afforded the title product **2** (18.3 g, 82%, mp 97–99 °C): ^{1}H NMR ($CDCl_3$) δ 2.16 (q, 3 H, 2-CH_3, J = 0.8 Hz), 2.09 (q, 3 H, 5-CH_3, J = 0.8 Hz); ^{2}H NMR ($CHCl_3$) δ 6.33 (s, 1 D, 4-D); mass spectrum m/e 223/225.

2-Bromo-*exo*-3-ethyl-1,4,6-trimethyl-*endo*-5-(1-propynyl)-7-thiatricyclo[2.2.1.0^{2,6}]heptane 7,7-Dioxide (6). A solution of ethylmagnesium bromide in anhydrous diethyl ether (1.9 mL of 3.0 M, 5.5 mmol) was added dropwise to a stirred solution of 3-bromo-2,5-dimethylthiophene 1,1-dioxide[1] (1.12 g, 5 mmol), in anhydrous ether (20 mL), at −20 °C under nitrogen. After being stirred for 2 h, the reaction mixture was hydrolyzed with saturated ammonium chloride. The organic phase was separated, and the aqueous phase was extracted three times with ether (3 × 25 mL). The combined ethereal phase was washed twice with water (2 × 50 mL), dried over magnesium sulfate, and concentrated. Column chromatography followed by recrystallization from ethanol afforded **6** (0.6 g, 73%, mp 83–85 °C): IR 2230 (C≡C stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.12 (q, 1 H, 5-H, J = 2.4 Hz), 2.67 (b t, 1 H, 3-H, J = 5.9, 0.6 Hz), 1.97 (dsxt, 1 H, 3-CH_2, J = 15.0, 7.6, 5.9 Hz), 1.88 (d, 3 H, acetylenic CH_3, J = 2.4 Hz), 1.81 (dsxt, 1 H, 3-CH_2, J = 15.0, 7.6, 5.9 Hz), 1.41 (d, 3 H, 4-CH_3, J = 0.6 Hz), 1.37 (s, 3 H, 1-CH_3), 1.30 (s, 3 H, 6-CH_3), 1.08 (t, 3 H, 3-CH_3, J = 7.6 Hz); HETCOR (^{13}C-^{1}H NMR) δ 52.65–2.67, 44.66–3.12, 18.41–1.97 and 1.81, 14.58–1.08, 10.20–1.30, 6.34–1.37, 3.85–1.41, 3.75–1.88.

The multiplicity was confirmed by DEPT (five CH_3 carbons at δ 3.75, 3.85, 6.34, 10.20 and 14.58, one CH_2 carbon at δ 18.41, two CH carbons at δ 44.66 and 52.65, and six carbons without hydrogen at δ 32.68, 40.52, 48.52, 64.16, 72.16, and 83.47).

Irradiation at δ 3.12 resulted in a singlet at δ 1.88. Irradiation at δ 2.67 resulted in a sextet at δ 1.97 (J = 15.0 and 7.6 Hz), a sextet at δ 1.88 (J = 15.0 and 7.6 Hz), and a singlet at δ 1.41: mass spectrum m/e 330/332. Anal. Calcd for $C_{14}H_{19}BrO_2S$: C, 50.7; H, 5.8; Br, 24.1. Found: C, 50.5; H, 5.8; Br, 24.3.

2-Bromo-*endo*-3,*exo*-5-dideuterio-*exo*-3-ethyl-1,4,6-trimethyl-*endo*-5-(1-propynyl)-7-thiatricyclo[2.2.1.0^{2,6}]heptane 7,7-Dioxide (7). A solution of ethylmagnesium bromide in anhydrous diethyl ether (3.8 mL of 3.0 M, 12 mmol) was added dropwise to a stirred solution of 3-bromo-4-deuterio-2,5-dimethylthiophene 1,1-dioxide (**2**; 2.24 g, 10 mmol) in anhydrous ether (40 mL) at −20 °C under nitrogen. After being stirred for 2 h, the reaction mixture was hydrolyzed with 10% hydrochloric acid, washed with saturated sodium bicarbonate, dried over magnesium sulfate, and concentrated. Column chromatography followed by recrystallization from ethanol afforded **7** (1.0 g, 60%, mp 82–83 °C): IR 2230 (C≡C stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.96 (qv, 1 H, 3-CH_2, J = 15.0, 7.6 Hz), 1.88 (s, 3 H, acetylenic CH_3), 1.81 (qv, 1 H, 3-CH_2, J = 15.0, 7.6 Hz), 1.41 (s, 3 H, 4-CH_3), 1.37 (s, 3 H, 1-CH_3), 1.29 (s, 3 H, 6-CH_3), 1.08 (t, 3 H, 3-CH_3, J = 7.6 Hz); ^{2}H NMR ($CHCl_3$) δ 3.07 (s, 1 D, 5-D), 2.63 (s, 1 D, 3-D); mass spectrum m/e 332/334.

2-Bromo-1,4,6-trimethyl-*exo*-3-*n*-propyl-*endo*-5-(1-propynyl)-7-thiatricyclo[2.2.1.0^{2,6}]heptane 7,7-Dioxide (8). A solution of *n*-propylmagnesium chloride in anhydrous diethyl ether (11 mL of 2 M, 22 mmol) was added dropwise to a stirred solution of 3-bromo-2,5-dimethylthiophene 1,1-dioxide (4.5 g, 20 mmol) in anhydrous ether (150 mL) at −20 °C under nitrogen. After being stirred for 2 h, the reaction mixture was treated as described previously for **7**. Column chromatography afforded **8** as an oil (1.8 g, 52%): IR 2230 (C≡C stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.10 (q, 1 H, 5-H, J = 2.4 Hz), 2.73 (b t, 1 H, 3-H, J = 5.5 Hz), 1.86 (d, 3 H, acetylenic CH_3, J = 2.4 Hz), 1.9–1.3 (qm, 4 H, 3-CH_2CH_2), 1.39 (s, 3 H, 4-CH_3), 1.34 (s, 3 H, 1-CH_3), 1.28 (s, 3 H, 6-CH_3), 0.93 (t, 3 H, 3-CH_3, J = 7.3 Hz).

The multiplicity was confirmed by DEPT (five CH_3 carbons at δ 3.69, 3.83, 6.18, 10.21, and 14.14, two CH_2 carbons at δ 23.16 and 27.20, two CH carbons at δ 44.58 and 50.62, and six carbons without hydrogen at δ 32.68, 40.45, 48.74, 64.09, 72.18, and 83.44): mass spectrum m/e 344/346. Anal. Calcd for $C_{15}H_{21}BrO_2S$: C, 52.2; H, 6.1; Br, 23.1. Found: C, 52.1; H, 6.1; Br, 23.2.

2-Bromo-*exo*-3-ethyl-1,4,6-trimethyl-*endo*-5-acetonyl-7-thiatricyclo[2.2.1.0^{2,6}]heptane 7,7-Dioxide (9). 2-Bromo-*exo*-3-ethyl-1,4,6-trimethyl-*endo*-5-(1-propynyl)-7-thiatricyclo-[2.2.1.0^{2,6}]heptane 7,7-dioxide (**6**; 0.5 g, 1.5 mmol) was added to an ice-cooled suspension of mercury(II) sulfate[10] (50 mg, 0.17 mmol) in aqueous formic acid (10 mL, 85%) with vigorous stirring. After the solution was stirred overnight, saturated ammonium sulfate (50 mL) was added to the reaction mixture, which was then extracted with toluene (3 × 25 mL). The combined extracts were dried over magnesium sulfate and filtered through silica, the silica being subsequently washed with dichloromethane. Evaporation of the solvents and recrystallization from ethanol produced **9** (0.48 g, 91%): mp 113–118 °C; IR 1715–1720 (C=O stretch) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.08 (dd, 1 H, 5-H, J = 7.5, 4.2 Hz), 2.54 (dd, 1 H, 5-CH_2, J = 18.0, 7.5 Hz), 2.44 (dd, 1 H, 5-CH_2, J = 18.0, 4.2 Hz), 2.24 (s, 3 H, 5-CH_3), 2.16 (t, 1 H, 3-H, J = 5.7 Hz), 1.99 (dsxt, 1 H, 3-CH_2, J = 15.0, 7.6, 5.7 Hz), 1.81 (dsxt, 1 H, 3-CH_2, J = 15.0, 7.6, 5.7 Hz), 1.42 (s, 3 H, 4-CH_3), 1.26 (s, 3 H, 1-CH_3), 1.09 (s, 3 H, 6-CH_3), 1.05 (t, 3 H, 3-CH_3, J = 7.6 Hz); mass spectrum m/e 348/350. Anal. Calcd for $C_{14}H_{21}BrO_3S$: C, 48.1; H, 6.1; Br, 22.9. Found: C, 48.3; H, 6.1; Br, 22.8.

3-Bromo-4-deuterio-2,5-dimethylthiophene (10). *n*-Butyllithium (107 mL, 2.06 N) in hexane was added dropwise to a solution of 3,4-dibromo-2,5-dimethylthiophene[11] (54.0 g, 0.2 mol) in anhydrous diethyl ether (500 mL) under a nitrogen atmosphere at −70 °C. After 30 min of vigorous stirring, deuterium oxide (30 mL) was added dropwise with continuous stirring at −70 °C for 1 h. The reaction mixture was allowed to reach room temperature, washed twice with water, and dried over magnesium sulfate. Distillation (85–86 °C (18 mmHg)) afforded **10** (34.2 g, 89%). According to ^{1}H NMR >98% deuteration occurred: ^{1}H NMR ($CDCl_3$) δ 2.40 (q, 3 H, 2-CH_3, J = 0.6 Hz), 2.33 (q, 3 H, 5-CH_3, J = 0.6 Hz); mass spectrum m/e 191/193; ^{2}H NMR ($CHCl_3$) δ 6.52 (s, 1 D, 4-D).

Acknowledgment. Grants from the Swedish Natural Science Research Council to S.G. and A.H. are gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, and complete descriptions of the X-ray structure determination of **6** (6 pages). Ordering information is given on any current masthead page.

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An Improved Synthesis of Isomerically Pure *cis*-1-Bromopropene

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Received December 7, 1990

As a part of a program to develop new synthetic approaches to the oral antibiotic candidate cefprozil monohydrate,[1-4] we required multikilogram quantities of isomerically pure (>99%) *cis*-1-bromopropene (**3**). Apart from careful spinning band distillation of the commercial mixture (Z/E = 70/30)[5-7] or desilicobromination of a 1,2-di-

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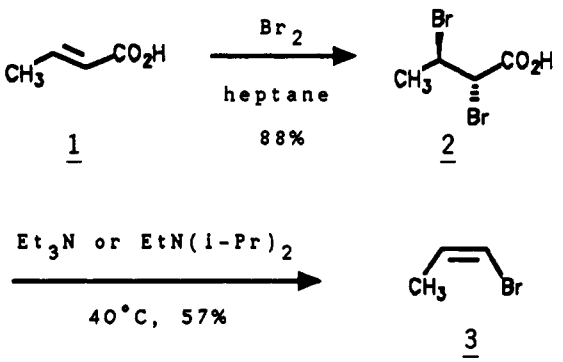
Scheme I



bromo(trialkylsilyl)propane derivative,[8,9] the most commonly employed synthesis of **3** involves bromination of *trans*-crotonic acid (**1**) followed by bromo decarboxylation of the resulting *erythro*-2,3-dibromobutanoic acid (**2**).[10-13] Unfortunately, the reported bromo decarboxylations of **2** to **3** with pyridine,[10] aqueous Na_2CO_3,[11,12] or $NaHCO_3$ in DMF[13] all proceed in poor yield.

In this paper we report a substantial improvement in the procedure (Scheme I) by carrying out the bromo decarboxylation of **2** in neat Et_3N or $EtN(i\text{-}Pr)_2$ at 40 °C. Use of either amine provided isomerically pure **3**[14] reproducibly in 57% yield (50% overall yield from **1**).

Storage of freshly distilled **3** in tightly sealed, light-excluding containers at −20 °C[15] showed no isomerization and/or decomposition of **3** over several months, as monitored by 360-MHz NMR spectroscopy. Thus, addition of either $NaHCO_3$[6] or K_2CO_3[7] as a stabilizing agent appears to be unnecessary for **3** prepared by this methodology.

We believe this improved synthesis provides a convenient and economical means for preparing isomerically pure *cis*-1-bromopropene. This bromoalkene is useful for synthetic applications requiring *cis*-propenyllithium[6,12,16] and *cis*-propenylmagnesium bromide.[5,16]

Experimental Section

Melting points are uncorrected. **Caution!** Heptane poses a dangerous fire and explosion hazard when exposed to heat or flame. Vapors are heavier than air and may travel a considerable distance to a source of ignition and flash back. Situtations which might cause electrostatic discharges should be avoided when handling this solvent.

***erythro*-2,3-Dibromobutanoic Acid (2).** A 500-mL flask equipped with an overhead stirrer, thermometer, and addition funnel was charged with *trans*-crotonic acid (**1**) (51.68 g, 0.60 mol, Aldrich) and 320 mL of heptane. The resulting mixture was stirred and brought to 30 °C (warm water bath) under dry N_2. Br_2 (34.4 mL, 0.63 mol, 1.05 equiv, Fisher) was added dropwise over ca. 45 min while maintaining a reaction temperature of 30 °C (cold water bath). Within 4–5 min after complete addition, crystallization of **2** commenced. A cold water bath was applied to maintain a reaction temperature of ca. 34 °C. The mixture was brought to ambient temperature, stirred an additional 16 h, and cooled in an ice water bath for 30 min. The colorless crystals were collected by suction filtration, washed with heptane (2 × 75 mL), and dried in vacuo at ambient temperature to constant weight to afford 130 g (88%) of **2**: mp 87–89 °C (lit.[11] mp 87–88 °C).

***(Z)*-1-Bromopropene (3).** A 2-L flask equipped with an overhead stirrer, thermometer, and reflux condenser with a mineral oil bubbler attached to the top of the condenser was charged with 517.5 mL (3.71 mol, 4.13 equiv) of 99% triethylamine (Aldrich). With vigorous stirring, a total of 221 g (0.90 mol) of acid **2** was added in ten portions at 5-min intervals. During this addition period, gas evolution (bubbler) and an exotherm to 40 °C were noted. The reaction was stirred at ambient temperature for 3.5 h followed by heating at 40 °C for an additional 3.5 h (gas evolution complete). The mixture was cooled to ambient temperature, and 321 mL of water was added. The solids were rinsed in and allowed to dissolve. Concentrated HCl solution (230 mL, Fisher) was added while maintaining a reaction temperature of 0 °C. Separation of the lower phase in a separatory funnel gave 82.2 g (75%) of crude **3**.[17] The aqueous phase was saved for recovery of triethylamine.

The crude **3** was washed twice with an equivalent volume of saturated $NaHCO_3$ solution and brine and dried (Na_2SO_4). Simple distillation at atmospheric pressure[18] afforded 62.4 g (57%)[19] of isomerically pure *cis*-1-bromopropene (**3**)[14,15] as a colorless liquid: bp 59–60 °C (lit.[10] bp 58–60 °C).

The acidic aqueous phase was cooled to 0–5 °C, and 750 mL of 25% aqueous NaOH solution was added dropwise with good stirring. Separation of the upper phase in a separatory funnel afforded a quantitative recovery of the triethylamine.

A similar result was obtained by substituting an equimolar amount of $EtN(i\text{-}Pr)_2$ for the Et_3N in the conversion of **2** to **3**.

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(10) Bachman, G. B. *J. Am. Chem. Soc.* **1983**, *55*, 4279; 28% yield.
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(14) Analysis of the distillate by NMR spectroscopy (360 MHz, $CDCl_3$/TMS) showed no contamination by *trans*-1-bromopropene when compared with an NMR spectrum of commercial material (Aldrich, Z/E = 70/30).
(15) Immediately after distillation, the distillate was transferred to a narrow-mouth screw-top amber bottle, tightly sealed with parafilm, and refrigerated at −20 °C until needed. Prior to use in a reaction, the *cis*-1-bromopropene was allowed to warm to ambient temperature.
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(17) The 360-MHz NMR spectrum showed *cis*-1-bromopropene and unidentified triethylammonium salt byproducts. No *trans*-1-bromopropene was detected.
(18) The product was distilled as one fraction; no forerun was collected.
(19) This yield represents a significant improvement over the best current literature yield[13] for preparation of *cis*-1-bromopropene (**3**) of high (>99%) isomeric purity.

6-Phenyl-2,4,6-trioxohexanoic Acid

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Received January 8, 1991

The title compound **1** is of current interest because of its relationship to the enolic acids **2** and **3**, which have been implicated in the bacterial oxidation of biphenyl[2] and certain polychlorobiphenyls,[3] respectively. In this paper,

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