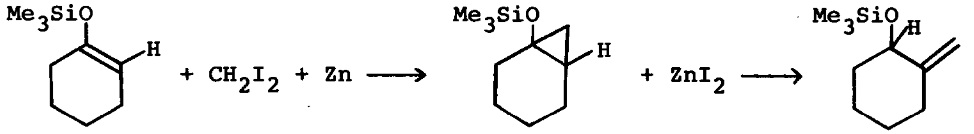
Tetrahedron Letters No. 23, pp 1995 - 1998, 1977. Pergamon Press. Printed in Great Britain.

SKELETAL REARRANGEMENT WITH RING EXPANSION IN THE SIMMONS-SMITH REACTION OF TRIMETHYLSILOXYMETHYLENECYCLOPENTANES

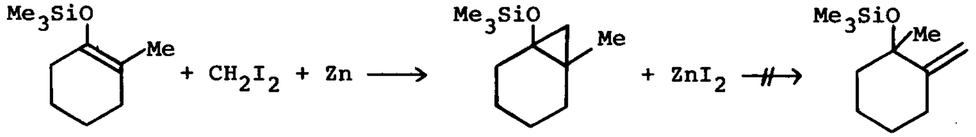
Ilhyong Ryu, Shinji Murai,* Shoji Otani, and Noboru Sonoda
Department of Petroleum Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565, Japan

(Received in Japan 28 March 1977; received in UK for publication 28 April 1977)

Recently cyclopropanation of enol silyl ethers by the use of Simmons-Smith reagent has been reported by this[1] and the other groups.[2] Cyclopropyl silyl ethers have been proved to be potential synthetic intermediates.[3] As reported previously,[4,5] the Simmons-Smith reaction of enol ethers (RO-C=C, R=alkyl, Me_3Si) has the unexpected aspect that zinc iodide, a by-product of this reaction, converts the initially formed cyclopropanated products to corresponding allylic ethers. This interesting isomerization reaction involves the cleavage of cyclopropane ring and consecutive 1,2-migration of hydrogen (eq 1). The corresponding 1,2-migration of methyl group, however, could not be achieved so far. For example, in the system of the Simmons-Smith reaction of 1-trimethylsiloxy-2-methylcyclohex-1-ene, 1,2-methyl migration has not been observed at all under any reaction conditions (eq 2).[6]



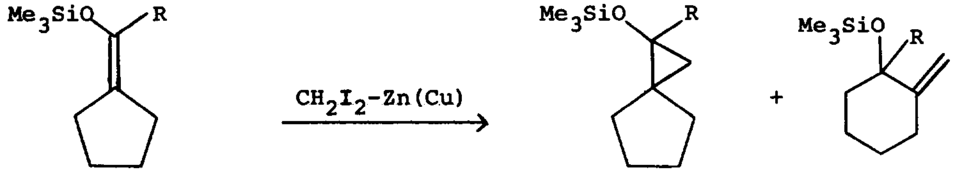
(1)



(2)

Now we wish to report the definite example of skeletal rearrangement accompanying 1,2-migration of carbon in the Simmons-Smith reaction of silyl ethers of the type 1. These compounds 1 give rise to strained spiro[4,2]-adducts 2 as initial products in the Simmons-Smith system.

Since it was found that the product distribution in the reaction of 1 were highly dependent on the concentration of the reaction mixture, we employed three reaction conditions (termed A, B,[7] and C) which were different only in the amounts of the solvent used. Generally, to the mixture of zinc-copper couple[8] (16 mmol) and an appropriate amount of anhydrous ether (Reaction conditions A 'diluted', 11 ml; Reaction conditions B 'concentrated', 4 ml; and Reaction conditions C 'highly concentrated', 2.5 ml) were added enol silyl ether 1 or 4 (5 mmol) and methylene iodide (8 mmol)and then the mixture was heated to 34° for 40 h with stirring. After mild acidic work-up[9] (aq NH_4Cl, aq $NaHCO_3$) the vacuum distillation of the ethereal solution gave the products. The results are given in the Table.



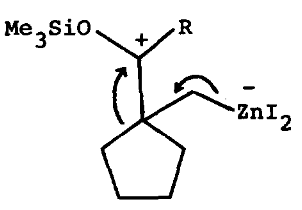
1a; R=Me
1b; R=H

2

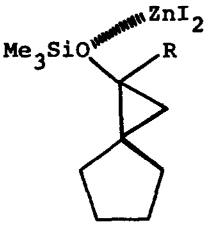
3

In the Simmons-Smith reaction of 1, merely expected cyclopropyl silyl ethers 2 were obtained exclusively under the 'diluted' conditions A. The more concentrated conditions gave the allylic products 3 in addition to 2. The most concentrated conditions (C or C') yielded the major product 3.

These unusual products 3 may be formed by the cleavage of cyclopropane ring of initially formed 2 by zinc iodide followed by the ring expansion with 1,2-migration of the carbon skeleton. Ionic intermediate 5 accounts for these processes reasonably.[10] This cation also explains the difference in the reactivity between 2a and 2b which are initial products from 1a and 1b, respectively.[11]



5

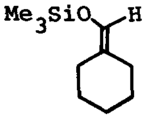


6

Dramatical changes of product distribution were observed under higher concentrated conditions (See results of B and C in 1a or C and C' in 1b). The species such as 6, in which cyclopropyl silyl ether occupies one of the coordination sites available for zinc iodide, would play an important role in the subsequent isomerization under these conditions.

The Simmons-Smith reaction of trimethylsiloxymethylenecyclohexane 4

Table. The Simmons-Smith Reaction of Enol Silyl Ethers 1 and 4.

Substrates	Reaction conditions (ml)[a]	Product distribution[b,c]		Total yields[b]
		'cyclopropyl' :	'allylic'[d]	
1a	A (11)	100	0	78 %
	B (4)	97	3	80 %
	C (2.5)	25	75	77 %
1b	A (11)	100	0	87 %
	B (4)	99	1	74 %
	C (2.5)	80	20	80 %
	C'(0.5)[e]	15	85	80 %
 4	A (11)	100	0	58 %
	B (4)	100	0	66 %
	C (2.5)	100	0	86 %

a) The amounts of the solvent used for every 5 mmol of the substrate.

b) Product distribution and yields were determined by glpc.

c) All new products showed satisfactory spectral and analytical data and 3b was identified with the authentic sample which was obtained from the Simmons-Smith reaction of 1-trimethylsiloxycyclohex-1-ene.[4]

d) The terms 'cyclopropyl' and 'allylic' correspond to 2 and 3 respectively.

e) Conditions: 1b (5 mmol), CH_2I_2 (8 mmol), Zn(Cu) (16 mmol), Et_2O (0.5 ml), 34°, 40 h.

gave nothing but normally expected spiro[5,2]-adduct, even when 'highly concentrated' conditions were employed. This suggests that the strain release from spiro[4,2]heptane system to methylenecyclohexane system may be the essential driving force in the isomerization of **2**.

Thus the proper choice of the reaction conditions is critically important in the reaction of enol ethers with zinc carbenoids.[12]

Referrences and Footnotes

(1) S. Murai, T. Aya, and N. Sonoda, J. Org. Chem., 38, 4354 (1973).

(2) a) J. M. Conia and C. Girard, Tetrahedron Lett., 2769 (1973).
  b) G. M. Rubottom and M. I. Lopez, J. Org. Chem., 38, 2097 (1973).
  c) R. LeGoaller and J. -L. Pierre, Bull. Soc. Chim. Fr., 1531 (1973).

(3) See refs. (1) and (2). Cyclopropyl silyl ethers can be easily converted to cyclopropanols.
  See also P. F. Hudrlik in "New Application of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., Elsevier Sci. Co., New York, N. Y., 1976, p 133.

(4) S. Murai, T. Aya, T. Renge, I. Ryu, and N. Sonoda, J. Org. Chem., 39, 858 (1974).

(5) I. Ryu, S. Murai, and N. Sonoda, Chemistry Lett., 1049 (1976).

(6) I. Ryu, S. Murai, and N. Sonoda, unpublished results.

(7) See refs. (4) and (5).

(8) R. J. Rawson and I. T. Harrison, J. Org. Chem., 35, 2057 (1976).

(9) Such mild conditions are indispensable in order to avoid the hydrolysis of products. Usual work-up involves the treatment with aq HCl.

(10) See refs. (4) and (5). The ionic intermediate has been proposed therein.

(11) The inductive effect of methyl group on **5** might be responsible for the easier achievment of this isomerization.

(12) The study using diethylzinc-methylene iodide is in progress.