**Table 1.** The ν(OH) bands of phenol involved in the H-bonds with **1—3**, the basicity factors, and the ν(CO) bands of **1—3** in the H-complexes and protonated forms after the addition of PFB and $HBF_4$

| Compound | ν(OH)/cm$^{-1}$ PhOH | Δν | $E_j$ | ν(CO)/cm$^{-1}$ | | |
|---|---|---|---|---|---|---|
| | | | | $CH_2Cl_2$ | PFB | $HBF_4$ |
| **1** | 3388 | 198 | 0.86 | 1978 vs | 2013 w, | 2085 m, 2063 s* |
| | | | | 1806 s | 1846 sh, 1760 m | 1867 s |
| **2** | 3360 | 226 | 0.94 | 1837 vs** | 1810 s | 1890 s |
| | | | | 1781 s | 1760 s | 1840 s |
| **3** | 3331 | 255 | 1.02 | 1706 sh | 1650 sh | 1744 sh |
| | | | | 1670 s | 1610 s | 1720 s |

* In $CH_3NO_2$ 2082, 2058, 1977, and 1869 cm$^{-1}$. ** All of the measurements for compounds **2** and **3** were carried out at $T$ = 200 K.

bridging carbonyl groups. The protonation occurs along an edge to give the symmetrical $Rh\overset{H}{\diagup\diagdown}Rh$ bridge.

## Experimental

Compounds **1—3** were prepared by the previously described procedures.[7] The IR spectra were recorded on Specord M-82 and Specord M-80 spectrophotometers. The $^1H$ NMR spectra were measured on Bruker AMX-400 and Bruker WP-200-SY instruments. The concentrations of the protic acids varied in the $5\times10^{-2}$—$1\times10^{-4}$ mol L$^{-1}$ range, those of the organometallic complexes were in the $1\times10^{-2}$—$1\times10^{-4}$ mol L$^{-1}$ range. The studies were carried out at 200—300 K in $CH_2Cl_2$.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 93-03-0461).

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*Received November 4, 1994*

# Electrosynthesis of tetraethylsilane from elemental silicon

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Electrolysis of alkylation reagents at silicon-containing electrodes results in alkylsilanes in both cathodic and anodic processes. A mechanism for the reaction is proposed.

**Key words**: electrosynthesis; silicon-containing electrodes; alkylsilanes.

At present, direct synthesis of chlorosilanes and/or silicon hydrides[1] followed by their treatment with organomagnesium (or lithium) reagents[2] or with unsaturated compounds is the main method for the preparation of organosilicon compounds from inorganic silicon derivatives. Previously[3] an alternative method for the synthesis of organosilicon compounds from silicon dioxide *via* pentacoordinated intermediates was reported. Whereas

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 388—389, February, 1995.

"direct" electrosyntheses of organic derivatives of Pb and Sn are well known,[4] for Si derivatives, it has only been reported that oxidation of Mg or Al halide at an organosilicon anode in the presence of organyl halides yields tetraorganylsilanes and polysiloxanes.[5] Nevertheless, the known electrochemical synthesis of siloxane using an "active" silicon electrode[6] prompted us to look for a direct electrosynthesis of organosilicon compounds from elemental silicon. We found that tetraethylsilane is formed at silicon-containing electrodes in the presence of alkylation reagents in both cathodic and anodic processes. The reaction mixture produced after oxidation of ethylmagnesium bromide at a platinum anode in the presence of finely divided silicon in THF exhibits an $^1$H NMR signal indicating that a compound with a Si—CH bond has appeared in the solution. When no electric current was passed through the solution, this signal did not appear in the spectrum. In order to intensify this process, we carried out the oxidation of the Grignard reagent in two ways: first, in an undivided cell with a solution that flowed through an anode made of powdered silicon doped with copper ions; second, in an undivided non-flow-through 60 mL cell with an anode made of a compact glassy carbon—silicon mixture (1 : 4, by volume) or an anode made of a platinum cylinder of diameter 1 cm surrounded by a 2 mm thick layer of powdered silicon. In both cases, a 0.25 *M* solution of freshly prepared ethylmagnesium bromide in THF was poured into the cell through a siphon in a flow of dry argon. The electrolysis was carried out without the addition of a supporting electrolyte. Since the working potential of the bulk anode is uncertain, the voltage at the cell was maintained within the limits 8—20 V at a current of 70 mA using a VSA-11 rectifier. The yield of tetraethylsilane was 9 %.

The formation of tetraethylsilane in the anodic process apparently involves radical species:

$$EtMgBr \xrightarrow{-e} MgBr^+ + Et^\cdot \quad \begin{cases} \xrightarrow{1/4\ Si} 1/4\ Et_4Si & (1) \\ \xrightarrow{Et^\cdot} Me(CH_2)_2\ Me & (2) \end{cases}$$

The addition of ethyl bromide, which may allow regeneration of the Grignard reagent at the cathode, does not noticeably change the yield of the product[4]

$$Mg^{2+} + EtBr \xrightarrow{+2e} EtMgBr, \qquad (3)$$

this is probably associated with the low conversion of ethyl magnesium bromide into tetraethylsilane. Thus, the process always occurs under the conditions of excess ethylmagnesium bromide.

Tetraethylsilane was also obtained by the reduction of 0.03 moles of ethyl bromide in 60 mL of THF at a "silicon" cathode in the presence of 0.02 moles of tetrabutylammonium bromide by passing $2F \cdot mol^{-1}$ of electricity.

$$EtBr \xrightarrow[-Br^-]{+2e} Et^\cdot \xrightarrow{1/4\ Si} 1/4\ Et_4Si \qquad (4)$$

The low current yield did not allow us to evaluate the number of electrons transferred per mole of electricity in the electrolysis or under the conditions of voltammetry, which would have confirmed the participation of ethyl radicals in the process. However, when ethyl chloride was used instead of ethyl bromide under the same conditions, the $^1$H NMR spectrum of the reaction mixture exhibited only a very weak signal of tetraethylsilane, which indicated that rather small amounts of alkylsilane were formed. This indirectly confirms that ethyl radicals act as the active species in this process: the fact that the potential difference, $\Delta E = E_{EtX/Et\cdot+X^-} - E_{Et\cdot/Et^-}$, is substantially smaller for bromide than for chloride[7] makes the existence of ethyl radicals and their participation in the process preferred in the case when they have been generated from ethyl bromide. When acetonitrile and allyl bromide were used as alkylating agents under the same conditions, no products with new Si—C bonds were detected.

Treatment of the electrolysis solution with ultrasound at a frequency of 25 kHz allowed us to intensify the process somewhat: in this case, tetraethylsilane was formed in a 23 % yield. Obviously, the form in which silicon participates in the process is of great importance. Silicon itself is not a conductor, and the formation of tetraethylsilane begins with the generation of alkylating intermediates at the conducting surface of an electrode. Therefore silicon alloys should be used as electrode materials, in order to make silicon accessible to radical attack in the near-electrode reaction layer. In addition, electrosynthesis in anodic and cathodic processes with Si alloys having various (n- or p-type) conductivities should be studied. After the appropriate optimization, the direct electrosynthesis of alkylsilanes may serve as an alternative method for the synthesis of organosilicon compounds.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Grant No. 94-03-09098).

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*Received November 16, 1994*

# 2-Alkoxyhexafluoropropyl-2-isocyanates

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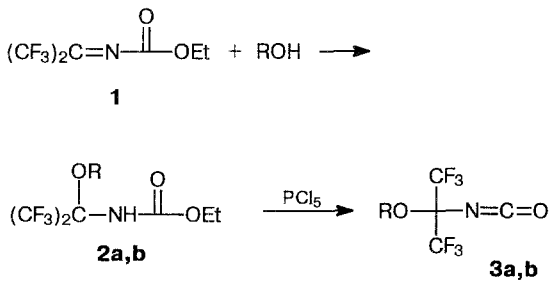
A convenient preparative method for the synthesis of 2-alkoxyhexafluoropropyl-2-isocyanates is proposed. The reactions of the isocyanates with amines and alcohols are studied.

**Key words:** 2-alkoxyhexafluoropropyl-2-isocyanates, synthesis; ureas, carbamates.

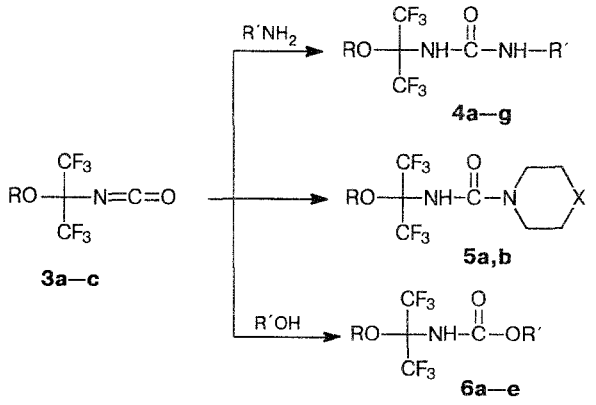
Alkylisocyanates are the main reagents for the modification of known physiologically active compounds and the synthesis of new ones. Isocyanates containing functional substituents at the α-position[1,2] occupy a special place in the series of alkylisocyanates. However, the data on the synthesis of α-alkoxypolyfluoroalkylisocyanates are scarce.[3] In the present report, a convenient preparative method for the synthesis of 2-alkoxyhexafluoropropyl-2-isocyanates is presented along with some of their chemical properties.

Previously we have found that the interaction of α-chlorohexafluoropropylisocyanate with EtOH in the presence of bases results in the formation of a mixture of the imine and ethoxyisocyanate. Therefore, the reaction of carbamates of the corresponding alcohols with $PCl_5$ is a more convenient and unambiguous method for the synthesis of the analogous isocyanates:




However, the reaction of the PhOH—α-chlorohexafluoropropylisocyanate adduct with one equivalent of a base (Py or $Et_3N$) turned out to be preferable for the preparation of phenoxyisocyanate **3c**.

Isocyanates **3a—c** are mobile low-boiling liquids, whose compositions and structures were confirmed by the data of elemental analysis, $^1H$ and $^{19}F$ NMR, IR spectra (Table 1, 2), and chemical transformations. Isocyanates **3** react with both primary and secondary amines to form the corresponding carbamide derivatives **4** and **5**, and react with alcohols to form carbamates **6**.




Compounds **4—6** are characterized by the $CF_3$ group signal in the 2 to 4 ppm range of the $^{19}F$ NMR spectra

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 390—392, February, 1995.