

dition of RLi to the triple bond. *ortho*-Metalation of benzene rings containing substituents which are inductively electron withdrawing is a well known phenomenon,⁵ and the inductive electron-withdrawing effect of the triple bond is apparent in the increased acidity of a number of acetylenic carboxylic acids in comparison to their saturated analogs.⁶ The dicarboxylic acids (III) are assigned the *trans* structure on the basis of the *trans* structure of the hydrolysis product from *n*-butyllithium and diphenylacetylene, in addition to the fact that the yield of indone, which requires a *trans* stereochemistry, may be increased by bubbling carbon dioxide through the reaction mixture, in contrast to our ordinary procedure of decanting onto a large excess of solid carbon dioxide. The *trans* nature of the products does not necessarily reflect the initial mode of addition of the *n*-butyllithium to the triple bond. Curtin and Koehl⁷ have shown that even at 2° in ether-benzene, *cis*-stilbenzylithium is completely isomerized to *trans*-stilbenzylithium in 30 min. In the present investigation, our olefinic lithium compounds remained in ethyl ether solution many hours. The situation in this case is more complicated, however, since we obtain a dilithium intermediate. Indeed, there seems to be some special stability to this dilithium compound (II), inasmuch as we recover after carbonation only starting material and products arising from V, nothing from a monolithium compound. The implications of this fact are being investigated.

In contrast to ethyl- and *n*-butyllithium, we find, in agreement with a recent report,⁸ that phenyllithium and diphenylacetylene give only triphenylacrylic acid (11%).

A still different course of reaction occurs between *t*-butyllithium and diphenylacetylene in ligroin (40 to 70°, 13 hr.). After hydrolysis, 1,2,3,4-tetraphenylbutadiene (30%) and *trans*-stilbene (5%) are isolated. The former compound was identified by comparison with an authentic sample prepared by the action of lithium metal on diphenylacetylene.⁹ The lithium-diphenylacetylene reaction may very well proceed by dimerization of the diphenylacetylene anion radical, and a strong possibility exists that at least a portion of the *t*-butyllithium and diphenylacetylene reaction proceeds by an anion-radical intermediate. In accord with this the reaction mixture displays on e.s.r. signal having no fine structure. The formation of radical anions from *n*-butyllithium and a number of aromatic compounds has recently been reported.¹⁰ *t*-Butyllithium would be expected to be an even better electron donor, since the process would presumably¹¹ involve the conversion of an unstable tertiary carbanion-like compound to a tertiary radical.¹²

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(12) P. D. Bartlett and S. J. Tauber have found a different course of reaction when *t*-butyllithium and diphenylacetylene react in ethyl ether at -30°. One of the products (after carbonation) is β -*t*-butyl- α,β -diphenyl-

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acrylic acid. We thank Professor Bartlett for communicating this information prior to publication.

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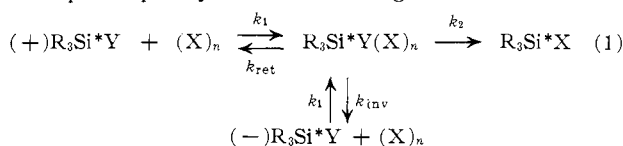
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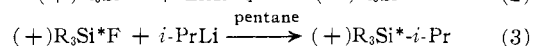
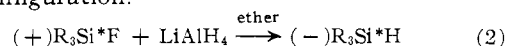
Racemization of an Optically Active Fluorosilane without Displacement of Fluoride Ion: Evidence for an Expanded-Octet Mechanism

Sir:

Previous studies have revealed highly stereospecific reactions of many optically active organosilicon compounds containing the α -naphthylphenylmethylsilyl group.¹⁻³ More recently, stereospecific reactions of optically active organogermanium compounds containing the same organic substituents have been reported.⁴ In all such cases of reactions proceeding with pure, or nearly pure, inversion or retention of configuration, it is clear that the mechanism may or may not involve expanded-octet intermediates (penta- or hexavalent silicon intermediates). However, it is equally clear that the mechanisms of such stereospecific reactions cannot involve fast equilibrium formation of an expanded-octet (addition) complex which returns to starting materials with inversion of configuration at a rate which approximates or exceeds its decomposition to products. Thus, for stereospecific reactions, mechanism 1, in which k_{inv} approximates k_{ret} and exceeds k_2 , cannot obtain if the optical purity of R_3Si^*X is high.



Stereospecific reactions of R_3Si^*F (α -naphthylphenylmethylfluorosilane), which cannot involve mechanism 1 having $k_{inv} \sim k_{ret} > k_2$, are known. Reaction 2 proceeds with inversion of configuration¹ and 3 with retention of configuration.⁵



Nevertheless, the high bond energy of Si-F (ca. 130 kcal./mole), the high electronegativity of fluorine, and its small size, as well as the existence of the stable SiF_6^{2-} ion, suggested to us that mechanism 1 might obtain for R_3Si^*F under certain conditions which would also lead to the relationship $k_{inv} > k_2$.

In the racemization experiments described below, the product in all cases is pure racemic fluorosilane. Macroscopic formation of a substitution product does not take place, and involvement of a substitution product in an equilibrium unfavorable to its isolation is ruled out by studies described later. Thus, it is clear that the rate of racemization greatly exceeds the rate of displacement of fluoride ion. In fact, the latter does not occur at all during the time required for complete racemization, under the designated conditions.

In sum, our observations and conclusions lead to the

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(2) L. H. Sommer, *Angew. Chem. Intern. Ed. Engl.*, **1**, 143 (1962).

(3) A. G. Brook and C. M. Warner, *Tetrahedron Letters*, **18**, 815 (1962).

(4) A. G. Brook and G. J. D. Peddle, *J. Am. Chem. Soc.*, **85**, 2338 (1963).

(5) L. H. Sommer, P. G. Rodewald, and G. A. Parker, *Tetrahedron Letters*, **18**, 821 (1962).

postulate of mechanism 1 in which $k_{inv} \gg k_2$ for the racemization studies described, and amount to the following.

(1) Optically active R_3Si^*F in pentane and *t*-butyl alcohol solvents is racemized by added methanol without displacement of $-F$.

(2) Such racemization cannot be due to fluoride-fluoride exchange engendered by formation of a small amount of HF. Addition of HF to the reaction medium strongly retards the rate of racemization.

(3) Such racemization cannot be due to the formation of ionic intermediates containing ionized fluorine. The high bond energy of Si-F and the low dielectric constants of the *t*-butyl alcohol and pentane solvents argue against such a possibility. Furthermore, in pure formic acid, a solvent of high ionizing power, the pseudo first-order rate constant for racemization of R_3Si^*F is only $3.7 \times 10^{-3} \text{ min.}^{-1}$, compared to $3.5 \times 10^{-2} \text{ min.}^{-1}$ in pentane containing 0.580 *M* methanol. Also, ionic intermediates containing ionic fluorine should be considerably stabilized by the presence of HF, due to probable formation of HF_2^- from such intermediates. Instead, rate-retardation is observed when HF is added.

Polarimetric rate data for racemization of R_3Si^*F (0.0358 *M*) in pentane by methanol (0.580 *M*) at 31.2° give a linear first-order plot, $k_1 = 3.5 \times 10^{-2} \text{ min.}^{-1}$. When racemization of an equimolar mixture of R_3Si^*F and optically active $R_3Si^*OCH_3$ (0.0179 *M* in each component) was carried out, the optical rotation only decreased to the expected value for the optically active methoxysilane and remained constant at that value for 26 hr. Thus, the racemization of the fluorosilane does not involve the methoxysilane as an intermediate, and racemization proceeds without displacement of fluoride ion. In the presence of HF ($7.5 \times 10^{-4} \text{ M}$), and keeping the methanol and fluorosilane concentrations constant, the rate constant for racemization decreased from $3.5 \times 10^{-2} \text{ min.}^{-1}$ to $4.0 \times 10^{-5} \text{ min.}^{-1}$, by a factor of almost 10^3 . In pentane solvent, racemization rate increases rapidly with increasing methanol concentration. Indeed, the order of reaction with respect to methanol was found to be approximately 4. In an extremely nonpolar solvent such as pentane, this does not mean that four molecules of methanol are covalently bonded to R_3Si^*F in the rate-controlling transition state.

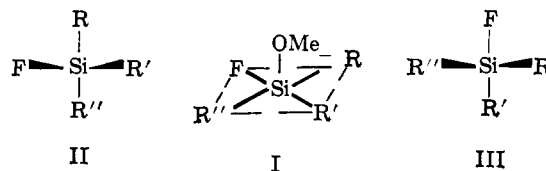
The rate data for racemization of R_3Si^*F (0.0358 *M*) in *t*-butyl alcohol by methanol (2.06 *M*) at 25° give a linear first-order plot, $k_1 = 2.0 \text{ min.}^{-1}$. In *t*-butyl alcohol solvent, as in pentane, an equimolar mixture of R_3Si^*F and $R_3Si^*OCH_3$ was racemized by methanol only to the point of complete racemization of R_3Si^*F and zero racemization of $R_3Si^*OCH_3$. Both HF ($8.44 \times 10^{-2} \text{ M}$) and boron trifluoride etherate (0.529 *M*) retard racemization of R_3Si^*F by methanol in the *t*-butyl alcohol solvent, the former by a factor of 17 and the latter by a factor of 4, for $[R_3Si^*F]$ equal to 0.0358 *M* and $[CH_3OH]$ equal to 0.580 *M*. Further studies are in progress.⁶

Addition of methoxide ion (from $MeOH_2^+ - MeO^-$) to the central silicon to give a geometrical arrangement in which R, R', R'', and F are coplanar constitutes a possible mechanism for the racemization.⁷ For a pen-

(6) Based on a solvolysis study of Ph_2SiF and *p*-tolylSiF in acetone-water (C. G. Swain, R. M. Esteve, and R. H. Jones, *J. Am. Chem. Soc.*, **71**, 965 (1949)), an expanded-octet mechanism was proposed for these reactions, but the evidence was inconclusive. It was also consistent with an SN_2 mechanism in which bond-formation exceeds bond-breaking in the rate controlling transition state. On the basis of the present stereochemical results and others, we now believe that the original mechanism postulate of Swain and co-workers for the solvolyses was probably correct.

(7) Structure I may also derive from reaction of R_3Si^*F with two molecules of methanol. In either case addition of HF should decrease the basicity of the medium and decrease rate. It is probable that I exists as one

tacovalent intermediate, the organic groups and the fluorine would be *basal* in a tetragonal pyramid and methoxide would be *apical*. Such an intermediate (I) would be optically active and could return to R_3Si^*F with *retention* or *inversion* of configuration, depending upon which pair of *trans* groups (R and R'' or R' and F) move toward the methoxy group as it leaves. In I the silicon atom need not be coplanar with R, R', R'', and F.



Structure III, resulting from movement of R and R'' toward MeO^- , is the enantiomer of structure II which results from movement of R' and F toward MeO^- .

An octahedral, hexacoordinate silicon intermediate, Si, R, R', R'', and F coplanar, which would be optically inactive if it contained *trans* methoxy groups, is also possible but seems less likely at present.

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component of an ion-pair which also contains $MeOH_2^+$ and that one or more molecules of methanol stabilize the ion-pair by solvation.

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Segregation of Benzoic Acid-*d* from Benzoic Acid by Zone Melting

Sir:

In an attempt to identify impurities segregated from benzoic acid by zone melting, the mass spectra of various fractions of zone-melted ingots were examined. It was found that samples taken from the tops of zone-melted ingots showed smaller ratios of mass 123 to mass 122 than did the original acid. The samples did not seem to contain any impurity in an amount that would account for the observed ratios. It was thought that isotopic fractionation might be responsible, and to test this the following experiment was carried out.

Benzoic acid-*d* (0.50 g., 95% isotopic purity) was mixed with 19.20 g. of benzoic acid that had been purified by zone melting, recrystallization from water, and sublimation. The mixture was melted in a sealed zone melting tube, shaken vigorously, and allowed to solidify.

The ingot was subjected to 274 passes in an automatic zone refiner.¹ Deuterium was determined by the infrared technique of Jones and MacKenzie² in samples taken from three points in the ingot. The top, middle, and bottom of the ingot gave water containing 0.23, 0.36, and 0.43 mole % D_2O , respectively. The original mixture contained 0.33 atom % deuterium. It is clear that $C_6H_5CO_2D$ is distributed in $C_6H_5CO_2H$ as an impurity whose distribution coefficient³ is less than unity.

Benzoic acid and benzoic acid-*d* probably form a continuous series of solid solutions. Since the melting point of $C_6H_5CO_2H$ is about 3° higher than that of $C_6H_5CO_2D$,⁴ it would be expected that the melting point of the former would be depressed by admixture with the latter. The observed distribution is consistent with this situation.

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