for $C_{10}H_{11}N_3OS$: C, 54.28; H, 5.01; N, 18.99. Found: C, 54.27; H, 5.04; N, 18.90.

***N*-Phenyl-*N'*-2-thiazolidinylideneurea (5).** To a stirring solution of 5.12 g (0.05 mol) of 1 in 60 mL of dry DMF at ambient temperature was added drop by drop over 25 min a solution of 4.77 g (0.04 mol) of phenyl isocyanate in 20 mL of dry DMF. The mixture was allowed to stir for 3 h and then poured onto excess ice and the crude solid collected, washed with H_2O, and dried. Recrystallization from EtOH and DMF-H_2O gave 9.0 g (81%) of pure **5** (R_f 0.1): mp 150-152 °C (lit.[3] mp 149.5-150 °C; lit.[15] mp 157-159 °C): ^{1}H NMR (DMF-d_7) δ 9.66 (1 H, br s, NH), 8.70 (1 H, s, N'H), 8.0-6.9 (5 H, m, Ph H), 3.44 (4 H, m, CH_2CH_2); IR (KBr) 3220 (NH), 1685 (C=O), 1620 (C=N) cm^{-1}. Anal. Calcd for $C_{10}H_{11}N_3OS$: C, 54.28; H, 5.01; N, 18.99. Found: C, 54.23; H, 5.02; N, 18.95.

Heating pure **4** neat and in solution in the same manner as **2** gave essentially clean conversion to **5**. Small amounts of two impurities (R_f 0.59 and 0.64, respectively) were observed on TLC. TLC of the 150-152 °C melt indicated significant amounts of **1**, the two front-running materials described, and an additional small impurity at R_f 0.73.

Preparation of **5** according to the directions of Klayman (1 mol:1 mol) in refluxing benzene also led, in our hands, to the formation of small amounts of bis adduct.[3]

Registry No. **1**, 1779-81-3; **1**·HBr, 13483-03-9; **2**, 101418-75-1; **3**, 13945-09-0; **4**, 14033-35-3; **5**, 14033-37-5; PhNCS, 103-72-0; PhNCO, 103-71-9.

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Reduction of Chiral β-Hydroxy Sulfoxides: Application to the Synthesis of Both Enantiomers of 4-Substituted Butenolides

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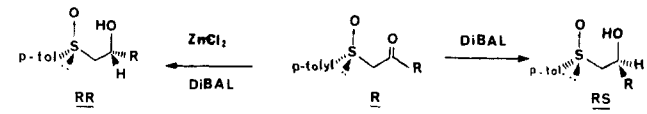
γ-Lactones and butenolides (1) are widely found as a moiety in many naturally occuring compounds such as insect pheromones or flavors. Numerous syntheses of such molecules in racemic form have been described,[1] but only a few reports of chiral synthesis of optically active butenolides have been published. Most of them deal with optical resolution of an intermediate[2] or transformation of an optically active precursor.[3] To our knowledge, only one asymmetric synthesis has been reported: asymmetric reduction of α,β-acetylenic ketones with lithium aluminum hydride complexed by *N*-methylephedrine and 3,5-dimethylphenol, yielding chiral propargylic alcohols which were transformed into butenolides.[4]

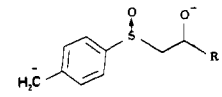
Scheme I



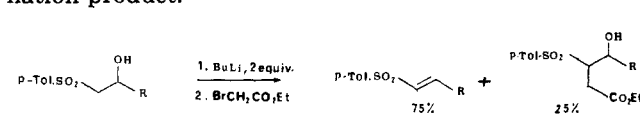
We recently reported[5,6] that the reduction of β-keto sulfoxides afforded both diastereomers of the corresponding β-hydroxy sulfoxides in high ee depending on the experimental conditions of the reduction (Scheme I). We report now the application of such a methodology to the chiral synthesis of butenolides.

For the synthesis of butenolides **1** (Scheme II), 2*R*-β-keto sulfoxides were prepared from the corresponding ethyl esters and (*R*-(+)-*p*-tolyl methyl sulfoxide.[6] The reduction step was performed either directly with DIBAL in THF at -78 °C affording the diastereomer (*RS*)-**3** or after complexation with zinc chloride followed by addition of DIBAL to give the diastereomer (*RR*)-**3**. Diastereomeric excesses were easily determined by ^{1}H NMR at 200 MHz. The two diastereomers (*RS*)-**3** and (*RR*)-**3** show quite different nonequivalences for the two protons α to the sulfoxide as well as quite different chemical shifts for the *tert*-butyl protons. The absolute configuration was deduced from our preceeding study on the reduction mechanism.[5] As indicated in Scheme II this reduction step was highly stereospecific. The smaller de observed with **3c** was the result of a reverse addition of DIBAL as shown in the preceeding paper[5] (method B).

β-Hydroxy *p*-tolyl sulfoxide **3** could not be alkylated on the carbon atom α to the sulfoxide. We demonstrated by labeling experiments that such a molecule gives a dianion having the following structure:



Therefore it was necessary to oxidize the sulfoxide to a sulfone. However, the alkylation of the corresponding dianion with ethyl bromoacetate gave mainly the elimination product:



Recently Tanaka[7] reported that the alkylation of racemic β-hydroxy sulfones could be performed by using sodium iodoacetate instead of any haloacetic ester. We have been able to repeat this experiment on the optically active sulfone (*S*)-**4** and (*R*)-**4** and without isolation of intermediates, convert the resulting hydroxyacids into the corresponding butenolides (*S*)-**1** and (*R*)-**1** by lactonisation in presence of *p*-toluenesulfonic acid and elimination of the sulfonyl group with triethylamine.

The enantiomeric purity of butenolide (*S*)-**1a** could be checked by NMR in presence of the chiral complex Eu(Tfc)$_3$. The racemic compound showed that for a molar ratio [Eu]/[butenolide] = 4, two nonequivalent *tert*-butyl groups can be detected ($\Delta\nu$ = 1.5 Hz). In these conditions

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(3) (a) David, U.; Silverstein, R. M. *Tetrahedron Lett.* **1977**, 423. (b) Tumilson, J. H.; Klein, M. G.; Doolittle, R. E.; Ladd, T. L.; Proveaux, A. T. *Science* **1977**, *197*, 789.

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(6) Solladié, G.; Demailly, G.; Greck, C. *J. Org. Chem.* **1985**, *50*, 1552.

(7) Tanaka, K.; Ootake, K.; Imai, K.; Tanaka, N.; Kaji, A. *Chem. Lett.* **1983**, 633. We are indebted to Prof. Tanaka for providing us the experimental part corresponding to this paper.

0022-3263/86/1951-1912$01.50/0

optically active (*S*)-**1a** did not show any splitting of the *tert*-butyl signal. Therefore one can conclude that no racemization occured during the transformation of the β-hydroxy sulfoxide into butenolide.

The methodology described in this paper is therefore a very efficient way to prepare either enantiomers of butenolides in very high ee using the highly stereospecific reduction of chiral β-keto sulfoxides.

Experimental Section

β-Keto Sulfoxides 2. General Procedure. To a solution of LDA (16 mmol) in 40 mL of THF at −30 °C was dropwise added (+)-(*R*)-methyl *p*-tolyl sulfoxide[8] (8 mmol) in 40 mL of THF. Temperature was then allowed to reach 0 °C and then cooled at −40 °C. A solution of 12 mmol of ester in 20 mL of THF was dropwise added. Temperature was then allowed to reach room temperature, and then the reaction mixture was heated under reflux for 4 h. The reaction mixture was decomposed with a saturated ammonium chloride solution (20 mL). The organic layer was separated, and the aqueous solution acidified with 10% HCl to pH 3–4 and extracted with CH_2Cl_2 (3 × 20 mL). After evaporation of the solvent, the residue was purified by chromatography on silica gel (eluent ether/hexane 60/40).

β-Keto Sulfoxide (*R*)-2a (R = *t*-Bu): yield, 84%; mp 110–111 °C; $[\alpha]_D$ +181° ($CHCl_3$, *c* 1).[9] IR ($CHCl_3$): 1705 (ν = 0), 1090 cm^{-1} ($\nu_{S\rightarrow O}$). NMR ($CDCl_3$): δ 1.0 (s, 9 H, *t*-Bu), 2.4 (s, 3 H, CH_3 benzyl), 4.0 (AB, 2 H, J_{AB} = 15 Hz, $\Delta\nu$ = 18.7 Hz, CH_2SO), 7.2–7.8 (m, 4 H, arom).

β-Keto Sulfoxide (*R*)-2b (R = *n*-C_8H_{17}): yield, 65%; mp 59–61 °C; $[\alpha]_D$ +138° ($CHCl_3$, *c* 1). IR ($CHCl_3$): 1705, 1090 cm^{-1}. NMR ($CDCl_3$): δ 0.8–1.7 (m, 15 Hz), 2.3–2.6 (m, 5 H, CH_3 benzyl, and CH_2CO), 3.8 (s, 2 H, CH_2SO), 7.7–7.8 (m, 4 H, arom). Anal. Calcd for $C_{17}H_{26}O_2S$: C, 69.33; H, 8.92. Found: C, 69.10; H, 8.91.

β-Keto Sulfoxide (*R*)-2c (R = *n*-C_5H_{11}): yield, 60%; mp 74–5 °C; $[\alpha]_D$ +190° ($CHCl_3$, *c* 1). IR ($CHCl_3$): 1705, 1090 cm^{-1}. NMR ($CDCl_3$): δ 0.7–1.8 (m, 9 H), 2.3–2.6 (m, 5 H, CH_3 benzyl and CH_2CO), 3.8 (s, 2 H, CH_2SO), 7.2–7.8 (m, 4 H, arom). Anal. Calcd for $C_{14}H_{20}O_2S$: C, 66.62; H, 8.00. Found: C, 66.87; H, 8.11.

Reduction of β-Keto Sulfoxides. General Procedure. A. With Diisobutylaluminium Hydride. To a solution of β-keto sulfoxide (2 mmol) in THF (20 mL) at −78 C was dropwise added 2.2 mL (2.2 mmol) of a 1 M solution of DIBAL in hexane.

After 1 h at −78 °C, the reaction mixture was decomposed by adding 20 mL of MeOH. The solvent was then evaporated and the residue was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with a 5% HONa solution, dried, and evaporated. The reaction was shown to be quantitative by TLC. The diastereoisomeric excesses were determined on the crude product by NMR. Finally the product was purified by chromatography on silica gel (eluent: ether/hexane, 60/40).

B. With DIBAL in the Presence of $ZnCl_2$. To a solution of β-keto sulfoxide (2 mmol) in THF (20 mL) was added 1.1 equiv of anhydrous zinc chloride (2.2 mmol) in solution in THF (20 mL). After 1 h at room temperature, the reaction mixture was cooled at −78 °C and 2.2 mL of a 1 M solution of DIBAL in hexane (2.2 mmol) was added. After 1 h at −78 °C, the same workup as in part A was used.

The reaction was shown to be quantitative by TLC. The diastereoisomeric excesses were determined by NMR on the crude product. Finally the product was purified as in part A.

β-Hydroxy Sulfoxide (*RS*)-3a: obtained by reduction with DIBAL; yield in isolated product, 80%; mp 124–6 °C; diastereoisomeric ratio, *RS*/*RR* > 95/5. IR ($CHCl_3$): 3400 (ν_{OH}), 1010 cm^{-1} ($\nu_{S\rightarrow O}$). NMR ($CDCl_3$): δ 0.85 (s, 9 H, Bu), 2.45 (s, 3 H, CH_3 benzyl), 2.82 (AB part of ABX, J_{AB} = 13.5 Hz, $\Delta\nu$ 57.4 Hz, J_{AX} = 10.5 Hz, J_{BX} = 1.5 Hz, 2 H, CH_2SO), 3.35 (d, 1 H *J* = 3 Hz, OH), 3.75–3.85 (m, 1 H, CHOH), 7.45 (A_2B_2, J_{AB} = 7.5 Hz, $\Delta\nu$ 35 Hz, 4 H, arom).

β-Hydroxy Sulfoxide (*RR*)-3a: obtained by reduction with DIBAL/$ZnCl_2$; yield in isolated product, 80%; mp 99–102 °C; diastereoisomeric ratio, *RR*/*RS* = 95/5. NMR ($CDCl_3$): δ 0.92 (s, 9 H, Bu), 2.45 (s, 3 H, CH_3 benzyl), 2.85 (AB part of ABX, J_{AB} = 13.5 Hz, $\Delta\nu$ = 6 Hz, J_{AX} = 5.5 Hz, J_{BX} = 6 Hz, 2 H, CH_2SO), 3.85 (d, 1 H, *J* = 2 Hz, OH) 3.95 (dt, 1 H, *J* = 6 Hz, *J* = 2 Hz, CHOH), 7.45 (A_2B_2, *J* = 7.5 Hz, $\Delta\nu$ = 35 Hz, 4 H, arom).

β-Hydroxy Sulfoxide (*RS*)-3b: obtained by reduction with DIBAL; yield in isolated product, 80%; diastereoisomeric ratio, *RS*/*RR* = 93/7. IR ($CHCl_3$): 3400 (ν_{OH}), 1080 cm^{-1} ($\nu_{S\rightarrow O}$). NMR ($CDCl_3$): δ 0.90 (m, 3 H, CH_3), 1.20–1.75 (m, 14 H), 2.45 (s, 3 H, CH_3 benzyl), 2.84 (AB part of ABX, J_{AB} = 13.5 Hz, $\Delta\nu$ = 84.0 Hz, J_{AX} = 10 Hz, J_{BX} = 2 Hz, 2 H, CH_2SO), 3.62 (d, *J* = 3 Hz, 1 H, OH), 4.05–4.20 (m, 1 H, CHOH), 7.45 (A_2B_2, J_{AB} = 7.5 Hz, $\Delta\nu$ 35 Hz, 4 H arom).

β-Hydroxy Sulfoxide (*RR*)-3b: obtained by reduction with DIBAL/$ZnCl_2$; yield in isolated product, 80%; diastereoisomeric ratio, *RR*/*RS* > 95/5. NMR ($CDCl_3$): 0.90 (m, 3 H, CH_3), 1.20–1.75 (m, 14 H), 2.45 (s, 3 H, CH_3 benzyl), 2.85 (AB part of ABX, J_{AB} = 13.5 Hz, $\Delta\nu$ = 32.5 Hz, J_{AX} = 9 Hz, J_{BX} = 2 Hz, 2 H, CH_2SO), 3.80 (d, *J* = 3 Hz, 1 H, OH), 4.25–4.40 (m, 1 H, CHOCH), 7.45 (A_2B_2, J_{AB} = 7.5 Hz, $\Delta\nu$ = 35 Hz, 4 H arom).

β-Hydroxy Sulfoxide (*RS*)-3c: obtained by reduction with DIBAL by reverse addition (5); yield in isolated product; 85%; diastereoisomeric ratio, *RS*/*RR* 85/15. IR ($CHCl_3$): 3400 (ν_{OH}), 1080 ($\nu_{S\rightarrow O}$). NMR ($CDCl_3$) δ 0.8–1.6 (m, 11 H), 2.45 (s, 3 H, CH_3 benzyl), 2.82 (AB, part of ABX, J_{AB} = 13.5 Hz, $\Delta\nu$ = 73.0 Hz, J_{AX} = 9 Hz, J_{BX} = 2 Hz, 2 H, CH_2SO), 4.1 (m, 1 H, CHOH), 7.45 (A_2B_2, J_{AB} = 7.5 Hz, $\Delta\nu$ = 3 Hz, 4 H, arom). Diastereomer **3c**-(*RR*): NMR ($CDCl_3$) δ 0.8–1.6 (m, 11 H) 2.45 (s, 3 H, CH_3, benzyl), 2.85 (AB part of ABX, J_{AB} = 13.5 Hz, $\Delta\nu$ = 34.6 Hz, J_{AX} = 8.5 Hz, J_{BX} = 2.5 Hz, 2 H, CH_2SO), 4.3 (m, 1 H, CHOH), 7.45 (A_2B_2, J_{AB} = 7.5 Hz, $\Delta\nu$ = 35 Hz, 4 H arom).

Oxidation of β-Hydroxy Sulfoxides to Sulfones 4. General Procedure. To a solution of β-hydroxy sulfoxide **3** (1 mmol) in CH_2Cl_2 (20 mL) was added at room temperature 1.1 equiv of *m*-CPBA in CH_2Cl_2 (20 mL). After 6 h at room temperature, the reaction mixture was washed with a 5% aqueous solution of sodium hydroxyde (20 mL) and then dried over sodium sulfate. After evaporation of the solvent, the crude sulfone obtained in 95–98% yield was used without any further purification.

β-Hydroxy Sulfones (*S*)-4a and (*R*)-4a: Sulfone (*S*)-**4a** was obtained by oxidation of the β-hydroxy sulfoxide (*RS*)-**3a** (de > 90%) with 98% yield and sulfone (*R*)-**4a** from the sulfoxide (*RR*)-**3a** (de > 90%) with 96% yield: mp 69 °C. IR ($CHCl_3$): 3500, 1300, 1135 cm^{-1}. NMR ($CDCl_3$): δ 0.88 (s, 9 H, *t*-Bu), 2.48 (s, 3 H, CH_3 benzyl), 3.15 (AB part of ABX, J_{AB} = 13 Hz, $\Delta\nu$ = 22.5 Hz, J_{AX} = 10 Hz, J_{BX} = 2 Hz, 2 H, CH_2SO_2), 3.20–3.30 (m, 1 H, CHOH), 7.60 (A_2B_2, J_{AB} = 7 Hz, $\Delta\nu$ = 80 Hz, 4 H arom).

β-Hydroxy Sulfones (*S*)-4b and (*R*)-4b. Sulfone (*S*)-**4b** was obtained from the (*RS*)-**3b** (de = 86%) with 95% yield and sulfone (*R*)-**4b** from sulfoxide (*RR*)-**4b** (de > 90%) with 95% yield. IR ($CHCl_3$): 3500, 1300, 1135 cm^{-1}. NMR ($CDCl_3$): δ 0.88 (t, *J* = 5 Hz, 3 H, CH_3), 1.15–1.65 (m, 14 H,), 2.45 (s; 3 H, CH_3 benzyl), 3.19 (AB part of ABX, J_{AB} = 13 Hz, $\Delta\nu$ = 6 Hz, J_{AX} = 4 Hz, J_{BX} = 7 Hz, 2 H, CH_2SO_2), 4.10–4.20 (m, 1 H, CHOH), 7.60 (A_2B_2, J_{AB} = 7 Hz, $\Delta\nu$ = 80 Hz, 4 H arom).

β-Hydroxy Sulfone (*S*)-4e. Sulfone (*S*)-**4c** was obtained from the sulfoxide (*RS*)-**3c** (de = 70%) with 96% yield. IR ($CHCl_3$): 3500, 1300, 1135 cm^{-1}. NMR ($CDCl_3$): 0.88 (t, *J* = 5 Hz, 3 H, CH_3), 1.15–1.65 (m, 8 H), 2.45 (s, 3 H, CH_3 benzyl), 3.18 (AB part of ABX, J_{AB} 13 Hz, $\Delta\nu$ = 6 Hz, J_{AX} = 4 Hz, J_{BX} = 8 Hz, 2 H, CH_2SO_2), 4.07–4.20 (m, 1 H, CHOH), 7.60 ppm (A_2B_2, J_{AB} = 7 Hz, $\Delta\nu$ = 80 Hz, 4 H, arom).

Butenolides 1. General Procedure. This synthesis involves three different steps without isolating the intermediate products.

(1) To a solution of β-hydroxy sulfone **4** (1 mmol) in THF (10 mL) at −78 °C was dropwise added 2.2 equiv of *n*-BuLi in hexane. After 2 h at −10 °C, the yellow solution was cooled at −78 °C and 1.2 equiv of sodium iodoacetate was added. After 1 h at −10 °C, the reaction mixture was allowed to react at room temperature for 15 h. After decomposition with saturated ammonium chloride (2 mL) and separation of the organic layer, the aqueous phase was acidified by 10% HCl and extracted with ether (3 × 5 mL). The organic layers were dried and evaporated giving a crude β-sulfonyl δ-hydroxy acid which was used in the next step without further purification.

(2) This crude product was dissolved in benzene (50 mL) and a catalytic amount of γ-toluenesulfonic acid was added. After

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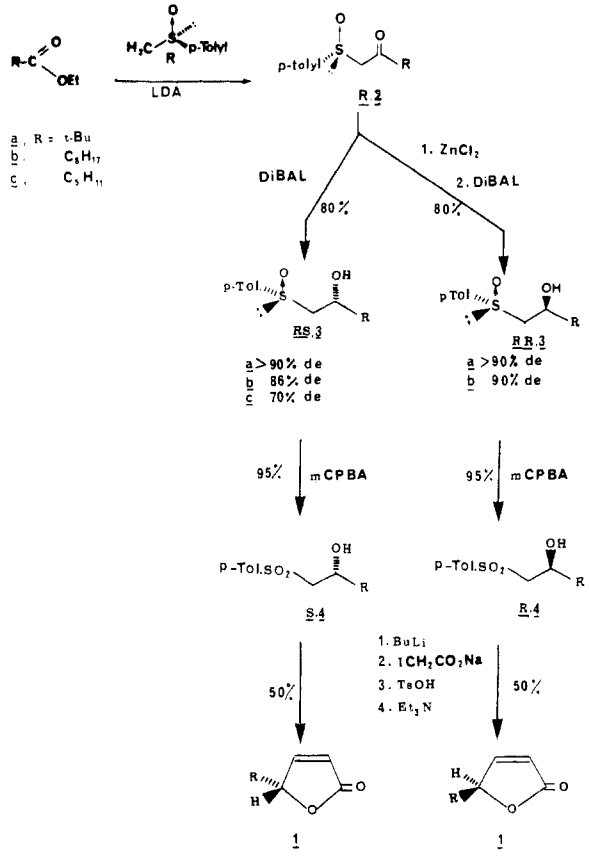
(9) Annunziata, R.; Cinquini, M.; Cozzi, F. *J. Chem. Soc. Perkin Trans 1* **1979**, 1687.

Scheme II



refluxing for 3 h in a soxhlet full of molecular sieves, the mixture was decomposed by adding a 5% aqueous solution of sodium bicarbonate (10 mL). After extraction with benzene, the organic layers were dried over sodium sulfate and concentrated to 50 mL.

(3) Triethylamine (4 equiv) was added to the solution and kept under stirring at room temperature for 15 h. The benzene solution was then washed with 10% HCl (10 mL), dried and evaporated.

The crude butenolide was finally purified by chromatography (eluent: ether/hexane 50/50). The overall yield for the three steps was around 50%.

Butenolides (*S*)-1a and (*R*)-1a. Butenolide (*S*)-**1a** was obtained from the β-hydroxy sulfone *S*-**4a** (ee > 90%) yield 50%, mp 59–61 °C; $[\alpha]_D$ +90° (dioxane, *c* 2). Anal. Calcd for $C_8H_{12}O_2$: C, 68.53; H, 8.64. Found: C, 68.37; H, 8.40. Butenolide **1a**-(*R*) was obtained from the β-hydroxy sulfone **4a**-(*R*) (ee > 90%): yield 47%, mp 59–61 °C; $[\alpha]_D$ −92° (dioxane, *c* 2); ee > 90% by RMN in presence of Eu(Tfc)$_3$ in the molar ratio (Eu)/[butenolide] = 0.4, nonequivalent *tert*-Butyl group, $\Delta\nu$ 1.5 Hz. IR ($CHCl_3$: 1740, 1160 cm^{-1}. NMR ($CDCl_3$): δ 1.0 (s, 9 H, *t*-Bu), 4.75 (m, 1 H, HC-CH=), 6.17 (dd, *J* = 5.5 Hz *J* = 2 Hz, =CHCO), 7.45 (dd, *J* = 5.5 Hz, *J* = 1.5 Hz, HC=).

Butenolides (*S*)-1b and (*R*)-1b. Butenolide (*S*)-**1b** was obtained from the β-hydroxy sulfone (*S*)-**4b** (ee = 86%); yield 45%; $[\alpha]_D$ +47° (dioxane, *c* 2).[4] There is some discrepancy with the optical rotation described in the literature probably due to the small scale experiment we performed. However, it was demonstrated in the case of butenolide **1a** that no racemization occured during the whole process.

Butenolide (*R*)-**1b** was obtained from the β-hydroxy sulfone (*R*)-**4b** (ee > 90%); yield 42%; $[\alpha]_D$ −49° (dioxane, *c* 2). IR ($CHCl_3$): 1740, 1160 cm^{-1}. NMR ($CDCl_3$): δ 0.90 (t, 3 H, CH_3), 1.20–1.85 (m, 14 H), 5.05 (m, 1 H, HCCH=), 6.12 (dd, *J* = 5.5 Hz, *J* = 2 Hz, 1 H, =HCCO), 7.45 (dd, *J* = 5.5 Hz, *J* = 1 Hz, 1 H, HC=).

Butenolide (*S*)-1c was prepared from the β-hydroxy sulfone (*S*)-**4c** (ee = 70%); yield 40%; $[\alpha]_D$ +51° (dioxane, *c* 2). Anal. Calcd for $C_9H_{14}O_2$: C, 70.08; H, 9.17. Found C, 69.41; H, 9.07. IR ($CHCl_3$): 1740, 1160 cm^{-1}. NMR ($CDCl_3$): 0.90 (t, 3 H, CH_3), 1.20–1.85 (m, 8 H), 5.05 (m, 1 H, HCCH=), 6.12 (dd, *J* = 5.5 Hz, *J* = 2 Hz, =HCCO), 7.47 (dd, *J* = 1 Hz, HC=).

Pentaphene via 1,2-Anthracyne: An Application of Repeated Aryne–Isobenzofuran Methodology

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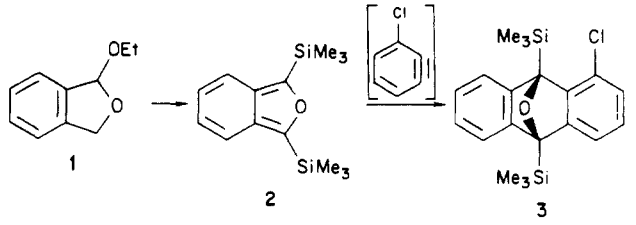
Received December 23, 1985

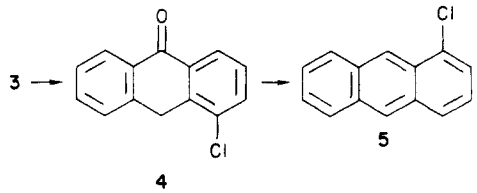
It appeared that recently developed methodology[1] which makes use of aryne cycloaddition to a protected form of isobenzofuran would allow a useful entry to the pentaphene skeleton, provided that 1,2-anthracyne could be generated. Of the various methods which in principle could be used to accomplish the formation of this reactive intermediate, strong base induced dehydrohalogenation is the only route that can avoid a potentially complex and multistep precursor synthesis. Even the 1-haloanthracenes are uncommon materials,[2] which apparently have not been examined as potential aryne-forming substrates.

A useful synthesis of 1-chloroanthracene has been developed, as outline in eq 1 and 2. By methods already described,[1] the acetal **1** was converted to 1,3-bis(trimethylsilyl)isobenzofuran (**2**); addition to the same reaction flask of *o*-dichlorobenzene and lithium tetramethylpiperidide (LTMP) generated the reactive intermediate 3-chlorobenzyne, which was efficiently trapped by **2** to give the cycloadduct **3** (62% after recrystallization).



(1)

As anticipated from the reactions of the 1-bromo and 1-methyl analogues[1b] of this material, treatment of **3** with trifluoroacetic acid (TFA) resulted in highly regioselective conversion to 4-chloroanthracen-9(10*H*)-one (**4**). This selectivity was evident from integration of the ^{1}H NMR spectrum, which exhibited a two-proton multiplet, attributed to the peri protons proximal to the carbonyl group, downfield from the major 5-proton aromatic absorption. Reduction of **4** by $LiAlH_4$ followed by acid-catalyzed dehydration gave 1-chloroanthracene (**5**) in 85% yield (based on **3**).



(2)

A separately prepared solution of **2** (1.5 equiv) was in turn treated with **5** and LTMP; that this method is suitable for the generation of 1,2-anthracyne (**6**) was shown by the isolation of the cycloadduct **7** (eq 3), as bright yellow needles (62% after recrystallization).[3]

(1) (a) Crump, S. L.; Netka, J.; Rickborn, B. *J. Org. Chem.* **1985**, *50*, 2746. (b) Netka, J.; Crump, S. L.; Rickborn, B. *Ibid.*, in press.

(2) Of the 1-haloanthracenes, only the chloride is commercially available, but the cost is prohibitive for many purposes.

(3) Anthracene itself serves well as a diene component in the Diels–Alder reaction with benzyne, and similar reaction of 1-chloroanthracene and 1,2-anthracyne is a possible competitive process in the formation of **7**. Integration of the aromatic proton region of the NMR spectrum of the crude product of eq 3 indicated that ≥70% of these absorptions are due to **7**, showing that alternative aromatics are not present in large amount.

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