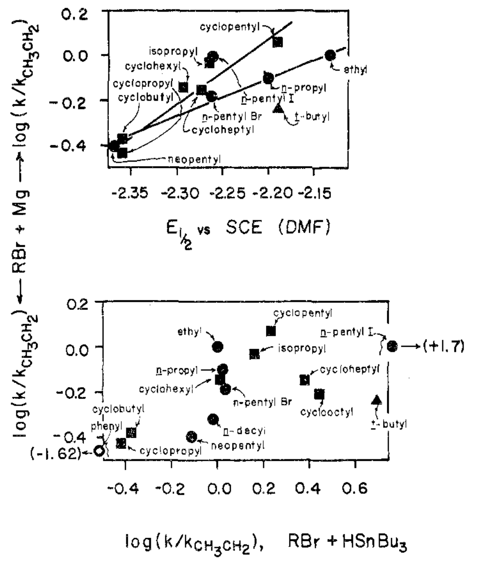

Figure 2. The relative rates of reactions of alkyl halides with magnesium correlate better with half-wave potentials for their reduction at a dropping mercury electrode than with their rates of reaction with tri-*n*-butyltin hydride. In this figure, primary halides are represented by ●, secondary by ■, the single tertiary halide by ▲, and phenyl, included on the plot for comparison, by ○.

the energy required to convert RX to $RX\cdot^-$ (2), we have used half-wave potentials, $E_{1/2}$, for reduction of alkyl halides.[11] For a reaction generating **2**, the log of the rate of electron transfer to RX at constant potential should be approximately proportional to $E_{1/2}$, provided, as we observe, that the rate is not diffusion limited. The correlation between log (k_{RX}/k_{EtBr}) from the Grignard reactions and $E_{1/2}$ for the corresponding alkyl bromides is again not particularly close over the limited range of compounds for which consistent electrochemical data are available, but appears better than that characterizing the tri-*n*-butyltin hydride reductions.[12,13]

These rate studies indicate that the rate-determining transition state in the formation of an alkyl Grignard reagent does not involve a heterolytic fission of the C-X bond, nor is it diffusion limited. The superiority of the correlation of log $(k_{RX}/k_{EtBr})_{Mg}$ with $E_{1/2}$ to that with $\log(k_{RX}/k_{EtBr})_{triBu_3SnH}$ suggests, but does not prove, that **2** rather than **3** describes the transition state for the reaction. Evidence implicating **2** as an intermediate in the formation of Grignard reagents has been described by others,[3,4] but these data have not been sufficient to characterize the rate-determining step, or, in the instance of CIDNP experiments, to establish that the **2** lies along the principal reaction path leading to product.

Acknowledgment. Preliminary work in this problem was carried out by E. V. Merry and C. H. Breckheimer.

Supplementary Material Available. Experimental procedures used to obtain the data summarized in Figure 1, and a representative plot of experimental data according to eq 3, will appear following this article in the microfilm addition of this journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-74-857.

References and Notes

(1) Supported by the National Science Foundation, Grant GP-28586X.

(2) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Compounds," Prentice Hall, New York, N. Y., 1954.

(3) H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **51,** 31 (1973); H. L. Goering and F. H. McCarron, *J. Amer. Chem. Soc.*, **80,** 2287 (1958).

(4) H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *Tetrahedron*, **29,** 719 (1973).

(5) W. C. Kossa, Jr., T. C. Rees, and H. G. Richey, Jr., *Tetrahedron Lett.*, 3455 (1971); C. Blomberg, *J. Organometal. Chem.*, **45,** 1 (1972); C. Rüchardt and H. Trautwein, *Ber.*, **95,** 1197 (1962).

(6) This observation and the fact that crude noncompetitive kinetics carried out using magnesium surfaces sufficiently large that their effective surface area does not change during the course of a kinetic run indicate that the assumption that $\alpha = 1$ is at least approximately justified: Y. Fujiwara, unpublished results.

(7) Supplementary material available. See paragraph at end of this communication.

(8) Data for these rate profiles were obtained from the following sources: A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; A. Streitwieser, Jr., and W. R. Young, *J. Amer. Chem. Soc.*, **91,** 529 (1969), and references cited therein; D. E. Applequist and P. F. O'Brien, *ibid.*, **85,** 743 (1963). Values for S_N2 reactions are Streitwieser's "average" values. The data for exchange of hydrocarbons with CsCHA have not been related to the rate of exchange of ethane. Since only the general forms of these profiles are important, the relative rate of exchange of cyclopropane has arbitrarily been given the same value as the equilibrium constant for metal-halogen exchange between ethyllithium and cyclopropyl iodide.

(9) C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9,** 830 (1970).

(10) H. G. Kuivila, *Accounts Chem. Res.*, **1,** 299 (1968).

(11) Details of the mechanism of electrochemical reduction of alkyl halides are still unclear; however, the bulk of the available evidence suggests one-electron transfer from the electrode to the alkyl halide as the potential-determining step; *cf.* C. K. Mann, J. L. Webb, and H. M. Walborsky, *J. Amer. Chem. Soc.*, **92,** 2042 (1970), and A. J. Fry and R. G. Reed, *ibid.*, **94,** 8475 (1972), for discussion of this point.

(12) All of the $E_{1/2}$ values included in Figure 2 are taken from a single source: F. L. Lambert and K. Kobayashi, *J. Amer. Chem. Soc.*, **82,** 5324 (1960). This study employed a dropping mercury electrode, DMF solvent, and $Bu_4N^+I^-$ as supporting electrolyte. Our efforts to obtain $E_{1/2}$ data in ethereal solvents have not been successful: C. L. Hill, unpublished work.

(13) The origin of the differences in the slopes of the lines correlating $E_{1/2}$ with log (k_{RX}/k_{EtBr}) for primary and secondary alkyl moieties is not obvious, but does not deserve speculation until it has been established that the difference persists in ethereal solvents.

(14) National Institutes of Health Predoctoral Fellow, 1966–1969.

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Received November 28, 1973

An Unusual Simmons-Smith Reaction Affording Noncyclopropyl Compounds. A New Route to 2-Methylenecycloalkanols from Silyl Alkenyl Ethers[1]

Summary: Reaction of silyl cycloalkenyl ethers under a certain Simmons-Smith reaction conditions gives silyl ethers of 2-methylenecycloalkanols, and these noncyclopropyl products have been shown to arise by the isomerization of initially produced silyl cyclopropyl ethers with zinc iodide which is formed during the course of Simmons-Smith reaction.

Sir: During the course of our study on the synthesis of cyclopropanols,[2] we found an interesting and unusual Simmons-Smith reaction which gave noncyclopropyl compounds.

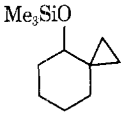
The reaction of trimethylsilyl cycloalkenyl ethers **1**[3] (0.05 mol) with methylene iodide (0.08 mol) and zinc-copper couple[4] (0.16 mol) *in 110 ml of anhydrous ether* at 34° for 40 hr (procedure A) gave the silyl cyclopropyl ethers **2** as expected. A dramatical change of the product was observed by merely changing the amount of the solvent in this reaction (Scheme I). When the same reaction was carried out using *40 ml of anhydrous ether* as a solvent while keeping all other reaction variables unchanged (pro-

Table I
Normal and Unusual Simons-Smith Reactions

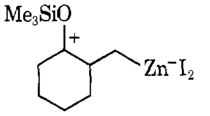
Compd	Procedure	Product	Yield, %[a]	Purity, %
1a	A	**2a**	76	>97[b]
1a	B	**3a**	71	100
1b	A	**2b**	71	>92[b]
1b	B	**3b**	68	100

[a] Isolated by distillation. [b] Impurities included were the starting olefin **1** and the isomeric product **3**, which could be easily removed.

cedure B), the products obtained were trimethylsilyl ethers of 2-methylenecycloalkan-1-ols **3**: **3a**, bp 60–61° (18 mm), ir (direct) 1666 cm^{-1}, nmr (CCl_4) δ 4.26 (1 H, CH) and 4.85 (2 H, $=CH_2$); **3b**, bp 60–65° (10 mm), ir (direct) 1660 cm^{-1}, nmr (CCl_4) δ 3.90 (1 H, CH) and 4.62 and 4.75 (2 H, $=CH_2$). The results are summarized in Table I. Both procedures A and B gave reproducible results and worked well on larger (fourfold) and smaller (one fifth) reaction scales. Under the reaction conditions of procedure B, **1b** gave no trace of a spiro compound **6** which would result from further cyclopropanation of **3b**. However, **6** was obtained in 42% yield in addition to **3b** (14%) under more forcing reaction condition, *i.e.*, when additional methylene iodide (0.13 mol), zinc-copper couple (0.26 mol), and ether (15 ml) were added at 40 hr and the reaction was continued for another 24 hr.

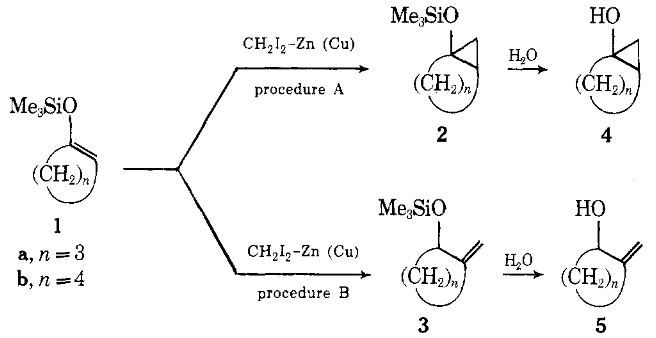


6



7

Scheme I



To clarify the nature of the unusual Simmons-Smith reaction, the product distribution was followed as a function of time by glc. This revealed that the reaction of **1b** using procedure B did afford cyclopropyl ether **2b** as the initial product. Its concentration increased with the decrease in that of **1b**; it reached maximum concentration after about 5 hr and then decreased with concomitant increase in the concentration of **3b**. This clearly demonstrates that **3b** is obtained by *in situ* isomerization of the initial product **2b**. This isomerization has been shown to be caused by zinc iodide which is produced during the course of the Simmons-Smith reaction. In a control experiment, cyclopropyl ether **2b** (0.01 mol) was treated with zinc iodide (0.01 mol) in 7 ml of ether at 34° for 40 hr to give a mixture containing **2b** (12%) and **3b** (88%). On the other hand, when 35 ml of the same solvent was used **3b** was not formed; **2b** was recovered unchanged.

Just as **2** have been converted to cyclopropanols **4**,[2] so the silyl ethers **3** can be hydrolyzed to 2-methylenecycloalkan-1-ols[5] (**5**) in quantitative yields by treating **3** (0.01 mol) with a mixture of 30 ml of CH_3OH and 3 ml of 1 *N* NaOH at room temperature for 3 hr. Thus, the above-described unusual Simmons-Smith reaction provides a new convenient synthetic route to 2-methylenecycloalkan-1-ols[6] whose synthesis is otherwise somewhat troublesome.[5,7]

By procedure B 2-methylene compounds similar to **3** were also obtained from 4-methyl and 4-*tert*-butyl derivatives of **1b**, but no unusual product was detected in the case of 1-trimethylsiloxycyclohept-1-ene and 1-trimethylsiloxy-5,6-benzocyclohex-1-ene.[8] The product obtained from 1-trimethylsiloxy-6-methylcyclohex-1-ene contained both the cyclopropanated and the allylic compounds.

It is tentatively assumed that the isomerization of **2** with zinc iodide proceeds *via* an intermediate **7**.[9] Internal strain of **2** and stabilization of the positive charge in **7** by the siloxy group would account for the ease of the isomerization. The reasons why procedure A and B give different results is not clear at this time. It could be attributed to the difference of coordination pattern around the zinc atom or merely to the function of reaction rate (*i.e.*, concentration of the reactants).

There has been no report,[10] to our knowledge, on the formation of noncyclopropyl compound by the reaction of an olefin under Simmons-Smith reaction conditions. The present results suggest that one should be very careful to identify products of the Simmons-Smith reaction, at least in the case of enol ethers. Indeed, preliminary result in this laboratory shows that 1-ethoxycyclohex-1-ene also gives 1-ethoxy-2-methylenecyclohexane. Further study of the scope and limitation, as well as mechanism, of this unusual Simmons-Smith reaction is in progress.

Acknowledgment. We wish to express our thanks to Professor Henry G. Kuivila for his helpful comments on the manuscript. We are grateful to Shin-Etsu Chemical Industry Co., Ltd., for providing the trimethylsilyl chloride.

References and Notes

(1) Synthesis *via* Silyl Alkenyl Ethers. V. For Part IV, see ref 2.
(2) S. Murai, T. Aya, and N. Sonoda, *J. Org. Chem.*, **38**, 1354 (1973).
(3) H. O. House, L. J. C. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
(4) R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).
(5) T. Tsuji, I. Moritani, and S. Nishida, *Bull. Chem. Soc. Jap.*, **40**, 2338 (1967). We wish to thank these authors for providing us with the ir and nmr spectra of **5**.
(6) Many naturally occurring compounds having this structural unit are known. For examples, see the following: A. S. Gupta and S. Dev, *Tetrahedron*, **27**, 635 (1971); A. I. Scott and A. D. Wrixon, *ibid.*, **27**, 4787 (1971).
(7) W. C. Still, Jr., A. J. Lewis, and D. Goldsmith, *Tetrahedron Lett.*, 1421 (1971); V. S. Joshi, N. P. Damodaran, and S. Dev, *Tetrahedron*, **27**, 475 (1971).
(8) The reasons why isomerized products are not obtained from these latter two compounds are not clear at present time. The H (C-4) and H (C-5) in the former or perihydrogen in the latter could possibly cause steric compression with trimethylsilyl group.
(9) Alternatively the formation of **7** and the following hydrogen migration could take place in a concerted manner.
(10) The formation and the partial isomerization of 1,1,2,2-tetramethoxycyclopropane by the reaction of bis(iodomethyl)zinc with tetramethoxyethylene have been reported by Hoffman and his coworkers.[11] Recent reports on the reaction of the Simmons-Smith reagent with **1a**[12] and **1b**[12,13] contain no mention of the formation of noncyclopropyl compound.
(11) R. W. Hoffman, U. Bressel, and G. Mühl, *Chem. Ber.*, **105**, 2104 (1972).
(12) J. M. Conia and C. Girard, *Tetrahedron Lett.*, 2769 (1973).
(13) G. M. Rubottom and M. I. Lopez, *J. Org. Chem.*, **38**, 2097 (1973).

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Received January 22, 1974