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FACTORS DETERMINING TRANSFORMATIONS OF SILICON-CONTAINING AROXYLS.

COMMUNICATION 1. DISPROPORTIONATION AND DIMERIZATION-REARRANGEMENT AS ALTERNATIVE TRANSFORMATION PATHS OF SILICON-CONTAINING AROXYLS

D. V. Muslin and N. Sh. Lyapina

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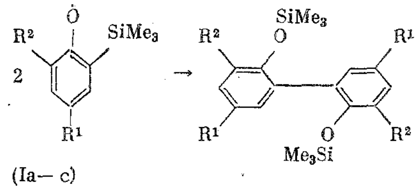
It is known [1] that replacement of at least one ortho-tert-butyl group of the stable 2,4,6-tri-tert-butylphenoxyl radical by the trimethylsilyl group leads to the appearance of a new type of transformation, namely, dimerization-rearrangement of silicon-containing aroxyls. The reaction products are tetrasubstituted 2,2'-bis(trimethylsilyloxy)diphenyls

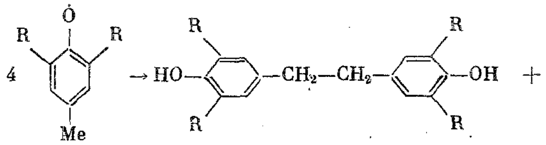


(Ia—c)

$R^1 = R^2 = t\text{-Bu}$ (Ia); $R^1 = t\text{-Bu}$, $R^2 = Me_3Si$ (Ib); $R^1 = R^2 = Me_3Si$ (Ic).

The stability of aroxyls obtained by oxidizing 2,6-di-tert-butyl-4-alkylphenols depends on the type of the para-alkyl substituent [2]. In the presence of para-alkyl groups with α-hydrogen atoms, the phenoxyl radicals disproportionate to form methylenequinone and the initial phenol. The rate of disproportionation decreases in the following series of para-alkyl substituents: $Me > Et > CHMe_2 > cyclo\text{-}C_6H_{11}$.

For 2,6-bis(trimethylsilyl)-4-alkylphenoxyls, both disproportionation and dimerization-rearrangement are, in principle, possible, and the character of the transformation of the aroxyl radical depends on the para-alkyl substituent. Thus, 2,6-bis(trimethylsilyl)-4-methylphenoxyl (II) disproportionates to form products of the same type as in the case of its carbon analog (R = t-Bu).



(II)

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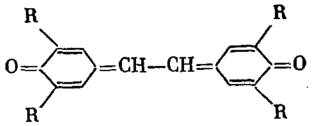
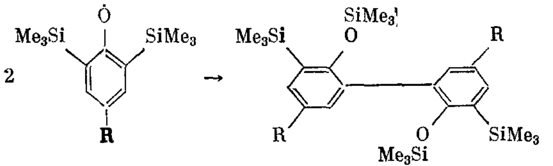


However, 2,6-bis(trimethylsilyl)-substituted 4-isopropylphenoxyl (III) [3] and 4-cyclohexylphenoxyl (IV), whose carbon analogs undergo disproportionation, convert into disiloxydiphenyls (V) and (VI) as the result of a dimerization-rearrangement

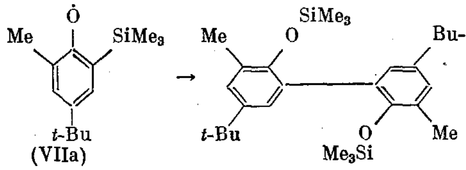


(III), (IV) (V), (VI)

R = CHMe$_2$ (III), (V); R = cyclo-C$_6$H$_{11}$ (IV), (VI).

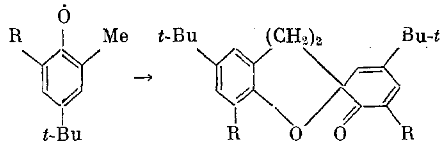
In the examples under consideration, with the same ortho-substituents, the possibility and the rate of disproportionation were determined by the para-alkyl substituent. It is known from [4] that the rate of dimerization-rearrangement of silicon-containing aroxyls depends on the spatial screening of the organosilyl group of the reaction center responsible for dimerization. It is thus possible to evaluate the competiveness of the disproportionation and dimerization-rearrangement reactions in a series of aroxyls of the same type with the same alkyl and different ortho-organosilyl substituents.

Among structurally similar aroxyls (VIIa-c), only aroxyl (VIIa) undergoes the dimerization-rearrangement [5]



(VIIa)

Aroxyls (VIIb) and (VIIc) disproportionate to form intraquinol ethers (VIIIa) and (VIIIb) as the end products, in the same way as the carbon analog of aroxyl (VIIa)



(VIIb), (VIIc) (VIIIa), (VIIIb)

R = Et$_3$Si (VIIb), (VIIIa); R = Ph$_3$Si (VIIc), (VIIIb).

EXPERIMENTAL

The synthesis of the silicon-containing analogs of 2,6-di-tert-butyl-4-methylphenol and the transformations of the corresponding aroxyls will be described later.

2,6-Dibromo-4-cyclohexyltrimethylsilane (IX). A mixture of 33.4 g (0.1 mole) of 2,6-dibromo-4-cyclohexylphenol, 16 ml (0.076 mole) of hexamethyldisilazane, and 50 ml of THF was boiled for 14 h. The solvent and the unreacted hexamethyldisilazane were then distilled and the residue was recrystallized from methyl ethyl ketone. Yield 27.75 g (68%) of aryloxysilane (IX), mp 83-84°C. Found: C 44.51; H 5.59; Br 39.56; Si 6.87%. $C_{15}H_{22}Br_2SiO$. Calculated: C 44.35; H 5.46; Br 39.34; Si 6.91%. IR spectrum (ν, cm^{-1}): 1260, 850 (SiMe)$_3$), 930 (SiOAr).

2-Bromo-4-cyclohexyl-6-trimethylphenol (X). A 38.5-ml portion of n-BuLi solution (0.05 mole) in hexane was added, with stirring and cooling in argon atmosphere, to a solution of 20.3 g (0.05 mole) of aryloxysilane (IX) in 50 ml of ether. After 5 min, the reaction mixture was hydrolyzed with 100 ml of saturated NH$_4$Cl solution. The organic layer was separated and dried over MgSO$_4$. The solvent was distilled in vacuo, and the residue was recrystallized from aqueous EtOH. Yield 10 g (62%) of phenol (X), mp 44.0-45.5°C. Found: C 54.03; H 6.83; Br 24.87; Si 8.18%. $C_{15}H_{23}BrSiO$. Calculated: C 55.04; H 7.08; Br 24.41; Si 8.58%. IR spectrum (ν, cm^{-1}): 1259, 840 ($SiMe_3$), 1160 (SiAr), 3520 (OH).

2-Bromo-4-cyclohexyl-6-trimethylphenoxytrimethylsilane (XI). A mixture of 9.43 g (0.03 mole) of phenol (X), 9.7 ml (0.03 mole) of Me_3SiCl and 4 ml of Et_3N in 25 ml of THF was boiled for 3 h, with stirring. After filtration, removal of solvent, and distillation of the residue in vacuo, 10 g (87%) of aryloxysilane (XI), bp 113-115°C (0.1 mm), were obtained. Found: C 53.87; H 7.73; Br 23.30; Si 13.69%. $C_{18}H_{31}BrSi_2O$. Calculated: C 54.11- H 7.82; Br 23.53; Si 14.96%. IR spectrum (ν, cm^{-1}): 1250, 840 ($SiMe_3$), 1085 (SiAr), 940 (SiOAr).

2,6-bis(trimethylsilyl-4-cyclohexylphenol (XII) was obtained in the same way as phenol (X) from aryloxysilane (XI), yield 73%, mp 20°C. Found: C 67.21% H 10.10; Si 17.93%. $C_{18}H_{32}SiO_2 \cdot Si_2O$. Calculated: C 67.41; H 10.06; Si 17.51%. IR spectrum (ν, cm^{-1}): 1250, 840 ($SiMe_3$), 1115 (SiAr), 3620 (OH).

2-Bromo-4-tert-butyl-6-methylphenoxytriethylsilane (XIII) was obtained in the same way as aryloxysilane (XI) from 2-bromo-4-tert-butyl-6-methylphenol and Et_3SiBr, yield 69%, bp 115-123°C (0.1 mm). Found: C 57.38; H 8.48; Br 22.57; Si 7.54%. $C_{17}H_{29}BrSiO$. Calculated: C 57.13; H 8.18; Br 22.36; Si 7.86%. IR spectrum (ν, cm^{-1}): 1015, 980 ($SiEt_3$), 935 (SiOAr).

2-Triethylsilyl-4-tert-butyl-6-methylphenol (XIV) was obtained in the same way as phenol (X) from aryloxysilane (XIII), yield 91%. Found: C 73.49; H 10.95; Si 9.61%. $C_{17}H_{30}SiO$. Calculated: C 73.34; H 10.85; Si 10.09%. IR spectrum (ν, cm^{-1}): 1012, 980 ($SiEt_3$), 1120 (SiAr), 3615 (OH).

2-Bromo-6-methyl-4-tert-butylphenoxytriphenylsilane (XV) was obtained in the same way as aryloxysilane (XI) from 2-bromo-4-tert-butyl-6-methylphenol and triphenylchlorosilane, yield 71%, mp 151-153°C. Found: C 69.28; H 5.18; Br 15.05; Si 4.08%. $C_{29}H_{29}BrSiO$. Calculated: C 69.45; H 5.83; Br 15.93; Si 4.60%. IR spectrum (ν, cm^{-1}): 1120 (SiPh), 950 (SiOAr).

2-Triphenylsilyl-4-tert-butyl-6-methylphenol (XVI) was obtained in the same way as phenol (X) from aryloxysilane (XV), yield 99%, mp 157-159°C (from hexane). Found: C 82.22; H 7.30; Si 6.23. $C_{29}H_{30}SiO$. Calculated: C 82.41; H 7.15; Si 6.65%. IR spectrum (ν, cm^{-1}): 1115 (SiPh), 3540 (OH).

Oxidation of Phenol (XII). A solution of 1.6 g (5 mmoles) of phenol (XII) in 25 ml of benzene was added to a solution of 5 g of $K_3[Fe(CN)_6]$ in 25 ml of 2 N aqueous KOH, and the mixture was stirred for 2 h in an argon atmosphere. The organic layer was separated and dried over $MgSO_4$. The solvent was distilled in vacuo and the residue was recrystallized from a mixture of methyl ethyl ketone and ethanol. Yield, 1.5 g (94%) of disiloxydiphenyl (VI), mp 129-130°C. Found: C 67.83; H 9.70; Si 17.24. $C_{36}H_{62}Si_4O_2$. Calculated: C 67.64; H 9.78; Si 17.57%. IR spectrum (ν, cm^{-1}): 1240, 845 ($SiMe_3$), 1110 (SiAr), 935 (SiOAr).

Oxidation of Phenol (XVI). In a similar way, from 4.24 g (5 mmoles) of phenol (XVI), 3.48 g (83%) of the quinol ether (VIIIb), mp 149-151°C (from ethanol) were obtained. Found: C 82.84; H 6.93; Si 6.56%. $C_{58}H_{56}Si_2O_2$. Calculated: C 82.81; H 6.71; Si 6.67%. IR spectrum (ν, cm^{-1}): 1110 (SiPh), 1685, 1665 (C=O).

CONCLUSIONS

The character of the transformations of silicon-containing phenoxyl radicals depends on both the type of the alkyl substituent (disproportionation in the case of para-methyl group, dimerization-rearrangement in the case of para-isopropyl and para-cyclohexyl groups) and type of organosilyl substituent (dimerization-rearrangement in the case of ortho-trimethylsilyl group, disproportionation in the case of ortho-triethylsilyl and orthotriphenylsilyl groups).

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