Detection of Aryl Radicals in Hydrodediazoniations[†]

Frederick W. Wassmundt* and William F. Kiesman[‡]

Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-4060

Received November 13, 1996 (Revised Manuscript Received September 9, 1997[⊗]*)*

Iodoacetic acid, an effective aryl radical trapping agent, was employed to investigate the reactive intermediates in several hydrodediazoniations. Isolation of an aryl iodide constitutes a positive result in the test for aryl radicals. Equally as important is the lower yield of the reduction product when the trap diverts radicals from their usual reaction path. Hydrodediazoniations performed in MeOH, EtOH, *i*-PrOH, benzyl alcohol, THF, tetramethylurea, formamide, and hypophosphorous acid all involve aryl radical intermediates. Ferrocene was found to be an effective initiator in most of these reactions; through its action as an electron donor, it serves to shorten reaction times and to improve yields of hydrodediazoniation products. All hydrodediazoniations examined, whether initiated or not, involve radical intermediates.

Introduction

Many investigators have sought to determine the mechanisms by which the diazonium group is replaced by hydrogen from a variety of organic substances.[1] In some of the more prominent reduction methods, careful consideration of the complex mechanistic evidence supports the intermediacy of radicals. What is lacking in these cases is a single simple yet convincing piece of evidence. In contrast, identification of the reactive intermediates in less prominent hydrodediazoniation methods has received scant attention. Unfortunately, very few generalizations have been made about the behavior of diazonium salts in these hydrodediazoniation reactions. Herein, we describe the systematic application of a simple aryl radical trap to a variety of hydrodediazoniation methods.

In general, a good radical trapping agent must be soluble, stable to the reaction conditions, inert to ionic reactions, and easily separable from the other products of the reaction. In addition, it should not foster the formation of radicals or substantially alter the original conditions of the reaction. Alkyl iodides have long been used as traps for alkyl radicals.[2] Bunnett and co-workers first demonstrated that aryl radicals abstract iodine from substituted iodobenzenes.[3] Iodobenzoic acid[4] and iodoacetic acid[5,6] have also been successfully employed as radical traps (eqs 1 and 2). Evidently, iodine transfer is

$$\mathrm{Ar^{\bullet} + IC_6H_4CO_2H \rightarrow ArI + {}^{\bullet}C_6H_4CO_2H} \qquad (1)$$

$$\mathrm{Ar^{\bullet} + ICH_2CO_2H \rightarrow ArI + {}^{\bullet}CH_2CO_2H} \qquad (2)$$

a reaction unique to radicals. Therefore, the replacement of the diazonium group by iodine from such sources demonstrates the presence of an aryl radical. For our investigations iodoacetic acid served as the iodine source.[7] The use of this functionalized trapping agent simplified the analysis of the product, because any surplus agent could be removed easily by washing with base.

Isolation of an aryl iodide from the reaction mixture constitutes a positive result in the primary, qualitative test for the presence of aryl radicals. A second confirmatory portion of the test involves an examination of the change in yield of the hydrodediazoniation product when the trap is added. If the normal product is formed through an aryl radical intermediate, then the yield of the normal radical product must decrease as the radicals are diverted toward aryl iodide formation. Thus a decrease of the normal product accompanying the aryl iodide formation confirms that the radical trap was interrupting the product-forming step.

Results and Discussion

For the investigation of hydrodediazoniations, which are usually performed under neutral or acidic conditions, iodoacetic acid functioned as the trap because of its excellent solubility in a wide range of solvents. First we wanted to test the effect that the presence of the trap had upon a reaction of known mechanism. The Schiemann reaction served as an ionic test reaction for iodoacetic acid.[8] A mixture of 2 equiv of iodoacetic acid and 4-bromobenzenediazonium tetrafluoroborate was boiled in CH_2Cl_2 for 14 days. The normal ionic product of the Schiemann reaction (4-bromofluorobenzene) was formed in 30% yield while no iodine transfer product (4-bromoiodobenzene) was detected in the reaction mixture. This simple experiment served to demonstrate that,

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[†] Part of the Ph.D. Thesis of W. F. Kiesman, University of Connecticut, 1995.

[‡] NSF Predoctoral Fellow (1993−1995). Present address: Biogen, Inc., 14 Cambridge Center, Cambridge, MA 02142.

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

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(7) In unpublished work, phenylacetic acid was isolated from the reaction mixtures of trapping experiments during the examination of Gomberg−Bachmann arylations in benzene. This result traces the fate of the alkyl radical generated in eq 2.

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S0022-3263(96)02128-7 CCC: $14.00

Table 1. Products from Traditional Reaction of 4-Bromobenzenediazonium Tetrafluoroborate in Selected Alcohols

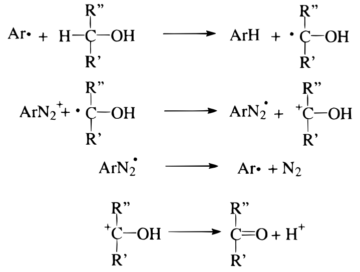
		products (% yield)[c]		
reagent[a]	conditions[b]	BrC_6H_4H	BrC_6H_4OR	BrC_6H_4I
MeOH	no trap	46	20	
	ICH_2CO_2H	2	16	49
EtOH	no trap	70	4	
	ICH_2CO_2H	4	11	58
i-PrOH	no trap	61	0	
	ICH_2CO_2H	13	0	64
BnOH	no trap	54	0	
	ICH_2CO_2H	18	0	56

[a] The reactions were carried out with 0.37 mmol of diazonium salt in 2 mL of reagent. [b] Two equivalents of iodoacetic acid were employed in the trapping experiments. [c] Yields were determined by GC analysis versus an internal standard.

under standard conditions, iodoacetic acid did not induce a radical reaction or interfere in any way with the normal course of the ionic reaction of the diazonium salt.

Reduction with H_3PO_2. A common method employed to replace a diazonium group by hydrogen uses hypophosphorous acid both as an electron donor and as a hydrogen atom source.[1a–d,5b] EPR[9] and CINDP[10] were used to study the mechanism of the reaction. Beckwith observed in the initiation stage of the reaction EPR signals which he assigned to the $HPO_2^{\bullet -}$ species. The extremely short lifetime of the aryl radical precludes its direct observation by EPR. However, in the presence of maleic acid signals were observed that were attributed to the product of reaction of the aryl radical and maleic acid. We thought it worthwhile to apply the iodoacetic acid trap to this reaction to intercept aryl radicals. Addition of iodoacetic acid to the hydrodediazoniation of 4-bromobenzenediazonium tetrafluoroborate in H_3PO_2 solution resulted in the formation of 4-bromoiodobenzene in 33% yield. This result confirms the existence of aryl radicals in the reaction and provides additional support for Kornblum's free-radical mechanism.[1a]

Hydrodediazoniations in Alcohols. Methanol, ethanol, isopropyl alcohol, and benzyl alcohol (BnOH) have all been used as reagents for hydrodediazoniations.[1d] Previous investigators found that the speed of the reaction is enhanced in basic methanol solutions but is retarded in acidic or neutral conditions.[3] We decided to investigate the hydrodediazoniations of 4-bromobenzenediazonium tetrafluoroborate not only in methanol but in all of the above alcohols. Under typical reaction conditions the diazonium salt was added to the alcohol and the solution boiled until the starting material was consumed. The reactions were performed both in the absence and presence of iodoacetic acid. The results are shown in Table 1. Even the slowest of these reactions was complete in about 2 h. In the absence of the trap, the reduction product (bromobenzene) is formed in preference to the aryl ethers in MeOH and EtOH. No ethers could be detected in the reactions performed in the less polar alcohols, *i*-PrOH and BnOH, and reduction remained the major reaction. Upon addition of the trap, the aryl iodide was formed and the amount of hydrodediazoniation product dropped sharply. Both the primary test and the confirmatory test indicated the presence of radical intermediates. The alcohol is undoubtedly the hydrogen atom source. Hodgson and Kershaw[11] found that byproducts of the abstraction of the hydrogen from the alcohols are the carbonyl compounds. One result confirmed their observation. We found in BnOH that benzaldehyde was formed in 42% yield in both the catalyzed and uncatalyzed reactions. These observations coincide with bond strength data which show that the weakest C−H bond in the alcohol involves the bond between the hydrogen atom α to the oxygen (the carbinyl hydrogen) and the carbinyl carbon. The results support the following general free-radical mechanism.[1a]



(3)

(4)

(5)

(6)

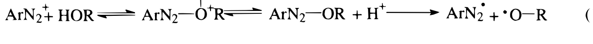
An important competing reaction in the more polar MeOH and EtOH is the formation of an ether by an ionic process (eq 7). The overall result is an increase in the amount of the ether product simultaneous with a decrease in reduction in the presence of iodoacetic acid.

$$\mathrm{ArN_2}^{+} \xrightarrow{-\mathrm{N_2}} \mathrm{Ar}^{+} \xrightarrow{\mathrm{ROH}} \mathrm{ArOR} + \mathrm{H}^{+} \tag{7}$$

In contrast to other diazonium salt reactions, no obvious catalyst is employed to initiate a radical mechanism. Apart from operations in base, there are two possible initiation pathways for the hydrodediazoniations in alcohols. In one, Bunnett and Yijima[12] proposed that in MeOH a direct oxidation of the alcohol by the diazonium salt occurs (eqs 8 and 9). Diazonium salts have been shown to oxidize, by a direct electron transfer, polycyclic aromatics[13] and tertiary amines.[5b] The oxidation potential of MeOH (ca. 0.8 V)[14] is certainly within the range that makes this transfer possible. Equally reasonable is an alternative initiation. Here, joining of the diazonium cation to the oxygen of the solvent is followed by proton loss and homolytic bond cleavage (eq 10). What results are the diazenyl radical and an alkoxy radical. Initiations involving this linkage−homolysis pathway in diazonium salt reactions have been postulated before.[15] A diazoether intermediate has been proposed in the reaction between alkyl nitrites and

$$\mathrm{ArN_2}^{+} + \mathrm{HOCH_3} \rightarrow \mathrm{ArN_2}^{\bullet} + [\mathrm{HOCH_3}]^{\bullet +} \tag{8}$$

$$\mathrm{ArN_2}^{\bullet} \rightarrow \mathrm{Ar}^{\bullet} + \mathrm{N_2} \tag{9}$$



$$\mathrm{ArN_2}^{+} + \mathrm{HOR} \rightleftharpoons \mathrm{ArN_2{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}^{+}}}\mathrm{R} \rightleftharpoons \mathrm{ArN_2{-}OR} + \mathrm{H}^{+} \longrightarrow \mathrm{ArN_2}^{\bullet} + {}^{\bullet}\mathrm{O{-}R} \tag{10}$$

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Table 2. Products from Ferrocene-Promoted Reactions of 4-Bromobenzenediazonium Tetrafluoroborate in Selected Alcohols

		products (% yield)[c]		
reagent[a]	conditions[b]	BrC_6H_4H	BrC_6H_4OR	BrC_6H_4I
MeOH	no trap	65	0	
	ICH_2CO_2H	3	0	72
EtOH	no trap	82	0	
	ICH_2CO_2H	8	0	72
i-PrOH	no trap	82	0	
	ICH_2CO_2H	10	0	81
BnOH	no trap	67	0	
	ICH_2CO_2H	18	0	57

[a] The reactions were carried out with 0.37 mmol of diazonium salt in 2 mL of reagent. [b] Two equivalents of iodoacetic acid were employed in the trapping experiments. [c] Yields were determined by GC analysis versus an internal standard.

arylamines and was thought to undergo homolytic bond cleavage to form a diazenyl radical and an alkoxy radical (eq 11).[16]

$$\mathrm{ArNH_2} \xrightarrow[-\mathrm{H_2O}]{\mathrm{RONO}} \mathrm{ArN_2{-}OR} \rightarrow \mathrm{ArN_2^{\bullet}} + {}^{\bullet}\mathrm{OR} \tag{11}$$

Initiated Hydrodediazoniations in Alcohols. The preceding discussion focused solely upon hydrodediazoniations performed in the absence of an initiator. In previous investigations of diazonium salt reactions we have used soluble electron donors to initiate free-radical reactions.[4,17,18] The donor gives up an electron to the diazonium cation (eq 12). The resulting diazenyl radical releases nitrogen, and the reactive aryl radical intermediate is formed (eq 13). The radical hydrodediazoniations in alcohols should benefit from the use of a promoter such as ferrocene. The effectiveness of the initiator was demonstrated by the results displayed in Table 2. In the presence of 10 mol % of ferrocene, the reactions were completed within 20 min, as compared with the uncatalyzed reactions which took several hours. This dramatic decrease in reaction time from only a small amount of ferrocene was attributed to more efficient initiation.

$$\mathrm{ArN_2^{+}} + \mathrm{Fc} \rightarrow \mathrm{ArN_2^{\bullet}} + \mathrm{Fc^{+}} \tag{12}$$

$$\mathrm{ArN_2^{\bullet}} \rightarrow \mathrm{Ar^{\bullet}} + \mathrm{N_2} \tag{13}$$

Addition of the ferrocene also increased the yields of the reduction products as a comparison of the yields in Table 2 with those in Table 1 shows. Furthermore, ferrocene, in the cases of MeOH and EtOH, suppressed the formation of the aryl ether products entirely. Clearly our introduction of an electron donor improved the efficiency of the radical hydrodediazoniation reactions.

These improved reactions also warrant mechanistic investigation. Upon the addition of the trap to the promoted reactions, the aryl iodide was formed and the yield of the reduction product dropped. Similar to the results of the uncatalyzed reactions, the primary and confirmatory tests both demonstrate that the ferrocene-initated reaction follows a radical pathway.

Table 3. Products from Reactions of 4-Bromobenzenediazonium Tetrafluoroborate in THF

		products (% yield)[c]	
catalyst	conditions[a,b]	BrC_6H_4H	BrC_6H_4I
none	no trap	65	
none	ICH_2CO_2H	20	41
ferrocene	no trap	68	
ferrocene	ICH_2CO_2H	21	55

[a] The reactions were carried out with 0.37 mmol of diazonium salt in 2 mL of THF. [b] Two equivalents of iodoacetic acid were employed in the trapping experiments. [c] Yields were determined by GC analysis versus an internal standard.

Interestingly, in the presence of iodoacetic acid, the yields of reduction product in the catalyzed reactions are almost identical with those found for the reactions performed in the absence of a promoter (Table 1). The use of a promoter speeds the radical reaction to the point where competing ionic reactions become negligible, and ether formation is thereby suppressed. In addition, benzaldehyde is a byproduct of the ferrocene promoted reactions performed in BnOH. This result mirrors that obtained in the reactions performed in the absence of a promoter.

THF. Hydrodediazoniations in THF share many of the traits of the reactions performed in alcohols. Whether the THF reductions were performed in the presence of an initiator or not, the addition of iodoacetic acid intercepted the aryl radical and interrupted the hydrogen atom abstraction (Table 3). These results concur with those obtained by Rüchardt et al. in their study of reductions performed in 1,3-dioxolane.[5] In the ferrocene-initiated reactions, the reaction time was greatly diminished and the yields were increased. Therefore, in THF as in the alcohols, the replacement of the diazonium group by hydrogen is a free-radical process.[19]

Hydrodediazoniations in Amides. In a previous paper the synthetic utility and mechanisms of hydrodediazoniations of diazonium salts in dimethylformamide and dimethylacetamide were described in detail.[4] The following discussion addresses separately the mechanistic investigations of hydrodediazoniations performed in the related amide solvents tetramethylurea (TMU) and formamide.

Tetramethylurea. Rutherford and Redmond[20] found that hydrodediazoniations could be performed in TMU and noted that the reactivity of the diazonium salts in this medium parallels that seen in EtOH and THF. Several years earlier DeTar[21] and Meerwein[22] had proposed that the latter reductions resulted from hydride abstraction by aryl cation intermediates. From the observed similarity, Rutherford and Redmond suggested that the reaction in TMU also followed an ionic pathway. They attempted to support this mechanistic choice by the unsubstantiated assertion that the PF_6^- counterion would not survive in a free-radical reaction. We and others[1a,19] have demonstrated that hydrodediazoniations in alcohols and THF follow radical pathways. Hence, this reaction is an attractive candidate for our radical test.

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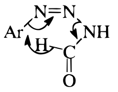
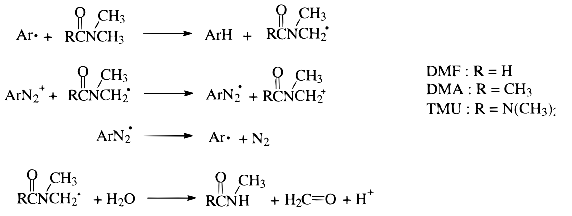


Figure 1.

Scheme 1

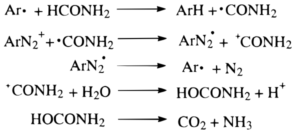


The hydrodediazoniation of 4-bromobenzenediazonium tetrafluoroborate in TMU was performed in the presence and absence of iodoacetic acid. The fluoroborate salt was substituted for the hexafluorophosphate for convenience. In the absence of the trap, bromobenzene was produced in 63% yield. Upon addition of the iodoacetic acid, the yield of bromobenzene dropped to 23% while the aryl iodide (53%) became the major product. In addition, in the presence of 10 mol % of ferrocene, the aryl iodide was formed in 65% yield while the yield of bromobenzene fell to 20%. Similar to other radical hydrodediazoniations, the formation of the aryl iodide clearly demonstrated the presence of aryl radicals in this reaction. Hydrodediazoniations in TMU are like those performed in DMF and DMA,[4] and our results support the following general free-radical chain mechanism (Scheme 1).

Formamide. In yet another hydrodediazoniation reaction, diazonium fluoroborates were converted into the corresponding hydrocarbons in moderate to good yields in a mixture of Et_3N and formamide.[23] Threadgill and Gledhill showed in an elegant labeling experiment that the sole source of hydrogen was that of the formyl position of formamide. The authors discounted the possibility of a radical pathway because no biphenyl derivatives could be detected in the reaction mixture; instead, they proposed that an intramolecular hydride transfer displaces nitrogen from an intermediate triazene derivative in a cyclic transformation (Figure 1). We felt our test could be used to advantage in the elucidation of the mechanism of this reaction.

When 4-bromobenzenediazonium fluoroborate was dissolved in formamide, gas evolution was spontaneous. The reaction was completed within 10 min and yielded 66% of the hydrogen replacement product. The transformation was achieved in the absence of Et_3N. Clearly Et_3N was not needed for the reaction. We chose to omit Et_3N for simplicity and to remove all ambiguity concerning the substance causing reduction. Meerwein and co-workers, for example, identify tertiary amines as reductants.[22] Upon addition of iodoacetic acid, the aryl iodide was formed in 56% yield while the yield of the reduction product dropped to 8%. The results of the primary and confirmatory tests demonstrate the presence of aryl radicals and deny the validity of the cyclic intermediate. Similarly, in the presence of 10 mol % of ferrocene, the aryl iodide was formed in 58% yield while the yield of bromobenzene fell to 11%. The site of hydrogen abstraction from formamide is also consistent with a free-radical reaction. For example, in a study of the abstraction of hydrogen from formamide by hydroxyl radicals it was found that the hydrogen abstraction occurs solely from the formyl position.[24] The aryl radical in a similar manner attacks the weakest bond in formamide, the formyl C−H bond. We propose the free-radical mechanism displayed in Scheme 2 for the hydrodediazoniation in formamide.

Scheme 2



The hydrodediazoniations in the amide family of reagents share a number of common features. The most likely initiation for the radical reaction in amide solvents is through a linkage−homolysis pathway discussed in our earlier paper.[4] The solvent is the hydrogen source. In TMU and DMA, the hydrogen comes from the *N*-methyl position. In DMF, the hydrogen abstraction takes place at both the *N*-methyl and formyl positions, and in formamide the formyl position is the sole hydrogen atom source.

Conclusions

Careful review of the literature pertaining to hydrodediazoniations reveals that aryl radicals have often been proposed as intermediates in these reactions but this view has not gained full acceptance. The primary test employed iodoacetic acid as an aryl radical trap, and our results are consistent with the presence of aryl radicals in these reactions. The intermediacy of an aryl radical in the product-forming step was established by the fact that the yield of the intended product decreased in the presence of the trap which diverts the intermediate toward aryl iodide formation. Importantly, all hydrodediazoniation methods examined, whether or not a promoter was present, involve radical intermediates.

Experimental Section

General. Diazonium salts were made and purified by methods previously described.[4] All liquids were reagent grade and were used as purchased. Melting points are uncorrected.

Schiemann Reaction with Iodoacetic Acid as a Trap. 4-Bromobenzenediazonium tetrafluoroborate (0.100 g, 0.370 mmol) and iodoacetic acid (0.138 g, 0.740 mmol) were dissolved in 10 mL of CH_2Cl_2. The solution was placed on a steam bath and heated under reflux for 14 days. GC analysis showed that the reaction mixture contained 1-bromo-4-fluorobenzene produced in 30% yield and 1-bromo-4-chlorobenzene in 5% yield, the latter substance presumably formed by Swain's ionic mechanism.[8] No 1-bromo-4-iodobenzene was detected.

Hydrodediazoniation Using Hypophosphorous Acid.[25] H_3PO_2 (1.47 g, 11.1 mmol) and iodoacetic acid (0.275 g, 1.48 mmol) were dissolved in 5 mL of water and chilled in an ice−water bath. Solid 4-bromobenzenediazonium tetrafluoroborate (0.200 g, 0.740 mmol) was added gradually with stirring to the chilled solution. The reaction mixture was kept between 5 and 10 °C for 3 h, allowed to warm to rt, and then stirred

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overnight. 4-Bromoiodobenzene (0.070 g, 33%) was isolated by suction filtration.

Trapping Experiments: Hydrodediazoniations in Various Solvents with Iodoacetic Acid as a Trap. Iodoacetic acid (0.138 g, 0.740 mmol) was dissolved in 2 mL of solvent in a 5-mL flask equipped with a magnetic stirrer and a reflux condenser. Solid 4-bromobenzenediazonium tetrafluoroborate (0.100 g, 0.370 mmol) was added gradually with stirring. The reaction mixture effervesced immediately. After being heated on a steam bath for 10 min, the reaction mixture was allowed to cool to rt and poured into 30 mL of Et_2O. The ether solution was extracted with three 10-mL portions of 10% KOH and dried with $MgSO_4$. GC analysis showed that bromobenzene and 1-bromo-4-iodobenzene were produced in 22.9% and 53.3% yields, respectively.

Product Analysis. Products were identified by comparison of retention times with authentic samples. Naphthalene was added, after workup, as an internal quantitative standard. Yields were calculated, based upon the response factors found for equimolar amounts of naphthalene standard vs known amounts of bromobenzene and 1-bromo-4-iodobenzene. The reported yields are the average of at least two determinations.

In formamide, under similar conditions, 1-bromo-4-iodobenzene was the isolated solid product.

Trapping Experiments: General Procedure for Ferrocene-Initiated Hydrodediazoniations in Various Solvents. Iodoacetic acid (0.138 g, 0.740 mmol) and ferrocene (0.007 g, 0.037 mmol) were dissolved in 2 mL of solvent in a 5-mL flask equipped with a magnetic stirrer and a reflux condenser. Solid 4-bromobenzenediazonium tetrafluoroborate (0.100 g, 0.370 mmol) was added to the catalyst solution gradually with stirring. The reaction mixture turned blue and effervesced immediately. After being heated on a steam bath for 10 min, the reaction mixture was allowed to cool to rt and poured into 30 mL of Et_2O. The ether solution was extracted with three 10-mL portions of 10% KOH, dried with $MgSO_4$, and analyzed by GC. Results for various alcohols are presented in Table 2.

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