^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 134.2, 131.1, 129.6, 124.8, 121.4, 50.1, 32.5, 28.1, 25.7, 17.6, 15.9; IR ($CHCl_3$) 3608, 3002, 1489 cm^{-1}; MS (FAB, positive ion, nitrobenzyl alcohol matrix) *m/z* 461 (MH^+, 1), 135 (100); FAB-HRMS calcd for $C_{32}H_{45}O_2$ 461.3420, found 461.3423. Low R_f diastereomer (white solid): mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.72 (s, 4 H, ArH), 4.88 (t, *J* = 6.8 Hz, 2 H, $CHCCH_3$), 4.47 (s, 2 H, ArOH), 2.42 (m, 2 H, ArCH), 2.24 (s, 12 H, $ArCH_3$), 1.79–0.86 (m, 12 H), 1.58 (s, 6 H, (*Z*)-$CHCCH_3$), 1.46 (s, 6 H, (*E*)-$CHCCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 136.4, 130.8, 128.4, 124.9, 122.3, 51.4, 34.1, 27.8, 27.7, 25.6, 17.6, 16.1; IR ($CHCl_3$) 3609, 2930, 1489 cm^{-1}; MS (FAB, positive ion, nitrobenzyl alcohol matrix) *m/z* 461 (MH^+, 1), 161 (25), 135 (100); MS (FAB, negative ion, 1-thioglycerol matrix) *m/z* 461 (MH^-, 52), 147 (100); HRMS (FAB, positive ion, nitrobenzyl alcohol matrix) calcd for $C_{32}H_{45}O_2$ (MH^+) 461.3420 found 461.3397.

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Registry No. **5**, 139229-99-5; **6**, 144180-67-6; **7**, 144180-68-7; **8**, 144180-69-8; **9**, 144180-70-1; **10**, 144180-71-2; **11**, 144180-72-3; (*E*)-**12**, 144180-73-4; (*Z*)-**12**, 144180-66-5; (*E*)-**13**, 144180-74-5; (*Z*)-**13**, 144180-93-8; (*E*)-**14**, 144180-75-6; (*Z*)-**14**, 144180-94-9; (*E*)-**15**, 144180-76-7; (*Z*)-**15**, 144180-95-0; (*E*)-**16**, 144180-77-8; (*Z*)-**16**, 144180-96-1; (*E*)-**17**, 144191-83-3; (*Z*)-**17**, 144191-84-4; **18**, 144180-78-9; **19**, 144180-79-0; **20**, 144180-80-3; **21**, 144180-81-4; **22**, 144180-82-5; *cis*-**23**, 144180-83-6; *trans*-**23**, 144180-97-2; **24**, 144180-84-7; *cis*-**25**, 144180-85-8; *trans*-**25**, 144180-98-3; **26**, 144180-86-9; *cis*-**27**, 144180-87-0; *trans*-**27**, 144180-99-4; (*E*)-**28**, 144180-88-1; (*Z*)-**28**, 144181-01-1; *cis*-**29**, 144180-89-2; *trans*-**29**, 144181-00-0; **30**, 144180-90-5; **32**, 144180-91-6; **32** quinone methide derivative, 144181-03-3; **33** isomer 1, 144180-92-7; **33** isomer 2, 144181-04-4; $Ph_3P{=}CHCO_2Et$, 1099-45-2; $(EtO)_2P(O)CH_2CN$, 2537-48-6; $Ph_3PPr\text{-}i^+$ Br^-, 1530-33-2; δ-valerolactone, 108-29-2; ε-caprolactone, 502-44-3; cyclopentene oxide, 285-67-6; 7-[3,5-dimethyl-4-[(*tert*-butyldimethylsilyl)oxy]phenyl]-2-methyl-2-heptene, 144181-02-2.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra for compounds **6**, **7**, **10**, **11**, **14**, **17**, **21**, **23**, **25**, **27**, **29**, **30**, **32**, and **33** and ^{1}H NMR spectra for compounds **18**, **19**, **20**, **22**, **24**, **26**, **28** (41 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Preparation and Reactivity of the Adducts of Ketene Alkylsilyl Acetals with Ethyl Propiolate in the Presence of Titanium Tetrachloride

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The reaction of ketene alkylsilyl acetals with ethyl propiolate in the presence of $TiCl_4$ led to intermediates whose reactivity was studied with electrophiles such as H_2O, D_2O, NBS, NCS, and PhSeCl to form glutaconate derivatives. Except in the case of the dimethylketene trimethylsilyl acetal, for which the reaction was stereospecific, with other ketene acetals the selectivity was lower. Similar results were observed in the reaction of these titanium intermediates with aldehydes and ketones. The results were interpretated as the formation of vinylic titanium intermediates (more stabilized in the case of the dimethylketene acetal) in equilibrium with the titanium allenolates.

Introduction

Numerous methods have been developed for preparing α-functionalized α,β-ethylenic esters. Among the straightforward procedures to access to such intermediates, the most promising for their simplicity employ the DABCO-catalyzed coupling of aldehydes with acrylates[1] or [α-(alkoxycarbonyl)vinyl]metal derivatives. Various metals have been used for the preparation of these vinylmetal compounds, such as Li,[2] Al,[3] Cu,[4] Sn,[5] Ge,[6] Pb,[7] Zn,[8] Pt,[9] Co,[10] Hg,[2b] Ru,[11] and Pd.[12,13] The most common way to prepare these metallic intermediates is the 1,4-addition of organometallic compounds to 2-alkynoates. Wide synthetic applications of this reaction were made in the case

(1) Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653.
(2) (a) Köbrich, G.; Trapp, H.; Akhtar, A. *Chem. Ber.* **1968**, *101*, 2644. (b) Elbe, H. L.; Köbrich, G. *Tetrahedron Lett.* **1974**, 2557. (c) Pitzcle, B. S.; Baran, J. S.; Steinman, D. H. *J. Org. Chem.* **1975**, *40*, 269. (d) Parham, W. E.; Boykin, D. W. *J. Org. Chem.* **1977**, *42*, 260. (e) Boykin, D. W.; Parham, W. E. *J. Org. Chem.* **1979**, *44*, 424. (f) Feit, B. A.; Melamed, U.; Schmidt, R. R.; Speer, H. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 1329. (g) See also: Adlington, R. M.; Barrett, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, 65.
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(4) (a) Bretting, C.; Munch-Peterson, J.; Jorgensen, P. M. *Acta Chem. Scand.* **1960**, *14*, 151. (b) Corey, E. J.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 1851. (c) Siddall, J. B.; Biskup, M.; Fried, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1853. (d) Klein, J.; Turkel, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 6186.
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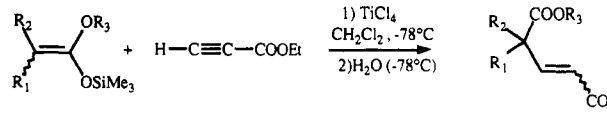
Table I. Reactions of Ketene Alkylsilyl Acetals 1 with Ethyl Propiolate



ketene acetal				product		
no.	R_1	R_2	R_3	no.	*E*:*Z* ratio	yield (%)[a]
1a	H	C_5H_{11}	Me	2a	70:30	75[b]
1b	H	*c*-C_6H_{11}	Me	2b	70:30	88
1c	Me	Me	Me	2c	100:0	81
1d		$-(CH_2)_5-$	Me	2d	80:20	86
1e	Me	Cl	Et	2e	78:22	47

[a] Refers to pure material isolated by liquid chromatography (SiO_2). [b] Reaction time: 0.5 h at −78 °C except for **2e** (7 h).

of copper reagents (mainly mixed cuprates), since the Michael addition was highly stereoselective and led to trisubstituted olefins after hydrolysis of the intermediates.[4,14] The second method, seldom used, consists in the metalation of α-bromoacrylates[14j,15,16] (eq 1).

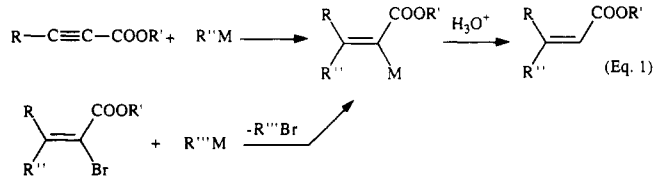
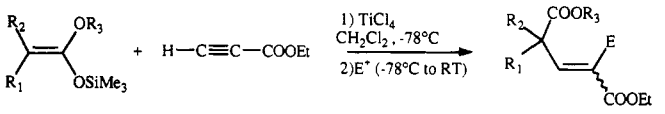


Table II. Reactions of Titanium Intermediates 4 with Electrophiles



ketene acetal	electrophile	glutaconate E	no.	yield (%)[a]	*E*:*Z* ratio
1a	NBS	Br	5a	74	20:80
1c	NBS	Br	5c	86	0:100
1e	NBS	Br	5e	46	20:80
1c	NCS	Cl	6c	71	46:54
1c	PhSeCl	SePh	7c	69	0:100
1a	PhSeCl	SePh	7a	66	20:80

[a] Refers to pure material isolated by liquid chromatography (SiO_2). Yields calculated from ketene acetals 1.

Alkylations of these [α-(alkoxycarbonyl)vinyl]metal derivatives have been reported. [(Alkoxycarbonyl)vinyl]lithium derivatives are more reactive and can be alkylated with alkyl halides,[2d-f,6,17] while [(alkoxycarbonyl)vinyl]copper and -aluminum derivatives are alkylated only with allylic[3a,15b] and (or) propargylic[15b] halides. Alkylations of [(alkoxycarbonyl)vinyl]tin derivatives with allylic halides[18] and of [(alkoxycarbonyl)vinyl]copper derivatives with vinyl and aryl halides[19] are also possible in the presence of palladium(0) complexes. Reactions of more reactive electrophiles such as epoxides, acyl chlorides, aldehydes, or ketones are also reported with [(alkoxycarbonyl)(vinyl]lithium,[2d-f] -copper,[14x,ab] and -aluminum[3b] derivatives.

Results

Our interest in the chemistry of ketene alkylsilyl acetals led us to examine the reactivity of these compounds with various electrophiles such as ketones,[20] acrylonitrile,[21] and chlorocarbenes.[22] Reactions of ketene acetals with propiolic derivatives have been scarcely studied. 1,1-Diethoxyethylene was reported to give a cyclobuteneone acetal by a thermal [2 + 2] cycloaddition.[23] We reported that

(14) Alkylcoppers: (a) Corey, E. J.; Chen, R. H. K. *Tetrahedron Lett.* **1973**, 1611. (b) Anderson, R. J.; Corbin, V. L.; Cotterrell, G.; Cox, G. R.; Henrick, C. A.; Schaub, F.; Siddall, J. B. *J. Am. Chem. Soc.* **1975**, *97*, 1197. (c) Poulter, C. D.; Wiggins, P. L.; Plummer, T. L. *J. Org. Chem.* **1981**, *46*, 1532. (d) Sundberg, R. J.; Pearce, B. C. *J. Org. Chem.* **1982**, *47*, 725. See also ref 19. Lithiocuprates: (e) Rämsby, S. *Acta Chem. Scand.* **1971**, *25*, 1471. (f) Näf, F.; Degen, P. *Helv. Chim. Acta* **1971**, *54*, 1939. (g) Corey, E. J.; Kim, C. U.; Chen, R. H. K.; Takeda, M. *J. Am. Chem. Soc.* **1972**, *94*, 4395. (h) Oida, S.; Ohashi, Y.; Ohki, E. *Chem. Pharm. Bull.* **1973**, *21*, 528. (i) Kluender, H.; Bradley, C. H.; Sih, C. J.; Fawcett, P.; Abraham, E. P. *J. Am. Chem. Soc.* **1973**, *95*, 6149. (j) Klein, J.; Levene, R. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1971. (k) Bowlus, S. B.; Katzenellenbogen, J. A. *Tetrahedron Lett.* **1973**, 1277. Bowlus, S. B.; Katzenellenbogen, J. A. *J. Org. Chem.* **1973**, *38*, 2733. (l) Cooke, M. P. *Tetrahedron Lett.* **1973**, 1281. (m) Carlson, R. M.; Oyler, A. R.; Peterson, J. R. *J. Org. Chem.* **1975**, *40*, 1610. (n) Michelot, D.; Linstrumelle, G. *Tetrahedron Lett.* **1976**, 275. (o) Alexakis, A.; Normant, J.; Villieras, J. *Tetrahedron Lett.* **1976**, 3461. (p) Marino, J. P.; Browne, L. J. *J. Org. Chem.* **1976**, *41*, 3629. (q) Obayashi, M.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1977**, 1807. (r) Alexakis, A.; Cahiez, G.; Normant, J. F.; Villieras, J. *Bull. Soc. Chim. Fr.* **1977**, 693. (s) Piers, E.; Morton, H. E. *J. Org. Chem.* **1980**, *45*, 4263. (t) Keck, G. E.; Nickell, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 3632. (u) Walba, D. M.; Edwards, P. D. *Tetrahedron Lett.* **1980**, *21*, 3531. (v) Alexakis, A.; Cahiez, G.; Normant, J. F. *Tetrahedron* **1980**, *36*, 1961. (w) Miginiac, P.; Daviaud, G.; Gérard, F. *Tetrahedron Lett.* **1979**, 1811. (x) Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1981**, *46*, 3696. (y) Rollinson, S. W.; Amos, R. A.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 4114. (z) Piers, E.; Chong, J. M.; Morton, H. E. *Tetrahedron Lett.* **1981**, *22*, 4905. (aa) Bourgain-Commerçon, M.; Foulon, J. F.; Normant, J. F. *Tetrahedron Lett.* **1983**, *24*, 5077. (ab) Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1983**, *48*, 4621. (ac) Cox, S. D.; Wudl, F. *Organometallics* **1983**, *2*, 184. (ad) Gardette, M.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1985**, *41*, 5887. (ae) Furber, M.; Tayler, R. J. K.; Burford, S. C. *Tetrahedron Lett.* **1985**, *26*, 3285. (af) Foulon, J. F.; Bourgain-Commerçon, M.; Normant, J. F. *Tetrahedron* **1986**, *42*, 1389. (ag) Ernst, L.; Hopf, H.; Krause, N. *J. Org. Chem.* **1987**, *52*, 398. (ah) Linderman, R. J.; Griedel, B. D. *J. Org. Chem.* **1991**, *56*, 5491. (ai) Piers, E.; Fleming, F. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1665. See also ref 5d. Magnesiocuprates: (aj) Liedtke, R. L.; Djerassi, C. *J. Org. Chem.* **1972**, *37*, 2111. (ak) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. lett.* **1981**, 905. (al) Klein, J.; Aminadev, N.; *J. Chem. Soc. C* **1970**, 1380. See also ref 14a,aa,af. Zincocuprates: (am) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1989**, *30*, 4799. (an) Retherford, C.; Chou, T. S.; Schelkun, R. M.; Knochel, P. *Tetrahedron Lett.* **1990**, *31*, 1833. (ao) Chou, T. S.; Knochel, P. *J. Org. Chem.* **1990**, *55*, 4791, 6232. (ap) Berk, S. C.; Yeh, M. C. P.; Jeong, N.; Knochel, P. *Organometallics* **1990**, *9*, 3053. (aq) Knoess, H. P.; Furlong, M. T.; Rozema, M. J.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 5974. (ar) Rozema, M. J.; Sidduri, A.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 1956. Aluminocuprates: (as) Semmelhack, M. F.; Stauffer, R. D. *J. Org. Chem.* **1975**, *40*, 3619. Borocuprates: (at) Yamada, K.; Miyaura, N.; Itoh, M.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3431. (au) Yamamoto, Y.; Yatagai, H.; Muruyama, K. *J. Org. Chem.* **1979**, *44*, 1744.

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(19) Tsuda, T.; Yoshida, T.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 607.

(20) Ali, S. M.; Rousseau, G. *Synlett* **1990**, 397.

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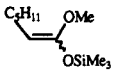
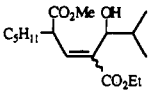
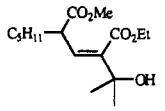
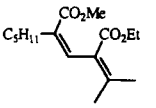
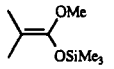
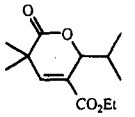
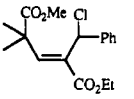
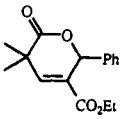
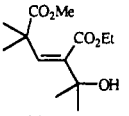
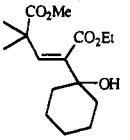
(23) Semmelhack, M. F.; Tomoda, S.; Hurst, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 7568. Semmelhack, M. F.; Tomoda, S.; Nagaoka, H.; Hurst, K. M. *J. Am. Chem. Soc.* **1982**, *104*, 747.

Table III. Reaction of Titanium Intermediates with Carbonyl Compounds

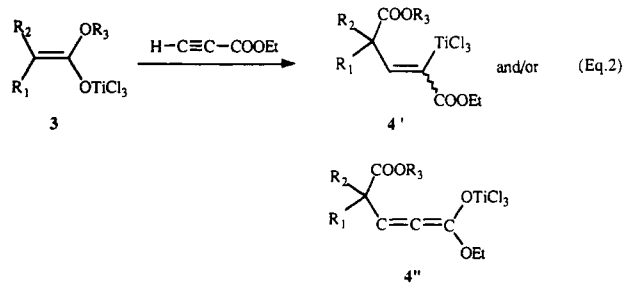
ketene acetal			product(s)			
structure	no.	electrophile[a]	major	no. (yield)	minor	no. (yield)
	1a	iPrCHO		9a (65%)[b]		
	1a	$(CH_3)_2CO$		10a (41%)		10b (26%)
	1c	iPrCHO		11a (56%)		
	1c	PhCHO		12b (47%)[c] 12b (76%)[d]		12a (34%)[c] 12a (4%)[d]
	1c	$(CH_3)_2CO$		13a (70%)		
	1c	$(CH_2)_5CO$		14a (73%)		

[a] The addition of the electrophile to the titanium intermediates was made at −78 °C, and then the reaction flask was slowly warmed to rt. [b] *E*:*Z* ratio 40:60 (mixture of diastereoisomers). [c] Reaction in the presence of 1 equiv of $TiCl_4$. [d] Reaction in the presence of 2 equiv of $TiCl_4$.

with ketene alkylsilyl acetals this cycloaddition took place in the presence of $ZrCl_4$.[8]

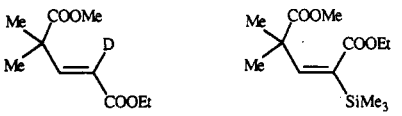
We decided to investigate the reactivity of ketene alkylsilyl acetals 1 with ethyl propiolate.[24] In dichloromethane, in the presence of $TiCl_4$ (30 min) at −78 °C, followed by a quenching with water at this temperature, glutaconates 2 were obtained (see Table I). These products were easily characterized by ^1H NMR and mass spectra. Satisfactory yields were obtained in all cases except with the chloroketene acetal 1e, which reacted slowly. Similarly Kelly and Ghoshal showed that the reaction of dimethylketene methyltrimethylsilyl acetal with propiolic acid gave by reaction with $TiCl_4$ a glutaconate derivative.[25]

We found that the reaction required 1 molar equiv of $TiCl_4$. This fact suggested the formation of titanium intermediates 4' and/or 4", by 1,4-addition of titanium enolates on the triple bond of ethyl propiolate (eq 2).



3 4' 4"

This was confirmed by the fact that D_2O quenching of the reaction mixtures at −78 °C allowed a deuterium incorporation, without modification of the *E*:*Z* ratios (example: glutaconate **2c**-d_2, yield 83%). These intermediates reacted with reactive electrophiles such as NBS, NCS, and phenylselenyl chloride. Results are reported in Table II.



2c-d_2 8c

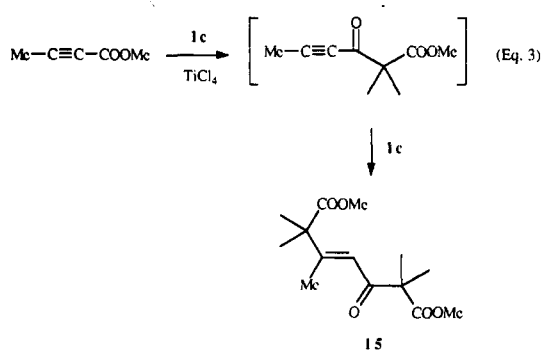
The products were characterized by ^1H NMR spectra, mass spectra, and elemental analysis. The *E*:*Z* ratios were determined from the VPC chromatograms and the ^1H NMR spectra. Interestingly, except with *N*-chlorosuccinimide, *E*:*Z* ratios were similar to those obtained in the respective water quenching reactions. These electrophiles allowed an easy introduction of heteroatoms at the vinyl position of these glutaconates. Other less reactive electrophiles were checked without success: ethylene oxide, methyl iodide, allyl bromide, phenyl isocyanate, isoamyl nitrite, 2,2-dimethoxypropane, and acrylonitrile. Additions of HMPA had no influence in these cases. Chlorotrimethylsilane in the presence of HMPA gave in low yield (20%) the C-silylated compounds **8c**.[8] A more complex reaction was observed with carbonyl compounds. In a preliminary experiment we have checked the reactivity of the titanium intermediate formed from the ketene acetal 1c with acetone and the allylic alcohol **13a** was isolated in moderate yield (Table III).

To improve this result we decided to use *distilled* $TiCl_4$ instead of the *commercial reagent*. In these conditions only the glutaconate **2c** was isolated! We checked titanium tetrachloride ordered from different suppliers and erratic results were obtained. Finally we were able to reproduce our initial result by adding a *catalytic amount of titanium oxide* to the titanium intermediate–ketone mixture formed with purified $TiCl_4$. In these conditions we observed a reaction with aldehydes and ketones. Electrophillic assistance of titanium(IV) oxide to the carbonyl compound

(24) For a preliminary report, see ref 8.
(25) Kelly, T. R.; Ghoshal, M. *J. Am. Chem. Soc.* **1985**, *107*, 3879.

probably increases its reactivity and allows the reaction to take place. Our results are reported in Table III. The reaction of the monoalkylketene acetal **1a** with isobutyraldehyde gave a mixture of *E* and *Z* hydroxy unsaturated diesters **9a**, while with acetone the dienic diester **10b** and the *Z* hydroxy unsaturated ester **10a** were isolated. We could not isolate any isomer posessing the *E* geometry; however we could not exclude the possibility that the dienic ester **10b** came from this one. Quenching of the reaction mixture with aqueous sodium bicarbonate instead of water gave the same result. With the more reactive ketene acetal **1c**, we observed the exclusive formation of *E* isomers with aldehydes and of the *Z* isomers with ketones. With benzaldehyde the primary reaction product was not isolated, and either the lactone **12a** or the chlorinated diester **12b** was isolated. In the presence of an excess of titanium tetrachloride, the lactonization could be almost completely suppressed. With isobutyraldehyde the lactone **11a** was the sole reaction product. The structures of all these compounds were established by ^{1}H NMR, IR, mass spectra, and elemental analysis. The correct stereochemistries of compounds **5a–c**, **6c**, **7c**, **9a**, **10a**, **13a**, and **14a** were determined by comparison of the ^{1}H NMR chemical shift of the vinyl proton with the value calculated for the two isomers. For example, the calculated shift values[26] of the vinylic hydrogen of *Z*-**9a** and *E*-**9a** were respectively δ 6.05 and 6.75 and the experimental values were respectively δ 6.20 and 6.85. Furthermore the lactonization of **10a**, **13a**, and **14a** was attempted without success (acidic and basic conditions). The fact that the lactone **11a** was isolated during the reaction of the ketene acetal **1c** with isobutyraldehyde and the *E* γ-hydroxy ester **9a** for the reaction of the ketene acetal **1a** with the same aldehyde is probably a consequence of the *gem*-dimethyl effect.[27]

The addition of the titanium enolate **3c** was also attempeted with methyl 2-butynoate. In the conditions used with ethyl propiolate, the sole isolated product was the enone **15** (22% yield, stereochemistry not assigned). We can explain the formation of this compound by the 1,2-addition of the ketene acetal **1a** on the acetylenic ester, followed by an 1,4-addition of the same ketene acetal on the triple bond of the intermediate ynone (eq 3).



(Eq. 3)

15

Discussion

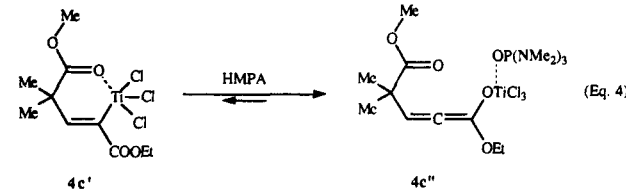
Structure of [α-(alkoxycarbonyl)vinyl]metals is still subject to discussion. Allenolates were proposed in the case of lithium[14j] and copper[14ab,28] compounds, while a vinylic structure was proposed for aluminum ones.[3b] With titanium, an allenolate structure seems, a priori, probable by comparison with the structure of titanium enolates.[29] However our experiments on the hydrolysis of the intermediates and the type of products isolated in the reaction with electrophiles argued against such structures. Indeed, these reactions should lead at least to a mixture of ethylenic compounds in which the *E* isomer should be major in the reaction with water and the *Z* isomer should be major with other electrophiles,[14ab] due to steric consideration in their approach. Further studies on the hydrolysis of the titanium intermediate **4c** are reported in Table IV.

Table IV. Hydrolysis Studies of the Titanium Enolate 4c

expt	reaction and quenching conditions	*E*:*Z* ratio in 2c	yield (%)
1	−78 °C, 30 min then H_2O (−78 °C)	100:0[a]	81
2	−78 °C, 2 h then H_2O (−78 °C)	100:0	80
3	−78 °C, 30 min then aq $NaHCO_3$ (−78 °C)	100:0[a]	82
4	−78 °C, 30 min then HMPA (5 min −78 °C) and H_2O (−78 °C)	47:53[a]	78
5	−78 °C, 30 min then HMPA (2 h, −78 °C) and H_2O (−78 °C)	47:53[a]	78
6	−78 °C, 30 min then warming at 0 °C and H_2O	60:40	40

[a] Quenching with D_2O gave the same ratio.

A loss of stereoselectivity was observed when the hydrolysis of the enoate **4c** was run in the presence of HMPA (experiments 4 and 5) or when the temperature of the reaction mixture was increased (experiment 6) before the quenching. To explain these results we can postulate the existence of the vinylic structure **4c′**, stable only at low temperature, stabilized by an interaction between the titanium atom and the carbonyl of the ester function. Addition of HMPA, or raising of the temperature of the reaction mixture, could favor the allenolate structure **4c″** and explain the selectivity observed after hydrolysis (eq 4).



(Eq. 4)

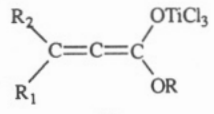
4c′ 4c″

In the same way with reactive electrophiles, such as NBS or PhSeCl, the reaction probably occurred at low temperature and should explain the good selectivity of the reaction (Table II), while with the less reactive NCS we observed a loss of selectivity due to the fact that the reaction occurred at higher temperature. The *Z* stereochemistry of the products observed during the reaction of the titanium intermediate **4c** with aldehydes (Table III) is probably also due to the fact that the reaction occurred at low temperature (reaction of **4c′**), while with the less reactive ketones the reaction occurred only at higher temperature (reaction of **4c″**). The exclusive *E* stereochemistry observed in this case could be due to steric interactions during the approach of the ketone to the allenolate **4c″**. A similar result had been reported with copper allenolates.[14ab] The hydrolysis of other titanium intermediates **4a**, **4b**, **4d**, and **4e** studied was less selective (Table I). We conclude that the stabilization of the vinylic intermediates **4′** is less effective and the proportion of allenolates is more important.[30] This difference can be attributed to the *gem*-dimethyl effect present in the inter-

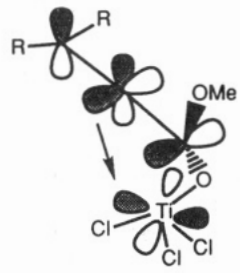
(26) Schraml, J.; Chvalovsky, V. *Collect. Czech. Chem. Commun.* **1970**, *35*, 709. Beeby, J.; Drake, L.; Duffin, R.; Sternell, S. *Org. Magn. Reson.* **1973**, *5*, 163. See also ref 14c.
(27) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.
(28) Krause, N. *Tetrahedron Lett.* **1989**, *30*, 5219.
(29) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer Verlag: Berlin, 1986.
(30) Work is under progress to verify spectroscopically these hypotheses.

mediate **4c**. The absence of specificity in the reaction of the intermediate **4a** (Table III), formed by reaction of the ketene acetal **1a** with ethyl propiolate and $TiCl_4$, with isobutyraldehyde suggests at the reaction temperature, an allenolate structure of the titanium intermediate.

Another less probable explanation of these results should be the unique formation of an allenolate, as suggested by Krause in the case of copper,[28] stabilized by interaction between the π system of the allenolate and unoccupied orbitals of the titanium atom, this weak stabilization being cancelled by addition of HMPA or warming of the reaction mixture.



16



In conclusion, we can tentatively conclude that the structure of simple organotitanium intermediates probably resembles an allenolate form **16** rather than an [α-(alkoxycarbonyl)vinyl]titanium form, the vinylic form being probably favored, in the cases reported here by the presence of a second ester function and for **4c** reinforced by the *gem*-dimethyl effect. Titanium derivatives **4** appear less reactive than the corresponding lithium,[2] copper,[14ab,19] and aluminum[3] derivatives.

Experimental Section

General.[1] H NMR spectra were recorded at 250 MHz. Mass spectra were determined at an ionizing voltage of 70 eV. Melting points were determined on a Reichert microscope. GC analyses were recorded with a 10% SE-30 2-m column. Column chromatography was performed with silica gel (70–230 mesh). TLC was performed on 0.25-mm silica gel (Merck 60 F_{254}). Dry solvents were obtained as followed: diethyl ether was distilled over $LiAlH_4$, THF over sodium benzophenone, and hexane over P_2O_5. Diisopropylamine was purified by distillation over CaH_2 and chlorotrimethylsilane by distillation over quinoline under argon. Other reagents were distilled before used. Ketene acetals **1a–e** have been prepared following a standard procedure.[31] All reactions were conducted under argon.

Preparation of Glutaconates 2a–c: Representative Procedure. To a solution of $TiCl_4$ (0.569 g, 3 mmol) in CH_2Cl_2 (8 mL) at −78 °C was added ethyl propiolate (0.441 g, 4.5 mmol), followed by the ketene acetal **1a** (0.649 g, 3 mmol) in solution in CH_2Cl_2 (3 mL). The reaction mixture was stirred 0.5 h and then quenched with water (7 mL). The mixture was vigorously stirred and warmed at rt. The organic layer was removed and the aqueous phase was extracted with ether (3 × 8 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Purification of the residue by silica gel column chromatography (hexane–ether 70:30) afforded liquid glutaconate **2a** (0.54 g, 75%) as a mixture of *E* and *Z* isomers (see Table I for the ratio). An analytical sample was then obtained by distillation under vacuum.

(*E*)- and (*Z*)-Ethyl 4-Carbomethoxy-2-nonenoates (2a). IR (neat) cm^{-1}: 1745, 1725 (CO), 1660 (CC). ^1H NMR δ: 0.80 (m, 5 H), 1.05–1.32 (m, 7 H), 1.58 (m, 1 H), 1.78 (m, 1 H), 3.15 (dt, J = 8.3 16.67 Hz, 1 H), 3.65 (s, 3 H), 4.15 (q, J = 6.0 Hz, 2 H), 5.80 (d, J = 8.3 Hz, 0.3H (*Z* isomer)), 5.85 (d, J = 13.9 Hz, 0.7 H (E isomer)), 6.20 (t, J = 8.3 Hz, 0.3H (*Z* isomer)), 6.85 (dd, J = 13.9 and 8.3 Hz, 0.7 H (*E* isomer)). MS: m/e 242 (M^+, 12.4), 197, 185, 171, 140, 126, 113, 109 (100), 95, 81, 67, 55, 43. Anal. Calcd for $C_{13}H_{22}O_4$: C, 64.42; H, 9.16. Found: C, 64.60; H, 9.27.

(*E*)- and (*Z*)-Ethyl 4-Carbomethoxy-4-cyclohexyl-2-butenoates (2b). Yield: 0.670 g (88%). IR (neat) cm^{-1}: 1745, 1730 (CO), 1660 (CC). ^1H NMR δ: 0.85–1.20 (m, 6 H), 1.28 (t, J = 6.0 Hz, 3 H), 1.50–1.70 (m, 5 H), 2.90 (dd, J = 10.0 Hz, 1 H), 3.68 (s, 3 H), 4.18 (q, J = 6.0 Hz, 2 H), 5.85 (d, J = 15.0 Hz, 0.7 H (E isomer)), 5.92 (d, J = 10.0 Hz, 0.3 H (*Z* isomer)), 6.28 (t, J = 10.0 Hz, 0.3 H (*Z* isomer)), 6.90 (dd, J = 10.0 and 15 Hz, 0.7 H (*E* isomer)). MS: m/e 254 (M^+, 3.1), 222, 194, 172, 140, 126 (100), 112, 98, 83, 79, 67, 55, 41. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.10; H, 8.72. Found: C, 66.30; H, 8.95.

(*E*)-Ethyl 4-Carbomethoxy-4-methyl-2-pentenoate (2c). Yield: 0.486 g (81%). IR (neat) cm^{-1}: 1740, 1725 (CO), 1655 (CC). ^1H NMR δ: 1.22 (t, J = 6.0 Hz, 3 H), 1.28 (s, 6 H), 3.65 (s, 3 H), 4.15 (q, J = 6.0 Hz, 2 H), 5.78 (d, J = 17.5 Hz, 1 H), 7.05 (d, J = 17.5 Hz, 1 H). MS: m/e 200 (M^+, 1.2), 141 (100), 127, 113, 95, 85, 67, 59, 41. Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.97; H, 8.06. Found: C, 60.12; H, 8.12.

(*E*)- and (*Z*)-Ethyl (1-Carbomethoxycyclohexyl)-2-propenoates (2d). Yield: 0.619 g (86%). IR (neat) cm^{-1}: 1745, 1730 (CO), 1650 (CC). ^1H NMR δ: 1.30 (t, J = 6.0 Hz, 3 H), 1.32–1.70 (m, 6 H), 1.85–1.95 (m, 4 H), 3.70 (s, 3 H), 4.18 (q, J = 6.0 Hz, 2 H), 5.85 (d, J = 17.4 Hz, 0.8 H (*E* isomer)), 5.88 (d, J = 13.0 Hz, 0.2 H (*Z* isomer)), 6.30 (d, J = 13.0 Hz, 0.2 H (*Z* isomer)), 6.85 (d, J = 17.4 Hz, 0.8 H (*E* isomer)). MS: m/e 240 (M^+, 3.7), 208, 181, 167, 162, 135 (100), 117, 107, 91, 72, 67, 55, 41. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.96; H, 8.39. Found: C, 65.21; H, 8.25.

(*E*)- and (*Z*)-Diethyl 4-Chloro-4-methyl-2-pentenedioates (2e). Yield: 0.331 g (47%). IR (neat) cm^{-1}: 1750, 1730 (CO), 1660 (CC). ^1H NMR δ: 1.30 (2 t, J = 6.0 Hz, 6 H), 1.90 (s, 3 H), 4.25 (2 q, J = 6.0 Hz, 4 H), 5.82 (d, J = 11.8 Hz, 0.22 H (*Z* isomer)), 6.15 (d, J = 16.5 Hz, 0.78 H (*E* isomer)), 6.51 (d, J = 11.8 Hz, 0.22 H (*Z* isomer)), 7.12 (d, J = 16.5 Hz, 0.78 H (*E* isomer)). MS: m/e 199 (M^+ − Cl, 48), 289, 162, 161, 136, 134 (100), 116, 105, 97, 89, 53, 43. Anal. Calcd for $C_{10}H_{15}ClO_4$: C, 51.27; H, 6.46. Found: C, 51.40; H, 6.59.

(*E*)-Ethyl 4-Carbomethoxy-4-methyl-2-pentenoate-2-d_1 (2c-d_2). Yield: 0.490 g (82%). IR (neat) cm^{-1}: 1740, 1720 (CO), 1640 (CC). ^1H NMR δ: 1.22 (t, J = 6.0 Hz, 3 H), 1.28 (s, 6 H), 3.65 (s, 3 H), 4.20 (q, J = 6.0 Hz, 2 H), 7.02 (s, 1 H). MS: m/e 201 (M^+, 1.0), 156, 142 (100), 128, 114, 96, 68, 59.

Preparation of Glutaconates 5a, 5c, 5e, 6c, and 7c: Representative Procedure. To a solution of $TiCl_4$ (0.569 g, 3 mmol) in CH_2Cl_2 (8 mL) at −78 °C under argon was added ethyl propiolate (0.441 g, 4.5 mmol), followed by the ketene acetal **1a** (0.649 g, 3 mmol) in solution in CH_2Cl_2 (3 mL). After 30 min at −78 °C NBS (0.641 g, 3.6 mmol) was added, and the flask was maintained 1 h more at this temperature. The cooling bath was removed and water (10 mL) was added at rt. The organic phase was separated and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Purification of the residue by silica gel column chromatography (hexane–ether 80:20) afforded glutaconate **5a** (0.713 g, 74%) as a mixture of *E* and *Z* isomers (see Table II for the ratio). Glutaconates **5c**, **5e**, **6c**, and **7c** were similary prepared. For **6c** the addition of NBS was made at −60 °C and the flask maintained 3 h at this temperature.

(*E*)- and (*Z*)-Ethyl 2-Bromo-4-carbomethoxy-2-nonenoates (5a). IR (neat) cm^{-1}: 1745, 1725 (CO), 1630 (CC). ^1H NMR δ: 0.90 (m, 5 H), 1.20–1.45 (m, 7 H), 1.55–1.95 (m, 2 H), 3.65 (m, 1 H), 3.70 (s, 3 H), 4.30 (q, J = 6.0 Hz, 2 H), 6.72 (d, J = 9.8 Hz, 0.2 H (*E* isomer)), 7.35 (d, J = 9.8 Hz, 0.8H (*Z* isomer)). MS: m/e 241 (M^+ − Br, 100), 206, 195, 163, 142, 107, 95, 87, 69, 59, 55, 43. Anal. Calcd for $C_{13}H_{21}BrO_4$: C, 48.74; H, 6.61; Br, 24.66. Found: C, 48.81; H, 6.43; Br, 24.40.

(*E*)-Ethyl 2-Bromo-4-carbomethoxy-4-methyl-2-pentenoate (5c). Yield: 0.720 g (86%). IR (neat) cm^{-1}: 1740, 1720 (CO), 1625 (CC). ^1H NMR δ: 1.35 (t, J = 6.0 Hz, 3 H), 1.45 (s, 6 H), 3.72 (s, 3 H), 4.30 (q, J = 6.0 Hz, 2 H), 7.42 (s, 1 H). MS: m/e 280, 278 (M^+, 0.2, 0.0), 221, 199 (100), 193, 181, 173, 153, 111, 67, 59, 41. Anal. CAlcd for $C_{10}H_{15}BrO_4$: C, 43.16; H, 5.44; Br, 28.63. Found: C, 43.33; H, 5.52; Br, 28.30.

(*E*)- and (*Z*)-Diethyl 2-Bromo-4-chloro-4-methyl-2-pentenedioates (5e). Yield: 0.433 g (46%). IR (neat) cm^{-1}: 1740, 1725 (CO), 1625 (CC). ^1H NMR δ: 1.35 (2 t, J = 6.0 Hz, 6 H), 1.98 (s, 3 H), 4.28 (2 q, J = 6.0 Hz, 4 H), 7.10 (s, 0.2 H (*E* isomer)),

(31) Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organometal. Chem.* **1972**, *46*, 59.

7.70 (s, 0.8 H (*Z* isomer)). MS: *m/e* 279, 277 (M^+ – Cl, 8.4, 7.8), 239, 214, 213, 177, 175 (100), 131, 97, 87, 51, 43. Anal. Calcd for $C_{10}H_{14}BrClO_4$: C, 38.46; H, 4.52. Found: C, 38.10; H, 4.30.

(*E*)- and (*Z*)-Ethyl 4-Carbomethoxy-2-chloro-4-methyl-2-pentenoates (6c). Yield: 0.500 g (71%). IR (neat) cm^{-1}: 1750, 1730 (CO), 1630 (CC). ^1H NMR δ: 1.35 (t, *J* = 6.0, 3 H), 1.45 (s, 6 H), 3.72 (s, 3 H), 4.30 (q, *J* = 6.0 Hz, 2 H), 6.40 (s, 0.46 H (*E* isomer)), 7.12 (s, 0.54 H (*Z* isomer)). MS: *m/e* 199 (M^+ – Cl, 100), 175, 147, 131, 129, 111, 101, 65, 59, 41. Anal. Calcd for $C_{10}H_{15}ClO_4$: C, 51.27; H, 6.46. Found: C, 51.41; H, 6.18.

(*Z*)-Ethyl 4-Carbomethoxy-2-(phenylseleno)-2-nonenoate (7a). Yield: 0.789 g (66% for the *E*/*Z* mixture). IR (neat) cm^{-1}: 1750, 1720 (CO), 1615 (CC). ^1H NMR δ: 0.89 (m, 5 H), 1.10 (t, *J* = 6.0 Hz, 3 H), 1.20 (m, 4 H), 1.50–1.80 (m, 1 H), 1.80–2.00 (m, 1 H), 3.69 (s, 3 H), 3.90 (m, 1 H), 4.20 (q, *J* = 6.0 Hz, 2 H), 7.25–7.55 (m, 6 H). MS: *m/e* 398, 396 (M^+, 59, 30) 366, 352, 293, 241, 195, 157, 135, 115, 107, 105 (100), 91, 77, 55. Anal. Calcd for $C_{19}H_{26}O_4Se$: C, 57.27; H, 6.58. Found: C, 57.51; H, 6.36.

(*Z*)-Ethyl 4-Carbomethoxy-4-methyl-2-(phenylseleno)-2-pentenoate (7c). Yield: 0.736 g (69%). IR (neat) cm^{-1}: 1745, 1720 (CO), 1615 (CC). ^1H NMR δ: 1.00 (t, *J* = 6.0 Hz, 3 H), 1.48 (s, 6 H), 3.62 (s, 3 H), 4.03 (q, *J* = 6.0 Hz, 2 H), 7.15–7.38 (m, 5 H), 7.41 (s, 1 H). MS: *m/e* 354–356 (M^+, 11.2, 24.6), 251, 223, 199 (100), 181, 171, 153, 142, 125, 111, 105, 91, 78, 77, 66, 59, 41. Anal. Calcd for $C_{16}H_{20}O_4Se$: C, 53.92; H, 5.66. Found: C, 54.24; H, 5.57.

(*E*)-Ethyl 4-Carbomethoxy-4-methyl-2-(trimethylsilyl)-2-pentenoate (8c). To a solution of $TiCl_4$ (0.569 g, 3 mmol) in CH_2Cl_2 (8 mL) at –78 °C was added ethyl propiolate (0.441 g, 4.5 mmol), followed by the ketene acetal **1a** (0.438 g, 3 mmol) in solution in CH_2Cl_2 (3 mL). After 30 min at –78 °C a mixture of $ClSiMe_3$ (0.490 g, 4.5 mmol) and HMPA (1.04 mL, 6 mmol) was added. The mixture was stirred 15 min at –78 °C, and then the cooling bath was removed and water (5 mL) was added at rt. The organic phase was separated and the aqueous phase extracted with ether (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Purification of the residue by silicagel column chromatography (hexane–ether 80:20) afforded 0.18 g (22%) of **8c** and 0.06 g (10%) of (*Z*)-**2c**. A workup following the procedure of Marino et al.[15x] gave the same **2c**–**8c** mixture (20%). IR (neat) cm^{-1}: 1745, 1720 (CO), 1610 (CC). ^1H NMR δ: 0.15 (s, 9 H), 1.25 (t, *J* = 6.0 Hz, 3 H), 1.35 (s, 6 H), 3.60 (s, 3 H), 4.10 (q, *J* = 6.0 Hz, 2 H), 6.00 (s, 1 H).

Reaction of the Titanium Intermediates 4a and 4c with Carbonyl Compounds: Representative Procedure. To a solution of $TiCl_4$ (0.569 g, 3 mmol) in CH_2Cl_2 (8 mL) at –78 °C was added ethyl propiolate (0.441 g, 4.5 mmol), followed by the ketene acetal **1c** (0.649 g, 3 mmol) in solution in CH_2Cl_2 (3 mL). After 30 min at this temperature isobutyraldehyde was added (0.216 g, 3 mmol) followed by 10 mg of TiO_2. After 1 h more at –78 °C, the cooling bath was removed and water was added at rt. The organic phase was separated and the aqueous phase extracted with ether (3 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Purification of the residue by silica gel column chromatography (hexane–ether 80:20 to 50:50 afforded 0.613 g (65%) of compound **9a** as a mixture of *E* and *Z* isomers (see Table III for ratio).

(*E*)- and (*Z*)-Ethyl 4-Carbomethoxy-2-(1-hydroxy-2-methylpropyl)-2-nonenoates (9a). IR (neat) cm^{-1}: 3500 (OH), 1745, 1725 (CO), 1650 (*Z* isomer) or 1645 (*E* isomer) (CC). ^1H NMR δ: 0.75 (*d*, *J* = 6.6 (*Z* isomer) or 6.8 Hz (*E* isomer), 3 H), 0.90 (*Z* isomer) or 0.85 (*E* isomer) (m, 3 H), 1.05 (d, *J* = 6.6 (*Z* isomer) or 6.8 Hz (*E* isomer), 3 H), 1.15–145 (m, 11 H), 1.60 (m, 1 H), 2.45–2.70 (m, 1 H), 3.60 (s, 3 H (*E* isomer)), 3.65 (s, 3 H and m, 1 H (*Z* isomer)), 3.45 (dt, *J* = 13.3 and 18.2 Hz, 1 H (*E* isomer)), 4.00 (d, *J* = 6.6 (*Z* isomer) or 5.9 Hz (*E* isomer), 1 H), 4.20 (*Z* isomer) or 4.25 (*E* isomer) (q, *J* = 6.0 Hz, 2 H), 6.05 (*Z* isomer) (d, *J* = 9.9 Hz, 1 H) or 6.75 (*E* isomer) (d, *J* = 13.3 Hz, 1 H). MS (*Z* isomer): *m/e* 297 (M^+ – OH, 0.2), 169, 141, 113, 97 (100), 70, 67, 55, 41. MS (*E* isomer): *m/e* 297 (M^+ – OH, 0.4), 225, 211, 193, 167, 95, 67, 55, 43, 41. Anal. Calcd for $C_{17}H_{30}O_5$ (*Z* isomer): C, 64.92; H, 9.62. Found: C, 65.21; H, 9.81.

(*E*)-Ethyl 4-Carbomethoxy-2-(1-hydroxy-1-methylethyl)-2-nonenoate (10a). Yield: 0.370 g (41%); IR (neat) cm^{-1}: 3450 (OH), 1740, 1720 (CO), 1650 (CC). ^1H NMR δ: 0.86 (m, 3 H), 1.20–1.38 (m, 9 H), 1.42 (s, 6 H), 1.50–1.90 (m, 2 H), 2.73 (bs, 1 H), 3.44 (dt, *J* = 6.8 Hz and 10.6 Hz, 1 H), 3.67 (s, 3 H), 4.28 (q, *J* = 7 Hz, 2 H), 6.00 (d, *J* = 10.6 Hz, 1 H). Anal. Calcd for $C_{16}H_{28}O_5$: C, 63.96; H, 9.40. Found: C, 64.12; H, 9.53.

(*Z*)-Ethyl 4-Carbomethoxy-2-ethylidene-3-nonenoate (10b). Yield: 0.220 g (26%); IR (neat) cm^{-1}: 1725 (CO), 1635 (CC). ^1H NMR δ: 0.86 (m, 3 H), 1.10–1.60 (m, 9 H), 1.84 (s, 3 H), 2.10 (s, 3 H), 2.35 (t, *J* = 7.0 Hz, 2 H), 3.67 (s, 3 H), 4.13 (q, *J* = 6.0 Hz, 2 H), 6.47 (s, 1 H). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.04; H, 9.29. Found: C, 68.29; H, 9.25.

4-Carboethoxy-2,2,6-trimethyl-3-hepten-5-olide (11a). Yield: 0.403 g (56%). Solid mp: 68 °C. IR ($CDCl_3$) cm^{-1}: 1800, 1720 (CO), 1650 (CC). ^1H NMR δ: 0.80 (d, *J* = 4.4 Hz, 3 H), 1.10 (d, *J* = 5.6 Hz, 3 H), 1.32 (t, *J* = 7 Hz, 3 H), 1.38 (s, 6 H), 2.12 (m, 1 H), 4.25 (q, *J* = 7 Hz, 2 H), 5.18 (d, 1 H), 6.70 (s, 1 H). MS: *m/e* 240 (M^+, 9.5), 198, 197 (100), 183, 170, 124, 97, 67, 55, 41. Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.96; H, 8.39. Found: C, 64.85; H, 8.43.

4-Carboethoxy-2,2-dimethyl-5-phenyl-3-penten-5-olide (12a). Yield: 0.280 g (34%). Solid mp: 64 °C. IR ($CDCl_3$) cm^{-1}: 1795, 1725 (CO). ^1H NMR δ: 1.25 (t, *J* = 7.0 Hz, 3 H), 1.45 (s, 3 H), 1.55 (s, 3 H), 4.25 (q, *J* = 7.0 Hz, 2 H), 6.40 (s, 1 H), 7.05 (s, 1 H), 7.45 (m, 5 H). MS: *m/e* 274 (M^+, 21.8), 246, 200, 157, 141, 122, 115, 105 (100), 77, 51. Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 6.62. Found: C, 70.10; H, 6.59.

(*Z*)-Ethyl 4-Carbomethoxy-2-(chlorobenzyl)-4-methyl-2-pentenoate (12b). Yield: 0.457 g (47%). IR (neat) cm^{-1}: 1735, 1720 (CO), 1655 (CC). ^1H NMR δ: 1.05 (t, *J* = 7.0 Hz, 3 H), 1.25 (s, 3 H), 1.35 (s, 3 H), 3.70 (s, 3 H), 4.05 (q, *J* = 7.0 Hz, 2 H), 5.40 (s, 1 H), 7.15 (s, 1 H), 7.30 (m, 5 H). MS: *m/e* 324 (M^+, 0.5), 289, 223, 187, 159, 143, 135, 115 (100), 91, 79, 59. Anal. Calcd for $C_{17}H_{21}O_4Cl$: C, 62.94; H, 6.53; Cl, 10.79. Found: C, 63.20; H, 6.59; Cl, 10.50.

(*Z*)-Ethyl 4-Carbomethoxy-2-(1-hydroxy-1-methylethyl)-4-methyl-2-pentenoate (13a). Yield: 0.542 g (70%); IR (neat) cm^{-1}: 3620–3230 (OH), 1745, 1720 (CO), 1630 (CC). ^1H NMR δ: 1.30 (t, *J* = 7.0 Hz, 3 H), 1.35 (s, 6 H), 1.42 (s, 6 H), 2.75–3.32 (m, 1 H), 3.62 (s, 3 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 5.95 (s, 1 H). MS: *m/e* 243 (M^+ – 15, 23.3), 197 (100), 169, 153, 137 (100), 125, 111, 107, 95, 67, 59, 43. Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.43; H, 8.59. Found: C, 60.57, H, 8.43.

(*Z*)-Ethyl 4-Carbomethoxy-2-(1-hydroxycyclohexyl)-4-methyl-2-pentenoate (14a). Yield: 0.652 g (73%); IR (neat) cm^{-1}: 3620–3230 (OH), 1745, 1720 (CO), 1745 (CC). ^1H NMR δ: 1.28 (t, *J* = 7.0 Hz, 3 H), 1.35 (s, 6 H), 1.38–1.78 (m, 10 H), 2.78–2.95 (m, 1 H), 3.62 (s, 3 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 5.88 (s, 1 H). MS: *m/e* 298 (M^+, 4.5), 197 (100), 151, 147, 123, 95, 81, 69, 55, 41. Anal. Calcd for $C_{16}H_{26}O_5$: C, 64.39; H, 8.79. Found: C, 64.50; H, 8.89.

Preparation of 15. The reaction of methyl 2-butynoate with ketene acetal **1c** and $TiCl_4$ was conducted in the same conditions than with ethyl propiolate except that the quenching with water was made at –20 °C. Chromatography on silica gel (ether-hexane 30–70 to 50–50) gave 0.178 g (22%) of methyl 6-carbomethoxy-3-oxo-2,2,5,6-tetramethyl-4-heptenoate (**15**): IR (neat) cm^{-1}: 1750, 1715 (CO), 1615 (CC). ^1H NMR δ: 1.35 (s, 6 H), 1.38 (s, 6 H), 1.98 (s, 3 H), 3.58 (s, 3 H), 3.70 (s, 3 H), 6.10 (s, 1 H). MS: *m/e* 239, 169, 141, 109 (100), 81, 73, 67, 59, 53, 41. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.19; H, 8.21. Found: C, 62.39; H, 8.09.