## Mechanism of Dimerization–Rearrangement of Organosilicon Aroxyls

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**Abstract**—Organosilicon aroxyls form disiloxybiaryls via C–C dimerization with simultaneous (or subsequent) isomerization of the dimeric intermediate, involving migration of the *ortho*-organosilyl substituents from carbon to oxygen.

Organosilicon aroxyls I containin *ortho*-organosilyl substituents can be converted to stable diamagnetic derivatives, tetrasubstituted O,O'-disiloxybiphenyls II [1–4].



 $\begin{array}{l} R_{3}Si = Me_{3}Si, \ R' = R'' = t\text{-Bu} \ (\mathbf{a}); \ R_{3}Si = Me_{2}EtSi, \ R' = R'' = t\text{-Bu} \ (\mathbf{b}); \ R_{3}Si = MeEt_{2}Si, \ R' = R'' = t\text{-Bu} \ (\mathbf{c}); \ R_{3}Si = Et_{3}Si, \ R' = R'' = t\text{-Bu} \ (\mathbf{d}); \ R_{3}Si = Me_{3}Si, \ R' = t\text{-Bu}, \ R'' = Me_{3}Si \ (\mathbf{e}); \ R_{3}Si = Me_{3}Si, \ R' = t\text{-Bu}, \ R'' = Ph_{3}Si \ (\mathbf{f}). \end{array}$ 

There are two routes biaryls II may form (Scheme 1). Route a involves isomerization of radicals I into aryl radicals III followed by recombination of the latter. Route b involves dimerization of the organosilicon aroxyls followed by isomerization of dimeric intermediate IV. Both isomerizations proceed via migration of the organosilyl substituents from carbon to oxygen.

Route *a* was first proposed to explain the conversion of aroxyl **Ia** via intermediate aryl radical **IIIa** formed by intramolecular homolytic substitution at silicon [1, 5]. However, later it was found that the rate of conversion of organosilicon aroxyls **I** into biaryls **II** depend on the size of the *ortho*-organosilyl substituents on the carbon atoms responsible for dimerization [4]. Moreover, the rate of decay of organosilicon aroxyls **I** follows a second-order equation [4]. This all argues in favor of route *b*.

The objects for study were 2,2'-bis(trimethylsiloxy)-3,3',5,5'-tetra-*tert*-butylbiphenylmercury (V) [6] and



4,6-di-*tert*-butyl-2-(trimethylsilyl)phenol (VI) [1, 2].

It is known that photolysis of organomercury compounds like  $Ar_2Hg$  gives free radicals which can be identified by their reaction products with the solvent [7]. Irradiation of biarylmercury **V** in hexane results in preferential formation of (2,4-di-*tert*-butylphenoxy)trimethylsilane (**VII**).

The reaction mixture, according to GLC and HPLC data, contains no disiloxybiphenyl **IIa**, the possible recombination product of aryl radicals **IIIa** formed by photolysis. Moreover, treatment of the reaction mixture with sodium methoxide in methanol gave 2,4-di*tert*-butylphenol (**IX**) and no dihydroxybiphenyl



 $\mathbf{R} = t$ -Bu.

VIII whose formation might be expected if biaryl IIa would form (Scheme 2).



Photolysis of biarylmercury V in  $CCl_4$  is complicated by the instability of certain products under experimental conditions. Chromatographic analysis showed that the reaction mixture contains [4,6-di(tertbutyl)-2-chlorophenoxy]trimethylsilane (X) and no biaryl IIa (Scheme 3). Phenoxysilane X partially decomposes under photolysis conditions, which was confirmed in separate experiment. Biaryl IIa is fairly stable under the same conditions. Treatment of the mixture of photolysis products of biaryl V with sodium methoxide in methanol gave 4,6-di-tertbutyl-2-chlorophenol (XI) and no dihydroxybiphenyl VIII (Scheme 3).

At the same time, phenoxyl radicals Ia obtained by a standard procedure of one-electron oxidation of phenols in hexane or carbon tetrachloride quantitatively convert into biaryl IIa. We found neither phenoxysilane **VII** nor chlorophenoxysilane **X**, which are formed by reaction of aryl radical III with hexane and carbon tetrachloride, respectively.

The resulting data generalized by Scheme 4 allow us to state that organosilicon phenoxyl radicals convert into tetrasubstituted disiloxybiphenyls via dimerization with simultaneous or subsequent isomerization of the intermediate, involving migration of the organosilyl groups from carbon to oxygen. This type of conversion can also be considered as a peculiar combination of dimerization of phenoxyl radicals with dienone-phenol and  $\alpha$ -silylketone rearrangements (Broock rearrangement [8].

OH

XI

Cl



$$\stackrel{\times}{\longrightarrow} \mathbf{IIa} \xrightarrow{\mathrm{CH}_3\mathrm{ONa}}_{\mathrm{CH}_3\mathrm{OH}} \rightarrow \mathbf{VIII}$$

 $\mathbf{R} = t - \mathbf{B} \mathbf{u}$ .

## EXPERIMENTAL

hν

Chromatographic analyses were performed on a Tsvet-212 gas chromatograph with a thermal conductivity detector, steel column (1000×4 mm), packing 5% SE-30 on Chromaton N-AW, carrier gas

helium, and a Tsvet-304 liquid chromatograph with a UV detector ( $\lambda$  254 nm), steel column (150×4 mm), packing Silasorb (5 µm), eluent hexane, flow rate 1 ml/min.

The IR spectra were measured on a Perkin-Elmer

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Scheme 4.



spectrophotometer for thin films or suspensions in Vaseline oil.

Photolysis was performed in sealed ampules under irradiation with a DRT-220 lamp.

**4,6-Di-***tert***-butyl-2-chlorophenol** (**XI**). Freshly distilled sulfuryl chloride, 26 ml, was added with stirring to 67.0 g of 2,4-di-*tert*-butylphenol in 150 ml of diethyl ether. The reaction mixture was stirred for 1 h at 20°C, washed with water and saturated with NaHCO<sub>3</sub>, and the organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed, and the residue was fractionated in a vacuum to obtain 55.0 g (70%) of compound **XI**, bp 105–106°C (1 mm) [9].

(4,6-Di-*tert*-butyl-2-chlorophenoxy)trimethylsilane (X). A solution of 2.4 g of chlorophenol XI, 2.0 ml of Me<sub>3</sub>SiCl, and 3.0 ml of Et<sub>3</sub>N in 50 ml of anhydrous benzene was heated under reflux with stirring under argon for 5 h. After cooling and filtering, the solvent was removed under reduced pressure to obtain 2.9 g (92%) of compound X, mp 89–90°C (from ethanol). IR spectrum, v, cm<sup>-1</sup>: 1245, 835 (Me<sub>3</sub>Si); 930 (Si–OAr). Found, %: C 65.43; N 9.335; Si 9.54. C<sub>17</sub>N<sub>29</sub>ClOSi. Calculated, %: C 65.24; H 9.35; Si 8.97.

(2,4-Di-*tert*-butylphenoxy)trimethylsilane (VII) was obtained similarly to phenoxysilane **X**, mp 32–33°C (from ethanol) [10].

**4,6-Di**-*tert*-**butyl-2-(trimethylsilyl)phenol (VI).** A solution of 20.0 g of 2-bromo-(4,6-di-*tert*-butyl-phenoxy)trimethylsilane [1] in diethyl ether was added dropwise with stirring under argon to 2.1 g of finely cut lithium in 50 ml of freshly distilled diethyl ether. After the reaction had began, the reaction mixture was stirred for 1 h and then cooled, the organic layer was separated, hydrolyzed with saturated aqueous  $NH_4CI$ ,

and extracted with benzene. The extract was dried with  $Na_2SO_4$ , and the solvent was removed to obtain 15.5 g (88%) of phenol **VI**, mp 70–71°C [1].

**Oxidation of phenol VI.** Phenol **VI**, 1 g, in 50 ml of a solvent (hexane or  $CCl_4$ ) was treated under argon with 10.0 g of  $K_3Fe(CN)_6$  in 50 ml of 2 M aqueous KOH. After the initially appreared blue color had disappered, the organic layer was separated, washed with water, dried, and the solvent was removed in a vacuum to obtain 0.95 g (95%) of biaryl **IIa**, mp 134–136°C [1].

2,2'-Bis(trimethylsiloxy)-3,3',5,5'-tetra-*tert*butylbiphenylmercury (V) was obtained according to [6] from 2.8 g of  $C_6H_5$ HgOH and 3.0 g of phenol VI. Yield 1.5 g (38%), mp 145–150°C.

**Photolysis of biarylmercury V.** *a*. Biarylmercury **V** (3.0 g in 50 ml of hexane) decomposed after 10-h irradiation with separation of 0.65 g (83.5%) of metallic mercury. We obtained 1.2 g (56%) of [2,4-di*tert*-butyl)phenoxy]trimethylsilane (**VI**), mp 32–33°C (from ethanol) [6].

b. Biarylmercury (V) (0.45 g in 7 ml  $CCl_4$ ) was irradiated for 10 h. The postreaction mixture was analyzed by GLC and HPLC and then treated with a saturated solution of sodium methoxide in methanol according to [11].

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