REACTIONS OF OXIDATION OF STERICALLY HINDERED SILICON-CONTAINING PHENOLS IN THE PRESENCE OF MOLECULAR OXYGEN

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It is known that silicon-containing phenoxyl radicals of the 2-di-tert-butylphenoxyl type and the series 2,6-bis-(trimethylsilyl)-4-R-phenoxyls, where $R = CH(CH_3)_2$, $-C(CH_3)_3$, $-Si(CH_3)_3$, undergo a rearrangement in solutions of inert solvents free of oxygen, consisting of migration of the orthotrimethylsilyl group of the phenyl ring to the oxygen of the aroxyl [1, 2]. The final products of oxidation of silicon-containing phenols by PbO₂ and an aqueous alkaline solution of $K_3Fe(CN)_6$ are substituted siloxydiphenyls. The phenols enumerated above are analogs of the known sterically hindered 2,6-di-tert-butyl-4-R-phenols, the oxidation of which by one-electron oxidizing agents of the type of PbO₂, Ag_2O , $K_3Fe(CN)_6$ in the presence of oxygen has been rather well studied. For example, in the oxidation of 2,4,6-tri-tert-butylphenol, a substituted peroxide of 4,4'-bicyclohexadienone is formed [3]. Under the action of a number of other oxidizing agents (benzoyl peroxide, lead tetraacetate, oxygen in alkaline alcohol solution), ortho- and paraquinoid derivatives are obtained [4]. The action of one-electron oxidizing agents on 2,6-di-tert-butyl-4-methylphenol leads to oxidative dimerization [5].

We were interested in determining the peculiarities of the course of oxidation of silicon-containing sterically hindered phenols in the presence of oxygen by one-electron oxidizing agents and in studying their oxidation under catalytic conditions, since we showed earlier that the oxidation of shielded phenols by oxygen in the presence of a copper-pyridine catalyst proceeds specifically: there is a stripping of the alkyl substituents on the para-position and the formation of the corresponding substituted 1,4-benzoquinones [6].

For the oxidation we selected 2-trimethylsilyl-4,6-di-tert-butylphenol (I) and 2,6-bis(trimethylsilyl)-4-tert-butylphenol (II). In the oxidation of the phenols (I) and (II) by one-electron oxidizing agents in the presence of oxygen, two basic processes take place: 1) dimerization of the silicon-containing aroxyls formed during oxidation after their rearrangement, as was observed earlier in oxygen-free medium, and the production of substituted siloxydiphenols (IV); 2) oxidation of the silicon-containing aroxyls obtained, forming the corresponding peroxides of 4,4'-bis-cyclohexadienone, like the formation of peroxides of this type in the oxidation of 2,4,6-trialkyl-substituted sterically hindered phenols in the presence of oxygen



Of the oxidation products, we isolated and identified for the first time bis-(1-trimethylsilyl-3,5-ditert-butyl-2,5-cyclohexadiene-4-one) peroxide (IX). The peroxide (IX) is changed in air; it is thermally stable and decomposes at the melting point (128-130°). In the thermal decomposition of (IX) we isolated

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	Mp, °C	UV spec- trum, nm	IR spectrum (ν , cm ⁻¹)			
Compound			он	Si(CH ₃) ₃	Si—O—C	C=0
(111)	39	255		850 1250	_	1665
(IV)	134	· -		850	930 4097	
(\mathbf{V})	194	-	3495		-	100
(1A)	130	-		1255	-	1640 1665
(VII)	125		. —	850 1248	930 1092	·
(VIII)	147	-	3505	845		
(VI)	51	254		855 1243	_	1655

TABLE 1. Oxidation Products of Silicon-Containing Phenols

and identified the corresponding substituted 1,4-benzoquinone (III). A certain amount of (III) is also formed in the oxidation of silicon-containing phenols. The production of (III) can be explained by the action of the oxidative system ($K_3Fe(CN)_6 + OH^-$) on the peroxide (IX), which is confirmed by special experiments.

The oxidation of the phenols (I) and (II) in the presence of the copper-pyridine complex also leads to two reaction pathways:



Like the oxidation of (I) and (II) by one-electron oxidizing agents in oxygen-free solutions of inert solvents, under the conditions of catalytic oxidation, the corresponding free radicals are formed, which undergo a rearrangement, then leading to substituted dimer siloxydiphenols (IV) and (VII) with yields of 30 and 41%, respectively. In addition to the siloxydiphenyls (IV) and (VII), in the presence of a copper-pyridine catalyst, 2-trimethylsilyl-6-tert-butyl- (III) and 2,6-bis(trimethylsilyl)-1,4-benzoquinones (VI) are formed with yields of 51 and 34%, respectively, i.e., the tendency for shielded phenols to strip an alkyl substituent from the paraposition under conditions of catalytic oxidation is preserved. Substituted benzo-quinones (III) and (VI) were isolated for the first time and were identified by various methods (Table 1).

In addition to the compounds indicated above, in the oxidation of the phenol (II) a product was isolated representing a complex of the copper-pyridine catalyst with one of the oxidation products -2,6-bis-(trimethylsilyl)-1,4-benzoquinone – which agrees with the data of [7], obtained in the oxidation of β -naphthol in the presence of a copper-collidine complex.

Thus, in the oxidation of shielded silicon-containing phenols under catalytic conditions, specificity of the action of the copper-pyridine complex is also observed. Otherwise, we might have expected the formation of a silicon-containing peroxide of 4,4'-bis-cyclohexadienone.

EXPERIMENTAL METHOD

2-Trimethylsilyl-4,6-di-tert-butyl- and 2,6-bis-(trimethylsilyl)-4-tert-butylphenols were synthesized according to modified methods of [8, 9], according to [2].

The oxidation of silicon-containing phenols was conducted under mild conditions: atmospheric pressure, temperature 20-22°, oxidizing agents PbO_2 in benzene solution and an aqueous alkaline solution of $K_3Fe(CN)_6$; catalytic system: copper-pyridine complex (at a ratio of phenol to the catalyst of 10:1, 10:2, calculated on the basis of cuprous chloride). The copper-pyridine complex was produced according to the method of [6]. All the experiments were conducted in an atmosphere of oxygen.

The reaction products were identified on the basis of the IR and UV spectrometric data, elemental analysis, and the molecular weight. The separation of the mixture of oxidation products was performed by the method of adsorption chromatography, followed by a fine separation by gas-liquid chromatography.

Oxidation of 2-Trimethylsilyl-4,6-di-tert-butylphenol (I) by an Aqueous Alkaline Solution of Potassium Ferricyanide in the Presence of Oxygen. To a mixture of 2.5 g K₃Fe(CN)₆ in 10.0 ml benzene and 25.0 ml 2 N KOH we added dropwise a solution of 0.5 g (I) in 20.0 ml of benzene over a period of 5 h, passing a strong current of oxygen into the solution. The mixture was mixed for 3 h in a stream of oxygen until disappearance of the blue color. The organic layer was removed, washed with water, and dried over MgSO4. After the solvent was distilled off under vacuum, the reaction mixture was chromatographed on a column of Al₂O₃, eluent hexane. The mixture of products was distributed in the form of four adsorption layers. The first, narrow layer represented traces of an unidentified compound, the second 2,2'-bis-(trimethylsiloxy)--3,3',5,5'-tert-butyldiphenol (IV), the third the 1,4-benzoquinone (III), and the fourth the peroxide (IX). The peroxide (IX) is a white crystalline substance, mp 128-130° (from ethanol), readily soluble in hexane, benzene, and ether. During thermal decomposition (130°), a bright-yellow compound, identified as a 1,4benzoquinone (III) on the basis of the IR and UV spectra, is formed. Chromatography ("Tsvet-4") by comparison of the retention of this compound and an addition of the individual compound (III) confirms the spectroscopic results. The IR spectrum of the peroxide (IX) does not contain the absorption bands of the OH and Si - O - Ar groups, and the absorption bands of the trimethylsilyl group (850, 1255 cm⁻¹) and carbonyl group (1640 and 1665 cm⁻¹) are present. Found: C 69.68; H 10.20%; molecular wt. 566 (cryoscopically in benzene). C₃₄H₅₈Si₂O₄. Calculated: C 69.56; H 9.95%; molecular wt. 586. Yields on the basis of the reacted phenol: (IX) -56%; (III) -7%; (IV) -23%; (V) -7%.

Oxidation of 2,6-bis-(Trimethylsilyl)-4-tert-butylphenol (II) with Oxygen in the Presence of a Copper -Pyridine Complex. To a solution of the copper-pyridine complex, prepared by saturation of 0.2 g Cu_2Cl_2 in 50 ml of pyridine by oxygen, we added 2.9 g 2,6-bis-(trimethylsilyl)-4-tert-butylphenol. The mixture was shaken in a vessel connected to a gas burette, on a mechanical mixer, until the absorption of oxygen ceased. Pyridine was distilled off under vacuum, a resin remained upon addition of methanol to which, white crystals of the dimer product 2,2'-bis-(trimethylsiloxy)-3,3'-bis-(trimethylsilyl)-5,5'-di-tert-butyldiphenyl (VII) with mp 125-126° (from ethanol), precipitated; yield 1.7 g (41%); molecular wt. found 580, calculated 586 (see (Table 1). A mixed sample with (VII) produced by countersynthesis gave no depression of the melting point.

In the hydrolysis of (VII) with sodium methylate, 3,3'-bis-(trimethylsilyl)-5,5'-di-tert-butyl-2,2'dihydroxydiphenyl (VIII), mp 146-147°, was obtained. A mixed sample with (VIII) produced by countersynthesis (mp 145°) gave no depression of the melting point.

The mixture of products remaining after the separation of the crystals of (VII) was dissolved in hexane and chromatographed on a column with Al_2O_3 , eluents: hexane and benzene. The mixture of products was distributed in the form of four adsorption layers. The first of them consisted of traces of Cu_2Cl_2 , the third, narrow layer consisted of traces of an unidentified compound. The high melting product (mp above 250°, yield 25%) obtained after removal of the eluent of the second adsorption band, was a complex of the copper -pyridine catalyst with 2,6-bis-(trimethylsilyl)-1,4-benzoquinone. To identify it the mixture was treated with dilute HCl (1:5), the solution extracted with benzene and analyzed by gas-liquid chromatography.

The eluent used to elute the products of the fourth band was removed. The resinous compound remaining (0.8 g) was treated with methanol; the 1,4-benzoquinone (VI) was isolated, yield 34%. The method of preparative gas-liquid chromatography was used to obtain pure (VI). The mixture was separated on a "Tsvet-4" analytical chromatograph according to a method analogous to [10]. (VI) was identified by methods of IR and UV spectroscopy (see Table 2 [sic]). The benzoquinone (VI) was a yellow-orange crystalline compound with mp 50-51° crystallizing from alcohol, readily soluble in n-hexane and benzene. The data of elemental analysis and molecular weight (cryoscopically in benzene) are in good agreement with the calculated data. Found: C 57.47, H 8.08; Si 22.04%; molecular wt. 267. $C_{12}H_{20}Si_2O$. Calculated: C 57.08; H 8.00; Si 22.20% molecular wt. 252. The UV spectrum has an intense absorption band at 254 nm, which is in good agreement with the absorption maximum characteristic of the series of 2,6-substituted 1,4-benzoquinones described in [4].

Oxidation of 2-Trimethylsilyl-4,6-di-tert-butylphenol (I) by Oxygen in the Presence of a Copper-Pyridine Complex. To a solution of the copper-pyridine complex (0.2 g Cu₂Cl₂, 50 ml of pyridine) we added 1.1 g butyl phenol (I). The oxidation was conducted analogously to that described above. After the pyridine was distilled off under vacuum and the solid residue extracted with petroleum ether, the solvent was distilled off. The mixture of products remaining was chromatographed on a column with AI_2O_3 ; for quantitative measurements chromatography was conducted on a "Tsvet-4" analytical chromatograph under the conditions described earlier. The components of the mixture were identified by comparing the retention times of the presumed components in the mixture to be analyzed and the individual compounds, as well as by the addition of the individual compounds to the mixture. The following were isolated: the benzoquinone (III), yield 51%; the siloxydiphenyl (IV) 19%; and (V) 10%. Previously synthesized compounds 2-trimethylsilyl-4,6-di-tert-butylphenol, 3,3',5,5'-tetra-tert-butyldihydroxydiphenyl, 2,2'-bis-(trimethylsiloxy)-3,3',5,5'-tetra-tert-butyldihydroxydiphenyl, 2,2'-bis-(trimethylsilox)-3,3',5,5'-tetra-tert-butyldihyd

The benzoquinone (III) was identified by the methods of IR and UV spectroscopy, the data of elemental analysis and molecular weight (see Table 2). Found: C 66.15; H 8.60; Si 11.96%; molecular wt. 258. $C_{13}H_{20}$ · SiO₂. Calculated: C 66.05; H 8.52; Si 11.88%; molecular wt. 264.

The solid residue, insoluble in petroleum ether, was treated with HCl (1:5), and the solution was extracted with benzene and petroleum ether. The mixture remaining after removal of the solvent was chromatographed on a "Tsvet-4" chromatograph. The basic product in the mixture was 2-trimethylsilyl-6-tert-butyl-1,4-benzoquinone.

CONCLUSIONS

1. In the oxidation of shielded silicon-containing phenols by one-electron oxidizing agents in the presence of molecular oxygen, stable aroxyls are formed, which react further along two pathways: they are rearranged and dimerized, giving substituted siloxydiphenyls, and they are oxidized to the peroxide of 4,4'bicyclohexadienone.

2. Oxidation in the presence of a copper-pyridine catalyst is specific, consisting of stripping of an alkyl substituent from the para-position and the formation of substituted 1,4-benzoquinones. The second pathway of the process is dimerization of the rearranged aroxyls with the formation of siloxydiphenyls.

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