

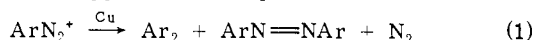
# Role of Radical and Organocopper Intermediates in Aromatic Diazonium Decomposition Induced by Cuprous Ion<sup>1a</sup>

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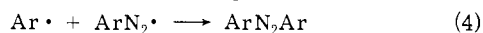
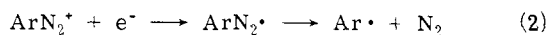
**Abstract:** When methyl iodide was used as a radical trap in the reaction of *p*-nitrobenzenediazonium tetrafluoroborate (**1**) with tetrakis(acetonitrile)copper(I) perchlorate in homogeneous acetone to produce 4,4'-dinitrobiphenyl (**2**) and 4,4'-dinitroazobenzene (**3**), it was found that *p*-iodonitrobenzene is formed at the expense of the dinuclear products (**2** and **3**), but that the ratio of the latter two remains essentially constant over a wide range of concentrations of methyl iodide. This finding is taken to indicate that aryl radicals are precursors of both **2** and **3**, and that the kinetic order in aryl radicals is identical for the production of **2** and **3**. The quantitative effect of methyl iodide in diverting the radicals from the production of dinuclear compounds leads to the conclusion that this order is between first and second. The effectiveness of radical traps in this system is methyl iodide > tetrahydrofuran > perdeuteriotetrahydrofuran > acetone; the latter three traps yield nitrobenzene. With a given radical trap, the ratio of atom transfer to dinuclear product formation increases with decreasing concentration of copper(I). In view of the effect of added methyl iodide and of the isotope effect for hydrogen transfer, this behavior is thought to result from cuprous ion mediated conversion of aryl radicals to dinuclear products. The ratio of biaryl to azoarene increases with increasing concentrations of diazonium and cupric ion and with decreasing concentrations of cuprous ion. A mechanism consistent with these facts involves the reversible reaction of an aryl radical with copper(I) followed by reaction of the resulting arylcopper(II) intermediate with another aryl radical to produce the key diarylcopper(III) species **5**. The latter can split out copper(I) to form the biaryl in a reductive elimination step, or it can become reversibly reduced by copper(I) to a diarylcopper(II) which, in turn, can be irreversibly reduced to an organocopper(I) compound capable of combining with diazonium ion to produce azoarene. Either diazonium or copper(II) ions are capable of reoxidizing the diarylcopper(II) intermediate to the diarylcopper(III) species. Apparent trapping of an organocopper intermediate by protonation with acids and by methylation and phenylation with methyl iodide and iodobenzene, respectively, lends support to this novel scheme which appears to be the simplest mechanism capable of explaining all known facts about this type of reaction.

Symmetrical biaryls and azoarenes are frequently major products of the reaction of aromatic diazonium ions with copper metal or copper(I) salts (eq 1).<sup>2-8</sup> It has been estab-

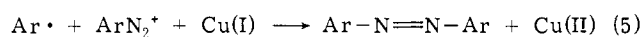


lished that the two nitrogen atoms of the azoarene are derived from a single diazonium ion<sup>9</sup> and that the new carbon-nitrogen and carbon-carbon bonds are formed at the carbon atom(s) formerly bearing the diazonium function.<sup>2-9</sup>

Although there has been a great deal of discussion of possible mechanisms for these couplings, very little convincing evidence is available. Many other copper-induced diazonium decompositions, such as the Sandmeyer, Meerwein, Pschorr and related reactions almost certainly proceed by free aryl radicals<sup>2,3,10-16</sup> which are produced by one-electron reduction of the diazonium ion and rapid decomposition of the resulting diazo radical (eq 2).<sup>17</sup> The mechanistic problem is particularly challenging since most of the interesting action apparently occurs in rapid steps following the rate-determining formation of aryl radicals.

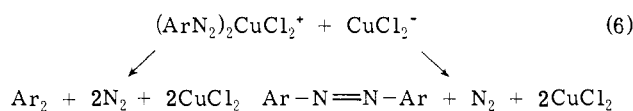


Probably because of the general acceptance of radical intermediates in copper-induced diazonium decomposition, the most frequently cited mechanism for biaryl production is the coupling of two aryl radicals (eq 3).<sup>5-7,8b,11,18</sup> Similarly, azoarene formation has been viewed as proceeding by the coupling of aryl and diazo radicals (eq 4);<sup>5,6</sup> an alternative mode of azoarene formation, involving the reaction of an aryl radical with a diazonium ion in the presence of a cuprous ion, has also been suggested (eq 5).<sup>4,11,12c,18,19</sup>

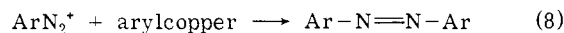


Cowdrey and Davies<sup>3</sup> proposed a nonradical scheme for

the production of biaryl and azoarene during Sandmeyer reactions. The salient feature of their proposal is the reduction by Cu(I) of a molecular complex,  $(\text{ArN}_2)_2\text{CuCl}_2^+$  (eq 6).



Cohen and Lewin recently advocated a reaction path involving arylcopper intermediates formed by the reaction of aryl radicals with Cu(I) (eq 7 and 8).<sup>20-22</sup> The oxidation



state of the copper in the organometallic was not specified since the arylcopper(II) derivative which would result from reaction of an aryl radical with a copper(I) species could undergo changes in oxidation state by subsequent reactions.<sup>23</sup> Arylcopper(I) compounds are known to self-couple both in the absence and, more rapidly, in the presence of an oxidizing agent<sup>22</sup> (a diazonium ion is an effective oxidizing agent<sup>17</sup>). The same intermediates could conceivably be involved in azoarene formation; not only have Grignard and organozinc compounds been reported to yield azo compounds upon treatment with diazonium salts,<sup>28</sup> but a case of an arylcopper(I) adding to a diazonium ion to produce azoarene has recently been observed.<sup>29</sup> The attractive feature of the arylcopper hypothesis is that it avoids the necessity of postulating the bimolecular reaction of two phenyl radicals, extremely reactive species which are presumably never present in substantial concentrations; it also avoids bypassing radicals altogether as in the Cowdrey-Davies<sup>3</sup> scheme.

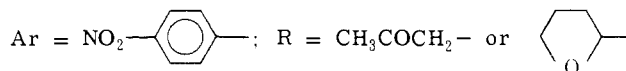
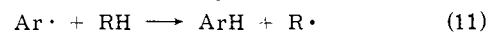
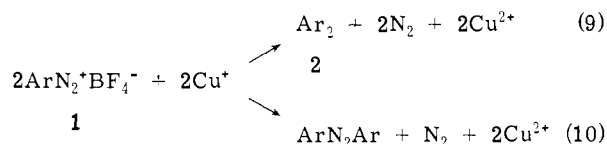
In this paper, we present evidence that in the copper(I)-induced decomposition of *p*-nitrobenzenediazonium tetrafluoroborate (**1**), aryl radicals are precursors of both 4,4'-

dinitrophenyl (**2**) and 4,4'-dinitroazobenzene (**3**) but that the biaryl is not formed by radical coupling. Evidence for an arylcopper intermediate in this reaction is also presented.

## Results

The decomposition of *p*-nitrobenzenediazonium tetrafluoroborate (**1**) was performed in a homogeneous solution consisting of tetrakis(acetonitrile)copper(I) perchlorate,  $(\text{CH}_3\text{CN})_4\text{Cu}^+\text{ClO}_4^-$ , dissolved in acetone containing a very small but known quantity of water; in the absence of the trace of water, the decomposition of the diazonium ion is slow and incomplete. At the concentrations used, about equal quantities of 4,4'-dinitrophenyl (**2**) and 4,4'-dinitroazobenzene (**3**) are produced, and, aside from a trace of nitrobenzene, no other products were observed (eq 9 and 10; Table I). Since cupric ion must be formed upon reduction of

expense of that of azo compound. The last entry in Table I indicates that in the presence of a strong acid nitrobenzene becomes a significant product.



**Table I.** Reaction of *p*-Nitrobenzenediazonium Fluoroborate with Tetrakisacetonitrilecopper(I) Perchlorate in Acetone in the Presence of Copper(II) Perchlorate, Water, or Perchloric Acid<sup>a</sup>

| Cu-<br>(ClO <sub>4</sub> ) <sub>2</sub> ·<br>4H <sub>2</sub> O,<br>mmol | Product composition, % <sup>b</sup> |                     |            | Yield,<br>% <sup>b</sup> |
|---|-------------------------------------|---------------------|------------|--------------------------|
|   | Ar <sub>2</sub>                     | ArN <sub>2</sub> Ar | ArH        |                          |
| 0   | 49.9 ± 1.0                          | 50.1 ± 1.0          | Trace      | 90.2                     |
| 1.0   | 75.2 ± 0.3                          | 24.8 ± 0.3          | Trace      | 80.7                     |
| 3.5   | 81.7 ± 0.5                          | 18.3 ± 0.5          | Trace      | 63.2 <sup>c</sup>        |
| 0 <sup>d</sup>  | 75.1 ± 1.4                          | 24.9 ± 1.3          | Trace      | 73.7                     |
| 0 <sup>e</sup>  | 52.5 ± 3.4                          | 11.8 ± 0.4          | 35.7 ± 1.0 | 100.4                    |

<sup>a</sup> All experiments were conducted using 0.50 mmol of diazonium salt, 1.5 mmol of tetrakis(acetonitrile)copper(I) perchlorate, and 30 ml of acetone containing 0.044 mmol of water. <sup>b</sup> Determined by comparison of the glpc peak areas with that of a standard; Ar = *p*-nitrophenyl. Reactions were performed in duplicate and sometimes in triplicate. Average deviations in product composition are given. <sup>c</sup> In this experiment, the product ratio was highly reproducible, but the absolute yields varied inexplicably from run to run. <sup>d</sup> In the presence of 18.4 mmol of water. <sup>e</sup> In the presence of 5.0 mmol of HClO<sub>4</sub> as a 70% aqueous solution.

the diazonium ion with copper(I), the effect of the concentration of cupric ion at a constant concentration of copper(I) was investigated by performing the reaction in the presence of different quantities of the tetrahydrate of cupric perchlorate. It is seen (Table I) that the latter reagent causes an increase in the ratio of biaryl to azoarene, but it is not clear to what extent this ratio change is caused by the water of hydration and to what extent by copper(II); water, albeit in a greater quantity than is present as water of hydration in entry 2 of Table I, causes a similar change in this ratio (see fourth entry). It thus appears likely that both water and cupric ion cause an increase in the yield of biaryl at the

Table II summarizes the effect on product composition of varying the concentration of cuprous ion and of adding the hydrogen atom donor tetrahydrofuran (THF) and the iodine atom donor methyl iodide.<sup>30</sup> In the absence of the added radical traps, lowering the concentration of copper(I) increases the ratio of biaryl to azoarene and increases the yield of nitrobenzene, presumably formed by hydrogen atom abstraction from the poor donor acetone (eq 11). Such hydrogen atom abstraction from acetone only becomes significant at concentrations of copper(I) below about 0.03 *M*.

At a concentration of cuprous ion (0.025 *M*) which results in the production of 7.7% nitrobenzene when acetone alone is the solvent, 30% of nitrobenzene is produced when a very small quantity of the far better hydrogen atom donor tetrahydrofuran is present in the acetone solution.<sup>31</sup> The view that in this experiment the nitrobenzene arises mainly by hydrogen atom donation from the tetrahydrofuran to a *p*-nitrophenyl radical and to some extent by such donation from acetone (eq 11) is supported by the isotope effect and tracer experiment in which perdeuteriotetrahydrofuran was used; the yield of nitrobenzene decreased sharply owing to an isotope effect, and the resulting nitrobenzene was monodeuterated to the extent of 38.1%. It is evident that in the presence of perdeuteriotetrahydrofuran, a minimum of 38% of the nitrobenzene is produced by reduction of the aryl radical by THF (any protium impurity in the labeled THF in combination with an isotope effect could raise this figure) and the remainder by similar reduction by acetone; in the case of protium THF the figure would, of course, be much larger. The significance of the isotope effect is discussed below.

The view that typical radical behavior becomes more evident the lower the concentration of copper(I) is reinforced by the results of experiments in which the diazonium ion was decomposed by cuprous ion present in varying concentrations in an acetone solution containing the iodine atom donor methyl iodide<sup>30</sup> (Table II). Even at concentrations of

**Table II.** Effects of the Concentration of Tetrakis(acetonitrile)copper(I) and of Radical Traps in Decomposition of *p*-Nitrobenzenediazonium Fluoroborate in Acetone<sup>a</sup>

| Reagents, mmol |                                  | Product composition, % <sup>b</sup> |                     |                         | ArI        | Yield, % <sup>b</sup> |
|----------------|----------------------------------|-------------------------------------|---------------------|-------------------------|------------|-----------------------|
| Cu(I)          | Additive                         | Ar <sub>2</sub>                     | ArN <sub>2</sub> Ar | ArH                     |            |                       |
| 1.5            |                                  | 49.9 ± 1.0                          | 50.1 ± 1.0          | Trace                   |            | 90.2                  |
| 1.0            |                                  | 54.0 ± 0.4                          | 46.0 ± 0.6          | Trace                   |            | 74.2                  |
| 0.75           |                                  | 57.0 ± 0.8                          | 35.3 ± 1.1          | 7.7 ± 0.2               |            | 83.2                  |
| 0.50           |                                  | 54.3 ± 5.1                          | 28.2 ± 3.0          | 17.6 ± 2.0              |            | 81.5                  |
| 0.75           | 25 (THF)                         | 40.0 ± 0.4                          | 30.0 ± 1.1          | 30.0 ± 1.5              |            | 93.8                  |
| 0.75           | 25 (THF- <i>d</i> <sub>5</sub> ) | 49.2 ± 0.4                          | 34.9 ± 0.9          | 15.9 ± 0.5 <sup>c</sup> |            | 81.3                  |
| 1.5            | 5 (MeI)                          | 48.2 ± 0.4                          | 36.4 ± 0.4          | Trace                   | 15.4 ± 0.1 | 79.5                  |
| 1.0            | 5 (MeI)                          | 44.1 ± 0.6                          | 30.0 ± 0.6          | Trace                   | 26.0 ± 0.0 | 73.1                  |
| 0.50           | 5 (MeI)                          | 29.8 ± 1.2                          | 19.8 ± 2.3          | 9.6 ± 0.1               | 41.8 ± 0.2 | 82.6                  |

<sup>a</sup> All experiments were conducted using 0.50 mmol of diazonium salt in 30 ml of acetone containing 0.044 mmol of water. <sup>b</sup> Determined by comparison of glpc peak areas with that of a standard; Ar = *p*-nitrophenyl. <sup>c</sup> Monodeuterated to the extent of 38.1%; determined by combined glpc-mass spectrometry.

**Table III.** Decomposition of *p*-Nitrobenzenediazonium Fluoroborate in Solutions Containing Varying Concentrations of Cuprous and Cupric Ions

| Rel concn <sup>a</sup><br>Cu(I):Cu(II):ArN <sub>2</sub> <sup>+</sup> | Product distribution, % <sup>b</sup> |                     |                                      | Yield, % <sup>c</sup> |
|--|--------------------------------------|---------------------|--------------------------------------|-----------------------|
|  | Ar <sub>2</sub>                      | ArN <sub>2</sub> Ar | Ar <sub>2</sub> /ArN <sub>2</sub> Ar |                       |
| 20:0:1.0   | 74.8 ± 0.8                           | 25.2 ± 0.8          | 3.0                                  | 99.0 ± 0.3            |
| 20:4.0:1.0   | 76.9 ± 0.1                           | 23.1 ± 0.1          | 3.3                                  | 92.7 ± 5.7            |
| 10:8.0:1.0   | 90.2 ± 1.8                           | 9.8 ± 1.8           | 9.2                                  | 62.1 ± 2.3            |
| 5:4.0:1.0  | 94.6 ± 0.9                           | 5.4 ± 0.1           | 17.5                                 | 82.8 ± 10.6           |
| 5:16:1.0   | 100 ± 2                              | <2                  | >50                                  | 81.7 ± 10.0           |

<sup>a</sup> All experiments were conducted using 0.13 mmol of *p*-nitrobenzenediazonium fluoroborate and the appropriate molar amounts of tetrakis(acetonitrile)copper(I) perchlorate and cupric perchlorate tetrahydrate in 70 ml of a 0.75 vol % acetonitrile solution in acetone containing 0.11 mmol of deionized water. Ar = *p*-nitrophenyl. <sup>b</sup> Each experiment was performed in duplicate and analyzed by glpc; the average deviation is given after each normalized yield. <sup>c</sup> The actual yields were determined from the ratio of peak areas of product to standard.

**Table IV.** Effects on Products of Decomposition of *p*-Nitrobenzenediazonium Fluoroborate of Varying the Concentration of Methyl Iodide

| CH <sub>3</sub> I, ml <sup>a</sup> | Product distribution, % <sup>b</sup> |                 |                     | Ar <sub>2</sub> /ArN <sub>2</sub> Ar | ArI/(Ar <sub>2</sub> + ArN <sub>2</sub> Ar) | Yield, % <sup>c</sup> |
|------------------------------------|--------------------------------------|-----------------|---------------------|--------------------------------------|---|-----------------------|
|                                    | ArI                                  | Ar <sub>2</sub> | ArN <sub>2</sub> Ar |                                      |   |                       |
| 0.0                                | 0.0                                  | 76.9 ± 0.1      | 23.1 ± 0.1          | 3.33                                 | 0   | 92.7 ± 5.7            |
| 1.0                                | 26.8 ± 2.4                           | 55.5 ± 2.0      | 17.7 ± 0.1          | 3.12                                 | 0.37  | 90.7 ± 7.9            |
| 2.0                                | 49.9 ± 1.3                           | 37.8 ± 0.9      | 12.3 ± 0.1          | 3.08                                 | 1.0   | 87.3 ± 4.1            |
| 4.0                                | 75.4 ± 3.9                           | 18.4 ± 2.5      | 6.2 ± 1.2           | 2.98                                 | 3.1   | 82.1 ± 14.5           |

<sup>a</sup> All experiments were conducted using 0.13 mmol of *p*-nitrobenzenediazonium fluoroborate, 2.60 mmol of tetrakis(acetonitrile)copper(I) perchlorate, and 0.51 mmol of cupric perchlorate tetrahydrate. The specified amount of methyl iodide was used and diluted to 70 ml with a 0.75 vol % acetonitrile solution of acetone containing 0.111 mmol of deionized water. Ar = *p*-nitrophenyl. <sup>b</sup> Each experiment was performed in duplicate and analyzed by glpc; the average deviation is given after each normalized yield. <sup>c</sup> The actual yields were determined from the ratio of peak areas of product to standard.

cuprous ion (0.05 and 0.033 *M*) at which no hydrogen atom abstraction occurs from acetone, significant quantities of *p*-nitroiodobenzene are produced in the presence of a small concentration of methyl iodide, and as the copper(I) concentration declines, the yield of the aryl iodide increases at the expense of that of the dinuclear products **2** and **3**. At the lowest concentration of copper(I) studied, 42% of the product consists of aryl iodide.

The results of the foregoing experiments indicate that the ratio of biaryl to azoarene produced depends on the concentration of both copper(I) and copper(II), and since the former is converted to the latter as the reaction proceeds, it is evident that the product ratio will vary throughout a given experiment. More importantly, any additive which changes the degree of cuprous ion oxidation during a reaction will lead to a change in the ratio of dinuclear products by this second-order effect, quite aside from the effect of the additive directly on the mechanism of formation of these products. For this reason, the changes that occur in the ratio of dinuclear products in the presence of additives are quite difficult to interpret. In order to avoid this problem, the experiments described below were conducted in solutions which were essentially buffered in both copper(I) and copper(II). This was accomplished by utilizing a quantity of solution and a concentration of copper ions such that the molar ratios of both types of copper ions to diazonium ions were high enough to preclude very substantial changes in the ratio of Cu(I):Cu(II) during the course of a reaction. Since at the higher concentrations of copper(I) the reaction rate was exceedingly rapid, a small quantity (0.75 vol %) of acetonitrile was added to the acetone solvent in order to moderate the reaction and ensure that no significant fraction of reaction would occur during the mixing process.

It can be seen that under these conditions an increase in the concentration of copper(II) perchlorate tetrahydrate at constant copper(I) concentration still causes an increase in the ratio of biaryl to azoarene and that this effect is most significant at relatively low concentrations of cuprous ion (Table III; entries 1, 2, 4, and 5). At constant copper(II) concentration, quadrupling the concentration of tetrakis(a-

acetonitrile)copper(I) perchlorate leads to a 5.3-fold decrease in the yield ratio of biaryl to azoarene (Table III, entries 2 and 4).

Utilizing the buffering technique, it became possible to determine the relative sensitivity to aryl radical trapping of biaryl and azoarene production and also the dependence of the degree of trapping on methyl iodide concentration. The relative yields of biaryl, azoarene, and aryl iodide as a function of methyl iodide concentration were monitored. The results (Table IV) indicate that the increase in the yield of *p*-iodonitrobenzene resulting from an increase in the concentration of methyl iodide occurs almost equally at the expense of biaryl and azoarene. The very small decrease in the ratio of biaryl to azoarene which occurs as the methyl iodide concentration increases can almost certainly be accounted for by the dilution of acetonitrile in the solvent by the methyl iodide; it was found in preliminary experiments that increased concentrations of acetonitrile in the solvent favor biaryl production.<sup>33</sup> Under conditions in which 75% of the product is *p*-iodonitrobenzene, the ratio of biaryl to azoarene only differs by about 5% from that observed under conditions in which only 27% of the product is the aryl iodide (Table IV). The ratio of aryl iodide to dinuclear compounds produced is not directly proportional to the methyl iodide concentrations; doubling the latter results in a threefold increase in this ratio, quadrupling the concentration in a ninefold increase. The possibility that the aryl iodide is produced not by abstraction of iodine atoms by aryl radicals but by reaction of the diazonium ion with a reaction product (*e.g.*, CuI) of methyl iodide and cuprous ion<sup>34</sup> was tested in two ways. (1) A solution of tetrakis(acetonitrile)copper(I) perchlorate in acetone containing 0.75 vol % acetonitrile and methyl iodide did not promote the generation of copper(II) ions (esr) over a period of 1 hr (or even after 3 days) at room temperature.<sup>34</sup> (2) A solution identical with that used for the experiments in Table IV but lacking the diazonium salt was maintained at room temperature for 1 hr, it was evaporated to dryness under nitrogen (in order to remove methyl iodide), and the residue was mixed with a solution identical with that used in Table IV but lacking

Table V. Effects of Varying the Concentration of *p*-Nitrobenzenediazonium Fluoroborate and of Adding *m*-Dinitrobenzene (DNB)

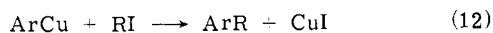
| Rel concn <sup>a</sup><br>ArN <sub>2</sub> <sup>+</sup> :<br>DNB | Product distribution <sup>b</sup> |                     | Ar <sub>2</sub> /<br>ArN <sub>2</sub> Ar | Yield, % <sup>c</sup> |
|--|-----------------------------------|---------------------|--|-----------------------|
|  | Ar <sub>2</sub>                   | ArN <sub>2</sub> Ar |  |                       |
| 2.0:0  | 85.8 ± 0.3                        | 14.2 ± 0.3          | 6.04                                     | 90.8 ± 10.7           |
| 1.0:0  | 76.9 ± 0.1                        | 23.1 ± 0.1          | 3.33                                     | 92.7 ± 5.7            |
| 0.25:0   | 57.8 ± 0.1                        | 40.2 ± 1.5          | 1.44                                     | 73.6 ± 7.1            |
| 1.0:4.0  | 81.7 ± 1.8                        | 18.3 ± 1.8          | 4.46                                     | 80.9 ± 5.1            |

<sup>a</sup> All experiments were conducted using 2.6 mmol of tetrakisacetonitrilecopper(I) perchlorate, 0.51 mmol of cupric perchlorate tetrahydrate, and the appropriate molar quantities of diazonium salt and DNB in 70 ml of a 0.75 vol % acetonitrile solution in acetone containing 0.11 mmol of deionized water. Ar = *p*-nitrophenyl. A relative concentration of 1.0 represents 0.13 mmol of the substance dissolved in 70 ml of solvent. <sup>b</sup> Each experiment was performed in duplicate and analyzed by glpc; the average deviation is given after each normalized yield. <sup>c</sup> The actual yields were determined from the ratio of peak areas of product to standard.

methyl iodide and copper salts; after 1 hr at room temperature, no *p*-iodonitrobenzene was generated, indicating that the residue did not contain a copper iodide salt capable of converting the diazonium salt to the aryl iodide.

The results of experiments in which the concentration of diazonium salt was varied are presented in Table V. The naive expectation that higher concentrations of diazonium salt would favor azoarene production is clearly not fulfilled; indeed it is evident that the yield ratio of biaryl to azoarene increases significantly as the concentration of diazonium salt increases. In order to test the hypothesis that the diazonium salt behaves as an oxidizing agent toward an organocopper intermediate, another, probably somewhat weaker oxidizing agent, *m*-dinitrobenzene, was added to the reaction mixture; this additive did indeed appear to cause a noticeable increase in the ratio of biaryl to azoarene (Table V).

A characteristic reaction of arylcopper(I) compounds is coupling with alkyl and aryl halides (eq 12).<sup>22</sup> No such coupling occurred in the experiments described above in which methyl iodide was present, and acetone was the solvent. However, some coupling was observed with both methyl iodide and iodobenzene in acetonitrile solution (Table VI). In these experiments, the cuprous perchlorate was generated by the reduction of the hydrated cupric salt by copper metal and a considerable excess of the latter was added in order to suppress the formation of *p*-nitrophenol; the phenol probably results<sup>13c,37</sup> from the oxidation of aryl radicals by cupric salt (generated by the oxidation of copper(I) by diazonium ion), and the concentration of the latter was minimized by the presence of copper metal which reduces the copper(II) to copper(I). The results in Table VI indicate that ca. 15–17% of the product is coupled material, but that the major products are 4,4'-dinitrophenyl and *p*-iodonitrobenzene.



## Discussion

The results of experiments in homogeneous, mainly acetone, solution which are summarized in Tables I–V reveal a great deal about the mechanisms involved. Perhaps the most significant result is that the ratio of biaryl to azoarene produced is independent of the concentration of the radical trap methyl iodide (Table IV), whereas the presence of the latter or of another radical trap, tetrahydrofuran, results in a marked reduction in the yields of both of these products (Tables II and IV). This indicates not only that aryl radicals are precursors of both dinuclear products, but that the order in aryl radicals is the same for the production of biaryl as for that of azoarene. These results rule out, at least in this system, the Cowdrey–Davies mechanism<sup>3</sup> for biaryl production since it does not involve radical precursors. Also incompatible with this mechanism is the finding that the concentrations of copper(I) and copper(II) influence the relative yields of biaryl and azoarene since, according to this mechanism, a common intermediate is reduced by copper(I) to both dinuclear products.

Furthermore, the finding that the production of both biaryl and azoarene is of the same order in aryl radicals clearly contradicts those literature mechanisms which involve radical precursors (see above) since, according to these mechanisms, biaryl production would be second order and azoarene production first order in aryl radicals. An indication of the actual order in aryl radicals is obtained by noting the threefold increase in the ratio of aryl iodide to dinuclear product which occurs when the methyl iodide concentration is doubled (Table IV). If it is assumed that each methyl iodide molecule which reacts destroys one aryl radical and produces one molecule of *p*-iodonitrobenzene,<sup>38</sup> then one must conclude that the order in aryl radicals is neither first nor second but is between these values.

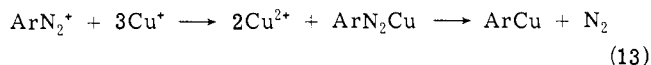
Another significant result is that the yields of atom abstraction products decrease, and those of the dinuclear products increase with increasing concentration of cuprous ion. This is consistent with the finding by Pfeil and Velten<sup>10b</sup> and by Cowdrey and Davies<sup>3</sup> that the formation of azoarene is of an order one higher in copper(I) chloride than formation of aryl chloride in the reaction of toluenediazonium ions with cuprous chloride; the production of aryl chloride results from chlorine atom abstraction from copper(II) chloride by the aryl radical.<sup>11,12</sup> We can conceive of three possible explanations of this phenomenon: (1) the higher the cuprous ion concentration, the higher the rate of diazonium ion decomposition and the concentration of aryl radicals. Higher concentrations of aryl radicals favor coupling (eq 3), which would be second order in aryl radicals, over atom abstraction, which would be first order in aryl radicals. This explanation can be rejected on the grounds that biaryl production has been shown to be less than second order in aryl radicals as indicated above. It may be significant in this respect that we have been unable to find an example of biaryl production in the radical decomposition of diazonium ions in the absence of copper except when biaryl production can be explained by substitution of an

Table VI. Reaction of *p*-Nitrobenzenediazonium Fluoroborate with Cuprous Perchlorate in Acetonitrile in the Presence of Methyl Iodide or Iodobenzene

| ArN <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup> | Reagents, mmol <sup>a,b</sup> |                                 |     |                                 | Product composition, % <sup>b,c</sup> |                     |     |     |      |                                 |
|--|-------------------------------|---------------------------------|-----|---------------------------------|---------------------------------------|---------------------|-----|-----|------|---------------------------------|
|  | Cu                            | CuClO <sub>4</sub> <sup>d</sup> | MeI | C <sub>6</sub> H <sub>5</sub> I | Ar <sub>2</sub>                       | ArN <sub>2</sub> Ar | ArH | ArI | ArMe | ArC <sub>6</sub> H <sub>4</sub> |
| 1.0  | 36                            | 28                              | 10  |                                 | 22                                    | 4                   | 4   | 56  | 15   |                                 |
| 1.0  | 86                            | 28                              |     | 10                              | 67                                    | 6                   | 3   | 25  |      | 17                              |

<sup>a</sup> Reactions performed in 25 ml of acetonitrile. <sup>b</sup> Ar = *p*-nitrophenyl. <sup>c</sup> By glpc utilizing an internal standard and uncalibrated flame ionization detectors. <sup>d</sup> Generated *in situ* by reduction of 14 mmol of cupric perchlorate tetrahydrate by copper powder.

aryl radical into an arene generated by reduction of the diazonium ion;<sup>8a</sup> this suggests a role for copper in mediating the coupling of aryl radicals. (2) Aryl radicals, although produced at low concentrations of copper(I), are bypassed at high concentrations as, for example, by a two-electron reduction of the diazonium ion to the copper salt of a diazene which could continue on to an arylcopper and thence to one



or both dinuclear products. (3) Aryl radicals are diverted to one or both of the dinuclear products by copper(I). The latter explanation appears more likely than (2) in view of the considerable increase in hydrogen atom donation that occurs when a small quantity of the excellent hydrogen atom donor tetrahydrofuran is present in the acetone, but the latter result could conceivably be due to a solvent effect; the THF may stabilize one of the copper species present. However, (3) is verified by the results of the deuterium isotope effect observed when the tetrahydrofuran is replaced with perdeuteriotetrahydrofuran. Only if the aryl radical has the choice of removing a hydrogen atom or proceeding to the dinuclear products will a decrease in nitrobenzene result from the replacement of hydrogen with the more difficultly removed deuterium in the THF. If (2) were correct, the extent of radical behavior would be dependent only on the concentration of copper(I).

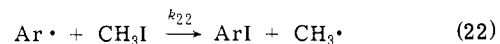
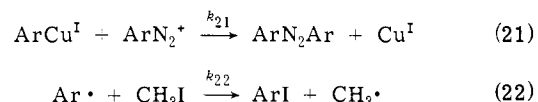
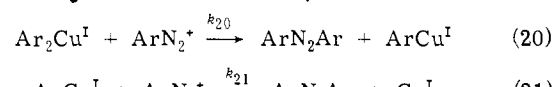
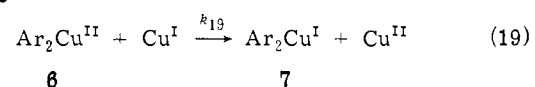
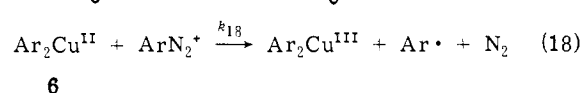
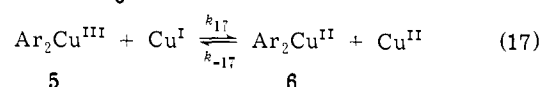
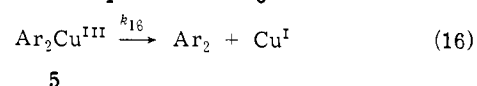
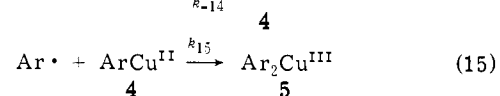
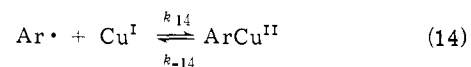
Confirmation of this view is found in the results of experiments in which methyl iodide is present. When the concentration of copper(I) is 1.0 or 1.5 mmol in 30 ml of solution, practically no hydrogen atom abstraction is observed from acetone, but when methyl iodide is present, the aryl iodide is produced in significant amounts (Table II); obviously, the abstraction of an iodine atom from methyl iodide is substantially more facile than that of a hydrogen atom from acetone. Since a typical radical abstraction process is made manifest by the presence of the iodine atom donor and not by the poorer atom donor acetone, it is clear that the radicals must be capable of either atom abstraction or dinuclear product formation. Once again, the atom abstraction reaction becomes more prominent as the cuprous ion concentration is decreased. It can thus be concluded that cuprous ions somehow mediate the conversion of *p*-nitrophenyl radicals to the dinuclear products. It is of interest in this respect that the production of symmetrical biaryl in copper-induced diazonium decomposition only occurs in those cases in which the copper(I) concentration is substantial; this is especially noticeable in aqueous systems in which ligands such as chloride,<sup>3,4</sup> ammonia,<sup>5-7</sup> and pyridines<sup>8b</sup> are required, presumably to stabilize the copper(I) enough for it to exist.

Any satisfactory mechanism must explain the following facts. (1) Both of the dinuclear products have radical precursors. (2) The production of both dinuclear products is of the same order, between first and second, in aryl radicals. (3) The conversion of the latter to one or both of the dinuclear products is mediated by cuprous ion. (4) Higher concentrations of cuprous ion favor azoarene over biaryl production, and there is some indication (Table III) that the ratio of azoarene to biaryl produced is dependent on a power of the cuprous ion concentration that is greater than 1 but less than 2. (5) Higher concentrations of copper(II) and diazonium ions favor the production of biaryl over that of azoarene; the sensitivity to the concentration of copper(II) is greater the lower the concentration to copper(I).

It is difficult to imagine how copper(I) could mediate dinuclear product formation without the intervention of arylcopper intermediates. There are several further pieces of evidence that such intermediates are present in the reaction mixtures. (1) In the presence of carboxyl-deuterated acetic

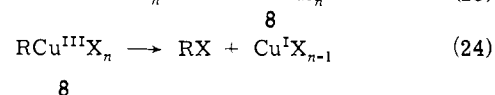
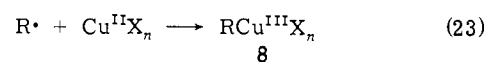
acid, a substantial yield of nitrobenzene, which is about one-half monodeuterated, is produced; the high O-H bond strength precludes hydrogen atom removal from the carboxyl group, and thus the protolysis of an organocopper intermediate is indicated as the process which produces at least one-half of the nitrobenzene. Evidence for organocopper intermediates in closely related systems has recently been presented.<sup>39</sup> (2) Nitrobenzene is formed in substantial yield in the presence but not in the absence of a small amount of perchloric acid when the diazonium salt is decomposed in acetone containing tetrakis(acetonitrile)copper(I) ions (last entry, Table I). (3) An intermediate can be methylated or phenylated, respectively, when the diazonium salt is decomposed in acetonitrile containing copper(I) and copper metal in the presence of methyl iodide or iodobenzene (Table VI).

The simplest mechanistic scheme which accounts for all our data is shown in eq 14-22 (ligands, which are certainly present, are omitted from these equations)



The data strongly indicate that the aryl radicals react with cuprous ions to form an organocopper. Equation 14, expressing this concept, is analogous to the reduction of organic radicals by several transition metal ions in their low oxidation states, a process believed to occur by organometallic intermediates.<sup>27b</sup>

Equation 15 is identical in principle with the extremely facile combination of organic radicals with various copper(II) species to form organocopper(III) intermediates (8, eq 23).<sup>27b</sup> In the oxidation of radicals by copper(II) chloride, part of the reaction is believed to proceed by an intermediate such as 8 (X = Cl) and the other part by the direct transfer of a chlorine atom from the coordination sphere of the copper(II) ion to the radical.<sup>27</sup> However, we prefer to view the complete reaction as proceeding by 8 which, in the case of an appropriate R group, can dissociate to a carbonium ion and which, when R does not form a stable carbonium ion, can collapse to RX and a copper(I) salt (eq 24).



Both of these reactions are examples of reductive elimination,<sup>41a</sup> the reverse of oxidative addition;<sup>41b</sup> many examples

of analogous reactions exist.<sup>41</sup> A similar collapse (reductive elimination) of **5** would yield biaryl and a copper(I) species (eq 16). The explanation for the identical order in aryl radicals for the production of both biaryl and azoarene is now seen to be that the organocopper(III) intermediate **5** is a common precursor with no further intervention of aryl radicals; the kinetic order in phenyl radicals will then be that for the production of **5**. If eq 14 were irreversible, the Ar-Cu<sup>II</sup> could only proceed on to dinuclear products, and thus the production of both would be first order in aryl radicals. By allowing some reversibility in eq 14, the order between first and second in aryl radicals becomes understandable.<sup>42</sup>

In competition with this reductive elimination by **5** (eq 16) is a reversible reduction of **5** by cuprous ion to an unstable diarylcopper(II) species **6** which, besides being reoxidizable to **5** by copper(II)<sup>43</sup> or by diazonium ions (eq 18), can be converted by subsequent transformations to azoarene. In order to avoid having the diazonium ion enter into the conversion of aryl radicals to azoarene in a first-order fashion, it is necessary for the diarylcopper(II) (**6**) to be irreversibly converted to an intermediate which can react with diazonium ion to produce azoarene. This intermediate (**7**, eq 19) is written here as an organocopper(I) species since these are known to add in this fashion to diazonium ions,<sup>29</sup> and any other type of intermediate is difficult to formulate. The specific assignment of the intermediate **7** as a diarylcuprate<sup>22,44</sup> is based on the data in Table III; however, since at present these data are rather scanty, we cannot completely rule out an alternative reaction, the fragmentation of **6** to Ar· and ArCu.<sup>45</sup>

According to this scheme, cuprous ions favor azoarene production by reducing the arylcopper(III) (**5**), which would otherwise produce biaryl, as well as by reducing the resulting organocopper(II) to **7**. On the other hand, oxidizing agents such as copper(II), *m*-dinitrobenzene, or a diazonium ion (eq 18) can reoxidize the organocopper(II) (**6**) to the organocopper(III), and they thus favor biaryl production. When the concentration of diazonium ion is increased, the consequent increase in the rate of biaryl formation is not counteracted by an increase in the rate of azoarene production, because the diazonium ion becomes involved in azoarene production only after the rate-determining step (eq 19) in the conversion of **5** to azoarene. In other words, reaction 20 is much faster than the reverse of reaction 19. The concept that the diazonium ion plays a role in the oxidation of an organocopper intermediate leads directly to an explanation of the often-discussed generalization<sup>3-8</sup> that electron-withdrawing groups on the diazonium ion favor biaryl production; obviously, such substituents increase the oxidizing power of the diazonium ion.<sup>17</sup> Furthermore, the role of acetonitrile in favoring biaryl production can be rationalized on this basis; the great stabilization of copper(I) by this reagent would probably drive equilibrium 17 to the left.

If the required irreversible process by which **6** becomes converted to an intermediate capable of adding to a diazonium ion involves reaction of **6** with a cuprous ion as in eq 19, the apparently greater than first-order dependence of the azoarene:biaryl ratio on cuprous ion concentration and the increased sensitivity of this ratio to the cupric ion concentration at low concentrations of cuprous ion (Table III) becomes understandable. Assuming steady-state concentra-

yield of Ar<sub>2</sub>/yield of ArN<sub>2</sub>Ar =

$$\frac{k_{16} \left( \frac{k_{-17}[\text{Cu}^{\text{II}}] + k_{18}[\text{ArN}_2^+]}{k_{19}[\text{Cu}^{\text{I}}]} + 1 \right)}{2k_{17}[\text{Cu}^{\text{I}}]} \quad (25)$$

tions of the various organocopper intermediates, we may derive expression 25.

It is clear that an increase in [Cu<sup>I</sup>] not only increases the denominator but decreases the numerator provided the fraction in the parentheses of the numerator is not much smaller than 1; this proviso appears secure in view of the increase in biaryl production that accompanies an increase in the concentration of copper(II) and of diazonium ion. It is also clear from this expression that an increase in [Cu<sup>II</sup>] will have a greater effect in increasing this yield ratio at low than at high concentrations of copper(I).

In view of the expectation that arylcopper compounds of lower oxidation state would become protonated to arene more readily than those of higher oxidation state,<sup>47</sup> the mechanism presented above would predict that a proton source would depress the production of azoarene to a greater extent than that of biaryl. It may be significant in this respect that the presence of a small quantity of concentrated perchloric acid in the reaction mixture sharply reduces the yield of azoarene while hardly influencing that of biaryl (Table I). However, since perchloric acid is an oxidizing agent as well as an acid, a more appropriate test of the prediction must await further work.

The scheme presented here is remarkably successful at explaining the known facts about this reaction, and, although it is novel, most of the steps are well precedented. Nevertheless, since the explanations may not be unique, the mechanism, and especially its details, must be regarded as tentative until it undergoes more extensive testing. It is also possible that some (but not all) of the the dinuclear product formation involves mechanisms which do not include organocopper intermediates; this seems particularly likely in the case of the generation of azoarene which can be produced from diazonium ions in the presence of reducing agents not containing transition metals.<sup>8a,49</sup> In any event, the concept<sup>26</sup> that a major characteristic of copper organic chemistry is the formation of new bonds by reductive elimination from organocopper(III) intermediates gains support from this work.

Finally, a new dimension may be added to the synthetic utility of diazonium ions by the realization that arylcoppers may be produced from aryl radicals. Whereas most diazonium displacements (Sandmeyer and Schiemann reactions, phenol syntheses, etc.) mentioned in textbooks are formally nucleophilic displacements, the arylation and methylation demonstrated here are electrophilic substitutions; other examples are almost certainly possible. The mechanistic scheme suggests substituents and reaction conditions for maximizing the trapping of arylcoppers in low oxidation states.

## Experimental Section

Melting points were determined on a Thomas-Kofler micro hot stage and are corrected. Infrared spectra were determined on a Beckman Model IR-8 spectrophotometer. Proton magnetic resonance spectra were determined using a Varian Associates Model A-60 nmr spectrometer and mass spectra on an LKB-9000 combined gas chromatograph-mass spectrometer at 70 eV. Gas-liquid partition chromatography (glpc) was performed on Varian Associates Model 1860-3 and Hewlett-Packard Model 5750 gas chromatographs equipped with flame ionization detectors and Disc integrators.

**Materials.** Acetone (Baker Analyzed Reagent) was dried by stirring over anhydrous potassium carbonate and then 4-Å Linde molecular sieve and by subsequent distillation.<sup>50</sup> Acetonitrile (Baker Analyzed or Matheson, Coleman, and Bell) was heated at reflux over calcium hydride for 25 hr, distilled on to 4-Å molecular sieve, and stored in sealed flasks in a desiccator. Copper powder (Englehard Magna 1107) was used as purchased. Copper(I) oxide (Fisher Reagent Grade) was stored in a vacuum desiccator before

use. Copper(II) perchlorate (G. F. Smith Reagent Grade), obtained as the deep blue hexahydrate, was dried in a vacuum oven at 80–85° in the presence of phosphorus pentoxide until the salt had been converted to the pale green tetrahydrate (*ca.* 24 hr).<sup>51</sup> Iodobenzene and methyl iodide (Baker Analyzed Reagents) were used as purchased. Tetrahydrofuran (Baker Analyzed Reagent) was heated at reflux over lithium aluminum hydride for 12 hr followed by distillation from the hydride. Tetrahydrofuran-*d*<sub>8</sub>, 99% (Norell Chemical Co.), was used as supplied.

Acetic acid-*d*<sub>1</sub> was prepared by the reaction of deuterium oxide with acetic anhydride;<sup>52</sup> the product was shown to contain 95% CH<sub>3</sub>CO<sub>2</sub>D by nmr analysis using chloroform as internal standard. 4,4'-Dinitroazobenzene was prepared by nickel peroxide oxidation of *p*-nitroaniline according to a literature procedure;<sup>53</sup> the orange product was recrystallized from acetone, mp 230.0–231.0° (lit.<sup>53</sup> mp 220–222°). *p*-Nitrophenyl acetate was prepared<sup>54</sup> by the reaction of acetic anhydride with the sodium salt of *p*-nitrophenol; white needles were obtained, mp 76.5–77.0° (lit.<sup>55a</sup> mp 77.5–78.0°; lit.<sup>55b</sup> mp 79.5–80.0°).

Tetrakis(acetonitrile)copper(I) perchlorate was prepared by the reduction of cupric perchlorate tetrahydrate by copper metal in acetonitrile.<sup>56a</sup> The white needles had mp 154–156° (sealed tube; lit.<sup>56a</sup> mp 164–166°); the infrared spectrum corresponded in detail with the published data.<sup>56b</sup> This material was stored in sealed vials under nitrogen in a desiccator over phosphorus pentoxide; eventually it developed a pale blue cast at which time it was considered no longer suitable for quantitative work.

*p*-Nitrobenzenediazonium tetrafluoroborate was prepared by the treatment of *p*-nitroaniline in concentrated aqueous fluoboric acid with sodium nitrite.<sup>57</sup> The yellow crystalline solid had mp *ca.* 165° dec (no melting point is reported in the "Organic Synthesis" preparation). The material was dried in a vacuum desiccator for 30 min. An infrared spectrum (Nujol) exhibited a strong absorption at 2300 cm<sup>-1</sup> (diazonium group) and no absorption in the OH and NH region, indicating the absence of solvation and of unreacted amine. The crystals could be stored indefinitely in the freezer. For quantitative work, the salt was recrystallized from 1:1 acetone: ether and dried for at least 1 hr in a vacuum desiccator.

**Diazonium Decompositions. (i) Decomposition in Acetic Acid-*d*<sub>1</sub>.** *p*-Nitrobenzenediazonium tetrafluoroborate (5 mmol) was added slowly from a solid addition funnel to 190 mmol of CH<sub>3</sub>CO<sub>2</sub>D containing 10 mmol of Cu<sub>2</sub>O at 5° under dry nitrogen. After the mixture had been stirred for 24 hr and allowed to reach ambient temperature, a negative  $\beta$ -naphthol test for diazonium ion was obtained. Dilution with water, filtration, and extraction with ethyl acetate yielded a product which, by glpc and mass spectral analysis (see below), contained 44% of nitrobenzene which was *ca.* 50% monodeuterated.

**(ii) Quantitative Experiments in Unbuffered Acetone.** A three-neck, 50-ml round-bottom flask was fitted with a magnetic stirring bar, a thermometer, a 25-ml addition funnel, a condenser, a gas inlet tube, and a gas outlet tube. A solution of tetrakis(acetonitrile)copper(I) perchlorate and any other reactants in 20 ml of acetone containing 0.044 mmol of water was placed in the reaction vessel, and a solution of the diazonium salt in 10 ml of anhydrous acetone was placed in the addition funnel and shielded from light. The entire system at 25° was flushed with prepurified nitrogen which was freed of traces of oxygen and moisture by passage through Fieser's solution<sup>58</sup> and Type 4-A Linde molecular sieve. The dropwise addition of the diazonium salt solution to the rapidly stirred solution in the reaction vessel was carefully regulated to be completed in 10 min; this procedure produced a 2° temperature rise. A  $\beta$ -naphthol test for the presence of diazonium ion, performed on a drop of solution, was found to be negative after completion of the addition. The mixture was diluted with 20 ml of ether and 20 ml of 5% aqueous ammonia and stirred for *ca.* 10 min. The aqueous layer was separated and extracted with ether (5 × 20 ml). The combined organic extract was dried over magnesium sulfate, the latter was removed by filtration and thoroughly washed with acetone, and the combined filtrate and washes were concentrated. The concentrate was redissolved in a 2:1 acetone: benzene solution, and, after the addition of biphenyl standard, was used for the glpc analysis.

Dual column operation was employed using 10 ft × 0.125 in. columns packed with 3% OV-17 on gas Chrom Q 100–120. Two program patterns were utilized, depending on the products to be

analyzed: 140 to 270° at 30°/min with a 10-min preprogram period and an 11-min postprogram period or 90 to 140° at 10°/min and an 8-min postprogram period, followed by a manual adjustment to isothermal operation at 270°. A nitrogen flow rate of 45 ml/min was used. All product yields were determined by integrating the areas under the curves after calibration of the relative flame response of an authentic sample with that of the biphenyl. All experiments were performed at least twice to verify reproducibility.

**(iii) Quantitative Experiments in Buffered Acetone.** Tetrakis(acetonitrile)copper(I) perchlorate, cupric perchlorate tetrahydrate, and any other additives were dissolved in 60 ml of a magnetically stirred solution of 0.75% acetonitrile (by volume) in acetone and 0.110 mmol of deionized water. A nitrogen purge, identical with that described above, was maintained; the temperature was 25°. One to five minutes after the addition of *p*-nitrobenzenediazonium tetrafluoroborate in 10 ml of the same solution (a temperature rise of no more than 1° was noted), the  $\beta$ -naphthol test indicated that the reaction was complete. After 10 min more of stirring, the internal standard (25 mg of benzophenone), 100 ml of diethyl ether, 50 ml of 20% aqueous ammonia, and 50 ml of 20% HCl were added in that order. In a separatory funnel, the layers were separated, and the aqueous layer was washed with two 50-ml portions of diethyl ether. The combined ether layers were concentrated to 2 ml on the rotary evaporator. Glpc quantitative analysis was performed with a 5 ft × 1/8 in. column packed with 3% OV-1 on Gas Chrom Q 100 mesh, operated at 100° for 12 min, 120° for 12 min, and 182° for 25 min, with a nitrogen flow rate of 25 ml/min. All experiments were performed twice to verify reproducibility.

**Control Tests to Detect the Reaction of Methyl Iodide with Copper(I).**<sup>59</sup> **(i) ESR Study.** In a glove bag containing a nitrogen atmosphere, tetrakis(acetonitrile)copper(I) perchlorate (0.85 g, 2.60 mmol) was added to 70 ml of a 0.75 vol % acetonitrile solution of acetone containing deionized water (2.71 mmol). The solution was thoroughly mixed, and a sample was removed and placed in a capillary tube, which was maintained under nitrogen. The tube was removed from the glove bag and sealed in a flame. After methyl iodide (4 ml) had been added to the remaining solution and the latter mixed thoroughly, another sample was sealed in a capillary tube in the same manner. Both sealed capillary tubes were set aside for 3 days along with the remaining reaction mixture, which was open to air. A sample of this reaction mixture was then placed in another capillary tube, which was sealed, and all three capillary tubes were individually placed into a Varian E-4 electron spin resonance spectrometer. The intensities of the signal for copper(II) from the first two samples, the copper solution and the copper solution plus methyl iodide, were identical. The intensity of the copper(II) signal from the sample of the solution that remained open to air for 3 days was about four times greater.

**(ii) Reaction of Diazonium Ion with Copper Salts Which Had Been Exposed to Methyl Iodide.** To 70 ml of a 0.75 vol % acetonitrile solution of acetone containing deionized water (0.11 mmol) were added tetrakis(acetonitrile)copper(I) perchlorate (0.85 g, 2.60 mmol), copper(II) perchlorate tetrahydrate (0.171 g, 0.51 mmol), and methyl iodide (4 ml). The solution was stirred under a nitrogen atmosphere for 1 hr. All the liquid was then evaporated under a nitrogen atmosphere, and to the residue was added 60 ml of a 0.75% acetonitrile solution of acetone containing deionized water (0.11 mmol). To the thoroughly mixed solution was added *p*-nitrobenzenediazonium fluoroborate (0.0308 g, 0.13 mmol) dissolved in 10 ml of a 0.75% acetonitrile solution of acetone. The solution was stirred under a nitrogen atmosphere for 1 hr. The only products visible by glpc on a 10-ft 3% OV-17 column were 4,4'-dinitrophenyl, 4,4'-dinitroazobenzene, and a trace of some other compound which was not *p*-iodonitrobenzene. The products were identified by coinjection with authentic samples.

**Identification of Products.** Identical retention times, by coinjection, for products and authentic samples were observed for nitrobenzene, *p*-nitrophenyl acetate, *p*-iodonitrobenzene (Baker Analyzed), *p*-nitrophenol (Fisher Reagent), *p*-nitroaniline (Eastman), 4-nitrobiphenyl<sup>61</sup> (Aldrich), 4,4'-dinitrobiphenyl (K&K), and 4,4'-dinitroazobenzene. In addition, the following products had mass spectra (by combined glpc-mass spectrometry) which matched those of authentic samples: *p*-nitrobiphenyl,<sup>61</sup> *m/e* (% of base, assignment) 199 (100, P<sup>+</sup>), 169 (30, P<sup>+</sup> – NO), 153 (80, P<sup>+</sup> – NO<sub>2</sub>), 141 (20, P<sup>+</sup> – NO – CO), 76 (35, P<sup>+</sup> – NO<sub>2</sub> – C<sub>6</sub>H<sub>5</sub>);

4,4'-dinitrophenyl, *m/e* 244 (100, P<sup>+</sup>), 214 (30, P<sup>+</sup> - NO), 152 (65, P<sup>+</sup> - 2NO<sub>2</sub>); 139 (25), 75 (15); 4,4'-dinitroazobenzene, *m/e* 272 (55, P<sup>+</sup>), 242 (35, P<sup>+</sup> - NO), 150 (10, P<sup>+</sup> - C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>), 122 (15, P<sup>+</sup> - NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>), 106 (15, P<sup>+</sup> - NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>2</sub> - O), 92 (100, C<sub>6</sub>H<sub>4</sub>O<sup>+</sup>), 76 (15). The mass spectrum of *p*-nitrotoluene matched that in the literature.<sup>60</sup> *m/e* 137 (80, P<sup>+</sup>), 107 (15, P<sup>+</sup> - NO), 91 (100, P<sup>+</sup> - NO<sub>2</sub>), 77 (20), 65 (70).

Deuterium incorporation into the nitrobenzene was determined by combined glpc-mass spectrometry.<sup>61</sup>

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## References and Notes

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- (39) It has been found that decomposition of *N,N*-dimethylbenzamide-*o*-diazonium tetrafluoroborate initiated by cuprous oxide in acetic acid produces *N,N*-dimethylbenzamide which is 52 and 29% monodeuterated on the ring, respectively, when the solvent is respectively CH<sub>3</sub>CO<sub>2</sub>D and CD<sub>3</sub>CO<sub>2</sub>H.<sup>40a</sup> No carbon dioxide is produced in these experiments. Evidently, both an aryl radical and an arylcopper intermediate are involved in this reaction. Hey, Jones, and Perkins<sup>40b</sup> have concluded independently that the reduction of the corresponding *N*-methyl-*N*-phenyl analog by copper in acetic acid involves protolysis of an organocopper intermediate.
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$$\frac{d([Ar_2] + [ArN_2Ar])}{dt} = \frac{k_{14}[Ar^*][Cu^I]}{k_{-14}/(k_{15}[Ar^*]) + 1}$$
 If eq 14 were irreversible,  $k_{-14} \ll k_{15}[Ar^*]$ , the rate of formation of dinuclear products would be first order in aryl radicals. On the other hand, if eq 14 were very reversible,  $k_{15}[Ar^*] \ll k_{-14}$ , the rate would be second order in aryl radicals. An intermediate situation apparently obtains.
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