crude **7** which was used in the next reaction without further purification.

Excess pyridine (2.4 g, 30 mmol) was added to a stirred solution of crude **7** (4 mmol) in 25 mL of dry CH_2Cl_2. Stirring was continued for 24 h at room temperature. The solution was washed twice with 0.1 N aqueous HCl (50 mL) and the organic layer was separated and dried (Na_2SO_4). After evaporation of the solvent, the dioxopiperazines were isolated either by column chromatography (**8d** and **8f**) on silica gel (Merck, Kieselgel H, CH_2Cl_2/CH_3OH 98:2 v/v as eluent) or by precipitation. To the stirred residue were added 5 mL of methanol and some water just to the point of turbidity. The precipitate was collected and washed several times with a 5% aqueous $NaHCO_3$ solution and then with water to give the dioxopiperazines **8** which were homogeneous on TLC (CH_2Cl_2/CH_3OH, 96:4 v/v). Recrystallization was achieved by using CH_2Cl_2/hexane mixtures. One isomer only crystallized with **8d** and **8f** as determined by using ytterbium tris-1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate as a ^1H NMR shift reagent. For the overall yields, melting points, and elemental analyses see Table I.

8a: ^1H NMR δ 7.39 (s, 10 H, 2 C_6H_5), 4.99 (s, 4 H, 2 $CH_2C_6H_5$), 3.98 (s, 4 H, 2 CH_2); IR (KBr) 1675 cm^{-1} (C=O); mass spectrum, *m/e* 326 $[M]^+\cdot$, 234 $[M - C_7H_8]^+\cdot$, 220 $[M - C_6H_5CHO]^+\cdot$, 181 $[C_{14}H_{13}]^+\cdot$, 91 $[C_7H_7]^+$.

8b,c: ^1H NMR δ 7.39 and 7.40 (2 s, 10 H, 2 C_6H_5), 4.99 (AB, 2 H, $CH_2C_6H_5$), 4.96 (s, 2 H, $CH_2C_6H_5$), 3.99 (q, 1 H, $CHCH_3$), 3.95 (s, 2 H, CH_2), 1.50 (d, 3 H, CH_3); IR (KBr) 1680 cm^{-1} (C=O); mass spectrum, *m/e* 340 $[M]^+\cdot$, 248 $[M - C_7H_8]^+\cdot$, 234 $[M - C_6H_5CHO]^+\cdot$, 181 $[C_{14}H_{13}]^+\cdot$, 91 $[C_7H_7]^+$.

8d: ^1H NMR δ 7.39 (s, 10 H, 2 C_6H_5), 4.97 (AB, 4 H, 2 $CH_2C_6H_5$), 3.99 (q, 2 H, 2 $CHCH_3$), 1.55 (d, 6 H, 2 CH_3); IR (KBr) 1675 cm^{-1} (C=O); mass spectrum, *m/e* 354 $[M]^+\cdot$, 262 $[M - C_7H_8]^+\cdot$, 248 $[M - C_6H_5CHO]^+\cdot$, 181 $[C_{14}H_{13}]^+\cdot$, 91 $[C_7H_7]^+$. Second isomer: ^1H NMR δ 7.39 (s, 10 H, 2 C_6H_5), 4.97 (s, 4 H, 2 $CH_2C_6H_5$), 4.03 (q, 2 H, 2 $CHCH_3$), 1.53 (d, 6 H, 2 CH_3).

8e: ^1H NMR δ 7.39 and 7.40 (2 s, 10 H, 2 C_6H_5), 4.99 (s, 2 H, $CH_2C_6H_5$), 4.94 (AB, 2 H, $CH_2C_6H_5$), 4.01 (s, 2 H, CH_2), 3.85 (d, 1 H, CHN), 2.48 [m, 1 H, $CH(CH_3)_2$)], 1.01 and 0.94 (2 d, 6 H, 2 CH_3); IR (KBr) 1670 cm^{-1} (C=O); mass spectrum, *m/e* 368 $[M]^+\cdot$, 276 $[M - C_7H_8]^+\cdot$, 262 $[M - C_6H_5CHO]^+\cdot$, 181 $[C_{14}H_{13}]^+\cdot$, 91 $[C_7H_7]^+$.

8f: ^1H NMR δ 7.39 (s, 10 H, 2 C_6H_5), 4.96 (s, 2 H, $CH_2C_6H_5$), 4.95 (AB, 2 H, $CH_2C_6H_5$), 4.13 (q, 1 H, $CHCH_3$), 3.87 (d, 1 H, CHN), 2.55 [m, 1 H, $CH(CH_3)_2$], 1.59 (d, 3 H, CH_3), 1.03 and 0.95 (2 d, 6 H, 2 CH_3); IR (KBr) 1675 cm^{-1} (C=O); mass spectrum, *m/e* 382 $[M]^+\cdot$, 290 $[M - C_7H_8]^+\cdot$, 276 $[M - C_6H_5CHO]^+\cdot$, 181 $[C_{14}H_{13}]^+\cdot$, 91 $[C_7H_7]^+$. Second isomer: ^1H NMR δ 7.39 (s, 10 H, 2 C_6H_5), 5.02 (AB, 2 H, $CH_2C_6H_5$), 4.96 (s, 2 H, $CH_2C_6H_5$), 4.13 (q, 1 H, $CHCH_3$), 3.94 (d, 1 H, CHN), 2.55 [m, 1 H, $CH(CH_3)_2$], 1.57 (d, 3 H, CH_3), 1.06 and 0.99 (2 d, 6 H, 2 CH_3).

1,4-Dihydroxy-2,5-dioxopiperazine (9a). A solution of **8a** (652 mg, 2 mmol) in 50 mL of dioxane was treated at room temperature and atmospheric pressure with H_2 and 10% Pd/C (50 mg) until 90 mL of H_2 (4 mmol) had been consumed, which took about 2 h. During this procedure **9a** precipitated. This precipitate and the catalyst were collected and separated by thorough washing with water. The dioxane and water layers were combined and the solvents evaporated. The residue was crystallized from hot CH_3OH to give **9a** (257 mg, 1.76 mmol), which was homogeneous on TLC ($BuOH/AcOH/H_2O$ 4:1:1 v/v): mp 180 °C dec; ^1H NMR (D_2O) δ 4.44 (s); IR (KBr) 3050 and 2700 (OH), 1690 and 1655 cm^{-1} (C=O); mass spectrum, *m/e* 146 $[M]^+\cdot$, 118 $[M - CO]^+\cdot$. Anal. Calcd for $C_4H_6N_2O_4$: C, 32.88; H, 4.14; N, 19.17. Found: C, 33.19; H, 4.14; N, 19.23.

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Registry No. 1 (R_1 = H), 298-12-4; 1 (R_1 = CH_3), 127-17-3; 1 (R_1 = i-C_3H_7), 759-05-7; **2** (R_1 = H), 77845-97-7; **2** (R_1 = CH_3), 77845-98-8; (*E*)-**2** (R_1 = i-C_3H_7), 77845-99-9; (*Z*)-**2** (R_1 = i-C_3H_7), 77846-00-5; **3** (R_1 = H), 77846-01-6; **3** (R_1 = CH_3), 77846-02-7; **3** (R_1 = i-C_3H_7), 77846-03-8; **4** (R_1 = H), 77846-04-9; **4** (R_1 = CH_3), 77846-05-0; **4** (R_1 = i-C_3H_7), 77846-06-1; **5** (R_2 = H), 77846-07-2; **5** (R_2 = CH_3), 77846-08-3; **6a**, 77846-09-4; **6b**, 77846-10-7; **6c**, 77846-11-8; **6d**, 77846-12-9; **6e**, 77846-13-0; **6f**, 77846-14-1; **7a**, 77846-15-2; **7b**, 77846-16-3; **7c**, 77846-17-4; **7d**, 77846-18-5; **7e**, 77846-19-6; **7f**, 77846-20-9; **8a**, 77846-21-0; **8b/8c**, 77846-22-1; **8d** (isomer 1), 77846-23-2; **8d** (isomer 2), 77846-24-3; **8e**, 77846-25-4; **8f** (isomer 1), 77846-26-5; **8f** (isomer 2), 77846-27-6; **9a**, 77846-28-7; benzylhydroxylamine·HCl, 2687-43-6.

Improved Preparation of (+)-(*R*)-Methyloxirane

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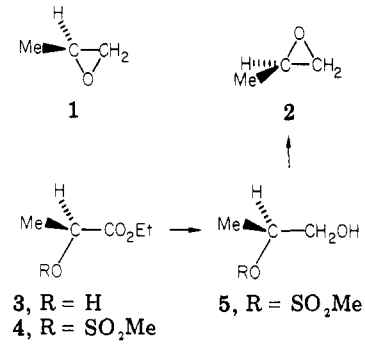
In the course of studies directed toward the synthesis of some macrocyclic dilactone antibiotics[1] we had need of optically active methyloxirane as a convenient chiral starting material.[2] Although preparations[3,4] for both (−)-(*S*)-methyloxirane (**1**) and (+)-(*R*)-methyloxirane (**2**)



3, R = H
4, R = SO_2Me
5, R = SO_2Me

have been reported, the methods reported for the latter are tedious and inefficient. Since the readily available ethyl (+)-(*S*)-lactate (**3**)[5] is a convenient precursor for (−)-(*S*)-methyloxirane, we investigated the possibility of also using this ester for the preparation of (+)-(*R*)-methyloxirane and herein report a rapid and efficient preparation for this useful chiral material in an overall yield of 71% from **3**.

Reaction of ethyl (+)-(*S*)-lactate (**3**) with methanesulfonyl chloride in toluene in the presence of triethylamine afforded the (−)-(*S*)-mesylate (**4**)[6] in 98% yield after distillation at reduced pressure. By this means, the chiral center was prepared for inversion during the epoxide-forming step. Selective reduction of the ethyl ester was

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(5) Aldrich Chemical Co. ethyl (+)-(*S*)-lactate, $[\alpha]^{20}_D$ −12° (neat). The observed rotation for this material was $[\alpha]^{22}_D$ −11.2°. The rotations for ethyl lactate vary due to the presence of impurities with high resolutions, e.g., the dimer 2,5-dimethyl-1,4-dioxane-3,6-dione, $[\alpha]_D$ −298°. See reference 4a.

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accomplished by reaction with AlH_3/THF at 0 °C for 30 min to afford (S)-2-(mesyloxy)-1-propanol (5) in high yield. This material proved to be extremely sensitive and decomposed vigorously upon attempted distillation[7]; however, it was smoothly converted to (+)-(R)-methyloxirane (2) upon slow addition to 66% aqueous KOH at 70 °C in a flask equipped with a distillation head. Redistillation of the wet distillate from KOH pellets afforded a 71% overall yield of 2 [bp 33-34 °C (730 mm); $[\alpha]^{22}_D$ +13.0° (neat)],[4,8] from ethyl (+)-(S)-lactate (3). The conditions for the cyclizations are critical since 5 appears to be extremely prone to polymerization under basic conditions. Attempts to form the epoxide under a variety of conditions (NaH/DMF, Na/ethylene glycol, KO-t-amyl/t-amyl alcohol, DBU/diglyme, Na_2CO_3/H_2O, K_2CO_3/EtOH, $LiN(SiMe_3)_2$) resulted in poor yields of epoxide.

Experimental Section

General Methods. Boiling points are uncorrected. Infrared spectra were obtained on films by using a Beckman Acculab 1 spectrophotometer. Nuclear magnetic resonance spectra were obtained in $CDCl_3/Me_4Si$ on a Varian Associates EM-360 spectrometer. Gas chromatograms were obtained on a Varian Aerograph Series 1700 instrument using 3 mm × 2.2 m glass columns packed with 3% OV-17 on 80/100 Chromosorb W-HP. Optical rotations were obtained on a Rudolph polarimeter in 1-dm cuvettes. Thin-layer chromatograms were run by using 250-μm Merck precoated silica gel layers.

Ethyl (-)-(S)-2-(Mesyloxy)propanoate (4). Redistilled ethyl (+)-(S)-lactate (3; 82.0 g, 0.695 mol) was combined with triethylamine (111.0 mL, 0.798 mol) in 1 L of toluene in a 2-L round-bottomed flask equipped with a magnetic stirrer. The mixture was cooled in an ice bath while methanesulfonyl chloride (56.6 mL, 0.73 mol) was added over a 15-min period. The light orange solution was kept an additional hour in the ice bath and then stored in a freezer (-15 °C) overnight. The mixture was then allowed to warm to room temperature, filtered (suction), and concentrated at reduced pressure to a light brown oil. Distillation through a 130-mm Vigreux column afforded 133 g (98%) of 4:[6] bp 75-76 °C (0.03 mm); $[\alpha]^{22}_D$ -52.9° (c 4.32, $CHCl_3$). This was shown by gas chromatography to be >99% pure (retention time, 2.0 min at 160 °C): NMR ($CDCl_3$) δ 5.15 (1 H, q, J = 7 Hz), 4.33 (2 H, q, J = 7.5 Hz), 3.15 (3 H, s), 1.62 (3 H, d, J = 7 Hz), 1.35 (3 H, t, J = 7.5 Hz).

(S)-2-(Mesyloxy)-1-propanol (5). The method of Brown[9] for the large-scale preparation of AlH_3 was modified. A 1-L three-necked flasked equipped with an N_2 inlet, a reflux condenser, and a large stirring bar was charged with 200 mL dry THF and 111.0 mL of a solution[10] of $LiAlH_4$ in THF (1.25 M, 0.139 mol). The flask was placed in an ice bath, and 100% H_2SO_4 (3.7 mL, 0.07 mol) was added cautiously. After 1 h, the mixture was cooled to -5 °C, and the ester 4 (23.5 g, 0.120 mol) in 50 mL THF was added during 10 min. After 30 min, the mixture was quenched with 20 mL of a 1:1 THF-H_2O solution followed by an additional 10-mL portion of H_2O and then stirred for 20 min before it was filtered (suction). The filter cake was washed with 100 mL of THF, 25 mL H_2O, and two additional 100-mL portions of THF. The filtrate was dried with anhydrous magnesium sulfate and concentrated at reduced pressure to afford 18.5 g of 5 as a yellow oil containing a small amount of suspended salts. This material could not be distilled without vigorous decomposition and was used directly in the next step without further handling. By thin-layer chromatography (25% petroleum ether-75% ether) the reaction was complete, and no ethyl ester remained: NMR ($CDCl_3$) δ 5.1-4.6 (1 H, m), 3.78 (2 H, d, J = 5 Hz), 3.15 δ (3 H, s), 2.92 (1 H, s), 1.42 (3 H, d, J = 7 Hz).

(+)-(R)-Methyloxirane (2). In a 250-mL round-bottomed flask equipped with a septum-sealed sidearm, a magnetic stirrer, and a distillation head were placed 100 g KOH and 50 mL of H_2O. The flask was heated to 70 °C, and then the mesylate 5 (18.5 g) was added dropwise with a syringe through the sidearm. The epoxide began to distill immediately. After the addition, a 25-mL portion of H_2O was added, and the temperature increased to 90 °C. After evolution of the epoxide ceased, the receiving flask was removed and the wet distillate redistilled from KOH pellets to afford 2: 5.0 g (72% from 4); bp 33-34 °C (730 mm); $[\alpha]^{22}_D$ +13.0° (neat)[8]; shown by gas chromatography to be >99% pure (retention time 0.5 min at 40 °C). This material was spectroscopically identical with a sample of racemic material.

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Registry No. 2, 15448-47-2; 3, 687-47-8; 4, 63696-99-1; 5, 77965-71-0.

(7) Havbrandt, O.; Osterman-Golkar, S.; Wachtmeister, C. A. *Acta Chem. Scand.* **1969**, *23*, 1072. These authors report vigorous decomposition of the racemic hydroxymesylates during attempted distillation. The compound appears to be stable below -15 °C for extended periods.

(8) Literature values reported for the rotation of (+)-(R)-methyloxirane are as follows: (a) $[\alpha]^{16}_D$ +12.53° (neat), Kumata, Y.; Furukawa, J.; Fueno, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3920. (b) $[\alpha]^{24}_D$ +13.9° (neat).[3a] (c) $[\alpha]^{20}_D$ +11.25° (neat).[3d] On the basis of our observed rotation for ethyl lactate, this preparation of (+)-(R)-methyloxirane was accomplished with no appreciable racemization.

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(10) Suspended material from $LiAlH_4$ if not removed by filtration results in reduced yield of 5.

Lithiation of *N,N*-Dimethylmethallylamine

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The generation of allylic anions derived from allylic ethers,[1] carbamates,[2] thioethers,[3] and amines[4] and their use as homoenolate equivalents have received widespread attention in recent years. In all these cases deprotonation takes place at the α position, producing typical allylic anions in which the α/γ-regioselectivity is determined by the nature of the metal as well as the character of the electrophile. Our recent interest in the dimetalation of *N-tert*-butylmethacrylamide[5] and its utility as a reagent have led to an investigation of reduced versions thereof, in particular of *N,N*-dimethylmethallylamine (1).

Only few related methallylic systems have been studied previously in terms of their metalation. *O*-Methallyl carbamates[2b] and *N*-methallylcarbazole[6] apparently behave very much like regular allylic systems in that their respective lithiated equivalents react both at the α and γ carbons with no observed reaction at the methyl group. The only known example of a methallylic system in which metalation occurs at the methyl group is that of methallyl alcohol.[7] Likely reasons for the modest yields reported are the heterogeneous character of the metalation reaction and the rather weak directing potential of the carbinol function, a property which has generally been recognized

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