sence of the minor diastereomer were hydrolyzed to the α-hydroxy acids (Table III). In this fashion, preparatively useful and enantiomerically pure acids **3** were obtained and characterized. The specific rotations of the acids are listed in Table III and may be assumed to represent at least 99% optical purity. As a check on the resolution efficiency, the α-methyl and the α-ethyl hydroxy acids previously described[4] gave $[\alpha]_D$ values in excellent agreement with those found in this work. The absolute configurations presented in Table III were all previously reported for the enantiomers presented except for the two cases of the *p*-anisyl and 2-thienyl acids. However, CD curves for all the acids in Table III were examined and gave the same general sense (negative) for the plot. Due to the low (215–220 nm) maxima, peaks and, therefore, molecular ellipticity (Θ) could not be ascertained. Since it is generally true[5] that compounds in a homologous series will exhibit the same sign for $\Delta\epsilon$ if they have the same absolute configuration at the chiral centers, this behavior provides further support to the assigned configuration for the *p*-anisyl and 2-thienyl derivatives.

In summary, diastereomers resulting from addition of organometallics to the benzoyloxazoline not only provide asymmetrically prepared α-hydroxy acids but may also be resolved with pressurized chromatography to enantiomerically pure products. It should be noted that no separation of diastereomers was possible by fractional crystallization (except for **2**, R = Me, previously reported[6]) or repeated elutions on preparative thin-layer plates.

Experimental Section

Medium-pressure liquid chromatography was performed on a home-built unit described in detail elsewhere.[1] The solvent system chosen for elution in Table I was based on obtaining an R_f of 0.1–0.15 on silica gel TLC plates (0.5 mm). Empirically this was found to be useful for achieving optimum separation and recovery of material. Samples of mixtures of **2** were introduced as 25–50% (by volume) solutions in the chosen eluting solvent and then chromatographed at a median pressure of 50 psi (extremes were 10–90 psi during the pump cycle) and at a flow rate of 15–20 mL/min. Fractions (5, 10, or 15 mL) were collected, and the presence of eluted materials was monitored by thin-layer chromatography (Merck, silica gel PF254, visualized by ultraviolet light). All the fractions possessing identical material and showing only a single spot were combined and the solvents evaporated to give pure material as indicated in Table I.

High-pressure liquid chromatography was performed on a Waters Associates instrument comprised of the following units: a Model 440 absorbance detector (UV); a Model R401 differential refractometer; a Model 6000A solvent delivery system; a Model U6K universal injector; a μ-Porasil No. 27477 3.9 mm × 30 cm column or a reverse-phase μ-Bondapak C_{18}, No. 27324, 3.9 mm × 30 cm column; a Houston Instrument Omniscribe Series B-5000 recorder. Samples of 0.5–2.0 μL were introduced as 5% (by volume) solutions in the appropriate eluting solvent and were chromatographed at pressures of 500–3000 psi at flow rates of 1–3 mL/min. Retention times and other parameters are given in Table II.

α-Substituted Madelic Acids 3. The fractions of **2** collected by medium-pressure LC which indicated the absence of any diastereomeric material were, after combination and concentration, subjected to the hydrolysis conditions reported in the accompanying paper.[3] The residue remaining, on concentration, gave analytically pure acids whose specific rotations are given in Table III.

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Registry No. 2a isomer 1, 63007-16-9; **2a** isomer 2, 63007-17-0; **2b** isomer 1, 69766-02-5; **2b** isomer 2, 69766-03-6; **2c** isomer 1, 73697-92-4; **2c** isomer 2, 73697-93-5; **2d** isomer 1, 73712-27-3; **2d** isomer 2, 73697-94-6; **2e** isomer 1, 73697-95-7; **2e** isomer 2, 73697-96-8; **2f** isomer 1, 73697-97-9; **2f** isomer 2, 73697-98-0; **2g** isomer 1, 73697-99-1; **2g** isomer 2, 73698-00-7; **2h** isomer 1, 73698-01-8; **2h** isomer 2, 73698-02-9; **2i** isomer 1, 73698-03-0; **2i** isomer 2, 73698-04-1; **3a**, 13113-71-8; **3b**, 24256-91-5; **3c**, 73698-05-2; **3d**, 73746-01-7; **3e**, 73698-06-3; **3f**, 52166-05-9; **3g**, 73698-07-4; **3h**, 73698-08-5; **3i**, 64471-38-1.

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Reactivity of Phenoxide Ion with Aryl Radicals[1]

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The $S_{RN}1$ mechanism of aromatic substitution has been proved to operate on different kinds of aromatic compounds and nucleophiles. Several types of carbanions, phosphanions, and amide ions have been found to participate as nucleophiles by this mechanism.[2] Among these nucleophiles those having an element belonging to the 6A group of elements with general structure $\mathrm{Ph{-}Z^-}$ have especially been objects of our attention.

Arenethiolate ions are known to react satisfactorily at saturated carbon sites,[3] at the 4-position of the isoquinoline system,[4] and at benzene ring sites by the $S_{RN}1$ mechanism.[2]

Recently we reported that phenyl selenide and phenyl telluride ions were two new nucleophiles probably operating by this mechanism.[5] These nucleophiles gave substitution products in photostimulated reactions in liquid ammonia, in yields that go from moderate to good, depending on the aromatic moiety and the leaving group of the substrate. These nucleophiles are supposed to follow the standard $S_{RN}1$ mechanism as sketched in Scheme I.[2]

Scheme I

$$\mathrm{ArX} + \text{electron donor} \rightarrow (\mathrm{ArX})^{-}\cdot \tag{1}$$

$$(\mathrm{ArX})^{-}\cdot \rightarrow \mathrm{Ar}\cdot + \mathrm{X}^{-} \tag{2}$$

$$\mathrm{Ar}\cdot + \mathrm{Ph{-}Z^{-}} \rightarrow (\mathrm{Ar{-}Z{-}Ph})^{-}\cdot \tag{3}$$

$$(\mathrm{Ar{-}Z{-}Ph})^{-}\cdot + \mathrm{ArX} \rightarrow (\mathrm{ArX})^{-}\cdot + \mathrm{Ar{-}Z{-}Ph} \tag{4}$$

$$\mathrm{Z} = \mathrm{S, Se, Te}$$

Steps 2–4 are the chain-propagation cycle of the proposed mechanism. The radical anion formed in step 3 transfers its extra electron to the substrate to give the substitution product. This has been the main reaction pathway with $\mathrm{PhS^-}$ and $\mathrm{PhSe^-}$ ions. $\mathrm{PhTe^-}$ ion gave not only the substitution product but also products coming from the decomposition of the intermediate radical anion.[5] The relative reactivity of $\mathrm{PhS^-/PhSe^-}$ is about 20 as determined in preliminary experiments.

Phenoxide ion instead is totally unreactive toward phenyl radicals in reactions stimulated by alkali metals,[6]

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by near-UV light,[7] or by electrons from a cathode[8] in liquid ammonia.

Besides, other nucleophiles such as the anion of anthrone, the dianion of hydroquinone, 9,10-dihydroanthracene, and 1,5-diamino-9,10-dihydroxyanthracene were unreactives toward 1-chloronaphthalene in photostimulated reactions in liquid ammonia.[7] Contrary to the PhO^- ion, most of these anions are soluble in liquid ammonia; the only slightly soluble one is the hydroquinone dianion; thus the lack of reactivity cannot be ascribed to their poor solubility.

On the other hand the report that halobenzenes react with PhO^- in 50% aqueous *tert*-butyl alcohol under stimulation by solvated electrons from dissolution of sodium amalgam, giving good yields of diphenyl ether,[9] prompts us to reinvestigate this reaction with the hope that under these reaction conditions we could study the relative reactivity of PhZ^- nucleophiles (Z = O, S, Se, and Te).

Unfortunately we were unable to reproduce those results, and the PhO^- ion was totally unreactive in our hands.

The experiments were conducted with bromobenzene as substrate and PhO^- ion in excess in 50% v/v aqueous *tert*-butyl alcohol with sodium amalgam as a source of electrons. All the reactions were conducted at 25 °C at concentrations of reactants identical with those reported and at two different ratios of substrate and sodium amalgam.

The reaction products were analyzed by GC, and the halide ion released was quantified by potentiometric titrations. In every case the reaction time which was required for the total dissolution of the sodium amalgam was the same. In reactions carried out with a bromobenzene–sodium amalgam ratio of 1:2 we could not find diphenyl ether or benzene by GC. In reactions with a ratio of 1:3 and in the presence of toluene as internal standard, benzene (6%) and bromide ion (7.5%) were found, but no traces of diphenyl ether (<0.5%) could be detected. Under the same experimental conditions, but with 10% external diphenyl ether added, the same results were obtained, with the diphenyl ether recovered unchanged, showing that it survives under our reaction conditions.

It is known that sodium amalgam dissolved in water generates hydrated electrons[10] which could produce phenyl radicals by reaction with bromobenzene (eq 1, Scheme I). The results reported in this paper show that PhO^- ion is unable to react with phenyl radical by the $S_{RN}1$ mechanism; instead it is reduced to benzene. This statement is reinforced by the fact that 5-chloro- and 5-bromo-2*H*,3*H*-benzo[*b*]thiophene-2,3-dione react with PhS^- in Me_2SO by the $S_{RN}1$ mechanism, but PhO^- gave only the reduction product.[11]

Experimental Section

General Methods. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with a flame-ionization detector, using a column packed with 4% silicon rubber SE-30 on Chromosorb G 80-100. Potentiometric titrations were carried out with a Seybold digital pH meter, Model GTE, using a combined silver–calomel electrode. Reagents were all commercially available materials and were purified by standard procedures.

Reaction of PhO^- ion with Bromobenzene and Sodium Amalgam. To a solution of phenol (2.688 g, 28.6 mmol) in 100 mL of 50% *tert*-butyl alcohol–doubly distilled water was added sodium hydroxide (1.517 g, 38 mmol), and the system was degassed and then constantly swept with nitrogen free of oxygen, under magnetic stirring. This was followed by the addition of bromobenzene (1 mL, 9.5 mmol) and toluene (0.5 mL) as internal standard. A 2-mL aliquot was removed at different reaction times to check the toluene/bromobenzene ratio, while sodium amalgam (containing 0.625 g, 27.2 mmol, of sodium) was added in small portions to the remaining solution. The total dissolution of the sodium amalgam took approximately 24 h. The toluene/bromobenzene ratio remained unchanged by GC in samples taken at 0.5, 1, and 2 h, and only one new peak, identified as benzene, was observed at a 24-h reaction time. The solution was then extracted with ether, and the aqueous layer was titrated for bromide ion.

Registry No. Phenoxide ion, 3229-70-7; bromobenzene, 108-86-1.

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Preparation and Synthetic Utility of Phase-Transfer Catalysts Anchored to Polystyrene[1]

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Phase-transfer catalysts[2] facilitate reactions between water-soluble reagents and water-insoluble organic compounds. The catalysts are generally not recovered and this becomes a problem when the relatively expensive cryptands and crown ethers are used. On the other hand, the inexpensive ammonium and phosphonium salts sometimes form stable emulsions. Development of polymer-supported, phase-transfer catalysts[3] allowed for greater ease in separation of the catalyst and isolation of the product. This paper describes the catalytic activity of several new polystyrene-immobilized tetraalkylphosphonium and ammonium salts and explores the extent to which they have synthetic utility.

Results and Discussion

For the determination of the most effective catalyst, different parameters such as the type of polystyrene used, the length of the spacer chain, the type of salt, and the degree of substitution on the polystyrene backbone were varied (Table I). Microporous polystyrene (cross-linked with 2% divinylbenzene, 200–400 mesh) was found to be superior to either macroporous or noncross-linked polystyrene. Regen[4] and Brown[5] studied catalysts similar to 1 and found them to possess much lower activity than nonimmobilized catalysts. Other investigators[5–8] reported increased activity when the catalytic center was attached to the polystyrene matrix by long (8–39 atoms) spacer

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