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# BONDING ISOMERS OF TRIORGANOSTANNYL ENOLATES ANALYZED BY $^{119}$Sn NMR SPECTROSCOPY

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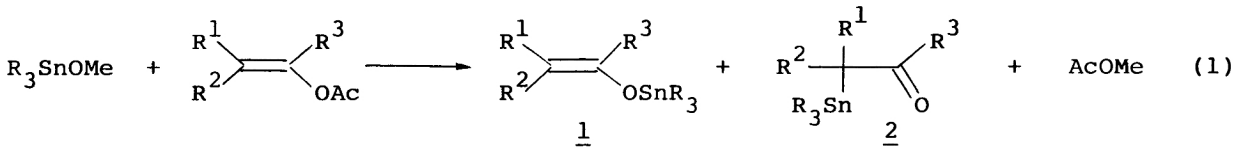
The bonding isomers of triorganostannyl enolates were analyzed by $^{119}$Sn NMR spectroscopy. In some cases the existence of an equilibrium between the O-stannyl enolate and C-stannyl derivative was confirmed by variable temperature $^{119}$Sn NMR spectra.

Application of triorganostannyl enolates to organic synthesis, such as diastereoselective cross aldol condensation, has been the subject widely developed.[1,2] The diastereoselectivity greatly depends on both reaction temperature and the type of triorganostannyl group. At -78 °C, tributylstannyl enolates showed threo selectivity,[2] whereas triphenylstannyl enolates gave erythro products.[1] On the contrary, at higher temperatures tributylstannyl enolates gave predominantly erythro adducts.[2]

Tributylstannyl enolates were reported to consist of O-stannyl enolates (1) and/or the corresponding C-stannyl derivatives (2).[3] However, the structures of trimethylstannyl and triphenylstannyl enolates have never been elucidated. In this communication, we wish to report the results on the bonding isomers of triorganostannyl enolates studied by $^{119}$Sn NMR spectroscopy, which may give further insight on the above-mentioned stereoselectivity.[4]

Triorganostannyl enolates were prepared by the reaction of alkenyl acetates with triorganotin methoxides,[3] and the reaction progress was followed by $^{119}$Sn NMR spectroscopy at room temperature in $CDCl_3$ (Eq. 1). The ratios of the O-stannyl enolates (1) to C-stannyl derivatives (2) were constant throughout the reaction course. Table 1 shows both the chemical shifts of some stannyl enolates and the ratio of 1 to 2 determined from integrated intensities in the $^{119}$Sn spectra. The O-stannyl isomers (1) of tributyl- and trimethylstannyl enolates are clearly differentiated from the C-stannyl isomers (2) by large separations of the chemical shifts (Table 1). The $^{119}$Sn NMR absorptions of 1 were observed at +100 — +130 ppm close to those of trialkyltin alkoxides,[5] while those of 2 were found at much higher fields near by those of tetraalkyltins.[5]



R = n-Bu, Me, Ph

a; $R^1 = R^2 = H$, $R^3 = Me$
b; $R^1 = R^2 = H$, $R^3 = Ph$
c; $R^1, R^3 = -(CH_2)_4-$, $R^2 = H$
d; $R^1, R^3 = -(CH_2)_3-$, $R^2 = H$
e; $R^1, R^2 = Me, H$, $R^3 = Et$
f; $R^1, R^2 = Me, H$, $R^3 = Ph$

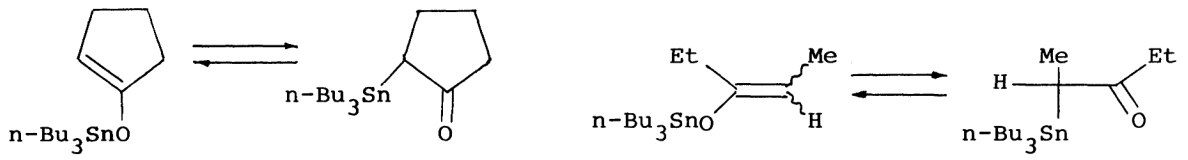
Table 1. $^{119}Sn$ chemical shifts of O-stannyl enolates (1) and C-stannyl derivatives (2), and the ratio of 1 to 2 at room temperature[a)]

| Entry | R = n-Bu | | R = Me | | R = Ph | |
|---|---|---|---|---|---|---|
| | 1(E, Z) | 2 | 1 | 2 | 1 | 2 |
| a | -- | -1.2 | -- | +16.1 | -- | -118.1 |
| | (0 : 100) | | (0 : 100) | | (0 : 100) | |
| | (0 : 100)[b)] | | | | | |
| b | +109.1 | +3.4 | -- | +20.5 | -- | -115.6 |
| | (20 : 80) | | (0 : 100) | | (0 : 100) | |
| | (22 : 78)[b)] | | | | | |
| c | +98.0 | -- | +125.2[d)] | -- | -103.1 | -- |
| | (100 : 0) | | (100 : 0) | | (100 : 0) | |
| | (100 : 0)[b)] | | | | | |
| d | +107.3 | +7.4 | -- | +28.5 | -- | -114.4 |
| | (57 : 43) | | (0 : 100) | | (0 : 100) | |
| | (57 : 43)[b)] | | | | | |
| e | +101.1, +96.0 | +7.5 | +135.4[d)] | +31.4 | -- | -114.1 |
| | (63 : 9 : 28) | | (43 : 57) | | (0 : 100) | |
| | (53 : 17 : 30)[b)] | | | | | |
| f | +114.7[d)] | -- | +140.0[d,e)] | -- | -111.8[e)] | -- |
| | (100 : 0) | | (100 : 0) | | (100 : 0) | |
| | (10 : 90)[c)] | | | | | |

a) $^{119}Sn$ NMR spectra were measured in the pulse Fourier transform mode using a JEOL-FX-90Q (33.37 MHz) spectrometer. The chemical shifts were determined relative to external $Me_4Sn$. b) Ref. 3, ratio determined by $^1H$ NMR. c) Ref. 2, ratio determined by $^1H$ NMR. d) Very broad peak. e) Ref. 6.

In the cases of triphenylstannyl enolates, however, the difference between the $^{119}Sn$ chemical shifts of 1 and 2 was very small. Therefore, the assignment of 1 and 2 to each isomer (R = Ph) was based on $^{1}H$ NMR spectra. Triphenylstannyl enolates (R = Ph, 1c and 1f) exhibited the alkenyl protons ($R^1$ or $R^2$ = H in 1) at 4.73 (t, J = 3 Hz) and 5.03 (q, J = 7 Hz), respectively. Other C-triphenylstannyl derivatives (R = Ph; 2a, 2b, 2d, and 2e) showed the α-methyne or α-methylene protons at 2.93 (s, $J_{Sn-CH_2}$ = 68.0 Hz), 3.43 (s, $J_{Sn-CH_2}$ = 65.7 Hz), 3.15 (t, J = 5 Hz), and 3.37 (q, J = 6 Hz), respectively. Entry a showed the presence of only C-stannyl derivative (2), while Entries c and f gave only O-stannyl enolate (1) in all cases (R = n-Bu, Me, Ph). However, the other enolates (Entries b, d, and e) exhibited different ratios of 1 to 2 according to the triorganostannyl groups. The ratio of 1e to 2e of tributylstannyl enolate larger than that of trimethylstannyl one is consistent with the generalization that sterically hindered enolate favors the O-stannyl form (1).[3] However, the reason for the selective formation of the C-triphenylstannyl derivative (R = Ph; 2e) is not clear.

The $^{119}Sn$ NMR spectra of the enolates were measured at -50 °C. In the cases of the enolates which consisted of a single bonding isomer at room temperature (O-stannyl enolates: c, f; R = n-Bu, Ph; or C-stannyl isomers: d, e; R = Ph), no isomerization was detected at -50 °C. On the contrary, when the spectra of tributylstannyl enolates consisted of the mixture of 1 and 2 were measured at lower temperatures (0, -25, -50 °C), the ratios of 1 and 2 decreased (Table 2). The alteration of the ratios induced by temperature change was confirmed to be reversible. This is an unequivocal evidence for the existence of the equilibrium between the O-stannyl enolate (1) and C-stannyl derivative (2). To the best of our knowledge, there has been no report concerning a proof of this equilibration (Scheme 1).




1d 2d 1e 2e

Scheme 1.

This $^{119}Sn$ NMR spectroscopic analysis has revealed its usefulness in discriminating the C-Sn from O-Sn bonding isomers of triorganostannyl enolates. Further studies are in progress on the elucidation of the reaction mechanism, especially of the different stereoselective behavior of triphenylstannyl enolates.

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Table 2. The ratio of 1 to 2 (d, e, R = n-Bu) at low temperatures

| Entry | Temperature | $^{119}$Sn Chemical Shift | | Ratio | |
|---|---|---|---|---|---|
| | °C | 1 | 2 | 1 | 2 |
| d (R = n-Bu) | 25 | +107.3 | +7.4 | 57 | 43 |
| | 0 | +109.1 | +8.6 | 46 | 54 |
| | -25 | +110.7 | +9.3 | 41 | 59 |
| | -50 | +112.7 | +11.3 | 21 | 79 |
| e (R = n-Bu)[a] | 25 | +101.6 | +7.6 | 72 | 28 |
| | 0 | +103.1 | +8.5 | 65 | 35 |
| | -25 | +104.3 | ---[b] | 39 | (61)[c] |
| | -50 | ----[d] | +10.7 | (22)[e] | 78 |

a) This sample was prepared by heating a solution of 3-pentenyl acetate (1 mmol) and n-$Bu_3$SnOMe (0.4 mmol) in 0.5 ml of $CDCl_3$ at 70 °C for 2 h. It includes 60% of e and 40% of a by-product n-$Bu_3$SnOAc. n-$Bu_3$SnOAc (+103.8 ppm at 25 °C) was used as a standard for calculation of the ratio of 1e to 2e. No absorption assigned to (Z)-1e[3] (+96.0, Table 1) was detected in this sample. b) Not detected. c) Estimated by comparing the integrated intensity of 1e signal with that of n-$Bu_3$SnOAc and assuming the rest of tin component was hidden in noise. d) Not detected, but might be hidden in noise. e) Estimated from the integrated intensities of n-$Bu_3$SnOAc (+110.5 ppm at -50 °C) and 2e signals.

## References


1) Y. Yamamoto, H. Yatagai, and K. Maruyama, J. Chem. Soc., Chem. Commun., 1981, 162.
2) S. Shenvi and J. K. Stille, Tetrahedron Lett., 23, 627 (1982).
3) M. Pereyre, B. Bellegrade, J. Mendelsohn, and J. Valade, J. Organometal. Chem., 11, 97 (1968).
4) K. Kobayashi, M. Kawanisi, T. Hitomi, and S. Kozima, Chem. Lett., 1983, 851.
5) n-$Bu_3$SnOMe; +109 — +111 ppm, $Me_3$SnOMe; +120 — +135 ppm, $Bu_4$Sn; -6 — -8 ppm, $Me_4$Sn; 0.0 ppm in $CDCl_3$.
6) It was confirmed by $^{119}$Sn and $^1$H NMR spectroscopy that these enolates consist of a single isomer of the O-stannyl form. However, the configurational assignment, E or Z, has not been made explicitly.


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