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2-ALKOXYCARBONYLALLYLTRIMETHYLSILANES AS NEW REAGENTS OF 2-ALKOXYCARBONYLALLYLATION OF ELECTROPHILES[1]

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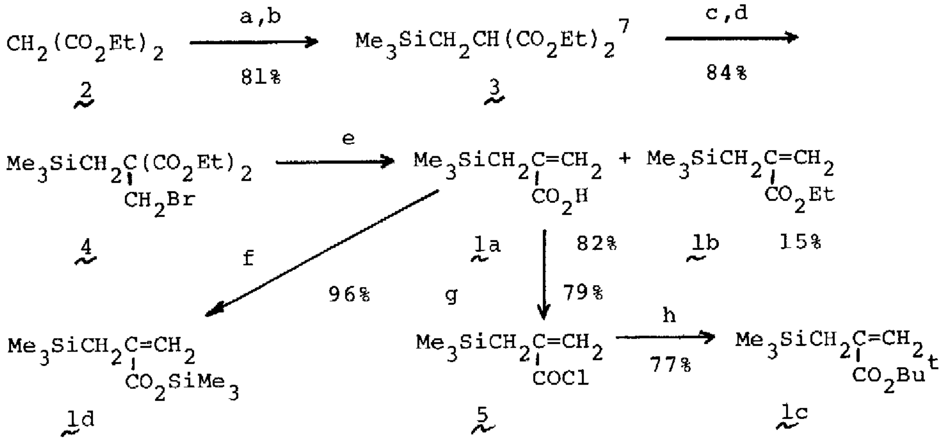
Summary: 2-Alkoxycarbonylallylsilanes are useful for 2-alkoxycarbonylallylation of acetals and carbonyl compounds with an aid of a Lewis acid; the products can be readily converted to α-methylene-γ-butyrolactones.

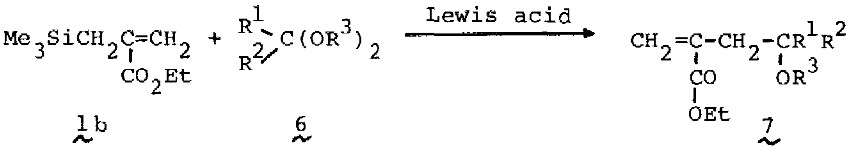
2-Carbethoxyallylation of carbonyl compounds is one of the most general routes to the synthesis of α-methylene-γ-butyrolactones, key structures of a number of naturally occurring sesquiterpenes with potential cytotoxic activity[2], and synthetic methods along this line attract much attention.[3] In eariler papers, we have demonstrated that allylsilanes are useful synthetic intermediates with a highly nucleophilic double bond.[4] During the course of studies on the introduction of a functionality to the allyl group of the allylsilanes, we have found a convenient method of preparation of 2-alkoxycarbonylallyltrimethylsilanes **1** which can be used as a useful reagent of introducing a 2-alkoxycarbonylallyl group into electrophilic centers in a single step. The products can be converted to α-methylene-γ-butyrolactones.

2-Alkoxycarbonylallyltrimethylsilanes **1**[5] are prepared by the following scheme.[6]



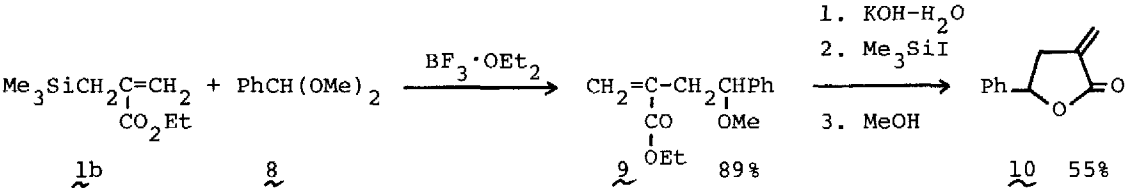
a. EtONa/EtOH, 30min. gentle heating; b. Me_3SiCH_2Cl, 24h, reflux; c. NaH, PhH, 1.5h; d. CH_2Br_2, reflux, 5h; e. KOH (3 equiv.), 20% H_2O-EtOH, reflux, 2.5h; f. Me_3SiCl/Py, Et_2O, 30min; g. $SOCl_2$, reflux, 4h; h. *t*-BuOLi (from *t*-BuOH and n-BuLi), THF, reflux, 1h.

2-Ethoxycarbonylallyltrimethylsilane (1b), thus obtained, reveals high reactivity toward various acetals in the presence of a Lewis acid to give 7. (eq. 1) The representative results are listed in Table 1.



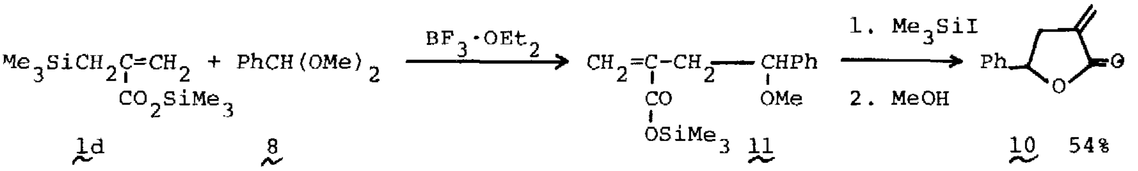
$$\underset{\mathbf{1b}}{\mathrm{Me_3SiCH_2\underset{\substack{|\\ CO_2Et}}{C}{=}CH_2}} + \underset{\mathbf{6}}{\mathrm{{}^{R^1}_{R^2}{>}C(OR^3)_2}} \xrightarrow{\text{Lewis acid}} \underset{\mathbf{7}}{\mathrm{CH_2{=}\underset{\substack{|\\ CO\\ |\\ OEt}}{C}\text{-}CH_2\text{-}\underset{\substack{|\\ OR^3}}{C}R^1R^2}} \qquad (1)$$

In all cases the reaction of 1b with acetals proceeds very smoothly to afford the corresponding carbethoxyallylation products in good yield, although the reaction is considerably slow than that of allyltrimethylsilane with acetals. Besides 1b, *t*-butyl ester (1c) and trimethylsilyl ester (1d) of 1a are also effective in the allylation of acetals. (run 7 and 8, respectively). The allylated compounds can be successfully converted to the corresponding α-methylene-γ-butyrolactones by the *in situ* dealkylation with iodotrimethylsilane.[8] (eq. 2 and 3)



(2)

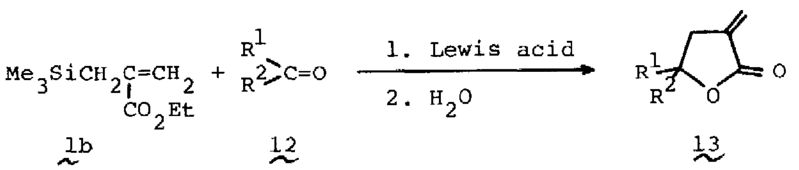
1b 8 9 89% 10 55%



(3)

1d 8 11 10 54%

The direct synthesis of α-methylene-γ-butyrolactones was also achieved by the reaction of 1b with carbonyl compounds. (eq. 4) However, unfortunately,



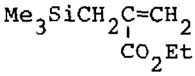
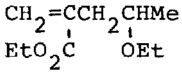
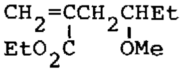
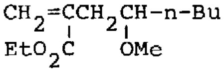
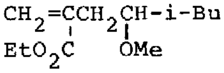
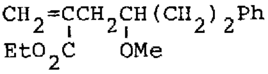
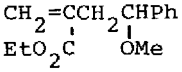
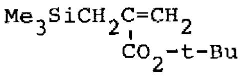
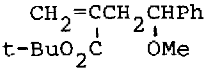
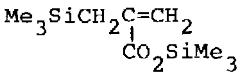
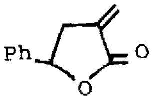
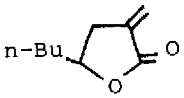
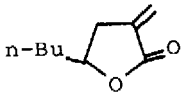
(4)

1b 12 13

yields are less satisfactory (20-30%) because of side reactions such as polymerization and aldol condensation of the starting materials or the products. (Table 1) The nucleophilicity of the double bond of 1 may decrease due to less effective σ-π conjugation in 1 rather than that in allyltrimethylsilane.[9]

As a general procedure, an allylsilane (1 mmol) in dichloromethane (2 ml) was added to a solution of an acetal (4 mmol) and a Lewis acid (4 mmol) in dichloromethane (8 ml) at 0°C. The mixture was stirred under a given condition in the Table, and hydrolyzed as a procedure employed in the previous papers.[4] After

Table 1. Reaction of 2-alkoxycarbonylallylsilanes **1** with various electrophiles promoted by a Lewis acid in dichloromethane.

Run	Allylsilane **1**	Electrophile	Lewis acid	Conditions	Product (% yield)[a]	
1	 $Me_3SiCH_2\underset{CO_2Et}{C}{=}CH_2$ **1b**	$MeCH(OEt)_2$	$TiCl_4$	0°, 6h	 $CH_2{=}\underset{EtO_2C}{C}CH_2\underset{OEt}{C}HMe$	(89)
2	**1b**	$EtCH(OMe)_2$	$TiCl_4$	0°, 5min then 25°, 30min	 $CH_2{=}\underset{EtO_2C}{C}CH_2\underset{OMe}{C}HEt$	(54)
3	**1b**	n-BuCH$(OMe)_2$	$TiCl_4$	0°, 11h	 $CH_2{=}\underset{EtO_2C}{C}CH_2\underset{OMe}{C}H$-n-Bu	(85)
4	**1b**	i-BuCH$(OMe)_2$	$TiCl_4$	0°, 7h	 $CH_2{=}\underset{EtO_2C}{C}CH_2\underset{OMe}{C}H$-i-Bu	(76)
5	**1b**	$Ph(CH_2)_2CH(OMe)_2$	$TiCl_4$	0°, 8h then 25°, 1h	 $CH_2{=}\underset{EtO_2C}{C}CH_2\underset{OMe}{C}H(CH_2)_2Ph$	(42)
6	**1b**	$PhCH(OMe)_2$	$BF_3{\cdot}OEt_2$	0°, 8h	 $CH_2{=}\underset{EtO_2C}{C}CH_2\underset{OMe}{C}HPh$	(89)
7	 $Me_3SiCH_2\underset{CO_2\text{-t-Bu}}{C}{=}CH_2$ **1c**	$PhCH(OMe)_2$	$BF_3{\cdot}OEt_2$	0°, 4h	 $CH_2{=}\underset{\text{t-BuO}_2C}{C}CH_2\underset{OMe}{C}HPh$	(67)
8	 $Me_3SiCH_2\underset{CO_2SiMe_3}{C}{=}CH_2$ **1d**	$PhCH(OMe)_2$	$BF_3{\cdot}OEt_2$	0°, 8h[b]		(54)
9	**1b**	n-BuCHO	$TiCl_4$	0°~25°, 3h		(25)
10	**1c**	n-BuCHO	$TiCl_4$	0°~rt, 4.5h		(23)

[a] Yields after isolation by TLC. [b] After demethylation with iodotrimethylsilane in CCl_4 (50°, 2h) followed by methanolysis.

work-up, a pure allylated product was isolated by TLC. The product (0.6 mmol) was treated with iodotrimethylsilane, prepared from allyltrimethylsilane (0.9 mmol) and iodine (0.8 mmol) in carbon tetrachloride by in situ method,[8b] at 50° for 2h. The mixture was then subjected to methanolysis and concentrated under the reduced pressure. The corresponding pure α-methylene-γ-butyrolactone was isolated by TLC.

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References and Notes

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4. For recent reports in this area, see a) A. Hosomi, M. Saito, and H. Sakurai, Tetrahedron Lett., 429 (1979); b) A. Hosomi, H. Hashimoto, and H. Sakurai, J. Org. Chem., 43, 2551 (1978), and references cited therein.
5. Physical and spectral properties of **1b** are: bp 35-40°C (2 mmHg); IR(neat) 1725, 1620, 1410, 1235, 905 cm^{-1}; NMR(CCl_4)δ -0.02(s, 9H, $SiCH_3$), 1.28(t, J= 6.5Hz, 3H, $OCH_2C\underline{H}_3$), 1.80(bs, 2H, $SiCH_2$), 4.14(q, J=6.5Hz, 2H, OCH_2), 5.23(m, 1H, trans proton to CO_2Et), 5.89(m, 1H, cis proton to CO_2Et). Anal. Calcd for $C_9H_{18}O_2Si$: C, 58.02; H, 9.74. Found: C, 57.94; H, 9.79. All other new compounds obtained in this work gave correct elemental analysis and satisfactory spectral data.
6. Similarly, stannyl analogs of **1** were prepared, starting from iodomethyltrimethylstannane instead of chloromethyltrimethylsilane.
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