REACTIONS OF ETHYLALUMINIUM COMPOUNDS WITH p-CHLORANIL *

Z. FLORJANCZYK, W. KURAN, S. PASYNKIEWICZ* and A. KRASNICKA

Institute of Organic Chemistry and Technology, Technical University (Politechnika), ul. Koszykowa 75, 00-662 Warsaw (Poland)

Summary

Reactions of ethylaluminium dichloride, diethylaluminium chloride and tri-ethylaluminium with p-chloranil have been investigated. Tetrachlorohydroquin-one and p-ethoxytetrachlorophenol are the main reaction products after hydroly-sis. Ethane, ethylene, butane, hexane, octane, higher aliphatic hydrocarbons, products of the chlorine substitution by an ethyl group in a molecule of p-chlor-anil or tetrachlorohydroquinone, and ethyltoluene or benzyltoluene isomers (when toluene was used as a solvent) may also be formed depending on the type of reactants and reaction conditions.

The reactions with p-chloranil of the ethylaluminium compounds studied were found to proceed involving in the first step the formation of donor—accep-tor complexes via the carbonyl group. These complexes were found to undergo reactions of two basic types. The first one is a homolytic dissociation of the Al—C bond with the formation of an aluminium derivative of semiquinone and an ethyl radical. The second type of reaction is the hydrogen transfer from the ethyl group bonded with the aluminium atom to the carbonyl group of quinone with the elimination of ethylene.

The reaction course leading to the formation of tetrachlorohydroquinone and p-ethoxytetrachlorophenol is proposed and discussed.

Introduction

In the reactions of 1,4-quinones with organolithium, -magnezium, -zinc, -cadmium and -boron compounds, 1,2-addition products of the organometallic compounds to the C=O or C=C bond, or 1,4-addition products to the conju-gated bond system C=C—C=O are formed [1—5]. Previously [6] ethylaluminium dichloride and isobutylaluminium dichloride were found to undergo in reactions

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with p-benzoquinone a 1,6-addition to the conjugated bond system O=C—C=C—C=O yielding the respective alkoxyphenols after hydrolysis. Hydroquinone was the second main reaction product after hydrolysis.

In the present work the reactions of ethylaluminium dichloride, diethylaluminium chloride and triethylaluminium with p-chloranil have been studied. It was hoped that the use of p-chloranil would lead to the reactions of the ethylaluminium compounds proceeding analogously to the ones mentioned above, but with higher selectivities than in the case of p-benzoquinone, and to the isolation of the stable intermediate products.

Results and discussion

The reaction of compounds of the type $EtAlX_2$ (where X = Et and/or Cl) with p-chloranil were carried out at $-78°C$ at a 1/1 molar ratio of the reactants. Immediately after mixing of the reactants, an orange-red, dark brown or black precipitate was isolated in the case of Et_3Al, Et_2AlCl and $EtAlCl_2$, respectively. In the reactions of Et_3Al and Et_2AlCl the isolation of the precipitate is accompanied by the evolution of a small quantity of ethane and ethylene.

ESR studies showed that in systems in which Et_2AlCl or $EtAlCl_2$ were used, comparatively stable paramagnetic compounds were formed. Their signal is a singlet of $g \approx 2.003$ and does not disappear at room temperature for a few days. It is much more intensive in the case of $EtAlCl_2$ than of Et_2AlCl. By analogy to the previously studied [6] reactions of organoaluminium compounds with p-benzoquinone it can be concluded to be the signal of the aluminium derivative of semiquinone (III) *.

Tetrachlorohydroquinone (I) and p-ethoxytetrachlorophenol (II) appeared to be the main products of the reaction of ethylaluminium compounds with p-chloranil after hydrolysis.

$$x = C_2H_5 \text{ and / or } Cl$$
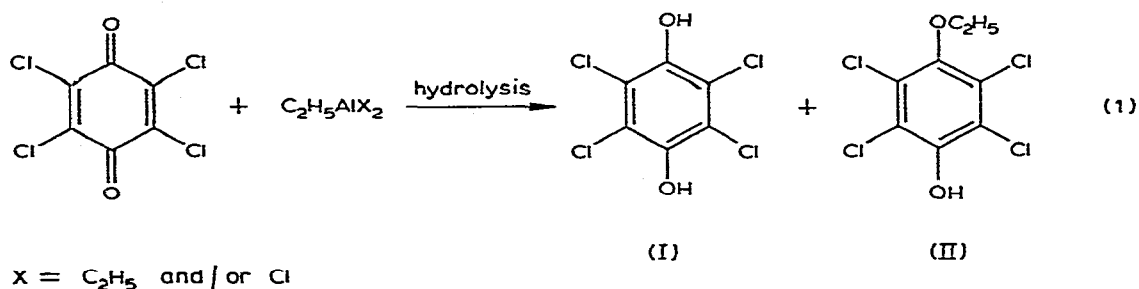
The yield of I increases and of II decreases on increasing the number of ethyl groups in $EtAlX_2$ (Table 1).

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* The formation of a semiquinone aluminium derivative (III, $O—C_6Cl_4—O—AlX_2$) was also postulated in the reactions of p-chloranil with aluminium halides [7]. It was suggested that III exists as an associate via tricentric bonds of the type
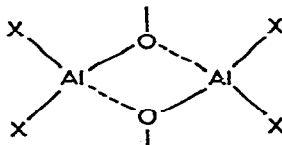
TABLE 1

YIELD OF TETRACHLOROHYDROQUINONE (I) AND p-ETHOXYTETRACHLOROPHENOL (II) IN THE REACTIONS [a] OF p-CHLORANIL WITH ETHYLALUMINIUM COMPOUNDS ($C_2H_5AlX_2$)

$C_2H_5AlX_2$	Molar ratio $C_2H_5AlX_2/p$-chloranil	Temp. (°C)	Yield (%)	
			I	II
$(C_2H_5)_3Al$	1	—78	64	6
$(C_2H_5)_2AlCl$	1	—78	51	27
$C_2H_5AlCl_2$	1	—78	23	53
$C_2H_5AlCl_2$	0.5	—78	15	60
$C_2H_5AlCl_2$	2	—78	60	26
$C_2H_5AlCl_2$	1	0	56	41
$C_2H_5AlCl_2$	1	25	65	18
$C_2H_5AlCl_2$	1	100	86	0

[a] p-chloranil: 12 g; solvent: toluene, 720 cm^3; time: 2 h.

In the reactions of $EtAlCl_2$ with p-chloranil, ethyltoluenes — products of the alkylation of the solvent — are formed. In reactions carried out at elevated temperature (100°C — Table 1) benzyltoluene isomers are also formed.
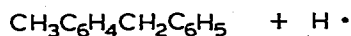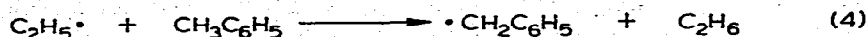
The above results indicate that the reactions of ethylaluminium compounds with p-chloranil may proceed according to a free-radical mechanism with the formation of III and an ethyl radical (reaction 2).
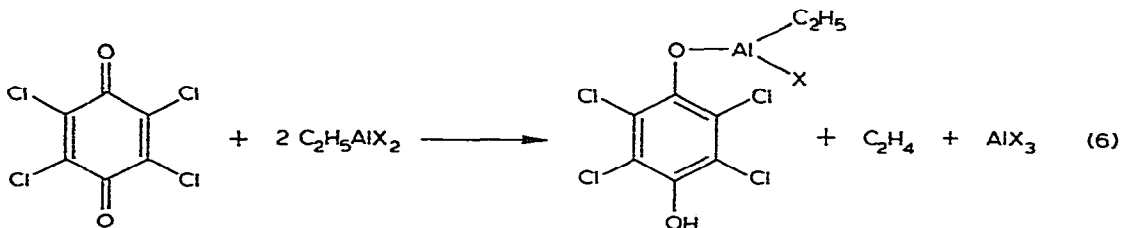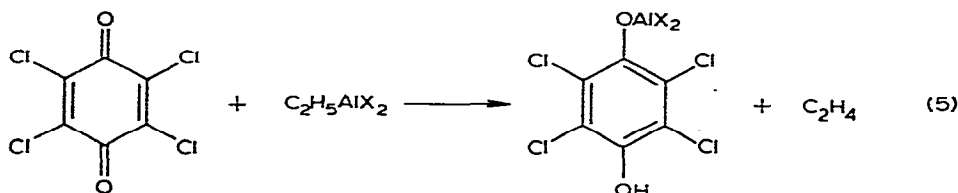

(III)
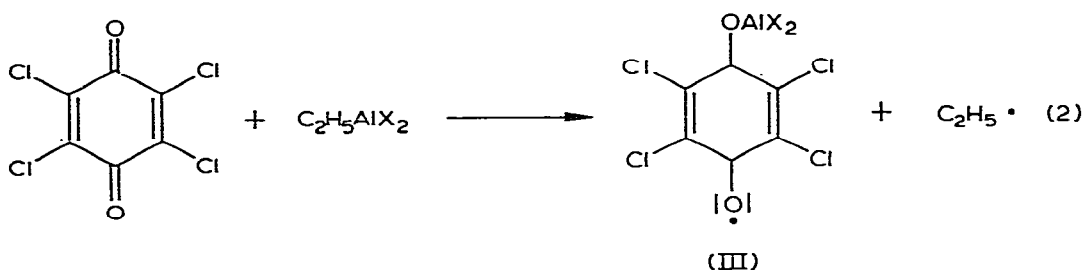
The formation of II can be explained by a recombination of the above radicals or further chain reactions initiated by the ethyl radical. The paramagnetic black precipitate in the reaction of $EtAlCl_2$ with p-chloranil yields I, after hydrolysis, as the only organic product. This indicates the possibility of the formation of I from the hydrolysis of III (or its oligomers). Other paths for the formation of I via III are also possible, e.g. the disproportionation of III or the addition of a hydrogen atom, formed from side reactions with the solvent (e.g. 3 and 4), to III.

The above side reactions (3, 4) of the ethyl radical with the solvent molecules take place particularly at elevated temperature. The deuterolysis of the precipitate isolated from the reaction of $EtAlCl_2$ with p-chloranil yields products containing an OH group as well as the OD one. This indicates the formation of part of the OH groups in I before the hydrolysis (i.e., the formation of HO—C_6Cl_4—$OAlCl_2$ in the reaction system).

As can be seen from Table 1 the yield of I increases and of II decreases when increasing the molar ratio $EtAlX_2/p$-chloranil and the reaction temperature.

$$C_2H_5 \cdot \ + \ CH_3C_6H_5 \longrightarrow CH_3C_6H_4C_2H_5 \ + \ H \cdot \qquad (3)$$

$$C_2H_5 \cdot \ + \ CH_3C_6H_5 \longrightarrow \cdot CH_2C_6H_5 \ + \ C_2H_6 \qquad (4)$$

$$(4a) \diagdown \ CH_3C_6H_5$$

$$CH_3C_6H_4CH_2C_6H_5 \ + \ H \cdot$$

When carrying out the reaction of $EtAlCl_2$ with p-chloranil in an excess of the organometallic compound (slowly dropping the toluene solution of p-chloranil into the toluene solution of $EtAlCl_2$) at 100°C, no black paramagnetic precipitate characteristic of a free radical reaction was observed. Also the products of the radical substitution of toluene were not found. The addition of p-chloranil was accompanied by the isolation of a white precipitate and the evolution of gaseous products, mainly ethane, ethylene and some HCl. After deuterolysis of this precipitate, I is obtained as the only organic product, containing both OD and OH groups. These facts allow us to assume that the formation of I can proceed via a transfer of a hydrogen atom from the ethyl group of the organoaluminium compound to the carbonyl group of p-chloranil without a previous homolytic cleavage of the Al—C bond (eqs. 5 and 6).

$$+ \ C_2H_5AlX_2 \longrightarrow \qquad + \ C_2H_4 \qquad (5)$$

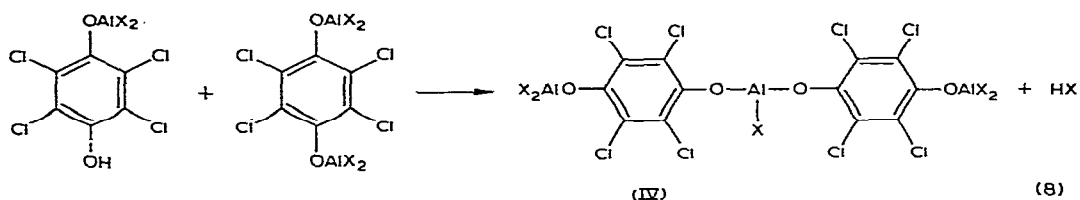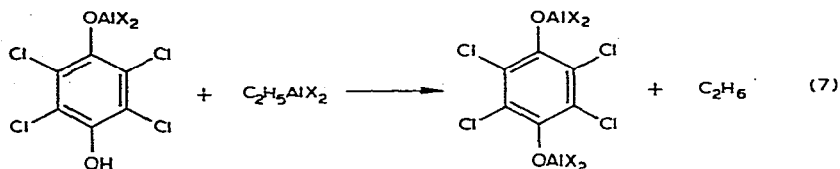$$+ \ 2 \ C_2H_5AlX_2 \longrightarrow \qquad + \ C_2H_4 \ + \ AlX_3 \qquad (6)$$

The hydroxyl group resulting from the above reactions reacts with ethyl groups or chlorine atoms bonded at the aluminium atoms with the evolution of ethane or HCl (eqs. 7 and 8) *.

For Et_3Al and Et_2AlCl, reactions 5—8 probably proceed much easier than for $EtAlCl_2$. For Et_3Al, even at 0°C (despite the method of introduction of reactants), I is exclusively formed with the elimination of ethane and ethylene.

The reactions of Et_3Al and $EtAlCl_2$ with p-chloranil were also carried out in a heptane suspension for the molar ratio $EtAlX_2/p$-chloranil = 2/1. In these

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* Bis[4-dichloroaluminoxy-2,3,5,6-tetrachlorophenoxy]aluminium chloride (IV when X = Cl) was isolated from the reaction of $EtAlCl_2$ with p-chloranil at a 1.1/1 molar ratio of the reactants, at 100°C, reaction time 3 h.

$$\text{(chlorinated phenol with } OAlX_2 \text{ and } OH) + C_2H_5AlX_2 \longrightarrow \text{(chlorinated ring with } OAlX_2 \text{ groups)} + C_2H_6 \quad (7)$$

$$\text{(chloro-OAlX}_2\text{ phenol, OH)} + \text{(chloro-OAlX}_2\text{ diester)} \longrightarrow X_2AlO\text{---}\underset{Cl}{\overset{Cl}{\bigcirc}}\text{---}O\text{---}\underset{X}{Al}\text{---}O\text{---}\underset{Cl}{\overset{Cl}{\bigcirc}}\text{---}OAlX_2 + HX$$

(IV)   (8)

conditions the reaction proceeds slowly and requires intensive heating. The conversion of p-chloranil after 6 h of reaction in boiling heptane was ca. 50%. During the reaction gaseous products, containing ethylene, ethane and small amounts of butane and ethyl chloride, were evolved. I was the main reaction product after hydrolysis. II was not found to be present in the hydrolysed postreaction mixture. Besides I small amounts of tar products containing OH, C=O, and C_2H_5 groups and an aromatic ring are also present. On the basis of elemental analysis they can be concluded to be a mixture of substitution products of chlorine atoms by ethyl groups in molecules of p-chloranil and I; 2,3,5-trichloro-6-ethyl-1,4-benzoquinone and 2,3,5-trichloro-6-ethylhydroquinone were isolated from this mixture. In these reactions hexane, octane and higher hydrocarbons were found to be formed, which, similarly to butane, probably result from the consecutive insertion of ethylene formed from reactions 5 and 6 * into the Al—C bond.

IR spectra of systems containing $EtAlX_2$, $AlCl_3$ or $EtOAlCl_2$ and p-chloranil indicate the formation of donor—acceptor complexes between the Lewis acids mentioned and p-chloranil via the carbonyl group. Characteristic bands for complexed carbonyl groups appear in the region 1480—1565 cm^{-1} (Table 2).

Considering this it seems quite probable that the reactions of ethylaluminium compounds with p-chloranil proceed via a complex step, in which the molar ratio $EtAlX_2/p$-chloranil = 1/1 as well as 2/1 **, e.g. V—VII.

The hydrogen transfer (which is facilitated by using an excess of $EtAlX_2$ with respect to p-chloranil) probably proceeds mainly according to eq. 6 via complex VII. The hydrogen transfer reaction proceeds most easily for triethylaluminium, which is similar to the reaction of ketones with ethylaluminium compounds [9].

The formation of III and ethyl radicals (reaction 2) probably results from the homolytic dissociation of the Al—C bond in complex V. The rate of this reaction increases with the increasing number of chlorine atoms in $EtAlX_2$ in the order $Et_3Al < Et_2AlCl < EtAlCl_2$ due to a decrease in the polarization of the Al—C bond.

* The ethylene content in the mixture of gaseous products is remarkably smaller than that of ethane.
** $AlCl_3$ is known to form complexes with ketones and esters in which the molar ratio $AlCl_3$/donor = 1/1 as well as 2/1 [8].

TABLE 2

STRETCHING FREQUENCIES OF THE CARBONYL GROUP IN p-CHLORANIL AND IN ITS COM-
PLEXES WITH ETHYLALUMINIUM COMPOUNDS, ALUMINIUM CHLORIDE AND ETHOXY-
ALUMINIUM DICHLORIDE (AlX$_3$)

| AlX$_3$	molar ratio AlX$_3$/p-chloranil	$\nu(C=O)$ (cm^{-1})
	0	1690s, 1680s [a]
Et$_3$Al	1	1690s, 1680s, 1565m, 1540w, 1520s [a]
Et$_2$AlCl	1	1690s, 1680s, 1565m, 1545w, 1515m [a]
EtAlCl$_2$	1	1688s, 1540w, 1510w, 1500s [a]
EtAlCl$_2$	10	1687m, 1540m, 1510s, 1498s [a]
(EtO)AlCl$_2$	1	1689m, 1545m, 1490m [b]
AlCl$_3$	1	1690m, 1682s, 1540w, 1510m, 1500m, 1495m [b]
AlCl$_3$	2	1685m, 1540m, 1498s [b]
AlCl$_3$	5	1540s, 1510(sh), 1500s, 1498(sh) [b]

[a] Nujol mull. [b] Saturated solution in CH$_2$Cl$_2$.
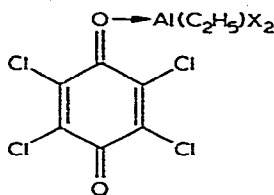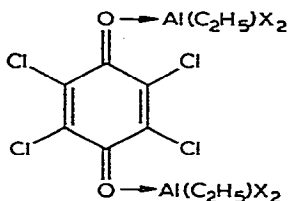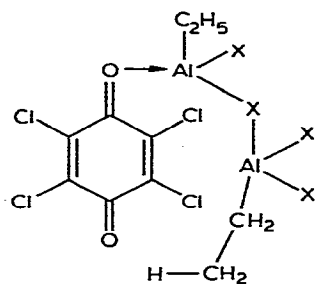
The course of reaction 2 involving an electron transfer from the Al—C bond
to the molecule of uncomplexed quinone does not seem to be very probable.
It was found that in the reaction of p-chloranil with (C$_2$H$_5$)$_3$(C$_6$H$_5$CH$_2$)N$^+$-
(C$_2$H$_5$)AlCl$_3^-$ in toluene or methylene chloride (1/1 molar ratio of reactants,
room temperature) I or II are not formed, despite the fact that the ethylalumini-
um chloride anion should be a considerably stronger electron donor than the
ethylaluminium compounds studied. 4-Ethyl-4-hydroxy-2,3,5,6-tetrachloro-2,5-
cyclohexadien-1-one, the product of the 1,2-addition to the carbonyl group, was
formed from this reaction.

Experimental

Materials

EtAlX$_2$ (Fluka) was purified by distillation under reduced pressure. p-Chlor-
anil was purified by recrystallization from acetic acid and dried in vacuum. Tri-
ethylbenzylammonium chloride was obtained by conventional methods and
dried over phosphorus pentoxide. Toluene, heptane and methylene chloride were
dried and purified by known methods.

Procedure

Each reaction was carried out under nitrogen atmosphere in a glass reaction vessel equipped with a stirrer and connected through a liquid seal to a gas burette. A toluene or heptane solution of 10—20 g of EtAlX$_2$ was prepared in the reaction vessel. p-Chloranil or its toluene solutions were then introduced while vigorously stirring the contents of the reaction vessel. In some reactions $(C_2H_5)_3(C_6H_5CH_2)N^+Cl^-$ was added to liquid $C_2H_5AlCl_2$ and then the complex formed was dissolved in toluene or methylene chloride. 60 cm^3 of toluene and ca. 100 cm^3 of heptane or methylene chloride were used per 1 g of p-chloranil. Gases formed during the reaction were collected and measured in a gas burette. After the reaction was completed, the reaction mixture was hydrolysed with water. The precipitate insoluble in water or an organic solvent was filtered off. The organic and water layers were separated. Both layers were concentrated and the reaction products were isolated from them.

In some cases the product, precipitated from the reaction mixture, was filtered off and subjected to further investigations.

Identification and isolation of products

Tetrachlorohydroquinone (I)
M.p. (benzene) 235—236°C (lit. [10] m.p. 236°C); IR spectrum (KBr); ν(OH) 3390, ν(C—O—H) 1415, 1205, ν(C—Cl) 710 cm^{-1} (Found: C, 29.21; H, 0.85; Cl, 56.02. $C_6H_2Cl_4O_2$ calcd.: C, 29.07; H, 0.81; Cl, 57.21%). The compound was mainly precipitated during hydrolysis, but also in small quantities after concentration of the water layer.

p-Ethoxytetrachlorophenol (II)
M.p. (hexane) 88—89°C; IR spectrum (KBr): ν(OH) 3380, ν(C—H) 2985, 2940, 2920, ν(C—O—H) 1390, ν(C—O) 1210, ν(C—Cl) 715 cm^{-1}; NMR spectrum (benzene): δ —1.12 (t), 3.30 (q), 4.70 (s) ppm. Molecular weight (MS) $M = 274$ (Found: C, 34.82; H, 2.19; Cl, 50.64. $C_8H_6Cl_4O_2$ calcd.: C, 34.82; H, 2.19; Cl, 51.38%). The toluene layer was washed with a NaOH solution. After acidifying the water layer, p-ethoxytetrachlorophenol was isolated as a precipitate.

2,3,5-Trichloro-6-ethyl-hydroquinone
M.p. (heptane) 133—136°C; IR spectrum (KBr): ν(OH) 3380, ν(C—H) 2980, 2940, 2882, ν(C—O—H) 1420, 1215, 1978; NMR spectrum (benzene): δ —1.16 (t), 2.83 (q), 5.30 (s), 7.06 (s) ppm. Molecular weight (MS) $M = 240$. (Found: C, 39.92; H, 3.01; Cl, 43.48. $C_8H_7Cl_3O_2$ calcd.: C, 39.78 H, 2.92; Cl, 44.05%). The compound was isolated by distillation from the mixture of tar products formed from reactions carried out in a heptane suspension, from the fraction soluble in a water solution of NaOH.

2,3,5-Trichloro-6-ethyl-1,4-benzoquinone
M.p. 116—119°C; IR spectrum (KBr): ν(C—H) 2985, 2945, 2882, ν(C=O) 1690, 1670, ν(C=C) 1580, ν(C—Cl) 760 cm^{-1}. Molecular weight (MS) $M = 238$, $M - CO = 210$, $M - Cl = 203$, $M - Cl - CO = 175$, $M - Cl - CO - C_2H_4 = 147$. The

compound was isolated upon sublimation from the mixture of tar products formed from reactions carried out in a heptane suspension, from the fraction insoluble in a water solution of NaOH.

4-Ethyl-4-hydroxy-2,3,5,6-tetrachloro-2,5-cyclohexadien-1-one

M.p. (benzene) 122—124°C; IR spectrum (KBr): ν(OH) 3380, ν(C—H) 2980, 2945, 2884, ν(C=O) 1678, ν(C=C) 1590, ν(C—O—H) 1111, ν(C—Cl) 740 cm^{-1}; NMR spectrum (benzene): δ —0.62 (t), 2.18 (q), 4.54 (s) ppm. Molecular weight (MS) M = 276 (Found: C, 34.70; H, 2.10; Cl, 50.79. $C_8H_6Cl_4O_2$ calcd.: C, 34.82; H, 2.19; Cl, 51.38%). The compound was precipitated during concentration of the toluene layer. It was isolated from the unreacted *p*-chloranil by dissolving in methanol and precipitation with water.

Bis[4-dichloroaluminoxy-2,3,5,6-tetrachlorophenoxy]aluminium chloride (IV)

(Found: C, 18.95; Cl inorganic, 23.92; Al, 10.95. $C_{12}Cl_{13}O_4Al_3$ calcd.: C, 19.22; Cl inorganic, 23.64; Al, 10.79%.)

Ethyltoluene and benzyltoluene isomers were distilled from the toluene layer after washing with NaOH at 160—165°C (760 Torr) and 140—150°C (19 Torr) and identified by gas chromatography and NMR spektroscopy. Hexane, octane and gaseous products were identified by gas chromatography.

Spectroscopy

NMR spectra were recorded on a JEOL C-100 H spectrometer using TMS as an internal standard. IR and ESR spectra were obtained on Zeiss UR and JEOL ME-3X machines, respectively.

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