## MIGRATORY APTITUDE OF THE TRIPHENYLGERMYL GROUP IN STERICALLY HINDERED PHENOLS AND PHENOXYL RADICALS

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UDC 541.515:547.558.5:547.56

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Phenoxyl radicals generated by the oxidation of phenols simultaneously substituted in the o-positions by organosilyl and organogermyl groups (Me<sub>3</sub>Ge, Me<sub>3</sub>Si, and Ph<sub>3</sub>Si) dimerize at the o-carbons to form substituted biphenyls with simultaneous migration of the heteroorganic group to oxygen [1, 2]. The migratory aptitude of the substituents decreases in the order Me<sub>3</sub>Ge > Me<sub>3</sub>Si > Ph<sub>3</sub>Si.

We have sought to find the position of the Ph<sub>3</sub>Ge group in this series by examining the oxidation of 2-trimethylsilyl-4-tert-butyl-6-triphenylgermylphenol (I) and 2-triphenylsilyl-4-tert-butyl-6-triphenylgermylphenol (II). We prepared phenols (I) and (II) by the procedure described in [1, 2] and verified their structures from the IR spectra, elemental analyses, and molecular weight measurements. Oxidation of these phenols in benzene solution by aqueous alkaline K<sub>3</sub>Fe(CN)<sub>6</sub> form phenoxyl radicals (III) and (IV), which we detected by electronic and ESR spectroscopy. The electronic spectra have absorption at 580 nm for (III) and at 588 nm for (IV). The ESR spectrum is a triplet due to the interaction of the unpaired electron with the ring m-protons ( $a_{\rm H}^{\rm m}$  = 1.8 0e). Each of the components of the triplet is further split by the interaction of the unpaired electron with the o-protons of the Ph<sub>3</sub>Ge phenyl rings  $[\alpha_{\rm M}=0.33$  in (III) and 0.35 Oe in (IV)]. The subsequent reactions of the phenoxyl radicals are controlled by the heteroorganic ring substituents. Radical (III) is converted to 2,2'bis(trimethylsiloxy)-3,3'-bis(triphenylgermyl)-5,5'-di-tert-butylbiphenyl (V). We verified the structure of (V) from its IR spectrum, which has bands  $(cm^{-1})$  due to Ar-O-Si (930), Ar-Ge (1100), and C-Si (860, 1260), but lacks the OH band, and by elemental analysis and molecular weight measurement



We also verified the structure of (V) by hydrolysis to 2,2'-dihydroxy-3,3'bis(triphenylgermyl)-5,5'-di-tert-butylbiphenyl (VI). The IR spectrum of (VI) lacks the bands of Ar-O-Si and C-Si, but contains the HO band (3500 cm<sup>-1</sup>). Elemental analysis and molecular weight measurement of the hydrolysis product support structure (VI). Consequently, in phenoxyl radical (III) the Me<sub>3</sub>Si group has a greater migratory aptitude than Ph<sub>3</sub>Ge. The Me<sub>3</sub>Ge fragment is known to be more mobile than Me<sub>3</sub>Si. The bulky phenyl substituents obviously reduce the mobility of the Ph<sub>3</sub>Ge group, and as a result this group does not migrate in radical (III).

2-Triphenylsilyl-4-tert-butyl-6-triphenylgermylphenol (II) is oxidized much more slowly than phenol (I). Complete oxidation requires 70 h under conditions in which phenol (I) is completely oxidized in 5 h. The stability of this phenol to oxidation probably stems from the efficient stabilization of its HO group by the phenyls of the  $Ph_3Ge$  and  $Ph_3Si$  groups as a result of intramolecular hydrogen bonding. This conjecture is supported by the presence

Institute of Chemistry, Academy of Sciences of the USSR, Gor'kii. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 604-608, March, 1979. Original article submitted September 12, 1977. in the IR spectrum of phenol (II) of only one HO band (3500 cm<sup>-1</sup>), which is characteristic of a group involved in intramolecular bonding. The IR spectrum of phenol (I) has two OH bands (3510 and 3550 cm<sup>-1</sup>); one (3550 cm<sup>-1</sup>) probably represents the hydroxyl that is not hydrogen-bonded.

We identified as the oxidation products of phenol (II) bis(siloxy)biphenyl (VII), bis-(germyloxy)biphenyl (VIII) and the quinol ether (IX). We can represent the reaction involved in their formation as



These products may well be accompanied in the reaction mixtures by the biphenyl  $$\rm Ph_3SiO~OGePh_3$$ 

Ph<sub>3</sub>Ge-SiPh<sub>3</sub>, though we were unable to isolate this. We verified the structure of dimer

(IX) from its IR and UV spectra. The IR spectrum contains a conjugated carbonyl band (1640 cm<sup>-1</sup>) and th UV spectrum an absorption maximum at  $\lambda 225$  nm, characteristic of p-quinol ethers [3]. We also identified quinol ether (IX) by elemental analysis and LiAlH<sub>4</sub> reduction, which gave phenol (II). We identified compounds (VII) and (VIII) by TLC of their hydrolysis products. The formation of compounds (VII), (VIII), and (IX) implies that the oxidation of phenol (II) involves two competing processes, firstly migration of the Ph<sub>3</sub>Ge and Ph<sub>3</sub>Si groups to the oxygen and C-C dimerization to form the bis(siloxy) - and bis(germyloxy) biphenyls, and secondly C-O dimerization of the phenoxyls to form the quinol ether, where both groups remain attached to the ring. This type of dimerization of phenoxyls (C-O dimerization) has previously been reported [4-6] in 4-acyl-, 4-acyloxy-, and 4-alkoxycarbonyl-2,6-di-tert-butylphenoxyls. Consequently, the mobility of the heteroorganic substituents in the phenoxyl radicals decreases in the order Me<sub>3</sub>Ge > Me<sub>3</sub>Si > Ph<sub>3</sub>Si ≈ Ph<sub>3</sub>Ge.

Trimethylgermyl-substituted phenols when heated to 200°C exchange the hydroxyl hydrogen for the Me<sub>3</sub>Ge group [2]. Phenols (I) and (II) behave similarly when heated to 200°C, being converted to silyl and germyl ethers (X)-(XIII)



We analyzed the thermal rearrangement products by IR spectroscopy, liquid, gas—liquid, and thin-layer chromatography using independently synthesized samples of the reaction products. We also hydrolyzed the reaction mixture and identified the known hydrolysis products —

phenols (XIV)-(XVI). The major pyrolysis product of phenol (I) is phenoxysilane (XII) and that of phenol (II) is phenoxygermane (XI). These results imply that the Me<sub>3</sub>Si group migrates to oxygen more readily than the Ph<sub>3</sub>Ge group and the Ph<sub>3</sub>Ge group more readily than Ph<sub>3</sub>Si. From our present and earlier results [2] we can rank the migratory aptitude of these groups in the order GeMe<sub>3</sub> > SiMe<sub>3</sub> > GePh<sub>3</sub>  $\ge$  SiPh<sub>3</sub>.

## EXPERIMENTAL

Spectra were recorded with: IR: a UR-20 as Vaseline oil mulls; ESR: and RÉ-1301; and UV: a Perkin-Elmer 402. The GLC and LC analyses were carried out on Tsvet-4 and Tsvet-304 chromatographs under the conditions specified in [1, 2]; TLC was carried out on Silufol plates in heptane-acetone (7:3) with visualization by iodine vapor. Molecular weights were measured by cryoscopy in benzene.

<u>2-Trimethylsilyl-4-tert-butyl-6-triphenylgermylphenol (I)</u> was prepared by the method described in [1, 2] in 20% yield as white crystals, mp 119°C. Found: C 70.90; H 6.93; Si 5.28; Ge 13.66%; mol. wt. 518.  $C_{31}H_{36}OSiGe$ . Calculated: C 70.88; H 6.91; Si 5.35; Ge 13.82%; mol. wt. 525.

<u>2-Triphenylsilyl-4-tert-butyl-6-triphenylgermylphenol (II)</u> was prepared after [1, 2] in 72% yield as white crystals, mp 214°C. Found: C 77.37; H 6.03; Si 3.96; Ge 10.22%; mol. wt. 706. C46H42OSiGe. Calculated: C 77.65; H 5.95; Si 3.94; Ge 10.20%; mol. wt. 711.

Oxidation of Phenol (I) by Alkaline Potassium Ferricyanide. A solution of (I) (1.84 g) in benzene (20 ml) was added dropwise under argon to a stirred solution of  $K_3Fe(CN)_6$  (3.5 g) and KOH (2 g) in water (20 ml). The benzene layer turned blue. After the discharge of the color (5 h) the organic layer was separated, washed with distilled water, and dried over MgSO<sub>4</sub>. The solvent was removed under vacuum to give compound (V) (1.74 g, 91%), as white crystals, mp 295°C (heptane). Found: C 70.84; H 7.04; Si 5.10; Ge 13.20%; mol. wt. 1027.  $C_{6_2}H_{70}O_2Si_2Ge_2$ . Calculated: C 71.03; H 6.73; Si 5.34; Ge 13.85%; mol. wt. 1048.38. Compound (V) (0.7 g) was dissolved in ether (50 ml) and a saturated solution (86 ml) of CH<sub>3</sub>ONa in CH<sub>3</sub>OH was added. The mixture was quenched with water. The ethereal layer was dried over MgSO<sub>4</sub>, the drying agent was filtered off, and the solvent was stripped off under vacuum. The residue was treated with heptane to give compound (VI) (0.53 g, 60%), as white crystals, mp 250°C. Found: C 70.62; H 6.17; Ge 15.77%; mol. wt. 890.  $C_{56}H_{54}O_2Ge_2$ . Cal-culated: C 74.38; H 6.02; Ge 16.06%; mol, wt. 904.17.

Oxidation of Phenol (II) by Alkaline Potassium Ferricyanide. A mixture of phenol (II) (1.77 g) in benzene (15 ml) with a solution of  $K_3Fe(CN)_6$  (5 g) and KOH (3 g) in water (30 ml) was shaken for 70 h in an evacuated ampul. The usual method of isolation gave a solid yellow product (1.7 g); recrystallization of this from heptane with added benzene (several drops) gave quinol ether (IX), as a cream-colored substance, mp 146-150°C. Found: C 77.77; H 5.81; Si 3.88; Ge 10.03%.  $C_{9_2}H_{8_2}O_2Si_2Ge_2$ . Calculated: C 77.77; H 5.81; Si 3.94; Ge 10.20%. The hydrolysis product of the reaction mixture of the oxidation of phenol (II) contained (TLC) 2,2'-dihydroxy-3,3'-bis(triphenylsilyl)-5,5'-di-tert-butylbiphenyl (VIII) and 2,2'-dihydroxy-3,3'-bis(triphenylgermyl)-5,5'-di-tert-butylbiphenyl (VII).

Thermal Rearrangement of Phenol (I). Phenol (I) (0.5 g) was heated at 200°C for 7 h in an evacuated ampul. The IR spectrum of the reaction mixture contained an intense band at 940 cm<sup>-1</sup> characteristic of the C-O-Si bond, which implied the formation of compound (XII) as major product. It was not possible to establish the presence of compounds with an Ar-O-Ge bond in the pyrolysis product from its spectrum, since the absorption of this group lies in the same region (1250 cm<sup>-1</sup>) as that of the SiMe<sub>3</sub> group. Germyl ether (X) was identified by LC and TLC (small quantity); it was also prepared independently by treatment of 2-trimethylsilyl-4-tert-butylphenol with Ph<sub>3</sub>GeBr in diethylamine, as white crystals, mp 88°C (ethanol). Found: C 70.73; H 6.67; Si 5.31; Ge 13.71%; mol. wt. 470. C<sub>31</sub>H<sub>36</sub>OSiGe. Calculated: C 70.88; H 6.90; Si 5.33; Ge 13.81%; mol. wt. 525.27. Phenols (XIV)-(XVI) were identified in the pyrolysis product of the reaction mixture by GLC and LC.

Thermal Rearrangement of Phenol (II). Phenol (II) (0.5 g) was heated at 200°C in an evacuated ampul. The IR spectrum of the pyrolysis product showed an intense band at 1245 cm<sup>-1</sup> and a weak band at 940 cm<sup>-1</sup> (C-O-Si), which was absent from the spectrum of phenol (II). The 1245 cm<sup>-1</sup> band was present in the IR spectrum of phenoxysilane (XI), prepared by reaction of 2-triphenylsilyl-4-tert-butylphenol with butyllithium and Ph<sub>3</sub>GeBr, as white crystals, mp 190-192°C (hexane). Found: C 77.82; H 5.97; Si 3.99; Ge 10.31%; mol. wt. 655.

 $C_{46}H_{42}OSiGe.$  Calculated: C 77.65; H 5.95; Si 3.94; Ge 10.20%; mol. wt. 711.47. 2-Triphenylsilyl-4-tert-butylphenol (XV) was identified in the hydrolysis product, mp 138°C. A sample of the hydrolysis product did not depress the melting point of a mixture with an authentic specimen.

## CONCLUSIONS

1. The phenoxyl radicals generated by oxidation of 2-trimethylsilyl-4-tert-butyl-6-triphenylgermylphenol with potassium ferricyanide rearrange by migration of the trimethyl-silyl group to the oxygen and dimerize, forming substituted bis(siloxy)biphenyls. The migratory aptitude of the groups in the phenoxyl radicals decreases in the order GeMe<sub>3</sub> >  $SiMe_3 > SiPh_3 \approx GePh_3$ .

2. Two types of reaction take place in the phenoxyl radical derived by one-electron oxidation of 2-triphenylsilyl-4-tert-butyl-6-triphenylgermylphenol, firstly, migration of the  $Ph_3Ge$  and  $Ph_3Si$  groups to the oxygen and C-C dimerization to form a bis(siloxy)biphenyl and a bis(germyloxy)biphenyl, and secondly C-O dimerization of the phenoxyls to form a quinol ether, where both heteroorganic groups remain attached to the ring.

3. 2-Trimethylsilyl-4-tert-butyl-6-triphenylgermylphenol (I) and 2-triphenylsilyl-4tert-butyl-6-triphenylgermylphenol (II) isomerize at 200°C to aryloxysilanes and germanes; phenol (I) forms mainly the aryloxysilane and phenol (II) the aryloxygermane.

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