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Regio- and Stereoselective Trapping of Pentadienyl Anion by a Tin Electrophile

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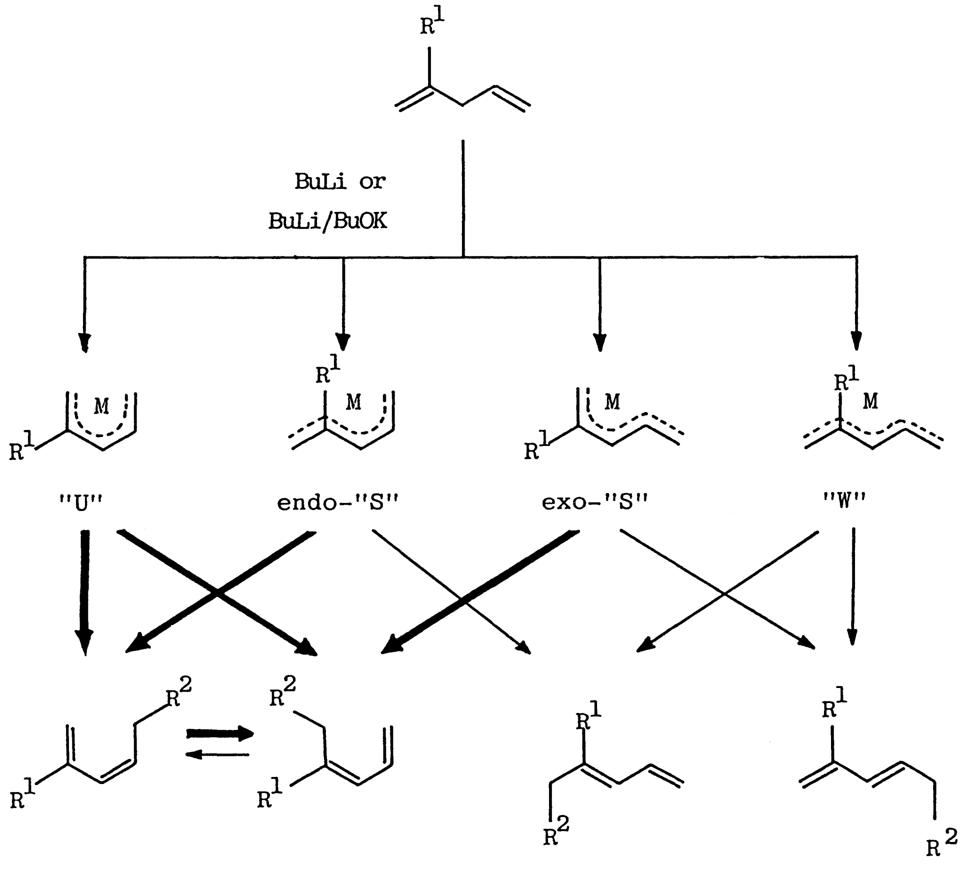
Electrophilic trapping of the pentadienyl anions bearing a methoxymethyl group with Me_3SnBr gives *Z*-pentadienylstannanes in high regioselectivity regardless of the structure of the anion.

Pentadienyl anion with an alkali metal counter cation has been well characterized by means of their trapping with electrophiles.[1,2] Generally the isomeric distribution of the resultant products corresponds to the distribution of the geometrical isomers of the intermediate anions, *i.e.*, "U", *endo*-"S", *exo*-"S", and "W" species.[2c] Since the lithium complex favors "S" or "W" form, its reaction with electrophiles has been reported to give preferentially the corresponding *E*-isomer (Scheme 1). On the other hand, the potassium complex affords the *Z*-isomer in high selectivity. This route via the pentadienyl anion is useful for the regio- and stereoselective synthesis of the corresponding main group metal derivatives, e.g. B,[2c] Si,[2d] Sn.[3] We examined electrophilic trapping of unsymmetrically substituted pentadienyl metals with Me_3SnBr and found highly regio- and stereoselective formation of *Z*-pentadienylstannanes when the dienyl anion possesses an oxygen functionality, regardless of the structure of the intermediate dienyl metals (Table 1). When the pentadienyl lithium bearing a nonpolar group (R^1=Pr) was quenched with Me_3SiCl, isomeric distribution of the four isomers[4] obtained (entry 2) was almost similar to that of the reported system (entry 1), regardless of the nature of the applied electrophile. Even in the electrophilic quenching with Me_3SiCl, introduction of a polar group (R^1=$MeOCH_2$)[5] to the dienyl moiety affected little perturbation on the isomeric distribution of the product (entry 4). Reaction of Me_3SnBr, however, with the same anion showed the formation of *Z*-**2d**[4] in



Z-3 Z-2 E-2 E-3

a, R^1 = n-Pr, R^2 = Me_3Si c, R^1 = $MeOCH_2$, R^2 = Me_3Si

b, R^1 = n-Pr, R^2 = Me_3Sn d, R^1 = $MeOCH_2$, R^2 = Me_3Sn

Scheme 1.

high selectivity (85%) and great decrease of E- and Z-3d.4) On the other hand, since pentadienyl potassium favors "U" shape, the resultant products predominantly consists of Z-2 and Z-3. As far as $FB(OMe)_2$2c) or Me_3SiCl were applied as electrophiles, there was no appreciable difference in the distribution of the isomers between methyl and methoxymethyl substitutions on the pentadienyl products (entries 6 and 7). But, quenching with Me_3SnBr showed preferential formation of Z-2d as observed in entries 5 and 8. The tin electrophile incidentally showed the same results regardless of the structure of the intermediate pentadienyl anion. These high selectivity can be explained by two possible ways. First, in the Z isomers, Z-2d and Z-3d, thermally-allowed [1,5] sigmatropic rearrangement is possible,3) but not in the E isomers. The rearrangement from Z-3d to Z-2d could be facilitated by means of intramolecular co-ordination of the ethereal oxygen to the tin atom.7)

Table 1. Isomeric Distribution of 2,4-Pentadienylmetals a)

Entry	M	R^1	R^2	Product ratio c)				**2** : **3**	Isolated Yield/ %
				Z-**3**	Z-**2**	E-**2**	E-**3**		
1b)	Li	Me	$(MeO)_2B$	13	16	23	48	39 : 62	77
2	Li	n-Pr	Me_3Si	19	18	8	55	26 : 74	70
3	Li	n-Pr	Me_3Sn	0	56	14	30	70 : 30	90
4	Li	$MeOCH_2$	Me_3Si	28	38	3	31	41 : 59	73
5	Li	$MeOCH_2$	Me_3Sn	0	85	8	7	93 : 7	70
6b)	K	Me	$(MeO)_2B$	63	34	3		34 63	65
7	K	$MeOCH_2$	Me_3Si	87	10	trace	3	10 : 90	43
8	K	$MeOCH_2$	Me_3Sn	0	88	4	8	92 : 8	53

a) Quenching of the pentadienyl lithium (or potassium) with metal halides (R^2X) was done at -78 °C. b) Taken from Ref. 2c. c) Determined by ^1H NMR.

Actually, Z-**2d** selectivity in entry 8 was close to the combined proportion of Z-**2c** and Z-**3c** in entry 7. Second, the selectivity in the lithium complex can be explained by the preferential attack at the vicinal carbon in exo-"S" due to the efficient co-ordination of the ethereal oxygen to the tin atom. Even in the reaction with Me_3SiCl the appreciable decrease of E-**2c** may be due to the less probable occurrence of the "W" form. At the present stage, the presence of the endo-"S" form in the lithium complex with an ether group is unclear, while low yields of E-**2c** and E-**2d**, both of which can form more easily than the corresponding Z-**3** by the intramolecular coordination of the oxygen atom to the tin atom, indicate the minor contribution of the endo-"S" form to the equilibrium.

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4) All isomers obtained were characterized by ^{1}H NMR. **2c** and **2d** have sufficient stability in chromatographic separation on silica gel. 400 MHz ^{1}H NMR data for selected products, δ($CDCl_3$): *Z*-**2d**, 0.10 (9H, J_{Sn-H}= 53 Hz, Me_3Sn), 1.91 (2H, J_{Sn-H}=58 Hz, CH_2), 3.28 (s, 3H, Me), 3.77 (2H, J_{Sn-H}= 11 Hz, CH_2O), 4.99 (dd, 1H, J= 2.0 and 10.2 Hz, terminal transoid H), 5.11 (dd, 1H, J= 2.0 and 16.4 Hz, terminal cisoid H), 5.83 (d, 1H, J= 10.5 Hz, olefinic H of the trisubstituted double bond), 6.47 (ddd, 1H, J= 10.2, 10.5, and 16.4 Hz, internal H of terminal olefin); *E*-**2d**, 0.10 (9H, J_{Sn-H}= 53 Hz, Me_3Sn), 1.87 (2H, J_{Sn-H}= 68 Hz, CH_2Sn), 3.28 (s, 3H, MeO), 3.97 (2H, J_{Sn-H}= 10 Hz, CH_2O), 4.89 (dd, 1H, J= 2.0 and 9.8 Hz, terminal transoid H), 5.02 (dd, 1H, J= 2.0 and 16.4 Hz, terminal cisoid H), 5.84 (d, 1H, J= 10.5 Hz, olefinic H of the trisubstituted double bond), 6.58 (ddd, 1H, J= 9.8, 10.5, and 16.4 Hz, internal H of the terminal olefin); *E*-**3d**, 0.08 (9H, J_{Sn-H}= 50 Hz, Me_3Sn), 1.81 (2H, J_{Sn-H}= 68 Hz, CH_2Sn), 3.31 (s, 3H, MeO), 4.94 (s, 2H, CH_2O), 4.92 and 4.93 (each s, 2H, $H_2C{=}C$), 5.88 (d, J= 15.7 Hz, $=C{-}C\underline{H}{=}C$), 5.98 (dt, J= 8.2 and 15.7 Hz, $=C\underline{H}CH_2$).

5) 2-Methoxymethylpentadienyl lithium (or potassium) was prepared as follows. Methylation (MeI, KOH, DMF, -20 °C) of 2-hydroxymethyl-1,4-pentadien$^{5)}$ gave the corresponding methyl ether in a 82% yield. Metallation of the obtained diene was performed in THF with *n*-BuLi for lithiation or with *t*-BuOK/*n*-BuLi for the preparation of the potassiun complex.$^{2c)}$

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7) Since only *Z*-**2b** among two possible *Z* isomers was observed in the alkyl substituted dienylstannane (entry 3), steric and/or electronic stabilization as well as the coordinative one would be responsible for the selection of *Z*-**2** isomer.

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