Synthesis and Polymerization of Alkyl α-(Alkylsulfonyl)acrylates[1a]

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Contrary to the reports in the patent literature, the title compounds could not be synthesized via the Mannich reaction with alkyl α-(alkylsulfonyl)acetate RSO_2CH_2COOR' (R = R' = CH_3 or other alkyl groups). A synthetic sequence which utilizes selenoxide elimination proved to be the most successful for obtaining the title compounds in high yields. The alkyl α-(alkylsulfonyl)acrylates polymerize much more readily than the corresponding unsubstituted acrylates. For example, the methyl and ethyl esters undergo spontaneous polymerization under the reaction conditions. The presence of bulky groups such as *tert*-butyl helped in moderating the propensity of these monomers to polymerize. Other routes to the title compounds and their synthetic applications are reported.

Synthetic routes to α-methylene carbonyl compounds have received considerable attention because of the importance of this class of compounds as useful synthetic intermediates.[1b-5] As part of a continuing program directed toward new organic intermediates incorporating the structural features of both sulfones and acrylates, we examined various approaches to the synthesis of the title compounds. A search of the literature revealed patent claims of a general synthesis of alkyl α-(alkylsulfonyl)-acrylates **2** from **1** by the usual Mannich reaction where the products had been distilled under vacuum (eq 1, where R and R' = CH_3 or C_2H_5).[6] Repeated efforts to reproduce

$$\underset{\mathbf{1}}{RSO_2CH_2COOR'} + (CH_2O)_n \xrightarrow[30\text{–}120\ ^\circ C]{\text{piperidine}} \underset{\mathbf{2}}{CH_2{=}C(SO_2R)COOR'} \quad (1)$$

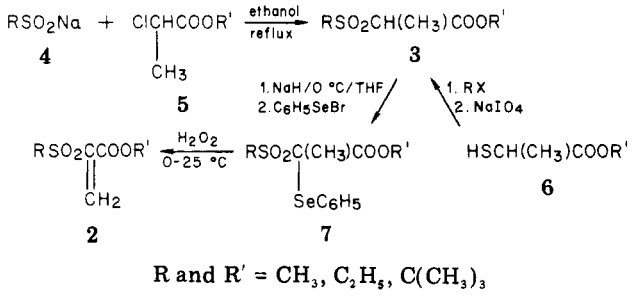
the literature synthesis were unsuccessful. Also, several modifications of this synthesis did not give the expected acrylate or any polymer. Alternative routes to the title compounds were extensively investigated, and a successful synthesis was developed that gave the intermediates in good to excellent yield. A description of the synthesis and the applicability of the reactive intermediate compounds with respect to new sources of sulfone esters is presented in this paper.

The precursors in this synthesis, alkyl α-(alkylsulfonyl)acetates **1**, were readily available from reaction of the sodium salt of methanesulfinic acid and the corresponding alkyl haloacetate in refluxing absolute alcohol.[7] Among the derivatives prepared, methyl α-(methylsulfonyl)acetate was used for further studies of the above reaction.

Repeated runs of the Mannich reaction produced oils and tars and failed to give the expected acrylates. Also, modified Mannich reactions were explored by using dimethylmethyleneammonium chloride (Eschenmoser's salt), which has been used to introduce the α-methylene moiety with ketone, ester, and lactone enolates.[5,8,9] Reaction of **1** using Eschenmoser's salt with lithium diisopropylamide or sodium hydride as the base followed by treatment of the amine with methyl iodide and then aqueous sodium bicarbonate did not afford the desired acrylate or the polymer.

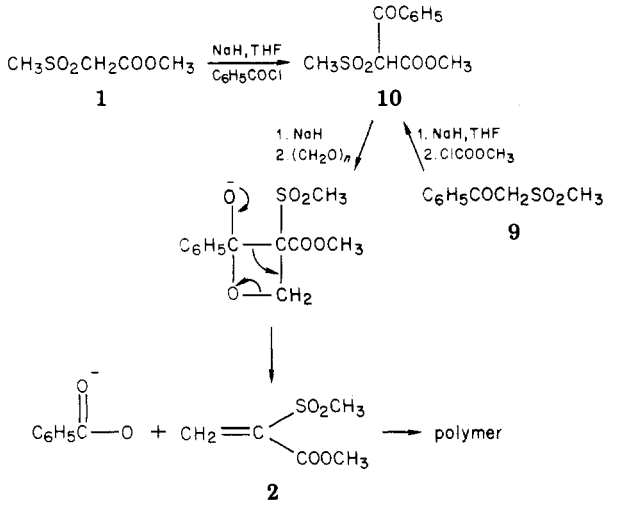
In a different approach to **2**, the α-sulfonylpropionates **3** were obtained by alkylation of the sulfinate **4** with α-halopropionate **5** or by alkylation of the thiol **6** and oxidation with sodium metaperiodate (Scheme I). Treatment of **3** with phenylselenyl bromide or chloride gave the α-(phenylselenyl)propionates **7** which upon treatment with hydrogen peroxide gave **2** in excellent yield.

Scheme I



R and R' = CH_3, C_2H_5, $C(CH_3)_3$

Scheme II



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Alkyl phenyl selenoxides have been shown to undergo facile elimination to form olefins.[10-13] This process is useful for introducing unsaturation into organic structures such as aldehydes, ketones, and esters under mild conditions.[11,12] In this reaction, the penultimate step involves oxidation of the α-phenylseleno carbonyl compound to the corresponding selenoxide which eliminates at or below room temperature to an olefin.

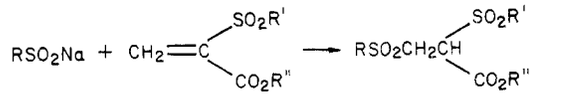
In view of the high cost of selenium compounds and the attendant waste disposal problems, the alternative sequence shown in Scheme II using deacylative methylenation[14,15] was investigated. The acylation reaction of **1** or **9** in each case gave a low yield (~30%) of **10** which was reacted with paraformaldehyde after deprotonation with NaH in THF to give the polymer of **2** (R = R′ = CH_3) in low yields. The mechanism suggested for this reaction is shown as a benzoyl transfer from carbon to an oxygen atom followed by elimination of the benzoate anion.[14] Studies with this route are continuing in order to explore further application of these reactive intermediates.

The alkyl α-(alkylsulfonyl)acrylates, in general, were much more reactive than the corresponding unsubstituted acrylates. For example, **2** (R = CH_3, R′ = CH_3 or C_2H_5) could only be observed in the NMR tube in $CDCl_3$ solution at 0 °C or below while at ambient temperatures spontaneous polymerization occurred, giving insoluble polymeric products. A two-phase system in which 2 equiv of pyridine or sodium bicarbonate was added to neutralize and buffer the reaction mixture and thereby prevent side reactions failed to suppress the polymerization.[11] The presence of bulky groups such as R or R′ = $C(CH_3)_3$ helped in moderating the propensity of these monomers to polymerize. For example, **2** [R = $C(CH_3)_3$ and R′ = CH_3 or R = CH_3 and R′ = $C(CH_3)_3$] could be stored at −5 °C for days without discernible polymer formation. The most stable homologue of **2** was with R = R′ = $C(CH_3)_3$, a white solid melting at 46–47 °C. This monomer showed no tendency to polymerize after standing many weeks at ambient temperature.

In an attempt to prepare high molecular weight polymers, the *tert*-butyl ester derivatives were polymerized at 25–50 °C by free-radical initiators and at −78 °C with anionic initiators. For the former, UV light, benzoyl peroxide, and azobis(isobutyronitrile) (AIBN) were used, while in the latter *n*-butyllithium in tetrahydrofuran was used.

Free-radical- and anionic-initiated polymerizations of **2** [R = CH_3, R′ = $C(CH_3)_3$ and R = $C(CH_3)_3$, R′ = CH_3] produced low molecular weight polymers (mol wt 10 000–20 000). The relatively low molecular weights compared with those of **2** [R = R′ = CH_3 and R = CH_3, R′ = C_2H_5] most likely are a reflection of the low ceiling temperatures of polymerization and steric constraints. This behavior has been observed for esters of α-alkylacrylic acids where the alkyl groups were ethyl, *n*-propyl, isopropyl, *n*-butyl, *tert*-butyl, *n*-amyl, isoamyl, and cetyl.[16-21] The presence of strain as a result of steric hindrance was shown to be an important factor in limiting the polymerizability of these esters to high molecular weight macromolecular products.

Table I. Michael Addition of Sulfinate and Mercaptide Anions to Alkyl α-(Alkylsulfonyl)acrylates[a]



R	R′	R″	yield, %	mp, °C
CH_3	*t*-Bu	*t*-Bu	90	(oil)
C_6H_5	*t*-Bu	*t*-Bu	84	149–150
p-ClC_6H_4	*t*-Bu	CH_3	90	67–68, sulfide[b,c] 118, sulfone
t-Bu	*t*-Bu	*t*-Bu	95	68.5–69.5, sulfide[b,c] 137–138, sulfone

[a] All products gave satisfactory ^1H NMR spectra, elemental analysis, and mass spectral *m/e* (*p*-SO_2-*t*-Bu, CO_2-*t*-Bu) analysis. [b] Reaction with mercaptide. [c] Oxidation with *m*-chloroperbenzoic acid.

The steric effect was shown to be most pronounced when **2** had R = R′ = $C(CH_3)_3$. Molecular models indicated that it was not possible to construct model sections of poly[*tert*-butyl α-(*tert*-butylsulfonyl)acrylate] either head to head, head to tail, or tail to tail. When this monomer was heated with benzoyl peroxide or AIBN in bulk or in solution no polymer precipitated on addition of methanol or petroleum ether. The product obtained after evaporation of the solvent was a tacky resin having a molecular weight equivalent to a hexamer. Under anionic conditions at −78 °C where the free energy of polymerization might be more favorable, a similar resinous product was isolated. It must be concluded that *tert*-butyl α-(*tert*-butylsulfonyl)acrylate is unable to polymerize to a product of high molecular weight. Free-radical copolymerization with equimolar quantities of methyl methacrylate gave higher molecular weight polymers which were predominantly poly(methyl methacrylate).

Michael addition products were prepared by the addition of sulfinates[22] and mercaptides to **2**. These compounds were prepared from the sulfinate salts in ethanol–acetic acid and from the mercaptides in dichloromethane catalyzed by potassium *tert*-butoxide. The resulting sulfides were oxidized with *m*-chloroperbenzoic acid to the sulfones (cf. Table I).

These syntheses provide efficient routes to a variety of new organic compounds containing sulfone and ester groups[23] under mild reaction conditions with readily available starting materials. The reactive intermediates should find application in the synthesis of more complex sulfone structures.

Experimental Section

General Methods. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were determined on a Perkin-Elmer 283 or Digilab FTS 15B spectrophotometer. Nuclear magnetic resonance (NMR) spectra were determined on a Varian T-60 or HA-100 spectrometer. Chemical shifts are given in τ units (*J* values in hertz) relative

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to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were taken on an AEI MS-30 mass spectrometer at an ionization energy of 70 eV.

Thin-layer chromatography was carried out on 200 × 400 × 1.5 mm layers of Merck silica gel PF-254 (E. Merck Ab Darmstadt). Compounds were separated in a mixture of hexane/ethyl acetate (5:1). Compounds were removed by washing with dichloromethane/methanol (2:1). Large-scale separations were carried out on a Waters Associates preparative liquid chromatograph, System 500, over two chromatographic Prepak silica gel columns. The solvent system was generally hexane/ethyl acetate in ratios from 3:1 to 5:1.

Microanalyses were performed by Childers Microanalytical Laboratories. Molecular weights relative to polystyrene were determined by gel-permeation chromatography by Analytical Services Inc.

Methyl α-(Methylsulfonyl)acetate. A solution of 102.9 g (1 mol) of sodium methylsulfinate, 108.5 g (1 mol) of methyl chloroacetate, and 500 mL of absolute ethanol was refluxed for 18 h. The solution was filtered to remove sodium chloride and concentrated by rotary evaporation to give a white crystalline solid. Recrystallization from an ethyl alcohol/isopropyl alcohol mixture (1:1) gave 201.5 g (76%) of colorless crystals: mp 65.5–66.5 °C; ^{1}H NMR ($CDCl_3$) τ 6.85 (3 H, s, SO_2CH_3), 6.22 (3 H, s, OCH_3), 6.00 (2 H, s, CH_2). Anal. Calcd for $C_7H_8O_4S$: C, 31.57; H, 5.30; S, 21.07. Found: C, 31.66; H, 5.21; S, 21.02.

Methyl α-(*tert*-butylthio)acetate: colorless liquid; bp 60 °C (3 mm); >95% yield; ^{1}H NMR ($CDCl_3$) τ 8.70 (9 H, s, S-*t*-Bu), 6.88 (3 H, s, OCH_3), 6.32 (2 H, s, CH_2).

Methyl α-(*tert*-butylsulfonyl)acetate: liquid; 95% yield; ^{1}H NMR ($CDCl_3$) τ 8.60 (9 H, s, SO_2-*t*-Bu), 6.26 (3 H, s, OCH_3), 6.10 (2 H, s, CH_2).

Similarly prepared were the following alkyl α-(alkylsulfonyl)propionates.

Methyl α-(methylsulfonyl)propionate: colorless crystals; mp 49–50 °C; 95% yield; ^{1}H NMR ($CDCl_3$) τ 8.48–8.27 (1 H, d, CH), 7.02 (3 H, s, OCH_3), 6.22 (3 H, s, SO_2CH_3), 6.13–6.65 (3 H, q, CH_3).

Ethyl α-(methylsulfonyl)propionate: colorless liquid; 90% yield; ^{1}H NMR ($CDCl_3$) τ 8.82–8.84 (3 H, t, CH_2H_5), 8.4–8.36 (3 H, d, CCH_3), 6.99 (3 H, s, SO_2CH_3), 6.25–6.02 (1 H, q, CH), 4.82–4.72 (2 H, d, CH_2CH_3).

***tert*-Butyl α-(methylsulfonyl)propionate**: colorless needles; mp 88.5–89.5 °C; 95% yield; ^{1}H NMR ($CDCl_3$) τ 8.55 (9 H, s, *t*-Bu), 8.48–8.52 (1 H, d, CH), 7.05 (3 H, s, SO_2CH_3), 6.22–6.42 (3 H, q, CH_3).

Methyl α-(*tert*-butylsulfonyl)propionate: colorless oil; 90% yield; ^{1}H NMR ($CDCl_3$) τ 8.72 (9 H, s, SO_2-*t*-Bu), 8.50–8.39 (1 H, d, CH), 6.30 (3 H, s, OCH_3), 6.00–5.72 (3 H, q, CH_3).

***tert*-Butyl α-(*tert*-butylthio)propionate**: colorless liquid; 73% yield; bp 81 °C (10 mm); ^{1}H NMR ($CDCl_3$) τ 8.62 (9 H, s, S-*t*-Bu), 8.50 (9 H, s, O-*t*-Bu), 8.36–8.28 (1 H, d, CH), 6.82–6.62 (3 H, q, CCH_3).

***tert*-Butyl α-(*tert*-butylsulfonyl)propionate**: colorless needles; 97% yield; mp 72.5–73.5 °C; ^{1}H NMR ($CDCl_3$) τ 8.50 (9 H, s, SO_2-*t*-Bu), 8.42 (9 H, s, O-*t*-Bu), 8.39–8.31 (1 H, d, CH), 6.20–5.82 (3 H, q, CCH_3).

Mass spectra of all the above compounds showed either a big P – 79 peak, a P – 56 peak, or a P – 120 peak, indicating loss of the SO_2CH_3, isobutylene, or isobutylenesulfonyl group, respectively.

Methyl α-(Methylsulfonyl)-α-(phenylselenyl)propionate. To a stirred suspension of 2.9 g (0.12 mol) of pentane-washed sodium hydride in 150 mL of absolute THF at −10 °C was added dropwise under nitrogen 19.9 g (0.12 mol) of methyl (methylsulfonyl)propionate in dry THF (50 mL). After 2 h the mixture was cooled to −20 °C, and 23.3 g (0.12 mol) of phenylselenyl chloride in 75 mL of dry THF was added over 15 min. After 2 h the mixture was allowed to warm to ambient temperature. The mixture was treated with a saturated solution of NH_4Cl (10 mL), and THF was removed under reduced pressure. The residue was extracted with three 100-mL portions of ether. The combined ether extracts were washed with brine and dried ($MgSO_4$). Evaporation of the solvent gave a light yellow oil which deposited colorless crystals (17.5 g, 50%): mp 62–63 °C; ^{1}H NMR ($CDCl_3$) τ 8.42 (3 H, s, CCH_3), 6.72 (3 H, s, OCH_3), 6.42 (3 H, s, SO_2CH_3), 2.9–2.18 (5 H, m, Ph); mass spectrum, *m/e* 243 (P – SO_2CH_3).

The following selenyl derivatives were prepared in an analogous manner.

Ethyl α-(methylsulfonyl)-α-(phenylselenyl)propionate: 65% yield; colorless oil (preparative LC); mass spectrum, *m/e* 336 (M^+); ^{1}H NMR ($CDCl_3$) τ 9.41–9.12 (3 H, t, CH_2CH_3), 8.95 (3 H, s, CH_3), 7.18 (3 H, s, SO_2CH_3), 6.18–6.50 (2 H, q, CH_2CH_3), 2.64–3.22 (5 H, m, SeC_6H_5).

***tert*-Butyl α-(methylsulfonyl)-α-(phenylselenyl)-propionate**: 75% yield; colorless oil (preparative TLC); mass spectrum, *m/e* 383 (M^+); ^{1}H NMR ($CDCl_3$) τ 8.78 (9 H, s, C-$(CH_3)_3$), 7.22 (3 H, s, CCH_3), 6.88 (3 H, s, SO_2CH_3), 3.01–2.38 (5 H, m, SeC_6H_5).

Methyl α-(*tert*-butylsulfonyl)-α-(phenylselenyl)-propionate: colorless crystals (preparative LC); 80% yield; mp 73.5–75 °C; ^{1}H NMR ($CDCl_3$) τ 8.57 (9 H, s, SO_2-*t*-Bu), 8.22 (3 H, s, CCH_3), 6.22 (3 H, s, OCH_3), 2.78–2.19 (5 H, m, SeC_6H_5).

***tert*-Butyl α-(*tert*-butylsulfonyl)-α-(phenylselenyl)-propionate**: slightly colored yellow crystals (preparative LC); 98% yield; mp 73.5–74.5 °C; ^{1}H NMR ($CDCl_3$) τ 8.45 (9 H, s, SO_2-*t*-Bu), 8.25 (3 H, s, CH_3), 2.80–2.10 (5 H, m, SeC_6H_5).

Oxidation of Selenides. Preparation of Acrylates. Oxidations of the selenides were carried out with an excess (2–3 equiv) of H_2O_2 in CH_2Cl_2 at 0 °C. The reaction vessel was momentarily taken out of the cold bath, and as the exothermic elimination started, it was cooled again to avoid polymerization. In spite of this precaution, the methyl and ethyl esters polymerized during workup. The product in each case was washed with sodium bicarbonate in methylene chloride, and after drying (Na_2SO_4) the solvent was evaporated at 0 °C under vacuum to give the product. Yields were 75–99%. For **2** (R = CH_3, R′ = *t*-Bu): ^{1}H NMR ($CDCl_3$) τ 8.50 (9 H, s, *t*-Bu), 6.82 (3 H, s, SO_2CH_3), 3.21–3.0 (2 H, d, vinyl). For **2** (R = *t*-Bu, R′ = CH_3): ^{1}H NMR ($CDCl_3$) τ 3.05 (2 H, d, *J* = 11.5 Hz, vinyl protons), 6.05 (3 H, s, CH_3 ester), 8.40 (9 H, s, SO_2-*t*-Bu). For **2** (R = *t*-Bu, R′ = *t*-Bu): colorless solid; 99+% yield; mp 46–47 °C; ^{1}H NMR ($CDCl_3$) τ 8.65 (9 H, s, SO_2-*t*-Bu), 8.50 (9 H, s, CO_2-*t*-Bu), 3.33–3.17 (2 H, d, vinyl). Anal. Calcd for $C_{11}H_{20}O_4S$: C, 53.20; H, 8.62; S, 12.91. Found: C, 52.99; H, 8.19; S, 13.50.

Polymerization of Alkyl α-(Alkylsulfonyl)acrylates. In general, the polymerizations were carried out as follows. (1) A 1.5-g sample of monomer and 1% of benzoyl peroxide or AIBN catalyst were placed in a 10-mm Schlenk Pyrex or quartz tube, connected to a vacuum line and degassed several hours before sealing at 10^{-6} mmHg. The monomer was either heated 24 h at 50–55 °C or exposed to the radiation from a 400-W mercury lamp. In each case the liquid monomer became viscous. The product was recovered as a solid by precipitation from hexane, a nonsolvent. (2) A 3-g sample of monomer was dissolved in 50 mL of absolute THF and cooled to −78 °C under nitrogen. Several drops of butyllithium initiator were added, and the mixture was stirred 16 h. The mixture was warmed to room temperature and the product recovered as a white solid from hexane. Anal. Calcd for poly[*tert*-butyl α-(methylsulfonyl)acrylate], $(C_8H_{14}O_4S)_n$: C, 46.54; H, 6.84; S, 15.54. Found: C, 45.76; H, 6.85; S, 15.46.

Methyl α-(methylsulfonyl)-α-(benzoyl)acetate. To a stirred suspension of sodium hydride (1.3 g, 0.05 mol) in dry THF (75 mL) at 0 °C was added 9.9 g (0.05 mol) of α-(methylsulfonyl)-acetophenone. Methyl chloroformate (4.7 g, 0.05 mol) was added dropwise after 1 h at −20 °C. The mixture was allowed to warm to ambient temperature after 2 h. After treatment with 75 mL of saturated aqueous NH_4Cl solution, the organic solvent was removed evaporatively. The residue was extracted into three 50-mL portions of ether, and the combined extracts were washed with brine and dried ($MgSO_4$). Removal of the solvent gave a semisolid which was purified by preparative TLC (1.5:1 EtOAc/hexane) to give 4.1 g (32%) of the desired compound.

Deacylative Methylenation. To a stirred suspension of sodium hydride (48 mg, 2 mmol) in THF (30 mL) was added methyl α-(methylsulfonyl)-α-(benzoyl)acetate (506 mg, 2 mmol) dissolved in the same solvent (10 mL) at 0 °C. After 30 min paraformaldehyde (100 mg) was added to the reaction mixture which developed a light yellow color. After 2 h the temperature was raised to 25 °C, and the reaction mixture was treated with saturated aqueous NH_4Cl (10 mL). The product was extracted into

four 30-mL portions of dichloromethane. The combined extracts were dried (Na_2SO_4) and evaporated to give a colorless semisolid. The NMR spectrum indicated it to be a polymer similar to the one obtained above by the selenide oxidation route for **2** (R = R′ = CH_3).

Michael Addition of Sulfinate and Mercaptide Ions to Alkyl α-(Alkylsulfonyl)acrylates. The following represent typical preparative procedures.

***tert*-Butyl 2-(*tert*-Butylsulfonyl)-3-(methylsulfonyl)-propionate.** A solution of sodium methylsulfinate (0.7 g, 14.5 mmol) in ethyl alcohol (10 mL) buffered with acetic acid (1 mL) was added dropwise to *tert*-butyl α-(*tert*-butylsulfonyl)acrylate (1.3 g, 5.2 mmol) in ethyl alcohol (10 mL) at 25 °C, and the mixture was stirred for 20 h. Water (30 mL) was added, and the mixture was extracted with two 25-mL portions of chloroform. The combined organic layers were washed with saturated aqueous $NaHCO_3$ (25 mL), dried over $MgSO_4$, and concentrated to give a viscous oil: 1.5 g (90%); ^1H NMR ($CDCl_3$) τ 8.62 (9 H, s, CO_2-*t*-Bu), 8.51 (9 H, s, SO_2-*t*-Bu), 7.18 (3 H, s, SO_2CH_3), 6.64–6.00 (1 H, m, CH), 5.61–5.46 (2 H, q, CH_2).

***tert*-Butyl 2-(*tert*-Butylsulfonyl)-3-(*tert*-butylthio)-propionate.** To a solution of *tert*-butyl α-(*tert*-butylsulfonyl)-acrylate (1.3 g, 5.2 mmol) in methylene chloride (20 mL) were added *tert*-butyl mercaptan (1.3 g, 14.5 mmol) and a trace of potassium *tert*-butoxide (~10 mg), and the mixture was stirred for 20 h. Workup as above furnished the desired adduct as a colorless oil which crystallized to give 1.6 g (95%) of white needles: mp 68.5–69.5 °C; ^1H NMR ($CDCl_3$) τ 8.79 (9 H, s, S-*t*-Bu), 8.67 (9 H, s, CO_2-*t*-Bu), 8.41 (9 H, s, SO_2-*t*-Bu), 7.68–6.73 (1 H, m, CH), 6.21–6.02 (2 H, q, CH_2). Oxidation of the sulfide to the corresponding sulfone proceeded quantitatively with 2.5 equiv of *m*-chloroperbenzoic acid in methylene chloride at 0 °C for 24 h.

Registry No. **1** (R = R′ = CH_3), 62020-09-1; **1** (R = *t*-Bu, R′ = CH_3), 63864-29-9; **2** (R = R′ = CH_3) monomer, 73017-61-5; **2** (R = R′ = CH_3) polymer, 73017-62-6; **2** (R = CH_3, R′ = *t*-Bu) monomer, 73017-59-1; **2** (R = CH_3, R′ = *t*-Bu) polymer, 73017-60-4; **2** (R = *t*-Bu, R′ = CH_3) monomer, 73017-57-9; **2** (R = *t*-Bu, R′ = CH_3) polymer, 73017-58-0; **2** (R = R′ = *t*-Bu), 73017-80-8; **3** (R = R′ = CH_3), 73017-81-9; **3** (R = CH_3, R′ = C_2H_5), 73017-82-0; **3** (R = CH_3, R′ = *t*-Bu), 73017-83-1; **3** (R = *t*-Bu, R′ = CH_3), 73017-84-2; **3** (R = R′ = *t*-Bu), 73017-85-3; **4** (R = CH_3), 20277-69-4; **4** (R = C_6H_5), 873-55-2; **4** (R = *p*-ClC_6H_4), 14752-66-0; **4** (R = *t*-Bu), 69152-35-8; **5** (R′ = CH_3), 17639-93-9; **5** (R′ = C_2H_5), 535-13-7; **5** (R′ = *t*-Bu), 40058-88-6; **7** (R = R′ = CH_3), 73017-86-4; **7** (R = CH_3, R′ = C_2H_5), 73017-63-7; **7** (R = CH_3, R′ = *t*-Bu), 73017-64-8; **7** (R = *t*-Bu, R′ = CH_3), 73017-65-9; **7** (R = R′ = *t*-Bu), 73017-66-0; **9**, 3708-04-1; **10**, 65020-08-8; methyl chloroacetate, 96-34-4; methyl α-(*tert*-butylthio)acetate, 49827-06-7; *tert*-butyl α-(*tert*-butylthio)propionate, 64041-97-0; phenylselenyl chloride, 5707-04-0; methyl chloroformate, 79-22-1; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(methylsulfonyl)propionate, 73017-67-1; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(*tert*-butylthio)-propionate, 73017-68-2; *tert*-butyl mercaptan, 75-66-1; *p*-chlorobenzenethiol, 106-54-7; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(phenylsulfonyl)propionate, 73017-69-3; methyl 2-(*tert*-butylsulfonyl)-3-(*p*-chlorobenzylthio)propionate, 73017-70-6; methyl 2-(*tert*-butylsulfonyl)-3-(*p*-chlorobenzenesulfonyl)propionate, 73017-71-7; *tert*-butyl 2-(*tert*-butylsulfonyl)-3-(*tert*-butylsulfonyl)propionate, 73017-72-8.

Reactions of (*E*)-2-*tert*-Butyl-3-phenyloxaziridine with Lithium Amide Bases

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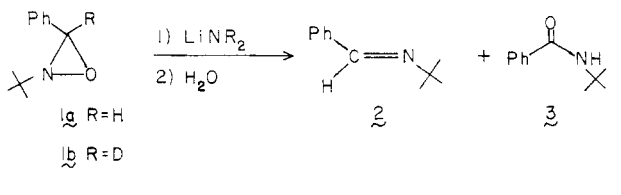
The reactions of (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**1a**) with lithium amide bases in tetrahydrofuran have been studied. In competing reactions, **1a** is reduced to *N*-*tert*-butylbenzaldimine (**2**) and isomerized to *N*-*tert*-butylbenzamide (**3**). The former reaction proceeds through an intermediate which accumulates and slowly decomposes to **2**; the reaction apparently occurs via an initial electron transfer from the base to the oxaziridine. The latter reaction occurs by simultaneous deprotonation and ring opening of the oxaziridine to give the anion of **3**.

The reactions of oxaziridines with strong bases have not been studied extensively, but limited studies have been reported which suggest that various reaction pathways exist. Deprotonation at an α position to the ring carbon or nitrogen and concomitant ring opening occurs when oxaziridines are treated with alkoxide or hydroxide.[1,2] However, when no protons are available at these positions [e.g., (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**1a**)], the oxaziridine is stable in the presence of alkoxides.[1] Rubottom reported that 2-*tert*-butyl-3-(*p*-nitrophenyl)oxaziridine reacted with sodium hydride in hexamethylphosphoramide to give *N*-*tert*-butyl-*p*-nitrobenzamide,[3] and Watt and Dinizo have found that a pyridine-substituted oxaziridine containing a proton on the carbon adjacent to the ring nitrogen produced the corresponding amide in 0–68% yield in reactions with various bases.[2] Recently, Davis et al.[4] have reported that oxaziridines react with lithium and Grignard reagents in ether to give coupling and/or hydroxylation products of the organometallic reagent; they postulated that mechanisms involving electron transfer and initial nucleophilic attack at oxygen occurred, respectively. We report here the results of our studies of the reaction of **1a** with lithium amide bases in tetrahydrofuran (THF); under these conditions the oxaziridine is both reduced to *N*-*tert*-butylbenzaldimine (**2**) and isomerized to *N*-*tert*-butylbenzamide (**3**) in competitive reactions.

Results and Discussion

We have investigated the reactions of **1a** with lithium diethylamide (LDEA), lithium diisopropylamide (LDA), and lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF under nitrogen. At 0 °C in the presence of excess base, **1a** was converted after protonation of the reaction mixture to imine **2** and amide **3**. Although imine **2** was isolated



1a R=H
1b R=D
2
3

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