REACTION OF SHIELDED SILICON-CONTAINING PHENOLS

### WITH PEROXIDES

COMMUNICATION 1. REACTION WITH DI-tert-BUTYL PEROXIDE AND

## DICYCLOHEXYL PEROXYDICARBONATE

I. L. Khrzhanovskaya, N. S. Vasileiskaya, UDC 542.91:547.1'128 and G. A. Razuvaev

Previously we had studied the oxidation of some shielded silicon-containing phenols, and specifically of the 2-trimethylsilyl-4, 6-di-tert-butyl-(I), 2, 6-bis(trimethylsilyl)-4-tert-butyl-(II), and 2, 4, 6-tris(trimethylsilyl)-(III) phenols, employing inorganic oxidizing agents [1-3], like oxygen in the presence of copper -pyridine catalyst [4], and peroxy radicals, which are obtained in the liquid-phase oxidation of hydrocarbons [5].

Organic peroxides can be used as oxidizing agents for phenols. We studied the oxidation of siliconcontaining phenols employing two peroxides, namely di-tert-butyl peroxide (DTBP) and dicyclohexyl peroxydicarbonate (DCPC), the decomposition of which yields alkoxy radicals. The reaction of alkylated phenols with these peroxides was studied by a number of authors [6-10].

The purpose of the present study was to ascertain the effect of  $(CH_3)Si$  groups in the molecule of the shielded phenol on the oxidation of the latter by DTBP and DCPC.

The reaction of the silicon-containing phenols with peroxides was run in benzene at the decomposition temperature of the peroxide (respectively 125 and 60° for DTBP and DCPC), either in an argon atmosphere or in evacuated ampuls. The phenol : peroxide ratio in moles was 2:1. The results of the studies are given in Tables 1 and 2. The reaction between the silicon-containing phenols and DTBP proceeds slowly and at high temperature. From 36 to 47% of the starting phenol reacts in 20 to 30 h (see Table 1). With a phenol : peroxide ratio of 1:2 the fraction of reacted phenol increases (for (I) at a 2:1 ratio the amount of starting phenol that had reacted in 23 h was 36%, and 60% at a 1:2 ratio), but the yield of the transformation products of the phenol remains the same. The principal transformation products of phenols (I)-(III) when reacted with DTBP are substituted disiloxybiphenyls (IV)-(VI) and 2-methyl-4, 6-substituted phenoxytrimethyl-silanes (VII)-(IX). Disiloxybiphenyls (IV)-(VI) are the conventional products of the one-electron oxidation of phenols (I)-(III), while phenoxysilanes (VII)-(IX) are compounds that are obtained as the result of the phenol reacting with a fragment of the peroxide molecule. A good material balance when based on reacted phenol (see Table 1) indicates the absence of noticeable amounts of unidentified transformation products of the silicon-containing phenols



tert-Butyl alcohol was detected in the reaction mixture in an amount corresponding to the reacted phenol. This indicates that the tert-butoxy radicals, formed in the thermal decomposition of DTBP, cleave hydrogen

### \*Based on reacted phenol.

Institute of Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2276-2283, October, 1972. Original article submitted June 30, 1971.

• 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00. TABLE 1. Reaction of  $\mathbf{R}^{\mathbf{L}}$   $\mathbf{Si}(CH_3)_3$ 

with DTBP in Benzene at

Reaction products in	$R^1 = R^2 = C(CH_3)_3$	${f R^i=Si(CH_3)_3}\ {f R^2=C(CH)_3}$	R <sup>1</sup> =R <sup>2</sup> =Si(CH <sub>3</sub> ) <sub>3</sub>
mole/mole of react-	Re	eaction time, hou	irs
eu phenor	23	37	34.
CH3COCH3 *	1,17	0,93	1,11
(CH <sub>3</sub> ) <sub>3</sub> COH	1,20	0,93	1,11
$(CH_3)_3SIO OSI(CH_3)_3$ $R^1 \qquad \qquad$	0,28	0,43	0,27
R <sup>1</sup> CH <sub>3</sub> )s R <sup>1</sup> CH <sub>3</sub> R <sup>2</sup>	0,28	0,14	0,22
Starting DTBP, mole /mole of reacted phenol	1,38	1,07	1,11
Reacted pheno1 Starting pheno1 .100, %	36	47	45

125° Phenol: DTBP, 2:1

\*Total amount of acetone, present in the reaction mixture and obtained from the undecomposed DTBP during chromatographic determination.

from the hydroxyl group of the phenol, giving tert-butanol and the phenoxyl radical. It is known that  $(CH_3)_3C-O$  is capable of decomposing into acetone and the methyl radical. Since the latter actively cleaves hydrogen from hydrogen-containing compounds, then it could be assumed that the reaction proceeds with its involvement. However, the slight amount of methane and the substantial amount of tert-butyl alcohol that are formed indicates that it is the tert-butoxyl radicals that mainly cleave hydrogen from phenols (I)-(III). The total amounts of tert-butyl alcohol and acetone that are detected correspond to double the amount of starting peroxide.



Disiloxybiphenyls (IV)-(VI) are formed as the result of the dimerization of the phenoxyls, while compounds (VII)-(IX) are formed by their reaction with the methyl radical. The formation of products where a methyl group is inserted into the aromatic ring of a phenoxyl was observed earlier by Ingold [6] when 2, 6di-tert-butyl-4-methylphenol was reacted with DTBP; here the ortho-tert-butyl group is cleaved, giving isobutylene. In silicon-containing phenoxyls the specific effect of silicon is manifested in the ease with which the silyl group migrates to the oxygen, as a consequence of which the substituted phenoxysilanes (VII)-(IX) are formed in the reaction with the methyl radical.

At 125° the starting phenols undergo thermal rearrangement to the 2,4-disubstituted phenoxysilanes. By means of a special experiment is was shown by us that phenoxysilanes do not react with DTBP in benzene at  $125^{\circ}$ 

The reaction of silicon-containing phenols with DCPC proceeds under milder conditions (60°) and is characterized by a higher degree of conversion of the phenols when compared with the reaction using DTBP.



Reaction products, mole	R1=R2=C(CH3)3	${}^{{ m R}^{1}={ m Si}({ m CH}_{3})_{3}}_{{ m R}^{2}={ m C}({ m CH}_{3})_{3}}$	R <sup>1</sup> =R <sup>2</sup> =Si(CH <sub>3</sub> ) <sub>3</sub>
/mole of reacted phenol	Rea	action time,	hours
	24	20	. 22
CO2	1,28	Not deter- mined	Not determined
i-C <sub>6</sub> H <sub>11</sub> OH	1,11	1,00	1,07
C <sub>6</sub> H <sub>11</sub> OCOOC <sub>5</sub> H <sub>11</sub>	0,11	Traces	
(CH <sub>3</sub> ) <sub>3</sub> SiO OSi(CH <sub>3</sub> ) <sub>3</sub>			
$ \begin{array}{c c} R^1 & & R^1 \\ & & & \\ R^2 & R^2 \end{array} $	0,45	0,36	0,46
$\begin{array}{c c} \operatorname{OSi}(\operatorname{CH}_{\mathfrak{s}})_{\mathfrak{d}} \\ R^{\mathfrak{1}} & & C_{\mathfrak{e}}H_{\mathfrak{s}} \\ & & \\ &$	0,06	0,06	· _
Starting DCPC, mole	0,69	0,63	0,72
/mole of reacted phenol			
Reacted phenol			
Starting phenol	72	80	72

zene at 60° Phenol : DCPC, 2:1

Thus, for (I) the amount that reacts with DTBP in 23-24 h is 36% of the starting phenol, while wnen reaction is



with DCPC the amount is 72% (cf. Tables 1 and 2). Disiloxybiphenyls (IV)-(VI) are formed in a high yield as a reaction result. The phenoxyl radicals are present in the system in a greater concentration. This was confirmed by us by the EPR method and by the formation of a characteristic blue color of the solution.

The phenoxyls are formed as a result of the reactions given below, since the amount of liberated  $CO_2$  is equivalent to double the amount of the starting peroxide (the reaction was run until all of the peroxide had decomposed), while the cyclohexanol :phenol (reacted) ratio is close to one



The reaction mixture contains a small amount of the 2-phenyl-4, 6-substituted derivatives, and specifically phenoxytrimethylsilanes (X)-(XI), the formation of which can be explained by the reaction of the silicon-containing phenoxyls as the isomeric C-radical with the aromatic solvent, namely benzene, similar to the known reaction of aryl radicals with aromatic solvents [11].

actions	of $R^{i}$ $R^{i}$ $R^{i}$ with DTBP and DCPC $R^{2}$						
		Chara	acteristics of	column	Thermo-	Helium flow	
reroxide	keaction products	length,m	liquid phase	sorbent	perature, C	rate,m1 /min	Internal standard
DTBP	(сн. <sub>3</sub> ,сон сн. <sub>5</sub> сосн.	2,0	PEGA (7%)	INZ600	80	20	ì∽C₀H₁₂
	R <sup>1</sup> OSI(CH <sub>3</sub> ), OH R <sup>2</sup> B <sub>1</sub> SI(CH <sub>3</sub> ), R <sup>1</sup> OH R <sup>3</sup> R <sup>3</sup> R <sup>3</sup> R <sup>4</sup> SI(CH <sub>3</sub> ), R <sup>1</sup> OSI(CH <sub>3</sub> ), R <sup>4</sup> CH <sub>3</sub>	0,5	Thermol-3	Shimalite B	160	40	R OH
	R OH R OH R OH CH3	1,0	Apiezon L (10%)	Chromosorb W	230	90	R Not determined quantita- tively
	R (CH <sub>3</sub> ) <sub>3</sub> SIO OSI(CH <sub>3</sub> ) <sub>3</sub>	0,5	Thermol-3	Shimalite B	230	40	и он и и и и и и и и и и и и и и и и и и
DCPC	Ita Ita i-CaHııC	2,0	PEGA (7%)	INZ-600	160	30	Cumene
	R1 OH K1 SI(CH3)3 K2	0,5	Thermol-3	Shimalite B	180	30	R OSH(CH4), R
	$\begin{array}{c} OSI(CH_{3,3} \\ R_1 \\ C_4H_6 \\ R_1 \\ R_2 \\ R_2 \\ R_2 \\ R_1 \\ R_1 \\ R_2 \\ R_1 \\ R_1 \\ R_1 \\ R_2 \\ R_1 \\ R_2 \\ R_2 \\ R_2 \\ R_2 \\ R_2 \\ R_2 \\ R_1 \\ R_2 \\ R_2 \\ R_2 \\ R_1 \\ R_2 \\ R_2 \\ R_2 \\ R_2 \\ R_2 \\ R_1 \\ R_2 \\ R_2 \\ R_2 \\ R_2 \\ R_1 \\ R_2 \\ R_1 \\ R_2 \\$	0,5	7	£	230	40	R HO OH R HO OH R HO OH
* R = t							

TABLE 3. Conditions for Chromatographic Determination of Individual Components of Reaction Mixture in the Re-

2213

#### EXPERIMENTAL

The silicon-containing phenols were obtained by a modification of the method given in [12, 13], as described in [1-3], and were purified by recrystallization from ethanol. The melting points of the phenols corresponded to those given in the literature. The DTBP was purified by vacuum-distillation, while the DCPC was purified by reprecipitation from chloroform solution with methanol. The benzene was dried and distilled over Na.

The reaction products were analyzed by GLC using a Tswett-1 chromatograph, equipped with a katharometer as the detector. The internal standard method was used for the quantitative analysis of the reaction products. The analysis conditions are given in Table 3.

<u>Reaction with Di-tert-butyl Peroxide</u>. The reaction was run in evacuated ampuls by the following typical method: a mixture of 1.39 g of phenol (I) and 0.37 g of DTBP in 12 ml of benzene was heated in an evacuated ampul for 23 h at 125°. A pale blue color was observed at the start, which is characteristic for phenoxyl. The color disappeared after 4 h. At the end of heating the reaction products were analyzed by GLC.

In order to identify products (VI)-(IX), we synthesized the previously unknown 2, 4-bis(trimethylsilyl)-6methylphenoxytrimethylsilane by a modification of the method given in [12, 13].

<u>2,4-Dibromo-6-methylphenoxytrimethylsilane</u>. To a stirred mixture of 26.6 g of 2,4-dibromo-6-methylphenol and 14 ml of  $(C_2H_5)_3N$  in 150 ml of m-xylene was added 13 ml of trimethylchlorosilane. The mixture was heated for 3 h at 120°, filtered, and the solvent was distilled off under reduced pressure. The residue, a yellow oil, was fractionally distilled in vacuo, collecting the fraction with bp 95-98° (0.5 mm). We obtained 21.5 g (64%) of product;  $n_D^{20}$  1.5500.

2.4-bis(Trimethylsilyl)-6-methylphenoxytrimethylsilane. With vigorous stirring, to a suspension of 5.7 g of Na in 150 ml of m-xylene at 120° was added a mixture of 16.9 g of 2,4-dibromo-6-methylphenoxy-trimethylsilane and 16 ml of  $ClSi(CH_3)_3$ . The mixture was heated at 120° for 3 h, filtered, the solvent was distilled off under reduced pressure, and the residue was distilled, collecting the fraction with bp 120-128° (2 mm);  $n_D^{20}$  1.4980. We obtained 6.1 g (38%) of a thick colorless liquid, which crystallized on standing. Found: C 59.38; H 9.88; Si 26.03%.  $C_{16}H_{32}OSi_3$ . Calculated: C 59.19; H 9.93; Si 25.95%. Absorption bands are present in the IR spectrum at 938 (ArO-Si), 850 and 1255 (-Si(CH\_3)\_3), and 1130 cm<sup>-1</sup> (Ar-Si). The composition of the reaction mixture was confirmed by hydrolysis with Na methylate. Here the trimethylsilyl group is removed and a mixture of known phenols is formed.

Reaction with Dicyclohexyl Peroxydicarbonate. The reaction was run either in a flask equipped with a reflux condenser, or in evacuated ampuls. In a typical experiment a mixture of 1.3 9 g of phenol (I) and 0.72 g of DCPC in 15 ml of benzene was heated in a flask under reflux, in an argon atmosphere, for 24 h at 60°. The liberated  $CO_2$  was absorbed by caustic solution and was determined by the weight increase. The reaction was run until all of the DCPC had decomposed (iodometric sample). The amount of individual components in the mixture was studied by GLC and IR spectroscopy. In order to identify product (X) the reaction mixture was hydrolyzed with a solution of  $CH_3ONa$  in methanol. The known 2-phenyl-4, 6-di-tert-butylphenol [14] was obtained after hydrolysis.

Disiloxybiphenyls (IV)-(VI) can be isolated preparatively in 60-70% yield by distilling off the solvent in vacuo and recrystallization of the residue from ethanol. The mixed melting point with authentic samples of (IV)-(VI) is not depressed.

#### CONCLUSIONS

1. Alkoxy radicals, formed during the thermal decomposition of di-tert-butyl peroxide (DTBP) and dicyclohexyl peroxydicarbonate (DCPC), dehydrogenate silicon-containing phenols, giving the corresponding alcohol and phenoxyl radical. The phenoxyl radicals undergo dimerization with the formation of disiloxybiphenyls, which are the main reaction products of silicon-containing phenols with DTBP and DCPC.

2. In the investigated reactions the specific effect of the  $(CH_3)_3$ Si groups in the shielded phenol is manifested in the addition of the methyl radical in the o-position of the aromatic ring, with a migration of the  $(CH_3)_3$ Si group to the oxygen (reaction with DTBP), and reaction of the phenoxyls with the aromatic solvent (reaction with DCPC).

# LITERATURE CITED

- 1. G. A. Razuvaev, N. S. Vasileiskaja, and D. V. Muslin, J. Organometal. Chem., 7, 531 (1967).
- 2. G. A. Razuvaev, N. S. Vasileiskaya, and D. V. Muslin, Dokl. Akad. Nauk SSSR, 175, 620 (1970).
- 3. G. A. Razuvaev, N. S. Vasileiskaya, D. V. Muslin, N. N. Vavilina, and S. N. Uspenskaya, Zh. Organ. Khim., 6, 980 (1970).
- 4. G. N. Bortnikov, N. S. Vasileiskaya, and L. V. Gorbunova, Izv. Akad. Nauk SSSR, Ser. Khim., 687 (1970).
- 5. I. L. Khrzhanovskaya and V. V. Kharitonov, Dokl. Akad. Nauk SSSR, 195, 1128 (1970).
- 6. K. U. Ingold, Can. J. Chem., 41, 2807 (1963).
- 7. K. U. Ingold, Can. J. Chem., 41, 2816 (1963).
- 8. K. M. Johnston, R. E. Jacobson, and G. H. Williams, J. Chem. Soc., 1425 (1969).
- 9. J. Pannel, Chem. Ind. (London), 1797 (1962).
- 10. A. L. Buchachenko, L. S. Lebedev, and M. B. Neiman, Zh. Struktur. Khim., 2, 558 (1961).
- G. A. Razuvaev, G. G. Petukhov, and B. T. Zateev, Dokl. Akad. Nauk SSSR, 127, 347 (1959);
   R. N. Milyutinskaya, Kh. S. Bagdasar'yan, and E. A. Izrailevich, Zh. Fiz. Khim., 31, 1019 (1957);
   G. A. Razuvaev, B. T. Zateev, and G. G. Petukhov, Dokl. Akad. Nauk SSSR, 130, 338 (1960).
- 12. C. D. Cooper, J. Org. Chem., 26, 925 (1961).
- 13. J. L. Speier, J. Am. Chem. Soc., 74, 1003 (1952).
- 14. E. Muller, A. Schick, R. Mayer, and K. Scheffler, Chem. Ber., 93, 2649 (1960).