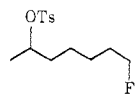
none (**10**). A separate experiment showed that **8** was, in fact, converted to **10** under our reaction conditions sufficiently rapidly to account for the **10** obtained from 5-fluoro-1-pentyne. We also observed the conversion of **4** to **10**, but the rate of reaction was insufficient for an appreciable proportion of the **10** obtained from 5-fluoro-1-pentyne to have arisen *via* the **4** → **10** pathway. That a special mechanism such as that of Scheme I is needed to account for loss of terminal fluorine (in **10**) was evident from a control experiment in which 1-fluorohexane was shown to be stable in trifluoroacetic acid–sodium trifluoroacetate. Perhaps our most important control experiment was a clear demonstration that **4** was not formed from **10** under carefully simulated reaction conditions involving added sodium fluoride and trifluoroacetic anhydride in addition to sodium trifluoroacetate. All of these results lend support to the postulated competition between "normal addition" and "fluorine-shift" pathways.

In a separate series of experiments the ω-fluoroalkyl tosylates shown in Table II were solvolyzed in trifluoroacetic acid in order to obtain possible rate evidence for fluorine participation. Analysis of these

Table II. First-Order Rate Constants for Solvolysis of ω-Fluoroalkyl Tosylates at 25°

Tosylate	10^5k, sec^{-1}	k_H/k_X
	0.0502	291
	2.14	8.87
	7.37	3.38

results depends on our earlier demonstration that large inductive effects upon rates of reaction of approximately 40 alkenes with trifluoroacetic acid[6] (also shown by the tosylates) could be correlated with an uncertainty of approximately ±10% by "attenuation plots," allowing even small participation effects to be evaluated.

The data in Table II, treated in this way, lead to a value of k_Δ/k_s (the ratio of rate constants for participation and for normal solvolysis) of 2.4. This modest but, in our judgment,[7] probably significant effect was approximately that which we expected, based on unpublished studies of the more strongly participating chloroalkyl tosylates. We conclude that our studies have provided moderately good rate evidence for fluorine participation in tosylate solvolyses and, in the reaction of 5-fluoro-1-pentyne, a probable example of a 1,4-fluorine shift which arises *via* a fluoronium ion intermediate or transition state.

(6) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *J. Am. Chem. Soc.*, **87**, 5163 (1965).

(7) We are aware that our judgment will be disputed, especially by those who make a comparison between our results and those obtained from solvolysis of cyclic and bicyclic systems, where interpretation of rate variations by factors as large as 10^2 or even 10^8 may be controversial. Our own studies have taken advantage of the very much greater predictability of rates in aliphatic systems, as evidenced especially by our discovery of 1,4-halogen shifts based originally on observation of an eightfold rate effect.

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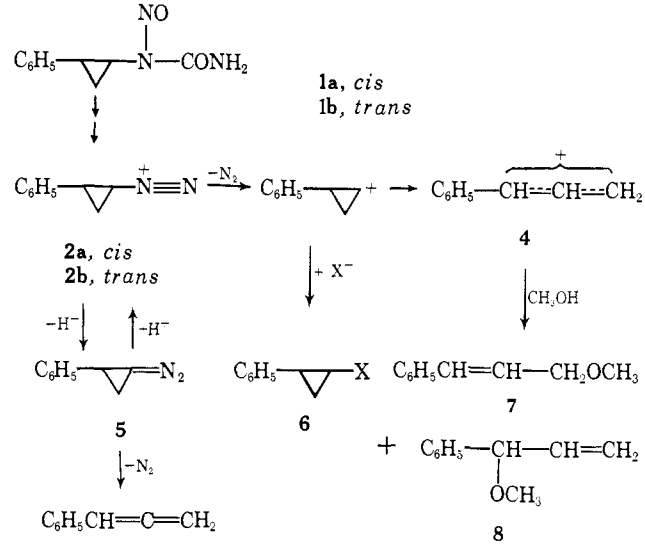
The Decomposition of Cyclopropyldiazonium Ions

Sir:

The solvolysis of cyclopropyl tosylates has recently been classified as a concerted process, with ring opening occurring in the transition state.[1] The cyclopropyl cation, presumably a highly energetic intermediate, is bypassed in the solvolysis of cyclopropyl tosylates.

We have studied the decomposition of cyclopropyldiazonium ions as a more promising route to cyclopropyl cations. Our arguments rest on product stereochemistry rather than kinetics. Therefore, two possible sources of error had to be eliminated: (i) acid-catalyzed equilibration of the (allylic) products; (ii) base-catalyzed equilibration of isomeric diazonium ions (*e.g.*, **2a,b**) *via* diazoalkane (*e.g.*, **5**). This type of reaction is readily detected in deuterated solvents. Intervention of the diazoalkane leads to incorporation of deuterium, while products free of deuterium result from decomposition of the diazonium ions prior to deprotonation.



Treatment of N-nitroso-N-2-phenylcyclopropylurea (*cis*- and *trans*-**1a,b**) with excess sodium formate in CH_3OD afforded phenylallyl methyl ethers (**7**, **8**) with 0.25 g-atom of D/mole (nmr).[2] Consequently, only 25% of the diazonium ions **2a,b** may have suffered *cis–trans* isomerization *via* **5**. However, both **1a** and **1b** afforded *trans*-cinnamyl methyl ether (*trans*-**7**) with only a trace of the *cis* isomer (Table I). If the decomposition

(1) C. H. De Puy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4007 (1965); **88**, 3343 (1966); P. von R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

(2) With $KDCO_3$–CH_3OD the deuterium content of **7** and **8** rose to 0.65 g-atom of D/mole; the yield of phenylallene was 0.5–0.8%. With 1 equiv of $NaOCH_3$ phenylallene was the major product (78–84%). Phenylallene results from the thermolysis of **5**; *cf.* W. M. Jones, *et al.*, *J. Am. Chem. Soc.*, **82**, 6200 (1960); **85**, 2754, 3309 (1963); **86**, 912 (1964).

of cyclopropyldiazonium ions and ring opening were concerted reactions (**2** → **4**), the Woodward–Hoffmann rules[3] should be obeyed to give *cis*-**7** from **1a** and *trans*-**7** from **1b**. Our contrary experience leads us to postulate the cyclopropyl cation **3** as a common intermediate of the *cis* and *trans* series.

Table I. Reaction of **1a,b** (0.82 g) in CH_3OD (32 ml) with Sodium Formate (4 g) at 25° (15 hr)

Starting Material	Products, %: Phenylallene	**6**, X = OCH_3 *cis*	**6**, X = OCH_3 *trans*	*trans*-**7**	*cis*-**7**	**8**
1a	0.1	0.03	0.30	25	0.1	60
1b	0.1	0.02	0.14	24	0.1	60

2-Phenylcyclopropyl methyl ether (**6**, X = OCH_3) was obtained in low yield, but very similar *cis*:*trans* ratio, from **1a** and **1b**.[4] Addition of lithium bromide to the reaction mixture gave rise to 1–2% of *trans*-2-phenylcyclopropyl bromide (**6**, X = Br) (*cis* <0.05%) from both **1a** and **1b**.[5] The nonstereospecific formation of **6** points toward **3** as the precursor of **6**.

Partial retention of the cyclopropyl structure was also encountered in the basic cleavage of N-nitroso-N-cyclopropylurea. In the presence of halide ions cyclopropyl halides were obtained in 3–9% yield. Treatment of the nitrosourea with a 2 *M* methanolic solution of lithium azide afforded the previously unknown cyclopropyl azide in 80% yield (bp 79.5°; $n^{23}D$ 1.4368; ν_{N_3} 2190 and 2105 cm^{-1}; nmr, 60 Mc in CCl_4, showed multiplets at 2.9 (1 H) and 0.7 ppm (4 H); cyclopropylamine was formed on reduction with sodium arsenite).

Although trapping of the cyclopropyl cation by strong nucleophiles may explain these observations, other reaction paths are conceivable and currently under investigation.

(3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(4) The assignment of the stereoisomers is tentative. A mixture rich in the presumed *cis* isomer was obtained from styrene and "methoxycarbene" according to U. Schöllkopf and J. Paust, *Chem. Ber.*, **98**, 2221 (1965).

(5) The assignment of the stereoisomers rests on the relative rates of solvolysis (*trans* > *cis*) and on the predominant formation of *cis*-2-phenylcyclopropyl bromide on partial reduction of 2-phenyl-1,1-dibromocyclopropane.

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Book Reviews

Stereochemistry, Mechanism and Silicon. An Introduction to the Dynamic Stereochemistry and Reaction Mechanisms of Silicon Centers. By LEO H. SOMMER, Professor of Chemistry, The Pennsylvania State University. McGraw-Hill Book Co., 330 West 42nd St., New York, N. Y. 1965. xvi + 189 pp. 16 × 23 cm. $9.75.

Occasionally, a single chemist with his co-workers is singlehandedly responsible for the development of an entire field of research. A good example is Professor Leo Sommer and the stereochemistry of silicon. The key to this area of research was the preparation, by Sommer and Frye, of functional, optically active silicon compounds in 1959. This well-written little book summarizes the ensuing research by Sommer and his students, which has contributed nearly everything we now know about organosilicon stereochemistry.

The first chapter, entitled "Fundamental Considerations," gives a good qualitative treatment of the evidence for penta- and hexacovalent silicon species and the problem of "siliconium ions." Here, and elsewhere, chemical bonding considerations are only mentioned. Chapter 2 briefly recounts the synthesis of the first optically active organosilicon compounds and the discovery of Walden inversion at silicon. Before proceeding onward from this point, readers new to the field should turn to Chapter 11 at the end of the book. Here is found a beautifully concise summary of the mechanistic possibilities for silicon and their stereochemical consequences, which are at once subtler and more complex than those for carbon.

Armed with this information, one is prepared to cut into the real meat of the book, Chapters 3 through 7. These all concern the detailed stereochemistry of various types of reactions at silicon. This story is complicated, and clear writing is vital to its successful telling. It is hard to see how Sommer's treatment could be improved on.

Chapter 8 treats structure–reactivity relationships in organosilicon chemistry; to this reviewer it seems less convincing than the rest of the book, perhaps because the author is writing about others' work rather than his own. He is on firm ground again in the final chapters, 9 and 10, dealing with reactivity of bridgehead silicon and "recent advances."

The book is attractively laid out and relatively errorless. No one who is seriously interested in organosilicon chemistry can afford to be without it.

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BOOKS RECEIVED, *January 1967*

LESLIE G. CHATTEN, Editor. "Pharmaceutical Chemistry." Volume 1. "Theory and Application." Marcel Dekker, Inc., 95 Madison Ave., New York, N. Y. 1966. 504 pp. $14.50.

F. ALBERT COTTON and GEOFFREY WILKINSON. "Advanced Inorganic Chemistry, A Comprehensive Text." Second Revised and Augmented Edition. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1966. 1136 pp. $14.50.