added to make the aqueous solution strongly alkaline. The organic layer was separated, dried over $MgSO_4$, concentrated in vacuo, and distilled to yield **57** (208 mg, 39% yield based on **52**): NMR (CCl_4) δ 2.23, 2.40 ($-CH_3$).

Reduction of Siloxymethylidenation Product (Enol Silyl Ether) Cyclohexanemethanol.[60b,61b] To a solution of $NaBH_4$ (1 mmol, 40 mg) in ethanol (8 mL) was added **3** (2 mmol, 430 mg). The mixture was stirred at 25 °C under nitrogen for 3 h. Solvent was removed in vacuo. Diethyl ether was added to the residue, and the solution was washed with dilute HCl solution. The organic layer was dried over $CaSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (silica gel, C_6H_6) to give cyclohexanemethanol (160 mg, 70% yield based on **3**): NMR (CCl_4) δ 3.15 (d, J = 5 Hz, OCH_2-).

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Highly Stereocontrolled Synthesis of Some Trioxygenated Cyclohexenes: An Asymmetric Total Synthesis of (-)-Methyl Triacetyl-4-epishikimate

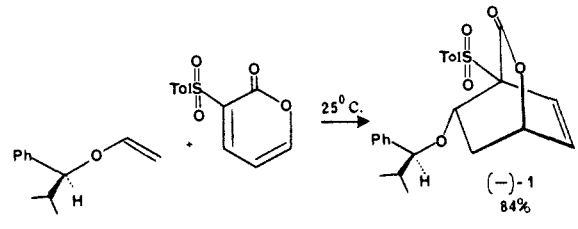
Gary H. Posner* and David G. Wettlaufer

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received May 19, 1986*

Abstract: Polyfunctional bicyclic lactone (-)-**1** serves as a chiron for preparation of 3,4,6-trioxygenated cyclohexene (-)-**5a** in 56.6% overall yield and for synthesis of (-)-methyl triacetyl-4-epishikimate, (-)-**12**, in 14 steps and in 23.4% overall yield. 3,4,5-Trioxygenated cyclohexene (-)-**12** is obtained in at least 98% enantiomeric purity.

Many polyoxygenated carbocycles produce potent biological responses, including antimicrobial,[1] antiviral,[1] and antitumor[2] as well as growth-promoting[3] effects. Because of these pronounced biological activities and because of their potential as versatile chemical intermediates, polyoxygenated carbocycles have been the targets of many synthetic efforts.[2a,4]

We recently reported using an α-pyrone sulfone[5] as an an electron-deficient diene in some highly asymmetric Diels-Alder cycloadditions with several chiral, nonracemic alkyl vinyl ethers as electron-rich dienophiles.[6] For example, such an inverse-electron-demand asymmetric (2 + 4) cycloaddition proceeded on a gram scale, as illustrated in eq 1, with formation of adduct (-)-**1**, which was isolated as a single diastereomer in 84% yield. This high level of stereocontrol was especially gratifying and somewhat surprising because the stereogenic center in the reactant alkyl vinyl



(1)

ether is insulated from the reacting vinyl moiety by a freely rotating ether linkage.[7] Chiron[8] (-)-**1** is a richly functionalized bicyclic lactone subject to a variety of chemoselective and stereoselective chemical operations. For example, hydroxylation of the olefinic bond in unsaturated lactone (-)-**1** would produce a *tetra*oxygenated cyclohexane; also the allylic carboxylate functionality within bicyclic lactone (-)-**1** affords opportunities for substitution reactions with various organometallic reagents.[9] We record here conversion of chiron (-)-**1** into some trioxygenated cyclohexenes of defined absolute stereochemistry, and we highlight the utility of chiron (-)-**1** by converting it in 14 steps and in 23.4% overall yield into (-)-methyl triacetyl-4-epishikimate, an intermediate for synthesis of (-)-chorismic acid and analogues. The important shikimate biosynthetic pathway in plants and microorganisms leads from carbohydrates to various aromatic compounds.[10] (-)-Methyl triacetyl-4-epishikimate has been prepared previously by resolution of a racemic precursor[11] and

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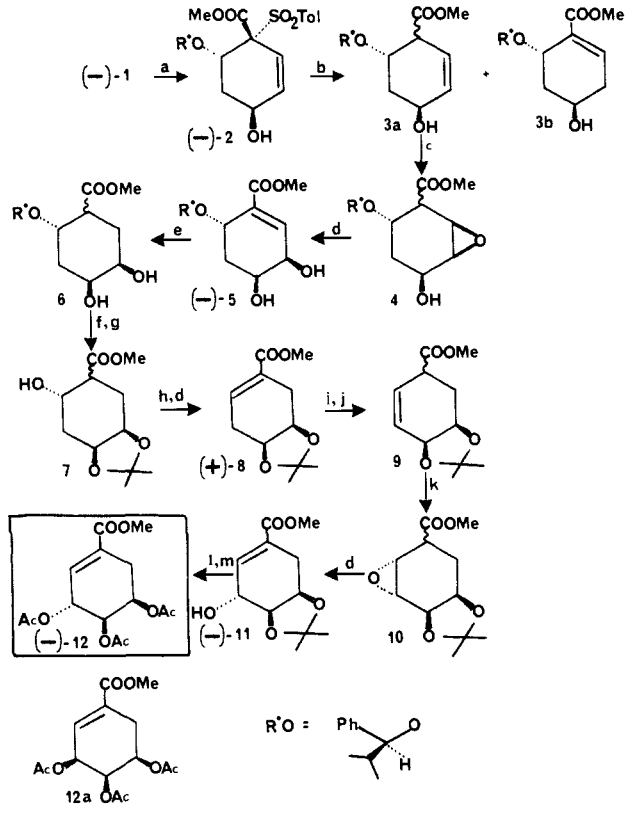
Scheme I[a]



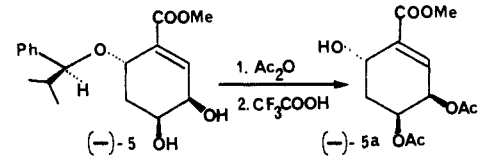
[a] (a) NaOMe; (b) Al–Hg; (c) p-$NO_2C_6H_4CO_3H$; (d) DBU; (e) H_2, Pd–C; (f) TFA; (g) 2,2-dimethoxypropane; (h) MsCl; (i) LDA; (j) HOAc; (k) m-CPBA; (l) TsOH; and (m) Ac_2O.

by synthesis from natural (−)-quinic acid.[12]

Results and Discussion

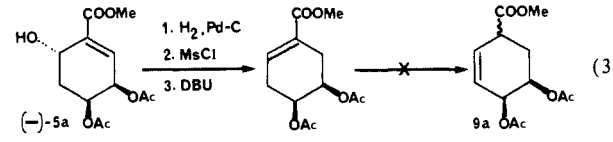
Low-temperature methanolysis[13] of lactone (−)-**1** led exclusively to allylic alcohol (−)-**2** in 93% yield (Scheme I). It was our plan to use the hydroxyl group of allylic alcohol (−)-**2** to direct syn vicinal oxygenation[14] via the corresponding epoxide. Toward this end, buffered trifluoroperacetic acid caused epoxidation of allylic alcohol (−)-**2**, but the β,γ-epoxy α-sulfonyl ester product was inert to a wide variety of conditions (e.g., Al–Hg, Na–Hg, and Raney nickel) which normally cause reductive cleavage of α-sulfonyl esters.[15] Therefore, the sequence of steps was reversed: first, reductive cleavage of the sulfonyl group was achieved to produce a mixture of two cyclohexene double-bond positional isomers, **3a** and **3b**, in which the desired β,γ-unsaturated ester **3a** predominated. The mixture of isomers **3a** and **3b** was immediately subjected to epoxidation using p-nitroperbenzoic acid;[16] the crude epoxide **4** was treated immediately with DBU to produce diol (−)-**5** in 70% overall yield from allylic alcohol (−)-**2**. The α,β-enoate **3b** survived the epoxidation and DBU procedure and thus could be recycled. To determine the degree of stereoselectivity in the epoxidation step, crude diol (−)-**5** was bisacetylated; the characteristic vinyl H resonances at δ 6.69 and at δ 6.63 in the 400-MHz ^{1}H NMR spectrum appeared in a 40:1 ratio. That the major vinyl H peak was due to the *cis*-diol diacetate was confirmed by performing p-nitroperbenzoic acid epoxidation directly on the acetate of allylic alcohol (−)-**2**, producing diacetates in a ratio of only 4:1 (δ 6.69 vs. 6.63) after DBU and acetyl chloride treatment; ultimate confirmation of the *cis*-diol stereochemical relationships in (−)-**5** was accomplished by conversion of this material into methyl triacetyl-4-epishikimate, (−)-**12**. As a sidelight, epoxidation of the trimethylsilyl ether of allylic alcohol (−)-**2** led to a 1:1 stereochemical mixture of epoxides.

To prepare a trioxygenated cyclohexene of very high enantiomeric purity, *cis*-diol (−)-**5** was acetylated and then subjected to trifluoroacetolysis, giving hydroxy diacetate (−)-**5a** in 87% overall yield (eq 2). Acid-promoted cleavages specifically of benzylic ethers have been reported.[17]



(2)

To complete a synthesis of 4-epishikimate (−)-**12**, our plan was to use a protected form of *cis*-diol (−)-**5** to direct anti epoxidation; it was necessary, therefore, to remove the phenylcarbinol chiral auxiliary and to introduce a double bond β,γ to the ester group (e.g., to prepare olefinic diacetate **9a**). Cyclohexene (−)-**5a** was catalytically hydrogenated, mesylated, and dehydrosulfonated to form a conjugated enoate diacetate (eq 3). All attempts to deconjugate this δ-acetoxy α,β-unsaturated ester failed, leading to a mixture of products in which aromatic material was evident.



(3)

Our successful route, shown in Scheme I, involved catalytic reduction of cyclohexene (−)-**5** (the benzyl ether chiral auxiliary survived this step[18a]),[18b] trifluoroacetolysis of the chiral auxiliary,[17] acetonide formation, mesylation, and dehydrosulfonation (i.e., **5** → **6** → **7** → **8**), operations which proceeded in 72% overall yield. LDA-promoted deconjugation of enoate *acetonide* (+)-**8** (in contrast to the corresponding enoate *diacetate*) led mainly to β,γ-unsaturated ester **9** which was subjected immediately to m-chloroperbenzoic acid anti epoxidation and DBU opening of the epoxide to form hydroxy acetonide (−)-**11**. The epoxidation step proceeded with at least 60:1 anti stereoselectivity, based on 400-MHz ^{1}H NMR measurements. To determine the enantiomeric purity of acetonide (−)-**11**, it was converted into the corresponding Mosher ester;[19] comparison of its ^{1}H NMR spectrum with that of the Mosher ester of an independently prepared *racemic* sample showed (−)-**11** to have an enantiomeric purity of

(11) (a) Grewe, R.; Hinricho, I. *Chem. Ber.* **1964**, *97*, 443. (b) Grewe, R.; Kersten, S. *Angew. Chem.* **1965**, *77*, 859. (c) Grewe, R.; Kersten, S. *Chem. Ber.* **1967**, *100*, 2546.

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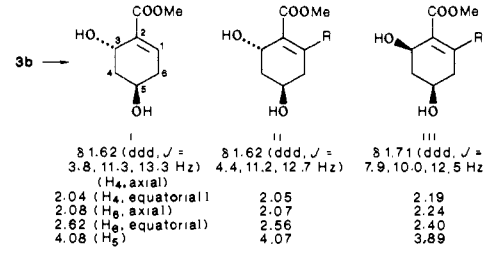
(16) Vilkas, M. *Bull. Soc. Chim. Fr.* **1959**, 1401.

(17) Marsh, J. P., Jr.; Goodman, L. *J. Org. Chem.* **1965**, *30*, 2491. To establish that trifluoroacetolysis caused no undesired solvolysis also of the *allylic* carbon–oxygen linkage, a detailed comparison was made of the ^{1}H NMR spectral data for model trifluoroacetolysis product i vs. those reported in the literature [Ohta, Y.; Abe, S.; Komura, H.; Kobayashi, M. *Phytochemistry* **1984**, *23*, 1607] for *trans*-diol ii and *cis*-diol iii; clearly the data strongly indicate that our model trifluoroacetolysis product i and, therefore, also intermediate **3a** both have a trans dioxygenation pattern.



(18) (a) Cf: Pugh, J. D.; Rooney, C. S.; Deana, A. A.; Ramjit, H. G. *Tetrahedron Lett.* **1985**, *26*, 2947. (b) All attempts at promoting direct β-elimination of R*OH from β-alkoxy ester **6** were unsuccessful.

(19) Dale, J. A., Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

>98% (see Experimental Section). The ^{19}F NMR spectrum was not informative in this case. Note that hydroxy acetonide (−)-**11** is a chiral, nonracemic trioxygenated cyclohexane in which two of the secondary hydroxyl groups are protected, thereby allowing chemospecific manipulation of the third secondary hydroxyl group.

Hydrolysis of hydroxy acetonide (−)-**11** and triple acetylation produced (−)-methyl triacetyl-4-epishikimate, (−)-**12**, in 50% overall yield from olefinic acetonide (+)-**8**. The spectral data of our synthetic (−)-**12** are identical with those reported in the literature[11,12] and different from those of methyl triacetylshikimate.[4a] For comparison purposes, we prepared racemic *all-cis*-triacetate **12a**;[20] our synthetic 4-epishikimate (−)-**12** was clearly different from *all-cis*-triacetate **12a**. The overall yield of epishikimate (−)-**12** from bicyclic lactone (−)-**1** via the 14 steps in Scheme I is 23.4%. A derivative of (−)-4-epishikimic acid has been converted previously into (−)-chorismic acid.[21]

In conclusion, we have shown here that bicyclic lactone (−)-**1** is a useful chiron for practical synthesis of some polyfunctionalized cyclohexenes in extremely high enantiomeric purity. These results and our total synthesis of trioxygenated cyclohexene 4-epishikimate (−)-**12** establish the absolute stereochemistry of bicyclic lactone (−)-**1** to be as shown. Starting with commercially available[22] (*R*)- instead of (*S*)-phenylisopropylcarbinol as the chiral auxiliary in the original Diels–Alder reaction (eq 1) would produce bicyclic lactone (+)-**1** and, utimately, antipodal 4-epishikimate (+)-**12**. One disadvantage of this scheme is that the chiral auxiliary is destroyed during its removal after having performed an excellent job of inducing chirality in the newly formed carbon–carbon bonds in Diels–Alder adduct (−)-**1**. One advantage of this scheme is that catalytic reduction of cyclohexene (−)-**5** into cyclohexane **6** can be done with D_2 (or even with T_2) to produce isotopically labeled products for use in various enzymatic and biosynthetic studies.

We are actively pursuing use of inverse-electron-demand Diels–Alder cycloadditions of sulfur-substituted pyrones for preparation of other polyfunctionalized cyclohexenes.

Experimental Section[23]

Hydroxy Ester Sulfone (−)-**2.** To an argon-flushed, 100-mL, round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet were added absolute methanol (42 mL) and sodium methoxide (4.45 mL of 25 wt % in methanol, 19.5 mmol). When this mixture cooled to −78 °C, a solution consisting of bicyclic lactone (−)-**1** (0.166 g, 0.39 mmol) and dichloromethane–methanol (1:1 by volume, 16 mL) was added dropwise. The temperature was maintained at −78 °C for an additional 5 min, at which time the reaction mixture was warmed to 0 °C. Stirring was continued at 0 °C until complete reaction was observed by TLC (40% EtOAc/hexanes, 1–1.25 h). Workup consisted of quenching with dilute aqueous ammonium chloride (50 mL), diluting with dichloromethane (30 mL) and ether (20 mL), and separating the layers. The aqueous layer was extracted with dichloromethane–ether (1:1 by volume, 2 × 30 mL). The combined organic layers were washed with dilute aqueous ammonium chloride (3 × 25 mL) and with brine. Drying (Na_2SO_4), filtering, and concentrating gave the crude hydroxy ester. Purification via PTLC (silica gel, 40% ether/30% dichloromethane/30% hexanes, R_f 0.36) afforded 0.165 g (93%) of hydroxy ester sulfone (−)-**2** as a foam: $[\alpha]^{23}_D$ −102° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2 H), 7.37–7.25 (m, 7 H), 6.11 (dd, *J* = 10.4, 3.5 Hz, 1 H), 5.83 (br d, *J* = 9.9 Hz, 1 H), 4.78–4.74 (m, 1 H), 4.39–4.34 (m, 1 H)8 4.35 (d, *J* = 7.3 Hz, 1 H), 3.45 (s, 3 H), 2.44 (s, 3 H), 2.17–1.98 (m, 2 H), 1.55 (br s, 1 H), 1.06–0.99 (m, 1 H), 0.91 (d, *J* = 6.7 Hz, 3 H), 0.66 (d, *J* = 6.7 Hz, 3 H); IR ($CHCl_3$) cm^{-1} 3590, 1760, 1750, 1145; HRMS, *m/z* calcd for $C_{22}H_{23}O_6S$ (M − C_3H_7) 415. 1216, found 415. 1219.

Desulfonation of Hydroxy Ester Sulfone (−)-**2.** To a 25-mL, round-bottomed flask fitted with a magnetic stir bar and reflux condenser were added hydroxy ester sulfone (−)-**2** (0.106 g, 0.231 mmol), THF (10.4 mL), and water (1.2 mL). Aluminum amalgam [prepared from aluminum foil (0.25 g, 9.2 mmol) which was subjected to one or two exposures to mercuric chloride][24] was added, and the flask was heated at reflux in a 105 °C oil bath. Heating was continued until complete reaction was observed by TLC (40% EtOAc/hexanes, 2.25–4.5 h). When the mixture cooled to room temperature, the gray suspension was filtered through a pad of Celite, and the solids were washed with EtOAc (50 mL). Drying (Na_2SO_4) followed by filtering and concentrating afforded the crude isomeric products in which the β,γ-unsaturated ester **3a** predominated over the α,β-enoate **3b** by about 6–7:1. ^1H NMR ($CDCl_3$) δ 7.37–7.24 (m, 5 H), 6.93 (dd, *J* = 5.5, 2.7 Hz, 0.2 H), 5.94–5.78 (m, 1.5 H), 5.69–5.64 (m, 0.1 H), 4.47–4.42 (m, 0.2 H), 4.34–4.24 (m, 0.7 H), 4.18–3.94 (m, 2.2 H), 3.78 (s, 0.6 H), 3.76 (s, 2.2 H), 3.72 (s, 0.2 H), 3.42–3.35 (m, 0.7 H), 3.25–3.20 (m, 0.1 H), 2.70–2.60 (m, 0.3 H), 2.12–1.67 (m, 2.4 H), 1.63–1.18 (m, 1.1 H), 0.95 (d, *J* = 6.7 Hz, 1.1 H), 0.92 (d, *J* = 6.7 Hz, 1.9 H), 0.68 (d, *J* = 6.7 Hz, 0.3 H), 0.63 (d, *J* = 6.7 Hz, 2.7 H); IR ($CHCl_3$) cm^{-1} 3582, 3420, 1730, 1710.

Dihydroxy Ester (−)-**5.** To a 25-mL, round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet was added the above mixture of unsaturated esters as a chloroform (9-mL) solution. The flask was flushed with argon and cooled to 0 °C and the solution treated with *p*-nitroperbenzoic acid (0.063 g, 0.35 mmol). The bath was removed, and the flask was allowed to warm to room temperature. Stirring was continued for 16 h, at which time the resulting solids were dissolved by the addition of ether (20 mL) and dichloromethane (20 mL). The mixture was extracted with dilute aqueous sodium bicarbonate (3 × 30 mL), and the combined aqueous layers were back-extracted with ether (1 × 20 mL). The organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated to give the crude epoxides **4** which were immediately ring-opened.

To a 25-mL, round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet was added a dichloromethane (11-mL) solution of the above epoxides. The flask was flushed with argon and cooled to −78 °C, and DBU (0.052 mL, 0.35 mmol) was added dropwise to the solution with stirring. The temperature was maintained at −78 °C for 5 min, at which time the bath was removed and the flask allowed to warm to room temperature. Stirring was continued an additional 2.5 h, after which dilute aqueous ammonium chloride (10 mL) and ether (20 mL) were added. The layers were separated, and the organic layer was washed with dilute aqueous ammonium chloride (2 × 20 mL). The combined aqueous layers were back-extracted with ether–dichloromethane (1:1 by volume, 1 × 15 mL), and the combined organic layers were washed with brine and dried (Na_2SO_4). Filtration and concentration afforded the crude product which was purified by PTLC (silica gel, 40% EtOAc/hexanes, R_f 0.21) to give *cis*-diol (−)-**5** (0.052 g, 70%) as a waxy solid: $[\alpha]^{24}_D$−148° (*c* 0.7, $CHCl_3$); mp 55–58 °C; ^1H NMR ($CDCl_3$) δ 7.35–7.24 (m, 5 H), 6.79 (d, *J* = 4.3 Hz, 1 H), 4.43 (t, *J* = 4.3 Hz, 1 H), 4.26 (t, *J* = 3.9 Hz, 1 H), 4.08–4.02 (m, 1 H), 4.06 (d, *J* = 8.3 Hz, 1 H), 3.79 (s, 3 H), 2.33 (br s, 1 H), 1.40 (br s, 1 H), 1.89–1.78 (m, 1 H), 1.60–1.43 (m, 2 H), 0.92 (d, *J* = 6.8 Hz, 3 H), 0.60 (d, *J* = 6.8 Hz, 3 H); IR ($CHCl_3$) cm^{-1} 3600–3300, 1719, 1260. Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.5, H, 7.5. Found: C, 67.4; H, 7.6.

Diacetate of (−)-**5.** To a flame-dried, 10-mL round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet were added diol (−)-**5** (0.027 g, 0.084 mmol), DMAP (0.5 mg), and dry dichloromethane (1.0 mL). The resulting solution was cooled to 0 °C and treated with triethylamine (0.117 mL, 0.84 mmol) and acetic anhydride (0.055 mL, 0.59 mmol) with stirring. The bath was removed and the mixture allowed to warm to room temperature. Stirring was continued for 1 h, at which time the reaction was quenched with dilute aqueous sodium bicarbonate

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(21) McGowan, D. A.; Berchtold, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 1153, 7036.

(22) Aldrich Chemical Company.

(23) Melting points were determined by using a Sybron/Thermolyne Model MP-12615 melting point apparatus; melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer 559B spectrometer and were calibrated by using the 1601-cm^{-1} polystyrene absorption as reference. ^1H NMR spectra were recorded by using a Varian XL-400 spectrometer operating at 400 MHz. Chemical shifts are reported in parts per million (ppm) downfield from a tetramethylsilane (Me_4Si) internal standard, and the resonances are noted as being a singlet (s), a doublet (d), a triplet (t), or a multiplet (m). Specific rotations were determined with a Perkin-Elmer 141 variable-wavelength polarimeter using a thermostated 1-dm quartz window cell of 1-mL capacity. Concentrations (*c*) for specific rotations are reported in units of g/100 mL. Mass spectra were performed by the mass spectrometry service laboratory at the University of Minnesota, Minneapolis. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. The following solvents were distilled from sodium/benzophenone before use: diethyl ether and tetrahydrofuran. Diisopropylamine was distilled from calcium hydride and dichloromethane from phosphorus pentoxide. *n*-Butyllithium was titrated by using 2,5-dimethoxybenzyl alcohol/tetrahydrofuran [Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87]. LDA was titrated by using 2-butanol in THF with 1,10-phenanthroline [Watson, S. C.; Eastham, J. R. *J. Organomet. Chem.* **1967**, *9*, 165]. All other reagents and solvents were used as received.

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(3 mL) and diluted with ether (6 mL). The layers were separated, and the organic layer was washed with dilute aqueous sodium bicarbonate (2 × 6 mL). The combined aqueous layers were back-extracted with ether (1 × 10 mL). The combined organic layers were washed with brine and dried (Na_2SO_4). Filtration, concentration, and purification by PTLC (silica gel, 20% EtOAc/hexanes, R_f 0.36) afforded 0.034 g (0.084 mmol, 100%) of the diacetate as a clear colorless oil: $[\alpha]^{23}_D$ −143° (*c* 1.06, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.37–7.23 (m, 5 H), 6.70 (d, *J* = 4.9 Hz, 1 H), 5.61 (t, *J* = 4.3 Hz, 1 H), 5.32 (t d, *J* = 11.4, 3.3 Hz, 1 H), 4 47 (t, *J* = 3.9 Hz, 1 H), 3.81 (s, 3 H), 2.01 (s, 3 H), 1.95 (s, 3 H), 1.87 (h, *J* = 6.65 Hz, 1 H), 1.71 (ddd, *J* = 13.4, 11.0, 4.3 Hz, 1 H), 1.51 (t d, *J* = 13.4, 3.5 Hz, 1 H), 0.94 (d, *J* = 6.65 Hz, 3 H), 0.61 (d, *J* = 6.65 Hz, 3 H); IR ($CHCl_3$) cm^{-1} 1740, 1723, 1250; HRMS, *m/z* calcd for $C_{19}H_{21}O_7$ (M − C_3H_7) 361.1287, found 361.1277.

Trioxygenated Cyclohexene (−)-5a. To a 10-mL round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet was added the above diacetate (0.034 g, 0.084 mmol) as a dichloromethane (2.6-mL) solution. The flask was flushed with argon and cooled to 0 °C, at which time trifluoroacetic acid (0.226 mL, 2.94 mmol) was added dropwise. The bath was removed, the reaction mixture was allowed to warm to room temperature, and stirring was continued (4 h and 20 min). Carbon tetrachloride (4 mL) was added and the mixture concentrated. Purification by PTLC (silica gel, 20% EtOAc/hexanes, R_f 0.13) afforded 0.020 g (0.073 mmol, 87%) of the desired alcohol as a clear colorless oil: $[\alpha]^{23}_D$ −158° (*c* 0.945, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 6.77 (d, *J* = 3 Hz, 1 H), 5.64–5.61 (m, 1 H), 5.49–5.44 (m, 1 H), 4.80–4.74 (m, 1 H), 3.83 (s, 3 H), 2.43–2.35 (m, 1 H), 2.08 (s, 3 H), 2.05 (s, 3 H), 1.95–1.88 (m, 1 H); IR (CCl_4) cm^{-1} 3540, 1745, 1705, 1230; HRMS, *m/z* calcd for $C_{12}H_{15}O_6$ (M − OH) 255.0869, found 255.0852.

Dihydroxy Ester 6. To a Fisher-Porter hydrogenation apparatus were added an absolute ethanol (10-mL) solution of diol (−)-**5** (0.076 g, 0.24 mmol) and 10% Pd–C (4.5 mg). The tube was purged with hydrogen (3 × 60 psig) and repressurized (60 psig), and the mixture was stirred rapidly for 12 h. The pressure was released and the catalyst removed by filtration through a pad of Celite. The solids were washed with EtOAc (20 mL). Concentration gave the crude saturated diol **6** which was used in the next step without purification.

An analytical sample of **6** was purified by PTLC (silica gel, 30% EtOAc/hexanes, two elutions, R_f 0.19): ^1H NMR ($CDCl_3$) δ 7.33–7.22 (m, 5 H), 4.14–3.96 (m, 2 H), 3.91–3.78 (m, 2 H), 3.72 (s, 2.8 H), 3.69, (s, 0.2 H), 2.81–2.74 (m, 0.9 H), 2.70–2.62 (m, 0.1 H), 2.21–2.11 (m, 1 H), 2.09–2.01 (m, 1 H), 1.82 (h, *J* = 7.2 1 H), 1.69–1.41 (m, 3.6 H), 0.92 (d, *J* = 6.8 Hz, 0.4 H), 0.91 (d, *J* = 6.8 Hz, 2.6 H), 0.65 (d, *J* = 7.1 Hz, 0.4 H), 0.60 (d, *J* = 7.2 Hz, 2.6 H); IR ($CHCl_3$) cm^{-1} 3560, 3400, 1722; HRMS, *m/z* calcd for $C_{15}H_{19}O_5$ (M − C_3H_7) 279.1233, found 279.1230.

Hydroxy Acetonide 7. To a 50-mL, round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet was added the above saturated diol **6** as a dichloromethane (7-mL) solution. The flask was flushed with argon and cooled to 0 °C, and trifluoroacetic acid (0.64 mL, 8.3 mmol) was added dropwise. Stirring was continued at 0 °C until complete reaction was observed by TLC (40% EtOAc/hexanes, followed by staining with aqueous $KMnO_4$, 40–60 min). The reaction mixture was diluted with CCl_4 (15 mL) and concentrated. Residual traces of acid were removed by the addition of benzene (10 mL) followed by concentration and high vacuum. The acetonide was immediately prepared.

The above triol was slurried in dichloromethane (4 mL) with stirring and treated with 2,2-dimethoxypropane (10 mL) and *p*-toluenesulfonic acid (3 mg). Stirring was continued at room temperature overnight (16–20 h), at which time ether (15 mL) was added and the mixture washed with dilute aqueous ammonium chloride (2 × 20 mL). The combined aqueous layers were back-extracted with ether (1 × 15 mL), and the combined organic layers were washed with brine and dried (Na_2SO_4). Filtration and concentration gave the crude hydroxy acetonide **7** which was used in the next step without purification.

An analytical sample of diastereomers **7** was purified by PTLC (silica gel, 30% EtOAc/hexanes, R_f 0.15, stained with phosphomolybdic acid): mp 74–78 °C; ^1H NMR ($CDCl_3$) δ 4.35–4.30 (m 1 H), 4.23–4.11 (m, 2 H), 3.74 (s, 3 H), 2.92 (br s, 1 H), 2.48–2.41 (m, 1 H), 2.35–2.27 (m, 1 H), 2.20–2.12 (m, 1 H), 1.75–1.66 (m, 2 H), 1.48 (s, 3 H), 1.34 (s, 3 H); IR ($CHCl_3$) cm^{-1} 3500, 1726, 1223; HRMS, *m/z* calcd for $C_{10}H_{15}O_5$ (M − CH_3) 215.0920, found 215.0917.

Olefinic Acetonide (+)-8. To a 10-mL, round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet was added the above hydroxy acetonide **7** as a dichloromethane (6-mL) solution. The flask was flushed with argon and cooled to 0 °C, and triethylamine (0.40 mL, 3.55 mmol) and methanesulfonyl chloride (0.137 mL, 1.77 mmol) were added dropwise. Stirring was continued at 0 °C for 3 h, at which time the reaction was quenched with dilute aqueous ammonium chloride (4 mL). Ether (10 mL) was added, and the layers were separated. The organic layer was washed with dilute aqueous ammonium chloride (2 × 4 mL), and the combined aqueous layers were back-extracted with ether (1 × 10 mL). The combined organic layers were washed with brine and dried (Na_2SO_4). Filtration and concentration afforded the crude mesylate as an oil which was used without purification.

To a 25-mL, round-bottomed flask fitted with a magnetic stir bar, septum, and argon inlet was added the above mesylate as a dichloromethane (10-mL) solution. The flask was flushed with argon, cooled to 0 °C, and treated with DBU (0.106 mL, 0.71 mmol). The bath was removed and the reaction mixture allowed to warm to room temperature. Stirring was continued until complete reaction was observed by TLC (40% EtOAc/hexanes, stained with aqueous $KMnO_4$ solution, 1–1.5 h) at which time the mixture was diluted with ether (10 mL) and washed with dilute aqueous ammonium chloride (2 × 25 mL). The aqueous layers were back-extracted with ether (1 × 10 mL). The combined organic layers were washed with brine and dried (Na_2SO_4). Filtration and concentration gave the crude enoate acetonide (+)-**8**. Purification by PTLC (silica gel, 20% EtOAc/hexanes) afforded 0.036 g (0.17 mmol, 72%) of the conjugated enoate acetonide (+)-**8** as a clear colorless oil: $[\alpha]^{24}_D$ +35° (*c* 0.92, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.04–7.00 (m, 1 H), 4.49–4.44 (m, 1 H), 4.43–4.38 (m, 1 H), 3.76 (s, 3 H), 2.74 (br dd, *J* = 16, 4 Hz, 1 H), 2.54–2.46 (m, 1 H), 2.38–2.25 (m, 2 H), 1.38 (s, 3 H), 1.32 (s, 3 H); IR (CCl_4) cm^{-1} 1715, 1265; HRMS, *m/z* calcd for $C_{11}H_{16}O_4$ 212.1049, found 212.1045.

Methyl Triacetyl-4-epishikimate [(−)-12]. A. Deconjugation of Enoate (+)-8. To a 100-mL, round-bottomed flask was added enoate acetonide (+)-**8** (0.036 g, 0.17 mmol) as a dichloromethane solution. The solvent was removed, and the flask was flushed with argon and fitted with a magnetic stir bar, septum, and argon inlet. THF (28 mL) was added and the resulting solution cooled to −100 °C (methanol/N_2 slush) with stirring. Lithium diisopropylamide (5.4 mL, 0.15 M, 0.81 mmol) was added over 3–4 min down the side of the flask. The side of the flask was rinsed with THF (2 mL), and the temperature was maintained at −100 °C for 70 min. The resulting light-green solution was quenched (over 2 min) with acetic acid (0.146 mL, 2.55 mmol) as a THF (6-mL) solution. The bath temperature was allowed to rise to −70 °C over 20 min, at which time the bath was removed and the flask allowed to warm to room temperature. The reaction mixture was diluted with ether (25 mL), dilute aqueous ammonium chloride (20 mL) was added, and the layers were separated. The aqueous layer was extracted with ether (2 × 25 mL). The combined organic layers were washed with dilute aqueous ammonium chloride (2 × 40 mL) and brine. Drying (Na_2SO_4) followed by filtering and concentrating gave the crude products which were used in the next step without purification.

An analytical sample was purified by PTLC (silica gel, 20% EtOAc, two bands staining with aqueous $KMnO_4$, R_f 0.4–0.6) and characterized as a 7:1 mixture of β,γ-enoate:α,β-enoate esters by ^1H NMR and IR: ^1H NMR ($CDCl_3$) δ 7.06–7.01 (m, 0.12 H), 6.12–6.06 (m, 0.66 H), 6.03–5.98 (m, 0.22 H), 5.92–5.86 (m, 0.66 H), 5.81–5.75 (m, 0.22 H), 4.50–4.33 (m, 1.30 H), 4.32–4.25 (m, 0.7 H), 3.76 (s, 0.36 H), 3.73 (s, 0.64 H), 3.71 (s, 2.00 H), 3.37–3.29 (m, 0.20 H), 3.07–3.00 (m, 0.68 H), 2.75 (dd, *J* = 16, 4, Hz, 0.12 H), 2.54–2.46 (m, 0.12 H), 2.38–2.25 (m, 0.24 H), 2.18–2.07 (m, 1.47 H), 1.95 (ddd, *J* = 15, 11, 3 Hz, 0.29 H), 1.42 (s, 2.00 H), 1.39 (s, 0.67 H), 1.38 (s, 0.95 H), 1.36 (s, 1.90 H), 1.33 (s, 0.48 H); IR (CCl_4) cm^{-1} 1735, 1715.

B. Epoxidation and Epoxide Opening of β,γ-Enoate 9. To a 10-mL round-bottomed flask were added the above acetonides as a dichloromethane solution. Upon concentration, the flask was flushed with argon and fitted with a magnetic stir bar, septum, and argon inlet. Dichloromethane (1.6 mL) was added and the resulting solution cooled to 0 °C and treated with *m*-CPBA (82% pure, 0.054 g, 0.255 mmol). The bath was removed and the mixture allowed to warm to room temperature, at which time the septum was replaced with a Teflon stopper. Stirring was continued (48 h) during which time solids formed. Addition of dichloromethane (3 mL) solvated the solids, and the solution was cooled to 0 °C and treated with DBU (0.084 mL, 0.56 mmol). The bath was removed and the reaction mixture allowed to warm to room temperature. Stirring was continued overnight (18 h), at which time the mixture was concentrated.

An analytical sample of hydroxy acetonide (−)-**11** was prepared via PTLC (silica gel, 65% EtOAc/hexanes, R_f 0.75): $[\alpha]^{24}_D$ −66.5° (*c* 0.43, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.00–6.97 (m, 1 H), 4.44–4.37 (m, 1 H), 4.34–4.29 (m, 1 H), 4.02 (dd, *J* = 7.4, 6.5 Hz, 1 H), 3.77 (s, 3 H), 3.16 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.32 (br s, 1 H), 2.31–2.23 (m, 1 H), 1.48 (s, 3 H), 1.37 (s, 3 H); IR ($CHCl_3$) cm^{-1} 3590, 1710; HRMS, *m/z* calcd for $C_{11}H_{17}O_5$ 228.0998, found 228.1016.

Mosher Esters of (±)-11 and of (−)-11. To a 5-mL, round bottomed flask were added hydroxy acetonide (±)-**11** (0.0055 g, 0.024 mmol) as a dichloromethane (1.0-mL) solution and DMAP (0.5 mg). The flask was flushed with argon and fitted with a magnetic stir bar, septum, and

argon inlet. The resulting solution was treated with triethylamine (0.034 mL, 0.24 mmol) and (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride[19] (0.018 g, 0.072 mmol) at room temperature with stirring. The reaction was quenched with dilute aqueous bicarbonate (1 mL) upon complete reaction, as determined by TLC (40% EtOAc/hexanes, followed by staining with aqueous $KMnO_4$, 1-2 h). The mixture was diluted with ether (5 mL), and the layers were separated. The organic layer was washed with dilute aqueous sodium bicarbonate (2 × 1 mL) and brine and dried (Na_2SO_4). Filtration and concentration afforded the crude esters. Analysis by ^1H NMR ($CDCl_3$) gave several diastereotopic protons that are as follows (with integration): δ 6.98-6.95 (m, 0.50 H), 6.88-6.85 (m, 0.50 H), 5.61-5.57 (m, 0.50 H), 5.56-5.52 (m, 0.50 H), 3.779 (s, 1.48 H), 3.765 (s, 1.52 H).

The Mosher ester of hydroxy acetonide (-)-**11** (0.0005 g, 0.0022 mmol) was prepared according to the above procedure with dichloromethane (0.4 mL), DMAP (0.3 mg), pyridine (0.006 mL, 0.074 mmol), and acid chloride (0.007 g, 0.028 mmol).

Analysis by ^1H NMR ($CDCl_3$) gave the following diastereotopic protons: δ 6.88-6.85, 5.56-5.52, 3.767. Expansions of the spectrum failed to show the characteristic peaks for the minor diastereomer.

C. Deprotection and Acetylation of Hydroxy Acetonide 11. The above light-brown oil was dissolved in methanol (2 mL), and *p*-toluenesulfonic acid (0.201 g, 1.06 mmol) was added with stirring at room temperature. Stirring was continued (9 h), at which time the mixture was concentrated. Residual methanol was removed under high vacuum. The flask was flushed with argon and fitted with a magnetic stir bar, septum, and argon inlet. Dichloromethane (6 mL) and 4-(dimethylamino)pyridine (0.5 mg) was added, and the resulting solution was cooled to 0 °C. Triethylamine (0.71 mL, 5.1 mmol) and acetic anhydride (0.32 mL, 3.4 mmol) were added dropwise. The bath was removed and the flask allowed to warm to room temperature. Stirring was continued (2 h), at which time the reaction mixture was diluted with ether (12 mL) and washed with dilute aqueous ammonium chloride (3 × 6 mL). The combined aqueous layers were back-extracted with ether (1 × 8 mL). The combined organic layers were washed with dilute aqueous sodium bicarbonate (3 × 6 mL) and brine and dried (Na_2SO_4). Filtration and concentration gave the crude products. Purification by PTLC (silica gel, 20% EtOAc/hexanes, two elutions, R_f 0.32) afforded 0.027 g (50%) of methyl triacetyl-4-epishikimate [(-)-**12**]: $[\alpha]^{24}_D$ -137° (*c* 1.17, MeOH); ^1H NMR ($CDCl_3$) δ 6.78-6.76 (m, 1 H), 5.68-5.62 (m, 1 H), 5.45-5.39 (m, 1 H, 5.13 (dd, *J* = 7.4, 2.4 Hz, 1 H), 3.76 (s, 3 H), 2.78-2.57 (m, 2 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H); IR (CCl_4) cm^{-1} 1745, 1720, 1215. *Literature*: $[\alpha]^{22}_D$ -140° (*c* 1.2, MeOH); ^1H NMR (60 MHz, $CDCl_3$) δ 6.73 (m, 1 H), 5.8-5.3 (m, 2 H), 5.13 (dd, *J* = 7, 2, Hz, 1 H), 3.77 (s, 3 H), 2.8-2.6 (m, 2 H), 2.10 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H).[11,12]

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Registry No. (-)-**1**, 104464-04-2; (-)-**2**, 104464-05-3; **3a** (isomer 1), 104464-06-4; **3a** (isomer 2), 104464-07-5; **3b**, 104487-42-5; **4** (isomer 1), 104530-70-3; **4** (isomer 2), 104464-21-3; (-)-**5**, 104464-08-6; (-)-**5** (diacetate), 104464-09-7; (-)-**5a**, 104464-22-4; **6** (isomer 1), 104464-10-0; **6** (R* = H, isomer 1), 104464-11-1; **6** (isomer 2), 104528-65-6; **6** (R* = H, isomer 2), 104528-64-5; **7** (isomer 1), 104464-12-2; **7** (isomer 2), 104528-63-4; **7** (mesylate, isomer 1), 104464-13-3; **7** (mesylate, isomer 2), 104528-66-7; (+)-**8**, 104464-14-4; **9** (isomer 1), 104464-15-5; **9** (isomer 2), 104464-16-6; **10** (isomer 1), 104464-17-7; **10** (isomer 2), 104528-67-8; (-)-**11**, 104464-18-8; (±)-**11**, 104528-68-9; (+)-**11** (mosher ester), 104464-19-9; (-)-**11** (mosher ester), 104464-20-2; (-)-**12**, 104528-69-0; (+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride, 20445-33-4.

The Preparation of Low-Spin *trans*-Polyacetylene

G. L. Baker,*† J. A. Shelburne, III,† and F. S. Bates‡

Contribution from Bell Communications Research, Red Bank, New Jersey 07701-7020, and AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received June 19, 1986*

Abstract: *trans*-Polyacetylene was prepared directly at 25 °C with a modification of the standard $AlEt_3/Ti(O\text{-}n\text{-}Bu)_4$ catalyst. The product was characterized by IR, transmission electron microscopy, electron diffraction, photothermal deflection spectroscopy, and electron spin resonance. The product was identical in all respects with *trans*-polyacetylene prepared by standard routes, except that the number of neutral defects (solitons) is reduced from ~1/3000 C atoms to ~1/47000 and the line width of the signal due to these defects increased from ~1 to 5 G. The reduced defect level makes this an extremely useful material for studying the effect of solitons on the physical properties of polyacetylene.

Perhaps the most distinguishing physical property of polyacetylene is its extreme physical intractability.[1,2] Since it neither dissolves in solvents nor can be thermally processed, the physical form of this polymer is set at the time of synthesis. Thus, different synthetic routes to polyacetylene might be expected to yield polyacetylenes with different purities, morphologies, and/or microstructures. The most widely used procedure for polyacetylene synthesis was developed by Ito et al.[3] and yields silvery films with a high cis isomer content. The trans isomer can be produced by a suitable thermal treatment, which also generates numerous (~1/3000 C atoms) free spins.[4]

A more recent approach to polyacetylene synthesis was developed by Feast and Edwards.[5,6] Their route, via a precursor polymer which can later be converted to polyacetylene, has led to the development of highly ordered crystalline films of *trans*-polyacetylene.[7,8] These films also contain numerous free spins[9] (~1/2000 C atoms) and can be converted to polymeric conductors by either oxidation or reduction.[10,11]

The spins observed in *trans*-polyacetylene prepared by the Shirakawa method are distinguished from those found in other conducting polymers by their postulated mobility in the conjugated

† Bell Communications Research.
‡ AT&T Bell Laboratories.

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