REARRANGEMENT OF HINDERED PHENOLS CONTAINING

SILICON OR GERMANIUM

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In continuing our studies of the reactivity of hindered phenols containing Si or Ge, or "mixed" phenols containing both Si and Ge [1], we have investigated the rearrangement of these phenols in order to compare the migration capabilities of the organosilicon and organogermanium substituents, when these two substituents are in analogue-molecules and also when they are both in the same molecule.

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2-Trimethylsilyl-4,5-di-tert-butylphenol (I), its germanium analogue (II), 2,6-di-tertbutyl-4-trimethylsilylphenol (III), its germanium analogue (IV), or 2-trimethylsilyl-4-tertbutyl-6-trimethylgermylphenol (V) can be stored indefinitely in evacuated ampuls; upon standing in air, they are rearranged to the corresponding phenoxysilanes or phenoxygermanes.



E = Si (III), (VIII); E = Ge (IV), (IX).

The phenols (I) and (II) remain unchanged after storage in air for 1 week. When stored for 0.5 months, they are rearranged to the extent of 35 and 55%, respectively, and in 6 months to the extent of 57 and 100%; i.e., the Ge-containing phenol is completely converted to the corresponding phenoxygermane. The rearrangement is accelerated by heating the phenols in air. Hence, we have investigated the interaction of these phenols with molecular oxygen. It was shown in [2] by means of electron emission spectroscopy that Group IVB organic compounds of the type Ph4M, where M = C, Si, Ge, Sn, or Pb, form labile complexes with oxygen, and that the capability of organometallic compounds for forming complexes can be characterized by the luminescence quenching constant K_q as calculated by the Stern-Volmer equation. The values of K_q that we have determined for a series of phenols containing silicon and/or germanium are listed in Table 1. The considerably larger values of K_{d} for the phenols (I) and (II) than for Ph4Si (0.8) and Ph4Ge (0.9) [2] indicate that the oxygen enters into complex formation with the phenols in the role of a π acceptor. In the series consisting of the phenol (I), the phenol (2), and 2,4,6-tri-tert-butylphenol, the constant for complex formation increases, owing to the increase in level of donor properties of the substituents (SiMe₃ < GeMe₃ < CMe₃), and complex formation takes place more readily. The effect of the substituents in these phenols is characterized by the values of the σ_p constant, which for the groups SiMe3, GeMe3, and CMe3 are 0.07, -0.01, and -0.19 respectively; i.e., the SiMe3 group has acceptor properties, and the GeMe₃ and CMe₃ groups have donor properties [3]. When the phenol forms a complex with oxygen, a partial positive charge appears on the nucleus, and this brings

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Phenol	K _q ·10 ⁻² liter/ mole	ν, cm ⁻¹	Phenol	$\begin{bmatrix} K_q \cdot 10^{-2} \\ liter / \\ mole \end{bmatrix}$	ν, cm ⁻¹
(I) (II) OH t-Bu	3,0 3,5 3,8	22 200 23 000 20 000	OH Me3Ge t-Bu	2,7	22 000
t-Bu (111) (IV) (V)	2,8 3,0 2,6	21 800 23 100 23 000	OH PhaGe SiPha f-Bu	2,8	23 000

TABLE 1. Values of $K_{\rm q}$ and Frequencies of Long-Wave Emission Bands for Phenols Containing Silicon and/or Germanium

about a redistribution of electron density in the phenol molecule, leading to the formation of an unstable quinolide compound that is converted to the phenoxysilane or phenoxygermane:



A correlation is observed between the phenol stability and the complex formation constant. The value of K_q is greater for the phenol (II) than for the phenol (I), and correspondingly, (II) is less stable than (I) when stored in air.

The p-substituted phenols (III) and (IV) are stable when stored in air; this is in accord with the low values of the complex formation constants for these compounds. The low values of K_q in this instance can be explained by direct polar conjugation, resulting in a lower level of π -donor properties of the phenols (III) and (IV):



For the mixed phenols with Ph_3M substituents, the values of K_q are considerably lower, evidently because of a lower level of donor properties of the groups when t-Bu is replaced by Ph_3M . Correspondingly, these phenols with Ph_3M substituents do not rearrange in air. The formation of complexes with charge transfer from a hindered phenol to oxygen, of the type $[PhOH^+O_2^-]$, was demonstrated recently in [4]. The final products of the reaction of alkylsubstituted phenols with oxygen are quinones, diphenoquinones, and quinols [5, 6]. When organosilyl or organogermyl groups are introduced into the phenol molecule, an unusual oxygeninitiated process is observed - rearrangement of the phenols to phenoxysilanes or phenoxygermanes. In the absence of oxygen, these phenols are stable when heated to 90°.

In Table 2, we have listed data on the conversion of the phenols (I)-(IV) to the phenoxysilanes or phenoxygermanes (VI)-(IX) upon heating in evacuated ampuls or in air at various temperatures. It had been shown previously [7] that poly(trimethylsilyl)phenols rearrange quantitatively to aryloxytrimethylsilanes when heated for 24 h at 250°.

From the values listed in Table 2, it can be seen that the phenol (II), which contains the GeMe₃ group in the o position, is more stable to heating than its silicon-containing analogue. The p-substituted phenols are considerably more stable than the o-substituted phenols. This suggests that, for the o-Si and o-Ge phenols, the basic role in the rearrangement is that of intramolecular coordination between the unshared electron pairs of the oxygen of the

TABLE 2. Conversion of Phenols to Phenoxysilanes or Phenoxygermanes as a Function of Temperature (4-h heating)

T ., ℃	Conversion, %								
	$(I) \rightarrow (VI)$		$(II) \rightarrow (VII)$		$(III) \rightarrow (VIII)$		$(IV) \rightarrow (IX)$		
	with O ₂	without O2	with O2	without O2	with O ₂	without O2	with _{O2}	without O ₂	
100 150 170 220	10 53 86 100	6 19 38 100	8 0 51 100	0 0 15 100	0 0 11 75	0 0 0 0	0 0 0 70	0 0 0 0	

*No reaction below 100°.

TABLE 3. Rearrangement of Phenols (I)-(IV) to Phenoxysilanes or Phenoxygermanes (VI)-(IX) under the Influence of Bases

Base	pK *	Conversion, %				
		$(I) \rightarrow (VI)$	$(II) \rightarrow (VII)$	$(III) \rightarrow (VIII)$	$(IV) \rightarrow (IX)$	
Piperidine Triethylamine Pyridine	11,28 10,33 5,21	90 3 2	100 80 4	45 0 0	100 24 4	

*According to [10].

OH group and the vacant d orbitals of the Si and Ge. Previously, in many studies that were summarized and correlated in the review [8], it was shown that intramolecular coordination is the driving force for migration of organosilyl and organogermyl groups in many organic compounds. The shielded phenols in the present study are less stable, since the contribution of the vacant d orbitals of the Si is more substantial than that of the d orbitals of the Ge. Moreover, in the case of the Ge-containing phenols, a more important role is played by the phenomenon of enhanced bond dissociation, since the polarizability of the C-element bond increases from Si to Ge. Hence, an external action (heating) has less effect on the more readily polarized molecule of the Ge-containing phenol.

In the p-substituted phenols (III) and (IV), there is no intramolecular coordination, but there is intermolecular coordination. In this particular case, the intermolecular coordination is apparently much weaker than the intermolecular coordination in the o-substituted phenols; hence, the p-substituted phenols (III) and (IV) are more stable than the corresponding o isomers. In the presence of atmospheric oxygen at 220°, the rearrangement of the phenol (IV) is accompanied by oxidation:



^{*}We have found that one-electron oxidation of the phenol (IV) by alkaline ferricyanide at ~20° forms 2,6-di-tert-butyl-diphenoquinone.

It was reported in [9] that α -hydroxysilanes are rearranged to silvl ethers by the action of bases. In the present work, we have investigated the influence of bases on the rearrangement of the phenols (I)-(IV). This study was carried out at 70° with a reaction time of 4 h; under these conditions, there is no thermal rearrangement. These results are presented in Table 3.

From a comparison of the yields of rearranged products from the o- and p-substituted Siand Ge-containing phenols (I)-(IV) under the influence of bases, we can draw the following conclusions: 1) The silicon-containing phenols are more stable than the germanium-containing phenols of the analogous structure; 2) p-substituted phenols are more stable than the corresponding o isomers.

The catalytic effect of the bases consists of the following: The basic catalyst removes the acidic proton, forming a phenolate anion, in which intramolecular coordination is stronger than in the neutral phenol molecule, owing to greater electron density on the oxygen; this facilitates intramolecular rearrangement of the anion. As a result of the rearrangement, a negative charge is fixed on the carbon, and the resulting carbanion is rapidly protonized.

In the anion, the migration capability of the SiMe₃ group is weaker than that of the GeMe₃, apparently because of a change in the geometric structure of the molecule when the anion is formed.

Thus we see that, in these analogue phenols, when they are subjected to conditions suitable for thermal rearrangement, the SiMe₃ group migrates more readily than does the GeMe₃. In catalytic processes, the rearrangement goes forward on the side of the germanium atom, regardless of the mechanism of the process (action of bases or complex formation with O_2).

EXPERIMENTAL

The phenols used in these studies (for synthesis, see [1]) were purified by recrystallization from ethanol, followed by vacuum drying over P_2O_3 . The phenol conversion products were analyzed by means of GLC and IR spectroscopy. The IR spectra were taken in a UR-20 spectrophotometer. The GLC analysis was performed in a Tsvet-4 chromatograph with a katharometer in a stream of helium (30 ml/min), in a steel column (1 m ×3 mm), on Chromaton N-AW-DMCS with 5% XE-60 silicone, at 150°.

The phenol—oxygen complexes were studied at 77°K. The luminescence spectra were obtained by a method described in [3]. The oxygen was dried by passage through 4-A molecular sieves. It was assumed that, under normal conditions and with rapid freezing to 77°K, the oxygen concentration in n-hexane is $1.5 \cdot 10^{-2}$ mole/liter [11].

Conversion of Phenols upon Heating. For complete removal of atmospheric oxygen from the phenol, the sample was dissolved in a minimal quantity of heptane, the ampul was evacuated and the sample refrozen, the solvent was removed under vacuum, and the ampul was sealed.

<u>Conversion of Phenols under the Influence of Bases</u>. The phenol and base (pyridine, piperdine, triethylamine, or triphenylphosphine) in al: 1 molar ratio were heated 4 h at 70° in an evacuated ampul or an open test tube, after which the reaction mixture was analyzed.

SUMMARY

1. Shielded phenols containing silicon and/or germanium have been found to rearrange to phenoxysilanes or phenoxygermanes under the influence of complex formation with oxygen.

2. The silicon- and germanium-containing phenols form π complexes with oxygen in which the oxygen acts as an acceptor. The constants of complex formation have been determined.

3. Silicon- and germanium-containing shielded phenols, when exposed to elevated temperatures or the action of bases, rearrange to phenoxysilanes or phenoxygermanes. The germanium-containing phenols are more stable at high temperatures than are the silicon-containing phenols, but are rearranged more readily under the influence of organic bases. The p isomers are more stable than the o isomers.

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