## FACTORS DETERMINING TRANSFORMATIONS OF SILICON-CONTAINING AROXYLS.

COMMUNICATION 2. CHANGE IN STABILITY IN THE SERIES OF o-TRIMETHYLSILYL-, o-PHENYLDIMETHYLSILYL-, AND o-METHYLDIPHENYLSILYL-CONTAINING AROXYLS

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UDC 541.124:542.91:542.952.1:547.1'128

We have already found [1] that the rate of dimerization-rearrangement of o-trialkylsilyl-substituted aroxyls depends on the steric screening by organosilyl substituents of the reaction center responsible for the dimerization. There is a linear dependence between the logarithms of the relative rate constants of the dimerization-rearrangement log  $k_{rel}$  and the sum of steric constants  $\Sigma E_s^{\circ}$  of the alkyl groups at the silicon atom.

To find whether there is a similar dependence on transition from o-trimethylsilyl to otriphenylsilyl group, we studied the change in the stability of silicon-containing aroxyls in the successive exchange of the methyl groups of the o-trimethylsilyl substituent for phenyl substituents.

The corresponding aroxyls (Ia-c) were obtained by the oxidation of phenols (IIa-c).



The transformation products of aroxyls (Ia-c) are substituted disilyloxydiphenyls (IIIa-c)



For each of the aroxyls (Ia-c), a linear dependence is observed in the  $x/(\alpha - x)$  vs. t coordinates, which indicates a second-order reaction.

The results of the kinetic measurements carried out by the EPR method are shown in Table 1 together with the data of [1].

TABLE 1. Data of Kinetic Investigations of Dimerization-Rearrangement Reaction of Organosilyl-Containing Aroxyls (2-R<sub>3</sub>Si-4,6-di-tert-butylphenoxyl radicals)

R₃Si	k <sub>re1</sub>	log k <sub>rel</sub>	$\Sigma E_{s}^{0}$	Reference
Me₃Si EtMe₂Si MeEt₂Si Et₃Si PhMe₂Si MePh₂Si	$\begin{array}{c c} 1,000\\ 0,391\\ 0,096\\ 0,057\\ 1,480\\ 0,050\end{array}$	$\begin{array}{r} 0,0000\\ -0,4075\\ -1,0155\\ -1,2448\\ 0,1703\\ -1,3010\end{array}$	$ \begin{vmatrix} 0,00 \\ -0,27 \\ -0,54 \\ -0,81 \\ 0,25 \\ 0,50 \end{vmatrix} $	[1] [1] [1] [1] -

Institute of Chemistry, Academy of Sciences of the USSR, Gorkii. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2344-2346, October, 1984. Original article submitted July 12, 1983.



Fig. 1. Dependence of rate of dimerization-rearrangement of silicon-containing aroxyls on steric effect of migrating oorganosilyl groups.

The linear dependence of log  $k_{rel}$  vs.  $\Sigma E_s^{\circ}$  is retained for o-phenyldimethylsilyl- and o-trialkylsilyl-containing aroxyls, but is absent in the series of o-trimethylsilyl-, o-phenyl-dimethylsilyl-, and o-methyldiphenylsilyl-containing aroxyls (Fig. 1).

The reasons for the absence of this correlation may be that the steric interaction of the phenyl groups on transition from phenyldimethylsilyl to methyldiphenylsilyl group and a change in the electron-acceptor ability of the silicon atom as the result of the electronic effect of the phenyl groups were not taken into account.

We were unable to synthesize 2-triphenylsilyl-4,6-di-tert-butylphenol and evaluate the migrating ability of the triphenylsilyl group in the corresponding aroxyl. The migrating ability of this group in 2-trimethylsilyl-4-tert-butyl-6-triphenylsilylphenoxyl (IV) obtained by the oxidation of phenol (V) is much lower than that of trimethylsilyl group, as indicated by the formation of disiloxyphenyl (VI) as the only product of the dimerization-rearrangement reaction of aroxyl (IV)



According to the relative migrating ability of trimethyl- and triphenylsilyl groups, and taking into account the tendency of the stability of the aroxyls to increase on transition from phenyldimethylsilyl to methyldiphenylsilyl group, the o-organosilyl substituents studied can be arranged in the following series, corresponding to decrease in the migrating ability: PhMe<sub>2</sub>Si > Me<sub>2</sub>Si > Ph<sub>2</sub>Si > Ph<sub>3</sub>Si.

## EXPERIMENTAL

Phenol's (IIa) and (IIb) were synthesized according to [1, 2]. The method of kinetic measurements is described in [1].

<u>2-Bromo-4,6-di-tert-butylphenoxymethyldiphenylsilane (VII).</u> A mixture of 10.25 g (0.036 mole) of 2-bromo-4,6-di-tert-butylphenol, 7.6 ml (0.04 mole) of MePh<sub>2</sub>SiCl, and 5.6 ml (0.04 mole) of Et<sub>3</sub>N in 50 ml of THF was heated, with stirring, for 11 h, and filtered, and the solvent was removed in vacuo. The residue was recrystallized from an ethanol-benzene mixture (3:1). Yield, 10 g (57.7%) of aryloxysilane (VII), mp 80.5-82.0°C. Found, %: C 67.55; H 6.80; Si 6.05; Br 17.07.  $C_{27}H_{33}SiBrO$ . Calculated, %: C 67.35; H 6.91; Si 5.83; Br 16.59. IR spectrum (v, cm<sup>-1</sup>): 1255, 790 (SiMe), 1120 (SiPh), 940 (SiOAr).

2-Methyldiphenylsilyl-4,6-tert-butylphenol (IIc). An 8-ml portion (0.001 mole) of a 1.3 N solution of n-BuLi in heptane was added with stirring, in an Ar atmosphere and cooling to a solution of 4.81 g (0.01 mole) of aryloxysilane (VII) in 50 ml of ether. After 5 min, the mixture was hydrolyzed by a saturated solution of NH<sub>4</sub>Cl. The organic layer was separated and dried over MgSO<sub>4</sub>, the solvent was distilled in vacuo, and the residue was recrystallized from EtOH. Yield, 3.05 g (75%) of phenol (IIc), mp 71-73°C. Found, %: C 80.32; H 8.85; Si 6.75. C<sub>21</sub>H<sub>29</sub>SiO. Calculated, %: C 80.54; H 8.51; Si 6.97. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1260, 790 (SiMe), 1118 (SiPh), 3500 (OH).

 $\frac{2,6-\text{Dibromo-4-tert-butylphenoxytriphenylsilane (VIII)}{1} \text{ was obtained in the same way as aryloxysilane (VII) from 2,6-dibromo-4-tert-butylphenol and Ph_3SiCl, yield 66%, mp 135.5-137.0°C (from acetone). Found, %: C 59.12; H 4.61; Si 5.00; Br 27.48. C_{2eH_26}SiBr_20. Calculated, %: C 59.39; H 4.63; Si 4.96; Br 28.21. IR spectrum (v, cm<sup>-1</sup>): 1125 (SiPh), 925 (SiOAr).$ 

 $\frac{2-\text{Bromo-4-tert-butyl-6-triphenylsilylphenol (IX)}{\text{from aryloxysilane (VIII), yield 95\%, mp 150-151°C.} Found, %: C 68.79; H 5.64; Si 5.79; Br 16.35. C_{26}H_2,SiBrO. Calculated, %: C 68.98; H 5.58; Si 5.76; Br 16.39. IR spectrum (v, cm<sup>-1</sup>): 1110 (SiPh), 3530 (OH).$ 

 $\frac{2-\text{Bromo-4-tert-butyl-6-triphenylsilylphenoxytrimethylsilane (X)}{\text{was obtained in the same way as aryloxysilane (VII) from phenol (IX) and Me_3SiCl, yield 97%. Found, %: Br 14.28. C_{31}H_{35}Si_2Br0. Calculated, %: Br 14.55. IR spectrum (v, cm<sup>-1</sup>): 1250, 850 (SiMe), 1110 (SiPh), 935 (SiOAr).$ 

 $\frac{2-\text{Trimethylsilyl-4-tert-butyl-6-triphenylsilylphenol (V)}{(Ic) \text{ from aryloxysilane (X), yield 82\%, mp 119-120°C. Found, %: C 77.43; H 7.47; Si 11.60. C_{31}H_{36}Si_{2}O. Calculated, %: C 77.44; H 7.55; Si 11.68. IR spectrum (v, cm<sup>-1</sup>): 1250, 870 (SiMe), 1110 (SiPh), 3525 (OH).$ 

Oxidation of Phenol (IIc). A solution of 2 g (5 mmoles) of phenol (IIc) in 35 ml of benzene was added with vigorous stirring in an Ar atmosphere to 10 g of  $K_3[Fe(CN)_6]$  in 50 ml of 2 N KOH. After 5 h of stirring, the reaction mixture was left to stand overnight, and the organic layer was separated and dried over MgSO<sub>4</sub>. The solvent was distilled in vacuo, and the residue was recrystallized from a benzene—ethanol mixture. Yield, 1.2 g (60%) of disiloxy-diphenyl (IIIc), mp 269.5-270.0°C. Found, %: C 80.76; H 8.47; Si 6.91.  $C_{4.2}H_{5.6}Si_2O_2$ . Calculated, %: C 80.74; H 8.28; Si 6.99. IR spectrum (v, cm<sup>-1</sup>): 1250, 790 (SiMe), 1115 (SiPh), 945 (SiOAr).

Oxidation of Phenol (V). Under conditions similar to those in the oxidation of phenol (IIc), 4.8 g (0.01 mole) of phenol (V) yielded 3.8 g (80%) of disiloxydiphenyl (VI), mp 297.5-300.0°C (from a mixture of benzene and ethanol). Found, %: C 77.69; H 7.33; Si 11.58.  $C_{62}$ • H<sub>70</sub>Si<sub>4</sub>O<sub>2</sub>. Calculated, %: C 77.60; H 7.35; Si 11.71. IR spectrum (v, cm<sup>-1</sup>): 1260, 850 (SiMe), 1110 (SiPh), 920 (SiOAr).

## CONCLUSIONS

In the dimerization-rearrangement of silicon-containing aroxyls, the relative migration ability of o-organosilyl substituents decreases in the series  $PhMe_2Si > Me_3Si > MePh_2Si > Ph_3Si$ .

## LITERATURE CITED

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