Journal of Organometallic Chemistry, 194 (1980) 1—7
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

NEW FUNCTIONAL ALLYLIC LITHIUM REAGENTS: *GEM*-DIALKOXYALLYLLITHIUM REAGENTS: A USEFUL ROUTE TO β-SILYL- AND β-STANNYLPROPIONATE ESTERS

DIETMAR SEYFERTH*, ROBERT E. MAMMARELLA and HELMUT A. KLEIN

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received January 21st, 1980)

Summary

The reaction of sec-butyllithium with acrolein dialkyl acetals in THF or in THF/Et_2O/pentane at —95°C results in formation of *gem*-dialkoxyallyllithium reagents, $Li[CH_2CHC(OR)_2]$. These react with organosilicon and organotin chlorides to give ketene acetals, $R_3SiCH_2CH{=}C(OR)_2$ and $R_3SnCH_2CH{=}C(OR)_2$. The acid hydrolysis of these products produces β-substituted propionic acid esters, $R_3SiCH_2CH_2CO_2R$ and $R_3SnCH_2CH_2CO_2R$. Reactions of these lithium reagents with allyl bromide gave esters of 5-hexenoic acid, $CH_2{=}CH(CH_2)_3CO_2R$ (R = Me, Et).

Introduction

The lithiation of allylic ethers provides useful reagents which are operationally equivalent to a β-acyl carbanion (eq. 1—3) [1].

$$ROCH_2CH = CH_2 + \text{sec-}C_4H_9Li \xrightarrow[\text{THF}]{-65^\circ C} Li[CH_2CHCHOR] + C_4H_{10} \quad (1)$$

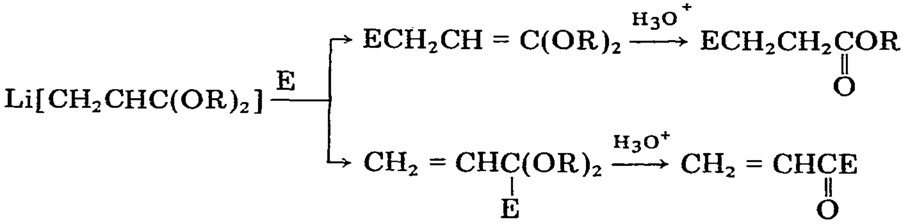
$$Li[CH_2CHCHOR] + R'X \rightarrow R'CH_2CH = CHOR + CH_2 = CHCH(R')\,OR \quad (2)$$

$$R'CH_2CH = CHOR + H_2O \rightarrow R'CH_2CH_2C(O)\,H + ROH \quad (3)$$

In this context, the possible lithiation of an allylic acetal, $CH_2{=}CHCH(OR)_2$, was of some interest. The expected product is a *gem*-dialkoxyallyllithium reagent (eq. 4) which potentially could react with an electrophile, E, at either

$$CH_2{=}CHCH(OR)_2 + R'Li \rightarrow Li[CH_2CHC(OR)_2] + R'H \quad (4)$$

the unsubstituted or the substituted terminus of the allyl group (eq. 5). If the new bond is formed at the substituted end, an allylic acetal would be formed. Hydrolysis of the latter would give a vinyl ketone. In this case the reagent



$$\mathrm{Li[CH_2CHC(OR)_2]} \xrightarrow{E} \begin{cases} \mathrm{ECH_2CH=C(OR)_2} \xrightarrow{H_3O^+} \mathrm{ECH_2CH_2\underset{\underset{O}{\|}}{C}OR} \\ \mathrm{CH_2=CH\underset{\underset{E}{|}}{C}(OR)_2} \xrightarrow{H_3O^+} \mathrm{CH_2=CH\underset{\underset{O}{\|}}{C}E} \end{cases} \qquad (5)$$

would function as a carbonyl anion equivalent, $CH_2{=}CHC(O)^-$. If, on the other hand, the new bond is formed at the unsubstituted terminus of the allyl group, a γ-substituted ketene acetal would result. Hydrolysis of such a product would give an ester, as shown in eq. 5. In this case the reagent would be operationally equivalent to a β-alkoxycarbonyl carbanion, $ROC(O)CH_2CH_2^-$.

Of special interest to us were the reactions of such $Li[CH_2CHC(OR)_2]$ reagents with organometallic halides, in particular trimethylchlorosilane and trimethyltin chloride. Alkyl- and aryl-substituted allylic lithium reagents of type $Li[CH_2CHCHR]$ and $Li[CH_2CHCR_2]$ had been found to react with both of these halides to give exclusively products of structure $Me_3MCH_2CH{=}CHR$ and $Me_3MCH_2CH{=}CR_2$ (M = Si and Sn), respectively [2,3]. On the other hand, trimethylchlorosilane reacted with *gem*-dichloro [4] and *gem*-difluoroallyllithium [5] to give $Me_3SiCX_2CH{=}CH_2$ (X = Cl and F). Trimethyltin chloride formed $Me_3SnCH_2CH{=}CCl_2$ on reaction with $Li[CH_2CHCCl_2]$. In the case of the Me_3SiCl reactions it was quite likely that products of kinetic control were obtained, while those derived from Me_3SnCl were products of thermodynamic control [4].

In view of the potential synthetic utility of reagents of $Li[CH_2CHC(OR)_2]$ and in view of the uncertainty of the regioselectivity in their reactions with various electrophiles, we have investigated their synthesis, stability and, to a limited extent, their reactions.

Results and discussion

We have found that acrolein dimethyl and diethyl acetals may be lithiated by sec-butyllithium in a THF/diethyl ether/pentane solvent mixture at $-90 \pm 5°C$ to give a yellow solution containing the respective *gem*-dialkoxyallyllithium reagents (eq. 4, R = Me and Et; R′ = sec-C_4H_9). The temperature range for successful preparation of these reagents is quite narrow: below −100°C the metalation reaction appears to be too slow; above −85°C the reagents begin to decompose slowly. Their decomposition is rapid at −65°C and above. Nonetheless, they find useful applications in synthesis.

We have thus far studied the reaction of these new allylic lithium reagents with several organosilicon and organotin chlorides and with allyl bromide (Table 1). Such reactions of $Li[CH_2CHC(OR)_2]$ with organosilicon and organotin chlorides, followed by nonhydrolytic work-up, gave silicon- and tin-substituted ketene acetals as the exclusive products (eq. 6). These acetals are acid-sensitive and decompose slowly on standing.

$$\mathrm{Li[CH_2CHC(OR)_2]} + \mathrm{R'_3MCl} \rightarrow \mathrm{R'_3MCH_2CH=C(OR)_2} + \mathrm{LiCl} \qquad (6)$$
$$(\mathrm{M = Si, Sn})$$

TABLE 1

REACTIONS OF *gem*-DIALKOXYALLYLLITHIUM REAGENTS [a] WITH CHLOROSILANES, TIN CHLORIDES AND ALLYL BROMIDE

Acrolein Dialkyl Acetal (mmol)	Substrate (mmol)	Work-up	Product (% Yield) [d]
$CH_2{=}CHCH(OMe)_2$ (21)	Me_3SiCl (27.6)	5% HCl	$Me_3SiCH_2CH_2CO_2Me$ (75)
$CH_2{=}CHCH(OMe)_2$ (42)	Me_3SiCl (45)	anhydrous	$Me_3SiCH_2CH{=}C(OMe)_2$ (70) [b]
$CH_2{=}CHCH(OMe)_2$ (43)	Me_2SiCl_2 (21)	5% HCl	$Me_2Si(CH_2CH_2CO_2Me)_2$ (61)
$CH_2{=}CHCH(OMe)_2$ (21)	Et_3SiCl (21)	5% HCl	$Et_3SiCH_2CH_2CO_2Me$ (70) [c]
$CH_2{=}CHCH(OMe)_2$ (42)	$PhMe_2SiCl$ (49)	5% HCl	$PhMe_2SiCH_2CH_2CO_2Me$ (77)
$CH_2{=}CHCH(OEt)_2$ (25)	Me_3SiCl (40)	H_2O	$Me_3SiCH_2CH_2CO_2Et$ (43)
$CH_2{=}CHCH(OEt)_2$ (63)	Et_3SiCl (86)	H_2O	$Et_3SiCH_2CH_2CO_2Et$ (86) (71% distilled)
$CH_2{=}CHCH(OEt)_2$ (63)	$PhMe_2SiCl$ (86)	H_2O	$PhMe_2SiCH_2CH_2CO_2Et$ (53)
$CH_2{=}CHCH(OMe)_2$ (42)	Me_3SnCl (60)	10% HCl	$Me_3SnCH_2CH_2CO_2Me$ (72)
$CH_2{=}CHCH(OMe)_2$ (42)	Me_3SnCl (60)	anhydrous	$Me_3SnCH_2CH{=}C(OMe)_2$ (69)
$CH_2{=}CHCH(OEt)_2$ (25)	Me_3SnCl (40)	5% HCl	$Me_3SnCH_2CH_2CO_2Et$ (27)
$CH_2{=}CHCH(OEt)_2$ (25)	Me_3SnCl (40)	H_2O	$Me_3SnCH_2CH_2CO_2Et$ (1 part) + $Me_3SnCH_2CH{=}C(OEt)_2$ (2 parts)
$CH_2{=}CHCH(OEt)_2$ (25)	Et_3SnCl (32)	5% HCl	$Et_3SnCH_2CH_2CO_2Et$ (24)
$CH_2{=}CHCH(OMe)_2$ (42)	$CH_2{=}CHCH_2Br$ (60)	5% HCl	$CH_2{=}CHCH_2CH_2CH_2CO_2Me$ (47)
$CH_2{=}CHCH(OEt)_2$ (25)	$CH_2{=}CHCH_2Br$ (40)	5% HCl	$CH_2{=}CHCH_2CH_2CH_2CO_2Et$ (22)

[a] Prepared at $-90 \pm 5^\circ$C by reaction with sec-butyllithium. [b] A 12 : 1 mixture of $Me_3SiCH_2CH{=}C(OMe)_2$ and $Me_3SiCH_2CH_2CO_2Me$ was produced. [c] The $Et_3SiOSiEt_3$ formed on hydrolysis of unconverted Et_3SiCl cannot be separated from the product and so it is better to use an excess of the lithium reagent. [d] By-products included the respective disiloxane in those reactions in which an excess of the chlorosilane was used.

The reaction shown in eq. 6 thus provides a useful new route to substituted ketene-*O*,*O*-acetals. Such reactions of *gem*-dialkoxyallyllithium reagents with silicon and tin chlorides, when followed by hydrolysis of the initially formed products, provide a new synthesis of β-silyl- and β-stannyl-propionic acid esters as shown in eq. 7. The yields of these products ranged from moderate to excellent.

$$\mathrm{Li[CH_2CHC(OR)_2] + R'_3MCl \rightarrow \xrightarrow{H_3O^+} R'_3MCH_2CH_2CO_2R + ROH + LiCl} \tag{7}$$

The conditions required for hydrolysis of the initially produced acetals differed for the reactions with organosilicon and organotin chlorides. In the case of the former, hydrolysis with neutral water was sufficient to give complete conversion to the esters. The organotin-substituted acetals were only incompletely hydrolyzed on treatment of the reaction mixtures with neutral water. Hydrolysis with 5%, or better, 10%, aqueous hydrochloric acid was required for production of the tin-substituted ester. The explanation for these observations is a simple one. Hydrolysis of unreacted chlorosilane, generally added in excess, generates an acid medium which facilitates hydrolysis of the acetal. Organotin chlorides, on the other hand, do not hydrolyze readily. Although their rate of hydrolysis is rapid, the hydrolysis equilibrium is not favorable [6]. Hence, insufficient acid is generated and external acid must be added to effect hydrolysis of the acetal.

The formation of products of type $R'_3MCH_2CH{=}C(OR)_2$ rather than $R'_3MC(OR)_2CH{=}CH_2$ in these reactions of $Li[CH_2CHC(OR)_2]$ with R'_3MCl may be understood in terms of the operation of steric effects. It is unlikely that allylic organosilicon compounds of either type (M = Si in the formulae above) would take part in transmetalation equilibria, so we assume that we are dealing with products of kinetic control. Products of type $R'_3SiC(OR)_2CH{=}CH_2$ would have been of some interest: their hydrolysis should have given α-silyl ketones, $R'_3SiC(O)CH{=}CH_2$.

Other methods for the preparation of β-silyl- and β-stannyl-propionic acid esters are available. Such silyl-substituted esters can be prepared by the acetoacetic ester and malonic ester syntheses when the appropriate halomethylsilanes, R_3SiCH_2X, are available [9]. Both silyl- and stannyl-substituted esters have been prepared by silicon or tin hydride addition to acrylate esters [10—13], while the reaction of β-halopropionic acid esters with tin foil provided another route to β-stannyl-substituted esters [14]. Thus the present procedure, which is based on the availability of the silicon or tin halide, complements these procedures.

Experimental

General comments

All reactions were carried out in flame-dried, nitrogen-flushed glassware under an atmosphere of prepurified nitrogen or argon. Solvents were rigorously dried prior to use. The reaction temperatures which are reported are uncorrected. They were obtained using a pentane total immersion thermometer which was immersed to a depth of about 3 cm into the stirred reaction mixture. Experiments showed that a stem correction of —8 to —10°C is appropriate.

sec-Butyllithium was purchased from Alfa Products, Thiokol/Ventron Corp., chlorosilanes from Petrarch Systems, Inc., the acrolein dialkyl acetals from Aldrich Chemical. Co. Methyltin starting materials were kindly donated by Cincinnati Milacron Chemicals, Inc.

Infrared spectra were recorded using a Perkin Elmer Model 457A grating infrared spectrophotometer, NMR spectra with a Varian Associates T60 spectrometer. Gas-liquid chromatography (GLC) was employed for analysis of reaction products, isolation of product samples and for yield determination by the internal standard method.

Preparation of gem-dialkoxyallyllithium reagents: general procedure

A Morton (creased) flask of appropriate size, equipped with a paddle-type stirrer, a no-air stopper and a Claisen adapter which was fitted with a low temperature thermometer and a gas inlet tube, was flame-dried and then allowed to cool under a stream of nitrogen or argon. The flask then was charged with the solvent mixture (75 ml of THF, 15 ml of diethyl ether and 15 ml of pentane), 21 mmol of the acrolein dialkyl acetal (2.5 ml in the case of $CH_2{=}CHCH(OMe)_2$) was added, and the solution was cooled to —90 ± 5°C by partial immersion in a liquid nitrogen Dewar flask. To this solution was added with stirring and under nitrogen (or argon) 20 ml of 1.1 *M* sec-butyllithium in

TABLE 2

REACTION PRODUCTS

Compound	n_D^t (°C)	Analysis, found (calcd.) (%)		^{1}H NMR, δ (ppm)
		Carbon	Hydrogen	
$Me_3SiCH_2CH_2CO_2CH_3$	1.4190 (20) [a]	52.42 (52.45)	10.04 (10.06)	0.00 (s, 9 H, Me_3Si), 0.63—1.00 (m, 2 H, $SiCH_2$), 2.1—2.44 (m, 2 H, CH_2CO), 3.6 (s, 3 H, OCH_3) (in $CDCl_3$)
$Me_2Si(CH_2CH_2CO_2Me)_2$	1.4396 (25)	51.25 (51.22)	8.60 (8.62)	0.00 (s, 6 H, Me_2Si), 0.65—1.05 (m, 4 H, $SiCH_2$), 2.1—2.5 (m, 4 H, CH_2CO), 3.6 (s, 6 H, OCH_3) (in $CDCl_3$)
$Et_3SiCH_2CH_2CO_2CH_3$	1.4409 (25)	59.19 (59.40)	10.67 (10.89)	0.15—1.25 (m, 17 H, Et_3Si and $SiCH_2$), 1.95—2.4 (m, 2 H, CH_2CO), 3.55 (s, 3 H, OCH_3) (in $CDCl_3$)
$PhMe_2SiCH_2CH_2CO_2CH_3$	1.4950 (25)	64.74 (64.86)	8.21 (8.11)	0.2 (s, 6 H, $SiMe_2$), 0.8—1.2 (m, 2 H, $SiCH_2$), 2.0—2.4 (m, 2 H, CH_2CO), 3.45 (s, 3 H, OCH_3), 7.2—7.5 (m, 5 H, Ph) (in $CDCl_3$)
$Me_3SiCH_2CH_2CO_2C_2H_5$	[b]	54.91 (55.12)	10.40 (10.41)	0.00 (s, 9 H, Me_3Si), 0.62—1.02 (m, 2 H, $SiCH_2$), 1.23 (t, *J* 7 Hz, 3 H, CH_3 of Et), 2.02—2.37 (m, 2 H, CH_2CO), 4.02 (q, *J* 7 Hz, CH_2 of Et) (in CCl_4)
$Et_3SiCH_2CH_2CO_2C_2H_5$	1.4407 (25) [c]	61.04 (61.05)	11.12 (11.18)	0.27—1.18 (m, 17 H, Et_3Si and $SiCH_2$), 1.27 (t, *J* Hz, 3 H, CH_3 of OEt), 2.03—2.38 (m, 2 H, CH_2CO), 4.05 (q, *J* 7 Hz, 2 H, OCH_2)
$PhMe_2SiCH_2CH_2CO_2C_2H_5$	1.4917 (25) [d]	66.09 (66.05)	8.52 (8.53)	0.32 (s, 6 H, Me_2Si), 1.05 (t, *J* 7 Hz, 2 H, $SiCH_2$), 1.33 (t, *J* 7 Hz, 3 H, CH_3 of OEt), 2.08—2.42 (m, 2 H, CH_2CO), 4.03 (q, 2 H, CH_2 of OEt), 6.88—7.57 (m, 5 H, Ph) (in CCl_4)
$Me_3SnCH_2CH_2CO_2CH_3$	1.4695 (20) [e]	33.44 (33.50)	6.49 (6.38)	0.07 (s, 9 H, Me_3Sn, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz), 1.00 (t, *J* 8 Hz, 2 H, $SnCH_2$), 2.50 (t, *J* 8 Hz, 2 H, CH_2CO), 3.63 (s, 3 H, OCH_3) (in $CDCl_3$)
$Me_3SnCH_2CH_2CO_2C_2H_5$	1.4638 (25) [f]	36.64 (36.27)	6.92 (6.85)	0.08 (s, 9 H, Me_3Sn, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz), 0.95 (t, *J* 7 Hz, 2 H, $SnCH_2$), 1.27 (t, *J* 7 Hz, 3 H, CH_3 of OEt), 2.50 (t, *J* 7 Hz, 2 H, CH_2CO), 4.08 (q, 2 H, OCH_2) (in CCl_4)
$Et_3SnCH_2CH_2CO_2C_2H_5$	1.4760 (25) [g]	43.51 (43.04)	7.90 (7.88)	0.33—1.48 (m, 20 H, Et_3Sn, $SnCH_2$ and CH_3 of OEt), 2.50 (t, *J*, 7 Hz, CH_2CO), 4.08 (q, *J* 7 Hz, 2 H, OCH_2) (in CCl_4)
$Me_3SiCH_2CH{=}C(OMe)_2$	1.4354 (20)	55.15 (55.17)	10.70 (10.34)	0.00 (s, 9 H, Me_3Si), 1.28 (d, *J* 8 Hz, 2 H, $SiCH_2$), 3.13—3.81 (m, 1 H, =CH), 3.50 and 3.56 (two s, each 3 H, OCH_3) (in $CDCl_3$)

TABLE 2 (continued)

Compound	n_D^t (°C)	Analysis, found (calcd.) (%)		^1H NMR, δ (ppm)
		Carbon	Hydrogen	
$Me_3SnCH_2CH{=}C(OMe)_2$	1.4845 (20)	36.15 (36.26)	6.82 (6.80)	0.05 (s, 9 H, Me_3Sn, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz), 1.52 (d, J 8 Hz, 2 H, $SnCH_2$), 3.15—3.90 (m, 1 H, =CH), 3.46 and 3.53 (two s, each 3 H, OCH_3) (in $CDCl_3$)
$Me_3SnCH_2CH{=}C(OEt)_2$	1.4640 (25)	40.90 (41.00)	7.65 (7.57)	0.07 (s, 9 H, Me_3Sn, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz), 1.25 and 1.28 (two t, J 7 Hz, each 3 H, CH_3 of OEt), 1.52 (d, J 8 Hz, 2 H, $SnCH_2$), 3.42 (m, 5 H, OCH_2 and =CH) (in CCl_4)

[a] Lit. [15] n_D^{20} 1.4480; [b] Lit. [9] n_D^{20} 1.4198; lit [16] n_D^{20} 1.4205; [c] Lit. [12] n_D^{20} 1.4422; [d] Lit. [9] n_D^{20} 1.4972; [e] Lit [14] n_D^{20} 1.4690; [f] Lit [14] n_D^{20} 1.4660; [g] Lit. [12] n_D^{20} 1.4762.

cyclohexane (22 mmol). The temperature was maintained at —90 ± 5°C during the course of this very slow, dropwise addition. The resulting yellow solution was stirred 2—3 h at —90°C.

To this reagent solution then was added the chlorosilane or the tin chloride (slight excess, ca. 25—30 mmol) by syringe over a 10 min. period. The resulting mixture, now milky white, was stirred at —90°C for 30 min and then was allowed to warm to room temperature.

In the non-hydrolytic work-up, the reaction mixture was transferred by cannula to a dry distillation flask. Solvents were removed at reduced pressure and the residue was trap-to-trap distilled at ca. 0.1 mm Hg into a flask cooled with liquid nitrogen. The distillate then was examined by GLC.

In the hydrolytic work-up, the cannulated solution was poured into a separatory funnel and treated successively with distilled water, two portions of 5 or 10% hydrochloric acid and, again, water. The aqueous phases were back-extracted with pentane and the combined organic phases were dried ($MgSO_4$) and the solvents removed at reduced pressure. The residue was trap-to-trap distilled, as above.

Some reactions were carried out on a larger scale (42 mmol of $CH_2{=}CHCH(OMe)_2$, 63 mmol of $CH_2{=}CHCH(OEt)_2$). In some cases THF alone, rather than the mixed solvent system, was used, but the mixed solvent is preferred.

Organosilicon and organotin products: characterization

Table 2 lists the organosilicon and organotin esters and acetals prepared, their refractive indices, analyses and spectroscopic properties. The infrared spectra of the esters (liquid film) showed strong ester carbonyl absorption at 1735—1740 cm^{-1}. The ketene acetals showed strong bands in their IR spectra at 1675 ($Me_3SiCH_2CH{=}C(OMe)_2$) and 1670 cm^{-1} ($Me_3SnCH_2CH{=}C(OMe)_2$).

The methyl and ethyl esters of 5-hexenoic acid are known compounds.

$CH_2{=}CHCH_2CH_2CH_2CO_2Me$, n_D^{20} 1.4205, a known compound [7], IR (film): ν(C=O) 1755, ν(C=C) 1640 cm^{-1}. NMR ($CDCl_3$): δ 1.6—2.5 (m, 6 H, $CH_2CH_2CH_2$), 3.6 (s, 3 H, CH_3) and 4.75—6.3 ppm (m, 3 H, $CH{=}CH_2$).

$CH_2{=}CHCH_2CH_2CH_2CO_2Et$, n_D^{20} 1.4225; lit. [8] n_D^{20} 1.4220, IR (film): ν(C=O) 1735, ν(C=C) 1640 cm^{-1}. NMR (CCl_4): δ 1.22 (t, 3 H, J 7 Hz, CH_3), 1.48—2.03 (m, 2 H, $CH_2C\underline{H_2}CH_2$), 2.10 and 2.22 (2t, 4 H, J 7 Hz, $C\underline{H_2}CH_2C\underline{H_2}$); 4.03 (q, 2 H, OCH_2), 4.73—6.17 (m, 3 H, $CH{=}CH_2$).

Acknowledgements

This work was supported in part by the Office of Naval Research. H.A.K. is grateful to the University of Kiel for a leave of absence and to the Max Kade Foundation for the award of a postdoctoral fellowship.

References

1 (a) D.A. Evans, G.C. Andrews and R. Buckwalter, J. Amer. Chem. Soc., 96 (1974) 5560; (b) W.C. Still and T.L. Macdonald, J. Amer. Chem. Soc., 96 (1974) 5561; (c) W.C. Still and T.L. Macdonaid, J. Org. Chem., 41 (1976) 3620; (d) A.P. Kozikowski and K. Isobe, Tetrahedron Lett., (1979) 833.

2 D. Seyferth and T.F. Jula, J. Organometal. Chem., 66 (1974) 195.

3 D. Seyferth and R.E. Mammarella, J. Organometal. Chem., 177 (1979) 53.

4 D. Seyferth, G.J. Murphy and R.A. Woodruff, J. Organometal. Chem., 141 (1977) 71.

5 D. Seyferth and K.R. Wursthorn, J. Organometal. Chem., 137 (1977) C17.

6 R.H. Prince, J. Chem. Soc., (1959) 1783.

7 P. Baudart, Bull. Soc. Chim. France, (1946) 86.

8 Yu.N. Ogibin, M.I. Katzin and G.I. Nikishin, Synthesis, (1974) 889.

9 L.H. Sommer and N.S. Marans, J. Amer. Chem. Soc., 72 (1950) 1935.

10 J.L. Speier, J.A. Webster and G.H. Barnes, J. Amer. Chem. Soc., 79 (1957) 974.

11 G.J.M. van der Kerk and J.G. Noltes, J. Appl. Chem., 9 (1959) 106.

12 F. Rijkens, M.J. Janssen, W. Drenth and G.J.M. van der Kerk, J. Organometal. Chem., 2 (1964) 347.

13 R.E. Hutton, J.W. Burley and V. Oakes, J. Organometal. Chem., 156 (1978) 369.

14 M. Nomuri, N. Matsui and S. Matsuda, Kogyo Kagaku Zasshi, 71 (1968) 1526; Chem. Abstr., 70 (1969) 47572.

15 A.D. Petrov, S.I. Sadykh-Zade and E.I. Filatova, Zh. Obshch. Khim., 29 (1959) 2936.

16 N.V. Komarov and N.V. Semenova, Zh. Obshch. Khim., 36 (1966) 103.