(4) Other factors being equal, in SN2 reactions having a neutral nucleophile and a neutral electrophile the transition state resembles the reactants more than is the case in SN2 reactions having a negative nucleophile and a neutral electrophile.[7]

The ready availability of $\Delta H^{\pm}$ values in several solvents for many reactions as well as the ease of measuring the heats of solution of the reactants and of the products in most cases makes this a promising method for obtaining an *experimental* measure of the effects of structural and other variables upon the structures of transition states.

(7) The suggestion that there is little charge separation in the transition state of the Menshutkin reaction was made recently by M. H. Abraham, *Chem. Commun.*, 1307 (1969).

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Received December 8, 1970

Halide–Halide Exchange at Asymmetric Silicon. New Evidence against a Siliconium Ion-Pair Mechanism

Sir:

In 1964 we published a preliminary report[1] containing data which seemed quite consistent with the proposal of a siliconium ion-pair mechanism for the chloride–radiochloride exchange of optically active α-NpPhMeSi*Cl (I) with c-$C_6H_{11}NH_3{}^{36}Cl$ in chloroform solvent. Despite the rather formidable array of evidence presented in our earlier report, we have now assembled completely convincing evidence that the siliconium ion-pair mechanism originally proposed for this reaction is incorrect.

We wish to communicate our new results because of their mechanistic importance. At present, the data in ref 1 favoring a siliconium ion-pair mechanism comprise, according to a recent reference,[2] "... the only well documented evidence for this mechanism in organosilicon chemistry ...."

Several lines of new evidence are summarized below.

Modern instrumentation unavailable to us in our previous studies was used for careful redetermination of the k_{rac}/k_{ex} ratio for α-NpPhMeSi*Cl (I). Radioactivity counting was done using a Packard Model 3002 Tri-carb liquid scintillation spectrometer. Racemization was followed using a Durrum-Jasco automatic digital polarimeter series J-180, accurate to ±0.002. Instead of our previous value of 1.0 ± 0.1 for the ratio, we now find k_{rac}/k_{ex} = 1.3 ± 0.1. This ratio is independent of any assumptions concerning the order of the exchange or racemization reactions in salt. The k's are first-order rate constants;[3] conditions and concentrations of reactants (chlorosilane and salt both at 0.089 M in chloroform at 25.5°) were identical for racemization and exchange studies. In addition, using the same conditions and concentrations of reactants in chloroform solvent, we have now determined the k_{rac}/k_{ex} ratios for two other optically active systems. For the new optically active chlorosilane,[4] α-$NpPh_FMeSi$*Cl (II), the perfluorophenyl analog of α-NpPhMeSi*Cl, k_{rac}/k_{ex} = 2.0 ± 0.1. For the optically active chlorosilane,[5] Ph_3SiSi*(Ph)(Me)Cl (III), k_{rac}/k_{ex} = 1.8 ± 0.1. Of itself, variation in the k_{rac}/k_{ex} ratio from 1.3 to 2.0 to 1.8 for I, II, and III, respectively, leads only to the conclusion that in the case of II each act of exchange proceeds with inversion, and that the ratios of 1.8 and 1.3 represent increasing importance of retention or racemization mechanisms for exchange reactions of III and I. However, comparing rate constants for exchange and racemization for chlorosilanes II and I gives the results: k_{ex}(II)/k_{ex}(I) = 1.1 and k_{rac}(II)/k_{rac}(I) = 1.7. Thus, replacement of a phenyl group in I by a perfluorophenyl group gives II and also gives somewhat *increased* rates of exchange and racemization. This is in direct conflict with a siliconium ion-pair mechanism. Operation of the latter should give greatly *decreased* rates for II because of its strongly electron-withdrawing perfluorophenyl substituent. Thus, these data point to a mixture of inversion and retention mechanisms for halide–halide exchange of I in chloroform.

The above conclusion, that the polar effects of substituents on the rate of chloride–chloride exchange of chlorosilanes, under the conditions defined above, is not in accord with a siliconium ion-pair mechanism, was reinforced by a study of the rates of chloride–chloride exchange for a series of optically inactive chlorosilanes. These had the general structure α-NpMe(Aryl)SiCl in which aryl comprised meta- and para-substituted phenyl groups suitable for a Hammett type σ–ρ study. Using phenyl substituents such as m-CF_3, p-CF_3, p-OCH_3, and p-CH_3, ρ was found to be very small and positive (ρ = 0.4 ± 0.1). Since ρ for a siliconium ion-pair mechanism would be expected to be large and negative (SN1 solvolyses have $\rho = \sim -3$ for tertiary organic halides), this study provides strong evidence against such a mechanism. Indeed it indicates very little change in charge for transition-state silicon compared to ground-state silicon in these halide–halide exchanges. Evidently, bond making and bond breaking have taken place to approximately equal extents in the rate-controlling transition states of these reactions.

Previously, we concluded from infrared studies of equilibrium 1 that an equimolar mixture of R_3Si*Br

$$R_3Si^*Br + c\text{-}C_6H_{11}NH_3Cl \rightleftharpoons R_3Si^*Cl + c\text{-}C_6H_{11}NH_3Br \quad (1)$$

and c-$C_6H_{11}NH_3Cl$ produced an equilibrium system containing less than 2% of the original R_3Si*Br. Using radiochloride salt we have now found that the equilibrium concentration of R_3Si*Br actually amounts to 9.9%. This revision of the equilibrium constant for eq 1 renders invalid one of the key links in the prior chain of evidence implicating a siliconium ion-pair mechanism. The incorrect earlier data led to the

(1) L. H. Sommer, F. O. Stark, and K. W. Michael, *J. Amer. Chem. Soc.*, 86, 5683 (1964); see also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, pp 98–100.

(2) M. W. Grant and R. H. Prince, *Chem. Commun.*, 1076 (1968).

(3) For racemization, k_{rac} is simply the pseudo-first-order rate constant; for exchange k_{ex} is the first-order rate contant defined by $k_1 = R/a$ in which R is the gross rate of exchange and a is the concentration of chlorosilane; for detailed treatment, see: (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 192–193; (b) M. W. Grant and R. H. Prince, *J. Chem. Soc. A*, 1138 (1969).

(4) Unpublished work of L. H. Sommer and M. A. Silverman; see M. A. Silverman, Ph.D. Thesis, University of California at Davis, 1970.

(5) L. H. Sommer and K. T. Rosborough, *J. Amer. Chem. Soc.*, 91, 7067 (1969).

conclusion, when coupled with rate data, that the rate of *racemization* of α-NpPhMeSi*Cl by *c*-$C_6H_{11}NH_3Br$ exceeds the rate of chloride–bromide *exchange* for these reactants by a factor of more than 15.

Previously, it was found that the racemization rate of α-NpPhMeSi*Cl with *c*-$C_6H_{11}NH_3X$ in chloroform is somewhat insensitive to the nature of X (X = Cl, Br, or I), a fact which also suggested a siliconium ion-pair mechanism; reaction rate variation was less than a factor of 4.[1] Although these data pointed to a certain lack of dependence of rate on the anionic component of the cyclohexylammonium salts investigated, the critical experiment, using cyclohexylammonium perchlorate, could not be carried out because of the extreme insolubility of this salt in chloroform. However, very recent work shows a sharp decrease in the rate of racemization of α-NpPhMeSi*Cl when the anionic component of quaternary ammonium and phosphonium salts is perchlorate. Thus, in chloroform solvent, comparing racemization rates with $PhCH_2Et_3NCl$ and $PhCH_2Et_3NClO_4$ gives a relative rate for the perchlorate salt of $\sim 10^{-3}$. Comparing racemization rates with $Ph_3(PhCH_2)PCl$ and $Ph_3(CH_3)PClO_4$ in chloroform solvent gives a relative rate for the perchlorate salt of $\sim 10^{-3}$.

It should be noted here that the fine work of Grant and Prince[2,3b] with $Li^{36}Cl$ in acetone–dioxane has shown that chloride–chloride exchange with α-NpPhMeSi*Cl in this system occurs with inversion of configuration for each act of exchange. Also, in another recent report, these authors have found for $(n\text{-}C_4H_9)_4N^{36}Cl$ in *benzene solvent* with α-NpPhMeSi*Cl that in this system the rate of exchange far exceeds the rate of racemization, k_{ex}/k_{rac} = 40–80. Thus, in this latter system the vast majority of exchanges are proceeding with retention of configuration.[6] For chloride–chloride exchange at asymmetric silicon, this work coupled with the new results reported herein demonstrates that the observed stereochemistry (per cent inversion *vs.* per cent retention) and the operation of competitive mechanisms are a sensitive function of the nature of the solvent, the reagent, and the chlorosilane structure. This is in sharp contrast to the usual situation for reactions of optically active acyclic chlorosilanes with strong nucleophiles which provide entering groups more basic than Cl—for such reactions an inversion SN2–Si mechanism operates in the vast majority of cases.[7,8]

Further discussion of the mechanistic implications of the above new data, and other data including the relative rate of chloride–chloride exchange at bridgehead silicon, will be presented in a later article.

Acknowledgment. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(6) M. W. Grant and R. H. Prince, *Nature (London)*, **222**, 1163 (1969).
(7) For example, *c*-$C_6H_{11}NH_3F$ and *c*-$C_6H_{11}NH_3OCOCH_3$ in chloroform solvent with α-NpPhMeSi*Cl give the fluorosilane and acetoxysilane products with better than 90% inversion of configuration; see L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Amer. Chem. Soc.*, **89**, 857 (1967).
(8) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, Chapter 4.

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*Book Reviews**

The Alkaloids. Chemistry and Physiology. Volume XII. Edited by R. H. F. MANSKE, Uni Royal Limited Research Laboratory. Academic Press Inc., New York, N. Y. 1970. xvii + 637 pp. $29.00.

Alkaloid chemists throughout the world will welcome the appearance of this twelfth volume of this standard and most comprehensive of treatises on all phases of alkaloid chemistry.

A number of varied topics are reviewed in this new volume, which consists of seven chapters. Chapters 1 and 2, by S. W. Pelletier and L. H. Keith, constitute a book within a book on the subject of the diterpene alkaloids of *Aconitum*, *Delphinium*, and *Garrya* species. Chapter 1 discusses the C_{19} diterpene alkaloids (*e.g.*, the aconitine type), while Chapter 2 discusses the C_{20} diterpene alkaloids (*e.g.*, the atisine type). The authors are to be congratulated for having accumulated most of the very complex chemistry of these polycyclic multifunctional bases, especially the C_{19} alkaloids, into one critical but thorough review.

Chapter 3, by J. E. Saxton, is concerned with *Alstonia* alkaloids. It is mostly a very readable account of the superb structure determinations of the unusual dimeric indole bases of *Alstonia* species, as carried out in recent years by Schmid, Hesse, Taylor, and their collaborators.

Chapter 4, by F. L. Warren, brings up to date the earlier review of N. J. Leonard on the "Senecio alkaloids," a special but large subgroup of pyrrolizidine alkaloids. Not only are the individual alkaloids described but also their hydrolysis products, the necine bases and the necic acids. The practical utility of this fine chapter would have been increased by the addition of a special section devoted to spectroscopic properties.

Chapter 5 by F. Šantavý, concerns recent studies of the alkaloids of the family *Papaveraceae*. The author has done an impressive job in discussing a wide variety of topics, from chemotaxonomy and biosynthesis to the chemistry of the fifteen different structural types of benzylisoquinoline-derived bases found to date in the *Papaveraceae*.

Chapter 6, by R. H. F. Manske, is a collection of brief abstracts of recent reports of alkaloids from various plant sources, Well-known alkaloids and new alkaloids of all types, some of which are of unknown structure, are included. This is a chapter of primarily practical use for the investigator doing current phytochemical research.

The volume closes with Chapter 7, by E. G. C. Clarke, on the subject of the forensic chemistry of alkaloids. This chapter appears to be a very good general review of such topics as poisoning and addiction by alkaloids, legal control of alkaloids, and extraction and analytical detection of alkaloids in animal tissues. This type of review is well worth publishing somewhere although one wonders

* Unsigned book reviews are by the Book Review Editor.