Three structurally similar complexes have been investigated: $Mg(NCS)_2$·benzo-15-crown-5,[6] $Co(H_2O)_2$·benzo-15-crown-5,[9] and $CuCl_2$·benzo-15-crown-5·$CHCl_3$.[10] A comparison of the structural data shows little variation for the conformation of the crown ether (e.g., Mg complex torsion angles vary less than 6% compared with those for the aluminum complex). However, the disparity in the Al–O distances for the title complex is not evident for any of the metal–oxygen lengths in the related complexes. This can be explained by both the increased charge and the smaller diameter of the aluminum cation ($d_{Mg^{2+}}$ = 1.84 Å, $d_{Cu^{2+}}$ = 1.88 Å, $d_{Co^{2+}}$ = 1.84 Å, all values corrected for seven-coordination using the method of Pauling,[20] whereas the corrected value for Al^{3+} = 1.44 Å). Thus the lesser donor capability of the "benzo" oxygens reported for $[Tl(CH_3)_2$·dibenzo-18-crown-6$]^+$ [21] becomes more evident for the smaller cation. The bonding system is an extension to that in SF_6 or PF_5, the ability of the oxygens to lie in a plane and the electronegativity of the chlorines combining to stabilize the filling of four bonding and three nonbonding orbitals. As only three of the former are bonding with respect to aluminum and oxygen, a six-electron ten-center pattern is formed, which is in agreement with the "eight-electron" rule and leads to the observed long and irregular bonding distances.[22]

Acknowledgment. We are grateful to the National Science Foundation and the Department of Energy (DE-FG22-83PC60780) for support of this research.

Supplementary Material Available: Tables of bond distances and angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

(20) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960; p 526.
(21) Henrick, K.; Matthews, R. W.; Podejma, B. L.; Tasker, J. *J. Chem. Soc., Chem. Commun.* **1982**, 118.
(22) Albright, T. A., personal communication.

Intramolecular Michael Addition of *O*-Carbamates to α,β-Unsaturated Esters. A New Diastereoselective Amination in an Acyclic System†[1]

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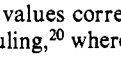
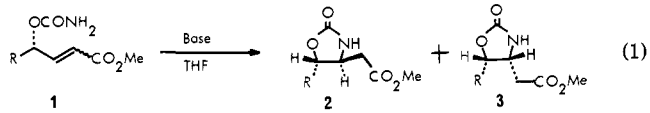
The synthesis of biologically important amino sugars from noncarbohydrate precursors is currently receiving considerable attention.[2] A challenging aspect of the effort is the stereocontrolled functionalization of acyclic olefinic systems. Though highly stereoselective oxygenation of double bonds of unsaturated amine derivatives has recently been reported,[3] alternative approaches starting from unsaturated alcohols have one obvious advantage that enantiomerically pure materials are readily accessible.[4,5] Compared with the two-step procedure, asymmetric epoxidation of allylic alcohols[5] and subsequent addition of nitrogen nucleophiles,[6] the direct addition of a nitrogen functionality to an unsaturated alcohol system has not generally been so stereoselective.[1,7] We disclose here a new aspect of carbamate-mediated functionalization[8] useful for diastereoselective introduction of a nitrogen functionality directly in the β-position of γ- and δ-hydroxy-α,β-unsaturated esters.

Table I. Diastereoselective Intramolecular Michael Addition of Allylic *O*-Carbamates **1**

entry	substrate R	substrate 2,3 double bond	conditions[a]	product ratio[b] **2**:**3**	product % yield[c]
1	**1a**, Me	*E*	25 min or 3 s	5:1	66
2	**1b**, Ph	*E*	30 min	12:1	85
3	**1b**, Ph	*E*	1.5 equiv, 30 min	7:1	68
4	**1c**, Ph	*Z*	30 min	>100:1	75
5		*E*	30 min	>20:1	79

[a] Carried out in an anhydrous THF and quenched with saturated aqueous NH_4Cl or pulverized NH_4Cl (1 equiv); 1.0 equiv of KO-*t*-Bu (0 °C) was used, unless otherwise indicated. [b] Product diastereomer ratio determined by 200-MHz ^1H NMR spectroscopy. [c] Yield of isolated mixture of **2** and **3**.

When allylic carbamate esters **1** were stirred with 1.0 equiv of KO-*t*-Bu (THF, 0 °C) under an argon atmosphere, a rapid cyclization via nitrogen occurred[1] producing mainly the *trans*-oxazolidinones **2**, equal to 1,2-*syn* amino alcohols (eq 1, Table I).[9,10] The ratio of **2**:**3** was not affected by changing the reaction time (entry 1), while it was diminished by excess KO-*t*-Bu (entries 2, 3). Other bases such as NaH (1.5 equiv, room temperature) resulted in the similar stereoselectivity with somewhat slower reaction rate. Higher 1,2-asymmetric induction was observed in the compounds with more sterically demanding R groups (entries



1 2 3 (1)

† Dedicated to the memory of Professor Kunio Sakan.
(1) Carbamate-mediated functionalization of unsaturated alcohols. 3. For part 2, see: Hirama, M.; Iwashita, M.; Yamazaki, Y.; Itô, S. *Tetrahedron Lett.* **1984**, *25*, 4963.
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(3) (a) Wang, Y.-F.; Izawa, T.; Kobayashi, S.; Ohno, M. *J. Am. Chem. Soc.* **1982**, *104*, 6465. (b) Hauser, F. M.; Ellenberger, S. R. *Ibid.* **1984**, *106*, 2458 and references cited therein.
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(6) (a) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109. (b) Roush, W. R.; Brown, R. J.; DiMare, M. *J. Org. Chem.* **1983**, *48*, 5083. Roush, W. R.; Brown, R. J. *Ibid.* **1983**, *48*, 5093 and references cited therein. (c) Behrens, C. H.; Sharpless, K. B. *Aldrichimica Acta* **1984**, *16*, 67 and references therein.
(7) (a) For iodocyclizations of allylic and homoallylic trichloroacetimidates, see: Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Chem. Soc., Chem. Commun.* **1982**, 1308. (b) For nitrile oxide cycloadditions to chiral allylic alcohol derivatives, see: Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jäger, V.; Schohe, R.; Fronczek, F. R. *J. Am. Chem. Soc.* **1984**, *106*, 3880 and references cited therein. (c) For other approaches, see ref 2a,c.
(8) While carbamate groups are long known to participate in neighboring group-assisted reactions (see: Capon, B. *Q. Rev. Chem. Soc.* **1964**, *18*, 45), renewed interest in stereocontrolled cyclofunctionalization has occurred recently. (a) For PhSeCl-initiated reactions of olefinic *N*-carbamates (urethanes) to afford pyrrolidines and piperidines, see: Clive, D. L. J.; Farina, V.; Singh, A.; Wong, C. K.; Kiel, W. A.; Menchen, S. M. *J. Org. Chem.* **1980**, 45, 2120. (b) For aminomercurations of olefinic *N*-carbamates, see: Harding, K. E.; Marman, T. H. *Ibid.* **1984**, *49*, 2838 and references cited therein. (c) For iodocyclizations of olefinic *N*-carbamates, see ref 3a and: Pauls, H. W.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1980**, *102*, 3956. Parker, K. A.; O'Fee, R. *Ibid.* **1983**, *105*, 654 and references therein. (d) For nucleophilic opening of epoxides by phenylurethane group, see ref 6. (e) For iodocyclizations of olefinic *O*-carbamates, see ref 1, ref 4c, and: Pauls, H. W.; Fraser-Reid, B. *J. Org. Chem.* **1983**, *48*, 1392.

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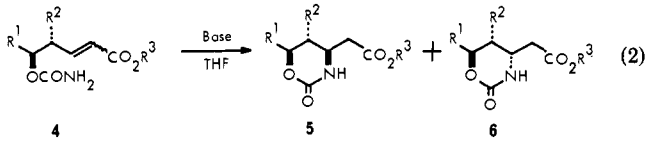
Table II. Diastereoselective Intramolecular Michael Addition of Homoallylic *O*-Carbamates **4**

entry	substrate R¹	R²	R³	2,3 double bond	conditions[a]	product ratio[b] **5**:**6**	% yield[c]
1	**4a**, Me	H	Me	*E*	NaH, 1 h	10:1	53
2	**4b**, 3-butenyl	H	Me	*E*	NaH, 1.5 h	10:1	70
3	**4c**, Me	H	Me	*Z*	NaH, 1 h	>20:1	70
4	**4d**, Me	*t*-OBu	Et	*E*	KOBu-t, 13 min	7:1	91
5	**4e**, Me	OAc	Et	*E*	KOBu-t, 2 min	19:1	52
6	**4f**, Me	OTBDMS	Et	*E*	KOBu-t, 10 min	36:1	90

[a] Carried out in anhydrous THF with 1.0 equiv of KO-*t*-Bu-t (0 °C) or with 1.5 equiv of NaH (room temperature). [b] Product diastereomer ratio determined by 200-MHz ^{1}H NMR spectroscopy. [c] Yield of isolated mixture of **5** and **6**.

2,5), and by use of the *Z* olefin **1c**, **2c** was formed almost exclusively (entry 4). These results suggest that the reaction is occurring under kinetic control.

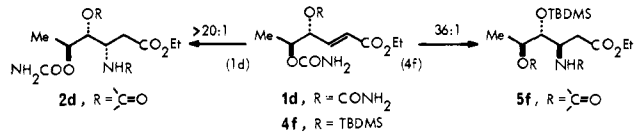
Homoallylic carbamates **4** also cyclized smoothly to 6-membered cyclic carbamates **5**[9] with high 1,3-*syn* asymmetric induction[11] in moderate to good yields (eq 2, Table II):[10] *Z* double



4 5 6 (2)

bond **4c** also improved the stereoselectivity greatly (entry 3) but to a lesser extent as compared with the case of **1c**. 1,3-Diastereoselectivity was affected by an additional substituent (R^2) at the γ-position. R^2 in the anti disposition to the δ-carbamate increased 1,3-syn-diastereoselectivity as expected (entries 5, 6), except in the reaction of **4d** (R^2 = O-*t*-Bu, entry 4). The unexpected decrease of selectivity in **4d** may reflect severe gauche interactions around the bulky *tert*-butoxyl group in the transition state.

A useful feature of these reactions is that either stereoisomer of amine derivatives can be synthesized in a specific manner from a common diol by proper choice between γ- and δ-hydroxyl groups as a carbamoyl group carrier, as is exemplified by the eq 3. In



2d, R = C=O **1d**, R = $CONH_2$ **4f**, R = TBDMS **5f**, R = C=O (3)

the competitive cyclization between allylic and homoallylic carbamate groups of the biscarbamate **1d**, the former added with greater selectivity (1,2-syn) to afford the 1,3-anti amino alcohol **2d** (Table I, entry 5). On the other hand, **5f** (1,3-syn) was obtained from the homoallylic carbamate **4f** (Table II, entry 6).

Further studies are in progress to evaluate the scope of this methodology and its application to stereoselective synthese of 3-amino-2,3-dideoxyhexoses will be reported in due course.

Acknowledgment. We are grateful to the Ministry of Education, Japan, for partial financial support of this research (Grant in Aid for Special Project Research 58110006 and 59104004).

Registry No. 1a, 94944-18-0; **1b**, 94944-19-1; **1c**, 94944-20-4; **1d**, 94944-21-5; **2a**, 94944-22-6; **2b**, 94944-23-7; **2d**, 94956-24-8; **3a**, 94944-24-8; **3b**, 94944-25-9; **3d**, 94956-25-9; **4a**, 94944-26-0; **4b**, 94944-27-1; **4c**, 94944-28-2; **4d**, 94944-29-3; **4e**, 94944-30-6; **4f**, 94944-31-7; **5a**, 94944-32-8; **5b**, 94944-33-9; **5d**, 94944-34-0; **5e**, 94944-35-1; **5f**, 94944-36-2; **6a**, 94944-37-3; **6b**, 94944-38-4; **6d**, 94944-39-5; **6e**, 94944-40-8; **6f**, 94944-41-9.

Supplementary Material Available: Spectroscopic data for the compounds **1**, **2**, **4**, and **5** (9 pages). Ordering information is given on any current masthead pages.

(9) (a) *O*-Carbamates (**1**, **4**, and **7**) were synthesized directly from the corresponding alcohols by the known procedure from $ClSO_2NCO$ (Graf, R. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 172) or CCl_3CONCO.[4c,6a] (b) Satisfactory spectral data and elemental analyses were obtained on all compounds reported herein.

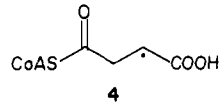
(10) (a) Minor diastereomers were not separated from major ones. (b) Unequivocal stereochemical assignments for **2d**, **5d**, **5f**, and **6d** were made by their transformations to the respective, known 3-amino-2,3,6-trideoxyhexoses.

(11) Completely different approach to syn-1,3 amino alcohols was recently reported. See: Narasaka, K.; Ukaji, Y. *Chem. Lett.* **1984**, 147.

Additions and Corrections

Free Radical Rearrangement Involving the 1,2-Migration of a Thioester Group. Model for the Coenzyme B_{12} Dependent Methylmalonyl-CoA Mutase Reaction [*J. Am. Chem. Soc.* **1984**, *106*, 8319–8321]. SUSAN WOLLOWITZ and JACK HALPERN*

Page 8319: Formula **4** should read



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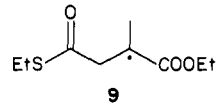
Page 8320: Formula **9** should read



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