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ADDITION REACTIONS OF METHYLALUMINOXANE ETHERATES TO 4-t-BUTYLCYCLOHEXANONE

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Summary

The reactions of methylaluminoxanes with 4-t-butylcyclohexanone have been studied. The methylaluminoxane etherates were found to methylate the ketone, however, with a lower yield than the trimethylaluminium etherate. 35—40% of the methylation products with aluminoxanes result from axial attack. No addition of the aluminoxane Al—O bond to the carbonyl group was observed.

On the basis of the ^{18}O isotopic effect in IR, the assignment of the absorption band at 800 cm^{-1} to the Al—O—Al grouping in aluminoxanes was confirmed.

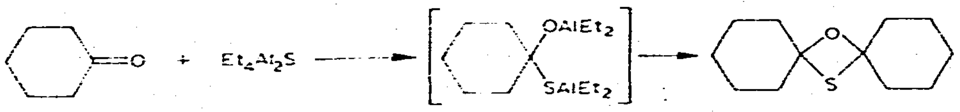
Introduction

Methylaluminoxanes $Me_nCl_{4-n}Al_2O$ ($n = 4, 3, 2$), similarly to the starting methylaluminium compounds Me_nAlCl_{3-n} ($n = 3, 2$), form donor—acceptor complexes with electron donors [1—3]. The stoichiometry and structure of the complexes formed depend on the acidity of the aluminium atoms, the basicity of the oxygen atom of the aluminoxane and on the electron donor used. Methylaluminoxanes are stronger Lewis acids as compared with the methylaluminium compounds used as their starting materials [2].

Aluminoxanes are catalysts of the stereoregular polymerization of polar monomers [4], and also active catalytic components in the polymerization of olefins.

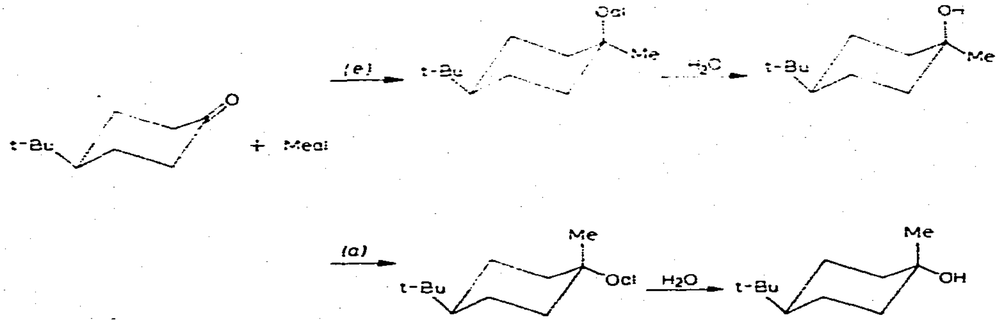
We hope that the studies undertaken on the structure and reactions of aluminoxane complexes with electron donors will lead to a better knowledge of the nature of these catalysts and the mechanism of catalysis.

The purpose of the present work was to study the paths of the methylaluminoxane's reactions with ketone. Until now, only the reactions of the sulphuric analogue of the aluminoxane Et_4Al_2S with electron donors containing a carbonyl group (ketones, esters, lactones) have been studied [5]. These reactions proceeded mainly with cleavage of the Al—S bond and resulted in the formation of respective thiocarbonyl compounds (eq. 1). Neither alkylation nor reduction products were observed.



(1)

4-t-Butylcyclohexanone was used for studies on the reactions of methylaluminoxanes ether complexes with ketone. The application of this ketone allowed the stereochemistry of the methylation to be determined. The t-butyl substituent causes a fixation of the chair conformation of the cyclohexanone ring in which the t-butyl group is in the equatorial position. During alkylation the attack on the carbonyl carbon atom can proceed from the equatorial side of the ring (2, *e*), or from the non-equivalent axial side (2, *a*), which give after hydrolysis an axial or equatorial alcohol, respectively (eq. 2).



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The stereochemistry of trimethylaluminium alkylation of 4-t-butylcyclohexanone was studied extensively by Ashby et al. [6]. The stereoselective activity of tetraisobutylaluminoxane was recently found in the heterolysis of some phosphorus esters [7].

Results and discussion

Ether complexes of tetramethyl-, trimethylchloro- and dimethyldichloroaluminoxanes were found to methylate 4-t-butylcyclohexanone. In reactions of 4-t-butylcyclohexanone with methylaluminoxanes and consecutive hydrolysis, mixtures of stereoisomeric 4-t-butyl-1-methylcyclohexanols are formed (eq. 3). Analogous products are formed from the reaction of the above ketone with the trimethylaluminium etherate.

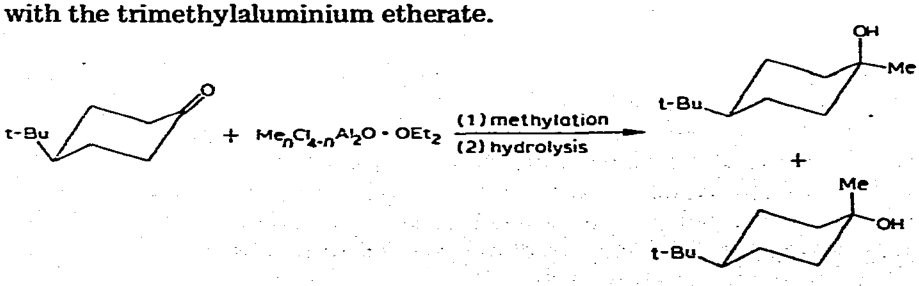

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TABLE 1

METHYLATION OF 4-t-BUTYLCYCLOHEXANONE WITH METHYLALUMINIUM COMPOUNDS

Exp. No.	Methylaluminium compound	Solvent	Mol ratio [b] OAC/ ketone	Reaction time (h)	Yield (%)	Axial alcohol [a] (%)	Equatorial alcohol [a] (%)
1	$Me_3Al \cdot OEt_2$	Ethyl ether	1.0	3	45	76	24
2	$Me_4Al_2O \cdot OEt_2$	Ethyl ether	1.0	3	25	65	35
3	$Me_3ClAl_2O \cdot OEt_2$	Ethyl ether	1.0	3	13	60	40
4	$Me_2Cl_2Al_2O \cdot OEt_2$	Ethyl ether	1.0	3	3	more	less
5	$Me_4Al_2O \cdot OEt_2$	Benzene	1.0	3	39	64	36
6	$Me_3Al \cdot OEt_2$	Benzene	3.0	19	67	74	26
7	$Me_4Al_2O \cdot OEt_2$	Benzene	3.0	19	65	65	35
8	$Me_3ClAl_2O \cdot OEt_2$	Benzene	3.0	19	57	58	42
9	$Me_2Cl_2Al_2O \cdot OEt_2$	Benzene	3.0	19	31	[c]	[c]
10	$Me_4Al_2O \cdot OEt_2$	Benzene	3.0	112	68	65	35
11	$Me_4Al_2O \cdot OEt_2$	Ethyl ether	3.0	19	35	65	35
12	$Me_4Al_2O \cdot OEt_2$ [d]	Benzene	3.0	12	58	65	35

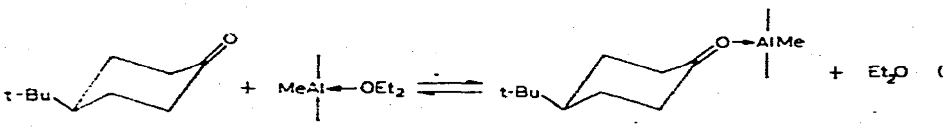
[a] Normalized as percent of axial alcohol + percent of equatorial alcohol 100. [b] Initial concentration of methylaluminium compound ca. 0.3 M. [c] Underwent dehydration during hydrolysis. [d] Aluminoxane enriched with ^{18}O.

The results of the methylation reactions are presented in Table 1.

If the methylation was carried out in benzene for 19 h, at 45°C and with an excess of the methylating agent (mol ratio 3/1) the ketone conversion was 65% for $Me_4Al_2O \cdot OEt_2$, 57% for $Me_3ClAl_2O \cdot OEt_2$, and 31% for $Me_2Cl_2Al_2O \cdot OEt_2$. In the same conditions $Me_3Al \cdot OEt_2$ methylated ketone with a yield of 67%. From the data presented it appears that the methylation ability of the studied organoaluminium compounds decreases in the order: $Me_3Al \cdot OEt_2 > Me_4Al_2O \cdot OEt_2 > Me_3ClAl_2O \cdot OEt_2 > Me_2Cl_2Al_2O \cdot OEt_2$, i.e. the opposite order to that of increasing acidity of organoaluminium compounds.

This is in agreement with our previous results regarding the influence of Lewis acidity on alkylation reactions [8].

No considerable effect of prolonged reaction time on yield was observed (Table 1, exps. 7 and 10). The yield of methylation, however, depends on the type of solvent used (Table 1, exps. 2 and 5; 7 and 11). The application of diethyl ether instead of benzene caused a considerable decrease in the conversion of ketone. This undoubtedly is concerned with the donors exchange reaction (eq. 4). The equilibrium between the complexes is confirmed by the IR spectra of the reaction mixture of 4-t-butylcyclohexanone and trimethylchloroaluminoxane (1/3) in diethyl ether, which exhibit absorption bands at 1721 and 1658 cm^{-1}, corresponding to the free and complexed carbonyl groups.

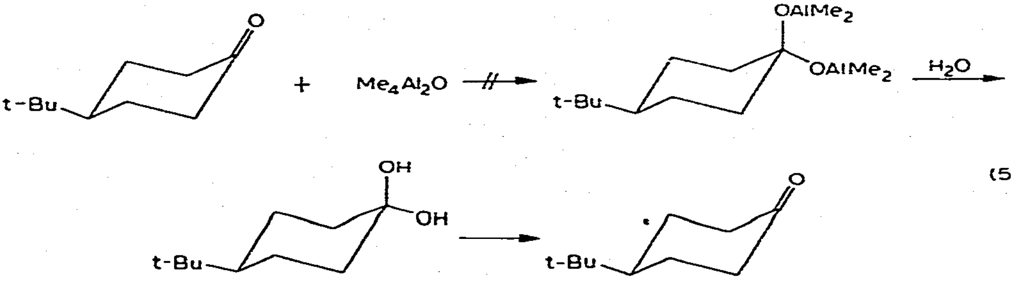


(4)

The data presented in Table 1 show that in the methylation of 4-t-butylcyclohexanone with methylaluminoxane ethereates an equatorial attack is favored and an axial alcohol is formed predominantly after hydrolysis. It is noteworthy that by using binuclear Lewis acids, as are aluminoxanes, the amount of the equatorial alcohol in the products increases, in comparison with the trimethylaluminium etherate products. This indicates that for aluminoxanes the sterically more hindered axial attack is relatively more favored. In the reaction with $Me_3Al \cdot OEt_2$ about 25% of equatorial alcohol is formed whereas with $Me_4Al_2O \cdot OEt_2$ it is 35% and with $Me_3ClAl_2O \cdot OEt_2$ 41%. The stereochemical results of the reaction of $Me_4Al_2O \cdot OEt_2$ with a ketone does not depend either on the molar ratio of the reactants or on the solvent (Table 1, exps 2, 5, 7), so it can be assumed that they depend on the structure of the aluminoxane molecule.

The structure of aluminoxane complexes and their stereochemical properties in reactions with electron donors continue to be the object of our interest.

According to the above-mentioned results [5] of the tetraethylaluminothiane reaction with donors possessing a carbonyl group (eq. 1) an analogous reaction could be expected for aluminoxane. This would involve the cleavage of the Al—O bond (eq. 5) resulting in the formation of an unstable hydrate of 4-t-butylcyclohexanone (4-t-butylcyclohexa-1,1-diol).



(5)

As it was impossible to observe directly the products of reaction 5, isotopic studies were undertaken. 4-t-Butylcyclohexanone, recovered from the products of the reaction with aluminoxane labelled with ^{18}O (Table 1, exp. 12), was studied by mass spectrometry (Table 2). The ^{18}O molar enrichment of the aluminoxane used was about 44%. Assuming a uniform distribution of the isotope between the alcohol, ketone and aluminoxane, as a result of the assumed complete reversibility of the methylation and addition reactions, the ^{18}O enrichment of the ketone isolated after hydrolysis should reach at least 16.5%. In the mass spectrum of the ketone the isotopic peak $P + 2$ should reach 19.8% of the molecular peak P. From data presented in Table 2 it appears that the use of

TABLE 2

ISOTOPIC PATTERNS OF THE PARENT MOLECULAR ION OF 4-t-BUTYLCYCLOHEXANONE RECOVERED AFTER METHYLATION $Me_4Al_2O \cdot OEt_2$ AND $Me_4Al_2{}^{18}O \cdot OEt_2$

$Me_4Al_2O \cdot OEt_2$		$Me_4Al_2{}^{18}O \cdot OEt_2$	
m/e	*P* (%)	*m/e*	*P* (%)
154 (*P*)	100.0	154 (*P*)	100.0
155 (*P* + 1)	16.3	155 (*P* + 1)	15.3
156 (*P* + 2)	3.8	156 (*P* + 2)	6.2

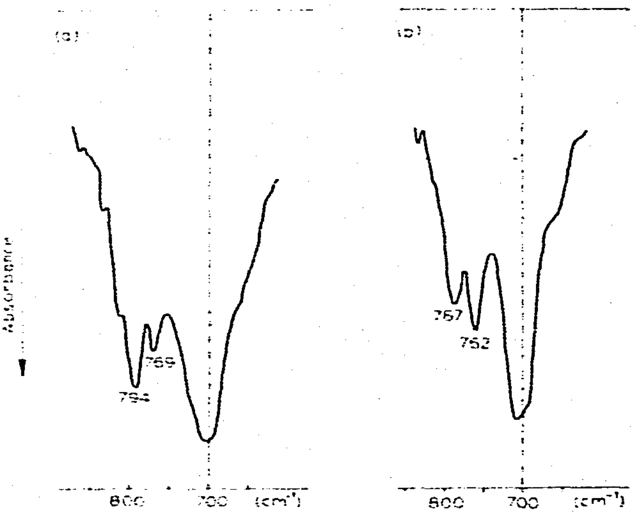


Fig. 1. Isotopic effect due to ^{18}O substitution in infrared spectra of (a) Me_4Al_2O etherate and (b) Me_4Al_2O isotopically enriched etherate.

$Me_2Al_2{}^{18}O \cdot OEt_2$ has practically no effect on the intensity of the ketone peak $P + 2$. Also in the mass spectra of 4-t-butyl-1-methylcyclohexanols obtained from the reactions of the ketone with the labelled and natural aluminoxanes no changes in intensity of the $P + 2$ peaks were observed (ca. 2.5% P). The results of isotopic studies and the yield of methylation suggest that the addition of an Al—Y bond to the carbonyl group, which does take place for sulphuric compounds (Y = S), practically does not occur in the case of oxygen derivatives (Y = O). This is in agreement with the higher stability of the Al—O bond in comparison with the Al—S bond, e.g. D(Al—O) 108 kcal mol^{-1} and D(Al—S) 82 kcal mol^{-1} [9].

The IR absorption of aluminoxanes has interested several authors [10—12]. From these works, and also from the correlation of the collected spectra it appeared that only the band at ca. 800 cm^{-1} could be assigned to the absorption of the Al—O—Al grouping, characteristic for this class of compounds. We confirmed correctness of this assignment by the observation of the isotopic effect in the IR spectra of both natural and ^{18}O labelled Me_4Al_2O etherates.

The recordings in the range 4000—400 cm^{-1} differ only in the region 800—750 cm^{-1}. The following differences between the spectra of natural (Fig. 1a) and labelled ^{18}O (molar enrichment ca. 44%, Fig. 1b) $Me_4Al_2O \cdot OEt_2$ occur: the band at 794 cm^{-1} in spectrum a is shifted to 787 cm^{-1} in spectrum b (this band is widened and its intensity decreased); the shape of the band at 787 cm^{-1} in spectrum b indicates an isotopic splitting. Position of component bands: 791 and 784 cm^{-1}; and the band at 769 cm^{-1} in spectrum a is shifted to 762 cm^{-1} in spectrum b, its intensity is not changed.

The observed isotopic effect shows that the absorption band at 794 cm^{-1} in the IR spectrum of aluminoxane derives from the stretching vibrations of the Al—O—Al grouping. Lynch et al. [13] performed IR measurements of matrixisolated Al_2O species and ^{18}O-enriched samples. For the stretching frequencies of Al_4O_2 the value of the ^{18}O isotopic effect ν/ν' is 1.021. For the dimeric $Me_4Al_2O \cdot OEt_2$ the value ν/ν' is 1.015.

The band at 769 cm^{-1} corresponds to the rocking vibrations of CH_2 groups of the ether [14]. The shift of the ether band can be explained by a different interference with it of the Al—O—Al band in spectra a and b.

Experimental

All operations were carried out under purified nitrogen.

Trimethylaluminium (b.p. 125—127°C) and dimethylaluminium chloride (b.p. 119—120°C) were distilled before use through the glass helix packed column.

Benzene and diethyl ether (P.O.Ch. Gliwice) were distilled over CaH_2 and then over potassium ketyl of benzophenone.

4-t-Butylcyclohexanone (Chemipan) was sublimed prior to use. Water, enriched with ^{18}O (molar enrichment 43.6%) supplied by OPDI-Swierk was used without purification, and tap water was redistilled.

Preparation of ether complexes of trimethylchloroaluminoxane and dimethyldichloroaluminoxane was described earlier, in refs. 15 and 1, respectively.

$Me_4Al_2O \cdot OEt_2$ was obtained from a partial hydrolysis of trimethylaluminium. 7.76 g of Me_3Al (108 mmol) was introduced into 30 cm^3 of cooled diethyl ether followed by 0.97 g of H_2O (54 mmol) dissolved in 120 cm^3 of diethyl ether, at —20°C with vigorously stirring. After introducing the water solution during 1 h, the reaction mixture was slowly heated to room temperature and then to the boiling point. The hydrolysis was completed when a stoichiometric amount of methane was evolved (ca. 2300 cm^3).

The solvent was distilled off under reduced pressure and the non-voltatile product was conditioned under 10^{-4} Torr at room temperature for 24 h, 10.4 g of product was obtained. Analysis: Found: Al, 26.2; Me (hydrolyzable), 30.4; mol. wt. 389 g mol^{-1}. $C_8H_{22}Al_2O_2$ calcd.: Al, 26.4; Me, 29.4%; mol. wt. 204 g mol^{-1}. In the IR spectrum of the cyclohexane solution of the product, the following main absorption bands were observed: 2979m, 1465w, 1390w, 1254w, 1203s, 1149w, 1123w, 1090m, 1033s, 996m, 895m, 833m sh, 794vs (Al—O—Al), 769s, 710vs, 520w.

The reactions of methylaluminium compounds with the ketone and the GLC analysis of the products were carried out according to the procedure described by Ashby et al. [6].

After hydrolysis the presence of 4-t-butyl-1-methylcyclohexenes was found among the products of some reactions, particularly for chloro derivatives of organoaluminium compounds. These compounds probably result from the dehydration of 4-t-butyl-1-methylcyclohexanol stereoisomers. The non-equivalent tendency of the axial and equatorial isomers towards dehydration may cause changes in the molar ratio of methylation products. No dehydration products were observed in the reactions discussed (Table 1).

Mass spectra were recorded on a Dupont 21-492 B apparatus connected with GLC, using an ionizing voltage of 70 V. IR spectra were recorded by means of a Perkin—Elmer 527 apparatus using KBr cells of 0.1 mm length.

References

1 M. Bolesławski, S. Pasynkiewicz, A. Minorska and W. Hryniów, J. Organometal. Chem., 65 (1974) 165.
2 S. Pasynkiewicz, M. Bolesławski and A. Sadownik, J. Organometal. Chem., 113 (1975) 303.
3 M. Bolesławski, S. Pasynkiewicz, A. Sadownik and H. Szachnowska, in preparation.
4 T. Araki, T. Aoyagi, N. Ueyama, T. Aoyama and H. Tani, J. Polym. Sci., 11 (1973) 699 and refs. therein.
5 H. Imaeda, Z. Hirabayashi, K. Itoh and Y. Ishii, Organometal. Chem. Syn., 1 (1970, 1971) 115.
6 J. Leammle, E.C. Ashby and P.V. Rolling, J. Org. Chem., 38 (1973) 2526.
7 Y. Kitabawa, S. Hashimoto, S. Iemura, H. Yamamoto and H. Nozaki, J. Amer. Chem. Soc., 98 (1976) 5030.
8 S. Pasynkiewicz and W. Arabas, Roczniki Chem., 39 (1965) 1393.
9 A.G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, 3rd. ed., Chapman and Hall, London, 1968.
10 A. Storr, K. Jones and A.W. Laubengayer, J. Amer. Chem. Soc., 90 (1968) 3173.
11 G.B. Sacharowskaja, N.N. Kornieyev, A.F. Popov, Yu.W. Kissin, S.M. Miezhikovskij and E.W. Kristalnyi, Zh. Obshch. Khim., 39 (1969) 788.
12 N. Ueyama, T. Araki and H. Tani, Inorg. Chem., 12 (1973) 2218.
13 D.A. Lynch, M.J. Zehe and K.D. Carlson, J. Phys. Chem., 78 (1974) 1567.
14 S. Takeda and R. Tarao, Bull. Chem. Soc. Jap., 38 (1965) 1567.
15 M. Bolesławski, S. Pasynkiewicz, K. Jaworski and A. Sadownik, J. Organometal. Chem., 97 (1975) 15.