THERMAL RACEMIZATION OF SOME ORGANOMETALLIC COMPOUNDS CONTAINING ELEMENTS OF THE FIRST, SECOND AND THIRD GROUP OF THE PERIODIC TABLE AND OPTICALLY ACTIVE ALKYL GROUPS

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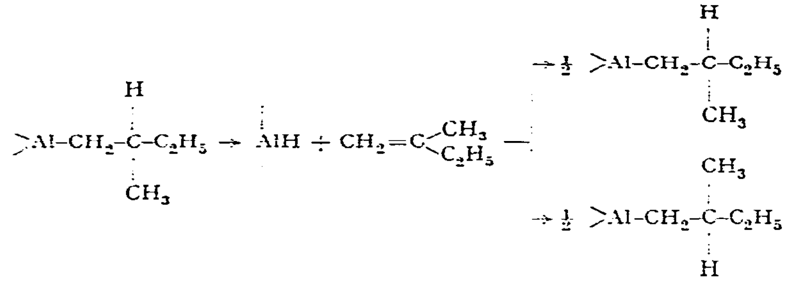
(Received April 10th, 1965)

In an earlier communication[1] we have proposed, on the basis of chemical and kinetic evidence, that the relatively rapid thermal racemization of tris[(*S*)-2-methylbutyl]aluminium takes place through the formation of dialkylaluminium monohydride according to scheme (1):



$$>\!Al{-}CH_2{-}\underset{CH_3}{\overset{H}{C}}{-}C_2H_5 \rightarrow AlH + CH_2{=}C\begin{matrix}CH_3\\C_2H_5\end{matrix} \rightarrow \begin{cases}\rightarrow \frac{1}{2}\ >\!Al{-}CH_2{-}\underset{CH_3}{\overset{H}{C}}{-}C_2H_5\\[2ex] \rightarrow \frac{1}{2}\ >\!Al{-}CH_2{-}\underset{H}{\overset{CH_3}{C}}{-}C_2H_5\end{cases} \qquad (1)$$

To obtain a better understanding of the chemical reactivity of other organometallic compounds containing a tertiary carbon atom in the β position with respect to the metal atom, we have extended our investigation to the (*S*)-2-methylbutyl-derivatives of lithium, beryllium, magnesium, zinc, cadmium and boron.

Compounds of boron or zinc having a tertiary asymmetric carbon atom in the γ or δ position with respect to the metal atom, have also been studied.

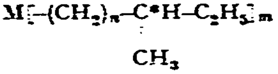
PREPARATION AND OPTICAL PURITY OF THE ORGANOMETALLIC COMPOUNDS USED

The preparation and the determination of the optical purity of the organometallic derivatives of zinc and boron used have already been described[2,3]. Bis[(*S*)-2-methylbutyl] magnesium was prepared according to the procedure of Mosher and Loeffler[4] and bis[(*R*)-2-methylbutyl]beryllium according to the procedure of Wood and Brenner[5]. The relationship between [α] and optical purity was determined by reacting the beryllium compound with CO_2 and determining the optical activity of (+)(*S*)-3-methylpentanoic acid[6] thus obtained. Although the corresponding aluminium, boron and zinc derivatives are monomeric, (+)bis[(*R*)-2-methylbutyl]beryllium was found to be dimeric in benzene, in agreement with the results obtained by Coates and Glocking[7] for diisopropylberyllium. Bis[(*S*)-2-methylbutyl]cadmium was prepared by a reported method[8] and the minimum optical purity evaluated by conversion of the organometallic compound to (+)(*S*)-4-methyl-2-hexanone[9]. (*R*)-1-lithium-2-methylbutane was not isolated but its optical purity was tested as indicated previously[6].

The physical properties and analyses of the organometallic compounds investigated are given in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND ANALYSIS OF SOME ORGANOMETALLIC COMPOUNDS OF GENERAL FORMULA



$M[-(CH_2)_n-\overset{*}{C}H(CH_3)-C_2H_5]_m$

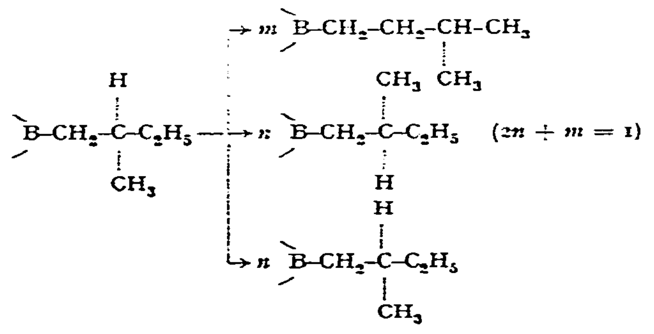
M	*n*	*B.p.* (°*C*/*mm*)	d_4^t	$[\alpha]_D^t$	*Analysis* (% *M*)		*Mol. wt.*[c]	
					Found	*Calcd.*	*Found*	*Calcd.*
Be	1	79–80/0.02–0.03		+35.47°[a,b]	5.84	5.96	308	151.29
Zn	1	40–41/0.1	0.983[a]	+ 9.92°[a]	31.49	31.47	212	207.65
Zn	2	64–65/0.1	0.982[a]	+ 7.68°[a]	27.73	27.74	238	235.71
Zn	3	81–82/0.07	0.962[a]	+14.36°[a]	24.84	24.78	268	263.76
Zn	4	104–105/0.05	0.947[a]	+10.40°[a]	22.38	22.40	296	291.81
Cd	1	48–49/0.02–0.03		+ 6.50°[d]	44.26	44.20		
B	1	68/0.5	0.773[e]	+39.00°[e]	4.85	4.83	225	224.22
B	2	115–116/1	0.783[e]	+15.65°[a]	4.03	4.06	255	266.29
Al	1	69–70/0.08–0.09	0.797[a]	+27.64°[a]	11.10	11.25		

[a] Determined at 25°. [b] In xylene (c = 8.456 g/100 ml). [c] By cryoscopy in benzene. [d] Observed rotation (l = 0.5, neat). [e] Determined at 20°.

RESULTS

Racemization experiments were carried out, when possible, by heating the organometallic compounds (in the presence or absence of solvents) in polarimeter tubes at constant temperature and following the decrease of rotatory power with time. In the case of (*R*)-1-lithium-2-methylbutane and bis[(*S*)-2-methylbutyl]magnesium, the thermal racemization was evaluated by carbonation to (+)(*S*)-3-methylpentanoic acid[6], after heating the organometallic compound for 10 h at 100°.

In those cases where a decrease of optical rotation was observed, the chemical structure of the racemized compounds was checked and only in the case of (+)tris[(*R*)-2-methylbutyl]boron did the racemized compound appear to be partially isomerized according to scheme (2)[10]:



(2)

Tables 2 and 3 show that only the 2-methylbutyl derivatives of beryllium, boron and aluminium racemize at an appreciable rate below 105° and the specific rate constant decreases in the order Be, Al, B.

TABLE 2

THERMAL RACEMIZATION OF SOME ORGANOMETALLIC COMPOUNDS OF Mg, Zn, Cd, B AND Al OF GENERAL FORMULA $M[-(CH_2)_n-\underset{\displaystyle CH_3}{\underset{|}{C^*H}}-C_2H_5]_m$ IN THE ABSENCE OF SOLVENTS

M	*n*	*Physical state*	*Temp. (°C)*	*Time (h)*	α_D^t *(l = 1) or optical purity*		*Racemization (%)*
					Initial	*Final*	
Mg	1	solid	100 ± 1	10	96.0^a	95.0^a	1.1
Zn	1	liquid	100 ± 1	10	$+9.76^{\circ b}$	$+9.74^{\circ b}$	0.5
	2	liquid	100 ± 1	10	$+7.56^{\circ b}$	$+7.52^{\circ b}$	0.5
	3	liquid	100 ± 1	10	$+13.82^{\circ b}$	$+13.78^{\circ b}$	0.6
Cd	1	liquid	103 ± 2	3	$+13.02^{\circ b}$	$+12.96^{\circ b}$	1.5
B	1	liquid	94.2 ± 0.1	7	$+22.50^{\circ c}$	$+21.58^{\circ c}$	4.1
	1	liquid	120 ± 0.1	7	$+16.00^{\circ c}$	$+9.87^{\circ c}$	38.3
	2	liquid	102.5 ± 0.1	10	$+9.99^{\circ c}$	$+9.99^{\circ c}$	0.0
Al	1	liquid	94.2 ± 0.1	5	$+13.26^{\circ c}$	$+6.90^{\circ c}$	48.0

[a] Determined by carbonation to (+)(*S*)-3-methylpentanoic acid. [b] Determined at 25°. [c] Determined at the experimental temperature.

Under these conditions, corresponding zinc, cadmium and lithium derivatives, do not racemize either in the presence or absence of hydrocarbon solvents. As bis[(*S*)-2-methylbutyl]magnesium is insoluble in hydrocarbons, its racemization was investigated in the solid state; practically no racemization was observed (Table 2) at 100°.

TABLE 3

INFLUENCE OF THE NATURE OF THE SOLVENT ON THE THERMAL RACEMIZATION OF SOME ORGANOMETALLIC COMPOUNDS OF Li, Be, Zn, B AND Al OF GENERAL FORMULA $M[-(CH_2)_n-\underset{\displaystyle CH_3}{\underset{|}{C^*H}}-C_2H_5]_m$

M	*n*	*Solvent*	*Concn. (w/v)*	*Temp. (°C)*	*Time (h)*	α_D^t *(l = 1) or optical purity*		*Racemization (%)*
						Initial	*Final*	
Li	1	decalin	11.7	100 ± 1	10	$96.0–99.0^a$	95.0^a	1–4
	1	*iso*-propyl ether	10.5–28.1	62 ± 1	6	$96.0–99.0^a$	$95.5–99.0^a$	0–3.5
Mg	1	dioxane	4.3	103 ± 2	10	96.0^a	95.3^a	0.8
Be	1	xylene	8.5	70 ± 0.1	3	$+1.73^{\circ b}$	$+0.68^{\circ a}$	62.7
	1	dioxane	5.9	70 ± 0.1	8	$+0.86^{\circ b}$	$+0.85^{\circ b}$	0.0
Zn	1	dioxane	25.0	104 ± 1	6	$+9.64^{\circ c}$	$+9.64^{\circ c}$	0.0
B	1	toluene	43.5	94.2 ± 0.1	7	$+11.53^{\circ b}$	$+11.02^{\circ b}$	4.4
	1	dioxane	46.5	94.2 ± 0.1	7	$+11.76^{\circ b}$	$+11.24^{\circ b}$	4.4
	1	tetralin	22.8	120 ± 0.1	7	$+6.21^{\circ b}$	$+2.95^{\circ b}$	52.4
Al	1	toluene	35.8	94.2 ± 0.1	5	$+3.67^{\circ b}$	$+1.83^{\circ b}$	50.0
	1	toluene	25.2	94.2 ± 0.1	5	$+4.54^{\circ b}$	$+2.22^{\circ b}$	51.1
	1	dioxane	7.1	94.2 ± 0.1	5	$+1.12^{\circ b}$	$+1.12^{\circ b}$	0.0

[a] Determined by carbonation to (+)(*S*)-3-methylpentanoic acid. [b] Determined at the experimental temp. [c] Determined at 25° (neat).

When the asymmetric carbon atom is in the γ or δ position with respect to the metal atom, no racemization has been observed for aluminium[11], boron[3] and zinc[2] alkyls (Table 2).

In the case of 2-methylbutyl-beryllium and -aluminium derivatives, racemization occurs below 100° with and without hydrocarbon solvents, but no change in optical rotation of these compounds with time was found at 70 and 94°, respectively, using ethereal solvents (Table 3).

On the other hand, for tris[(*R*)-2-methylbutyl]boron the rate of racemization does not appear to be much dependent on the type of solvent (Table 3); furthermore, the ratio $v_{rac}/c_{MR^*_3}$, which in the case of aluminium alkyl is independent of the concentration of the organometallic compound, increases with decrease in the boron alkyl concentration (Tables 2 and 3)[10].

The investigation of the thermal racemization of (*R*)-1-lithium-2-methylbutane in ethereal solvents is complicated by the reaction between lithium alkyls and ethers[12]. Using diisopropyl ether, the decomposition rate of which, in the presence of lithium alkyls, is sufficiently low, practically no racemization was observed in the unreacted (*R*)-1-lithium-2-methylbutane (Table 3).

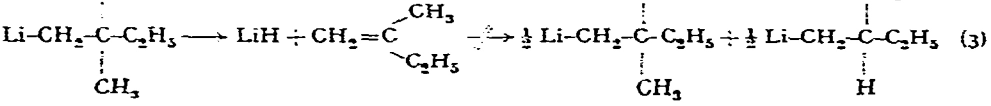
DISCUSSION

On the basis of the racemization mechanism suggested for tris[(*S*)-2-methylbutyl]aluminium (scheme 1), it is possible to correlate hydride formation and racemization for the other organometallic compounds we have investigated.

In fact, bis[(*R*)-2-methylbutyl]beryllium, which very easily undergoes thermal decomposition, like other beryllium alkyls[13], with formation of 2-methylbutylberyllium hydride, shows the highest racemization rate (about 15 times that of the corresponding aluminium alkyl).

According with the slow dialkyl monohydride formation of boron alkyls[14,15] at 100–130°, tris[(*R*)-2-methylbutyl]boron slowly racemizes at 100° but the racemization is accompanied by partial isomerization of the alkyl group[10,16].

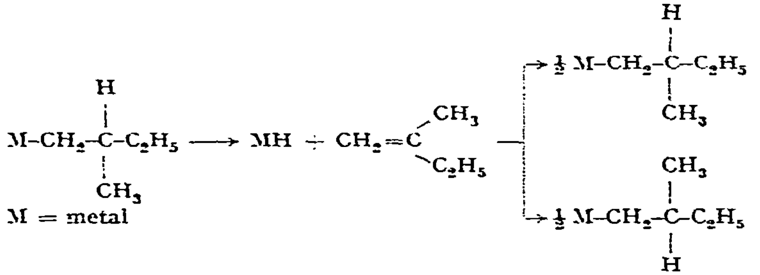
In the case of (*R*)-1-lithium-2-methylbutane, which like other lithium alkyls, undergoes thermal decomposition with formation of lithium hydride[17,18], no racemization was observed (Table 3). In our opinion the lack of racemization, which is expected according to scheme (1), is due to the fact that, under the conditions used for our experiment, the olefine does not react at an appreciable rate with lithium hydride (scheme 3):



$$\text{Li–CH}_2\text{–}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{–C}_2\text{H}_5 \longrightarrow \text{LiH} + \text{CH}_2\text{=C}\begin{matrix}\diagup\text{CH}_3\\ \diagdown\text{C}_2\text{H}_5\end{matrix} \nrightarrow \tfrac{1}{2}\,\text{Li–CH}_2\text{–}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{–C}_2\text{H}_5 + \tfrac{1}{2}\,\text{Li–CH}_2\text{–}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{–C}_2\text{H}_5 \quad (3)$$

Bis[(*S*)-2-methylbutyl]magnesium does not racemize at 100° either in the solid state (Table 2) or in dioxane solution (Table 3) as expected on the basis of the above assumptions. In fact, magnesium alkyls give hydrides only at temperatures above 100° (ref. 19). Zinc and cadmium derivatives which, on heating, easily undergo homolytic cleavage of the metal–carbon bond[2,20] and do not usually give hydrides, do not racemize at 100°, but partially decompose with formation of metallic zinc and cadmium[2,20]. The lack of racemization of bis[(*R*)-2-methylbutyl]beryllium in dioxane solution is in keeping with the results obtained for tris[(S)-2-methylbutyl]aluminium in dioxane solution (Table 3); it seems that the ether prevents the formation of the metal–hydrogen bond, the affinity of the metal for the ethereal oxygen being higher than the affinity of the metal for the hydrogen in the β position. Boron alkyls do not yield etherates at room temperature in the presence of ethers[21] and therefore the racemization rate of tris[(*R*)-2-methylbutyl]boron is not affected by the presence of these solvents.

From the above evidence we conclude that organometallic compounds containing a tertiary asymmetric carbon atom in the β position have relatively low racemization temperatures only when the metal is able to form hydrides and olefines reversibly according to scheme (4):



(4)

Further experiments are in progress to clarify the racemization mechanism of tris[(*R*)-2-methylbutyl]boron which appears be more complicated as shown by the isomerization phenomena accompanying the racemization and by the dependence of the overall reaction rate on BR^*_3 concentration.

EXPERIMENTAL

Solvents

Petroleum ether, benzene and xylene were purified by H_2SO_4 treatment, dried by distillation over sodium and stored under nitrogen. Isopropyl ether, tetralin and decalin were purified by rectification over sodium; dioxane was purified by the procedure of Pestemer[22].

Known organometallic compounds

(+)(*R*)-1-Lithium-2-methylbutane[6], (+)bis[(*S*)-2-methylbutyl]magnesium chloride[6], (+)bis[(*S*)-2-methylbutyl]magnesium[4], (+)bis-[(*S*)-2-methylbutyl]zinc[2], (+)-tris[(*R*)-2-methylbutyl]boron[3] and (+)tris[(*S*)-2-methylbutyl]aluminium[23] were prepared from (+)(S)-1-chloro-2-methylbutane ($[\alpha]_D^{25}$ +1.60–1.62°) as previously published.

(+)Bis[(*S*)-3-methylpentyl]zinc[2] and (+)tris[(*S*)-3-methylpentyl]boron[3] were prepared as described previously from (+)(*S*)-1-chloro-3-methylpentane ($[\alpha]_D^{25}$ +19.00°). (+)Bis[(*S*)-4-methylhexyl]zinc was obtained from (+)(*S*)-1-chloro-4-methylhexane ($[\alpha]_D^{25}$ +10.61°)[2]. The physical properties and analyses of the organometallic compounds investigated are reported in Table 1. The pressure in the vacuum distillation apparatus was measured by a McLeod gauge.

(+)Bis[(R)-2-methylbutyl]beryllium

To 0.41 moles of (+)(*R*)-1-lithium-2-methylbutane [from (+)(*S*)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ +1.60°] in 220 ml of petroleum ether, were added with stirring 16.5 g of beryllium chloride sublimed at reduced pressure[24]. The mixture was gently refluxed for 3 h after the addition of 15.3 g of anhydrous ether, under an atmosphere of dry nitrogen and then left to cool overnight.

The upper liquid phase was transferred under a nitrogen atmosphere to a distillation apparatus and petroleum ether was eliminated by vacuum distillation. The residue was distilled at reduced pressure and a product, b.p. 75–78° (0.05 mm) (Be, 5.37 %)[25] was recovered; this fraction afforded on redistillation (+)bis[(*R*)-2-methylbutyl]beryllium, $[\alpha]_D^{25}$ +35.47° (c = 8.456 g/100 ml, xylene) (40 % yield based on (+)(*R*)-1-lithium-2-methylbutane).

In order to determine its optical purity (+)bis[(*R*)-2-methylbutyl]beryllium in ether (1.0 g) was carbonated by pouring the solution on to "dry ice"[26]. By distillation of the ether extracts, 0.3 g of (+)(*S*)-3-methylpentanoic acid, b.p. 102–103° (20 mm), n_D^{25} 1.4143, $[\alpha]_D^{25}$ +8.31°, was obtained (20 % yield).

In a repeat experiment, (+)bis[(*R*)-2-methylbutyl]beryllium in ether [1.07 g, $[\alpha]_D^{25}$ +34.90° (xylene)] was carbonated by solid CO_2. The weight of distilled (+)(*S*)-3-methylpentanoic acid, b.p. 102–103° (19–20 mm), n_D^{25} 1.4142, $[\alpha]_D^{25}$ +8.17°, was 0.75 g (46 % yield).

Carbonation of racemized (+)bis[(R)-2-methylbutyl]beryllium. Several samples of (+)bis[(*R*)-2-methylbutyl]beryllium (1.10 g) racemized by heating (70° for 5–8 h) were carbonated by solid CO_2 in the usual manner. Pure (+)(*S*)-3-methylpentanoic acid (0.5 g), b.p. 100–101° (18 mm), n_D^{25} 1.4140, $[\alpha]_D^{25}$ +0.61°, was recovered (31 % yield). No traces of other C_6 carboxylic acids were found on examining the methyl ester by gas chromatography.

Bis[(S)-2-methylbutyl]cadmium

To 0.43 moles of (+)(*S*)-2-methylbutylmagnesium chloride [from (+)(*S*)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ +1.60°] in ether, was added with stirring 39.5 g of anhydrous cadmium chloride[8] (30 min). The mixture was gently refluxed for 2 h, cooled and the upper liquid phase transferred under a nitrogen atmosphere to a distillation apparatus. The first distillation afforded a fraction, b.p. 55–60° (0.04 mm); a second distillation of this fraction gave (+)bis[(*S*)-2-methylbutyl]cadmium, α_D^{25} +6.50° (l = 0.5 dm, neat) (30 % yield based on the (+)(*S*)-2-methylbutylmagnesium chloride).

This organometallic compound decomposes at room temperature with separation of metallic cadmium.

The optical purity was determined by treating 6.3 g of the compound with acetyl chloride in the usual manner[9]; (+)(*S*)-4-methyl-2-hexanone, b.p. 140°, n_D^{25} 1.4061, $[\alpha]_D^{25}$ +6.42° (ref. 9) was obtained (29 % yield). The crude ketone was purified through its semicarbazone as described in the literature[27].

Thermal racemization experiments

For (+)bis[(*R*)-2-methylbutyl]beryllium, (+)tris[(*R*)-2-methylbutyl]boron,

-aluminium, -aluminium etherate and (+)tris[(S)-3-methylpentyl]boron, racemization experiments were carried out by heating the organometallic compound directly with or without a solvent using polarimetric tubes (1 or 0.5 dm length), at constant temperature (± 0.1°). In the case of (+)bis[(S)-2-methylbutyl]zinc, -cadmium, (+)bis-[(S)-3-methylpentyl]zinc and (+)bis[(S)-4-methylhexyl]zinc, which decompose thermally with separation of metal, the organometallic compound was heated with or without solvents under an atmosphere of dry, purified nitrogen and distilled directly into the polarimetric tube.

Thermal racemization of (+)(R)-1-lithium-2-methylbutane. (+)(R)-1-Lithium-2-methylbutane [0.28 moles, from (+)(S)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ +1.60°–1.62°] in 190 ml of decalin, were heated for 10 h at 100 ± 1°, under an atmosphere of dry, purified nitrogen. By successive carbonation of the reaction mixture and the usual procedure[26] (+)(S)-3-methylpentanoic acid, b.p. 102–103° (20 mm), n_D^{25} 1.4143, $[\alpha]_D^{25}$ +8.40° was obtained (3% yield).

In a repeat experiment, 0.37 moles of (+)(R)-1-lithium-2-methylbutane [from (+)(S)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ +1.60°] in 150 ml of decalin, were heated for 1 h at 120–125°. The apparatus was provided with an effective condenser so that the gaseous products evolved did not escape into the atmosphere. By carbonation of the mixture, cooled overnight at 0° in presence of 650 ml of anhydrous ether, (+)(S)-3-methylpentanoic acid, n_D^{25} 1.4142, $[\alpha]_D^{25}$ +8.45°, was obtained (3.5% yield). On heating at 100–125°, (+)(R)-1-lithium-2-methylbutane in decalin decomposes mainly to 2-methylbutene and lithium hydride; this thermal decomposition is complete in 8 h at *ca.* 140°.

(+)(R)-1-Lithium-2-methylbutane [0.65 moles, from (+)(S)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ +1.61°] in 180 ml of isopropyl ether were heated for 6 h at 62–63°. During this period 6.2 l of propylene were evolved and 16 g of practically pure 2-methylbutane were obtained in an ice–NaCl cooled trap. By carbonation of the reaction mixture, (+)(S)-3-methylpentanoic acid [n_D^{25} 1.4142, $[\alpha]_D^{25}$ +8.44°–8.46°] was obtained (12% yield).

Thermal racemization of (+)bis[(S)-2-methylbutyl]magnesium. (+)(S)-2-Methylbutylmagnesium chloride [0.26 moles, from (+)(S)-1-chloro-2-methylbutane, $[\alpha]_D^{25}$ +1.60°] in ethyl ether was slowly (2 h) added to boiling xylene and distillation of the mixture continued until the refractive index of the distillate was that of xylene. Xylene was added at intervals to maintain the liquid level in the distillation apparatus[28] approximately constant. The (+)(S)-2-methylbutylmagnesium chloride suspension in 180 ml of xylene was heated for 10 h at 100 ± 1°. By carbonation, (+)(S)-3-methylpentanoic acid [n_D^{25} 1.4141, $[\alpha]_D^{25}$ +8.44°] was obtained (71% yield).

(+)Bis[(S)-2-methylbutyl]magnesium (2.0 g), prepared by the Mosher and Loeffler procedure[4], from (+)(S)-2-methylbutyl magnesium chloride in ether, was carbonated to (+)(S)-3-methylpentanoic acid, b.p. 102° (20 mm), n_D^{25} 1.4142, $[\alpha]_D^{25}$ +8.45° (42% yield).

(+)Bis[(S)-2-methylbutyl]magnesium (2.2 g) were heated, under an atmosphere of dry nitrogen, for 10 h at 100 ± 1°; by carbonation of the mixture, (+)(S)-3-methylpentanoic acid, n_D^{25} 1.4144, $[\alpha]_D^{25}$ +8.40°, (41% yield) was obtained.

A dioxane solution of (+)bis[(S)-2-methylbutyl]magnesium (50 ml of 0.26 *M*) were heated for 10 h at 103 ± 2°. The mixture was cooled, carbonated and (+)(S)-3-methylpentanoic acid [n_D^{25} 1.4143, $[\alpha]_D^{25}$ +8.42°] was recovered (53% yield).

SUMMARY

The chemical reactivity of organometallic compounds containing a tertiary carbon atom in the β position with respect to the metal atom, was studied by investigation of the thermal racemization of some organometallic compounds of Li, Mg, Be, Zn, Cd, B and Al containing optically active alkyl groups. At a temperature of 100° only the 2-methylbutyl derivatives of Be, B and Al racemize at an appreciable rate. When the asymmetric carbon atom is in the γ or δ position with respect to the metal atom, no racemization was observed. The influence of solvents on the optical activity decay rate and a reasonable mechanism of the thermal racemization of the investigated organometallic compounds are discussed.

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