

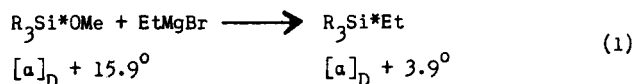
STEREOCHEMISTRY OF ASYMMETRIC SILICON:
COUPLING REACTIONS WITH ORGANOMETALLIC REAGENTS

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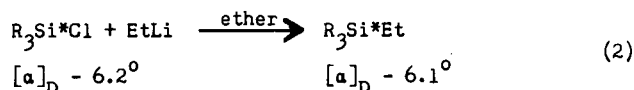
(Received 12 June 1962)

ONE of the most useful methods for establishing carbon-silicon bonds is the coupling reaction of organometallic reagents with silicon-halogen and silicon-alkoxy compounds. We wish to report new stereochemical data which bear on the problem of the mechanisms of these interesting reactions. These data relate to reactions of optically active α -naphthylphenylmethylsilanes,¹ α -NpPhMeSiY, designated R_3Si^*Y below.

Reaction of R_3Si^*OMe with ethylmagnesium bromide in ether is slow at room temperature. Removal of most of the ether and heating at 90° for several hours gave:



Reaction of R_3Si^*Cl with ethyllithium proceeds rapidly at room temperature and gave the following result:



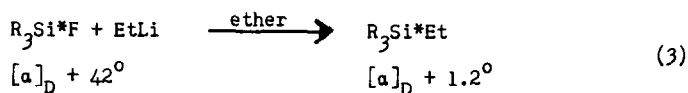
Reactions (1) and (2) follow opposite stereochemical paths on the basis of assignment of the same configuration² to (+) R_3Si^*OMe and (-) R_3Si^*Cl . Furthermore, the reactions of R_3Si^*Cl with diverse nucleophilic reagents

¹ L.H. Sommer and C.L. Frye, *J. Amer. Chem. Soc.* **81**, 1013 (1959).

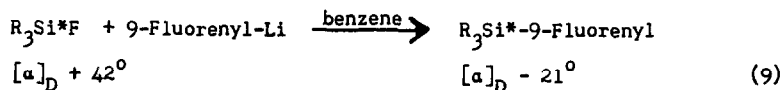
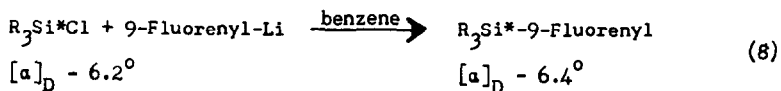
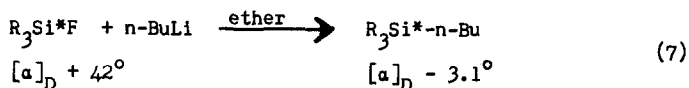
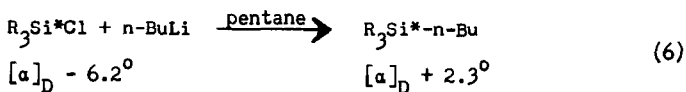
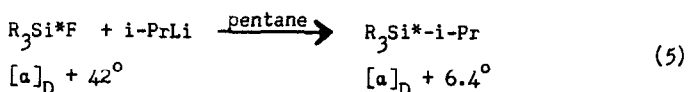
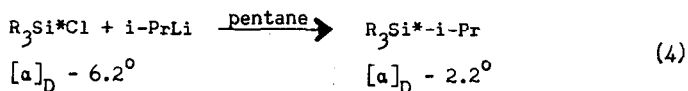
² For a recent review, see L.H. Sommer, *Angew. Chem.* **1**, 143 (1962).

follow an inversion stereochemistry, whereas R_3Si^*OMe gives retention of configuration with many bases, including lithium aluminum hydride.² Thus, it seems very probable that (1) proceeds with retention of configuration and (2) with inversion of configuration.

Reaction of R_3Si^*F with ethyllithium in ether at room temperature gave:

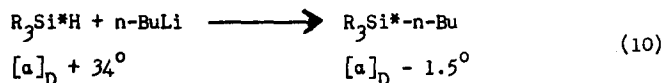


Stereochemical equations given below compare reactions of other organolithium reagents with R_3Si^*Cl and R_3Si^*F .



$(-)$ R_3Si^*Cl and $(+)$ R_3Si^*F have been assigned the same configuration.² Thus, opposite stereochemical paths are indicated for R_3Si^*Cl and R_3Si^*F with ethyl-, isopropyl- and n-butyl-lithium. The same predominant stereochemistry obtains for both compounds with 9-fluorenyllithium.

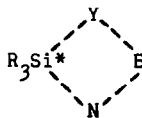
Reaction of R_3Si^*H with n-butyllithium in a pentane-heptane solvent at 68° for 20 hr gave:



Since $(-)-R_3Si^*H$ and $(-)-R_3Si^*F$ have the same configuration,² reactions (7) and (10) have the same predominant stereochemistry.

Taken together, reactions (1)-(10) and previous studies² suggest that inversion of configuration is predominant for reactions of R_3Si^*Cl with organolithium reagents.³ Retention of configuration for R_3Si^*H in reaction (10) is consistent with many other retention reactions for this substance.² Retention of configuration for R_3Si^*F in reactions (3), (5) and (7), and inversion in (9), indicate that the stereochemistry of R_3Si^*F is sensitive to reagent structure. This situation has been noted before in the reactions of R_3Si^*F with lithium aluminum hydride and R_3Si^*OK . The former gives inversion of configuration² and the latter, unlike the reaction with R_3Si^*Cl , pursues a retention path.⁴

In the present studies, a retention stereochemistry probably derives from quasi-cyclic transition states or intermediates (E and N represent electrophilic and nucleophilic parts of the attacking reagent):



whereas an inversion stereochemistry probably derives from trigonal bipyramidal transition states or intermediates in which Y and N are apical.

³ The available sparse evidence indicates that inversion is also the predominant stereochemistry (accompanied by considerable racemization) for the corresponding reactions of optically active organic halides. Cf. H.D. Zook and R.N. Goldey, *J. Amer. Chem. Soc.* **75**, 3975 (1953).

⁴ Unpublished studies of C.L. Frye and L.H. Sommer.

The results of Brook and Warner⁵, concerning stereospecific synthesis and rearrangement of an α -hydroxysilane, $R_3Si^*COH(C_6H_5)_2$, and the very reasonable assignment of a retention stereochemistry for the intramolecular rearrangement of this substance to $R_3Si^*OCH(C_6H_5)_2$ with Na-K alloy, require assignment of an inversion stereochemistry to the reaction of R_3Si^*Cl with diphenylmethyl lithium. Thus, the stereochemistry assignments made in the present studies receive important support from the excellent work of Brook and Warner.

The yields of product in (1)-(10) averaged about 90 per cent and products were adequately characterized by infrared spectra and analyses. It is clear that some racemization occurs, especially in reactions which require heating for long periods of time.

We thank Dow Corning Corporation for generous support.

¹ A.G. Brook and C.M. Warner, Tetrahedron Letters 815 (1962), preceding paper.