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Reactions of trimethylaluminium with *cis*-2-buten-1,4-diol

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Abstract

The reaction of trimethylaluminium with *cis*-2-buten-1,4-diol was studied. The complex $[AlMe][OCH_2CH{=}CHCH_2O]_2[AlMe_2]_2$ (**1**) was formed. The structure of **1** was determined by means of ^1H, ^{13}C, ^{27}Al NMR, elemental analysis and molecular weight measurements. It appears from our current and previous studies that trimethylaluminium reacts with 2-buten-1,4-diol derivatives, independently of their structure, to form complexes possessing one five- and two four-coordinated aluminium atoms.

Key words: Aluminium

1. Introduction

We have previously studied reactions of trimethylaluminium with 1,2-dihydroxymethylbenzene [1] and with 2-[methyl-bis(trimethylsiloxy)silyl[but-2-ene-1,4-diol [2]. The complexes formed have similar structures when the molar ratio of the reactants is 3:2. In these complexes a central five-coordinated aluminium atom is bonded to four oxygen atoms and to one methyl group; two four-coordinated aluminium atoms are bonded to two oxygen atoms and to two methyl groups. For the molar ratios of trimethylaluminium/diol = 1:1 and 2:3, dimers and/or higher associates, insoluble or sparingly soluble in organic solvents, are formed. Köster *et al.* [3] obtained the complex $[R_4Al_3B_4Hal_5O_6]$, which is similar in structure, by reacting aluminium trihalides $[AlHal_3]$ with triorganoboroxins $[RBO_3]$ at molar ratios of 3:2.

The purpose of this work was to study the reaction of trimethylaluminium with *cis*-2-buten-1,4-diol, to identify its products and to determine their structure.

2. Results and discussion

The reaction of *cis*-2-buten-1,4-diol with trimethylaluminium proceeds according to eqn. (1).

$$2HOCH_2(H)C{=}C(H)CH_2OH + 3AlMe_3 \longrightarrow \underset{\mathbf{1}}{[AlMe][OCH_2(H)C{=}C(H)CH_2O]_2[AlMe_2]_2} + 4MeH \qquad (1)$$

The structure of product **1** (Fig. 1) was determined by means of ^1H, ^{13}C, and ^{27}Al NMR. The ^1H spectrum (Fig. 2) prove that both hydroxy groups of diol reacted completely with $AlMe_3$. The ^1H NMR signals of diol, the doublet of $-CH_2$ at 4.11 ppm and the singlet of $-OH$ at 4.10 ppm, disappeared from the spectrum of the product **1**.

The structure of the olefinic ligand has been retained in the product **1**. The signals corresponding to

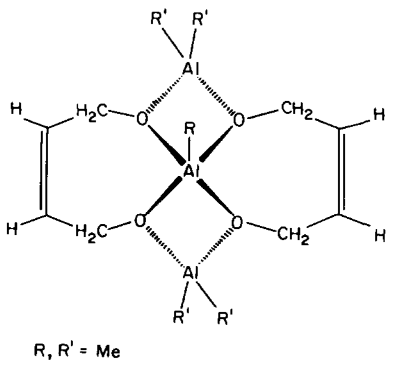

Fig. 1. Structure of complex **1**.

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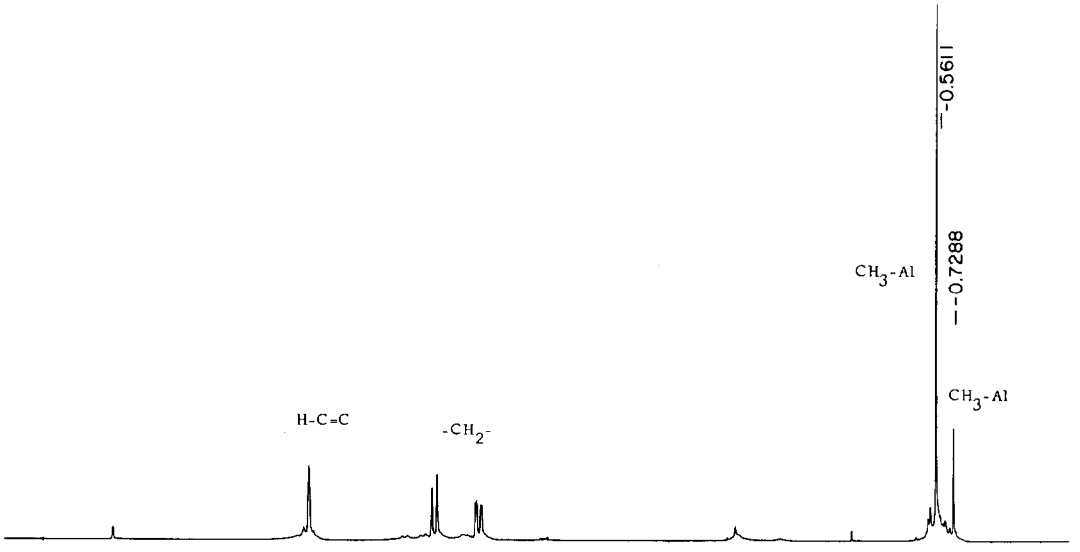


Fig. 2. ^{1}H NMR spectrum of the product 1, in C_6D_6 solution, standard C_6D_5H = 7.15 ppm.

=CH vinylic and $-CH_2-$ protons were observed with proper integration at 5.31 ppm (4H) and 4.2–3.7 ppm (8H) respectively (Fig. 2). Surprisingly, the doublet of doublets expected for $-CH_2-$ protons with hindered rotation (AB system) was split into the multiplet shown in Fig. 3. In order to simplify the spectrum, we have run the spectrum with irradiating frequency applied at 5.29 ppm. The typical doublet of doublets (Fig. 4) was obtained with δ_A = 4.08 ppm, δ_B = 3.67 ppm and J_{AB} = 13.1 Hz, similar to that described for $[1,2\text{-}C_6H_4(CH_2O)_2]_2Al_3Me_5$ isolated from the reaction of trimethylaluminium with 1,2-dihydroxymethylbenzene [1]. The ^{1}H NMR spectrum of $[1,2\text{-}C_6H_4(CH_2O)_2]_2\text{-}Al_3Me_5$ shows a typical doublet of doublets of CH_2 groups with δ_A = 4.57 ppm, δ_B = 4.30 ppm and J_{AB} = 12 Hz. The corresponding signals of the product **1** are shifted upfield in comparison to the corresponding signal for $[1,2\text{-}C_6H_4(CH_2O)_2]_2Al_3Me_5$, which is in agreement with the deshielding effect of an aromatic ring.

For the =CH and $-CH_2-$ signals a higher order of splitting was observed (Fig. 3) than that predicted from

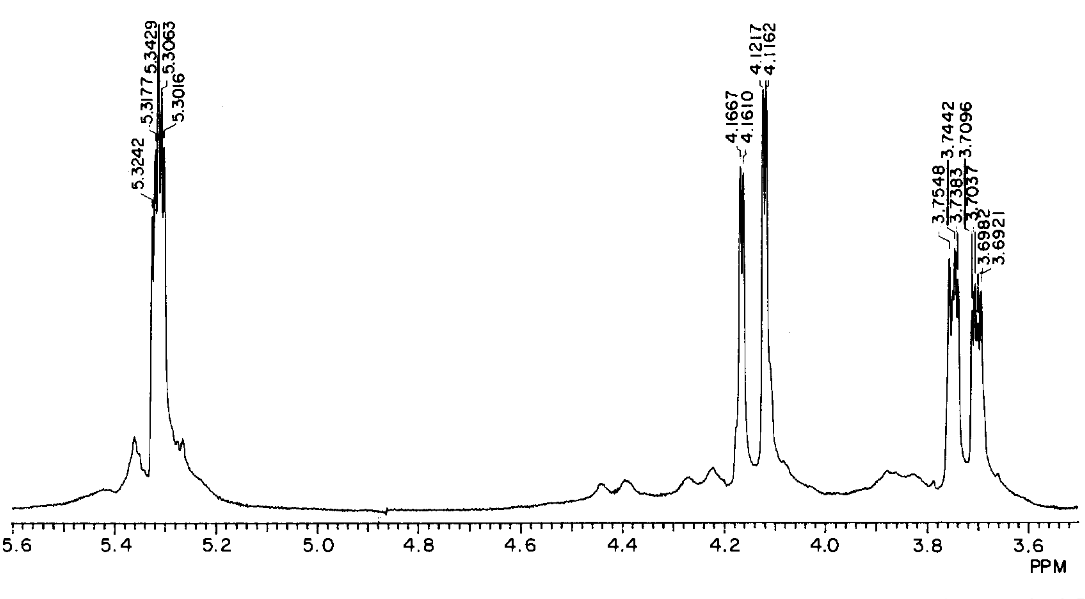


Fig. 3. ^{1}H NMR spectrum of the product 1, the signals of H–C=C and $-CH_2-$ groups, in C_6D_6 solution, standard C_6D_5H = 7.15 ppm.

the number of neighbouring protons. Most probably these protons in our compound should be considered as an ABX system.

At higher field two types of methyl groups bonded to aluminium were observed at -0.56 ppm (12H, 4 methyl groups) and at -0.73 ppm (3H, 1 methyl group) (Fig. 2). The integration of the signals shows that the molecule consists of 4 protons of the type HC=CH, 4 $-CH_2$ groups and 5 $-CH_3$ groups bonded to aluminium, one of which is decidedly different from the others.

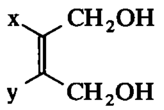
The ^{13}C NMR spectrum shows that the product is an individual compound. The olefinic part of the molecule is observed as a singlet at 130.41 ppm (C=C), and the singlet at 58.64 ppm ($-CH_2-$). The methyl groups bonded to aluminium were recorded at -12.10 ppm as a broad signal, due to a quadrupole effect.

In the ^{27}Al NMR spectrum two signals are present at 153.0 and 75.0 ppm indicating two coordination types on aluminium centres. These two signals correspond to four- and five-coordinated aluminium atoms respectively. The presence of two different types of aluminium centre is consistent with the expectation based on the above mentioned ^1H spectrum of methyl groups $Al-CH_3$. It can be stated, based on the ^1H and ^{27}Al NMR spectra, that one CH_3 group is bonded to a five-coordinated aluminium atom, and the remaining four CH_3 groups are bonded to two four-coordinated aluminium atoms.

The association degree of the product **1**, determined by the cryoscopic method in benzene, was 1.38, which is higher than 1 due to the presence of oligomeric aluminium compounds. These compounds were soluble in pentane and therefore hard to remove in the process of purification of the product. After evaporation of the solvent the product was obtained as fine, coalesced crystals. They were freely soluble in benzene, toluene, diethyl ether, pentane and methylene chloride. However, attempts failed to recrystallize them from the above solvents at low temperature (−20°C).

3. Conclusions

It appears from our studies [1,2 and present work] that trimethylaluminium reacts with 2-buten-1,4-diol derivatives of the general structure



where x = H, $SiMe(OSiMe_3)_2$; y = H; x,y = −C≡C−C≡C−

to form complexes possessing one five- and two four-coordinated aluminium atoms. For the molar ratio of reactants Me_3Al : diol = 3 : 2 the complexes are formed with high yield. The yield depends on steric hindrances of the diol. The more the diol is hindered the higher the yield of the complex.

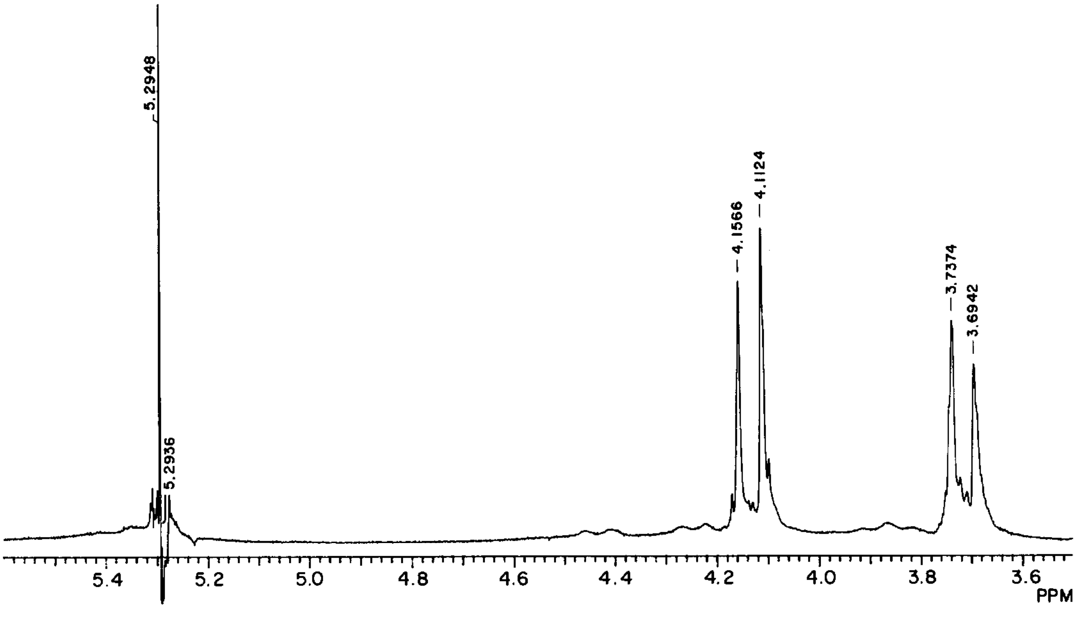
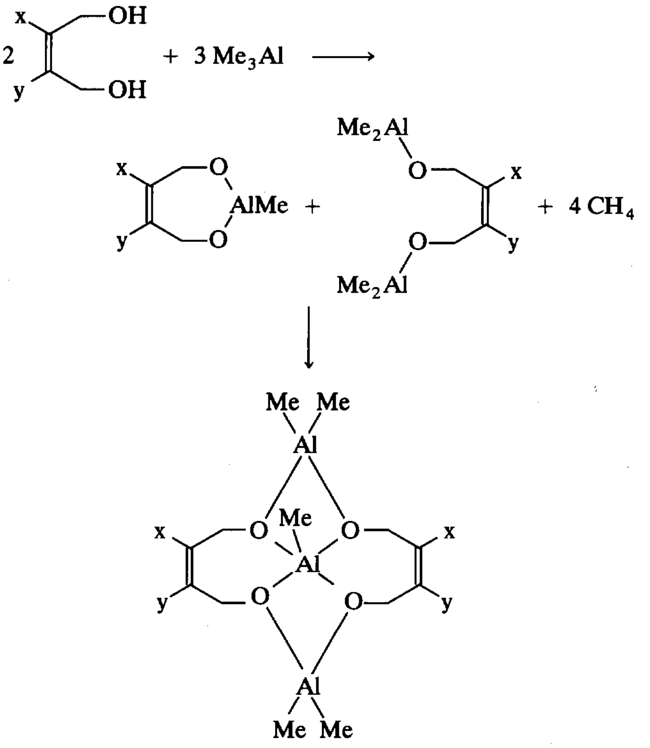


Fig. 4. ^1H NMR spectrum of the product **1**, the signals of $-CH_2-$ groups irradiated at 5.29 ppm in C_6D_6 solution, standard C_6D_5H = 7.15 ppm.

The general scheme of the reaction can be presented thus:



4. Experimental section

^1H NMR spectra were recorded with a Varian VXR 300 spectrometer, at 299.9 MHz, using acquisition time 3.74 s, flip angle 30° and spectral width 4000 Hz. Chemical shifts were referenced to the residual proton signal of C_6D_6 solvent (7.15 ppm). ^{13}C NMR spectra were run on the same instrument at 75.4 MHz. ^{27}Al spectra were run at 78.2 MHz, using acquisition time 0.079 s and spectral width 40000 Hz.

cis-2-Buten-1,4-diol (from Aldrich, 95% *cis*); ^1H NMR (acetone-d_6); δ 5.57 ppm (t, $J = 2.9$ Hz, 2H, H–C=C); δ 4.11 ppm (d, $J = 3.1$ Hz, 4H, CH_2); δ 4.10 ppm (s, 2H, OH); standard: acetone $C_2HD_5C{=}O = 2.04$ ppm. ^{13}C NMR (acetone-d_6); δ 131.45 ppm (C=C); δ 58.39 ppm (CH_2); δ 58.36 ppm (CH_2); standard: ^{13}C $CD_6C{=}O = 29.80$ ppm.

4.1. *The reaction of diol with $AlMe_3$ at 2:3 molar ratio*

A solution of 0.648 g (9 mmol) of $AlMe_3$ in 15 ml of diethyl ether was added drop by drop within 1 h to a vigorously stirred emulsion of 0.528 g (6 mmol) of *cis*-2-buten-1,4-diol in 20 ml of diethyl ether at −76°C. The reaction mixture was then allowed to warm to room temperature within 2 h. Gases already evolved slowly at −76°C, and faster during the warming. The mixture became turbid and white solid precipitated. Diethyl ether was evaporated and pentane was added to the solid residue. After vigorous stirring, the liquid was decanted from the precipitate. The residue was a white, amorphous solid insoluble in organic solvents. It was probably a mixture of polymeric organoaluminium compounds. Pentane was evaporated from the decanted solution. White solid (product **1**) was obtained (0.396 g, 40.2%). Attempts to recrystallize it from various organic solvents failed.

4.2. *NMR spectra*

^1H (C_6D_6): δ 5.31 ppm (q, $J = 1.7$ Hz, 2H, =CH); δ 4.17–3.69 ppm (m, 4H, $-CH_2-$) (Fig. 3); δ −0.56 (s, 12H, $Al-CH_3$); δ −0.73 (s, 3H, $Al-CH_3$); standard: benzene $C_6D_6H = 7.15$ ppm.

^{13}C (C_6D_6): δ 130.41 (C=C); δ 58.79 ($-CH_2-$); δ −12.10 (CH_3); standard: benzene ^{13}C $C_5D_6 = 128.00$ ppm.

^{27}Al (C_6D_6): δ 153.0; δ 75.0; standard: $Al(acac)_3 = 0.0$ ppm.

References

1 S. Pasynkiewicz and W. Ziemkowska, *J. Organomet. Chem.*, *423* (1992) 1.
2 S. Pasynkiewicz and W. Ziemkowska, *J. Organomet. Chem.*, *437* (1992) 99.
3 R. Köster, K. Angermund, J. Serwatowski and A. Sporzyński, *Chem. Ber.*, *119* (1986) 1301.