m/e (%) 127 (M − 35, 2.7), 99 (5.4), 92 (8.9), 70 (100), 57 (51.8), 41 (75.0).

Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.7; H, 6.82. Found: C, 51.7; H, 6.75.

3-Cyclohexenespiro-3′,3′-dichloro-4′-(trimethylsiloxy)cyclobutan-2′-one (2c).[1] From 9.1 g (0.05 mol) of silyl enol ether **1c**, 5.88 g (0.04 mol) of dichloroacetyl chloride, and 5.56 g (0.055 mol) of triethylamine was isolated 8.2 g (70%) of **2b** as a pale yellow oil with spectra identical with those of an authentic sample.

3-Cyclohexenespiro-3′,3′-dichloro-4′-hydroxycyclobutan-2′-one (3c).[1] Hydrolysis of **2c** with methanol afforded **3c** as previously described. Spectra were identical with those of an authentic sample.

3-Cyclohexenespiro-3′-chloro-3′-methyl-4′-(trimethylsiloxy)cyclobutan-2-one (4c). From 7.28 g (0.04 mol) of silyl enol ether **1c**, 6.62 g (0.045 mol) of 2-chloropropanoyl chloride, and 6.06 g (0.06 mol) of triethylamine in refluxing hexane was isolated 5.35 g (49%) of **4c** as a pale yellow oil after distillation at 92–98 °C (0.04 mm); IR 1790, 1610, 1445, 1252, 1170, 845 cm^{-1}; NMR δ 5.74 (m, 2 H), 4.28 (m, 1 H), 2.3–1.9 (m, 6 H), 1.6–1.4 (m, 3 H), 0.26 (s, 9 H); mass spectrum, *m/e* (%) 274 (M + 2, 0.2), 272 (0.5), 237 (8.3), 182 (16.7), 166 (15.3), 164 (44.4), 128 (16.7), 110 (53.0), 92 (92.0), 73 (100).

3-Cyclohexenespiro-3′-chloro-4′-hydroxy-3′-methylcyclobutan-2-one (5c). Hydrolysis of 1.25 g (0.0046 mol) of **4c** gave 0.72 g (78%) of **5c** as a pale yellow oil after distillation at 88–94 °C (0.07 mm): IR 3550–3200, 1785, 1625, 1438, 1250, 1170, 1090 cm^{-1}; NMR δ 5.5 (m, 2 H), 4.15 (s, 1 H), 3.2 (s, 1 H), 2.3–1.7 (m, 6 H), 1.6–1.4 (m, 3 H); mass spectrum, *m/e* (%) 202 (M + 2, 0.5), 200 (1.4), 110 (95.0), 92 (77.9), 81 (54.9), 79 (100), 77 (51.9), 63 (93.5).

Acknowledgment. We express appreciation to the Robert A. Welch Foundation and to the North Texas State University Faculty Research Fund for support of this investigation.

Registry No. 1a, 19980-43-9; **1b**, 6651-34-9; **1c**, 51075-25-3; **2a**, 73210-23-8; **2b**, 66324-00-3; **2c**, 70320-74-0; **3a**, 66324-06-9; **3b**, 66324-05-8; **3c**, 70320-75-1; *endo*-**4a**, 73199-34-5; *exo*-**4a**, 73245-86-0; **4b**, 73199-35-6; **4c**, 73199-36-7; *endo*-**5a**, 73199-37-8; *exo*-**5a**, 73245-87-1; **5b**, 73199-38-9; **5c**, 73199-39-0; *endo*-**6a**, 73199-40-3; *endo*-**7a**, 73199-41-4; *endo*-**8a**, 73199-42-5; *endo*-**9a**, 73199-43-6; *endo*-**10a**, 73199-44-7; *endo*-**11a**, 73199-45-8; *endo*-**12a**, 73199-46-9; *endo*-**13a**, 73199-47-0; *endo*-**14a**, 73199-48-1; *endo*-**15a**, 73199-49-2; phenylchloroacetyl chloride, 2912-62-1; 2-phenoxypropanoyl chloride, 122-35-0; methoxyacetyl chloride, 38870-89-2; phenoxyacetyl chloride, 701-99-5; 2-chloropropanoyl chloride, 7623-09-8; dichloroacetyl chloride, 79-36-7; 2-methylpropenyl 2-chloropropanoate, 73199-50-5.

Ion Pairing of Arenediazonium Salts in Solvents of Low Polarity

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Due to the ionic nature of arenediazonium salts, their reactions are usually conducted in aqueous media or in highly polar organic solvents, such as methanol or dimethyl sulfoxide. In such solvents, significant interactions between an arenediazonium cation and its counterion are usually absent. For example, Penton and Zollinger[1] have observed that the azo coupling rates of *p*-toluenediazonium tetrafluoroborate and bisulfate with *N*,*N*-dimethylaniline are exactly the same in either acetonitrile or nitromethane.

Solubility of arenediazonium salts in less polar organic solvents such as chlorocarbons and benzene may be achieved by attaching lipophilic groups to the aromatic ring of the arenediazonium cation,[2-4] by anion interchange,[5] or by complexation with crown ethers.[6] For the determination of the importance of ion pairing for arenediazonium salts in organic solvents of low polarity, a kinetic and spectroscopic investigation was undertaken. The results of this study are now reported.

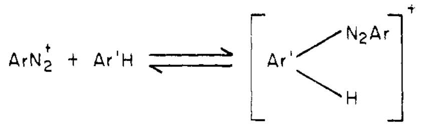
Table I. Observed Pseudo-First-Order Rate Constants for the Coupling of *p*-*tert*-Butylbenzenediazonium Hexafluorophosphate (2) with *N*,*N*-Dimethylaniline (3) in 1,2-Dichloroethane at 25.0 °C

10^4[2], M	10^4[3], M	$10^4 k_{obsd}$, s^{-1}
0.149	2.56	4.22
0.149	4.25	9.18
0.149	5.94	16.0

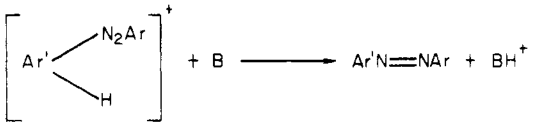
Results and Discussion

The arenediazonium salts employed in this investigation are *p*-*tert*-butylbenzenediazonium tetrafluoroborate[4] and hexafluorophosphate, **1** and **2**, respectively. Observation of anion effects with counterions as similar as tetrafluoroborate and hexafluorophosphate would indicate that even more important effects should be expected for dissimilar anions. Both arenediazonium salts have reasonable solubility in chlorocarbon solvents, but the solubility of **1** is greater than that of **2** in such media.

Azo Coupling Reactions. We have previously reported[7] a detailed kinetic study of the reaction of **1** with excess *N*,*N*-dimethylaniline (**3**) in 1,2-dichloroethane at 25 °C. The reaction was found to be first order in arenediazonium salt and second order in **3**, with a third-order rate constant of 7.05×10^2 s^{-1} M^{-2}. The observed rate expression is consistent with an S_E2 mechanism (eq 1) in which proton abstraction from the σ complex by a second molecule of **3** is rate limiting.



(1a)



(1b)

When the reaction of the hexafluorophosphate salt **2** with **3** was conducted under the same conditions, the observed pseudo-first-order rate constants listed in Table I were obtained. Yields of the anticipated coupling product 4-*tert*-butyl-4′-(dimethylamino)azobenzene were quantitative. For the coupling reaction of **2** and **3**, a simple second-order behavior in **3** is not observed. Instead the kinetic data are consistent with the rate expression[8] in eq 2. Apparently, the hexafluorophosphate anion is sufficiently basic to compete with **3** in removing the proton

$$\text{rate} = k_2[\mathbf{2}][\mathbf{3}] + k_3[\mathbf{2}][\mathbf{3}]^2 \qquad (2)$$

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(8) If the rate = $k_2[2][3] + k_3[2][3]^2$ under the pseudo-first-order conditions employed, $k_{obsd}/[3] = k_{appar} = k_2 + k_3[3]$. A plot of k_{appar} vs. [3] was perfectly linear with an intercept of k_2 and a slope of k_3.

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Table II. Observed First-Order Rate Constants for the Thermal Decomposition of *p-tert*-Butylbenzenediazonium Salts[a] 1 and 2 in 1,2-Dichloroethane at 50.0 °C in the Presence and Absence of 18-Crown-6

anion	equiv of 18-crown-6	$10^4 k_{obsd}$, s^{-1} [b]	retardation effect,[c] %
BF_4^-	0	2.51	
	1.0	1.35	46
PF_6^-	0	3.27	
	1.0	1.44	56

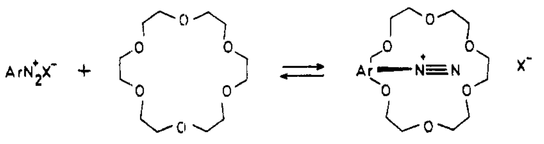
[a] $[ArN_2^+X^-] = 5.8 \times 10^{-5}$ M. [b] Reproducible to ±3% of the stated value. [c] Retardation effect = $100 - 100(k_1/k_0)$, where k_0 is the rate constant in the absence of crown ether and k_1 is the rate constant with 1 equiv of crown ether present.

from the σ complex (eq 1). Calculated rate constant values[8] for the kinetic expression in eq 2 are $k_2 = 8.58 \times 10^{-1}\ s^{-1}\ M^{-1}$ and $k_3 = 3.08 \times 10^3\ s^{-1}\ M^{-2}$. Comparison of this third-order rate constant with that obtained for the analogous azo coupling reaction of the tetrafluoroborate 1 reveals an approximately fourfold faster coupling reaction when the arenediazonium counterion is hexafluorophosphate. Ion pairing of the arenediazonium ion with its anion would be expected to decrease the electrophilicity of the cation.[9] Therefore, the more rapid coupling rate for 2 reveals a lesser degree of ion pairing when the anion is hexafluorophosphate as compared with tetrafluoroborate.

These results contrast sharply with the aforementioned insensitivity of azo coupling to anion variation in more polar organic solvents reported by Penton and Zollinger.[1]

Thermal Decomposition of Arenediazonium Salts. Thermolysis rates for 1 and 2 in 1,2-dichloroethane at 50.0 °C (Table II) were measured by using a previously employed ultraviolet spectroscopic kinetic method.[10] The thermolysis is approximately 30% faster for the hexafluorophosphate salt 2 than for the corresponding tetrafluoroborate 1. If the free aryldiazonium ion is assumed to be the kinetically active species in the thermolysis, lesser ion pairing for the hexafluorophosphate counterion is again evident.

As expected, the thermal decompositions of both 1 and 2 are retarded in the presence of the crown ether 18-crown-6 (4) due to partial conversion of the diazonium salts into their thermally stabilized[10] crown ether complexes 5 (eq 3). The "retardation effect" (Table II) caused by 1 equiv of 18-crown-6 is somewhat greater for the hexafluorophosphate salt 2 than for the tetrafluoroborate 1. If ion pairing of the arenediazonium salt is less important for the hexafluorophosphate, attraction of the more electropositive arenediazonium cation for the crown ether should be greater than with the tetrafluoroborate. This will shift the equilibrium represented in eq 3 further to the right when the counterion is hexafluorophosphate. Conversion of a relatively larger proportion of the total arenediazonium salt into the thermally stabilized complex 5 results in a larger "retardation effect" for the arenediazonium hexafluorophosphate.



(3)

4 5

Table III. Products from the Thermal Decomposition of *p-tert*-Butylbenzenediazonium Salts[a] in 1,2-Dichloroethane at 50.0 °C

counterion	rel yields, % *p-tert*-butylfluorobenzene	 *p-tert*-butylchlorobenzene
BF_4^-	39.0 ± 1.4[b]	61.0 ± 1.4
PF_6^-	28.8 ± 0.4[c]	71.2 ± 0.4

[a] $[ArN_2^+X^-] = 0.01$ M. [b] Average and standard deviation from five reactions. [c] Average and standard deviation from two reactions.

Table IV. ^{19}F NMR Data for *p-tert*-Butylbenzenediazonium Salts 1 and 2 in 1,2-Dichloroethane in the Absence and Presence of 18-Crown-6

counterion	equiv of crown ether	chemical shift,[a] Hz
BF_4^-	0	14 105[b]
	1.0	14 344[b]
	5.0[c]	14 362[b]
PF_6^-	0	6 720[d]
	1.0	6 853[d]
	5.0[c]	6 864[d]

[a] Upfield with respect to $CFCl_3$. [b] Center of the quartet. [c] Larger amounts of 18-crown-6 did not produce additional chemical shift changes. [d] Center of the doublet, $J_{FP} = 712$ Hz.

Products from the thermal decomposition of 1 and 2 in 1,2-dichloroethane were analyzed by gas chromatography and are recorded in Table III. The Schiemann reaction product and *p-tert*-butylchlorobenzene are formed from both 1 and 2. These products arise via an aryl cation intermediate.[4] Fluoride ion abstraction from the counterion[4] by the aryl cation produces *p-tert*-butylfluorobenzene, while chloride ion abstraction from the solvent[4,11] yields *p-tert*-butylchlorobenzene.

If in these thermolysis reactions the aryl cation precursor is the free arenediazonium cation, the relative amount of Schiemann product would be expected to be higher for the hexafluorophosphate counterion than for tetrafluoroborate. (The P–F bond strength is considerably less than that for a B–F bond,[12] and a statistical factor should also favor removal of a fluoride ion from hexafluorophosphate relative to tetrafluoroborate.) However, the relative product proportions listed in Table III reveal that the yield of *p-tert*-butylfluorobenzene is higher in the thermolysis of the tetrafluoroborate salt 1. This result indicates that for the thermolysis of arenediazonium salts in organic solvents of low polarity, diazonium cation–anion ion pairs as well as free diazonium cations are kinetically active diazonium ion species.

Nuclear Magnetic Resonance Studies. Cation–anion interactions for 1 and 2 in 1,2-dichloroethane were further probed by measuring ^{19}F NMR chemical shifts for the respective anions in the absence and presence of 18-crown-6 (Table IV).

Addition of sufficient 18-crown-6 to a solution of 1 or 2 in dichloroethane should convert the diazonium salt into crown ether separated ion pairs 5 (eq 3). For such species, cation–anion interactions should be minimal, and the ^{19}F NMR chemical shift should essentially be that of the free anion. In agreement, the distorted quartet observed for the tetrafluoroborate anion of 1 in the absence of crown

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Table V. ^{1}H NMR Data for *p-tert*-Butylbenzenediazonium Salts 1 and 2 in Deuterated Dimethyl Sulfoxide in the Absence and Presence of 18-Crown-6

counter-ion	equiv of crown ether	chemical shift, ppm[a,b]	proton
BF_4^-	0	1.37	$C(CH_3)_3$
	1.0	1.37	
	0	8.60	aromatic (2,6)
	1.0	8.53	
	0	8.04	aromatic (3,5)
	1.0	8.04	
PF_6^-	0	1.37	$C(CH_3)_3$
	1.0	1.37	
	0	8.60	aromatic (2,6)
	1.0	8.52	
	0	8.04	aromatic (3,5)
	1.0	8.04	

[a] Relative to Me_4Si. [b] Chemical shifts for the aromatic protons refer to the center of the doublet in each leg of the A_2B_2 pattern.

ether became symmetrical in the presence of 5 equiv of 18-crown-6.

Comparison of the chemical shift data for the anions of 1 and 2 in the absence and presence of 5 equiv of 18-crown-6 reveals a change of 257 Hz for 1 and 144 Hz for 2. The smaller chemical shift change observed for 2 is again consistent with a lesser degree of ion pairing when the counterion is hexafluorophosphate.

Central to this argument is the formulation of the crown ether–diazonium salt complex 5 as resulting from insertion of the neck of the arenediazonium cation into a crown ether collar.[6,13,14] Previous evidence for this arrangement includes steric effects of substituents in solubilization[6,13] and titration calorimetric[14] studies and ^{1}H NMR spectral changes of certain macrocyclic polyethers in the presence of arenediazonium salts.[6,13]

Because of insufficient solubility of uncomplexed 2 it was not possible to probe for changes in the ^{1}H NMR spectra of 1 and 2 in 1,2-dichloroethane upon addition of 18-crown-6. However, such measurements could be made in dimethyl sulfoxide and are summarized in Table V.

Although the chemical shifts of the *tert*-butyl group hydrogens and the 3,5 aromatic ring hydrogens of 1 and 2 are unaffected by the presence of 18-crown-6, the 2,6 aromatic ring hydrogens are shifted upfield by 7–8 Hz in the presence of 18-crown-6. This chemical shift change for only the ortho hydrogens provides further evidence for the proposed diazonium ion–crown ether complex 5.

Experimental Section

General Methods. Melting points were measured with a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 infrared spectrophotometer, using sodium chloride plates. NMR spectra were measured with either a Varian A-60 or XL-100 spectrometer. Abbreviations used in identifying signal multiplicities are s (singlet) and m (multiplet). Gas chromatographic analysis was performed on an Antek 400 or a Varian 2400 flame-ionization gas chromatograph.

Materials. The compounds 1,2-dichloroethane (Aldrich, Gold Label), 18-crown-6 (4, PCR Research Chemicals), *tert*-butylbenzene (Aldrich), and *N,N*-dimethylaniline (Mallinckrodt, reagent grade) were obtained from the indicated sources and used directly. *p-tert*-Butylbenzenediazonium tetrafluoroborate[4] (1), 4-*tert*-butyl-4′-(dimethylamino)azobenzene,[7] and *p-tert*-butylchlorobenzene[15] were prepared according to the cited literature procedures. An authentic sample of *p-tert*-butylfluorobenzene was prepared by the thermal decomposition of solid *p-tert*-butylbenzenediazonium tetrafluoroborate by using a standard procedure.[16]

p-tert-Butylbenzenediazonium hexafluorophosphate (2) was prepared from *p-tert*-butylaniline[4] in 80% yield by the procedure of Rutherford, Redmond, and Rigamonti.[17] The crude salt was washed with cold anhydrous diethyl ether, dissolved in a minimum amount of acetone, precipitated by adding pentane, and then dried in vacuo. The resulting white solid had the following: mp 125 °C dec; ^{1}H NMR δ 7.8–8.6 (m, 4 H), 1.34 (s, 9 H); IR (Nujol mull), characteristic bands at 2289 (NN stretch) and 820 (PF_6^-) cm^{-1}.

Kinetic methods for studying the thermal decomposition of the arenediazonium salts and their coupling reactions with *N,N*-dimethylaniline were the same as those previously reported.[7,10]

Product analysis in thermolysis reactions was accomplished by gas chromatography on a 10 ft × $^1/_8$ in. column of 15% Carbowax 20-M on Chromosorb W at temperatures of 90–110 °C. Anisole was used as the internal standard, and molar response corrections were made. In all cases, quantitative yields of *p-tert*-butylchlorobenzene and *p-tert*-butylfluorobenzene resulted from the thermolysis of 0.01 M solutions of 1 and 2 in 1,2-dichloroethane at 50.0 °C.

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Registry No. 1, 52436-75-6; 2, 73286-45-0; 3, 121-69-7.

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Convenient and Inexpensive Procedure for Oxidation of Secondary Alcohols to Ketones

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In connection with certain studies concerned with the total synthesis of chirally pure natural products,[1] we required large quantities of (−)-camphor. This substance can be obtained from relatively inexpensive (−)-borneol by oxidation with an almost bewildering array of reagents.[2] However, the need for repeated large-scale work forced us to consider fractors such as cost, ease of operation, and total reaction volume in the selection of an oxidation procedure. In our previous work[1] we had employed *tert*-butyl hypochlorite. However, the somewhat tedious preparation[3] of this reagent and its potentially explosive nature,[3] especially during large-scale preparations, led us

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