

DIASTEREOSELECTIVE REACTION OF CROTYLSILANES WITH ACETALS.  
 IMPORTANCE OF THE ELECTRONIC EFFECT IN ACYCLIC STEREOSELECTION<sup>1)</sup>

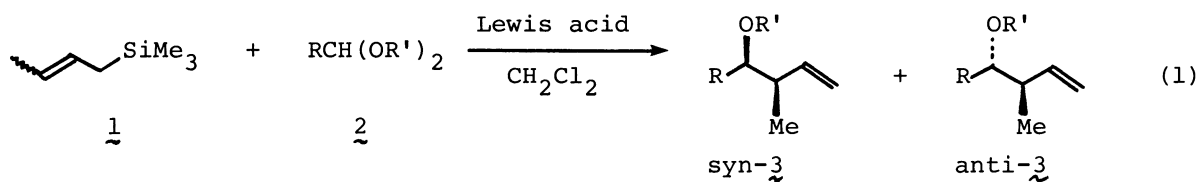
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Acyclic stereoselection of aromatic acetals in the reaction with crotylsilanes depends upon the geometry of crotylsilanes. It was also disclosed for the first time that the electronic effect plays an important role on controlling the diastereochemistry.

Control of acyclic stereoselection is one of the most important targets in synthetic organic chemistry and, therefore, much attention has been focused on the highly diastereoselective reaction of crotyl organometallics with aldehydes.<sup>2,3)</sup> We report herein that the diastereoselectivity in the reaction of crotylsilanes (1) with aromatic acetals<sup>4)</sup> is cleanly controlled by the geometry of the starting 1 and, in addition, by the substituent on the aromatic nucleus, contrary to the remarkable syn selectivity reported for the reaction of 1 with aliphatic acetals irrespective of the starting geometry. To our knowledge, this is the unprecedented example showing that the electronic effect, rather than the steric effect, plays an important role on diastereofacial control.

At first the stereochemistry in reactions of Z- and E-1 with a variety of acetals (2) was examined and the results are listed in Table 1.<sup>5)</sup>



Reactions of crotylsilanes (1) with aliphatic acetals such as pivalaldehyde dimethylacetal (2a) and isovaleraldehyde dimethylacetal (2b) proceed very smoothly in a regiospecific and highly syn selective mode, irrespective of the geometry of 1. However aromatic acetals such as benzaldehyde dimethylacetal (2c) react with Z-1 with high anti preference, although the syn selectivity was observed with E-1.  $\alpha$ -Chloro ether (2e) also affords similar results.<sup>4b)</sup> The stereoselectivity does not depend on the nature of Lewis acids or activators among examined such as titanium chloride, boron trifluoride etherate, iodotrimethylsilane, and trimethylsilyl trifluoromethanesulfonate.

Interestingly, the stereoselectivity can be dramatically controlled by the

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Table 1. Reactions of Z- and E-1 with Acetals (2) in  $\text{CH}_2\text{Cl}_2$ <sup>a)</sup>

Entry	Acetal (2)	Activator	$Z-1$ <sup>b)</sup>		$E-1$ <sup>c)</sup>	
			Yield/% <sup>d)</sup>	(syn/anti) <sup>e)</sup>	Yield/% <sup>d)</sup>	(syn/anti) <sup>e)</sup>
1	t-BuCH(OMe) <sub>2</sub>	TiCl <sub>4</sub>	83	(93/7)	63	(96/4)
2	(2a)	10 mol% Me <sub>3</sub> SiI	71	(92/8)		
3		1 mol% Me <sub>3</sub> SiOTf	70	(92/8)	66	(97/3)
4	Me <sub>2</sub> CHCH <sub>2</sub> CH(OMe) <sub>2</sub> (2b)	TiCl <sub>4</sub>	99	(91/9)	90	(91/9)
5	PhCH(OMe) <sub>2</sub>	BF <sub>3</sub> ·OEt <sub>2</sub>	78	(28/72)	94	(75/25)
6	(2c)	10 mol% Me <sub>3</sub> SiI	82	(28/72)	99	(69/31)
7		1 mol% Me <sub>3</sub> SiOTf	76	(20/80)	66	(79/21)
8	PhCH(OEt) <sub>2</sub> (2d)	BF <sub>3</sub> ·OEt <sub>2</sub>	82	(31/69)	75	(71/29)
9	PhCHCl(OMe) (2e)	1 mol% Me <sub>3</sub> SiOTf	80	(29/71)	53	(84/16)

a) At -78-0 °C for 3-6 h under the standard conditions.<sup>4a)</sup> b) Z/E=89/11. c) Z/E=6/94. d) Yield after isolation by TLC. e) Determined by NMR.

Table 2. Reactions of Z- and E-1 with Aromatic Acetals (2)<sup>a)</sup>

Entry	Acetal (2)	$Z-1$ <sup>b)</sup>		$E-1$ <sup>c)</sup>	
		Yield/% <sup>d)</sup>	(syn/anti) <sup>e)</sup>	Yield/% <sup>d)</sup>	(syn/anti) <sup>e)</sup>
1	p-MeO-C <sub>6</sub> H <sub>4</sub> -CH(OMe) <sub>2</sub>	66	(46/54)	56	(45/55)
2	p-Me-C <sub>6</sub> H <sub>4</sub> -CH(OMe) <sub>2</sub>	87	(32/68)	77	(65/35)
3	C <sub>6</sub> H <sub>5</sub> -CH(OMe) <sub>2</sub>	78	(28/72)	94	(75/25)
4	p-NC-C <sub>6</sub> H <sub>4</sub> -CH(OMe) <sub>2</sub>	92	(20/80)	84	(80/20)

a) All the reactions were conducted by the promotion of BF<sub>3</sub>·OEt<sub>2</sub> in  $\text{CH}_2\text{Cl}_2$ .<sup>4a)</sup> b) Z/E=89/11. c) Z/E=6/96. d) Yield after isolation by TLC. e) Determined by NMR.

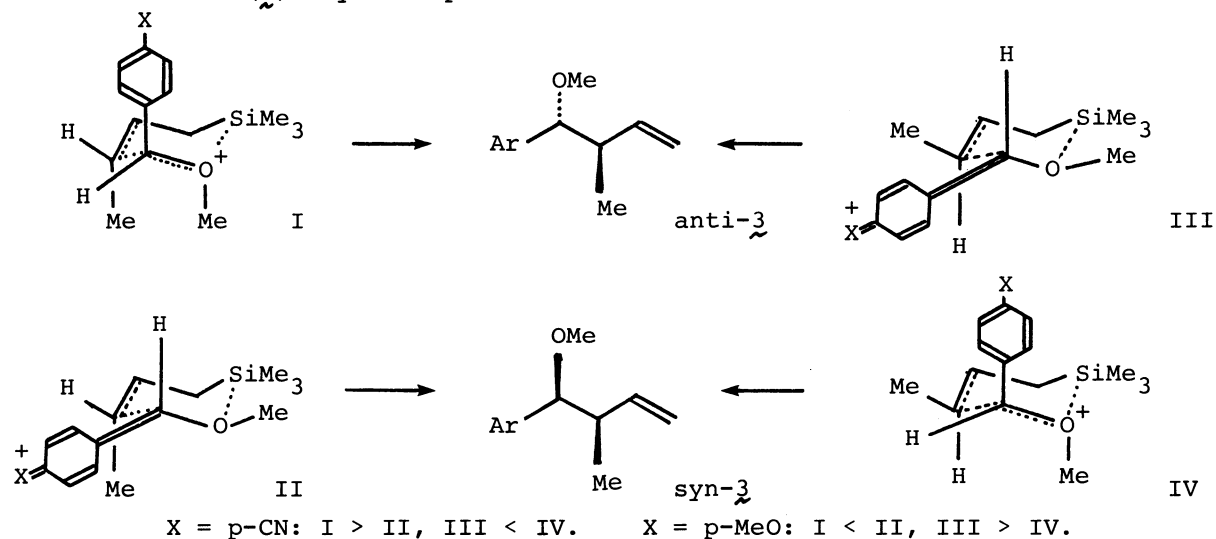
substituent on the ring of aromatic acetals, the results being listed in Table 2.

Increasing anti selectivity is observed in the case of  $Z-1$  with increasing electron-withdrawal due to the substituent in the order of p-CN>H>p-Me>p-MeO. On the other hand, with  $E-1$ , syn selectivity increases with electron-withdrawing substituents. It is worth to note that the Hammett plot between logarithms of the diastereomer ratio,  $[\ln(\text{syn/anti})_{\text{corr}}]$ ,<sup>6)</sup> with Brown-Okamoto's  $\sigma^+$  revealed good linear correlations ( $\rho=-1.25$ ,  $r=0.996$  for  $Z-1$  and  $\rho=1.26$ ,  $r=0.988$  for  $E-1$ ). Appar-

ently diastereoselectivity is controlled by the electronic effect.

The observed selectivity is inconsistent with an acyclic-transition-state mechanism proposed for the reactions of 1 with aldehydes.<sup>2,3a)</sup> A simple six-membered cyclic transition state with the most stable conformation in the chair form,<sup>2,3,7)</sup> also cannot reasonably explain the results of the present reaction.

The origin of this unprecedented stereochemistry in the aromatic acetals is not completely clear at this stage, but the mechanism of the reaction of 1 with aromatic acetals (2) may be explained as follows.



Scheme 1. Mechanism of diastereoselection in the allylation.

In marked contrast to aliphatic acetals, aromatic acetals can be activated by an acid to undergo the C-O bond cleavage, resulting in the intermediary formation of benzylic cationic species. If the six-membered cyclic transition states (I and IV) are involved as shown in Scheme 1,<sup>8)</sup> an electron-withdrawing p-cyano group on the aromatic ring produces a partial double bond between the benzylic carbon and the ether oxygen due to the donation of electrons from the oxygen. Then aryl and methyl groups should occupy the anti position each other.<sup>10)</sup> Therefore, anti and syn isomers are dominantly produced from Z-1 and E-1, respectively. However such a double bond nature between benzylic carbon and alkoxy oxygen atoms may disappear or decrease the extent by the introduction of electron-donating p-methoxy group, resulting in the formation of the transition states (II and III) predominantly. Thus E-1 increases the anti selectivity and the reverse selectivity is induced in Z-1. This might be the reason why reversal of the diastereoselectivity from reactions of the crotyl metallics (B, Al, Mg, Zn, Li, Ti, Zr etc) with aldehydes is induced, where the six-membered cyclic transition state is similarly involved.<sup>2)</sup>

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- 5) All the new compounds obtained in this work gave satisfactory spectral data and elemental analysis.
- 6) Observed syn/anti ratios shown in Table 2 were converted to the corrected values [(syn/anti)<sub>corr</sub>] for pure Z-1 and E-1.
- 7) Usually the syn product is obtained from Z-1 through the six-membered cyclic transition state, although the anti adduct is formed from E-1.
- 8) Since the ether oxygen reveals relatively higher basicity than the carbonyl oxygen,<sup>9)</sup> the cyclic transition state that had not been considered for the reaction with aldehydes might be possible for reactions of aromatic acetals with allylsilanes.
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