to be a highly applicable reaction.[3] Phenylthio- or phenylselenodesilylation of allylsilanes followed by oxidative rearrangement of the resulting allylsulfides or allylselenides to give allyl alcohols has been shown to be an effective process.[3,4] We wish to report a new useful direct oxidation of 2-substituted allylsilanes 1 to conjugated enals 2 with hypervalent organoiodine compound.



Hypervalent organoiodine compounds have been known as mild oxidizing reagents; oxidation of alcohols, carbonyl compounds, sulfides, and ketenes has been published.[5] Allylsilanes 1 on treatment with iodosobenzene (2 equiv.) activated by the coordination with boron trifluoride etherate (BF_3-Et_2O) (1 equiv.)[6] in dry dioxane afforded conjugated enals 2 in good yield. Representative results are indicated in Table 1.

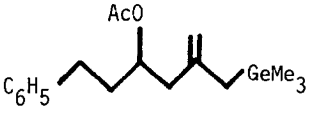
In this reaction, the formation of iodobenzene was usually observed on TLC.[8] The use of

Table 1 Oxidation of Allylsilanes to Conjugated Enals with Iodosobenzene and BF_3-Et_2O[a]

Allylsilane[b]	1	Conjugated Enal	2	Yield, %[c]
	1a		2a	63
	1b		2b	72
	1c		2c	71
	1d		2d	65
	1e		2e	63

a) To a stirred suspension of allylsilane 1 and iodosobenzene (2 equiv.) in dry dioxane (ca. 250 ml/mmol of 1) was added BF_3-Et_2O (1 equiv.) dropwise at room temperature in nitrogen; the mixture was stirred for 12 hr. After adding ice-cooled aqueous $NaHCO_3$ solution, the mixture was extracted with ether. The extract was washed with brine and dried. Evaporation gave after preparative TLC (hexane-ethyl acetate, 5 ∿ 7 : 1) pure conjugated enal 2. b) For preparation of 1a and 1b-1e, see ref. 7 and 6, respectively. c) Isolated yield.

ether as the solvent instead of dioxane afforded a complex mixture of the products. Chemoselectivity of the reaction was observed: the isolated double bond was kept intact (see 1e → 2e). Allylgermane 3 was also oxidized in a same manner, but enal 2d was obtained in only 30% yield.



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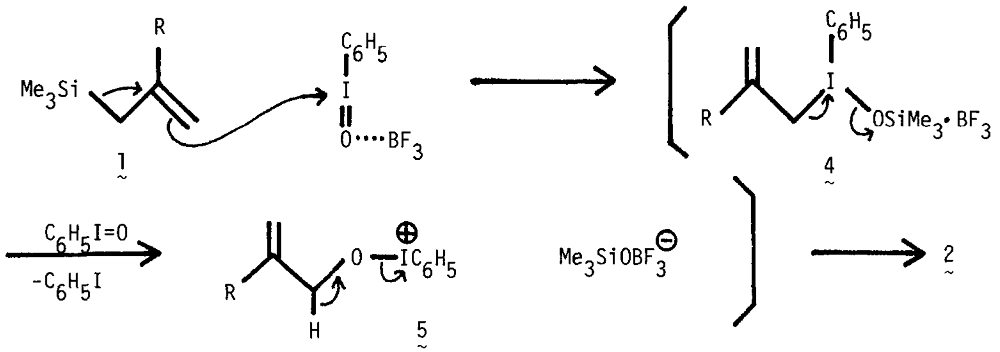
The activation of iodosobenzene by the coordination of BF_3-Et_2O to its oxygen atom seems to be very important, because the oxidation of 1 does not proceed without BF_3-Et_2O. In the reaction more than 2 equiv. of iodosobenzene were required.[9] In view of these observations, the reaction sequence shown in Scheme 1 seems to be plausible.

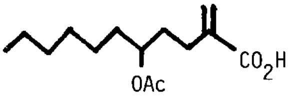
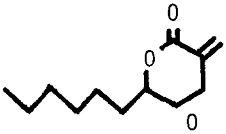
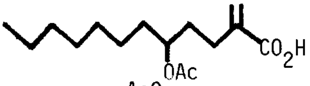
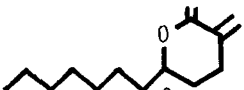
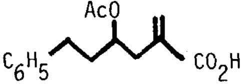
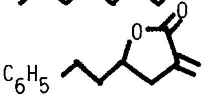
The first step of the reaction may be the formation of the highly reactive species 4[10] as a transient intermediate, which will be attacked by the nucleophilic oxygen of another molecule of iodosobenzene to give 5.[11] Decomposition of 5 produces enal 2.[12]

Conjugated enals 2 were smoothly coverted to α-methylene γ- and δ-lactones 7.[4b] The



Scheme 1

Table 2 Synthesis of α-Methylene γ- and δ-Lactones from Conjugated Enals

Enal	α,β-Unsaturated Acid		Yield, %	γ- and δ-Lactone		Yield, %
2b		6b	83		7b	72
2c		6c	99		7c	70
2d		6d	91		7d	59
2e		6e	89		7e	76

aldehyde 2b on treatment with sodium chlorite in the presence of a chlorine scavenger, 2-methyl-2-butene,[13] gave α,β-unsaturated acid 6b in 83% yield. Alkaline hydrolysis of 6b ($NaOH/H_2O/MeOH$) followed by the treatment with dicyclohexylcarbodiimide in pyridine afforded the desired δ-lactone 7b in 72% yield. The results of the lactone synthesis are summarized in Table 2.

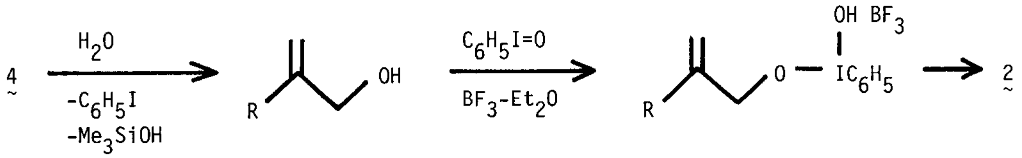
Thus we developed a new convenient method for the oxidation of 2-substituted allylsilanes 1, yielding conjugated enals 2, by using hypervalent organoiodine compound.

References and Notes

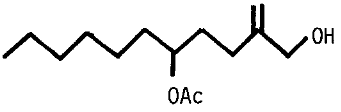
1. (a) H. Sakurai, *Pure Appl. Chem.*, 54, 1 (1982); (b) T. H. Chan and I. Fleming, *Synthesis*, 1979, 761; (c) M. Ochiai and E. Fujita, *J. Synth. Org. Chem., Jpn.*, 40, 508 (1982).
2. J. M. Reuter, A. Sinha, and R. G. Salomon, *J. Org. Chem.*, 43, 2438 (1978).
3. (a) I. Fleming and B.-W. Au-Yeung, *Tetrahedron*, 37, Supplement, No. 9, 13 (1981); (b) M. J. Carter and I. Fleming, *J. Chem. Soc., Chem. Comm.*, 1976, 679; (c) Epoxidations of

allylsilanes are reported to give poorly characterized mixtures of cleavage procudts: P. F. Hudrlik and G. P. Withers, *Tetrahedron Lett.*, **1976**, 29.

4. (a) H. Nishiyama, K. Itagaki, K. Sakuta, and K. Itoh, *Tetrahedron Lett.*, **22**, 5285 (1981); (b) Cf. H. Nishiyama, H. Yokoyama, S. Narimatsu, and K. Itoh, *ibid.*, **23**, 1267 (1982).
5. (a) A. Varvoglis, *Chem. Soc. Rev.*, **10**, 377 (1981); (b) D. F. Banks, *Chem. Rev.*, **66**, 243 (1966); (c) R. B. Sandin, *ibid.*, **32**, 249 (1943): (d) T. Takaya, H. Enyo, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **41**, 1032 (1968).
6. M. Ochiai, E. Fujita, M. Arimoto, and H. Yamaguchi, *J. Chem. Soc., Chem. Comm.*, in press.
7. M. Ochiai, E. Fujita, M. Arimoto, and H. Yamaguchi, *Chem. Pharm. Bull.*, in press.
8. In the oxidation of allylsilane **1a**, iodobenzene was obtained in 72% yield (GLC yield) based on iodosobenzene.
9. Allylsilane **1a** on treatment with 1 equiv. of iodosobenzene gave conjugated enal **2a** in only 33% yield.
10. Umemoto amd co-workers recently reported the useful perfluoroalkylations of carbanions, alkenes, arenes, and thiols with (perfluoroalkyl)phenyliodonium salts: T. Umemoto, Y. Kuriu, S. Nakayama, and O. Miyano, *Tetrahedron Lett.*, **23**, 1471 (1982) and references cited therein.
11. The reaction initiated by the attack of oxygen of iodosobenzene to electron deficient carbon atoms has been reported: (a) J. Wicha, A. Zarecki, and M. Kocor, *Tetrahedron Lett.*, **1973**, 3635; (b) R. M. Moriarty, S. C. Gupta, H. Hu, D. R. Berenschot, and K. B. White, *J. Am. Chem. Soc.*, **103**, 686 (1981).
12. The partial participation of the following alternative reaction sequence cannot be ruled out. Water may be produced by the condensation of trimethylsilanol during the reaction.



In fact allyl alcohol **8** on treatment with iodosobenzene (1 equiv.) and BF_3-Et_2O (1 equiv.) in dioxane at room temperature afforded enal **2b** in 59% yield.



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13. B. S. Bal, W. E. Childers, and H. W. Pinnick, *Tetrahedron*, **37**, 2091 (1981).

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