Regioselective 1,4-Addition to α,β-Unsaturated Ketones with Grignard Reagents Mediated by (N,N,N′,N′-Tetramethylethylenediamine)zinc(II) Chloride

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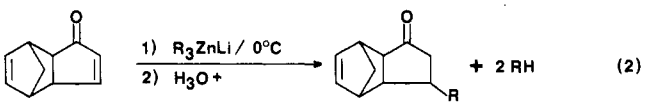
The reaction of α,β-unsaturated ketones with a THF solution of RMgX (3 mol equiv) and $ZnCl_2$·TMEDA (1 mol equiv) followed by NH_4Cl gave 1,4-addition products. The products were contaminated by 1,2-addition products when R = Ph and Me but were essentially free of those compounds when R = *n*-Bu or *i*-Pr. The yields were highest when X = Cl. Thus the reaction of 2-cyclohexen-1-one with a solution of *n*-BuMgCl and $ZnCl_2$·TMEDA gave 3-*n*-butylcyclohexanone (1) in 96% yield.

Throughout the last 4 decades chemists have had the ability to add alkyl groups to α,β-unsaturated ketones in a 1,4-fashion without appreciable contamination by the unwanted 1,2-addition product. Perhaps the most well-known reagents for this are the organocuprates (R_2CuM, M = Li or MgX),[1] but more recently higher order cuprates such as $RR'Cu(CN)Li_2$ have received much attention due to their thermal stability and high efficiency.[2]

Lithium triorganozincates (R_3ZnLi) are another type of reagent that can be used to add alkyl groups in a 1,4-fashion to α,β-unsaturated ketones.[3] They have not, however, been studied as extensively as cuprates. Isobe[3a] and co-workers demonstrated that lithium triorganozincates which were prepared from $ZnCl_2$ (eq 1), or much

$$ZnCl_2 + 3\,RLi \xrightarrow{0°C\,/\,THF} R_3ZnLi + 2\,LiCl \qquad (1)$$



(2)

more conveniently[4] from $ZnCl_2$/*N,N,N′,N′*-tetramethylethylenediamine complex ($ZnCl_2$·TMEDA), react with the enone shown in eq 2 to give excellent yields of 1,4-addition products. They also showed that these triorganozincates can be prepared and used at 0 °C and that an indicator can be used to signal the end point in the addition of 3 equiv of alkyllithium to the $ZnCl_2$ or $ZnCl_2$·TMEDA. Thus, lithium triorganozincates are very convenient to prepare and use. Langer and Seebach[3b] showed that, like cuprates, the 1,4-addition reactions of zincates are enantioselective when carried out in a chiral medium. Watson and Kjonaas[3c] showed that mixed lithium triorganozincates (RMe_2ZnLi) selectively transfer the R group (R = *n*-Bu or *sec*-Bu) rather than methyl.

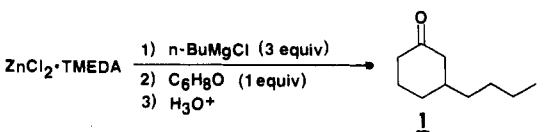
As part of our search for carbon–carbon bond formation methods which complement existing methods, we decided to prepare a variety of triorganozincates from Grignard reagents rather than from alkyllithiums and to study the reactivity of these reagents toward α,β-unsaturated ketones. Reported herein are the results of those experiments.

Results and Discussion

Isobe[3a] and co-workers had used triphenylmethane as an indicator to mark the end of the addition of the third equivalent of alkyllithium to $ZnCl_2$·TMEDA when preparing lithium triorganozincates. Since the reaction of Grignard reagents with triphenylmethane does not give a colored species, we chose to use 2,2′-bipyridine as our indicator.

Thus, we began adding *n*-butylmagnesium chloride via syringe to a solution of 1.00 mmol of $ZnCl_2$·TMEDA and about 2 mg of 2,2′-bipyridine in THF. Surprisingly, the red color of the indicator–Grignard complex began to appear after only a small amount of Grignard reagent had been added. This faint color slowly intensified as more Grignard reagent was syringed into the THF solution. After the concentration of the Grignard was confirmed by two titration methods,[5,6] the experiment was repeated except that another indicator, *N*-phenyl-1-naphthalenamine, was used. Again, the light red color began to appear long before 3.00 mmol of Grignard had been added to the 1.00 mmol of $ZnCl_2$·TMEDA. Similar results were obtained when 1,10-phenanthroline was used as the indicator.

Because of these observations, we decided to prepare the reagents without using an indicator. Addition of 3.00 mmol of *n*-BuMgCl to 1.00 mmol of $ZnCl_2$·TMEDA in THF gave a solution which, when treated with 1.00 mmol of 2-cyclohexen-1-one, gave a 96% yield of 3-*n*-butylcyclohexanone (1) as shown in eq 3. This product contained



(3)

1

less than 1% of the 1,2-addition product. Further experiments in which the ratio of *n*-BuMgCl to $ZnCl_2$·TMEDA was 1:1, 2:1, and 4:1 gave 1 in much lower yield than the 96% obtained with the 3:1 ratio.

It might be expected that the 1:1 and 2:1 mixtures of *n*-butylmagnesium chloride and $ZnCl_2$·TMEDA are actually solutions of *n*-butylzinc chloride and di-*n*-butylzinc respectively. Indeed, a common procedure for preparing

(1) Posner, G. H. *Org. React.* **1972**, *19*, 1. Posner, G. H. *An Introduction to Synthesis Using Oganocopper Reagents*; Wiley: New York, 1980.

(2) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *J. Org. Chem.* **1984**, *49*, 3938–3942.

(3) (a) Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* **1977**, 679–682. (b) Langer, W.; Seebach, D. *Helv. Chim. Acta* **1979**, *62*, 1710–1722. (c) Watson, R. A.; Kjonaas, R. A. *Tetrahedron Lett.* **1986**, *27*, 1437–1440.

(4) $ZnCl_2$·TMEDA is more convenient to use than $ZnCl_2$ since it is nonhygroscopic. Because of experimental difficulties encountered in our previous experiences with anhydrous $ZnCl_2$ solutions, we limited this study to $ZnCl_2$·TMEDA. Unfortunately, $ZnCl_2$·TMEDA is only slightly soluble in ether.

(5) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.

(6) Bergbreiter, D. E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219–220.

0022-3263/86/1951-3993$01.50/0

Table I. Effect of Time and Temperature on the Reaction of "(n-Bu)$_3$ZnMgCl" with 2-Cyclohexen-1-one

reaction time, min	temp, °C	% yield of 1[a,b]
5	0	86
5	−84	71
5	25	69[c]
30	0	96
30	−84	78
1000	0	44

[a] Yields were determined by GC analysis with an internal standard and appropriate response factor. [b] Less than 1% yield of tertiary alcohol derived from 1,2-addition unless otherwise noted. [c] 3% yield of 1,2-addition product.

alkylzinc halides (RZnX) and dialkylzinc reagents (R_2Zn) is the treatment of $ZnCl_2$ with Grignard reagents.[7] The literature is unclear, however, on the ability of RZnX and R_2Zn reagents to add in a 1,4-fashion to α,β-unsaturated ketones.[8]

The result obtained with the 3:1 mixture of n-BuMgCl and $ZnCl_2$·TMEDA (eq 3) suggests that a magnesium triorganozincate species ($R_3ZnMgCl$) might have formed in spite of the puzzling result obtained with the three different indicators mentioned above. Although there is evidence in the literature for the existence of *lithium* triorganozincates,[9] our experiments offer no real evidence for the existence of a *magnesium* triorganozincate. Thus, we use the formula "R_3ZnMgX" only to denote the stoichiometry involved in preparing the solutions used in this study.

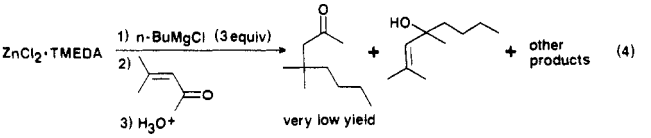
Encouraged by the result shown in eq 3, we carried out a series of experiments in which a THF solution of n-BuMgCl (3.00 mmol) and $ZnCl_2$·TMEDA (1.00 mmol) was prepared at 0 °C and then treated with 2-cyclohexen-1-one (1.00 mmol) at various temperatures and allowed to react for various lengths of time prior to aqueous workup. The results (Table I) suggest that 0 °C and 30 min are the best conditions. Reaction times that were considerably longer than 30 min invariably led to lower yields, as exemplified by the last entry in Table I. Also, the use of excess reagent ("$R_3ZnMgCl$") led to lower yields.

The scope of the reaction is more clearly defined by the examples in Table II. The reaction appears to be of very little utility for 1,4-addition of a methyl group to methyl vinyl ketone (MVK) because of the low yields and because of the competing 1,2-addition. The same trend is seen with 2-cyclohexen-1-one except when the reagent is derived from CH_3MgCl rather than CH_3MgBr or CH_3MgI and when it is used at −84 °C. Even then, a 9% yield of the unwanted 1,2-addition product accompanies the 84% yield of 1,4-addition product (entry 8).

Addition of n-butyl and isopropyl groups to 2-cyclohexen-1-one, 2-cyclopenten-1-one, and MVK is much more regioselective than addition of either methyl or phenyl. With the exception of one example (entry 25), the 1,2-addition products appeared in no more than trace amounts. Although the yields of 1,4-addition of n-butyl and isopropyl groups to MVK are not as good as those involving 2-cyclohexen-1-one, they are, nonetheless, quite acceptable in view of the well-known reluctance of MVK to undergo 1,4-addition efficiently with dialkylcuprates.

Except for the fact that unreacted starting material could be detected in virtually every reaction, the reactions in Table II were very clean. In the reaction of "(i-pr)$_3$ZnMgCl" with 2-cyclopenten-1-one (entry 26), most of the ketone that was not converted to 1,4-addition product could be recovered intact. Attempts to decrease the amount of unreacted ketone in that reaction by using more reagent or longer reaction times were unsuccessful. This observation is consistent with the assumption that deprotonation is a competing reaction.

Production of a quaternary carbon by 1,4-addition of n-butyl to mesityl oxide is very inefficient by this method (eq 4). In contrast, higher order mixed organocuprate



reagents have been shown by Lipshutz[2] and co-workers to give excellent yields of 1,4-addition to mesityl oxide as well as some even more hindered α,β-unsaturated ketones. It should be noted, however, that those excellent yields could be obtained in diethyl either but not in THF. Our reactions were run in THF[4].

Conclusions

Although there is no evidence for the formation of an actual Grignard-derived triorganozincate species (R_3ZnMgX), Grignard reagents can be used in place of alkyllithium reagents in a 3:1 molar ratio with $ZnCl_2$·TMEDA in order to effect 1,4-addition to α,β-unsaturated ketones. Unlike the preparation of triorganozincates from alkyllithium reagents, it does not appear to be possible to use an indicator to signal the end point in the addition of 3 molar equiv of Grignard to the $ZnCl_2$·TMEDA.

The use of the Grignard/($ZnCl_2$·TMEDA) solutions to transfer n-butyl and isopropyl in a 1,4-fashion offers an advantage over the use of both lower and higher order cuprates in that the yields are comparable but the reactions are carried out at 0 °C. This is a more convenient temperature than the low temperatures reported in the use of cuprate reagents.[1,2] An accurate comparison of the efficiency of Isobe's R_3ZnLi reagents to that of the reagents reported in this study cannot be made since the enones used in the two studies are not the same. It appears, however, that the method described here is more efficient than the R_3ZnLi method when transferring primary, secondary, and aryl moieties.

The general availability of Grignard reagents along with the thermal stability and, in some cases, the efficient reactivity of the Grignard/($ZnCl_2$·TMEDA) solutions make this a viable synthetic method.

Experimental Section

^{1}H NMR spectra were recorded on a Varian T-60 and resonances are reported in δ with tetramethylsilane as the internal standard. Infrared spectra were recorded on a Perkin-Elmer 700.

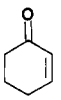
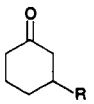
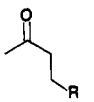
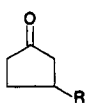
(7) Boershma, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. Ed.; Pergamon: New York, 1982; Vol. 2, p 832. Sheverdina, N. I.; Kocheshkov, K. A. "Methods of Elemento-Organic Chemistry" *The Organic Compounds of Zinc and Cadmium*; North-Holland: Amsterdam, 1967; Vol. 3.

(8) It was shown by Gilman and Kirby (ref 8a) that diphenylzinc gives a 91% yield of 1,4-addition product with benzalacetophenone, but benzalacetophenone does not appear to be a very good test case since even phenylmagnesium bromide gives that same product in 94% yield (ref 8b). To our knowledge, a general study involving the reactions of RZnX and R_2Zn with α,β-unsaturated ketones does not exist, but there are numerous reports of related work (see, for example, ref 8c–g). (a) Gilman, H.; Kirby, R. H. *J. Am. Chem. Soc.* **1941**, *63*, 2046–2048. (b) Sullivan, W. I.; Swamer, R. W.; Humphlett, W. J.; Hauser, C. R. *J. Org. Chem.* **1961**, *26*, 2306–2310. (c) Luche, J-L.; Petrier, C.; Lansard, J-P.; Greene, A. E. *J. Org. Chem.* **1983**, *48*, 3837–3839. (d) Shono, T.; Nishiguchi, I.; Sasaki, J. *J. Am. Chem. Soc.* **1978**, *100*, 4314–4315. (e) Bellassaued, M.; Frangin, Y.; Gaudemar, M. *Synthesis*, **1977**, 205–208. (f) Kataoka, K.; Tsuratu, T. *Polym. J.* **1977**, *9*, 595–604. (g) Kohler, E. P.; Heritage, G. L.; MacLeod, A. L. *J. Am. Chem. Soc.* **1911**, *46*, 217–236.

(9) Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1963**, *85*, 2861–2863. See also: Wittig, G.; Meyer, F. J.; Lang, G. *Justus Liebigs Ann. Chem.* **1951**, 167–201.

Table II. Reaction of "R_3ZnMgX" with α,β-Unsaturated Ketones

$$ZnCl_2\cdot TMEDA \xrightarrow[THF]{RMgX\ (3\ equiv)} \text{"}R_3ZnMgX\text{"} \xrightarrow[(2)\ NH_4Cl\ (aq)]{(1)\ enone\ (1\ equiv)} \text{products} + RH$$

entry	enone	R	X	conditions[a]	products: compd number,	products: % yield[b]
						
1		*n*-butyl	Cl		1, 96	2, <1
2			Br		1, 79	2, <1
3		isopropyl	Cl		3, 87	3, 0
4			Br		3, 88[c]	4, 0
5		phenyl	Cl		5, 93	6, 4
6			Br		5, 61	6, 30
7		methyl	Cl		7, 39	8, 32
8			Cl	−84 °C[d]	7, 84	8, 9
9			Br		7, 33	8, 39
10			Br	−84 °C[d]	7, 29	8, 10
11			I		7, 26	8, 45
12			I	−84 °C[d]	7, 42	8, 4
						
13		*n*-butyl	Cl		9, 68	10, <1
14			Br		9, 50	10, <1
15		isopropyl	Cl		11, 73	12, <1
16			Br		11, 70	12, <1
17		phenyl	Cl		13, 64	14, <3
18			Br		13, 59	14, <3
19		methyl	Cl		15, 45	16, 50
20			Cl	−84 °C ↑[e]	15, 55	16, 43
21			Br		15, 9	16, 9
22			Br	−84 °C ↑[e]	15, 12	16, 1
23			I		15, 4	16, 4
24			I	−84 °C ↑[e]	15, 6	16, 5
						
25		*n*-butyl	Cl		17, 78	18, 3
26		isopropyl	Cl		19, 58	20, 0

[a] 0 °C/30 min unless otherwise noted. [b] Yields were determined by GC integration with an internal standard and appropriate response factor. [c] 88% isolated yield. [d] The Grignard/($ZnCl_2$·TMEDA) solution was prepared at 0 °C, cooled to −84 °C, treated with the α,β-unsaturated ketone, allowed to stir 30 min at −84 °C, and then quenched by pouring into aqueous NH_4Cl. [e] After the reaction mixture had stirred at −84 °C for 15 min, the cold bath was removed and the reaction was allowed to stir an additional 15 min before being quenched by pouring into aqueous NH_4Cl.

A Varian Aerograph 90-P with a 0.25 in. × 6 ft column packed with 3% SE-30 on 100/120 Varapact #30 was used for preparative gas chromatography. Analytical GC was performed on either a Varian 3300 equipped with a stainless steel ($^1/_8$ in. × 6 ft.) column packed with 10% OV-1 on WHP 80/100, or a Hewlett-Packard 5710A equipped with the same column. Recording and integration were done by either a Houston Instruments OmniScribe recorder or a Shimadzu C-R3A Chromatopac. Microanalysis were done by Galbraith Laboratories, Inc., Knoxville, TN.

All glassware and syringes were oven-dried. The reactions were run under an atmosphere of N_2 that had passed through concentrated H_2SO_4, solid NaOH, and solid anhydrous $CaSO_4$.

Chemicals. THF (Burdick and Jackson Laboratories) was stored under reflux with sodium and benzophenone. The α,β-unsaturated ketones were obtained commercially and, except for 2-cyclopenten-1-one, were distilled prior to use. Methylmagnesium chloride in THF and methylmagnesium bromide in diethyl ether were purchased from Alfa and methylmagnesium iodide in diethyl ether was purchase from Aldrich. The other Grignard reagents were prepared by standard methods from the corresponding organohalides and magnesium. The concentrations varied from 1.0 to 1.9 M.

$ZnCl_2$·TMEDA was prepared by Isobe's method;[3a] i.e., 19 mL of saturated $ZnCl_2$/THF solution and 5 mL of TMEDA were mixed and allowed to stand several hours at 25 °C. The crude crystals were separated and recrystallized from THF; white needles, mp 176–177.

Titration of Grignard Reagents. The concentration of each Grignard reagent except methylmagnesium iodide was determined by the following procedure and in some cases was confirmed by two well-known procedures.[5,6] Approximately 2 mg of 2,2′-bipyridine or 1,10-phenanthroline was dissolved in 5 mL of THF at 0 °C. The Grignard was then added via syringe until a light red color appeared. A carefully weighed amount (usually about 1 mmol) of menthol (Fisher) was then dissolved in this solution and treated with enough Grignard via a 1-mL syringe to reproduce the light red color. Results of these titrations were reproducible to approximately ±2.0% for all of the Grignard reagents except CH_3MgBr (±4.0%) and CH_3MgI. The latter of these gave nebulous results by this method as well as by two other methods.[5,6] For this reason, the CH_3MgI concentration reported on the label was employed.

General Procedure for 1,4-Addition. To a stirred solution of 1.00 mmol of $ZnCl_2$·TMEDA (252 mg) in 5 mL of THF at 0 °C under an atmosphere of dry N_2 was added 3.00 mmol of Grignard (approximately 2 M in ether except C_6H_5MgCl and CH_3MgCl which were in THF) followed immediately by 1.00 mmol of the α,β-unsaturated ketone. After being stirred at 0° C for 30 min, the solution was poured into 5 mL of saturated aqueous NH_4Cl and then diluted with 5 mL of diethyl ether. The organic

phase was separated, washed with 5 mL of saturated aqueous NH_4Cl, dried with Na_2SO_4 or $CaCl_2$, and the evaporated. When yields were determined by GC, an internal standard (often benzylacetone) was added after the 5 mL of ether, and the organic phase was not evaporated. In those cases in which the temperature in Table II is cited as "−84 °C", the reaction mixture was cooled to −84 °C (N_2/ethyl acetate) prior to the addition of the α,β-unsaturated ketone. Thirty minutes after the addition, the reaction mixture, still at −84 °C, was poured into 5 mL of saturated aqueous NH_4Cl and worked up as described above. In those cases in which the temperature is cited as "−84 °C↑" in Table II, the cold bath was removed half way through the 30-min reaction time. At the end of the 30 min, the reaction mixture, now near room temperature, was worked up as described above.

Identification of Products. Except for entry 26 in Table II, the identity of each 1,4- and 1,2-addition product was confirmed by comparing the ^1H NMR spectrum and the GC retention time (coinjection) with that of authentic materials. The sources of the authentic materials are as follows: **7**, **9**, **11**, **13**, **15**, and **16** were obtained commercially; **1** was prepared by Isobe's method;[3a] **2**, **3**,[10] **4**,[10] **6**,[11] and **8**[10] were prepared by treating 2-cyclohexen-1-one with the corresponding Grignard reagent and were purified by preparative GC; **10**, **12**, and **14** were prepared by treating vinylmagnesium bromide (Aldrich) with the corresponding methyl ketone; **5** was prepared from lithium diphenylcuprate and 2-cyclohexen-1-one;[12] **17** was prepared from 2-cyclopenten-1-one and n-$Bu_2Cu(CN)Li_2$;[2] **18** was prepared from 2-cyclopenten-1-one and n-butyllithium.

3-Isopropylcyclopentanone (19). Following the general procedure and preparative GC, **19** was isolated as an oil: IR (neat) 1730 cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (d, 6 H), 1.2–1.8 (m, 4 H), 1.8–2.3 (m, 4 H). Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.32; H, 11.30.

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Registry No. **1**, 39178-69-3; **3**, 23396-36-3; **5**, 20795-53-3; **6**, 60174-90-5; **7**, 591-24-2; **8**, 23758-27-2; **9**, 111-13-7; **11**, 110-12-3; **13**, 2550-26-7; **15**, 107-87-9; **16**, 115-18-4; **17**, 57283-81-5; **19**, 10264-56-9; 2-cyclohexenone, 930-68-7; methyl vinyl ketone, 78-94-4; 2-cyclopentenone, 930-30-3; butylmagnesium chloride, 693-04-9; butylmagnesium bromide, 693-03-8; isopropylmagnesium chloride, 1068-55-9; isopropylmagnesium bromide, 920-39-8; phenylmagnesium chloride, 100-59-4; phenylmagnesium bromide, 100-58-3; methylmagnesium chloride, 676-58-4; methylmagnesium bromide, 75-16-1; methylmagnesium iodide, 917-64-6.

(10) Whitmore, F. C.; Pedlow, G. W. *J. Am. Chem. Soc.* **1941**, *63*, 758–760.
(11) Brown, H. C.; Ravindranathan, M.; Rho, M. M. *J. Am. Chem. Soc.* **1976**, *98*, 4216–4218.
(12) House, H. O.; Giese, R. W.; Kronberger, K.; Kaplan, J. P.; Simeone, J. F. *J. Am. Chem. Soc.* **1970**, *92*, 2800–2810.

Electrochemical Synthesis of Organosilicon Compounds

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Electrochemical reduction of allyl, aryl, and vinyl halides in the presence of a silylating agent (Me_3SiCl, HMe_2SiCl, and $PhMe_2SiCl$) in a solution of tetraethylammonium tosylate in dimethylformamide (DMF) gave the corresponding organosilicon compounds. The regioselectivity of the reaction of allylic halides depends on the nature of the silylating agent. Trimethylsilyl and dimethylphenylsilyl groups were introduced to the less substituted end of the allyl group, whereas the dimethylsilyl group was introduced to both ends of the allyl group. High chemoselectivity of the present approach was demonstrated by selective monosilylations of *p*-bromoiodobenzene and *p*-bromocinnamyl chloride to obtain (*p*-bromophenyl)trimethylsilane and (*p*-bromocinnamyl)trimethylsilane, respectively. A mechanism involving a carbanion intermediate is suggested.

The usefulness of organosilicon compounds as synthetic intermediates[2] opens the question of their methods of preparation. Although several methods, including the direct method,[3] transmetalation,[4] hydrosilylation,[5] reductive silylation,[6] and methods using silyl anions[7] and disilanes,[8] have been developed so far, simple and versatile methods are still required especially from a view point of chemoselectivity. Recently we have reported an electro-

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(2) (a) Weber, W. P. *Silicon Reagent for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (c) Magnus, P. D.; Sarkar, T.; Djuric, S. *Comp. Organomet. Chem.* **1982**, *7*, 515. (d) Fleming, I. *Compr. Org. Chem.* **1979**, *3*, 539. (e) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (f) Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; Vol. 1, Chapter 6.
(3) Rochow, E. G. *J. Am. Chem. Soc.* **1945**, *67*, 963.
(4) For example: (a) Kipping, F. S. *J. Chem. Soc.* **1907**, *91*, 209. (b) Kipping, F. S. *Ibid.* **1907**, *91*, 717. See also ref 1f.
(5) For example: (a) Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; MacDiamid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1. (b) Lukevics, E. Y.; Voronkov, M. G. *Organic Insertion Reactions of Group IV Elements*; Consultant Bureau: New York, 1966. (c) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Library*, **1977**, *5*, 1. (d) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.
(6) For example, (a) Calas, R.; Dunogues, J. *J. Organomet. Chem. Library*, **1976**, *2*, 277. (b) Calas, R. *J. Organomet. Chem.* **1980**, *200*, 11. (c) Benkeser, R. A. *Acc. Chem. Res.* **1971**, *4*, 94.
(7) For example, Si–Li: (a) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 608. (b) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063. Si–Na, Si–K: (c) Shippey, M. A.; Dervan, P. B. *J. Org. Chem.* **1977**, *42*, 2654. (d) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511. (e) Sakurai, H.; Kondo, F. *J. Organomet. Chem.* **1975**, *92*, C46. Si–Al: (f) Altnau, G.; Roesch, L. *Tetrahedron Lett.* **1983**, *24*, 45. (g) Hayami, H.; Sato, M. Kanemoto, S.; Morizawa, Y.; Oshima, K.; Nozaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 4491. (h) Trost, B. M.; Yoshida, J.; Lautens, M. *Ibid.* **1983**, *105*, 4494. (i) Trost, B. M.; Yoshida, J. *Tetrahedron Lett.* **1983**, *24*, 4895. Si–Cu: (j) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520. Metal free: (k) Hiyama, T.; Obayashi, M.; Mori, I.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912.
(8) For example: (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Matsumoto, H,; Matsubara, I.; Kato, T.; Shono, K.; Watanabe, H.; Nagai, Y. *J. Organomet. Chem.* **1980**, *199*, 43. (c) Matsumoto, H.; Yoshihiro, K.; Nagashima, S.; Nagai, Y. *Ibid.* **1977**, *128*, 409.

0022-3263/86/1951-3996$01.50/0