to give the bicyclic ketone 23 as a gum. This gum was taken up in 4 mL of acetonitrile, and the solution was cooled at 0 °C. To this solution was added successively diphenyl chlorophosphate (190 μL, 0.92 mmol), diisopropylethylamine (160 μL, 0.92 mmol), and DMAP (<1 mg). After the mixture was stirred at 0 °C under Ar for 1 h, 3-pyridinemethanethiol (137 mg, 1.09 mmol) was added followed by additional diisopropylethylamine (190 μL, 1.09 mmol). The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for 1 h. The resulting mixture was diluted with EtOAc–ether (1:1), and this solution was washed (10% saturated $NaHCO_3$, 10% saturated NH_4Cl, brine), dried (Na_2SO_4), and evaporated to give a gum. Flash chromatography (SiO_2, EtOAc then MeCN) of this gum gave the title compound (138 mg, 47%) as a white foam: $[\alpha]^{25}_D$ +71.0° (c 0.5, $CHCl_3$); IR ($CDCl_3$), 3420, 1770, 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.50–8.56 (m, 2 H), 7.66–7.72 (m, 1 H), 7.23–7.30 (m, 1 H), 5.85–6.04 (m, 1 H), 5.37–5.48 (m, 1 H), 5.20–5.28 (m, 1 H), 4.61–4.87 (m, 2 H), 3.91–4.12 (m, 5 H), 3.41–3.47 (m, 1 H), 3.30 (dq, J = 7.3, 9.1 Hz, 1 H), 1.8 (br s, 1 H), 1.25 (d, J = 7.3 Hz, 3 H). Anal. Calcd for $C_{18}H_{20}N_2O_4S{\cdot}0.6H_2O$: C, 58.24; H, 5.76; N, 7.55. Found: C, 58.19; H, 5.43; N, 7.77.

Potassium (4*R*,5*S*,6*S*)-3-[(Pyridin-3-ylmethyl)thio]-6-(hydroxymethyl)-4-methyl-7-oxo-1-azabicyclo[3.2.0]hept-2-ene-2-carboxylate (26). To a solution of the allyl ester 25 (58 mg, 0.16 mmol) in 500 μL of acetonitrile was added a solution of tetrakis(triphenylphosphine)palladium (4 mg, 2 mol %) and triphenylphosphine (4 mg) in 100 μL of CH_2Cl_2, followed by a solution of potassium 2-ethylhexanoate (32 mg, 0.176 mmol) in 250 μL of EtOAc. After the mixture was stirred at room temperature under Ar for 1.5 h, it was diluted with ether and the supernatant was decanted. Ether was again added, the supernatant was decanted, and the residue was dried in vacuo to give a tan powder. Reverse-phase chromatography (C_{18} Bonda-Pak/H_2O) of this powder gave, after lyophilization, the title compound (41 mg, 72%) as off-white glassy beads: IR (KBr) 3400, 1750, 1595 cm^{-1}; ^1H NMR (D_2O) δ 8.52 (d, J = 2.3 Hz, 1 H), 8.43 (dd, J = 1.5, 4.9 Hz, 1 H), 7.90 (dt, J = 1.9, 8.0 Hz, 1 H), 7.44 (dd, J = 5.0, 8.0 Hz, 1 H), 4.18, 4.05 (AB q, J = 14.1 Hz, 2 H), 3.82–4.05 (m, 4 H), 3.50–3.56 (m, 1 H), 3.33 (dq, J = 7.3, 9.0 Hz, 1 H), 1.16 (d, J = 7.2 Hz, 3 H); UV (H_2O, pH 7) 206 (ε 10209), 270 (ε 5707), 304 (ε 9157) nm.

Acknowledgment. We wish to thank Drs. H. Mastalerz, A. Martel, and R. Vanga for useful discussions and to acknowledge the interest and encouragement of (the late) Professor B. Belleau and Dr. M. Ménard during the course of this work.

Direct Epoxidation of Fluorinated Olefins Using the F_2–H_2O–CH_3CN System

Ming H. Hung, Bruce E. Smart, Andrew E. Feiring, and
Shlomo Rozen*

Du Pont, Central Research & Development, Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

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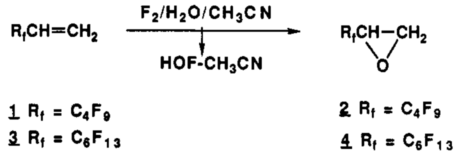
Fluorine-containing epoxides are important intermediates in the synthesis of surfactants, oligomers, and polymers with special properties.[1] Since most polyfluorinated olefins are too deactivated for direct electrophilic epoxidation, their epoxides are usually made by either using special catalysts or employing indirect methods. For example, our attempts to epoxidize the electron deficient double bond of 3,3,4,4,5,5,6,6,6-nonafluorohexene (1) with *m*-chloroperoxybenzoic acid or trifluoroperacetic acid were unsuccessful; only starting material was recovered.

One of us recently developed a new method using elemental fluorine to epoxidize olefins.[2] When fluorine is passed through a water–acetonitrile mixture, a relatively stable HOF–acetonitrile complex is formed.[3] This is a rare case of an oxidizing system where the partial charge on the oxygen atom is permanently positive,[4] which is responsible for the complex's very efficient epoxidation of moderately electron rich olefins. We report here on the ability of the HOF–CH_3CN system to epoxidize 1 and related electron-deficient fluoroolefins.

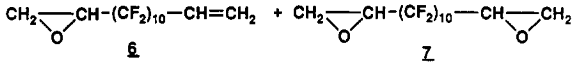
When a hydrocarbon olefin is reacted with the F_2–H_2O–CH_3CN oxidizing mixture at 0 °C or lower, it usually takes less than a minute for complete epoxidation to occur.[2] Under similar conditions, however, fluoroolefin 1 failed to react. Since HOF is stabilized by CH_3CN[5] and can be easily prepared in relatively large amounts, it was possible to use a considerable excess of the reagent,[6] raise the temperature to about 25 °C, and prolong the reaction time to a few hours. Under these conditions the electron-deficient olefin smoothly reacted to form the corresponding epoxide 2 in over 70% yield. Similar results also were obtained with olefins possessing longer perfluorinated chains, such as 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctene (3), which formed the corresponding epoxide 4 in 80% yield.



With two identical double bonds in a molecule, as in the fluorinated diene 5,[7] it is difficult to differentiate their reactivity. The deactivating effect of the oxygen atom of the first-formed monoepoxide is hardly felt by the remaining double bond, especially when compared to the strong electron-withdrawing effect of the CF_2 groups. Thus, when only a moderate excess of the reagent is used, a mixture of the mono- (6) and bis-epoxide (7) was formed. With a very large excess of the reagent the reaction could be driven to completion to form the bis-epoxide 7 in 72% yield.

$$CH_2{=}CH{-}(CF_2)_{10}{-}CH{=}CH_2$$

5



6 **7**

With more differentiated double bonds, however, the more electron rich olefin can be regiospecifically epoxidized. Thus, 1,1,2-trifluoro-1,5-hexadiene (8) reacted with the in situ prepared HOF–CH_3CN reagent in less than 2 min to produce only 5,6-epoxy-1,1,2-trifluoro-1-hexene (9). Similarly, 1,1,2-trifluoro-1,7-octadiene (10) and

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* Direct correspondance to this author at School of Chemistry, Tel-Aviv University, Tel-Aviv 69978, Israel.

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(5) Unlike pure HOF, which is unstable above –70 °C, the HOF–CH_3CN complex has a half-life of several hours at room temperature.

(6) In contrast with the olefin epoxidations described in ref 2, most of the alkenes in this work had to be treated with a considerable excess of HOF–CH_3CN to achieve near quantitative conversion.

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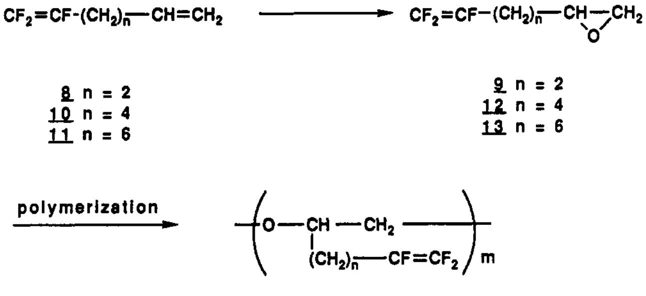
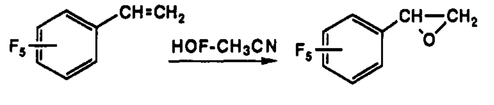
1,1,2-trifluoro-1,9-decadiene (11)[8] were converted in good yields to the corresponding epoxides 12 and 13 without affecting the trifluoroethylene moiety. These monoepoxides could be polymerized through the epoxy group to yield polymers with pendant fluorovinyl substituents that could be used for cross-linking and other chemical modifications.[9] Regioselective epoxidation is also possible when both aromatic and other π centers are present in the same molecule. For example, pentafluorophenylethene (14) reacted with the oxidizing mixture in 5 min to form the corresponding epoxide 15[10] in 85% yield.[11]



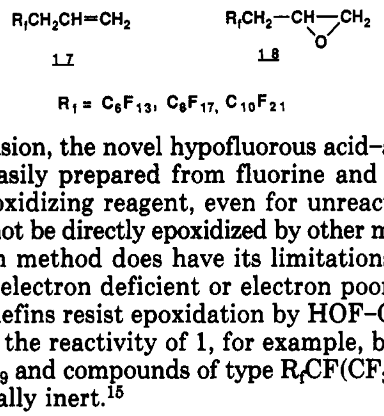
8 n = 2
10 n = 4
11 n = 6

9 n = 2
12 n = 4
13 n = 6



14 15

Another potentially important group of olefins are the 3-(perfluoroalkyl)-1-propenes (17)[12] whose epoxides[13] are particularly useful intermediates to surfactants.[14] Since the double bonds in these olefins are separated from the electron withdrawing perfluorinated chains by a methylene unit they are more susceptible to electrophilic attack and treatment with a moderate excess of HOF–CH_3CN rapidly converts them to the corresponding epoxides 18 in very good yields.



17 18

In conclusion, the novel hypofluorous acid–acetonitrile complex, easily prepared from fluorine and water, is a general epoxidizing reagent, even for unreactive olefins which can not be directly epoxidized by other means. This epoxidation method does have its limitations, however. Extremely electron deficient or electron poor, sterically hindered olefins resist epoxidation by HOF–CH_3CN. In contrast to the reactivity of 1, for example, both $C_4F_9CH{=}CHC_4F_9$ and compounds of type $R_fCF(CF_3)CH{=}CH_2$ are practically inert.[15]

Experimental Section

Caution! Molecular fluorine is a very toxic and corrosive gas. The following reactions should be carried out in an efficient fume hood, and the experimenter should be familiar with the precautions necessary for safe handling of fluorine.[16] Since molecular fluorine diluted with an inert gas is much safer to handle than pure fluorine, the use of a fluorine/nitrogen mixture comprising no more than 20% fluorine is recommended. A reaction apparatus for working with elemental fluorine has been described.[17]

General Procedure for Producing the HOF–CH_3CN Oxidizing System. Mixtures of 10–15% F_2 diluted with nitrogen were used. This mixture was passed at a rate of about 400 mL/min through a cold (−10 °C) and vigorously stirred mixture of 400 mL of CH_3CN and 40 mL of H_2O. The level of the oxidizing power was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with a standard aqueous sodium thiosulfate solution. Concentrations of oxidizing agent of more than 1 mol/L can be generated.

General Epoxidation Procedure. The olefin (5–20 g) was dissolved in about 50 mL of CH_2Cl_2, cooled to 0 °C, and added in one portion to the reaction vessel in which the oxidizing agent had been prepared. Except for reactions with the more reactive olefins, the cooling bath was removed and the reaction was stopped after 3 h by neutralization with solid sodium bicarbonate or its saturated aqueous solution. Reactions can be left for longer periods, but most of the reagent decomposes after 3–4 h. The reaction mixture was then poured into 1.5 L of water, extracted with $CFCl_3$, and washed with aqueous $NaHCO_3$ and water until neutral. The organic layer was dried over $MgSO_4$, and the solvent was removed by distillation. The residue containing the crude product was usually distilled at either atmospheric or reduced pressure.

Epoxidation of 3,3,4,4,5,5,6,6,6-Nonafluorohexene (1). The olefin 1[18] (15 g, 61 mmol) dissolved in 30 mL of CH_2Cl_2 was added to 250 mmol of the oxidizing solution. The reaction was left until no more oxidizing reagent could be detected and worked up as described above. The epoxide was distilled to give 3 g of the starting material and 10 g (63%) of the epoxide 2: bp 81–83 °C; IR (KBr) 1240 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.0 (2 H, dm, J = 10 Hz), 3.5 (1 H, tm, J = 10 Hz); ^{19}F NMR ($CDCl_3$) δ −81.6 (3 F, tm, J = 10 Hz); MS *m/z* 262 (M$^+$). Anal. Calcd for $C_6H_3F_9O$: C, 27.48; H, 1.15; F, 65.27. Found: C, 27.63; H, 1.32; F, 65.01.

Epoxidation of 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctene (3). To a solution of 230 mmol of the oxidizing reagent in 440 mL of CH_3CN-H_2O (10:1) was added 20 g (58 mmol) of 3[18] in 20 mL of CH_2Cl_2. After 2 h the reaction was neutralized with solid sodium bicarbonate. The reaction mixture was distilled at 80 mm to afford 230 mL of liquid consisting mainly of acetonitrile and epoxide 4. It was poured into 1 L of water and worked up as above. The epoxide (80% yield at 60% conversion) distilled at 20–22 °C (1 mm): IR (KBr) 1200, 1240 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.0 (2 H, dm, J = 10 Hz), 3.5 (1 H, tm, J = 10 Hz); ^{19}F NMR (CD_2Cl_2) δ −81.4 (3 F, tm, J = 10 Hz); MS *m/z* 362 (M$^+$). Anal. Calcd for $C_8H_3F_{13}O$: C, 26.52; H, 0.83; F, 68.23. Found: C, 26.73; H, 1.02; F, 67.89.

Epoxidation of Fluorinated Diene 5. Following the above procedure, a solution of 240 mmol of the oxidizing reagent was prepared in 440 mL of acetonitrile–water (10:1). To this solution 10 g of 5[7] dissolved in 30 mL of CH_2Cl_2 was added, and the reaction was allowed to stand at room temperature until no oxidizing power remained. The reaction was worked up as described above. GC/MS analysis indicated the formation of both mono- (6) and bis-epoxides (7) in 30% and 55% yields, respectively. MS, *m/e* (6) 551 [(M − F)$^+$], 77 [($CF_2CH{=}CH_2$)$^+$]. When the epoxidation was repeated using the above mixture of 6 and 7 as a substrate, the yield of 7 increased to 72%: mp 93 °C (from cyclohexane); ^{1}H NMR (CD_2Cl_2) δ 3.5 (1 H, m), 3.0 (2 H, m); MS *m/z* (7) 586 (M)$^+$, 536 [(M − CF_2)$^+$], 486 [(M − $2CF_2$)$^+$], 100 [($(CF_2)_2$]$^+$. Anal. Calcd for $C_{14}H_6F_{20}O_2$: C, 28.67; H, 1.02; F, 64.85. Found: C, 28.63; H, 0.99; F, 64.81.

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[8] In general, synthesis of 8, 10, and 11 involves reaction between trifluoroiodoethene and an appropriate hydrocarbon olefin, followed by dehydroiodination. A full report on the preparation of these dienes will appear later.

[9] Hung, M., unpublished results. A separate report on the polymerizations and polymer properties will be published later.

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[11] If a large excess of the HOF–CH_3CN reagent is allowed to react with aromatic compounds for prolonged periods of time, the aromatic ring can be attacked. This chemistry is currently under investigation.

[12] Matsubara, S.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 5857. Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 439.

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[14] Brace, N. O. U.S. Patent 3,145,222 (1964).

[15] After 10 h with a large excess of the HOF–CH_3CN reagent less than 5% of $C_4F_9CH{=}CHC_4F_9$ was converted to its epoxide and $R_fCF(CF_3)CH{=}CH_2$ had not detectably reacted. In a competition experiment, perfluorohex-1-ene actually reacted faster than n-$C_4F_9CH{=}CH_2$ but produced a complex mixture which contained carbonyl compounds and little epoxide.

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[17] Umemoto, T.; Tomita, K.; *Org. Synth.* **1990**, *69*, 129.

[18] Available from PCR, Inc., Gainesville, FL.

Epoxidation of Fluorinated Diene 8. A solution of 9.5 g (70 mmol) of 8[8] in 30 mL of CH_2Cl_2 was added to 200 mmol of the oxidizing reagent. After 2 min at 0 °C the reaction was worked up as described above. After the solvent was removed by distillation, the residual oil was fractionated to give the monoepoxide **9** (60%): bp (30 mm) 58 °C; IR (KBr) 1200, 1300 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.8–2.95 (2 H, dm), 3.31 (1 H, m), 1.9–2.67 (4 H, m); ^{19}F NMR (CD_2Cl_2) δ −100.8 to −102.9 (1 F, four m), −114.5 to −117.7 (1 F, four m), −166.9 to −169.3 (1 F, two m); MS *m/z* 151 [$(M - 1)^+$]; calcd mass for $C_6H_7F_3O$ 151.0371, found 151.0367. Anal. Calcd for $C_6H_7F_3O$: C, 47.37; H, 4.61; F, 37.50. Found: C, 47.35; H, 4.61; F, 37.86. In this case the only effect of lowering the ratio of the oxidizer/reactant as well as the temperature was to lower the conversion of the starting material from 100 to 70%.

Epoxidation of Fluorinated Diene 10. Olefin **10**[8] (9.7 g, 60 mmol) dissolved in CH_2Cl_2 (30 mL) was cooled to −40 °C and added to the oxidizing solution (160 mmol) also cooled to −40 °C. After 2 min the reaction was worked up as described above to afford the mono epoxide **12** (50%): bp (7 mm) 50–59 °C; ^1H NMR (CD_2Cl_2) δ 2.95 (1 H, m), 2.78 (1 H, t, J = 4 Hz), 2.49 (1 H, q, J = 6 Hz, 4 Hz) 1.4–2.4 (8 H, m); ^{19}F NMR (CD_2Cl_2) δ −106 (1 F, m), −125.4 (1 F, m), −175 ppm (1 F, m); MS *m/z* 180 (M^+), 108 [$(CF_2{=}CFCH_2CH_2 - 1)^+$], 95 [$(CF_2{=}CFCH_2)^+$]. Anal. Calcd for $C_8H_{11}F_3O$: C, 53.33; H, 6.11; F, 31.67. Found: C, 53.27; H, 6.13; F, 31.02.

Epoxidation of Fluorinated Diene 11. A solution of 5 g (26 mmol) of the olefin[8] dissolved in 20 mL of CH_2Cl_2 was added at −10 °C to 65 mmol of the oxidizing reagent. After 10 min the reaction was worked up as before to give 19% recovered starting materal and 55% monoepoxide **13**: ^1H NMR (CD_2Cl_2) δ 2.95 (1 H, m), 2.78 (1 H, t, J = 4 Hz), 2.46 (1 H, q, J = 6 Hz, 4 Hz) 1.3–2.4 (12 H, m); ^{19}F NMR (CD_2Cl_2) δ −106.5 (1 F, m), −125.7 (1 F, m), −175.1 (1 F, m); MS *m/z* 207 [$(M - 1)^+$]; calcd mass for $C_{10}H_{14}F_3O$ 207.0997, found 207.1029; 95 [$(CF_2{=}CFCH_2)^+$].

Epoxidation of Pentafluorophenylethylene (14). A solution of 8 g of **14**[18] in 20 mL of CH_2Cl_2 was added to the reagent solution (100 mmol in 440 mL of 10:1 $CH_3CN–H_2O$). After 5 min the reaction was neutralized with solid sodium bicarbonate. Most of the liquid was distilled off under reduced pressure (80 mm). The remaining liquid (50 mL) was poured into water, extracted with $CFCl_3$, and worked up as usual to give 6.7 g (85% yield) of epoxide **15**:[10] bp 34–37 °C (0.1 mm); ^1H NMR (CD_2Cl_2) δ 3.2 (2 H, 2 m), 4.0 (1 H, m); ^{19}F NMR (CD_2Cl_2) δ −143.9 (2 F, m), −154.1 (1 F, t, J = 21 Hz), −162.5 (2 F, m); MS *m/z* 210 (M^+).

Epoxidation of a Mixture of 3-(Perfluoroalkyl)-1-propenes (17).[12] To a solution of 100 mmol of the oxidizing reagent in 440 mL of $CH_3CN–H_2O$ (10:1) was added 20 g of a 1:1:1 mixture of $C_6F_{13}CH_2CH{=}CH_2/C_8F_{17}CH_2CH{=}CH_2/C_{10}F_{21}CH_2CH{=}CH_2$ in 50 mL of CH_2Cl_2. After 10 min the reaction was neutralized with solid sodium bicarbonate. The reaction mixture was poured into water, extracted with $CFCl_3$, and worked up as usual. The crude product (16.3 g) was shown to be a 1:1:1 mixture of epoxides **18**: MS ($R_f = C_6F_{13}$) *m/z* 360 (M^+), ($R_f = C_8F_{17}$) *m/e* 460 (M^+), ($R_f = C_{10}F_{21}$) *m/e* 560 (M^+).

A Convenient Synthesis of γ-Hydroxy α,β-Unsaturated Sulfones

Barry M. Trost* and Timothy A. Grese

Department of Chemistry, Stanford University, Stanford, California 94305-5080

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The synthetic versatility offered by γ-hydroxy α,β-unsaturated sulfones, especially as acceptors in our [3 + 2] cycloadditions, induced us to explore more convenient syntheses.[1-3] Extension of the excellent method of Tanikaga for the synthesis of γ-hydroxy α,β-unsaturated esters, which employs a Knoevenagel condensation in tandem with an allylic sulfoxide–sulfenate rearrangement,[4] to sulfones is highly attractive.[5-7] A recent communication, employing (phenylsulfinyl)(phenylsulfonyl)methanes,[8] leads us to give a full account of our work in this area.

Scheme I.[a] Synthesis of ((4-Chlorophenyl)sulfinyl)(phenylsulfonyl)methane

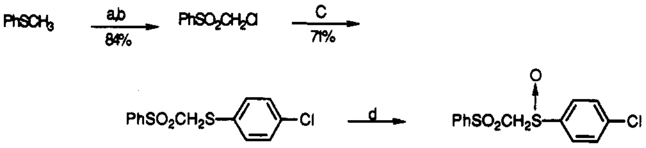

Table I. Synthesis of γ-Hydroxy α,β-Unsaturated Sulfones

entry	R	R′	temp, °C	time, h	% yield
1	H	H	rt	–	–
2	CH_3	H	rt	2	53
3	CH_3	CH_3	62–80	16	41
4	TBDMSO$(CH_2)_4$	H	rt	1	66
5	$CH_3(CH_2)_3$	H	rt	2	79
6	$CH_2{=}CH(CH_2)_7$	H	rt	2	90
7	$(CH_3)_2C{=}CHCH_2CH_2CH(CH_3)$	H	rt	2	94[a]
8	$PhCH(CH_3)$	H	rt	2	94[b]
9	Ph	H	rt	–	–
10	$(CH_3)_3CCH_2CH(CH_3)$	H	rt	2	93[c]

[a] dr 1:1. [b] dr 1.2:1. [c] dr 1.4:1.

We chose to employ ((4-chlorophenyl)sulfinyl)(phenylsulfonyl)methane (**1**) as our preferred reagent. Scheme I outlines its synthesis in 47% overall yield from thioanisole (MCPBA = *m*-chloroperoxybenzoic acid). Condensations with aldehydes according to eq 1 and Table I were normally performed by allowing an acetonitrile solution of equivalent quantities of reactants to stir with 1 equiv of piperidine at room temperature. The products show characteristic infrared absorbances at approximately 3600 cm^{-1} for the hydroxyl group and 1350–1150 cm^{-1} for the sulfone groups. ^1H NMR coupling constants for the vinyl hydrogens indicate only the *E* isomers are obtained in every case.

(1)

The reaction is relatively insensitive to the presence of water or impurities, so that anhydrous solvents or inert atmosphere conditions are not required. Substitution of the aldehyde at the α-position required higher temperatures and resulted in somewhat lower yield (Table I, entry 3), but β-substitution was not deleterious (Table I, entries 7, 8, and 10). The reaction failed with acetaldehyde and phenylacetaldehyde, possibly due to preferential self-condensation reactions.

Condensation of β-alkyl-substituted aldehydes (Table I, entries 7, 8, and 10) gave essentially nonselective mixtures of diastereomers. On the other hand, reaction of **1** with the carbohydrate-derived aldehyde **3** (prepared from **2** by the method of Nicolaou)[9] gave sulfone **5** as a 7.6:1

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