Table I. Products from the Crown Ether–Copper-Catalyzed Decomposition of Arenediazonium Fluoroborates

Reactant[a,b]	Registry no.	Reaction conditions	Products[d] (yields)[e]	Registry no.
2a	326-87-4	10 mol % **1**,[g] CH_2Cl_2, 30 min, 40 °C	**3a** (95%); **4a** (0)	372-18-9 (**3a**)
2b[c]	456-27-9	10 mol % **1**,[g] CH_2Cl_2, 30 min, 40 °C	**3b** (91%); **4b** (0)	58777-17-6 (**3b**)
2c	41136-80-5	10 mol % **1**,[g] CH_2Cl_2, 30 min, 40 °C	**3c** (93%); **4c** (0)	88-73-3 (**3c**)
2d	58801-43-7	10 mol % **1**,[g] CH_2Cl_2, 3 h, 40 °C	**3d** (17%); **4d** (60%)	71-43-2 (**3d**) 462-06-6 (**4d**)
2e	459-44-9	10 mol % **1**,[g] CH_2Cl_2, 3 h, 40 °C	**3e** (56%); **4e** (29%)	108-88-3 (**3e**) 352-32-9 (**4e**)
5	61702-20-3	10 mol % **1**,[g] CH_2Cl_2, 3 h, 40 °C	**6** (83%); **7** (6%)[f]	6009-10-5 (**6**) 61702-21-4 (**7**)

[a] All diazonium salts were prepared by standard techniques see ref 7. [b] Identity confirmed by comparison of physical properties with literature values and by IR, ^{1}H NMR, and elemental analyses. [c] The authors thank Dr. D. Mulvey for a sample of this compound. [d] Identity determined by isolation and VPC/mass spectrum. [e] Yields determined by VPC vs. standard. [f] Decomposition occurred upon attempted distillation. [g] Registry no., 16069-36-6.

interesting to note the lack of biaryl coupling products, despite the assumed presence of aryl radicals.

We are currently exploring the synthetic utility of these crown ether catalyzed decompositions in the generation of coupling and Sandmeyer type products. We anticipate that crown ethers may also facilitate other gas evolving decompositions, such as those involving diazomethane, α-diazo ketones, and *p*-toluenesulfonylhydrazones.

Experimental Section

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Analysis of the products of decomposition of the diazonium salts was carried out on a Hewlett-Packard 6830 gas chromatograph with use of an SP-2401 column.

Preparation of Diazonium Salts. All salts were prepared by standard techniques (ref 7). The only compound which was prepared for the first time was **5**, which had a decomposition point of 145–150 °C.

Arenediazonium Fluoroborate Decomposition. All salts were decomposed in identical fashion with the only variable being the heating period as shown in Table I. A representative procedure is given below for the decomposition of **2a**.

Decomposition of 2,4-Difluorobenzenediazonum Tetrafluoroborate (2a). A 100-mL round-bottom flask was charged with 1.33 g (5.9 mmol) of **2a**, 11 mL of methylene chloride, and 0.19 g (0.5 mmol) of dicyclohexyl-18-crown-6 (**1**) under a nitrogen atmosphere. With continuous nitrogen flow, 0.1 g of copper powder was added in one portion and the reaction mixture was heated at 40 °C for 15 min with magnetic stirring. The cooled reaction mixture was then filtered and analyzed by VPC to indicate that 1,3-difluorobenzene (**3a**) was the sole product in 95% yield vs. internal standard. A portion of the reaction mixture was distilled to give a pure sample of **3a**, which had boiling point, IR, and NMR identical with published values. Another portion of the reaction mixture was subjected to VPC/mass spectrum analysis, indicating a single peak at *m/e* 113, correct for **3a**.

Registry No.—Copper, 7440-50-8.

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Reduction of Aryldiazonium Compounds in Nonpolar Media

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Received November 8, 1976

While studying diazonium ion reactivity in nonpolar media, we required a convenient method for protodediazoniation (reduction) of these substances. In particular, the method had to afford high yields of reduction product at low temperatures in a short period of time and be applicable in such nonpolar media as chloroform and methylene chloride. Numerous methods are available for reduction of aryldiazonium salts (particularly chlorides) in aqueous media,[1] but these are commonly ineffective for reduction of BF_4^- and PF_6^- salts which are more stable than chlorides but much less soluble in water. Reducing systems which have been reported for the reduction of BF_4^- or PF_6^- salts include zinc in ethanol,[2] tributyltin hydride in tetrahydrofuran or diethyl ether and triethylsilane in acetonitrile,[3] rhodium complexes in dimethylformamide,[4] tetramethylurea,[5] sodium borohydride in methanol or dimethylformamide,[6] 1,4-dioxane in the presence of Cu_2O,[7] and 1,4-dioxane, tetrahydrofuran, 1,3-dioxolane, and 1,2-dimethoxyethane in aqueous sodium acetate.[8] Moreover, the potential of hypophosphorous acid for our requirements could be inferred from Lamm's observation[9] that 2-bromo-4,6-dichloro-, 2,4,5-trichloro-, and 2,4-dichloro-6-nitrobenzenediazonium tetrafluoroborates were reduced by 10 equiv of hypophosphorous acid in 5 M HCl in 83, 77, and 64% yields, respectively.

We wish to report that hypophosphorous acid[10] in chlorocarbon solution in the presence of trace cuprous oxide fulfills the conditions set forth above. Thus, excellent yields of reduction products were obtained in eight of the nine cases examined (see Table I). The single exception is *p*-methoxybenzenediazonium tetrafluoroborate, which undergoes reduction in only 67% yield. Apparently, electron-attracting substituents favor the reduction and mildly electron-releasing

Table I. Reduction of Diazonium Ions in Chloroform

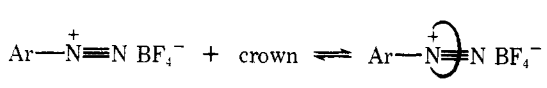
$$\mathrm{Ar{-}N{\equiv}N^+BF_4^-} \xrightarrow[\mathrm{Cu_2O}\atop \mathrm{CHCl_3}]{\mathrm{H_3PO_2}} \mathrm{ArH}$$

Diazonium tetrafluoroborate	Registry no.	Product[a]	% yield[b]	Registry no.
p-Bromobenzene-	673-40-5	Bromobenzene	99	108-86-1
o-Bromobenzene-	10448-07-4	Bromobenzene	99	
p-Chlorobenzene-	673-41-6	Chlorobenzene	97 (90)[c]	108-90-7
o-Chlorobenzene-	1956-97-4	Chlorobenzene	97	
2,4-Dichlorobenzene-	21872-70-8	*m*-Dichlorobenzene	97	541-73-1
p-Methylbenzene-	459-44-9	Toluene	99	108-88-3
3,4-Dimethylbenzene-	2192-34-9	*o*-Xylene	92	95-47-6
p-Methoxybenzene-	459-64-3	Anisole	67[e]/88[d]	100-66-3
p-Nitrobenzene-	456-27-9	Nitrobenzene	99	98-95-3

[a] The identities of products were confirmed by spectral analysis of samples obtained by preparative GLC. [b] Yields were determined by GLC using a 5 ft × 0.25 in. 10% SE-30 on Chromosorb P column utilizing an internal standard and are corrected for detector response. All yields represent at least four replicate experiments and are reproducible to ±2%. [c] Isolated yield. Reaction carried out on a 44-mmol scale using 7 equiv of H_3PO_2. [d] 0.075 equiv of 18-crown-6 added. [e] Extension of the reaction time to 3 h and addition of 14 equiv of H_3PO_2 did not alter the yield.

substituents do not appreciably hinder the reduction. The difficulty encountered in the latter case may be overcome by addition of a small amount of 18-crown-6 polyether.[11] When 0.075 equiv (7.5 mol %) of 18-crown-6 was added to the reducing mixture containing *p*-methoxybenzenediazonium tetrafluoroborate, the yield of reduction product was increased to 88%. It should be noted that neither in the presence or absence of crown were chlorinated or fluorinated by-products isolated.

We presume that the reduction involves aryl radical formation and hydrogen atom capture as proposed by Kornblum and co-workers some years ago.[9b] The crown effect is somewhat more difficult to explain. There are three obvious explanations we have considered. The first is that crown is enhancing the solubility of the diazonium salt, a now well-established phenomenon.[12] The second possibility is that the crown complexed diazonio function is more prone to reduction than the noncomplexed function, an unlikely prospect in light of the recent results reported for the Schiemann reaction.[13] The third possibility is that the crown and copper ion interact to enhance the reduction process. No increase in yield was observed, however, when 15-crown-5 was substituted for 18-crown-6. The smaller crown is of the appropriate size to



$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N\ BF_4^-} + \text{crown} \rightleftharpoons \mathrm{Ar{-}\overset{+}{N}{\equiv}N\ BF_4^-}$$

complex cuprous or cupric but not diazonium ion. The latter possibility therefore seems unlikely. We are currently considering the two aforementioned and other possibilities, although this in no way affects the efficacy of the method herein reported.

Experimental Section

The diazonium tetrafluoroborates were prepared by standard methods[14] from commercially available anilines. Hypophosphorous acid (50% aqueous, Fisher) was used as obtained. The chloroform used was ACS reagent grade, although substitution of carefully dried, alcohol-free reagent gave identical results.

Reduction Procedure.[15] To a stirred suspension of the diazonium tetrafluoroborate (1.5 mmol) in chloroform (10 mL) cooled in an ice water bath was added 0.80 mL (7.5 mmol) of H_3PO_2 and a few milligrams (trace) of Cu_2O. The mixture was stirred for 5 min, after which time Na_2CO_3 was added continuously until the pH was 8. The mixture was then washed with water and the aqueous layer backwashed with chloroform; the combined organic layers were filtered (if necessary), dried over sodium sulfate, and subjected to GLC analysis.

Acknowledgment. We warmly thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for grants which supported this work.

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Metal Ion Promoted Lactonizations

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Received September 28, 1976

The acid-catalyzed lactonization of hydroxy acids of fixed conformation has been a topic of considerable interest.[1] Alkyl substituents on the aromatic nucleus enhance lactonization rates of derivatives of **1**.[1d] The terms "stereopopulation control" [1b] and "trialkyl lock" [1e] have been applied to methylated