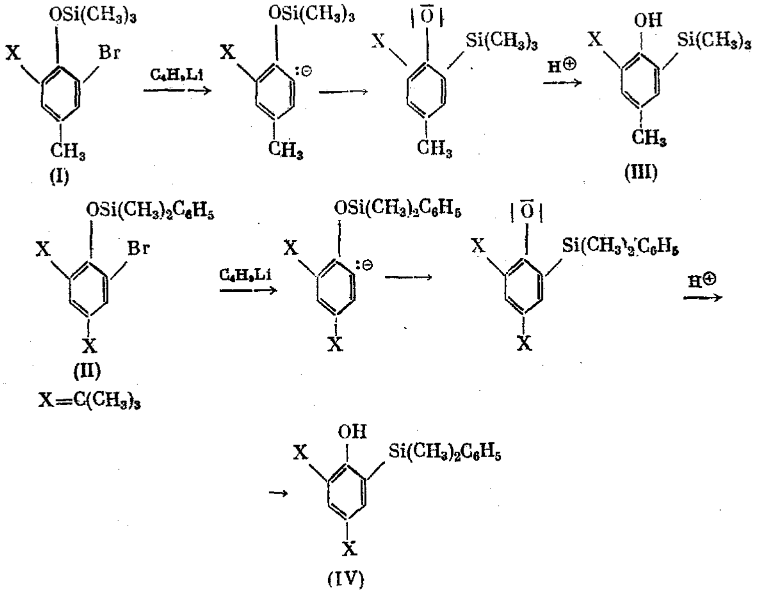
REACTIONS OF HALOARYLOXYSILANES WITH ORGANOLITHIUM COMPOUNDS

D. V. Muslin, N. Sh. Lyapina,
A. P. Kut'in, and N. S. Vasileiskaya

UDC 542.91:547.1'128:547.253.4

We have reported [1, 2] the anionic rearrangement induced by the action of n-butyllithium (BL) on o-bromophenoxysilanes, which provides a convenient preparative method for various silicon-containing phenols. The reactions of o- and p-bromophenoxysilanes with t-butyllithium [3] under the conditions of rearrangement of α-carbanions of benzyloxysilanes and benzyloxygermanes [4] proceed similarly.

This 1,3-anionic rearrangement can be considered as an intramolecular conversion of the silyloxyarenide ion to the silylarenolate ion; this is supported by the reaction of a mixture of (2-bromo-4-methyl-6-t-butylphenoxy)trimethylsilane (I) and (2-bromo-4,6-di-t-butylphenoxy)dimethylphenylsilane (II) with BL, which forms 2-(trimethylsilyl)-4-methyl-6-t-butylphenol (III) and 2-(dimethylphenylsilyl)-4,6-di-t-butylphenol (IV)



The reaction mixture did not contain the cross products, 2-(trimethylsilyl)-4,6-di-t-butylphenol and 2-(dimethylphenylsilyl)-4-methyl-6-t-butylphenol, whose formation would be expected from an intermolecular mechanism.

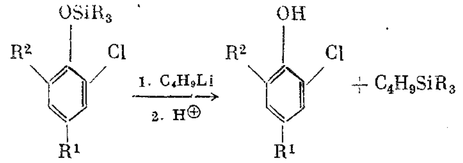
Examination of the interaction of o-bromoaryloxytrimethyl(dimethylethyl, triethyl, dimethylphenyl, diphenylmethyl, triphenyl)silanes with BL shows that the nature of the organosilyl group does not determine whether the rearrangement takes place. The necessary condition for rearrangement is formation of the carbanion (or of the potential carbanion of the organolithium compound) as a result of halogen–lithium exchange [1], the rate of which depends on the nature of the halogen and on the organolithium reagent. Organolithium compounds are known to cleave the Si–O bond. Thus the product distribution will be controlled by the relative rates of exchange and cleavage.

The interaction of chloroaryloxysilanes with BL forms exclusively chlorophenols (X)-(XIV) and the corresponding tetraorganosilanes as a result of Si–O cleavage, as in the case of phenoxytrimethylsilane

---

Institute of Chemistry, Academy of Sciences of the USSR, Gor'kii. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 890-893, April, 1978. Original article submitted December 21, 1976.

$$C_6H_5OSi(CH_3)_3 \xrightarrow[2.\ H^{\oplus}]{1.\ n\text{-}C_4H_9Li} C_6H_5OH + C_4H_9Si(CH_3)_3$$



R=CH_3, R^1=R^2=H (V), (X); R=CH_3, R^1=Cl, R^2=H (VI), (XI);
R=CH_3, R^1=H, R^2=Cl (VII), (XII); R=CH_3, R^1=R^2=Cl (VIII),) (XIII);
R=C_6H_5, R^1=H, R^2=Cl (IX), (XIV)

The products of the reaction of bromoaryloxysilanes (XV)-(XVII) with BL are silicon-containing phenols (XVIII)-(XX), implying the predominance of the exchange reaction, which precedes anionic rearrangement

TABLE 1

Compound	Yield, %	bp, deg C (p, mm Hg)/mp, deg C	n_D^{20}	$\frac{\text{Found}}{\text{Calculated}}$, % C	H	Si	Hal	Empirical formula	IR spectrum ν, cm⁻¹ Si–OAr	OH
(I)	80	86—88 (0,5)	1,5227	$\frac{53,75}{53,33}$	$\frac{7,71}{7,35}$	$\frac{9,19}{8,91}$	$\frac{25,42}{25,34}$	$C_{14}H_{23}SiBrO$	925	—
(III)	90	53—54	—	$\frac{71,15}{71,12}$	$\frac{10,32}{10,23}$	$\frac{11,56}{11,88}$	$\frac{—}{—}$	$C_{14}H_{24}SiO$	—	3645 3620
(IX)	66	87—89	—	$\frac{68,51}{68,40}$	$\frac{4,49}{4,30}$	$\frac{6,64}{6,66}$	$\frac{16,58}{16,82}$	$C_{24}H_{18}Cl_2SiO$	910	—
(XVI)	96	67—69 (0,1)	1,5445	$\frac{33,28}{33,34}$	$\frac{3,80}{3,73}$	$\frac{8,96}{8,66}$	$\frac{49,70}{49,31}$	$C_9H_{12}SiBr_2O$	920	—
(XIX)	75	63—65 (0,1)	1,5518	$\frac{44,11}{44,08}$	$\frac{5,65}{5,35}$	$\frac{12,30}{11,44}$	$\frac{32,07}{32,58}$	$C_9H_{13}SiBrO$	—	3530
(XXI)	97	78(0,1)	1,5422	$\frac{34,51}{34,41}$	$\frac{3,56}{3,53}$	$\frac{8,79}{8,94}$	$\frac{47,99}{48,10}$	$C_9H_{11}Cl_2BrSiO$	925	—
(XXII)	49	120—122	—	$\frac{57,52}{57,61}$	$\frac{3,60}{3,42}$	$\frac{5,93}{5,61}$	$\frac{30,38}{30,14}$	$C_{24}H_{17}SiCl_2O$	920	—
(XXIII)	67	52(0,1)	1,5380	$\frac{45,81}{45,96}$	$\frac{5,48}{5,14}$	$\frac{11,73}{11,94}$	$\frac{30,09}{30,15}$	$C_9H_{12}SiCl_2O$	—	3540
(XXIV)	77	179—181	—	$\frac{68,64}{68,40}$	$\frac{4,46}{4,30}$	$\frac{6,68}{6,66}$	$\frac{16,75}{16,82}$	$C_{24}H_{18}SiCl_2O$	—	3500
(XXV)	77	100—102 (0,1)	1,5657	$\frac{36,54}{36,55}$	$\frac{4,83}{4,72}$	$\frac{6,47}{6,57}$	$\frac{48,42}{48,41}$	$C_{13}H_{20}SiBrIO$	920	—
(XXVI)	88	79—82 (0,2)	1,5274	$\frac{52,09}{51,82}$	$\frac{7,24}{7,03}$	$\frac{9,20}{9,32}$	$\frac{26,32}{26,52}$	$C_{13}H_{21}SiBrO$	—	3530

TABLE 2

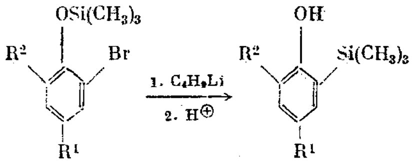
Aryloxysilane	R_3Si	Hal	R^1	R^2	Type of reaction*	Phenol	R^3
(V) [6]	$(CH_3)_3Si$	Cl	H	H	A	(X)	Cl
(VI) [6]	$(CH_3)_3Si$	Cl	Cl	H	A	(XI)	Cl
(VII) [7]	"	Cl	H	Cl	A	(XII)	Cl
(VIII) [7]	"	Cl	Cl	Cl	A	(XIII)	Cl
(IX)	$(C_6H_5)_3Si$	Cl	H	Cl	A	(XIV)	Cl
(XV) [6]	$(CH_3)_3Si$	Br	H	H	B	(XVIII) [6]	$(CH_3)_3Si$
(XVI)	"	Br	Br	H	B	(XIX)	$(CH_3)_3Si$
(XVII) [1]	$(CH_3)_3Si$	Br	Br	Br	B	(XX) [1]	"
(XXI)	"	Br	Cl	Cl	B	(XXIII)	"
(XXII)	$(C_6H_5)_3Si$	Br	Cl	Cl	B	(XXIV)	$(C_6H_5)_3Si$
(XXV)	$(CH_3)_3Si$	I	$(CH_3)_3C$	Br	B	(XXVI)	$(CH_3)_3Si$
(I)	$(CH_3)_3Si$	Br	CH_3	$(CH_3)_3C$	B	(III)	"
(II) [8]	‡	Br	$(CH_3)_3C$	$(CH_3)_3C$	B	(IV) [8]	‡
(I)	$(CH_3)_3Si$	Br	CH_3	$(CH_3)_3C$	A†	(XXV)	Br

---

*A denotes Si–O cleavage in the aryloxysilane; B halogen–lithium exchange followed by 1,3-rearrangement; AlkLi = n-C_4H_9Li.

† AlkLi = CH_3Li.

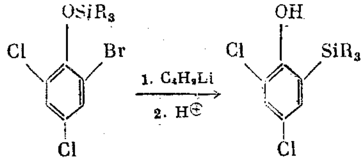
‡ R_3Si = $C_6H_5(CH_3)_2Si$.



$R^1=R^2=H$ (XV), (XVIII); $R^1=Br$, $R^2=H$ (XVI), (XIX); $R^1=R^2=Br$ (XVII), (XX)

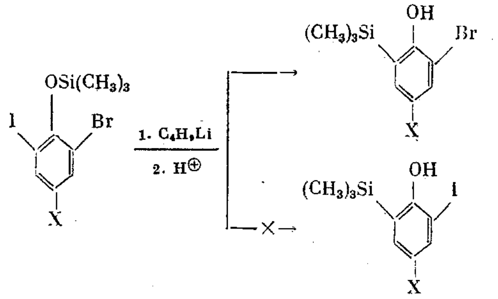
The contribution of the cleavage reaction diminishes in aryloxysilanes in the order (XV), (XVI), and (XVII), apparently as a result of the increased rate of the exchange reaction when bromine is present at positions 4 and 4,6 of aryloxysilanes (XVI) and (XVII) [4].

That the relative rate of bromine–lithium exchange is higher than those of chlorine exchange and of Si–O cleavage causes silicon-containing phenols (XXIII) and (XXIV) to be formed in the reactions of (2-bromo-4,6-dichlorophenoxy)trimethylsilane (XXI) and (2-bromo-4,6-dichlorophenoxy)triphenylsilane (XXII) with BL



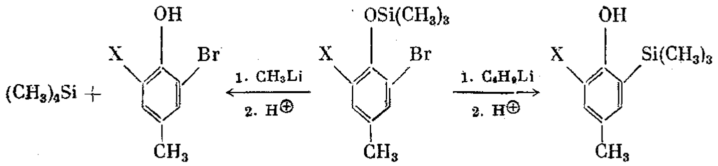
$R=CH_3$ (XXI), (XXIII); $R=C_6H_5$ (XXII), (XXIV)

The formation of 2-bromo-4-t-butyl-6-(trimethylsilyl)phenol (XXVI) in the reaction of (2-bromo-4-t-butyl-6-iodophenoxy) trimethylsilane (XXV) with BL is consistent with our experimental results and with the reported increase in the rate of halogen–lithium exchange in the order Cl < Br < I [5]



The reactivity of the organolithium reagent also affects the product distribution from its reaction with the halogenoaryloxysilane.

Methyllithium cleaves the Si–O bond of aryloxysilane (I), forming bromophenol (XXVII) and tetramethylsilane. Interaction of aryloxysilane (I) with BL involves mainly bromine–lithium exchange and forms silicon-containing phenol (III) by 1,3-anionic rearrangement



EXPERIMENTAL

Aryloxysilanes (I), (V)-(VIII), (XV)-(XVII), (XXI), and (XXV) were prepared by silylation of the appropriate halophenols with trimethylchlorosilane in the presence of triethylamine or hexamethyldisilazane. Aryloxydimethylphenylsilanes (II) and aryloxytriphenylsilanes (IX) and (XXII) were synthesized by heating equimolar quantities of the relevant chlorosilane, halophenol, and triethylamine in THF.

The properties of aryloxysilanes (II), (V)-(VIII), (XV), and (XVII) accorded with literature data [6-8]. The yields, physical constants, elemental analyses, and IR parameters of aryloxysilanes (I), (IX), (XVI), (XXI), (XXII), and (XXV) are summarized in Table 1.

The reaction of haloaryloxysilanes with organolithium compounds was carried out by the procedure of [1]. Table 2 summarizes the starting aryloxysilanes and the products of their reaction with the organolithium compounds. The new silicon-containing phenols synthesized as a result of the rearrangement are summarized in Table 1.

CONCLUSIONS

The 1,3-anionic rearrangement of aryloxysilanes is an intramolecular process that does not depend on the nature of the migrating organosilyl group but is controlled by the reactivities of the labile halogen of the aryloxysilane and of the organolithium compound in the halogen–lithium exchange reaction, which generates the silyloxyarenide ion.

LITERATURE CITED

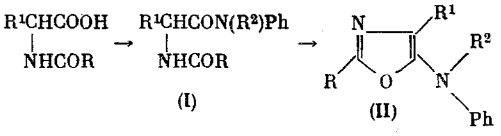
1. D. V. Muslin, G. A. Razuvaev, N. N. Vavilina, and N. S. Vasileiskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 1975, 182.
2. G. A. Razuvaev, D. V. Muslin, N. S. Vasileiskaya, and F. B. Gershanov, Proceedings of the Fourth International Symposium on the Chemistry of Organosilicon Compounds, Vol. 1, Part 2, p. 160 (1975).
3. R. West, R. Lowe, H. F. Stewart, and A. Wright, J. Am. Chem. Soc., 93, 282 (1971).
4. W. J. Trepka and R. J. Sonnenfeld, J. Organomet. Chem., 16, 317 (1969).
5. D. E. Applequist and D. F. O'Brien, J. Am. Chem. Soc., 85, 743 (1963).
6. J. L. Speier, J. Am. Chem. Soc., 74, 1003 (1952).
7. G. D. Cooper, J. Org. Chem., 26, 925 (1961).
8. G. A. Razuvaev, N. S. Vasileiskaya, D. V. Muslin, N. N. Vavilina, and S. N. Uspenskaya, Zh. Org. Khim., 6, 980 (1970).

SYNTHESIS OF 5-R_2N-OXAZOLES FROM α-N-ACYLATED AMINO ACIDS

G. Ya. Kondrat'eva, M. A. Aitzhanova,
V. S. Bogdanov, and Z. N. Ivanova

UDC 542.91:547.787

In the present work we synthesized aminooxazoles (II), including compounds of type II with R^1=H, from α-acylated amino acids and secondary amines [$C_6H_5NHCH_3$ and $(C_6H_5)_2NH$] without isolating the amides (I) formed as intermediates according to the scheme



The condensation is carried out in the presence of an excess of the dehydrating agent, viz., halogen-containing compounds of phosphorus or P_2O_5, in a medium of boiling $CHCl_3$. The alkalinization of the reaction mass is followed by the isolation of the 5-R_2N-oxazole, often in a mixture with the methylphenyl amide (or the diphenyl amide) of the original acylated amino acid (Table 1). The presence of the latter is due to the incompleteness of the reaction I→II or (and) the splitting of the oxazole ring upon the neutralization of the acidic mixtures. The conversion of I into II depends on the reaction time and the relative amounts of the reactants, the extent of decomposition of II is influenced by the concentration of the base, the neutralization temperature, and the stirring rate. The stability of the individual compounds of type II in acidic aqueous media (and, therefore, the extent of splitting upon neutralization) is closely related to the structure of the radicals R and R^1. The C-phenyl-substituted oxazoles (II, R or $R^1 = C_6H_5$) are the most stable with respect to hydrolysis, and compounds of type II with R^1=H are most easily hydrolyzed. The control experiments showed that the 5-methylphenylaminooxazoles with a phenyl substituent on the ring, for example, 2-phenyl-4-methyl-5-methylphenylaminooxazole (IIh) and even 2-phenyl-5-methylphenylaminooxazole (IIc), remain unchanged during brief heating with water, while the 2-methyl-5-methylphenylamino compound (IIa) splits to the methylphenyl amide of glycine not only in aqueous media, but also upon standing in the air. The method is not applicable to N-formylated α-amino acids (formylglycine and formylalanine) and yields unsatisfactory results in the case of

---

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 894-898, April, 1978. Original article submitted December 30, 1976.