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

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Various 1-alkynes were converted to 1-alkoxy-3-chloro-2-alkenes using alkoxymethyl esters and dichlorobis(trifluoromethanesulfonato)titanium(IV) [$TiCl_2(OTf)_2$, 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-phenoxycarbonyloxy-, and 5-methoxycarbonyloxy-1-alkynes. Among them, 3- and 4-dimethylcarbamoyloxy-1-butynes 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 $Sn(OTf)_2$. As a functionalization of the obtained vinyl chloride, 3-chloro-4-dimethylcarbamoyloxy-1-methoxy-2-pentene was converted into the corresponding ketone using $Hg(OCOCF_3)_2$.

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) [$TiCl_2(OTf)_2$, 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 alkoxymethyl 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]

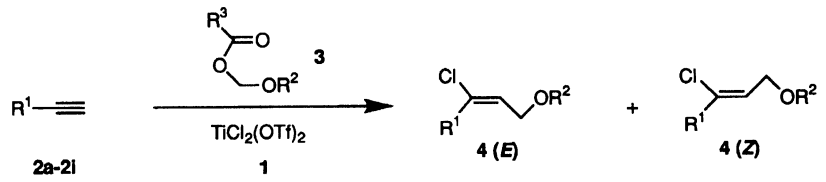
In due consideration, the reaction between 1-alkynes **2** and alkoxymethyl esters **3** promoted by **1** were possibly promising, because the alkoxymethyl cations will be more easily generated than the acyl cations. We report here an effective method for the preparation of 1-alkoxy-3-chloro-2-alkenes **4** from 1-alkynes **2** and alkoxymethyl esters **3**, i.e., a carbon homologation, promoted by titanium(IV) bis(triflate) (**1**) as shown in Scheme 1. Alkoxymethyl 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 dimethylaluminium 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

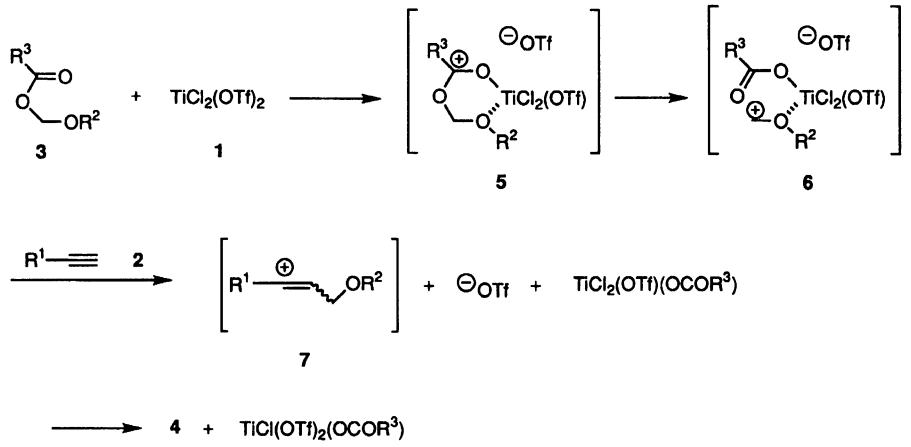
First, the addition reaction of 1-heptyne (**2a**) with methoxymethyl benzoate (**3a**) in the presence of titanium(IV) bis(triflate) (**1**) at 0 °C for an hour gave 3-chloro-1-methoxy-2-octene (**8**) in 75% yield ($E/Z=35:65$) according to Markownikoff's rule. The configurations (*E* or *Z*) of **8**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

A plausible reaction mechanism of the carbon homologation is illustrated in Scheme 2. The alkoxymethyl 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 alkoxymethyl esters **3**



Scheme 1.



Scheme 2.

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

Various alkoxymethyl 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-methoxyl-2-alkenes **13** and **14**, respectively.

The reactions of several 5-benzoyloxy-, 5-phenoxycarbonyloxy-, 3- or 5-methoxycarbonyloxy-, and 3- or 4-dimethylcarbamoyloxy-1-alkynes **2d**—**2i** also proceeded 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 alkoxycarbonyl 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).

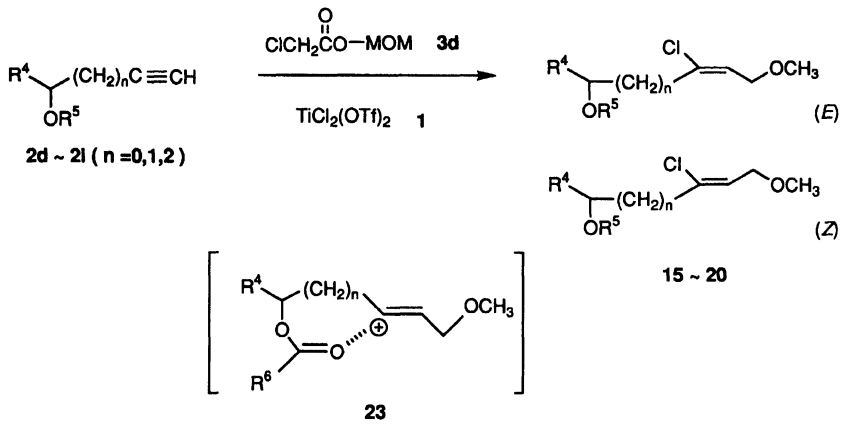
Table 1. Addition Reactions of 1-Heptyne (**2a**) with Alkoxymethyl Esters **3a**—**3h** Promoted by $TiCl_2(OTf)_2$ (**1**)[a]

Entry	Alkoxymethyl ester		Product	Yield/%	E/Z[b]
1	$PhCO_2$–MOM[c]	(**3a**)	**8**	75	40/60
2	$MeCO_2$–MOM	(**3b**)	**8**	62	38/62
3	$PhCH_2CH_2CO_2$–MOM	(**3c**)	**8**	55	38/62
4	$ClCH_2CO_2$–MOM	(**3d**)	**8**	73	35/65
5	$^tBuCO_2$–MOM	(**3e**)	**8**	64	37/63
6	Cl_2CHCO_2–MOM	(**3f**)	**8**	32	31/69
7	$ClCH_2CO_2CH_2OCH_2Ph$	(**3g**)	**11**	35	37/63
8	$ClCH_2CO_2CH_2O^iPr$	(**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- =$MeOCH_2$-.

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 [Sn(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 hydrolysis[10] and di- or tri-substituted olefins by regioselective displacement of the chlorine atom upon treatment with suitable nucleophiles[11] 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

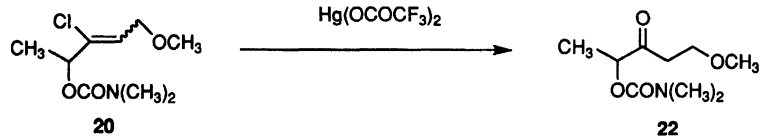


Scheme 3.

Table 2. Addition Reactions of Several Alkynes with Methoxymetyl Chloroacetate (**3d**)[a)]

Entry	Substrate				Product	Yield (%)	E/Z
	n	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_2Ph	(**2e**)	**16**	55	30/70[c)]
6	2	H	CO_2Me	(**2f**)	**17**	56	30/70[c)]
7	1	H	CO_2NMe_2	(**2g**)	**18**	66	30/70[c)]
8	0	H	CO_2Me	(**2h**)	**19**	27	35/65[c)]
9	0	Me	CO_2NMe_2	(**2i**)	**20**	65	30/70[b)]
10[d)]	0	Me	CO_2NMe_2	(**2i**)	**20**	57	24/76[b)]
11	4-Octyne			(**2j**)	**21**	12	—

a) These reactions were carried out in CH_2Cl_2 at 0 °C for an hour and at room temprature 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 $TiCl_4$ vs. the substrate were added to this system.



Scheme 4.

ketone **22** by hydrolysis was examined. Hydrolyses of **22** using H_2SO_4[10a)] and $TiCl_4$[10b)] were first tried, but these reactions gave complex mixtures. When $Hg(OCOCF_3)_2$[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-phenoxycarbonyloxy-, 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 $CDCl_3$. 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) [$TiCl_2(OTf)_2$=titanium(IV) bis-

(triflate) (**1**)] was prepared by the previously reported procedure.[4c] Alkoxymethyl esters **3a**,[12] **3b**,[13] **3d**,[4c] **3e**,[6c] and **3f**[14] 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. ($C_{11}H_{14}O_3$) C, H.

Benzyloxymethyl 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. ($C_{10}H_{11}ClO_3$) 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. ($C_6H_{11}ClO_3$) 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 (Na_2SO_4). 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. ($C_9H_{17}ClO$) C, H.

1-Benzyloxy-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. ($C_{15}H_{21}ClO$) 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. ($C_{11}H_{21}ClO$) 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. ($C_{12}H_{23}ClO$) 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. ($C_{10}H_{17}ClO$) C, H.

4-Pentynyl benzoate (2d). Reaction of 4-pentyn-1-ol and benzoyl chloride in the presence of Et_3N (1.10 equiv) in CH_2Cl_2 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 mm Hg; IR (film) 2120, 1715 cm^{-1}; ^1H NMR δ=1.70—2.40 (5H, m), 4.25 (2H, t, J=7 H), 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-butyn-1-ol and dimetylcarbamoyl 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-butyn-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 $TiCl_4$ 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. ($C_{14}H_{17}ClO_3$) C, H. Methyl benzoate was obtained as a by-product in 25% yield, and in 33% yield when $TiCl_4$ 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. ($C_{14}H_{17}ClO_4$) 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 $\delta=1.65$—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. ($C_9H_{15}ClO_4$) 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 $\delta=2.20$—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. ($C_9H_{16}ClNO_3$) 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 $\delta=1.60$ (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. ($C_8H_{13}ClO_4$) C, H.

3- Chloro- 1- methoxy- 4- dimethylcarbamoyloxy- 2- pentene (20). Colorless oil: Yield 65% (57% when $TiCl_4$ 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 $\delta=1.60$ (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. ($C_9H_{16}ClNO_3$) C, H, N.

4-Chloro-5-methoxymethyl-4-octene (21). Colorless oil: ^1H NMR $\delta=0.60$—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 (Na_2SO_4). 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 $\delta=1.60$ (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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