Anal. Calcd for $C_{15}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.27; H, 8.24.

The 2,4-dinitrophenylhydrazone was synthesized in the usual manner: mp 200–201 °C; $[\alpha]^{21}_D$ +225°.

Regeneration of Alcohols 4. A sample of dihydroestafiatone (**5**) (100 mg, 0.40 mmol) was dissolved in 5 mL of methanol at 0 °C under nitrogen and treated with sodium borohydride (70 mg, 1.8 mmol). After stirring for 1.5 h, water was added and the product was isolated with ether to give 94 mg of alcohols **4** as a colorless oil: IR (film) 3420, 3090, 1760, 1640, 900 cm^{-1}; NMR ($CDCl_3$) δ 4.86 (s, 2 H), 1.16 (d, J = 7 Hz, 3 H).

Trisubstituted Olefin 6 and Disubstituted Δ^2-Olefin. A 327-mg (1.3 mmol) sample of alcohols **4** (from sodium borohydride reduction of dihydroestafiatone) was dissolved in 45 mL of HMPA and heated at 250 °C for 50 min.[10] The cooled reaction mixture was then diluted with water and exhaustively extracted with hexane. The resulting oil (228 mg) was chromatographed on 45 g of 10% silver nitrate–silica gel with 10% ethyl acetate–hexane to furnish trisubstituted olefin **6** as an oil (82 mg), which could be further purified by bulb-to-bulb distillation (80 °C (0.25 mm)): $[\alpha]^{21}_D$ +46°; IR (film) 3080, 3040, 1780, 1640, 990, 900, 810 cm^{-1}; NMR (CCl_4) δ 5.36 (broad s, 1 H), 4.73 (broad s, 2 H), 3.82 (pseudo t, J = 8 Hz, 1 H), 1.83 (broad s, 3 H), 1.15 (d, J = 6 Hz, 3 H); mass spectrum m/e 232 (M^+).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.61; H, 8.80.

The disubstituted Δ^2-olefin (73 mg) was eluted in subsequent fractions. Recrystallization from hexane provided colorless needles: mp 77.5–79 °C; $[\alpha]^{21}_D$ −41°; IR (Nujol) 3070, 3040, 1760, 1630, 1455, 980, 900 cm^{-1}; NMR (CCl_4) δ 5.58 (broad d, J = 6 Hz, 1 H), 5.30 (dd, J = 2 and 6 Hz, 1 H), 4.72 (broad s, 1 H), 4.60 (broad s, 1 H), 3.83 (pseudo t, J = 9 Hz, 1 H), 3.33 (broad d, J = 10 Hz, 1 H), 1.16 (d, J = 7 Hz, 3 H); mass spectrum m/e 232 (M^+).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.45; H, 8.67.

In general, the crude alcohol mixture **4** from the $NaBH_4$–pyridine reduction of dienone **3** was dehydrated directly to produce a comparable mixture of olefins in somewhat lower yield.

Triene 8. Trisubstituted olefin **6** (117 mg, 0.50 mmol) in 0.5 mL of THF was added dropwise over 30 min to a solution of lithium diisopropylamide [from n-BuLi (0.75 mmol, hexane removed) and diisopropylamine (0.77 mmol) in THF (1.5 mL)] at −78 °C under nitrogen.[12] The resulting mixture was stirred for 20 min after which a solution of diphenyl diselenide (234 mg, 0.75 mmol) and HMPA (134 mg, 0.75 mmol) in 0.5 mL of THF was rapidly added. After 20 min at −78 °C and 1.5 h at −35 °C the reaction was quenched with 0.1 N HCl and the crude product was isolated with ether. Chromatography on silica gel using 10% ethyl acetate–hexane gave 147 mg of **7** as a crystalline solid: NMR (CCl_4) δ 7.56–7.00 (m, 5 H), 5.40 (broad s, 1 H), 4.83 (s, 1 H), 4.76 (s, 1 H), 3.95 (pseudo t, J = 9 Hz, 1 H), 1.82 (broad s, 3 H), 1.43 (s, 3 H).

The phenylseleno compound **7** (147 mg, 0.38 mmol) was dissolved in 2 mL of THF containing 0.06 mL of acetic acid and treated at 0 °C with 0.28 mL of 30% H_2O_2. After stirring for 0.5 h, the reaction mixture was poured into cold saturated sodium bicarbonate. Isolation with ether gave an oil which was chromatographed on silica gel using 5% ethyl acetate–hexane to give 75 mg of triene **8**, further purified by bulb-to-bulb distillation: mp 37–40 °C; $[\alpha]^{21}_D$ +113°; IR (film) 3090, 3050, 1765, 1655, 1640, 1005, 900, 820 cm^{-1}; NMR (CCl_4) δ 5.95 (d, J = 3 Hz, 1 H), 5.37 (broad s, 1 H), 5.26 (d, J = 3 Hz, 1 H), 4.78 (s, 2 H), 3.86 (pseudo t, J = 9 Hz, 1 H), 1.83 (broad s, 3 H); mass spectrum m/e 230 (M^+).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.05; H, 7.71.

(−)-Estafiatin (9). To a solution of triene **8** (60 mg, 0.26 mmol) in 5 mL of chloroform at −8 °C was added m-chloroperbenzoic acid (85%, 154 mg, 0.76 mmol) in three portions over 20 min. The temperature was slowly allowed to increase to 5 °C over 2.25 h. The reaction mixture was then washed with 10% sodium hydroxide and brine, dried, and concentrated under reduced pressure. Chromatography on silica gel using 10% ethyl acetate–hexane afforded 41 mg of an ca. 4:1 (by NMR) mixture of two epoxides, from which 26 mg of pure estafiatin was obtained by crystallization from ether–hexane: mp 104.5–105.5 °C; $[\alpha]^{21}_D$ −10°, $[\alpha]^{24}_{578}$ −15°, $[\alpha]^{24}_{546}$ −15°, $[\alpha]^{24}_{436}$ − 28°, $[\alpha]^{24}_{365}$ −60° (lit.[2] mp 104–106 °C; $[\alpha]^{20}_D$ −9.9°, $[\alpha]^{24}_{578}$ −13.9°, $[\alpha]^{24}_{546}$ −16.1°, $[\alpha]^{24}_{436}$ −30.6°, $[\alpha]^{24}_{365}$ −59.6°); IR (Nujol) 3080, 3020, 1760, 1660, 1645, 1150, 990, 910, 820 cm^{-1}; NMR ($CDCl_3$) δ 6.10 (d, J = 3 Hz, 1 H), 5.36 (d, J = 3 Hz, 1 H), 4.85 (s, 1 H), 4.79 (s, 1 H), 4.00 (dd, J = 8 and 10 Hz, 1 H), 3.30 (s, 1 H), 1.59 (s, 3 H); mass spectrum m/e 246 (M^+).

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.03; H, 7.48.

The pyrazoline derivative was synthesized with diazomethane, mp 118 °C dec [lit.[2] mp 120 °C dec].

Estafiatin was also synthesized in comparable yield by epoxidation of the trisubstituted olefin **6** followed by the introduction of the α-methylene group.

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Registry No.—**1**, 7759-23-1; **2**, 1618-98-0; **3**, 23811-43-0; **4**, 68151-24-6; **5**, 38142-65-3; **6**, 38236-17-8; **7**, 68151-25-7; **8**, 68151-26-8; **9**, 10180-89-9.

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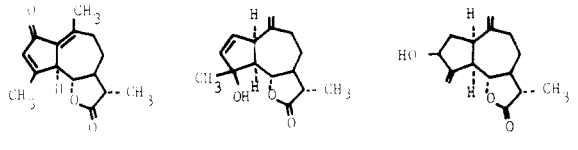

oxidation [P. A. Grieco, *ibid.*, **37**, 2363 (1972)], and treatment with sodium acetate.

An Improved Preparation of Sulfinate Salts and Their Michael Addition to Enones[1]

Harold W. Pinnick* and Michael A. Reynolds

Department of Chemistry, University of Georgia, Athens, Georgia 30602

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Arylsulfinic acids and their salts are available from the corresponding arylsulfonyl chlorides by zinc reduction.[2] On the other hand, aliphatic sulfinic acids and their salts are not easily prepared. The most common method is metal reduction of sulfonyl chlorides as with the aryl systems, but the yields are much lower and the reaction product is contaminated with other sulfur compounds.[2] Another preparation involves the reaction of Grignard reagents and organolithiums with sulfur dioxide, but this also suffers from competing side reactions.[2,3]

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Table I. Preparation of Sulfinate Salts

organometallic	registry no.	sulfinate salt (g; % yield)[a]	registry no.
n-BuLi	109-72-8	*n*-$BuSO_2Li$ (3.23; 102)	55163-93-4
t-BuLi	594-19-4	*t*-$BuSO_2Li$ (2.83; 92)	68152-32-9
MeLi	917-54-4	$MeSO_2Li$ (3.66; 80)	55163-92-3
$C_6H_5CH_2$-MgCl	6921-34-2	$C_6H_5CH_2SO_2MgCl$ (5.50; 101)	68152-33-0
sec-BuMgCl	15366-08-2	*sec*-$BuSO_2MgCl$ (4.40; 97)	68152-34-1

[a] All salts give satisfactory ^1H and ^{13}C NMR spectra.

Experimental Section

Proton nuclear magnetic resonance spectra were recorded on a Varian T-60 instrument. Carbon-13 nuclear magnetic resonance spectra were obtained with a JEOL PFT-100 spectrometer (resolution of 1.52 Hz). All chemical shifts are recorded in parts per million downfield from tetramethylsilane (0.0). Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected.

A typical procedure for each preparation is given below.

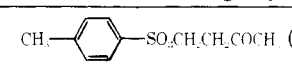
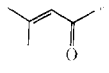
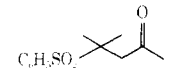
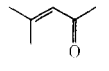
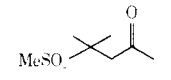
Preparation of Lithium *n*-Butylsulfinate. Sulfur dioxide (10 mL, 230 mmol) was condensed in a dry flask at −78 °C, and 40 mL of cold ether was added. A 2.45 M hexane solution of *n*-butyllithium (10.0 mL, 24.5 mmol) was added dropwise over 10 min. The reaction mixture was stirred for another 30 min at −78 °C and then was allowed to warm up to room temperature for 24 h. All volatile materials were removed on a rotary evaporator to leave 3.23 g (102%) of the sulfinate salt as a white powder: ^1H NMR (D_2O) 0.72 (t, J = 6 Hz, 3 H), 1.30 (m, 4 H), 2.18 (t, J = 8 Hz, 2 H) ppm; ^{13}C NMR (D_2O) 14.36, 22.72, 25.09, 61.55 ppm.

Preparation of Magnesium Chloride Benzylsulfinate. Benzyl magnesium chloride was prepared from 3.16 g (20.2 mmol) of benzyl chloride and 0.67 g (0.028 g-atom) of magnesium turnings in 25 mL of ether after refluxing for 1.5 h. This solution was added to 10 mL of SO_2, stirred, and concentrated as above to give 5.50 g (97%) of the white solid sulfinate salt: ^1H NMR (D_2O) 3.45 (s, 2 H), 7.15 (s, 5 H) ppm; ^{13}C NMR (D_2O) 68.80, 127.87, 129.22, 130.50, 132.63 ppm.

Preparation of 4-(*n*-Butylsulfonyl)butan-2-one. A solution of 0.928 g (7.25 mmol) of lithium *n*-butylsulfinate and 0.435 g (7.25 mmol) of glacial acetic acid in 10 mL of 95% ethanol was added over a 5-min period to 0.364 g (5.20 mmol) of MVK, and the reaction mixture was stirred for 12 h. Water (30 mL) was added, and the mixture was extracted with two 20-mL portions of chloroform. The combined organic layers were washed with 20 mL of saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated to give a viscous oil. Trituration with hexane and recrystallization from ethanol–ether gave 0.853 g (85%) of colorless plates: mp 57–58 °C; ^1H NMR ($CDCl_3$) 1.00 (m, 3 H), 1.67 (m, 4 H), 2.25 (s, 3 H), 3.13 (m, 6 H) ppm; ^{13}C NMR ($CDCl_3$) 13.41, 21.52, 23.78, 29.57, 34.87, 46.51, 52.98, 203.24 ppm.

Registry No.—Sulfur dioxide, 7446-09-5.

Table II. Michael Addition of Sulfinate Salts to Enones

sulfinate salt	registry no.	enone	michael adduct (g; % yield; mp, °C)[a]	registry no.
p-$MeC_6H_4S(=O)ONa$	824-79-3	MVK[d]	 (3.75; 83; 74–75[b])	61476-94-6
n-$BuSO_2Li$		MVK	*n*-$BuSO_2CH_2CH_2COCH_3$ (0.85; 85; 57–58)	68152-35-2
t-$BuSO_2Li$		MVK	*t*-$BuSO_2CH_2CH_2COCH_3$ (0.36; 42; 54–55)	68152-36-3
$MeSO_2Li$		MVK	$MeSO_2CH_2CH_2COCH_3$ (0.28; 38; 88–89)	68152-37-4
$C_6H_5CH_2SO_2MgCl$		MVK	$C_6H_5CH_2SO_2CH_2CH_2COCH_3$ (0.58; 52; 99–100)	68152-38-5
sec-$BuSO_2MgCl$		MVK	*sec*-$BuSO_2CH_2CH_2COCH_3$ (1.50; 53; *c*)	68152-39-6
$C_6H_5SO_2Na$	873-55-2		 (1.81; 38; 84–85)	24731-40-6
$MeSO_2Li$			 (1.01; 44; 65–66)	68152-40-9

[a] All sulfones give satisfactory ^1H and ^{13}C NMR spectra. [b] Literature[6] mp 74.5–75 °C. All other products are new compounds. [c] Liquid sulfone, bp 104–108 °C (0.1 mm). [d] Registry no., 78-94-4. [e] Registry no., 141-79-7.

A recent method employs 2 equiv of *m*-chloroperbenzoic acid to oxidize mercaptans directly to sulfinic acids.[4] Besides the unpleasantness of using mercaptans, particularly those of low molecular weight, this approach requires tedious low temperature work since many of the aliphatic sulfinic acids decompose rapidly even at room temperature.[4]

We needed a variety of aliphatic sulfinic acid salts and felt that the sulfur dioxide approach seemed like the most promising method if its shortcomings could be circumvented. Since the main side reaction is the formation of the corresponding sulfoxide[3] (presumably by reaction of the sulfinate salt with the organometallic), we reasoned that addition of the organometallic to excess sulfur dioxide would eliminate this problem. Indeed, this is the case.

Addition of either an organolithium reagent or a Grignard reagent to roughly 10 equiv of sulfur dioxide in ether gives a nearly quantitative yield of the corresponding sulfinate salt. Table I summarizes the results with a variety of organometallics.[5] For example, *sec*-butylmagnesium chloride gives a 97% yield of magnesium chloride *sec*-butylsulfinate.

Although ^1H and ^{13}C NMR spectra are consistent with the assigned structures, we sought additional evidence as confirmation. A recent paper[6] describes the Michael addition of sodium *p*-tolylsulfinate to methyl vinyl ketone (MVK), and this would seem to fill our need as well. Combination of the sulfinate salts in Table I with MVK in ethanol/acetic acid gives the corresponding keto sulfones (see Table II). Thus, lithium *n*-butylsulfinate gives an 85% yield of the corresponding pure keto sulfone. Mesityl oxide is also an effective Michael acceptor for sulfinate salts. For example, lithium methanesulfinate gives a 44% yield of the adduct. Consequently, either MVK or mesityl oxide provides a useful entry into the preparation of keto sulfones.

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