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# FORMATION OF α-TRICHLOROSTANNYL KETONES IN THE REACTION OF STANNIC CHLORIDE WITH ENOL SILYL ETHERS

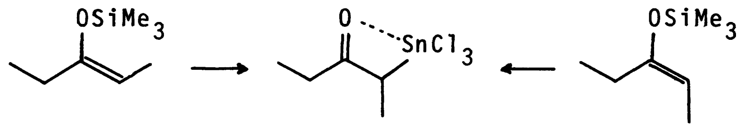
Eiichi NAKAMURA and Isao KUWAJIMA*
Department of Chemistry, Tokyo Institute of Technology, Ookayama
Meguro-ku, Tokyo 152

The enol silyl ethers of ketones reacted with $SnCl_4$ to give α-trichlorostannyl ketones in moderate to good yields, and their structures were determined by chemical and spectral means. The reaction mechanism is also discussed.

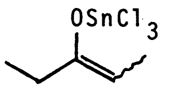
In spite of the tremendous recent advances in the chemistry of metallo enolates, not that much progress has been recorded for the reactions of their isomers, α-metallo ketones. This situation has arised presumably not because of the lack of the interest in this chemistry, but because of the lack of the suitable preparative methods and of the solid data on the structure of these species.[1] In fact, a very recent report by Yamamoto[1] demonstrated that such chemistry in the aldol reaction is no less interesting than the enolate chemistry: A highly stereoselective aldol reaction was found to occur with α-mercurio ketones.[2] Our interests in the process of converting homoenol derivatives to β-metallo carbonyl compounds[3] have led us to examine the possibility of converting enol derivatives to α-metallo ketones, and this has indeed proven to be a workable reaction.

The enol silyl ether is a useful stable metal enolate, and has been transformed to a variety of enolate anions,[4] but not too often to α-metallo carbonyl compounds.[2] We now found that, on reacting with $SnCl_4$, the enol silyl ethers of certain ketones give α-trichlorostannyl ketones, and report herein the preliminary results on the formation and the properties of these products.

At the start, we examined the reaction of the enol silyl ether Z-1 and $SnCl_4$ (1 equiv) in $CDCl_3$. Instantaneous reaction occurred on mixing these reactants (35 °C), yielding the α-stannyl ketone 2 (67% yield) and chlorotrimethylsilane (75%). Although attempts to purify this organometallic failed, the following pieces of information were solid enough to deduce the structure. The IR spectrum ($CCl_4$) showed an intense absorption at 1660 $cm^{-1}$ (with relatively weak ones at 1700 and 1640 $cm^{-1}$) assignable to the C=O group coordinated to a metal atom.[5] $^1H$ NMR exhibited the following signals: 1.28 (t, J = 7.0 Hz, $CH_3$), 1.92 (d, J = 8.0 Hz, $CH_3$), 2.77 (q, J = 7.0 Hz, $CH_2$), and 4.27 (q, J = 8.0 Hz, CH). The chemical shift of the methyne proton is incompatible with the trichlorostannyl enolate 3.[6,7] The absence of the fine allylic coupling in the methyl doublet (ca. 1 Hz), which was seen in the $^1H$ NMR of 1, is also in agreement with the proposed formulation. That the same product formed from the E-isomer of 1 (E-1) provided a chemical implication of the nature of the transmetallation process. The stannyl ketone 2, as well as others described below, underwent smooth aldol reaction with aldehydes as expected.[8] These stannyl ketones were stable at room temperature in solution, and showed no sign of isomerization to the enolate form, e.g., 3. The reactions were performed either in $CH_2Cl_2$ or in $CDCl_3$.



Z-1 (>99% Z) 2 E-1 (~75% E)



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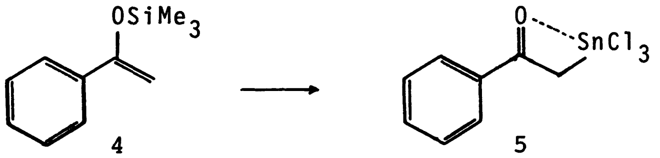
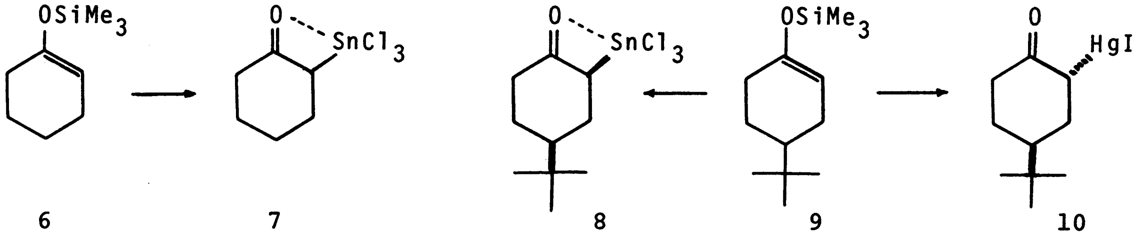
The reaction of 4 initially gave 5 (δ 4.27, s) in about 40% yield, which then gradually suffered in situ protonation to yield the parent ketone (31% isolated yield).



4 5

The enol silyl ether of cyclohexanone (6) gave 7 in 40-50% yield. The reaction did not complete with 1 equiv of $SnCl_4$, and about 30% of 6 remained. Total consumption of 6 was seen with excess $SnCl_4$ (1.4 equiv). The crucial $^1H$ NMR resonance of the α-proton appeared at δ 3.98, notably as a doublet of doublets (J

= 6, 13 Hz), showing that the metal is (nearly) in the plane of the carbonyl group, occupying the equatorial position. This behavior is in consonance with the internal chelation. The stannyl ketone 8 ($\sim$35% from 9) also have the metal on the equatorial side (δ 4.07, dd, J = 7, 13 Hz), and was tentatively assigned as the 1,3-cis isomer on the basis of the similarity of the $^1$H NMR of 7 and 8. Interestingly, the metal atom occupies the axial position in the mercurio ketone 10 prepared by mercuration of 9,[2] the assignment being deduced from a broad signal of the α-proton at δ 3.66, $W_{1/2}$ = 8 Hz. This stereochemistry must reflect the kinetic course of the mercuration reaction; for equilibration should have given a mixture of diastereomers.[9]

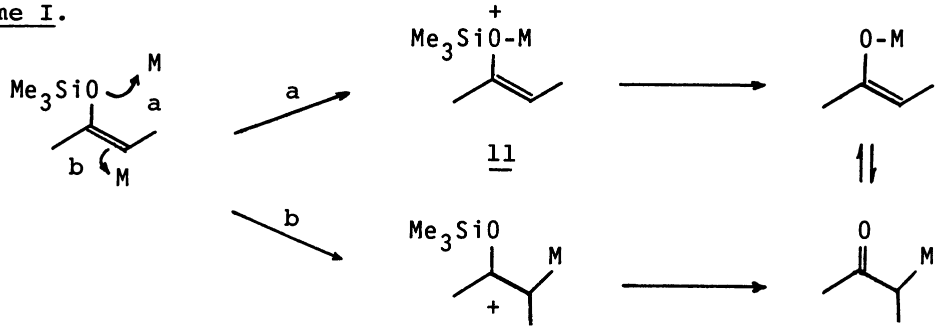


6 7 8 9 10

The reaction reported here appears very sensitive to the structure of the enol silyl ether, particularly to the substituent on the olefin. For instance, the $\Delta^{1,2}$-isomer of the enol silyl ether of 1-phenylthio-2-propanone (E/Z mixture) was inert to $SnCl_4$ in $CDCl_3$ (35 °C).[10] The examination of the scope of the reaction as well as the optimization of the conditions are yet to be done.

There are two ways of viewing this stannylation reaction (Scheme I). One contains the transmetallation reaction on oxygen, which is followed by ketonization. The alternative is analogous to the oxymercuration of olefins.[2]

Scheme I.



Dialkylboron triflates react with enol silyl ethers to give boron enolates.[11] This process, being stereospecific, is thought to involve the transition state 11. A somewhat related reagent, trimethylsilyl triflate, however, was inert to 1 ($^1$H NMR

35 °C, $CDCl_3$). The silyl triflate suffers rapid silyl exchange with the silyl ether of a secondary alcohol, e.g., l-menthol, and the complete lack of the exchange with 1 indicates the high energy barrier in going through 11. Consideration of the electronic effects of the olefin justifies the poor reactivity of the enol oxygen. It was revealing, in this respect, to find that $SnCl_4$, which does react with enol silyl ethers, was inert to the menthyl silyl ether. This fact makes the Si-Sn exchange route (a) via 11 highly unlikely. On the other hand, the sensitivity of the reaction to the substituent of the olefin implies the direct interaction of the metal atom with the olefin. For the moment, we take the second mechanism (b) as something close to the reality.

## References

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2) H. O. House, R. A. Auerbach, M. Gall, and H. P. Peet, J. Org. Chem., 38, 514 (1973).
3) E. Nakamura and I. Kuwajima, submitted for publication.
4) G. Stork and P. F. Hudrlik, J. Am. Chem. Soc., 90, 4464 (1968).
5) This band itself does not preclude the enolate structure, e.g., 3: Cf. M. Pereyre and J. Valade, Bull. Soc. Chim. Fr., 1967, 1928; ref 2.
6) The underlying logic in the NMR analysis is the presumed correlation between the electron availability and the chemical shift of the olefinic proton of the enolate (ref 2 and 4). Thus, the olefinic proton of a trichlorostannyl enolate should resonate in much lower field than that of the corresponding tributylstannyl enolate, which appears between $\delta$ 4 (ref 5) and $\delta$ 5 (ref 1).
7) $^{13}C$ NMR of the material under discussion showed one major carbonyl carbon but no olefinic one. The assignment will be deferred, however, till purer material becomes available.
8) Details will be reported later.
9) The conformational A value of a mercury atom is almost zero: J. A. Hirsch, Topics in Stereochemistry, 1, 199 (1967).
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