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OXIDATION OF DISUBSTITUTED SILICON-CONTAINING PHENOLS

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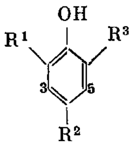
Despite the substantial number of papers devoted to the oxidation of phenols, the reactivity of disubstituted phenols with organosilicon substituents in the aromatic ring and the products formed by their oxidation have received little study. Only some information exists on the reactivity of disubstituted silicon-containing phenols when reacted with organomercury compounds [1].

The oxidation of disubstituted silicon-containing phenols (I), which are analogs of the 2,4- and 2,6-di-tert-butylphenols, by alkaline potassium ferricyanide was studied in the present paper. The effect of O_2 on this process was also studied.



(Ia—c)

R^1=$Si(CH_3)_3$, R^2=$C(CH_3)_3$, R^3=H (a); R^1=R^2=$Si(CH_3)_3$, R^3=H (b); R^1=R^3=$Si(CH_3)_3$, R^2=H (c).

Phenoxyl radicals, generated by the one-electron oxidation of dialkylphenols with free o- or p-positions, usually dimerize with the formation of C−C or C−O bonds. Thus, from 2,4-dialkylphenols are formed dimers with a C−C bond between the o-C atoms of the phenoxyls [2], while from 2,6-dialkylphenols are formed dimers with a C−C bond between the p-C atoms. Here coupling at the C−C bonds leads to substituted diphenoquinones, while coupling at the C−O bonds leads to polyphenyl ethers [3-5].

When phenol (Ia) is oxidized in an inert atmosphere, the first to be formed is dihydroxydiphenyl (IIa), which is then converted to two products. These products correspond to the dihydroxydiphenyl dimers, contain organosilicon fragments, and their IR spectra have a band that is characteristic for the OH group (3550 cm^{-1}). As a whole, their structure could not be ascertained. The oxidation of (Ia) in the presence of O_2 leads to spiroketals (IIIa) and (IVa), and also to a small amount of the oxidation products of dihydroxydiphenyl (IIa).

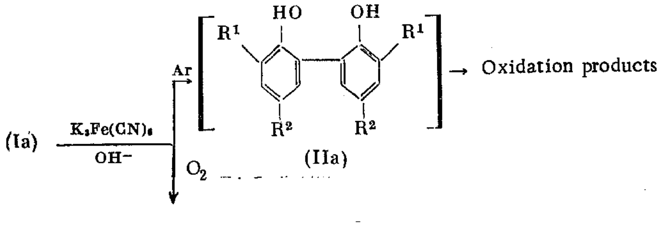


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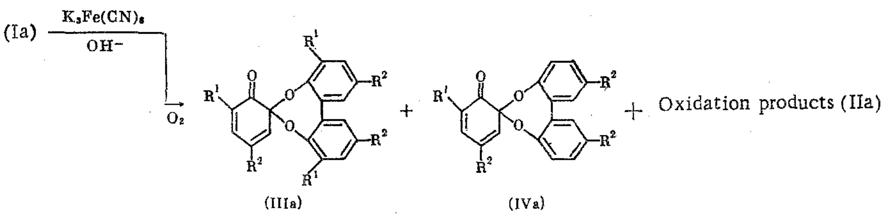
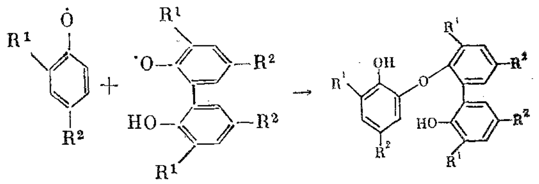
TABLE 1. PMR Spectra of Starting Compounds

Compound	δ, ppm						SSCC, Hz		
	3-H	4-H	5-H	6-H	R^1	R^2	$J_{3,4}$	$J_{3,5}$	$J_{5,6}$
(Ia)	7,29	–	7,14	6,51	0,24	1,20	–	2,5	8,5
(Ib)	7,40	–	7,28	6,56	0,21	0,14	–	1,7	8,0
(Ic)	7,31	6,89	7,31	–	0,29	–	7,60	–	–



(IIIa) (IVa)

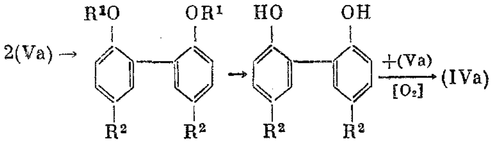
The structure of the preparatively isolated (IIIa) and (IVa) was confirmed by the elemental analysis data, molecular weight, IR and PMR spectra, and reduction by $LiAlH_4$. Spiroketals are formed by the reaction of the phenoxyl radicals that are obtained from the starting phenol and intermediate dihydroxydiphenyl [6]. A similar mechanism is probably realized in the formation of spiroketals (IIIa) and (IVa).



(Va)

Spiroketal (IIIa) is isolated in higher yield (~ 75%) when a mixture of (Ia) and (IIa) is oxidized, which confirms the mechanism of its formation by the above given scheme.

Spiroketal (IVa) is obtained the same as (IIIa), but a characteristic trait of organosilyl-substituted phenols appears in the given case, which consists in the dimerization of the formed phenoxyls with simultaneous migration of the triorganosilyl group from the o-positions of the aromatic ring to the oxygen of the phenoxyl [7]. The formed disiloxydiphenyl is hydrolyzed under the reaction conditions to alkyldihydroxydiphenyl (VIa). The subsequent oxidation of (VIa) in the presence of (Va) leads to spiroketal (IVa).



(VIa)

As a result, in the presence of O_2, besides the oxidation products of dihydroxydiphenyl (IIa), the silicon-containing spiroketals, the products of the simultaneous coupling of the formed phenoxyls at the C–C and C–O bonds, were isolated.

The insertion of a second $(CH_3)_3Si$ group in the p-position has a noticeable effect on the direction of the oxidation. Employing liquid adsorption chromatography (LAC), we were able to isolate two types of compounds in the oxidation of phenol (Ib). On the basis of the elemental analysis data, molecular weight, and the IR and PMR spectra, we proposed the structures of phenylene oxides for compounds (VIIb) and (VIIIb), and the structure of a spiroketal for compound (IVb).

Small amounts of compounds with a lower Si content were also found, whose IR spectra resembled those of (VIIb) and (VIIIb). These compounds are probably also phenylene oxides, which are formed by the oxidation of phenol (Ib) and 4-trimethylsilylphenol. The latter is obtained from (Ib) by the migration of its o-$(CH_3)_3Si$ group to the oxygen of the phenoxyl and subsequent hydrolysis of the phenoxysilane. The compounds with a low

TABLE 2. Oxidation Products of Phenols (Ia-c) in Presence of O_2

Oxidation product	Yield, %	Color of product	mp, °C	Found / Calculated				Empirical formula	Infrared spectrum (ν, cm^{-1})		PMR spectrum (δ, ppm)	
				C, %	H, %	Si, %	mol. wt.					
(IIIa)	55	Light pink	112–114	70,73 / 70,84	9,23 / 9,14	12,51 / 12,74	659 / 663	$C_{39}H_{60}Si_3O_3$	850, 1250 1125 1665 1590, 3030	($(CH_3)_3Si$) (Si–Ph) (C=O) (Ph)	$(CH_3)_3C/(CH_3)_3Si$=1/1	
(IVa)	23	Light brown	142–145	74,29 / 76,68	8,82 / 8,58	6,02 / 5,43	560 / 517	$C_{33}H_{44}SiO_3$	850, 1250 1125 1660 1590, 3030	$(CH_3)_3Si$ (Si–Ph) (C=O) (Ph)	$(CH_3)_3C/(CH_3)_3Si$=3/1	
(IVb)	14	Light yellow	66–68	63,66 / 63,79	8,28 / 7,90	19,97 / 19,90	571 / 564	$C_{30}H_{44}Si_4O_3$	845, 1250 1125 1665 1590, 3030	$(CH_3)_3Si$ (Si–Ph) (C=O) (Ph)		
(VIIb)*	40	Light brown	84–86	62,37 / 62,06	8,50 / 8,50	21,69 / 21,94	672 / 640	$C_{33}H_{54}Si_5O_3$	845, 1250 1125 1590, 3030 3550	$(CH_3)_3Si$ (Si–Ph) (Ph) (OH)	$(CH_3)_3Si$ CH	0,25 s (18H) 0,32 s (9H) 0,34 s (9H) 0,35 s (9H) 6,7–7,8 m (8H)
(VIIIb)*	23	Brown	98–100	62,41 / 62,78	8,18 / 8,28	20,82 / 20,97	875 / 804	$C_{42}H_{66}Si_6O_4$	845, 1250 1125 1590, 3030 3550	$(CH_3)_3Si$ (Si–Ph) (Ph) (OH)	$(CH_3)_3Si$ CH	0,25 s (18H) 0,31 s (9H) 0,32 s (9H) 0,34 s (9H) 0,35 s (9H) 6,7–7,8 m (11H)
(IXc)	92	Reddish violet	220–221	61,04 / 60,94	8,67 / 8,53	23,43 / 23,75	463 / 473	$C_{24}H_{40}Si_4O_2$	845, 1245 1125 1590	$(CH_3)_3Si$ (Si–Ph) (C=O)	$(CH_3)_3Si$ CH	0,16 s (36H) 8,00 (4H)

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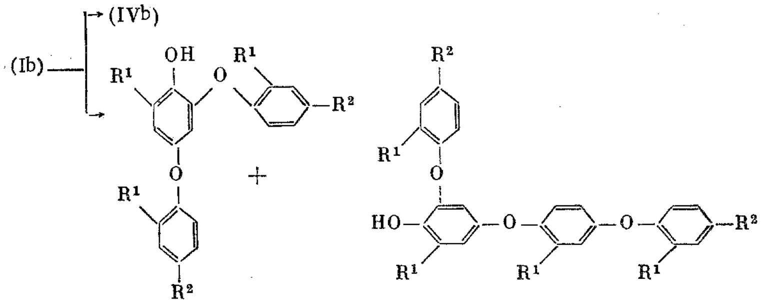
* The PMR spectra were taken in Me_2CO solution.

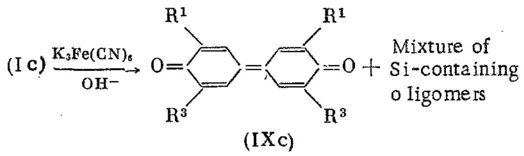


(VIIb) (VIIIb)

Si content are possibly also formed by the common oxidation of phenol (Ib) and 4,4'-bistrimethylsilyldihydroxydiphenyl, which is obtained from (Ib) in the same manner as (VIa). O_2 has practically no effect on the process for the oxidation of (Ib).

Phenol (Ic) is an analog of 2,6-di-tert-butylphenol. Differences in their oxidation products can be due to a distinctive trait of the Si−C chemical bond, which is determined by three factors: The lower electronegativity of silicon, its inability to form a double bond, and the presence of unfilled d orbitals on Si.

The results of oxidizing phenol (Ic) show that two competing reactions also proceed in this case, which lead to the C−C and C−O coupling products of the phenoxyls formed in the reaction.



(IXc)

The oxidation of (Ic) in an inert atmosphere gave the Si-containing diphenoquinone (IXc) in ~45% yield, and also a dark brown resin, which represents a mixture of oligomers of the phenylene oxide type. However, a low Si content in all of the preparatively isolated fractions indicates that the ability of the $(CH_3)_3Si$ group to migrate from the o-position of the aromatic ring to the phenoxyl oxygen is also retained in the oxidation of phenol (Ic). Subsequent hydrolysis of the phenoxysilane formed in the reaction leads to 2-trimethylsilylphenol with the loss of one $(CH_3)_3Si$ group. This is probably followed by the common oxidation of phenol (Ic) and 2-trimethylsilylphenol. When (Ic) is oxidized in the presence of O_2, the equilibrium of the reaction is shifted toward the formation of diphenoquinone (IXc) (~ 92% yield).

EXPERIMENTAL

Phenols (Ia-c) were synthesized by a modification of the methods given in [8-10]. The oxidation of the phenols was run at 20°C in an argon atmosphere, in the presence of O_2, using alkaline $K_3Fe(CN)_6$ solution. The reaction products were isolated and purified employing LAC. The compounds were identified via IR and PMR spectroscopy, molecular weight determination (cryoscopically in benzene), and elemental composition. The IR spectra were obtained on a UR-20 spectrophotometer, and the PMR spectra were obtained on a Tesla BS-487C spectrometer (80 MHz), using either CH_2Cl_2 (δ, 5.20 ppm) or $(CH_3)_2CO$ (δ 2.08 ppm) as the internal standard and solvent (Table 1).

Oxidation of Phenols (Ia-c). With vigorous stirring, to 5 g of $K_3Fe(CN)_6$ in 40 ml of 2 N KOH solution was added in 0.5 h a solution of 1 g of the phenol in 10 ml of benzene. The reaction was run until the color of the reaction mixture ceased to change (5-6 h), after which the organic layer was separated from the aqueous layer. The latter was extracted with benzene, the extract was combined with the organic layer, the whole was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was separated into the components by LAC, using Al_2O_3 as the adsorbent and a set of successive eluants (hexane, benzene, methanol). The isolated products (Table 2) were purified by repeated chromatography.

2,2'-Bistrimethylsilyl-4,4'-di-tert-butyldihydroxydiphenyl (IIa) was obtained as described in [11]; PMR spectrum (δ, ppm in CH_2Cl_2): 0.20 s (18H, $(CH_3)_3Si$), 1.18 s (18H, $(CH_3)_3C$), 7.12 d and 7.33 d (2H, CH, J= 2.6 Hz).

Reduction of (IIIa) with $LiAlH_4$. With stirring, to 0.5 g of (IIIa) in 60 ml of abs. ether was added an ether solution of $LiAlH_4$ (50 ml) and the mixture was left standing for a day. Then the mixture was poured into water, acidified with HCl solution, and extracted with ether. The extract was dried over $MgSO_4$, the ether was distilled off, and the residue was analyzed by GLC on a Tswett-4 chromatograph, equipped with a katharometer and a 100 × 0.3 cm stainless steel column packed with Silicone XE-60 deposited on Chezasorb AW, at temperatures of 180 and 220°, and using helium as the carrier gas. The reduction products were identified by comparing the retention times of the postulated components in the analyzed mixture and the pure compounds. In the reduction product were detected phenol (Ia) and dihydroxydiphenyl (IIa), which were preparatively isolated by LAC (using Al_2O_3 as the adsorbent and hexane and benzene as the eluants).

CONCLUSIONS

1. When disubstituted Si-containing phenols are oxidized in an inert atmosphere, the main directions of the transformations of the phenoxyls formed in the reaction, which are characteristic for their alkyl analogs, are retained. An increase in the number of trimethylsilyl groups and the presence of a Me_3Si group in the p-position of the aromatic ring enhances the tendency of the aroxyls formed in the oxidation to undergo C−O coupling with the formation of Si-containing phenylene oxides.

2. Phenoxyls, obtained by the oxidation of 2,4-disubstituted Si-containing phenols in the presence of O_2, exhibit the ability to undergo simultaneous coupling at the C−C and C−O bonds with the formation of Si-containing spiroketals. In the oxidation of 2,6-bistrimethylsilylphenol the equilibrium of the reaction is shifted toward the formation of the Si-containing diphenoquinone.

3. Phenoxyls, obtained by the oxidation of disubstituted Si-containing phenols, retain the ability to dimerize with simultaneous migration of the Me_3Si group from the o-position of the aromatic ring to the oxygen atom with the formation of tetrasubstituted disiloxydiphenyls.

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