active 2-halooctanes (and by extension, other 2-haloalkanes) in generally high optical purity. It should be further noted that only 2-halooctanes were observed. Rearranged halocarbons were not detected. Taken together, these data are consistent with a mechanism for carbon–halogen bond formation which involves an S_N2 displacement at carbon. Finally, and not unexpectedly, nucleophiles other than halide ions appear to behave similarly. Thus, for example, (+)-(*S*)-2-octyl tosylate reacts with lithium azide to yield (−)-(*R*)-2-azidooctane (93%, α^{20}_{589} −40.20°).[8]

Experimental Section[9]

(+)-(*S*)-2-Octyl tosylate was prepared from (+)-(*S*)-2-octanol (α^{20}_{589} +7.97°) by the procedure described by Streitwieser and coworkers.[10]

(−)-(*R*)-2-Fluorooctane (1). Into a dry two-neck 50-ml flask containing a Teflon-coated stirrer bar was placed 7.25 g (125 mmol) of anhydrous potassium fluoride. One neck was capped with a rubber septum, the other was connected to a cold trap, and the apparatus was flushed with nitrogen. Anhydrous triethylene glycol (25 ml) and 7.10 g (25 mmol) of the tosylate of (+)-(*S*)-2-octanol (α^{20}_{589} +7.97°, optical purity 99.4%) were added by syringe. The rubber septum was replaced with a glass stopper and the flask was heated to 110° with vigorous stirring under reduced pressure (4 Torr). The volatile materials were allowed to distil from the reaction mixture and collected in the cold trap (−50°) over a period of 3 hr. Analysis of the crude distillate by GLC indicated a 52% yield of 2-fluorooctane accompanied by a 27% yield of octene(s). The crude distillate was treated with a slight excess of bromine in carbon disulfide, washed with aqueous sodium thiosulfate, dried ($MgSO_4$), and distilled to afford 1.45 g (44%) of (−)-(*R*)-2-fluorooctane (1): α^{20}_{589} −9.99°, bp 55–57° (43 Torr) [lit.[11] bp 139° (760 Torr)]; ^1H NMR (CCl_4) δ 4.50 [1 H, d of multiplets, $J(HCF) = 48$ Hz], ~1.4 [10 H, br, complex multiplet, $(CH_2)_5$], 1.26 [3 H, d of d, $J(\mathbf{CH_3}\text{–}CH\mathbf{F}) = 23$ Hz, $J(\mathbf{CH_3}\text{–}\mathbf{CH}F) = 7.0$ Hz], 0.96 (3 H, t); ir (CCl_4) 870 cm^{-1} (vs, C–F).

(−)-(*R*)-2-Chlorooctane was prepared from 4.24 g (100 mmol) of anhydrous lithium chloride and 5.68 g (20.0 mmol) of the tosylate of (+)-(*S*)-2-octanol in 20 ml of triethylene glycol by a procedure analogous to that described for the synthesis of **1**. After treatment with a slight excess of bromine (CS_2) and subsequently with aqueous sodium thiosulfate, the crude product mixture was dried ($MgSO_4$) and fractionated to yield 1.80 g (61%) of (−)-(*R*)-2-chlorooctane, bp 74–76° (25 Torr) [lit.[12] bp 61–62° (17 Torr)], α^{20}_{589} −30.72°.

(−)-(*R*)-2-Bromooctane was synthesized by a procedure similar to that described for the preparation of **1** using anhydrous potassium bromide (1.97 g, 18.0 mmol) and 4.26 g (15.0 mmol) of the tosylate of (+)-(*S*)-2-octanol in 15 ml of triethylene glycol at 65° (0.1 Torr). The reaction was conducted over a period of 2 hr. Direct fractionation of the crude product afforded 1.84 g (63%) of (−)-(*R*)-2-bromooctane, bp 74–76° (14 Torr) [lit.[12] bp 72° (9 Torr)], α^{20}_{589} −41.56°.

(−)-(*R*)-2-Iodooctane was prepared according to the procedure outlined for the preparation of **1** using lithium iodide (0.806 g, 6.00 mmol) and 1.42 g (5.00 mmol) of the tosylate of (+)-(*S*)-2-octanol in 10 ml of tetraethylene glycol. The reaction was carried out under a reduced pressure of 0.1 Torr at a temperature of 90° over a period of 90 min. Direct fractionation of the crude product gave 0.80 g (67%) of (−)-(*R*)-2-iodooctane, bp 54–55° (1.5 Torr) [lit.[12] bp 42° (0.5 Torr)], α^{20}_{589} −19.32°.

(−)-(*R*)-2-Azidooctane was prepared from 2.45 g (50.0 mmol) of lithium azide and 2.84 g (10.0 mmol) of the tosylate of (+)-(*S*)-2-octanol by a procedure analogous to that described for the preparation of **1**. Direct fractionation of the crude product yielded 1.11 g (72%) of (−)-(*R*)-2-azidooctane: bp 59–60° (5 Torr) [lit.[13] bp 68° (9 Torr)]; α^{20}_{589} −40.20°; ^1H NMR (CCl_4) δ 3.33 (1 H, sextet), 1.9–1.2 (13 H, br, complex multiplets), 0.90 (3 H, t); ir (CCl_4) 2110 cm^{-1} (vs, $-N_3$).

Acknowledgment. We thank Professor Donald B. Denney for a generous gift of optically active 2-octanol.

Registry No.—2-Fluorooctane, 54632-06-3; 2-chlorooctane, 18651-57-5; 2-bromooctane, 5978-55-2; 2-iodooctane, 29117-48-4; (+)-(*S*)-2-octyl tosylate, 34817-25-9; (−)-(*R*)-2-azidooctane, 53475-02-8.

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(6) The best-fit equation, calculated for the points Cl, Br, I shown in Figure 1, is $[M]^{20}_{589} = 7.58[R]^{20}_{589} + 5.64$, which leads to a molecular rotation of $[M]^{20}_{589}$ −16.6° for optically pure (−)-(*R*)-2-fluorooctane, *calculated* for carbon–fluorine bond refraction of 1.44. The molecular optical rotation (molecular rotation, M) as used here corresponds to the quantity $[M] = [\alpha](\text{mol wt})/100$; [R] is the common bond refraction.[5] The density of 2-fluorooctane is unavailable. The density of 1-fluorooctane, $d^{20} = 0.810$ ["Handbook of Chemistry and Physics", 53rd ed, 1972, p C-399], was substituted.

(7) For a review of these procedures, see H. R. Hudson, *Synthesis*, **1**, 112 (1969).

(8) Yield determined by GLC analysis. The observed rotation for purportedly optically pure 2-azidooctane is $|\alpha|^{20}_{589}$ 38.6° [R. A. Moss and P. E. Schueler, *J. Am. Chem. Soc.*, **96**, 5792 (1974)].

(9) All boiling points are uncorrected. Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were determined with a Varian T-60 NMR spectrometer. ^1H chemical shifts are reported in parts per million relative to internal tetramethylsilane. All coupling constants are in hertz. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute product yields were calculated from peak areas using internal standard techniques with response factors obtained from authentic samples. Reported rotations were recorded as neat liquids in a 1-dm cell using a Perkin-Elmer Model 141 spectropolarimeter. Alkali salts were purchased from Alfa Inorganics. Solvents were distilled immediately prior to use.

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Sodium Bismuthate as a Phenolic Oxidant

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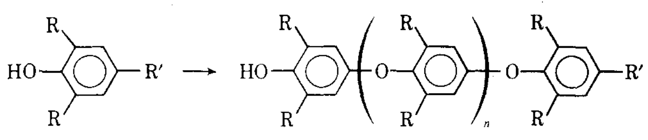
The oxidative polymerization of 2,6-xylenol (I) to its corresponding polyphenylene oxide (II) has been carried out with homogeneous and heterogeneous one-electron oxidants. An excellent catalytic oxidant is the homogeneous cuprous halide–oxygen–pyridine system developed by Hay and coworkers.[1] Heterogeneous oxidants such as silver oxide,[2] activated manganese dioxide,[3] lead dioxide,[3] and nickel peroxide[4] have been reported to be noncatalytic and less effective in achieving with facility the high molecular weights of the Hay system. Nonetheless, studies of these heterogeneous oxidants have been important in eliciting the mechanism of the polymerization and understanding the oxidative capabilities of nonstoichiometric oxides. Despite the disparity of oxidants for this polymerization, the mechanism is a free-radical one characterized by a polycondensation via quinone–ketal intermediate.[3,5,6]

Sodium bismuthate is another interesting and possibly more useful heterogeneous oxidant for the polymerization of I and other phenols (Table I). Scant attention has been given to sodium bismuthate as an oxidant for phenols, even though its potential was indicated by Hewitt, who used it to oxidize the monobenzyl ether of bis-2-hydroxy-1-naphthylmethane to a spironaphthalenone in 90% yield.[7]

Table I
Products of Phenolic Oxidation by Sodium Bismuthate



I, IV, VI   II, V, VII

Compd	R	R'	Compd	R	R'
I	CH_3	H	II	CH_3	H
IV	CH_3	CH_3	V	CH_3	CH_3
VI	OCH_3	H	VII	OCH_3	H

When a benzene solution of 2,6-xylenol was refluxed with sodium bismuthate in 2 molar excess, a 74% yield of II was obtained. The polymer's infrared spectrum contained the characteristic peaks at 8.4, 9.8, 10.4, 11.6, and 12.0 μ. The two NMR peaks at 2.1 and 6.5 ppm relative to $(CH_3)_4Si$ were in the ratio of 3:1. In the mass spectrum peaks which were multiples of 120 were displayed. The polymer had an intrinsic viscosity of 0.33, which corresponds to an approximate molecular weight of 1.1×10^4.[8] A comparable experiment with activated manganese dioxide gave a polymer with an intrinsic viscosity of 0.14. An examination of variations of reaction conditions is presented in Table II. A noteworthy point is that reactions at room temperature afford polymers of higher molecular weight than those obtained at temperatures of refluxing solvents. Other points of interest from these variable studies are that polymer viscosities did not change appreciably after 2 hr of reaction time or with an increase of oxidant to phenol molar ratio beyond 6:1.

Table II
Polymerization of 2,6-Xylenol with Sodium Bismuthate

Wt $NaBiO_3$, g	Benzene, ml	Temp	Reaction time, hr	% yield[a] of polymer	Intrinsic viscosity[b]	Approx mol wt[c]
16.5	100	Ambient	0.33	24	0.07	1.3×10^3
16.5	100	Ambient	2	67	0.15	3.6×10^3
33.0	100	Reflux	2	74	0.33	1.1×10^4
33.0	100	Ambient	2	70	0.59	2.3×10^4
55.0	200	Reflux	2	73	0.49	1.8×10^4
55.0	200	Ambient	2	79	0.59	2.3×10^4

[a] The yield is calculated on initial amount (4.1 g) of 2,6-xylenol. [b] All intrinsic viscosities were determined in benzene at 30°. [c] Molecular weights were estimated from the formula of Price and Chu.[8]

The bismuthate-mediated polymerization had the polycondensation feature of similar reactions in that when an oily oligomer devoid of monomer was treated with bismuthate at room temperature, a 72% yield of solid polymer melting at 190° was obtained.

The bismuthate reaction mixtures of most polymerizations in benzene contained minor amounts of tail-to-tail products, such as 3,3',5,5'-tetramethyldiphenoquinone (III). Indeed this product and its reduced precursor were not recovered even when I was in 2 molar excess—in contrast to the activated manganese dioxide reactions.[3] Small amounts of III were formed if these bismuthate mixtures were not refluxed or the reaction solvent was chloroform or the bismuthate was pretreated with a 10% sulfuric acid washing. An oxidation of authentic III with excess bismuthate yielded neither organic products nor starting material. III is quite stable to a similar treatment by activated manganese dioxide. This decomposition of III, however, can be carried out with nickel peroxide. The polymer itself was recovered in 89% yield with no change in viscosity after a 2-hr reflux in benzene over excess bismuthate.

Not all tail-to-tail couplings suffer complete oxidation with bismuthate. 2,6-Di-*tert*-butylphenol was oxidized to the tetra-*tert*-butyldiphenoquinone in 91% yield with a 2-hr refluxing of a benzene solution over a 2 molar excess of bismuthate.

Bismuthate attack on specialized tail-to-tail products was exemplified by the oxidation of mesitol (IV). The principal products were 4-hydroxy-3,5-dimethylbenzaldehyde and that polymeric mixture (V) formed by oxidative dealkylation of mesitol, which was first observed in activated manganese dioxide oxidations.[9] The yields of the aldehyde, which was absorbed on the surface of the bismuthate as a sodium salt, and the polymer were 26 and 30%, respectively, for a 2 molar excess bismuthate oxidation. Only a small amount of mesitol was recovered; copious amounts of CO_2 were evolved upon acidification. In a separate experiment, the aldehyde was recovered in 50% yield after stirring at room temperature for 5 days over 3 molar excess bismuthate.

Carbon dioxide formation was not unique to the mesitol reaction. Acidification of the water washings of bismuthate surfaces from 2,6-xylenol oxidations after extensive benzene washings afforded carbon dioxide. Furthermore, titration of such basic water wishes indicated amounts of base equivalent approximately to the polymer yield. The formation of strongly basic sites on the oxidizing bismuthate surfaces might be implicated in the diphenoquinone breakdown via proton abstraction on the methyl groups. Such anions could be oxidized further or lead to Diels–Alder adducts susceptible to bismuthate degradation.

Another peculiarity of the xylenol oxidation is the appearance of a green coating on the oxidant during the initial stage of the reaction. When the mole ratio of bismuthate to xylenol was more than 1:1, the reaction viscosity gradually decreased and the green color disappeared. With equimolar ratios the thinning out was observed but the residual bismuthate remained green. No color was observed when bismuthate was used to oxidize oligomer to polymer. One source of the green could be the diphenoquinone precursor. When the sodium salt of reduced III was treated with bismuth trinitrate to give a monobismuth salt, the latter turned green upon contact with light and/or air.

Despite its ability to attack tail-to-tail or alkyl groups in the para position of phenols, bismuthate is ineffectual as an oxidant for benzyl alcohol. Even the use of bismuthate which had oxidized partially 2,6-xylenol and hence contained basic sites gave no oxidation. This represents a distinct difference from that workhorse of benzylic oxidations, activated manganese dioxide,[10] and its more powerful relative, nickel peroxide.[11]

In order to examine the bismuthate reaction products, 2,4,6-tri-*tert*-butylphenol was treated with sodium bismuthate to give the corresponding stable phenoxyl radical. This reaction with excess of the phenol was used to completely exhaust the oxidizing power of a bismuthate sample. After benzene and water washings, the remaining residue was Bi_2O_3. Titration of the washes indicated amounts of sodium hydroxide almost equivalent to the initial sodium bismuthate. These results suggest that the stoichiometry of bismuthate oxidations is $2NaBiO_3 + 4(H) \rightarrow H_2O + Bi_2O_3 + 2NaOH$. It should be borne in mind that the formula of the bismuthate does not fully express its structure. Commercial bismuthate usually has a 5–6% water content as determined by benzene azeotrope. Bismuthates with or without this water are equally effective in xylenol polymerization. Azetropic distillation has little effect on "chemical hydration" as indicated by ir bands at 2.95 and 5.95 μ.[12] The structure of the bismuthate undergoes a substantial change in refluxing acetic acid, wherein the 2,6-xylenol oxidation products are 2-acetoxy-2,6-dimethylcyclohexadien-3,5-one (63%) and diphenoquinone (III, 15%). No polymer was formed. Without the xylenol the sodium bismuthate in refluxing acetic acid evolves oxygen, as demonstrated by trapping the oxygen by a nitrogen sweep into a separate flask containing the 2,4,6-tri-*tert*-butylphenoxyl radical. Acidity causes a drop in active oxygen content. Commercial sodium bismuthate possesses an active oxygen content of 3.1×10^{-3} g-atoms of oxygen per gram. This is indicative of 91% purity, if correction is made for 5% water. The value for bismuthate treated with 10% sulfuric acid is 1.2×10^{-3} g-atoms of oxygen per gram. The sodium bismuthate, however, does not change in oxidizing power on standing in acetic acid at room temperature for several days.

Other phenols which have been polymerized by sodium bismuthate are durenol and 2,6-dimethoxyphenol. The durenol (2,3,5,6-tetramethylphenol) was treated with a 2 molar excess of bismuthate in refluxing benzene for 2 hr to give a 64% yield of a polymer (mp 215–230°) whose ir and NMR spectra were identical with those reported by Price and Nakagawa.[13] A similar treatment of 2,6-dimethoxyphenol afforded a polymer VII which adhered strongly to the bismuthate surface. Soxhlet extraction with chloroform was used to obtain a 66% yield of a polymer melting at 205–210°. Its NMR spectrum had two singlet peaks at 3.7 (6 H) and 6.3 ppm (2 H) relative to $(CH_3)_4Si$. Significant ir bands were at 8.2, 8.35, 10.1, 10.6, 11.3, and 12.1 μ.

Experimental Section

Materials and Instruments. Phenols were obtained from Aldrich Chemical Co. and were used without further purification. Sodium bismuthate was obtained from J. T. Baker Chemical Co., Fisher Scientific Co., and Allied Chemical Co. Spectral determinations were determined as follows: infrared, Perkin-Elmer Model 137; nuclear magnetic resonance, Varian Associates Model A-60; mass spectra, Varian Associates Model M-66. Melting points were determined on a Thomas-Hoover Unimelt apparatus. The thermometer was calibrated against melting point standards supplied by A. H. Thomas Co.

An Oxidation Procedure. Sodium bismuthate (33.0 g, 0.118 mol) was added to a solution of 2,6-xylenol (4.1 g, 0.033 mol) in 100 ml of benzene. The mixture was refluxed for 2 hr with magnetic stirring. After being cooled to 20° the mixture was filtered and the residual sodium bismuthate was washed with 150 ml of benzene. The combined benzene solutions were washed with a 5% solution of NaOH. Acidification of the basic layer did not yield any organic matter. The dried benzene solution was evaporated to give a crude polymer, which was dissolved in 25 ml of chloroform. The latter solution was poured into 200 ml of methanol to coagulate the polymer, which was then filtered and dried. It weighed 3.05 g and melted at 186–215°. The alcoholic mother liquor was concentrated to near dryness and yielded 0.047 g of diphenoquinone (III), as determined by superimposition of its infrared spectrum with that of an authentic sample. A portion of the dried recovered sodium bismuthate–bismuth oxide mixture was dissolved in concentrated hydrochloric acid without any residue.

Registry No.—I, 576-26-1; II repeating unit, 24938-67-8; II homopolymer, 25134-01-4; III, 4906-22-3; IV, 527-60-6; V homopolymer, 30140-67-1; VI, 91-01-1; VII repeating unit, 25667-13-4; VII homopolymer, 25511-61-9; $NaBiO_3$; 12125-43-8; 2,6-di-*tert*-butylphenol, 128-39-2; tetra-*tert*-butyldiphenoquinone, 2455-14-3; 4-hydroxy-3,5-dimethylbenzaldehyde, 2233-18-3; 2-acetoxy-2,6-dimethylcyclohexadien-3,5-one, 7218-21-5; durenol, 527-35-5.

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Ionization Constants of Substituted 2-Aminoacetanilides and Benzylamines. Transmission of Electronic Effects through Amide Links

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Previous papers in this series have reported the effect of aromatic ring substituents on the rates of reaction at the methylene group adjacent to the carbonyl in substituted anilides.[1] A typical study was the displacement rate of 4-nitrophenoxide with 2-bromoacetanilides.[1d] The reaction center was immediately adjacent to the carbonyl group, and Hammett ρ values[2–7] appeared to indicate efficient transfer of activation effects through the amide link. Two studies have indicated low transmission efficiencies through the amide functionality: the ionization constants of 4-substituted 4′-aminobenzanilides[8] and the ^{19}F chemical shifts in substituted trifluoroacetanilides.[9]

In a continuation of these studies, and because of possible interest from the biochemical area, we have prepared a group of ring-substituted 2-aminoacetanilides and have measured the p*K*'s in water solution. For comparison the p*K*'s of a group of ring-substituted benzylamines have been determined; previous determinations[3,10–12] of the Hammett ρ for these amines gave values ranging from 0.72[3,10] to 1.06[11] to 1.13 (data from ref 12 fit to the Hammett equation in this work; $r = 0.987$). Values of ρ refer to eq 1. It was

$$BH^+ \rightleftarrows B + H^+ \qquad (1)$$

thought desirable to remeasure the benzylamines to ensure consistency of measurement with the 2-aminoacetanilides.

The benzylamines and their hydrochlorides are known compounds; they were purchased or prepared by reported