

of cyclopropyldiazonium ions and ring opening were concerted reactions ($2 \rightarrow 4$), the Woodward-Hoffmann rules⁸ 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 CH₃OD (32 ml) with Sodium Formate (4 g) at 25° (15 hr)

Starting Material	Phenylallene	Products, %				
		6, X = OCH ₃		<i>trans</i> -7	<i>cis</i> -7	8
		<i>cis</i>	<i>trans</i>			
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 = OCH₃) was obtained in low yield, but very similar *cis:trans* ratio, from **1a** and **1b**.⁴ Addition of lithium bromide

(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).

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 nitroso urea with a 2 M methanolic solution of lithium azide afforded the previously unknown cyclopropyl azide in 80% yield (bp 79.5°; *n*^{23D} 1.4368; ν_{N} 2190 and 2105 cm⁻¹; nmr, 60 Mc in CCl₄, 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.

(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 single-handedly 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 hexavalent 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

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