silyl)chloroamine was prepared by the method of Wiberg and Raschig.[16]

Analytical Procedures. Conversions of carboxylic esters to their chloro derivatives were determined by GLC analysis on an HP 5830 gas chromatograph with SCOT columns (50 ft Carbowax or 50 ft DEGS). Complete separation of isomers was accomplished for the chloro esters up to dodecanoate and appeared in order from the 5 to the 12 isomer. For longer chain lengths (C_{14}–C_{18}), ω, ω-1, ω-2, and ω-3 isomers were completely separated from the mid-chain isomers.

Chlorinations. In a three-necked flask equipped with a thermometer and a mechanical stirrer and containing concentrated sulfuric acid (10 mL) was added the methyl ester (20 mmol) while the temperature was maintained below 5 °C via an ice–alcohol bath. The *N*-chlorodiisopropylamine (22 mmol) was then carefully added dropwise. The ferrous sulfate heptahydrate (2 mmol) was added, and the mixture was vigorously stirred. The ice bath was removed and the temperature rose to 34 °C within 2–5 min. After being stirred for 1 h, the mixture was poured over ice and extracted three times with methylene chloride (75 mL). The combined extracts were washed with water and dried over sodium sulfate, and the solvent was removed via a rotary evaporator at ambient temperature. Any free carboxylic acid present was esterified by diazomethane, and the crude product was analyzed by GLC. When amides were used as substrates, they were hydrolyzed and reesterified by refluxing with HCl/MeOH for 18 h.

Registry No. Methyl hexanoate, 106-70-7; methyl octanoate, 111-11-5; methyl decanoate, 110-42-9; methyl dodecanoate, 111-82-0; methyl tetradecanoate, 124-10-7; methyl hexadecanoate, 112-39-0; methyl octadecanoate, 112-61-8; methyl 6-chlorohexanoate, 14273-89-3; methyl 5-chlorohexanoate, 35783-67-6; methyl 4-chlorohexanoate, 71194-26-8; methyl 8-chlorooctanoate, 16195-75-8; methyl 7-chlorooctanoate, 67963-60-4; methyl 6-chlorooctanoate, 67963-59-1; methyl 10-chlorodecanoate, 71194-27-9; methyl 9-chlorodecanoate, 71194-28-0; methyl 8-chlorodecanoate, 71194-29-1; methyl 12-chlorododecanoate, 71194-30-4; methyl 11-chlorododecanoate, 71194-31-5; methyl 10-chlorododecanoate, 71194-32-6; methyl 14-chlorotetradecanoate, 71194-33-7; methyl 13-chlorotetradecanoate, 71194-34-8; methyl 12-chlorotetradecanoate, 71194-35-9; methyl 16-chlorohexadecanoate, 71194-36-0; methyl 15-chlorohexadecanoate, 71194-37-1; methyl 14-chlorohexadecanoate, 71194-38-2; methyl 18-chlorooctadecanoate, 71194-39-3; methyl 17-chlorooctadecanoate, 71194-40-6; methyl 16-chlorooctadecanoate, 71215-21-9; methyl nonanoate, 1731-84-6; nonanoamide, 1120-07-6; *N*-hydroxyethyl-*N*-methylnonanamide, 35627-81-7; *N*,*N*-bis(hydroxyethyl)nonanamide, 3077-37-0; *N*-[2-(2-hydroxyethoxy)ethyl]nonanamide, 32368-60-8; *N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-41-7; NCDA, 24948-81-0; *N*-chloro-2-ethoxy-*N*-(2-ethoxyethyl)ethanamine, 71194-42-8; methyl 4-(chloromethylamino)-3,5-dichlorobenzoate, 71194-43-9; *N*-chloro-*N*-methylacetamide, 5014-39-1; NCTs, 2350-10-9; TCIA, 87-90-1; TCM, 7673-09-8; TSCA, 4148-01-0; methyl 5-chlorononanoate, 71194-44-0; methyl 6-chlorononanoate, 71194-45-1; methyl 7-chlorononanoate, 71194-46-2; methyl 8-chlorononanoate, 63318-22-9; methyl 9-chlorononanoate, 22457-33-6; 4-chlorononanamide, 71194-47-3; 5-chlorononanamide, 71194-48-4; 6-chlorononanamide, 71194-49-5; 7-chlorononanamide, 71194-50-8; 8-chlorononanamide, 71194-51-9; 9-chlorononanamide, 71194-52-0; 5-chloro-*N*-(2-hydroxyethyl)-*N*-methylnonanamide, 71194-53-1; 6-chloro-*N*-(2-hydroxyethyl)-*N*-methylnonanamide, 71194-54-2; 7-chloro-*N*-(2-hydroxyethyl)-*N*-methylnonanamide, 71194-55-3; 8-chloro-*N*-(2-hydroxyethyl)-*N*-methylnonanamide, 71194-56-4; 9-chloro-*N*-(2-hydroxyethyl)-*N*-methylnonanamide, 71194-57-5; 5-chloro-*N*,*N*-bis(2-hydroxyethyl)nonanamide, 71194-58-6; 6-chloro-*N*,*N*-bis(2-hydroxyethyl)nonanamide, 71194-59-7; 7-chloro-*N*,*N*-bis(2-hydroxyethyl)nonanamide, 71194-60-0; 8-chloro-*N*,*N*-bis(2-hydroxyethyl)-nonanamide, 71194-61-1; 9-chloro-*N*,*N*-bis(2-hydroxyethyl)nonanamide, 71194-62-2; 5-chloro-*N*-[2-(2-hydroxyethoxy)ethyl]nonanamide, 71194-63-3; 6-chloro-*N*-[2-(2-hydroxyethoxy)ethyl]nonanamide, 71194-64-4; 7-chloro-*N*-[2-(2-hydroxyethoxy)ethyl]nonanamide, 71194-65-5; 8-chloro-*N*-[2-(2-hydroxyethoxy)ethyl]nonanamide, 71194-66-6; 9-chloro-*N*-[2-(2-hydroxyethoxy)ethyl]nonanamide, 71194-67-7; 5-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-68-8; 6-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-69-9; 7-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-70-2; 8-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-71-3; 9-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-72-4; 10-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-73-5; 11-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-74-6; 12-chloro-*N*,*N*-bis(2-ethoxyethyl)dodecanamide, 71194-75-7; methyl 3-chlorododecanoate, 71194-76-8; methyl 4-chlorododecanoate, 71194-77-9; methyl 5-chlorododecanoate, 71194-78-0; methyl 6-chlorododecanoate, 71194-79-1; methyl 7-chlorododecanoate, 71194-80-4; methyl 8-chlorododecanoate, 71194-81-5; methyl 9-chlorododecanoate, 71194-82-6; methyl 4-chlorodecanoate, 71194-83-7; methyl 5-chlorodecanoate, 71194-84-8; methyl 6-chlorodecanoate, 71194-85-9; methyl 7-chlorodecanoate, 71194-86-0; methyl 2-chlorodecanoate, 20589-84-8; methyl 3-chlorodecanoate, 71194-87-1; methyl 5-chlorooctanoate, 67963-58-0; decanoic acid, 334-48-5; 5-chlorodecanoic acid, 71194-88-2; 6-chlorodecanoic acid, 71194-89-3; 7-chlorodecanoic acid, 71194-90-6; 8-chlorodecanoic acid, 71194-91-7; 9-chlorodecanoic acid, 71194-92-8; 10-chlorodecanoic acid, 37027-56-8; decanoamide, 2319-29-1; 5-chlorodecanoamide, 71194-93-9; 6-chlorodecanoamide, 71215-22-0; 7-chlorodecanoamide, 71194-94-0; 8-chlorodecanoamide, 71194-95-1; 9-chlorodecanoamide, 71194-96-2; 10-chlorodecanoamide, 71194-97-3.

Supplementary Material Available: Table III (variables on chlorination of methyl decanoate) and Table IV (variation of substrates and molar concentration) (2 pages). Ordering information is given on any current masthead page.

(16) N. Wiberg and F. Raschig, *J. Organomet. Chem.*, **10**, 15 (1967).

Side Reactions in Peptide Synthesis. 12.[1] Hydrogenolysis of the 9-Fluorenylmethyloxycarbonyl Group

Jean Martinez,[2] John C. Tolle, and Miklos Bodanszky*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Received April 13, 1979

When an attempt was made to selectively remove the benzyl ester group from (9-fluoroenylmethyloxycarbonyl)-β-benzyl-L-aspartic acid α-(2,4,5-trichlorophenyl ester) by Pd-catalyzed hydrogenation, parallel to the disappearance of the starting material, formation of a ninhydrin-positive compound was noted. This prompted a second experiment in which a solution of (9-fluorenylmethyloxycarbonyl)-L-alanine (FMOC-L-Ala) in methanol was hydrogenated in the presence of a small amount of acetic acid and a 10% Pd-on-charcoal catalyst. Under similar conditions Carpino and Han[3] recovered an FMOC derivative unchanged. Yet, in our experiment after 4 h of hydrogenation at 0 °C we could not detect the starting material, FMOC-L-alanine, but found instead free alanine. These observations were surprising because the resistance of the FMOC protecting group to hydrogenolysis was emphasized in the papers[3] which introduced this new method of protection and was mentioned again in the literature.[4] In an attempted reduction of FMOC-aniline Carpino and Han[3] recovered the starting material unchanged, while benzyl carbanilate, also present in the mixture, was completely cleaved. Because of these conflicting results we carried out additional experiments. First, we subjected FMOC-glycine to catalytic hydrogenation and found complete removal of the protecting group. The free glycine produced in the reaction was

(1) For the preceding paper in this series cf. M. Bodanszky, S. S. Deshmane, and J. Martinez, *J. Org. Chem.*, **44**, 1622 (1979).

(2) Visiting scientist on leave from Equipe de Recherche No. 195 du Centre National de la Recherche Scientifique, Ecole Normale Superieur de Chimie de Montpellier, France.

(3) L. A. Carpino and G. Y. Han, *J. Am. Chem. Soc.*, **92**, 5748 (1970); *J. Org. Chem.*, **37**, 3404 (1972); **38**, 4218 (1973).

(4) E. Wünsch, *Methoden Org. Chem. (Houben-Weyl), 4th Ed.*, **15**(1), 94 (1974).

0022-3263/79/1944-3596$01.00/0

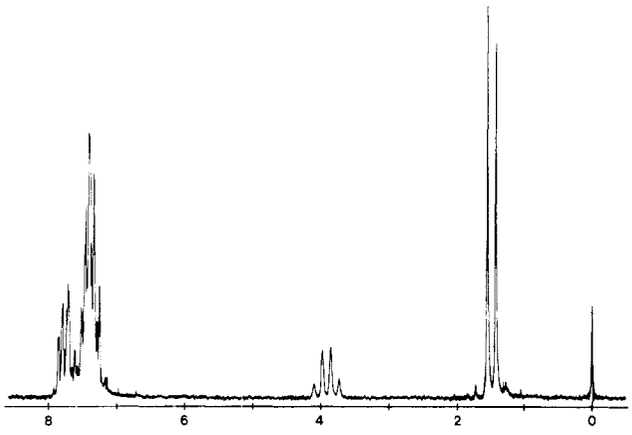


Figure 1. Proton NMR spectrum (in $CDCl_3$) of 9-methylfluorene produced in the Pd-catalyzed hydrogenolysis of FMOC-glycine.

identified by TLC and the second product, 9-methylfluorene, by its NMR spectrum which at 1.47 ppm from Me_4Si exhibited a characteristic doublet of its methyl group, coupled with the neighboring CH proton, that appeared as a quartet, at 3.93 ppm (cf. Figure 1). The spectrum also showed the absence of dibenzofulvene. Also, we hydrogenated FMOC-L-leucine in aqueous ethanol in the presence of some acetic acid. After 4 h all of the starting material was converted to the free amino acid and 9-methylfluorene.

The discrepancy between our observations and those of Carpino and Han[3] might be attributed to some difference in the quality of the catalysts used in the two laboratories. A partially poisoned catalyst could be active enough to reduce a benzyl group but sufficiently inactive to leave an FMOC derivative intact. It should be noted that the FMOC group has already been applied[5,6] with considerable success in the solid-phase synthesis of biologically active peptides and is being employed in conventional syntheses (in solution) in our laboratory. The mere fact that this group can be removed by catalytic hydrogenation does not diminish its value as a novel kind of protection. It is conceivable that in some schemes an additional possibility for the removal of this important protecting group represents a distinct advantage. Yet, it seemed necessary to call attention to an observation which is in variance with the literature.[3,4]

Experimental Section

Thin-layer plates of silica gel (Merck) were run in the following solvent systems: A, $CHCl_3$–MeOH–AcOH (24:1:1); B, $CHCl_3$–hexane (1:1); C, 1-BuOH–AcOH–H_2O (4:1:1); D, EtOAc–1-BuOH–AcOH–H_2O (1:1:1:1); E, $CHCl_3$–MeOH–AcOH (8:1:1); F, $CHCl_3$–MeOH (9:1). A Varian A60 instrument was used for recording NMR spectra.

Attempted Preparation of FMOC-L-aspartic Acid α-(2,4,5-Trichlorophenyl Ester). A sample (2.23 g) of L-aspartic acid β-benzyl ester (Bachem) was suspended in a 10% solution of Na_2CO_3 in H_2O (20 mL) and treated with a solution of 9-fluorenylmethyl chlorocarbonate (2.5 g, Chemalog) in dioxane (20 mL).[3] The mixture was stirred overnight. According to TLC, a small amount of the aspartic acid β-benzyl ester remained unchanged; therefore, more chlorocarbonate (0.10 g) was added. Two hours later the reaction mixture was neutralized with dilute HCl and concentrated in vacuo to about half of its volume. Water (10 mL) was added and the solution was acidified to about pH 2. It was extracted with EtOAc and the solvent was removed from the organic phase in vacuo. The residue (4.3 g) was chromatographed on a silica gel column (150 g, Baker). Elution with $CHCl_3$ removed small amounts of impurities. Subsequently the main product was eluted with $CHCl_3$–CH_3OH (8:2 (v/v)). Evaporation of the fractions which showed a single spot on TLC with R_f(A) 0.3 left a white solid (2.9 g): mp 121–124 °C; NMR ($CDCl_3$ with Me_4Si as an internal standard) δ 3.05 (d, 2, Asp β-CH_2), 4.0–5.0 (m, 4, Asp C_α-H + fluorenyl 9-H + 9-CH_2), 5.5 (s, 2, benzyl CH_2), 5.95 (d, 1, NH), 7.25–7.9 (m, 13, aromatic).

The protected amino acid (0.58 g) was dissolved in pyridine (5 mL), and the solution was cooled in an ice–water bath; 2,4,5-trichlorophenol (0.32 g) and dicyclohexylcarbodiimide (DCC, 0.27 g) were added. After 0.25 h at 0 °C and 12 h at room temperature some starting material could still be detected. Therefore, more DCC (50 mg) was added. After a further 2 h the separated *N,N'*-dicyclohexylurea was removed by filtration. The solvent was evaporated in vacuo, the residue was dissolved in EtOAc, and the mixture was concentrated and refiltered. Evaporation of the filtrate left a solid residue which was triturated with ether (10 mL), filtered and washed with a small volume of ether and then with a mixture of ether and hexane (1:1), and dried in vacuo. The product (0.61 g) was homogeneous on TLC R_f ($CHCl_3$) 0.70, R_f(B) 0.20; mp 99–101 °C; NMR ($CDCl_3$, Me_4Si standard) δ 3.15 (d, 2, Asp β-CH_2), 4.1–5.0 (m, 4, Asp α-CH + fluorenyl 9-H and 9-CH_2), 5.2 (s, benzyl CH_2), 5.9 (d, 1, NH), 7.25–7.9 (m, 15, aromatic); IR (KBr) 1775 (active ester C=O) cm^{-1}.

The active ester (0.50 g) was dissolved in dimethylformamide (2.5 mL); MeOH (25 mL) and AcOH (0.5 mL) were added followed by a 10% Pd-on-charcoal catalyst (Matheson Coleman and Bell, 0.1 g). Hydrogen was passed over the solution for 2 h. An examination of the solution by TLC revealed (with I_2 vapors) no more starting material but a complex mixture. Since the major product was ninhydrin positive, this mixture was not further studied and the experiment was abandoned.

Hydrogenation of FMOC-L-alanine. A solution of the protected amino acid (20 mg, Chemalog, R_f(C) 0.82) in MeOH (10 mL) was cooled in an ice–water bath while stirred and hydrogenated in the presence of 2 drops of AcOH and a 10% Pd-on-charcoal catalyst (Pfaltz and Bauer, ca. 10 mg). After 4 h TLC showed no more starting material. The free amino acid (alanine) was detected with ninhydrin (R_f(C) 0.24). A minor, unidentified component (R_f(C), 0.17) was also present.

Hydrogenation of FMOC-glycine. A sample of FMOC-glycine (100 mg, Chemalog) was dissolved in 95% EtOH (5 mL). A 10% Pd-on-charcoal catalyst (20 mg, Pfaltz and Bauer) was added, and after the mixture was flushed with N_2 a slow stream of H_2 was passed over the stirred solution for 22 h. The catalyst was removed by filtration and the solvent evaporated in vacuo. The residue was taken up in $CHCl_3$ and H_2O (5 mL each), and the phases were separated. The organic layer contained only one material (R_f(D) 0.96, R_f(F) 0.82) which had a strong UV absorption and was subsequently identified as 9-methylfluorene. Evaporation of the solvent left an oil which crystallized on standing. The NMR spectrum ($CDCl_3$) is shown in Figure 1. The aqueous layer contained glycine, revealed by ninhydrin (R_f(D) 0.25).

Hydrogenation of FMOC-L-leucine. A sample of the protected amino acid (706 mg), prepared according to the procedure of Carpino and Han[3] with commercially available (Chemalog) 9-fluorenylmethyl chlorocarbonate, was dissolved in 95% EtOH (30 mL). Two drops of AcOH and a 10% Pd-on-charcoal catalyst (140 mg, Pfaltz and Bauer) were added. The stirred mixture was hydrogenated at room temperature for 1 day. At that time TLC showed about one-third of the the starting material unchanged, a larger amount of 9-methylfluorene, and free leucine. After removal of the catalyst and the solvent, the residue was dissolved in $CHCl_3$ and H_2O. The aqueous layer left on evaporation a white crystalline material (160 mg), identified as leucine by its IR and NMR spectra (D_2O). The organic layer was extracted with a 5% solution of $NaHCO_3$ and evaporated. The residual oil, 9-methylfluorene (240 mg), gradually solidified to a crystalline mass, mp 44–45 °C (lit.[7] 46–47 °C). The NMR spectrum was the same as that shown in Figure 1. The $NaHCO_3$ extract was acidified and extracted with $CHCl_3$. The organic layer

(5) E. Atherton, H. Fox, D. Harkiss, C. J. Logan, R. C. Sheppard, and B. J. Williams, *J. Chem. Soc., Chem. Commun.*, 537 (1978); E. Atherton, H. Fox, D. Harkiss, and R. C. Sheppard, *ibid.*, 539 (1978).

(6) C. D. Chang and J. Meienhofer, *Int. J. Pept. Protein Res.*, 11, 246 (1978).

(7) W. Wislicenus and A. Densch, *Ber. Dtsch. Chem. Ges.*, 35, 762 (1902).

was washed with H_2O and evaporated. The recovered starting material (184 mg) was identified by TLC (R_f(E) 0.74). The reduction did not go to completion because the free leucine produced in the reaction separated on the catalyst.

In a second experiment FMOC-L-leucine (35 mg) was hydrogenated in a mixture of ethanol (3 mL), H_2O (1 mL), and AcOH (1 drop) in the presence of a 10% Pd-on-charcoal catalyst (10 mg, Matheson Coleman and Bell). According to TLC, the conversion to leucine and 9-methylfluorene was complete in 4 h.

Acknowledgment. This study was supported by grants from the National Science Foundation (CHE 76-15652) and from the U.S. Public Health Service (NIH AM-12473).

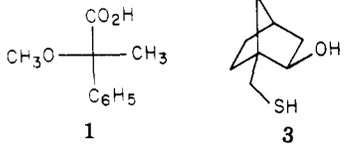
Registry No. FMOC-L-aspartic acid α-(2,4,5-trichlorophenyl) ester, 71359-85-8; L-aspartic acid β-benzyl ester, 2177-63-1; 9-fluorenylmethyl chlorocarbonate, 28920-43-6; FMOC-L-alanine, 35661-39-3; alanine, 56-41-7; FMOC-glycine, 29022-11-5; 9-methylfluorine, 2523-37-7; glycine, 56-40-6; FMOC-L-leucine, 35661-60-0; leucine, 61-90-5.

Communications

Asymmetric Synthesis of Nearly Optically Pure Atrolactic Acid Methyl Ether

Summary: A synthesis of atrolactic acid methyl ether, $C_6H_5C(OCH_3)(CH_3)CO_2H$, in 97 ± 2% enantiomeric excess based on 10-mercaptoisoborneol [readily available by lithium aluminum hydride reduction of (+)-camphor-10-sulfonyl chloride from natural (+)-camphor] as the chiral auxiliary substance is described.

Sir: In a previous publication[1] we described the preparation of (*S*)-(+)-atrolactic acid methyl ether (**1**) in nearly 100% optical yield using 4,6,6-trimethyl-1,3-oxathiane (**2**)

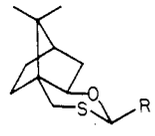


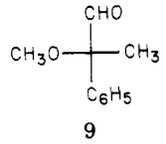
1 **3**

as the chiral auxiliary substance (henceforth called "chiral adjuvant"). The enantiomeric excess (ee) of the product was, however, only 44%, which was the ee of the chiral adjuvant used. While optically pure chiral adjuvant **2** can be obtained by methods described,[2] the resolution involved is tedious. Obviously, a better approach is to prepare a chiral adjuvant from a natural product and we here describe such an approach based on enantiomerically pure (+)-camphor.

(+)-10-Camphorsulfonic acid,[3] either commercially available material or prepared[5] from (+)-camphor, $[\alpha]^{23}_D$ 43.5° (lit.[4] 43.8°), was converted to (+)-10-camphorsulfonyl chloride, $[\alpha]_D$ 28.8° ($CHCl_3$, *c* 4.2), after recrystallization from heptane, by means of thionyl chloride.[6] The acid chloride, in ether, was reduced by means of lithium aluminum hydride (4:1 mole ratio) in ether, initially at −78 °C, warming up to room temperature, and then refluxing for 6 h. Acidic workup gave a 4:1 mixture (proton NMR analysis using H(2)) of *exo*- and *endo*-2-hydroxy-10-mercaptonorbornanes from which the exo isomer was separated by column chromatography on silica gel, eluting with 1.5% (v/v) ethyl acetate in hexane. This yielded 10-mercaptoisoborneol (**3**, 50–55%), mp 76–78 °C, $[\alpha]^{24}_D$ −55.4° ($CHCl_3$, *c* 10), along with 8–10% of 10-mercaptoborneol.

Treatment of **3** with paraformaldehyde in benzene containing a small amount of *p*-toluenesulfonic acid at reflux with a Dean–Stark trap to remove water gave, after the usual workup and Kugelrohr distillation [air bath 100–120 °C (0.1 torr)], oxathiane **4**, mp 57.5–59 °C (after sublimation), $[\alpha]^{24}_D$ −114.7° ($CHCl_3$, *c* 16.4), in 84–86% yield.[7,8]





9

4, R = H
5, R = $CHOHC_6H_5$
6, R = COC_6H_6
7, R = $C(OH)(CH_3)C_6H_5$
8, R = $C(OCH_3)(CH_3)C_6H_5$

Oxathiane **4** resisted the usual[1] deprotonation with *n*-butyllithium at −78 °C and significant decomposition was observed at 0 °C or above. Therefore, deprotonation was effected with *sec*-butyllithium in THF at −78 °C; subsequent treatment with benzaldehyde (20% excess) gave alcohol **5** as a mixture of stereoisomers. Although this mixture could be separated by column chromatography on silica gel (eluting with 2% ethyl acetate in hexane) it was normally oxidized directly to ketone **6** by addition to a mixture of oxalyl chloride, dimethyl sulfoxide, and dichloromethane[9] at −78 °C followed by treatment with triethylamine, allowing the temperature to rise from −78 °C to room temperature. Recrystallization from heptane yielded pure **6**, mp 135–136 °C, $[\alpha]^{25}_D$ −103.2° ($CHCl_3$, *c* 5.2);[8] the overall yield of **6** from **4** was 65%.

(1) Eliel, E. L.; Koskimies, J. K.; Lohri, B. *J. Am. Chem. Soc.* **1978**, *100*, 1614.
(2) Cf. Hagberg, C.-E.; Allenmark, S. *Chem. Scr.* **1974**, *5*, 13.
(3) Acid prepared by us had $[\alpha]^{23}_D$ +21.7° (H_2O, *c* 2.3) and was presumably anhydrous. Purchased material had $[\alpha]^{23}_D$ +20.5° and was probably the hemihydrate. The rotation given in ref 4 is $[\alpha]^{20}_D$ +21.5°, but rotations as high as +24° are listed in Beilstein's Handbuch.
(4) "The Merck Index", 9th Ed., Merck and Co.: Rahway, N.J., 1976.
(5) Bartlett, P. D.; Knox, L. H. "Organic Syntheses"; Collect. Vol. 5; Wiley: New York, 1973; p 194.
(6) Smiles, S.; Hilditch, T. P. *J. Chem. Soc.* **1907**, *91*, 519. Read, J.; Storey, R. A.; *Ibid.* **1930**, 2761. Sutherland, H.; Shriner, R. L. *J. Am. Chem. Soc.* **1936**, *58*, 62.
(7) **Note Added in Proof** (August 16, 1979, observations by N. P. Müller): We have now also prepared (+)-**4**, $[\alpha]^{25}_D$ +116.4° (*c* 3.0, $CHCl_3$), starting from (commercially available) ammonium (−)-10-camphorsulfonate, which was recrystallized (acetone, 12 parts, ethanol, 2 parts, water, 1 part) to constant rotation, $[\alpha]^{25}_D$ −20.35° (*c* 1.7, H_2O). Treatment of the ammonium salt with thionyl chloride (tenfold excess, room temperature, 20 h) yielded (75–80%) (−)-10-camphorsulfonyl chloride, $[\alpha]^{25}_D$ −31.9° (*c* 3.2, $CHCl_3$). (The absolute rotation decreases on standing or repeated recrystallization.) Compounds (+)-**3**, $[\alpha]^{24}_D$ +56.7° (*c* 2.9, $CHCl_3$, after sublimation), and (+)-**4**, prepared essentially as described above, had slightly higher rotations than reported above, suggesting that the optical purity of the levorotatory materials may have been only 98–99%.
(8) These compounds had correct C,H elemental analyses.
(9) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.

0022-3263/79/1944-3598$01.00/0