Letter

Electrochemical activation of diorganyl dialkoxysilanes for siloxane backbone extension

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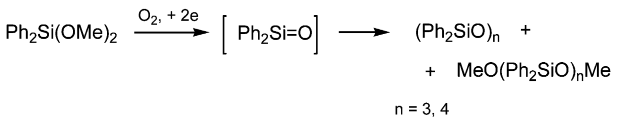
The reaction of diorganyl dialkoxysilanes $PhRSi(OAlk)_2$ (R = Ph, vinyl, OMe; Alk = Me, Et) with electrochemically reduced forms of oxygen provides reactive intermediates that insert into hexamethyldisiloxane or permethyl cyclosiloxanes, D_3 and D_4, to give siloxane products with one additional PhRSiO fragment; the process is thought to occur with the intermediacy of diorganylsilanones.

Diorganyl silanones, silicon analogs of ketones, are thought to be intermediates in many reactions of organic silicon compounds.[1,2] These species have never been observed in solution at room temperature nor has their formation been unequivocally proven, yet their transient formation was supposed in thermal transformations of oxygen-containing silicon compounds,[3–6] in reactions of silenes with carbonyl compounds,[7] in oxidation of silylenes by DMSO[8] and epoxides[9] and in the oxidation of dichlorosilanes by O-donor reagents under relatively mild conditions.[2,10,11] We recently proposed an electrochemical method for the *in situ* generation of diorganyl silanones from diorganyl dichlorosilanes.[12] On the other hand, although silicon chloro derivatives remain one of the most common starting materials for various synthetic processes, the use of easily available non-chlorinated organosilicon reagents is among the utmost priorities in silicon chemistry. Here, we report initial results of the use of diorganyl dialkoxysilanes as a source of an electrogenerated reagent, presumably diorganyl silanone, allowing to selectively incorporate a PhRSiO group into linear and cyclic siloxanes.

To check the hypothesis that diorganyl dialkoxysilanes would react with nucleophilic forms of O_2, it was first shown that they do not react with molecular oxygen itself under the experimental conditions used: bubbling oxygen for 4 h through a 10^{-2} mol L^{-1} solution of $Ph_2Si(OMe)_2$ in DMF containing 0.1 M Bu_4NPF_6 did not cause the formation of any new products. When the same solution was electrolyzed in a divided three-electrode cell at the reduction potentials of O_2, where $Ph_2Si(OMe)_2$ is electrochemically inactive, a mixture of siloxane products was formed (Scheme 1).

The main product, hexaphenylcyclotrisiloxane (**1**), was obtained with an 18% isolated yield [there was also 31% of unreacted $Ph_2Si(OMe)_2$ left] along with octaphenyltetracyclosiloxane (**2**) and higher diphenylsiloxanes of linear structure The conditions and yields of the electrolyses are summarized in Table 1. Siloxane products supposedly result from cyclooligomerization of electrogenerated transient silanone, $Ph_2Si{=}O$. The insertion of the latter into Si–O bonds of the starting $Ph_2Si(OMe)_2$ or of primarily formed siloxanes, one of the typical reactions of silanones,[2] might account for the formation of the higher siloxanes.

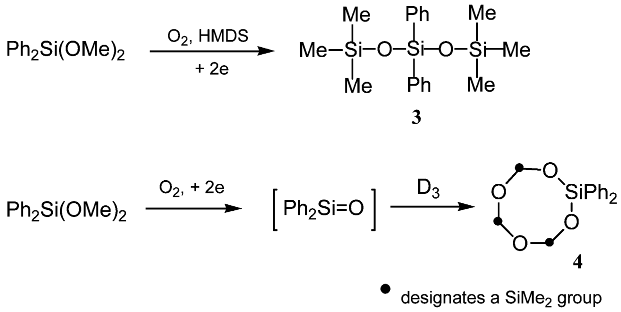


Scheme 1

Cathodic generation of diphenylsilanone from $Ph_2Si(OMe)_2$ was attempted using hexamethyldisiloxane (HMDS) as a silanone trap. Thus, the reduction of molecular oxygen in the presence of $Ph_2Si(OMe)_2$ and HMDS in a 0.1 M solution of Bu_4NPF_6 in DMF resulted in the formation of 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane (**3**) as shown in Scheme 2. When permethylcyclosiloxanes,[13] D_n (n = 3, 4), were used instead of HMDS, the corresponding cyclic products $D_nD^{Ph_2}$ were obtained (Table 1). Some amount of linear insertion product **3** was also found in the reaction mixture, probably due to HMDS formed from Me_3SiCl, which was usually added to the solution, prior to the main electrolysis, in order to remove traces of water. In principle, HMDS could also arise from ring-chain equilibration[14] of D_3 or D_4, though such processes usually need heating or a catalyst.

Similar results were obtained when using diphenyl diethoxysilane as the silanone precursor: in the experiment with no trap, the product distribution was as in the case of $Ph_2Si(OMe)_2$ (Table 1, run 1), whilst the addition of HMDS gave rise to the linear insertion product **3**. In general, the product distribution with diorganyl dialkoxysilanes is much narrower compared to that observed when diorganyl dichlorosilanes are used as silanone precursors[12] and less by-products were formed.

As seen from Table 1, cyclic siloxanes diverge during the electrolysis[15] giving rise, under the usual conditions, to multiple products so that the yield of each is generally not very high. However, with HMDS, forming but a single product, the isolated physical yield (taking into account the 60% conversion



Scheme 2

Table 1 Electrochemically induced extension[a] of the siloxane backbone using diorganyl dialkoxysilanes $PhRSi(OAlk)_2$

Run	$PhRSi(OAlk)_2$	Silanone trap	Q/F mol^{-1} [b]	Products (% yield)[c]
1	$Ph_2Si(OMe)_2$	No trap	1.9	$(Ph_2SiO)_3$ (**1**, 18%), $(Ph_2SiO)_4$ (**2**, 2%), $MD^{Ph_2}M$ (**3**, 5%)[d]
2		HMDS	1.7	**3** (46%)
3		D_3	2.1	$D_3D^{Ph_2}$ (**4**, 24%), $D_4D^{Ph_2}$ (**5**, 5.3%), **3** (6.1%)
4		D_4	2.2	**4** (21%), **5** (4.6%), **3** (2.8%)
5		D_4	2.0	**5** (29%), **4** (13%)[e]
6	$Ph_2Si(OEt)_2$	No trap	2.0	**1** (23%), **2** (5%), **3** (5.2%)
7		HMDS	1.8	**3** (43%)
8	$PhSi(OMe)_3$	D_3	1.9	$D_3D^{Ph,MeO}$ (**6**, 26%), $D_4D^{Ph,MeO}$ (**7**, 3.8%)
9	$PhVinSi(OMe)_2$	D_3	2.0	$D_3D^{Ph,Vin}$ (**8**, 18%)

[a] In DMF + 0.1 M Bu_4NPF_6, $T = 45\,°C$. [b] Related to the total amount of dialkoxysilane taken, typical conversion of $PhRSi(OAlk)_2$ was α = 60–75%. [c] Non-optimized isolated yields after column chromatography on SiO_2. [d] HMDS resulted from the hydrolysis of Me_3SiCl. [e] $T = -10\,°C$.

of the starting $Ph_2Si(OEt)_2$) amounts to 71%. When using cyclic traps for the silanones, there are two points worth addressing. First, there is a remarkable formation of polysiloxanes in the process compared to the experiments with HMDS as the trap (Table 1), and second, products resulting from siloxanes other than the starting siloxane (*e.g.*, D_3D^{PhR} products from D_4 and D_4D^{PhR} products from D_3) are obtained. Ring disproportionation (usually promoted by high concentrations and temperature[14]) might account for these phenomena. Since the concentration of permethyl cyclosiloxane in the electrolyte is not high enough to favor this process considerably, we ran the electrolysis at a lower temperature.[16] Now, the reduction of O_2 in the presence of $Ph_2Si(OMe)_2$ and D_4, carried out at $-10\,°C$, shows a more correct product distribution (Table 1, runs 4 and 5). The product yields were higher, the amount of higher siloxanes was smaller and the ratio of $D_4D^{Ph_2}$ to $D_3D^{Ph_2}$ was 2:1 instead of 1:3 under the usual conditions. The process is therefore much more selective at low temperature.

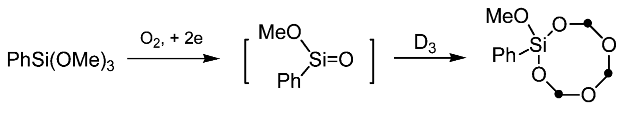
To check that the "silanone path" is the only one leading to the PhRSiO insertion products and to rule out other possible reaction pathways, a series of experiments was carried out. First, after stirring $Ph_2Si(OMe)_2$ and D_3 in a solution of 0.1 M Bu_4NPF_6 in DMF for 4 h (a typical duration of the electrolysis), no new products were observed. The same results were observed in the electroreduction of O_2 in the presence of either HMDS or D_3 and by saturating the solution of $Ph_2Si(OMe)_2$ and D_3 in DMF + 0.1 M Bu_4NPF_6 with oxygen and stirring it for 4 h without passing the current.

The presence of two alkoxy groups is essential for the process since no products were obtained when using monoalkoxysilanes. Methoxytrimethylsilane only served as a silanone trap, reacting with diphenylsilanone to give $Me_3SiOSi(Ph)_2OMe$. On the other hand, when organyl trialkoxysilanes were used, $RSi(OAlk)_3$, only two OAlk groups reacted to form the intermediate silanone (Scheme 3) whereas the third one was incorporated and conserved in the ring extension product.

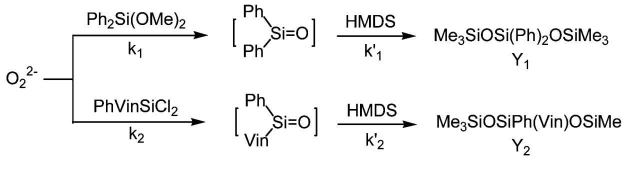
Given that in the absence of an appropriate silanone trap diorganylsilanones tend to undergo autocyclization,[2] the rate of this process is apparently slower than that of silanone insertion into the Si–O bond of HMDS or that of permethylcyclosiloxanes, since practically no perphenylated siloxane products were observed in the electrolyses with these silanone traps. This fact can have a purely kinetic reason. Indeed, though the starting ratio of $Ph_2Si(OMe)_2$ to HMDS was in favor of the dimethoxy compound (10:4), the conditions of electrogeneration of $Ph_2Si{=}O$ are such that its instantaneous concentration is very low and the process occurs with a large bulk excess of HMDS practically until the end of the electrolysis. This observation allowed the relative efficiency of diorganyl dialkoxysilanes *versus* diorganyl dichlorosilanes for the electrogeneration of diorganyl silanones to be evaluated. Since silanones were never observed in solution, their rate of consumption must be faster than their rate of formation. This seems to be true, whatever is the substituent at Si, at least for ordinary substituents like Me, vinyl (Vin), Et, Ph.[12] As no autocyclization products were obtained in the electrolyses, one can assume this is also true in the competitive kinetic scheme (Scheme 4), that is $k_1 \ll k_1'$ and $k_2 \ll k_2'$.

From the ratio $k_1/k_2 = Y_1/Y_2$ it follows that $k_1 = k_2(Y_1/Y_2)$ with $k_1 = k^{OMe}_{Ph_2} = k_{Ph_2} \times k^{OMe}$ and $k_2 = k^{Cl}_{PhVi} = k_{PhVi} \times k^{Cl}$.

Therefore, assuming k_1 and k_2 to be limiting steps and taking an excess of HMDS, one can estimate the relative rates of reaction of two silanone precursors with reduced oxygen by the ratio of the yields (Y_1 and Y_2) of silanone insertion products in two competitive pathways [given that the mechanism of the process is similar in both cases, that $C_{Ph_2Si(OMe)2} = C_{PhVinSiCl_2}$ and both concentrations are much higher than $C_{O_2}{}^{2-}$, and that the conversion is low, $\alpha \approx 5\%$[17]]. Keeping in mind that the apparent rate constants have contributions k_R from the electronic and steric properties of the organyl groups on Si on the one hand, and on the other from the leaving groups, k^{OMe} and k^{Cl}, these terms were estimated in two series of experiments. In the reaction series with similar leaving groups, $Ph_2SiCl_2/PhVinSiCl_2$ and $Ph_2Si(OMe)_2/PhVinSi(OMe)_2$, the ratio of constants is the same, $k_{Ph_2}/k_{PhVin} = 0.31$, indicating that the organyl groups at Si affect the reactivity of diorganyl dimethoxy and diorganyl dichlorosilanes in the same way. Then the cross experiments with the couples $Ph_2Si(OMe)_2/PhVinSiCl_2$ and $Ph_2SiCl_2/PhVinSi(OMe)_2$ gave the ratios $k_1/k_2 = 1/5.8$ and $1/1.794$, respectively. Taking into account that $k_{PhVin} = 3.22 \times k_{Ph_2}$ and thus correcting the data for the replacement of Ph with Vin, one obtains the ratio $k^{OMe} = 0.556 \times k^{Cl}$. Thus, the diorganyl dialkoxysilanes are about two times less reactive than diorganyl dichlorosilanes and this is presumably the reason why the process in the first case is more selective (*cf.* ref. 12). Studies aiming to reveal the exact nature of the electrogenerated active intermediate in the process and to track the transformations of the eliminated alkoxy groups are in progress.



Scheme 3



Scheme 4

Experimental

Typical experimental procedure for the electrolyses was as follows. A solution of 0.1 mmol of Me_3SiCl and 2.5×10^{-3} mol Bu_4NPF_6 in 25 ml of dry DMF was electrolyzed for 1.5 h to reduce H^+ formed in the hydrolysis of the chlorosilane by residual water. Diorganyl dialkoxysilane (5 mmol) was then added (and, when necessary, 2 mmol of silanone trap) and the electrolysis was carried out at a constant O_2 flow rate (5 ml min^{-1}) in the galvanostatic mode with a current density $j = 5$–7 mA cm^{-2}. Graphite cathode and glassy carbon felt anode were used. After passing about 2 F of electricity, Bu_4NPF_6 was precipitated with hexanes, the solution concentrated and separated on a column with SiO_2.

Characterization of products

MS and NMR spectra were recorded using a Shimadzu QP-5000 quadrupole spectrometer, ionization voltage 70 kV, and a Bruker 200 MHz spectrometer ($CDCl_3$, TMS), respectively.

$(Ph_2SiO)_3$ (1). NMR ^{1}H: 7.20–7.24 (6H, m), 7.42–7.46 (12H, m), 7.96–7.98 (12H, m); NMR ^{13}C ($CDCl_3$): 125.91 (C_3, C_5), 128.99 (C_4), 137.11 (C_2, C_6), 144.21 (C_1); MS m/z: 594 (M^+), 439, 219, 197, 144, 131, 77.

$(Ph_2SiO)_4$ (2). NMR ^{1}H: 7.19–7.24 (8H, m), 7.39–7.43 (16H, m), 7.90–7.92 (16H, m); NMR ^{13}C ($CDCl_3$): 125.21 (C_3, C_5), 129.21 (C_4), 138.01 (C_2, C_6), 145.41 (C_1).

$MD^{Ph_2}M$ (3). NMR ^{1}H ($CDCl_3$): 0.104 (18H, s), 7.30–7.66 (10H, m); NMR ^{13}C ($CDCl_3$) 2.47 ($SiCH_3$), 126.5 (C_3), 130(C_4), 135.4 (C_2), 142.2 (C_1); MS m/z: 360 (M^+), 345 ($M^+ - CH_3$), 330, 267, 197, 73.

$D_3D^{Ph_2}$ (4). NMR ^{1}H ($CDCl_3$): 0.09 (12H, s), 0.11 (6H, s), 7.36–7.69 (10H, m); NMR ^{13}C ($CDCl_3$): 0.80 ($SiCH_3$), 1.32 ($SiCH_3$), 126.4 (C_3 and C_5 of Ph), 129.4 (C_4 of Ph), 135.4 (C_2 and C_6 of Ph), 143.6 (C_1 Ph); MS/EI m/z: 420 (M^+), 405 ($M^+ - CH_3$), 207, 197, 135, 73.

$D_4D^{Ph_2}$ (5). NMR ^{1}H ($CDCl_3$): 0.086 (12H, s), 0.136 (12H, s), 7.30–7.66 (10H, m); NMR ^{13}C ($CDCl_3$): 0.80 ($SiCH_3$), 1.32 ($SiCH_3$), 126.4 (C_3, C_5), 129.3 (C_4), 134.6 (C_2, C_6), 143.1 (C_1); MS m/z: 479 ($M^+ - CH_3$), 417 ($M^+ - C_6H_5$), 340, 207, 197, 137, 73.

D_3D^{PhMeO} (6). NMR ^{1}H: 0.08 (12H, s), 0.12 (6H, s), 3.55 (3H, s), 7.14–7.78 (5H, m); NMR ^{13}C: 0.80 ($SiCH_3$), 1.81 ($SiCH_3$), 52.88 (OCH_3), 127.71 (C_3, C_5 of Ph), 128.64 (C_4), 135.6 (C_2, C_6), 141.5 (C_1); MS m/z: 374 (M^+), 359 ($M^+ - CH_3$), 343, 207, 151, 89, 31.

D_4D^{PhMeO} (7). NMR ^{1}H: 0.08 (12H, s), 0.11 (12H, s), 3.50 (3H, s), 7.14–7.71 (5H, m); NMR ^{13}C ($CDCl_3$): 0.80 ($SiCH_3$), 1.72 ($SiCH_3$), 52.80 (OCH_3), 127.1 (C_3, C_5), 128.5 (C_4), 134.2 (C_2, C_6), 141.1 (C_1); MS m/z: 433 ($M^+ - CH_3$), 371 ($M^+ - C_6H_5$), 207, 181, 137, 73.

D_3D^{PhVin} (8). NMR ^{1}H: ($CDCl_3$) 0.14 (6H, s), 0.18 (12H, s), 5.82–6.32 (3H, m), 7.36–7.67 (5H, m); MS m/z: 370 (M^+), 355 ($M^+ - CH_3$), 251, 207, 73.

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