and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the diene **4c** (353.7 mg, 83%): ^1H NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9 H), 0.45–2.30 [m, 20 H, includes 0.85 (br d, J = 5.5 Hz, 3 H), 1.34 (s, 3 H), 1.37 (s, 3 H), 2.13 (s, 3 H)], 3.45 (dt, J = 10.1, 2.0 Hz, 1 H), 4.16 (dd, J = 4.8, 2.0 Hz, 2 H), 6.36 (s, 1 H), 7.23 (br s, 5 H).

Acknowledgment. This research was supported by PHS Grant HL49784. NMR spectra were obtained through the auspices of the Northeast Regional NSF/NMR Facility at Yale University which was supported by NSF Chemistry Division Grant CHE 7916210. A Dox Fellowship to Mark Bednarski and a Heyl Fellowship to Clarence Maring are gratefully acknowledged.

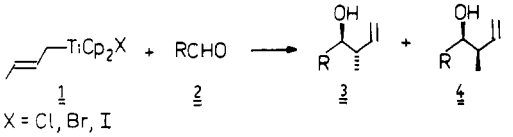
Registry No. **4a**, 88146-66-1; **4b**, 90130-49-7; **4c**, 90084-13-2; **5a**, 4652-27-1; **5b**, 79010-92-7; **5c** (*l*-menthol), 90084-14-3; **5d**, 90084-15-4; **5e** ((+)-phenethyl), 90084-16-5; **5f**, 90084-17-6; **6a**, 56279-34-6; **6b**, 90084-18-7; **6c**, 90084-19-8; **6d**, 56279-35-7; **6e**, 90084-20-1; **6f**, 90084-21-2; **6g** ((+)-phenethyl), 90084-22-3; **7**, 74441-37-5; **8**, 90084-23-4; **9**, 90084-24-5; **10**, 90084-25-6; *l*-phenmenthol, 65253-04-5; *l*-menthol, 2216-51-5; (+)-phenethyl alcohol, 1517-69-7; trimethylsilyl trifluoromethanesulfonate, 27607-77-8; 3-cholestanol, 80-97-7.

Communications

Reversal of Diastereoselectivity in the BF_3-Promoted Addition of Halobis(cyclopentadienyl)crotyltitanium Compounds to Aldehydes

Summary: Diastereoselectivity in the reaction of halobis(cyclopentadienyl)crotyltitanium reagents with aldehydes is reversed if BF_3 is added, erythro adducts being formed preferentially.

Sir: The idea that crotylmetal reagents can be used as enolate equivalents in the stereoselective construction of β-hydroxy carbonyl compounds has been applied in numerous cases.[1] Generally, the stereochemical outcome (threo or erythro adducts) depends upon the geometry of the crotylmetal reagent (*E* or *Z* configuration, respectively). For example, Sato's titanium compounds **1**, which are



accessible only in the *E* form, react with aldehydes to afford threo adducts **3** preferentially.[2,3] The necessity of having to prepare prochirally pure *E* or *Z* reagents does not apply to the BF_3-promoted addition of crotyltin compounds, which react stereoconvergently to produce erythro adducts **4**.[4] This surprising result has been explained by Yamamoto on the basis of an open-chain transition state as opposed to the conventional cyclic mechanism.[4] In this communication we report that *diastereoselectivity in the addition of 1 to aldehydes can be reversed by the use of BF_3.*

The reaction of the crotyltitanium reagents **1** with a mixture of aldehyde **2** and BF_3 at −78 °C afforded erythro adducts **4** preferentially as summarized in Table I. The data is relevant to the present preoccupation with cyclic vs. noncyclic transition states.[4,5] The degree of threo selectivity in the noncatalyzed reaction depends markedly upon the nature of the halogen ligand, and this has been interpreted by Sato by assuming the conventional pericyclic transition state.[1,2] The use of BF_3 in the present reactions not only favors the formation of erythro adducts but the degree of diastereoselectivity is also almost independent of the nature of the halogen at titanium. Al-

Table I. Addition[a] of 1 to Aldehydes 2

X	R	threo:erythro with BF_3[b]	threo:erythro without BF_3 according to Sato[2]
Cl	C_6H_5	14:86 (98)	60:40
Cl	n-C_6H_{13}	9:91 (85)	
Cl	$(CH_3)_2CH$	9:91 (85)	
Cl	$(C_2H_5)_2CH$	7:93 (84)	
Br	C_6H_5	14:86 (90)	100:0
Br	$(CH_3)_2CH$	9:91 (75)	99:1
Br	$(C_2H_5)_2CH$	6:94 (90)	
I	C_6H_5	24:76 (90)	94:6
I	$(C_2H_5)_2CH$	12:88 (70)	

[a] In the catalyzed reaction a mixture of 10 mmol of aldehyde and 20 mmol of BF_3 etherate in 5 mL of THF was added at −78 °C to 10 mmol of the crotyltitanium reagent **1**[2] in THF. After 2 h aqueous workup afforded the products **3**/**4**, the ratio of which was determined by GC. Configurational assignments were made by comparison of the NMR spectra of authentic samples reported in ref 2 and 4 as well as by Zeiss (Zeiss, H. J. Dissertation, University of Marburg, 1980) and Hoffmann and Zeiss (Hoffmann, R. W.; Zeiss, H. J. *J. Org. Chem.* **1981**, *46*, 1309). [b] Numbers in parentheses refer to percent conversion.

(1) Hoffmann, R. W. *Angew. Chem.* **1982**, *94*, 569; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.

(2) Sato, F.; Iida, K.; Ijima, S.; Moriya, H.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1140.

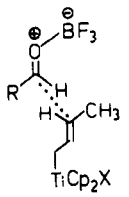
(3) Reviews of organotitanium reagents in organic synthesis: (a) Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1. (b) Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In "Comprehensive Organometallic Chemistry" Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon Press: Oxford, England, 1982; Chapter 22.3. (c) Weidmann, B.; Seebach, D. *Angew. Chem.* **1983**, *95*, 12; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31.

(4) Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107. Yamamoto, Y.; Maruyama, K. *Heterocycles* **1982**, *18*, 357.

(5) Noncyclic transition states have been discussed in other cases. (a) Aldol-type additions involving TAS enolates: Noyori, R.; Nishida, I.; Sakata, *J. J. Am. Chem. Soc.* **1981**, *103*, 2106; **1983**, *105*, 1598, and references cited therein. (b) Aldol-type additions involving zirconium enolates: Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980**, *21*, 4607. See, however: Evans, D. A.; McGee, L. R. *Ibid.* **1980**, *21*, 3975. (c) Aldol-type additions involving tin enolates and α-mercurio ketones: Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1981**, 162. Yamamoto, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1982**, *104*, 2323. (d) $TiCl_4$-induced addition of crotylsilanes: Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 2865 and references cited therein. See also: Denmark, S. E.; Weber, E. J. *Helv. Chim. Acta* **1983**, *66*, 1655. (e) Concerning HOMO–LUMO interactions in the addition of dianions of carboxylic acids to aldehydes, see: Mulzer, J.; Brüntrup, G.; Finke, J.; Zippel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7723.

0022-3263/84/1949-2292$01.50/0

though these findings certainly do not prove a noncyclic mechanism **5**, they are consistent with such a transition state.[6]



5

Interestingly, BF_3 does *not* reverse diastereoselectivity in the case of $CH_3CH{=}CHCH_2Ti(O\text{-}i\text{-}Pr)_3$, which has been shown to be a threo-selective reagent.[7] We have observed that it reacts considerably faster than **1** in the absence of BF_3. η^5-Cyclopentadienyl ligands as in **1** are powerful π donors[8] which reduce the Lewis acidity of titanium drastically.[9]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(6) A referee has noted that BF_3-induced removal of halide from **1** followed by addition of $CH_3CH{=}CHCH_2{}^+TiCp_2$ via a cyclic transition state could also explain the lack of a halogen effect on diastereoselectivity. We have also considered other possibilities such as BF_3 complexation at RCHO anti to the R group followed by a chair-like pericyclic transition state in which R occupies the quasi-axial position instead of the usual equatorial position. This would make Ti–O coordination possible but also raises the question whether *two* metals can complex at the aldehyde oxygen simultaneously; if C–C bond formation is far advanced in the transition state, electron density at oxygen increases, making double coordination more likely. The initial product would be a Lewis acid complexed titanium alkoxide, for which there is precedence Gmelin Handbuch, Titan-Organische Verbindungen, Springer-Verlag: Berlin, 1977; Part 1, p 63 and 207). These speculations also apply to such reactions as the Mukaiyama aldol addition of silyl enol ethers to $RCHO/TiCl_4$, the mechanism of which is also unclear.

(7) (a) See p 40 of ref 3a. (b) Widler, L.; Seebach, D. *Helv. Chim. Acta* **1982**, *65*, 1085.

(8) Concerning π bonding in bis(cyclopentadienyl)titanium compounds, see: Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

(9) We have observed that $CpTiCl_3$ does not induce allylsilane addition to aldehydes, in contrast to $TiCl_4$ (Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 2195).

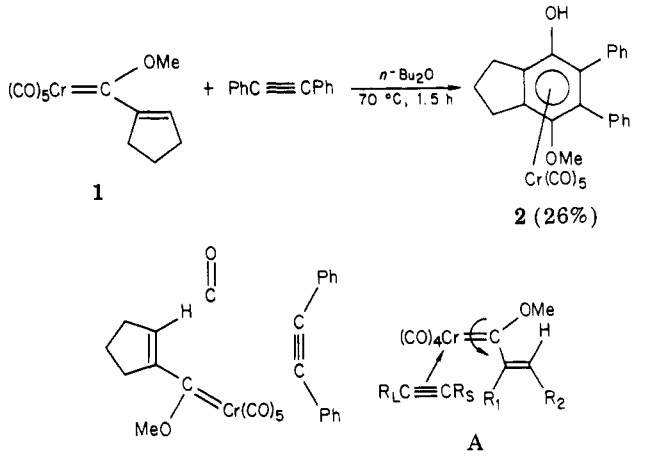
M. T. Reetz,* M. Sauerwald
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse
3550 Marburg, West Germany
Received January 18, 1984

Benzannulation of α,β-Unsaturated Fischer Carbene Complexes with Acetylenes[1]

Summary: The reaction of acetylenes with α,β-unsaturated chromium carbene complexes allows for the controlled construction of an aromatic nucleus under neutral conditions at near ambient temperatures. The synthetic scope of the reaction is examined for eight different carbene complexes with a variety of acetylenes to give three different types of benzannulated products depending on the type of oxidative workup employed.

(1) This work was presented at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 28–Sept 2, 1983.

Scheme I



Sir: Fischer carbene complexes of chromium are known to undergo facile reactions with acetylenes leading to products resulting from a benzannulation of one of the carbene carbon substituents. This reaction was first reported by Dötz[2] and has since been developed to the point where applications to natural product syntheses are beginning to appear in the literature.[3,4] However, all of the investigations of this reaction have been limited to those complexes for which the annulated substituent is an aryl group, with the singular exception of the reaction of the cyclopentenyl complex **1** (Scheme I). This complex has been reported to react with diphenylacetylene to give the indanechromium tricarbonyl complex **2** in 26% yield.[5,6] This result suggests that the benzannulation reaction of alkenyl-substituted chromium carbene complexes may also have potential for synthetic applications. We now report the results of an investigation designed to delineate the synthetic scope of this reaction and to explore its applications in natural product synthesis.[7]

The data in Table I establish that this annulation reaction will be synthetically useful for a variety of α,β-unsaturated chromium carbene complexes and acetylenes. The benzannulated products can be obtained in good to moderate yields and in the oxidation state of choice as illustrated in Scheme II for the cyclohexenyl complex **3**.[8] Rather than isolating the air-sensitive chromium tricarbonyl complex **5**, an oxidative workup with $FeCl_3$·DMF complex[9] gives the 4-methoxytetrahydronaphthol **6f** in 64% yield, or an oxidative workup with $(NH_4)_2Ce(NO_3)_6$[9] can give either the quinone **7e** (65%) or the quinone

(2) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 644.

(3) (a) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.* **1981**, *204*, C4. (b) Dötz, K. H.; Pruskil, I.; Muhlemeier, J. *Chem. Ber.* **1982**, *115*, 1278.

(4) Semmelhack, M. F.; Bozell, J. J.; Sato, T.; Wulff, W.; Spiess, E.; Zask, A. *J. Am. Chem. Soc.* **1982**, *104*, 5850.

(5) Dötz, K. H.; Dietz, R. *Chem. Ber.* **1978**, *111*, 2517.

(6) (a) A preliminary report on the reactions of one other alkenyl complex has appeared: Semmelhack, M. F. *Pure Appl. Chem.* **1981**, *53*, 2379. (b) Subsequent to the disclosure of this work and the preparation of this manuscript, two communications appeared describing five additional examples: Dötz, K. H.; Kuhn, W. *J. Organomet. Chem.* **1983**, *252*, C78. Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732.

(7) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434.

(8) The carbene complexes in Table I are prepared by the standard Fischer method involving addition of an alkenyllithium (cyclopentenyllithium in the case of **3**) to chromium hexacarbonyl followed by methylation. For example, the cyclopentenyl complex **3** can be prepared in 71% yield from cyclopentenyl bromide.

(9) The procedures for the use of these oxidants in the workup of other benzannulations has been previously described.[10] The workup with tri-*n*-butylphosphine involves stirring the reaction mixture with 3 equiv at 25 °C for 36 h followed by destruction of the excess phosphine by sequential treatment with excess methanol and carbon tetrachloride.

0022-3263/84/1949-2293$01.50/0