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NEW SYNTHESIS OF METHYL 2-TRIORGANOSILYL-3-BUTENOATES AS A NEW SYNTHON OF 3-METHOXYCARBONYLALLYL ANION

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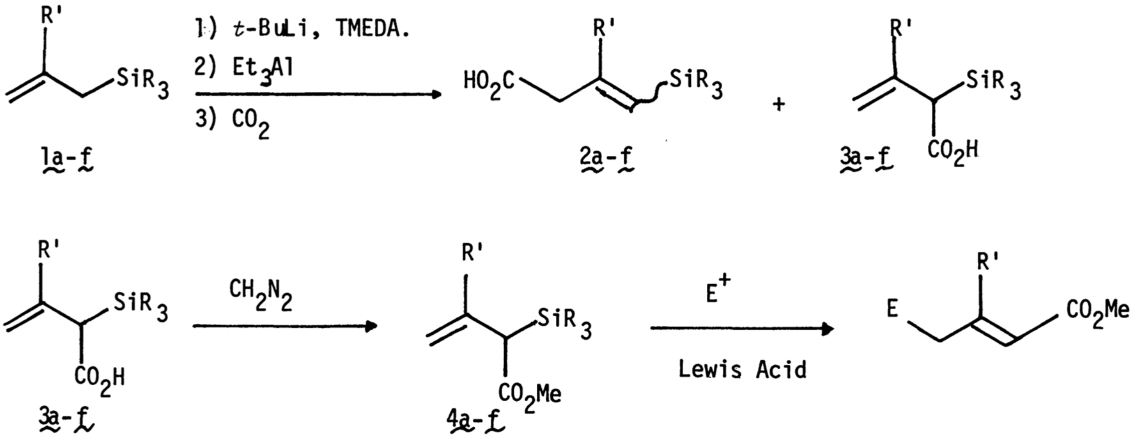
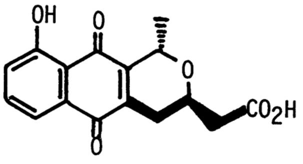
Methyl 2-triorganosilyl-3-butenoates, which are selectively obtained from the carboxylation of the corresponding allylsilanes via allylic aluminates, react with various kinds of electrophiles to give γ substituted (E)-α,β-unsaturated esters in highly regio- and stereoselective manner with the aid of a Lewis acid.

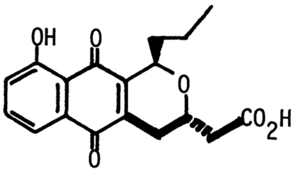
For the synthesis[1] of nanaomycin A and deoxyfrenolicin, we have developed a new synthon of 3-methoxycarbonyl-2-propenyl anion. The requisites for the synthon are (a) high regioselectivity at the γ position and (b) sufficient nucleophilicity toward electrophiles under acidic conditions. Silyldienolate has been reported to be a candidate as such synthon by Fleming[2] and Mukaiyama,[3] and copper dienolate by Katzenellenbogen,[4] while their nucleophilic reactions generally lack regioselectivity because of their electronic character. The high γ selectivity of allylsilane[5] in the reaction could afford a solution to the above problems. Very recently, Katzenellenbogen[6] reported the γ selective substitution of ethyl 3-methyl-2-trimethylsilyl-3-butenoate prepared via nickel-catalyzed coupling reaction of lithium enolate with vinylic bromide. We have independently prepared methyl 2-triorganosilyl-3-butenoates and found it reacted with electrophiles in a regio- and stereoselective manner in the presence of a Lewis acid.[1] In this report, we describe the preparation of methyl 2-triorganosilyl-3-butenoates from allylsilanes and their wide applicabilities in the reaction with various electrophiles.

Scheme I





Nanaomycin A



Deoxyfrenolicin

Table I Carboxylation of Allylic Aluminate

Run	Allylsilane		Product Ratio	Yield (%)^a
	R'	R_3	2/3	
1	1a H	Ph_3	30/70	55
2	b H	Me_3	25/75	35
3	c H	Me_2Ph	~0/~100	85
4	d H	Me_2(*p*-Tol)	~0/~100	50
5	e H	Me_2(*t*-Bu)	~0/~100	20
6	f Me	Me_2Ph	~0/~100	70

a) Isolated yield of 3.

Our efforts were focused on the introduction of a methoxycarbonyl group to the α position of allylsilanes in high regioselectivity. Carboxylation of the allylic anion, which was prepared from allylsilane by Grignard method,[7] lacks both synthetic efficiency and regioselectivity at the α position. So, we overcame the regiochemical difficulty by using allylic aluminate[8] as well as the synthetic defficiency.

The typical reaction was performed as follows. To a solution of allyl carbanion[9] obtained by treating an allylsilane 1 (20mmol) with *t*-BuLi (25mmol) and TMEDA (25mmol) in THF at -30°C was added a hexane solution of Et_3Al at -78°C to afford aluminate, which was quenched by dry CO_2 gas at -78°C. Exclusively α product (3c-f) was obtained in runs 3-6. In runs 1 and 2, a considerable amount of γ product (2a,b) was accompanied (Table I). These α carboxylic acids 3 were purified by column chromatography (silica gel, CH_2Cl_2 as eluent), and were treated with CH_2N_2 to give methyl 2-triorganosilyl-3-butenoates 4.[10]

Lewis acid mediated reaction of 4 with a variety of electrophiles was examined and the results are summarized in Table II. Dimethylphenylsilyl derivative 4c has enough reactivity to attack to various kinds of electrophiles in good yields. In entries 6,7,11,12,13,and 14, chlorination of the initially formed products was observed. Unexpectedly, they reacted with *n*-pentanal to afford the corresponding methyl ether, presumably because of the occurrence of acetalization prior to the nucleophilic reaction.

Let us focus our attention on the stereochemical course of the present reaction. The coupling constants of $J_{H^1-H^2}$ in 4a-e are ca. 10Hz. This fact suggests that the dihedral angle between silicon-carbon bond and olefinic double bond is ca. 90°. This configuration could also afford maximum σ-π conjugation and minimum steric interaction as shown in Scheme II. Nucleophilic attack from the opposite site of the large silyl group in the γ carbon would be favored by the stereo- and electrochemical reasons predominantly to give an (E)-α,β-unsaturated ester.[11]

With respects to the reactivity and the accessibility, dimethylphenylsilyl derivative 4c is useful as a new synthetic equivalent of (E)-3-methoxycarbonyl-2-propenyl anion. Further extention of this chemistry is under progress.

Table II Reaction of Methyl 2-Triorganosilyl-3-butenoates with Electrophiles

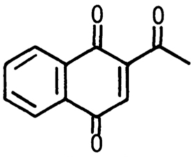
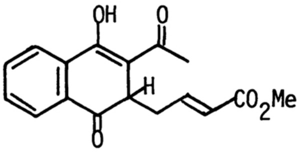
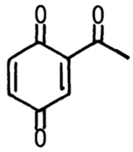
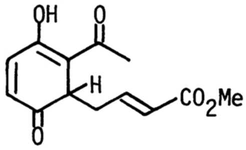
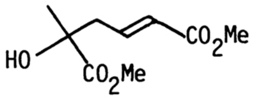
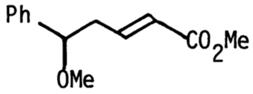
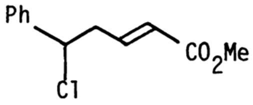
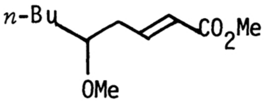
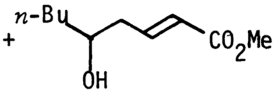
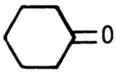
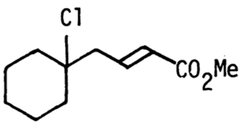
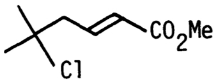
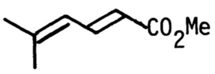
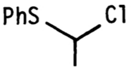
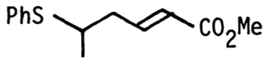
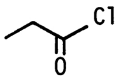
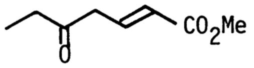
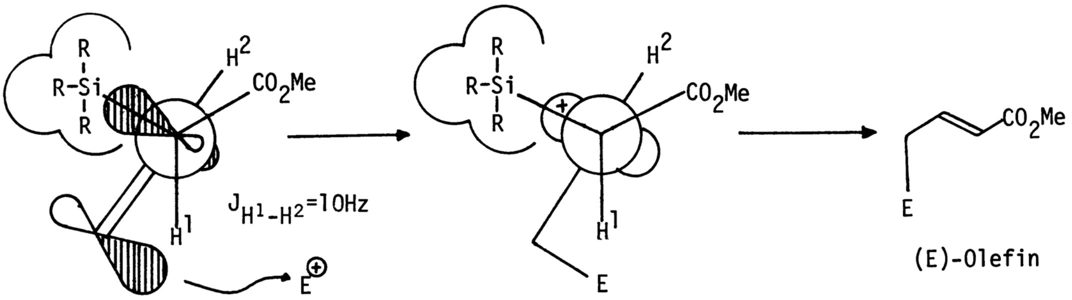
Entry	Electrophile	Silane	Conditions[a]	Product[b]	Yield (%)[c]
1		**4a**	A		(76)[d]
2		**4c**	A		100(72)[e]
3	$MeCOCO_2Me$	**4c**	B		94(89)
4		**4d**	B		99
5	PhCHO	**4a**	C		(24)[f]
6		**4c**	B		80
7		**4d**	B		81(43)
8	*n*-BuCHO	**4c**	B	 + 	46(22) 21
9		**4c**	D		trace (60)
10		**4d**	B		trace 59
11		**4c**	B		22
12		**4d**	B		31(17)
13	$Me_2C(OMe)_2$	**4c**	B	 + 	48(45) 29
14		**4c**	D		48 48
15		**4c**	E		71(63)

Table II (continued)

Entry	Electrophile	Silane	Conditions[a]	Product[b]	Yield (%)[c]
16		**4c**	E		66[g]

[a] Conditions: A; $SnCl_4$(1.2eq.), -78°C→r.t., 1h. B; $TiCl_4$(1.2eq.), r.t., overnight. C; $AlCl_3$(1.2eq.), r.t., overnight. D; $TiCl_4$(4eq.), r.t., 1.5h. E; $TiCl_4$(4eq.), -78°→0°C, 2.5h. [b] All new compounds exhibited ^1H-NMR, IR, and MS consistent with the assigned structures. No (Z)-olefin could be detected by GLC analysis. [c] Yields in the parentheses are of isolated products. Others are estimated by ^1H-NMR using *cis*-dichloroethylene as an internal standard. [d] Isolated yield as the corresponding hydroquinone diacetate. [e] Isolated yield as the corresponding hydroquinone bis-*t*-butyldimethylsilyl ether.

Scheme II



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10) **4c**: ^1H-NMR($CDCl_3$) δ 0.38(s,6H),3.10(d,1H,J=10Hz),3.48(s,3H),4.56-5.00(m,2H), 5.93(dt,1H,J=17,10Hz),7.24-7.52(m,5H); IR(neat) 1720(vs), 1630(m), 1250cm^{-1}(v).
11) Similar SE2' reaction of allylsilane has been reported; T. Hayashi, M. Konishi, H. Ito, and M. Kumada, 28th Symposium on Organometallic Chemistry, B111,(1981).

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