Intramolecular Nucleophilic Acyl Substitution Reactions Mediated by XTi(O-*i*-Pr)$_3$ (X = Cl, O-*i*-Pr)/2*i*-PrMgBr Reagent. Efficient Synthesis of Functionalized Organotitanium Compounds from Unsaturated Compounds

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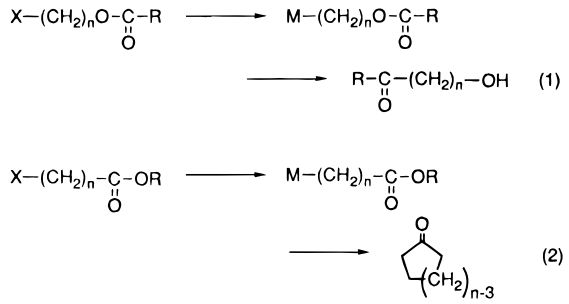
Abstract: Treatment of acetylenic or olefinic carbonates and esters with a low-valent titanium reagent diisopropoxy-(η^2-propene)titanium (**1**), readily generated by the reaction of Ti(O-*i*-Pr)$_4$ or ClTi(O-*i*-Pr)$_3$ with 2*i*-PrMgX, resulted in an intramolecular nucleophilic acyl substitution (INAS) reaction to afford organotitanium compounds having a carbonyl functional group, in good to excellent yields. Thus, the treatment of alkyl alkynyl carbonates **2** or alkyl alkenyl carbonates **4** with **1** gave organotitanium compounds having a lactone and/or ester group. Similarly, alkyl alkynoates **10** or alkynyl esters **14** of carboxylic acids reacted with **1** to give organotitanium compounds having a cyclic or acyclic ketone group, respectively. Thus, the reaction provides, after hydrolysis, five- or six-membered α-alkylidene lactones and/or α,β-unsaturated esters from **2**, γ-butyrolactone derivatives from **4**, five- or six-membered α-alkylidene cyclic ketones from **10**, and acyclic α,β-unsaturated ketones **15** from **14**. In all cases, the yields are excellent and the generation of the organotitanium compounds was confirmed by deuterolysis. The organotitaniums **6** and **11c** reacted smoothly with iodine to afford 2-(iodomethyl)-4-butanolide (**9**) and α-[iodo(trimethylsilyl)-methylidene]cyclopentanone, respectively. The organotitanium compounds obtained here also reacted with aldehydes to give the corresponding adducts, thus opening up a new access to substituted α,β-butenolides from **2**, to γ-butyrolactones from **4**, and to the corresponding tetrasubstituted furan from **10** and **14**.

Intramolecular nucleophilic acyl substitution (INAS) reactions can be classified into two types: one which enables the transfer of carbon fragments from oxygen to carbon as represented in eq 1 and the other which affords cyclic ketones from acyclic esters and related compounds as shown in eq 2. In spite of their high synthetic potential,[2] however, INAS reactions are rather rare because of the intrinsic difficulty entailed in carrying them out. One of the difficulties associated with INAS reactions is that a reactive nucleophilic species must be generated in the presence of a carbonyl functional group, and at the same time this nucleophile is expected to react only with the carbonyl group in an intramolecular fashion, but not intermolecularly, with the one present in the reaction product. Organometallics such as zinc and boron compounds lack the nucleophilicity to undergo INAS reactions, while organolithiums and -magnesiums are generally too reactive.[3] Thus, most of the published INAS reactions involve the use of stabilized carbanions as exemplified by base-promoted cyclization of diesters and keto esters as well as rearrangement of *o*-(acyloxy)phenyl ketones.[4]



With respect to INAS reactions which do not involve stabilized carbanions, samarium(II) iodide-mediated reaction of

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(2) As represented by Claisen rearrangements (recent review: Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 305) and 2,3-sigmatropic Wittig rearrangements (recent review: Nakai, T.; Mikami, K. *Org. React.* **1994**, *46*, 105), synthetic sequences involving the transfer of carbon fragments from oxygen to carbon play an important role in organic synthesis. Methodology for synthesis of cyclic alkanones: Shaman, P. D., Jr.; Papa, A. J. Ketones. *Kirk-Othmer Encyclopedia of Chemical Technology,* 3rd ed.; Grayson, M., Eckroth, D., Eds.; Wiley: New York, 1981; Vol. 13, p 894. Waring, A. J. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, D., Eds.; Pergamon: Oxford, 1979; Vol. 1, p 1017. Jung, M. E. *Tetrahedron* **1976**, *32*, 3. Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron,* **1990**, *46*, 1385.

(3) INAS reaction *via* organolithium intermediates affording cyclic ketones has been attained in some cases, see: Fadel, F.; Canet, J.-L.; Salaun, J. *Synlett* **1990**, 89. Souchet, M.; Clark, R. D. *Synlett* **1990**, 151. Kitano, Y.; Okamoto, S.; Sato, F. *Chem. Lett.* **1989**, 2163. Van der Does, T.; Klumpp, G. W.; Schakel, M. *Tetrahedron Lett*. **1986**, *27*, 519. Cooke, M. P., Jr.; Houpis, I. N. *Tetrahedron Lett.* **1985**, *26*, 4987. Negishi, E.; Miller, J. A. *J. Am. Chem. Soc*. **1983**, *105*, 6761.

(4) Hauser, C. R.; Swammer, F. W.; Adams, J. T. *Org. React.* **1954**, *8*, 59. Kraus, G. A.; Futton, B. S.; Woo, S. H. *J. Org. Chem.* **1984**, *49*, 3212. Ohtsuka, Y; Oishi, T. *Tetrahedron Lett.* **1979**, *20*, 4487. Yates, P.; Anderson, C. D. *J. Am. Chem. Soc.* **1963**, *85*, 2937. Wallace, P. Warren, S. *Tetrahedron Lett.* **1985**, *26*, 5713. Wallace, P.; Warren, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2971. Schweitzer, E. E.; Creasy. W. S. *J. Org. Chem.* **1971**, *36*, 2379. Arey, P. M.; Warren, S. *Tetrahedron Lett.* **1989**, *30*, 4581. Jacobs, H. K.; Gopalan, A. S. *J. Org. Chem.* **1994**, *59*, 2014. For the reaction using Michael addition followed by Dieckmann condensation, see: Nugent, W. A.; Hobbs, F. W., Jr. *J. Org. Chem.* **1983**, *48*, 5364. Honda, T.; Mori, M. *Chem. Lett*. **1994**, 1013. Crimmins, M. T.; Nantermet, P. G. *J. Org. Chem*. **1990**, *55*, 4235. Crimmins, M. T.; Nantermet, P. G.; Trotter, B. W.; Vallin, I. M.; Watson, P. S.; McKerlie, L. A.; Reinhold, T. L.; W.-H. Cheung, A.; Stetson, K. A.; Dedopoulou, D.; Gray, J. L. *J. Org. Chem*. **1993**, *58*, 1038. Crimmins, M. T.; Watson, P. S. *Tetrahedron Lett.* **1993**, *34*, 199. Crimmins, M. T.; Guise, L. E. *Tetrahedron Lett.* **1994**, *35*, 1657. Crimmins, M. T. Huang, S.; Guise, L. E.; Borden Lacy, D. *Tetrahedron Lett.* **1995**, *36*, 7061.

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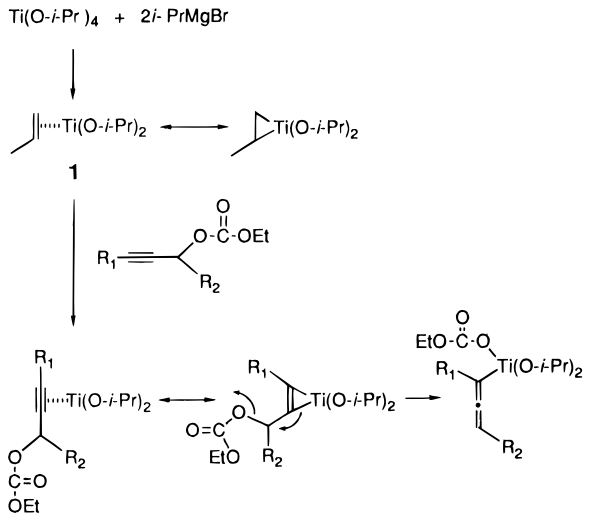
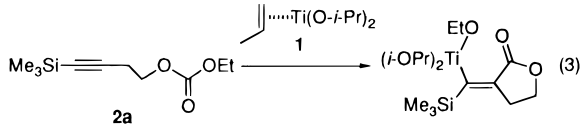
Scheme 1



alkyl iodides represents an exceptional, successful endeavor. The reaction is applicable to both types of reaction and its scope and limitations have been extensively investigated by Molander and co-workers.[5] The INAS reactions involving organochromium, -copper (derived by transmetalation reaction from organomercuric compounds), and -tin compounds have been reported;[6] however, the scope of these reactions has remained unexplored. We report here a titanium-promoted INAS reaction which is characterized by the fact that (i) the reaction provides for the first time an organometallic compound as the product, thus affording the opportunity for further functionalization through manipulation of the resulting carbon−metal bond, and (ii) the reaction is applicable to both types of reaction as shown in eqs 1 and 2 and has a wide range of applicability.

Recently we have disclosed a highly efficient and practical protocol for preparation of allenyltitanium compounds by the reaction of propargyl alcohol derivatives including carbonates with a Ti(O-*i*-Pr)$_4$/2*i*-PrMgBr reagent.[7] This formal oxidative addition reaction can be explained by the plausible reaction mechanism shown in Scheme 1 which involves generation of diisopropoxy(η^2-propene)titanium (**1**) from Ti(O-*i*-Pr)$_4$ and 2 equiv of *i*-PrMgBr[8] and subsequent replacement of the propene coordinated in **1** by the acetylenic moiety of the substrate to furnish a titanium-alkyne intermediate which then undergoes β-elimination.

With these results in hand, our attention turned to the reaction of the Ti(O-*i*-Pr)$_4$/2*i*-PrMgBr reagent with homopropargylic carbonate **2a** which has one additional carbon atom between the carbonate group and triple bond, and we found that the reaction afforded an INAS product, i.e., an alkenyltitanium compound having a lactone moiety as shown in eq 3.[9]



Further studies on the scope of this unprecedented type of titanium(II)-mediated INAS reaction have revealed that it affords a general and practical method for synthesis of a variety of organotitanium compounds having functional groups, thus opening up a synthetically versatile new methodology.[10,11]

Results and Discussion

Ti(II)-Mediated INAS Reaction of Carbonates of Acetylenic Alcohols.[9] The reaction of carbonates of a variety of substituted acetylenic alcohols **2** with the Ti(O-*i*-Pr)$_4$/2*i*-PrMgBr reagent provided alkenyltitanium compounds having a lactone and/or ester moiety in good to excellent yields, which was confirmed by hydrolysis, deuterolysis, and the reaction with aldehydes as summarized in Table 1.[12] However, carbonates having a terminal triple bond such as ethyl 3-butynyl carbonate gave no INAS reaction product.

The reaction can be explained by the plausible reaction mechanism shown in Scheme 2. Thus, the ligand exchange reaction of the propene moiety in **1** with **2** affords titanacyclopropene intermediate **3** which undergoes INAS reaction *via* path a and/or path b. The fact that no product with an endocyclic double bond was obtained by the attack of the other Ti−C bond to the carbonate group in **3** presumably can be attributed to conformational requirements. With acetylenic carbonates in which the carbonate group and triple bond are separated by two or three carbons, the acyl substitution proceeded mainly *via* path a to provide the corresponding alkenyltitanium compounds having a five- or six-membered lactone moiety (entries 1−7 in Table 1). In contrast, the reaction of the carbonate where both the functional groups are separated by four carbons proceeded *via* path b providing the alkenyltitanium compound having an ester group presumably due to lower stability of the seven-membered lactone ring compared to five- or six-membered ones (entry 8). The carbonates having an aromatic ring as a tether between the triple bond and carbonate group react similarly, thus providing an easy access to 3-isochromanone derivatives[13] (entries 9 and 10).

It should be noted that the vinyltitanium compounds derived here are rather stable and versatile and afford addition products with aldehydes.[14] It is also noteworthy that the reaction products

(5) Molander, G. A.; Christina, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3705. Molander G. A.; Shakya, S. R. *J. Org. Chem.* **1994**, *59*, 3445. Molander, G. A.; McKie, J. A. *J. Org. Chem.* **1993**, *58*, 7216. Molander, G. A.; McKie, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 5821. Molander, G. A. *Chem. Rev.* **1992**, *92*, 29.

(6) *Via* organochromium compound: Ledoussal, B.; Gorgues, A.; Le Coq, A. *J. Chem. Soc., Chem. Commun.* **1986**, 171. Ledoussal, B.; Gorgues, A.; Le Coq, A. *Tetrahedron* **1987**, *43*, 5841. *Via* organocopper compound: Kocovsky, P.; Grech, J. M.; Mitchell, W. L. *J. Org. Chem.* **1995**, *60*, 1482. *Via* organotin compound: Mori, M.; Kaneta, N.; Isono, N.; Shibasaki, M. *Tetrahedron Lett.* **1991**, *32*, 6139. Mori, M.; Isono. N.; Kaneta. N.; Shibasaki, M. *J. Org. Chem.* **1993**, *58*, 2972.

(7) Nakagawa, T.; Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3207.

(8) (a) Kasatkin, A.; Nakagawa, T.; Okamoto, S.; Sato, F. *J. Am. Chem. Soc*. **1995**, *117*, 3881. (b) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A.; Prityts kaya, T. S. *Zh. Org. Khim.* **1989**, *25*, 2244. (c) Kulinkovich, O. G.; Sviridov, S. V.; Vasilevskii, D. A. *Synthesis* **1991**, 234. (d) Corey, E. J.; Rao, A.; Noe, M. C. *J. Am. Chem. Soc.* **1994**, *116*, 9345.

(9) For a preliminary account of this work, see: Kasatkin, A.; Okamoto, S.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 6075.

(10) Other applications of the reagent **1** in organic synthesis: (a) Harada, K.; Urabe, H.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 3203. (b) Urabe, H.; Hata, T.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 4261. (c) Kasatkin, A.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 6079. (d) Gao, Y.; Harada, K.; Sato, F. *Tetrahedron Lett.* **1995**, *36*, 5913.

(11) Utility of functionalized organometallic reagents has been well exemplified by zinc compounds, see: Knochel, P. *Synlett*, **1995**, 393. Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117.

(12) For reviews on α-alkylidene- and α-arylidenebutyrolactones, see: Lu, X.; Ma, S.; Ji, J.; Zhu, G.; Jiang, H. *Pure Appl. Chem.* **1994**, *66*, 1501. Petragnani, N.; Ferraz, H. M. L.; Silva, G. V. *Synthesis* **1986**, 157. Hoffmann, H. M. R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94 and see also reference 18.

(13) Kobayashi, K.; Mannami, T.; Kawakita, M.; Tokimatsu, J.; Konishi, H. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 582 and references cited therein.

(14) Weidmann, B.; Maycock, C. D.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 1552. Mead, K.; MacDonald, T. L. *J. Org. Chem.* **1985**, *50*, 423. Boeckman, R. K.; O'Connor, K. J. *Tetrahedron Lett.* **1989**, *30*, 3271. Reetz, M. T. Titanium in Organic Synthesis In *Organometallics in Synthesis*; Schlosser, M., Ed.; Wiley: New York, 1994; p 195.

Table 1. Preparation of Alkenyltitanium Reagents Starting from **2** and Their Reactions with Electrophiles[a]

entry	2	reaction product with H_2O[b] % yield[d]	reaction product with PhCHO[c] % yield[d]
1	R^1 = $SiMe_3$, R^2 = H, n = 1	68[e]	65
2	R^1 = $SiMe_3$, R^2 = Et, n = 1	58, 84[e,f]	50
3	R^1 = $SiMe_3$, R^2 = Ph, n = 1	78	
4	R^1 = *n*-Hex, R^2 = H, n = 1	72[e,g]	
5	R^1 = Ph, R^2 = H, n = 1	81	40[h]
6	R^1 = $SiMe_3$, R^2 = H, n = 2	76[e]	70, 93[i]
7	R^1 = Et, R^2 = H, n = 2	55	74[i]
8	R^1 = $SiMe_3$, R^2 = H, n = 3	66[e,j]	38[j]
9	R = H	74	78[i,k]
10	R = Me	69	83[i,l]

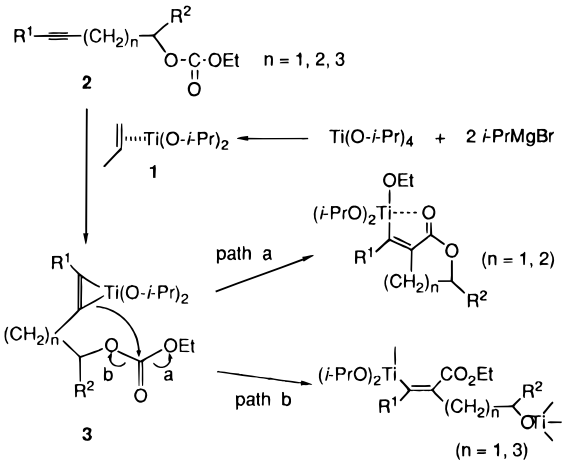
[a] All reactions were carried out using 1.0 equiv of an acetylenic carbonate, 1.3 equiv of Ti(O-*i*-Pr)$_4$, and 2.6 equiv of *i*-PrMgBr unless stated otherwise. An alkenyltitanium compound was prepared in Et_2O at −45 ∼ −40 °C (1 h), and then an electrophile was added at −40 °C. [b] Only one stereoisomer was observed in all cases according to ^{1}H- and ^{13}C-NMR data. The assignment of the double-bond stereochemistry is based on the chemical shift value of the vinyl proton (see refs 27−29 and 40). [c] After addition of 2.0 equiv of PhCHO, the reaction mixture was warmed up to 0 °C for 1 h. [d] Isolated yields based on the acetylenic carbonates unless stated otherwise. [e] Deuterolysis of the reaction mixture gave the product containing >98% D (^{1}H-NMR analysis). [f] 2.0 equiv of Ti(O-*i*-Pr)$_4$ and 4.0 equiv of *i*-PrMgBr were used. [g] Included 24% of (*E*)-3-(ethoxycarbonyl)-3-decen-1-ol. [h] EtCHO instead of PhCHO was used, after addition of EtCHO, the reaction mixture was stirred at 20 °C for 20 h. [i] 0.5 equiv of PhCHO was used, isolated yield based on PhCHO. [j] An alkenyltitanium reagent was prepared from 2.0 equiv of Ti(O-*i*-Pr)$_4$ and 4.0 equiv of *i*-PrMgBr at −45 ∼ −40 °C (2.5 h) followed by warming up to −15 °C for 1 h. [k] The 74:26 mixture of two diastereoisomers (rotamers) according to ^{1}H-NMR data. [l] H-NMR data. [l] The 43:37:20 mixture of three diastereomers according to ^{1}H-NMR data.

with aldehydes are recyclized substituted butenolides[15] rather than the initially formed α-alkylidene butanolides.

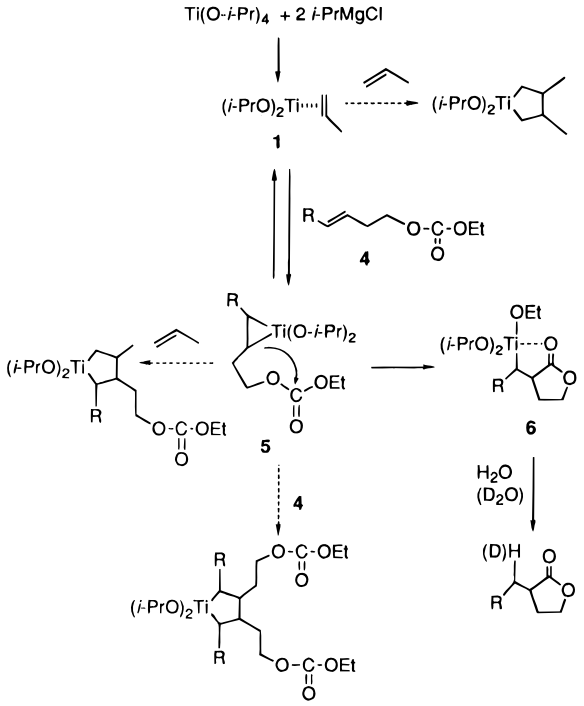
INAS Reaction with Olefinic Carbonates. Ti(II)-Mediated INAS reaction of acetylenic carbonates reported above is noteworthy for its efficient transfer of carbon fragments from oxygen to carbon and for providing an easy access to functionalized organotitanium compounds which are otherwise difficult to get, thus providing a powerful synthetic methodology for synthesis of a variety of butenolides. We next considered the application of Ti(II)-promoted INAS reactions to olefinic carbonates **4**.

Although the reaction of **1** with alkynes provided titanium−alkyne compounds quantitatively *via* a ligand exchange reaction,[10a] the reaction with alkene furnished a complex mixture of titanacyclopentanes due to the equilibrium between the two

Scheme 2



Scheme 3



titanium−alkene compounds (**1** and that derived from the alkene added) and their further coupling reactions with propene and/or the alkene added.[16] We, however, anticipated that the facile INAS reaction of the intermediate **5** generated by the reaction of **1** and **4** might act as a driving force for shifting the equilibrium, thus impeding these side reactions, and afford the acyl substitution product in a synthetically useful yield as shown in Scheme 3.[17]

As expected, a variety of ethyl carbonates of homoallyl alcohols provided the corresponding γ-butyrolactones in excellent yields on reaction with **1** and subsequent hydrolysis. The presence of alkyltitanium compound **6** was confirmed by subjecting the reaction mixture to deuterolysis. The results are summarized in Table 2.

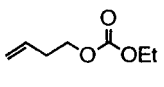
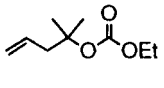
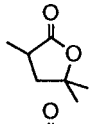
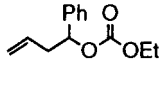
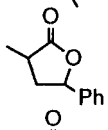
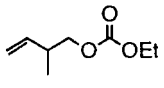
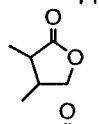
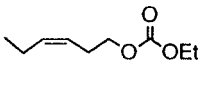
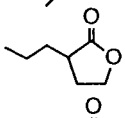
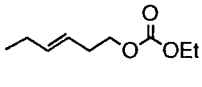
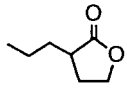
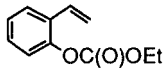
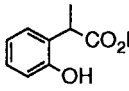
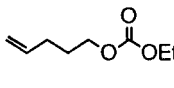
In contrast, the reaction of **1** with ethyl carbonate of 4-penten-1-ol (the carbonate of bishomoallyl alcohol) did not afford the

(15) For reviews, see: Knight, D. W. *Contemp. Org. Synth.* **1994**, *1*, 287. Jacobi, P. A. *Adv. Heterocycl. Nat. Prod. Synth.* **1992**, *2*, 251.

(16) Harada, K.; Sato, F. Unpublished result. A similar result was reported in the zirconium chemistry, see: Swanson, D. R.; Rousset, C. J.; Negishi, E.; Takahashi, T.; Seki, T.; Saburi, M.; Uchida, Y. *J. Org. Chem.* **1989**, *54*, 3521.

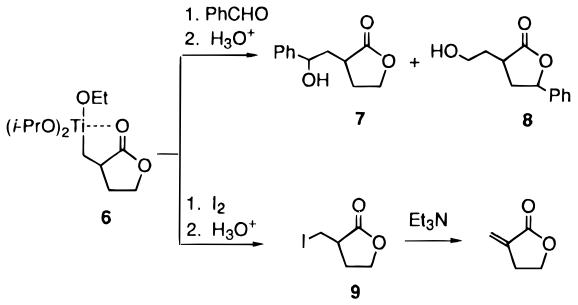
(17) The reaction of **1** with allyl carbonate provides allyltitanium compound; see reference 8a.

Table 2. Ti(II)-Mediated INAS Reaction of Olefinic Carbonates **4**[a]

entry	4	product[b]	% yield[c]
1			92
2			92
3			89[d]
4			86[d]
5			79
6			30
7			89
8		—	[e]

[a] All reactions were carried out using 1.0 equiv of an olefinic carbonate (**4**), 1.3 equiv of Ti(O-*i*-Pr)$_4$, and 2.6 equiv of *i*-PrMgCl. The reaction mixture was stirred for 1 h at −45 ∼ −40 °C, and then 3 N HCl was added at −40 °C. [b] Treatment of the reaction mixture with D_2O instead of 3 N HCl gave the product containing >98% D (^{1}H-NMR analysis). [c] Isolated yield based on **4**. [d] Obtained as a 1:1 mixture of diastereomers. [e] No INAS product was observed by ^{1}H NMR (see text).

Scheme 4

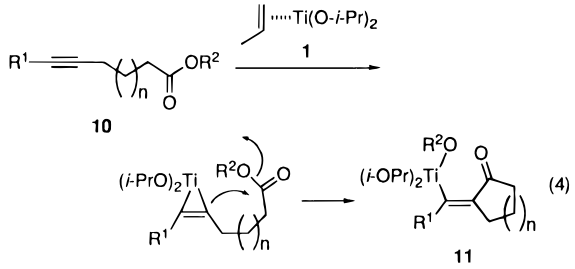


expected δ-lactone derivative, but gave a complex mixture of products including the coupling product with propene (entry 8). This finding strongly indicates the importance of a facile INAS path for the success of the reaction with olefinic substrates. The sluggish reaction of ethyl carbonate derived from (*E*)-3-hexen-1-ol which resulted in a lower yield compared to the corresponding *Z* isomer (entry 5 *vs* 6) may also be attributed to the slower reaction rate of the INAS path because of steric and/or conformational requirements.

The titanium compounds **6** can be intercepted with benzaldehyde or iodine as exemplified by the reactions shown in Scheme 4. Thus, starting from **6**, the addition product with benzaldehyde was obtained as a mixture of lactones **7** and **8** in 61% total yield. It should be noted, however, that the reaction with aliphatic aldehydes such as propanal did not proceed in contrast with the alkenyltitanium compound obtained by the INAS reactions of **2** (see entry 5 in Table 1). Treatment with excess of iodine provided the iodo lactone **9** in 90% yield which, upon treatment with Et_3N, underwent elimination to furnish α-methylene γ-butyrolactone in essentially quantitative yield.

Although many methods for synthesis of substituted γ-butyrolactones have been reported,[18] the present method is unique with respect to its reaction mode and starting materials and is potentially useful as an attractive complementary methodology.

INAS Reaction of Esters of Acetylenic Acids. The INAS reaction of carbonates of acetylenic alcohols mediated by **1** described above suggested that the analogous INAS reaction of esters **10** of acetylenic acids should provide a convenient method for synthesis of alkenyltitanium compounds containing a cyclic ketone fragment (**11**) as shown in eq 4.



Realization of the INAS reaction of **10**, however, was expected to encounter problems associated with the enhanced reactivity of the resulting ketone to nucleophiles. Thus, the present goal of the methodology requires that the generated titanium−alkyne intermediate reacts only with the ester group of the substrates in an intramolecular fashion but not intermolecularly, with the more reactive keto group of **11** formed; moreover, **11** must be free of the self-condensation problem.

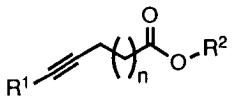
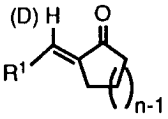
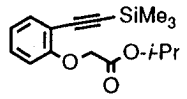
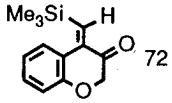
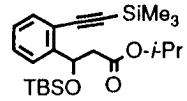
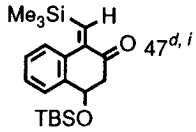
With the goal of developing the INAS reaction of **10** to **11**, the esters derived from 6-(trimethylsilyl)hex-5-ynoic acid were chosen as substrates and subjected to the reaction with **1** under various conditions. The yields of the expected α-alkylidene cyclopentanone obtained by hydrolysis of the reaction mixture are shown in entries 1−5 of Table 3. The results indicated that the use of ClTi(O-*i*-Pr)$_3$ instead of Ti(O-*i*-Pr)$_4$ resulted in better yield (entry 1 *vs* 2).[19] It can also be seen that the yield was dependent on the nature of the ester group, and the isopropyl ester **10c** gave the highest and most synthetically useful yield of 73%.

Although explanation of the effect of R^2 in **10** on the yield of the INAS reaction product must await further study, isopropyl esters of a variety of acetylenic acids were subjected to the reaction. As revealed by entries 6−8 in Table 3, the carbonate **10e** which has one more carbon between the triple bond and ester group compared to **10c**, reacted similarly to afford the corresponding α-alkylidene cyclohexanone in good yield, while the substrates **10f** and **10g** which have two more or one less carbon, respectively, did not provide the corresponding INAS reaction products. These results might be caused by the fact that the formation of transition states leading to four/seven-membered cyclic ketones are disfavored by entropy as well as enthalpy compared to those giving rise to five/six-membered

(18) For reviews, see: Kano, S.; Shibuya, S.; Ebata, T. *Heterocycles* **1980**, *14*, 661. Rao, Y. S. *Chem. Rev.* **1976**, *76*, 625. Grieco, P. A. *Synthesis* **1975**, 67.

(19) The synthesis of **1** from ClTi(O-*i*-Pr)$_3$ and *i*-PrMgX was reported by Corey.[8d] One of the referees suggested (η^2-propene)Ti(*i*-PrO)Cl as the most likely species. However, this possibility seems to be slight because use of Cl_2Ti(O-*i*-Pr)$_2$/2*i*-PrMgBr for the INAS reaction of **10c** resulted in low yield of INAS product (less than 10% yield) and recovery of **10c** (∼70% yield).

Table 3. Preparation of α-Alkylidenecycloalkanones by Reaction of Esters **10** of Acetylenic Acids Using ClTi(O-*i*-Pr)$_3$/2*i*-PrMgBr[a]

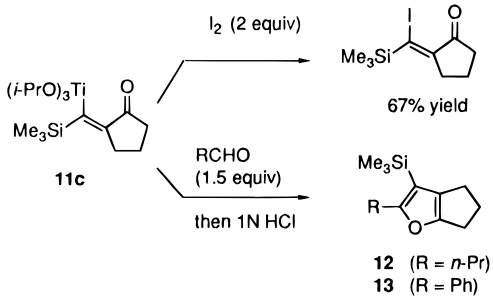
entry	10	product[b] isolated yield, %
		
1	**a**; R^1 = $SiMe_3$, R^2 = Me, n = 2	30
2	**a**; R^1 = $SiMe_3$, R^2 = Me, n = 2	15[c]
3	**b**; R^1 = $SiMe_3$, R^2 = Et, n = 2	28[d]
4	**c**; R^1 = $SiMe_3$, R^2 = *i*-Pr, n = 2	73[e]
5	**d**; R^1 = $SiMe_3$, R^2 = *t*-Bu, n = 2	12[d]
6	**e**; R^1 = $SiMe_3$, R^2 = *i*-Pr, n = 3	79[e, f]
7	**f**; R^1 = $SiMe_3$, R^2 = *i*-Pr, n = 4	trace[g]
8	**g**; R^1 = Et, R^2 = *i*-Pr, n = 1	trace[h]
9	**h**; R^1 = *t*-Bu, R^2 = *i*-Pr, n = 3	60
10	**I**; R^1 = Ph, R^2 = *i*-Pr, n = 3	83
11	**j**; 	 72
12	**k**; 	 47[d, i]

[a] Conditions: 1.0 equiv of **10**, 1.5 equiv of ClTi(O-*i*-Pr)$_3$, and 3.0 equiv of *i*-PrMgBr in Et_2O at −50 ∼ −40 °C for 1 h. [b] Only one stereoisomer was observed in all cases according to ^{1}H- and ^{13}C-NMR data. The double-bond stereochemistry is (*E*)-configuration determined by NOE-difference experiments. [c] The reaction was carried out using Ti(O-*i*-Pr)$_4$ instead of ClTi(O-*i*-Pr)$_3$. [d] ^{1}H-NMR yields using an internal standard. [e] Deuterolysis of the reaction mixture gave the product containing >98% D (^{1}H-NMR analysis). [f] The same product was obtained in 36% yield from methyl 6-(trimethylsilyl)hex-5-ynoate. [g] 41% yield of isopropyl (*Z*)-8-(trimethylsilyl)oct-7-enoate was obtained. [h] 35% yield of isopropyl (*Z*)-hept-4-enoate was obtained. [i] 45% of **10k** was recovered; the product and **10k** were inseparable.

ketones. It can also be seen that the reaction of **10** which contains a phenyl and/or ether group(s) as a part of the tether between the triple bond and ester group proceeded smoothly to afford the corresponding cyclic ketones in good to excellent yields (entries 11 and 12). In any event, the present reaction provides an efficient and general method for synthesis of alkenyltitanium compounds having five- or six-membered cyclic ketone fragment.[20]

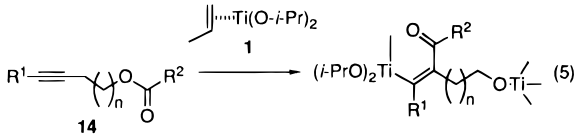
The presence of the titanium intermediate **11** was confirmed by deuterolysis (entries 4 and 6). The alkenyltitanium **11** can also be intercepted with iodine or aldehydes as exemplified by Scheme 5. In the case of the reaction with aldehydes, as expected, the addition products were converted into the corresponding furans during acidic workup.[21] Thus, addition of butanal or benzaldehyde to the reaction mixture of **10c** and **1**

Scheme 5



afforded the corresponding furan **12** or **13** in 44% or 69% yield, respectively.[22]

INAS Reaction of Esters Derived from Acetylenic Alcohols. Since α,β-unsaturated ketones are valuable intermediates in organic synthesis, development of an efficient methodology for their preparation has attracted continued interest.[20] The results of Ti(II)-mediated INAS reactions of acetylenic carbonates and esters of acetylenic acids led us to anticipate that acetylenic esters of the type **14** might react in a similar fashion and, thus, to afford a new general method for synthesis of α,β-unsaturated ketones (eq 5).



Viability of the above concept was studied using 5-(trimethylsilyl)-4-pentynyl acetate (**14a**) as the substrate. To a solution of **14a** and Ti(O-*i*-Pr)$_4$ (1.0 equiv) in ether was added *i*-PrMgBr (2.0 equiv) at −78 °C, and the mixture was stirred at −50 ∼−40 °C for 1 h to furnish the expected α,β-unsaturated ketone **15a** in only 15% yield as the sole identified product even though the starting **14a** was consumed completely. Although the yield is low, presumably due to further intermolecular carbonyl addition reactions because of the enhanced reactivity of the resulting ketone,[10a,14] it was reproducible and was not reduced even under prolonged reaction time. These findings suggested to us that the reaction might involve at least two different alkenyltitanium species, one of which must be free of the problems arising from intermolecular condensation. With the expectation of this possibility, we continued our efforts to find the reaction conditions for the development of this approach to a synthetically useful level, and we found that the use of 2 equiv of ClTi(O-*i*-Pr)$_3$/2*i*-PrMgBr reagent resulted in 68% yield of **15a**.

Encouraged by this finding, we subjected a variety of esters derived from acetylenic alcohols to the reaction with 2 equiv of ClTi(O-*i*-Pr)$_3$/2*i*-PrMgBr, and the results are summarized in Table 4. It can be seen from the table that the esters **14** having two, three, or even four carbons between the acetylene and ester groups were good substrates, although in the last case (entry 2) the yield is a little bit lower. It should be noted that in some cases the reaction products were isolated as the corresponding hemiacetals.

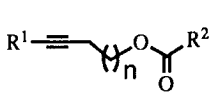
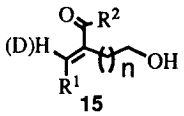
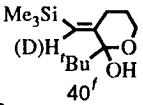
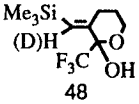
Since a variety of **14** can be readily obtained by reactions of acetylenic alcohols with carboxylic acids or their derivatives, the present reaction which enables the transfer of the acyl group

(20) Patai, S.; Rappoport, Z., Eds. *The Chemistry of Enones*; Wiley: Chichester, 1989; Vol 1. Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988**, *60*, 57. For tri- and tetrasubstituted α,β-enones, see: Dieter, R. K.; Silks, L. A., III. *J. Org. Chem.* **1986**, *51*, 4687 and references cited therein.

(21) Nishiyama, H.; Sasaki, M.; Itoh, K. *Chem. Lett.* **1981**, 1363 and references cited therein.

(22) For reviews on substituted furans and their utility, see: *Comprehensive Heterocyclic Chemistry*; Meth-Cohn, O., Ed.; Pergamon Press: New York, 1984; Vol. 1. Meyers, A. I. *Heterocycles in Organic Synthesis*; Wiley and Sons: New York, 1973. Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. For recent synthetic methods, see: Katritzky, A. R.; Li, J.; Gordeer, M. F. *J. Org. Chem.* **1993**, *58*, 3038 and references cited therein.

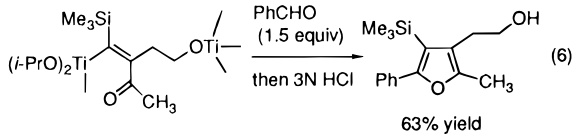
Table 4. Preparation of α,β-Unsaturated Ketones by Reaction of Esters **14** Derived from Acetylenic Alcohols Using $ClTi(O\text{-}i\text{-}Pr)_3$/2*i*-PrMgBr[a]

entry	14	product[b, c] isolated yield, %
		
		15
1	**a**; $R^1 = SiMe_3$, R^2 = Me, n = 2	58 (68)[d]
2	**b**; $R^1 = SiMe_3$, R^2 = Me, n = 3	47[e]
3	**c**; $R^1 = SiMe_3$, R^2 = Ph, n = 1	76
4	**d**; $R^1 = SiMe_3$, R^2 = Ph, n = 2	77
5	**e**; $R^1 = SiMe_3$, R^2 = (E)-CH=CHCH$_3$, n = 2	38
6	**f**; $R^1 = SiMe_3$, $R^2 = {}^t$Bu, n = 2	 40[f]
7	**g**; $R^1 = SiMe_3$, $R^2 = CF_3$, n = 2	 48
8	**h**; R^1 = Ph, R^2 = Ph, n = 2	49

[a] Conditions: 1.0 equiv of **14**, 2.3 equiv of $ClTi(O\text{-}i\text{-}Pr)_3$, and 4.6 equiv of *i*-PrMgBr in E_2O at −50 ∼ −40 °C for 1 h. [b] Only one stereoisomer was observed in all cases according to ^{1}H- and ^{13}C-NMR data. The double-bond stereochemistry is (*E*)-configuration determined by NOE-difference experiments. [c] Treatment of the reaction mixture with D_2O afforded **15** contain >99% D (^{1}H-NMR analysis) in all cases. [d] ^{1}H-NMR yield using an internal standard. [e] 9% of (*Z*)-6-(trimethylsilyl)hex-5-en-1-yl acetate was coproduced. [f] 19% of (*Z*)-6-(trimethylsilyl)hex-5-en-1-yl pivaloate was coproduced.

from oxygen to carbon provides a practical and general method for preparation of a wide range of α,β-unsaturated ketones.

So far we have described the synthesis of α,β-unsaturated ketones **15** by hydrolysis of the reaction product of **14** and **1**. Since the reaction affords the alkenyltitanium intermediate shown in eq 5, which was confirmed by deuterolysis (see footnote *c* in Table 4), it potentially expands the synthetic application of this reaction. For example, condensation with aldehydes can be used for synthesis of tetrasubstituted furan derivatives[22] as exemplified by eq 6.



63% yield (6)

Conclusion

$Ti(O\text{-}i\text{-}Pr)_4$/2*i*-PrMgBr and/or $ClTi(O\text{-}i\text{-}Pr)_3$/2*i*-PrMgBr reagent mediates INAS reactions of unsaturated compounds to afford organotitanium compounds containing functional groups. Because of the versatility of organotitanium compounds, the chemistry developed here provides an efficient, general method for the synthesis of butenolides, butanolides, vinyl cyclic ketones, α,β-unsaturated ketones, and furans. Moreover, the reaction is practical since the reaction uses nontoxic, commercially available inexpensive starting materials, and the reaction procedure is operationally simple. Thus, the reaction would be widely applicable in synthetic organic chemistry.

Experimental Section

General. Infrared spectra were recorded on a JASCO A-100 IR spectrometer. ^{1}H-NMR spectra were measured at 300 MHz on a Varian Gemini-300 spectrometer with $CDCl_3$ as a solvent at ambient temperature, and the chemical shifts were described in parts per million downfield from tetramethylsilane (δ = 0 ppm) or based on residual $CHCl_3$ (δ = 7.26 ppm) as an internal standard. ^{13}C-NMR spectra were recorded at 75 MHz on a Varian Gemini-300 spectrometer with $CDCl_3$ as a solvent and referenced to the central line of the solvent (δ = 77.0 ppm) The coupling constants (*J*) are reported in hertz. Mass spectra (MS, EI, 70 eV) were measured on a Shimadzu QP-5000 GC mass spectrometer. High resolution mass spectra (HRMS, EI, 70 eV) were measured on a JEOL JMS-SX102 spectrometer. Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}). Visualization was accomplished by UV light (254 nm), $KMnO_4$, phosphomolybdic acid, iodine, and vanillin. All experiments were conducted under argon atmosphere in oven-dried flasks. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl immediately prior to use.

Materials. $Ti(O\text{-}i\text{-}Pr)_4$, benzaldehyde, propanal, and butanal were distilled and stocked under argon. $ClTi(O\text{-}i\text{-}Pr)_3$ was prepared from $Ti(O\text{-}i\text{-}Pr)_4$ and $TiCl_4$ according to the procedure described in the literature[23] and stocked as a 2.0 M of ethereal solution under argon. *i*-PrMgBr and *i*-PrMgCl were prepared from commercial magnesium turnings and 2-bromo- or 2-chloropropane according to the conventional procedure as a 1.1−1.8 M of ethereal solution, titrated, and stocked under argon. The carbonates **2** and **4** were prepared from the corresponding acetylenic or olefinic alcohols by treatment with ethyl chloroformate and pyridine in ether.[24] Compounds **10a**−**i** were prepared from the acetylenic acids, which were obtained by Jones oxidation reaction of the corresponding alcohols, by treatment with oxalic acid monochloride in benzene followed by addition of alcohol (MeOH or EtOH) or a THF solution of lithium alcoholate (*i*-PrOLi or *t*-BuOLi). Compound **10j** was obtained from 2-[(trimethylsilyl)ethynyl]-phenol[25] by treatment with isopropyl iodoacetate and NaH in THF. Compound **10k** was synthesized from 2-[(trimethylsilyl)ethynyl]benzaldehyde[26] by Reformatsky reaction using isopropyl iodoacetate followed by silylation. Compounds **14a**−**h** were prepared from acetylenic alcohols by treatment with the corresponding acid chloride or anhydride in pyridine. Compounds **2**, **4**, **10**, and **14** thus prepared were purified by distillation and/or column chromatography prior to use. Other reagents were purchased from commercial source and were used without purification.

Ti(II)-Mediated INAS Reaction of Carbonates 2 of Acetylenic Alcohols. Preparation of Vinyl Titanium Reagents. To a solution of $Ti(O\text{-}i\text{-}Pr)_4$ (0.65 mmol) and an acetylenic carbonate (**2**) (0.50 mmol) in ether (7.5 mL) was added dropwise *i*-PrMgBr (1.30 mmol, in ether) at −50 °C. The resulting yellow solution was stirred for 1 h at −45 °C to −40 °C (the color of the mixture became red brown) to give a solution of the alkenyltitanium reagent ready for the next reactions.

Hydrolysis. To a solution of the alkenyltitanium reagent prepared above was added 1 N HCl (5 mL) at −40 °C. The mixture was warmed up to room temperature and stirred for 30 min. The organic layer was separated, and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (5 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford an α-alkylidene lactone and/or an α,β-unsaturated ester. **Deuterolysis.** To a solution of the alkenyltitanium reagent was added D_2O (1.0 mL) at −40 °C. The mixture was warmed up to room temperature and stirred for 15 min. To the resulting white suspension was added 1 N HCl (5 mL), and the mixture was stirred for additional 30 min. Usual extractive workup with ether as described above and concentration of the combined organic extracts furnished the crude

(23) Reetz, M. T.; Steinbach, R.; Kesseler, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 864. *Angew. Chem. Suppl.* **1982**, 1899.
(24) Tsuji, J.; Sato, K.; Okumoto, H. *J. Org. Chem.* **1984**, *49*, 1341.
(25) Barton, T. J.; Groh, B. L. *J. Org. Chem.* **1985**, *50*, 158.
(26) Austin, W. B.; Bilow, N.; Kelleghn, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

monodeuterated product which was analyzed by ^{1}H NMR. In all cases only one stereoisomer was observed on ^{1}H- and ^{13}C-NMR analysis, and the assignment of double bond stereochemistry is based on the chemical shift value of the vinyl proton (for α-alkylidene lactones, see: references 27−29; for α,β-unsaturated esters, see: references 40).

(*E*)-2-[(Trimethylsilyl)methylene]-4-butanolide[27] (entry 1 in Table 1): ^{1}H-NMR and IR spectral data were in good agreement with those described in the literature.

(*E*)-2-[(Trimethylsilyl)methylene]-4-ethyl-4-butanolide (entry 2 in Table 1): ^{1}H NMR δ 0.17 (s, 9H), 0.98 (t, *J* 6.9, 3H), 1.67 (m, 2H), 2.50 (ddd, *J* 17.4, 6.0, 2.4, 1H), 3.01 (ddd, *J* 17.4, 6.6, 2.4, 1H), 4.43 (tt, *J* 6.3, 6.3, 1H), 6.88 (t, *J* 2.4, 1H); ^{13}C NMR δ −1.5, 8.9, 29.2, 33.0, 78.2, 138.9, 140.2, 170.0; IR (neat) 2960, 1755, 1630, 1345, 1300, 1245, 1180, 1000, 960, 835, 750, 685 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15. Found: C, 60.85; H, 9.62.

(*E*)-2-[(Trimethylsilyl)methylene]-4-phenyl-4-butanolide (entry 3 in Table 1): ^{1}H NMR δ 0.20 (s, 9H), 2.86 (ddd, *J* 17.1, 6.6, 3.0, 1H), 3.40 (ddd, *J* 17.1, 8.1, 2.7, 1H), 5.51 (t, *J* 7.4, 1H), 7.02 (m, 1H), 7.37 (m, 5H); ^{13}C NMR δ −1.4, 36.4, 77.7, 125.4, 128.5, 128.8, 139.5, 140.0, 170.0; IR (Nujol) 1730, 1640, 1300, 1280, 1170, 1005, 970, 855, 820, 740, 680 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2Si$: C, 68.25; H, 7.36. Found: C, 68.46; H, 7.46.

(*E*)-2-Heptylidene-4-butanolide[28] and (*E*)-3-(Ethoxycarbonyl)-3-decen-1-ol (entry 4 in Table 1): ^{13}C NMR δ 13.9, 22.4, 25.0, 28.0, 28.9, 30.2, 31.5, 65.3, 125.1, 140.9, 171.1 (^{1}H NMR and IR spectral data were in good agreement with those described in the literature) and ^{1}H NMR δ 0.89 (t, *J* 6.9, 3H), 1.31 (m, 9H), 1.45 (m, 2H), 1.90 (br s, 1H), 2.22 (dt, *J* 7.5, 7.2, 2H), 2.60 (t, *J* 6.6, 2H), 3.69 (t, *J* 6.6, 2H), 4.20 (q, *J* 6.9, 2H), 6.98 (t, *J* 7.5, 1H); IR (neat) 3425, 2970, 2940, 2860, 1710, 1645, 1470, 1370, 1280, 1190, 1145, 1100, 1045, 860, 760 cm^{-1}. Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.08; H, 10.61, respectively.

(*E*)-2-Benzylidene-4-butanolide[29] (entry 5 in Table 1): mp 117 °C; ^{1}H NMR δ 3.26 (dt, *J* 7.2, 2.7, 2H), 4.47 (t, *J* 7.2, 2H), 7.40−7.55 (m, 5H), 7.58 (t, *J* 2.7, 1H); ^{13}C NMR δ 27.4, 65.4, 123.5, 128.9, 129.8, 129.9, 134.6, 136.6, 172.2.

(*E*)-2-[(Trimethylsilyl)methylene]-5-pentanolide (entry 6 in Table 1): ^{1}H NMR δ 0.14 (s, 9H), 1.92 (tt, *J* 6.6, 5.4, 2H), 2.65 (t, *J* 6.6, 2H), 4.30 (dt, *J* 2.1, 5.4, 2H), 7.18 (t, *J* 2.1, 1H); ^{13}C NMR δ −1.5, 23.2, 27.8, 69.0, 139.9, 145.6, 165.6; IR (neat) 2975, 1725, 1615, 1410, 1325, 1255, 1170, 1120, 1090, 980, 960, 850, 770, 700 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2Si$: C, 58.65; H, 8.75. Found: C, 58.28; H, 8.85.

(*E*)-2-Propylidene-5-pentanolide[29a] (entry 7 in Table 1): ^{13}C NMR δ 12.4, 21.4, 22.5, 23.3, 68.4, 124.8, 147.6, 166.5. ^{1}H NMR and IR spectral data were in good agreement with those described in the literature.

(*E*)-4-[(Trimethylsilyl)methylene]-3-isochromanone (entry 9 in Table 1): mp 68.5−69.0 °C; ^{1}H NMR δ 0.20 (s, 9H), 5.23 (s, 2H), 7.16 (s, 1H), 7.20−7.50 (m, 4H); ^{13}C NMR δ 0.26, 69.0, 124.5, 127.1, 128.0, 128.8, 132.0, 132.5, 139.7, 143.1, 168.3; IR (Nujol) 1750, 1730, 1250, 1225, 1180, 1170, 1035, 940, 905, 865, 840, 795, 760, 695 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2Si$: C, 67.20; H, 6.94. Found: C, 66.94; H, 7.11.

(*E*)-1-Methyl-4-[(trimethylsilyl)methylene]-3-isochromanone (entry 10 in Table 1): ^{1}H NMR δ 0.18 (s, 9H), 1.68 (d, *J* 6.6, 3H), 5.42 (q, *J* 6.6, 1H), 7.14 (s, 1H), 7.20−7.50 (m, 4H); ^{13}C NMR δ 0.24, 20.8, 75.9, 123.6, 127.3, 127.9, 128.9, 132.0, 136.7, 140.2, 142.4, 168.3; IR (neat) 1960, 1900, 1730, 1600, 1580, 1485, 1450, 1370, 1350, 1325, 1250, 1205, 1185, 1170, 1075, 1040, 1015, 915, 885, 860, 840, 790, 760, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2Si$: C, 68.25; H, 7.36. Found: C, 68.63; H, 7.80.

Ethyl (*E*)-2-(4-Hydroxybutyl)-3-(trimethylsilyl)propenoate (entry 8 in Table 1): ^{1}H NMR δ 0.19 (s, 9H), 1.30 (t, *J* 6.9, 3H), 1.45−1.70 (m, 4H), 2.09 (br s, 1H), 2.41 (m, 2H), 3.66 (t, *J* 6.0, 2H), 4.19 (q, *J* 6.9, 2H), 6.81 (s, 1H); IR (neat) 3375, 2940, 2850, 1705, 1595, 1450, 1360, 1240, 1215, 1090, 1045, 1020, 850, 830, 755, 680 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O_3Si$: C, 58.97; H, 9.90. Found: C, 59.56; H, 10.02.

Reaction with Benzaldehyde. To a solution of the alkenyltitanium reagent prepared above from 1.3 mmol of Ti(O-*i*-Pr)$_4$, 1.0 mmol of **2**, and 2.6 mmol of *i*-PrMgBr was added PhCHO (212 mg, 2 mmol or 53 mg, 0.5 mmol) at −40 °C. The mixture was slowly warmed to 0 °C over 1 h and hydrolyzed by addition of 1 N HCl (5 mL). After stirring at ambient temperature for 30 min and the following extractive workup as described above, the crude product was purified by column chromatography on silica gel.

2-(2-Hydroxyethyl)-3-(trimethylsilyl)-4-phenyl-2-buten-4-olide (entry 1 in Table 1): ^{1}H NMR δ 0.04 (s, 9H), 2.77 (t, *J* 5.8, 2H), 3.87 (t, *J* 5.8, 2H), 5.88 (s, 1H), 7.17 (m, 2H), 7.36 (m, 3H); ^{13}C NMR δ −1.1, 29.9, 61.1, 87.7, 128.0, 128.8, 129.5, 134.8, 138.4, 165.0, 175.1; IR (Nujol) 3450, 1740, 1705, 1245, 1065, 1050, 1035, 975, 880, 840, 760, 690 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_3Si$: C, 65.18; H, 7.29. Found: C, 65.22; 7.45.

2-(2-Hydroxybutyl)-3-(trimethylsilyl)-4-phenyl-2-buten-4-olide (entry 2 in Table 1): ^{1}H NMR δ 0.02 (s, 9H), 1.01 (t, *J* 6.0, 3H), 1.58 (m, 2H), 2,56 (dd, *J* 11.7, 6.6, 1H), 2.70 (d, *J* 11.7, 1H), 2.75 (br s, 1H), 3.86 (m, 1H), 5.88 (s, 1H), 7.20 (m, 2H), 7.36 (m, 3H); ^{13}C NMR δ −1.1, 10.0, 30.9, 34.0, 71.8, 87.8, 128.0, 128.8, 129.5, 134.9, 138.7, 164.8, 175.3; IR (Nujol) 3450, 2950, 1720, 1240, 1115, 1075, 980, 835, 745, 685 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.06; H, 7.94. Found: C, 66.64; H, 8.11.

2-(2-Hydroxyethyl)-3-phenyl-4-ethyl-2-buten-4-olide (entry 5 in Table 1): ^{1}H NMR δ 0.87 (t, *J* 7.2, 3H), 1.50 (m, 1H), 1.82 (br s, 1H), 1.91 (m, 1H), 2.73 (m, 2H), 3.90 (m, 2H), 5.38 (m, 1H), 7.39−7.50 (m, 5H); ^{13}C NMR δ 8.1, 25.5, 28.0, 60.8, 83.4, 125.8, 127.7, 129.1, 129.9, 131.2, 162.0, 175.0; IR (Nujol) 3375, 1720, 1630, 1320, 1160, 1100, 1065, 1025, 960, 750, 680 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 71.79; H, 6.99.

2-(3-Hydroxypropyl)-3-(trimethylsilyl)-4-phenyl-2-buten-4-olide (entry 6 in Table 1): ^{1}H NMR δ 0.01 (s, 9H), 1.84 (tt, *J* 7.5, 6.0, 2H), 2.57 (t, *J* 7.5, 2H), 2.70 (br s, 1H), 3.69 (t, *J* 6.0, 2H), 5.81 (s, 1H), 7.14 (m, 2H) 7.33 (m, 3H); ^{13}C NMR δ −1.2, 22.2, 32.2, 61.4, 87.2, 127.9, 128.7, 129.4, 135.0, 140.9, 163.2, 175.0; IR (neat) 3400, 2950, 1740, 1620, 1460, 1320, 1260, 1105, 1070, 1000, 845, 760, 705 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_3Si$: C, 66.17; H, 7.63. Found: C, 66.78; H, 7.76.

2-(3-Hydroxypropyl)-3-ethyl-4-phenyl-2-buten-4-olide (entry 7 in Table 1): ^{1}H NMR δ 0.98 (t, *J* 7.8, 3H), 1.81 (tt, *J* 7.5, 6.0, 2H), 2.02 (dq, *J* 15.6, 7.8, 1H), 2.45 (dq, *J* 15.6, 7.8, 1H), 2.47 (t, *J* 7.5, 2H), 2.78 (br s, 1H), 3.67 (t, *J* 6.0, 2H), 5.75 (s, 1H), 7.20 (m, 2H), 7.38 (m, 3H); ^{13}C NMR δ 12.3, 19.4, 19.7, 31.1, 61.2, 83.9, 126.1, 126.8, 128.9, 129.2, 134.6, 165.4, 175.0; IR (neat) 3400, 2920, 1735, 1660, 1450, 1300, 1255, 1160, 1030, 1000, 840, 750, 695 cm^{-1}. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.66; H, 7.15.

2-[2-(Hydroxymethyl)phenyl]-3-(trimethylsilyl)-4-phenyl-2-buten-4-olide (entry 9 in Table 1) (74:26 mixture of two diastereomers): ^{1}H NMR δ −0.20 and −0.27 (s, 9H), 3.2 and 2.6 (br s, 1H), 4.48 and 4.55 (d, *J* 12.8, 1H), 4.60 and 4.71 (d, *J* 12.8, 1H), 6.08 and 6.04 (s, 1H), 7.15−7.60 (m, 9H); ^{13}C NMR δ −0.94 and −0.71, 63.2 and 63.5, 87.7 and 88.0, 127.6, 127.9, 128.8, 129.0, 129.4, 129.6, 129.7, 129.9, 130.0, 130.5, 130.7, 134.5, 139.9, 141.0, 166.4, 168.0, 174.1; IR (Nujol) 3520, 1735, 1245, 1160, 1090, 1010, 995, 895, 845, 765, 750, 700 cm^{-1}. Anal. Calcd for $C_{20}H_{22}O_3Si$: C, 70.97; H, 6.55. Found: C, 70.69; H, 6.56.

2-[2-(1-Hydroxyethyl)phenyl]-3-(trimethylsilyl)-4-phenyl-2-buten-4-olide (entry 10 in Table 1) (the mixture of three diastereomers): ^{1}H NMR δ −0.22 and −0.17 (s, 9H) 1.48 and 1.55 (d, *J* 7.5, 3H), 4.78, 4.83 and 4.96 (q, *J* 7.5, 1H), 6.04, 6.07 and 6.10 (s, 1H), 7.10−7.70 (m, 9H); ^{13}C NMR (the two main diastereomers) δ −1.56 and −1.10, 225 and 24.8, 66.7 and 68.0, 87.2 and 88.1, 125.8, 126.1, 126.9, 127.2, 127.9, 128.0, 128.9, 129.6, 129.7, 130.0, 130.2, 130.3, 134.8, 135.0, 141.4, 144.3, 144.6, 166.6 and 167.0, 173.5 and 174.2; IR (Nujol) 3425, 1740, 1310, 1245, 1195, 1155, 1070, 995, 960, 895, 840, 750, 690 cm^{-1}. Anal. Calcd for $C_{21}H_{24}O_3Si$: C, 71.55; H, 6.86. Found: C, 71.34; H, 6.71.

2-(4-Hydroxybutyl)-3-(trimethylsilyl)-4-phenyl-2-buten-4-olide (entry 8 in Table 1): ^{1}H NMR δ 0.06 (s, 9H), 1.71 (m, 4H), 1.89 (br s,

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1H) 2.52 (m, 2H), 3.76 (m, 2H), 5.82 (s, 1H), 7.17 (m, 2H) 7.38 (m, 3H); ^{13}C NMR δ −1.1, 25.5, 25.9, 32.5, 62.3, 86.9, 127.9, 128.8, 129.4, 135.2, 141.4, 162.1, 174.5; IR (neat) 3440, 2960, 2875, 1745, 1620, 1500, 1460, 1415, 1320, 1255, 1110, 1075, 1035, 995, 880, 845, 770, 760, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_3Si$: C, 67.06; H, 7.94. Found: C, 67.02; H, 7.94.

INAS Reaction with Olefinic Carbonates 4. Preparation of Organotitanium Reagent 6. To a stirred solution of Ti(O-*i*-Pr)$_4$ (1.3 mmol) and an olefinic carbonate (**4**) (1.0 mmol) in ether (7 mL) was added dropwise *i*-PrMgCl (2.6 mmol, in ether) at −50 °C. The resulting mixture was stirred for 1 h at −45 °C to −40 °C to give the titanium reagent having lactone moiety (**6**) ready for the next reactions.

Hydrolysis. To a solution of the organotitanium reagent **6** prepared above was added 3 N HCl (5 mL), and the reaction mixture was allowed to stir for 30 min at room temperature. The organic layer was separated, and the aqueous layer was extracted with ether (2 × 20 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and chromatographed on silica gel to give the butenolide. **Deuterolysis.** In a similar way quenching the organotitanium reagent **6** with D_2O followed by usual workup affords the monodeuterated product which was analyzed by ^{1}H NMR.

Spectral data of 2-methyl-4-butanolide[30] (entry 1), 2,4-dimethyl-4-pentanolide[31] (entry 2), 2-methyl-4-phenyl-4-butanolide[32] (entry 3), 2,3-dimethyl-4-butanolide[33] (entry 4), 2-propyl-4-butanolide[34] (entry 5 and 6), and ethyl 2-(2-hydroxyphenyl)propionate[35] (entry 7) obtained by the reactions in Table 2 are in good agreement with those described in the literature.

Reaction with Benzaldehyde. Benzaldehyde (2.0 mmol) was added at −45 °C to the titanium reagent **6** prepared as above, and the reaction mixture was allowed to warm to ambient temperature over 1 h. After stirring for additional 6 h, usual acidic workup followed by chromatography afforded the butanolide as a mixture of isomers **7** and **8**.

2-(2-Phenyl-2-hydroxyethyl)-4-butanolide (7) and 2-(2-Hydroxyethyl)-4-phenyl-4-butanolide (8). **7** and **8** were inseparable from each other by chromatography, and ^{1}H-NMR analysis was performed using the mixture. ^{1}H NMR δ 2.05 (m, 2H), 2.20−2.31 (m, 2H), 4.12−4.35 (m, 2H), 5.02 (dd, *J* 7.8, 4.3, 1H), 7.35 (m, 5H) and ^{1}H NMR δ 1.86 (m, 1H), 2.03 (m, 1H), 2.49 (dd, *J* 9.0, 6.0, 2H), 2.87 (m, 1H), 3.81 (m, 2H), 5.62 (t, *J* 6.9, 1H), 7.35 (m, 5H), respectively.

For confirmation of the structure, the mixture of **7** and **8** was treated with $LiAlH_4$ (2 equiv) in ether (2.5 h, refluxing) to afford a single product, 5-phenyl-3-(hydroxymethyl)pentane-1,5-diol, in 86% yield: ^{1}H NMR δ 1.45−1.85 (m, 4H), 1.92 (m, 1H), 2.33 (br s, 1H), 3.50−3.73 (m, 4H), 4.17 (br s, 2H), 4.79 (m, 5H); ^{13}C NMR δ 34.8, 34.9, 41.5, 60.2, 65.7, 71.7, 125.6, 127.3, 128.4, 145.0; IR (neat) 3330, 2950, 1610, 1505, 1465, 1340, 1210, 1120, 1050, 1015, 920, 760, 705 cm^{-1}.

Iodolysis. Addition of I_2 (5.0 equiv) in THF to the organotitanium reagent **6** at −40 °C followed by usual acidic workup afforded the intermediate 2-(iodomethyl)-4-butanolide (**9**) which upon treatment with triethylamine in CH_2Cl_2 underwent dehydroiodination to furnish 2-methylene-4-butanolide. Spectral data of the product thus obtained are in good agreement with those described in the literature.[36] A small amount of unstable intermediate **9** was purified by passing through a short silica gel column for ^{1}H-NMR analysis.

2-(Iodomethyl)-4-butanolide (9): ^{1}H NMR δ 2.19 (m, 1H), 2.53 (m, 1H), 2.91 (m, 1H), 3.33 (dd, *J* 10.3, 7.9, 1H), 3.51 (dd, *J* 10.3, 3.9, 1H), 4.25 (m, 1H), 4.41 (m, 1H); ^{13}C NMR δ 3.4, 29.3, 41.4, 65.8, 175.8.

INAS Reaction of Esters 10 of Acetylenic Acids. Preparation of Vinyltitanium Reagent 11. To a solution of ClTi(O-*i*-Pr)$_3$ (0.75 mL, 2.0 M in ether, 1.5 mmol) and **10** (1.0 mmol) in ether (10 mL) was added dropwise *i*-PrMgBr (3.0 mmol, in ether) at −78 °C. The resulting mixture was warmed up to −50 °C over 0.5 h and stirred for 1−1.5 h at −50 °C to −45 °C to give the vinyltitanium reagent **11** ready for the next reactions.

Hydrolysis or Deuterolysis. To a solution of the vinyltitanium reagent **11** prepared above was added H_2O or D_2O (0.5 mL) at −45 °C. The mixture was warmed up to room temperature over 0.5 h. After addition of NaF (1.5 g) and Celite (1.5 g), the mixture was stirred for 1 h and then filtered through a pad of Celite. After concentration of the filtrate *in vacuo*, the residue was purified by column chromatography on silica gel to afford the α-alkylidene cycloalkanone. Deuterolysis gave the product contained >98% D on ^{1}H NMR analysis (for entries 4 and 6 in Table 3). Only one stereoisomer was obtained in all cases on ^{1}H- and ^{13}C-NMR analysis, and the double bond stereochemistry is (*E*)-configuration determined by NOE-difference experiments.

Spectral data of (*E*)-2-[(trimethylsilyl)methylene]cyclohexanone[37] (entry 6), (*E*)-2-(2,2-dimethylpropylidene)cyclohexanone[38] (entry 9), and (*E*)-2-benzylidenecyclohexanone[39] (entry 10) obtained by the reactions shown in Table 3 are in good agreement with those described in the literature.

(*E*)-2-[(Trimethylsilyl)methylene]cyclopentanone (entries 1−5 in Table 3): ^{1}H NMR δ 0.15 (s, 9H), 1.86−2.00 (m, 2H), 2.31 (t, *J* 7.9, 2H), 2.68 (dt, *J* 2.6, 7.3, 2H), 6.65 (t, *J* 2.6, 1H); ^{13}C NMR δ −1.2, 19.5, 29.5, 37.3, 133.4, 150.8, 205.8; IR (neat) 2960, 1720, 1620, 1410, 1250, 1160, 840, 760, 690 cm^{-1}; MS (EI) *m/z* (relative intensity, proposed ion), 168 (3.3, M$^+$), 153 (100, M$^+$ − CH_3), 140 (20.1, M$^+$ − CH_2CH_2); HRMS calcd for $C_9H_{16}OSi$ 168.0970, found 168.0970.

(*E*)-4-[(Trimethylsilyl)methylene]chroman-3-one (entry 11 in Table 3): ^{1}H NMR δ 0.21 (s, 9H), 4.55 (s, 2H), 7.00 (s, 1H), 7.02−7.12 (m, 2H), 7.31 (dt, *J* 1.6, 7.7, 1H), 7.42 (d, *J* 7.7, 1H); ^{13}C NMR δ −0.26, 72.3, 118.0, 122.4, 124.1, 128.6, 130.4, 139.0, 142.2, 155.1, 197.3; IR (neat) 29060, 2900, 1710, 1600, 1580, 1560, 1480, 1460, 1250, 1050, 855, 755 cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_2Si$: C, 67.20; H, 6.94. Found: C, 66.73; H, 6.96.

(*E*)-4-[(Trimethylsilyl)methylene]-1-[(*tert*-butyldimethylsilyl)oxy]-1,2,3,4-tetrahydronaphthalen-3-one (entry 12 in Table 3): The product and **10k** were inseparable from each other by preparative HPLC and distillation, and ^{1}H-NMR spectra was measured using the mixture. ^{1}H NMR δ −0.01 (s, 3H), 0.12 (s, 3H), 0.14 (s, 9H), 0.85 (s, 9H), 2.71 (dd, *J* 6.2, 16.4, 1H), 2.77 (dd, *J* 4.3, 16.4, 1H), 4.97 (dd, *J* 4.3, 6.2, 1H), 7.00 (s, 1H), 7.22−7.48 (m, 4H). [Compound **10k**: ^{1}H NMR δ −0.17 and −0.06 (2s, each 3H), 0.28 (s, 9H), 0.85 (s, 9H), 1.24 (d, *J* 8.1, 6H), 2.56 (dd, *J* 8.6, 14.7, 1H), 2.63 (dd, *J* 4.2, 14.7, 1H), 4.95−5.08 (m, 1H), 5.67 (dd, *J* 4.2, 8.6, 1H), 7.18 (dt, *J* 1.5, 7.7, 1H), 7.32 (dt, *J* 1.6, 7.7, 1H), 7.39 (d, *J* 7.7, 1H), 7.53 (d, *J* 7.7, 1H); ^{13}C NMR δ −5.3, −4.8, 18.0, 21.9, 25.7, 45.0, 67.5, 69.6, 99.8, 102.3, 120.0, 126.0, 126.9, 128.7, 131.7, 146.5, 170.2; IR (neat) 2950, 2880, 2150, 1740, 1480, 1380, 1250, 1115, 1085, 960, 870, 840, 760 cm^{-1}. Anal. Calcd for $C_{23}H_{38}O_3Si_2$: C, 65.98; H, 9.15. Found: C, 66.07; H, 9.08.].

Iodolysis. To a solution of the vinyltitanium reagent was added a solution of iodine (508 mg, 2.0 mmol) in ether (8 mL) at −45 °C. The mixture was warmed up to 0 °C over 0.5 h and quenched by addition of 1 N HCl (5 mL). The organic layer was separated, and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with saturated aqueous $Na_2S_2O_3$ (10 mL) and $NaHCO_3$ (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the alkenyl iodide.

(*Z*)-2-[Iodo(trimethylsilyl)methylene]cyclopentanone. This compound is not stable to stock for a long time, and the following analyses were performed immediately after rapid column chromatography. ^{1}H NMR δ 0.28 (s, 9H), 1.90−2.03 (m, 2H), 2.52 (t, *J* 8.0, 2H), 2.73 (t,

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J 7.4, 2H); IR (neat) 2960, 2900, 1720, 1560, 1410, 1240, 1180, 860, 840, 750 cm^{-1}.

Reaction with Aldehyde. To a solution of the vinyltitanium reagent **11** prepared from 1.0 mmol of **10** was added aldehyde (1.5 mmol) at −45 °C. The mixture was warmed up to room temperature over 0.5 h. After addition of 1 N HCl (5 mL), the organic layer was separated and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the furan.

2-Propyl-3-(trimethylsilyl)-4,5-dihydrocyclopenta[*b*]furan (12): ^{1}H NMR δ 0.20 (s, 9H), 0.95 (t, *J* 7,4, 3H), 1.56−1.71 (m, 2H), 2.35−2.47 (m, 2H), 2.47−2.55 (m, 2H), 2.57 (t, *J* 7.5, 2H), 2.56−2.68 (m, 2H); ^{13}C NMR δ 0.03, 13.9, 23.0, 24.2, 24.6, 27.8, 31.7, 110.8, 130.6, 157.0, 164.8; IR (neat) 2910, 1760, 1710, 1470, 1260, 840 cm^{-1}; MS (EI) *m/z* (relative intensity, proposed ion), 222 (46.4, M^+), 207 (13.2, $M^+ - CH_3$), 193 (100, $M^+ - C_2H_5$), 179 (5.2, $M^+ - C_3H_7$), 149 (2.7, $M^+ - Si(CH_3)_3$). Anal. Calcd for $C_{16}H_{22}OSi$: C, 70.21; H, 9.97. Found: C, 69.64; H, 10.30.

2-Phenyl-3-(trimethylsilyl)-4,5-dihydrocyclopenta[*b*]furan (13): ^{1}H NMR δ 0.21 (s, 9H), 2.41−2.53 (m, 2H), 2.62 (t, *J* 6.4, 2H), 2.74 (t, *J* 7.1, 2H), 7.25−7.62 (m, 5H); ^{13}C NMR δ 0.25, 24.2, 25.1, 27.9, 103.6, 113.0, 123.1, 127.6, 128.0, 128.6, 132.7, 158.9; IR (neat) 2970, 2860, 1600, 1540, 1480, 1250, 840, 760 cm^{-1}; MS (EI) *m/z* (relative intensity, proposed ion), 256 (100, M^+), 241 (34.9, $M^+ - CH_3$). Anal. Calcd for $C_{16}H_{20}OSi$: C, 74.95; H, 7.86. Found: C, 74.88; H, 8.12.

INAS Reaction of Esters Derived from Acetylenic Alcohols. Preparation of a Vinyltitanium Reagent. To a solution of an ester derived from acetylenic alcohol (**14**) (1.0 mmol) and $ClTi(O\text{-}i\text{-}Pr)_3$ (2.3 mmol) in ether (10 mL) was added *i*-PrMgBr (4.6 mmol, in ether) at −78 °C. The resulting mixture was warmed up to −50 °C over 0.5 h and was stirred for 1 h at −50 to −40 °C to give the vinyltitanium reagent ready for the next reactions.

Hydrolysis. To a solution of the vinyltitanium reagent prepared above was added 3 N HCl (5 mL) at −40 °C. The mixture was warmed up to room temperature over 0.5 h. The organic layer was separated, and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL) and dried over $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography on silica gel to afford **15**. **Deuterolysis.** To a solution of the vinyltitanium reagent was added D_2O (1.0 mL) at −40 °C. The mixture was warmed up to 0 °C over 1 h, and then 3 N HCl (5 mL) was added. After stirring for 10 min at ambient temperature, the organic layer was separated and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL) and dried over $MgSO_4$. After concentration *in vacuo*, the residue was purified by column chromatography on silica gel to afford **15** containing >98% D which was determined by ^{1}H-NMR analysis. Only one stereoisomer was obtained in all cases on ^{1}H and ^{13}C NMR analysis and the double bond stereochemistry is (*E*)-configuration determined by NOE-difference experiments.

(*E*)-5-(Trimethylsilyl)-4-acetylpent-4-en-1-ol (15a): ^{1}H NMR δ 0.20 (s, 9H), 1.57−1.62 (m, 2H), 2.34 (s, 3H), 2.42 (t, *J* 7.6, 2H), 3.56 (t, *J* 6.2, 2H), 6.69 (s, 1H); ^{13}C NMR δ −0.4, 25.7, 26.4, 33.2, 62.0, 142.7, 155.9, 201.0; IR (neat) 3400, 2930, 1660, 1580, 1360, 1240, 840 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06. Found: C, 59.82; H, 9.95.

(*E*)-6-(Trimethylsilyl)-5-acetylhex-5-en-1-ol (15b): ^{1}H NMR δ 0.16 (s, 9H), 1.30−1.41 (m, 2H), 1.54 (tt, *J* 6.9, 6.9, 2H), 2.29 (s, 3H), 2.31 (t, *J* 7.6, 2H), 3.6 (t, *J* 6.5, 2H), 6.59 (s, 1H); ^{13}C NMR δ −0.4, 25.8, 26.1, 30.3, 32.6, 62.2, 141.4, 156.4, 200.6; IR (neat) 3400, 3050, 1770, 1700, 1518, 1410, 1360, 1217, 1005 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34. Found: C, 61.45; H, 10.45.

(*E*)-4-(Trimethylsilyl)-3-(phenylcarbonyl)but-3-en-1-ol (15c): ^{1}H NMR δ 0.21 (s, 9H), 2.80 (t, *J* 6.1, 2H), 3.77 (t, *J* 6.1, 2H), 6.3 (s, 1H), 7.40−7.59 (m, 3H), 7.74 (d, *J* 7.7, 2H); ^{13}C NMR δ −0.2, 35.6, 62.7, 128.2, 129.9, 132.4, 137.3, 144.3, 152.5, 200.0; IR (neat) 3450, 2960, 2900, 1750, 1660, 1595, 1450, 1250, 1140, 1060, 1030, 870, 840, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.89; H, 8.37.

(*E*)-5-(Trimethylsilyl)-4-(phenylcarbonyl)pent-4-en-1-ol (15d): ^{1}H NMR δ 0.19 (s, 9H), 1.65−1.75 (m, 2H), 2.65 (t, *J* 7.7, 2H), 3.62 (t, *J* 6.3, 2H), 6.18 (s, 1H), 7.38−7.44 (m, 2H), 7.48−7.54 (m, 1H), 7.69−7.72 (m, 2H); ^{13}C NMR δ −0.3, 28.2, 32.4, 62.1, 128.1, 129.6, 132.1, 137.6, 142.2, 154.9, 199.3; IR (neat) 3380, 2920, 1650, 1600, 1450, 1240, 1060, 850 cm^{-1}. Anal. Calcd for $C_{15}H_{22}O_2Si$: C, 68.65; H, 8.45. Found: C, 68.14; H, 8.66.

(*E*)-5-(Trimethylsilyl)-4-[[(*E*)-prop-1-enyl]carbonyl]pent-4-en-1-ol (15e). The product (colorless oil) contained a small amount of impurity even after column chromatography, and the yield was calculated based on ^{1}H-NMR analysis using an internal standard which indicated 97% chemical purity on weight. ^{1}H NMR δ 0.21 (s, 9H), 1.59−1.68 (m, 2H), 1.92 (dd, *J* 6.4, 1.5, 3H), 2.52 (t, *J* 7.4, 2H), 3.57 (t, *J* 6.2, 2H), 6.55 (s, 1H), 6.69 (dd, *J* 15.2, 1.5, 1H), 6.82−6.94 (m, 1H); ^{13}C NMR δ −0.3, 18.4, 27.1, 32.9, 62.0, 127.3, 140.3, 143.8, 156.4, 193.4; IR (neat) 3400, 2950, 1720, 1660, 1615, 1440, 1245, 1050, 850 cm^{-1}.

(*E*)-2-Hydroxy-2-*tert*-butyl-3-[(trimethylsilyl)methylene]tetrahydropyran (15f): ^{1}H NMR δ 0.17 (s, 9H), 1.22 (s, 9H), 1.57−1.63 (m, 2H), 2.42 (t, *J* 7.8, 2H), 3.61 (t, *J* 6.2, 2H), 5.76 (s, 1H); ^{13}C NMR δ −0.02, 28.2, 30.3, 32.4, 43.6, 62.3, 131.2, 156.7, 213.8; IR (neat) 3430, 2960, 1730, 1680, 1600, 1260, 1140, 860 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O_2Si$: C, 64.41; H, 10.81. Found: C, 64.25; H, 10.67.

(*E*)-2-Hydroxy-2-(trifluoromethyl)-3-[(trimethylsilyl)methylene]-tetrahydropyran (15g): ^{1}H NMR δ 0.16 (s, 9H), 1.65−1.78 (m, 1H), 1.94−2.08 (m, 1H), 2.55−2.63 (m, 1H), 2.94 (s, 1H), 6.05 (s, 1H); ^{13}C NMR δ 0.3, 24.9, 26.4, 61.2, 120.7, 124.7, 131.3, 146.9; IR (neat) 3400, 2890, 1720, 1630, 1450, 1250, 1190, 1080, 960, 860, 840, 750 cm^{-1}. Anal. Calcd for $C_{10}H_{17}F_3O_2Si$: C, 47.23; H, 6.74. Found: C, 47.00; H, 7.07.

(*E*)-5-Phenyl-4-(phenylcarbonyl)pent-4-en-1-ol (15h): ^{1}H NMR δ 1.78−1.90 (m, 2H), 2.87 (t, *J* 7.4, 2H), 3.66 (t, *J* 6.0, 2H), 7.17 (s, 1H), 7.28−7.62 (m, 8H), 7.77 (d, *J* 6.9, 2H); ^{13}C NMR δ 23.6, 31.5, 61.8, 128.2, 128.6, 128.7, 129.2, 129.6, 131.9, 135.3, 138.4, 140.9, 142.6, 199.9; IR (neat) 3400, 2950, 2850, 1720, 1650, 1595, 1500, 1450, 1320, 1250, 1060, 960, 760, 720, 700 cm^{-1}. Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.79; H, 6.99.

Reaction with Benzaldehyde. To a solution of the vinyltitanium reagent prepared from 1.0 mmol of 4-(trimethylsilyl)-3-butynyl acetate was added PhCHO (1.5 mmol) at −45 °C. The mixture was warmed up to room temperature over 1 h, and then 1 N HCl (5 mL) was added. After stirring for 0.5 h at ambient temperature, the organic layer was separated and the aqueous layer was extracted with ether (10 mL). The combined organic layers were washed with brine (5 mL), dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give the furan.

2-Phenyl-3-(trimethylsilyl)-4-(2-hydroxyethyl)-5-methylfuran: ^{1}H NMR δ 0.16 (s, 9H), 2.31 (s, 3H), 2.74 (t, *J* 6.9, 2H), 3.76 (t, *J* 6.9, 2H), 7.34−7.41 (m, 3H), 7.44−7.47 (m, 2H); ^{13}C NMR δ 1.1, 11.5, 29.0, 63.1, 114.9, 120.5, 127.8, 128.1, 129.1, 133.4, 148.9, 158.0; MS (EI) *m/z* (relative intensity, proposed ion), 274 (75.7, M^+), 259 (100, $M^+ - CH_3$), 243 (57.4, $M^+ - CH_2OH$); HRMS calcd for $C_{16}H_{22}O_2Si$ 274.1389, found 274.1378.

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Supporting Information Available: Copies of ^{1}H NMR spectra (47 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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