

Carbon Homologation of 1-Alkynes Using Alkoxyethyl Esters Mediated by Dichlorobis(trifluoromethanesulfonato)titanium(IV)

YOO TANABE

School of Science, Kwansei Gakuin University, 1-1-155 Uegahara, Nishinomiya 662

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Various 1-alkynes were converted to 1-alkoxy-3-chloro-2-alkenes using alkoxyethyl esters and dichlorobis(trifluoromethanesulfonato)titanium(IV) [$\text{TiCl}_2(\text{OTf})_2$, titanium(IV) bis(triflate)]. This carbon homologation proceeded in the case of not only simple 1-alkynes but also for several 3- or 4-dimethylcarbamoyloxy-, 5-benzoyloxy-, 5-phenoxy-carbonyloxy-, and 5-methoxycarbonyloxy-1-alkynes. Among them, 3- and 4-dimethylcarbamoyloxy-1-butyne underwent the reaction without loss of their functionalities compared with the other oxy substrates. The stereoselectivity was *Z* predominant, especially in the case of the above mentioned 3-, 4-, and 5-oxy substituted 1-alkynes. Addition of TiCl_4 to this system was somewhat effective for enhancing the *Z* ratios. Titanium(IV) bis(triflate) was the only effective catalyst among several Lewis acids such as AlCl_3 , TiCl_4 , SnCl_4 , ZnCl_2 , and $\text{Sn}(\text{OTf})_2$. As a functionalization of the obtained vinyl chloride, 3-chloro-4-dimethylcarbamoyloxy-1-methoxy-2-pentene was converted into the corresponding ketone using $\text{Hg}(\text{OCOCF}_3)_2$.

Metal trifluoromethanesulfonates (triflates) systems have enjoyed various types of significant C–C bonds formation in organic synthesis, and are continuously being developed.¹⁾ The triflates of B, Si, Sn(II), Sn(IV), and Al are well recognized as effective aldol-type reaction mediators. Recently, lanthanide metals (for example, Yb) and Sc triflates have been introduced as water-tolerable catalysts for the aldol reaction.²⁾

During the course of synthetic studies on the dichlorobis(trifluoromethanesulfonato)titanium(IV) [$\text{TiCl}_2(\text{OTf})_2$, titanium(IV) bis(triflate)] (**1**) mediated selective acylation reactions, we noted two important facts: (1) titanium(IV) bis(triflate) (**1**) would smoothly generate the vinyl cationic species from 1-alkynes **2** with carboxylic anhydride during the acylation of **2**, although the use of acyl chlorides were almost ineffective for the acylation,³⁾ and (2) the crossed type-Claisen condensation of alkoxyethyl esters **3** toward methyl esters was conducted using **1** and tertiary amines, wherein **1** interacted more preferentially with **3** than the methyl esters.⁴⁾ Accordingly, both of these reactions proceed via the formation of strong six-membered chelate complexes between **1** and carboxylic anhydride or **3**. In addition, it has been very recently reported, that titanium(IV) bis(triflate) (**1**) became an efficient catalyst for macrolide synthesis, wherein intramolecular esterification (a kind of acylation) of hydroxy carboxylic acid was performed.⁵⁾

In due consideration, the reaction between 1-alkynes **2** and alkoxyethyl esters **3** promoted by **1** were possibly promising, because the alkoxyethyl cations will be more easily generated than the acyl cations. We report here an effective method for the preparation of 1-alkoxy-3-chloro-2-alkenes **4** from 1-alkynes **2** and alkoxyethyl esters **3**, i.e., a carbon homologation, promoted by titanium(IV) bis(triflate) (**1**) as shown in Scheme 1. Alkoxyethyl esters **3** were easily prepared from carboxylic acids and the corresponding alkyl chloromethyl ethers or vinyl ethers.⁶⁾ Although ZnCl_2 catalyzed

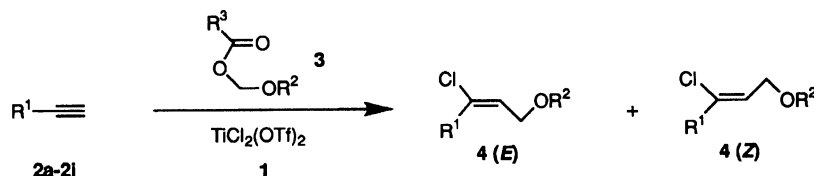
such a homologation reaction of simple 1-alkynes using the chloromethyl methyl ether (**9**),⁷⁾ 1,3-dichloro-2-alkenes are frequently liable to be produced together with 1-alkoxy-3-chloro-2-alkenes **4**.⁸⁾ A similar example of dimethylaluminum halide- CH_2O promoted homologation of simple 1-alkynes was also reported: This reaction gave mixtures of allenic alcohols and 3-chloroallylic alcohols which were prepared with high *Z* selectivities via a *syn* Friedel–Crafts type addition.⁸⁾

Results and Discussion

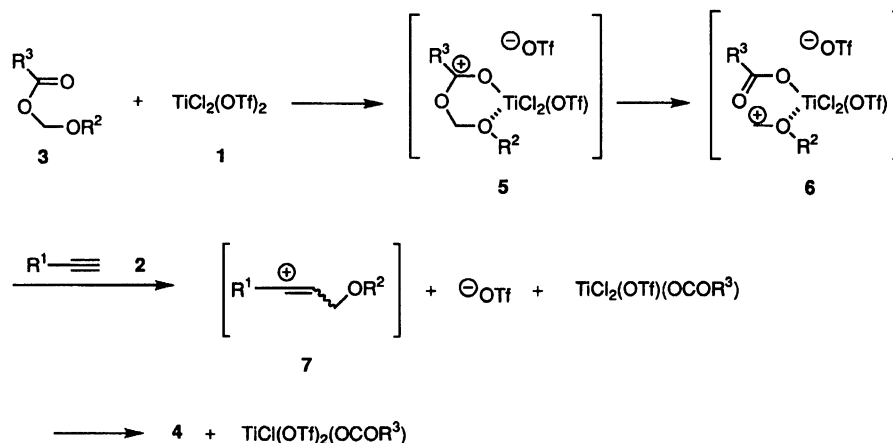
First, the addition reaction of 1-heptyne (**2a**) with methoxymethyl benzoate (**3a**) in the presence of titanium(IV) bis(triflate) (**1**) at 0 °C for an hour gave 3-chloro-1-methoxy-2-octene (**8**) in 75% yield (*E/Z* = 35 : 65) according to Markovnikoff's rule. The configurations (*E* or *Z*) of **8** were determined by the comparison of olefinic proton using ^1H NMR: Chemical shift of the *E* isomer located downfield than that of the *Z* isomer.⁹⁾

A plausible reaction mechanism of the carbon homologation is illustrated in Scheme 2. The alkoxyethyl cation **6** produced from a six-membered chelate intermediate **5** would work as the reactive species. Alkyne **2** reacts with the reactive cation **6** to afford the vinyl chloride **4** via the vinyl cationic intermediate **7**. It is notable that the vinyl cation **7** is trapped with a chloride ion to afford the vinyl chloride **4**. This fact is in contrast to that of the related reaction of 1-alkynes **2** with acid anhydrides to give 1,3-diketones wherein the vinyl cation would be reacted with quenching water.³⁾

Next, the carbon homologation using other methoxymethylchlorinating reagents such as chloromethyl methyl ether (**9**)⁷⁾ and dimethoxymethane (**10**) were examined under the same conditions. The reaction of 1-heptyne (**2a**) with **10** gave the desired 3-chloro-1-methoxy-2-octene (**8**) in 53% (*E/Z* = 43 : 57) yield. But the yield was only 15% when **9** was used. These results would indicate that the chelate-type coordination of **1** with reagents such as alkoxyethyl esters **3**



Scheme 1.



Scheme 2.

and dimethoxymethane (**10**) is essential to generate the methoxymethyl cation during the present reaction.

Various alkoxy methyl carboxylates **3** were screened as reagents using 1-heptyne (**2a**) as the substrate to examine their reactivity and the stereoselectivity (*E/Z*) as shown in Table 1. Although the steric bulkiness of substituent R^2 or R^3 in **3** caused a slight effect on enhancement of the *Z* ratios, their values were within the range of *E/Z* = 40 : 60—31 : 69. Other simple terminal alkynes, i.e., 1-decyne (**2b**) and cyclohexylacetylene (**2c**) underwent the similar reactions using methoxymethyl chloroacetate (**3d**) to give the corresponding 3-chloro-1-methoxy-2-alkenes **13** and **14**, respectively.

The reactions of several 5-benzoyloxy-, 5-phenoxy carbonyloxy-, 3- or 5-methoxycarbonyloxy-, and 3- or 4-dimethylcarbamoyloxy-1-alkynes **2d—2i** also proceeded

Table 1. Addition Reactions of 1-Heptyne (**2a**) with Alkoxy methyl Esters **3a—3h** Promoted by $\text{TiCl}_2(\text{OTf})_2$ (**1**)^{a)}

Entry	Alkoxy methyl ester	Product	Yield/%	<i>E/Z</i> ^{b)}
1	$\text{PhCO}_2\text{—MOM}^{\text{c)}$ (3a)	8	75	40/60
2	$\text{MeCO}_2\text{—MOM}$ (3b)	8	62	38/62
3	$\text{PhCH}_2\text{CH}_2\text{CO}_2\text{—MOM}$ (3c)	8	55	38/62
4	$\text{ClCH}_2\text{CO}_2\text{—MOM}$ (3d)	8	73	35/65
5	$^t\text{BuCO}_2\text{—MOM}$ (3e)	8	64	37/63
6	$\text{Cl}_2\text{CHCO}_2\text{—MOM}$ (3f)	8	32	31/69
7	$\text{ClCH}_2\text{CO}_2\text{CH}_2\text{OCH}_2\text{Ph}$ (3g)	11	35	37/63
8	$\text{ClCH}_2\text{CO}_2\text{CH}_2\text{O}^i\text{Pr}$ (3h)	12	55	34/66

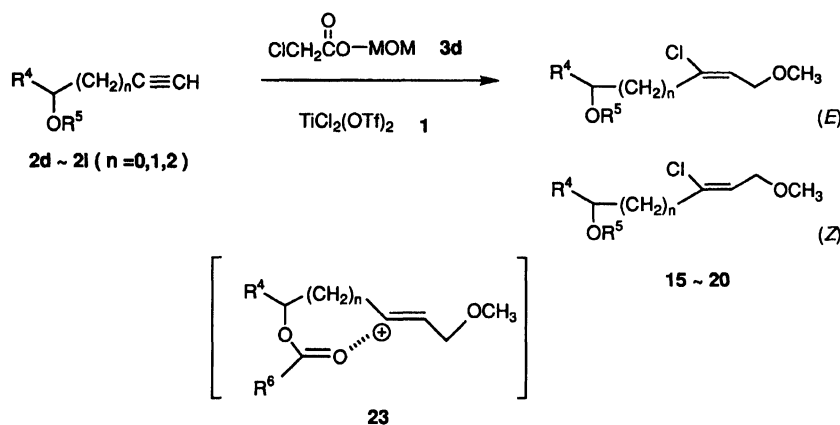
a) These reactions were carried out in CH_2Cl_2 at 0 °C for 2 h. Molar ratios of **2a**:**3a—3h**:**1** were = 1.0 : 1.6 : 1.1. b) Determined by GLC analysis.

c) MOM- = $\text{MeOCH}_2\text{—}$.

as shown in Scheme 3, whose results are summarized in Table 2. The *Z* ratios of these products **15—20** somewhat increased compared with those in the case of simple 1-alkynes **2a**, **2b**, and **2c** perhaps due to the formation of intermediate **23** by the anchimeric assistance of these carbonyloxy groups during the reactions. Although the acyl- and alkoxy carbonyl type protective groups of the hydroxy function in **2d—2f**, **2h** were apt to be cleaved to some extent during the reactions (Entries 3—6 and 8), the dimethylcarbamoyl group in **2g** and **2i** was found to be stable so as to affect the increase of the yields (Entries 7, 9, and 10). Addition of TiCl_4 to this system was also slightly effective for enhancing the *Z* ratios (Entries 4 and 10). The reaction of 4-octyne (**2j**), an internal alkyne proceeded to give **21** with a low yield (Entry 11).

The present reaction employing these oxy-substituted alkynes **2d—2i** with **3d**, and even with chloromethyl methyl ether (**9**) or dimethoxymethane (**10**) did not proceed by the reported methods catalyzed by AlCl_3 ^{7a)} or ZnCl_2 .^{7b)} When TiCl_4 , SnCl_4 or tin(II) triflate [$\text{Sn}(\text{OTf})_2$] was used in the reaction of **2i**, the desired product **20** was obtained in poor yield (10%) and **2i** was almost totally recovered. These facts indicate the high Lewis acidity of titanium(IV) bis(triflate) (**1**).

Vinyl chlorides are well recognized as a class of important precursor of ketones by the hydrolysis¹⁰⁾ and di- or tri-substituted olefins by regioselective displacement of the chlorine atom upon treatment with suitable nucleophiles¹¹⁾ such as Grignard reagents catalyzed by nickel complex.^{11d)} As an application of the present reaction, conversion of 3-chloro-4-dimethylcarbamoyloxy-1-methoxy-2-pentene (**20**) to the corresponding

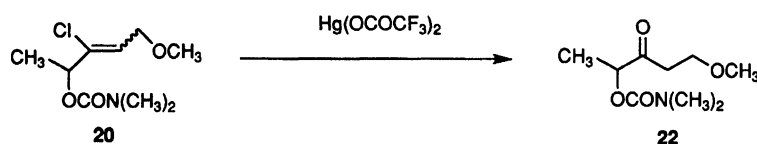


Scheme 3.

Table 2. Addition Reactions of Several Alkynes with Methoxymethyl Chloroacetate (**3d**)^{a)}

Entry	Substrate			Product	Yield (%)	<i>E/Z</i>	
	<i>n</i>	R ⁴	R ⁵				
1		1-Decyne	(2b)	13	68	40/60 ^b)	
2		Cyclohexylacetylene	(2c)	14	39	47/53 ^b)	
3	2	H	COPh	(2d)	15	43	25/75 ^c)
4 ^d)	2	H	COPh	(2d)	15	37	15/85 ^c)
5	2	H	CO ₂ Ph	(2e)	16	55	30/70 ^c)
6	2	H	CO ₂ Me	(2f)	17	56	30/70 ^c)
7	1	H	CO ₂ NMe ₂	(2g)	18	66	30/70 ^c)
8	0	H	CO ₂ Me	(2h)	19	27	35/65 ^c)
9	0	Me	CO ₂ NMe ₂	(2i)	20	65	30/70 ^b)
10 ^d)	0	Me	CO ₂ NMe ₂	(2i)	20	57	24/76 ^b)
11		4-Octyne	(2j)	21	12	—	

a) These reactions were carried out in CH₂Cl₂ at 0 °C for an hour and at room temperature for 5 h. Molar ratios of **2b**—**2j**:**3d**:**1** were =1.0 : 1.6 : 1.1. b) Determined by GLC analysis. c) Determined by ¹H NMR measurement of the olefinic proton. d) 1.10 Molar amounts of TiCl₄ vs. the substrate were added to this system.



Scheme 4.

ketone **22** by hydrolysis was examined. Hydrolyses of **22** using H₂SO₄^{10a)} and TiCl₄^{10b)} were first tried, but these reactions gave complex mixtures. When Hg(OCOCF₃)₂^{10c)} was used, the desired ketone **22** was successfully obtained in 62% yield, wherein the labile functional groups such as α-dimethylcarbamoyloxy and β-methoxyl groups in the ketone **22** were retained during the reaction (Scheme 4).

This method will provide a carbon homologation of not only simple 1-alkynes but also for several 3- or 4-dimethylcarbamoyloxy-, 5-benzoyloxy-, 5-phenoxy-carbonyloxy-, and 5-methoxycarbonyloxy-1-alkynes with alkoxymethyl esters **3** in moderate to good yields with *Z*

predominant stereoselectivities promoted by titanium(IV) bis(triflate) (**1**).

Experimental

Apparatus and Materials. Boiling points are uncorrected. ¹H NMR spectra were recorded on a Hitachi R-24B (60 MHz) and a JEOL FX-90Q (90 MHz) spectrometers using TMS as an internal standard in CDCl₃. IR spectra were recorded on a Hitachi 270-30 spectrophotometer. MS spectra were obtained with a Hitachi GC/MS M-80 instrument. Analytical GLC was performed on a Shimadzu GC9A with a 5% SE-30 (1.5 m×3 mm) or a 5% XE-60 (1.5 m×3 mm) packed column. Dichlorobis(trifluoromethanesulfonato)titanium(IV) [TiCl₂(OTf)₂=titanium(IV) bis-

(triflate) (**1**)] was prepared by the previously reported procedure.^{4c)} Alkoxy methyl esters **3a**,¹²⁾ **3b**,¹³⁾ **3d**,^{4c)} **3e**,^{6c)} and **3f**⁴⁾ were prepared according to the reported procedure. Other reagents and the solvents were of commercial grade and were used without further purification. Silica-gel column chromatography was performed on a Merck Art. 7734.

Methoxymethyl 3-Phenylpropionate (3c). Reaction of 3-phenylpropionic acid and chloromethyl methyl ether gave **3c** in 82% yield by the known method.^{6a)} Bp 180 °C (oven temp)/1.0 mmHg (1 mmHg=133.3 Pa) by bulb to bulb distillation; IR (film) 1730 cm⁻¹; ¹H NMR δ =2.30–2.90 (4H, m), 3.30 (3H, s), 5.10 (2H, s), 7.00–7.40 (5H, m); MS (70 eV) m/z 194 (M⁺); Anal. (C₁₁H₁₄O₃) C, H.

Benzoyloxymethyl Chloroacetate (3g). Reaction of chloroacetic acid and benzyl chloromethyl ether gave **3g** in 62% yield by the known method.^{6a)} Bp 200 °C (oven temp)/1.0 mmHg by bulb to bulb distillation; IR (film) 1730 cm⁻¹; ¹H NMR δ =4.00 (2H, s), 4.50 (2H, s), 5.15 (2H, s), 7.00–7.20 (5H, m); MS (70 eV) m/z 214 (M⁺); Anal. (C₁₀H₁₁ClO₃) C, H.

Isopropoxymethyl Chloroacetate (3h). Reaction of chloroacetic acid and chloromethyl isopropyl ether gave **3h** in 75% yield by the known method.^{6a)} Bp 150 °C (oven temp)/20 mmHg by bulb to bulb distillation; IR (film) 1730 cm⁻¹; ¹H NMR δ =1.05 (6H, d, J =7 Hz), 3.50–4.00 (1H, m), 3.95 (2H, s), 5.25 (2H, s); MS (70 eV) m/z 166 (M⁺); Anal. (C₆H₁₁ClO₃) C, H.

3-Chloro-1-methoxy-2-octene (8). A typical procedure (Table 1, Entry 1): To a stirred suspension of titanium(IV) bis(triflate) (**1**, 191 mg, 0.46 mmol) in dichloromethane (1.0 ml) was added methoxymethyl benzoate (**3a**, 114 mg, 0.69 mmol) in dichloromethane (0.5 ml) at 0 °C under an argon atmosphere. To the resultant mixture, 1-heptyne (**2a**, 40 mg, 0.42 mmol) in dichloromethane (0.5 ml) was added at 0 °C followed by stirring at this temperature for 2 h. Then, phosphate buffer solution (pH 7.0; 2.0 ml) was added to the mixture followed by filtration with Celite. The mixture was extracted with dichloromethane (20 ml×2) and washed with water, brine, and dried (Na₂SO₄). Evaporation of the solvent and purification with silica-gel chromatography (hexane/ether=10:1) gave **8** (56 mg; 75%). Colorless oil: E/Z =40:60 by GLC analysis (SE-30; column temp 150 °C); IR (film) 1120 cm⁻¹; ¹H NMR δ =0.75–1.05 (3H, m), 1.05–1.70 (6H, m), 2.15–2.55 (2H, m), 3.30 (3H, s), 3.85–4.15 (2H, m), 5.25–5.60 (1H, m; *Z*-form), 5.60–5.85 (1H, m; *E*-form); MS (70 eV) m/z 176 (M⁺); Anal. (C₉H₁₇ClO) C, H.

1-Benzoyloxy-3-chloro-2-octene (11). Colorless oil: E/Z =37:63 by GLC analysis (SE-30; column temp 180 °C); IR (film) 1130 cm⁻¹; ¹H NMR δ =0.70–1.00 (3H, m), 1.00–1.50 (6H, m), 2.00–2.40 (2H, m), 3.85–4.20 (2H, m), 4.40 (2H, s), 5.20–5.50 (1H, m; *Z*-form), 5.50–5.80 (1H, m; *E*-form), 7.15–7.30 (5H, m); MS (70 eV) m/z 252 (M⁺); Anal. (C₁₅H₂₁ClO) C, H.

3-Chloro-1-isopropoxy-2-octene (12). Colorless oil: E/Z =34:66 GLC analysis (SE-30; column temp 150 °C); IR (film) 1120 cm⁻¹; ¹H NMR δ =0.60–1.00 (3H, m), 0.90–1.70 (6H, m), 1.05 (6H, d, J =7 Hz), 2.00–2.50 (2H, m), 3.50 (1H, q, J =7 Hz), 3.80–4.10 (2H, m), 5.15–5.45 (1H, m; *Z*-form), 5.45–5.70 (1H, m; *E*-form); MS (70 eV)

m/z 204 (M⁺); Anal. (C₁₁H₂₁ClO) C, H.

3-Chloro-1-methoxy-2-undecene (13). Colorless oil: E/Z =40:60 by GLC analysis (SE-30; column temp 180 °C); IR (film) 1120 cm⁻¹; ¹H NMR δ =0.75–1.05 (3H, m), 1.05–1.75 (12H, m), 2.15–2.55 (2H, m), 3.30 (3H, s), 3.85–4.15 (2H, m), 5.25–5.60 (1H, m; *Z*-form), 5.60–5.85 (1H, m; *E*-form); Anal. (C₁₂H₂₃ClO) C, H.

1-Chloro-1-cyclohexyl-3-methoxy-1-propene (14). Colorless oil: E/Z =47:53 by GLC analysis (SE-30; column temp 150 °C); IR (film) 1120 cm⁻¹; ¹H NMR δ =1.50–2.65 (11H, m), 3.30 (3H, s), 3.85–4.15 (2H, m), 5.30–5.65 (1H, m; *Z*-form), 5.65–5.90 (1H, m; *E*-form); Anal. (C₁₀H₁₇ClO) C, H.

4-Pentynyl benzoate (2d). Reaction of 4-pentyn-1-ol and benzoyl chloride in the presence of Et₃N (1.10 equiv) in CH₂Cl₂ at 0 °C for 5 h gave **2d**. Colorless oil: Bp 89–90 °C/0.08 mmHg; IR (film) 2120, 1715 cm⁻¹; ¹H NMR δ =1.50–2.40 (5H, m), 4.25 (2H, t, J =7 Hz), 7.00–8.10 (5H, m).

5-Phenoxycarbonyloxy-1-pentyne (2e). Reaction of 4-pentyn-1-ol and phenoxycarbonyl chloride in a similar procedure of preparation of **2d** gave **2e**. Colorless oil: Bp 82–84 °C/0.08 mmHg; IR (film) 2120, 1715 cm⁻¹; ¹H NMR δ =1.70–2.40 (5H, m), 4.25 (2H, t, J =7 Hz), 7.00–7.50 (5H, m).

5-Methoxycarbonyloxy-1-pentyne (2f). Reaction of 4-pentyn-1-ol and methoxycarbonyl chloride in a similar procedure of preparation of **2d** gave **2f**. Colorless oil: Bp 150 °C (oven temp)/20 mmHg by bulb to bulb distillation; IR (film) 2110, 1720 cm⁻¹; ¹H NMR δ =1.50–2.40 (5H, m), 3.70 (3H, s), 4.10 (2H, t, J =7 Hz).

4-Dimethylcarbamoyloxy-1-butyne (2g). Reaction of 3-butyne-1-ol and dimethylcarbamoyl chloride in a similar procedure of preparation of **2d** gave **2g**. Pale yellow oil: Bp 80 °C (oven temp)/1.5 mmHg by bulb to bulb distillation; IR (film) 2110, 1650 cm⁻¹; ¹H NMR δ =2.30 (1H, t, J =2 Hz), 2.35–2.70 (2H, m), 2.95 (6H, s), 4.15 (2H, t, J =7 Hz).

3-Dimethylcarbamoyloxy-2-butyne (2i). Reaction of 3-butyne-2-ol and dimethylcarbamoyl chloride in a similar procedure of preparation of **2g** gave **2i**. Yellow oil: Bp 80 °C (oven temp)/1.5 mmHg by bulb to bulb distillation; IR (film) 2110, 1650 cm⁻¹; ¹H NMR δ =1.50 (3H, d, J =7 Hz), 2.45 (1H, d, J =2 Hz), 2.95 (6H, s), 5.40 (1H, dd, J =7 Hz, J =2 Hz).

For the syntheses of **15**–**21**, the reactions were carried out by almost the same procedure of **8** except the conditions of footnote a) in Table 2.

3-Chloro-1-methoxy-6-benzoyloxy-2-hexene (15). Colorless oil: Yield 43% (37% when TiCl₄ was added); E/Z =25:75 (15:85) by ¹H NMR measurement of the olefinic proton; ¹H NMR δ =1.65–2.10 (2H, m), 2.20–2.60 (2H, m), 3.25 (3H, s), 3.85–4.40 (4H, m), 5.30–5.55 (1H, m; *Z*-form), 5.60–5.90 (1H, m; *E*-form), 7.00–7.45 (5H, m); MS (70 eV) m/z 268 (M⁺); Anal. (C₁₄H₁₇ClO₃) C, H. Methyl benzoate was obtained as a by-product in 25% yield, and in 33% yield when TiCl₄ was added.

3-Chloro-1-methoxy-6-phenoxycarbonyloxy-2-hexene (16). Colorless oil: E/Z =30:70 by the same procedure of **15**; IR (film) 1715, 1120 cm⁻¹; ¹H NMR δ =1.65–2.10 (2H, m), 2.20–2.60 (2H, m), 3.25 (3H, s), 3.80–4.30 (4H, m), 5.30–5.60 (1H, m; *Z*-form), 5.60–5.90 (1H, m; *E*-form), 7.00–7.45 (5H, m); MS (70 eV) m/z 284 (M⁺);

Anal. (C₁₄H₁₇ClO₄) C, H. Methyl phenyl carbonate was obtained as a by-product in 13% yield.

3-Chloro-1-methoxy-6-methoxycarbonyloxy-2-hexene (17). Colorless oil: *E/Z*=30:70 determined by the same procedure of **15**; IR (film) 1720, 1120 cm⁻¹; ¹H NMR δ =1.65–2.60 (4H, m), 3.25 (3H, s), 3.70 (3H, s), 3.70–4.25 (4H, m), 5.30–5.60 (1H, m; *Z*-form), 5.60–5.90 (1H, m; *E*-form); MS (70 eV) *m/z* 222 (M⁺); Anal. (C₉H₁₅ClO₄) C, H.

3-Chloro-1-methoxy-5-dimethylcarbamoyloxy-2-pentene (18). Colorless oil: *E/Z*=30:70 determined by the same procedure of **15**; IR (film) 1720, 1650 cm⁻¹; ¹H NMR δ =2.20–2.55 (2H, m), 3.35 (3H, s), 3.70 (3H, s), 4.00–4.40 (4H, m), 5.35–5.65 (1H, m; *Z*-form), 5.60–5.90 (1H, m; *E*-form); Anal. (C₉H₁₆ClNO₃) C, H, N.

3-Chloro-1-methoxy-4-methoxycarbonyloxy-2-pentene (19). Colorless oil: *E/Z*=35:65 determined by the same procedure of **15**; IR (film) 1720, 1120 cm⁻¹; ¹H NMR δ =1.60 (3H, d, *J*=7 Hz), 3.20 (3H, s), 3.70 (3H, s), 3.90–4.30 (2H, m), 4.60 (1H, d, *J*=7 Hz), 5.70–6.00 (1H, m; *Z*-form), 6.00–6.25 (1H, m; *E*-form); Anal. (C₈H₁₃ClO₄) C, H.

3-Chloro-1-methoxy-4-dimethylcarbamoyloxy-2-pentene (20). Colorless oil: Yield 65% (57% when TiCl₄ was added); *E/Z*=30:70 (24:76) by GLC analysis (XE-60; column temp 180 °C); IR (film) 1650, 1120 cm⁻¹; ¹H NMR δ =1.60 (3H, d, *J*=7 Hz), 2.95 (6H, s), 3.35 (3H, s), 4.00–4.30 (2H, m), 4.60–4.75 (1H, m), 5.80–6.15 (1H, m); MS (70 eV) *m/z* 221 (M⁺); Anal. (C₉H₁₆ClNO₃) C, H, N.

4-Chloro-5-methoxymethyl-4-octene (21). Colorless oil: ¹H NMR δ =0.60–1.00 (6H, m), 1.00–1.70 (4H, m), 1.70–2.50 (4H, m), 3.10 (3H, s), 3.85 (2H, s); MS (70 eV) *m/z* 190 (M⁺).

4-Dimethylcarbamoyloxy-1-methoxy-3-pentanone (22). To a stirred solution of mercury(II) trifluoroacetate (447 mg, 1.5 mmol) in trifluoroacetic acid (5 ml), **20** (221 mg, 1.0 mmol) was added at room temperature followed by stirring for 2 h. After removal of trifluoroacetic acid under reduced pressure, the residue was filtered with Celite and extracted with dichloromethane (20 ml×2). The organic phase was washed with water, brine, and dried (Na₂SO₄). Evaporation of dichloromethane followed by purification with silica-gel chromatography (hexane/ether=3:1) gave **22** (125 mg, 62%). Colorless oil; IR (film) 1720, 1650 cm⁻¹; ¹H NMR δ =1.60 (3H, d, *J*=7 Hz), 2.95 (6H, s), 3.20–3.80 (4H, m), 3.35 (3H, s), 5.20 (1H, q, *J*=7 Hz); MS (70 eV) *m/z* 203 (M⁺).

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