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# ALKYL EXCHANGE REACTIONS IN THE SYNTHESIS OF OPTICALLY ACTIVE TRIALKYLALUMINIUM COMPOUNDS

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## SUMMARY

Alkyl exchange reactions between optically active organometallic compounds of Group II and III elements, containing an asymmetric carbon atom in the $\beta$ position with respect to the metal atom, have been investigated, and the results show that no significant racemization takes place. In the light of this, the syntheses of several optically active trialkylaluminium compounds have been carried out by treating the appropriate alkylboron compound with triethylaluminium. The minimum optical purity of the prepared $AlR_3^*$ has been evaluated, and this confirms that this method provides a satisfactory method of preparing optically active organometallic compounds.

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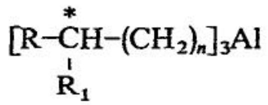
## INTRODUCTION

Exchange reactions between organometallic compounds of non-transition elements have been much studied in respect of the mechanistic pathways involved[1-8] and of the synthetic applications[9-13]. The reactions offer a convenient route to organometallic compounds not otherwise available; for instance, organo-lithium[14-16], -zinc[17] and -cadmium[18] compounds containing certain alkyl groups and also optically active lithium[19,20] and magnesium[20] derivatives have been prepared in this way.

In connection with our studies on the alkyl group redistribution between metal centres, we have carried out investigations of (*i*) the stereospecificity of the exchange reactions using optically active organometallic compounds of Group II and III elements, and (*ii*) the application of these reactions to the synthesis of optically active organoaluminium compounds (I).



$$[R-\overset{*}{\underset{R_1}{CH}}-(CH_2)_n]_3Al \qquad (I)$$

$R$ = Me, Et, i-Pr
$R_1$ = Et, Ph
$n$ = 1, 2, 3, ...

Until now, optically active aluminium trialkyls containing an asymmetric carbon atom in the β position with respect to the metal atom, have been prepared by treating the appropriate alkyllithium compounds with aluminium halides[21], or organomercury compounds with metallic aluminium[22,23]: in the latter case however, much racemization (60–70%) occurs. It seems likely to us that a more reliable and more general procedure for the synthesis of optically active aluminium trialkyls could be based on the exchange reaction.

## EXPERIMENTAL

### *Materials*

(+)-Bis[(*R*)-2-methylbutyl]beryllium[24], (+)-bis[(*S*)-2-methylbutyl]zinc[25], (+)-tris[(*R*)-2-methylbutyl]boron[26] and (+)-tris[(*S*)-2-methylbutyl]aluminium[21] were prepared as previously described. $Be(i\text{-}Bu)_2$, $Zn(i\text{-}Bu)_2$ and $B(i\text{-}Bu)_3$ were prepared by similar procedures. $Al(i\text{-}Bu)_3$ (Texas Alkyls Inc.) and $AlEt_3$ (Montedison S.p.A.) were obtained by purifying the commercial products. Distillations and handling of the organometallic compounds were carried out under dry, purified nitrogen. Benzene, purified by treatment with $H_2SO_4$, was heated over, and distilled from, metallic sodium and then stored under nitrogen.

### *Exchange reactions between organometallic compounds*

In order to determine the optical purity of the optically active organometallic compounds, these were distilled into a polarimeter tube (0.5 dm length) before use.

Benzene solutions of the organometallic compounds were prepared in 10 ml volumetric flasks: the solutions were then introduced by glass syringes into a polarimeter tube (2 dm length) fitted with a T-tube, so that a stream of purified nitrogen could be maintained.

Optical rotations were determined at 25°±0.1 with a Schmidt–Haensch polarimeter (sensitivity ±0.005°).

### *Preparation of optically active organoaluminium compounds by the exchange reaction*

*(+)-Tris[(S)-2-methylbutyl]aluminium.* To 0.1 mole of (+)-tris[(*R*)-2-methylbutyl]boron[26] ($[\alpha]_D^{20}$ +40.93°) in a distillation apparatus were added 12.0 g of $AlEt_3$. The mixture was stirred for 2 h and the $BEt_3$ was removed as it was formed during 24 h at reduced pressure (0.5 mmHg). The residue on distillation gave 18.0 g (75% yield) of (+)-tris[(*S*)-2-methylbutyl]aluminium, b.p. 54–55° (0.03 mmHg), $[\alpha]_D^{25}$ +28.20°. (Found: Al, 11.20, mol.wt. (cryoscop. in benzene), 243. $C_{15}H_{33}Al$ calcd.: Al, 11.22%; mol.wt., 240.4.)

In a second experiment, [from (+)-tris[(*R*)-2-methylbutyl]boron (0.1 mole), $[\alpha]_D^{20}$ +37.64°] (+)-tris[(*S*)-2-methylbutyl]aluminium ($[\alpha]_D^{25}$ +27.87°) was isolated in 87% yield by molecular distillation of the reaction residue at 0.03 mmHg (oil bath temperature ca. 40°).

*(+)-Tris[(S)-4-methylhexyl]aluminium.* To 0.031 moles of (+)-tris[(*S*)-4-methylhexyl]boron[27] ($[\alpha]_D^{25}$ +15.88°) [from (+)(*S*)-1-chloro-4-methylhexane[28] $[\alpha]_D^{25}$ +10.57°], were added 3.64 g of $AlEt_3$. The mixture was stirred for 20 h at reduced pressure (0.5 mmHg) to remove the $BEt_3$. Molecular distillation of the residue at $4\text{–}6 \times 10^{-5}$ mmHg (oil bath temperature 110°) yielded 7.65 g (76%) of (+)-tris-[(*S*)-4-methylhexyl]aluminium, $d_4^{25}$ 0.998, $[\alpha]_D^{25}$ +19.58°. (Found: Al, 8.30; mol.wt.

(cryoscop. in benzene), 650. $C_{21}H_{45}Al$ calcd.: Al, 8.31%; mol.wt., 324.5.)

Hydrolysis of 1.62 g of the aluminium trialkyl gave (+)(*S*)-3-methylhexane[29], b.p. 91°, $n_D^{25}$ 1.3891, $[\alpha]_D^{25}$ +9.47°, 71% yield.

(+)-*Tris[(S)-2-phenylbutyl]aluminium.* This was prepared according to the above procedure by treating 0.032 moles of (+)-tris[(*S*)-2-phenylbutyl]boron[30] ($[\alpha]_D^{25}$ +46.77°) with 4.02 g of $AlEt_3$. After removal of $BEt_3$, molecular distillation of the residue at $4–6 \times 10^{-5}$ mmHg (oil bath temperature 140°), gave 10.0 g (73% yield) of (+)-tris[(*S*)-2-phenylbutyl]aluminium, $d_4^{25}$ 0.986, $[\alpha]_D^{25}$ +4.93°. (Found: Al, 6.31; mol.wt. cryoscop. (in benzene), 433. $C_{30}H_{32}Al$ calcd.: Al, 6.32%; mol.wt., 426.5.)

Hydrolysis of a sample of the compound (0.76 g) gave (+)(*S*)-2-phenylbutane[30], $[\alpha]_D^{25}$ +23.11° ($c$=1.622 g/100 ml, n-hexane) (71% yield).

(+)-*Tris[(S)-2-phenyl-3-methylbutyl]aluminium.* To 0.044 moles of (+)-tris-[(*S*)-2-phenyl-3-methylbutyl]boron[30] ($[\alpha]_D^{25}$ +58.73°) ($c$=3.022 g/100 ml, toluene) were added 5.9 g of $AlEt_3$. $BEt_3$ was removed at reduced pressure (0.5 mmHg). Molecular distillation of the residue at $4–6 \times 10^{-5}$ mmHg (oil bath temperature 170°) gave 15.1 g (73% yield) of (+)-tris[(*S*)-2-phenyl-3-methylbutyl]aluminium, $[\alpha]_D^{25}$ +42.11° ($c$=1.401 g/100 ml, toluene). (Found: Al, 5.74; mol.wt. (cryoscop. in benzene), 470. $C_{33}H_{45}Al$ calcd.: Al, 5.75%; mol.wt., 468.6.)

Hydrolysis of the compound (3.0 g) gave 89% of (+)(*S*)-2-phenyl-3-methylbutane[31], $[\alpha]_D^{25}$ +25.26°.

## RESULTS AND DISCUSSION

### *A*

The stereospecificity of the exchange reactions between organometallic compounds of Group II and III elements containing a tertiary carbon atom in the $\beta$ position with respect to the metal atom was investigated by measuring the optical rotations of $MR_n^*/M'R_m$ organometallic systems in benzene. Table 1 presents our experimental data and the rotations calculated on the basis of the following hypotheses:

(*a*). The optical activity of the species $MR_n^*$, $MRR_{n-1}^*$, $MR_2R_{n-2}^*$, ... in the mixture is proportional to the number of metal-borne R* groups and is dependent only on the nature of metal M[*],

(*b*). The alkyl groups are statistically distributed between the metal centres present.

The results of Expt. No. 3 (Table 1), which refers to the (*S*)-2-methylbutyl zinc/aluminium system[32], provide a significant test of these assumptions. Within the accuracy limits of the method adopted, the results indicate that there is a high stereospecificity in the reactions investigated. The small differences between experimental and calculated values (0.0–4.7%) can be attributed to the fact that there is some departure from additivity of the optical rotations of the single species in solution, and/or to the existence of a small deviation from the statistical distribution of the alkyl groups which would be explicable in terms of hybridization changes, non-bonding interactions, etc.[1,5,10]. The transfer of an (*S*)-2-methylbutyl group from one metal

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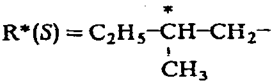
[*] The optical activity of $Al(i\text{-}Bu)_3/AlR_3^* \cdot Et_2O$ mixtures is in fact proportional to the number of (*S*)-2-methylbutyl groups present in the optically active species (unpublished results).

TABLE 1

OPTICAL ROTATIONS OF BENZENE SOLUTIONS OF GROUP I AND II ORGANOMETALLIC SYSTEMS AT ROOM TEMPERATURE:

$m\,R^*_n M + n\,R_m M' \rightleftarrows m\,R_m M + n\,R^*_m M'$



$R^*(S) = C_2H_5\text{-}\overset{*}{C}H(CH_3)\text{-}CH_2\text{-}$

| Expt. | $R^*_n M$ | | | $R_m M'$ | | | | $\alpha_D^{25}$ ($l=2$) | |
|---|---|---|---|---|---|---|---|---|---|
| | M | O.p. (%) | Concn. (mmoles) | R | M' | O.p. (%) | Concn. (mmoles) | Found | Calcd.[a] |
| 1 | Zn | 96.0 | 36.5 | i-Bu | Be | | 32.1 | +2.51°±0.01 | +2.60°±0.01 |
| 2 | | 96.1 | 23.9 | i-Bu | B | | 20.6 | +1.79°±0.01 | +1.85°±0.03 |
| 3 | | 97.0 | 192.2 | R* | Al | 84.6 | 188.2 | +8.65°±0.01[b] | +8.65°±0.01[b,c] |
| 4 | B | 93.8 | 17.9 | i-Bu | Zn | | 33.3 | +1.83°±0.01 | +1.84°±0.04 |
| 5 | | 93.7 | 17.9 | i-Bu | Al | | 21.7 | +2.58°±0.01[d] | +2.57°±0.01 |
| 6 | Al | 84.6 | 34.7 | i-Bu | Zn | | 36.0 | +3.34°±0.01 | +3.19°±0.01 |

[a] The following rotations were assumed: for the optically pure beryllium, zinc, boron and aluminium derivatives: $[\alpha]_{D\,\max}^{25}$ (benzene), +38.5° ($c=4.211$ g/100 ml), +9.1–10.0° ($c=2.105$–$3.905$ g/100 ml), +38.2° ($c=1.792$ g/100 ml) and +29.4° ($c=3.736$ g/100 ml) respectively (ref. 32). [b] $l=0.5$ dm, neat. [c] By assuming rotations for the optically pure zinc and aluminium compounds of $[\alpha]_{D\,\max}^{25}$ (neat) +10.20° (ref. 25) and +33.71° (ref. 27), respectively. [d] After heating at 40° for 5 h.

centre to another thus takes place without significant racemization, in accordance with previous observations for the tris[(*S*)-2-methylbutyl]aluminium etherate/triisobutylaluminium system[33].

## B

In view of the above result, we carried out the synthesis of some optically active trialkylaluminium compounds, (I), via exchange between the appropriate trialkylboron and $AlEt_3$: a similar procedure has previously been used for the preparation of tris[(*S*)-3-methylpentyl]aluminium (50% yield)[27].

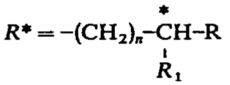
The yields and the optical purities of the trialkylaluminium compounds prepared are listed in Table 2, and it will be seen that the compounds were obtained in good yields, with negligible racemization.

With (+)-tris[(*S*)-2-methylbutyl]aluminium the extent of the slight racemization depends mainly on the method used for purification (Table 2), which is not surprising since this compound is known to undergo a fairly fast thermal racemization involving reversible formation of the dialkylaluminium monohydride and the olefin[24]. The absence of racemization in the synthesis and in the purification of tris[(*S*)-4-methylhexyl]aluminium is consistent with this explanation[24]. It is noteworthy that when a phenyl group is present on the asymmetric carbon atom of (I), the optically active aluminium compounds have higher thermal stability than the (*S*)-2-methylbutyl derivatives, at least under the conditions of purification we have used (Table 2). Even though the degree of racemization in the synthesis of (+)-tris[(*S*)-2-methylbutyl]aluminium is comparable with that encountered in the preparation from the alkyllithium[21], the present method has the advantage of simplicity and, therefore, higher yields. Furthermore, the use of optically active reagents such as trialkylboron

TABLE 2

YIELDS AND DEGREE OF RACEMIZATION IN THE SYNTHESIS OF ALKYL ALUMINIUM COMPOUNDS BY EXCHANGE REACTIONS:

$BR_3^* + AlEt_3 \rightarrow BEt_3 + AlR_3^*$



$R^* = -(CH_2)_n-\overset{*}{\underset{R_1}{CH}}-R$

| R | $R_1$ | n | $BR_3^*$ O.p. (%) | $AlR_3^*$ $[\alpha]_D^{25}$ (°) | O.p. (%) | Yield (%) | Racemization (%) |
|---|---|---|---|---|---|---|---|
| Me | Et | 1 | 96.7 | +28.20 | 83.6 | 75 | 13.5 |
| | | | 88.9 | +27.87[a] | 82.7[a] | 87[a] | 7.0[a] |
| Me | Et | 3 | 95.6 | +19.58[a] | 95.6[a,b] | 76[a] | 0.0[a] |
| Et | Ph | 1 | 95.0 | +5.07[a] | 94.6[a,c] | 73[a] | 0.4[a] |
| i-Pr | Ph | 1 | 90.0 | +42.11[a,d] | 89.5[a,c] | 73[a] | 0.6[a] |

[a] Recovered by molecular distillation. [b] By hydrolysis to (*S*)-3-methylhexane. [c] By hydrolysis to the corresponding optically active phenylalkanes. [d] $c = 1.401$ g/100 ml, toluene.

compounds appears to be especially effective in the synthesis of phenylalkylaluminium derivatives.

Since the optically active organoaluminium compounds (I) in the other cases studied had practically the same optical purities as the starting alkylboron compounds (Table 2), we can conclude that the actual transfer of (*S*)-2-methylbutyl groups between different metal centres (Table 1) also occurs stereospecifically. The results are consistent with the mechanistic pathways ("four-center transition state")[6], generally assumed for such reactions.

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