of white crystals: mp 77-78 °C; IR ($CDCl_3$) 1640 cm^{-1}; NMR δ 3.5 (8 H, m, CH_2N), 1.9 (8 H, m, CH_2). Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.22; H, 8.16. Found: C, 61.34; H, 8.15.

Oxalyl Bis(tetrahydroquinolinide) (2f). A 1.5-g (11 mmol) sample of tetrahydroquinoline was acylated with oxalyl chloride in benzene–pyridine. After workup, crystallization afforded 1.54 g (43.7%) of white crystals: mp 138-140 °C; IR 1660 cm^{-1}; NMR δ 7.13 (8 H, m, Ar H), 3.6 (4 H, m, CH_2N), 1.63 (8 H, m, CH_2). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.97; H, 6.29. Found: C, 75.00; H, 6.40.

Methyl *N*-Methyl-*N*-carbethoxyphthalamate (4). A 2.4-g (10 mmol) sample of *N*-carbethoxyphthalamic acid[17] was methylated with an excess of sodium hydride and methyl iodide in DMF to give 2.2 g (83%) of **4** as an oil, which was chromatographed: IR 1720, 1700, 1670 cm^{-1}; NMR δ 7.90 (1 H, dd, Ar H, ortho to CON), 7.33 (3 H, m, Ar H), 3.90 (2 H, q, CH_2O), 3.73 (3 H, s, CH_3O), 3.33 (3 H, s, CH_3N), 0.87 (3 H, t, CH_3). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.66; N, 5.28. Found: C, 58.74; H, 5.66; N, 5.11.

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Registry No. **1a**, 5470-26-8; **1b**, 5325-94-0; **1c**, 59325-17-6; **1d**, 2621-79-6; **1e**, 603-52-1; **1f**, 54915-68-3; **1g**, 33923-02-3; **2a**, 85802-71-7; **2b**, 17506-94-4; **2c**, 14288-21-2; **2d**, 14288-22-3; **2e**, 109124-48-3; **2f**, 109124-49-4; **3a**, 85-91-6; **3b**, 35472-56-1; **4**, 109124-50-7; **5**, 550-44-7; $EtO_2CN(Me)$-2-$C_6H_4CO_2H$, 79228-33-4; $Cl_2(CO)_2$, 79-37-8; HO_2C-2-$C_6H_4CONHCO_2Et$, 49599-18-0; tetrahydroquinoline, 25448-04-8.

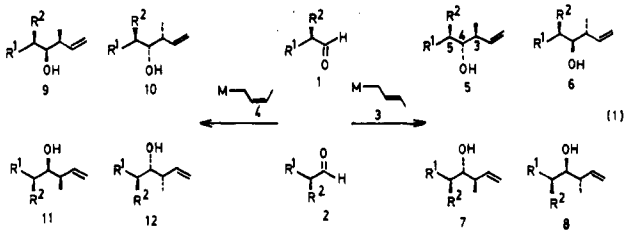
Communications

A Highly Diastereoselective Addition of (*E*)- and (*Z*)-Crotyldiisopinocampheylboranes to α-Substituted Aldehydes

Summary: (*E*)- and (*Z*)-Crotyldiisopinocampheylboranes **13-16** were used for diastereofacial selectivity in their reaction with α-substituted chiral aldehydes (*S*)-2-methylbutyraldehyde (**17**) and (*S*)-2-(benzyloxy)propionaldehyde (**18**).

Sir: The reaction of certain allylmetal and crotylmetal reagents with chiral carbonyl compounds constitutes a powerful method for control of acyclic stereochemistry and their value as biosynthetic intermediates has been amply demonstrated.[2-5] A variety of crotylmetal compounds with high stereochemical purity are now available. Many of the crotylmetals, especially crotyl boron compounds, undergo reaction with aldehydes in which the olefin geometry is transmitted predictably via cyclic transition states to either a syn (from *Z*) or anti (from *E*) relationship around the newly formed C–C bond in the product alcohols.[6] An as yet unsolved problem involves control of facial selectivity in reactions of crotylmetals with α-substituted chiral aldehydes.

Like enolates, crotyl organometallic reagents react with α-substituted chiral aldehydes to furnish diastereomeric mixtures of (3,4- and 4,5)-anti,anti (**5** and **7**), -anti,syn (**6** and **8**), -syn,anti (**10** and **12**), and -syn,syn (**9** and **11**) adducts (eq 1).[3e,4a] Enantiomeric homoallyl alcohol units (R_1 = CH_3; R_2 = C_2H_5, OBz) constitute a characteristic structural feature of numerous macrolide and polyether antibiotics.[7] The major problem in stereocontrol concerns the selectivity in the relative configuration of the newly formed C–C bond to the configuration present in the aldehydes. Although considerable effort has been devoted to the elucidation of the stereochemistry of the reaction of crotylmetal compounds with α-substituted chiral aldehydes, relatively little information is available regarding such reactions. Hence, the development of new crotyl organometallic reagents possessing high stereoselectivities remains a desirable goal.



(1)

We recently described the stereochemistry of the reactions of allyldiisopinocampheylboranes [derived from (+)- and (−)-α-pinene] with α-substituted chiral aldehydes.[8] In general, these reactions are highly stereoselective, with high

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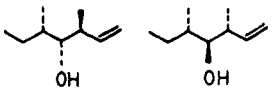
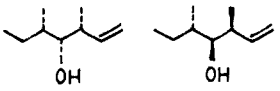
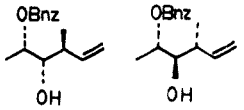
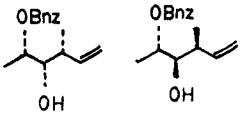
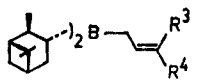
Table I. Reaction of Chiral Aldehydes 17 and 18 with the Reagents 13–16[a]

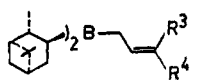
aldehydes[b]	reagents	products: yield,[c] %	products: diastereomeric ratio[d,f]
17			
	13	(75)	96:4
	14	(70)	9:91[e]
			
	15	(73)	82:18[e]
	16	(79)	4:96[e]
18			
	13	(80)	95:5
	14	(85)	3:97
			
	15	(74)	73:27
	16	(78)	1:99

[a] The reactions were carried out at −78 °C under a nitrogen atmosphere[10] by utilizing a 1:1 molar ratio of reagent to chiral aldehyde. [b] Chiral aldehydes (17, 96–97% ee; 18, 99% ee) were prepared and used in solution. The optical purity of the aldehydes were routinely checked by comparing the optical rotations of the corresponding alcohols produced by BMS reduction of the aldehydes. [c] Isolated yield. [d] The ratios of diastereomers were determined by capillary GC analysis of the product alcohols using a column of methylsilicon, 50 M × 0.25 mm. [e] In addition to the presence of the desired two diastereomers, the capillary GC analysis revealed the presence of 1–2% of the other two diastereomers, presumably arising from the presence of small amounts of the other diastereomeric reagent. [f] Configurations of the newly formed C–C bond to the configuration present in the aldehyde are predicted by analogy to the configuration realized in the products obtained in the reaction of crotyldiisopinocampheylborane derivatives with achiral aldehydes.[6a]

facial selectivities. In order to further explore the factors controlling aldehyde facial selectivity, we have examined and report herein the stereochemical features of the reactions of crotyldiisopinocampheylboranes **13–16** with aldehydes (*S*)-2-methylbutyraldehyde (**17**) and (*S*)-2-(benzyloxy)propionaldehyde (**18**).



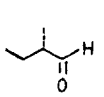
13 $R^3 = H$, $R^4 = CH_3$



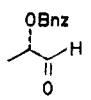
14 $R^3 = H$, $R^4 = CH_3$

15 $R^3 = CH_3$, $R^4 = H$

16 $R^3 = CH_3$, $R^4 = H$



17



18

The reagents, *B*-crotyldiisopinocampheylboranes **13–16**, are readily obtained in high stereochemical purity according to the procedure previously reported from our laboratory.[6a] All crotylboration reactions were carried out at −78 °C in ether solvent. These reactions are observed to be rapid and require less than 3 h at −78 °C. The reaction mixture was worked up by using alkaline hydrogen peroxide to remove the boron intermediate.[9] The diastereofacial selectivities of the reagents **13–16** with chiral aldehydes **17** and **18** are easily assessed by monitoring the overall diastereoselectivities achieved in the reaction. The results are summarized in Table I.

It is immediately striking that the reactions of crotylboranes **13**, **14**, and **16** with aldehydes **17** and **18** are highly stereoselective and the corresponding (3,4- and 4,5)-anti,syn, -anti,anti, and -syn,anti products have been obtained in very high facial selectivities. Even the reaction of **15** with aldehydes **17** and **18** furnished the syn,syn product in moderately good facial selectivity.

It is clear from these results that the crotyldiisopinocampheylboranes **13–16** are highly diastereoselective reagents with α-substituted chiral aldehydes **17** and **18**. The stereochemistry at the newly formed C–C bond is controlled simply by selecting the appropriate enantiomeric reagent; thus, the chirality of the reagent controls the overall diastereofacial selectivity achieved in the reaction. This synthesis is operationally very simple, providing access to all possible stereoisomers in high optical purity merely by selecting the proper antipode of the reagents and aldehydes.[11] Further, ozonification of these homoallyl alcohols should provide the corresponding aldehydes, which, on further treatment with (*E*)- or (*Z*)-crotyldiisopinocampheylboranes, would provide the homoallyl alcohols with an additional two stereocenters in high stereoselectivity. Hence, this repeating process should provide a convenient route to the numerous macrolide and polyether antibiotics.

Acknowledgment. The financial support from the National Institutes of Health (Grant GM 10937-24) is gratefully acknowledged.

(9) Alternatively, the boron intermediate can be removed by precipitation with enthanolamine. Brown, H. C.; Jadhav, P. K.; Bhat, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 2564.

(10) For techniques, see: Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975; p 191.

(11) Attention is called to a recent paper[12] which describes the reaction of the (*Z*)- and (*E*)-crotylboronate with β-alkoxy-α-methylpropionaldehyde. The reaction takes the same course. In this case, it was possible to assign the structure by comparison of the spectral data for the known material.

(12) Roush, W. R.; Palkowitz, A. D.; Palmer, M. A. *J. Org. Chem.* **1987**, *52*, 316.

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Charge Reversal of Electrophilic π-Allylpalladium Intermediates: Carbonyl Allylation by Allylic Acetates with $Pd(PPh_3)_4$–Zn

Summary: Allylic acetates were reduced by zinc in the presence of a catalytic amount of $Pd(PPh_3)_4$ to serve as nucleophilic allylating agents, which reacted with aldehydes to afford the corresponding homoallylic alcohols.

Sir: Addition reaction of various allylic organometallic compounds to aldehydes has attracted notice for possible applications to stereocontrolled synthesis in the conformationally nonrigid acyclic system.[1] The allylic organo-

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