Titanium Tetrachloride-Catalyzed Reaction of Diketene with Unsaturated Organosilanes. A Useful Synthesis of β-Dicarbonyl Compounds

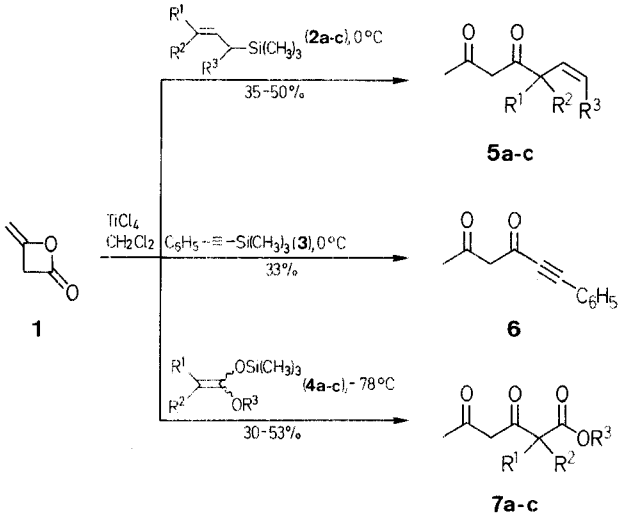
Masatomi Ohno, Shotaro Matsuoka, Shoji Eguchi*

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464, Japan

Allylsilane and silyl ketene acetal were acetoacetylated with diketene in the presence of titanium tetrachloride.

Diketene (**1**) is a reactive and versatile compound used for the introduction of functionalized C_2, C_3, and C_4 units. As an electrophile, this reagent gives primarily acetoacetylated products in reaction with a variety of carbon and heteroatom nucleophiles. An extensive review on this reagent appeared recently.[1] In the past decade unsaturated organosilanes have been widely utilized in organic synthesis.[2] Their applicabilities are based on the characteristic properties of the silicon atom; the unsaturated bond with a β-silyl group has moderately enhanced nucleophilicity. Thus, the combination of these reagents, **1** and allylic or enolic silanes, could provide a new method for preparing β-dicarbonyl compounds. We wish to report here the results of such synthesis of some β-dicarbonyl derivatives.

The reaction of **1** with allylic silanes **2a–c** proceeded at 0 °C under the influence of titanium tetrachloride as a catalyst, and the acetoacetylated product **5a–c** was obtained in a moderate yield after chromatographic separation. Similarly the reaction with acetylenic silane **3** afforded acetylenic 1,3-diketone **6**. The reactions of silyl enol ether **9** and silyl ketene acetals **4a–c** were carried out at −78 °C with the same catalyst.[3] Although both enolic silanes were reactive with **1**, **4a–c** gave the expected 3,5-dioxo-esters **7a–c**, but silyl enol ether **9** did not give triones. This difference may be due to the instability of the product under the employed conditions. In reactions, the catalyst is critical; the other Lewis acids such as stannic chloride, ether-



2, 5	R^1	R^2	R^3	4, 7	R^1	R^2	R^3
a	H	H	H	a	CH_3	H	C_2H_5
b	H	$-(CH_2)_2-$		b	C_6H_5	H	CH_3
c	C_6H_5	H	H	c	CH_3	CH_3	CH_3

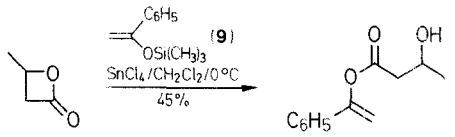
Table. β-Dicarbonyl Compounds **5–7** Prepared

Product	Reaction Time	Yield[a] (%)	Molecular Formula[b]	IR (neat)[c] ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS)[d] δ, J(Hz)
5a	3 min	35	$C_7H_{10}O_2$ (126.2)	1720, 1615, 990, 910	2.05 (s, 2.1H); 2.24 (s, 0.9H); 3.06 (d, 1.4H, J = 7); 3.08 (d, 0.6H, J = 7); 3.60 (s, 0.6H); 5.14, 5.18 (2d, each 1H, J = 18, 10); 5.51 (s, 0.7H); 5.70–6.26 (m, 1H); 15.29 (s, 0.7H)
5b	1 min	50	$C_9H_{12}O_2$ (152.2)	1720, 1700, 1615	1.55–2.80 (m, 4H); 2.06 (s, 2.4H); 2.24 (s, 0.6H); 3.45 (m, 1H); 3.62 (s, 0.4H); 5.51 (s, 0.8H); 5.81 (m, 2H); 15.41 (s, 0.8H)
5c	3 hr	36	$C_{13}H_{14}O_2$ (202.2)	1720, 1700, 1615, 990, 910	2.01 (s, 2.1H); 2.11 (s, 0.9H); 3.55 (s, 0.6H); 4.24 (d, 0.7H, J = 8); 4.49 (d, 0.3H, J = 8); 5.13, 5.25 (2d, each 1H, J = 18, 10); 5.51 (s, 0.7H); 6.25 (ddd, 1H, J = 17, 10, 8); 7.30 (s, 5H); 15.78 (s, 0.7H)
6	12 min	33	$C_{12}H_{10}O_2$ (186.2)	2210, 1670, 1600	2.13 (s, 2.7H); 2.32 (s, 0.3H); 3.82 (s, 0.2H); 5.84 (s, 0.9H); 7.30–7.65 (m, 5H); 14.93 (s, 0.9H)
7a[e]	3 min	30	$C_9H_{14}O_4$ (186.2)	1740, 1615	1.26 (t, 3H, J = 7); 1.39 (d, 3H, J = 7); 2.07 (s, 2.4H); 2.25 (s, 0.6H); 3.36 (q, 1H, J = 7); 3.72 (s, 0.4H); 4.19 (q, 2H, J = 7); 5.58 (s, 0.8H); 15.20 (s, 0.8H)
7b	1 min	40	$C_{13}H_{14}O_4$ (234.2)	1740, 1615	2.00 (s, 2.4H); 2.10 (s, 0.6H); 3.59 (s, 0.4H); 3.74 (s, 3H); 4.59 (s, 0.8H); 5.00 (s, 0.2H); 5.49 (s, 0.8H); 7.36 (s, 5H); 14.99 (s, 0.8H)
7c	1 min	53	$C_9H_{14}O_4$ (186.2)	1740, 1615	1.41 (s, 6H); 2.06 (s, 2.4H); 2.24 (s, 0.6H); 3.65 (s, 0.4H); 3.72 (s, 3H); 5.54 (s, 0.8H); 15.20 (s, 0.8H)

[a] Yield of isolated product based on the organosilanes **2–4**.
[b] Satisfactory microanalyses obtained: C ±0.30, H ±0.25.
[c] Recorded on a JASCO IRA-1 Infrared spectrophotometer.
[d] Obtained on a JEOL 60-HL spectrometer.
[e] Ref. 5.

boron trifluoride and zinc chloride were unsatisfactory. The β-dicarbonyl compounds **5–7** obtained exist in a 3:7 to 1:9 keto/enol ratio (^{1}H-NMR, see Table).

Ring strain relief seemed to be a driving force for the above reactions. Therefore, a similar type of reaction of the related β-lactone **8** with unsaturated orgaosilanes was also attempted. In this case, however, **8** reacted limitedly only with **9** in the presence of stannic chloride to give only *O*-acylated product **10**.[4]



8 **10**

6-Alken-2,4-diones 5a–c and 3,5-Dioxoalkanoic Esters 7a–c; General Procedure:

To a solution of diketene (**1**; 126 mg, 1.5 mmol) and the appropriate allylic silane **2** (1 mmol) in dry CH_2Cl_2 (3 mL) is added $TiCl_4$ (0.11 mL, 1 mmol) by syringe at 0 °C under N_2, and the mixture is stirred for the period indicated in the Table. The resultant brown solution is poured into dil. aq. HCl, and the product is extracted with ether (2 × 20 mL). The organic layer is separated, washed with brine (20 mL) and dried (Na_2SO_4). After evaporation of the solvent, the residue is chromatographed on a silica gel column (Fuji-Davison BW-300) using hexane/EtOAc (100:3, v/v) to give an oily product **5a–c** (Table).

Dioxo esters **7a–c** are obtained from **4a–c** in a similar fashion, except for reaction temperature of −78 °C, extraction with EtOAc, and chromatography with hexane/EtOAc (10:1, v/v) (Table).

6-Phenyl-5-hexyn-2,4-dione (6):

The same treatment of **3** with **1** as above gives a mixture of diketone **6** and its silyl enol ether.

The partly retained trimethylsilyl group is removed by treating the raw product with KF (60 mg) in MeOH (2 mL) for 5 min at room temperature. Purification by silica gel chromatography (hexane/EtOAc, 100:3, v/v) affords oily **6** (Table).

α-Styryl 3-Hydroxybutyrate (10):

To a solution of **8** (86 mg, 1 mmol) and **9** (192 mg, 1 mmol) in dry CH_2Cl_2 (3 mL) is added $SnCl_4$ (0.12 mL, 1 mmol) by syringe at 0 °C, and the mixture is stirred for 11 min. The reaction mixture is poured into ice-water (20 mL) followed by extraction with ether (2 × 20 mL), and the separated organic layer is dried Na_2SO_4. Evaporation of the solvent and purification of the residue by silica gel chromatography (hexane/EtOAc, 20:3 v/v) affords **10** as an oil; yield: 93 mg (45%).

$C_{12}H_{14}O_3$	calc.	C 69.89	H 6.84
(206.2)	found	69.82	6.91

IR (neat): ν = 3400, 1740, 1640 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS): δ = 1.30 (d, 2H, J = 6 Hz); 2.72 (d, 2H, J = 6 Hz); 4.31 (br s, 1H); 4.33 (sext. 1H, J = 6 Hz); 5.05, 5.49 (2d, each 1H, J = 3 Hz); 7.17–7.64 (m, 5H).

Received: 28 March 1987; revised: 15 July 1987

(1) Clemens, R.J. *Chem. Rev.* **1986**, *86*, 241.
(2) Colvin, E.W. *Silicon in Organic Synthesis*, Butterworth, London, 1981.
(3) Chan, T.H., Brownbridge, P. *J. Chem. Soc. Chem. Commun.* **1979**, 578.
(4) Ref. 2, p. 233.
(5) Suzuki, E., Inoue, S. *Synthesis* **1975**, 259.