in THF (2 mL) was added. The precipitate that formed was removed by filtration and was washed with THF. The filtrate and the washing were combined, and the solvent was evaporated. Distillation of the residue under reduced pressure afforded 768 mg (96%) of **2a**: IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 6 Hz), 1.4–3.3 (m, 3 H), 4.1–4.3 (m, 2 H); MS m/z (relative intensity) 41 (100), 42 (41), 56 (70), 100 (16, M$^+$). Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 59.97; H, 8.05.

Reaction in the presence of the crown ether was performed in similar manner. However, in this case, a THF solution of equimolar quantities of the γ-lactone and the crown ether was added drop-by-drop to the potassium naphthalenide solution.

The following α-alkyl γ- and δ-lactones were obtained in a similar manner:

Dihydro-3-ethyl-2(3*H*)-furanone (α-ethyl γ-butyrolactone, 2b): yield, 811 mg (89%); IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0 (t, 3 H, J = 7.5 Hz), 1.5–2.7 (m, 5 H), 4.2–4.6 (m, 2 H); MS m/z (relative intensity) 114 (10, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.15; H, 8.80.

Dihydro-3,5-dimethyl-2(3*H*)-furanone (α-methyl γ-valerolactone, 2c): mixture of two stereoisomers (mole ratio = 3:2 by GC); yield, 866 mg (95%); IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 6.4 Hz), 1.4 (d, 3 H, J = 6.3 Hz), 1.5–2.9 (m, 3 H), 4.2–4.6 (m, 1 H); MS m/z (relative intensity) 114 (16, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.14; H, 8.85.

Dihydro-3-ethyl-5-methyl-2(3*H*)-furanone (α-ethyl γ-valerolactone, 2d): mixture of two stereoisomers (mole ratio = 2:1 by GC); yield, 880 mg (86%); IR (capillary cell) ν_{max} = 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0 (t, 3 H, J = 7.0 Hz), 1.2–2.6 (m and d, 8 H, J = 6.2 Hz), 4.1–4.5 (m, 1 H); MS m/z (relative intensity) 128 (4, M$^+$). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.61; H, 9.46.

Tetrahydro-3-methyl-2*H*-pyran-2-one (α-methyl δ-valerolactone, 2e): yield, 857 mg (94%); IR (capillary cell) ν_{max} = 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (d, 3 H), 1.38–2.80 (m, 5 H), 4.20–4.50 (m, 2 H); MS m/z (relative intensity) 114 (3.7, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C,63.14; H, 8.83. Found: C, 63.12; H, 8.85.

Tetrahydro-3-ethyl-2*H*-pyran-2-one (α-ethyl δ-valerolactone, 2f): yield, 890 mg (87%); IR (capillary cell) ν_{max} = 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.99 (t, 3 H), 1.20–2.70 (m, 7 H), 4.20–4.50 (m, 2 H); MS m/z (relative intensity) 128 (2.7, M$^+$). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.63; H, 9.41.

The reaction of the potassium naphthalenide/18-crown-6 complex with β-propiolactone (2-oxetanone) **3a** and β-butyrolactone (4-methyl-2-oxetanone) **3b** to yield the esters **4** was conducted in a similar manner. The following compounds were obtained after treatment of the enolate solutions with methyl and ethyl iodide, respectively.

2-Propenoic acid methyl ester (4a): yield, 564 mg (82%); IR (capillary cell) ν_{max} = 1740, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 3 H), 5.75–6.43 (m, 3 H); MS m/z (relative intensity) 42 (12), 55 (100), 56 (70), 85 (12), 86 (2, M$^+$). Anal. Calcd for $C_4H_6O_2$: C, 55.81; H, 7.02. Found: C, 55.83; H, 7.08.

2-Propenoic acid ethyl ester (4b): yield, 648 mg (81%); IR (capillary cell) ν_{max} = 1730, 1670 cm^{-1}; ^{1}H NMR ($CDCL_3$) δ 1.30 (t, 3 H, J = 7.1 Hz), 4.21 (q, 2 H, J = 7.1 Hz), 5.76–6.44 (m, 3 H); MS m/z (relative intensity) 29 (15), 55 (100), 57 (12), 73 (8), 85 (5), 100 (2, M$^+$). Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 59.97; H, 8.04.

2-Butenoic acid methyl ester ((*E*)-4c): yield, 704 mg (88%); IR (capillary cell) ν_{max} = 1745, 1665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.89 (dd, 3 H), 3.73 (s, 3 H), 5.86 (dq, 1 H), 6.9–7.1 (m, 1 H); MS m/z (relative intensity) 15 (10), 28 (5), 29 (4), 38 (3), 39 (25), 41 (48), 43 (3), 53 (2), 55 (3), 59 (5), 68 (3), 69 (100), 70 (5), 85 (23), 100 (19, M$^+$), 101 (2). Anal. Calcd for $C_5H_8O_2$: C, 59.99; H, 8.05. Found: C, 59.99; H, 8.06.

2-Butenoic acid ethyl ester ((*E*)-4d): yield, 775 mg (85%); IR (capillary cell) ν_{max} = 1740, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3 H, J = 7.0 Hz), 1.88 (dd, 3 H), 4.2 (q, 2 H, J = 7.0 Hz); 5.85 (dq, 1 H), 6.9–7.2 (m, 1 H); MS m/z (relative intensity) 39 (17), 41 (22), 45 (4), 68 (6), 69 (100), 70 (5), 86 (8), 99 (30), 100 (4), 114 (2, M$^+$). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.16; H, 8.80.

2-Propenoic acid (5a) was prepared according to the general procedure. However, when the reaction of potassium naphthalenide with lactone **3a** was complete, the THF was partly evaporated and the precipitate that formed was collected by filtration and was washed with THF. Then, the precipitate was dissolved in Et_2O which also contained ion-exchange resin (Lewatit S 1080), acid form, Merck). The mixture was filtered to remove the resin. Evaporation of solvent from the filtrate afforded 461 mg (80%) of **5a**: IR (capillary cell) ν_{max} = 1700, 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.7–6.8 (m, 3 H), 10.2 (s, 1 H); MS m/z (relative intensity) 55 (60), 72 (70, M$^+$). Anal. Calcd for $C_3H_4O_2$: C, 50.01; H, 5.60. Found: C, 50.03; H, 5.58.

Similarly obtained was the following.

2-Butenoic acid ((*E*)-5b): yield, 571 mg (83%); IR (capillary cell) ν_{max} = 1700, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.9 (d, 3 H), 5.9 (d, 1 H), 7.0–7.2 (m, 1 H), 9.1 (s, 1 H); MS m/z (relative intensity) 69 (30), 86 (100, M$^+$). Anal. Calcd for $C_4H_6O_2$: C, 55.81; H, 7.02. Found: C, 55.80; H, 7.09.

Registry No. **1a**, 96-48-0; **1b**, 108-29-2; **1c**, 542-28-9; **2a**, 1679-47-6; **2b**, 13888-01-2; **2c**, 5145-01-7; **2d**, 19639-00-0; **2e**, 10603-03-9; **2f**, 32821-68-4; **3a**, 57-57-8; **3b**, 3068-88-0; **4a**, 96-33-3; **4b**, 140-88-5; **4c**, 623-43-8; **4d**, 623-70-1; **5a**, 79-10-7; **5b**, 110-17-8; potassium naphthalenide, 4216-48-2.

Hypochlorite-Induced Substitution of Chlorine for Bromine in Aromatic Compounds

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Aqueous hypochlorite and phase-transfer catalysts induce oxidation of aldehydes, amines, and primary and secondary alcohols,[1] oxidative decarboxylation of certain trisubstituted acetic acids with oxidative cleavage of corresponding tertiary alcohols,[2] and formation of alkyl and aromatic chlorides from alkanes and activated aromatics via substitution for hydrogen.[3]

In research focusing on defining the role of pH in such hypochlorite reactions, chlorinated benzenes show considerable utility as internal standards for gas and liquid chromatographic analysis.[2,4] Specifically, chlorobenzene and 1,4-dichlorobenzene are stable to conditions and have suitable retention times for inclusion with reactants to serve as quantitative and qualitative "bench marks" for monitoring the course of reactions.

In contrast, the present research has revealed that brominated benzenes are demonstrably unstable, reacting with aqueous hypochlorite in a biphasic system including the phase-transfer catalyst, tetra-*n*-butylammonium bisulfate, to give the corresponding chloroaromatics. At ambient temperature and pH 7.5–9, conventional for hypochlorite oxidations, bromobenzene is converted to chlorobenzene with a reaction half life of 2–5 h. The

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0022-3263/92/1957-0391$03.00/0

Table I[a]

substrate (QPhBr) Q	conversion ratios[b]	conversion (%) to QPhCl[c]
4-nitro (1b)	<0.01	
4-benzoyl (1c)	0.37–0.38	16–18
3-chloro (1d)	0.26–0.4	15–20
4-chloro (1e)	1.0	30–35
H (1a)	(1)	
4-*tert*-butyl[d] (1f)	2.2–2.4	14–20
4-phenoxy (1g)	5.5–6.3	35–40
4-phenyl (1h)	5.8–6.8	19–21

[a] 3–5 h reactions, pH monitored and maintained at 7.5–9. [b] {[2]/([1] + [2])}/{[2a]/([1a] + [2a])} from GC analyses. [c] Higher conversions observed after longer reaction times. [d] Side-chain chlorination byproducts detected (see Experimental Section).

two-stage transformation of 1,4-dibromobenzene to 1,4-dichlorobenzene, proceeding by way of the 4-chlorobromobenzene intermediate, requires days. Review of the literature indicates that these observations reveal hitherto unrecognized chemistry of hypochlorite.

$$\mathrm{ArBr} + \mathrm{OCl^-} \xrightarrow{\text{phase transfer catalyst}} \mathrm{ArCl}$$

At pH >10, bromobenzene is essentially inert to aqueous hypochlorite, even in the presence of phase-transfer catalyst. After 14 h of stirring at high pH, only a trace of chlorobenzene is detectable by gas chromatography.

However, at pH 4–5 in ambient light and with phase-transfer catalyst, bromobenzene is converted to chlorobenzene in nearly quantitative yield in 1 h. In the same time period, only a trace of product is formed during biphase reactions in the absence of catalyst and under "dark" conditions of severely reduced illumination. A sluggish reaction proceeds in ambient light with no catalyst, but with catalyst, reactions of bromobenzene proceed about as effectively in "dark" as in illuminated reactions. However, at this low pH, substituted bromoaromatics, such as 4-bromo-*tert*-butylbenzene, are subject to competing substitution reactions.[3]

At pH 7.5–9, under normal room lighting conditions, monobromoaromatics generally may be converted to the corresponding chloro compounds, without significant formation of alkyl or aromatic substitution byproducts. Results of reactions of brominated aromatics are summarized in Table I. To assess the influence of substituents, conversions of a series of bromobenzenes, QPhBr (1), to chlorobenzenes, QPhCl (2), were carried out competitively in the presence of bromobenzene (1a, Q = H). Except as indicated, corresponding unbrominated aromatics (QPhH) and chlorine substitution products (QPhCl, 2) were shown to be stable to reaction conditions employed.

Substrates with electron-donating substituents showed enhanced relative reactivities compared to bromobenzene, and those with electron-withdrawing groups generally exhibited lower reactivities. However, the results are not correlated linearly by the Hammett equation, using either σ or σ "+" values. Consequently, the predictive value for specific reaction rates of other substituted substrates is limited.

Plausible chlorinating agents responsible for the replacement of bromine by chlorine include hypochlorite (OCl^-), hypochlorous acid (HOCl), chlorine monoxide (Cl_2O), and chlorine (Cl_2) as well as intermediates such as chlorine atoms ($Cl^\bullet$) and chloroxy radicals ($ClO^\bullet$). The photochemically induced replacement of bromine in ArBr by chlorine in carbon tetrachloride has been suggested to proceed through intermediacy of chlorine atoms and/or π complexes involving X_2 molecules.[5]

Alternately, phase transfer catalyzed reactions with hypochlorite are known to effect substitution of chlorine for aromatic and/or aliphatic hydrogens in activated substrates such as toluene and anisole.[3] The mechanisms of these processes were projected to be free radical in nature and specifically to involve chloroxy radicals and the intermediacy of chlorine monoxide, based on selectivity of hydrogen abstraction. These reactions were found to be modestly sensitive to light and the presence of oxygen. The pH of reaction mixtures also was determined to be an important reaction parameter, with reactivity at pH 5 > 8.5 > 10.5.

The light-induced reactivity noted here in biphasic, no catalyst hypochlorite reactions at pH 4–5 enhances the likelyhood that a free radical is involved, at least at the lower pH. If so, some nonionic precursor to the chlorinating agent, perhaps HOCl, Cl_2 or Cl_2O, must be extracted from the aqueous phase. Otherwise, the chlorinating species must be very active at the interface.

A significant amount of chloroform was detected at pH 4–5 and 7.5–9 in reactions run using dichloromethane as the nonaqueous phase. Chloroform also was found on mixing catalyst, hypochlorite, and dichloromethane with no substrate present. Some chloroform may have resulted from degradation of the catalyst, but given the known propensity for R–H chlorination under these conditions,[3] it is likely that the solvent was the main precursor. Formation of chloroform from dichloromethane probably accounts for consumption of a substantial amount of hypochlorite in these reactions, but preliminary studies showed no advantage in using other solvents such as chloroform, carbon tetrachloride, nitrobenzene, or ethyl acetate instead of dichloromethane.

This study indicates that caution should be exercised in assessing levels of bromo- and/or chloroaromatic compounds in biphasic systems that contain aqueous hypochlorite along with materials that might serve as phase-transfer catalysts.

Experimental Section

Materials and General Procedures. All compounds employed were obtained from commercial suppliers. Aqueous hypochlorite ("5.25%") was obtained in the form of commercial Clorox. In all cases, the phase-transfer catalyst (PTC) employed was tetra-*n*-butylammonium hydrogen sulfate. Gas chromatographic (GC) analyses were accomplished with a Perkin-Elmer 3920B system fitted with a 6 ft, $^1/_4$ in. 3% SP2100 glass column and FID detector. Liquid chromatography (LC) was performed with a Perkin-Elmer Series 10 gradient system with C_{18} reversed-phase column. Reaction pH's were monitored with Orion 501 pH meters equipped with plastic (high pH) or glass (low pH) combination electrodes dipped into top, aqueous layers of biphasic solutions. Reaction mixtures were stirred magnetically, and progress of reactions was followed by GC analysis of aliquots withdrawn from the organic phases. Except where noted, organic reactants and products were identified by comparison with chromatographic retention times derived from authentic samples. "Dark" reactions were conducted using reaction vessels covered with black tape in a room with lighting cut to the minimum.

Comparative Reactions of Bromobenzene. All reactions utilized aqueous phases consisting of 200 mL (0.1 mol) of hypochlorite (initial pH >11) to which had been added 0.2 g of PTC (6×10^{-4} mol) and HCl to adjust down to the desired pH. Runs at pH <7.5 tended quickly to drop further in pH, and adjustments upward were made with small portions of Clorox. Reactions to establish relative reactivities at pH 4–5 and 7.5–8.5 were conducted with an organic phase consisting of 6×10^{-4} mol of substrate and an equal molar amount of 1,4-dichlorobenzene as internal

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standard, dissolved in 25 mL of dichloromethane. Reactions to establish reactivity at pH >10, in light vs dark reactions, and in runs conducted without catalyst employed organic phases consisting $1-3 \times 10^{-3}$ mol of substrate with equal molar amounts of 1,4-dichlorobenzene as internal standard, in 50 mL of CH_2Cl_2.

Comparative Reactions of Substituted Bromobenzenes (Table I). Substrates (1×10^{-3} mol) and equal molar amounts of bromobenzene and internal standards were dissolved in 50 mL of dichloromethane and stirred magnetically with 200 mL (0.1 mol) of hypochlorite containing 0.2 g (6×10^{-4} mol) of PTC in three-necked 250-mL round-bottom flasks. The pH's of aqueous layers were monitored and adjusted continuously to maintain pH 8-9 for periods indicated. The identity of 1-chloro-2-(4-chlorophenyl)-2-methylpropane as a byproduct from reaction of 4-bromo-*tert*-butylbenzene (**1f**) was indicated by gas chromatography/mass spectrometry.

The above procedure, modified by replenishment of the aqueous hypochlorite layer and catalyst twice during stirring for 2 weeks at pH 7.5-9, resulted in conversion of over 90% of 1,4-dibromobenzene to a 6:1 mixture of 1,4-dichlorobenzene and 1-bromo-4-chlorobenzene. Analysis of reactions in progress showed initial buildup of the bromochloro intermediate followed by its diminishment as the dichloro product accumulated.

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Registry No. **1a**, 108-86-1; **1b**, 586-78-7; **1c**, 90-90-4; **1d**, 108-37-2; **1e**, 106-39-8; **1f**, 3972-65-4; **1g**, 101-55-3; **1h**, 92-66-0; $ClCH_2C(CH_3)_2C_6H_4$-*p*-Cl, 13099-56-4; BrC_6H_4-*p*-Br, 106-37-6; ClC_6H_4-*p*-Cl, 106-46-7; ClC_6H_4-2-Br, 106-39-8; Clorox, 7681-52-9.

Synthesis of Pentasubstituted 3-Hydroxy-1,2-dioxolanes

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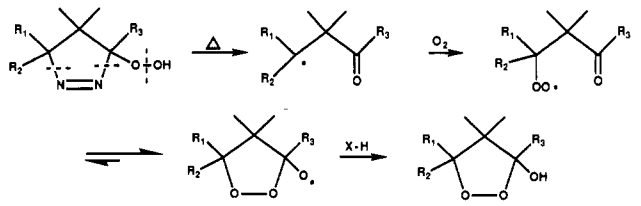
Introduction

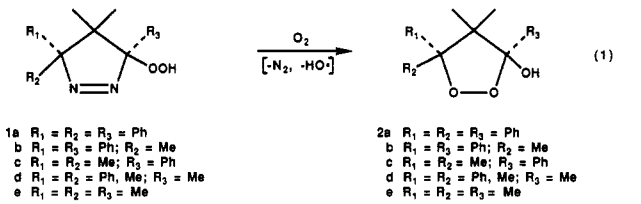
Five-membered cyclic peroxides are of synthetic and mechanistic importance.[1-3] Several examples of 3-hydroxy-1,2-dioxolanes (hemiperketals) and related ring systems have been found as natural products.[2,4] Synthetic routes to 3-hydroxy-1,2-dioxolanes and closely related ring systems usually involve the reaction of singlet oxygen[5] or hydrogen peroxide[6] with α,β-unsaturated carbonyl compounds. Autoxidation or photooxidation of cyclopropanols has been shown[7] to produce hemiperketals in several specialized examples. We report here the synthesis of a series of 3,4,4,5,5-pentasubstituted-3-hydroxy-1,2-dioxolanes via O_2 trapping of intermediates generated during the thermolysis of cyclic α-azo hydroperoxides.

Scheme I



Results and Discussion

The thermal decomposition of a series[8] of cyclic α-azo hydroperoxides **1a-e** in benzene or acetone in the presence of 100% O_2 (at one atmosphere) yielded the corresponding 3,4,4,5,5-pentasubstituted 3-hydroxy-1,2-dioxolanes in moderate yields (eq 1). The hemiperketals (isolated in 35-50% yields by chromatographic methods) were characterized by physical and spectral techniques. The 3-hydroxy-1,2-dioxolanes were of remarkable stability and appeared not to be in rapid equilibrium[9] with the ring-opened form. No reaction (ambient temperature) with dimethyl sulfide was observed, while reaction with trivalent phosphorus compounds required days to reach completion. ^{17}O NMR[10] data on **2b** and **2d** in CH_2Cl_2 at 25 °C (for **2b** δ 304 ± 2 ppm ($\nu_{1/2}$ = 2600 Hz) peroxy oxygens, unresolved and δ 78 ± 1 ppm ($\nu_{1/2} \approx$ 850 Hz) hydroxy oxygen; for **2d** δ 302 ± 2 ppm peroxy oxygens, unresolved and δ 74 ± 2 ppm hydroxy oxygen) also were in agreement with the closed structure. However, compound **2b** was noted to



(1)

1a $R_1 = R_2 = R_3 = Ph$
b $R_1 = R_3 = Ph$; $R_2 = Me$
c $R_1 = R_2 = Me$; $R_3 = Ph$
d $R_1 = R_2 = Ph$, Me; $R_3 = Me$
e $R_1 = R_2 = R_3 = Me$

2a $R_1 = R_2 = R_3 = Ph$
b $R_1 = R_3 = Ph$; $R_2 = Me$
c $R_1 = R_2 = Me$; $R_3 = Ph$
d $R_1 = R_2 = Ph$, Me; $R_3 = Me$
e $R_1 = R_2 = R_3 = Me$

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