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REACTIONS OF CUMYL AND t-BUTYL HYDROPEROXIDES WITH ALKYLALUMINIUM DICHLORIDE

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Summary

The reactions of cumyl hydroperoxide and t-butyl hydroperoxide with methyl- and ethylaluminium dichloride (1 : 1 molar ratio) in toluene, cyclopentadiene, diethyl ether, 1,2-dimethoxyethane and anisole have been studied. The final product of the reaction of methylaluminium dichloride with cumyl hydroperoxide is the 1 : 1 complex $PhOAlCl_2 \cdot O{=}C(CH_3)_2$ (I). In the reaction of methylaluminium dichloride with cumyl hydroperoxide in 1,2-dimethoxyethane (DME) the unstable aluminium peroxide $Ph(CH_3)_2COOAlCl_2$ is formed which rearranges to I.

In the reaction of alkylaluminium dichloride with t-butyl hydroperoxide the aluminium peroxide t-$BuOOAlCl_2$ is formed. A stabilizing effect of the donor solvent on the peroxide was found. This effect increases with the increase of the solvent's electron-donor ability in the order

$DME \geqslant Et_2O > PhOME > C_6H_5CH_3$

Introduction

Peroxidic compounds of the Main Group metals are intermediate products of oxidation of organometallic compounds [1,2]. The formation of peroxidic compounds of aluminium was also postulated in the oxidation of organoaluminium compounds [3—7]. The instability of these compounds is due to the high reactivity of the R—OO—Al group with respect to carbon—aluminium bonds, and alkoxyaluminium compounds are formed accordingly [3—7].

Only few peroxidic aluminium compounds have been isolated up to now. Razuvaev [8] obtained dimeric $PhMe_2COOAl(OEt)_2$ from the reaction of diethoxyaluminium chloride with the sodium salt of cumyl hydroperoxide. On the other hand, Anisimov [9] isolated monomeric peroxide compounds of formula $ROOAl(OEt)_2$, (R = cumyl, t-butyl) from the reaction of cumyl and t-butyl hydroperoxides with diethoxyaluminiumchloride in the presence of ammonia.

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Davies [7] established the formation of tris(decahydro-9-naphthylperoxy)-aluminium in the reaction of decahydro-9-naphthyl hydroperoxide with aluminium t-butoxide. Tris(decahydro-9-naphthylperoxy)aluminium decomposed partially when the solvent was removed.

The purpose of this work was to synthesise peroxidic aluminium compounds of formula $ROOAlCl_2$. The formation of these compounds was postulated in the oxidation of alkylaluminium dichloride with molecular oxygen [6].

Results and discussion

1. Reaction of cumyl hydroperoxide with methylaluminium dichloride

The reaction of cumyl hydroperoxide with methylaluminium dichloride (1 : 1 molar ratio) was carried out in toluene, cyclopentane and diethyl ether at temperatures shown in Table 1. Irrespective of the solvent used, one mole of methane evolved with respect to one mole of the hydroperoxide.

A white solid, not containing peroxidic oxygen, was obtained from the reaction. After hydrolysis, acetone and phenol were found as shown chromatographically. On the basis of GC, IR (ν(C=O) at 1675 cm^{-1}) and NMR (singlet at τ = 7.93 ppm) spectra and elemental analysis (Table 1), the product was identified as the 1 : 1 complex of phenoxyaluminium dichloride with acetone, $PhOAlCl_2 \cdot O{=}CMe_2$ (I). Its formation was also confirmed by comparison of its IR and NMR spectra with those of the complex (I) obtained in the reaction of $PhOAlCl_2$ with acetone.

In order to explain the course of the reaction of cumyl hydroperoxide with methylaluminium dichloride (1 : 1 molar ratio), low temperature NMR spectra of the reaction mixture in 1,2-dimethoxyethane were recorded (Fig. 1). The reaction was found to start at 0° C, the signal of methane protons appears (τ = 9.83 ppm) and the peaks of the CH_3—Al protons of methylaluminium dichloride complexed with DME (10.7—10.8 ppm) and of the —OOH proton (0.27 ppm) and —$(CH_3)_2C$— protons (8.51 ppm) of cumyl hydroperoxide diminish. At the same time, a new signal at 8.56 ppm appears (Fig. 1b). After keeping the reaction mixture at 0° C for about 1 h, no signals of methylaluminium dichloride or cumyl hydroperoxide are observed and only the signal at τ = 8.56 ppm is present. A rise of temperature above 10° C causes the appearance of three signals at 7.93, 7.98 and 8.07 ppm. Simultanously, the signal at 8.56 ppm disappears.

TABLE 1

ANALYTICAL DATA FOR THE PRODUCT OBTAINED IN THE REACTION OF CUMYL HYDROPEROXIDE WITH METHYLALUMINIUM DICHLORIDE (1 : 1 MOLAR RATIO) CARRIED OUT IN DIFFERENT SOLVENTS

Organo-aluminium compound	Solvent	Reaction temp. (°C)	Methane evolved (mol %)	Analysis Found (%) [a]	
				Al	Cl
$MeAlCl_2$	toluene	—70 to 10	90	12.0	28.0
	cyclopentane	—70 to 10	90	11.8	25.2
	Et_2O	—10 to 25	92	12.1	27.5

[a] Calcd. for $Ph(Me)_2COOAlCl_2$: Al, 10.84; Cl, 28.51%.

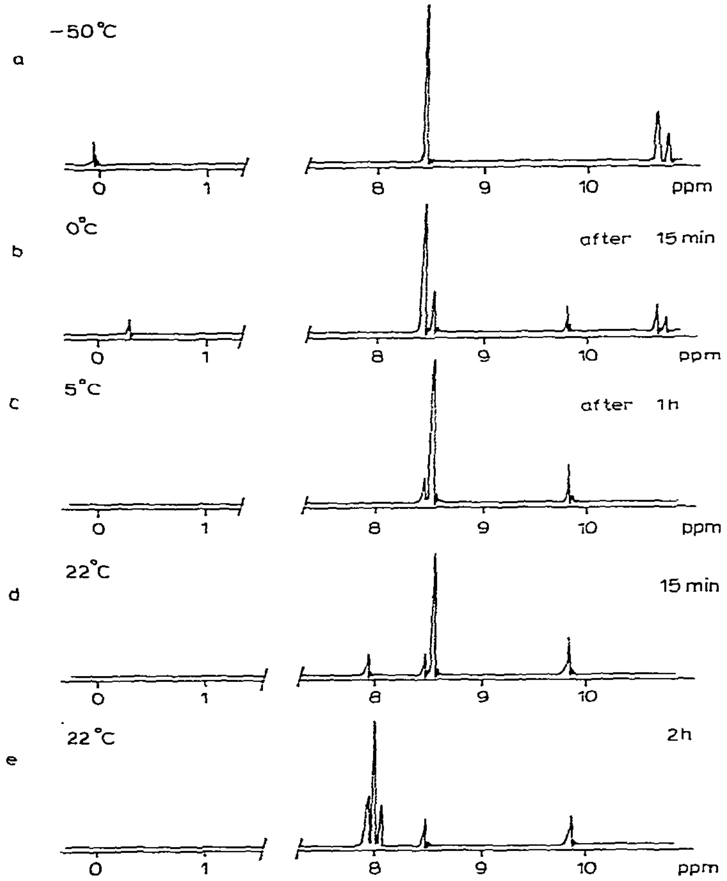
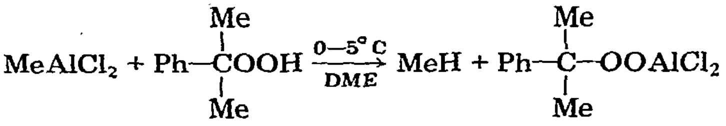


Fig. 1. The PMR spectra of the reaction $\mathrm{MeAlCl_2} : \mathrm{PhMe_2COOH} = 1 : 1$ carried out in NMR tube (dimethoxyethane solution). Assignments of the signals; τ: 10.7—10.8 ppm, $\mathrm{CH_3}$—Al protons of $\mathrm{MeAlCl_2}$ complexed with 1,2-dimethoxyethane: 0.27 ppm, HOO— protons of $\mathrm{PhMe_2COOH}$; 8.51 ppm, $\mathrm{(CH_3)_2C}$— protons of $\mathrm{PhMe_2COOH}$: 9.85 ppm, protons of methane; 8.56 ppm protons of $\mathrm{Ph(CH_3)_2OOAlCl_2}$, 7.93—8.07 ppm, protons of $\mathrm{(CH_3)_2C{=}O}$.

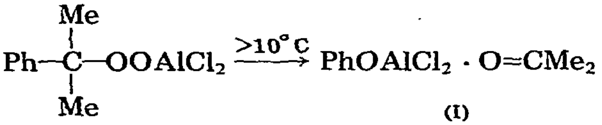
The presence of three signals in the NMR spectrum at ~8.0 ppm was found only when DME was used as a solvent. It can be presumed that this is caused by the formation of different complexes of acetone with the aluminium compounds, resulting from the known cleavage of ethers by strong Lewis acids.

On the basis of the above studies it was found that the reaction between methylaluminium dichloride and cumyl hydroperoxide in DME proceeds according to equations 1 and 2.



$$\mathrm{MeAlCl_2} + \mathrm{Ph}\!-\!\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\mathrm{OOH} \xrightarrow[\mathrm{DME}]{0\text{—}5^\circ\,\mathrm{C}} \mathrm{MeH} + \mathrm{Ph}\!-\!\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\!-\!\mathrm{OOAlCl_2} \qquad (1)$$

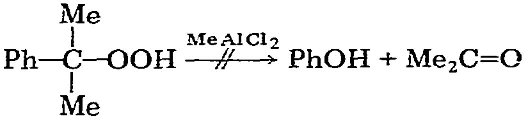
(II)



$$\mathrm{Ph}\!-\!\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{C}}}\!-\!\mathrm{OOAlCl_2} \xrightarrow{>10^\circ\,\mathrm{C}} \mathrm{PhOAlCl_2}\cdot\mathrm{O{=}CMe_2} \qquad (2)$$

(I)

These results suggest that the formation of complex I in the reaction of methylaluminium dichloride with phenol, formed from the decomposition of cumyl hydroperoxide by a Lewis acid, does not proceed (equations 3—5).



$$Ph-\overset{\overset{\large Me}{|}}{\underset{\underset{\large Me}{|}}{C}}-OOH \xrightarrow[]{MeAlCl_2} \!\!\!\!\!\!\!\!\!/\;\;\;\;\; PhOH + Me_2C{=}O \qquad (3)$$

$$PhOH + MeAlCl_2 \not\rightarrow MeH + PhOAlCl_2 \qquad (4)$$

$$PhOAlCl_2 + Me_2C{=}O \not\rightarrow \underset{(I)}{PhOAlCl_2 \cdot O{=}CMe_2} \qquad (5)$$

2. Reaction of t-butyl hydroperoxide with methyl- and ethylaluminium dichloride

(a) Reaction in 1,2-dimethoxyethane and diethyl ether. The rate of rearrangement of the alkyl group at the tertiary carbon of organic hydroperoxide, leading to the formation of a ketone and alcohol, is much smaller than that of the aryl group. Thus it was expected that the addition of t-butyl hydroperoxide to the reaction with alkylaluminium dichloride would slow down the reaction analogous to eq. 2, and would permit the formation of the aluminium peroxide $t\text{-}BuOOAlCl_2$ (III).

On the basis of NMR spectra, it was found that the reaction of t-butyl hydroperoxide with methylaluminium dichloride in DME starts at 0—10° C (Fig. 2). At 0° C a signal of methane protons appears (9.83 ppm) and the signals of the CH_3Al protons of methylaluminium dichloride (10.7—10.8 ppm), the —OOH proton (0.50 ppm) and of the $(CH_3)_3C$— protons (8.86 ppm) of the hydroperoxide disappear (Fig. 2b). At the same time a new signal of $(CH_3)_3C$— protons at a lower field (8.80 ppm) is observed. After about 2 h at 10°C, no signals of the OOH and CH_3Al protons are observed; only a signal at 8.83 ppm and the methane signal are present. At room temperature there are no changes in the spectrum, even after prolonged storage of the solution.

Thus, it can be assumed that no rearrangement of the aluminium peroxide $t\text{-}BuOOAlCl_2$ with formation of acetone takes place in the reaction of t-butyl hydroperoxide with alkylaluminium dichloride in DME. When $EtAlCl_2$ was used in the reaction only signals of the $(CH_3)_3C$ group and of ethane (9.14 ppm) were observed in the NMR spectrum at room temperature. This excludes the oxidation of ethylaluminium dichloride by the peroxide III, according to reaction 6.

$$EtAlCl_2 + t\text{-}BuOOAlCl_2 \rightarrow t\text{-}BuOAlCl_2 + EtOAlCl_2 \qquad (6)$$

On the basis of the NMR spectrum, the analysis of the post-reaction solution for aluminium, chlorine and peroxidic bonds and the determined ratio Al : Cl : O—O = 1 : 2.5 : 1.2, it is indicated that the aluminium peroxide $t\text{-}BuOOAlCl_2$ is formed in the reaction of t-butyl hydroperoxide with methyl- and ethylaluminium dichloride (1 : 1 molar ratio). After distilling off DME from the solution a considerable decrease in the content of peroxidic bonds (6—12 mole %) was found in the solid product.

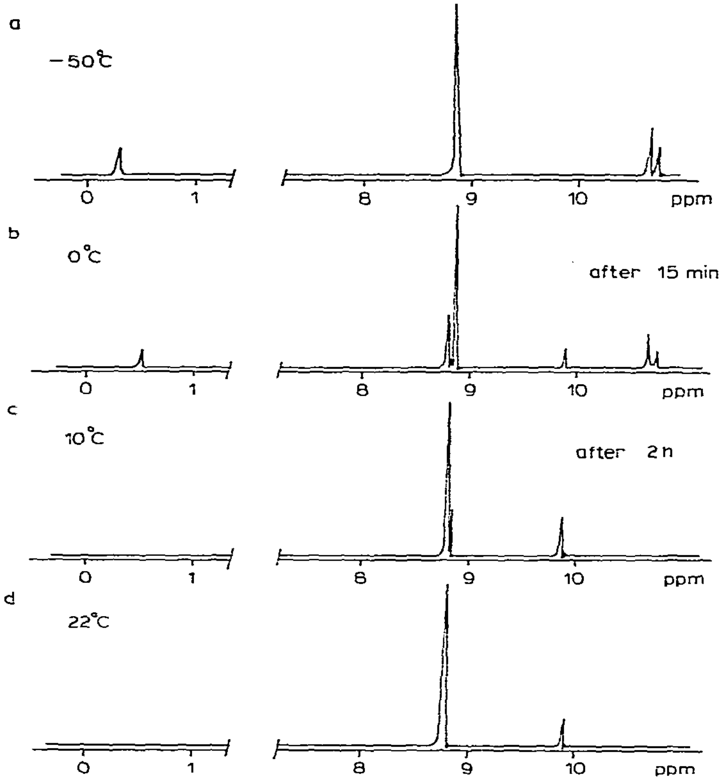


Fig. 2. The PMR spectra of the reaction MeAlCl : t-BuOOH = 1 : 1 carried out in NMR tube (dimethoxyethane solution). Assignments of the signals, τ: 10.70—10.80 ppm, CH_3—Al protons of $MeAlCl_2$ complexed with dimethoxyethane; 0.27—0.51 ppm, HOO— proton of t-BuOOH; 9.85 ppm, protons of methane: 8.86 ppm, protons of $(CH_3)_3C$ of t-BuOOH.

In an analogous reaction carried out in diethyl ether a white precipitate was formed during the distillation of the solvent, which at the end of the process decomposed violently. t-BuO$AlCl_2$ was the main decomposition product (NMR spectrum in anisole: signal of $(CH_3)_3C$— group at 8.48 ppm).

On the basis of the above results it can be stated that in the reaction of t-butyl hydroperoxide with methyl- and ethylaluminium dichloride, carried out in diethyl ether and dimethoxyethane, the aluminium peroxide, t-BuOO$AlCl_2$, is formed. This peroxide is stable in the solution of these solvents.

(b) Reaction in anisole. In order to confirm the stabilizing electron-donating effect of the solvent on the aluminium peroxide, the reaction of t-butyl hydroperoxide with methylaluminium dichloride was carried out in anisole.

The reaction starts at —25°C (Fig. 3a). At that temperature the signal of the methane protons appears (τ = 9.50 ppm). After increasing the temperature to —10°C the reaction proceeds much faster, the peak of the CH_3—Al protons at τ = 9.92 ppm disappears and the intensity of the $(CH_3)_3C$— protons of the hydroperoxide at τ = 8.44 ppm decreases. Simultaneously, at τ = 8.23 ppm, a signal of the newly formed compounds appears (Fig. 3b). Despite the complete disappearance of the signal of the CH_3—Al protons at —10°C (Fig. 3c), the signal at τ = 8.44 ppm of the hydroperoxide $(CH_3)_3C$— group protons did not vanish

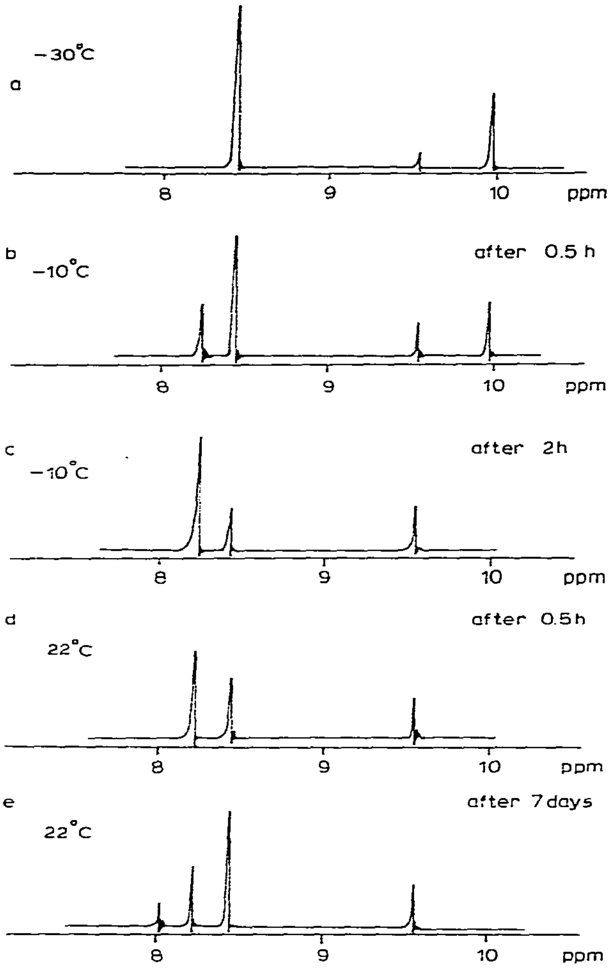


Fig. 3. The PMR spectra of the reaction $MeAlCl_2$: t-BuOOH = 1 : 1 carried out in NMR tube (anisole solution). Assignments of the signals, τ: 9.92 ppm, CH_3—Al protons of $MeAlCl_2$ complexed with anisole; 8.44 ppm $(CH_3)_3C$—, protons of t-butyl hydroperoxide; 9.50 ppm, protons of methane; 8.23 ppm, $(CH_3)_3C$— protons of t-$BuOOAlCl_2$; 8.48 ppm, $(CH_3)_3C$— protons of t-$BuOAlCl_2$.

completely. After increasing the temperature to 22° C, a signal at τ = 8.48 ppm appeared and slowly increased in intensity. This signal was assigned to the $(CH_3)_3C$— group protons of t-$BuOAlCl_2$. The spectrum recorded after the sample had been kept for 7 days at room temperature (Fig. 3e) showed that further decomposition had taken place. The signal at τ = 8.23 ppm was assigned to the protons of the $(CH_3)_3C$ group of t-$BuOOAlCl_2$, which at temperatures higher than —10° C slowly decomposed to t-$BuOAlCl_2$.

On the basis of the above results it was concluded that the reaction of t-butyl hydroperoxide with methylaluminium dichloride in anisole proceeds according to equation 7.

$$\begin{tikzcd} \text{t-BuOOH} + \text{MeAlCl}_2 \arrow[r, "-\text{MeH}", "-10^\circ\text{C}"'] & \text{t-BuOOAlCl}_2 \arrow[dl, "\text{room temperature}"] \\ \text{t-BuOAlCl}_2 & \end{tikzcd} \qquad (7)$$

The use of anisole, a much weaker electron donor than diethyl ether and 1,2-dimethoxyethane, accelerates the decomposition of the aluminium peroxide formed.

(c) Reaction in toluene. Methane evolved and a gelatinous precipitate separated from the reaction of t-butyl hydroperoxide with methylaluminium dichloride in 1 : 1 molar ratio in toluene. The precipitate did not contain peroxidic bonds after evaporation of the solvent. The presence of acetone, t-butanol and methanol in the hydrolysis products of the precipitate was shown chromatographically . The presence of acetone was also confirmed by the IR spectrum of the hydrolysis product ($\nu(C{=}O) = 1675\ cm^{-1}$).

The above studies (a, b, c) indicate that the stability of aluminium peroxide depends mainly on the solvent. The stability of the peroxide $ROOAlCl_2$ decreases with decreasing electronegativity of the solvent:

$$DME \geqslant Et_2O > C_6H_5OCH_3 > C_6H_5CH_3$$

This is in agreement with the statement of Davies and Hall [7], that the stability of tris(decahydro-9-naphthylperoxy)aluminium depends on the solvent used for its synthesis.

Experimental

All solvents used were dried with 4 A molecular sieves and, then distilled off and stored under nitrogen.

Methyl- and ethylaluminium dichloride were prepared by conventional methods. Phenoxyaluminium dichloride was obtained according to ref. 10. Cumyl hydroperoxide [11] and t-butyl hydroperoxide [12] were obtained by methods described in the literature.

All reactions were carried out under a blanket of dry and deoxygenated nitrogen. The solutions of organoaluminium compounds in ethers were prepared on a high vacuum line.

NMR spectra were recorded on a JEOL 100 MHz spectrometer, using CH_3— group protons of the solvent as an internal standard. Chemical shifts were measured using the following τ values as standards: DME 6.74 ppm; anisole 6.27 ppm. IR spectra were run on a Zeiss UR 10 Spectrometer in Nujol mulls.

Reactions of $MeAlCl_2$ and $EtAlCl_2$ with cumyl hydroperoxide (1 : 1 molar ratio)

The organoaluminium compound solution was added to a solution of cumyl hydroperoxide in toluene, cyclopentane or ethyl ether at temperatures given in Table 1. Such an order of adding the reactants prevented the oxidation of alkylaluminium dichloride by the aluminium peroxide being formed. The reaction course was monitored by the rate of evolution of the alkane during the rise of temperature to room temperature. The precipitate formed in the reaction carried out in hydrocarbons was isolated by decantation, washed with the solvent and dried under reduced pressure at room temperature. The product of the reaction carried out in ether was isolated by distilling off the solvent under reduced pressure.

The white product, insoluble in hydrocarbons and soluble in ethers, was identified as the 1 : 1 complex $PhOAlCl_2 \cdot O{=}C(Me)_2$. The aluminium and chlorine analyses are given in Table 1. A singlet at $\tau = 7.93$ ppm was found in the NMR spectrum of the product in 1,4-dioxane. In the IR spectrum the ν(C=O) band was at 1675 cm^{-1}. On the basis of an iodometric analysis no active oxygen bondings were found.

Synthesis of $PhOAlCl_2 \cdot O{=}C(Me)_2$

0.7 g (12 mmol) of acetone in 10 cm^3 of benzene were added to the solution of 2.3 g (12 mmol) of phenoxyaluminium dichloride in 40 cm^3 of benzene. The white precipitate was filtered off, washed with benzene, and dried under reduced pressure. Found: Al, 10.5; Cl, 27.1. $C_9H_{11}AlCl_2O_2$ calcd.: Al, 10.48; Cl, 28.51%. NMR (1,4-dioxane): $\tau = 7.93$ ppm, IR: ν(C=O) 1675 cm^{-1}.

Reactions of $MeAlCl_2$ *with cumyl hydroperoxide and t-butyl hydroperoxide in an NMR tube*

A known quantity of a solution of $MeAlCl_2$ in dimethoxyethane or anisole was introduced to a NMR tube, cooled with liquid nitrogen and the required amount of hydroperoxide was added. The tube was then sealed, and the NMR spectra were recorded while slowly increasing the temperature.

Synthesis of t-butoxyaluminium dichloride

2.25 g of methylaluminium dichloride in 40 ml of cyclopentane were added dropwise to 1.5 g of t-BuOH in 40 ml of cyclopentane at —30 to 5° C. The reaction mixture was then stirred for about 1 h at room temperature and filtered. The solvent was removed from the filtrate under vacuum and pale yellow crystals were obtained. Found: Al, 15.4; Cl, 39.9. $C_4H_9AlCl_2O$ calcd.: Al, 15.78; Cl, 41.52%. NMR (anisole): singlet at $\tau = 8.48$ ppm.

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