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Preliminary communication

PHENOXYALUMINIUM COMPOUNDS

IV*. SYNTHESES AND STRUCTURES OF MONOMERIC (2,6-DI-t-BUTYL-4-METHYLPHENOXY)ALUMINIUM COMPOUNDS

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Summary

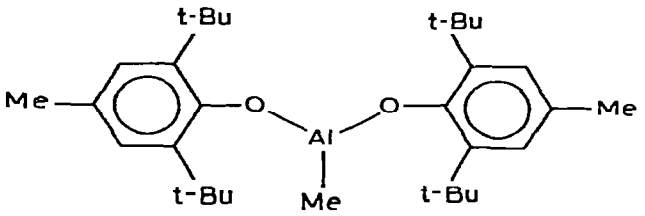
The preparations of monomeric dialkyl(2,6-di-t-butyl-4-methylphenoxy)-aluminium (alkyl = methyl, i-butyl) and i-butylbis(2,6-di-t-butyl-4-methylphenoxy)aluminium are described and their reactions, PMR and ESR spectra are reported.

It was stated that even strongly sterically hindered aluminium and beryllium compounds react with 2,6-dimethylphenoxy (DMP) substituents to form stable dimers e.g. $[Me_2Al(DMP)]_2$ [2] or $[CpBe(DMP)]_2$ [3].

We report here the preparation of $R_2Al(DBMP)$** (R = Me, i-Bu), compounds which we would expect to be monomeric in nature.

Reaction of 2 moles of 2,6-di-t-butyl-*p*-methylphenol with 1 mole of trimethylaluminium dimer was carried out in toluene and/or cyclopentane. The low temperature PMR spectrum indicated that in the reaction mixture trimethylaluminium was present together with another methyl-containing aluminium compound. After evaporation of solvent together with Me_3Al, and crystallization from cyclohexane, the product was obtained as colourless crystals. It was deduced from the evidence of the PMR spectrum and aluminium content (found: 5.4, calcd.: 5.63%) that compound I was obtained as a product of this reaction.

* For part III see ref. 1.
** DBMP = 2,6-di-t-butyl-4-methylphenoxy group.



(I)

Similarly, reaction of triisobutylaluminium with 2,6-di-t-butyl-*p*-methylphenol in the molar ratio 1/1 leads to the formation of i-Bu_2 Al(DBMP) (II). i-BuAl(DBMP)$_2$ (III) can be obtained on disproportionation of II at 110°C/10^{-4} mmHg, when i-Bu_3 Al is distilled off. III is also formed in the reaction of i-Bu_3 Al with 2,6-di-t-butyl-*p*-methylphenol in molar ratio 1/2.

All compounds studied were characterized by PMR spectra and aluminium content determinations. Their molecular weights, found cryoscopically in benzene, correspond closely with the values calculated for monomeric species of I, II and III.

Compounds I and III are very sensitive to oxygen. Even small amounts of air cause rapid darkening and formation of fairly stable free radicals. ESR spectra of free radicals obtained after introduction of oxygen to I or III are more complex than that of the 2,6-di-t-butyl-4-methylphenoxyl radical [4], which suggests the presence of an aluminium-containing radical.

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