

DIRECT PREPARATION OF HEXAALKYLDISILOXANES FROM TRIALKYLSILANES AND CYCLOSILOXANES FROM DIALKYLSILANES USING POTASSIUM SUPEROXIDE-CROWN ETHER

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Abstract. Trialkylsilanes were readily transformed to the corresponding hexaalkyldisiloxane in high yields with KO_2 -18-crown-6. Meanwhile, dialkylsilanes gave mainly hexaalkylcyclotrisiloxanes under the same reaction conditions.

The chemical reactivity, including mechanistic details, for the reaction of potassium superoxide (KO_2) with organic substrates has been reviewed. Predominating reactions among these are oxidation of organic substrates.¹ The extended works using KO_2 are dehydrohalogenation², desulfurization³, N-alkylation of pyrrole⁴, decyanation⁵, and cleavage of ether⁶. Typically, the reactions are carried out in the presence of crown ether to increase the solubility of KO_2 in aprotic solvents. Among such KO_2 reactions, however, no example has been reported for the KO_2 induced oxidation of alkylsilanes. In this paper, we wish to report that alkylsilanes are readily transformed into the corresponding siloxane compounds using KO_2 /crown ether in acetonitrile. Our results are summarized in table-1.

High yields and short reaction times are the obvious advantages to this reagent. Reaction went to completion under stirring (except *iso*-propyl, run 1) within 1-2 hours in most cases. Trialkylsilanes such as triethylsilane, dimethylphenylsilane gave the corresponding hexaalkyldisiloxane in high yields. The bulky triisopropylsilane also gave the hexaisopropylidisiloxane in 85% along with triisopropylsilanol in 15% (GLC analysis). For diarylsilanes such as diphenylsilane, only octaphenylcyclotetrasiloxane⁷ was obtained quantitatively (run 4). No other cyclotrisiloxane was formed. In contrast, methylphenylsilane under the same reaction conditions, a mixture of 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane and 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclopentasiloxane were formed in 67% and 33% respectively (run 5). Dialkylsilanes (such as cyclohexylmethylsilane and methyl-*n*-octylsilane) gave a mixture of the corresponding cyclotrisiloxane and cyclotetrasiloxane in high yield (runs 6 and 7). Interestingly, cyclopentasiloxanes such as 1,3,5,7,9-pentacyclohexyl-1,3,5,7,9-pentamethyl-cyclopentasiloxane and 1,3,5,7,9-pentamethyl-1,3,5,7,9-penta-*n*-octyl-cyclopentasiloxane were not formed in this case.

Diethylsilane was also examined under the same reaction condition. Cyclo(tri, tetra or penta)siloxanes were formed (GLC) (run 8). The cyclotetrasiloxane **c** was the major product in most cases (runs 4-8). Acetonitrile was the best choice of solvent for this investigation. In our hands, neither tetrahydrofuran nor dimethoxyethane, common organic solvents, produced high yields even after several hours of stirring.

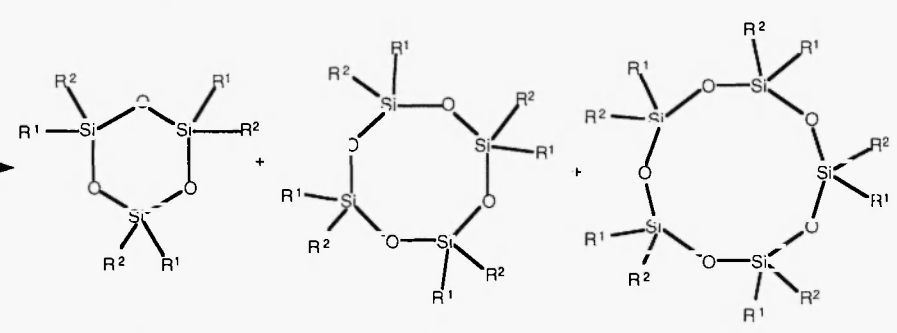
In a general procedure, trialkylsilane (2mmol), KO_2 (4 mmol) and catalytic amount of 18-crown-6 were added in dry acetonitrile (4 ml). The reaction mixture was stirred under a nitrogen atmosphere for 1-2 h. The work-up procedure was very simple. After the reaction, KO_2 was removed by filtration and washed with dichloromethane. The solvents were evaporated. The residue was chromatographed on a short column of silica gel (ϕ : 1cm, 1:3 cm, eluent: methylene chloride) to give the corresponding hexaalkyldisiloxane compounds (table 1, run 1-3). Our yields are based on quantities obtained after this step. The products were identified by mass, IR and NMR spectroscopy. Similarly, dialkylsilanes gave the corresponding cyclotrisiloxanes in 87-95% yields (runs 4-8). For comparison, tri-*iso*-propylsilane was treated with KOH instead of KO_2 under the same reaction conditions. Hexa-*iso*-propylidisiloxane and tri-*iso*-propylsilanol were then formed (51% and 39%) along with 10% of unchanged tri-*iso*-propylsilane (GLC) even under reflux for 4 h. With stirring under the same reaction condition for 8 h, hexa-*iso*-propylidisiloxane was formed in only 1% along with tri-*iso*-propylsilanol (5%) and starting material was recovered (GLC).

In summary, it has been shown here that disiloxane and cyclopentasiloxane are readily obtained from the corresponding trialkylsilane and dialkylsilane using potassium superoxide-crown ether in

acetonitrile. We are presently investigating the organic functional group transformation using our reagents and will report on them in due course.

Table 1. Direct Preparation of Hexaalkyldisiloxanes from Trialkylsilanes and Cyclosiloxanes from Dialkylsilanes using Potassium Superoxide-Crown ether

(Trialkylsilane) ^a						
$\text{R}^1\text{R}^2\text{R}^3\text{SiH} \xrightarrow[\text{CH}_3\text{CN}]{\text{KO}_2 / 18\text{-Crown-6}} \text{R}^1\text{R}^2\text{R}^3\text{Si-O-SiR}^1\text{R}^2\text{R}^3$						
Entry	R ¹	R ²	R ³	Reaction Condition	Product ^c	% Yield (isolated)
1	<i>i</i> -Pr	<i>i</i> -Pr	<i>i</i> -Pr	Reflux 1h	a	85
2	Et	Et	Et	Stir. 2h	a	90
3	Ph	Me	Me	Stir. 1h	a	95

(Dialkylsilane) ¹							
$\text{R}^1\text{R}^2\text{SiH}_2 \xrightarrow[\text{CH}_2\text{CN}]{\text{KO}_2 / 18\text{-Crown-6}}$ 							
Entry	R ¹	R ²	Reaction Condition	Product ^c			% Yield (isolated)
				b	c	d	
4	Ph	Ph	Stir. 1h	-	100 ^d	-	95
5	Ph	Me	Stir. 2h	-	67	33	96
6	<i>n</i> -Oct	Me	Stir. 1h	11	89	-	93
7	Cyclohex	Me	Stir. 1h	17	83	-	90
8	Et	Et	Stir. 1h	11	83	6	87

^a Reactions were run at 25° (except entry 1) by using 1:2 molar ratios of silane: KO₂. ^b Same conditions as in a with 1:3 molar ratios of silane: KO₂. ^c Products are assigned by selected ¹H NMR, IR, and GC-Mass spectral data. ^d Product was crystallized and identified with previous report: ref. 7.

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