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

COMMUNICATION 2. OXIDATION OF MONO-, DI- AND TRISILICON-SUBSTITUTED PHENOLS

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The previously started [1, 2] oxidation of shielded phenols, containing trimethylsilyl (TMS) groups in different positions, was studied in the present paper. For the study we selected: 2-TMS-4,6-di-tert-butylphenol (I), 2,6-bis-TMS-4-tert-butylphenol (II), 2,4-bis-TMS-6-tert-butylphenol (III), 4-TMS-2,6-di-tert-butylphenol (IV), and 2,4,6-tris-TMS-phenol (V). The oxidative system was the copper–pyridine complex (CPC) in an O_2 atmosphere. The oxidation results for phenols (I)-(V) are given in Table 1. When the sterically hindered 2,4,6-trisubstituted phenols are oxidized with O_2 in the presence of CPC the formed phenoxyl radical either undergoes C–C dimerization, or oxidation with cleavage of the p-alkyl(alkoxy) substituent, or else it is oxidized to dimeric quinolide compounds [3, 4].

Two competing reactions take place when the silicon-containing shielded phenols are oxidized. One of them consists in the migration of the TMS group from the o-position of the formed phenoxyl to the oxygen and the formation of the substituted siloxybiphenyls (VII), (IX) and (X) (Table 1). The other reaction consists in the oxidation of the obtained phenoxyl radical to the silicon-containing 1,4-benzoquinones (VI), (VIII) and (XI). Consequently, the specificity of the action of the CPC, which is characterized by the cleavage of the substituent from the p-position, is also retained for the silicon-containing phenols.

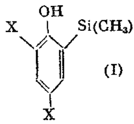
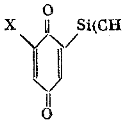
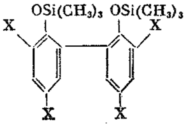
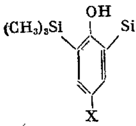
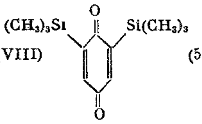
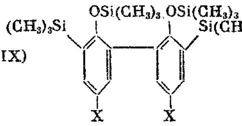
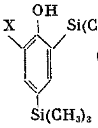
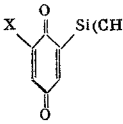
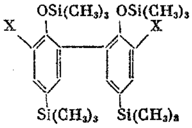
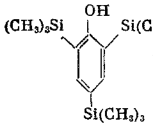
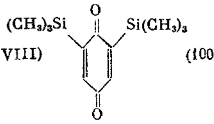
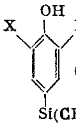
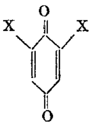
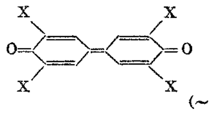
With increase in the number of TMS groups in the benzene ring the reaction for the formation of the 1,4-benzoquinone suppresses the rearrangement, the end product of which is the siloxybiphenyl. Thus, the oxidation of (I) gives 2-TMS-6-tert-butyl-1,4-benzoquinone (VI) in 51% yield, and siloxybiphenyl (VII) in 30% yield. The rearrangement of 2,4-bis-TMS-6-tert-butylphenoxyl, obtained by the oxidation of phenol (III), is suppressed by the competing formation of the 1,4-benzoquinone (VI), and the siloxybiphenyl (X) was isolated in low yield (0.4%). The rearrangement was not observed when (V) was oxidized under analogous conditions, and only the 2,6-bis-TMS-1,4-benzoquinone (VII) was obtained in quantitative yield (see Table 1). If the TMS group is found in the p-position of the shielded phenol (IV), the oxidation proceeds with cleavage of this group. The obtained unstable radical is dimerized to 3,3',5,5'-tetra-tert-butyldiphenoquinone (XII), since the 2,6-di-tert-butyl-1,4-benzoquinone (XI) was detected in traces.

The mentioned peculiarities in the oxidation of phenols (I)-(V) are associated with the action of O_2 in the presence of the CPC. A study was also made of the effect of O_2 on the oxidation of silicon-containing phenols when they were treated with one-electron oxidizing agents of the $K_3Fe(CN)_6$ type. Previously it was shown that when phenol (I), having one TMS substituent in the o-position, is treated with $K_3Fe(CN)_6$ the oxidation goes in two directions [1]. One of them is the rearrangement of the formed stable phenoxyls to the substituted siloxybiphenyl (VII), while the other is the oxidation of these radicals to bis(1-TMS-3,5-di-tert-butyl-2,5-cyclohexadien-4-one) peroxide (XIII).

In the present paper we oxidized phenols (II)-(V) with $K_3Fe(CN)_6$ in an O_2 atmosphere; the results obtained are given in Table 2.

Institute of Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2755-2760, December, 1972. Original article submitted June 21, 1971.

TABLE 1. Oxidation of Silicon-Containing Shielded Phenols with Oxygen in the Presence of Copper–Pyridine Complex X = $C(CH_3)_3$

Starting phenol	Reaction time,	Products obtained (yield, %)	
 (I)	6	(VI)  (51)	(VII)  (30) *
 (II)	7	(VIII)  (59)	(IX)  (41) *
 (III)	6	(VI)  (94)	(X)  (0,4)
 (V)	5	(VIII)  (100)	
 (IV)	1	(XI)  (traces)	(XIII)  (~100)

*From [2].

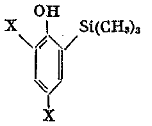
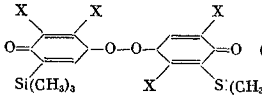
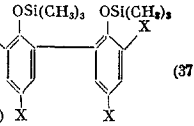
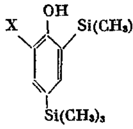
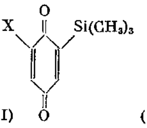
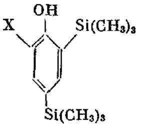
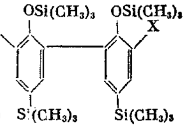
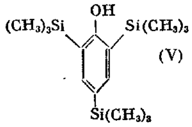
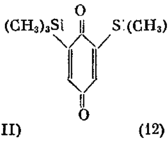
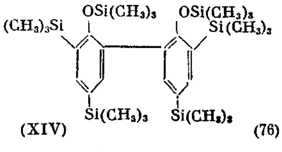
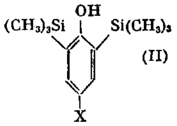
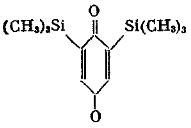
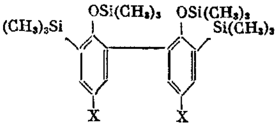
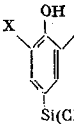
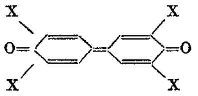
Competing reactions are observed when phenols (II) and (V) are oxidized. The predominant reaction is rearrangement of the TMS group from the o-position and the formation of siloxybiphenyls (XIV) and (IX), while the other isolated product is 2,6-bis-TMS-benzoquinone (VIII). It is possible to assume that a 4,4'-bis-cyclohexadienone peroxide of the (XIII) type is obtained as an oxidation result of the silicon-containing phenoxyl, which is unstable and decomposes under the oxidation conditions with the formation of (VIII).

The oxidation of the 2,4-bis-TMS-substituted phenol (III) proceeds practically in one direction, the rearrangement of the phenoxyls is suppressed, while the oxidation rate of the phenol is lower than that of the other phenols [(I), (II), (IV), (V)]. Phenol (III) is oxidized to the extent of 30% in 6 h, whereas the oxidation of (I), (II), (IV) and (V) is completely ended in this length of time. A study of the oxidation products of (III) by TLC disclosed that a cyclohexadienone peroxide is present in the mixture, which is responsible for the formation of benzoquinone (VI). The oxidation of phenol (IV), having a TMS substituent in the p-position, under the same conditions gives diphenoquinone (XII) in quantitative yield. As a result, the competition between the oxidation and the rearrangement of the formed silicon-containing phenoxyls in the presence of O_2 depends on the position of the TMS substituents in the benzene ring (Table 2).

EXPERIMENTAL METHOD

The silicon-containing phenols (II)-(V) were synthesized as described in [5]. The oxidation of the phenols was run at 20-21°C and atmospheric pressure using $K_3Fe(CN)_6$ solution, or in the presence of the CPC [4] (the ratio of the phenol to the catalyst was 10 : 1 when based on CuCl). All of the experiments were run in an O_2 atmosphere. The reaction products were identified by GLC and by IR and UV spectroscopy, and also by counter synthesis. The GLC analysis was run on a Tswett-4 chromatograph, equipped with a detector based on the heat conductivity. The 100 × 0.3 and 50 × 0.3 cm stainless steel columns were filled with Apiezon L (10%) deposited on Chromosorb W (80-100 mm), or with Thermol Q deposited on Shimalite A. The temperature was 200-230°, and the velocity of the carrier gas (helium) was 30 ml/min. The constants of the compounds obtained are given in Table 3.

TABLE 2. Oxidation of Silicon-Containing Shielded Phenols with Potassium Ferricyanide in Alkaline Medium in the Presence of Oxygen

Starting phenol	Reaction time, h	Products obtained (yield,%)
 (I)	6	 (XIII) (56)  (VII) (37)*
 (III)		 (VI)  (III)  (X)
	6	(VI) (30); (III) (70); (X) (traces)
	13	(VI) (70); (III) (24); (X) (traces)
	25	(VI) (91); (III) (8); (X) (traces)
 (V)	5	 (VIII) (12)  (XIV) (76)
 (II)	6	 (VIII) (3)  (IX) (88)
 (IV)	1	 (XII) (~100)

*From [1].

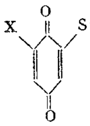
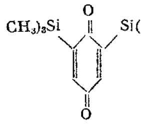
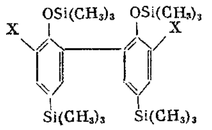
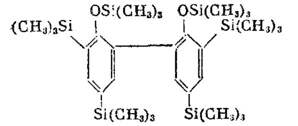
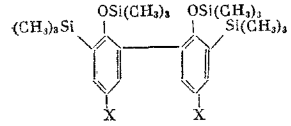
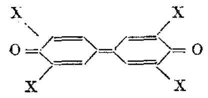
Oxidation of Phenol (III) in the Presence of Copper–Pyridine Complex. To a stirred solution of the CPC was added in drops a solution of 0.5 g of phenol (III) in benzene; after 6 h the pyridine was vacuum-distilled, the residue was extracted with ether, and the insoluble part was filtered. The filtrate was evaporated under reduced pressure, and the residual product was chromatographed on Al_2O_3. We isolated (VI) in 94% yield and (X) in 0.4% yield.

Oxidation of Phenol (IV) or (V) in the Presence of Copper–Pyridine Complex. A solution of 0.15 g of phenol (IV) in pyridine was added to a solution of the CPC, after which the reaction mixture was worked up as described above, in which connection diphenoquinone (XII) was isolated and traces of (XI) were detected. The oxidation of 0.6 g of phenol (V) gave quinone (VIII) in quantitative yield.

Oxidation of Phenol (III) with $K_3Fe(CN)_6$. With stirring, to 5 g of $K_3Fe(CN)_6$ in 40 ml of 2 N KOH solution was added in drops a solution of phenol (III) in 20 ml of benzene. The organic layer was separated from the aqueous layer, washed until neutral, dried over $MgSO_4$, evaporated in vacuo, and the residue was chromatographed on an Al_2O_3 column (using hexane as the eluant). Analysis of the reaction mixture by GLC disclosed that (VI) and (X) are present in ratios that depend on the reaction time (see Tables 2 and 3).

Oxidation of Phenols (II), (IV) and (V) with $K_3Fe(CN)_6$. The oxidation of 1 g of (II), followed by GLC analysis of the obtained mixture, disclosed the presence of (VIII) and (IX), the oxidation of 0.15 g of (IV) (30-60 min) gave (XII) in quantitative yield, while the oxidation of (V) gave (VIII) and (XIV).

TABLE 3. Oxidation Products of Silicon-Containing Shielded Phenols in the Presence of Oxygen

Oxidation product	Mp, °C	IR spectrum, ν, cm^{-1}			UV spectrum
		$Si(CH_3)_3$	Si—O—Ar	C=O	nm
 (VI)	39—40	850 1250	—	1660	255
 (VIII)	50—51	855 1213	—	1628 1650	255
 (X)	225	850 1240	928 1085	—	—
 (XIV)	139—140	850 1240	930 1095	—	—
 (IX)	125	845 1245	920 1090	—	—
 (XII)	240	—	—	1612 1645	400 418

CONCLUSIONS

1. When silicon-containing shielded phenols are oxidized with oxygen in the presence of the copper–pyridine catalyst the direction of the reaction that predominates with increase in the number of trimethylsilyl groups is oxidation to silicon-containing benzoquinones; both rearrangement and dimerization of the phenoxyls are practically suppressed.

2. In the presence of O_2 the stable silicon-containing phenoxyls that are formed by the action of one-electron oxidizing agents are then transformed along two routes: they are oxidized to cyclohexadienone derivatives or else they are rearranged to siloxybiphenyls.

LITERATURE CITED

1. G. A. Razuvaev, N. S. Vasileiskaya, L. V. Gorbunova, G. N. Chevkinova, and G. N. Bortnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2392 (1971).
2. G. N. Bortnikov, N. S. Vasileiskaya, L. V. Gorbunova, N. P. Nikulina, and Ya. I. Yashin, Izv. Akad. Nauk SSSR, Ser. Khim., 687 (1970).
3. L. V. Gorbunova, N. S. Vasileiskaya, M. L. Khidekel', and G. A. Razuvaev, Zh. Organ. Khim., 2, 1233 (1966); 2, 1236 (1966).
4. L. V. Gorbunova, O. N. Efimov, V. V. Karpov, G. A. Razuvaev, V. V. Turchaninov, and M. L. Khidekel', Transactions of the Conference on the Mechanism and Kinetics of Enzymatic Catalyst [in Russian], Nauka (1964), p. 227.
5. G. A. Razuvaev, N. S. Vasileiskaya, and D. V. Muslin, Dokl. Akad. Nauk SSSR, 175, 620 (1967); G. A. Razuvaev, N. S. Vasileiskaya, D. V. Muslin, N. N. Vavilina, and S. N. Uspenskaya, Zh. Organ. Khim., 6, 980 (1970); Y. D. Cooper, J. Org. Chem., 26, 925 (1961).