Stereochemistry of Hydroperoxide Cyclization Reactions

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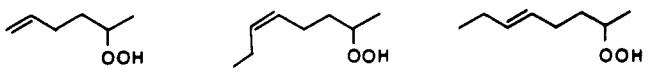
The 6-exo cyclization of three unsaturated hydroperoxides has been studied. These hydroperoxides, **1**, (5-hexen-2-yl hydroperoxide), **2** ((*Z*)-5-octen-2-yl hydroperoxide), **3** ((*E*)-5-octen-2-yl hydroperoxide), were cyclized by free radical and mercury-catalyzed reactions. The mercury-catalyzed reactions were followed by reductive demercuration and the products isolated here and from the free radical cyclization were alkyl substituted tetrahydrofuranols. The stereochemistry of the products of cyclization has been determined and the preferred stereoselectivity of cyclization may be understood by assuming an equatorially substituted chair-like transition state.

The importance of cyclization reactions of unsaturated hydroperoxides in several biological and nonbiological systems has led to many studies of this important reaction.[1] Recent model studies for polyolefin oxidation establish a multiple peroxy radical cyclization pathway (Scheme I) involving a 6-exo cyclization and indicate a marked preference for the formation of 3,6-trans disubstituted 1,2-dioxanes.[2,3] This observation of 6-exo regioselectivity and 1,4-stereochemical induction prompted us to further explore this system and we report here the results of that effort.

Results

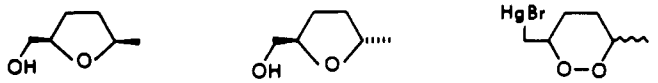
Three unsaturated hydroperoxides, **1–3**, were studied. Two methods of cyclizing the peroxide were employed.



1 **2** **3**

Radical abstraction of the hydroperoxy hydrogen with a free radical initiator was one method utilized,[4] and intramolecular peroxy mercuration[5,6] was the second set of reaction conditions used. The peroxy mercuration reaction was generally coupled to subsequent borohydride demercuration reactions of the intermediate cyclic peroxides.

Reactions of Hydroperoxides 1–3. Reaction of hydroperoxide **1** with di-*tert*-butyl peroxyoxalate[7] in degassed benzene at 25 °C for 5 days followed by treatment of the reaction mixture with a catalytic amount of trichloroacetic acid led to two primary products, **4** and **5**, which were

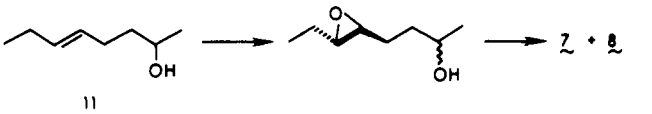


4 **5** **6**

isolated by preparative gas chromatography. These products compare in every respect to the two tetrahydrofurans prepared previously by Brown and Djerassi.[8,9]

Scheme I

Scheme II



11

12

Table I. Product Distribution for Reactions of Hydroperoxides 2 and 3

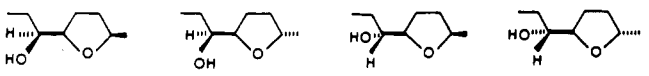
reactant	conditions	products 7	8	9	10
2	free radical	68	21	8	3
3	free radical	65	20	11	4
2	mercuric pivalate[a]/BH_4^-	79	11	9	1
3	mercuric pivalate[b]/BH_4^-	74	19	6	1
2	mercuric nitrate[c]/BH_4^-	63	22	11	4

[a] Mercuric pivalate at −20 °C, 12 h. [b] Mercuric pivalate at room temperature. [c] Mercuric nitrate at room temperature.

The ratio of products **4**:**5** was 65:35.

Use of mercuric pivalate[10] to cyclize **1**, followed by potassium bromide workup, led to β-mercuri-cyclic peroxide compounds such as **6**. Reduction of these cyclic peroxides with sodium borohydride (CH_2Cl_2/aqueous solvent) followed by treatment of the resulting product mixture with trace trichloroacetic acid gave compounds **4** and **5** in a 90:10 product ratio.

Reaction of the hydroperoxides **2** and **3** under conditions identical with those described for hydroperoxide **1** led to analogous cyclic peroxides and tetrahydrofurans. Thus, reaction of **2** under free radical conditions gave four tetrahydrofuran products, **7–10**, with structures as shown.



7 **8** **9** **10**

Compounds **7** and **8** have erythro stereochemistry at the

(1) Porter, N. A.; Funk, M. O.; Gilmore, D.; Isaac, R.; Nixon, J. *J. Am. Chem. Soc.* **1976**, *98*, 6000–6005.
(2) Roe, A. N.; McPhail, A. T.; Porter, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 1199–1203.
(3) Porter, N. A.; Roe, A. N.; McPhail, A. T. *J. Am. Chem. Soc.* **1980**, *102*, 7574–7576.
(4) See ref 1.
(5) Nixon, J. R.; Cudd, M. A.; Porter, N. A. *J. Org. Chem.* **1978**, *43*, 4048–4052.
(6) Bloodworth, A. J.; Loveitt, M. E. *J. Chem. Soc., Perkin. Trans. 1* **1978**, 522.
(7) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762.
(8) Brown, H. C.; Lynch, G. J. *J. Org. Chem.* **1981**, *46*, 930–939.
(9) Djerassi, C.; Cook, M. M. *J. Am. Chem. Soc.* **1973**, *95*, 3678–3686.
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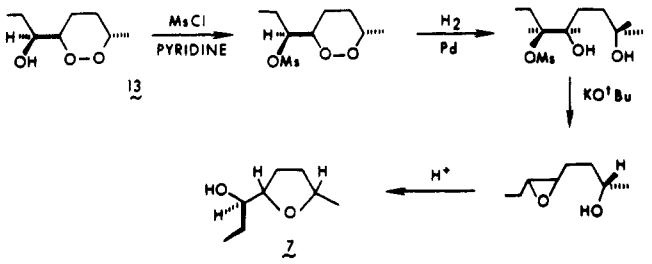
Scheme III

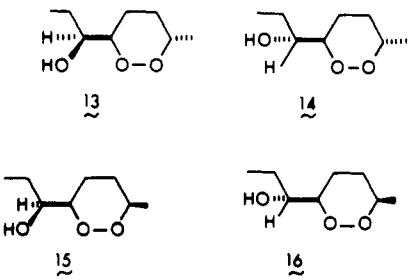


adjacent ring carbinol centers while compounds **9** and **10** have threo stereochemistry at those centers.

The distribution of products, **7–10**, from reactions carried out under several conditions are presented in Table I.

Assignment of Structures 7–10. Several lines of evidence were used to assign the structures **7–10**. The erythro pair (**7** and **8**) and the threo pair (**9** and **10**) were assigned simply by peracid epoxidation of alcohols **11** and **12** (Scheme II) followed by TCA workup. Separation of the diastereomeric pair formed from epoxidation of both **11** and **12** by HPLC and comparison of these products with those formed from the hydroperoxide precursors (Table I) allowed identification of the threo and erythro compounds in the product mixtures.

Further identification of the compounds was achieved by correlating the stereochemistry of **7–10** with the stereochemistry of compounds **13–16**. These 1,2-dioxanes



were prepared from the hydroperoxides **2** and **3** by free radical cyclization in the presence of molecular oxygen followed by treatment of the product cyclic peroxide hydroperoxides with triphenylphosphine to reduce the hydroperoxide to alcohol[11] (See Scheme V). The ring stereochemistry of compounds **13–16** may be assigned by ^1H and ^{13}C NMR spectroscopy. The cis or trans substitution on the 1,2-dioxane may be simply assigned by analysis of coupling patterns of protons on carbons α to the peroxide linkage. For the trans substituted compounds, **13** and **14**, J values of $\sim$3 and 10 Hz are observed as is expected for coupling of axial protons with the two vicinal ring protons. Couplings of corresponding α protons for the cis substituted compounds are lower and more equal as is expected. It should also be noted that signals for several carbons are observed to be shifted upfield in the ^{13}C spectrum of **15** and **16** relative to the shifts observed for **13** and **14**. This upfield shift is consistent with the increased steric crowding in the cis substituted dioxane ring which must have one substituent axially placed. (A detailed discussion of the ^1H and ^{13}C spectra of compounds **13–16** is presented in the supplementary material to this paper.) From ^1H and ^{13}C spectroscopy, the relative stereochemistry of the ring chiral centers can thus be unambiguously assigned.

The final link in the product identification is provided by conversion of the cyclic peroxides, **13–16**, to the tetrahydrofuran derivatives **7–10** by the sequence outlined in Scheme III. The conversion was achieved for three of the peroxides and is illustrated here only for **13**. In this way **13**, one of the trans substituted dioxanes is converted to **7**, a cis substituted tetrahydrofuran. The complete stereochemistry of the four tetrahydrofurans **7–10** as well as the dioxanes **13–16** may thus be unambiguously assigned by this sequence of reactions. The identification matrix utilized is presented in Scheme IV. As seen from Scheme IV, one of the two trans substituted dioxanes leads to a tetrahydrofuran that has erythro stereochemistry and is therefore **7** while the other trans dioxane is converted to a furan product that has threo configuration and is thus assigned the structure **9**. The identity of **8** and **10** are similarly revealed from the cis dioxane pair **15** and **16**.

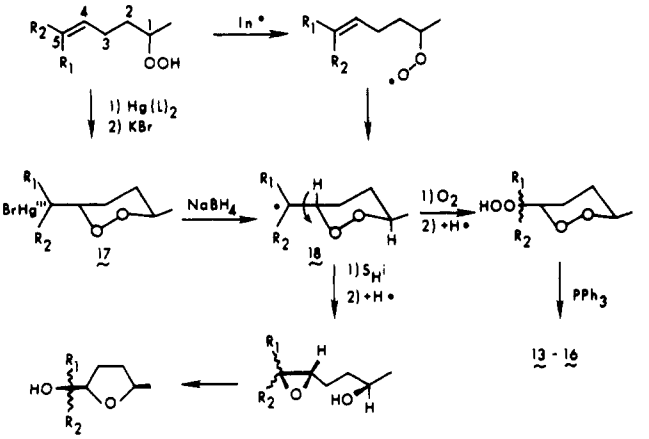
Scheme IV. Structural Assignments of Compounds 7–10

	7 and 8 (erythro pair)	9 and 10 (threo pair)
THFs		
dioxanes		

13 and 14[a] → 7 (erythro, cis) + 9 (threo, cis)
15 and 16[a] → 8 (erythro, trans) + 10 (threo, trans)

[a] Trans substituted dioxanes are converted to cis substituted tetrahydrofurans by the sequence as outlined in Scheme III.

Scheme V



Discussion

The mechanistic pathways described in Scheme V may be used to discuss the cyclization reactions studied. Both the radical cyclization[12] and mercury cyclization modes[13] have ample precedent as do the S_Hi sequence[14] and the epoxide conversion to tetrahydrofurans.[15] The 1,4-stereochemistry is defined in the cyclization step and depends on the substrate and method of cyclization. Cyclization reactions leading to 3,6-trans disubstituted dioxanyl intermediates as shown in Scheme V ultimately lead to cis substituted tetrahydrofurans via the S_Hi and epoxide cyclization steps. The trans substituted dioxanes should be favored (diequatorial substituents) and consistent with this is the fact that in all cases studied the cis substituted tetrahydrofurans (derived from trans dioxanes) are the major products isolated.

(11) Funk, M. O.; Isaac, R.; Porter, N. A. *J. Am. Chem. Soc.* **1975**, *97*, 1281.

(12) Beckwith, A. L.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099.

(13) Bloodworth, A. J.; Khan, J. A. *J. Chem. Soc., Perkin Trans. 1*, **1980**, 2450.

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(15) Staude, E.; Patat, F. In "The Chemistry of Ethers"; Patai, S., Ed.; Interscience: New York, 1967.

Peroxy radical cyclization is apparently less stereoselective than mercury-catalyzed cyclizations. Free radical cyclization of **1** gives a 65:35 ratio of **4**:**5** while mercuric pivalate catalyzed reaction of the same substrate leads, after borohydride reduction, to a 90:10 product ratio. Radical cyclization of **2** and **3** gives a 76:24 ratio of cis:trans products (**7** + **9**:**8** + **10**) while mercuric pivalate gives an 88:12 product ratio for **2** and a 79:21 product distribution for **3**. The cis:trans ratios obtained were maximum for mercuric pivalate catalyzed reactions with mercuric nitrate and other derivatives being less selective.

It should be noted that significant erythro:threo selectivity is observed in the cyclization reactions of **2** and **3**. This selectivity, which is independent of mode of cyclization is on the order of 88:12, the erythro configuration being favored. The erythro stereochemistry indicates that there is a marked preference for formation of the trans substituted epoxide in the S_Hi reaction of carbon radical **18** (Scheme V). This trans epoxide preference from **18** is undoubtedly steric in origin and reflects crowding in the S_Hi reaction of **18** leading to cis substituted epoxide. Note that there is free rotation in the crucial α-bond or radical **18** and the conformation about this bond in the transition state defines product threo–erythro stereochemistry.

Experimental Section

The hydroperoxides **1**, **2**, and **3** were prepared from the corresponding alcohols, 5-hexen-2-ol, *cis*-5-hepten-2-ol, and *trans*-5-hepten-2-ol. The details for the synthesis of these alcohols is given in the supplementary material.

The alcohols were converted to corresponding methanesulfonates by reaction with pyridine and methanesulfonyl chloride. The methanesulfonate was then converted to the hydroperoxide by treatment with basic hydrogen peroxide. The general procedure used is described here.

5-Hexen-2-yl Methanesulfonate. 5-Hexen-2-ol (2.01 g, 0.02 mol) was combined with methanesulfonyl chloride (2.30 g, 0.02 mol) and cooled under argon to 0–5 °C. Pyridine (3.37 g, 0.04 mol) was added dropwise to the combined reagents over 1 h. The reaction mixture stirred an additional 2 h before it was poured over 15 mL of ice cold 10% hydrochloric acid solution. The resulting reaction mixture was extracted with three 20-mL portions of diethyl ether, which were combined and washed with two 20-mL portions of water and 20 mL of saturated sodium bicarbonate solution. After the ether layer was dried with anhydrous potassium carbonate and filtered, and the solvent was removed, the resulting product was purified by using a 1-in. Waters semiprep column packed with 230–400 mesh silica gel: 2.83 g (0.016 mol, 80%); 80 MHz NMR ($CDCl_3$) δ 1.4 (3 H, d), 1.6–2.3 (4 H, m), 3.0 (3 H, s), 4.6–5.2 (3 H, m), 5.6–6.0 (1 H, m); ^{13}C ($CDCl_3$) δ 22.2, 29.3, 35.8, 38.7, 79.5, 115.6, 137.1.

***trans*-5-Octen-2-yl Hydroperoxide.** The methanesulfonate (1.1 g, 0.0053 mol) was dissolved in 9 mL of methanol and 1 mL of water and cooled to 0–5 °C. 30% Hydrogen peroxide (2.39 g, 0.02 mol) was added to the cool solution followed by 50% aqueous potassium hydroxide (0.65 g, 0.003 mol). The reaction mixture was allowed to warm slowly to room temperature and stir for 20 h. Additional equivalents of hydrogen peroxide and potassium hydroxide were added at 24 h and 48 h.

At 72 h, 75 mL of methanol was added and the reaction mixture cooled to 0 °C. The reaction mixture was acidified with the dropwise addition of concentrated hydrochloric acid. White flocculent material formed.

50 mL of brine and 25 mL of water were added. The aqueous phase was extracted seven times with 50-mL portions of diethyl ether. The ether extracts were combined and dried with anhydrous sodium sulfate. After filtering, the diethyl ether was removed under reduced pressure. The crude product was redissolved in benzene and dried with anhydrous sodium sulfate. Filtration and removal of benzene from the product mixture was followed by purification using a 1 in. Waters semiprep column packed with 230–400 mesh silica gel. 5% ethyl acetate and 95% hexane was used as the eluting solvent. The product was obtained as a clear oil: 0.329 g (0.0023 mol, 43%); 250 MHz NMR δ 0.95 (3 H, t), 1.22 (3 H, d), 1.40–1.54 (2 H, m), 1.61–1.77 (2 H, m), 1.93–2.13 (4 H, m), 4.01–4.13 (1 H, m), 5.31–5.54 (2 H, m), 7.63 (1 H, s). Decoupling at 2.03 gives δ 5.48 (d, 15.2 Hz coupling) and 5.37 (d, 15.3 Hz coupling). While the hydroperoxide was not analyzed for C and H, the corresponding alcohol gave an acceptable analysis. Calcd for $C_8H_{10}O$: C, 75.0; H, 12.6. Found: C, 74.75; H, 12.49.

Cyclization Reactions, Typical Procedures. 1. Free Radical. *cis*-5-Octen-2-yl hydroperoxide (0.02 g, 1.4×10^{-4} mol) dissolved in 140 μL of benzene-d_6 was combined with di-*tert*-butyl peroxyoxalate (0.0005–0.001 g) in 170 μL of benzene-d_6 and an additional 100 μL of benzene-d_6 was added. The mixture was freeze–pump–thawed through five cycles and then the tube sealed under vacuum. The tube was allowed to stand at room temperature for five days, after which time the tube was opened and a trace quantity of trichloroacetic acid added at 0 °C.

After stirring for 1 h, methylene chloride (15 mL) was added and the reaction mixture was washed with 5 mL of saturated sodium bicarbonate solution and 10 mL of brine. The organic layer was dried over anhydrous magnesium sulfate (0.0125 g, 8.7×10^{-5} mol, 62%).

2. Mercuric Pivalate Catalyzed. *cis*-5-Octen-2-yl hydroperoxide (0.052 g, 3.6×10^{-4} mol) in 10 mL of methylene chloride was added dropwise to a solution of mercuric pivalate[10] (0.214 g, 5.4×10^{-4} mol) in 15 mL of methylene chloride at −20 °C. After stirring for 12 h at −20 °C, 10 mL of saturated potassium bromide solution was added. The mixture was stirred for 1.5 h at room temperature.

Methylene chloride (100 mL) was added and the aqueous potassium bromide phase removed. The methylene chloride was washed five times with 50-mL portions of water, then dried over anhydrous sodium sulfate, filtered, and removed in vacuo. The product is a slightly opaque oil (0.146 g, 3.4×10^{-4} mol, 94%) and one spot on thin layer chromatography. Material purified by HPLC gives an acceptable C and H analysis. Calcd for $C_8H_{15}O_2HgBr$: C, 22.7; H, 3.6. Found: C, 22.92; H, 3.72.

3. Reduction of Alkyl Mercuric Bromides with $NaBH_4$. Alkyl mercuric bromide (0.055 g, 1.3×10^{-4} mol) in 25 mL of methylene chloride and 8 mL of water was purged with argon and then cooled in an ice bath. Sodium borohydride (0.006 g, 1.6×10^{-4} mol) in 17 mL of 2 N sodium hydroxide was purged with argon and then added dropwise to the solution of mercuric bromide over 30 min. The reaction was stirred for an additional 30 min. Methylene chloride (200 mL) was added to the reaction mixture which was then washed three times with 50-mL portions of water, dried over anhydrous sodium sulfate, and filtered, and the solvent removed in vacuo.

Methylene chloride (10 mL) was added to the residue and the solution cooled in an ice bath. Trichloroacetic acid (0.02 M) in methylene chloride (5 mL) was added to the above solution and stirred for 1 h at room temperature.

Additional methylene chloride (15 mL) was added and the mixture was washed with 10 mL each of 5% sodium bicarbonate and water (0.0077 g, 5.3×10^{-5}, 41%). A mixture of GC purified tetrahydrofuranols **9** and **10** gave an acceptable C and H analysis. Calcd for $C_8H_{16}O_2$: C, 66.6; H, 11.2. Found: C, 66.61; H, 11.32.

4. Free Radical Cyclization under Oxygen. *cis*-5-Octen-2-yl hydroperoxide (0.5 g, 0.0035 mol) dissolved in 88 mL of benzene and saturated with oxygen prior to the addition of di-*tert*-butyl peroxyoxalate (0.16 g, 0.0007 mol). After stirring for 24 h the benzene was removed under reduced pressure and 50 mL of anhydrous diethyl ether was added to the residue. Triphenylphosphine (0.44 g, 0.0017 mol) in 15 mL of diethyl ether was added to the ether solution at 0 °C and stirred at 0 °C for 1 h. The ether was removed under reduced pressure and the precipitate filtered and washed with hexane. After removal of the hexane the crude material was purified on a 1 in. Waters semiprep column and then further purified on a Whatman partisil M 9 column.

Conversion of Dioxanes 13–16 to THF 7–10. The general procedure is given here for the conversion of **15** → **8**. The dioxane–alcohol (0.017 mg, 1.1×10^{-4} mol) was dissolved in 10 mL of CH_2Cl_2 and cooled to 0 °C with an ice bath. Triethylamine (0.089 mL, 6.4×10^{-4} mol) was added followed by mesyl chloride (1.04 mL, 5.3×10^{-4} mol) to the methylene chloride solution at 0 °C. The mixture was stirred under argon at 0 °C for 1 h and at room temperature for 1 h.

Diethyl ether (10 mL) was added to the reaction mixture. It was washed six times with 8-mL portions of water and each with 10 mL of saturated sodium bicarbonate and 10 mL of brine solution. The organic layer was dried over anhydrous potassium carbonate and filtered, and the solvent was removed under reduced pressure: thin-layer chromatography showed one spot (0.025 g, 1.05×10^{-4} mol, 95%); 80 MHz NMR δ 1.08 (3 H, t), 1.17 (3 H, d), 1.50–2.10 (6 H, m), 3.12 (3 H, s), 4.12–4.40 (2 H, m), 4.50–4.72 (1 H, m).

The mesylate (0.006 g, 2.5×10^{-5} mol) was dissolved in 2 mL of absolute ethanol. 5% Palladium on carbon (1.35 mg) was added to the ethanol solution and it was allowed to stir at room temperature under hydrogen pressure (balloon) for 12 h.

The reaction mixture was filtered through Celite and the solvent was removed under reduced pressure. No further purification was necessary (one spot on thin-layer chromatography) (0.0048 g, 2×10^{-5} mol, 80%); 80 MHz NMR δ 1.04 (3 H, t), 1.24 (3 H, d), 1.41–1.98 (6 H, m), 1.98–2.77 (2 H, m), 3.08 (3 H, s), 3.67–4.02 (2 H, m), 4.52–4.79 (1 H, m).

The diol (0.0057 g, 2.4×10^{-5} mol) was dissolved in 1 mL of anhydrous diethyl ether and cooled to 0 °C. Potassium *tert*-butoxide (0.014 g, 1.2×10^{-4} mol) was added in one portion and allowed to stir at 0 °C for 1 h and at room temperature for 2.5 h.

The reaction mixture was diluted with diethyl ether and filtered through a Celite plug. The ether was removed under reduced pressure giving crude epoxy alcohol that was converted to the THF **8** by reaction with trichloroacetic acid in methylene chloride. Gas chromatography of the THF derivatives **7–10** was carried out on a Carbowax 20M capillary column at 75 °C. The elution order of products is **9** (30 min), **10** (36 min), **7** (44 min), and **8** (60 min).

Registry No. **1**, 89122-01-0; **2**, 89122-02-1; **3**, 89122-03-2; **4**, 16015-08-0; **5**, 54774-28-6; **7**, 89122-04-3; **8**, 89194-24-1; **9**, 89194-25-2; **10**, 89194-26-3; **11**, 89122-05-4; **12**, 55968-41-7; **13**, 89122-06-5; **14**, 89194-27-4; **15**, 89194-28-5; **15** mesylate, 89122-08-7; **16**, 89194-29-6; $CH_2{=}CH(CH_2)_2CH(OH)CH_3$, 626-94-8; $MeSO_2Cl$, 124-63-0; $CH_2BrCH_2CH{=}CH_2$, 5162-44-7; CH_3CHO, 75-07-0; CH_3Br, 74-83-9; mercuric pivalate, 32276-77-0; 5-hexen-2-yl methanesulfonate, 89122-07-6; (3*R**,4*R**,7*R**)-4,7-dihydroxyoct-3-yl methanesulfonate, 89122-09-8; *cis*-5-octen-2-ol, 55968-41-7; *cis*-4-hepten-1-ol, 6191-71-5; *cis*-5-octen-2-ol tetrahydropyranyl ether, 63043-82-3; 5,6-epoxyoctan-2-ol tetrahydropyranyl ether, 89122-10-1; *trans*-5-octen-2-ol tetrahydropyranyl ether, 89122-11-2.

Supplementary Material Available: Procedures for synthesis of the alcohol precursors to **2** and **3** and spectral data for THF's **4**, **5**, and **7–10** and dioxanes **13–16** (5 pages). Ordering information is given on any current masthead page.

Synthesis of Phenoxyamines

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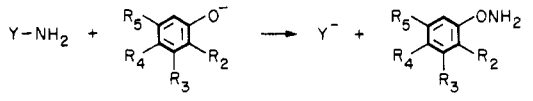
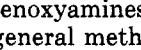
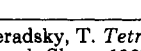
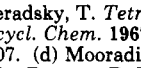
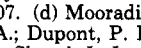
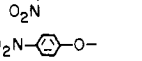
Treatment of phenols with 2,4-dinitrophenoxyamine leads to the synthesis of phenoxyamines through an amine exchange reaction. Yields for this reaction are sensitive to the pK_a of the phenol in a manner explainable in terms of a competing bimolecular decomposition reaction involving the 2,4-dinitrophenoxyamine. By use of an appropriately substituted phenol, this phenomenon can be exploited to give high yields of phenoxyamines having oxygenated substitution patterns that were unattainable by previous methods.

It is well established that *O*-aryl oximes can be converted to benzofurans, presumably through a mechanism paralleling the one postulated for the Fischer indole synthesis.[1,2] These oximes, in turn, can be readily synthesized from phenoxyamines **3**[3] by condensation with a ketone or aldehyde. Thus, phenoxyamines offer the potential for a more convenient, higher yielding, and more general sequence to benzofurans than more conventional methods.[4] Unfortunately, this potential has never been fully realized due to difficulties encountered in the synthesis of the requisite phenoxyamines. In this report we describe an efficient, general method for the synthesis of phenoxyamines.

Scheme I. Synthesis of Phenoxyamines by Amine Exchange



1 **2**$^-$ **3**

Y		R_2	R_3	R_4	R_5
a SO_4^-	a	H	OCH_3	H	OCH_3
b 	b	H	OCH_3	H	H
c Cl^-	c	H	H	H	H
d 	d	H	OTs	H	H
e 	e	H	OMs	H	OMs
f 	f	H	OTs	H	OTs
	g	OMs	H	H	H
	h	OTs	H	H	H
	i		H	H	H
	j	H	H	OTs	H
	k	H	CH_3	Cl	H

The methodologies used in the synthesis of phenoxyamines **3** can be divided into two major categories. In one category, the key step involves an aryl S_N2 substitution of a halobenzene with an oximate anion.[5] This reaction is restricted to halobenzenes having strong ortho or para

(1) (a) Sheradsky, T. *Tetrahedron Lett.* **1966**, 5225. (b) Sheradsky, T. *J. Heterocycl. Chem.* **1967**, *4*, 413. (c) Mooradian, A. *Tetrahedron Lett.* **1967**, 407. (d) Mooradian, A.; Dupont, P. E. *Ibid.* **1967**, 2867. (e) Mooradian, A.; Dupont, P. E. *J. Heterocycl. Chem.* **1967**, *4*, 441. (f) Kaminsky, D.; Shavel, J., Jr.; Meltzer, R. I. *Tetrahedron Lett.* **1967**, 859. (g) Sheradsky, T.; Elgavi, A. *Isr. J. Chem.* **1968**, *6*, 895. (h) Sheradsky, T.; Salemnick, G. *J. Org. Chem.* **1971**, *36*, 1061. (i) Cattanach, C. J.; Rees, R. G. *J. Chem. Soc.* **1971**, 53. (j) Sharkova, L. M.; Aksanova, L. A.; Kucherova, I. F.; Zagorevski, V. A. *Khim. Geterotsikl. Soedin.* **1971**, 762. (k) Bender, D. R.; Hearst, J. E.; Rapoport, H. *J. Org. Chem.* **1979**, *44*, 2176. (l) Moron, J.; Nguyen, C. H.; Bisagni, E. *J. Chem. Soc., Perkin Trans. 1* **1983**, 225.

(2) Robinson, B. *Chem. Rev.* **1969**, *69*, 227.

(3) These compounds are also known as *O*-arylhydroxylamines.

(4) For reviews, see: (a) Cagniant, P.; Cagniant, D. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R.; Boulton, A. J., Eds.; Academic Press: New York, 1975; Vol. 18, p 338. (b) Mustafa, A. "Benzofurans"; Wiley-Interscience, New York, 1974.

(5) For examples, see: Tamura, Y.; Minamikawa, J.; Ikeda, M. *Synthesis* **1977**, 1.

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