[cf. also A. E. Jukes, S. S. Dua, and H. Gilman, *J. Organomet. Chem.* **24**, 791 (1970)]. For example, NMR spectroscopy reveals that a suspension of polymeric 2-$Me_2NC_6H_4Cu$ in $CDCl_3$ decomposes into CuCl and secondary products, 2-$Me_2NC_6H_4D$ and (2-$Me_2NC_6H_4\!\!+_2$. The formation of CuCl can be deduced from the observation of the resonance pattern of chloroform-soluble (2-$Me_2NC_6H_4)_4Cu_6Cl_2$. This hexanuclear arylcopper–copper halide is much more stable toward chloroform than the parent organocopper: G. van Koten and J. T. B. H. Jastrzebski, unpublished results.

(25) J. A. Jarvis, B. T. Kilbourn, R. Pearce, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 475 (1973).

(26) A. Cairncross and W. A. Sheppard, *J. Am. Chem. Soc.*, **93**, 247 (1971).

(27) Nuclear quadrupole resonance spectra of samples of 2-$Me_2NC_6H_4Cu$ polymer show NQR frequencies for both copper isotopes. The observation of two signals at 21.794 (very weak) and 35.892 MHz (medium) (^{63}Cu resonance positions) indicates that the copper atoms occupy chemically inequivalent sites. This conclusion supports the proposed structure (cf. figure in ref 3) having three-coordinate copper atoms in the polymeric chain whereas the copper atoms at the end of the chains are essentially two-coordinate. H. van Dam and G. van Koten, unpublished results.

(28) H. O. House, *Acc. Chem. Res.*, **9**, 59 (1976).

(29) R. G. Pearson and C. D. Gregory, *J. Am. Chem. Soc.*, **98**, 4098 (1976).

(30) Bulky ortho substituents enlarge the barrier for rotation of a 2e–3c bonded aryl group around the C(bridge)–C(4) axis: G. van Koten and J. G. Noltes, Abstracts, XVIIth Conference on Coordination Chemistry, 1976, p 236.

(31) The formation of asymmetric biaryls in the reaction of CuOTf with premixed benzene solutions of (2-$Me_2NCH_2C_6H_4)_4Cu_4$ (Ar_4Cu_4) and (4-$MeC_6H_4)_4Cu_4$ (Ar'_4Cu_4) (see Experimental Section) indicates that (1) interaggretate exchange between these tetranuclear species takes place resulting in the formation of a mixed arylcopper–copper triflate precursor complex $Ar_xAr'_yCu_{x+y+z}OTf_z$, and (2) an even number of aryl groups ($x + y$) is present in the precursor complex because arenes are formed in very low yields.

A Simple Preparation of Phenols from Diazonium Ions via the Generation and Oxidation of Aryl Radicals by Copper Salts[1a]

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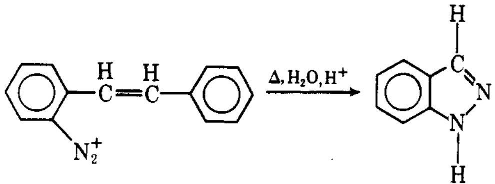
The standard method of preparation of phenols from diazonium salts consists of heating the latter in highly acidic aqueous solution; the high temperature and acidity often cause a variety of unwanted side reactions. We advocate an entirely different procedure which can be performed in a few minutes in neutral solution at room temperature, or below. The method is based on our previous observation that aryl radicals can be oxidized to phenols by cupric ion and it consists of adding cuprous oxide to a dilute solution of the diazonium salt dissolved in a solution containing a large excess of cupric nitrate. In one case the presence of silver(I) appeared to accelerate the radical oxidation. Not only is the redox procedure simpler than the thermal method, but in all cases studied to date, the yields are equivalent or superior to those obtained by the thermal procedure. In four cases in which the latter is unsatisfactory, the redox method is quite successful and it is considered the method of choice for new cases.

As indicated in all textbooks in organic chemistry the standard method for the conversion of an aromatic diazonium ion to a phenol is thermal decomposition of the diazonium ion in a highly acidic aqueous medium. The great deal of controversy concerning the mechanism of this reaction[2] has apparently been resolved recently in favor of a substantially free, singlet, aryl cation intermediate (eq 1).[3]

$$ArN_2^+ \longrightarrow N_2 + Ar^+ \xrightarrow{H_2O} ArO^+H_2 \longrightarrow ArOH + H^+ \quad (1)$$

The high acidity is required in order to suppress the ionization of the product phenol to phenoxide ion which couples readily with unreacted diazonium ion to produce an azo compound.[4,5] In order to obtain high yields of phenol uncontaminated with azo compound, it is frequently necessary to add a solution of the diazonium salt to a boiling sulfuric acid solution,[6] if possible with simultaneous removal of the phenol by steam distillation.[7]

The coupling reaction is only one of a variety of competing reactions which plague the synthesis of phenols by this route. Intramolecular nucleophiles or potential nucleophiles can also attack the diazonium group. For example, an ortho carboxamido group reacts with a diazonium function to yield a benzo-1,2,3-triazene.[8] Similarly, an ortho hydroxyl group leads to the production of a diazoxazole,[9] while an ortho thiol group leads to a benzothiadiazole.[10] Intramolecular diazo coupling with a suitably placed electron-rich ring has also been observed.[11] Nucleophilic attack on the diazonium function by an ortho vinyl group to form an indazole (1) is also common (eq 2).[12]



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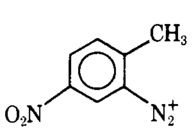
$$+ \; PhCHO + H^+ \quad (2)$$

Even a saturated carbon atom in the ortho position to a diazonium function can serve as a nucleophile, presumably after deprotonation.[13-15] For example, the diazonium ion 2



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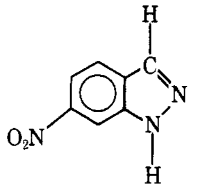
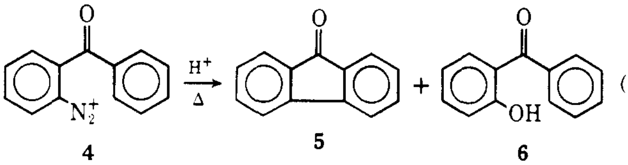


3

yields 85% of the indazole 3 when heated in acid solution,[13] although the phenol can be produced instead by adding the diazonium solution to a boiling sulfuric acid solution.[14]

Another problem sometimes encountered during thermal decomposition of a diazonium ion is replacement of an ortho or para substituent with a hydroxyl group.[16]

In addition to these competing reactions in which the two nitrogen atoms are retained in the product, several reactions in which nitrogen is lost are known to occur in place of phenol production. One of these involves attack of the aryl cation on the phenolic product to yield arylphenol and diaryl ether.[17] A more serious and widespread competing reaction of this type is intramolecular attack of the aryl cation intermediate upon a suitably placed aromatic ring;[11,18–20] the most common of these is the thermal Pschorr[18–20] reaction as illustrated in eq 3.[18–20] Two types of nitrogen-free products are frequently observed involving saturated carbon atoms four atoms removed from the carbon atom bearing the diazonium function. One of these is direct carbon–carbon bond formation leading to a five-membered ring[21–23] and the other involves a 1,5-hydrogen transfer to the carbon bearing the diazonium function.[22,24]



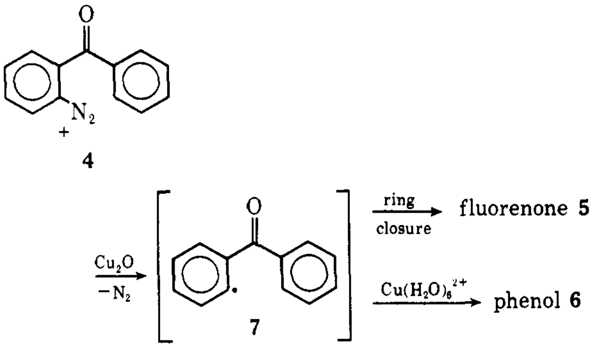
(3)

4 **5** **6**

65-68% 32-35%

Finally, the high acidity and temperature required in the conventional conversion of diazonium salt to phenol would obviously be detrimental to acid-sensitive functions such as acetals, phenol or enol esters, and lactones. Examples are given below.

In this paper we indicate the details and something of the scope of a procedure which does not require high temperatures, extreme acidities, and long reaction times. It is based upon a previous observation from this laboratory that aryl radicals, produced by cuprous oxide induced diazonium decomposition, could be oxidized to phenols by hydrated cupric ion.[20] Whereas diazonium ion **4** is converted mainly to fluorenone (**5**) by heating in acid (eq 3) and almost entirely to **5** by radical decomposition induced by cuprous oxide, 88% of the product is phenol when the latter reaction is conducted in the presence of a high concentration of cupric nitrate (eq 4). Formally, the process is a Sandmeyer reaction[25] with the transfer to the radical site of $H_2O^{+}\cdot$ instead of a halogen atom or CN radical from the ligand shell of copper(II). A reasonable mechanism involves the attack of cupric ion on the radical **7** and reductive elimination of copper(I) from the resulting arylcopper(III) hydrate (eq 5).[26]



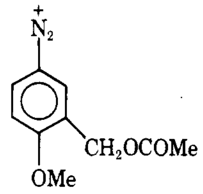
(4)

$$\mathrm{Ar}\cdot + \mathrm{Cu(H_2O)}_n^{2+} \longrightarrow \mathrm{ArCu(H_2O)}_m^{2+} \longrightarrow \mathrm{ArO^+H_2} + \mathrm{Cu(H_2O)}_{m-1}^{+} \qquad (5)$$

A closely related reaction in which a vinyl radical is apparently oxidized to an aldehyde by hydrated cupric ion has recently been described by Walling.[27]

The conversion of diazonium ions to phenols by the generation and oxidation of aryl radicals is, of course, fundamentally different from the thermal method proceeding via aryl cations and it has been suggested as a new phenol synthesis.[20] It was also demonstrated that p-bromophenol could be generated in 87% yield by the radical procedure from p-bromobenzenediazonium ion whereas a simple thermal decomposition in acid solution resulted in only 53% of phenol contaminated with "diazo resins".[20]

Since this early publication,[20] several groups have successfully utilized our procedure.[28–30] Two interesting cases which did not yield to the traditional hydrolysis procedure are **8**[29] and **9**,[30] which produced the corresponding phenols in 79 and 95% yield, respectively; it is of interest that both possess acid-sensitive functions, **8** an ester and **9** both acetal and enol lactone groups.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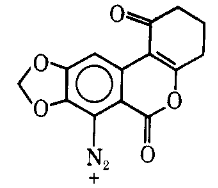
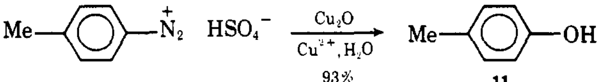

9

In order to provide information concerning the scope and utility of the copper-catalyzed conversion of diazonium ions to phenols, five diazonium salts in aqueous solutions containing cupric nitrate were subjected to the action of solid cuprous oxide. The facility of the procedure and the yields of phenol were then compared with those for the noncatalytic (thermal) method. A limited number of optimization experiments were also conducted.

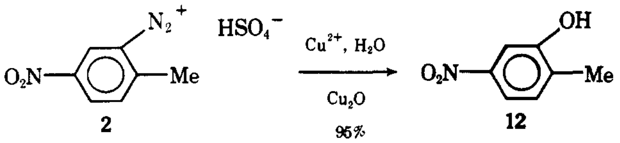
Results

Although the thermal conversion of p-toluenediazonium bisulfate (**10**) to p-cresol (**11**) proceeds in 89% yield,[7] the procedure is cumbersome, as indicated above. The copper-catalyzed reaction occurred in 93% yield (GLC) and was performed at room temperature over a period of less than 1 min. In a larger scale experiment, 88% of p-cresol could be isolated. The only two drawbacks to this procedure are that large quantities of cupric nitrate are required and that the concentration of diazonium salt must be maintained very low; both of these requirements have the same basis, that the rate of oxidation of the radical by cupric ion should be high compared to the rate of reaction of the radical with substrate or product. At a constant concentration of cupric nitrate (41 mmol/100 mL of water), the yield of p-cresol increased from 66% to 93% as the concentration of diazonium salt was lowered from 8.1 mmol to 2.6 mmol in 100 mL of water (1.8 mmol of cuprous oxide was used). Inspection of the gas chromatograms for a number of experiments in which the cupric nitrate concentration was varied indicate that the yields of phenol decreased when the concentration of copper(II) decreased much below about 41 mmol/100 mL of water.



10 **11**

As indicated above, thermal decomposition of 5-nitro-2-methylbenzenediazonium bisulfate (**2**) gives mainly the indazole **3** if it is heated in aqueous acid;[13] phenol could be produced, however, by adding the cold solution of diazonium salt to a boiling solution of concentrated sulfuric acid–water (1:2).[14] We have obtained a 95% yield (GLC) of the phenol (**12**) in a 1-min reaction at 0 °C. A higher concentration of cupric ion (205 mmol/100 mL of water) than in the case of p-cresol

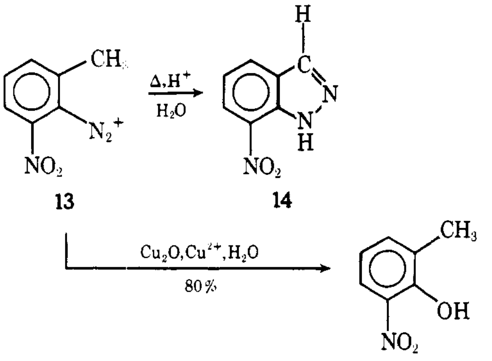


2 **12**

formation was required to obtain this yield (concentration of diazonium salt, 2.1 mmol/100 mL). The lower concentration of 123 mmol of Cu^{II}/100 mL gave an only slightly inferior yield (90%), but still lower concentrations of copper(II) caused substantial reduction in the yield of phenol and an increase in that of by-products as indicated by gas chromatograms of the reaction mixture. The by-products consisted of *p*-nitrotoluene, an aryl chloride thought to be 5-nitro-2-methylchlorobenzene (undoubtedly due to a Sandmeyer reaction involving adventitious traces of chloride ion, probably contaminating the cupric nitrate), and a biaryl (molecular ion 272 amu).

The next substrate submitted to the redox procedure for phenol formation was 6-nitro-2-methylbenzenediazonium ion (**13**). Although the amine precursor is commercially available, a careful search of the literature revealed that there are no reports of the conversion of this diazonium ion to the phenol (**15**). The reason became clear when it was discovered that the major product (42% yield) of thermal decomposition is the indazole **14**, even when the diazonium solution was added to a boiling solution of extremely strong acid (concentrated sulfuric acid–water, 2:1); the yield of phenol in this thermal decomposition was only 10% and 9% of *m*-nitrotoluene was also produced.

Several redox conversions of **13** to phenol (**15**) were performed. In all cases 0.50 mmol of diazonium salt was decomposed by 1.4 mmol of cuprous oxide in a solution containing 210 mmol of cupric nitrate in 50 mL of water. The poorest isolated yield (55% from the amine) was obtained when the diazonium bisulfate was not isolated but decomposed in situ in the still acidic solution. The yield improved to 60% (average of two experiments) when the diazonium tetrafluoroborate was decomposed in situ, also in an acidic solution. In the latter case, 14% of *m*-nitrotoluene and 8% of a biaryl were also produced. The best yields of phenol (80% based on diazonium ion, 74% based on amine) were obtained when the isolated diazonium fluoroborate was decomposed in neutral solution; in this case the yields of the two by-products were reduced to about 2% each. As in the other examples the reaction was over in 1–2 min.



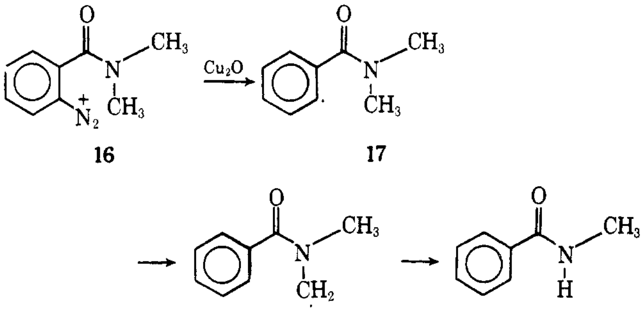
13 **14** **15**

Since aryl radicals are produced very rapidly from diazonium ions in the presence of cuprous oxide, it is clear that the phenol yield would be determined by the competition between oxidation of this radical and other reactions available to it. In order to simplify the interpretation of the data, this type of competition was studied in a system in which only a single nonoxidative reaction is available to the radical. Previous work in this laboratory[22,31,32] has established that the radical **17**, formed by the reaction of diazonium ion **16** with cuprous oxide, undergoes an extremely efficient 1,5-hydrogen atom transfer to produce the new radical **18** which, in the presence of cupric ion, is converted to *N*-methylbenzamide (**19**) and formaldehyde. Yields of **19** in excess of 95% can be obtained when cupric ion is not purposely added to the solution; the only other detected product is reduced material, *N,N*-dimethylbenzamide.

Table I. Cuprous Oxide Induced Decomposition of *N,N*-Dimethylbenzamide-*o*-diazonium Tetrafluoroborate at Room Temperature in the Presence of Cupric Nitrate and Silver Nitrate[a]

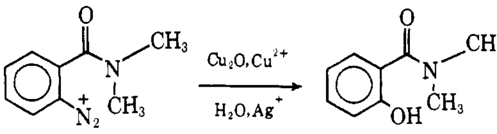
Reagents, mmol			Phenol[b]/ *N*-methylbenzamide	Phenol[b]/ *N,N*-dimethylbenzamide
ArN_2^+	$Cu(NO_3)_2$	$AgNO_3$		
2.3	4.1		0.17	v large
2.5	20		0.39	v large
2.3	20	30	2.8	5.0
2.3	40	15	3.6	1.2
2.5	40	30	5.8	8.2
2.4	40	30	5.5	9.2
2.3	40	60	7.1	6.6
2.1	60	30	9.8	11
2.4	60[c]	60[c]	12	7.5
2.4	80[c]	60[c]	12	7.5
2.4	100[c]	60[c]	12	7.5

[a] 100 mg of Cu_2O in 10 mL of H_2O used in each case except run 3, in which 540 mg was used. [b] Ratios determined by gas chromatography. [c] The cupric and silver nitrates were not completely soluble at these concentrations.



16 **17** **18** **19**

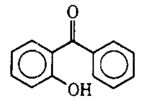
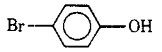
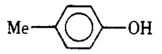
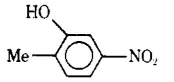
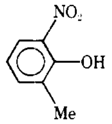
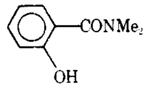
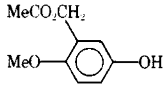
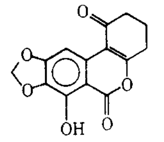
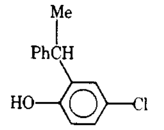
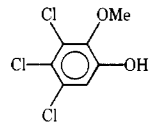
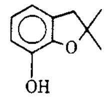
It was found that the aryl radical **17** can be intercepted and converted to phenol (**20**), although inefficiently, by high concentrations of cupric ion (Table I). However, the interception becomes far more efficient when silver nitrate is also present in the solution and, at a given concentration of cupric ion, the ratio of phenol (**20**) to *N*-methylbenzamide (**19**) produced increases with increasing concentration of silver(I) (Table I). Unfortunately, the yield of reduced material, *N,N*-dimethylbenzamide, also has a tendency to increase when the silver ion concentration is increased, particularly at high concentrations of the latter. Nevertheless, a yield of 54% of *N,N*-dimethylsalicylamide could be obtained in the three runs at the bottom of Table I; this represents a fairly efficient diversion of the aryl radical when it is considered that no detectable phenol is produced without the deliberate addition of copper(II) and silver(I). The thermal decomposition of the diazonium ion gives about the same yield of phenol accompanied by *N*-methylbenzamide and *N*-methylphthalimidine.[22]



16 **20**

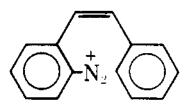
Finally, the redox procedure was applied to *cis*-stilbene-2-diazonium ion (**21**). As indicated in eq 2, DeTar and Chu[12] reported that thermolysis in aqueous acid yielded indazole (**1**, 62% yield) and benzaldehyde as the major products. However,

Table II. Yields in the Conversion of Diazonium Ions to Phenols by the Redox Method

Entry	Phenol prepared	Yield, %[a]	Ref
1		76–85	20
2		87	20
3		93	*b*
4		95	*b*
5		80	*b*
6		54	*b*
7		79	29
8		95	30
9		38[c]	28a
10		*d*	28b
11		88–93	28c

[a] Yields are the maximum obtained if more than one set of conditions was tried. [b] Present work. [c] No attempt was made to improve this yield. [d] Yield not reported.

at higher temperatures, the isomerized olefin, *trans*-2-hydroxystilbene, and the product of Pschorr ring closure, phenanthrene (**22**), predominated; no *cis*-2-hydroxystilbene was produced. Treatment of this diazonium ion (**21**), as its



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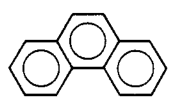

22

tetrafluoroborate salt, with cuprous oxide in a solution containing cupric nitrate gave 64% (GLC yield) of phenanthrene and a trace of stilbene. Apparently, the radical undergoes such rapid ring closure that it is not intercepted by cupric ion. Supplementation of the cupric nitrate with silver nitrate did not lead to the cis phenol; phenanthrene was produced in 86% yield.

Conclusions

The redox procedure is the method of choice for the conversion of diazonium salts to the corresponding phenols. Table II is a compilation of all of the examples of its successful use of which we are aware. The only unsuccessful case of which we know is that of the *cis*-stilbene-2-diazonium ion (**21**); the thermal method is also unsuccessful in this case. It may be that other metal ions would lead to a successful phenol synthesis from **21**. We are unaware of any example in which the thermal method is significantly more successful than the redox procedure and the latter has been successful in at least four cases in which the thermal method gives extremely poor yields or fails entirely (entries 1, 5, 7, and 8, Table II). The redox method should be especially advantageous in the case of diazonium ions which undergo indazole formation readily or those which bear groups which are sensitive to the strong acid or high temperatures ordinarily required in the thermal method. However, even in cases in which the latter gives satisfactory yields of phenol, the redox procedure is very much preferable owing to its great ease and rapidity. The major disadvantage of the procedure is that fairly high dilutions are necessary for optimum results.[33] However, it appears likely that the use of silver nitrate will permit higher concentrations to be used since in the case of diazonium ion **16** this salt apparently increases the rate of radical oxidation.

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. Mass spectra were obtained on an LKB-9000 combined gas chromatograph–mass spectrometer at 70 eV. Gas–liquid chromatography (GLC) was performed on Varian Associates Model 1860-3 and Hewlett-Packard Model 5750 gas chromatographs equipped with flame ionization detectors and either a Disc or an electronic integrator.

***p*-Cresol (11).** *p*-Toluidine (0.213 g, 1.98 mmol) was dissolved in 2 mL of hot 35% sulfuric acid and then allowed to cool to below 15 °C. Ice (2 g) was added and the amine bisulfate precipitated. A solution of 0.176 g (2.55 mmol) of sodium nitrite in 2 mL of ice water was added dropwise under the surface of the ice-cooled solution with stirring at such a rate as to maintain the temperature at 0–5 °C. After the solution had been stirred for an additional 5 min, a few crystals of urea were added to decompose any excess sodium nitrite.

To the cold (0 °C) solution of *p*-methylbenzenediazonium bisulfate was added a solution of 7.5 g (31 mmol) of cupric nitrate trihydrate in 70 mL of water (total volume 76 mL of H_2O) at room temperature. With vigorous stirring, 0.265 g (1.82 mmol) of cuprous oxide was added to the solution. The liquid became dark blue and rapidly changed to green. About 1 min after the addition of cuprous oxide the nitrogen evolution ceased and a negative test with alkaline β-naphthol indicated that the reaction was complete. The mixture was extracted with ether and this extract was used for the GLC analysis.

p-Cresol was identified by comparison of its GLC retention times with those of an authentic sample via the coinjection technique and by its combined GLC–mass spectrum:[34] *m/e* (rel intensity, assignment) 109 (7, P + 1), 108 (90, P), 107 (base, P − H), 90 (8, P − OH_2), 79 (15), 77 (20). The yield of *p*-cresol by GLC (hexadecane as internal standard) was 93%. An isolated yield of 88% for this phenol was realized from 5.34 g (50.0 mmol) of the amine by base extraction of the organic extract, reacidification of the aqueous solution, and extraction with ether.

5-Nitro-2-methylphenol (12). By a similar procedure, using 0.319 g (2.08 mmol) of 5-nitro-2-methylaniline (Matheson Coleman and Bell), 5 mL of sulfuric acid, 5 g of ice, 2.5 mmol of sodium nitrite in 2 mL of ice water, 205 mmol of cupric nitrate trihydrate in 90 mL of water, and 1.96 mmol of cuprous oxide, a 95% (GLC) yield of 5-nitro-2-methylphenol was obtained. It was identified by the melting point of an isolated sample, 115–117 °C (after recrystallization from petroleum ether–benzene) (lit.[14] mp 118 °C), and by its combined GLC–MS: *m/e* (rel intensity, assignment) 154 (10, P + 1), 153 (base, P), 107 (30, P − NO_2), 95 (7, P − NO, CO), 79 (17, P − NO_2, CO), 77 (52). Three very minor peaks had mass spectra which were consistent with those expected for *p*-nitrotoluene,[35] 5-nitro-2-methylchlorobenzene, and a biaryl (molecular ion 272).

2-Methyl-6-nitrobenzenediazonium Tetrafluoroborate. A solution of 2-methyl-6-nitroaniline (2.00 g, 13.2 mmol, Aldrich) and 5.4 g (30 mmol) of fluoroboric acid (48–50%) in 100 mL of absolute ethanol was stirred and cooled to 0 °C. To the resulting solution was added, dropwise over a 15-min period, 2.12 g (18.0 mmol) of freshly distilled *n*-amyl nitrite. The resulting solution was stirred for 30 min at 0 °C and poured into 100 mL of cold ether causing precipitation of 3.0 g (92% yield) of 2-methyl-6-nitrobenzenediazonium tetrafluoroborate: mp 117.5–118.0 °C dec; IR (Nujol) 2300 (s, $N{\equiv}N^+$), 1560 (s, NO_2), and 1050 cm^{-1} (s, broad, BF).

2-Methyl-6-nitrophenol (15). A. From Isolated 2-Methyl-6-nitrobenzenediazonium Tetrafluoroborate. The reaction was performed using 0.125 g (0.50 mmol) of the diazonium salt, 75 g (0.31 mol) of cupric nitrate trihydrate, 67 mg (1.4 mmol) of cuprous oxide, and 50 mL of water at room temperature. The decomposition seemed to be complete within a matter of minutes, but stirring was continued for an additional 30 min. The mixture was filtered free of cuprous oxide. The filtrate was made basic by the addition of 10 mL of 1 N sodium hydroxide and the resulting solution was extracted with methylene chloride. The base extract was reacidified with dilute hydrochloric acid and extracted with methylene chloride. The extract was dried (sodium carbonate) and filtered, and the solvent evaporated to leave 59 mg (0.38 mmol, 77% yield) of light yellow crystals of 2-methyl-6-nitrophenol: mp 68.0–68.5 °C (lit.[14] mp 69.5 °C); *m/e* (rel intensity, assignment) 154 (8, P + 1), 153 (base, P), 136 (8, P − OH), 107 (14, P − NO_2), 105 (9, P − NO, H_2O), 79 (11, P − NO_2, CO), 77 (32). GLC analysis of the organic extract from the basic solution indicated the presence of *m*-nitrotoluene, a biaryl (base peak 226 for P − NO_2), and a trace of 2-chloro-3-nitrotoluene.

B. From 2-Nitro-6-methylbenzenediazonium Bisulfate Prepared in Situ. The procedure was identical with that used for *p*-toluidine described above. The quantities used were 0.50 mmol of amine, 2.5 mL of sulfuric acid, 2 g of ice, 0.64 mmol of sodium nitrite in 2.5 mL of water, 21 mmol of cupric nitrate trihydrate in 50 mL of water, and 1.4 mmol of cuprous oxide. The 2-methyl-6-nitrophenol prepared (55% yield) in this manner was not as clean (dull yellow crystals, broad mp range, 59–64 °C) as that produced from the isolated 2-methyl-6-nitrobenzenediazonium tetrafluoroborate. Analysis of the neutral fraction by GLC indicated that *m*-nitrotoluene (13% yield), the biaryl (5%), and a trace of aryl chloride were also produced.

C. From 6-Nitro-2-methylbenzenediazonium Tetrafluoroborate Prepared in Situ. A solution of 76 mg (0.50 mmol) of 2-methyl-6-nitroaniline and 10.4 mL (60 mmol) of fluoroboric acid (48–50%) was magnetically stirred at room temperature for 0.5 h. The solution was cooled to 0 °C and treated dropwise over a 15-min period with 2 mL of an aqueous solution of sodium nitrite (44 mg, 0.64 mmol). The decomposition procedure and workup were identical with those described above. The yield of phenol was 62%; *m*-nitrotoluene (14%), the biaryl (8%), and a trace of aryl chloride were also formed.

Thermal Decomposition of 2-Nitro-6-methylbenzenediazonium Tetrafluoroborate. An aqueous solution containing 125 mg (0.500 mmol) of 2-methyl-6-nitrobenzenediazonium tetrafluoroborate in 25 mL of water was added dropwise to a boiling solution of aqueous sulfuric acid and sodium sulfate [25 g of concentrated sulfuric acid, 12.5 mL of water, and 18.7 g (157 mmol) of sodium sulfate].[6b] The resulting solution was heated at reflux for 2 h, cooled to room temperature, and extracted with methylene chloride. A GLC analysis indicated the presence of 3-nitrotoluene (9.2%) and 2-methyl-6-nitrophenol (9.7%), as well as a major component of longer retention time. The solution was extracted with 10 mL of a 1 N sodium hydroxide solution. The aqueous layer was made slightly acidic (pH 6, litmus) by the addition of 1 N hydrochloric acid; the resulting solution was extracted with methylene chloride, and the combined extracts were dried (magnesium sulfate), filtered, and concentrated, leaving 34 mg (42% yield) of a light yellow crystalline compound, mp of 7-nitro-1*H*-indazole 184–185 °C (lit. mp[36] 187 °C). The mass spectrum was also consistent with this structure: *m/e* (rel intensity, assignment) 164 (9, P + 1), 163 (base, P), 117 (22, P − NO_2), 90 (46), 63 (21).

***o*-Amino-*N,N*-dimethylbenzamide.** A mixture containing 1.01 g (5.15 mmol) of *o*-nitro-*N,N*-dimethylbenzamide[22a] and 0.101 g of 10% palladium on charcoal in 25 mL of absolute ethanol was hydrogenated at room temperature and atmospheric pressure. The hydrogen uptake was approximately 400 mL. The solution was filtered free of catalyst and the solvent was evaporated leaving an almost colorless oil that was induced to crystallize to give 0.80 g (95% yield) of white amine: mp 61.0–61.5 °C (lit.[37] mp 61–62 °C); IR ($CHCl_3$) 3480 (w), 3370 (w), and 1610 cm^1 ($C{=}O$).

***N,N*-Dimethylbenzamide-*o*-diazonium Tetrafluoroborate.** The procedure was the same as that used for the preparation of 2-methyl-6-nitrobenzenediazonium tetrafluoroborate. From 0.800 g (4.87 mmol) of *o*-amino-*N,N*-dimethylbenzamide, there was obtained 1.17 g (92% yield) of *N,N*-dimethylbenzamide-*o*-diazonium tetrafluoroborate, after recrystallization from cold acetone–ether: mp 96–97 °C dec; IR (Nujol) 2280 (s, $N{\equiv}N^+$), 1620 (s, $C{=}O$), and 1050 cm^{-1} (s, broad, BF).

Decomposition of *N,N*-Dimethylbenzamide-*o*-diazonium Tetrafluoroborate. The following representative procedure is the one that gives the optimum yield of the phenol; in other experiments the quantities of copper(II) and silver(I) salts were varied as indicated in Table I. The diazonium salt (62.4 mg, 0.237 mmol) was added to a stirred suspension of 100.0 ± 2 mg of cuprous oxide in 10 mL of distilled water containing 15 g (60 mmol) of cupric nitrate trihydrate and 10 g (59 mmol) of silver nitrate at room temperature, under a positive pressure of prepurified nitrogen. As the diazonium salt was added to the suspension an immediate evolution of nitrogen gas was observed. The reaction was over almost immediately and was considered complete when a negative β-naphthol test was obtained; stirring was continued for an additional 30 min. The reaction mixture was filtered free of cuprous oxide and other inorganic salts, the reaction vessel being rinsed well first with water and then with methylene chloride. The aqueous layer was extracted with four 15-mL portions of methylene chloride and the combined extracts were dried (sodium carbonate) and concentrated. The residue was taken up in 3 mL of acetone, the GLC standard, *p*-tolyl benzoate, was added, and the solution was analyzed by GLC. The chromatogram exhibited three peaks which were identified by a comparison of retention times with those of authentic samples of *N,N*-dimethylbenzamide (Eastman Organic Chemicals), *N*-methylbenzamide,[22d] and *N,N*-dimethylsalicylamide.[22c] Coinjection with authentic samples caused peak enhancements for each of the three compounds.

***cis*-2-Nitrostilbene.** *trans*-*o*-Nitro-α-phenylcinnamic acid was decarboxylated by the method of Cohen and Schambach.[38] In a 500-mL, three-neck, round-bottom flask fitted with a nitrogen inlet which entered below the surface of the liquid and a thermometer that was immersed in the liquid were placed 11 g (40 mmol) of *trans*-*o*-nitro-α-phenylcinnamic acid,[12] 2.9 g (20 mmol) of cuprous oxide, and 250 mL of quinoline. The mixture was then heated slowly until the rate of carbon dioxide evolution (noted via a change in weight of an Ascarite tube) reached a maximum (155 °C). Carbon dioxide evolution was monitored until the reaction was nearly complete (97% yield of CO_2) after which time the reaction mixture was allowed to cool to room temperature. Cuprous oxide and other inorganics were removed by filtration, the quinoline was removed by vacuum distillation (55 °C at 0.1 mmHg), and the residue was chromatographed on a 4-ft glass column packed with neutral alumina. The *cis*- and *trans*-2-nitrostilbene isomers were eluted with a 5% ether–95% *n*-hexane mixture, the cis isomer eluting first and yielding bright yellow needles, mp 63.0–63.5 °C (lit.[12] mp 63.0–63.5 °C), in a 55% yield.

***cis*-Stilbene-2-diazonium Tetrafluoroborate.**[12] Reduction of 3.0 g of the nitrostilbene to the hydrochloride (mp 203–204 °C lit.[12] mp 202–203 °C) of *cis*-2-aminostilbene was accomplished in 60% yield by the method of Ruggli and Staub.[39] This hydrochloride (1.85 g, 8.0 mmol) was dissolved in 50 mL of a 10% aqueous sodium hydroxide solution, shaken vigorously, and extracted four times with 10-mL portions of methylene chloride. The combined extracts were dried over sodium carbonate and concentrated, leaving 1.54 g (7.9 mmol) of a colorless oil, presumed to be *cis*-2-aminostilbene, which showed one peak via a GLC analysis. To a stirred solution of this oil in 50 mL of absolute ethanol at 0 °C was added 5.4 g (30 mmol) of fluoroboric acid (48–50%) and the resulting solution was allowed to stir for 15 min. Freshly distilled *n*-amyl nitrite (1.42 g, 12.0 mmol) was then added dropwise over a 15-min period, whereupon the reaction mixture changed from colorless to bright yellow. After the solution had been stirred for 2 h at 0 °C, 200 mL of cold anhydrous ether was added to precipitate the bright yellow diazonium salt. The material was then filtered and purified by solution in a mixture of 40 mL of methanol–10 mL of dimethylformamide followed by precipitation with about 250 mL of anhydrous ether. The yield of reprecipitated fluoroborate (yellow crystals) was 1.45 g (65%): mp 87.0–87.5 °C dec; IR (Nujol) 2240 (s, $N{\equiv}N^+$), 1470 (s), and 1050 cm^{-1} (s, broad, BF).

Decomposition of *cis*-Stilbene-2-diazonium Tetrafluoroborate. The procedure was nearly identical with that for the decomposition of *N,N*-dimethylbenzamide-*o*-diazonium tetrafluoroborate except that the cupric nitrate trihydrate (15 g, 62 mmol) and silver nitrate (10 g, 59 mmol) were added to a solution of the diazonium salt in 50 mL of water. This mode of addition was used in order to ensure the complete dissolution of the diazonium salt prior to adding the catalyst, cuprous oxide. GLC analysis showed one peak which was identified by comparison of retention times and peak enhancement via the dual injection technique with an authentic sample (Aldrich), as phenanthrene. Based on the internal standard, *p*-tolyl benzoate, the yield of phenanthrene was 88% for duplicate runs. No *cis*-2-hydroxystilbene was formed.

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Registry No.—**10** bisulfate, 32066-79-8; **11**, 106-44-5; **12**, 5428-54-6; **13** BF_4, 1427-01-6; **13** HSO_4, 62058-61-1; **15**, 13073-29-5; **16** BF_4, 54616-48-7; **21** BF_4, 62058-63-3; *p*-toluidine, 106-49-0; 5-nitro-2-methylaniline, 99-55-8; 2-methyl-6-nitroaniline, 570-24-1; fluoroboric acid, 16872-11-0; 7-nitro-1*H*-indazole, 2942-42-9; *o*-amino-*N,N*-dimethylbenzamide, 6526-66-5; *o*-nitro-*N,N*-dimethylbenzamide, 2018-71-5; *cis*-2-nitrostilbene, 52208-62-5; *trans*-*o*-nitro-α-phenylcinnamic acid, 19319-35-8; *cis*-2-aminostilbene, 62058-64-4.

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Protonated Cyclopropanes. 9. Protonated Methylcyclopropane Intermediates in the Trifluoroacetolysis of 1-Butyl-*1*-^{14}C-mercuric Perchlorate

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The trifluoroacetolysis of 1-butyl-*1*-^{14}C-mercuric perchlorate was carried out at 35, 50, and 72 °C. At 35 °C, ^{14}C was scrambled only between C-1 and C-4 in the major 2-butyl product and there was no isotopic scrambling in the minor 1-butyl product. At 50 or 72 °C, all four isomeric butyl products were obtained. In the major product, 2-butyl-^{14}C trifluoroacetate, the label was scrambled over all four carbon positions. There was a small amount of ^{14}C scrambling from C-1 to C-2 in the 1-butyl product, while in the isobutyl ester, a 50:50 split of the label between C-1 and the rest of the molecule was observed. These results indicated that at 35 °C, the only scrambling processes were successive 1,2-hydride shifts involving classical 1-butyl and 2-butyl cations. At 50 or 72 °C, however, the scrambling data could be explained only by invoking some involvement (about 8–14%) of equilibrating protonated methylcyclopropanes in the overall reaction.

Work on protonated cyclopropanes has been the subject of a number of reviews,[1] and much of the evidence implicating such species as reaction intermediates has been derived from studies using isotopes as labels. In contrast to the unsubstituted protonated cyclopropane intermediates, definitive evidence from isotopic scrambling for protonated methylcyclopropane has been rather limited. Deno et al.[2] have reported that according to NMR studies, the addition of DCl to