ELSEVIER

Journal of Organometallic Chemistry 493 (1995) 27–32

Journal of Organometallic Chemistry

Stereoselective electrochemical synthesis of silyl enol ethers using a sacrificial magnesium anode

Dominique Bonafoux, Michel Bordeau *, Claude Biran *, Jacques Dunoguès

Laboratoire de Chimie organique et organométallique, (URA 35 CNRS), Université Bordeaux I, F-33405 Talence, France

Received 29 July 1994

Abstract

The 2-pyrrolidone magnesium salt electrogenerated in an undivided cell fitted with a sacrificial magnesium anode allowed the stereoselective synthesis of Z-silyl enol ethers upon deprotonation of enolizable ketones in the presence of a complexing agent.

Keywords: Silyl enol ethers; Stereoselective synthesis; Electrogenerated bases; Sacrificial magnesium anode

1. Introduction

The synthetic utility of silyl enol ethers is now well established [1], but among the numerous methods known for their preparation [1,2] few are readily regio- [3] and stereo-selective [4]. The most widely used reagents for the latter are bases such as lithium diisopropylamine (LDA) which are employed in the presence of hexamethylphosphoramide (HMPA) or tetramethylethylenediamine (TMEDA) under conditions of thermodynamic control [5] when a Z-enolate with good selectivity is desired [4b–7]. Otherwise, the use of tertiary amines as bases causes formation of amine hydrochlorides which are often hard to remove from the enoxysilanes.

This paper concerns a new stereoselective route for the synthesis of silyl enol ethers, using electrogenerated bases (EGBs) [8] obtained in an undivided cell fitted with a sacrificial anode. Such anionic species, which behave rather as bases than as nucleophiles, are generally generated in divided cells by the cathodic reduction of precursors called probases (PBs), but the use of undivided cells is now more common [9,10]. An important advantage of the electrochemical approach is that it is very easy to control both the solvent and the counterion because the basic and nucleophilic reactivities of anions depend strongly on these factors. For example, Shono and coworker's showed that the reactivity of the base electrogenerated from 2-pyrrolidone (**1**) [11–16] depends on the size of the associated quaternary ammonium cation of the supporting electrolyte [17].

Here we report first results on the use of the 2-pyrrolidone EGB (**1a**) associated with magnesium cations produced by the oxidation of a sacrificial magnesium anode for the deprotonation of enolizable ketones. The formation of magnesium enolates was further demonstrated and studied by quenching them with trimethylchlorosilane.

2. Results and discussion

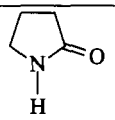
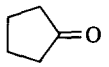
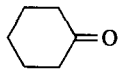
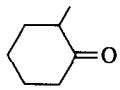
Because the reduction of PB (**1**) occurs in dimethoxyethane (DME) at a potential (-2.44 V/SCE) (Table 1) of the same order as that of the ketones studied (-2.3 to -2.6 V/SCE, Table 1), the enolate preparation had to be carried out in a two-step procedure: (1) electrochemical reduction of PB (**1**) generating the corresponding MgEGB (**1a**); (2) reaction of the ketone (the active-hydrogen compound) after complete electrolysis of PB (**1**).

PB (**1**) (0.51 mol l^{-1}) was dissolved in a mixture of DME and 10% by volume HMPA (complexing cosolvent) containing a small amount (3.8×10^{-2} mol l^{-1} or 7×10^{-2} eq/PB (**1**)) of a supporting electrolyte (Bu_4NBr or Et_4NBF_4). The electrochemical reduction of PB (**1**) was performed at room temperature at con-

* Corresponding authors.

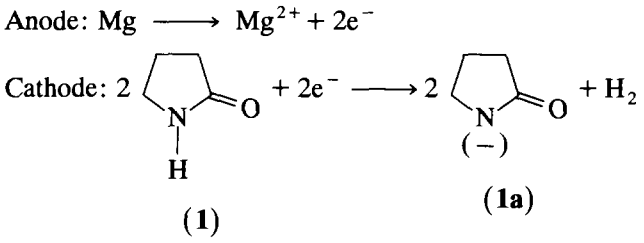
SSDI 0022-328X(94)05368-5

Table 1
Peak potentials of 2-pyrrolidone and ketones obtained by cyclic voltammetry in DME-0.1M Bu_4NBF_4 at a 1-mm-diameter Pt Disk (sweep rate 200 mV s^{-1})

Compound	2-Pyrrolidone and ketones	Ep (V/SCE)
1		−2.44 [a]
2	$PhCH_2COCH_2Ph$	−2.58
3	$PhCH_2COPh$	−2.27
4	$PhCH_2COCH_3$	−2.35
5	CH_3CH_2COPh	−2.5
6		−2.61
7		−2.38
8		−2.44
9	$(CH_3CH_2CH_2)_2C{=}O$	−2.45
10	$(CH_3)_2CHCH_2COCH_3$	−2.54

[a] Ep = −2.4 V/SCE from [8b].

stant current (0.10 A dm^{-2}) in an undivided cell using a magnesium bar as the anode and a cylindrical stainless steel grid as the cathode until 1.5 F mol^{-1} of PB (**1**) had passed. The reactions then occurring are shown in Scheme 1.

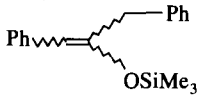
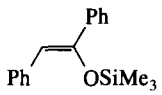
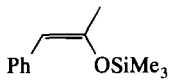
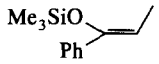
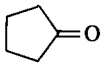
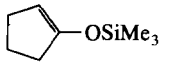
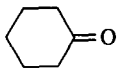
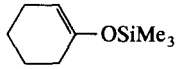
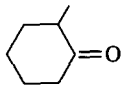


Scheme 1.

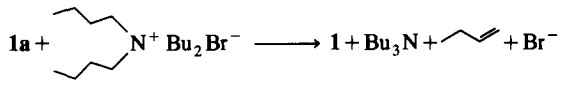
Under these conditions all PB (**1**) was reduced and the resulting magnesium salt MgEGB was quite stable and could be kept for 10 h at room temperature without any decomposition. The anodic current efficiency (percentage of metal consumed relative to the theoretical mass corresponding to the charge passed) was 125%, showing very minor participation of the anodically scoured magnesium in a chemical reductive process.

The quaternary ammonium salts used as supporting electrolytes are not totally inert in this medium and we noticed the formation of tributyl amine, from tetrabutylammonium bromide as shown by GC/MS and IR spectroscopy (Scheme 2). This reaction can be com-

Table 2
Silyl enol ethers obtained from electrogenerated base MgEGB

	Ketone	Conversion (%)		Enoxysilane	Isomer (%)	Yield [a]	Yield [b]
2	$PhCH_2COCH_2Ph$	100	**14**		100 only one isomer is obtained [c]	88	56
3	$PhCH_2COPh$	90	**15**		100(Z)	80	50
4	$PhCH_2COCH_3$	100	**16**		95(Z) 5(E)	82	50
5	$PhCOCH_2CH_3$	85	**17**		100(Z)	[d]	[d]
6		100	**18**		–	85	50
7		100	**19**		–	80	55
8		0 [e]					
9	$(CH_3CH_2CH_2)_2CO$	0 [e]					
10	$(CH_3)_2CHCH_2COCH_3$	0 [e]					

[a] Yield after elimination of by-product (**11**) by distillation. [b] Yield of doubly distilled colourless and odourless silyl enol ether. [c] Stereochemistry unknown. [d] Silyl enol ether not separated from by-product (**11**). [e] 1-trimethylsilyl-2-pyrrolidone (**11**) was formed.



Scheme 2.

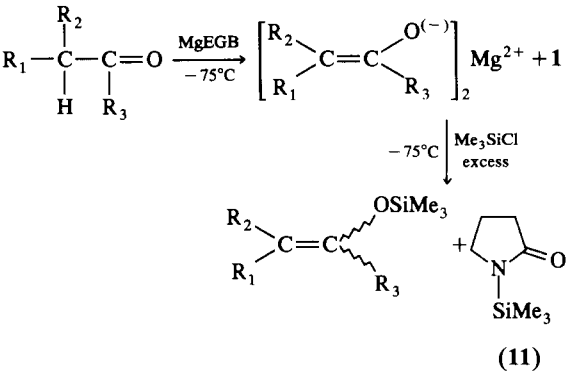
pared to the α-β elimination from Bu_4NBr promoted by organolithium compounds [18].

Thus, as Bu_3N is difficult to separate from the final silyl enol ether because of its marked lipophilicity, we preferred to use tetraethylammonium tetrafluoroborate which leads to easily removable water-soluble triethylamine.

A ketone (one equivalent) was then immediately added to the solution of EGB (two equivalents) at −75°C and was allowed to react at this temperature for 3 h to give the corresponding magnesium enolate which was then trapped with an exces of Me_3SiCl. Besides the enoxysilane, *N*-trimethylsilyl-2-pyrrolidone (**11**) was formed, because of the excess both of resulting EGB and Me_3SiCl (Scheme 3).

The conversion of aryl ketones (**2–5**), cyclopentanone (**6**) and cyclohexanone (**7**) to their silyl enol ethers occured in high yield under these conditions, but 2-methylcyclohexanone (**8**) and linear aliphatic ketones (**9**, **10**) failed to react (Table 2). In this context Fuchigami et al. [8h] have already reported that (R_4N^+) EGB is not basic enough to generate the enolate anion efficiently to α-alkyl (**8**).

When several stereoisomers were possible (ketones **3–5**), the electrochemical route led selectively to the single *Z*-isomer. The stereochemistry of the single isomer of (**14**) (from ketone **2**) is unknown and could not be determined, but it is most likely also to be Z. The stereoselectivity of the reaction is not surprising because of the presence of HMPA (0.04 mol or one equivalent/PB (**1**)), initially used to ensure good conductivity during the electrolysis, but which is also responsible for the equilibration of enolates [4b–7] and which usually favours the *Z*-enolate.



Scheme 3.

Comparison of the regio- and stereo-selectivities obtained by this electrochemical route with that of the main chemical methods was made for benzyl methyl ketone (**4**) (Table 3). In general, two regioisomers of enolate anions are formed from unsymmetrical ketones, and their ratio can be changed by varying the bases used and the reaction conditions. Thus (**4**) can generate the kinetic product (**12**) with the terminal C=C bond and the thermodynamic product with the more substituted C=C bond, in two stereoisomeric forms *Z* (**13a**) and *E*(**13b**) (Scheme 4).

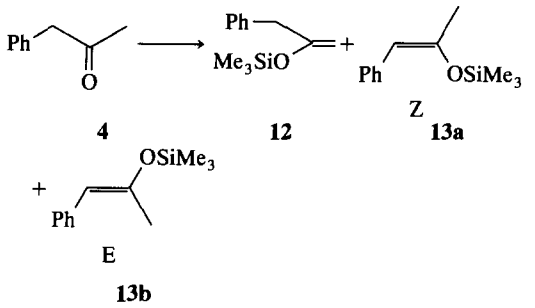
The regio- and stereo-selectivities obtained by the electrochemical route are similar to the best obtained chemical under equilibration conditions (LDA/HMPA or $(Me_3Si)_2NNa$/HMPA as reported by Davis et al. [4b], but the EGB is much easier to prepare. Another advantage is that the use of MgEGB avoids large quantities of amine so that the enoxysilanes are not contaminated with amine hydrochlorides.

HMPA plays a very important part in this synthesis as the cosolvent (0.04 mol in a typical run). By dissociating the supporting electrolyte it ensures a good conductivity. Being highly polar, it facilitates the equilibration of enolates and is responsible for the high stereoselective *Z*-enolate formation. It also enhances the reactiv-

Table 3
Enolisation of benzyl methyl ketone promoted by MgEGB and by the principal chemical routes

Silyl enol ether	Et_3N Me_3SiCl $ZnCl_2$ [19] (%)		Et_3N Me_3SiCl [20] (%)		Et_3N Me_3SiCl NaI [21] (%)		LDA [d] Me_3SiCl [4b] (%)		LDA [d] Me_3SiCl HMPA [4b] (%)		HMDS [d] Na Me_3SiCl HMPA [4b] (%)		HMDS [d] Na Me_3SiCl [4b] (%)		BSA [d] Na HMPA [22] (%)		MgEGB [a] (%)	
12	15		0		40		50		0		0		0		15		0	
13a	75	85	67	100	85	60	11	50	95	100	94	100	60	100	98	85	95	100
13b	25		33		15		89		5		6		40		2		5	
global yield	52		42		56										65		82 [b] / 50 [c]	

[a] This work. [b] Yield after elimination of product (**11**). [c] Yield of distilled, colourless, odourless silyl enol ether. [d] LDA = Lithium diisopropylamide; HMDS = hexamethyldisilazane; BSA = bis(trimethylsilyl)acetamide



Scheme 4.

ity of metal enolates towards electrophiles [22–25], which promotes easier formation of the silyl enol ethers.

In order to define the complexing role of HMPA in this reaction and to discover alternatives because it is presumed to be toxic, the effect of other complexing agents was investigated in the case of ketone (**4**).

These experiments were conducted under the same experimental conditions as before (Et_4NBF_4, supporting electrolyte), but without HMPA, using a DME 10% by volume *N*-methylpyrrolidone (NMP) mixture. The conductivity was sufficient during the electrolysis of PB (**1**), but no deprotonation reaction occured after the addition of (**4**), the ketone and (**11**) being recovered after silylation, the latter proving formation of MgEGB (Table 4). Enolate formation took place on adding 0.04 mol (one equivalent/PB (**1**)) of tris(3,6-dioxaheptyl) amine (TDA-1) [26] or TMEDA after the electrolysis of PB (**1**). This lead to the corresponding enoxysilanes with conversion ratios of 43% and 80%, respectively, arising from the increasing complexing power of these complexing agents. This clearly demonstrates that Mg^{2+} cations need to be complexed to enhance the basic reactivity of EGB by formation of looser ion-pairs. HMPA is the best complexing agent (100% conversion of (**4**)) and NMP alone the worst (0% conversion of (**4**)) (Table 4). Moreover, the regio- and stereo-selectivities of enolate formation was almost the same with TDA-1 or TMEDA as with HMPA, certainly because of their high polarity.

3. Conclusion

In conclusion, this is the first time that silyl enol ethers have been synthesised using an electrogenerated base. We have shown that the stereoselective synthesis of *Z*-stereoisomers from ketones is possible using the 2-pyrrolidone magnesium salt and HMPA, but alternative complexing agents such as TMEDA or TDA-1 can be used.

Table 4
Influence on the enolate conversion of (**4**) during 3 h at −75°C of a complexing agent added after the formation of MgEGB in DME/NMP medium

Added complexing agent (one equivalent/PB1)	Conversion (%)	Formed enoxysilanes		
		(12) (%)	(13a) (%)	(13b) (%)
none	0	0	0	0
TDA-1	43	0	93	7
TMEDA	80	0	93	7

4. Experimental details

4.1. Chemicals and reagents

All the materials used for silyl enol ether synthes were of reagent grade and used without preliminary purification, except for TDA-1 and Me_3SiCl which were distilled under vacuum and over magnesium powder, respectively. For cyclic voltammetry experiments, DME and tetrabutylammonium tetrafluoroborate (Fluka) were dried over sodium benzophenone ketyl and by heating overnight at 80°C in vacuo, respectively. All glassware was oven-dried and manipulations involving air-sensitive materials were performed under argon.

4.2. Cyclic voltammetry

Experiments were performed under argon in DME containing the supporting electrolyte Bu_4NBF_4 in 0.1 M solution. The reference electrode was an aqueous saturated calomel electrode. Ferrocene (10^{-3} M) was also used as an internal standard ($E_{pa} = 0.63$ V, $E_{pc} = 0.56$ V). The working electrode was a platinum disk of 1 mm diameter. The instrumentation used has been described elsewhere [27].

4.3. General procedure for the preparation of silyl enol ethers

Electrolyses were carried out in an undivided cell described previously [27], fitted with a sacrificial magnesium anode and a stainless-steel grid cathode separated by a polypropylene mesh.

To a solution of 0.6 g (3×10^{-3} mol) Et_4NBF_4 in DME (70 ml) and HMPA (7 ml) in the cell was added 3 ml (3.9×10^{-2} mol) of 2-pyrrolidone (**1**). A constant current of 0.1 A was applied at room temperature under argon until 1.5 F mol^{-1} were passed. The resulting solution of about two equivalents Mg EGB was transferred under argon to a three-necked round bottom flask and cooled to −75°C, 2×10^{-2} M of ketone (one equivalent) were added immediately. After 3 h stirring at this temperature, 20 ml (0.25 mol) of Me_3SiCl were added to the magnesium enolate and the temperature held constant for 1 h. After the excess of Me_3SiCl and DME had been evaporated off, 80 ml of cold pentane were added and then 20–50 ml of ice-cold water were slowly added with good stirring. The aqueous layer was then extracted several times with pentane.

The combined extracts were washed with cold 2% aqueous HCl and then with water until neutrality. After drying over anhydrous magnesium sulfate, pentane was evaporated off and the silyl enol ether separated from *N*-silyl-2-pyrrolidone (**11**) by distillation (yields: note a, Table 2). Finally, a second distillation yielded enoxysilane (yields: note b, Table 2). Analysis of the products was achieved by GC, and ^{1}H, ^{13}C NMR and IR spectroscopies. Gas chromatography was performed with a temperature-programmable Hewlett Packard 5890 apparatus equipped with a 25 m × 0.25 μm CP-Sil capillary column. ^{1}H NMR (250 MHz) and ^{13}C NMR (62.86 MHz) spectra were recorded from solutions in $CDCl_3$ using a Bruker AC 250 spectrometer. All chemical shifts reported are downfield from tetramethylsilane. IR spectra were recorded using a spectrometer with pure liquid films (NaCl sheets).

4.4. Characteristics of the obtained compounds

4.4.1. 2-trimethylsiloxy-1,3-diphenylprop-1-ene (Z) (14)

Only one isomer was formed. ^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9H, $SiMe_3$), 3.62 (s, 2H, CH_2), 5.53 (s, 1H,–CH=), 7.3–7.63 (m, 10H, H arom). ^{13}C NMR ($CDCl_3$): δ 1.1 (3P, $SiMe_3$), 44.32 (1S,–CH_2), 110.55 (1T,–CH=), 125.89, 126.79, 127.32, 126.26, 128.44, 128.70, 128.98, 129.21, 129.48, 129.78, 136.93, 138.26 (12 C arom), 152.08 (1 Q,=C($OSiMe_3$)(CH_2Ph)). IR (neat): 3060 (f), 3040 (m), 2940 (m), 2910 (f), 1960 (f), 1720 (f), 1650 (F, ν (C=C)), 1610 (m), 1500 (F), 1460 (m), 1380 (m), 1260 (F), 1170 (F), 1090 (f), 1050 (f), 990 (F), 850 (F), 760 (F), 700 (F) cm^{-1}.

4.4.2. 1-trimethylsiloxy-1,2-diphenylethylene (Z) (15)

^{1}H NMR ($CDCl_3$): δ 0.25 (s, 9H,$SiMe_3$), 6.34 (s, 1H,–CH=), 7.38–7.8 (m, 5H,*Ph*–CH=), 7.85–7.88 (m, 5H,*Ph*C($OSiMe_3$)=), in accordance with [4b] for the *Z* isomer ($CDCl_3$): *Z*: δ 6.14 (s, 1H,–CH=),*E*: δ 6.08 (s, 1H,–CH=). ^{13}C NMR ($CDCl_3$): δ 0.93 (3P, $SiMe_3$), 110.7 (1T, *C*H(Ph)=), 126.3, 126.36, 127, 128.26, 128.32, 128.36, 128.86, 129.7, 133.31, 136.84, 139.8 (11 C arom), 151.1 (1Q,=*C* Ph($OSiMe_3$)). IR (neat): 3040 (m), 3020 (m), 2950 (F), 1950 (f), 1630 (F,ν (C=C)), 1600 (m), 1490 (m), 1440 (m), 1345 (F), 1280 (m), 1250 (F), 1200 (m), 1050 (F), 1025 (m), 920 (F); 890 (F), 840 (F), 760 (F), 690 (F) cm^{-1}.

4.4.3. 2-trimethylsiloxy-1-phenylprop-1-ene (Z) (16)

^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9H, $SiMe_3$), 1.97 (s, 3H, CH_3), 5.41 (s, 1H,–CH=), 7–7.5 (m, 5H, H arom), in accordance with [21] for the *Z* isomer ($CDCl_3$): *Z*: δ 5.31 (s, 1H,–CH=), *E*: δ 5.73 (s, 1H,–CH=). ^{13}C NMR ($CDCl_3$): δ 24.1 (1P, CH_3), 108.53 (1 s, –*C*H(Ph)=), 125.34, 127.15, 127.86, 128.1 (4 C arom), 137.14 (1 Q arom), 149.39 (1 Q,=*C*(CH_3)$OSiMe_3$). IR (neat): 3040 (f), 3000 (f), 2960 (m), 2900 (f), 1650 (F,ν(C=C)), 1590 (f), 1490 (m), 1430 (m), 1380 (m), 1350 (F), 1250 (F), 1170 (F), 1020 (m), 980 (F), 960 (F), 830 (F), 750 (m), 690 (m) cm^{-1}.

4.4.4. 1-trimethylsiloxy-1-phenylprop-1-ene (Z) (17)

^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9H, $SiMe_3$), 1.58 (d, 2H,–CH_3,J^3 = 6.8 Hz), 5.16 (q, 1H,–CH=,J^3 = 6.8 Hz), 7.24–7.38 (m, 5H, Harom). ^{13}C NMR ($CDCl_3$): δ 0.47 (3P, $SiMe_3$), 11.58 (1P,*C*H_3) 105.1 (1T,=CHMe), 127.2, 127.84, 127.91, 128.4 (4 C arom), 149.78 (1 Q,=*C*PhO$SiMe_3$), in accordance with [4b] ($CDCl_3$): δ 0.1 (3P, $SiMe_3$), 11.6 (1P, CH_3), 105.2 (1T,=CHMe), 127–137.01 (Carom), 149.0 (1 Q,=CPhO$SiMe_3$).

No absorption for the allylic carbon of an *E*-isomer was observed.

4.4.5. 1-trimethylsiloxycyclopent-1-ene (18)

^{1}H NMR ($CDCl_3$): δ 0.13 (s, 9H, $SiMe_3$), 2.0–2.14 (m, 2H, –CH_2–C($OSiMe_3$)=), 2.16–2.25 (m, 4H, =C(*C*H_2)$_2$), 4.53 (s, 1H,–CH=). ^{13}C NMR ($CDCl_3$): δ −0.12 (3P, $SiMe_3$), 21.21 (1S,–CH_2–*C*H_2–CH=), 28.64 (1S,–*C*H_2–CH=), 33.42 (1S,–(*C*H_2–C($OSiMe_3$)=), 101.87 (1T,–*C*H=), 154.9 (1 Q,–*C*($OSiMe_3$)=).

4.4.6. 1-trimethylsiloxycyclohex-1-ene (19)

^{1}HNMR ($CDCl_3$): δ 0.11 (s, 9H, $SiMe_3$), 1.38–2.29 (m, 2H, –CH_2), 4.78 (s, 1H, –CH=). ^{13}CNMR ($CDCl_3$): δ 0.26 (3P,$SiMe_3$), 22.30, 23.12, 24.48, 30.0 (4S,(–*C*H_2)$_4$), 104.15 (–*C*H=), 150.3 (=*C*–O$SiMe_3$).

Acknowledgment

Financial support for this work by Electricité de France, Rhône-Poulenc, CNRS, and Région Aquitaine is gratefully acknowledged.

References

[1] P. Brownbridge, *Synthesis*, (1983) 1 and 85.
[2] (a) E.W. Colvin, *Silicon in Organic Synthesis*, Butterworths, London, 1981, p. 198; (b) W.P. Weber, *Silicon Reagents for Organic Synthesis*, Springer-Verlag, Berlin, 1983, p. 206.
[3] See for example some recent results: (a) P.F. Hudrlik, A.M. Hudrlik and A.K. Kulkarni, *J. Am. Chem. Soc., 107* (1985) 4260; (b) I. Matsuda, S. Sato, M. Hattori, and Y. Izumi, *Tetrahedron Lett., 26* (1985) 3215; (c) H.J. Reich, R.C. Holtan and S.L. Borkowsky, *J. Org. Chem., 52* (1987) 312; (d) K. Takai; Y. Kataoka, T. Okazoe and K. Utimoto, *Tetrahedron Lett., 29* (1988) 1065; (e) F.A. Davis, G.S. Lal and J. Wei, *J. Org. Chem., 29* (1988) 4269.
[4] (a) A.G. Brook, *Adv. Organomet. Chem., 7* (1968) 146; (b) F.A. Davis, A.C. Sheppard, B.C. Chen and M. Haque, *J. Am. Chem. Soc., 112* (1990) 6679; (c) G.L. Larson, R. Berrios, J.A. Prieto and H. America, *Tetrahedron Lett., 30* (1989) 283.
[5] Z.A. Fataftah, I.E. Kopka and M.W. Rathke, *J. Am. Chem. Soc., 102* (1980) 3959.

[6] R.E. Ireland, R.H. Mueller and A.K. Willard, *J. Am. Chem. Soc.*, *98* (1976) 2868.
[7] E.J. Corey and A.W. Gross, *Tetrahedron Lett.*, *25* (1984) 495.
[8] (a) M.M. Baizer, in H. Lund and M.M. Baizer (eds.), in *Electrogenerated Bases and Acids in Organic Electrochemistry*, Dekker, New York, 1991, pp. 1265–1282, and references therein; (b) J.H.P. Utley, Electrogenerated bases, in *Topics in Current Chemistry*, *142* Springer, Berlin, 1987, pp. 131–165, and references therein; (c) M.M. Baizer, *Tetrahedron*, *40* (1984) 935; (d) P.E. Iversen and H. Lund, *Tetrahedron Lett.*, *20* (1969) 3523; (e) M.M. Baizer, J.L. Chruma and D.A. White, *Tetrahedron Lett.*, *24* (1973) 5209; (f) H. Lund, H. Doupeux, M.A. Michel, G. Mousset and J. Simonet, *Electrochem. Acta*, *19* (1974) 629; (g) M.A. Michel, G. Mousset, J. Simonet and H. Lund, *Electrochem. Acta*, *20* (1975) 143; (h) T. Fuchigami, K. Suzuki and T. Nonaka, *Electrochem. Acta*, *35* (1990) 239.
[9] M.E. Niyazymbetov and D.H. Evans, *Tetrahedron*, *49* (1993) 9627.
[10] R. Barhdadi, J. Gal, M. Heintz, M. Troupel and J. Périchon, *Tetrahedron*, *49* (1993) 5091.
[11] T. Shono, S. Kashimura and H. Nogusa, *J. Org. Chem.*, *49* (1984) *2043*.
[12] T. Shono, S. Kashimura, K. Ishigaki and O. Ishige, *Chem. Lett.*, (1983) 1311.
[13] T. Shono, O. Ishige, H. Uyama and S. Kashimura, *J. Org. Chem.*, *51* (1986) 546.
[14] T. Shono and Y. Nakagawa, *J. Org. Chem.*, *52* (1987) 5276.
[15] T. Shono, S. Kashimura, M. Sawamura and T. Soegina, *J. Org. Chem.*, *53* (1988) 907.
[16] T. Shono, M. Ishifune, O. Ishige, H. Uyama and S. Kashimura, *Tetrahedron Lett.*, *31* (1990) 7181.
[17] T. Shono, M. Ishifune, T. Okada and S. Kashimura, *J. Org. Chem.*, *56* (1991) 2.
[18] J. March, *Advanced Organic Chemistry, Reactions, Mechanisms and Structure*, 4th edn., Wiley Interscience, 1992, p. 1017.
[19] Rhône-Poulenc Society, *Belg. Patent 670.769* (Chem. Abstr. 65 5487 d).
[20] H.O. House, L.J. Czuba, M. Gall and H.D. Olmstead, *J. Org. Chem.*, *34* (1969) 2324.
[21] P. Cazeau, F. Duboudin, F. Moulines, O. Babot and J. Dunoguès, *Tetrahedron*, *43* (1987) 2075.
[22] J. Dédier, P. Gerval and E. Frainnet, *J. Organomet. Chem.*, *185* (1980) 183.
[23] L.M. Kackman and B.C. Lange, *J. Am. Chem. Soc.*, *103* (1981) 4494.
[24] D. Seebach, R. Amstutz and J.D. Dunitz, *Hev. Chim. Acta*, *64* (1981) 2622.
[25] W. Bauer, T. Laube and D. Seebach, *Chem. Ber.*, *118* (1985) 764.
[26] G. Soula, *J. Org. Chem.*, *50* (1985) 3717.
[27] D. Deffieux, M. Bordeau, C. Biran and J. Dunoguès, *Organometallics*, *13* (1994) 2415.