for the reactivity comes from the first term in eq 5. Then, the remaining ca. half of ρ^+ for the reactivity can be attributed to the positive $\gamma\rho^+$(polar transition state); positive γ suggests the resonance structures such as [p-$\mathrm{XC_6H_4S^-}$,$\mathrm{RNO^{+}}$·].[31] This polar transition state is similar to that proposed for the benzoyloxy radical trapping with substituted phenyl *N*-*tert*-butylnitrones by Janzen, Evans, and Nishi,[32] while the opposite tendency was reported for the *tert*-butoxy radical[2] and the primary alkyl radical.[4]

Solvent Effect. For the alkyl radical Ingold et al. found the polar solvent effect on the spin-trapping rates.[33] In Table III, the rate constants for p-$\mathrm{CH_3C_6H_4S}$· and p-$\mathrm{NH_2C_6H_4S}$· in various solvents are shown in Table III. Other substituents such as Cl and $\mathrm{CH_3O}$ groups show a similar effect to the $\mathrm{CH_3}$ group. Although we can find some tendencies that polar solvents accelerate the rates for p-$\mathrm{CH_3C_6H_4S}$· compared with that in benzene and that the rate in cyclohexane is the fastest, differences are too small to distinguish from the experimental errors. On the other hand, the rates for p-$\mathrm{NH_2C_6H_4S}$· are greatly reduced in benzene and in polar solvents compared with that in cyclohexane. Neither the solvation of nitroso compounds nor that of the spin adducts can be attributed to such large solvent effects. The specific solvation of p-$\mathrm{NH_2C_6H_4S}$· was found in the solvent shifts of the absorption maxima[34,35] and in the addition rates with styrene.[35] Therefore, the decreases of the rates in the polar solvents and in benzene are interpreted as follows: the polar solvents that stabilize p-$\mathrm{NH_2C_6H_4S}$· in the reactants desolvate in the transition state, which results in an increase in the activation energy of the reaction.

Experimental Section

Commercially available 2-methyl-2-nitrosopropane (Aldrich) was used without further purification. Nitrosobenzene was used after recrystallization in the dark. Pentamethylnitrosobenzene was prepared by the method of Smith and Taylor.[36] Disulfides were purified by recrystallization. Solvents were of spectrophotometric grade. Samplings and measurements were made in the dark to prevent inadvertent photolysis.[37]

The ESR spectra of the spin adducts were measured with a Varian E4 EPR spectrometer during the photolysis of disulfides (ca. 10^{-3} M) with the light between 350 and 450 nm (500-W high-pressures Hg lamp) in the presence of nitroso compounds (ca. 10^{-3} M). Decay of the ESR signals was followed by a fast recorder or by a transient memory. The xenon flash photolysis apparatus was of standard design; input energy was 150 J and the half-duration of xenon flash lamps was ca. 10 μs. By the use of light filters, disulfides were flash decomposed with light between 350 and 450 nm and the photolysis of the nitroso compounds was avoided.[37] In the case of 2-methyl-2-nitrosopropane, formation of di-*tert*-butyl nitroxide, which is produced by the inadvertent photolysis of the nitroso compound, was observed in small amounts (less than 5% compared to the spin adduct with the thiyl radical). In order to reduce the photodecomposition of 2-methyl-2-nitrosopropane by the monitoring light at ca. 500 nm, band-path filters of 10 nm were used.

Acknowledgment. We are extremely grateful to Professor Y. Ikegami, Dr. S. Tero-Kubota, and Dr. T. Chiba of Tohoku University for their kind suggestions in the kinetic ESR measurements and for the donation of the authentic sample of pentamethylnitrosobenzene.

Registry No. Ph(p-$\mathrm{BrC_6H_4S}$)NO·, 84751-91-7; Ph(p-$\mathrm{ClC_6H_4S}$)NO·, 84751-92-8; Ph(PhS)NO·, 62991-74-6; Ph(p-t-$\mathrm{C_4H_9C_6H_4S}$)NO·, 84751-93-9; Ph(p-$\mathrm{CH_3C_6H_4S}$)NO·, 72054-13-8; Ph(p-$\mathrm{OCH_3C_6H_4S}$)NO·, 84751-94-0; Ph(p-$\mathrm{NH_2C_6H_4S}$)NO·, 84751-95-1; t-$\mathrm{C_4H_9}$(p-$\mathrm{BrC_6H_4S}$)NO·, 84751-96-2; t-$\mathrm{C_4H_9}$(p-$\mathrm{ClC_6H_4S}$)NO·, 71899-51-9; t-$\mathrm{C_4H_9}$(PhS)NO·, 59504-24-4; t-$\mathrm{C_4H_9}$(p-t-$\mathrm{C_4H_9C_6H_4S}$)NO·, 84751-97-3; t-$\mathrm{C_4H_9}$(p-$\mathrm{CH_3C_6H_4S}$)NO·, 66729-86-0; t-$\mathrm{C_4H_9}$(p-$\mathrm{OCH_3C_6H_4S}$)NO·, 74928-94-2; t-$\mathrm{C_4H_9}$(p-$\mathrm{NH_2C_6H_4S}$)NO·, 84751-98-4; (p-$\mathrm{BrC_6H_4}$)$_2$S$_2$, 5335-84-2; (p-$\mathrm{ClC_6H_4}$)$_2$S$_2$, 1142-19-4; Ph$_2$S$_2$, 882-33-7; (p-t-$\mathrm{C_4H_9C_6H_4}$)$_2$S$_2$, 7605-48-3; (p-$\mathrm{CH_3C_6H_4}$)$_2$S$_2$, 103-19-5; (p-$\mathrm{OCH_3C_6H_4}$)$_2$S$_2$, 5335-87-5; (p-$\mathrm{NH_2C_6H_4}$)$_2$S$_2$, 722-27-0; p-$\mathrm{BrC_6H_4S}$·, 31053-90-4; p-$\mathrm{ClC_6H_4S}$·, 31053-91-5; PhS·, 4985-62-0; p-t-$\mathrm{C_4H_9C_6H_4S}$·, 81372-23-8; p-$\mathrm{CH_3C_6H_4S}$·, 31053-92-6; p-$\mathrm{OCH_3C_6H_4S}$·, 31053-93-7; p-$\mathrm{NH_2C_6H_4S}$·, 31053-95-9; 2-methyl-2-nitrosopropane, 917-95-3; nitrosobenzene, 586-96-9; pentamethylnitrosobenzene, 65594-36-7.

---

(31) Walling, C.; Briggs, E. R.; Wolfstrin, K. B.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 1537.

(32) Janzen, E. G.; Evans, C. A.; Nishi, Y. *J. Am. Chem. Soc.* **1972**, *94*, 8236.

(33) Maeda, Y.; Schmid, P.; Griller, D.; Ingold, K. U. *J. Chem. Soc., Chem. Commun.* **1978**, 525.

(34) Morine, G. H.; Kuntz, R. R. *Chem. Phys. Lett.* **1979**, *67*, 552.

(35) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 568.

(36) Smith, L. I.; Taylor, F. L. *J. Am. Chem. Soc.* **1935**, *57*, 2460.

(37) Chatgilialoglu, C.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 4833.

Mechanistic Investigation of the Copper-Catalyzed Reactions of Diphenyliodonium Salts

Thomas P. Lockhart

Contribution from the General Electric Company, Corporate Research and Development, Schenectady, New York 12301. *Received August 20, 1982*

Abstract: The reaction of diphenyliodonium hexafluoroarsenate (PIFA) with copper(II) benzoate in alcohol solvent gives iodobenzene and alkyl phenyl ether, the arylation product, in high yield along with small amounts of phenyl benzoate and benzene. With diphenyliodonium bromide (PIBr), a substantial yield of bromobenzene is obtained along with iodobenzene and the ether. In nonnucleophilic solvent, $\mathrm{CH_2Cl_2}$, PIFA yields appreciable amounts of iodobenzene, benzene, biphenyl, and phenyl benzoate. In $\mathrm{CH_2Cl_2}$, PIBr gives a high yield of bromobenzene and iodobenzene and low yields of benzene and biphenyl. $\mathrm{Cu^I}$ is shown to be the catalytically active oxidation state of copper, based in part on the chemistry observed with independently prepared copper(I) benzoate. Phenyl radical intermediates are ruled out in the reactions of PIFA and PIBr in methanol and $\mathrm{CH_2Cl_2}$, and their chemistry is contrasted with that observed with a benzenediazonium salt. A mechanism involving a phenylcopper(III) intermediate is proposed which concisely accounts for the reaction products observed with PIFA and PIBr in both nucleophilic and nonnucleophilic solvents.

Diaryliodonium salts have been the subject of considerable research interest since the turn of the century. In particular, they have been investigated for their ability to arylate a wide variety of nucleophilic substrates.[1] More recently, their utility in initiating cationic polymerization has been reported.[2] Evidence for the occurrence of both nucleophilic aromatic substitution (S$_{\mathrm{N}}$Ar) and electron-transfer pathways in the reaction of diaryliodonium salts

---

(1) Beringer, F. M.; Brierly, A.; Drexler, M.; Gindler, E. M.; Lumpkin, C. C. *J. Am. Chem. Soc.* **1953**, *75*, 2708.

(2) Crivello, J. V.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 539. Crivello, J. V.; Lockhart, T. L.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 97.

Table I. Reaction of Diphenyliodonium Salts[a] with Copper[b] in Methanol

						absolute yield,[c] %				
run no.	iodonium salt[a]	catalyst	catalyst concn, M	temp, °C	reaction time, min	C_6H_6	C_6H_5-OCH_3	C_6H_5Br	C_6H_5I	phenyl benzoate
1	PIFA	Cu^{II}	1×10^{-3}	120	120	1	82		100	6
2	PIFA	Cu^{II} + Sn^{II}[d]	2×10^{-3}	23	21	3	69		92	4
3	PIFA	Cu^{I}	5×10^{-3}	23	5	3	84		100	3
4	PIFA	Cu^{II}	1×10^{-3}	120	20	1	43		53	3
5	PIFA[e]	Cu^{II}	1×10^{-3}	120	20	0.5	<9		18	trace
6	PIBr	Cu^{I}	1×10^{-2}	23	125	0	62	33	93	0

[a] [Iodonium salt] = 1×10^{-2} M. [b] Copper(*n*) benzoate salts used; copper compounds required for significant conversion of iodonium salts. [c] Based on iodonium salt present; determined by FID-equipped VPC using internal standard method. [d] Tin(II) (2-ethylhexanoate)$_2$ (5×10^{-3} M). [e] Solution contained 1.3×10^{-3} M cuproin.

Table II. Reaction of Iodonium Salts with Copper(I) Benzoate in CH_2Cl_2

					absolute yield,[b] %				
run no.	iodonium salt[a]	copper(I) benzoate concn, M	temp	reaction time	C_6H_6	C_6H_5Br	C_6H_5I	C_6H_5-C_6H_5	phenyl benzoate
1	PIFA	2×10^{-3}	room temp	96 h	4.5		25	3.5	4
2	PIFA	1×10^{-2}	room temp	96 h	14		74	23	12
3	PIBr	1×10^{-3}	room temp	140 min	0	86	86	trace	0
4	PIBr	1×10^{-2}	room temp	10 min	3	49	91	8.4	0

[a] [Iodonium salt] = 1×10^{-2} M. [b] Determined as per Table I.

with various carbanions and inorganic substrates have been found.[1,3]

Arylation of nucleophiles by diaryliodonium salts is greatly facilitated by the presence of catalytic amounts of copper salts. The mechanism by which copper salts catalyze the reaction of iodonium salts, however, is not well understood, although some general features have been delineated.[4,5] From studies of the copper-catalyzed hydrolysis of iodonium tosylates, kinetic evidence for the role of Cu^I was obtained. On the basis of product studies, aryl radicals and diaryliodine have been proposed[5] as possible reaction intermediates although Beringer and co-workers[4] argued against the formation of aryl radicals in the reaction of diaryliodonium salts with chlorine and iodine in several solvents.

In this paper are disclosed results observed in the copper benzoate catalyzed reaction of diphenyliodonium salts having both nucleophilic (Br^-) and nonnucleophilic (AsF_6^-) counterions in nonaqueous solvents (methanol and CH_2Cl_2). Observations relevant to the critical role of Cu^I and to the strong dependence of the reaction pathway on the nucleophilicity of the solvent and the iodonium salt counterions are made.

Results and Discussion

The reaction of diphenyliodonium hexafluoroarsenate (PIFA) with copper benzoates has been examined in several solvents. In methanol (Table I) anisole and iodobenzene were obtained in high yield, while smaller amounts of benzene, phenyl benzoate, and traces of methyl benzoate and biphenyl were formed. In ethanol solution, similar products were observed, ethyl phenyl ether (phenetole) appearing instead of anisole. Under the same conditions, little or no reaction was observed in the absence of copper. The ratio of products showed little variation whether the reaction was conducted at room temperature with Cu^I, Cu^I produced in situ by the reduction of Cu^{II} with Sn^{II}, or at elevated temperature with Cu^{II}. When the principal reaction products, anisole and iodobenzene, were each combined with copper(I) benzoate in methanol at room temperature, no reaction was detected, demonstrating that the principal reaction products are stable to the reaction conditions.

The reaction of diphenyliodonium bromide (PIBr) in methanol led to the formation of similar products with the exceptions that a new product, bromobenzene, was formed in appreciable yield and that no benzene or phenyl benzoate was detected.

Reaction of the iodonium salts in dichloromethane resulted in a very different distribution of products (Table II). Benzene, biphenyl, and phenyl benzoate were produced in significant yield from the reaction of PIFA in CH_2Cl_2; with PIBr, bromobenzene was formed in high yield and a variable yield of biphenyl was observed. With both PIFA and PIBr in CH_2Cl_2, the yield of biphenyl appears to depend directly on the Cu^I concentration. Particularly noteworthy is the *stoichiometric* reaction of Cu^I with PIFA in CH_2Cl_2; in contrast, the reaction of PIBr with Cu^I was *catalytic* in copper.

Role of Cu^I. Experiments have been carried out to determine the oxidation state of copper responsible for inducing reaction of the diphenyliodonium salts. Toward this end, authentic copper(I) benzoate was prepared and isolated as a white, air-sensitive solid. The data in Table I demonstrate that the product distribution obtained with copper(I) benzoate (independently synthesized or from the in situ reduction of copper(II) benzoate with tin(II) octoate) is virtually identical with that obtained in thermal reactions using copper(II) benzoate (Table I, run 1 vs. 2, 3). Furthermore, the rate of reaction was many orders of magnitude greater in the presence of the Cu^I salt. These two observations demonstrate that copper(I) benzoate is a permissible and sufficient description of the copper species responsible for the reaction of the iodonium salts.

Further evidence implicating Cu^I in the reaction of Cu^{II} with iodonium salts was obtained in a Cu^I "trapping experiment" similar to that employed in an earlier study of the hydrolysis of a diphenyliodonium salt in aqueous solution catalyzed by $CuCl_2$.[5] For this experiment 2,2′-biquinoline (cuproin), which binds strongly to Cu^I salts producing a characteristic intense purple color,[6] was used. When PIFA and copper(II) benzoate were heated in methanol solution in the presence of cuproin, the reaction rate was significantly inhibited (Table I, runs 4 and 5) and a deep purple color evolved. Appearance of the purple color may be

---

(3) (a) Tanner, D. D.; Reed, D. W.; Setiloane, B. P. *J. Am. Chem. Soc.* **1982**, *104*, 3917. (b) Beringer, F. M.; Falk, R. A. *J. Chem. Soc.* **1964**, 4442. (c) Beringer, F. M.; Forgione, P. S. *Tetrahedron* **1963**, *19*, 739. (d) Lubinkowski, J. J.; Knapczyk, J. W.; Calderon, J. L.; Petit, L. R.; McEwen, W. E. *J. Org. Chem.* **1975**, *40*, 3010. (e) Holm, B. Ph.D. Thesis, University of Lund, Sweden, 1974.

(4) Beringer, F. M.; Bodlaender, P. *J. Org. Chem.* **1969**, *34*, 1981. Beringer, F. M.; Gindler, E. M.; Rapoport, M.; Taylor, R. J. *J. Am. Chem. Soc.* **1959**, *81*, 351.

(5) Caserio, M. C.; Glusker, D. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 336. Roberts, J. D. In "Theoretical Organic Chemistry", Kukulé Symposium; Butterworths: London, 1959.

(6) (a) Breckenridge, J. G.; Lewis, R. W.; Quick, L. A. *Can. J. Res. Sect. B* **1939**, *17*, 258. (b) Hoste, J. *Anal. Chim. Acta* **1950**, *4*, 23.

Scheme I

$$(\mathrm{A})\quad ArN_2{}^+X^- + Cu(I)X \xrightarrow{\text{electron transfer}} ArN_2CuX_2$$

$$ArN_2CuX_2 \longrightarrow Ar\cdot \quad N_2 \quad Cu(II)X$$

$$Ar\cdot + Cu(II)X_2 \longrightarrow ArX + Cu(I)X$$

$$(\mathrm{B})\quad ArN_2{}^\bullet + Cu(I) \xrightarrow{\text{electron transfer}} Ar\cdot \quad N_2 \quad Cu(II)$$

$$Ar\cdot + Cu(II) \xrightarrow{H_2O} ArOH + Cu(I) + H^+$$

Scheme II

$$Cu(II)Y_2 \longrightarrow Cu(I)Y$$

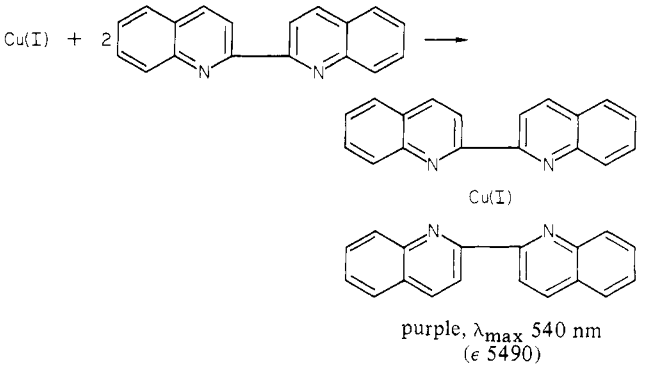
$$(C_6H_5)_2I^+X^- + Cu(I)Y \longrightarrow C_6H_5\cdot \quad Cu(II)XY \quad C_6H_5I$$

$$C_6H_5\cdot + Cu(II)XY \longrightarrow C_6H_5Cu(III)XY$$

$$C_6H_5Cu(III)XY + CH_3OH \longrightarrow Cu(I)Y + HX + C_6H_5OCH_3$$

$$C_6H_5\cdot + CH_3OH \longrightarrow C_6H_6 + \dot{C}H_2OH$$

directly attributed to formation of the copper(I)–2cuproin complex during the reaction. The coincident inhibition of the reaction rate strongly implies that, in scavenging Cu^I, the rate of reaction of the diphenyliodonium salt has been reduced.[7]



The ease of production of *catalytically significant* amounts of copper(I) benzoate from copper(II) benzoate in methanol is suggested by the observation that, upon heating copper(II) benzoate in methanol in the presence of cuproin, the purple color of copper(I)–2cuproin appeared in the course of several minutes.[8] Thus, significant reduction of Cu^{II} occurs upon heating in methanol, presumably with the concurrent oxidation of methanol.[9]

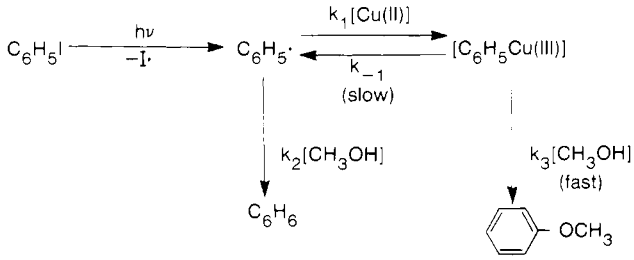
Mechanism of the Reaction—Diazonium Salt Model. Several features of the diphenyliodonium salt reactions suggested that the reaction pathways might be similar to those of several other organic reactions catalyzed by copper. Kochi has summarized these for diazonium salt[10] and peroxide[11] decompositions catalyzed by copper: copper cycles between the 1+ and 2+ oxidation states alternately reducing the starting compound (by electron transfer from Cu^I) and oxidizing radical intermediates (by Cu^{II}).

Table III. Oxidation of Phenyl Radical[a] by Copper(II) Caprylate

[(Cu^{II})], ×10^{-2} M	ratio[b] of yields anisole/benzene
0.00	0.00
0.60	0.0096
0.80	0.011
1.0	0.015
1.5	0.054
2.0	0.11
4.0	0.22

[a] Phenyl radical produced by photolysis of iodobenzene.
[b] Ratios represent data averaged from two reaction solutions each with duplicate VPC analyses.

Scheme III



The mechanism widely proposed[12] to account for the reaction of diazonium salts with copper halides (the Sandmeyer reaction) is shown in Scheme IA. Electron transfer from Cu^I (generated from Cu^{II} in the reaction medium) to the diazonium salt produces an aryl radical which abstracts halide from CuX_2 to give the aryl halide. When water is employed as solvent and halides are excluded as counterions (Scheme IB),[10] oxidation of the aryl radical by Cu^{II} occurs followed by nucleophilic attack on water, yielding ArOH and Cu^I. The oxidation of aryl radicals may take place via a short-lived aryl–copper complex, ArCu^{III}.[13] Similar copper complexes of alkyl radicals are well-established intermediates in other reactions.[11,14]

A mechanism for the reaction of iodonium salts with copper in methanol modeled after that for diazonium salts is presented in Scheme II. Electron transfer from Cu^I to the iodonium salt followed by rapid homolysis of a phenyl–iodine bond would generate Cu^{II} and a phenyl radical. Combination of the phenyl radical and Cu^{II} to yield phenylcopper(III),[13] followed by reaction with solvent, would lead to $ArOCH_3$. In competition with this reaction, abstraction of hydrogen from the solvent by phenyl would produce benzene.

Recommending a comparison of the iodonium and diazonium salt reaction mechanisms are the following considerations: (1) The reduction potentials of both organic salts are very similar.[15] (2) Cu^I is the catalytic species in both reactions. (3) Similar reactivity is observed when the reactions are conducted in nucleophilic solvents in the absence of halide (e.g., oxidation of the aryl fragment to give products of nucleophilic attack, such as phenol in aqueous solution). (4) The observation of small amounts of benzene in the iodonium salt reactions (Table I) appeared, prima facie, to be consistent with the presence of phenyl radicals on the reaction pathway. Competition between oxidation of the aryl radical by Cu^{II}, leading to anisole, and abstraction of hydrogen from solvent, leading to benzene, could account for the formation of these products.

---

(7) **Caveat**: In interpretation of the cuproin experiments, the assumption was made that the presence of cuproin in the reaction solution did not influence, positively or negatively, the rate of formation of Cu^I from Cu^{II} nor that it reduced the reactivity of Cu^{II}.

(8) When a methanol solution of Cu^{II} and cuproin (no PIFA) was heated under vacuum to 120 °C for 15 min, a deep purple color developed, just as in the reaction with PIFA present. A similar observation was reported by Quick et al.[6a]

(9) Nigh, W. G. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; p 35.

(10) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978; Chapter 9.

(11) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1.

(12) Zollinger, H. *Acc. Chem. Res.* **1973**, *6*, 335.

(13) Assignment of an oxidation state to the arylcopper species is problematic, with 1+ through 3+ states found in the literature.[10,14] Upon consideration that the aryl group behaves as an electrophile, a Cu^I oxidation state seems justified. In this paper, however, following the usual formalism of assigning anionic counterions and σ-bonded hydrocarbons a formal charge of 1−, the arylcopper complex is considered to be in the 3+ oxidation state.

(14) (a) Ferraudi, G. *Inorg. Chem.* **1978**, *17*, 2506. (b) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1977**, 127. (c) Freiberg, M.; Meyerstein, D. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1825.

(15) (a) Elofson, R. M.; Gadallah, F. F. *J. Org. Chem.* **1969**, *34*, 854. (b) Beringer, F. M.; Messing, S. *J. Org. Chem.* **1972**, *37*, 2484.

Tests of Mechanism. A critical feature of the reaction mechanism proposed in Scheme II is the required intermediacy of the phenyl radical. A critical evaluation of this model would involve determining whether or not the products of the reaction of PIFA with copper in methanol are consistent with a phenyl radical-mediated pathway. The proposed mechanism further requires that Cu^{II} be capable of oxidizing phenyl radicals; oxidation of alkyl radicals by Cu^{II} is well-known,[11,14] but no direct demonstration of the reaction with phenyl radicals was found in the literature.[16]

Kinetic Test. A simple kinetic test of the mechanism was devised, such that the rate of oxidation by Cu^{II} vs. H abstraction of independently generated phenyl radicals could be determined. When phenyl radicals were generated in methanol by photolysis of iodobenzene[17] (as well as from several other sources: photolysis of PIFA and photolysis and thermolysis of benzoyl peroxide) in the presence of copper(II) benzoate, both benzene and the oxidation product, anisole, were produced. The ratio of anisole/benzene formed was small but showed a marked dependence on the amount of copper in solution (Table III).

The proposed mechanism (Scheme II) requires that the oxidation of phenyl radicals by Cu^{II} be extremely fast; the dependence of the anisole/benzene ratio on the concentration of Cu^{II} suggested an approach that would allow the absolute rate constant for the oxidation reaction to be determined. As outlined in Scheme III, a phenyl radical generated by photolysis of iodobenzene either may be oxidized by Cu^{II} (k_1) or may abstract hydrogen from the solvent (k_2). The ratio of the yield of anisole and benzene is given by eq I. Assuming irreversible formation of the phenylcopper

$$\text{yield}\left(\frac{\text{anisole}}{\text{benzene}}\right) = \frac{k_1}{k_2[\mathrm{CH_3OH}]}[\mathrm{Cu^{II}}] \qquad \text{(I)}$$

intermediate under the reaction conditions ($k_3[CH_3OH] >> k_{-1}$) and given that neither Cu^{II} nor methanol concentrations change appreciably during the reaction, a plot of the anisole/benzene ratio vs. $[Cu^{II}]$ should be linear with a slope of $k_1/(k_2[CH_3OH])$. Because the concentration of methanol is known, and the absolute rate constant for the abstraction of hydrogen from methanol by phenyl has been measured at room temperature ($k_2 \geq 1.4 \times 10^5$ M^{-1} s^{-1}),[18,19] the absolute rate constant for the oxidation of phenyl radical by Cu^{II} (k_1) can be determined.

Photolysis of iodobenzene was chosen as the phenyl radical source because it is a very clean reaction, producing only benzene (in high yield) and a trace of biphenyl in dilute methanol solution in the absence of copper. Copper(II) caprylate was used in the kinetic experiments because of its reasonable solubility in methanol. Solutions were irradiated under vacuum in quartz tubes in a water bath (23 ± 1 °C). Longer photolysis times were required to obtain equal conversion of solutions containing the higher concentrations of Cu^{II}, perhaps due to absorption of incident light or quenching by the copper salt. The range of copper concentrations investigated was restricted by the very small amount of anisole formed at the lower concentrations and by the limited solubility of Cu^{II} in methanol at the higher end.

Appropriate controls showed that in the absence of Cu^{II} no anisole was formed upon photolysis. The concentration of Cu^{II} was held approximately constant during photolysis by carrying the reactions to less than 50% completion; the yield of anisole based on Cu^{II} present never exceeded 5%. As stated previously, both iodobenzene and anisole are inert to Cu^I, thus removing possible complications from the presumed formation of small amounts of Cu^I during the photolysis. Photolysis of copper(II) caprylate alone in methanol resulted in slow formation of an unidentified volatile product. The amount of this product produced during photolyses of iodobenzene was small and represented only minor conversion of the copper salt.

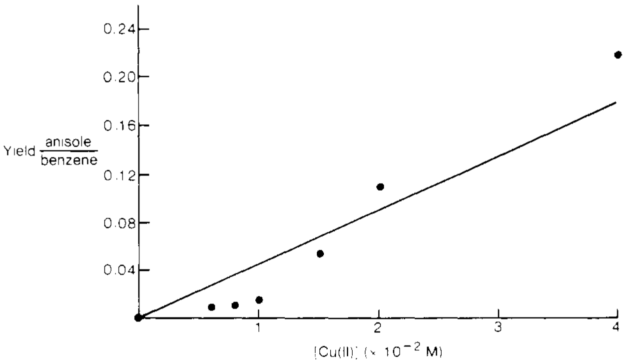


Figure 1. Plot of ratio anisole/benzene obtained in the photolysis of iodobenzene as a function of Cu^{II} concentration.

Table IV. Ionization Potential (IP) and Rates of Oxidation by Copper(II) (Carboxylates)

R·	carboxylate	IP, eV	k_{oxid}, M^{-1} s^{-1}	k_{oxid} ref
CH_3	O_2CCH_3	9.98[a]	1.5×10^6	23
C_6H_5	$O_2CC_7H_{15}$	8.8–9.2[b]	1×10^7	this work
$CH_3CH_2CH_2$	O_2CCH_3	8.69[a]	4.4×10^7	11
CH_3CHCH_3	O_2CCH_3	7.90[a]	5.0×10^7	11
$(CH_3)_3C$	O_2CCH_3	7.43[a]	5.5×10^8	11

[a] Reference 11. [b] Reference 21.

The data from the kinetic experiment (Table III) obey a linear relationship, slope = 4.5 ± 1, correlation coefficient = 0.99 (Figure 1). The line is constrained to pass through the origin since, for $[Cu^{II}] = 0$, anisole/benzene = 0, as predicted by the kinetic analysis and observed experimentally. When the value of the slope is combined with the value of the rate constant k_2 ($\geq 1.4 \times 10^5$ M^{-1} s^{-1}) and the concentration of methanol (25 M), the absolute rate constant for oxidation of phenyl radicals by copper(II) caprylate is found to be about 1×10^7 M^{-1} s^{-1} at 23 °C. When photolysis of benzoyl peroxide was employed as the source of phenyl radicals, a similar value was obtained.

The value determined for k_1 compares quite well with the rates of oxidation reported for the reaction of alkyl radicals with copper(II) acetate.[11] A general trend is observed (Table IV) for alkyl radicals such that the higher the oxidation potential the slower the rate of oxidation; thus, the rate of oxidation of methyl < 1° < 2° < 3°. The phenyl radical has an oxidation potential (8.8–9.2 eV)[21] slightly higher than that of *n*-propyl (8.7 eV), and the oxidation rate constant determined is somewhat slower (1×10^7 vs. 4×10^7 M^{-1} s^{-1}, respectively).

Having obtained the rate constant for oxidation of the phenyl radical, it may be asked whether or not oxidation by copper(II) carboxylates is sufficiently fast to produce the ratio of products observed (i.e., anisole/benzene = 82/1, Table I) in the reaction of iodonium salts with copper.[22] For a free phenyl radical in the reaction solution, the ratio of anisole/benzene expected is only 0.003 if $[Cu^{II}] = 1 \times 10^{-3}$ M. Only by the operation of a dramatic "cage effect" could a mechanism generating a phenyl radical/Cu^{II}

---

(16) The trapping of aryl radicals by copper(I) carboxylates has been examined; reactions of the arylcopper(II) intermediates thus generated show some similarity to those of the putative phenylcopper(III) intermediate produced here. Cohen, T.; Lewin, A. H. *J. Am. Chem. Soc.* **1966**, *88*, 4521.

(17) Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 528.

(18) Packer, J. E.; House, D. B.; Rasburn, E. J. *J. Chem. Soc. B* **1971**, 1574.

(19) The experimental absolute rate constant for abstraction of hydrogen from methanol by phenyl[18] compares favorably with that reported for abstraction by *tert*-butoxy radicals (3.4×10^5 M^{-1}, 21 ± 2 °C)[20] which are also highly reactive.

(20) Paul, H.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520.

(21) Johnstone, R. A. W.; Mellon, F. A. *J. Chem. Soc., Faraday Trans 2* **1972**, *68*, 1209. Ambroz, H. B.; Kemp, T. J. *Chem. Soc. Rev.* **1979**, *8*, 353.

(22) It is possible that the Cu^{II} salt produced upon electron transfer to PIFA (copper(II) benzoate hexafluoroarsenate), having the extremely nonnucleophilic AsF_6^- counterion, is somewhat more reactive toward phenyl than in copper(II) benzoate. Kochi found[23] the rate of oxidation of *n*-butyl by copper(II) triflate to be about 10 times faster than by copper(II) acetate.

(23) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843.

Scheme IV

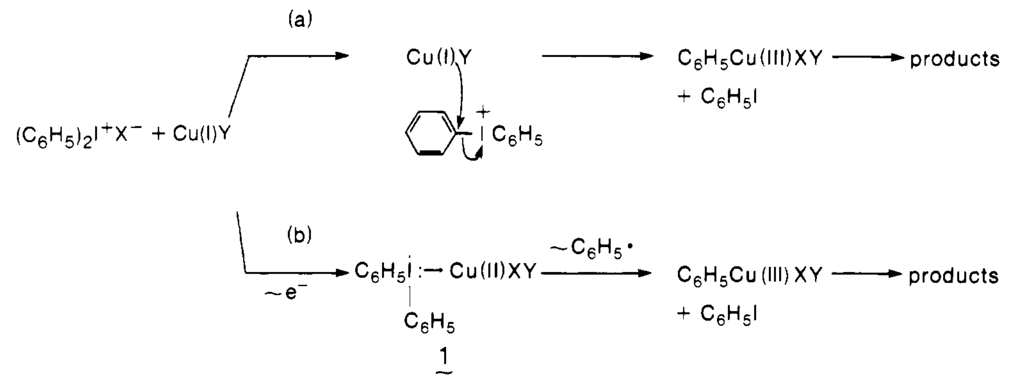


Table V. Reaction of $C_6H_5N_2^+BF_4^-$ and PIFA with Cu^I in Methanol[a]

run no.	salt[b]	absolute yield, % benzene	absolute yield, % anisole
1	$C_6H_5N_2^+BF_4^-$	82	2
2	$(C_6H_5)_2I^+AsF_6^-$	1	82

[a] $[Cu^I] = 1 \times 10^{-2}$ M in run 1, 5×10^{-3} in run 2. [b] [Onium salt] $= 1 \times 10^{-2}$ M.

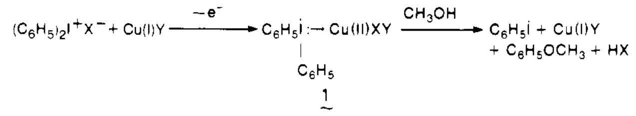
solvent-caged pair account for the ratio of anisole to benzene observed.[24] From these arguments, it appears that a mechanism which invokes the formation of aryl radical intermediates is tenuous.

It should be noted, however, that the phenylcopper species which is a likely intermediate in the oxidation of phenyl radicals by Cu^{II}, does lead to anisole formation in methanol. Such a species remains attractive as a possible intermediate in the reaction of diphenyliodonium salts with Cu^{II}.

Direct Comparison of Iodonium and Diazonium Salt Reactions. The incompatibility of a phenyl-mediated pathway in the iodonium salt reactions and the fundamental difference between the reaction of iodonium and benzenediazonium salts with Cu are emphasized by a comparison of the products observed from the two salts under identical reaction conditions. Typically, in preparative reactions involving aryldiazonium salts and Cu, solvents that are relatively inert toward radicals and high concentrations of copper salts (usually >0.1 M) are used. Under such conditions, only small amounts of reduction products (ArH) are observed. However, when benzenediazonium tetrafluoroborate reacted with 0.01 M Cu^I in methanol solution (Table V), benzene was the predominant product, as expected for a phenyl radical mediated reaction (vide supra). The contrast with the results obtained with PIFA are dramatic and firmly demonstrate the fundamental differences between the two reactions.

Test for Phenyl Radicals in CH_2Cl_2 Solution. In analogy to the experiments in methanol, it must be asked whether or not the ratio benzene/bromobenzene observed with PIBr in CH_2Cl_2 [Table II; 3 and 4] is that expected for a phenyl radical intermediate. A phenyl radical would have an opportunity to abstract hydrogen from CH_2Cl_2 or bromine from copper(II) bromobenzoate, which would be formed upon electron transfer between PIBr and Cu^I. This question was evaluated by independently generating phenyl radicals (by photolysis of iodobenzene to low conversion) in CH_2Cl_2 in the presence of 0.005 M $CuBr_2$ ($CuBr_2$ should be an appropriate kinetic model for copper(I) bromobenzoate). From phenyl radicals, benzene/bromobenzene was obtained in the ratio 3/1. Therefore, if phenyl radicals are significant intermediates in the reaction of PIBr in CH_2Cl_2, a high yield of benzene should be obtained. Instead, the reaction of PIBr with Cu^I [Table II; 3 and 4] produced a benzene/bromobenzene ratio <1/16.

Scheme V



In contrast, PIFA reacted with Cu^I in CH_2Cl_2 to produce a significant amount of benzene, presumably from a phenyl radical intermediate. One may speculate that the reactions of PIBr and PIFA with Cu^I in CH_2Cl_2 proceed initially along the same reaction coordinate (electron transfer) and diverge only at a subsequent stage, the PIFA reaction leading to phenyl radicals and PIBr to bromobenzene (vide infra).

Alternate Mechanistic Proposals. Given the failure of the mechanism modeled upon diazonium salt chemistry, several alternate mechanisms are proposed (Schemes IV and V) to account for the chemistry observed in methanol solution.

The pathways in Scheme IV have the common feature of postulating the intermediacy of a phenylcopper species. As pointed out above, such a complex remains viable as an intermediate on the reaction pathway, although it cannot be formed from a phenyl radical precursor. Pathway a corresponds to a formal nucleophilic displacement on aromatic carbon by Cu^I. A related pathway would be oxidative addition of the diphenyliodonium salt to Cu^I followed by subsequent loss of iodobenzene to give the phenylcopper intermediate. Pathway b illustrates inner sphere electron transfer resulting in a copper-complexed diphenyliodine radical **1**, analogous to the electron-transfer complex proposed in the reaction of diazonium salts with copper. Subsequent intramolecular migration of a phenyl group to copper would produce the phenylcopper species from which the phenyl ether is obtained.

Pathway b in Scheme IV receives some support from the report of Reutov and co-workers[25] that formally related aryl migrations from diaryliodonium chloride to metal have been observed in a number of cases (eq II). $HgCl_2$ on the left side of the equation

$$Ar_2I^+Cl^-{\cdot}HgCl_2 + M \rightarrow ArHgCl + ArI + MCl_2 \quad (II)$$

$$M = Hg,\ Fe,\ Sn,\ \text{and}\ Cu$$

may be replaced by chlorides of Sn, As, Sb, and Bi.

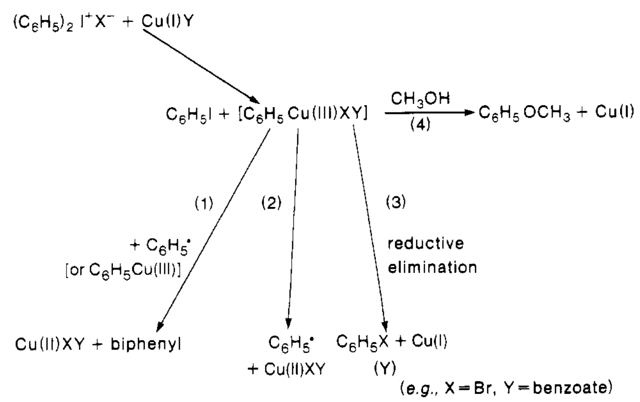
Although it has been demonstrated that Cu^{II} oxidizes phenyl radicals, presumably via phenylcopper, to produce anisole in

---

(24) The magnitude of the cage effect that would be required to produce the observed benzene/anisole ratio can be illustrated by the following argument: the rate of diffusive encounter of phenyl and Cu^{II} in solution is between 10^9 and 10^{10} s^{-1}, but the rate of oxidation is only 10^7 s^{-1}; therefore, only one in every 10^2 to 10^3 encounters is "productive" (results in oxidation). The phenyl/Cu^{II} pair in Scheme II (eq 2) should be roughly equivalent to a single diffusive encounter of phenyl and Cu^{II} (perhaps somewhat more favorable in orientation than an average diffusive encounter). Barring an extraordinary effect then, escape from the solvent cage should still dominate the reactions of the phenyl/Cu^{II} pair. This picture is consistent with kinetic studies of cage reactions, notably those of Greene et al. (Greene, F. D.; Berwick, M. A.; Stowell, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 867) and Kopecky and Gillan (Kopecky, K. R.; Gillan, T. *Can. J. Chem.* **1969**, *47*, 2371).

(25) Reutov, O. A.; Khu, K. V. *Dokl. Akad. Nauk SSSR* **1958**, *122*, 825. Reutov, O. A. In "Theoretical Organic Chemistry", Kukulê Symposium; Butterworths: London, 1959. Ptitsyna, O. A.; Reutov, O. A.; Ertel, G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1961**, 285.

Scheme VI



methanol solution, and other experimental observations are entirely consistent with their presence on the reaction pathway, phenylcopper species are not *required* as intermediates on the pathway to the products of aromatic substitution (anisole). In Scheme V, a mechanism is proposed in which anisole is produced from the iodonium salt without the formation of a phenylcopper intermediate. The electron-transfer complex **1** could produce anisole directly, either by attack of free methanol or methanol complexed to Cu^{II}. A similar proposal was offered by Roberts[5] and Beringer[4] and co-workers to account for formation of aromatic substitution products from diphenyliodonium salts.

Invoking a phenylcopper(III) intermediate in the reaction of PIFA with Cu^I, however, permits a number of observations in methanol and CH_2Cl_2 solvents to be correlated in a single, concise mechanistic scheme (Scheme VI). Thus, reaction of nucleophiles (methanol) with the phenylcopper intermediate [pathway 4] leads to the formation of aromatic substitution products (anisole)[26] with regeneration of catalytically active Cu^I. In contrast, in CH_2Cl_2 solution containing only poor nucleophiles ($X = AsF_6^-$), the primary products are benzene and biphenyl. Benzene is presumably derived from a phenyl radical which could be formed by homolytic cleavage of the phenylcopper bond [pathway 2].[16] The route leading to biphenyl is complex.[27] A strong dependence of the biphenyl yield on the concentration of Cu^I was observed for both PIFA and PIBr in CH_2Cl_2, suggesting that biphenyl may result from a bimolecular reaction involving the phenylcopper intermediate [pathway 1]. Both benzene and biphenyl, if formed from a phenylcopper intermediate would not lead to regeneration of Cu^I. As observed experimentally, the reaction of PIFA with Cu^I in CH_2Cl_2 is not catalytic in Cu^I.

The reaction of PIBr (X = Br) in CH_2Cl_2 differed dramatically from the reaction of PIFA, bromobenzene appearing as a major product at the expense of benzene, biphenyl, and phenyl benzoate. As demonstrated above, bromobenzene is not formed from phenyl radical intermediates. The failure of the phenylcopper complex to suffer phenyl–copper bond cleavage may be attributed to the presence of the nucleophilic bromine counterion in the phenylcopper complex. Reductive elimination, yielding bromobenzene, regenerates Cu^I [pathway 3], and the reaction with PIBr is catalytic in Cu^I. The diversion of reaction products in CH_2Cl_2 as a function of Br^- vs. AsF_6^- counterion suggests that when a nucleophilic ligand is available, reductive elimination is favored over phenylcopper bond homolysis. Similarly, in methanol solution, electrophilic attack on solvent[26] occurs in almost complete preference to bond homolysis.

The modest yield of phenyl benzoate observed in the reaction of PIFA in CH_2Cl_2 compared with the yield of reductive elimination products using PIBr is presumably due to the strong preference of Cu^{n} for relatively nucleophilic counterions; thus, reductive elimination of phenyl benzoate from phenylcopper(III) benzoate hexafluoroarsenate, which would produce Cu^IAsF_6, is disfavored relative to homolysis. The same factor (i.e., counterion nucleophilicity) may likewise favor reductive elimination of Br over benzoate in the PIBr reaction.

Lastly, the ratio of anisole/bromobenzene observed with PIBr in methanol (6, Table I), suggests that given a choice between reductive elimination and reaction with methanol,[26] the phenylcopper(III) bromobenzoate intermediate has a slight preference for the latter pathway.

Attempts to Demonstrate Phenylcopper Existence. Alkylcopper(III) intermediates, produced upon trapping of alkyl radicals with Cu^{II}, have been observed spectroscopically,[14] and their lifetimes in aqueous solution have been determined by fast kinetic techniques (CH_3Cu^{III}, in water, disappears with a pseudo-first-order rate constant of $7 \times 10^2\ s^{-1}$ at 25 °C).[14a] Given the surprisingly long lifetimes of alkylcopper intermediates in aqueous solution, it seemed worthwhile to explore the possibility that in a nonnucleophilic solvent such as dichloromethane the phenylcopper intermediate produced in the reaction of Cu^I with iodonium salts might be observed directly.

Reaction of PIFA with Cu^I in CH_2Cl_2 provided no evidence of a long-lived intermediate (the reaction was conducted in an NMR probe, but no transient NMR signals were observed; the experiment was complicated by line broadening due to the formation of Cu^{II} during the reaction). If a sufficiently long-lived intermediate was produced in the reaction, then iodobenzene might be formed much more rapidly than other products early in the reaction; the ratio of products observed by VPC, however, did not vary appreciably over the course of the reaction. Lowering the temperature to between −10 and −20 °C slowed the reaction of the iodonium salt, but again without providing evidence for the buildup of an intermediate (the product ratio was unchanged).

Resolution of the question of phenylcopper formation may require application of fast kinetics techniques such as those used to observe alkylcopper species.[14] Comparison of the UV–visible spectrum of an intermediate formed upon trapping of phenyl radicals (generated photolytically) by Cu^{II} with intermediates formed in the reaction of PIFA with Cu^I would most directly address this question.

Conclusions

Assignment of the reactive form of copper to the 1+ oxidation state has been firmly established in experiments demonstrating the high reactivity of a Cu^I complex. Also, inhibition of the thermal reaction of a diphenyliodonium salt with copper(II) benzoate by cuproin, which acts as a Cu^I trap, was observed.

A mechanism which invokes intermediate phenyl radicals, such as that favored for the chemistry of aryldiazonium salts, has been questioned on the basis of a comparison of the products obtained from diphenyliodonium and benzenediazonium salts under similar reaction conditions. Furthermore, the rate of oxidation of phenyl radicals by Cu^{II} was measured and appears inconsistent with any mechanism that invokes phenyl radical intermediates on the pathway to aryl ether formation from the reaction of diphenyliodonium salts with Cu^I in alcohol solvents. Alternative mechanisms, notably postulating the intermediacy of a phenylcopper species, have been proposed.

Experimental Section

Materials. Diphenyliodonium hexafluoroarsenate and diphenyliodonium bromide were generously supplied by J. L. Lee and J. V.

---

(26) A referee has suggested the possibility that anisole formation may take place via reductive elimination from a $C_6H_5Cu^{III}(OCH_3)(Y)$ intermediate rather than from nucleophilic attack of methanol on the $C_6H_5Cu^{III}(X)(Y)$ intermediate. According to this scheme, methanol exchange in (i) may occur, generating the copper(III) methoxide (ii). Reductive elimination from (ii) could produce both anisole and C_6H_5Y (Y = benzoate, Br^-).

$$\underset{\text{i}}{C_6H_5Cu^{III}XY} + CH_3OH \rightleftharpoons \underset{\text{ii}}{C_6H_5Cu^{III}(OCH_3)(Y)} + HX \qquad (a)$$

$$C_6H_5OCH_3 + CuY \leftarrow \text{ii} \rightarrow C_6H_5Y + Cu(OCH_3) \qquad (b)$$

We have no information on the relative importance of eq a and at the present time cannot discriminate unambiguously between this mechanism for anisole formation and direct nucleophilic attack of methanol on (i).

(27) Biphenyl does not result from simple combination of phenyl radicals, as was demonstrated by the photolysis of iodobenzene in CH_2Cl_2: in the photolysis, a much higher rate of conversion (to phenyl radical) was attained, yet the yield of biphenyl never exceeded a few percent of the yield of benzene.

Crivello; the synthesis of these compounds has been described elsewhere.[28] Benzenediazonium tetrafluoroborate was prepared according to the procedure of Bunnett and co-workers.[29] Copper(II) benzoate and copper(II) caprylate were obtained from Pfaltz and Bauer and used without additional purification. Methanol (MCB Omnisolve) was stored over oven dried 3-Å sieves before use. CH_2Cl_2 (Burdick and Jackson glass distilled) was redistilled from P_2O_5 and stored over 4-Å sieves before use.

The synthesis of copper(I) benzoate has been described by Edwards and Richards.[30] An alternate route was employed in this study: in an inert atmosphere glovebox ($[O_2] < 10$ ppm), a mixture of copper(II) benzoate (0.016 mol) and a reducing agent, tin(II) 2-ethylhexanoate (0.009 mol), in 25 mL CH_2Cl_2 was prepared. When the mixture was stirred at room temperature, the color of the solution changed from light blue (due to Cu^{II}) to a faint grey-green over about 4 h. The very fine precipitate (the Cu^I salt) was isolated by suction filtration under N_2. The product was washed 4× with CH_2Cl_2 leaving a very light grey solid which was dried under dynamic vacuum (0.005 torr) for 12 h. The moderately air-sensitive copper(I) benzoate was isolated in 84% yield and stored under nitrogen. Examination of the product by IR (KBr pellet) revealed no evidence of carboxylate exchange (2-ethylhexanoate for benzoate) during the synthesis.

Instrumentation. Analytical VPC was performed on a Varian 3700 FID-equipped chromatograph with a 6 ft × $^1/_8$ in. 10% OV-101 column. Typical temperature program—initial temperature 40 °C for 4 min, program rate 14 °C per min, final temperature 220 °C for 4 min. A helium flow rate of 30 mL/min was used. The injector temperature was kept at 80 °C in order to avoid decomposition of the diphenyliodonium salts in the injector port. It was also necessary to clean the glass injector liner in methanol after every two or three injections (to avoid the appearance of "ghost" peaks). The VPC was interfaced with a Spectra Physics SP4000 computing integrator. ^{1}H NMR experiments were run on a Varian EM-390 90-MHz spectrometer. VPC-mass spectra (VPC-MS) were obtained on either of two instruments: The first was a GC/GC-MS (Varian MAT III) equipped with a 10 ft × $^1/_8$ in. 3% OV-17 primary column and a 25-m WCOT wide-bore secondary column. This instrument has been described in detail elsewhere.[31] The second VPC-MS used was a Varian MAT 311a employing a 10 ft × $^1/_8$ in. 3% OV-17 column.

Thermal Reactions. Solution pyrolyses of the iodonium and diazonium salts were performed in the following way: a 50-mL solution of the organic salt, copper catalyst, and the internal standard (i.s.), octane, was prepared in a foil-covered Erlenmeyer flask. Small portions of the solution were pipetted into small glass tubes (2 or 6 mm i.d.) fitted with 14/20 female ground glass joints. After three freeze-pump-thaw cycles (to 0.005 torr) the tubes were sealed under vacuum (the aryldiazonium salt reactions were carried out under an air atmosphere, for reasons described below). The solutions were immersed in an oil bath heated to the desired temperature; the temperature of the bath was regulated to ±2 °C with an I^2R Therm-o-Watch controller. After pyrolysis, the reaction tubes were allowed to cool to room temperature and then opened and analyzed immediately by VPC. Products were identified by coinjection with authentic samples and by comparison of their mass spectra (obtained by VPC-MS) either with the published spectra[32] or with spectra of authentic samples obtained under identical conditions. Quantitative determination of product yields was accomplished by comparison of the VPC peak area of reaction products with that of the (known amount of) i.s. in solution. The relative response factors of the products were measured for a range of concentrations using solutions of the authentic compounds and the i.s. Product yields are accurate to ca. ±5%, except for benzene which, when present in low yields (<10%) has a considerably larger uncertainty.

Reactions of diphenyliodonium salts with copper(I) benzoate (or copper(II) benzoate + tin(II) 2-ethylhexanoate) were conducted at room temperature in a three-neck flask fitted with an N_2 inlet and a rubber septum (through which reactants and aliquots of the reaction solution could be transferred) and solutions were stirred magnetically. The Cu^I salt was loaded into the reaction flask either in an inert atmosphere glovebox or, outside the glovebox, under a rapid flow of N_2. Iodonium salt solutions were added by syringe after purging with N_2. Lastly, the i.s. was added. Aliquots were removed periodically and analyzed by VPC. Conducting these reactions in the presence of a partial air atmosphere appeared to have little influence on the product distribution in CH_3OH or CH_2Cl_2 solution.

Reactions of the benzenediazonium salt were carried out under an air atmosphere because, as demonstrated by Bunnett and co-workers,[29] radical chain-induced decomposition of diazonium salts may occur in methanol. Bunnett and co-workers found that the presence of an air atmosphere was sufficient to completely inhibit the chain decomposition in the systems they examined.

Analysis of the diazonium salt reaction solutions was more difficult than for PIFA and PIBr solutions due to decomposition of unreacted diazonium salt in the VPC injector port, even at 80 °C. To avoid this problem, solutions were bulb-to-bulb distilled under static vacuum (0.005 torr) before VPC analysis; this separated the reaction products from unreacted diazonium salt. The data obtained with this procedure appear to be accurate to better than ±10%.

A further complication arose from the fact that benzenediazonium tetrafluoroborate reacts readily with methanol at room temperature in the absence of copper to give anisole. To avoid the problem of direct reaction, the diazonium salt was added last to the methanol/Cu^I reaction solution. Under these conditions, direct reaction with solvent was insignificant.

Photochemical Reactions. The procedure for carrying out photochemical experiments was similar to that employed for pyrolysis reactions: aliquots from a 50-mL solution of the reactant(s) and i.s. were placed in quartz tubes fitted with female joints and capped with Teflon vacuum stopcocks. After three freeze-pump-thaw cycles, the sample tubes were closed under vacuum and photolyzed by immersing in a large water bath (23 ± 1 °C) next to the light source (a Hanovia 450-W medium-pressure mercury arc lamp which rested inside a quartz well cooled by circulating water).

The photolysis of iodobenzene with $CuBr_2$ in CH_2Cl_2 requires additional comment. Because of poor solubility of $CuBr_2$ in CH_2Cl_2, methanol (4% v/v) was added. CD_3OH was used so that the contribution of methanol to the benzene product could be determined by VPC-MS. The experimental ratio C_6H_5D/C_6H_6 (<1/20) demonstrates that the presence of methanol did not significantly contribute to the yield of benzene in the reaction. Secondary photolysis of the bromobenzene product occurred to a modest extent, as demonstrated by the slight decrease in C_6H_5Br/C_6H_6 ratio as a function of photolysis time. A simple plot of this ratio (with data from 24, 40, and 50% conversion of iodobenzene) extrapolated back to zero time gave a ratio of C_6H_6/C_6H_5Br of about $(3 \pm 0.5)/1$.

Acknowledgment. I am grateful for insightful discussions with J. V. Crivello and for generous loans of material from J. V. Crivello and J. L. Lee. I also appreciate the expert assistance of R. J. May and H. Grade in obtaining VPC-MS data.

Registry No. PIFA, 62613-15-4; PIBr, 1483-73-4; copper(II) benzoate, 533-01-7; phenyl radical, 2396-01-2; copper(II) caprylate, 3890-89-9; benzenediazonium tetrafluoroborate, 369-57-3; copper(1+), 17493-86-6; iodobenzene, 591-50-4.

---

(28) Crivello, J. V.; Lam, J. H. W. *J. Org. Chem.* **1978**, *43*, 3055. Reference 1.

(29) Bunnett, J. F.; Yijima, C. *J. Org. Chem.* **1977**, *42*, 639. Broxton, T. J.; Bunnett, J. F.; Paik, C. H. *Ibid.* **1977**, *42*, 643.

(30) Edwards, D. A.; Richards, R. J. *J. Chem. Soc., Dalton Trans.* **1973**, 2463.

(31) Ligon, W. F., Jr.; May, R. J. *Anal. Chem.* **1980**, *52*, 901.

(32) "Eight Peak Index of Mass Spectra"; Mass Spectrometry Data Centre, AWRE, Reading, U.K., 1974; Vol. 1.