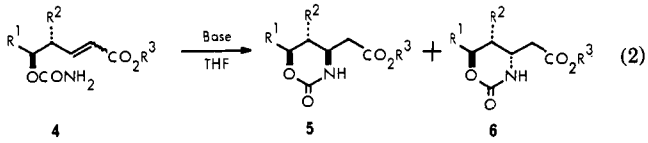
**Table II.** Diastereoselective Intramolecular Michael Addition of Homoallylic *O*-Carbamates **4**

| 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.

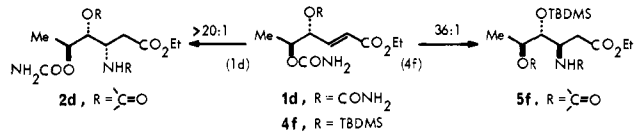
Homoallylic carbamates **4** also cyclized smoothly to 6-membered cyclic carbamates **5**[9] with high 1,3-*syn* asymmetric induction[11] in moderate to good yields (eq 2, Table II):[10] *Z* double




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.

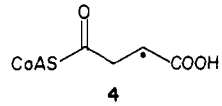
(10) (a) Minor diastereomers were not separated from major ones. (b) Unequivocal stereochemical assignments for **2d**, **5d**, **5f**, and **6d** were made by their transformations to the respective, known 3-amino-2,3,6-trideoxyhexoses.

(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*

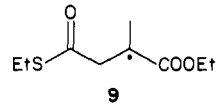
**Free Radical Rearrangement Involving the 1,2-Migration of a Thioester Group. Model for the Coenzyme $B_{12}$ Dependent Methylmalonyl-CoA Mutase Reaction** [*J. Am. Chem. Soc.* **1984**, *106*, 8319–8321]. SUSAN WOLLOWITZ and JACK HALPERN*

Page 8319: Formula **4** should read




**4**

Page 8320: Formula **9** should read




**9**