REACTION OF SHIELDED SILICON-CONTAINING PHENOLS WITH PEROXIDES

COMMUNICATION 2. REACTION WITH BENZOYL PEROXIDE

I. L. Khrzhanovskaya and N. S. Vasileiskaya

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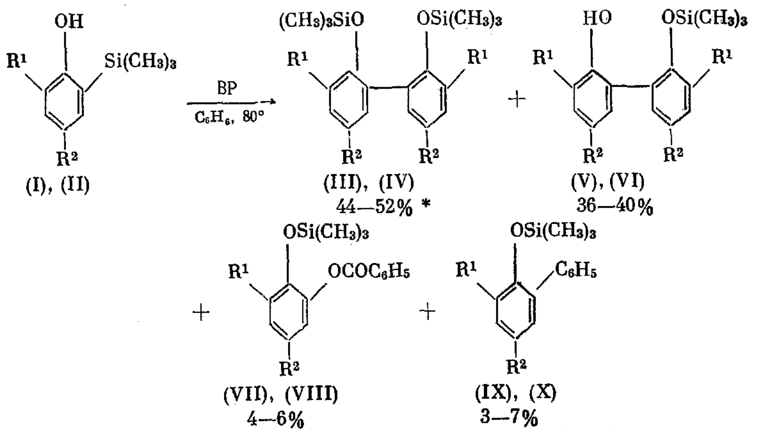
In the present paper, which is a continuation of our studies begun previously on the reactions of shielded silicon-containing phenols with peroxides [1], we studied the reaction of the 2-trimethylsilyl-4,6-di-tert-butyl- (I) and 2,6-bis(trimethylsilyl)-4-tert-butyl- (II) phenols with benzoyl peroxide (BP). The reactions of various mono-, di-, and tri-substituted phenols with BP were investigated previously [2-7], in which connection for the tri-substituted alkylphenols, which are carbon analogs of (I) and (II), the formation of quinol benzoates was observed [3, 6].

The reaction of phenols (I) and (II) with BP was run in benzene at 80° and a molar ratio of phenol : BP = 2 : 1.6. The reaction fails to go at a lower temperature (20 and 50°). The appearance of an intense blue color, which is characteristic for phenoxyls, indicates the radical mechanism of the process. The main transformation products of the phenol are the dimers: (III) and (IV), and (V) and (VI); the 2-trimethylsiloxy-3,5-disubstituted phenyl benzoates (VII) and (VIII), and the 2-phenyl-4,6-disubstituted phenoxytrimethylsilanes (IX) and (X), are found in small amounts (Table 1).



(1)

(I), (III), (V), (VII), (IX), (XI) $R^1 = R^2 = C(CH_3)_3$
(II), (IV), (VI), (VIII), (X), (XII); $R^1 = Si(CH_3)_3$, $R^2 = C(CH_3)_3$

Quinol benzoates, described for the carbon analogs, are not formed here (absorption bands at 1640-1670 cm^{-1} are absent in the IR spectrum, and at 230-250 nm in the UV spectrum). The disiloxybiphenyls (III) and (IV) are obtained via the dimerization of the phenoxyl radicals by the usual scheme [8]; the formation of dimers (V) and (VI) proceeds via secondary processes.

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* Based on reacted phenol.

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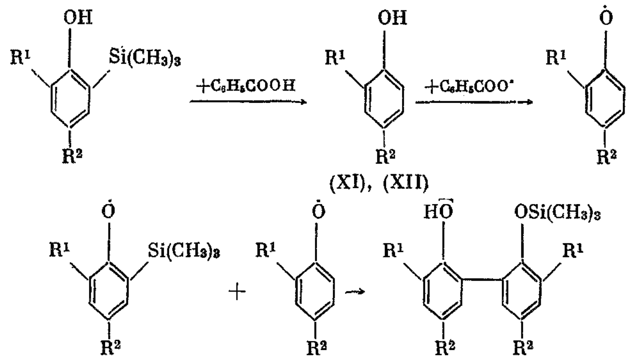
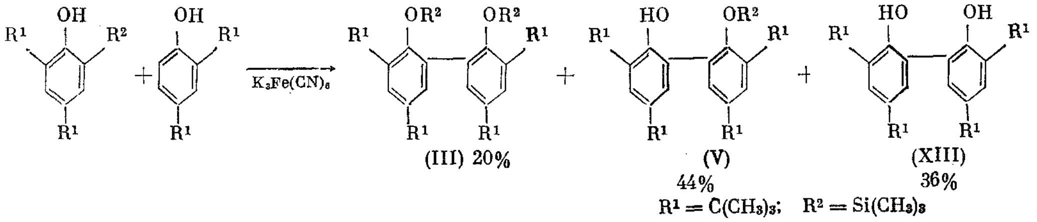


(2)

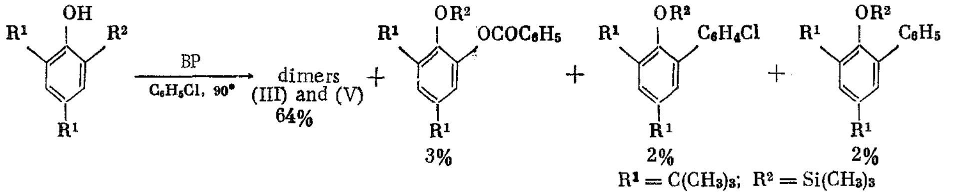
The formation of dimers (V) and (VI) can be assumed to proceed via the scheme of cleaving the O–Si bond in (III). However, our attempts to cleave this bond by treatment even with a large excess of benzoic acid proved unsuccessful (benzene used as solvent, and a temperature of 80°). The reactions that are indicated by Scheme (2) proceed easily, as was shown by us in special experiments. Thus, benzoic acid, similar to many inorganic acids, destroys the C_{Ar}–Si bond in silicon-containing phenols; disubstituted phenols are formed here. In the case of phenol (II) in benzene, at 80° and a phenol : C_6H_5COOH molar ratio = 1 : 1, the reaction goes to the extent of 40% in 20 h. As confirmation that the last step in the sequence of transformations depicted by Scheme (2) can take place is the formation of dimer (V) when a benzene solution of two phenols, namely the trisubstituted (I) and the disubstituted 2,4-di-tert-butylphenol (XI) (taken in a 1 : 1 ratio), is subjected to oxidation with potassium ferricyanide. Besides dimer (V), the usual products of the one-electron oxidation of phenols (I) and (XI), namely dimers (III) and (XIII), are formed in this reaction:



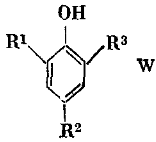
(3)

The reaction of phenols (I) and (II) with BP gave only traces of the disiloxybiphenyls (XIII) [cf. with 36% in reaction (3)]. This is explained by the fact that due to the low concentration of the disubstituted phenoxyls, corresponding to phenols (XI) and (XII) [see the corresponding reactions in Scheme (2)], their recombination with the phenoxyls from (I) and (II), the concentration of which is substantially greater, predominates over the dimerization of the phenoxyls from (XI) and (XII).

The formation of products (VII) and (VIII), and of (IX) and (X), in reaction (1) is associated with the characteristic ability of the o-$(CH_3)_3Si$ groups of phenoxyls to migrate to the oxygen atom, as a consequence of which the addition of the peroxide moieties (C_6H_5COO and C_6H_5) goes in the o-position of the ring. Compounds (IX) and (X) are also obtained due to reaction with an aromatic solvent [1], which is confirmed by running the reaction in chlorobenzene:

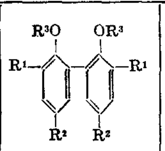
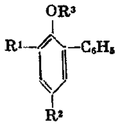
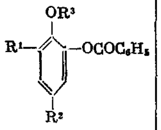
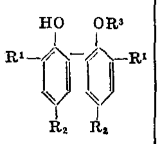


When phenols (I) and (II) are reacted with PB in benzene the amount of benzoic acid that is formed is equivalent to the amount of reacted phenol, i.e., this reaction is the main reaction for the dehydrogenation of the phenols. The phenyl radicals dehydrogenate the phenol to a very slight degree; as was shown by a determination of the benzene when the reaction was run in C_6H_5Cl, 0.80 M of C_6H_5COOH and 0.04 M of C_6H_6 are formed per mole of BP. When phenols (I) and (II) are reacted with BP the total amount of benzoate

TABLE 1. Reaction Products of 

with Benzoyl Peroxide (BP)

(80°, benzene; phenol : BP = 2 : 1.6; yield, M/M of reacted phenol)

Reaction products	$R^1=R^2=C(CH_3)_3$ $R^3=Si(CH_3)_3$	$R^1=R^3=Si(CH_3)_3$ $R^2=C(CH_3)_3$	Reaction products	$R^1=R^2=C(CH_3)_3$ $R^3=Si(CH_3)_3$	$R^1=R^3=Si(CH_3)_3$ $R^2=C(CH_3)_3$
	23 h	23 h		23 h	23 h
CO_2	0,66	0,63		0,22	0,26
C_6H_5COOH	0,95	0,83		0,07	0,03
$C_6H_5COOSi(CH_3)_3$		0,22		0,04	0,06
$C_6H_5—C_6H_5$	0,15	0,17	Starting BP	0,97	0,86
$C_6H_5COOC_6H_5$	Traces	Traces	$\frac{\text{Reacted phenol}}{\text{Starting phenol}} \times 100\%$	82%	88%
	0,18	0,20			

radicals corresponds to the total amount of BP: 1/2 [CO_2] + 1/2 [C_6H_5COOH + $C_6H_5COOSi(CH_3)_3$] + 1/2 [(VII), (VIII)] ≅ [starting peroxide*].

EXPERIMENTAL

Phenols (I) and (II) were obtained and purified as described in [1]. The BP was reprecipitated from $CHCl_3$ solution with methanol.

Reaction of Phenols (I) and (II) with Benzoyl Peroxide. In a typical experiment, a mixture of 0.004 mole of phenol (I) and 0.003 mole of BP in 15 ml of benzene was heated at 80° for 23 h in an argon stream. The evolved CO_2 was absorbed by alkali and was determined by the weight increase. The reaction was ended when iodometric titration disclosed the absence of peroxide. The benzoic acid was extracted with $NaHCO_3$ solution and determined gravimetrically after acidification and partial evaporation of the solution (0.003 M). Trimethylsilyl benzoate, $C_6H_5COOSi(CH_3)_3$, is easily hydrolyzed, for which reason this method gives the total amount of benzoic acid. We used GLC [1] for the separate determination of these components. The conditions for the determination of the C_6H_5COOH and $C_6H_5COOSi(CH_3)_3$ were: 0.5 m × 3 mm column filled with 10% Thermol 3 deposited on Shimalite B, 150°, He flow rate 30 ml/min, and internal standard = $C_6H_5 \cdot NO_2$. After removal of the C_6H_5COOH, the amounts of the other components in the reaction mixture, namely unreacted phenols (I) and (II), biphenyl, dimers (III), (IV) and (V), (VI), and products (VII), (VIII) and (IX), (X), were determined by GLC (see [1] for the analysis conditions). In order to identify the products we synthesized a number of the compounds.

$C_6H_5COOSi(CH_3)_3$. From 12.4 g of benzoic acid and 15 ml of $(CH_3)_3SiCl$ in triethylamine was obtained 12.2 g (61%) of $C_6H_5COOSi(CH_3)_3$, bp 110° (0.5 mm); n_D^{20} 1.4860. Found: C 62.41; H 7.25; Si 13.92%. $C_{10}H_{14} \cdot O_2Si$. Calculated: C 61.81; H 7.25; Si 14.45%.

2-Hydroxy-2'-trimethylsiloxy-3,3',5,5'-tetra-tert-butylbiphenyl (V). To 0.82 g of 2,2'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl (XIII) in 10 ml of benzene were added 0.5 ml of $(C_2H_5)_3N$ and 0.4 ml of $(CH_3)_3SiCl$. The course of the reaction was followed by taking samples and analyzing them by GLC. The starting (XIII) was not detected in the reaction mixture after 0.5 h at ~20° and heating at 80° for 15 min. The mixture was filtered from the precipitate, the solvent was removed, and the residue was recrystallized

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*The reaction was run until all of the BP was decomposed.

from ethanol. We obtained 0.60 g (60%) of (V) as a white crystalline compound, mp 155-157°. Found C 77.13; H 10.37; Si 5.42%. $C_{31}H_{50}O_2Si$. Calculated: C 77.12; H 10.44; Si 5.82%.

2-Trimethylsiloxy-3,5-di-tert-butylphenyl Benzoate (VII). a) Preparation of 2-Hydroxy-3,5-di-tert-butylphenyl Benzoate (XIV). To 2.22 g of 2,4-di-tert-butylcatechol, obtained as described in [9], in pyridine, at ~20°, was added 0.70 g of benzoyl chloride. The product was isolated in the usual manner and was dissolved in ethanol. The initial precipitate was 0.30 g of the difficultly soluble 2,4-di-tert-butylpyrocatechol dibenzoate, mp 186°. Found: C 78.33; H 6.96%. $C_{28}H_{30}O_4$. Calculated: C 78.11; H 7.02%. The mother liquor on cooling deposited 1.90 g (55%) of (XIV), mp 156°. Found: C 77.38; H 8.04%. $C_{21}H_{26}O_3$. Calculated: C 77.27; H 8.03%.

b) Preparation of (VII). From 0.49 g of (XIV), by reaction with 0.3 ml of $(CH_3)_3SiCl$ and 0.3 ml of $(C_2H_5)_3N$ in 10 ml of toluene, was obtained 0.45 g (75%) of (VII) as a white crystalline compound, mp 135-140° (from methanol). Found: C 72.35; H 8.46; Si 6.70%. $C_{24}H_{34}O_3Si$. Calculated: C 72.31; H 8.59; Si 7.05%. The purity of the obtained compounds was verified by GLC.

CONCLUSIONS

1. The reaction of shielded silicon-containing phenols (2-trimethylsilyl-4,6-di-tert-butylphenol and 2,6-bis(trimethylsilyl)-4-tert-butylphenol) with benzoyl peroxide in benzene at 80° leads to a dehydrogenation of the phenols with the formation of benzoic acid and phenoxyl radicals. The latter dimerize to give the corresponding disiloxybiphenyls.

2. The indicated phenols under the influence of benzoic acid form 2,4-disubstituted phenols, which react with a new molecule of the starting phenol to give the combined oxidation products, namely 2-hydroxy-2'-trimethylsiloxy-3,3',5,5'-tetrasubstituted biphenyls.

LITERATURE CITED

1. I. L. Khrzhanovskaya, N. S. Vasileiskaya, and G. A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim., 2276 (1972).
2. P. D. Bartlett and K. Nazaki, J. Amer. Chem. Soc., 69, 2299 (1947).
3. S. L. Cosgrove and W. A. Waters, J. Chem. Soc., 3189 (1949); 399 (1951).
4. T. Suehiro, J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zassi), 72, 301 (1951).
5. H. Unoue, O. Simamura, and K. Takamizawa, Bull. Chem. Soc. Japan, 35, 1958 (1962).
6. C. D. Cook and C. B. Depatie, J. Org. Chem., 24, 1144 (1959).
7. C. Walling and R. B. Hodgdon, J. Amer. Chem. Soc., 80, 228 (1958).
8. G. A. Razuvaev, N. S. Vasileiskaya, D. V. Muslin, N. N. Vavilina, and S. N. Uspenskaya, Zh. Organ. Khim., 6, 980 (1970).
9. H. H. Schulze and W. Flaig, Ann. Chem., 547, 231 (1952).