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THE REACTION OF ENOL ETHERS WITH SIMMONS-SMITH REAGENT. THE FORMATION OF ALLYLIC ETHERS

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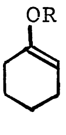
The Simmons-Smith reaction of methyl and ethyl cyclohexenyl ethers has resulted in the formation of allylic ethers, in addition to expected cyclopropyl ethers. In one case the allylic ether was obtained as the major product of this reaction.

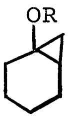
There have been many reports on the cyclopropanation of enol ethers with the Simmons-Smith reagent.1) The cyclopropyl ethers obtained by this reaction can be converted to α-methyl ketones by hydrolysis,2) and such transformation has been utilized in the synthesis of steroids or terpens.3)

Recently we have found that the Simmons-Smith reaction of silyl alkenyl ethers gave not only cyclopropyl ethers but also ring-opened allylic ethers and that the latter was formed by the further reaction of the former with zinc iodide, a by-product of this reaction.4) Since silyl compounds are known by their different properties from the carbon analog in various reactions,5) this unexpected result in the case of silyl alkenyl ethers (RO-C=C, R=Me_3Si) led us to reinvestigate the Simmons-Smith reaction of enol ethers (RO-C=C, R=alkyl). To our knowledge, there has been no description of the formation of such non-cyclopropyl compounds in the literature reported.

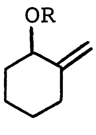
As the representative enol ethers, 1-methoxycyclohexene (Ia)6) and 1-ethoxycyclohexene (Ib) were prepared for present study.7) Two kinds of reaction conditions were employed according to the previous work.4,8) The differences in them are only those in the amounts of the solvent used. Generally, to a suspension of zinc-copper couple9) (0.16 mol) in anhydrous ether (reaction conditions A, 110 ml; reaction conditions B, 40 ml) were added an enol ether I (0.05 mol) and methylene iodide (0.08 mol) and then the mixture was refluxed for 40 hr. The results are given in the Table.



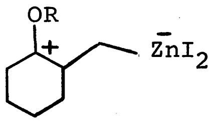
Ia; R=Me
Ib; R=Et



II



III



IV

Formation of allylic ethers was observed in all cases studied (see the Table). The results are reproducible. The assignment of the structure of allylic ethers III follows clearly from the spectral data. For example, 1-methoxy-2-methylenecyclohexane (IIIa) has following spectral properties: m/e 126 (M^+), IR (neat) 1660 cm^{-1}, NMR (CCl_4)

δ 4.72 ppm (s, $=CH_2$).[10,11]

Table. The Simmons-Smith reaction of enol ethers I

Enol Ether	Reaction Conditions	II	: III[a]	Total Yield[b]
Ia	A	98	2	72%
	B	83	17	59%
Ib	A	86	14	66%
	B	44	56	87%

[a] Product distribution was determined by glc analysis using SE-30 (Cromosorb W 5%).
[b] Isolated yields.

Ethoxy compound IIb is easier to isomerize than methoxy compound IIa. Such tendency is reconcilable with the ionic intermediate IV which was proposed previously.[4)] The isomerization of II (cyclopropyl alkyl ether) to III is relatively slow, when compared with the results of silyl ethers.[8)] This may be attributed to the widely recognized property of organosilicon group to stabilize the cation at the β-position.[12)]

We are extending these isomerization accompanying 1,2-hydrogen migration to the systems in which the hydrogen is replaced with an alkyl group.

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