manner to give a 56% yield of **1a** and **1b**.

Diene 4. A. Preparation from 2. To a solution of **2** (18.94 g, 45 mmol) and diethyl (cyanomethyl)phosphonate (8.77 g, 45 mmol) in 175 mL of THF at 0 °C was added 100 mL of 1 M LiHMDS in THF. After stirring for 4.5 h at ambient temperature, considerable starting material remained by TLC, so additional phosphonate (0.88 g, 4.5 mmol) and 1 M LiHMDS in THF (20 mL, 20 mmol) were added at room temperature and the solution was stirred overnight. The reaction mixture was then treated with water, and the product was extracted into ether, washed with brine, dried ($MgSO_4$), filtered, and concentrated. The crude product was chromatographed on a Waters Prep-500 HPLC (ethyl acetate/hexane, 35:65) to give 6.50 g of **4** (43%): $[\alpha]^{20}_D$ +22.9° (c 0.20, CCl_4); MS, *m/e* 336 (M + 1); UV (MeOH) λ_{max} 261.5 nm (ϵ 10 228); ^1H NMR δ 2.47 (m, 1 H), 3.34 (dd, 1 H, *J* = 7.0, 9.6 Hz, C_7H_a), 3.45 (dd, 1 H, *J* = 3.7, 9.6 Hz, C_7H_b), 4.51 (m, 2 H), 4.69 (m, 1 H, *J* = 3.7, 7.0, 8.6 Hz, C_6H), 4.80 (m, 2 H, $PhCH_2O$ on C_4), 5.42 (d, 1 H, *J* = 8.6 Hz, C_5H), 5.58 (d, 1 H, *J* = 16.1 Hz, C_2H), 6.77 (d, 1 H, *J* = 16.1 Hz, C_3H), 7.3 (m, 10 H) [2D-NOESY data indicated a positive interaction of the resonance at 6.77 ppm with those at 5.58 and 5.42 ppm, as well as the resonance at 5.58 ppm with those at 4.80 and 6.77 ppm, indicating the *E,Z* geometry]; 15.0-MHz ^{13}C NMR δ 66.0 (d, C-6), 73.1 (t), 73.5 (t), 74.3 (t), 98.1 (d, C-3), 117.4 (q, C-1), 125.6 (d), 127.0 (d), 127.8-128.7 (10 C), 136.3 (q), 137.7 (q), 145.8 (d, C-5), 152.5 (q, C-4). Anal. Calcd for $C_{21}H_{21}NO_3$: C, 75.21; H, 6.31; N, 4.18. Found: C, 74.46; H, 6.30; N, 4.15.

B. Preparation from 1a and 1b. To a 76:24 mixture of **1a** and **1b** (110 mg, 2.5 mmol) in 5 mL of THF was added 0.25 mL of 1 M LiHMDS in tetrahydrofuran. After 2 h of stirring at ambient temperature, the reaction mixture was treated with ether, washed with water, dried ($MgSO_4$), filtered, and concentrated. The crude material was chromatographed by preparative TLC (ethyl acetate/hexane, 3:7) to give 40 mg of **4** (48%).

Diels-Alder Reaction of 4 with *N*-Phenylmaleimide. A solution of **4** (1.0 g, 3.0 mmol) and *N*-phenylmaleimide (0.78 g, 4.5 mmol) in 10 mL of benzene was heated at reflux for 21 h. The solution was concentrated, and 10% of the product was purified on silica gel (ethyl acetate/hexane; 45:55). The major band was isolated, giving 77 mg of **8** (51% yield). With the exception of the isomer described below, each UV-active or H_2SO_4-charring impurity constituted <5% of the product. Upon standing the product solidified (mp 80-95 °C, dec). The lactone structure was inferred by ^1H NMR, IR, and literature precedence.[8,9] A 2D-COSY NMR experiment was run on this compound in order to make the ^1H assignments listed below; $[\alpha]^{20}_D$ -104° (c 0.70 CH_2Cl_2); MS, *m/e* 509 (M + 1), 537 (M + 29); IR (KBr) λ_{max} 3300-3550 cm^{-1} (N-H stretch); 2900-3000: 2250 (CN); 1777 (lactone stretch); 1678, 1600 (amide stretch), 1547 (N-H bend); 1497; 1444; 1200. ^1H NMR δ 3.16 (t, 1 H, *J* = 4.8 Hz, *CH*CONH), 3.30 (ddd, 1 H, *J* = ca. 0.5, ca. 1.0, 8.8 Hz, H_b coupled with C=C*H*, H_a, and $CHCO_2$),[12] 3.64 and 3.81 (both dd, *J* = 2.2, 11.0 Hz, 1 H each, CH_2OCH_2Ph coupled geminally and with H_a), 3.8 (m, 1 H, $CHCO_2$), 3.90 (ddd, 1 H, *J* = 5.2, 5.2, 1.5 Hz, *CH*CN coupled with *CH*CON and C=C*H*), 4.47 (d, 1 H, *J* = 12.0 Hz), 4.58 (d, 1 H, *J* = 12.0 Hz), 4.73 (d, 1 H, *J* = 11.2 Hz), 4.80 (d, 1 H, *J* = 11.3 Hz), 4.89 (q, 1 H, *J* = 2.3 Hz, H_a), 5.01 (dd, 1 H, *J* = ca. 0.3, 5.3 Hz, C=C*H*), 7.12 (t, 1 H, *J* = 7.3 Hz, 4-*H*PhNH), 7.2-7.4 (m, 12 H), 7.60 (d, 2 H, *J* = 8.6 Hz, 2-*H*PhNH), 10.0-10.4 (br s, 1 H, N*H*) [Irradiation of the resonance at 3.63 ppm resulted in enhancements of 5% and 8% at 3.33 and 4.88 ppm, respectively. Irradiation at 3.83 ppm gave enhancements of 9% and 10% at 3.33 and 4.88 ppm, respectively]; 90.6-MHz ^{13}C NMR δ 27.4 (d), 39.8 (d), 43.5 (d), 70.0 (t), 71.2 (t), 73.7 (t), 81.1 (d), 92.1 (d), 118.1 (q), 120.7 (d), 127-129 (d, 14C), 135.5 (q), 137.2 (q), 137.6 (q), 155.0 (q), 167.0 (q), 176.6 (q). Anal. Calcd for $C_{31}H_{28}N_2O_5$: C, 73.21; H, 5.55; N, 5.51. Found: C, 73.79; H, 6.03; N, 5.20. High-resolution mass spectrum, *m/e* calcd for $C_{31}H_{28}N_2O_5$ 508.19982, found 508.19240.

Also isolated was 24 mg (16%) of an isomeric material that did not convert to **8** upon continued refluxing in benzene, although there was decomposition to several near-origin spots on TLC (ethyl acetate/hexane; 45:55). It did not have the N*H* singlet at 10-10.4 ppm in the ^1H NMR spectrum, as does **8**: mp 50-65 °C dec; MS, *m/e* 509 (M + 1); IR (KBr) λ_{max} 3280-3550 cm^{-1}, 2880-2970, 1777, 1693, 1601, 1545, 1499, 1445, 1162; ^1H NMR δ 2.7 (m, 2 H), 3.27 (m, ca. 1 H), 3.39-4.09 (m, ca. 4 H), 4.37-4.62 (m, 2 H), 4.66-4.87 (m, 2 H), 5.17 (m, ca. 1 H), 7.1 (d, ca. 1 H), 7.16-7.40 (m, ca. 12 H), 7.5-7.64 (m, ca. 1 H). High-resolution mass spectrum, *m/e* calcd for $C_{31}H_{28}N_2O_5$ 508.19982, found 508.20001.

Acknowledgment. We thank Dr. G. Caldwell and J. Masucci for mass spectral results and M. S. Mutter for ^1H NMR data. We also thank Professors R. W. McClard (Reed College) and R. W. Franck (Hunter College) for helpful suggestions.

Registry No. **1a**, 110116-77-3; **1b**, 110116-78-4; **2**, 37776-25-3; **4**, 110116-79-5; **8**, 110116-80-8; diethyl (cyanomethyl)phosphonate, 2537-48-6; *N*-phenylmaleimide, 941-69-5.

(12) Professor Franck (private communication, 1986) has indicated that the ^1H NMR data of his lactones[8] were actually for compounds epimeric at the carbon bearing the CONHPh functionality. The correct coupling constant for H_a and H_b of the trans-configured major isomer is 2.4 Hz (instead of 7.3 Hz).

Chemistry of 3,4-Epoxy Alcohols. Fragmentation Reactions

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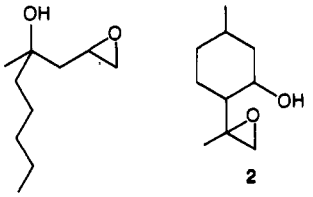
Recent interest in the chemistry of 3,4-epoxy alcohols has centered on applications toward the synthesis of the taxane ring system,[1] on models for the biosynthesis of secolongifolene[2] and the antitumor xanthanolides,[3] and on studies related to the structural effects governing the formation of oxetanes[4] and fragmentation products.[5-7] Despite this attention, factors favoring fragmentation over other possible reaction pathways (e.g., addition to epoxide) need to be more clearly recognized.[5,6] To this end, we have treated selected 3,4-epoxy alcohols with excess aluminum isopropoxide and report herein some significant results.

1,2-Epoxy-4-hydroxy-4-methylnonane (**1**) was prepared by addition of allylmagnesium bromide to 2-heptanone followed by epoxidation of the tertiary alcohol with MCPBA.[5] Compound **1**, presumably a mixture of stereoisomers, was treated with 5 equiv of aluminum isopropoxide in refluxing toluene for 70 h. A complex mixture of products resulted, containing a 33% yield (by GC) of 2-heptanol, identified by GC/MS analysis and by GC comparison to authentic material. 2-Heptanol is formed in this reaction by a Grob-type fragmentation followed by a Meerwein-Ponndorf reduction of 2-heptanone.[8] We have reported that the action of potassium *tert*-butoxide converted **1** into the oxetane (by intramolecular nucleophilic addition) and the *tert*-butoxide adduct, with no detectable fragmentation.[5] Thus, for fragmentation to

(1) Holton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 5731.
(2) Yadav, J. S.; Chawla, H. P. *Indian J. Chem., Sect. B* **1983**, *22B*, 212.
(3) Herz, W. *Isr. J. Chem.* **1977**, *16*, 32.
(4) Masamune, T.; Ono, M.; Sato, S.; Murai, A. *Tetrahedron Lett.* **1978**, 371; *J. Chem. Soc., J. Chem. Commun.* **1976**, 864; *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2895.
(5) Waddell, T. G. *Tetrahedron Lett.* **1985**, *26*, 6277.
(6) Holton, R. A.; Kennedy, R. M. *Tetrahedron Lett.* **1984**, *25*, 4455.
(7) Patil, D. G.; Chawla, H. P.; Dev, S. *Indian J. Chem., Sect. B.* **1983**, *22B*, 206.
(8) Holland, H. L.; Khan, S. R. *Can. J. Chem.* **1985**, *63*, 2763.

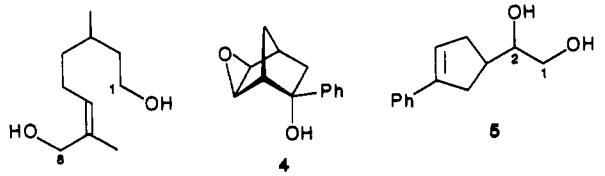
0022-3263/87/1952-4802$01.50/0

occur here, a Lewis *acid* is required.



1 2

Epoxidation of commercially available isopulegol with MCPBA provided isopulegol epoxide (2), homogeneous on TLC, but a mixture of diastereomers by NMR analysis. Treatment of 2 in the usual way with aluminum isopropoxide afforded a 97% crude yield of 8-hydroxycitronellol (3) as a 2:1 mixture of *Z*/*E* isomers (homogeneous on TLC). NMR and MS analyses of 3 and its diOTMS derivative confirmed the structure (see the Experimental Section). In addition, compound 3 was one of the products formed by SeO_2 oxidation of citronellol (TLC analysis). 8-Hydroxycitronellol (3) must be produced by an efficient Lewis acid induced fragmentation followed by reduction.[8] It is interesting to note that the starting material 2 gave no reaction with the strong base potassium *tert*-butoxide.[5]



3(*Z*) 4 5

As reported earlier 2-*endo*-hydroxy-2-*exo*-phenyl-5,6-epoxybicyclo[2.2.1]heptane (4) gave only the corresponding oxetane by intramolecular cyclization when treated with potassium *tert*-butoxide.[5] However, when 4[5] was treated with excess aluminum isopropoxide in refluxing toluene, the novel rearrangement product 5 was obtained in good yield (81%) as a pair of diastereomers (see the Experimental Section). We propose that the point of isomerism is C-2 (see 5) since in excess aluminum isopropoxide, reversible Meerwein–Ponndorf hydride transfers can take place at this carbon producing *R* and *S* configurations.[8]

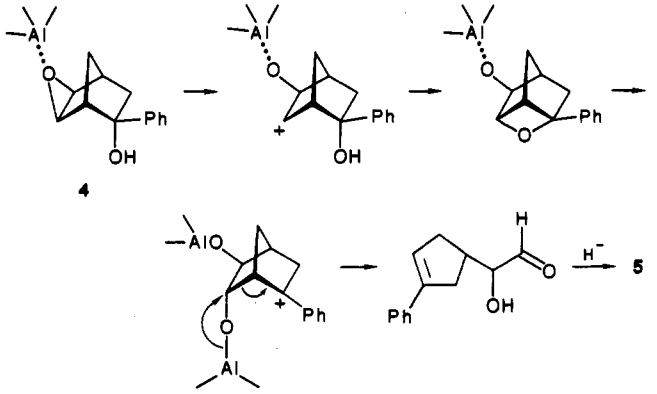
A likely mechanism for the conversion of 4 to 5 is shown in Scheme I. The intermediacy of the oxetane is supported by the fact that 4 readily forms this structure in base- or acid-promoted reactions.[5] The driving force for this new rearrangement appears to be the transient production of a tertiary benzylic carbocation and the ultimate carbonyl formation in the fragmentation step.

In addition, we have shown that those 3,4-epoxy alcohols that resist fragmentation with the base potassium *tert*-butoxide do fragment with the Lewis acid aluminum isopropoxide. Thus, these successful Grob fragmentations of 3,4-epoxy alcohols are initiated by electrophilic attack of the Lewis acid on the epoxide oxygen, as illustrated in the first step of the scheme.

Experimental Section

All melting points are uncorrected. IR spectra were recorded with a Beckman FT 1100 instrument, and NMR data were obtained on a JNM-PMX60 JEOL spectrometer (signals reported in ppm from TMS as an internal standard). The UV spectra were recorded using a Hitachi 100-80 spectrophotometer. The ^{13}C NMR spectra were run in the Department of Chemistry, University of Tennessee, Knoxville, TN, and GC/MS data were obtained from the Laboratory of Chemistry, National Institutes of Health, Bethesda, MD, using an LKB-Bromma 2091 instrument. The column was a HP ultraperformance capillary (25 m × 0.31 mm) packed with cross-linked methyl silicone. The temperature was

Scheme I



programmed from 70 to 270 °C at 10 °C/min. Combustion analyses were performed by Galbraith Laboratories, Knoxville, TN.

Fragmentation of 1,2-Epoxy-4-hydroxy-4-methylnonane (1). To a solution of 0.240 g of 1 (1.4 mmol) in 10 mL of dry toluene was added dropwise by syringe a solution of 1.438 g (7.05 mmol) of freshly distilled aluminum isopropoxide in 12 mL of dry toluene. The resulting solution was stirred and refluxed under N_2 for 70.5 h, cooled to room temperature, and poured into 50 mL of 1 M HCl. After shaking, the layers were separated, and the aqueous phase was extracted with 2 × 20 mL of ether. The combined organic phases were washed with water, dried ($MgSO_4$), and carefully concentrated under reduced pressure. The final toluene solution was subjected to GC/MS analysis where 2-heptanol was determined to be present (33% yield). TLC indicated 2-heptanol and a complex mixture of lower R_f products.

Preparation of Isopulegol Epoxide (2). To a solution of 0.507 g isopulegol (Aldrich, 3.29 mmol) in 5 mL of CH_2Cl_2 at 0 °C was added dropwise over 17 min a chilled solution of 0.833 g MCPBA (4.80 mmol) in 15 mL of CH_2Cl_2. The reaction mixture was left at 4 °C for 21 h and gravity filtered. After dilution with Et_2O, the filtrate was washed with 35 mL of saturated $NaHSO_3$ and three times with saturated $NaHCO_3$. The total aqueous phase was extracted with 10 mL of CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$), filtered, and evaporated to dryness. Isopulegol epoxide (0.453 g, 81%) was a clear, colorless oil, a single circular spot on TLC (solvent Et_2O, R_f 0.75): IR (neat) 3420 (OH), 869 (epoxide) cm^{-1}; NMR (CCl_4) δ 3.60 (1 H, complex, HCO), 2.77 (2 H, complex, epoxide CH_2), 1.40 (s, CH_3CO), 1.05 (d, CH_3CH). The complex nature of the epoxide CH_2 signal implied that stereoisomers were present.

Fragmentation of Isopulegol Epoxide (2). A solution of 2.63 g (12.9 mmol) of distilled aluminum isopropoxide in 12 mL of dry toluene was added slowly by syringe to a solution of 2 (0.450 g, 2.64 mmol) in 15 mL of dry toluene. The resulting solution was stirred and refluxed under N_2 for 70.5 h and worked up as described for 1, except that the final organic solution was evaporated to dryness. The product 3 was a thick oil (0.436 g, 97%), a single, circular spot on TLC (Et_2O, R_f 0.66). This oil was chromatographed on silica gel, eluting with Et_2O to obtain an analytical sample. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.77; H, 11.62. Found: C, 69.73; H, 11.34.

Compound 3: positive Baeyer test; IR (neat) 3350 (OH), 1653 (C=C) cm^{-1}; NMR (CCl_4) δ 5.1 (1 H, complex, H-6), 3.8, 3.9 (2 H, 2 s, H-8, *E*/*Z* isomers, 1:2 ratio),[9] 3.5 (2 H, t, J = 5 cps, H-1),[10] 1.66, 1.57 (H-7, CH_3, 2 isomers), 0.87 (H-3, CH_3). GC/MS analysis showed two isomeric compounds (2:1) with nearly identical mass spectra, m/z 154 $(M - H_2O)^{\cdot+}$, 139 $(M - H_2O - CH_3)$, 121, 109, 82. Compound 3 readily formed a diOTMS derivative, which gave two peaks in the GC (2:1). As expected for *Z*/*E* isomers, the MS of each component was nearly identical and confirmed the structural assignment, m/z 316 (M^+), 226 $(M^+ - HOTMS)$, 211, 169, 156, 143 (base peak, $CH{=}C(CH_3)CH_2OTMS^{\cdot+}$), 121, 117 $(CH_2CH_2OTMS^{\cdot+})$, 103 $(CH_2OTMS)^{\cdot+}$.

(9) Bhalerao, U.; Rapoport, H. *J. Am. Chem. Soc.* **1971**, *93*, 4835.
(10) Pouchert, C. J. *Aldrich Library of NMR Spectra*; Aldrich: Milwaukee, 1983; p 135.

Fragmentation of 4. A solution of distilled aluminum isopropoxide (2.57 g, 12.6 mmol) in 15 mL of dry toluene was added slowly by syringe to a solution of **4**[5] (0.504 g, 2.5 mmol) in 15 mL of dry toluene. This mixture was stirred and refluxed under N_2 for 71 h and worked up as described above. The product (**5**) was a pale yellow oil (0.409 g, 81%, one spot on TLC), which slowly began depositing crystalline material, assisted by ether trituration.

Crop 1: mp 106-107 °C (recrystallized from Et_2O); 0.110 g; positive Baeyer and CrO_3 tests. Anal. Calcd for $C_{13}H_{16}O_2 \cdot 0.1H_2O$: C, 75.80; H, 7.87. Found: C, 75.48; H, 7.89. IR (mull) 3200, 1600, 751, 723, 692 cm^{-1}; ^1H NMR δ 7.35 (5 H, aromatic), 6.12 (1 H, br s, olefinic H), 3.70 (3 H, complex, HCO), 2.60 (5 H, complex) (the complex pattern at 3.70 ppm was nearly identical with that found at the same chemical shift in the NMR spectra of model 1,2 glycols);[11] ^{13}C NMR δ 35.8, 35.9, 40.6 (alkane), 65.6, 76.0 (CO), 124.3, 136.3 (alkene), 125.5, 127.0, 128.3, 141.7 (aromatic); UV λ_{max} 246 nm (ϵ 17 500) (styrene chromophore).[12]

Crop 2: mp 82-84 °C (recrystallized from Et_2O); 0.052 g; positive Baeyer test. Anal. Calcd for $C_{13}H_{16}O_2 \cdot 0.1H_2O$: C, 75.80; H, 7.87. Found: C, 75.98; H, 7.92. IR (mull) 3348, 1600, 761, 723, 694 cm^{-1}; UV λ_{max} 247 nm; ^1H NMR δ 7.35 (5 H, aromatic), 6.12 (1 H, br s, olefinic H), 3.65 (3 H, complex, HCO), 2.60 (5 H, complex); ^{13}C NMR δ 35.7, 35.9, 40.6 (alkane), 65.7, 75.9 (CO), 124.9, 136.2 (alkene), 125.5, 127.0, 128.3, 141.2 (aromatic).

Acknowledgment. We express appreciation to Taysir Jaouni, Dr. H. M. Fales (NIH), and L. Jay Stewart (University of Tennessee) for assistance in obtaining spectral data. We also thank Tony Zimmerman for his help during the course of this work.

(11) Reference 9, p 127c.
(12) Williams, D. H.; Fleming, I. *Spectroscopic Methods in Organic Chemistry*, 3rd ed.; McGraw-Hill: London, 1980; p 24.

Reaction of β-Hydroxy α-Amino Acid Derivatives with (Diethylamino)sulfur Trifluoride (DAST). Synthesis of β-Fluoro α-Amino Acids

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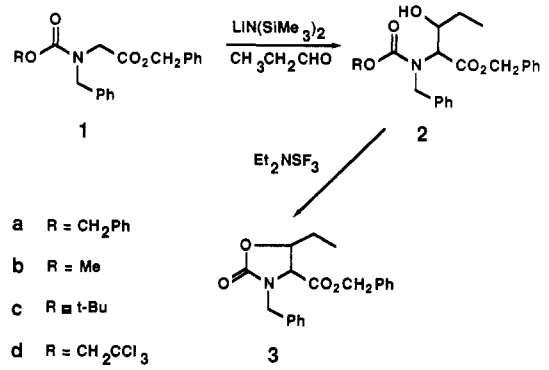
Amino acids that bear fluorine at a β-carbon can act as mechanism-based irreversible inactivators of certain enzymes and can block important metabolic pathways.[1] For example, alanine racemase, an enzyme which provides D-alanine for bacterial cell wall formation, is inactivated by β-fluoroalanine and its analogues.[2] Such chemotherapeutic potential has encouraged development of methods for synthesis of α-amino acids bearing the β-fluorine directly on the parent side chain. Previous approaches include the following: ammonolysis of 2-bromo-3-fluoro carboxylic acids;[3] reaction of azirines,[4] aziridines[5] or glycidonitriles[5b,6] with hydrogen fluoride in pyridine; fluorodehydroxylation or -desulfurization of β-hydroxy or β-thiol amino acids with sulfur tetrafluoride in liquid hydrogen fluoride;[7,8] reductive amination of fluoropyruvic acids;[5c,9] and fluoroalkylation of glycinate anions.[10] Although generally applicable, these procedures often require special precautions due to the toxicity of the reagents. The present work describes the use of the mild fluorinating agent, (diethylamino)sulfur trifluoride (DAST),[11] for synthesis of aliphatic β-fluoro amino acids.

Scheme I



As a mild reagent for substitution of hydroxyl groups by fluorine, DAST has been employed extensively in the synthesis of fluorinated carbohydrates[12] but has not been utilized on a general basis in the preparation of free β-fluoro α-amino acids from corresponding β-hydroxy derivatives.[13] Previous studies on the reaction of DAST with N-protected β-hydroxy amino acid esters have usually yielded[13] the corresponding dehydro compounds[14] or the rearranged α-fluoro β-amino acids.[15] However, since the dehydration occurred in the presence of pyridine and the rearrangement required a nucleophilic amino group, we decided to investigate the reaction in the absence of amines.

Initially the enolate of benzyl [*N*-benzyl-*N*-(benzyloxycarbonyl)glycinate (**1a**) was generated ($LiN(SiMe_3)_2$, THF, -78 °C) and condensed with propionaldehyde to afford **2a**

(1) (a) Kollonitsch, J. In *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Ed.; Kodansha: Tokyo, 1982; pp 93-125. (b) Walsh, C. *Adv. Enzymol. Relat. Areas Mol. Biol.* **1983**, *55*, 197-289. (c) Walsh, C. *Annu. Rev. Biochem.* **1984**, *53*, 493-535. (d) Bey, P. *Ann. Chim. Fr.* **1984**, *9*, 695-702. (e) Rathod, P. K.; Tashjian, A. H., Jr.; Abeles, R. H. *J. Biol. Chem.* **1986**, *261*, 6461-6469.
(2) See references in: (a) Esaki, N.; Walsh, C. T. *Biochemistry* **1986**, *25*, 3261-3267. (b) Flynn, G. A.; Beight, D. W.; Bohme, E. H. W.; Metcalf, B. W. *Tetrahedron Lett.* **1985**, *26*, 285-288.
(3) Gershon, H.; McNeil, M. W.; Bergman, E. D. *J. Med. Chem.* **1973**, *16*, 1407-1409.
(4) (a) Wade, T. N.; Guedj, R. *Tetrahedron Lett.* **1979**, 3953-3954. (b) Wade, T. N.; Kheribet, R. *J. Org. Chem.* **1980**, *45*, 5333-5335.
(5) (a) Ayi, A. I.; Guedj, R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2045-2051. (b) Guedj, R.; Ayi, A. I.; Remli, M. *Ann. Chim. Fr.* **1984**, *9*, 691-694. (c) Tsushima, T.; Kawada, K.; Nishikawa, J.; Sato, T.; Tori, K.; Tsuji, T.; Misaki, S. *J. Org. Chem.* **1984**, *49*, 1163-1169.
(6) Ayi, A. I.; Remli, M.; Guedj, R. *Tetrahedron Lett.* **1981**, *22*, 1505-1508.
(7) (a) Kollonitsch, J.; Marburg, S.; Perkins, L. M. *J. Org. Chem.* **1977**, *44*, 771-777. (b) Vidal-Cros, A.; Gaudry, M.; Marquet, A. *Ibid.* **1985**, *50*, 3163-3167.
(8) Kollonitsch, J.; Marburg, S.; Perkins, L. M. *J. Org. Chem.* **1976**, *41*, 3107-3111.
(9) Dolling, U. H.; Douglas, A. W.; Grabowski, E. J. J.; Schoenewaldt, E. F.; Sohar, P.; Sletzinger, M. *J. Org. Chem.* **1978**, *43*, 1634-1640.
(10) O'Donnell, M. J.; Barney, C. L.; McCarthy, J. R. *Tetrahedron Lett.* **1985**, *26*, 3067-3070.
(11) Middleton, W. J. *J. Org. Chem.* **1975**, *40*, 574-578.
(12) For some examples, see references in: (a) Klemm, G. H.; Kaufman, R. J.; Sidhu, R. S. *Tetrahedron Lett.* **1982**, *23*, 2927-2930. (b) Card, P. J. *J. Org. Chem.* **1983**, *48*, 393-395. (c) Rosenbrook, W., Jr.; Riley, D. A.; Lartey, P. A. *Tetrahedron Lett.* **1985**, *26*, 3,4. (d) Posner, G. H.; Haines, S. R. *Ibid.* **1985**, *26*, 5-8.
(13) Fluoro-dehydroxylation with DAST has been used in the preparation of β-fluorovaline methyl ester and β-fluorophenylalanine methyl ester from diketopiperazine bis(lactim ether) derivatives (Groth, U.; Schöllkopf, U. *Synthesis* **1983**, 673-675). However, saponification of such methyl ester products frequently leads to decomposition with loss of fluoride.[5c,10] Dehydration during the DAST reaction was also observed.
(14) Somekh, L.; Shanzer, A. *J. Org. Chem.* **1983**, *48*, 907-908.
(15) Somekh, L.; Shanzer, A. *J. Am. Chem. Soc.* **1982**, *104*, 5836-5837.

0022-3263/87/1952-4804$01.50/0