Journal of Organometallic Chemistry, 293 (1985) 139–146
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS WITH ORGANOBORANES

I. SYNTHESIS OF ALLYLIC DIETHYLBORANES AND *B*-ALLYLIC BORINANES VIA METALATION OF OLEFINS. CONTRATHERMODYNAMIC ISOMERIZATION OF OLEFINS

MAREK ZAIDLEWICZ
Institute of Chemistry, Nicolas Copernicus University, 87–100 Torun (Poland)

(Received April 23rd, 1985)

Summary

Allylic organopotassium compounds prepared by metalation of olefins with trimethylsilylmethylpotassium reacted with chlorodiethylborane and *B*-chloroborinane to give allylic diethylboranes and *B*-allylic borinanes, respectively. Hydrolysis of these organoboranes proceeding with allylic rearrangement leads to isomerized olefins. In this way, (*E*,*Z*)-2-pentene, (*Z*)-2-heptene, 1-methylcyclohexene and (+)-α-pinene were cleanly transformed into 1-pentene, 1-heptene, methylenecyclohexane and (+)-β-pinene, respectively. Stereochemistry of the addition of myrtenyldiethylborane to formaldehyde and 2-cyclohexenyldiethylborane to 4-t-butylcyclohexanone is described.

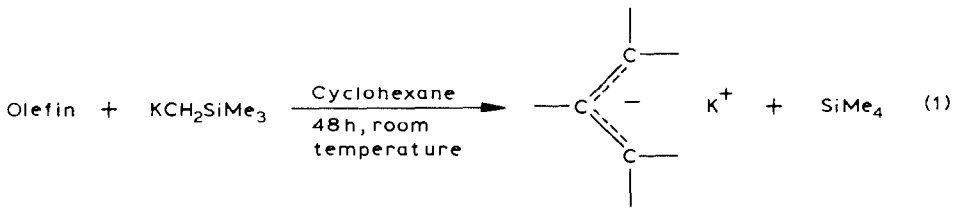
Introduction

Among organoboron compounds widely used as synthetic intermediates, allylic organoboranes play an important role due to their high reactivity [1,2]. In contrast to trialkylboranes, they readily react with acetylenes, aldehydes and ketones. These reactions find applications in the formation of C–C bonds [1–4]. The synthetic potential of allylic organoboranes, however, is not fully developed since the scope of the existing methods for their preparation is limited. The approaches most often used involve transmetalation reactions and hydroboration of conjugated dienes and allenes [1,2,5]. The usefulness of transmetalation, being in principle a very general method, depends on the availability of allylic organometallics. Considerable progress has been achieved recently in metalation reactions providing a convenient access to these compounds from readily available olefins [6–8]. This prompted me to study the synthesis of allylic dialkylboranes from olefins via their metalation, with the objective to develop new synthetic applications of these organoboranes.

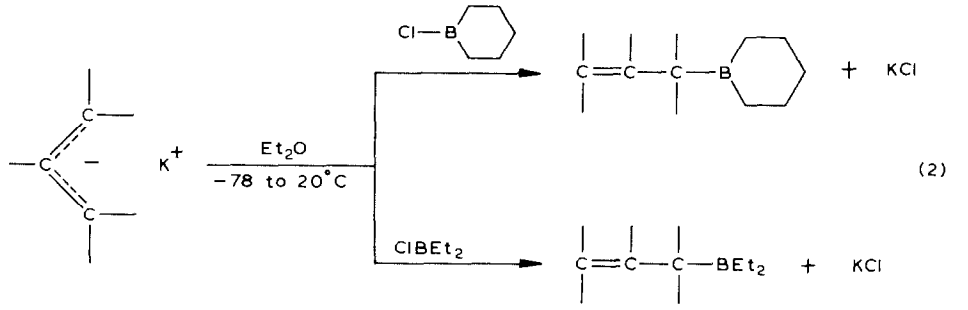
0022-328X/85/$03.30

Results and discussion

Trimethylsilylmethylpotassium was chosen as the metalating agent. It is a strong base requiring no activation for the reaction with olefins [9]. The metalation was carried out in cyclohexane solution or without the solvent (eq. 1). The reaction



mixture does not contain compounds interfering in the synthesis of allylic dialkylboranes. Consequently, this procedure allows the use of allylic organopotassium intermediates without isolation. These compounds, insoluble in cyclohexane, were separated from the unreacted olefin which could be recovered. The solid material consisting of the intermediate, the unreacted metalating agent and mercury was dried and added to a solution of chlorodiethylborane or *B*-chloroborinane in diethyl ether or THF to give allylic diethylboranes and *B*-allylic borinanes, respectively (eq. 2). The products are shown in Table 1. Although THF was found to be a better

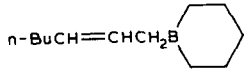
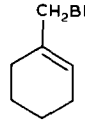
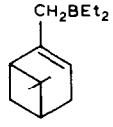
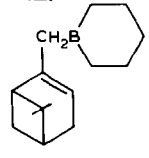
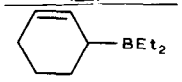


solvent for the organopotassium derivatives than diethyl ether, the latter was preferred since the product isolation was easier and the yields were higher.

These organoboranes oxidized with hydrogen peroxide under standard conditions or by simultaneous addition of hydrogen peroxide and an aqueous sodium hydroxide solution gave mainly olefins. The hydrolytic cleavage of the allylic group was suppressed by carrying out the oxidation with hydrogen peroxide in the presence of an excess of trimethylamine. However, even under these conditions, hydrolysis could not be stopped completely. The oxidation products are shown in Table 2.

Oxidation of II derived from (*Z*)-2-heptene gave a mixture of (*E*)- and (*Z*)-2-hepten-1-ols. The IR spectrum of II showed an intense absorption at 970 cm^{-1} characteristic of a *trans* disubstituted double bond [10]. This indicates that II is a mixture of geometric isomers. Consequently, the overall transformation of *Z*-2-heptene into II proceeds with loss of configurational identity of the double bond. The change of configuration could take place either in the metalation step or in the product due to its allylic rearrangement well known to occur in allylic dialkylboranes [1,5]. No attempt was made to clarify this problem. It was important, however, to

TABLE 1. SYNTHESIS OF ALLYLIC DIETHYLBORANES AND *B*-ALLYLIC BORINANES FROM OLEFINS

Olefin	Organoborane	Yield (%)	B.p. (°C/ mmHg)	^{1}H NMR (neat + TMS)	Molecular formula (mol. wt.)	B (Found (calcd.) (%))
2-Pentene (*E*,*Z*)	$EtCH{=}CHCH_2BEt_2$ (*E*,*Z*) (I)	61	46–47 5.0	0.91 (t, *J* 6 Hz, 9H, Me), 1.06–1.50 (m, 4H, CH_2), 2.04 (m, 4H, $CH_2C{=}C$), 5.10–5.70 (m, 2H, HC=CH).	$C_9H_{19}B$ (138.06)	7.92 (7.83)
2-Heptene (*Z*)	$n\text{-}BuCH{=}CHCH_2BEt_2$ (*E*,*Z*) (II)	65	46–47 0.1	0.93 (t, *J* 6 Hz, 9H, Me), 1.06–1.50 (m, 8H, CH_2), 2.00 (m, 4H, $CH_2C{=}C$), 5.00–5.67 (m, 2H, HC=CH).	$C_{11}H_{23}B$ (166.12)	6.41 (6.50)
2-Heptene (*Z*)	 (*E*,*Z*) (III)	62	55–56 0.1	0.90 (t, *J* 6 Hz, 3H, Me), 1.12–1.40 (m, 8H, CH_2), 1.55 (m, 6H, CH_2), 1.97 (m, 4H, $CH_2C{=}C$), 5.00–5.75 (m, 2H, HC=CH).	$C_{12}H_{23}B$ (178.13)	6.15 (6.07)
1-Methyl-cyclohexene	 (IV)	53 [a]	45–46 0.1	0.94 (t, *J* 6 Hz, 6H, Me), 1.06–1.40 (m, 4H, CH_2), 1.54 (m, 4H, CH_2), 1.87 (m, 4H, $CH_2C{=}C$), 1.97 (s, 2H, $BCH_2C{=}C$), 5.20 (m, 1H, HC=C).	$C_{11}H_{21}B$ (164.10)	6.45 (6.59)
(+)-α-Pinene	 (V)	57	48–50 0.05	0.85 (s, 3H, Me), 0.94 (t, *J* 6 Hz, 6H, Me), 1.22 (s, 3H, Me), 1.04–1.40 (m, 5H, CH, CH_2), 2.06 (s, 2H, $BCH_2C{=}C$), 1.62–2.50 (m, 5H, CH, CH_2), 5.05 (m, 1H, HC=C).	$C_{14}H_{25}B$ (204.16)	5.18 (5.30)
(+)-α-Pinene	 (VI)	51	58–60 0.05	0.85 (s, 3H, Me), 1.20 (m, 5H, CH, CH_2), 1.24 (s, 3H, Me), 1.50 (m, 6H, CH_2), 1.97 (s, 2H, $BCH_2C{=}C$), 1.75–2.50 (m, 5H, CH, CH_2), 5.06 (m, 1H, HC=C).	$C_{15}H_{25}B$ (216.18)	5.12 (5.00)
Cyclohexene	 (VII)	63 [a]	38–40 0.05	0.93 (t, *J* 6 Hz, 6H, Me), 1.06–1,38 (m, 4H, CH_2), 1.57 (m, 4H, CH_2), 1.93 (m, 2H, $CH_2C{=}C$), 2.15 (m, 1H, CH), 5.62 (m, 2H, HC=CH).	$C_{10}H_{19}B$ (150.07)	7.17 (7.20)

[a] Neat olefin metalated.

TABLE 2

OXIDATION AND HYDROLYSIS OF ALLYLIC DIETHYLBORANES AND *B*-ALLYLIC BORINANES

Organo-borane	Oxidation		Hydrolysis	
	Product (% composition)	Yield (%)	Product [d,f]	Yield (%)
I	2-Penten-1-ol [a,b] (76 (*E*), 24 (*Z*))	76	1-Pentene	92
II	2-Hepten-1-ol [a,c] (80 (*E*), 20 (*Z*))	85	1-Heptene	95
III	2-Hepten-1-ol [a,c] (78 (*E*), 22 (*Z*))	82	1-Heptene	95
IV	1-Hydroxymethyl-1-cyclohexene [c,d]	72	Methylene-cyclohexane	96
V	(+)-Myrtenol [c,d,e]	65	(+)-β-Pinene [g]	95
VI	(+)-Myrtenol [c,d,e]	60	(+)-β-Pinene [g]	93
VII	2-Cyclohexen-1-ol [d,f]	77.5	Cyclohexene	93

[a] Identified by GLC (25 m capillary column Carbowax 20M). [b] Authentic samples prepared by the reduction of (*E*)- and (*Z*)-2-pentenoic acid with AlH_3. (*E*)-2-Penten-1-ol, b.p. 137–139°C, n_D^{20} 1.4335 (lit., b.p. 74–74.5°C/45 mmHg, $n_D^{22.5}$ 1.4335 [37]), ^{1}H NMR(CCl_4), δ 1.01 (t, *J* 7.5 Hz, 3H, Me), 2.04 (m, 2H, CH_2), 3.95 (m, 2H, CH_2O), 4.19 (s, 1H, OH), 5.58 (m, 2H, HC=CH). (*Z*)-2-Penten-1-ol, b.p. 136–137°C, n_D^{20} 1.4345 (lit., b.p. 135–137°C, n_D^{25} 1.4350 [37], ^{1}H NMR CCl_4, δ 0.98 (t, *J* 7.5 Hz, 3H, Me), 2.06 (quintet, *J* 7.5 Hz, 2H, CH_2), 4.07 (d, *J* 5.5 Hz, 2H, CH_2O), 4.75 (s, 1H, OH), 5.44 (m, 2H, HC=CH). [c] Authentic samples prepared according to the literature; (*E*)- and (*Z*)-2-hepten-1-ol [38], (+)-myrtenol [19], 1-hydroxymethyl-1-cyclohexene [39]. [d] Identified by GLC (2.5 m column Carbowax 20M 5% on Chromosorb G). [e] $[\alpha]_D^{20}$ +31.4°. [f] Commercial authentic samples. [g] (−)-β-Pinene used for GLC ananlysis as an authentic sample.

establish the position of the boron atom in the organoboranes, I–VI. Examination of their ^{1}H NMR spectra, obtained at room temperature, revealed the boron atom at the primary position. GLC analysis of their oxidation products did not show 1-penten-2-ol, 1-hepten-2-ol, 2-methylenecyclohexanol and pinocarveol, respectively. Hydrolysis of I–VI gave in each case only one olefin derived from the organoborane having the boron atom at the primary position. Organoboranes with the boron atom at the secondary position, which may be involved in the allylic rearrangement, must be present in very low concentration.

The organoboranes I–VII hydrolized under very mild conditions. Stirring with water at room temperature for one hour was sufficient. The stoichiometric amount of sodium hydroxide was added to keep the corresponding dialkylborinic acid in the aqueous phase. Separation of the organic phase and distillation gave an olefin in high yield and purity. The products obtained are shown in Table 2, these are isomers of the olefins used for metalation and are uncontaminated with the starting material. Thus, the overall transformation involving a 1,2-transposition of the double bond is the contrathermodynamic isomerization of these olefins.

By this convenient two-step procedure the conversion of (+)-α-pinene into (+)-β-pinene in 54% yield and 90.8% optical yield was achieved. In contrast to (−)-β-pinene, a chiral material used in synthesis, the (+)-enantiomer occurring in a few plants [11], is not readily available. Several preparations of this enantiomer have been reported. It has been obtained from (+)-α-pinene via hydroboration with diborane, thermal isomerization of the intermediate organoborane and displacement

with a high-boiling olefin [12]. In another preparation based on hydroboration the thermally isomerized organoborane derived from (+)-α-pinene reacts with benzaldehyde to give (+)-β-pinene in 51% yield and 93.5% optical yield [13]. It has also been prepared in low yield from (+)-10-camphensulphonyl chloride [14]. The conversion of α- into β-pinene, 53% yield, 94% purity, by photooxidation/reduction has been described for the (−)-enantiomer [15]. Finally, β-pinene is the minor constituent of the equilibrium mixture produced by catalytic isomerization of α-pinene [16–18]. The product isolation in these preparations requires either chromatographic separation or an efficient fractional distillation. This is avoided in the conversion of (+)-α-pinene into (+)-β-pinene, 25% yield, 90% optical yield, 99% isomeric purity, by a four-step synthesis via (+)-myrtenol [19].

The preparation of (+)-β-pinene described here gives isomerically pure material in high optical yield. The intermediate is stable and may be easily purified. No solvent is required in the hydrolysis step and the product is isolated by simple distillation. The procedure is amenable to scaling up.

The addition of allylic organoboranes to aldehydes and ketones provides a ready access to homoallylic alcohols [1–3,20]. Stereochemistry of this addition is actively investigated [4,21–23]. In this study the stereochemical course of the reaction of myrtenyldiethylborane (V) with formaldehyde and 2-cyclohexenyldiethylborane (VII) with 4-t-butylcyclohexanone was examined. The reaction of V with formaldehyde gave (−)-*trans*-2-methylene-3-hydroxymethyl-7,7-dimethylbicyclo[4.1.1]heptane (VIII) in 91% yield. The alcohol showed identical GLC retention time, ^{1}H NMR and IR spectra with an authentic sample obtained in 6% yield from (+)-α-pinene by the Prins reaction [24]. The *trans* position of the hydroxymethyl group and the *gem*-dimethyl bridge was corroborated by ^{1}H NMR through a comparison of lanthanide-induced shifts of the methyl groups. Thus, the gradient of shift diagram [25], $\Delta\delta \cdot \text{VIII/Eu(DPM)}_3$, of the 8 and 9 methyl groups (standard pinane numbering employed [26,27]) was 2.8 and 4.4, respectively. The value for the 9 methyl group is much smaller than may be expected if the hydroxymethyl group is in a *cis* position to the bridge. For example, the gradients of the 8 and 9 methyl groups in isoborneol and borneol are 4.4, 4.0, 11.0 and 4.7, respectively [28]. The synthesis of VIII by this method is highly stereoselective and proceeds with much better yield than reported previously [24].

The reaction of VII with 4-t-butylcyclohexanone gave the 8/2 mixture of *cis*- and *trans*-1-(2-cyclohexenyl)-4-t-butylcyclohexanols indicating predominant equatorial attack on the carbonyl group. Thus, both reactions described above show preference of the addition from the less hindered side of the organoborane or the ketone.

Experimental

All glassware was dried at 150°C for at least 5 h, assembled hot and allowed to cool under an argon purge. All reactions were carried out under a static argon pressure. ^{1}H NMR spectra were recorded on a Tesla 80 MHz spectrometer and ^{13}C NMR spectra on a Tesla BS-567 25 MHz spectrometer. GLC analyses were performed on a Chrom-4 instrument using, if not otherwise stated, a 2.5 m column packed with 5% Carbowax 20M on Chromosorb G. IR spectra were recorded with a Carl Zeiss Jena Specord 75 KSR 4100 spectrophotometer. Mass spectra were obtained on an MX-1320 spectrometer (electron ionisation). Melting points were

determined on a Boetius apparatus and are uncorrected. C and H analyses were carried out with a Perkin–Elmer 240 microanalyser. B was determined by the oxygen-flask method [29].

Chlorodiethylborane [30], *B*-chloroborinane [31], trimethylsilylmethylpotassium [32] and bis(trimethylsilylmethyl)mercury [33] were prepared according to the literature. Diethyl ether, THF, (*Z*)-2-heptene (Merck), (*E*,*Z*)-2-pentene (Fluka) and all other hydrocarbons were distilled from $LiAlH_4$ prior to use.

Synthesis of allylic diethylboranes and B-allylic borinanes

General procedure. A mixture of potassium, 2.0 g, 50 mmol, and mineral oil 20 ml, was placed in a centrifugal vial provided with a rubber septum. The mixture was heated until the potassium melted and the vial was vigorously shaken to form potassium sand. After cooling to room temperature, cyclohexane, 20 ml, was added and a magnetic stirring bar was placed in the vial. The potassium sand was washed with cyclohexane, 3×20 ml. Cyclohexane, 50 ml, was added followed by bis(trimethylsilylmethyl)mercury, 9.4 g, 25 mmol, added all at once with stirring. A slightly exothermic reaction started and a trimethylsilylmethylpotassium precipitate was formed. After 1 h an olefin, 100 mmol, was added and the mixture was stirred at room temperature for 48 h and then centrifuged. The liquid was decanted and the solid was washed with cyclohexane and dried under vacuum at room temperature. The vial was connected to a flask containing a solution of chlorodiethylborane, 5.2 g, 50 mmol, or *B*-chloroborinane, 5.8 g, 50 mmol, in diethyl ether and the solid organopotassium derivative was added to the stirred solution at −78°C. The mixture was allowed to warm up to room temperature and left overnight. The solution was separated from the solid material by centrifugation/decantation and the product was isolated by distillation.

Hydrolysis of allylic diethylboranes and B-allylic borinanes. A typical example is as follows. Myrtenyldiethylborane, 5.1 g, 25 mmol, derived from (+)-α-pinene ($[\alpha]_D^{20}$ +35.1° (neat), 68.0%, enantiomeric excess, (e.e.) [34]) was added to water, 4.5 g, 250 mmol, at 0°C and the mixture was stirred for 1 h at room temperature. Sodium hydroxide, 1.2 g, 30 mmol, was added at 0°C and stirring was continued for 0.5 h at this temperature. The organic layer was separated, washed with water, 1 ml, dried over magnesium sulfate and distilled to give (+)-β-pinene, 3.2 g, 95% yield, b.p. 60–61°C at 15 mmHg, n_D^{20} 1.4772, $[\alpha]_D^{20}$ +14.1° (neat), 61.8% e.e. [14], 90.8% optical yield. GLC analysis of this product did not show contamination with α-pinene.

Oxidation of allylic diethylboranes and B-allylic borinanes. The following is a typical example. 2-Cyclohexenyldiethylborane, 3.8 g, 25 mmol, was added to a solution of trimethylamine, 1.8 g, 30 mmol, in THF, 10 ml. The oxidation was done by the addition of 30% aqueous hydrogen peroxide solution, 10.2 ml, 100 mmol, at 0°C with stirring for 2 h at room temperature. The organic layer was separated, washed with saturated brine, dried over magnesium sulfate and distilled to give 2-cyclohexen-1-ol, 1.9 g, 77.5% yield, b.p. 60–61°C at 10 mmHg, n_D^{20} 1.4856, identified by comparison (GLC, ^1H NMR) with an authentic sample.

(−)-trans-2-Methylene-3-hydroxymethyl-7,7-dimethylbicyclo[4.1.1]heptane (VIII). Formaldehyde, 0.9 g, 30 mmol, was passed into a solution of myrtenyldiethylborane, 5.1 g, 25 mmol, in diethyl ether, 25 ml, at 0°C and the mixture was left for 1 h at room temperature. An aqueous 3 *M* sodium hydroxide solution, 10 ml, 30 mmol, was added at 0°C and the mixture was stirred for 0.5 h at room temperature. The

organic layer was separated and the aqueous layer was extracted with diethyl ether. The etheral solutions were combined, washed with water and dried over magnesium sulfate. Distillation gave VIII, 3.8 g, 91% yield, b.p. 62–64°C at 0.1 mmHg, n_D^{20} 1.4990, $[\alpha]_D^{20}$ −28.8° (neat) (lit., b.p. 86–87°C at 2 mmHg, n_D^{20} 1.5019, $[\alpha]_D^{20}$ −17.3° (neat) [24]). Anal. Found: C, 79.46; H, 10.92. $C_{11}H_{18}O$ calcd.: C, 79.46; H, 10.91%. ^{1}H NMR (CCl_4), δ 0.75 (s, 3H, CH_3), 1.77 (s, 1H, OH), 1.44–2.84 (m, 7H, CH, CH_2), 3.50 (d, J 7 Hz, 2H, CH_2–O), 4.73 (m, 2H, C=CH_2). The product showed identical ^{1}H NMR spectrum and GLC retention time with an authentic sample prepared from (+)-α-pinene by Prins reaction [24].

Cis- and trans-1 (2-cyclohexenyl)-4-t-butylcyclohexanol. A solution of 2-cyclohexenyldiethylborane, 7.5 g, 50 mmol, in diethyl ether, 25 ml, was added to a solution of 4-t-butylcyclohexanone, 7.7 g, 50 mmol, in diethyl ether, 50 ml, at 0°C and the mixture was left for 2 h at room temperature. An aqueous 3 *M* sodium hydroxide solution, 19 ml, 57 mmol, was added and the mixture was stirred for 1 h. The organic layer was separated, washed with water and dried over magnesium sulfate. The product isolated by distillation, 11.0 g, 93% yield, b.p. 87–89°C/0.1 mmHg, solidified in the receiver. GLC analysis showed two components 8/2. The major component isolated by crystallization from n-pentane was *cis*-1-(2-cyclohexenyl)-4-t-butylcyclohexanol, m.p. 90–92°C. Anal. Found: C, 81.30; H, 12.09. $C_{16}H_{28}O$ calcd.: C, 81.29; H, 11.93%. ^{1}H NMR ($CDCl_3$): δ 0.85 (s, 9H, $(CH_3)_3C$), 1.12–2.12 (m, 16H, CH, CH_2), 1.25 (s, 1H, OH), 5.80 (m, 2H, HC=CH). ^{13}C NMR ($CDCl_3$): δ 129.68, 127.29, 72.56, 48.00, 46.88, 35.39, 34.04, 32.33, 27.55, 25.23, 23.67, 22.47, 22.32. Mass spectrum: no molecular ion, 154 (10), 155 (100), 137 (12), 95 (10), 81 (30), 67 (13), 57 (27). IR (CS_2): 954 cm^{-1} (axial OH, [35,36]).

The 8/2 mixture, 0.3 g, was dissolved in ethanol and hydrogenated in the presence of platinum black until hydrogen absorption ceased. GLC analysis of the solution showed cis- and trans-4-tert-butylcyclohexanol, 8/2, identified by comparison with an authentic sample prepared by the reaction of 4-t-butylcyclohexanone with cyclohexylmagnesium bromide.

Acknowledgment

The finantial support given by the Polish Academy of Sciences under the project MR.I.12 is acknowledged.

References

1 B.M. Mikhailov and Yu.N. Bubnov, Bororganicheskie Soedinieniya v Organicheskom Sinteze, Nauka, Moscow, 1977, p. 398.
2 E. Negishi, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 7, Pergamon Press, Oxford, 1982, p. 349.
3 A. Pelter, Chem. Soc. Rev., 11 (1982) 191.
4 R.W. Hoffmann, Angew. Chem., 94 (1982) 569.
5 G.W. Kramer and H.C. Brown, J. Organomet. Chem., 132 (1977) 9.
6 J. Klein, Tetrahedron, 39 (1983) 2733.
7 M. Stahle and M. Schlosser, J. Organomet. Chem., 220 (1981) 277.
8 M. Stahle, J. Hartmann and M. Schlosser, Helv. Chim. Acta, 60 (1977) 1730.
9 J. Hartmann and M. Schlosser, Helv. Chim. Acta, 59 (1976) 453.
10 M. Golfier, in H.B. Kagan (Ed.), Stereochemistry, Vol. 1, G. Thieme, Stuttgart, 1977, p. 4.

11 E. Gildemeister and F. Hoffmann, Die Ätherische Öle, Vol. IIIa, Akademie-Verlag, Berlin, 1960, p. 164.
12 H.C. Brown and M.V. Bhatt, J. Am. Chem. Soc., 82 (1960) 2074.
13 M.M. Midland, J.E. Petre, S.A. Zderic and A. Kazubski, J. Am. Chem. Soc., 104 (1982) 528.
14 W. Krimse and W. Gruber, Chem. Ber., 105 (1972) 2764.
15 Y F. Min, B W. Zand and Y. Cao, Synthesis, (1982) 875.
16 US Pat., 3325553, 3359342, 3360581; Chem. Abstr., 67 (1967) 108795k, 68 (1967) 49816p, 49817q.
17 Neth. Appl., 6501986, 6610235; Chem. Abstr., 64 (1966) 3619a, 67 (1967) 73718h.
18 G.A. Rudakov, L.S. Ivanova, T.N. Pisareva and A.G. Borovskaya, Zh. Org. Khim., 11 (1975) 2275.
19 M. Harwood and M. Julia, Synthesis, (1980) 456.
20 G.W. Kramer and H.C. Brown, J. Org. Chem., 42 (1977) 2292.
21 Y. Yamamoto and K. Maruyama, Heterocycles, 18 (1982) 357.
22 R.W. Hoffmann, H.J. Zeiss, W. Ladner and S. Tabche, Chem. Ber., 115 (1982) 2357.
23 H.C. Brown and P.K. Jadhav, J. Am. Chem. Soc., 105 (1983) 2092.
24 J. Kapuscinski, Roczniki Chem., 40 (1966) 331.
25 A.F. Cockerill, G.L.O. Davies, R.C. Harden and D.M. Rackham, Chem. Rev., 73 (1973) 553.
26 A. Pelter and S.H. Harper, in S. Coffey, (Ed.), Rodd's Chemistry of Carbon Compounds, 2nd edit., Vol. IIc, Elsevier, Amsterdam, 1969, p. 167.
27 J.M. Coxon, G.J. Hydes and P.J. Steel, J. Chem. Soc., Perkin II, (1984) 1351.
28 P.V. Demarco, T.K. Elzey, R.B. Lewis and E. Wenkert, J. Am. Chem. Soc., 92 (1970) 5734.
29 A. Mazzeo Farina, Il Farmaco Ed. Sci., 28 (1973) 937.
30 Inorg. Synth., XV (1974) 149.
31 H.C. Brown and M. Zaidlewicz, J. Am. Chem. Soc., 98 (1976) 4917.
32 A.J. Hart, D.H. O'Brien and C.A. Russell, J. Organomet. Chem., 72 (1974) C19.
33 D. Seyferth and W. Freyer, J. Org. Chem., 26 (1961) 2604.
34 H.C. Brown, P.K. Jadhav and M.C. Desai, J. Org. Chem., 47 (1982) 4583.
35 R.A. Pickering and C.C. Price, J. Am. Chem. Soc., 80 (1958) 4931.
36 M.C. Deschamps, A. Marchand and J. Valade, C.R. Acad. Sci., Paris, Ser. C, 265 (1967) 232.
37 D.A. Thomas and W.K. Warburton, J. Chem. Soc., (1965) 2988.
38 L.F. Hatch, H.D. Weiss and T.P. Li, J. Org. Chem., 26 (1961) 61.
39 R.J.W. Cremlyn, R.M. Ellam and T.K. Mitra, J. Chem. Soc., Perkin I, (1972) 1727.