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Control of γ vs. ε Regioselectivity on the Nucleophilic Addition of 2,4-Pentadienylstannane to Aldehydes by Lewis Acid Co-ordination

Yoshinori NARUTA,* Yutaka NISHIGAICHI, and Kazuhiro MARUYAMA*

Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606

The BF_3-mediated nucleophilic addition of 2- and 4-methoxymethyl-2,4-pentadienylstannanes to aldehydes selectively gives the corresponding γ adducts, while the reaction with sterically hindered aldehydes affors the corresponding ε adducts regardless of the tin reagents applied.

Recently we reported the selective pentadienyl transfer to carbonyl compounds from 2,4-pentadienylstannanes,[1] which are known to be fluxional molecules.[2] These stannyl reagents, in contrast with the corresponding silyl derivatives, showed marked reactivity toward versatile carbonyl compounds, including quinones and α,β-unsaturated carbonyl compounds. Generally, the pentadienyl transfer from the stannyl reagents occurs exclusively at the ε position of the pentadienyl moiety, though the selective γ addition has never been reported (Eq. 1).[3,4] These

(1)

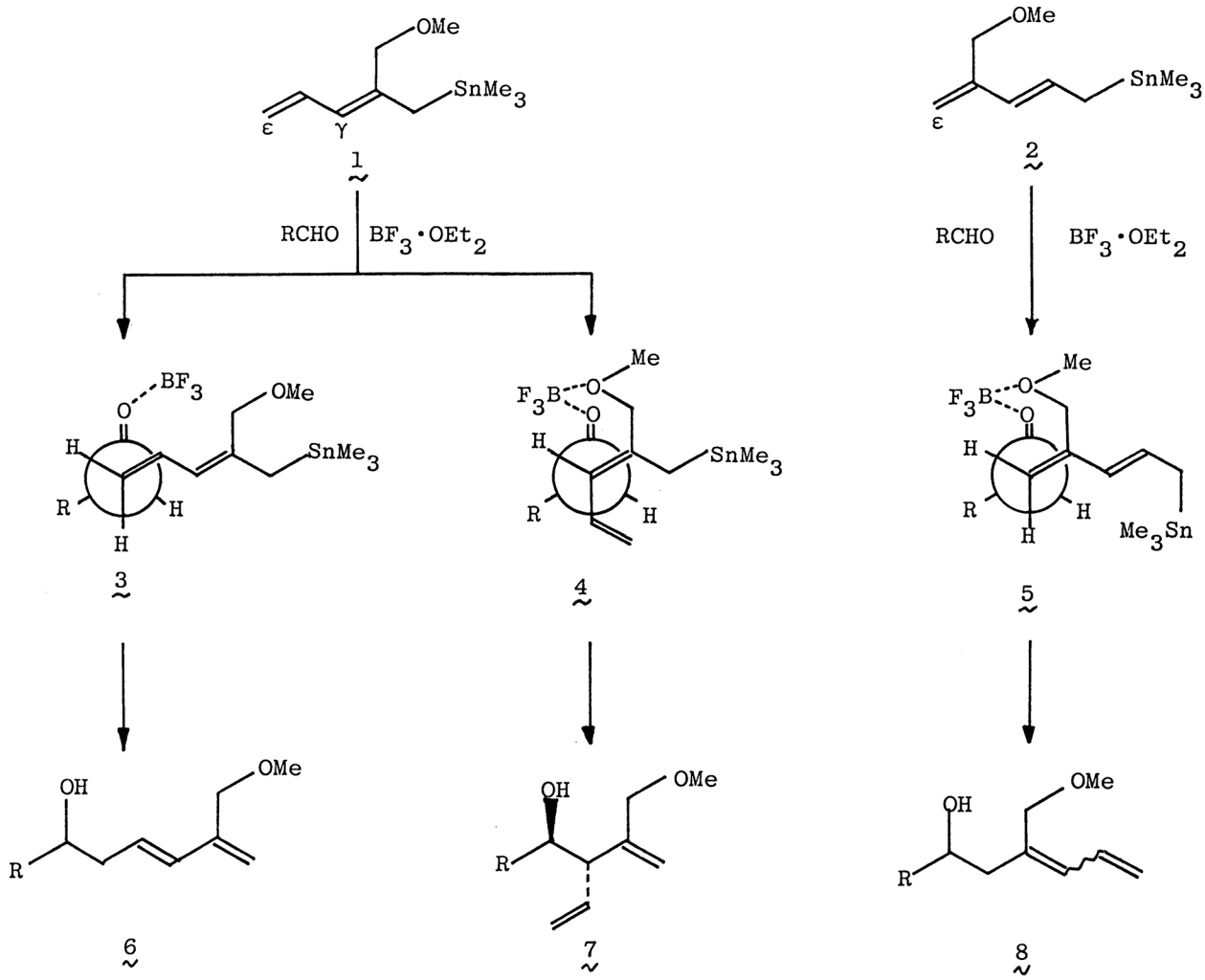
regioselectivity can be well elucidated by means of frontier molecular orbital theory and the steric effect.[5] In the preceding paper,[7] we reported the highly regioselective preparation of 2,4-pentadienylstannane with an ethereal functionality. We reported herein (1) control of the γ/ε regioselectivity in the pentadienyl transfer reaction to aldehydes by coordiantion of Lewis acid to the ethereal functionality on the pentadienylstannane and (2) remarkable steric effect of the aldehydes on this regioselectivity.

Table 1[a)]

Run	RCHO/ R	Tin reagent[b)]	Product ratio[c)] 6	7	8
1	Ph	1	7	93[d)]	trace
2	p-MeC_6H_4	1	7	89[d)]	4
3	p-ClC_6H_4	1	4	88[d)]	8
4	p-$O_2NC_6H_4$	1	2	89[d)]	7
5	(E)-MeCH=CH	1	trace	93[d)]	7
6	n-C_6H_{13}	1	22	71[d)]	7
7	o-ClC_6H_4	1	84[e)]	13	3
8	2,6-$Cl_2C_6H_3$	1	94[e)]	0	6
9	o-$O_2NC_6H_4$	1	74[e)]	16	10
10	Ph	2	0	0	100[f)]
11	2,6-$Cl_2C_6H_3$	2	0	0	100[f)]
12	(E)-MeCH=CH	2	0	0	100[f)]

a) All reactions gave the corresponding adducts in more than 90% total yields. b) stereoisomeric purity; 1, Z : E = 95 : 5; 2, Z : E = 0 : 100. c) Determined by ^1H NMR of the crude product. d) anti : syn > 100 : 1. e) trans : cis = 99 : 1. f) E : Z ≃ 1 : 1.

When the reaction of (E)-2-methoxymethylpentadienylstannane 1[8)] with PhCHO was conducted in the presence of $BF_3 \cdot OEt_2$ in CH_2Cl_2 at -78 °C, the corresponding γ adduct 7 was formed in 93% selectivity (Table 1). This is the first demonstration of the γ addition reaction in the nucleophilic reaction of 2,4-pentadienylstannane. Other aldehydes also gave the corresponding γ adducts in good yields and in high selectivity (runs 2 - 6). On the other hand, the reaction of the same stannane 1 with sterically hindered aldehydes afforded the corresponding ε adduct 6 in excellent selectivities (runs 7 - 9), which rose to 94% in the reaction with 2,6-dichlorobenzaldehyde. This marked contrast can be elucidated in terms of both Lewis acid co-ordination and steric effect (Scheme 1). In the reaction with less sterically hindered aldehydes, Lewis acid would co-ordinate both to the formyl oxygen atom and to the ethereal oxygen. This co-ordination can accelerate the nucleophilic attack on aldehydes at the nearby γ carbon atom of the pentadienyl moiety via transition state 4. However, this γ selectivity is very sensitive to the



Scheme 1.

structure of the substrates. Increased steric hindrance around the substrate aldehyde becomes unfavorable to the γ attack, which requires more crowded transition state than the ε one, swiching the selectivity from the γ attack to the ε one (Table 1, runs 7-9).

It is worth mentioning of the stereoselectivity of the γ adducts 7, which in runs 1-6 were assigned to possess anti configuration in extremely high ratio.[9] This selectivity makes a marked contrast to the syn addition, which was observed in the reaction of 2-butenyl-[11] and 2,4-hexadienylstannane[1b] with aldehydes. The above results support the presence of the bidentatively co-ordinated transition state 4, thus the ethereal oxygen atom on the stannyl reagent plays a key role in a reversal of the stereoselectivity. The isomeric stannane, 4-methoxymethyl-2,4-pentadienylstannane 2,[8] gave the corresponding ε adduct in 100% selectivity,

regardless of the structure of aldehydes. In this case, the ethereal oxygen can easily co-ordinate to BF_3 and the steric factor at the transition state also favors the formation of the ε adduct.

References

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2) M.J.Halis, B.E.Mann, and C.M.Spencer, J. Chem. Soc., Dalton Trans., 1983, 729.

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4) The BF_3-mediated reaction of 2,4-hexadienyltrimethylstannane with aldehydes exclusively gave the corresponding ε adducts,[1a] although the tributylstannyl derivative afforded the corresponding γ and ε adducts in a 1:1 ratio.[12]

5) The ε carbon atom of 2,4-pentadienylstannane possesses a larger HOMO coefficient than the γ one.[6] At the stage of the pentadienyl transfer from the stannyl reagent to aldehydes, less steric hindrances are expected at the ε position of 1 than at the γ one.

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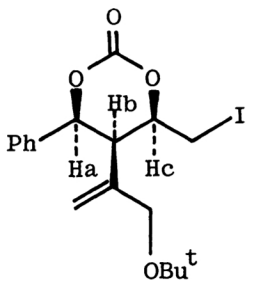
8) The stannyl compounds, 1 and 2, were used after purification with silica gel-chromatography as described in the preceding paper.[4] Isomeric purities of 1 and 2 were determined to be >95% Z- and 100% E-, respectively.

9) The stereochemistry of the γ adduct 7 (R = Ph) was confirmed by the iodolactonization according to the literature method[10] (BuLi, Et_2O, -78 °C to r.t.; BOC-ON, THF, r.t.; I_2, CH_3CN, -20 °C). The product 9 was assigned to be 4,5-syn and 5,6-syn: 9 (R = Ph) ^1H NMR ($CDCl_3$): δ 1.43 (s, 9 H), 2.99 (dd, J=10.4, 6.1 Hz, 1H), 3.02 (m, 1H, H_b), 3.19 (dd, J=10.4, 4.6 Hz, 1H), 4.09 (dt, J=6.1, 4.9 Hz, H_c) 4.33 (ddt, J=12.8, 2.1, 1.8 Hz, 1H), 4.40 (dt, J=12.8, 1.8 Hz, 1H), 4.53 (q, J=2.1 Hz, 1H), 4.94 (q, J=2.1 Hz, 1H), 5.64 (d, J=7.6 Hz, H_a), 7.35 (m, 5H).



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The stereochemistry of the other γ products obtained in runs 2-6 was assigned to have anti configuration in comparison with the ^1H NMR data (J_{H1-H2}=6.1 Hz) of 7 (R = Ph). Coupling constants J_{H1-H2} of the other γ products were in the range from 4.6 to 6.4 Hz.

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