# ANIONIC REARRANGEMENT IN REACTION OF o-BROMOPHENOXYSILANES WITH n-BUTYLLITHIUM

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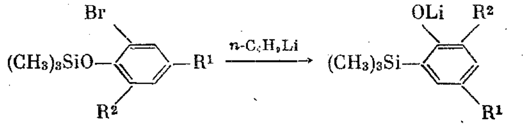
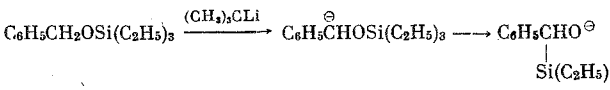
The halogen-metal exchange reaction is a convenient method for the preparation of aryllithium compounds [1]. Its attempted use to obtain aromatic organolithium compounds that contain the trimethylsiloxy group as one of the substituents proved unsuccessful. Vigorous reaction occurs when an o-bromophenoxytrimethylsilane in the series of substituted o-bromophenoxytrimethylsilanes is treated with n-butyllithium, which gives, instead of the expected aryllithium compound, the Li salt of the isomeric hydroxyaromatic compound, which contains the trimethylsilyl group in the aromatic ring. The reaction proceeds exceedingly fast and is completed simultaneously with the termination of adding the n-butyllithium.



(I)—(IV) (V)—(VIII)

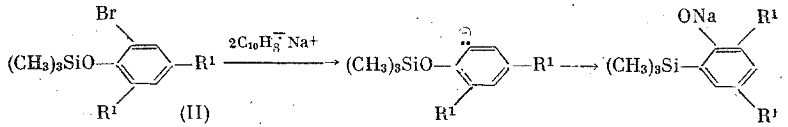
$R^1 = (CH_3)_3C$, $R^2 = H$ (I), (V); $R^1 = R^2 = (CH_3)_3C$ (II), (VI);
$R^1 = Br$, $R^2 = (CH_3)_3C$ (III), (VII); $R^1 = R^2 = Br$ (IV), (VIII)

According to [2], benzyloxytriethylsilane when treated with excess tert-butyllithium is converted to the isomeric $\alpha$-triethylsilylbenzyl alcohol; it is postulated that the carbanion, formed by metalation, migrates to the more stable alkoxy anion. The observed 1,2-anionic rearrangement: alkoxysilane-$\alpha$-silylcarbinol is formally analogous to the Wittig rearrangement



$$C_6H_5CH_2OSi(C_2H_5)_3 \xrightarrow{(CH_3)_3CLi} C_6H_5\overset{\ominus}{C}HOSi(C_2H_5)_3 \longrightarrow C_6H_5\underset{\displaystyle Si(C_2H_5)_3}{\underset{|}{C}}HO^{\ominus}$$

The reaction product of 2-bromo-4,6-di-tert-butylphenoxytrimethylsilane (II) with the anion-radical of sodium naphthalene under conditions that lead to the carbanion of the aryloxysilane is the Na salt of 2-hydroxy-3,5-di-tert-butylphenyltrimethylsilane. This testifies to the fact that the migration of the organosilyl group precedes the formation of the corresponding carbanion



(II)

$R^1$ $(CH_3)_3C$

As a result, the reaction discovered by us represents the 1,3-anionic rearrangement: phenoxysilane-hydroxyphenylsilane, which is also caused by a migration of the carbanion to the hydroxy anion.

1,3-Anionic rearrangement with a migration of the trimethylsilyl group, which proceeds in the same direction, i.e. from oxygen to carbon, was observed previously when hexamethyldisiloxane was reacted with tert-butyllithium in the presence of tetramethylethylenediamine (TMEDA) [3]

$$(CH_3)_3SiOSi(CH_3)_3 \xrightarrow[TMEDA]{(CH_3)_3CLi} \overset{\ominus}{C}H_2(CH_3)_2SiOSi(CH_3)_3 \longrightarrow (CH_3)_3Si(CH_3)_2SiO^{\ominus}$$

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TABLE 1

| Starting compound | Amount of RLi, equiv (solvent) | Reaction time | Type of migration | Rearrangement product | Yield, % | Literature reference |
|---|---|---|---|---|---|---|
| Benzyloxytriethylsilane | $(CH_3)_3CLi$, 1,2 (pentane) | 48 h | 1,2 | α-Triethylsilylbenzyl alcohol | 75 | [2] |
| Benzyloxytriethylsilane | $(CH_3)_3CLi$, 5 (pentane) | 144 h | 1,2 | α-Triethylsilylbenzyl alcohol | 96 | [2] |
| Hexamethyldisiloxane | $(CH_3)_3CLi$, 0.5 (TMEDA, 0.1 equiv) | 264 h | 1,3 | Trimethylsilyldimethylsilanol | 30 | [3] |
| 2-Bromo-4-tert-butylphenoxytrimethylsilane (I) | n-$C_4H_9Li$, 1 (ether-hexane) | 5 min | 1,3 | 2-Hydroxy-5-tert-butylphenyltrimethylsilane (V)* | 96 | — |
| 2-Bromo-4,6-di-tert-butylphenoxytrimethylsilane (II) | n-$C_4H_9Li$, 1 (ether-hexane) |  | 1,3 | 2-Hydroxy-3,5-di-tert-butylphenyltrimethylsilane (VI)* | 95 | — |
| 2-tert-Butyl-4,6-dibromophenoxytrimethylsilane (III) | n-$C_4H_9Li$, 1 (ether-hexane) |  | 1,3 | 2-Hydroxy-3-tert-butyl-5-bromophenyltrimethylsilane (VII)* | 85 | — |
| 2,4,6-Tribromophenoxytrimethylsilane (IV) | n-$C_4H_9Li$, 1 (ether-hexane) |  | 1,3 | 2-Hydroxy-3,5-dibromophenyltrimethylsilane (VIII)* | 92 | — |

Note. The numbers with an asterisk represent the substituted o-hydroxyphenylsilanes, whose corresponding Li salts are designated by the numbers without an asterisk.

TABLE 2

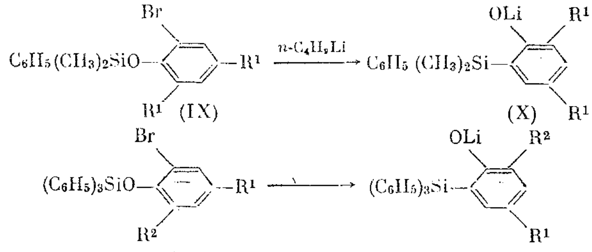
| Compound | Yield, % | mp., °C | Found, % |  |  |  | Empirical formula | Calculated, % |  |  |  | Cited lit. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H | Si | Br |  | C | H | Si | Br |  |
| (V) * | 95 | 76—77 | 70,26 | 9,93 | 12,71 | — | $C_{13}H_{22}OSi$ | 70,21 | 9,97 | 12,63 | — | [4] |
| (VI) * | 95 | 70—72 | 73,10 | 10,95 | 9,85 | — | $C_{17}H_{30}OSi$ | 73,31 | 10,86 | 10,08 | — | [5] |
| (VII) * | 85 | 52—53 | 51,46 | 7,05 | 9,21 | 25,97 | $C_{13}H_{21}SiBrO$ | 51,85 | 7,03 | 9,32 | 26,52 | — |
| (VIII) * | 92 | 56—57 | 33,40 | 3,88 | 8,40 | 49,34 | $C_9H_{12}SiBr_2O$ | 33,36 | 3,73 | 8,67 | 49,31 | — |
| (X) * | 90 | 63—64 | 76,83 | 9,71 | 8,33 | — | $C_{22}H_{32}OSi$ | 77,58 | 9,47 | 8,25 | — | [6] |
| (XIII) * | 96 | 157—159 | 82,22 | 7,30 | 6,23 | — | $C_{29}H_{30}OSi$ | 82,22 | 7,15 | 6,65 | — | — |
| (XIV) * | 95 | 150—151 | 68,97 | 5,64 | 5,62 | 16,35 | $C_{28}H_{27}SiBrO$ | 68,98 | 5,58 | 5,76 | 16,39 | — |

The intramolecular mechanism postulated by West [2] for rearrangements of this type, which includes involvement of the pentacoordination silicon atom in the transition state, is apparently also valid for the rearrangement of the aryloxysilanes. However, mention should be made of the difference in the conditions and degree of progress of the three mentioned examples of the rearrangements. In the examples described by West a substantial excess of tert-butyllithium or of the complex of tert-butyllithium with TMEDA is used; the 1,2- and 1,3-migrations of the organosilyl groups to benzyloxytriethylsilane and hexamethyldisiloxane precede the metalation of the $sp^3$-hybridized carbon atom, while the degree of progress of the anionic rearrangements of West depends on the length of reaction with the metalating agent.

The reaction of o-bromophenoxysilanes with n-butyllithium leads to the formation of the carbanion at the $sp^2$-hybridized carbon atom, proceeds with exceeding speed, is accompanied by the evolution of heat, and does not require amounts of the organolithium reagent that exceed the stoichiometric amount. As a rule, the yields of the rearranged products are quantitative. The comparative data on the rearrangement conditions and yields of rearranged products are given in Table 1.

The reaction of 2,4-dibromo-6-tert-butylphenoxytrimethylsilane (III) and 2,4,6-tribromophenoxytrimethylsilane (IV) with n-butyllithium revealed that the progress of the rearrangement is independent of the total number and position of the bromine atoms substituted in the aromatic ring. When o- and p-bromo atoms are simultaneously present the rearrangement leads exclusively to the o-isomers (VII) and (VIII).

The phenyldimethyl- and triphenylaryloxysilanes (IX)-(XI) rearrange in the same manner as the trimethylaryloxysilanes. It is difficult to estimate the relative migration capacity of the trimethylsilyl, phenyldimethylsilyl, and triphenylsilyl groups due to the high reaction rate with n-butyllithium



$R^1 = (CH_3)_3C$, $R^2 = CH_3$ (XI), (XIII); Br (XII), (XIV)

## EXPERIMENTAL METHOD

All of the reactions of the o-bromophenoxysilanes with n-butyllithium were run under the same conditions as described below.

Reaction of 2-Bromo-4-tert-butylphenoxytrimethylsilane (I) with n-Butyllithium. To 6.4 g (0.02 mole) of phenoxysilane (I) in 20 ml of absolute ether was added in drops 15.2 ml of a 1.4 N solution of n-butyllithium (0.02 mole) in n-hexane. The reaction was run in an argon atmosphere, with stirring and cooling, The cooled reaction mixture was hydrolyzed with saturated aqueous $NH_4Cl$ solution and then 30 ml of ether was added, and the mixture was stirred for another 5 min. The organic layer was separated, dried over $MgSO_4$, and the solvent was removed in the vacuum of a water-jet pump. The residue is 2-hydroxy-5-tert-butylphenyltrimethylsilane (V)* with mp 76-77° (from n-hexane) (cf. [4]). The yield of (V)* was 4.5 g (95%).

The rearrangement products or substituted o-hydroxyphenylsilanes are listed in Table 2.

## CONCLUSIONS

1. The reaction of substituted o-bromophenoxysilanes with n-butyllithium leads to the lithium salts of substituted o-hydroxyphenylsilanes.

2. The formation of the lithium salts of substituted o-hydroxyphenylsilanes, instead of the expected aromatic organolithium compounds, is explained by anionic rearrangement, where 1,3-migration of the organosilyl groups occurs.

## LITERATURE CITED

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