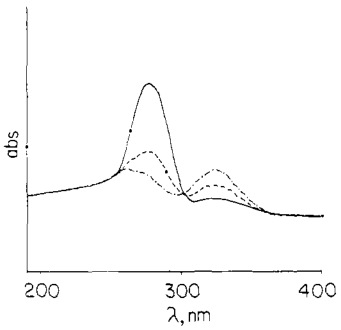
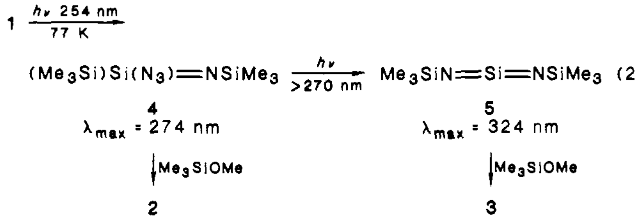


Figure 1. (—) Ultraviolet spectrum of $Me_3SiSi(N_3)=NSiMe_3$ (**4**), generated by irradiation (254 nm) of **1** at 77 K. The 274-nm band is due to **4** while the band at 324 nm is due to a small amount of $Me_3SiN=Si=NSiMe_3$ (**5**) formed in the photolysis: (- - -) UV spectrum after photobleaching (>270 nm) for 30 min; (- · · -) UV spectrum after photobleaching for 60 min.

Irradiation (254 nm) of **1** in glassy 3-methylpentane (3-MP) at 77 K results in the appearance of two new bands in the UV at 274 and 324 nm (Figure 1). At first, the 274-nm band grows in more rapidly than the 324-nm band, showing that two different species are responsible for the UV spectrum. This is confirmed by bleaching experiments. Longer wavelength irradiation (>270 nm) reduces the 274-nm band with a concomitant increase in the 324-nm band (Figure 1).

The structures of the compounds responsible for the UV spectra were determined by trapping experiments. When the 254-nm irradiation is performed at 77 K in a 3-MP glass containing 0.2% Me_3SiOMe, compounds **2** and **3** are the only products observed after warming the sample to room temperature and analyzing the photolysate by GC.[10] The combined yields of **2** and **3** were 75–90% on the basis of consumed **1**. The molar ratio of **3**:**2** varies from 0.2 to 0.9, increasing with the duration of the 254-nm photolysis. If the glass is then irradiated at >270 nm (the same conditions that produce the changes in the UV spectrum shown in Figure 1) prior to warmup, the combined yields of **2** and **3** are unchanged, but the ratio of **3**:**2** increases to between 1.1 and 2.0.[11] 2.0.[11] These results, together with the information obtained from UV spectroscopy, indicate that (a) the azidosilanimine **4** is responsible for the 274-nm band, (b) **4** is a photochemical precursor of the silanediimine **5**, and (c) **5** has an absorption maximum at 324 nm (see eq 2).[12,13]



$$\mathbf{1}\xrightarrow[77\ \mathrm{K}]{h\nu\ 254\ \mathrm{nm}}\underset{\substack{\mathbf{4}\\ \lambda_{max}=274\ \mathrm{nm}\\ \downarrow Me_3SiOMe\\ \mathbf{2}}}{(Me_3Si)Si(N_3)=NSiMe_3}\xrightarrow[>270\ \mathrm{nm}]{h\nu}\underset{\substack{\mathbf{5}\\ \lambda_{max}=324\ \mathrm{nm}\\ \downarrow Me_3SiOMe\\ \mathbf{3}}}{Me_3SiN=Si=NSiMe_3}\quad(2)$$

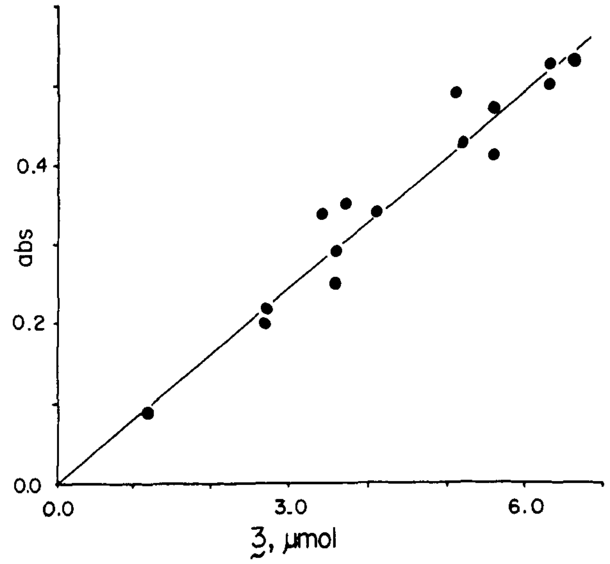


Figure 2. Plot of number of moles of **3** produced in the photolysis of **1** at 77 K versus the absorbance measured at 324 nm.

Further support for our assignment of the 324-nm band to **5** can be gained by plotting the number of moles of **3** produced vs. the absorbance measured at 324 nm. From the slope of the least-squares line of such a plot (Figure 2), the molar absorptivity (ϵ) of **5** is found to be 2130 ± 260 M^{-1} cm^{-1}. The linear nature of this plot provides convincing evidence that the absorption maximum at 324 nm is due to the precursor of **3**.[13]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Contracts F49620-86-C-0010 and 84-0065, and the National Science Foundation, Grant CHE-8318820-02. We thank Greg Gillette for obtaining ^{13}C NMR spectra.

Registry No. **1**, 106865-42-3; **2**, 106865-43-4; **3**, 106865-44-5; **4**, 106865-45-6; **5**, 106865-46-7; Me_3SiOMe, 1825-61-2; $EtMe_2SiOMe$, 52686-75-6; $(Me_3Si)_2SiCl_2$, 5181-42-0.

---

[8] Photolysis of $Ph_2Si(N_3)_2$ in the presence of *tert*-butyl alcohol has been reported[9] to give the product from migration of each phenyl group to a nitrogen and addition of 2 mol of alcohol (see below). The authors interpret

$$Ph_2Si(N_3)_2\xrightarrow{h\nu}[PhN=Si=NPh]\xrightarrow{2(t\text{-}BuOH)}PhHNSi(O\text{-}t\text{-}Bu)_2NHPh$$

this as evidence for the intermediacy of *N,N'*-diphenylsilanediimine. Our results suggest that the silanediimine is not formed directly and that a mechanism involving two sequential migration–addition steps is operative.

[9] Ando, W.; Tsumaki, H.; Ikeno, M. *J. Chem. Soc., Chem. Commun.* **1981**, 597–598.

[10] UV spectra identical with those shown in Figure 1 are observed when 0.2% Me_3SiOMe is present in the glass.

[11] Control experiments demonstrated that **2** and **3** are not produced on irradiation (>270 nm) of **1** at 77 K for short periods of time (15 m). However, prolonged irradiation (4 h) does result in the formation of small amounts of both **2** and **3**.

[12] $EtMe_2SiOMe$ was also used as a trapping agent. Solution and glass experiments both produced the same products, identified as $Me_3SiSi(OMe)(N_3)N(SiMe_3)(SiMe_2Et)$ and $[(Me_3Si)(EtMe_2Si)N]_2Si(OMe)_2$.

[13] This analysis assumes that **5** is quantitatively trapped by Me_3SiOMe to give **3**. Our value of ϵ, therefore, represents an upper limit to the true value.

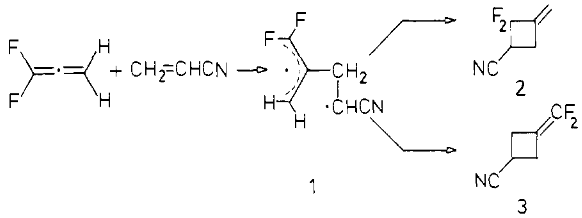
Pressure and Viscosity Effects on the [2 + 2] Cycloaddition of Styrene and Difluoroallene

William R. Dolbier, Jr.,* and Mark J. Seabury

Department of Chemistry, University of Florida
Gainesville, Florida 32611

Received January 26, 1987

The [2 + 2] cycloadditions of allenes provide special opportunities for probing the behavior of diradicals formed in nonconcerted cycloaddition processes. As exemplified for the reaction of difluoroallene with acrylonitrile,[1] all [2 + 2] cycloadditions involving allenic addends involve initial C–C bond formation at C_2 of the allene to form diradicals such as **1** which still must



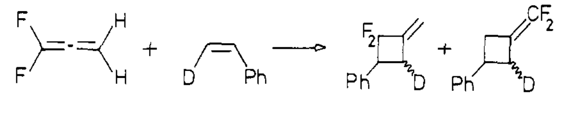
partition between two competitive cyclizations to form regioisomeric products **2** and **3**. In similar cycloadditions *not* involving

---

[1] Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1984**, *49*, 2381.

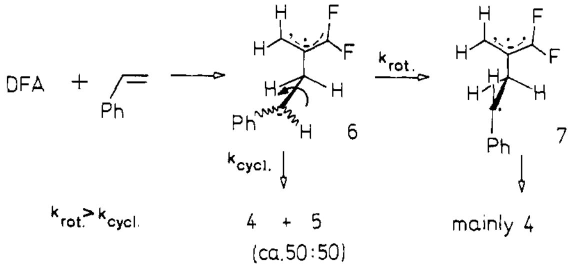
allenic components total regiochemical determination is accomplished with initial bond formation. Hence, the existence of a *second* point of partitioning provides the potential for much additional insight being obtained from the careful study of allene [2 + 2] cycloadditions.

We have already demonstrated the efficacy of such studies in our probe of the stereochemistry of the reaction of difluoroallene (DFA) with (*Z*)-*β*-deuteriostyrene.[2] In this reaction a significantly greater degree of retention of stereochemistry was observed for the minor product product **5**-*d* than for the major product **4**-*d*.



4-d 5-d

This finding required the proposition of a mechanism involving at least two kinetically distinct diradicals, i.e., **6** and **7**. The properties attributed to initially formed diradical **6** were those of a kinetically unstable species, i.e., lack of regioselectivity and high stereoselectivity in its cyclization plus rapid conversion via C–C bond rotation to a more stable diradical, such as **7**, which itself would cyclize with greater regio- and less stereoselectivity.



Various probes of such a mechanism can be envisioned including those wherein either the allene or the styrene component would be structurally modified. Indeed, we have recently completed a study of the effect of *α*-substitution on the styrene component,[3] while Pasto and co-workers have examined the stereochemistry of dimethylallene–dimethyl maleate/fumarate cycloadditions,[4] with the results of such studies being generally consistent with the mechanistic scheme above.

On the other hand, it was considered that a more subtle perturbation of the dynamics of this mechanism, wherein structural change along with its concomitant complications regarding steric and electronic effects on the kinetic and thermodynamic picture would not be required, might be able to provide unique insight. The probability of significant effects of very high pressure and/or increased viscosity of the medium upon the regio- and stereochemical outcome of the reaction was considered to be such a potentially subtle and thus dramatic probe. It was predicted, because of an expected $-\Delta V^{\ddagger}$ for the cyclization of diradical **6** as compared to little expected ΔV for any rotational conversion of **6** to **7**, that under increasingly high pressure the reaction should become less regioselective and more stereoselective. Similarly, according to propositions of Firestone,[5] increasing viscosity should cause a similar influence.

In this communication we wish to report preliminary results which bear upon the effect of pressure and viscosity on the *regiochemistry* of the DFA–styrene cycloaddition. As can be seen in Table I, increasing pressure does indeed give rise to a discernable diminishment in the regioselectivity of the reaction,[6,7] a result consistent with our mechanistic suppositions. Similarly, as shown in Table II, there is observed a significant reduction in the regioselectivity of this reaction as one increases the viscosity of the medium.

Table I. Pressure Effects on the Regiochemistry of the DFA/Styrene Cycloaddition[a]

pressure, kbar	ratio **4**:**5**	% **4**
2.95	7.33 ± 0.02	88.0
3.57	7.02 ± 0.02	87.5
4.32	6.22 ± 0.05	86.1
5.03	5.58 ± 0.06	84.8
5.70	5.39 ± 0.05	84.3
6.18	5.01 ± 0.02	83.4

[a] In pentane at 25 °C for 4 h.

Table II. Viscosity Effects on the Regiochemistry of the DFA/Styrene Cycloaddition[a]

solvent	η^b	η_{rel}	ratio **4**:**5**	% **4**
heptane	0.31	1	4.34 ± 0.06	81.3
Nujol	5.8	18	4.13 ± 0.08	80.5
N/P-3[c]	11.3	36	3.98 ± 0.10	79.9
N/P-2[c]	26.7	86	3.75 ± 0.04	78.9
N/P-1[c]	55.4	179	3.13 ± 0.03	75.8

[a] At 120 °C for 2.5 h. [b] Experimentally determined with a Brookfield Model LVT Viscometer. [c] Mixtures of Nujol and soluble Aldrich high-density polyethylene pellets (ca. 1–3 g of polyethylene/100 mL of Nujol).

A question, of course, thus arises as to the degree that the observed pressure effects can be attributed to an increase in viscosity that will inevitably take place at high pressures. The effect of pressure on viscosity for hydrocarbon solvents such as pentane has been measured and is found to be relatively small.[8] Over the range of pressures utilized in our study a change in viscosity of only 10–12-fold would be expected.[9] Therefore viscosity changes can realistically explain only a small part of the high pressure effects.

Another question is whether the diminishment of regioselectivity for this reaction can be explained simply as a leveling effect resulting from rate enhancement due to pressure (or viscosity). For a Diels–Alder reaction ($\Delta V^{\ddagger} \approx 35$ cm^3/mol), a rate change of ~10-fold would be expected by increasing pressure from 3 to 6 kbar.[10] Moreover, for a [2 + 2] cycloaddition, observed rate enhancements due to pressure have been shown to be about *half* those for Diels–Alder reactions.[11] In fact, the DFA/styrene reaction appeared to undergo only about a 2.5-fold rate increase in going from 3 to 6 kbar.[12] In our earlier study of the effect of temperature upon the regiochemistry of the DFA/styrene reaction,[2] a 30 °C increase (70 → 100 °C), which certainly should give rise to a comparable if not greater rate enhancement than that due to the pressure change, resulted in a much smaller change in regioselectivity (from 4.88 to 4.26). It was also found that over the viscosity range studied there was little observed change in rate for the DFA/styrene reaction.[13]

Therefore it seems clear that increases in either viscosity or pressure have an intrinsic and predictable, unambiguously significant effect upon the regiochemical outcome of the DFA/styrene cycloaddition, a result which is consistent with the earlier hypothesized two-intermediate picture of the mechanism of this

---

(2) Dolbier, W. R., Jr.; Wicks, G. E. *J. Am. Chem. Soc.* **1985**, *107*, 3626.

(3) Dolbier, W. R., Jr.; Seabury, M. J. *Tetrahedron Lett.* **1987**, *28*, 1491.

(4) Pasto, D. J.; Yang, S. H. *J. Am. Chem. Soc.* **1984**, *106*, 152.

(5) Firestone, R. A.; Vitale, M. A. *J. Org. Chem.* **1981**, *46*, 2160.

(6) The greater regioselectivities observed for the DFA/styrene reactions in this study (88% major product at 2.95 kbar, 25 °C), compared to those in our earlier study[2] (83% major product at 1 bar, 70 °C) can reasonably be attributed to a variation deriving from reaction temperature differences. Such temperature-dependent variations in product ratio were observed in the earlier study.

(7) The reaction was *very slow* under these conditions, never proceeding to as much as 10% conversion, even at the higher pressures.

(8) Brazier, D. W.; Freeman, G. R. *Can. J. Chem.* **1969**, *47*, 893.

(9) This is assuming that our reaction medium, a mixture of pentane, styrene, and DFA, will behave as far as viscosity is concerned like pure pentane. It was in fact only 70–80% pentane by weight.

(10) (a) Rimmelin, J.; Jenner, G. *Tetrahedron* **1974**, *30*, 3081. (b) Walling, C.; Peisach, J. *J. Am. Chem. Soc.* **1958**, *80*, 5819.

(11) Stewart, C. A., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 635.

(12) Our crude rates were based simply upon the relative amount of adducts actually formed at each pressure.

(13) The measured relative rates for the DFA/styrene reaction in solvents N/P-3, Nujol, and heptane were 1.50, 1.48, and 1.0, respectively.

reaction as well as with earlier pressure studies which were utilized to emphasize the mechanistic differences in competing concerted and nonconcerted processes.[11,14] The effect of pressure and viscosity on the *stereochemical* outcome of this reaction, which study is currently in progress, should provide even more clear-cut insights into these questions.

Acknowledgment. Support of this research in part by the National Science Foundation and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are also indebted to Dr. Philip de Shong for his generosity in allowing us to use his high pressure apparatus at Penn State University.

(14) Klarner, F. G.; Dogan, B. M. J.; Ermer, O.; Doering, W. von E.; Cohen, M. P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 108.

A New Type of Stable, Storable, and Selective Alkylating Reagent, R_4Pb

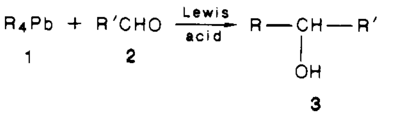
Yoshinori Yamamoto* and Jun-ichi Yamada

Department of Chemistry, Faculty of Science
Tohoku University, Sendai 980, Japan

Received February 3, 1987

Needless to say, organomagnesium, organolithium, and organocopper derivatives are classical and widely used carbanionic alkylating reagents. Since the mid-1970s, a new current has appeared in this field. Several air-stable and storable reagents for the C–C bond formation of carbonyl compounds have been developed, which are normally used under nonbasic conditions.[1] Unfortunately, however, the transfer from the hitherto known reagents is limited to the particular functional groups such as allyl,[1b,c] alkynyl,[2] and enols.[1a] The transfer of alkyl groups is entirely unknown despite its potential synthetic importance.[3] We report for the first time a new method for the alkyl transfer via a stable and storable reagent, R_4Pb.

Tetraalkylleads[4] reacted quite smoothly with aldehydes in the presence of Lewis acids such as $TiCl_4$ and BF_3 (eq 1). The results are summarized in Table I. Titanium tetrachloride gave the best result among the Lewis acids examined. A possibility that $RTiL_n$ may be a real intermediate is eliminated by the following reasons. *n*-Alkyl groups and even a cyclohexyl group underwent the transfer reaction. It is well-known that *n*-alkyl and *sec*-alkyl titanium compounds of the type $Cl_3Ti–R$ (R = alkyl) easily undergo *β*-elimination reactions.[5] Further, formation of **3** by use of BF_3-OEt_2 clearly indicates that transmetalation from R_4Pb to RBL_n does not take place under lower temperature, since RBL_n cannot alkylate aldehydes under the reaction conditions.



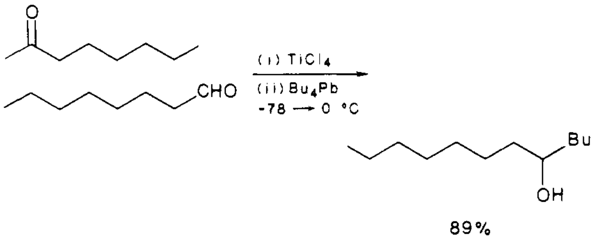
$$\underset{\mathbf{1}}{R_4Pb} + \underset{\mathbf{2}}{R'CHO} \xrightarrow[\text{acid}]{\text{Lewis}} \underset{\mathbf{3}}{R-\underset{OH}{CH}-R'} \quad (1)$$

Table I. Alkyl Transfer from R_4Pb to Aldehydes[a]

entry	R_4Pb (**1**) R	R'CHO (**2**) R'	reaction condn temp (°C)	reaction condn **1** (equiv)	isolated yield of **3**, %
1	Et	C_6H_5	−78 → −30	1.8	96
2	Et	C_6H_{11}	−78 → −30	1.3	98
3	Et	$CH_3(CH_2)_6$	−78 → −30	1.3	94
4	Bu	C_6H_{11}	−78 → 0	1.3	84
5	Bu	C_6H_{11}	−78 → −30	1.3	70
6	Bu	$CH_3(CH_2)_6$	−78 → 0	1.3	88
7	Bu	$CH_3(CH_2)_6$	−78 → −30	1.3	73
8	C_6H_{11}	C_6H_{11}	−70 → 0	2.0	38
9	C_6H_{11}	C_6H_{11}	−70 → −30	1.3	32
10	C_6H_{11}	$CH_3(CH_2)_6$	−70 → 0	2.0	46
11	C_6H_{11}	$CH_3(CH_2)_6$	−70 → −30	1.3	41

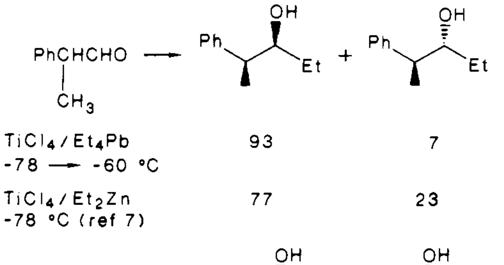
[a] The procedure of entry 1 is representative. To a solution of benzaldehyde (1 mmol) in CH_2Cl_2 (1 mL) was added at −78 °C a solution of $TiCl_4$ in CH_2Cl_2 (1 M, 1.2 mmol), and then Et_4Pb–CH_2Cl_2 solution (1 M, 1.8 mmol) was added.[6] The reaction mixture was gradually warmed to −30 °C. Then, the reaction was quenched with aqueous $NaHCO_3$–MeOH. The product was isolated by column chromatography on silica gel (entries 1 ~ 3) or on alumina (entries 4 ~ 11), by using *n*-hexane–ether as an eluant. Excess Et_4Pb and Bu_4Pb were recovered and could be utilized repeatedly. When the reaction was incomplete (entries 4 ~ 11), the starting aldehyde was recovered.

As is apparent from Table I, transfer of an ethyl group occurs rapidly in essentially quantitative yields (entries 1–3). Transfer of a butyl group is relatively slow in comparison with ethyl transfer (entries 4–7), and cyclohexyl group can be transferred slowly at 0 °C (entries 9–11). Another important aspect of $R_4Pb/TiCl_4$ is its chemoselectivity. Only aldehydes underwent the alkylation in the presence of ketones (for example, eq 2). Cyclohexanone and related ketones did not react with Bu_4Pb at room temperature for a prolonged period of time.

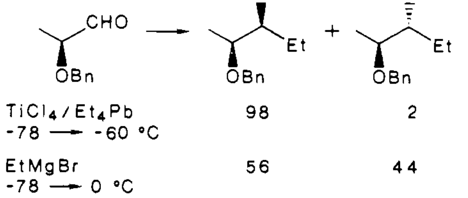


(2)

Very high 1,2- and 1,3-asymmetric induction was realized with this new reagent (eq 3–5). Especially noteworthy is the high asymmetric alkylation of eq 3 and 5. Such a high diastereoselective alkylation cannot be achieved by using the previous reagents. The ethylation of 2-phenylpropionaldehyde took place



(3)



(4)

---

(1) (a) Silyl enol ethers: Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973**, 1011. (b) Allylsilanes: Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (c) Allyltins: Tagliavini, G.; Peruzzo, V.; Plazzogna, G.; Marton, D. *Inorg. Chim. Acta* **1977**, *24*, L24. Naruta, Y.; Ushida, S.; Maruyama, K. *Chem. Lett.* **1979**, 919. (d) Allylboranes; allylaluminums, and related compounds react under nonbasic conditions, but they are air and moisture sensitive.

(2) (a) Stannylacetylenes: Yamamoto, Y.; Nishii, S.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, *102*. (b) Silylacetylenes: Kuwajima, I.; Nakamura, E.; Hashimoto, K. *Tetrahedron* **1983**, *39*, 975.

(3) Dialkylzinc compounds, which are moisture and air sensitive, transfer alkyl groups to aldehydes in the presence of $TiCl_4$ (ref 7).

(4) Et_4Pb and Bu_4Pb were prepared essentially according to the literature procedure: Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1950**, *72*, 1760. $(C_6H_{11})_4Pb$ was prepared as described in the literature: Gruttner, G. *Chem. Ber.* **1914**, *47*, 3257.

(5) *n*-Alkyl titanium compounds of the type $(i\text{-}PrO)_3Ti–R$ do not undergo *β*-elimination reactions: (a) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer-Verlag: New York, 1985. (b) Seebach, D. *Mod. Synth. Methods* **1983**, *3*, 216.

(6) Clean reactions did not occur upon the reversed addition: (i) R_4Pb, (ii) $TiCl_4$, and then (iii) aldehydes. Apparently, the transmetalation took place first and $RTiL_n$ was involved as an intermediate in the reversed addition.

(7) Reetz, M. T.; Steinbach, R.; Wenderoth, B. *Synth. Commun.* **1981**, *11*, 261.

0002-7863/87/1509-4395$01.50/0