We interpret this result to mean either that deuterium substitution has little effect on the tautomeric equilibria or that $\Delta G^{\ddagger}$ for the tautomeric hydrogen shift is small compared with the total free energy of activation.[15] It is of interest that $\Delta G^{\ddagger}$ compares favorably with $\Delta G^{\ddagger}$ for fluxional processes in polyolefin–iron complexes.[7] Nevertheless the proton shift is a necessary prerequisite for fluxionality in these 1(1*H*),2-diazepine complexes since **3d**–**g** are not dynamic at room temperature and attempts to induce fluxionality by raising the temperatures to +100° were unsuccessful. In contrast to azepine complexes,[16,17] dynamic behavior is not expected for iron tricarbonyl complexes of N-substituted 1(1*H*),2-diazepines since the two alternative π sites are nonequivalent.

Further insight was provided by the synthesis of **3a** (yellow crystals, 85%; mp 99°; ir (C_6H_{14}) ν(CO) 2050 (s), 1987 (s), 1974 (s) cm^{-1}; mass spectrum M$^+$ *m/e* 248) from **3f**[4] and **3b** (yellow crystals, 62%, mp 97°; ir (C_6H_{14}) ν(CO) 2049 (s), 1987 (s), 1973 (s) cm^{-1}) from **3g**. Nmr spectral parameters are given in Table I. **3b** exhibited an nmr spectrum characteristic of a dynamic molecule ($\Delta G^{\ddagger}$ = 15 ± 0.4 kcal mol^{-1}) while **3a** gave a well-resolved nonfluxional temperature-invariant spectrum. For **3a** one tautomer, that in which the $Fe(CO)_3$ moiety is bonded to carbon atoms C_4–C_7, is stabilized.

These results suggest that π complexation may be of general utility for modifying tautomeric equilibria. Furthermore dynamic behavior can be expected for π complexes of other heterocycles exhibiting tautomerism.

Acknowledgment. We thank the National Research Council of Canada for financial support.

[15] The entire process, *viz.*, hydrogen migration, ring double bond shift, and movement of the $Fe(CO)_3$ moiety may be concerted.

[16] L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).

[17] H. Günther and R. Wenzl, *Tetrahedron Lett.*, 4155 (1967).

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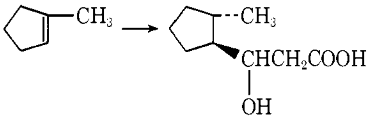
An Intramolecular Michael Reaction Involving Borate Complexes. A Novel Synthesis of β-Hydroxycarboxylic Acids

Sir:

We wish to report an intramolecular version of the Michael reaction involving borate complexes, which provides a novel route to β-hydroxycarboxylic acids from olefins with the possibility of incorporating stereochemically defined groups in the β position (for example eq 1).

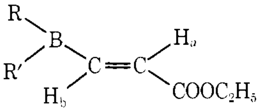


1

(1)

The conjugate addition of organic moieties to α,β-unsaturated carbonyl derivatives, such as the Michael reaction, represents one of the most important classes of carbon–carbon bond-forming reactions.[1] Recently, it has been established that trialkylboranes undergo conjugate addition *via* a free-radical mechanism.[2–4] Although the reaction appears to be of wide applicability, satisfactory reaction conditions have not so far been found to induce successful conjugate addition to α,β-unsaturated carboxylic acids and their derivatives. Furthermore, in accordance with the free-radical mechanism, partial loss of the stereochemistry at the γ carbon of the products has been observed.[2c] These limitations led us to explore the possible use of the borate anions in the conjugate addition reaction. However, when lithium tetraalkylborates, such as lithium tetra-*n*-butylborate, were allowed to react with α,β-unsaturated carbonyl compounds, such as ethyl acrylate, there was little indication for the formation of the desired Michael products.

It then occurred to us that such a reaction might be greatly facilitated by making the process intramolecular.[5] Indeed, we have found that disiamyl(2-ethoxycarbonylethenyl)borane (**2**a) undergoes a facile reaction, on treatment with sodium methoxide, to produce an intermediate which can be oxidized to 3-hydroxy-4,5-dimethylhexanoic acid (47% overall yield). Pmr examination has revealed that the hydroboration product consists of a 67:33 mixture of **2a** and **3a**:[6] pmr (THF, TMS) δ 7.70 (H_a, d, J = 19 Hz), 6.23 (H_b, double d, J = 19 Hz), 6.44 (H_c, d, J = 3 Hz), 5.54 (H_d, d, J = 3 Hz) ppm. The combined yield of **2a** and **3a** by pmr was 98% (benzene as an internal standard). The results of hydroboration are in marked contrast to those reported with β-substituted propiolic acid esters,[8] in-



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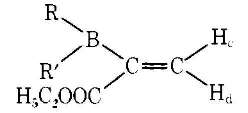

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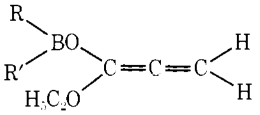

4

a, R = R′ = siamyl; **b**, R = alkyl; R′ = thexyl

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[1] See, for example, the following: (a) E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. React.*, **10**, 179 (1959); (b) G. H. Posner, *ibid.*, **19**, 1 (1972); (c) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972.

[2] (a) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972; (b) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92**, 710 (1970); (c) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 3777 (1971).

[3] A few methods for the synthesis of β-dimethylamino[3a] and β-hydroxycarbonyl[3b] compounds involving the free-radical conjugate addition of organoboranes have been reported: (a) J. Hooz and J. N. Bridson, *J. Amer. Chem. Soc.*, **95**, 602 (1973); (b) T. Mukaiyama, K. Inomata, and M. Muraki, *ibid.*, **95**, 967 (1973).

[4] For the related works on organoaluminum compounds, see (a) J. Hooz and R. B. Layton, *J. Amer. Chem. Soc.*, **93**, 7320 (1971); (b) R. Pappo and P. W. Collins, *Tetrahedron Lett.*, 2627 (1972); (c) G. W. Kabalka and R. F. Daley, *J. Amer. Chem. Soc.*, **95**, 4428 (1973).

[5] The presence of an appropriately located boron atom has made certain otherwise difficult substitution reactions extremely facile. See, for example, (a) ref 2a; and (b) D. S. Matteson, *Progr. Boron Chem.*, **3**, 117 (1970).

[6] In contrast to the facile formation of vinyloxyboranes,[7] no indication for the formation of **4** by the tautomerization of **3** was obtained.

[7] D. J. Pasto and P. W. Wojtkowski, *Tetrahedron Lett.*, 215 (1970).

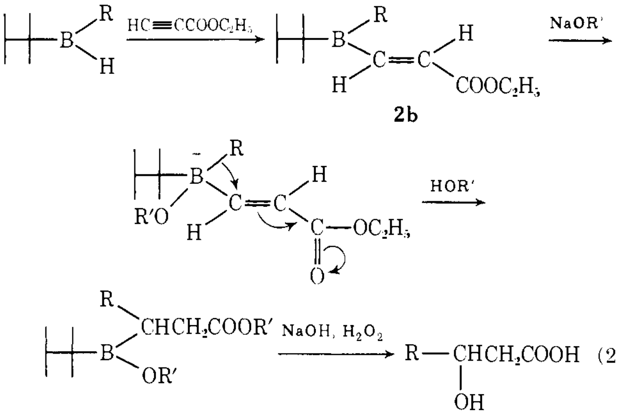
[8] A preferential attack of the α-carbon atom by the boron atom has been reported: J. Plamondon, J. T. Snow, and G. Zweifel, *Organometal. Chem. Syn.*, **1**, 249 (1971).

Table I. Preparation of Thexylalkyl(2-ethoxycarbonylethenyl)boranes and Their Conversion into β-Hydroxycarboxylic Acids

Alkyl group (R) of thexylmonoalkylborane	Hydroboration product: Yield (2b + 3b) by pmr,[a] %	Isomer distribution,[a] %		β-Hydroxycarboxylic acids[b]: Yield, %[a]		
		2b	3b	Glpc[c]	Isolated	Mp, °C
Cyclohexyl	94	>99	Trace	74	60	79.5–80.0
Norbornyl	93	90	10	57	51	80–82
3-Methyl-2-butyl	101	>99	Trace	72	68	50.5–51.5
trans-2-Methylcyclopentyl	89	>99	Trace	81	69	69.5–70.0
2-Methyl-1-pentyl	94	67	33	46[d]	*e*	

[a] Based on pmr examination of vinyl protons (benzene as an internal standard). The chemical-shift ranges: H_a (d, J = 19 Hz) 7.63–7.70; H_b (d, J = 19 Hz) 5.90–6.04; H_c (d, J = 3 Hz) 6.40–6.42, and H_d (d, J = 3 Hz) 5.31–5.40. [b] All new, isolated products yielded satisfactory analytical and spectral data. [c] By glpc examination of silylated products (SE-30). [d] By glpc examination after treatment of the product with an excess of diazomethane (SE-30). [e] Isolated by glpc as methyl 2-methoxy-4-methyloctanoate.

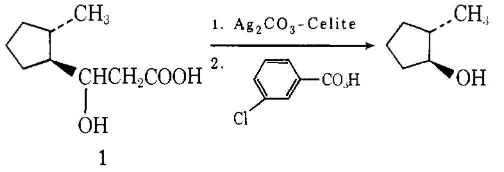
dicating that steric effect can be significant in determining the orientation in this reaction. Accordingly, we tested a series of thexylmonoalkylboranes[9] containing a highly bulky thexyl group as hydroborating agents. Fortunately, all but one of the thexylmonoalkylboranes of different steric requirements we tested placed at least 90% of the boron atoms in the desired β positions, producing only minor amounts of the isomeric products **3b**[6] (Table I). Moreover, the usual reluctance of the thexyl group to participate in the ionic reactions of organoboranes[10] was observed in the subsequent reaction of **2b** with base, thereby making the one-pot procedure shown by eq 2 a highly practical synthetic method which permits the maximum conversion of the starting olefins into β-hydroxycarboxylic acids.[11] The experimental results are summarized in Table I.



(2)

R = alkyl; R' = H, methyl, or ethyl

That the transfer of an alkyl group from boron to carbon must involve an ionic mechanism is indicated by the following observations. First, use of a base is necessary to induce the facile transfer reaction. Second, addition of free-radical scavengers (5 mol %), such as galvinoxyl, does not have any noticeable effect on the rate of reaction. Finally, the stereochemistry of the group R is totally retained when R is *trans*-2-methylcyclopentyl as demonstrated by glpc analysis of 2-methyl-1-cyclopentanol obtained by oxidation of **1** with silver carbonate followed by the Baeyer–Villiger oxidation (eq 3). It should be noted that the procedure reported here provides a unique, new route to the Reformatsky products[12] with the possibility of incorporating, in a simple manner, stereochemically defined moieties in the β position.



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(3)

The following procedure for the preparation of **1** is representative. To a dry 250-ml flask equipped with a septum inlet, a reflux condenser, and a magnetic stirring bar was placed 16.8 ml (30 mmol) of 1.78 *M* thexylborane in THF after flushing the system with nitrogen. To this were added in sequence 3.20 ml (30 mmol) of 1-methylcyclopentene (1 hr at −25 to −30°), 3.20 ml (30 mmol) of ethyl propiolate (1 hr at −25 to −30°), and 25 ml (75 mmol) of 3 *N* sodium hydroxide (5 min at −25°, then 1 hr at room temperature). The reaction mixture was oxidized with 10 ml of 30% hydrogen peroxide and heated for 2 hr at 40–50° to complete oxidation and hydrolysis. After the usual workup, 4.10 g (79%) of crude product (*ca.* 90% pure) was obtained. After recrystallization (ether–pentane), the combined yield of pure **1** was 3.20 g (62%): mp 69.5–70°; ir (Nujol) 3150, 1690 cm^{-1}; pmr (CCl_4, TMS) δ 1.05 (d, J = 6 Hz, 3 H), 1.2–2.2 (m, 8 H), 2.45 (d, J = 6 Hz, 2 H), 3.6–4.2 (m, 1 H), 7.62 (s, 2 H) ppm.

We continue to explore the scope and synthetic applicability of this new carbon–carbon bond forming reaction.

Acknowledgment. We thank Syracuse University for financial support.

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(9) (a) G. Zweifel and H. C. Brown, *J. Amer. Chem. Soc.*, **85**, 2066 (1963); (b) E. Negishi, J. J. Katz, and H. C. Brown, *Synthesis*, 555 (1972).

(10) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **89**, 5285, 5477 (1967).

(11) Only a trace quantity (<2%), if any, of the by-product corresponding to the transfer of the thexyl group was observed in each case.

(12) R. L. Shriner, *Org. React.*, **1**, 1 (1942).

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Dynamic Nuclear Magnetic Resonance Investigations of Intramolecular Catalysis in Amide Proton Exchange

Sir:

We have used dynamic nmr methods to explore neighboring group participation in the amide proton exchange of ortho-substituted *N*-methylbenzamides. Although the mechanism of amide proton exchange