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REACTIONS OF ORGANOALUMINIUM COMPOUNDS WITH *p*-BENZOQUINONE

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Summary

The reactions of *p*-benzoquinone (BQ) with alkylaluminium compounds of the R_3Al (R = Et, i-Bu) and $RAlCl_2$ (R = Me, Et, i-Bu) type have been investigated. It was found that hydroquinone and a respective alkylhydroquinone are formed after hydrolysis, from the reaction of BQ with R_3Al; hydroquinone and a respective *p*-alkoxyphenol are formed from reaction of BQ with $RAlCl_2$ (R = Et, i-Bu). In addition to the products mentioned in the reactions above, oligomerization compounds and products resulting from the reaction of BQ with toluene (when used as a solvent) were obtained.

With the aid of ESR studies it was shown from the reaction of BQ with $RAlCl_2$ that aluminium derivatives of semibenzoquinone are formed.

On the basis of the results obtained, a carbanionic mechanism for the reaction of BQ with R_3Al (1,4-addition) and a radical mechanism for the reaction of BQ with $RAlCl_2$ (1,6-addition) are proposed and discussed.

Introduction

BQ can react with organo-zinc, -cadmium and -boron compounds by a carbanionic mechanism to yield products of 1,2-addition to the carbonyl group and 1,4-addition to the conjugated system of double bonds [1—4]. The 1,2-addition products were obtained in reactions with diallylzinc [1] and triallylboron [2]; addition to both carbonyl groups of BQ takes place. The 1,4-addition products were obtained in reactions with diethylcadmium [3], triallylboron [2] and trialkyl derivatives of boron [4]. In these reactions the addition takes place only at one conjugated system of double bonds of the BQ molecule to form respective derivatives of hydroquinone, after hydrolysis. Reactions of BQ with Grignard reagents have been reported [5] to produce, after hydrolysis, hydroquinone as the only identified product.

Reactions of BQ with organoaluminium compounds have not been reported hitherto in the literature. We found during studies on the $EtAlCl_2$ catalyzed alternating copolymerization of acrylonitrile with propylene, that the addition of BQ to the polymerization system enhances the amount of active radical centres [6]. This might indicate that the reaction between BQ and $EtAlCl_2$ proceeds according to a radical mechanism.

The purpose of this work was to investigate the reaction of BQ with organoaluminium compounds of the R_3Al (R = Et, i-Bu) and $RAlCl_2$ (R = Me, Et, i-Bu) type.

Results and discussion

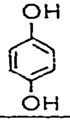
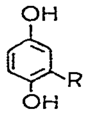
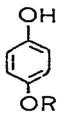
Reactions of BQ with Et_3Al, $i\text{-}Bu_3Al$, $MeAlCl_2$, $EtAlCl_2$ and $i\text{-}BuAlCl_2$ were carried out in ether solution at —78°C with the R_nAlCl_{3-n}/BQ molar ratio 2/1. After mixing the reactants the colour of the reaction mixture turned dark violet in all cases (in the case of Et_3Al and $i\text{-}Bu_3Al$ the colour of the reaction mixture changed to red after a longer period of time). In neither of the reactions were any gaseous products found to be produced.

It was found that hydroquinone, a respective alkylhydroquinone (Table 1) and a mixture of oligomeric compounds with an average molecular weight > 200 are the products of the reaction of BQ with Et_3Al or $i\text{-}Bu_3Al$, after hydrolysis. IR and NMR spectra of the oligomeric products showed the presence of carbonyl ($\nu(C{=}O) = 1660\ cm^{-1}$) and hydroxyl ($\nu(OH) = 3400\ cm^{-1}$) groups, aromatic rings ($\nu(C{-}H) = 2965\ cm^{-1}$, $\nu(C{-}C) = 1610, 1470\ cm^{-1}$; $\delta = 6.69$ (m) ppm alkyl with ($\delta(CH_2$ in $C_2H_5) = 2.60$, $\delta(CH_2$ in $i\text{-}C_4H_9) = 2.34$ ppm) and alkoxyl ($\nu(C{-}O) = 1240\ cm^{-1}$; $\delta(CH_2$ in $OC_2H_5) = 3.89$, $\delta(CH_2$ in $O\text{-}i\text{-}C_4H_9) = 3.66$ ppm) substituents in the aromatic ring.

Hydroquinone, a respective *p*-alkoxyphenol (Table 1) and small amounts of oligomeric compounds are the products of the reaction of BQ with $EtAlCl_2$ or

TABLE 1

YIELD OF HYDROQUINONE, ALKYLHYDROQUINONES AND *p*-ALKOXYPHENOLS IN THE REACTIONS OF *p*-BENZOQUINONE (BQ) WITH ORGANOALUMINIUM COMPOUNDS (R_nAlCl_{3-n}) IN DIETHYL ETHER [a]

R_nAlCl_{3-n}	Yield [b] (%)		
			
$(C_2H_5)_3Al$	21.4	9.4	0
$(i\text{-}C_4H_9)_3Al$	25.0	28.3	0
CH_3AlCl_2	0	0	0
CH_3AlCl [c]	24.0	0	0
$C_2H_5AlCl_2$	18.8	0	11.2
$i\text{-}C_4H_9AlCl_2$	50.0	0	15.0

[a] R_nAlCl_{3-n}/BQ molar ratio 2/1, temperature —78°C, time 4 h. [b] Calculated with respect to BQ. [c] Reaction carried out at diethyl ether boiling point, time 2 h.

TABLE 2

YIELD OF HYDROQUINONE, *p*-ALKOXYPHENOLS AND GASEOUS PRODUCTS IN REACTIONS OF *p*-BENZOQUINONE (BQ) WITH ORGANOALUMINIUM COMPOUNDS ($RAlCl_2$) IN TOLUENE [a]

$RAlCl_2$	Temperature (°C)	Yield [b] (%)		
				R—H
CH_3AlCl_2	—78	54.0	0	91.5
CH_3AlCl_2	65	14.9	0	85.5
$C_2H_5AlCl_2$	—78	32.0	14.0	0
$C_2H_5AlCl_2$ [c]	0	37.5	6.5	0
$C_2H_5AlCl_2$	65	60.0	4.0	39.0
$C_2H_5AlCl_2$ [d]	—78	27.5	2.5	0
$C_2H_5AlCl_2$ [e]	—78	traces	25.8	0
$C_2H_5AlCl_2$ [ce]	0	14.9	12.8	13.0

[a] $RAlCl_2$/BQ molar ratio 2/1, time 4 h. [b] Yield of hydroquinone and *p*-alkoxyphenol calculated with respect to BQ; yield of R—H calculated with respect to $RAlCl_2$. [c] Reaction time 15 min. [d] $RAlCl_2$/BQ molar ratio 1/1. [e] Acrylonitrile was added (acrylonitrile/$C_2H_5AlCl_2$ molar ratio 10/1); yield of polyacrylonitrile at —78°C = 2.1% and at 0°C = 15.0%.

i-$BuAlCl_2$, after hydrolysis. In the reaction of BQ with $MeAlCl_2$, at —78°C, none of the above mentioned products were obtained after hydrolysis, and unreacted BQ was recovered. In boiling ether this reaction gave hydroquinone (Table 1) and a dark violet oligomer, after hydrolysis. In the IR and NMR spectra of the oligomer are signals characteristic of carbonyl ($\nu(C{=}O) = 1640\ cm^{-1}$) and hydroxyl ($\nu(OH) = 3280\ cm^{-1}$) groups, and of aromatic rings ($\nu(C—C) = 1600, 1457\ cm^{-1}$; $\delta = 6.61$ (m) ppm).

Reactions of BQ with $MeAlCl_2$ and $EtAlCl_2$ were also carried out in toluene solution (Table 2). After mixing the reactants at —78°C a dark violet product precipitated from the solution and in the case of $MeAlCl_2$, methane was evolved (when $EtAlCl_2$ was used, ethane evolved only after raising the temperature above 0°C). The reaction of BQ with $MeAlCl_2$ yielded hydroquinone (Table 2) and a mixture of products resulting from the reaction of BQ with toluene. 2,5-Di-*p*-tolyl-1,4-benzoquinone * was isolated from this mixture. The reaction of BQ with $EtAlCl_2$ yielded hydroquinone, *p*-ethoxyphenol (Table 2) and oligomers with properties similar to those obtained in reactions carried out in ethyl ether.

Reaction of BQ with $EtAlCl_2$ in a toluene solution, in the presence of acrylonitrile, was also carried out. Besides hydroquinone, *p*-ethoxyphenol and oligomeric products, polyacrylonitrile was also formed (Table 2). The IR spectrum of the polyacrylonitrile thus obtained showed no bands attributable to the C=N group (or the C=O group after hydrolysis). This indicates that the polymerization of acrylonitrile is not anionically initiated [8].

From Table 2 it appears that raising the temperature in the reaction of BQ

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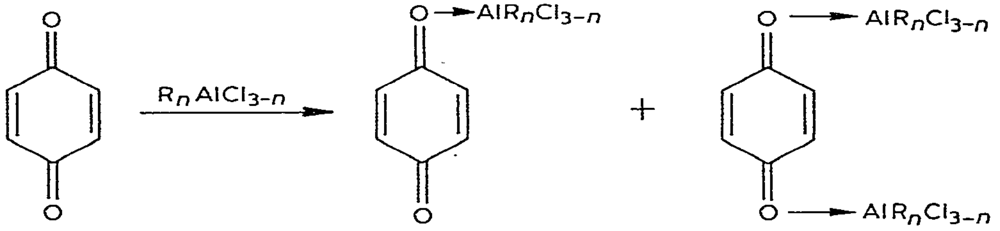
* 2,5-Di-*p*-tolyl-1,4-benzoquinone is also formed from the reaction of BQ with toluene in the presence of $AlCl_3$ [7].

with $EtAlCl_2$ causes an increase in the hydroquinone yield and a decrease in the *p*-ethoxyphenol yield. For a $EtAlCl_2$/BQ molar ratio 2/1, the yield of hydroquinone and *p*-ethoxyphenol is higher than when the molar ratio is 1/1. The addition of acrylonitrile to the reaction system causes a decrease in the hydroquinone yield and an increase in the *p*-ethoxyphenol yield. For the reaction of BQ with $MeAlCl_2$, an increase in temperature causes a decrease in the hydroquinone yield.

Taking into account the relatively strong electron-accepting properties of organoaluminium compounds, it can be expected that the formation of donor—acceptor complexes I or II will be the first stage in the reaction of BQ with these compounds (eq. 1). The isolation of these complexes, however, was not successful.



(1)

(I) (II)

The IR spectra of products precipitated in the reaction of BQ with $EtAlCl_2$ (molar ratio 1/1), carried out in toluene, showed bands at 1640, 1580 and 1505 cm^{-1} attributable to the stretching vibrations of C=O and C=C bonds in the complexed BQ.

The possibility of the formation of donor—acceptor complexes between BQ and organoaluminium compounds is confirmed by comparison with the IR spectra of the mixture of BQ and $AlCl_3$ (Table 3) ($AlCl_3$ has similar complexing properties to alkylaluminium dichlorides). The IR spectrum, in CH_2Cl_2 solution, of the product of the reaction of $AlCl_3$ with BQ (molar ratio 1/1) showed bands at

TABLE 3

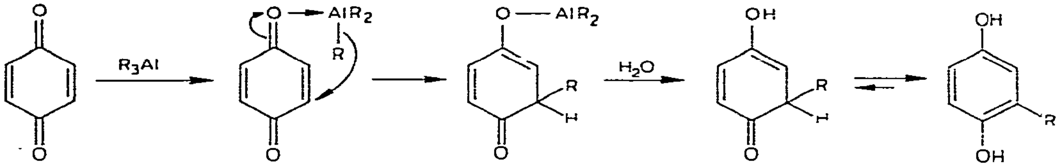
CHARACTERISTIC BAND FREQUENCIES IN IR SPECTRA OF *p*-BENZOQUINONE AND ITS COMPLEXES WITH $AlCl_3$ [a]

$AlCl_3$/BQ molar ratio	Frequency (cm^{-1})					
	ν(C=O)					ν(C=C)
0 [b]	1680m	1660s				1590m
1 [b]	1680m	1660s	1640sh		1505s	1590m
2 [b]			1640s		1505s	1588m
5 [b]			1640s	1552s	1505s	1590m
2 [c]	1680m	1660s	1640m	1552m	1505sh	1580m
2 [d]	1680m	1660s	1640sh		1505m	1590sh

[a] Spectra recorded in the range 1700—1500 cm^{-1}. [b] Saturated solution in CH_2Cl_2. [c] Saturated solution in diethyl ether. [d] Saturated solution in acrylonitrile.

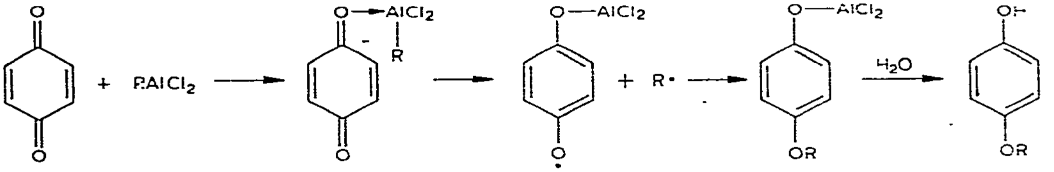
1680 and 1660 cm^{-1} attributable to vibrations of C=O groups in free BQ [9], and bands at 1640 and 1505 cm^{-1} that also occur in the spectrum of the precipitate formed in the reaction of BQ with $EtAlCl_2$. In the IR spectrum of the product of the reaction of $AlCl_3$ with BQ (molar ratio 2/1) bands characterisitc of the C=O vibrations of free BQ do not occur, only the bands at 1640 and 1505 cm^{-1} remain. When the $AlCl_3$/BQ molar ratio is 5/1, besides bands at 1640 and 1505 cm^{-1}, a band at 1552 cm^{-1} occurs. It seems that bands at 1640 and 1505 cm^{-1} can be attributed to the stretching vibrations of carbonyl groups in complexes of BQ with $AlCl_3$ (BQ/$AlCl_3$ molar ratio 1/1) (I), and the band at 1552 cm^{-1} to complexes formed when the molar ratio of the reactant is 2/1 (II). Complexes of BQ with $AlCl_3$ are formed also in ether and acrylonitrile solutions (Table 3).

The formation of alkylhydroquinones from the reactions of BQ with R_3Al can be explained by a 1,4-addition proceeding via complex I according to the carbanionic mechanism shown in eq. 2.



(2)

The formation of *p*-alkoxyphenols from the reactions of BQ with $RAlCl_2$ indicates the possibility of these reactions proceeding according to the radical mechanism shown in eq. 3 *.



(III)

(3)

The formation of free radicals in these reactions is confirmed by ESR studies. In Fig. 1 an ESR spectrum of the reaction mixture BQ and $MeAlCl_2$ in toluene is shown. This spectrum consists of 30 lines. Taking into account that the spectrum of semibenzoquinone consists of 5 lines [11] and the nuclear spin of Al is 5/2, it can be assumed that the spectrum obtained represents the signal due to radical III **.

The formation of aluminium derivatives of semibenzoquinone can be explained by the homolytic dissociation of the C—Al bond in complex I. It seems that homolytic cleavage of the C—Al bond in the $RAlCl_2$ molecule complexed with BQ proceeds much easier than that in the R_3Al molecule complexed with BQ. The inductive effect of two chlorine atoms towards the aluminium atom causes

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* In a similar manner Blomberg et al. [10] explained the formation of phenoxy derivatives from the reactions of *o*-quinones with organomagnesium compounds.

** The splitting of signals of semibenzoquinone was also observed when it was complexed with sodium or lithium ions [12].

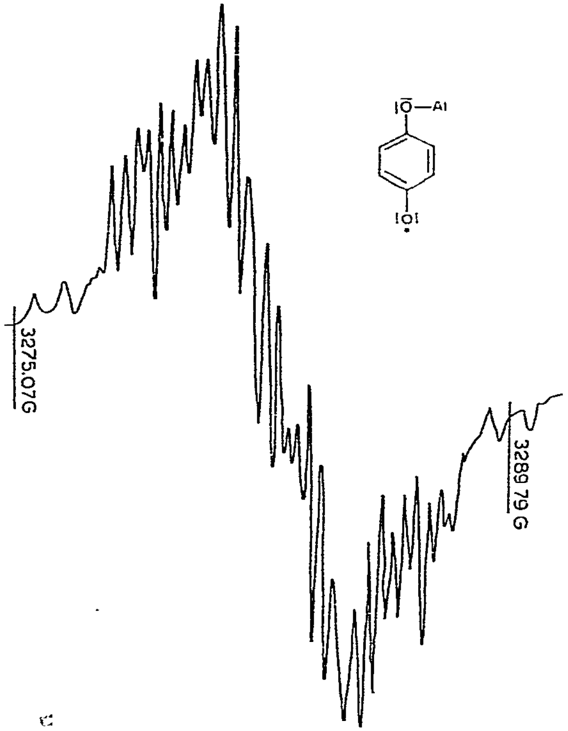

Fig. 1. The ESR spectrum obtained immediately after mixing methylaluminium dichloride and *p*-benzoquinone (BQ) ($MeAlCl_2$/BQ molar ratio 2/1); 2.18 mmol of BQ in 30 ml toluene, temperature 25°C.

a decrease in the partial negative charge on the carbon atom and in the C—Al bond polarization in a $RAlCl_2$ molecule. The first stage of the reaction of BQ with $RAlCl_2$ is probably a one electron transfer from the C—Al bond to a BQ molecule. Due to a further reaction between the radicals thus formed, the 1,6-addition product of the organoaluminium compound with BQ is obtained (eq. 3).

The radicals formed in eq. 3 can also initiate the oligomerization of BQ and the polymerization of acrylonitrile (if it is present in the reaction system).

In complexes formed from BQ and R_3Al derivatives the C—Al bond is strongly polarized in comparison to that formed from BQ and $RAlCl_2$. Therefore the heterolytic cleavage of the former, leading to the formation of the 1,4-addition products, is more probable (eq. 2).

Experimental

Materials

Organoaluminium compounds were obtained by conventional methods and purified by distillation under reduced pressure. BQ was purified by sublimation. Ethyl ether, toluene and acrylonitrile were dried and purified by known methods.

Procedure

Each reaction was carried out under a nitrogen atmosphere in a glass reaction vessel equipped with a stirrer and connected through a liquid seal to a gas burette. An ether or toluene solution of 10—20 g of an organoaluminium compound was prepared in the reaction vessel. A BQ solution was then dropped into the organoaluminium solution while the contents of the reaction vessel were vigorously stirred at —78° C. If a higher reaction temperature was required the reaction vessel was placed in a thermostatted bath. Gases formed during the reaction were collected and measured in a gas burette. After the reaction was complete, the reaction mixture was hydrolyzed with water. In the case of the reaction carried out in ether, toluene was added to the hydrolyzed reaction mixture and then ether was distilled off. The toluene and water layers were separated. Both layers were concentrated and the reaction products were isolated from them.

Identification and isolation of products

Hydroquinone, m.p. (CCl_4/CH_3OH) 170° C (lit. [13] m.p. 172°C); IR spectrum (KBr): ν(OH) 3370, ν(C—H) 3035, ν(C—C) 1525, 1475, ν(C—O) 1200, ν(C—H) 825 cm^{-1}. The compound was isolated from the water layer of the post-reaction mixture by extraction with ethyl ether and crystallization from a methyl alcohol/carbon tetrachloride mixture (1/5 v/v).

Ethylhydroquinone, m.p. (n-C_6H_{14}) 108—110° C (lit. [14] m.p. 112°C); NMR spectrum ($CDCl_3$): δ —1.23 (t), 2.58 (q), 4.42 (s), 6.60 (m) ppm; IR spectrum (KBr): ν(OH) 3300, ν(C—H) 2980, ν(C—C) 1620, 1520, ν(CH_2) 1470, ν(C—O) 1200, δ(C—H) 800, 870 cm^{-1}. (Found: C, 68.76; H, 7.14. $C_8H_{10}O_2$ calcd.: C, 69.56; H, 7.25%.) The compound isolates during concentration of the toluene layer as a yellow oil. After crystallization from n-hexane it yielded a white precitate.

Isobutylhydroquinone, m.p. (n-C_6H_{14}) 105—106° C; NMR spectrum ($CDCl_3$): δ —0.9 (d), 1.89 (m), 2.37 (d), 4.62 (s), 4.95 (s), 6.57 (quin) ppm; IR spectrum (KBr): ν(OH) 3280, ν(C—H) 2965, ν(C—C) 1610, 1520, ν(CH_2) 1455, ν(C—O) 1200, δ(C—H) 880, 830 cm^{-1}. (Found: C, 72.39; H, 8.41. $C_{10}H_{14}O_2$ calcd.: C, 72.29; H, 8.43%.) The compound was distilled from the toluene layer (b.p. 140° C/1 Torr) and crystallized from hexane.

p-Ethoxyphenol, m.p. (petroleum ether) 63—63.5° C (lit. [15] m.p. 65—66° C); NMR spectrum (CCl_4): δ —1.23 (t), 3.78 (q), 4.28 (s), 6.55 (s) ppm; IR spectrum (KBr): ν(OH) 3370, ν(C—H) 2980, ν(C—C) 1610, 1518, ν(C—O) 1240, δ(C—H) 831 cm^{-1}. (Found: C, 69.24; H, 7.26. $C_8H_{10}O_2$ calcd.: C, 69.56; H, 7.25%.) The water layer was washed with a NaOH solution. This ether extraction, after acidification, gave, *p*-ethoxyphenol which was then crystallized from petroleum ether.

p-Isobutoxyphenol, m.p. 52—54° C; NMR spectrum (CCl_4): δ —0.98 (d) 1.89 (m), 3.57 (d), 4.65 (s), 6.57 (s) ppm. IR spectrum (KBr): ν(OH) 3260, ν(C—H) 2960 cm^{-1}, ν(C—C) 1610, 1518, ν(CH_2) 1455, ν(C—O) 1240, δ(C—H) 830 cm^{-1}. (Found: C, 71.93; H, 8.41. $C_{10}H_{14}O_2$ calcd.: C, 72.29; H, 8.43%.)

2,5-Di-*p*-tolyl-1,4-benzoquinone, m.p. 218° (lit. [7] m.p. 220° C); NMR spectrum (CCl_4): δ —2.35 (s), 6.54 (s), 7.17 (q) ppm; IR spectrum (KBr): ν(C=O) 1650, ν(C—C) 1602, 1510, ν(C=C) 1580, δ(C—H) 840 cm^{-1}. The compound was isolated upon sublimation from a mixture of products left after distilling toluene from the organic layer. Methane and ethane were identified by gas chromatography.

Spectroscopy

NMR spectra were recorded on a JEOL C-100H spectrometer using TMS as an internal standard. IR and ESR spectra were obtained on Zeiss UR-10 and JEOL ME-3X machines, respectively.

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