Journal of Organometallic Chemistry, 259 (1983) 127–137
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

ON THE 1,6-ADDITION OF ALKYLALUMINIUM COMPOUNDS TO *para*-QUINONES

ZBIGNIEW FLORJAŃCZYK* and EWA SZYMAŃSKA-ZACHARA

Faculty of Chemistry, Technical University (Politechnika), Koszykowa 75, 00-662 Warsaw (Poland)

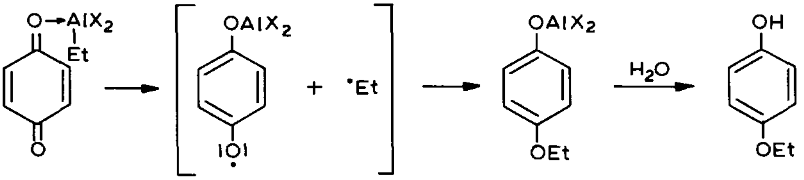
(Received June 30th, 1983)

Summary

Ethyl, n-butyl and i-butylaluminium dichlorides undergo 1,6-addition to a conjugated bond system O=C–C=C–C=O of *para*-quinones. Methylaluminium dichloride is inactive in this addition, and triethylaluminium gives low yields. The reactivities of the quinones vary with their electron affinities, and the highest yields of 1,6-addition are obtained in the reactions of chlorine derivatives of 1,4-benzoquinone. The results are discussed in terms of a radical mechanism involving a homolytic cleavage of the Al–C bond in the donor-acceptor complex formed between the reactants followed by combination of alkyl radicals and aluminium derivatives of semiquinone within a cage. The stable donor-acceptor complexes and aluminium derivative of semiquinone were isolated and characterized from the reactions of aluminium trichloride with 2,3,5,6-tetramethyl-1,4-benzoquinone and 2,3,5,6-tetrachloro-1,4-benzoquinone, respectively.

Introduction

It has been previously shown that ethyl aluminium compounds undergo 1,6-addition to 1,4-benzoquinone [1] and 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-chloranil) [2] to give, after hydrolysis, the corresponding 4-ethoxyphenols. The plausible reaction pathway is shown in eq. 1.



(1)

According to this scheme, the Al–C bond in the donor-acceptor complex formed between the reactants undergoes homolytic cleavage to give ethyl radicals and

0022-328X/83/$03.00

aluminium derivatives of semiquinones, which combine within a cage.

The aluminium derivatives of semiquinones have been observed by several authors as an intermediate or long lived paramagnetic species formed in reactions between *ortho*- and *para*-quinones with alkylaluminium compounds or halides [1–10]. The structures of some *ortho*-quinone derivatives were proved by means of ESR spectroscopy [4–9]. The reactions leading to paramagnetic species are usually very fast even at −80°C, and thus the donor-acceptor complexes between quinones and aluminium compounds were not isolated.

In this paper we describe the results of examination of the reactions of various *para*-quinones with alkylaluminium compounds aimed at determining the factors affecting the 1,6-addition. The isolation of the donor-acceptor complex and aluminium derivative of semiquinone formed in the reaction between $AlCl_3$ and some quinones is also described.

Results and discussion

Reactions of various *para*-quinones with $EtAlCl_2$ were carried out in toluene at −78°C with a 1/1 mol ratio of the reactants. After hydrolysis, the corresponding dihydroxyaromatic compounds and their monoethyl ethers were the main products (Table 1). It can be observed that the yield of monoethers from the 1,6-addition depends on the electron acceptor properties of the quinones. The chlorinated derivatives of 1,4-benzoquinone, which exhibit high electron affinity, are the most reactive. The reactivities of other quinones decrease in the order 1,4-naphthoquinone

TABLE 1

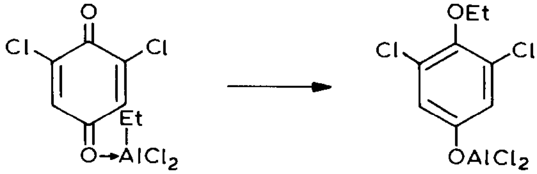
YIELD OF 1,4-DIHYDROXYAROMATIC COMPOUNDS (I) AND THEIR MONOETHYL ETHERS (II) IN REACTIONS OF $EtAlCl_2$ AND Et_3Al WITH *p*-QUINONES [a]

Quinone	Electron affinity [b]	Organoaluminium compound	Yield (%)	
			I	II
2,3,5,6-tetrachloro-1,4-benzoquinone	1.4	$EtAlCl_2$	23	58
		Et_3Al	65	6
2,3,5-trichloro-1,4-benzoquinone	1.3	$EtAlCl_2$	13	67
2,6-dichloro-1,4-benzoquinone	1.2	$EtAlCl_2$	12	60
2,5-dichloro-1,4-benzoquinone	1.1	$EtAlCl_2$	9	59
1,4-naphthoquinone	0.7	$EtAlCl_2$	26	44
		Et_3Al	14	4
1,4-benzoquinone	0.6	$EtAlCl_2$	29	20
		Et_3Al	56	8
2,3,5,6-tetramethyl-1,4-benzoquinone	$\leqslant 0.5$	$EtAlCl_2$	1	traces
		Et_3Al	11	1

[a] Mol ratio: quinone/organoaluminium compound = 1, solvent: toluene, 500 cm^3, quinone concentration 0.07 mol l^{-1}; temp. −78°C; time 2 h. [b] Ref. 11.

> 1,4-benzoquinone > 2,3,5,6-tetramethyl-1,4-benzoquinone. The last compound, which is the weakest acceptor among the quinones studied, forms only traces of the monoether.

In the reactions with 2,6-dichlorobenzoquinone of among the two theoretically possible isomers only 3,5-dichloro-4-ethoxyphenol is formed. This indicates that the aluminium atom interacts with the carbonyl group which is less sterically hindered and possesses a higher electron density.



(2)

In the case of 2,3,5-trichlorobenzoquinone the differential effect of the substituents is smaller, and a mixture of 2,3,5-trichloro-4-ethoxyphenol and 2,3,6-trichloro-4-ethoxyphenol in an approximately 4/1 mole ratio is formed.

The yield of dihydroxyaromatic compound in the reactions of most of the quinones with $EtAlCl_2$ at $-78°C$ is markedly lower than that of monoethers, with the exception of the reactions involving benzoquinone and tetramethylbenzoquinone. However, it is known that the yield of dihydroxyaromatic compounds rises rapidly with increase in the temperature [1,2].

The ^1H NMR spectra of the mixture of products obtained after hydrolysis show that some of the ethyl groups derived from $EtAlCl_2$ undergo also addition to the carbon atoms of quinones. The largest yield of C-alkylation products is formed in reactions of 1,4-benzo- and 1,4-naphthoquinone; as indicated by the NMR data, 10–20% of all the ethyl groups are consumed in this process. In the case of benzoquinone, naphthoquinone, and chloranil, Et_3Al was also used as an alkylating agent. As can be seen from Table 1 this compound is much less reactive in 1,6-addition than $EtAlCl_2$, and it gives mainly dihydroxyaromatic compounds and C-alkylation products *.

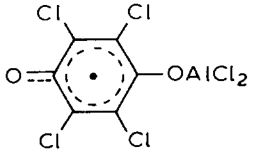
ESR observations show that long lived paramagnetic products are formed in the reactions of $EtAlCl_2$ with the quinones studied. Their spectra are not well resolved, however, and no conclusions about the structure of radicals can be drawn.

From the studies carried out for *p*-benzoquinone and *p*-chloranil it results that stable paramagnetic products are formed also in reactions with various alkylaluminium chlorides and with $AlCl_3$. In the reaction of Et_3Al with those quinones the signals in the ESR spectra were very weak and were observed only at low temperatures ($\sim -70°C$). The stable paramagnetic product formed in reactions of $AlCl_3$ or $EtAlCl_2$ with *p*-chloranil was isolated. On the basis of an analysis of the aluminium and chloride ion content in the mixture after hydrolysis and of the IR

---

* The C-alkylation of *para*-quinones by organoaluminium compounds has been reported previously [1,2,10,12].

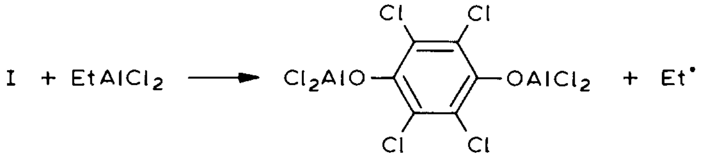
spectrum it appeared to be the aluminium derivative of semiquinone I.



(I)

In the IR spectrum, the most intense absorption bands appear at 1589, 1524, 1475, 1175, 960 and 722 cm^{-1}. By analogy with the spectra of paramagnetic salts of *p*-chloranil with alkali metals [13], it can be assumed that the band at 1524 cm^{-1} corresponds to stretching vibrations of the CO bond of an order lower than in the free quinone, but still having a π bond character. The second CO bond has a bond order close to one, and its characteristic absorption band appears at 1175 cm^{-1}. The bands at 1589 and 1475 cm^{-1} are assigned to the stretching vibrations of carbon atoms in the ring and their frequencies are slightly lower than those observed for the bis(dichloroaluminium) salt of 2,3,5,6-tetrachlorohydroquinone (1602, 1493 cm^{-1}). The band at 722 cm^{-1} is characteristic of vibrations of the C–Cl bond in chloranil anion-radicals [13].

I reacts with $EtAlCl_2$ to give the bis(dichloroaluminium) salt of 2,3,5,6-tetrachlorohydroquinone (II), ethane, and small quantities of ethylene. Free radical substitution probably takes place in this case, as in the case of phenoxy radicals [14].



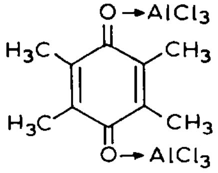
(II)

(3)

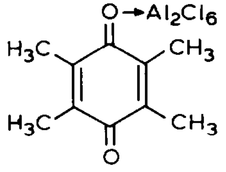
Treatment of I with Lewis acids caused disproportionation to *p*-chloranil and II. IR and ESR observations showed that the disproportionation proceeds slowly in solutions of weak donors, such as nitromethane and anisole, and very rapidly in THF or water. At the same time water brings about hydrolysis of II to 2,3,5,6-tetrachlorohydroquinone.

The reactions of $AlCl_3$ with 2,3,5,6-tetramethyl-*p*-benzoquinone (TMBQ) give stable coordination complexes in which the halide/quinone mole ratio is 2. Their IR spectra indicate that the complexation proceeds via the carbonyl groups, since there is a characteristic shift of the stretching frequency of this group towards lower values. In free TMBQ the $\nu(C{=}O)$ appears at 1640 cm^{-1}. In the isolated complexes the band of the carbonyl groups bonded with the aluminium atom appears as a broad peak with two maxima at 1570 and 1558 cm^{-1} and a shoulder at 1540 cm^{-1} (Fig. 1a). A band characteristic of the free carbonyl group at 1645 cm^{-1} is also present. The presence of three frequencies of the carbonyl group stretching vibrations probably results from the existence of two types of complexes with 2/1 mole stoichiometry. In the first (III) both carbonyl groups are coordinated to an $AlCl_3$

monomer, and in the second (IV) one carbonyl group is coordinated to an Al_2Cl_6 dimer *.



(III)



(IV)

With an equimolar ratio of reactants or when an excess of quinone is present, an intense band of the free carbonyl groups vibrations and a band characteristic for the complex with the maximum at 1558 cm^{-1} are present in the IR spectrum (Fig. 1b). Bands assigned to complexed carbonyl groups are observed also in the IR spectra of mixtures of TMBQ with Me_2AlCl and $MeAlCl_2$ at 1563 and 1560 cm^{-1}, respectively.

^{13}C NMR studies showed that the chemical shifts of the TMBQ carbon atoms increase under the influence of $AlCl_3$. The changes are greater for the olefinic carbon atoms than for the carbonyl carbon atoms (Table 2). This indicates that the quinone is an electron donor in the complexes studied and the inductive effect caused by the complexation of the oxygen atoms is transferred along the conjugated system of double bonds.

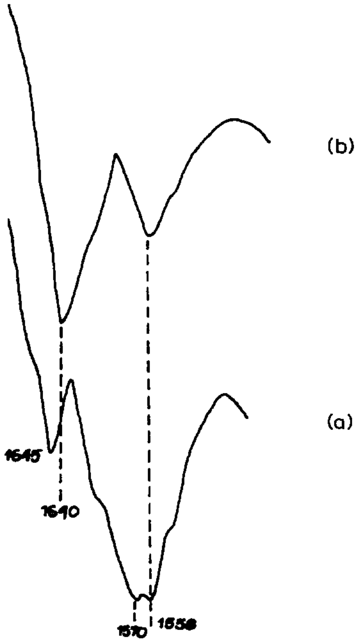


Fig. 1. ν(C=O) region of IR spectra of the system $AlCl_3$/2,3,5,6-tetramethyl-1,4-benzoquinone at 2/1 (a) and 1/1 (b) mol ratios.

---

* The coordination of Al_2Cl_6 or dimers of methylaluminium chlorides by one carbonyl group was previously observed for ketone and ester complexes. The most probable structure of these complexes is a six-centred ring composed of a C=O bond and a dimer with one chlorine bridge [15].

TABLE 2

INFLUENCE OF $AlCl_3$ ON THE CHEMICAL SHIFTS (δ) OF CARBON ATOMS IN 2,3,5,6-TETRAMETHYL-1,4-BENZOQUINONE (TMBQ)[a]

Mol ratio $AlCl_3$/TMBQ	δ ($\Delta\delta$)[b] (ppm)		
	C=O	C=C	CH_3
0	188.68	141.62	12.99
0.5	189.96 (1.28)	143.51 (1.48)	13.22 (0.83)
1.0	192.56 (3.88)	146.51 (4.89)	14.11 (1.72)
2.0	193.49 (4.71)	147.61 (5.99)	14.80 (2.41)
3.0	193.40 (4.62)	147.41 (5.79)	14.33 (1.97)

[a] Solvent, nitromethane; lock ext. D_2O; reference ext. dioxane-d_8 (67.08 ppm), ambient temperature, proton decoupled, ~10000 pulses. [b] Difference between the δ observed and δ in free TMBQ.

Changes in the distribution of electron density due to the complexation of the quinone by organoaluminium compounds lead to the heterolytic or homolytic cleavage of the Al–C bond. Polar addition or reduction reactions are governed by the polarization of the Al–C bond, and trialkylaluminium compounds are the most reactive organoaluminium compounds. The C-alkylation products and dihydroxyaromatic compounds are formed by this pathway in the reactions with *p*-quinones [1,2,10,12]. The homolytic cleavage of the Al–C bond is probably preceded by an inner sphere electron-transfer in the donor-acceptor complex.

Quinones are σ donors and π acceptors in these complexes. The formation of a coordination complex is known to lower the energies of Lewis bases orbitals and increase those of Lewis acids orbitals [16,17]. Because of this a single electron transfer from the organoaluminium compound to the LUMO of quinone becomes possible. This process seems to be governed by the electron acceptor properties of complexed quinone, as indicated by (a) the fact that the largest yield of 1,6-addition products is in reactions with quinones of high electron affinities and (b) by the

TABLE 3

YIELD OF 1,4-DIHYDROXYAROMATIC COMPOUNDS (I) AND THEIR MONOALKYL ETHERS (II) IN REACTIONS OF 1,4-BENZOQUINONE AND 2,3,5,6-TETRACHLORO-1,4-BENZOQUINONE WITH VARIOUS ALKYLALUMINIUM DICHLORIDES ($RAlX_2$)[a]

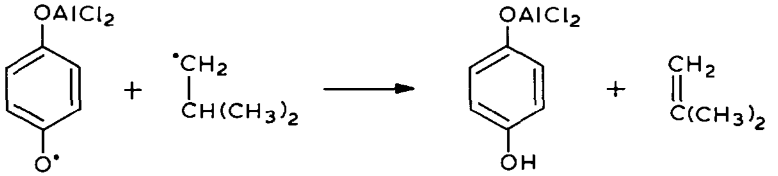
Quinone	$RAlX_2$	Mol ratio $RAlX_2$/Quinone	Yield (%)	
			I	II
1,4-benzoquinone	CH_3AlCl_2	2	54	0
	$C_2H_5AlCl_2$	1	29	20
	$C_2H_5AlCl_2$	2	50	26
	n-$C_4H_9AlCl_2$	2	35	43
	i-$C_4H_9AlCl_2$	2	52	12
2,3,5,6-tetrachloro-1,4-benzoquinone	CH_3AlCl_2	1	65	0
	$C_2H_5AlCl_2$	1	23	58
	$C_2H_5AlCl_2$	2	60	26
	n-$C_4H_9AlCl_2$	1	30	17
	i-$C_4H_9AlCl_2$	1	60	11

[a] For reaction conditions see Table 1.

higher reactivity of quinone complexes in radical reactions with $EtAlCl_2$ (which is a strong Lewis acid) than with Et_3Al.

The electron affinity of the quinone and acidity of the aluminium compound must also affect the electron-acceptor properties of the semiquinone aluminium derivative, and its recombination with alkyl radicals (see eq. 1) which exhibit electron donor properties. The effectiveness of recombination also depends on the type of alkyl radical derived from the organoaluminium compound. Studies of the reaction of *p*-benzoquinone and *p*-chloranil with various alkylaluminium chlorides (Table 3) showed that the 1,6-addition gave ethyl, n-butyl and i-butyl monoethers, but no methyl ethers. During the reaction with $MeAlCl_2$ vigorous evolution of methane is observed and the corresponding hydroquinones are the main products after hydrolysis. The methyl radicals probably diffuse from the cage much faster than higher alkyl radicals, and so do not undergo recombination with an aluminium derivative of semiquinone even at −78°C.

From previous observations [1,2] it is known that in the case of ethyl derivatives the efficiency of recombination falls considerably with a rise of temperature, and above 0°C the yield of monoethers is very small. As can be seen from Table 3 the yield of monoethers is low in reactions of isobutylaluminium dichloride and after hydrolysis the corresponding hydroquinones are the main products. During the reactions isobutylene is also formed, and alkylates toluene to give 4-t-butyltoluene. The formation of hydroquinones and isobutylene may result from reduction (via hydride anion transfer) or from disproportionation between the semiquinone aluminium derivative and isobutyl radical * (eq. 4).



(4)

Aluminium derivatives of semiquinone, which do not react with alkyl radicals, can form hydroquinone derivatives by the disproportionation or radical substitution of an alkyl group in the organoaluminium compound. Alkyl radicals, which escape from the cage can abstract a hydrogen atom from toluene [2] and can also induce the polymerization of vinylic monomers [19]. It is probable that some of the C-alkylation products result from radical substitution in the quinone or hydroquinone derivatives.

Experimental

Materials

Alkylaluminium dichlorides were obtained from reactions of corresponding aluminium trialkyls with $AlCl_3$ and were distilled under reduced pressure. 2,6-Di-

---

* A similar radical reduction mechanism was recently proposed by Ashby and Goel for the reactions of dimesityl and mesitylphenyl ketones with alkylaluminium compounds [18].

chloro-1,4-benzoquinone, 2,5-dichloro-1,4-benzoquinone and 2,3,5-trichloro-1,4-benzoquinone were made as described by Ling [20]. Other quinones (commercial reagents) and $AlCl_3$ were purified by sublimation.

Procedure

The reactions were carried out under nitrogen in a vessel equipped with a stirrer and connected through a liquid seal to a burette. A toluene solution of quinone was prepared in the vessel, and a toluene solution of an organoaluminium compound or a nitromethane solution of $AlCl_3$ was then introduced with vigorous stirring. When reaction was complete, the mixture was treated with water or 1 *M* HCl and the organic and aqueous layers were separated. Both layers were concentrated and the products isolated from them as indicated below. In some cases the mixture was concentrated before hydrolysis and the product which separated was filtered off and subjected to further investigations.

Identification and isolation of products

Monoethers of 1,4-dihydroxyaromatic compounds

4-Ethoxyphenol. M.p. (petroleum ether) 63–64°C (lit. [21] 65–66°C). Anal. Found: C, 69.24; H, 7.26. $C_8H_{10}O_2$ calcd.: C, 69.56; H, 7.25%. ^1H NMR (CCl_4): $\delta(CH_3)$ 1.23; OCH_2, 3.78; OH, 4.28; H aromatic, 6.55 ppm. IR (KBr): ν(OH) 3370, ν(C–H) 2980, ν(C–C aromatic) 1610, 1518, ν(C–O) 1240 cm^{-1}.

4-n-Butoxyphenol. M.p. (petroleum ether) 48°C. Anal. Found: C, 72.36; H, 7.95. $C_{10}H_{14}O_2$ calcd.: C, 72.29; H, 8.43%. ^1H NMR (CCl_4): $\delta(CH_3)$ 0.93; CCH_2CH_2C, 1,23–1.83; OCH_2, 3.85; OH, 5.20; H aromatic, 6.68 ppm.

4-i-Butoxyphenol. M.p. (petroleum ether) 52–54°C. Anal. Found: C, 72.36; H, 7.95. $C_{10}H_{14}O_2$ calcd.: C, 72.29; H, 8.43%. ^1H NMR (CCl_4): $\delta(CH_3)$ 0.98; CH, 1.89; OCH_2, 3.57; OH, 4.65; H aromatic, 6.57 ppm.

4-Ethoxytetrachlorophenol. M.p. (hexane) 88–89°C. Anal. 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%. ^1H NMR (benzene): $\delta(CH_3)$ 1.12; OCH_2, 3.30; OH, 4.70 ppm. IR (KBr): ν(OH) 3380, ν(C–H) 2985, 2940, 2920, ν(C–OH) 1390, ν(C–C–O) 1210, ν(C–Cl) 715 cm^{-1}.

4-n-Butoxytetrachlorophenol. M.p. (pentane) 52–53°C. Anal. Found: C, 39.57; H, 3.25. $C_{10}H_{10}Cl_4O_2$ calcd.: C, 39.49; H, 3.32%. ^1H NMR (CCl_4): $\delta(CH_3)$ 0.98; CCH_2CH_2C, 1.37–1.94; OCH_2, 3.88; OH, 5.73 ppm.

4-Ethoxytetramethylphenol. M.p. (CH_3OH/H_2O) 118–120°C. MS: $M = 194$, $M - C_2H_4$ 166, $M - C_2H_5CH_3$ 151. ^1H NMR (CCl_4): $\delta(CH_3{-}CH_2)$ 1.36; CH_3, 2.12; OCH_2, 3.66 ppm. IR (KBr): ν(OH) 3395, ν(C–H) 2920, ν(C–OH) 1245 cm^{-1}.

2,5-Dichloro-4-ethoxyphenol. M.p. (petroleum ether) 56–58°C. Anal. Found: C, 46.35; H, 3.89; Cl, 33.65. $C_8H_8Cl_2O_2$ calcd.: C, 46.30; H, 3.87; Cl, 34.29%. ^1H NMR (CCl_4): $\delta(CH_3)$ 1.39; CH_2, 3.95; OH, 5.21; H aromatic, 6.71, 6.92.

3,5-Dichloro-4-ethoxyphenol. M.p. (hexane) 99–101°C. Anal. Found: C, 46.83; H, 4.04; Cl, 33.93. $C_8H_8Cl_2O_2$ calcd.: C, 46.30; H, 3.87; Cl, 34.29%. ^1H NMR (CCl_4): $\delta(CH_3)$ 1.40; OCH_2, 4.02; OH, 5.51; H aromatic 6.70 ppm. In order to find which of the two possible isomers (2,6- or 3,5-dichloro) was isolated from the reaction with 2,6-dichloro-*p*-benzoquinone, the ^1H NMR spectra of a sodium salt of the product and sodium salt of 2,5-dichloro-4-ethoxyphenol were recorded. The formation of a salt is known to cause a considerably greater chemical shift for protons bonded at the *ortho* than at the *para* with respect to the OH groups [22,23]. For 2,5-dichloro-4-ethoxyphenol those shifts are −0.48 and −0.13 ppm, respectively, and the isolated isomer shift is −0.61 ppm. Thus it is assumed that the hydrogens in the ring are *ortho* to the OH group.

2,3,5-Trichloro-4-ethoxyphenol and 2,3,6-trichloro-4-ethoxyphenol (mixture of isomers). M.p. (pentane) 41.5–53.5°C. Anal. Found: C, 38.15; H, 2.89; Cl, 44.92. $C_8H_7Cl_3O_2$ calcd.: C, 39.79; H, 2.92; Cl, 44.04%. ^{1}H NMR (CCl_4): $\delta(CH_3)$ 1.43; OCH_2, 3.93; OH, 5.59; H aromatic, 6.71, 6.91 (1/4 mol ratio). The difference in chemical shift between the stronger aromatic signal of the ether and that of its sodium salt in DMSO is −0.50 ppm.

1-Ethoxy-4-hydroxynaphthalene. M.p. (hexane) 92–94°C, (lit. [24] 90°C). Anal. Found: C, 75.71; H, 5.31. $C_{12}H_{12}O_2$ calcd.: C, 76.59; H, 6.30%. ^{1}H NMR ($CDCl_3$): $\delta(CH_3)$ 1.45; OCH_2, 4.08; H aromatic, 6.59, 7.43, 8.79 ppm. IR (KBr): ν(OH) 3250, ν(C–H) 2900, ν(C–C–O) 1280 cm^{-1}.

The above compounds were isolated by crystallization from hexane of the residue after concentration of the organic layer (in the case of derivatives containing chlorine atoms) or by washing of the organic layer with aqueous NaOH followed by separation of the water layer and acidification of it with aqueous HCl and extraction with ethyl ether. The yields of monoethers obtained from the reactions of 1,4-benzoquinone, 1,4-naphthoquinone and of 2,3,5-trichlorobenzoquinone were determined from the ^{1}H NMR spectra of the product mixtures.

Dihydroxyaromatic compounds

Hydroquinone. M.p. (CCl_4/CH_3OH) 170°C (lit. [25] 172°C). IR (KBr): ν(OH) 3370, ν(C–C aromatic) 1525, 1475, ν(C–O) 1200 cm^{-1}.

2,3,5,6-Tetrachlorohydroquinone. M.p. (benzene) 235–236°C (lit. [26] 236°C). Anal. 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%. IR (KBr): ν(OH) 3390, ν(C–O–H) 1415, ν(C–O) 1205, ν(C–Cl) 710 cm^{-1}.

2,3,5,6-Tetramethylhydroquinone. M.p. (C_2H_5OH) 229–233°C (lit. [27] 234–235°C). Anal. Found: C, 72.37; H, 8.43. $C_{10}H_{14}O_2$ calcd.: C, 72.43; H, 8.43%. ^{1}H NMR (1,4-dioxane): $\delta(CH_3)$ 2.12; OH, 6.09 ppm. IR (KBr): ν(OH) 3400, ν(C–H) 2950, ν(C–C–O) 1375, 1320, ν(C–O–H) 1325 cm^{-1}.

2,5-Dichlorohydroquinone. M.p. (benzene) 166–168°C (lit. [28] 166°C). Anal. Found: C, 40.16; H, 2.39; Cl, 38.30. $C_6H_4Cl_2O_2$ calcd.: 40.70; H, 2.26; Cl, 40.13%. ^{1}H NMR ($CDCl_3$): δ(H aromatic) 7.06; OH, 7.29 ppm. IR (KBr): ν(OH) 3350, ν(C–C–O) 1305, ν(C–O–H) 1205, 1180, ν(C–Cl) 700 cm^{-1}.

2,6-Dichlorohydroquinone. M.p. (toluene) 158–160°C (lit. [29] 157–158°C). Anal. Found: C, 40.51; H, 2.43; Cl, 38.72. $C_6H_4Cl_2O_2$ calcd.: C, 40.70; H, 2.26; Cl, 40.13%. ^{1}H NMR ($CDCl_3$): δ(H aromatic) 6.80; OH, 7.21 ppm. IR (KBr): ν(OH) 3250, ν(C–C–O) 1340, 1305, ν(C–O–H) 1200, ν(C–Cl) 685 cm^{-1}.

2,3,5-Trichlorohydroquinone. M.p. (toluene) 209°C. Anal. Found: C, 32.07; H, 1.49; Cl, 48.46. $C_6H_3Cl_2O_2$ calcd.: C, 33.76; H, 1.42; Cl, 49.82%. IR (KBr): ν(OH) 3387, ν(C–C–OH) 1407, ν(C–O) 1306, 1202, ν(C–Cl) 706 cm^{-1}.

1,4-Dihydroxynaphthalene. M.p. (toluene) 176–177°C (lit. [25] 176°C), diacetate m.p. 126–128°C (lit. [25] 128–130°C).

Dihydroxyaromatic compounds separate during hydrolysis of the initial product mixture. Small amounts of them can also be isolated by extraction of the water layer with ethyl ether, and something appears during concentration of the organic layer.

Dichloroaluminium salt of semi-p-benzoquinone (III). Black powder, m.p. ~ 145°C. Anal. Found: Al, 7.89; Cl (inorganic), 21.46. $C_6H_5O_2AlCl_2$ calcd.: Al, 7.85; Cl (inorganic), 20.63%. The above compound was obtained from the reaction of $AlCl_3$ with *p*-chloranil in the 2/1 mol ratio in a mixture of toluene and nitromethane. It separated out during concentration of the product mixture. At lower mol ratio halide (or alkylaluminium dichloride)/quinone, the radical contains some *p*-chloranil impurities (15–20 mol%). IR spectra were recorded as a Nujol mull, in CH_2Cl_2 and in KBr pellets.

Bis(dichloroaluminium) salt of 2,3,5,6-tetrachlorohydroquinone. Anal. Found: Al, 12.53; Cl (inorganic), 33.15. $C_6Cl_4O_2Al_2Cl_4$ calcd.: Al, 12.23; Cl (inorganic), 32.11%. IR (Nujol mull or CH_2Cl_2): ν(C–C aromatic) 1602, 1493; ν(C–O–Al) 1415, ν(C–Cl) 695 cm^{-1}. The above compound was obtained from the reaction of III with $EtAlCl_2$ in toluene and from that of 2,3,5,6-tetrachlorohydroquinone with $EtAlCl_2$.

TMBQ · 2 $AlCl_3$ complexes. Anal. Found: Al, 12.32 and 12.68. $C_{10}H_{12}O_2Al_2Cl_6$ calcd.: Al, 12.53%. These complexes were isolated from the reaction of $AlCl_3$ and TMBQ used in 1/1 and 2/1 mol ratios in a toluene and nitromethane mixture. After removal of the solvents, the residue was extracted with toluene to separate the complexes from the unreacted $AlCl_3$. The complexes were extracted from the toluene solution with heptane.

4-t-Butyltoluene was distilled from the toluene layer after washing with NaOH, and was identified by GLC and ^1H NMR spectroscopy.

Acknowledgement

The authors thank the Polish Academy of Sciences for financial support within the scientific programme MR.I.12.

References

1 Z. Florjańczyk, W. Kuran, S. Pasynkiewicz and G. Kwas, J. Organomet. Chem., 112 (1976) 21.
2 Z. Florjańczyk, W. Kuran, S. Pasynkiewicz and A. Kraśnicka, J. Organomet. Chem., 145 (1978) 21.
3 G.A. Abakumov, E.S. Klimov and G.A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 1827.
4 G.A. Abakumov and E.S. Klimov, Dokl. Akad. Nauk SSSR, 202 (1972) 827.
5 G.A. Abakumov, E.S. Klimov, V.V. Ershov and I.S. Belostotskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 927.
6 G.A. Abakumov and E.S. Klimov, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 1199.
7 G.A. Razuvaev, G.A. Abakumov, E.S. Klimov, E.N. Gladyshev and P.Ya. Bayshkin, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 1128.
8 P.E. Barker, A. Hudson and R.A. Jackson, J. Organomet. Chem., 208 (1981) C1.
9 A.G. Davies, Z. Florjańczyk, E. Lusztyk and J. Lusztyk, J. Organomet. Chem., 229 (1982) 215.
10 A. Alberola, A.M. Gonzalez Nogal, J.A. Martinez de Ilarduya and F.J. Polido, An. Quim. Ser. C, 78 (1982) 166.
11 E. Briegleb, Angew. Chem., 76 (1964) 326.
12 A. Alberola, A.M. Gonzalez Nogal and J.A. Martinez de Ilarduya, An. Quim. Ser. C, 73 (1977) 1227.
13 A. Girlando, I. Zanon, R. Bozio and C. Pecile, J. Chem. Phys., 68 (1978) 1.
14 E. Müller, P. Ziemek and A. Rieker, Tetrahedron Lett., (1964) 207.
15 K.B. Starowieyski, S. Pasynkiewicz and A. Sporzyński, J. Organomet. Chem., 117 (1976) 117.
16 P.A. Kollman and L.C. Allen, Chem. Rev., 72 (1972) 283.
17 Z. Latajka, H. Ratajczak and K. Romanowska, J. Organomet. Chem., 131 (1977) 347.
18 E.C. Ashby and A.B. Goel, J. Organomet. Chem., 221 (1981) C15.
19 Z. Florjańczyk, W. Kuran and E. Lusztyk, Makromol. Chem., 181 (1980) 2279.
20 A.R. Ling, Soc., 61 (1892) 558.

21 E. Klarmann, L.W. Gatyas and V.A. Shternov, J. Am. Chem. Soc., 54 (1932) 298.
22 J.M. Brown, Tetrahedron Lett., 32 (1964) 2215.
23 T. Bisanz and P. Szczeciński, Roczniki Chem., 49 (1973) 1615.
24 Russig, J. Praktische Chemie, [2] 62 (1900) 52.
25 CRC Handbook of Tables for Organic Compounds Identification, CRC Press, Cleveland 3rd ed. 1976.
26 Beilstein Handbuch der Organischen Chemie, Springer Berlin 1923, Vol. VI, p. 851.
27 J.M. Snell and A. Weissberger, J. Am. Chem. Soc., 61 (1939) 453.
28 S. Levy and G. Schultz, Ann. Chem., 210 (1881) 148.
29 A. Faust, Ann. Chem., 149 (1869) 155.