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Preliminary communication

CONCERNING REVERSAL OF DIASTEREOSELECTIVITY IN THE BF_3 PROMOTED ADDITION OF CROTYL—ORGANOMETALLIC COMPOUNDS TO ALDEHYDES

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Summary

The addition of a mixture of benzaldehyde and $BF_3 \cdot OEt_2$ to crotyl-organometallic reagents C_4H_7MLn (1) (M = Cu, Cd, Hg, Tl, Ti, Zr and V) produces predominantly the *erythro* homoallyl alcohol as well as the α-adduct, while without $BF_3 \cdot OEt_2$ the *threo* isomer is formed preferentially.

A recent communication by Reetz and Sauerwald [1] on the reversed diastereoselectivity in BF_3-mediated reactions of crotyltitanium reagents with aldehydes has prompted us to report our own findings [2] in this area. When we found that the BF_3-mediated reaction of crotyltrialkyltins with aldehydes proceeds in a stereoconvergent manner to produce *erythro* homoallyl alcohols predominantly and proposed an antiperiplanar transition state [3,4], we anticipated that a similar reaction of other crotyl-organometallic compounds may exhibit selective inversion from *threo* to *erythro* by BF_3 coordination to aldehydes (eq. 1).

We therefore examined the reaction of benzaldehyde with several crotyl-metals in the presence and in the absence of $BF_3 \cdot OEt_2$. The results are summarized in Table 1.

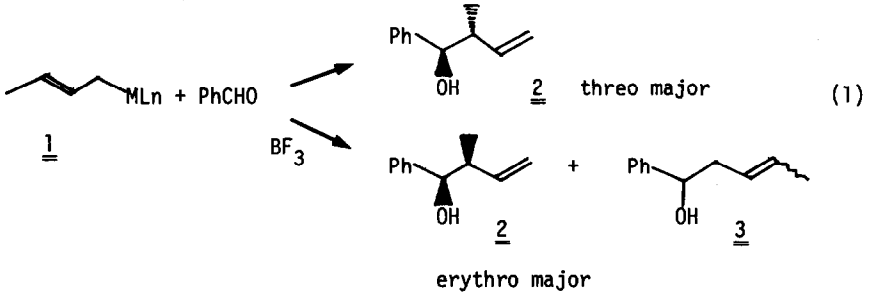

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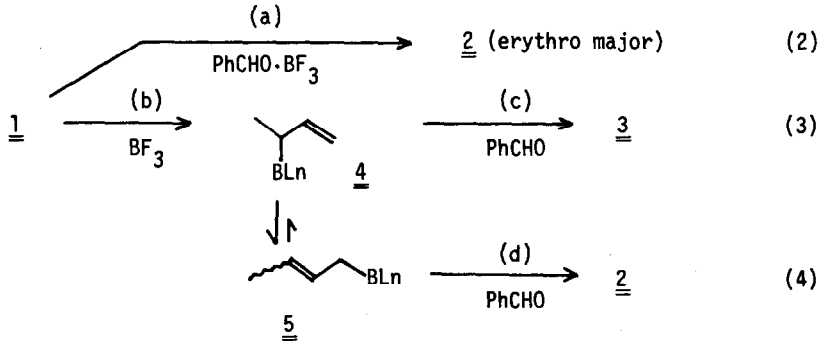
TABLE 1

SELECTIVE INVERSION FROM *threo* TO *erythro* [a]

Entry	1 (MLn)	with BF_3			without BF_3
		γ-adduct (2) *erythro/threo*	ratio γ/α	α-adduct (3) *trans/cis*	*erythro/threo*
1	MgCl	48/52	70/30	60/40	48/52
2	ZnBr	56/44	81/19	65/35	56/44
3		30/70	100/—		30/70
4	Cu [b]	98/2	35/65	57/43	48/52
5	CdI [c]	60/40	57/43	65/35	50/50
6	HgI [c]	70/30	65/35	75/25	34/66
7	TlI [c]	98/2	50/50	65/35	50/50
8	$TiCl_2Cl$	55/45	80/20	60/40	20/80
9	$ZrCp_2Cl$	96/4	34/66	50/50	19/81 [d]
10	VCp_2Cl	70/30	65/35	70/30	43/57

[a] A mixture of PhCHO (1 mmol) and $BF_3 \cdot OEt_2$ (2 mmol) in dry ether (1 ml) was added at −78°C to the crotylmetal reagent (1.1 mmol) in ether (or in ether/THF), except where otherwise indicated, and the reaction was quenched at 0°C. The reagent was prepared in situ by addition of crotylmagnesium chloride (1.1 mmol) to MLn (1.1 mmol) ($ZnBr_2$ in THF, CuI in ether, CdI_2 in ether, HgI_2 in ether, TlI_2 in ether, $TiCp_2Cl_2$ in ether, $ZrCp_2Cl_2$ in THF and VCp_2Cl_2 in ether). The product ratio and yield were determined by GLC and ^1H NMR spectroscopy. The structure determination was made by comparison with authentic samples [3]. Total yields are almost quantitative except for entries 5, 7 and 10, where also small amounts of $PhC(O)CH(CH_3)CH{=}CH_2$ were formed presumably due to the Meerwein–Pondorf oxidation. [b] The reagent was made at −30°C, and $PhCHO \cdot BF_3$ was added at this temperature. [c] The reagent was made at 0°C and PhCHO was added at 0°C. [d] Data from Y. Yamamoto and K. Maruyama, Tetrahedron Lett., 22 (1981) 2895.

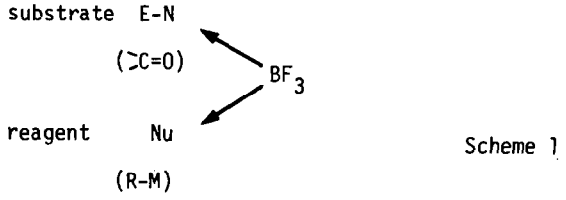
The *erythro/threo* ratio in the reaction of Mg, Zn, and B is not influenced by the presence of BF_3 (entries 1–3). Reversal of the diastereoselectivity is observed in the reactions of Cu, Cd, Hg, Tl, Ti [5], Zr, and V (entries 4–10). Especially, the use of BF_3 in the reactions of Cu, Tl, and Zr causes very predominant formation of the *erythro* isomer. Furthermore, the α-isomer 3 is formed as a by-product, and sometimes as the major product, if BF_3 is used. Without BF_3 the γ-isomer is obtained in an essentially quantitative yield [6]. The inversed regioselectivity may be explained by transmetallation via an S_E2' process (path b) followed by a rapid reaction with benzaldehyde (path c) [7] (eq. 3).



If such a transmetallation process is involved, the γ/α isomer ratio should depend on the addition sequence of BF_3. The addition of 1 equiv. of BF_3 to crotylmagnesium chloride at —78°C followed by the addition of benzaldehyde produced 30% of the γ-adduct (*erythro/threo* = 75/25) and 70% of the α-adduct (*trans/cis* = 64/36) (cf. entry 1). Allylic rearrangement from 4 to 5 followed by the reaction with benzaldehyde (path d) again produces 2 (eq. 4). In fact, when the mixture of 1 equiv. of $BF_3 \cdot OEt_2$ and crotylmagnesium chloride, prepared at —78°C, was allowed to warm up to room temperature and then cooled to —78°C, a similar reaction with benzaldehyde gave exclusively the γ-adduct (*erythro/threo* = 39/61).

We also examined the reaction of isobutyraldehyde (6) to investigate whether in the BF_3 mediated reaction of an aliphatic aldehyde besides the γ-adduct some α-adduct is also formed. The reaction of crotyl-$ZrCp_2Cl$ with 6-BF_3 produced 98% of the γ-adduct (*erythro/threo* = 60/40) [8] along with 1% of the α-adduct (*trans/cis* = 1/1). A similar reaction of crotyl-$SnBu_3$, our original reaction in this series, gave 99% of the γ-adduct (*erythro/threo* = 96/4) along with 0.2% of the α-isomer. Consequently, the γ/α ratio is highly dependent upon the structure of the aldehyde, the metal (M), and the reaction conditions, owing to the complex competitive processes (eqs. 2—4). Until now it is not possible to clarify whether 2 is produced via eq. 2 or eq. 4. However, when the formation of the α-isomer can be neglected, the reversed diastereoselectivity must occur via an antiperiplanar transition state (path a, eq. 2).

In conclusion, reversal of the diastereoselectivity from *threo* to *erythro* is observed for a wide range of crotylmetals with relatively low Lewis acidity. Furthermore, the use of BF_3 often induces reversal of the regioselectivity, which is ascribed to the fact that BF_3 can interact with both nucleophilic sites (Scheme 1). The E—N·BF_3 interaction produces predominantly the γ-*erythro* isomer, and the Nu·BF_3 interaction preferentially the α-isomer. A similar double function of Lewis acids has been observed recently with several reagents and reactions, e.g. RCu·BF_3 [9], $R_2CuLi \cdot BF_3$ [9], RLi·BF_3 [10], allylsilane·$TiCl_4$ [11], and silyl enol ether·$TiCl_4$ [12].



SCHEME 1

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2 Presented orally at the post ICOS-IV Kyoto symposium, August 1982.
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6 This means that 1, prepared in situ from crotylmagnesium chloride and MLn, does not take an α-metallyl geometry but possesses a crotyl structure.
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