Formation and Reactions of Functional Silyl Anions

By HAMAO WATANABE,* KAZUAKI HIGUCHI, MITSUNOBU KOBAYASHI, MASAHIRO HARA, YUKO KOIKE, THORU KITAHARA, and YOICHIRO NAGAI

(*Department of Chemistry, Gunma University, Kiryu, Gunma* 376 *Japan*)

Summary Functionalized silyl anions such as methyldimethoxysilyl anion and methoxydimethylsilyl anion were first prepared in common solvents and allowed to react with organic halides giving rise to functional organosilicon compounds.

ALTHOUGH organosilyl-metal compounds have been extensively studied,[1] the formation of silicon-functional compounds has not yet been reported. We now report that *sym*-methylmethoxydisilanes were cleaved readily by sodium methoxide to give a new class of organosilyl-metal compounds, mono- and di-methoxysilyl-sodium (**1**). The silicon-functional silyl-sodium compounds thus formed

TABLE. Reactions of methoxysilyl-sodium (**1**) with organic halides in tetrahydrofuran.[a]

Silyl-sodium	Halide	Molar ratio (anion : halide)	Reaction time/h	Yield of (**2**) %[b]
(**1a**)[c]	PhBr	2 : 1	2	80
"	PhCl	2 : 1[d]	5	53
"	Bu^nBr	1·5 : 1[e]	24	60
"	Bu^nCl	2 : 1[d]	"	60
(**1b**)[c]	PhBr	2 : 1	"	90
"	p-$C_6H_4Br_2$	4 : 1	"	74[f]

[a] All the reactions were carried out at room temperature under argon using 20 mmol of disilane. Other solvents could be used; benzene, triethylamine, *etc.* [b] G.l.c. yield based on the halide used. [c] Prepared from an equimolar mixture of the disilane and sodium methoxide. [d] 18-Crown-6 ether (10 mol % relative to the halide) was added (ref. 3). [e] 15 mmol of the disilane was used. [f] Value for *p*-bis(methoxydimethylsilyl)benzene (R. L. Merker and M. J. Scott, *J. Polymer Sci., Part A*-1, *Polymer Chem.*, 1964, **2**, 15).

reacted with organic halides to yield the corresponding mono- and di-methoxyorganosilanes (**2**), respectively. The reactions were conveniently carried out by adding disilane to a mixture of sodium methoxide and organic halides in tetrahydrofuran. The products were obtained in good yields (Table).

$$(\mathrm{MeO})_m\mathrm{Si}_2\mathrm{Me}_{6-m} \xrightarrow{\mathrm{NaOMe}} (\mathrm{MeO})_n\mathrm{Me}_{3-n}\mathrm{Si}^-\mathrm{Na}^+$$

$m = 2$ and 4

(**1**)

a; $n = 1$

b; $n = 2$

$$(\mathbf{1a,b}) \xrightarrow{\mathrm{RX}} \mathrm{RSiMe}_{3-n}(\mathrm{OMe})_n$$

(**2**)

a; $n = 1$

b; $n = 2$

These reactions have an advantage in that the generation of the silyl anions can be quite easily accomplished in common solvents, since the cleavage of hexamethyldisilane requires the use of strongly co-ordinating aprotic solvents, such as hexamethylphosphoramide[2] and 1,3-dimethyl-2-imidazolidone.[3]

The present reaction may provide a novel and convenient method for preparation of silicon-functional organosilicon compounds starting from dimethyltetramethoxydisilane and dimethoxytetramethyldisilane which are readily accessible in large amounts.[4]

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