tering through alumina just before use: bp 46–47 °C (15 mmHg).

Benzyl hydroperoxide (BHP) was prepared in low yield by the method of Walling and Buckler[1] and purified by column chromatography (silica gel, CH_2Cl_2) and vacuum transfer to give material 96% pure by iodometric titration.[17] The NMR spectrum in $CDCl_3$ is δ 4.83 (s, 2 H, CH_2), 7.28 (m, 5 H, phenyl), 8.6 (br s, variable with temperature, 1 H, OOH).[18] The BHP prepared in this way is identical in all respects with the product of oxidation of 5-methylene-1,3-cyclohexadiene.

Samples were prepared in 10-mL drying ampules fitted with "O" ring seals for attachment to a vacuum line. The ampules were cleaned by soaking in concentrated HNO_3, washing thoroughly with water, and drying at 110 °C. The appropriate amount of hydroperoxide was dissolved in solvent and samples were pipetted into the reaction vessels. The ampules were degassed by at least three freeze-thaw cycles and then sealed at 5×10^{-5} mmHg.

Decomposition in octane was carried out by immersion of ampules containing 1-mL samples in a 100.2 °C oil bath. Concentration of hydroperoxide was followed through 80% reaction by titration[17] of samples removed at regular intervals.

Decomposition in styrene was carried out as above on 5-mL samples through 40% reaction at 60.0 °C. Due to the increase in viscosity of the styrene solutions and probably the trapping of hydroperoxide in the polymer (which precipitates during analysis), the precision is less than in octane.

Polymerization rates at 60.0 °C were determined gravimetrically by precipitation of the polymer in cold methanol. The styrene solution (5 mL) was first diluted with a small amount of toluene (2–3 mL) and then very slowly pipetted into 400 mL of reagent-grade methanol at 10 °C. The precipitated polymer was filtered on a sintered glass funnel and brought to constant weight under vacuum. Rates were determined for the first 5% conversion of monomer.

Chain-transfer constant of benzyl hydroperoxide was determined by standard methods[12] from the intrinsic viscosity of polymer solutions in benzene. Concentrations of hydroperoxide from 9×10^{-4} to 8×10^{-3} M were used.

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Registry No.—BHP, 3071-34-9; octane, 111-65-9; styrene, 100-42-5.

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Direct α-Lithiation of Phenoxyacetic Acid and Electrophilic Substitution

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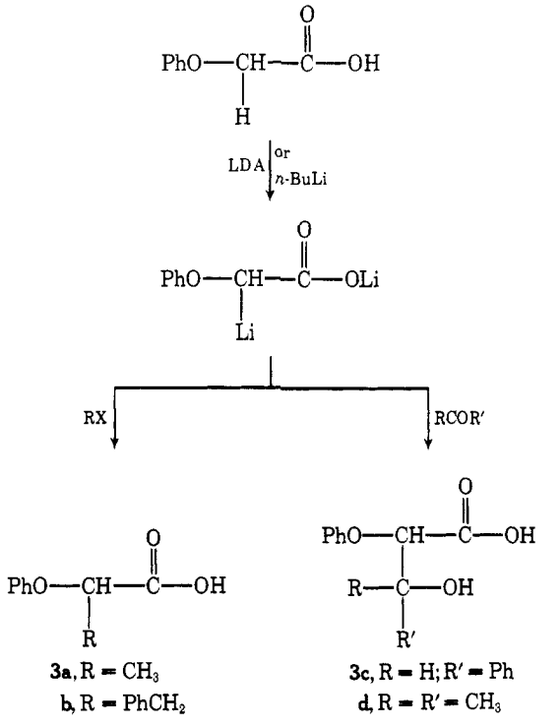
The destabilization exerted by juxtaposed oxygen atoms on carbanionic centers is well recognized.[2] This effect is most dramatically accentuated in the side-chain metalation of thioanisole vs. ring metalation of anisole by *n*-butyllithium.[3] A powerful synthetic utilization has been the Corey–Seebach reagent,[4] prepared by direct metalation of 1,3-dithiane with *n*-butyllithium, conditions which fail to produce the corresponding 2-carbanion from 1,3-dioxane.[2a] However, allylic ethers were recently[5] converted efficiently into allyloxy carbanions with *sec*-butyllithium, and α-alkoxynitrile carbanions[6] have been used as synthons, showing that the destabilizing influence of the α-oxygen atom can be moderated by conjugation. In fact the enolate ion of 2-carbomethoxy-1,3-dioxolane was formed only fivefold slower than that of the carbocyclic analogue, i.e., 2-carbomethoxycyclopentane, in the methoxide-catalyzed deuterium exchange.[7]

These facts suggested that it should be possible to prepare stable solutions of the hitherto unknown enolate **2** by metalation of phenoxyacetic acid with strong bases such as *n*-butyllithium or lithium diisopropylamide (LDA).[8] The potential usefulness of such a α-lithiocarboxylate **2** as synthon encouraged us to explore the direct lithiation of phenoxyacetic acid (1). Presently we report our successful generation of this enolate and its reaction with electrophiles.

Treatment of phenoxyacetic acid (1) in THF with stoichiometric amounts (2 mol) of *n*-BuLi at −78 °C generated



3a, R = CH_3 **3c**, R = H; R' = Ph
b, R = $PhCH_2$ **d**, R = R' = CH_3

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a clear yellow solution. Deuteration of the reaction mixture with excess D_2O and NMR analysis of the reisolated acid **1** confirmed that the enolate **2** was formed in ca. 80% yield. Some carbonyl addition had also taken place. Since excess *n*-BuLi had to be avoided in view of the troublesome carbonyl addition, we decided to use LDA as base catalyst. At −78 °C in THF and 100% excess LDA the phenoxyacetic acid (**1**) was converted in over 90% yield to the α-lithiocarboxylate **2** as yellow solution, confirmed by NMR analysis of the deuterated reaction mixture.

The reaction of the phenoxy enolate **2** with common electrophiles proceeded smoothly. Discoloration of the characteristic yellow color of the α-lithiocarboxylate **2** took place immediately on addition of the electrophile. Thus, the enolate **2** afforded 2-phenoxypropionic acid (**3a**) with methyl iodide, 2-phenoxy-3-phenylpropionic acid (**3b**) with benzyl bromide, and the diastereomeric 3-hydroxy-2-phenoxy-3-phenylpropionic acids (**3c**) with benzaldehyde in good yields. These condensation products were identified on the basis of literature reported physical constants and NMR and IR spectral data. With acetone as electrophile the enolate **2** gave the unknown 3-hydroxy-3-methyl-2-phenoxybutyric acid (**3d**) in ca. 80% yield, mp 62 °C (from hexane–benzene, as hydrate) and 77 °C (sublimed, as free acid). The structure of **3d** is based on the correct elemental analysis and IR and NMR spectral data.

We are now extending this direct lithiation method to alkoxy-, diaryloxy-, and dialkoxyacetic acids and are planning to utilize these novel enolates as synthons.

Experimental Section

Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn. Melting points are uncorrected. NMR spectra were run on an Hitachi Perkin-Elmer R-24B instrument and IR spectra on a Perkin-Elmer 237B Infracord. Solvents and reagents were purified and starting materials were prepared and purified according to standard, published procedures.

General Procedure. A dry, 50-mL, two-necked, round-bottom flask, provided with magnetic spinbar, rubber septum, and three-way stopcock, was attached to a nitrogen manifold and flushed with dry nitrogen for at least 5 min while flame-drying. While under a positive nitrogen gas pressure (ca. 50 mm, regulated with a mercury bubbler), the reaction vessel was charged by means of a syringe with 1.62 g (16 mmol) of diisopropylamine (freshly distilled from calcium hydride) and 20 mL of anhydrous THF (freshly distilled from benzophenone ketyl radical). By means of a dry ice–methanol bath the reaction flask was cooled to −78 °C and while stirring vigorously 16 mmol of *n*-butyllithium in *n*-hexane (standardized by acidimetry) was added by means of a syringe. After complete addition (ca. 5 min) the cooling bath was removed and the reaction mixture was allowed to reach room temperature (ca. 30 °C) while stirring. After ca. 10 min the contents were cooled again to −78 °C and by means of a syringe 608 mg (4 mmol) of phenoxyacetic acid in 5 mL of anhydrous THF was added while magnetically stirring. The yellow solution was stirred at −78 °C for 15 min and subsequently ca. 8 mmol (200% excess) of the electrophile was added and allowed to stir at −78 °C for 15–60 min until complete disappearance of the yellow color.

The reaction mixture was poured onto ca. three to five times crushed ice and extracted with 2 × 20 mL of ether and the aqueous layer acidified with 10% hydrochloric acid until pH ca. 3. The product was extracted with 5 × 20 mL of ether, the combined extracts were dried over anhydrous $MgSO_4$, and after rotoevaporation, first at ca. 30 °C (25 mmHg) and finally at ca. 30 °C (1 mmHg), the residue was purified by recrystallization. The individual cases are detailed below. Yields have not been optimized.

2-Phenoxypropionic acid (3a) was prepared in 70% yield by the above procedure, mp 112–114 °C from water (lit.[9] mp 115–116 °C), by adding 1.15 g (8 mmol) of methyl iodide at −78 °C and stirring for 30 min.

2-Phenoxy-3-phenylpropionic acid (3b) was prepared in 50% yield by the above procedure, mp 82 °C from methanol/water (1:2) (lit.[10] mp 81 °C), by adding 1.37 g (8 mmol) of benzyl bromide at −78 °C and stirring for 60 min.

3-Hydroxy-2-phenoxy-3-phenylpropionic acid (3c) was prepared in 50% yield by the above procedure, mp 116–117 °C from hexane/benzene (1:1) (lit.[11] mp 93–94 °C), by adding 0.85 g (8 mmol) of benzaldehyde at −78 °C and stirring for 15 min.

3-Hydroxy-3-methyl-2-phenoxybutyric acid (3d) was prepared in 80% yield by the above procedure, mp 62 °C as hydrate (needles from benzene/hexane) and 77 °C after sublimation, by adding 0.93 g (16 mmol) of acetone at −78 °C and stirring for 15 min. The spectral data are: IR ($CHCl_3$) 3500–2500 (OH and CO_2H) and 1740 cm^{-1} (C=O); ^1H NMR (60 MHz) δ ($CDCl_3$, Me_4Si) 1.45 (6 H, s, CH_3), 4.40 (2 H, s, OH and CO_2H), 4.45 (1H, s, O–C–H), and 6.7–7.4 (5 H, m, C_6H_5); mass spectrum (70 eV) *m/e* (rel) 210 (11.0), 152 (99.6), and 107 (100). Anal. Calcd for $C_{11}H_{14}O_4H_2O$: C, 57.89; H, 7.07. Found: C, 57.75; H, 7.15.

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Registry No.—**3a,** 940-31-8; **3b,** 64682-83-3; **3c,** 64682-84-4; **3d,** 64682-85-5; phenoxyacetic acid, 122-59-8; LDA, 4111-54-0; *n*-butyllithium, 109-72-8; methyl iodide, 74-88-4; benzyl bromide, 100-39-0; benzaldehyde, 100-52-7; acetone, 67-64-1.

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Pyrolysis of *N*-*p*-Toluenesulfonylsulfilimines[1]

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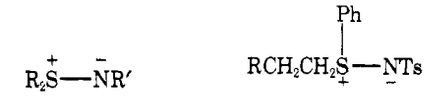
Sulfilimines (**1**) have received considerable attention in the past several years with respect to their synthesis[2] as well as their chemistry.[3] Of particular interest to us have been studies relating to the pyrolysis of sulfilimines. Both Swern[4] and Oae[5] have noted that pyrolysis of sulfilimines in which one of the sulfur substituents contains a β hydrogen (e.g., **2**)



1 **2**

results in a facile elimination yielding an alkene and a sulfenamide. More recently the pyrolysis of *N*-toluenesulfonylsulfilimines in which no β hydrogens are present has been reported.[6] Various solvents were used, and the products obtained depended markedly on the nature of the solvent. We have found[1] that in the absence of solvent the pyrolysis of *N*-toluenesulfonylsulfilimines yields a significantly different mixture of products, and we wish to report those results.

Results and Discussion

The pyrolytic decomposition of *S*,*S*-dimethyl-*N*-*p*-tosylsulfilimine **3** in the absence of solvent at 300 °C yielded the

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