A Product Analytical Study of the Thermal and Photolytic Decomposition of Some Arenediazonium Salts in Solution

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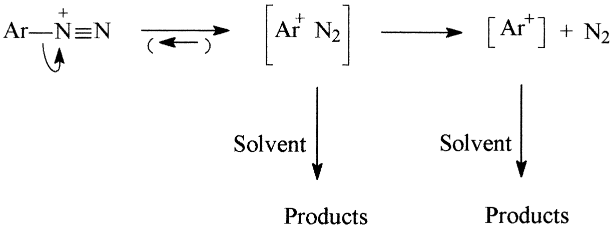
(Received August 13, 2001)

Products of thermal and photochemical reactions of eleven arenediazonium tetrafluoroborates in various solvents have been analyzed. All compounds in most solvents undergo unimolecular heterolysis to give singlet aryl cations which are captured by solvent. This mechanism is dominant for arenediazonium ions without electron-withdrawing substituents in all solvents, and the only reaction observed in water. Additionally, appreciable yields of fluoroarenes are obtained by fluoride abstraction by the aryl cation from fluorinated solvents and from tetrafluoroborate in fluorinated solvents. Yields from photochemical processes are very similar to those from thermal reactions indicating that the main reactions proceed through common or very similar intermediates. Aryl cations formed from ion-paired diazonium ions may react with the counterion, but fragmentation of dissociated diazonium ions leads only to solvent-derived product. Some arenediazonium ions in some solvents undergo an alternative radical reaction leading principally to hydrodediazoniation. It is proposed that this reaction involves initial rate-limiting electron transfer from ethanol to the arenediazonium ion followed rapidly by homolysis of the resultant aryldiazenyl radical. Within the same solvent cage, the aryl radical then either abstracts an α-hydrogen from the ethanol radical cation generated in the first step to give the reduction product and protonated acetaldehyde, or combines with it at the oxygen to give a protonated aryl ethyl ether.

Reactions of arenediazonium salts are both synthetically useful and mechanistically interesting,[1] they are exploited industrially in the manufacture of, for example, pharmaceuticals and dyestuffs, their mechanisms have been studied by wide-ranging techniques from the earliest days of organic chemistry, and they still find new applications in contemporary organic synthesis.[2] The usual simple equations of correlation fail to yield satisfactory analyses of their kinetics in aqueous and nonaqueous solution,[3,4] and few of the reported rate studies have been accompanied by reliable product analyses. Consequently, mechanistic understanding of the relationships between molecular structure of reactant, solvent, and reaction conditions is less than complete.

The origin of this investigation was a search for a cleaner, safer, and more efficient procedure for fluorodediazoniation (replacement of the diazonium group by a fluorine) than methods currently employed, i. e. a practical method which could be employed on a manufacturing scale for introducing fluorine into an aromatic system in a site-specific manner. The Balz–Schiemann reaction is the synthetic route of fluoroarenes (ArF) generally favoured on a laboratory scale;[5] the isolation of the arenediazonium tetrafluoroborate is followed by its thermal decomposition to form the fluoroarene. No solvent is required for this reaction, although one may be used, or it may be carried out on a slurry using an organic liquid to facilitate controlled heat transfer. This site-specific introduction of the fluorine into the aromatic ring proceeds by heterolytic loss of nitrogen and transfer to the aryl cation of a fluoride from the tetrafluoroborate counter-ion. In dichloromethane, 4-*t*-butylbenzenediazonium tetrafluoroborate gives chloroarene (ArC1), as well as ArF,[6] so the electrophilic intermediate is sufficiently reactive to abstract chloride from a nonpolar haloalkane. Similarly, when 1,2-dichloroethane is used as the reaction medium for arenediazonium tetrafluoroborate thermolysis, chloroarenes are obtained as well as fluoroarenes.[4,7] In alkane systems, only the most reactive carbenium ions will abstract halide from a halogenated solvent.[8] Variations to the original Balz–Schiemann procedure have been reported, including the use of counter-ions other than tetrafluoroborate,[9] and photochemical methods have been reported to give higher yields of fluoroarenes.[10]

The widely accepted mechanism in Scheme 1 is based upon kinetics results (including kinetic isotope effect measurements)[3,4,11] and diverse evidence for two intermediates (an ion-molecule pair and a fully dissociated aryl cation)[12] supported by theory.[13] The proportion of product from each of the sequentially formed intermediates and the degree of return of each to its precursor depend upon the solvent and the external nitrogen pressure. In water, the first-formed ion-molecule pair does not live long enough to undergo significant dissociation



Scheme 1. Heterolytic mechanism for dediazoniation of dissociated arenediazonium ions in solution.

whereas, in less nucleophilic but still ionizing solvents such as 2,2,2-trifluoroethanol,[14] it does. Under normal atmospheric pressure, capture of the dissociated aryl cation by nitrogen in 2,2,2-trifluoroethanol is negligible hence the second step may normally be regarded as essentially irreversible. Return from the ion-molecule pair to diazonium ion was detected by measuring rearrangement in unreacted starting material when the two nitrogens are distinguishable by isotopic labelling.[12] Clearly, return without rearrangement will be easier than with, consequently the extent of rearrangement necessarily underestimates the true extent of internal return. The rate-enhancing effects of some potent nucleophiles are now more convincingly interpreted as reducing the extent of internal return rather than in terms of a direct bimolecular displacement on the covalent arenediazonium ion.[15]

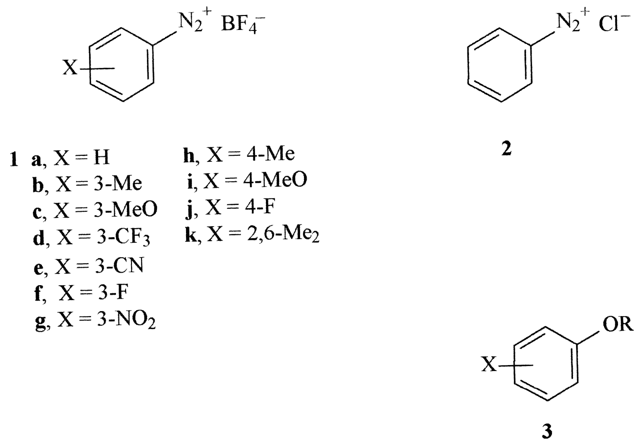
Considerable effort has been applied to the direct observation of aryl cation intermediates,[16] and their generation by methods other than dediazoniation.[17] In 1998, Steenken and colleagues reported laser flash photolysis studies on *para* substituted benzenediazonium ions in the weakly nucleophilic 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with and without an added electron-rich arene such as 1,3,5-trimethylbenzene.[18] Absorption bands for triplet cations and radicals were not seen but, in reactions when the electron-rich arene was added, bands corresponding to the formation of substituted cyclohexadienyl cations were observed. These cations were stable in the microsecond to millisecond range in the absence of added nucleophiles, and represent proof (albeit indirect) that singlet aryl cations were produced even though their lifetimes were too short to allow direct observation. Most recently, the parent phenyl cation has been generated at 8 K in an argon matrix (but not from the benzenediazonium ion) and shown to be a singlet.[19]

Other methods of decomposing arenediazonium ions in potentially useful ways include reactions with transition metal salts[20,21] and nucleophilic anions,[22] and reductive methods (hydrodediazoniation) at an electrode[23] or using, for example, ethanol or hexamethylphosphoric triamide as reductant and solvent.[24,25] These reactions, especially of substrates with electron-withdrawing substituents and using nucleophilic solvents in an oxygen-free environment, unquestionably involve radical intermediates.[20,26] Understanding of the relationships between the ionic and homolytic mechanisms of fragmentation of arenediazonium ions, however, is incomplete.

We reported recently our kinetics studies on thermal solvolytic decomposition of arenediazonium ions;[27] much of that report's introductory account of previous studies relates to this complementary report on our product analytical investigation. This report also includes results of photochemical decompositions of arenediazonium ions in the same solvolytic media but not considered earlier.

Methods

Preparations. Preparations of our arenediazonium tetrafluoroborates (**1**) and benzenediazonium chloride (**2**) followed well established methods and have already been described.[27,28] Other preparations followed literature methods with only occasional minor modifications. Samples of the major solvolytic products in 2,2,2-trifluoroethanol (TFE), i.e. aryl 2,2,2-trifluoroethyl ethers (**3**, R = CF_3CH_2) (Fig. 1), were made from the appropriate arenediazonium tetrafluoroborate (**1**) and TFE with final product isolation by preparative GLC; purity was checked by capillary GLC and identification confirmed by ^1H NMR. In this manner, nine aryl 2,2,2-trifluoroethyl ethers and (using other solvents) one 1,1,1,3,3,3-hexafluoro-2-propyl ether and five ethyl ethers were prepared, isolated, characterized, and shown to be pure enough to be used for GLC molar response factor determinations, or construction of HPLC correlation graphs. The yield of ethyl 3-fluorophenyl ether was too low by this method, so was prepared by reaction of ethyl 4-toluenesulfonate with 3-fluorophenol in alkaline solution. Other aryl ethers, arenes, haloarenes, and phenols required were available either commercially or from our previous work.



1 **a**, X = H
b, X = 3-Me
c, X = 3-MeO
d, X = 3-CF_3
e, X = 3-CN
f, X = 3-F
g, X = 3-NO_2
h, X = 4-Me
i, X = 4-MeO
j, X = 4-F
k, X = 2,6-Me_2

2

3

Fig. 1. Structures of **1**, **2**, and **3**.

Qualitative GLC Product Analysis. Solutions of arenediazonium salts (with and without solutes as required) in the solvolytic media—TFE, 2,2-difluoroethanol (DFE), 2-fluoroethanol (FE), ethanol, aqueous TFE, water, HFIP, and trifluoroacetic acid (TFA)—were reacted for at least ten half lives. The reaction mixtures were then either analyzed by GLC directly, or quenched and products extracted into ether, pentane, or dichloromethane for analysis. Although all other major potential solvolytic reaction products were available for identification of peaks in chromatograms of product mixtures, this was not true of aryl 2-fluoroethyl and aryl 2,2-difluoroethyl ethers (**3**, R = FCH_2CH_2 and F_2CHCH_2). Consequently, ether extracts of products from reactions in DFE and FE were first analyzed by GLC-mass spectrometry to facilitate peak identification. 3-Fluoroiodobenzene, a possible product from reactions of 3-fluorobenzenediazonium tetrafluoroborate (**1f**) in the presence of iodoacetic acid (a well known radical trap),[29] was commercially available. No major peaks remained unidentified in chromatograms from any reactions.

Photolysis reactions were carried out at room temperature with water cooling as appropriate using an immersion well photochemical reactor with a 6 watt or 125 watt low-pressure mercury lamp with maximum emission at 254 nm following preliminary investigation using a semi-micro scale apparatus. Product solutions from the photolysis reactions were analyzed in the same way as those from the corresponding thermal reactions. Since the photochemical reactions were much faster than the thermal ones, products from the latter are unlikely to contaminate the former.

Molar Response Factors (MRF). Molar response factors of major reaction products were determined by analyzing standard solutions of pure authentic samples with either undecane or octane as internal standard in the usual way.[30] Results were reproducible to about 2%, but we observed systematic differences between gas chromatographs, so always used MRFs appropriate to the particular instrument. Pure samples of aryl 2-fluoroethyl ethers and aryl 2,2-difluoroethyl ethers (**3**, R = FCH_2CH_2 and F_2CHCH_2) were not available in sufficient quantities to the purity required for molar response factor determination. However, since MRFs of corresponding aryl ethyl and aryl 2,2,2-trifluoroethyl ethers (**3**, R = Et and R = CF_3CH_2) had been determined, reliable estimates of the MRFs of FCH_2CH_2OAr and F_2CHCH_2OAr could be made.[31] MRFs of aryl 1,1,1,3,3,3-hexafluoro-2-propyl ethers and aryl trifluoroacetates were also estimated,[32] and it was established by the non-detection of phenols from reactions in TFA that the trifluoroacetate esters were hydrolytically stable to the work-up and analytical conditions.[33]

Quantitative Analysis by GLC. Quantitative GLC analyses were carried out from reactions on accurately known amounts of arenediazonium salts as described for the corresponding qualitative analyses except that a known amount of internal standard was added either at the very beginning or to the product mixture immediately before analysis. Significant known possible products that were not detected were assigned maximum possible yields based on the largest peak at the known retention time that could have escaped detection; this was always $< 1\%$ and generally $< 0.1\%$. Absolute recoveries were usually in the range 85–105% and have been normalized ($\Sigma = 100\%$) to facilitate comparison and for presentation in the Tables; except when a product is shown to be absent (see above), estimated maximum uncertainties are ±3% or 15% of the yield quoted, whichever is the larger.

Analysis by UV. Yields of phenols from some reactions in water were determined by comparison of the UV absorption at the λ_{max} of the isolated phenol, or of the reaction mixture, made up to a known volume in water or methanol with that of a standard solution of the authentic pure phenol in the same solvent. All such reactions were carried out at least in duplicate and yields of phenols were generally close to 100%.

Analysis by HPLC. For HPLC analyses, correlation graphs were constructed from pure samples of phenols and fluoroarenes which allowed their absolute yields to be determined. Yields of aryl 2,2,2-trifluoroethyl ethers by this method were calculated by difference assuming the total recovery to be 100%.

Some reactions were analyzed quantitatively by more than one method and agreement between the methods was generally satisfactory.[31,32,34]

Results

Reactions in Water. 4-Methyl- and 4-methoxy-benzenediazonium tetrafluoroborates (**1h,i**) were decomposed thermally and photolytically in water, and water saturated with potassium fluoride (ca. 10 mol dm^{-3}). In all reactions, fluoroarenes were sought and not detected ($< 1\%$); the only products were the phenols and, when quantified by UV, HPLC, or GLC, yields were close to 100%. Fluorobenzene and 1,3-difluorobenzene were rigorously sought from the reaction of 3-fluorobenzenediazonium tetrafluoroborate (**1f**) in water, and the upper limit on their formation is estimated by their non-detection by GLC to be $< 0.1\%$. Similarly, no trace of 4-fluorotoluene was observed from thermolysis of 4-toluenediazonium tetrafluoroborate (**1h**) in water containing ammonium hexafluorophosphate; virtually 100% yields of phenols were also observed from the hydrolysis of benzenediazonium and 3-methoxybenzenediazonium tetrafluoroborates (**1a**) and (**1c**), respectively, and the photolysis of 4-fluorobenzenediazonium tetrafluoroborate (**1j**) in water.[35]

Reactions in 2,2,2-Trifluoroethanol.[14] As shown in Table 1, yields of ArF are generally in the range 30–45%, the remainders being exclusively the 2,2,2-trifluoroethyl (TFEt) ether, with no obvious trend according to the nature of the substituent, and no systematic difference between thermal and photolytic modes of decomposition. In all cases where the products of hydrodediazoniation (reduction) were sought, they were not detected. Also included in Table 1 are the results for benzenediazonium chloride (**2**) which was used to estimate the yield of fluorobenzene which is formed by the phenyl cation abstracting fluoride from TFE (rather than from tetrafluoroborate);[36] chlorobenzene was considered as a possible product,[37] but was shown to be absent. The yield of fluorobenzene from **2** is lower than from the tetrafluoroborate (**1a**) in this solvent, but still appreciable. Significantly, reaction of 3-fluorobenzenediazonium tetrafluoroborate (**1f**) in TFE saturated with io-

Table 1. Product Analysis from Thermal (Δ) and Photolytic ($h\nu$) Reactions of Arenediazonium Tetrafluoroborates (**1**) in 2,2,2-Trifluoroethanol

Substituent	Δ or $h\nu$	ArF/%	$ArOCH_2CF_3$/%
H[a)]	Δ	28	72
H[b)]	Δ	10	90
H	$h\nu$	43	57
3-Me[a)]	Δ	42	58
3-Me	$h\nu$	44	56
3-MeO	Δ	29	71
3-MeO	$h\nu$	31	69
3-CF_3	Δ	27	73
3-CF_3	$h\nu$	33	67
3-F[a),c)]	Δ	35	65
3-F[a)]	$h\nu$	33	67
3-CN	Δ	37	63
3-CN	$h\nu$	33	67
3-NO_2	Δ	44	56
3-NO_2	$h\nu$	43	57
4-Me	Δ	37	63
4-Me	$h\nu$	45	55
4-OMe[d)]	Δ	~35	~65
4-OMe	$h\nu$	49	51

a) $< 0.1\%$ ArH detected. b) Reactant = PhN_2Cl rather than PhN_2BF_4; PhCl was sought but not detected. c) No 3-fluoroiodobenzene was detected ($< 1\%$) when the reaction mixture was saturated with ICH_2CO_2H. d) Approximate results; the thermal reaction was too slow to allow a reliable analysis.

doacetic acid gave no detectable 3-iodofluorobenzene which confirms that radical intermediates are not involved in these reactions.[29] Table 2 shows the product yields from reactions of benzenediazonium tetrafluoroborate (**1a**) in TFE containing various fluoride-containing salts—$NaPF_6$, $NaBF_4$, and $NaSbF_6$—as potential fluoride donors that are soluble in TFE. Only $NaBF_4$ has an effect possibly outside experimental uncertainty. As the results in Table 3 show, there is a modest increase in the yield of ArF from 4-toluenediazonium tetrafluoroborate (**1h**) as the proportion of trifluoromethoxybenzene (TFMOB) as cosolvent increases. More limited studies with (**1h**) using difluoromethyl 2,2,2-trifluoroethyl ether indicated that this cosolvent has a smaller effect.

Reactions in Aqueous 2,2,2-Trifluoroethanol.[38] Only the 4-methyl compound (**1h**) was solvolysed in H_2O:TFE = 4:1 (molar radio), Table 4; a low yield of fluorodediazoniation is observed (11%) and the ratio of phenol to phenyl TFEt ether (2.7:1) is lower than the ratio of water to TFE in the solvent. In H_2O:TFE = 1:1, the yields of fluoroarenes range from 5% for the parent (**1a**) to 24% for the 4-methyl-substrate (**1h**). For (**1h**), addition of ammonium hexafluorophosphate (but not tetrabutylammonium tetrafluoroborate) leads to an increased yield of fluorodediazoniation. Ratios of aryl TFEt ethers to phenols range from about 1:1 to 2:1 although the 2,6-dimethyl-substrate (**1k**), the most reactive one, is exceptional with a ratio of 3.8:1. In the least aqueous medium, 97TFE, the yield of fluoroarene from **1h** is 32%, and the ratio of TFEt ether to phenol (9:1) is again higher than the molar ratio of TFE:H_2O in the solvent (5.8:1).

Reactions in 1,1,1,3,3,3-Hexafluoro-2-propanol. HFIP has been widely used as a highly-ionizing, weakly-nucleophilic solvent,[39,40] the low nucleophilicity of the hydroxy being ascribed to the electron-withdrawing effect of the six β-fluorine atoms. So many fluorines will also reduce the ability of one of them to act as a nucleophilic centre compared with one in TFE. It was difficult, therefore, to predict which of the two sites (OH or F) would be most effective in capturing the (highly reactive) electrophile in the dediazoniation. Table 5 shows the product yields obtained for the thermal and photolytic reactions of various arenediazonium tetrafluoroborates. The yields of ArF are systematically lower than from reactions in TFE, there is little variation with the nature of the substituent, and photolysis generally gives a lower yield of the fluoroarene than the thermal process.

Reactions in Trifluoroacetic Acid. TFA was identified as a weak fluoride donor which is also only weakly nucleophilic at oxygen;[41] products of thermal and photolytic reactions are given in Table 6. They are very similar to those in HFIP (results from the thermal reaction of the parent compound appear out of line and may be inaccurate) except that now photolysis

Table 2. Product Analysis from Thermal Reactions of Benzenediazonium Tetrafluoroborate (**1a**) in 2,2,2-Trifluoroethanol with Added Inorganic Salts

Salt (concn/mol dm^{-3})	PhF/%	$PhOCH_2CF_3$/%
0	28	72
$NaPF_6$ (1.76)	27	73
$NaBF_4$ (0.63)	34	66
$NaSbF_6$ (0.60)	29	71

Table 3. Product Analysis from Thermal Reactions of 4-Methylbenzenediazonium Tetrafluoroborate (**1h**) in 2,2,2-Trifluoroethanol:Trifluoromethoxybenzene (TFE:TFMOB)

Solvent molar ratio	$4\text{-}MeC_6H_4F$/%	$4\text{-}MeC_6H_4OCH_2CF_3$/%
TFE (100%)	28	72
TFE:TFMOB (10:1)	34	66
TFE:TFMOB (5:1)	39	61
TFE:TFMOB (2.5:1)	40	60

Table 4. Product Analysis from Thermal Reactions of Substituted Benzenediazonium Tetrafluoroborates in Aqueous Trifluoroethanol

Substituent	Water:TFE[a)]	ArF/%	$ArOCH_2CF_3$/%	ArOH/%
4-Me	4:1	11	24	65
H	1:1	5	40	55
4-Me	1:1	24	42	34
4-Me[b)]	1:1	21	44	35
4-Me[c)]	1:1	43	34	23
2,6-di-Me	1:1	18	65	17
3-F	1:1	7	61	32
3-Cl	1:1	22	44	34
4-Me	3:97[d)]	32	61	7

a) Molar ratio. b) Containing 0.7 mol dm^{-3} Bu_4NBF_4. c) Containing 1.2 mol dm^{-3} NH_4PF_6. d) By weight.

Table 5. Product Analysis from Thermal (Δ) and Photolytic (*hν*) Reactions of 3-Substituted Benzenediazonium Tetrafluoroborates in 1,1,1,3,3,3-hexafluoro-2-propanol

3-Substituent	Δ or *hν*	ArF/%	$ArOCH(CF_3)_2$/%
H	Δ	26	74
H	*hν*	15	85
Me	Δ	24	76
Me	*hν*	15	85
MeO	Δ	12	88
MeO	*hν*	13	87
CF_3	Δ	33	67
CF_3	*hν*	11	89

Table 6. Product Analysis from Thermal (Δ) and Photolytic (*hν*) Reactions of 3-Substituted Benzenediazonium Tetrafluoroborates in Trifluoroacetic acid

3-Substituent	Δ or *hν*	ArF/%	CF_3CO_2Ar/%
H	Δ	4	96
H	*hν*	18	82
Me	Δ	15	85
Me	*hν*	20	80
MeO	Δ	11	89
MeO	*hν*	15	85
CF_3	Δ	18	82
CF_3	*hν*	19	81
CN	Δ	14	86
CN	*hν*	21	79
NO_2[a]	Δ	~9	~91
NO_2	*hν*	21	79

a) This reaction is very slow and the results may be inaccurate.

generally gives the higher yield of ArF.

Reactions in Ethanol. Results in Table 7 show that substrates with strongly electron-withdrawing substituents give high yields of ArH and no ArF, the residue being the aryl ethyl ether (ArOEt). In contrast to what was observed in TFE, when iodoacetic acid was added to the ethanol for the reaction of 3-fluorobenzenediazonium tetrafluoroborate (**1f**), 3-iodofluorobenzene was detected amongst the products—a positive and well established test for the involvement of radical intermediates.[29] Only very low yields of ArH are observed for the parent compound (**1a**) and analogues with electron-releasing substituents.[42] In these reactions, the major product is ArOEt, with a low yield of PhF from the parent compound and higher yields of ArF from substrates with electron-releasing substituents. In ethanol, therefore, unlike reactions in less nucleophilic but more ionizing solvents, there is unambiguous evidence for radical *and* heterolytic pathways, and which route is dominant depends upon the substituents in the arene ring and the experimental conditions.[43]

Reactions of 3-Fluoro- and 3-Nitro-benzenediazonium Tetrafluoroborates (1f, g) in 1,1-$^2H_2$-Ethanol. The major product from the thermal dediazoniation reaction of 3-nitrobenzenediazonium tetrafluoroborate (**1g**) in 1,1-dideuterioethanol was isolated and purified by preparative GLC, then investigated by ^1H and ^2H NMR. Comparison of the integrated ^1H NMR spectrum with that of a sample of unlabelled nitrobenzene established that the nitrobenzene from the reaction in 1,1-dideuterioethanol has a single deuterium atom. The chemical shifts in the ^1H spectrum, and the details of the ^2H NMR spectrum, confirmed that the deuterium is *meta* to the nitro group, i.e. where the diazonium group was originally bonded. 3-Fluorobenzenediazonium tetrafluoroborate (**1f**) was also solvolyzed in 1,1-dideuterioethanol but preliminary studies had shown that we were unable to isolate by preparative GLC or microdistillation from a small scale solvolysis a sample of fluorobenzene sufficient in quantity and purity for NMR analysis. Consequently, the products from the quenched reaction were first extracted into pentane, then back-extracted into DMSO-d_6. The ^1H NMR spectrum of this sample was then compared with the spectrum from an identical run using unlabelled ethanol, and with that of a sample of authentic pure unlabelled fluorobenzene in the same solvent. It was possible to conclude from the integrated ^1H NMR spectra that a single deuterium was present in the fluorobenzene from the run in 1,1-dideuterioethanol, but overlapping signals from contaminants prevented more detailed deductions.

Table 7. Product Analysis from Thermal Reactions of 3-Substituted Benzenediazonium Tetrafluoroborates in Ethanol

3-Substituent	ArH/%	ArF/%	EtOAr/%
H[a]	7	5	88
H[b]	4	2	94
Me	3	15	82
MeO	4	17	79
F[c]	80[d] (85)	< 0.1 (< 0.1)	20 (15)
NO_2	92[e]	< 1	8

a) $[PhN_2BF_4]_0 = 0.0066$ mol dm^{-3}. b) $[PhN_2BF_4]_0 =$ 0.013 mol dm^{-3}; previously reported < 1:4:96.[36] c) An unquantified yield of 3-fluoroidobenzene was observed when the reaction was carried out in the presence of 0.18 mol dm^{-3} iodoethanoic acid;[29] yields in parentheses are for photolysis. d) 3-Deuteriofluorobenzene obtained in CH_3CD_2OH. e) 3-Deuterionitrobenzene obtained in CH_3CD_2OH.

Reactions in 2-Fluoroethanol and 2,2-Difluoroethanol. In view of the dramatic differences in product analyses between reactions in ethanol (Table 7) and 2,2,2-trifluoroethanol (Table 1), solvolyses were carried out for a limited range of substrates in mono- and difluoro-ethanols, and results are shown in Tables 8 and 9. For benzenediazonium tetrafluoroborate (**1a**), the results in both solvents are virtually the same as for reaction in TFE; for the 3-methyl analogue **1b**, the only difference is an inversion in the proportions of fluorobenzene and the ether in these two solvents compared with reaction TFE. In neither solvent for neither substrate, **1a** or **1b**, was there any

Table 8. Product Analysis from Thermal Reactions of 3-Substituted Benzenediazonium Tetrafluoroborates in 2-Fluoroethanol

3-Substituent	ArH/%	ArF/%	$ArOCH_2CH_2F$/%
H	< 0.1	36	64
Me	< 0.1	76	24
F	2	32	66

Table 9. Product Analysis from Thermal Reactions of 3-Substituted Benzenediazonium Tetrafluoroborates in 2,2-Difluoroethanol

3-Substituent	ArH/%	ArF/%	$ArOCH_2CHF_2$/%
H	< 0.1	33	67
Me	< 0.1	77	23
F	0.5	53	47

Table 10. Product Analysis from Thermal Reactions of 4-Toluenediazonium Tetrafluoroborate (**1h**) in Other Media

Medium	$4\text{-}MeC_6H_4F$/%	Other products/%
1,2-Dichloroethane	74	4-chlorotoluene (26)
Toluene	77	—[a)]

a) Three nonpolar minor products were observed but not identified.

hydrodediazoniation. Only for 3-fluorobenzenediazonium tetrafluoroborate (**1f**) in these solvents, with low yields of hydrodediazoniation in both, is there any tendency towards the outcome in ethanol—the main reactions are still formation of the ethers (**3**) and the fluoroarene. Both FE and DFE give higher yields of fluoroarenes than TFE.

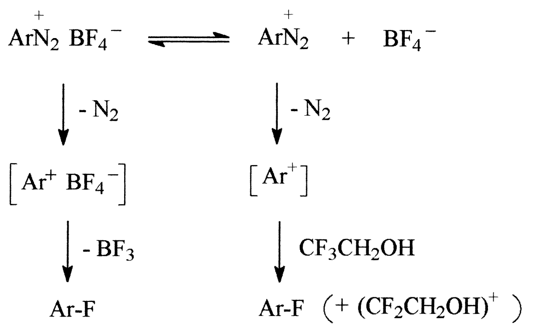
Reactions in Nonpolar, Nonnucleophilic Media. Few reliable complete product analyses have been reported for reactions using nonpolar, nonnucleophilic solvents possibly because reaction reproducibility is difficult to achieve, a difficulty we also encountered. Analysis for 4-fluorotoluene by HPLC from 4-toluenediazonium tetrafluoroborate (**1h**) in 1,2-dichloroethane and in toluene led to results in Table 10. In 1,2-dichloroethane, 4-chlorotoluene was identified as a significant additional product, but the three minor by-products from reaction in toluene were not identified. Attempts to obtain satisfactory reproducible quantitative analyses from reactions of 3-fluorobenzenediazonium tetrafluoroborate (**1f**) in 1,2-dichloroethane, toluene, 4-fluorotoluene, and chlorobenzene were not successful.

Discussion

Reaction in Aqueous Solution. Dilute arenediazonium salts will be fully dissociated in highly aqueous solution,[44] so reactions will be of independently solvated diazonium ions, Scheme 1. In water with no cosolvent, products of thermal and photolytic reactions are exclusively phenols; even saturation of the water with potassium fluoride (ca. 10 mol dm^{-3}) led to no detectable yield of fluoroarene which, in other solvents, is always found from the heterolytic mechanism. There is already evidence that aryl cations are extremely short-lived,[45] and will not survive extensive diffusion through even only weakly nucleophilic media; additionally, fluoride is strongly hydrated in aqueous solution and consequently a very weak nucleophile.

In water–TFE mixtures, the dilute reactant will also be fully dissociated,[44] consequently the products are overwhelmingly formed from independently solvated dissociated arenediazonium cations and solvent molecules. In these reactions, the ratio of TFEt ethers to phenols is generally greater than the ratio of TFE:H_2O in the solvent, Table 4. Similar selectivities in favour of TFE over water have been reported for vinyl cations whereas simple alkyl carbenium ions generally show selectivity in favour of reaction with water over TFE.[40,46] However, fluoroarenes are significant additional products formed from the TFE (see below), i.e. the aryl cation combines with and abstracts a fluoride from the trifluoromethyl end of a TFE molecule—a reaction previously detected in the gas phase.[47] Consequently, the ratio of TFEt ether to phenol under-estimates the ratio of *total* reaction of the aryl cation with TFE compared with water, and there are two issues: (i) why is there selectivity in favour of TFE? and (ii) why is there so much fluoride abstraction in aqueous TFE? The selectivity for TFE cannot be due to better hydrogen bonding with the nucleofuge by the more acidic OH of TFE compared with an OH of water, which accounts for similar selectivities involving oxygen-bonded nucleofuges.[46] Nor does the encounter-controlled nature of the product-forming reactions alone provide a satisfactory explanation.[48] Arenediazonium ions are both positively charged and lipophilic, and consequently will be more effectively solvated by TFE than by water molecules. Moreover, the interactions between the arenediazonium ions and solvent molecules must be predominantly electrostatic ion–dipole interactions, and the CF_3 end will be the more negative end of the TFE molecule dipole. Consequently, combination of the extremely reactive aryl cation with a lone pair on one of three fluorines may well involve less molecular reorganization than combination with a lone pair on the hydroxy.

Reactions in 2,2,2-Trifluoroethanol, 1,1,1,3,3,3-Hexafluoro-2-propanol, and Trifluoroacetic acid. Results in Table 1 show that, using chloride as the counter ion in TFE, 10% of the products is ArF (and no chloroarene was detected) compared with 28% ArF from the tetrafluoroborate; the major reaction for both is capture of the electrophile by the hydroxy of TFE. The absence of fluoroarene from reactions in water without any TFE rules out reaction between the aryl cation and dissociated tetrafluoroborate. We deduce that, in TFE, the aryl cation has two routes to fluoroarene—fluoride abstraction from TFE (as in aqueous TFE, but in higher yield) and fluoride abstraction from tetrafluoroborate *within an ion pair*, these occur in the ratio of about 1:2, Scheme 2. The phenyl cation, therefore, is captured by a TFE molecule, either though the oxygen (~70%) or a fluorine (~10%) or by an ion-paired tetrafluoroborate anion (~20%). The absence of chloroarene from the arenediazonium chloride in TFE indicates either a lower degree of ion pairing with chloride than with tetrafluoroborate, or stron-



Scheme 2. Formation of fluoroarenes from reaction of aryl cation with ion-paired tetrafluoroborate and with trifluoroethanol.

ger solvation of chloride within the ion pair which prevents direct access to the chloride by the aryl cation. Although photochemical reactions in TFE are much faster, the product analyses are very similar indicating that the same or very similar intermediates are involved. And, although substituents have appreciable effects upon rate constants for solvolysis, product ratios are relatively insensitive to the substituents in the arene ring, again indicative of a highly reactive short-lived electrophile.

In an attempt to increase the yield of fluoroarenes in TFE, two types of solutes were tried. The marginal increase in ArF yield in the presence of sodium tetrafluoroborate (Table 2) probably reflects a higher proportion of reaction through the arenediazonium tetrafluoroborate ion pair whose dissociation will have been suppressed. Correspondingly, the increase in ArF in the presence of NH_4PF_6 (Table 4) could be due to reaction through the additional ion pair formed from the additional fluorine-containing additive. Phenyl trifluoromethyl ether has an oxygen bonded to the fluorine-bearing carbon which, by resonance, has the potential to assist the delivery of fluoride to an aryl cation. However, as results in Table 3 show, the enhancement of the ArF yield is modest at TFMOB mole fraction = 0.29, and does not indicate a route to a viable practicable synthesis of fluoroarenes.

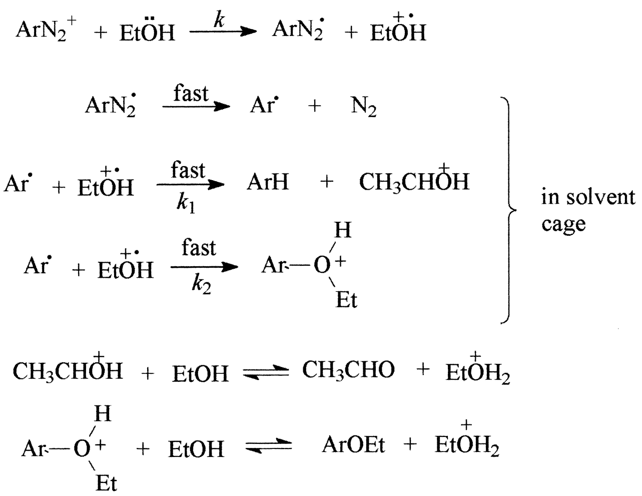
1,1,1,3,3,3-Hexafluoro-2-propanol and trifluoroacetic acid may be considered together, Tables 5 and 6. No arenediazonium tetrafluoroborate in either solvent shows significantly increased yields of ArF in thermal or photolytic reactions compared with reactions in TFE; indeed, they are generally lower. There are two credible explanations. The higher ionizing power of these solvents will cause a greater degree of reaction through dissociated arenediazonium ions, consequently there will be less reaction of the aryl cation with tetrafluoroborate anion. (In agreement, much higher yields of fluoroarene are obtained in nonpolar solvents such a 1,2-dichloroethane and toluene (see below) in which ions will be overwhelmingly ion-paired). Secondly, in both HFIP and TFA, the strongly electron-attracting rest of the molecule inhibits fluoride transfer more than in TFE so, by default, the aryl cation is trapped mainly through oxygen.

Reactions in Ethanol, 2-Fluoroethanol, and 2,2-Difluoroethanol. Thermolysis of arenediazonium salts in ethanol is a well-cited hydrodediazoniation (reduction) method.[20,24,29] In practice, however, yields are variable and depend upon the other substituents in the arene and the precise experimental conditions. This was corroborated in our studies, Table 7. For the parent (**1a**) and derivatives with electron-releasing substituents, there are only low yields of reduction in ethanol, the major products being the ethyl ethers with some formation of ArF especially for reactants with electron-releasing substituents. Comparison of rate constants[27] and product ratios indicates that these compounds, e.g. (**1b,c**), react in ethanol largely by the same mechanism as in other solvents, Schemes 1 and 2. With electron-withdrawing substituents, however, reduction yields are high but still invariably accompanied by some ethyl ether although, significantly, no fluoroarene. There is an early report that, using methanol as the reducing solvent, it is one of the methyl hydrogens which is transferred.[49] Our present results using 3-nitro and 3-fluoro-benzenediazonium tetrafluoroborates in CH_3CD_2OH establish that, in ethanol, it is a hydrogen from the methylene group which is transferred. And showing that the deuterium in the nitrobenzene from **1g** is *meta* to the nitro group also establishes that, as for reactions of phenyl cations in solution,[50] but not in the gas phase,[47,51] hydrodediazoniation in ethanol does not involve rearrangement of the intermediate whatever its nature.

The parent and analogues with electron-donating and -withdrawing substituents were also solvolyzed in mono- and di-fluoroethanol to investigate the discontinuity in mechanisms between TFE and ethanol. We see from Tables 8 and 9 that for the parent in both solvents the results are virtually the same as in TFE, i.e. heterolytic nucleophilic substitution. For 3-methylbenzenediazoniium tetrafluoroborate, there is also no trace of hydrodediazoniation although there is an inversion of the ratio of ArF to ether (for which we have no explanation). Only for 3-fluorobenzenediazonium tetrafluoroborate is any reduction product detected but even here yields are very low. Of the solvents we have investigated, therefore, only ethanol provides useful yields of hydrodediazoniation, and this occurs only for arenediazonium salts with electron-withdrawing substituents.[52]

Mechanisms. Both the heterolytic nucleophilic substitution reactions and the hydrodediazoniation reactions reported here follow first-order kinetics, but their activation parameters are characteristically different. In general, the former have large $\Delta H^{\ddagger}$ values and positive $\Delta S^{\ddagger}$ values, and the previously reported heterolytic mechanism, Scheme 1, through either dissociated or ion-paired arenediazonium ions (depending upon the solvent), Scheme 2, satisfactorily accounts for the results.[27]

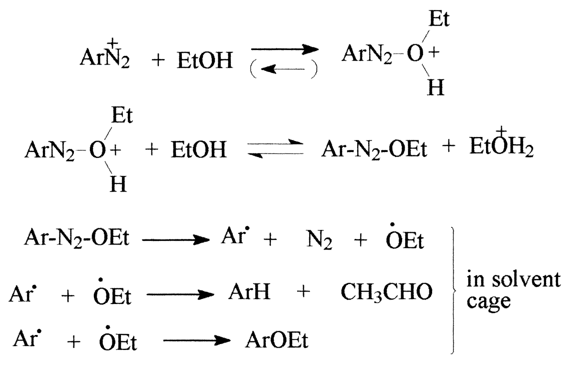
Formation of 3-iodofluorobenzene from reaction of 3-fluorobenzenediazonium tetrafluoroborate in ethanol containing iodoacetic acid confirmed the involvement of radical intermediates in the hydrodediazoniation reactions,[29] but they do not have the kinetic complexities of some types of radical reactions.[53] However, rate constants are much faster than expected on the basis of results in other solvents, and activation parameters are characteristically different; generally, $\Delta H^{\ddagger}$ values are smaller and $\Delta S^{\ddagger}$ values substantially negative. Significantly, hydrodediazoniations, even when yields are high, are invariably accompanied by the formation of some aryl ethyl ether. Rate constants for the heterolytic mechanism of ca. $10^{-6}\ s^{-1}$ at 25 °C can be estimated for the reactions for arenediazonium tetrafluoroborate with strongly electron-withdrawing substituents from results in other solvents; actual rate constants for these compounds in ethanol are between 200 and 900 times larger.[27] It follows, therefore, that the appreciable yields of aryl ethyl ethers in ethanol cannot have been formed by the heterolytic route in parallel with the homolytic path as has usually been assumed in the past. We propose that the ethyl ethers from arenediazonium ions with electron-withdrawing substituents are formed by a product-forming path, which competes with the main hydrodediazoniation path, within a single composite homolytic mechanism.[20,26,43,54] Strongly supportive of this conclusion is the total absence in ethanol from arenediazonium ions with electron-withdrawing substituents of any ArF which, for all reactants in other solvents (except pure water for reasons given above), and reactants without electron-withdrawing substituents in ethanol, characterises the heterolytic mechanism. Scheme 3 involves a rate-limiting bimolecular



Scheme 3. Electron transfer-homolysis mechanism for dediazoniation of arenediazonium ions in ethanol.

electron transfer from ethanol to the arenediazonium ion probably via an encounter complex of the sort identified by Kochi.[55] Then, before the ethanol radical cation can diffuse away, fragmentation of the very short-lived arenediazenyl radical gives the aryl radical.[56] This then partitions between alternative competing product-forming routes: hydrogen atom abstraction from the methylene of the proximate ethanol radical cation with elementary rate constant k_1, and combination with the ethanol radical cation through the oxygen with elementary rate constant k_2. This mechanism for reactions in ethanol accounts for the kinetics parameters,[27] the reduction product, the ether formation, the rate-enhancing effect of electron-withdrawing substituents in the arene ring, the rate-enhancing effects of nucleophilic solutes and co-solvents,[43] and the isotopic labelling results,[36,49] and is well precedented.[20,21,57,58] Solvents or solutes such as low valence state metal ions and iodide which are effective electron donors should facilitate this process but may, as in the case of iodide, lead to additional products.[20,22] An alternative radical mechanism shown in Scheme 4 via intermediate aryl diazo ethers, ArN=NOR,[26,59] seems less likely as such compounds are known to react by acid catalyzed heterolysis, i.e. the reverse of the first two steps of Scheme 4.[60]

Formation of both 1,3-fluorobenzene and fluorobenzene indicates that heterolytic and homolytic routes are concurrent for 3-fluorobenzenediazonium tetrafluoroborate only in FE and DFE, and the heterolytic path predominates in both. For substrates without electron-withdrawing substituents, formation of fluoroarene and arene indicates that both mechanisms run in parallel in ethanol, but again the heterolytic path predominates. In such cases, the lower $\Delta H^{\ddagger}$ values for the homolytic reaction indicate that hydrodediazoniation will compete more effectively at lower temperatures.



Scheme 4. Alternative homolytic mechanism for dediazoniation of arenediazonium ions in ethanol.

Photolytic Reactions. Product analyses from thermally and photolytically induced reactions are generally very similar and are satisfactorily explained in terms of common or very similar intermediates—either cations or radicals.[61] It has already been shown that arenediazonium ions are excellent triplet quenchers,[62] and that direct irradiation of an arenediazonium ion can lead to an excited singlet state of the diazonium ion and then, by intersystem crossing, the triplet state.[63] However, the present results for substrates without electron-withdrawing groups indicate involvement of only the singlet phenyl cation. The singlet excited arenediazonium ion, therefore, fragments faster than it crosses to the triplet state under the experimental conditions used. Photolysis of the 3-fluoro-substrate in ethanol, likewise, gives a product analysis very similar to that obtained by thermolysis which proceeds via electron transfer and homolysis. Like comparable reactions already reported, this also appears to be a homolytic reaction.[61,64]

Experimental

2,2,2-Trifluoroethanol was distilled and stored over 4 Å molecular sieves. 2-Fluoroethanol (Aldrich), 2,2-difluoroethanol (Lancaster), and HPLC grade ethanol (Lancaster) were used as supplied. ***2-Fluoroethanol is highly toxic and should be handled with extreme care***. Samples of octane and undecane (Lancaster) used as GLC internal standards were shown to be pure by GLC. Ether means diethyl ether and, unless otherwise stated, deuteriochloroform was used as solvent for ^{1}H and ^{13}C NMR spectra on a Bruker WP200 spectrometer, for ^{19}F NMR spectra on a Jeol Lambda 500, and for ^{2}H NMR spectra on Bruker WM300-WB; coupling constants (J) are given in Hz. Analysis by GLC was carried out on Pye 104, Hewlett-Packard 5890, Pye Unicam 15503 GCD, Packard 427, and Perkin Elmer Sigma 4b instruments, and peak integrations were recorded with chromatograms. Preparative GLC was on a Varian Aerograph 2700. Analysis by reverse phase HPLC was carried out on a dual pump Gilson system fitted with a manual Rheodyne injection valve and an Applied Biophysics UV detector (set at 254 nm) controlled by Gilson software on an Opus PC IV.

Small scale photolytic work was first carried out using a Photochemical Reactors semi-micro instrument (model RS-55, 4 watt maximum emission, 254 nm). An immersion well photochemical reactor was used for larger samples (model RQ 125, 6 watt or 125 watt low-pressure mercury lamp, maximum emission 254 nm). For most reactions, the solution of reactant was placed in a 150 mL standard reaction flask containing the water-cooled borosilicate-glass immersion well. For reactions in TFA, HFIP, and TFE, a 3 mL quartz UV cell was filled with the reaction solution and clamped to the outside of the immersion well.

Preparations. Preparations of benzenediazonium chloride and arenediazonium tetrafluoroborates have already been reported.[27,28,65]

Ethyl 3-fluorophenyl Ether. A solution of ethyl tosylate

(3.64 g, 18 mmol) in acetonitrile (10 mL) was added drop-wise over 1 h to a magnetically stirred solution of sodium hydroxide (0.867 g, 22 mmol) and 3-fluorophenol (2.02 g, 18 mmol) in water (15 mL) at 0 °C. The pale yellow solution was next allowed to stand at room temperature for 1 h, then was heated with stirring under reflux at 100 °C for 3 h during which time it became colorless, and a small amount of white suspension disappeared. The solution was allowed to cool, then was extracted with ether (2×20 mL), and the extracts were combined, dried ($MgSO_4$), filtered, and evaporated under reduced pressure until the total volume was approximately 1 mL. A pure sample of the product was isolated by preparative GLC (10% Carbowax 20M, 8ft by 1/4 inch column; ^{1}H NMR: δ 1.40 (3H, t, J = 6.9 Hz), 3.99 (2H, q, J = 6.9 Hz), 6.63 (3H, m), 7.17 (1H, m)). Capillary GLC analysis showed that the same product had been formed in the reaction of 3-fluorobenzenediazonium tetrafluoroborate in ethanol.

Isolation of Reaction Products. The following are representative.

(i) 3-Fluorophenyl 2,2,2-Trifluoroethyl Ether. A solution of the arenediazonium salt (4.0 g, 19 mmol) in TFE (45 mL) was heated under reflux for 4 h then cooled, and extracted between ether (80 mL) and aqueous sodium hydroxide (2 mol dm^{-3}, 80 mL). The organic phase was separated and combined with two further ether extracts of the aqueous phase. The dried ether solution was evaporated under reduced pressure, and a sample of 3-fluorophenyl 2,2,2-trifluoroethyl ether was isolated from the residue by preparative GLC and shown by capillary GLC to be pure (^{1}H NMR: δ 4.31 (2H, q, J = 8.1 Hz), 6.72 (3H, m), 7.23 (1H, t, J = 7.4 Hz).

(ii) Phenyl 2,2,2-Trifluoroethyl Ether. The procedure described above was followed using benzenediazonium tetrafluoroborate (6.0 g, 31 mmol) in TFE (40 mL); ^{1}H NMR: δ 4.34 (2H, q, J = 8.2 Hz), 6.95 (2H, d, J = 7.3 Hz), 7.05 (1H, t, J = 7.5 Hz), 7.33 (2H, m).

(iii) 1,1,1,3,3,3-Hexafluoro-2-propyl 3-Methylphenyl Ether. A solution of 3-methylbenzenediazonium tetrafluoroborate (3.7 g, 18 mmol) in HFIP (10 mL) was heated at 60 °C for 24 h. The reaction was worked up in the usual way and a sample of the product purified by preparative GLC; ^{1}H NMR: δ 2.3 (3H, s), 4.7 (1H, sept., J = 5.7 Hz), 6.9 (3H, m), 7.2 (1H, m).

(iv) 3-Deuterionitrobenzene. 3-Nitrobenzenediazonium tetrafluoroborate (0.25 g, 1.1 mmol) was dissolved in 1,1-$^2H_2$-ethanol (99%, 2 mL). The reaction mixture was heated under reflux at 80 °C for 48 h. A sample of the product (^{1}H NMR: δ 7.5 (1H, m, Ar), 7.7(1H, m, Ar), 8.2(2H, m, Ar); ^{2}H NMR: δ 7.6 (1D, t, J = 1.2 Hz), EIMS m/z 124 (M^+, 100%), 94, 78, 52) was isolated and purified by preparative GLC.

Qualitative Product Analysis by GLC. All reactions were carried out at least in duplicate. Thermal solvolyses were for 10 half-lives or longer before (in most cases) direct GLC analysis followed by GLC and GLC-mass spectrometric analysis of the ether (or pentane or dichloromethane) extract of an aqueous quench of the reaction. Photolytic reactions were monitored by UV to ensure completion before analysis as for the thermal reactions. Products were identified and characterized either by the usual spectroscopic methods following isolation, or by comparison with authentic samples.

Determination of GLC Molar Response Factors. The following procedure is representative. A solution (25 mL) of undecane (0.1660 g, 1.06 mmol) and 1,3-difluorobenzene (0.1875 g, 1.64 mmol) in ether (in some determinations, ethanol or pentane were used) was analyzed six times by capillary GLC. It was then diluted by a factor of two and analyzed a further six times. This procedure was carried out two or three times with different amounts of compounds to allow two or three separate determinations of the MRF from which an average was taken.

Quantitative Product Analysis of Thermal Solvolysis Reactions by GLC: General Aspects. Reactions were carried out at least twice for not less than ten half-lives, and GLC analyses were usually carried out six times and average results taken. The following are representative.

(i) 3-Fluorobenzenediazonium Tetrafluoroborate in TFE. A solution of 3-fluorobenzenediazonium tetrafluoroborate (0.2015 g, 0.9601 mmol) in TFE (3.00 mL) was heated under reflux for 4 h, then extracted between water (8 mL) and ether (8 mL). Undecane (0.1345 g, 0.8605 mmol) was added to the ether phase which was then analyzed by GLC.

(ii) 3-Fluorobenzenediazonium Tetrafluoroborate in Ethanol. A solution of 3-fluorobenzenediazonum tetrafluoroborate (0.1200 g, 0.5718 mmol) and undecane (0.0640 g, 0.4094 mmol) in ethanol (6 mL) was heated under reflux for 3 h at 78 °C, then cooled and analyzed directly by GLC.

(iii) Benzenediazonium Tetrafluoroborate in Ethanol. This reaction was carried out at two different concentrations of substrate: (a) 0.013 mol dm^{-3} and (b) 0.0066 mol dm^{-3}.

(a) The procedure was as described above for 3-fluorobenzenediazonium tetrafluoroborate in TFE (except that pentane was used for the organic extraction) using benzenediazonium tetrafluoroborate (0.0265 g, 0.138 mmol), octane (0.0165 g, 0.1445 mmol), and ethanol (10.4 mL). The procedure was repeated using the arenediazonium salt (0.0191 g, 0.0995 mmol), octane (0.0337 g, 0.0295 mmol), and ethanol (7.5 mL).

(b) The procedure was as under (a) but using benzenediazonium tetrafluoroborate (0.0240 g, 0.125 mmol), octane (0.0370 g, 0.324 mmol), and ethanol (18.8 mL). The procedure was repeated twice (i) using the arenediazonium salt (0.0290 g, 0.151 mmol), octane (0.042 g, 0.368 mmol), and ethanol (22.8 mL), and (ii) using the arenediazonium salt (0.0166 g, 0.0865 mmol), octane (0.0346 g, 0.303 mmol), and ethanol (13.1 mL).

(iv) 3-Fluorobenzenediazonium Tetrafluoroborate in 2,2-Difluoroethanol. A solution of 3-fluorobenzenediazonium tetrafluoroborate (0.0198 g, 0.0943 mmol), octane (0.0378 g, 0.331 mmol), and 2,2-difluoroethanol (0.5 mL) was heated under reflux for 2 h at 90 °C then allowed to cool. The reaction mixture was extracted between ether (2 mL) and aqueous sodium hydroxide (3 mol dm^{-3}, 2 mL), then the organic phase was separated and analyzed by GLC.

(v) 4-Methoxybenzenediazonium Tetrafluoroborate in Saturated Aqueous Potassium Fluoride. A solution of 4-methoxybenzenediazonium tetrafluoroborate (877 mg) in water (200 mL) containing potassium fluoride (120 g) was heated under reflux for 12 h with constant stirring. The cooled reaction mixture was diluted with water (50 mL) and extracted with ether (4×50 mL). The combined extract was evaporated under reduced pressure and the residue diluted in methanol to 500 mL. Analysis by GLC showed 4-methoxyphenol to be the only product, and comparison by UV spectroscopy (at 292.5 nm) with a standard solution of 4-methoxyphenol (829 mg) in methanol (500 mL) indicated a yield of 96%.

Quantitative Product Analysis of Thermal Reactions by HPLC: General Aspects. Correlation graphs were constructed by reverse phase HPLC analysis (aqueous methanol) of standard solutions of 4-fluorotoluene, *p*-cresol, and 1,3-difluorobenzene which were shown to be pure by GLC. Typically, each of two or three stock solutions would be diluted to give three or four different solutions for analysis.

Quantitative Photolytic Reactions. The following are representative.

(i) 3-Fluorobenzenediazonium Tetrafluoroborate in TFE. A solution of the arenediazonium salt (0.0185 g, 0.0882 mmol) and undecane (0.022 g, 0.142 mmol) in TFE (3.0 mL) in a UV cell was clamped to the outside of the photochemical reactor and irradiated. The reaction was monitored by UV, then, upon completion, was extracted between water and ether, and the ether phase was analyzed.

(ii) 4-Methoxybenzenediazonium Tetrafluoroborate in Saturated Aqueous Potassium Fluoride. A stirred solution of 4-methoxybenzenediazonium tetrafluoroborate (730 mg) in saturated aqueous potassium fluoride solution (10.2 mol dm^{-3}, 200 mL) was photolyzed in the usual way and monitored by UV spectroscopy. Upon completion (ca. 2 h), the products were extracted into ether (4×50 mL); the combined extract was dried ($MgSO_4$), filtered, and evaporated under reduced pressure. GLC analysis showed 4-methoxyphenol to be the only product.

We thank the EPSRC for studentships to KMcC, BS, and PSJC, and Zeneca (formerly ICI) for financial support. We also thank Drs J.H. Atherton and D. J. Moody for helpful discussions, and Mss H. Dowling and N. Martin for supportive experimental work. HM thanks members of the Institute for Fundamental Research in Organic Chemistry (IFOC) at Kyushu University for hospitality during the writing of this manuscript, and Professors S. Kobayashi and T. Sonoda for many helpful discussions.

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