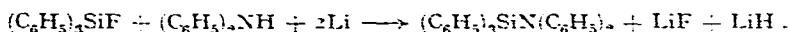


A convenient route to triphenylsilyllithium, using triphenylsilyl fluoride

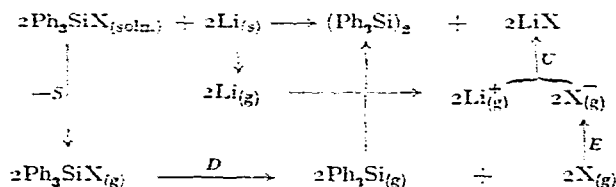
Triphenylsilyllithium has proved to be a useful reagent for preparing organosilicon compounds, and has been used extensively since 1954¹. The formation and reactions of organosilvylmetallic compounds has been reviewed².

When triphenylsilyllithium is prepared from one of the triphenylsilyl halides, as is now the usual procedure, the chloride is invariably chosen. This is convenient when this compound is commercially available, but the authors have been unable to find a source of it. This compound can be prepared by the reaction of silicon tetrachloride with three equivalents of phenylmagnesium bromide, but mixed products are often obtained and the yields are low*. However, when a triphenylsilyl compound is required, the fluoride has definite advantages⁴. When silicon tetrafluoride gas is bubbled into a solution of phenylmagnesium halide in diethyl ether, triphenylsilyl fluoride is formed in good yield⁵, the fourth fluorine being inert to further reaction with the Grignard reagent. The silicon tetrafluoride can be readily prepared from calcium fluoride, silica, and sulphuric acid.

We have found that triphenylsilyl fluoride reacts with lithium in tetrahydrofuran solution to give triphenylsilyllithium in good yield. The reaction proceeds in the same manner as for triphenylsilyl chloride. The mixture initially precipitates a white solid, identified as hexaphenyldisilane; this subsequently reacts to give a black solution. On addition of trimethylchlorosilane, 1,1,1-trimethyl-2,2,2-triphenyldisilane is precipitated from solution. The only example in the literature of a reaction of triphenylsilyl fluoride in the presence of lithium is that given by Chugunov⁶, it is likely that this reaction goes via triphenylsilyllithium:



Although organosilicon fluorides are less reactive than the chlorides there are few examples where the chloride reacts but not the fluoride⁷. Bond energies are not a satisfactory guide to the reactivity of silicon-halogen bonds⁸ and use has been made of the ionic bond energies of Remick⁹. Another approach is to examine a thermodynamic cycle for the reaction:



[This reaction is followed by $(\text{Ph}_3\text{Si})_2 + 2\text{Li} \longrightarrow 2\text{Ph}_3\text{SiLi}$]. The terms in the cycle that are changed in going from $\text{X} = \text{Cl}$ to $\text{X} = \text{F}$ are: *S*, the energy of solution of the gaseous triphenylsilyl halide; *D*, the silicon-halogen bond dissociation energy;

* We have found that the most satisfactory preparation of triphenylsilyl chloride is to treat diphenyldichlorosilane (commercially available) with phenylmagnesium bromide, extract the product with toluene and wash out impurities with petrol ether³.

E , the electron attachment energy of the halogen (this being the electron affinity with the opposite sign); and U , the lattice energy of the lithium halide if it is a solid, or the sum of the solvation energies of the Li^+ and X^- ions if the lithium halide is in solution. The values of S are not known, but it is reasonable to assume that they are very similar. In going from $\text{X} = \text{Cl}$ to $\text{X} = \text{F}$, E hardly changes ($E = -79.5$ and -83.3 kcal./mole respectively), and there is the well known increase in D . There is also a decrease in U due to the small size of the fluoride ion¹⁰. The increased strength of the Si-F bond compared with the Si-Cl bond is compensated for by the more negative lattice energy of the lithium fluoride or solvation energy of the fluoride ion, so that the total energy change is about the same for both halides.

Experimental

Triphenylsilyl fluoride was prepared by the method of Medoks⁵ and recrystallised from ethanol¹¹.

Triphenylsilyllithium was prepared from triphenylsilyl fluoride (0.025 M) and lithium (0.1 g-atom) in tetrahydrofuran solution, with stirring, under nitrogen. After $\frac{1}{2}$ h, white hexaphenyldisilane precipitated. On stirring for $2\frac{1}{2}$ h, the solution became black and gave a positive test to the Gilman¹² colour test I. After filtration, addition of trimethylchlorosilane gave a white precipitate of 1,1,1-trimethyl-2,2,2-triphenyldisilane in 84% yield (based on triphenylsilyl fluoride). The two silanes prepared were identified by infrared and elemental analysis.

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