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).

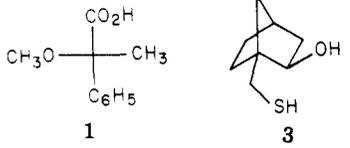
Registry No. FMOC-L-aspartic acid α-(2,4,5-trichlorophenyl) ester, 71359-85-8; L-aspartic acid β-benzyl ester, 2177-63-1; 9-fluorenylmethyl chlorocarbonate, 28920-43-6; FMOC-L-alanine, 35661-39-3; alanine, 56-41-7; FMOC-glycine, 29022-11-5; 9-methylfluorine, 2523-37-7; glycine, 56-40-6; FMOC-L-leucine,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

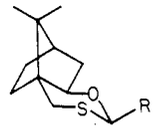


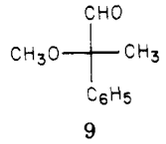
1 **3**

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.

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Addition of a solution of ketone **6** in 2:1 ether–THF to methylmagnesium iodide in ether at 0–25 °C gave alcohol **7** ($[\alpha]^{24}_D$ −133.3° ($CHCl_3$, *c* 4.25)) as a single stereoisomer (^{13}C NMR[10]) in 92–100% yield. Protection of the hydroxyl group in **7** was effected by treatment with NaH in THF followed by the addition of methyl iodide; methyl ether **8** ($[\alpha]^{24}_D$ −68.5° ($CHCl_3$, *c* 21.5)) was thus obtained in 87–98% yield. ^{13}C NMR confirmed **8** to be a single stereoisomer.

Hydrolysis of **8** to atrolactic aldehyde methyl ether **9** required somewhat more carefully controlled conditions than in the previous study,[1] since extended reaction times led to decomposition. However, treatment of **8** with methyl iodide and calcium carbonate in 80% aqueous acetonitrile[1] at reflux for 4–5 h gave aldehyde **9** in fair yield (62–65%). Oxidation of **9** with Jones reagent[1] gave atrolactic acid methyl ether **1** $[\alpha]^{25}_D$ + 37.6° (CH_3OH, *c* = 8.8), whose ee was determined after conversion to the methyl ester by diazomethane[1] to be 97 ± 2% by proton NMR spectroscopy using the chiral shift reagent Eu(hfbc)$_3$.[11]

The present method is competitive with that recently reported by Mukaiyama et al.[12] which yields **1** in about 95% ee.

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1, 24190-10-1; *exo*-**3**, 71242-58-5; *endo*-**3**, 71242-59-6; **4**, 71215-16-2; **5** isomer 1, 71215-17-3; **5** isomer 2, 71242-60-9; **6**, 71215-18-4; **7**, 71215-19-5; **8**, 71215-20-8; **9**, 66221-50-9; (+)-10-camphorsulfonic acid, 3144-16-9; (+)-10-camphorsulfonyl chloride, 21286-54-4.

(10) A mixture of the two diasteromers was produced, for NMR comparison, by reaction of the lithium derivative of **4** with acetophenone.

(11) Goering, H. L.; Eikenberry, J. N.; Koermer, G. S.; Lattimer, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 1493.

(12) Mukaiyama, T.; Sakito, Y.; Asani, M. *Chem. Lett.* **1978**, 1253.

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Ketene Bis(phenylthio)acetals. Easily Prepared Intermediates for the Conversion of Acids and Esters to α-Alkylidene Ketones and Sulfur-Substituted Dienes

Summary: Treatment of acids or esters with $Al(SPh)_3$ produces ketene bis(phenylthio)acetals which, by independent manipulation of the phenylthio groups, are capable of a varity of transformations.

Sir: Aluminum thiophenoxide (**1**), which at 25 °C converts carboxylic esters into thioesters,[1] has now been found to react at the temperatures of refluxing benzene and xylene with carboxylic esters and acids, respectively, to produce in the case of unconjugated substrates (**2**) simple ketene bis(phenylthio)acetals (**3**) and in the case of α,β-unsaturated esters (**4**) 1,1,3-tris(phenylthio)-1-alkenes (**5**; eq 1 and 2). The yields in the nonconjugated cases are excellent

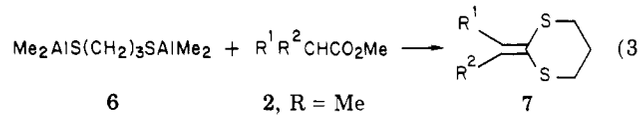
$$\underset{\mathbf{1}}{Al(SPh)_3} + \underset{\mathbf{2}}{R^1R^2CHCO_2R} \rightarrow \underset{\mathbf{3}}{R^1R^2C{=}C(SPh)_2} \quad (1)$$

R = H or CH_3

$$\mathbf{1} + \underset{\mathbf{4}}{R^3R^4C{=}CHCO_2R} \rightarrow \underset{\mathbf{5}}{R^3R^4C(SPh)CH{=}C(SPh)_2} \quad (2)$$

except when a carboxylic acid in which there is no branching at the α- or β-positions is used (Table I);[2] in these cases, an important byproduct is a 1,1,1-tris(phenylthio)alkane, and a modification of this procedure can be used to prepare tris(phenylthio)orthoacetate, a precursor of the useful ketene bis(phenylthio)acetal (**3**, $R^1 = R^2 = H$).[3] The yields are somewhat lower for conjugated esters.[4]

Corey and Kozikowski[5] have reported a somewhat analogous transformation to that in eq 1; they showed that alkylidenedithianes (**7**) are produced by reaction of esters (**2**) with **6** (eq 3). Although most discussions[5-7] of the uses

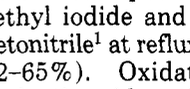


(3)

6 **2**, R = Me **7**

of simple ketene thioacetals as synthetic intermediates have focused on alkylidenedithianes produced by eq 3 or by Peterson or Wittig type olefinations,[6,8,9] we are convinced that the synthetic utility of ketene thioacetals is

Table I. Ketene Bis(phenylthio)acetals from the Reaction of Aluminum Thiophenoxide with Acids (A) and Methyl Esters (E)

product	from	refluxing solvent	time, h[a]	yields, %
$MeCH{=}C(SPh)_2$	A	xylene	17	56[b]
$EtCH{=}C(SPh)_2$	A	xylene	17	65[b]
$Me_2CHCH{=}C(SPh)_2$	A	xylene	12	98[c]
c-C_6H_{11}-$CH{=}C(SPh)_2$	A	xylene	17	97[c]
$Me_2C{=}C(SPh)_2$	A	xylene	17	96[c]
$Me_2C{=}C(SPh)_2$	E	benzene	4	89[b]
c-$C_6H_{10}{=}C(SPh)_2$	A	xylene	17	100[c]
c-$C_6H_{10}{=}C(SPh)_2$	E	benzene	4	96[c]
	A	xylene	17	97[c]
	E	benzene	4	100[c]
$MeCH(SPh)CH{=}C(SPh)_2$	E[d]	benzene	17	70[b]
$PhCH(SPh)CH{=}C(SPh)_2$	E[e]	benzene	17	70[b]
$Me_2C(SPh)CH{=}C(SPh)_2$	E[f]	benzene	17	85[c]

[a] At reflux. [b] After silica chromatography. [c] Obtained spectroscopically pure directly from reaction. [d] Methyl crotonate. [e] Methyl cinnamate. [f] Methyl 3-methyl-2-butenoate.

(1) T. Cohen and R. E. Gapinski, *Tetrahedron Lett.*, 4319 (1978).

(2) New compounds were characterized by ^1H NMR, IR, and mass spectroscopy and by their exact masses, as determined by high-resolution mass spectroscopy.

(3) (a) T. Cohen, G. Herman, J. R. Falck, and A. J. Mura, Jr., *J. Org. Chem.*, **40**, 812 (1975); (b) T. Cohen, R. B. Weisenfeld, and R. E. Gapinski, submitted for publication.

(4) Unsaturated acids (**4**, R = H) could also be converted to **5**, but the yields (~50%) were less satisfactory.

(5) E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, 925 (1975).

(6) For an excellent review, see: B.-T. Gröbel and D. Seebach, *Synthesis*, 357 (1977).

(7) N. H. Anderson, P. F. Duffy, A. D. Denniston, and D. B. Grotjahn, *Tetrahedron Lett.*, 4315 (1978); N. H. Anderson, Y. Yamamoto, and A. D. Denniston, *ibid.*, 4547 (1975).

(8) B.-T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 852 (1977).

(9) M. Mikolajczyk, S. Grzejszczak, A. Zatorski, B. Mlotkowska, H. Gross, and B. Costisella, *Tetrahedron*, **34**, 3081 (1978).

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