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Superoxide-stable ionic liquids: new and efficient media for electrosynthesis of functional siloxanes

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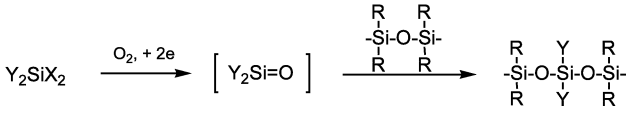
Received (in Cambridge, UK) 31st October 2003, Accepted 23rd January 2004
First published as an Advance Article on the web 10th February 2004

The electrogeneration of diorganylsilanones from difunctional precursors $Y(CH_2)_3(Me)SiX_2$ and Ph_2SiX_2 (Y = NH_2, CF_3, CN; X = Cl, OEt, OMe), performed in the presence of hexamethyldisiloxane or hexamethylcyclotrisiloxane (D_3) in the ionic liquids $[C_5H_5NC_8F_{18}]\cdot NTf_2$, $[C_5H_5NC_{18}H_{38}]\cdot NTf_2$ and $Me_3BuN\cdot NTf_2$, which reveal high solubility of oxygen and are inert toward superoxide anion, allows functionalized siloxanes to be produced selectively in good isolated yields.

Besides their use as "green chemistry" solvents,[1] room temperature ionic liquids (IL) are attracting increasing attention for electrochemical investigations.[2] The conductivity of ILs, their good electrochemical stability and selective miscibility with common organic solvents make them very appealing quasi-permanent and non-volatile electrolytic media. Yet electrochemical studies of IL are mainly limited to the consideration of their potential window, conductivity, diffusion and ion-pair formation in these systems,[3] and voltammetry of several metal complexes and model compounds.[3d,4] Papers on electrosyntheses in IL are much scarcer. A few known examples come from electropolymerization of benzene,[5] anthracene,[6] pyrrole,[7] formation of silane polymer films.[8] Even less is known on the electrosynthesis of molecular products.[9]

Recently, we found that the reaction of reduced forms of oxygen with diorganyl dichloro[10] or dialkoxy[11] silanes, supposedly occurring *via* a transient diorganylsilanone species $R_2Si{=}O$, allows the insertion of an R_2SiO group into cyclic and linear permethylated siloxanes to give various products according to Scheme 1 (Y is a substituent, other than R, and X = Cl, OAlk).



Scheme 1

Here we report the first organosilicon electrosynthesis based on cathodic activation of O_2 in IL, $Me_3BuN\cdot NTf_2$ and $[C_5H_5NR]\cdot NTf_2$ (R = C_8F_{18}, $C_{18}H_{38}$), a process combining the advantages of both the unique properties of the IL and the electrochemical functionalization of siloxanes.

Although the reduction of oxygen in IL has been the object of several studies,[12] special attention should be drawn to the choice of an IL appropriate for this process because three problems are met here: i) low normal pressure solubility of O_2, ii) its diffusion rate in IL is much slower than in conventional organic solvents (DMF, THF [ref. 12*c*, see also refs. 3*c*,4*d*,9*b*]) which decreases the electrolysis current by 15–20 times, and iii) stability of electrogenerated $O_2^{\cdot-}$ in these media.

Given that CH_3CN is one of the best electrochemical solvents on the one hand, and that silanone-based functionalization occurs smoothly when using Bu_4NBF_4 supporting salts in aprotic solvents[10] on the other, we tried $[NC(CH_2)_4]_4N\cdot NTf_2$ IL which we thought would be an analog of the $CH_3CN/(C_4H_9)_4NBF_4$ system. Surprisingly, the solubility of O_2 was too small and the resistance too high to use this IL for electrosynthesis.[13]

Knowing that fluorinated solvents allow much higher O_2 solubility, eventually up to 50 ml of O_2 in 100 mL of solvent and higher,[14] it would be very advantageous to add a fluorinated co-solvent to the IL to boost O_2 concentration. Indeed, the addition of C_6F_6 or decafluorobiphenyl $C_{12}F_{10}$ increases the solubility of O_2 by 15% and 76%, respectively (Fig. 1), but these media, though stable against O_2, are not suitable for generation of $O_2^{\cdot-}$ because the latter reacts with fluoroaromatics.[15] In contrast to this, a pyridinium-based IL with a grafted aliphatic perfluorinated chain, $[C_5H_5N^+C_8F_{18}]\cdot NTf_2$, revealed a 105% increase of O_2 solubility (Fig. 1) and allowed the observation of a stable oxidation signal of superoxide anions.[16] A comparable effect (87% gain) was observed for a parent ionic liquid with longer alkyl chain, $[C_5H_5N^+C_{18}H_{38}]\cdot NTf_2$, though the conductivity in this case was substantially lower.

To make sure that the mechanism of the silanone-based functionalization of siloxanes[11b] does not change in the IL, we ran control experiments first stirring O_2-saturated solutions of hexamethyldisiloxane (HMDS) and silanone precursors in IL for 4 h without polarization, and second reducing O_2 in the IL in the presence of HMDS. In both cases, no new products were observed. Only the reduction of O_2 in the presence of a mixture of silanone precursor/silanone trap resulted in products of R_2SiO group insertion (Scheme 2, Table 1).

When $PhSi(OMe)_3$, $Cl(CH_2)_3Si(OMe)_3$ or alkylmethylsilanes $R(Me)SiX_2$ with alkyl substituents terminated with CN, NH_2 and CF_3 groups were used in this process, corresponding linear and cyclic functional siloxane derivatives were obtained (Scheme 3,

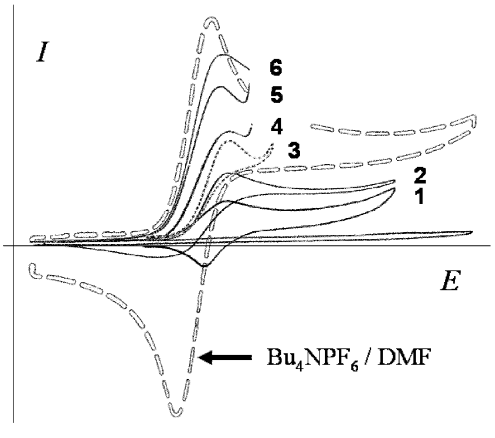
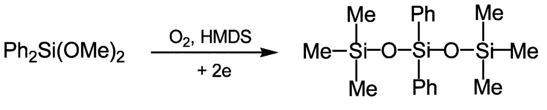


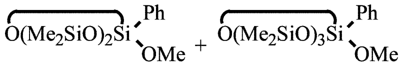
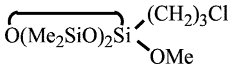
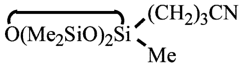
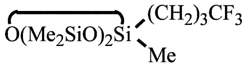
Fig. 1 Voltammograms of saturated solutions of O_2 in different IL. From the baseline upward: (1) $Me_3BuN\cdot NTf_2$ (magnified 5×); (2) $[NC(CH_2)_4]_4N\cdot NTf_2$ (magnified 10×); (3) the same, after addition of 20 mmol $C_{12}F_{10}$ (×7); (4) $[C_5H_5N^+C_8H_{18}]\cdot NTf_2$ (×10); (5) $C_5H_5N^+C_8F_{18}]\cdot NTf_2$ (×10); (6) $[C_5H_5N^+C_{18}H_{38}]\cdot NTf_2$ (×7). For comparison, the current of O_2 in DMF/0.1 M $(n\text{-}Bu)_4NPF_6$ is outlined; 0.8 mm GC disk electrode; v = 200 mV s^{-1}; T = 22 °C.



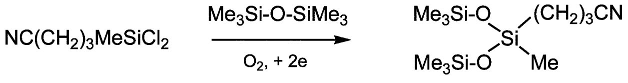
Scheme 2

DOI: 10.1039/b313832a

Table 1 The functionalization of hexamethylsiloxanes in IL ($P = 1$ bar, $T = 22$ °C)

Run	Silanone precursor	Siloxane	Medium	Q/F mol^{-1}	Products	Yield (%)[a]
1	$Ph_2Si(OMe)_2$	HMDS	$(n\text{-Bu})_4NPF_6$/DMF	2.2	$(Me_3SiO)_2SiPh_2$	46[b]
2	$Ph_2Si(OMe)_2$	HMDS	$Me_3BuN{\cdot}NTf_2$	2.3	$(Me_3SiO)_2SiPh_2$	71
3	$PhSi(OMe)_3$	D_3	$[C_5H_5N^+C_{18}H_{38}]{\cdot}NTf_2$	1.6		28 + 7
4	$NC(CH_2)_3(Me)SiCl_2$	HMDS	$[C_5H_5N^+C_8H_{18}]{\cdot}NTf_2$	2.2	$(Me_3SiO)_2Si(Me)(CH_2)_3CN$	67
5	$NC(CH_2)_3(Me)SiCl_2$	D_3	$Me_3BuN{\cdot}NTf_2$	2.0		39
6	$H_2N(CH_2)_3(Me)Si(OEt)_2$	HMDS	$[C_5H_5N^+C_8F_{18}]{\cdot}NTf_2$	2.1	$(Me_3SiO)_2Si(Me)(CH_2)_3NH_2$	32
7	$Cl(CH_2)_3Si(OMe)_3$	D_3	$[C_5H_5N^+C_8F_{18}]{\cdot}NTf_2$	2.0		48
8	$CF_3(CH_2)_3(Me)SiCl_2$	D_3	$[C_5H_5N^+C_8F_{18}]{\cdot}NTf_2$	2.1		64
9	$CF_3(CH_2)_3(Me)SiCl_2$	D_3	″[c]	2.4	″	59

[a] Isolated yields. [b] Literature data.[11a] [c] The IL used in run 8, after the extraction of products and addition of a new load of $CF_3(CH_2)_3(Me)SiCl_2$ and D_3.



Scheme 3

Table 1). After run 8 had been accomplished and the product was extracted from the electrolyte with diethyl ether, new portions of the starting compounds were added to the same IL and the electrolysis (run 9) continued till 2.4 F mol^{-1} of electricity were passed. Thorough extraction withether gave 59% more of the cyclic methyl(trifluoromethylpropyl)siloxo product. Thus no visible degradation of the efficiency of this second load electrolysis (run 9) was found compared to that with the first load (run 8).

The viscosity of the used IL remarkably decreases when dissolving HMDS and silanone precursor which allows to intensify mass transfer and to reduce ohmic drops. So the studied IL provided sufficiently high concentrations of O_2 for practical electrosynthetic purposes, good conductivity and allowed the formation of functional siloxanes selectively, easily and in good isolated yields. The study of these and other IL for silicon electrochemistry and their turn-over efficiency is in progress.

Voltammetric tests were performed using a PAR-362 potentiostat with a glassy carbon (GC) 0.8 mm disk used as working electrode and a GC rod as auxiliary electrode. The reference electrode was Ag/0.1 M $AgNO_3$ in CH_3CN. In large-scale electrolyses a porous graphite cathode and a GC felt anode were used. Diorganosilanes, HMDS and D_3 were purchased from ABCR and used as received. The ionic liquids were prepared according to refs. 1*a*,17 and dried overnight in vacuum (3 mmHg at 80 °C) before use. Oxygen (Air Liquide, France) was dried passing it through a cartridge filled with P_2O_5 on glass wool. All experiments were performed under inert argon atmosphere. A typical electrolysis procedure was as follows. 1 mmol Me_3SiCl was added to 7.5 ml IL and electrolyzed for about 2.5 h to reduce H^+ formed in hydrolysis of the chlorosilane by residual water. A silanone precursor (50 mmol) and a silanone trap (55 mmol) were then added *via* a syringe and the electrolysis was carried out with a constant flow of O_2 (5 ml min^{-1}) with the current density $j = 0.5$–1 mA cm^{-2}. After passing 2 F mol^{-1}, the products were isolated by thorough extracting the IL with diethyl ether, evaporation of the latter and column separation of the organic residue.

The authors are grateful to Rennes Metropôle for the financial support of this work.

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