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## Evidence for Phenyl Cation as an Intermediate in Reactions of Benzenediazonium Salts in Solution<sup>1,2</sup>

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Abstract: Displacements on benzenediazonium cation,  $C_6H_5N_2^+$ , in solution in the absence of strong bases, reducing agents, or light proceed by rate-determining cleavage to a singlet phenyl cation intermediate,  $C_6H_5^+$ , rather than by the bimolecular mechanism proposed in 1969. In aqueous solution at 25°, only unrearranged products are obtained, and negligible incorporation of deuterium from solvent D<sub>2</sub>O occurs, showing that aryne processes do not occur to a significant extent. The low selectivity between nucleophiles nevertheless requires a highly reactive intermediate. In the hydrolysis of  $C_6H_5N_2^+$ , the high entropy of activation (+10.5 cal mol<sup>-1</sup> deg<sup>-1</sup>) and the constancy of  $k_1$  (within 4%) from H<sub>2</sub>O to D<sub>2</sub>O demonstrate that water is not involved as a nucleophile in the rate-determining step. The constancy of  $k_1$  (within 10%) in solutions as diverse as 14-21 M H<sub>2</sub>SO<sub>4</sub> and 100% CH<sub>3</sub>CO<sub>2</sub>H and CH<sub>2</sub>Cl<sub>2</sub> is in accord with a common rate-determining step over this whole range of solvents. Para-substituent effects can be dissected into nearly equal field (predominantly transition state) and resonance (predominantly reactant) contributions by an analysis using dual substituent constants (previously published), with a correlation coefficient of 0.992, although analysis using the Hammett  $\rho\sigma$  equation, *i.e.*, with only a single set of substituent constants, yields a correlation coefficient worse than zero.

The purpose of this work was to determine whether a weakly basic nucleophile Y (e.g., H<sub>2</sub>O, Br<sup>-</sup>, Cl<sup>-</sup>, or F<sup>-</sup>) replacing the  $N_2^+$  group in an ordinary substitution reaction ("dediazoniation") of benzenediazonium cation (I) in solution is in the transition state or not.<sup>6</sup> The observed kinetics



with benzenediazonium bromide, chloride, bisulfate, or fluoborate in water at 5-64° is first order in diazonium salt.<sup>7</sup> However, when Y is a solvent molecule  $(H_2O)$ , the kinetics must be first order even with a bimolecular rate-determining step. When Y is a solute anion (Br<sup>-</sup> or Cl<sup>-</sup>), a bimolecular mechanism involving Y could still give deceptive firstorder kinetics because of compensating salt effects, as shown by excellent first-order kinetics for bimolecular reactions of trimethyl- or tribenzylsulfonium ion with chloride ion in 90% acetone-10% water and 16 other solvents and solvent mixtures at 18-100°.8 Analogous bimolecular possibilities for reactions of I with anions have not been eliminated in any previously published work by recourse to kinetic studies at constant ionic strength.

Possible Mechanisms. At the outset of this work, there appeared to be eight possibilities for the rate-determining step, where Y may be H<sub>2</sub>O, Br<sup>-</sup>, Cl<sup>-</sup>, or F<sup>-</sup>. Mechanism 1 is a one-step bimolecular displacement. This simplest mech-

$$I + Y \longrightarrow \bigotimes_{III} Y^{+} + N_{2}$$
(1)

$$I + Y \longrightarrow \bigvee_{II}^{-} \bigvee_{N_2^+}^{Y^+}$$
(2)

$$II \longrightarrow C_6H_5Y^+ + N_2 \tag{3}$$

$$I \longrightarrow \bigotimes_{IV}^{+} + N_2$$
 (4)

$$I + Y \longrightarrow \bigotimes_{Y} + HY^{+} + N_{2}$$
 (5)

$$I + Y \longrightarrow \bigotimes_{VI}^{-} N_2^+ + HY^+ \qquad (6)$$

$$VI \longrightarrow V + N_2$$
 (7)

$$V + Y \longrightarrow \bigotimes_{V \mid I} Y^+ \tag{8}$$

anism was rejected for a long time, because it appeared difficult to reconcile with the kinetics, e.g., with first-order

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rate constants that vary less than 50% with hydrochloric acid concentration, while the product ratio  $C_6H_5Cl/C_6H_5OH$  changes from 0.05 to  $3.^{7c}$  Nevertheless, it was adopted in 1969 as the preferred mechanism for reaction of arenediazonium ions with  $H_2O$ , SCN<sup>-</sup>, Br<sup>-</sup> or Cl<sup>-</sup> in aqueous solution in best accord with all the evidence in much excellent published work.<sup>7g,9</sup> We too expected this mechanism or one of its stepwise addition-elimination variants (mechanism 2 or 3)<sup>10</sup> to be the one to survive further scrutiny when we began our experimental work in 1962.

Mechanism 4, first proposed in 1942 by Waters,<sup>11</sup> does not involve Y in its transition state. This two-step mechanism proceeds through the reactive phenyl cation (IV) in which the positive charge cannot be delocalized by conventional forms of resonance. The intermediate in mechanism 2 or 3 seems much more likely, because it avoids such concentrated charge development. Singlet phenyl cation is perhaps the most implausible hydrocarbon carbonium ion that can be imagined, save for various antiaromatic cations (e.g., cyclopentadienyl), since its electron deficiency is localized in an orbital of relatively high s character  $(sp^2)$ . It is generally better to give vacant orbitals maximum p character. Formally similar vinyl cation intermediates have recently been demonstrated in several reactions of acetylenes and vinyl halides and vinyl esters.<sup>12</sup> However, ab initio calculations<sup>12b</sup> indicate that the preferred structure of the vinyl cation is linear at the carbonium carbon, the bent sp<sup>2</sup> structure being higher in energy by more than 30 kcal  $mol^{-1}$ . Experimentally,<sup>12d</sup> 1-cyclooctenyl and 2-cis-2-butenyl triflates (trifluoromethanesulfonates) solvolyze 105 times faster than 1-cyclopentenyl triflate and 104 times faster than 1-cyclohexenyl triflate in 50% ethanol at 100°, presumably because they can give linear carbonium ions more easily than 1-cyclopentenyl and 1-cyclohexenyl. It would be about as difficult for phenyl cation to be linear at  $C_1$  as for cyclohexenyl. A phenyl group is also more electronegative than a methyl group and unlikely to be transformed into a cation on that account also. Therefore one should be exceedingly skeptical about any interpretation requiring IV.

A variant of mechanism 4 involves not singlet IV but instead a triplet (biradical) phenyl cation, which might provide resonance stabilization and delocalization of the positive charge around the ring and even onto meta substituents, as was thought to be required to explain the peculiar effects of substituents on rate of dediazoniation of metaand para-substituted benzenediazonium salts.<sup>13</sup>

Mechanisms 5-8 all involve a benzyne intermediate. Other possibilities seem to be only minor variants of these eight.<sup>14</sup>

**Products.** Benzyne mechanisms 5-8 are all excluded for decomposition of I in aqueous solutions without strong bases by the absence of isomerized products such as are formed from reactions known to proceed via a benzyne intermediate under the same conditions. For example, decomposition of o-toluenediazonium chloride in water yields ocresol but no m-cresol; likewise m-toluenediazonium ion yields m-cresol but no o-cresol, although as little as 0.1% could be detected (see Experimental Section). No rearrangements during decomposition of simple arenediazonium ions in aqueous solutions have been reported, although the reaction has been used widely for a century.<sup>7e,15</sup>

For I itself, the absence of benzyne mechanisms is demonstrated by negligible formation of ring-deuterated phenol during the decomposition of I BF<sub>4</sub><sup>-</sup> in DCl-D<sub>2</sub>O. As shown in Table I, the amount of phen- $d_1$ - ol formed is only 0.05% during solvolysis for 16 hr at 25°. At the acidities employed, phenol and phenoxide both undergo significant acid-catalyzed exchange.<sup>19</sup> On the basis of control experi-

Table I. Deuterium Incorporation into Phenol in DCl or HCla

|                                  |          | $\frac{m/e \ 95/(m/e \ 95 + m/e \ 94)}{$ |        |        |      |
|----------------------------------|----------|--|--------|--------|------|
| Reactant                         | $H^+, M$ | hr                                       | $D_2O$ | $H_2O$ | % D  |
| I BF4 <sup>-b</sup>              | 0.01     | 16                                       | 0.0635 | 0.0629 | 0.06 |
| $I BF_4^{-b}$                    | 0.01     | 16                                       | 0.0646 | 0.0642 | 0.04 |
| C <sub>6</sub> H₅OH              | 0.0087   | 44.5                                     | 0.0640 | 0.0636 | 0.04 |
| C <sub>6</sub> H <sub>5</sub> OH | 0.0434   | 44.0                                     | 0.0642 | 0.0636 | 0.06 |

<sup>a</sup> At 25°; hydroxyl protons exchanged before analysis. <sup>b</sup> Initial concentration, 0.05 M.

Table II. Yields of Halobenzenes from Dediazoniation of  $0.03-0.05 M I BF_4^-$  in Aqueous 1.0 M HBr

| $H_2SO_4, M$ | T, °C | $C_6H_5Br, \%$ | $C_6H_5F, \%$ |
|--------------|-------|----------------|---------------|
| 0.0          | 25    | 13.4           | 0.85          |
| 2.0          | 25    | 11.9           | 0.88          |
| 10.0         | 25    | 9.7            | 0.89          |
| 0.0          | 50    | 12.0           | 0.92          |
| 2.0          | 50    | 10.9           | 0.82          |
| 8.0          | 50    | 10.1           | 0.76          |

ments, the incorporation of deuterium from exchange of the phenol under the reaction conditions is calculated as 0.02%. Thus, the contribution of benzyne mechanisms (0.03% from Table I) is less than 0.05% and may be essentially zero within experimental error (estimated 0.02%). That benzyne would have given rise to phen- $d_1$ -ol is shown by the formation of greater than 90% phen- $d_1$ -ol when benzyne is generated in D<sub>2</sub>O containing  $\leq 10^{-2} M$  NaOD.<sup>20</sup>

The products also exclude various free radical mechanisms. Formation of phenyl radicals<sup>6</sup> or of a triplet phenyl cation<sup>13</sup> is ruled out by the low yields (<5%) of benzene obtained when I BF<sub>4</sub><sup>-</sup> is decomposed in acetone or acetic acid, solvents that are good donors of hydrogen atoms, and by failure of any intermediate to undergo addition of bromine under our conditions. In 75% CH<sub>3</sub>CO<sub>2</sub>H-25% H<sub>2</sub>O solutions with 1-4 *M* Br<sub>2</sub> as a trap, no dibromide is formed initially. Some bromobenzene is formed, and this is later further brominated to *p*-dibromobenzene, but these are slower minor reactions (maximum 28%) and not zero order in Br<sub>2</sub> (see Experimental Section on products). Deuterium isotope effects<sup>4</sup> also provide convincing evidence against a triplet mechanism. Thus only mechanisms 1-4, in which electrons stay paired throughout, remain.

A practical difficulty in distinguishing between mechanisms 1-4 by using reactions where Y is a solute molecule or ion, rather than the solvent, is the low selectivity between nucleophiles shown by whatever species it is (I or IV) that reacts with Y in the product-determining step. For example, hydrolysis strongly dominates and therefore obscures all other reactions in aqueous solutions. Experiments designed to influence product distribution or rate by decreasing the concentration of water had surprisingly little effect (*cf.* next section).

Effect of Concentration of Water. Tables II and III show that product distribution and rate are affected amazingly little by changes in concentration of sulfuric acid. The yields of bromobenzene and fluorobenzene are nearly constant at  $11 \pm 2$  and  $0.9 \pm 0.1\%$ . The major products are phenol and sulfonated derivatives of phenol.<sup>2</sup> No doubt, the protonation of Br<sup>-</sup> to HBr in 8-10 *M* H<sub>2</sub>SO<sub>4</sub> decreases its reactivity and accounts for the continuing low yield of C<sub>6</sub>H<sub>5</sub>Br. However, as a practical matter, this means that one cannot make reaction with any anion predominate over reaction with water, as would in practice be necessary if one had to choose between mechanisms 1-3 and mechanism 4 solely from kinetic order at constant ionic strength or con-

Table III. First-Order Rate Constants for Dediazoniation  $0.0003-0.0015 MI BF_4^-$  at  $25.0^\circ$ 

| Run<br>no.² | Solvent   | $10^{5}k_{1}$ , sec <sup>-1</sup> |
|-------------|---|-----------------------------------|
| 25          | $0.001\% (0.0001 M) H_2 SO_4$                               | $4.59 \pm 0.03$                   |
| 24          | $0.10\% (0.010 M) H_2 SO_4$                                 | $4.55\pm0.03$                     |
| 66          | $9.5\% (1.0 M) H_2 SO_4$                                    | $4.12 \pm 0.01$                   |
| 20          | 23% (2.7 M) H <sub>2</sub> SO <sub>4</sub>                  | $3.56\pm0.02$                     |
| 15          | 50% (6 M) H <sub>2</sub> SO <sub>4</sub>                    | $2.68\pm0.01$                     |
| 62          | 80% (14 M) H <sub>2</sub> SO <sub>4</sub>                   | $2.13\pm0.02$                     |
| 22          | 96% (18 M) H <sub>2</sub> SO <sub>4</sub>                   | $2.11\pm0.01$                     |
| 121         | 105% (21 M) H <sub>3</sub> SO <sub>4</sub>                  | $2.15\pm0.01$                     |
| 60          | $0.0001 \ M \ D_2 SO_4$                                     | $4.76 \pm 0.04$                   |
| 59          | $0.010 \ M \ D_2 SO_4$                                      | $4.71 \pm 0.04$                   |
| 67          | $1.0 M D_2 SO_4$  | $4.11 \pm 0.07$                   |
| 40          | 100% CH3CO2H  | $2.26 \pm 0.01$                   |
| 43          | 100% CH <sub>3</sub> CO <sub>2</sub> H + 0.13 <i>M</i> LiCl | $3.71 \pm 0.07$                   |
| 42          | 100% CH <sub>3</sub> CO <sub>2</sub> H + 1.0 M LiCl         | $4.51 \pm 0.02$                   |
| 73          | $CH_2Cl_2$  | $2.20 \pm 0.05$                   |
| 122         | 3-Methylsulfolane   | $1.36 \pm 0.03$                   |
| 71          | 97 % sulfolane–3 % ( $C_2H_5$ ) <sub>2</sub> O              | $1.24 \pm 0.01$                   |
| 72          | Dioxane   | $1.15 \pm 0.02$                   |

stant high concentration of some inert salt. Fortunately, there are other ways to distinguish between them.

The selectivity of whatever species it is (I or IV) that reacts with H<sub>2</sub>O, Br<sup>-</sup>, Cl<sup>-</sup>, or F<sup>-</sup>, although very low, is nevertheless measurable. Lewis and Cooper<sup>21</sup> reported dimensionless competition factors  $k_x/k_w$  relative to water (55 *M*) of 1.4 for SO<sub>4</sub><sup>2-</sup>, 3 for Cl<sup>-</sup> or the N of SCN<sup>-</sup>, and 6 for the S of SCN<sup>-</sup>, comparable to our 6 for Br<sup>-</sup>.

Selectivity between nucleophiles is indicative of the structure of the intermediate (or other) species that is doing the also are intermediates like trityl cation  $(C_6H_5)_3C^+$ , that are well stabilized by resonance.<sup>23a</sup> As little as 0.0013 *M* NaN<sub>3</sub> in 50% water-50% acetone solution at 25° can intercept over 90% of all trityl ions generated, although competing with 27 *M* water  $(k_{N_3}-/k_{H_2O} = 280,000; k_{Cl}-/k_{H_2O} =$ 3100).<sup>23a</sup> On the other hand, benzhydryl cation is much less selective  $(k_{Cl}-/k_{H_2O} = 120)$ , and *tert*-butyl has a selectivity so low that it is hard to measure  $(k_{Cl}-/k_{H_2O} \simeq 4)$ .<sup>22,24</sup> What should one expect for I  $(C_6H_5N_2^+)$  in mechanism 1?

$$\bigwedge_{I}^{+} \overset{+}{N = N} : \longleftrightarrow \bigwedge_{N = N}^{+} \overset{-}{N = N} : \longleftrightarrow + \bigwedge_{N = N}^{+} \overset{-}{N = N} : \overset{-}{N = N} : (9)$$

Surely it has excellent resonance stabilization, is stabler than trityl ion, and ought to be as selective in mechanisms 1 and 3. On the other hand, in mechanism 4, the activated complex for reaction of IV ( $C_6H_5^+$ ) with solvent or other nucleophiles should be much closer in structure to IV than to the final product III ( $C_6H_5Y^+$ ), in accord with the very low selectivities found (*e.g.*,  $k_{Cl}$ -/ $k_{H_2O}$  = 3),<sup>21</sup> even lower than those for *tert*-butyl cation.

A surprising observation that excludes all mechanisms except mechanism 4 out of the eight considered is the less than 2% change in first-order rate constant  $(k_1)$  for hydrolysis from 80 to 105% H<sub>2</sub>SO<sub>4</sub>, in spite of the facts that (1) the activity of water changes more than 1000-fold just from 80 to 98% H<sub>2</sub>SO<sub>4</sub>, (2) HSO<sub>4</sub><sup>-</sup> is a much poorer nucleophile than water, and (3) even HSO<sub>4</sub><sup>-</sup> drops rapidly above 100% H<sub>2</sub>SO<sub>4</sub>.<sup>26</sup> Evidently the extent of covalent-bond formation between carbon and the nucleophile Y (here H<sub>2</sub>O or HSO<sub>4</sub><sup>-</sup>) at the transition state is extremely small or zero. This is confirmed by the large positive entropy of activation and by the absence of a solvent isotope effect (*cf.* next two sections).

Effect of Temperature. Additional evidence against cova-

lent bonding of water to carbon at the transition state of the hydrolysis reaction can be deduced from the large entropy of activation,  $\pm 1.0$  gibbs (cal mol<sup>-1</sup> deg<sup>-1</sup>) for 0.1 M I Cl<sup>-</sup> in water at 25°.<sup>7</sup>c This is within 2 gibbs of that for tert-butyl chloride,<sup>27</sup> where it is generally thought that water is not covalently bonded to carbon at the transition state, but 20-24 gibbs (the translational entropy of one water molecule) higher than that for hydrolysis of benzyl chloride, methyl bromide, or methyl p-toluenesulfonate, where water is bonding to carbon in the transition state. Similarly, the entropy of activation  $\Delta S^*$  for hydration of isobutylene or 1-methylcyclopentene, where the rate-determining step is formation of a carbonium ion, and water enters only after this step, is 18-25 gibbs higher than that for crotonaldehyde, where water adds to carbon during the rate-determining step, although the overall entropies of hydration ( $\Delta S^{\circ}$ ) for these two hydrocarbons are within 2 gibbs of that for crotonaldehyde.<sup>28</sup>

**Solvent** (H<sub>2</sub>O-D<sub>2</sub>O) **Isotope Effect.** Rates in light and heavy water are identical within experimental error (±4%, Table III), in agreement with previous results<sup>7c</sup> for 0.1 *M* I Cl<sup>-</sup> at 35°. The best value of  $k_{H_2O}/k_{D_2O}$  based on all of the data is 0.98 ± 0.01. The predicted values<sup>29</sup> are (1.5)<sup>3</sup> = 3.4 or (1.5)<sup>2</sup> = 2.2 for complete conversion to hydronium or phenyloxonium ion at the transition state (mechanisms 7, 8, or 4) or slightly less than 3.4 or 2.2 for formation of unstable benzyne or anionic intermediates (mechanisms 5, 6, or 3); (2.2)<sup>1/2</sup> = 1.5 for a mechanism 1 transition state midway between reactants and products, or less for earlier transition states; and unity (as observed) for mechanism 4. These 1.5 factors are equilibrium constants for complete conversion of a DO<sup>+</sup> bond to an HO<sup>+</sup> bond, which, for example, happens six times ( $K = (1.5)^6 = 11$ ) in

$$2D_3O^* + 3H_2O \rightleftharpoons 3H_3O^* + 2D_2O$$

Evidently, even with the weak base water, the strength of Y-C bonding at the transition state is below RT and less than 2% of a normal O-C single bond. Operationally, this excludes all mechanisms except mechanism 4 out of the eight considered. This evidence based on rate measurements (high activation entropy and insensitivity of hydrolytic rate to %  $H_2SO_4$  or water deuteration) results of course from only the difference between transition-state and reactant structures. However, if the transition state does not bind Y, neither can any product or intermediate among the immediate products of the rate-determining step, because the descent from transition state to these first products occurs at the rate of a molecular vibration (RT/Nh), which is faster than Y can approach, if it is not already on hand and appreciably bonded. Furthermore, the evidence of at least some selectivity between nucleophiles,<sup>21</sup> albeit low, shows that Y is involved in the activated complex for the product-determining step, which must therefore be different from that for the rate-determining step. The evidence therefore specifically excludes the proposed one-step mechanism 19 and addition-elimination mechanisms 2 and 310 but still allows Water's elimination-addition mechanism 4 proceeding through the phenyl cation intermediate IV.<sup>11</sup>

Nitrogen and Aromatic Hydrogen Isotope Effects. The evidence against mechanisms 1-3 and 5-8 cited in the preceding three sections seems to us to be irrefutable. Nevertheless, we summarize here two other lines of evidence that add still more weight to the disproof of these mechanisms.

I is much less stable than III, and  $N_2^+$  is a better leaving group than any Y<sup>+</sup> that we are considering. Therefore, if the one-step mechanism 1 were correct, the transition state should be closer to I than to III in structure. Then the  $\alpha$ -nitrogen isotope effect should be substantially less than that for halfway breakage of the C-N bond (1.02, based on a calculated N isotope effect of 1.04-1.045 for complete breakage of a C-N bond). If mechanism 2 or 3 were correct, the transition state should be close to the unstable intermediate II, and the  $\alpha$ -N isotope effect should be close to unity. In the second paper following this one,<sup>5</sup> we present data that show an  $\alpha$ -N isotope effect of 1.038. This large kinetic isotope effect is inconsistent with mechanisms 1-3 but in accord with mechanism 4 since its transition state should resemble the high-energy phenyl cation IV more closely than I, and hence the C-N bond should be extensively broken at its transition state.

The large kinetic hydrogen secondary isotope effect  $k_{\rm H}/k_{\rm D}$  of 1.22 for each ortho hydrogen (see following paper<sup>4</sup>) indicates an extremely electron-deficient transition state, as one close to the carbonium ion (IV, C<sub>6</sub>H<sub>5</sub><sup>+</sup>) in mechanism 4 would be, but one close to the resonance-stabilized diazonium ion (I, structure 9) in mechanism 1 [or to the anionic intermediate (II) in mechanism 2 or 3] would not. Hyperconjugation is expected to become this important only when better possibilities for stabilization by resonance, solvation, or other covalent participation by leaving, entering, or neighboring groups are all absent.

Other Solvent Effects. Products vary widely in different solvents, but rates vary remarkably little (Table III).<sup>2</sup> In glacial acetic acid with 0-1 *M* LiCl added,  $10^{-3} M$  I BF<sub>4</sub> yields  $\geq 69\%$  phenyl acetate, 2-3% phenol, 29-0% fluorobenzene, and 0-27% chlorobenzene; in methanol, the products are 91-93% anisole, 5-6% fluorobenzene; in methylene chloride, they are 66% chlorobenzene and 34% fluorobenzene; in 3-methylsulfolane, they are 54% phenol and 17% fluorobenzene.<sup>30</sup>

The similarity of rate constants shown in Table III for three solvents of widely different polarity,  $CH_2Cl_2$  (2.2),  $CH_3CO_2H$  (2.3), and fuming  $H_2SO_4$  (2.2), is striking. It seems to us to imply that the rate-determining step does not change, and that these solvents solvate I\* and I only very feebly. The twofold decrease in rate constant in the sulfolanes and dioxane is puzzling, but it may result from tighter association into large ionic aggregates approaching the stability of solid I  $BF_4^-$  in these solvents of especially low anion-solvating ability.

The small (twofold) increase in rate from 14 M (80%)  $H_2SO_4$  to  $10^{-4}$  M  $H_2SO_4$  may at first appear to suggest a change or partial change to a new mechanism in  $10^{-4} M$ H<sub>2</sub>SO<sub>4</sub> in which water is involved as a nucleophile, as in mechanism 1, 2, or 3. However, this deduction is unjustified because water activity or vapor pressure increases 30-fold over this range, and this is a region already noted for large and highly specific changes in ionic activity coefficients (and consequent inconstancy of rate constants for ionic reactions), in contrast to the relative constancy of activity coefficients in 83-100% H<sub>2</sub>SO<sub>4</sub>.<sup>26</sup> This small change (doubling) of rate is in fact completely reasonable for mechanism 4, as a consequence of differing effects of water solvation on I and I\*. The activity coefficient of I should be lowered less than that of I\* by increasing water activity, even though there may be the same number of water molecules in the innermost shells of I and I\* at any given concentration of  $H_2SO_4$ . Because the charge in I is better delocalized by resonance (eq 9), it benefits less from replacement of neighboring H<sub>2</sub>SO<sub>4</sub> molecules by H<sub>2</sub>O molecules. In short, no water is involved in the rate-determining step from 21 M  $H_2SO_4$  down to 14 M  $H_2SO_4$ . It is weakly involved in 10<sup>-4</sup> M H<sub>2</sub>SO<sub>4</sub> but only to an extent that is reasonably attributed to a more reduced activity coefficient for I\*, owing to differentially stronger solvation of I\* at the highest water concentration.31

A similar (twofold) increase in rate occurs in 100% acetic

acid solution when 1 M LiCl is added (Table III). Since the yield of C<sub>6</sub>H<sub>5</sub>Cl reaches only 27%, this is again due to better solvation of I\* than of I, this time with stronger solvation by Cl<sup>-</sup> ion than by CH<sub>3</sub>CO<sub>2</sub>H solvent molecules.

The fact that the rate constant decreases no more than twofold on loss of this strong *external* solvation by  $Cl^-$  (in 100%  $CH_3CO_2H$ ) or by  $H_2O$  (from dilute to 100%  $H_2SO_4$ ) suggests that there must be substantial compensation by some *internal* stabilization, such as resonance delocalization of the positive charge in the transition state I\* just preceding II, obviously not as great as in I (eq 9) but nevertheless considerable. A mechanism for such delocalization in I\* (hyperconjugation) is suggested by the kinetic secondary isotope effects observed when deuterium is present in ortho or meta positions, described in the paper immediately following this one.<sup>4</sup>

Meta- and Para-Substituent Effects. Table IV shows observed and calculated substituent effects at 25°. The observed log  $(k/k_{\rm H})$  values are those determined in the first major investigation of substituent effects for this reaction<sup>7c</sup> supplemented by two data for *tert*-butyl<sup>2,36</sup> but excluding data for anionic or partially anionic substituents.<sup>37</sup> These observed rate constants range over five powers of ten, from  $6 \times 10^{-9} \, {\rm sec^{-1}}$  for *p*-OCH<sub>3</sub> to  $7 \times 10^{-4} \, {\rm sec^{-1}}$  for *m*-*t*-C<sub>4</sub>H<sub>9</sub>.

The calculated effects are

$$\log (k/k_{\rm H})_{\rm m} = f_{\rm m} \mathfrak{F} + r_{\rm m} \mathfrak{R} + i_{\rm m} = (-2.74 \pm 0.20) \mathfrak{F} + (-3.18 \pm 0.36) \mathfrak{R} + (0.27 \pm 0.12)$$

and

log 
$$(k/k_{\rm H})_{\rm p} = f_{\rm p} \mathfrak{F} + r_{\rm p} \mathfrak{R} + i_{\rm p} = (-2.60 \pm 0.16) \mathfrak{F} + (5.08 \pm 0.37) \mathfrak{R} + (-0.25 \pm 0.10)$$

using  $\mathfrak{F}$  and  $\mathfrak{R}$  ("field" and "resonance") substituent constants defined and tabulated previously,<sup>38</sup> without any change. These f, r, and i values were fitted by leastsquares, and the  $\pm$  numbers are their standard deviations.<sup>39</sup>

The  $f_m$  and  $f_p$  reaction constants represent the sensitivities of these reactions to the field constants  $\mathcal{F}$  of meta and para substituents (representing all influences except those transmitted by resonance or  $\pi$  bonds). They are comparable (-2.74 and -2.60) and of the expected sign and magnitude, because electron-supplying (negative  $\mathcal{F}$ ) substituents should facilitate departure of N<sub>2</sub> with its previously bonding electron pair, by stabilizing the transition state I\* (which is close to the electron-deficient phenyl cation IV in structure) much more strongly than the reactant I.

The  $r_m$  and  $r_p$  reaction constants represent the sensitivities of these reactions to the resonance constants  $\Re$  of meta and para substituents. For the ten meta substituents, resonance with electron-supplying (negative  $\Re$ ) substituents significantly stabilizes the transition state leading to phenyl cation by supplying negative charge to the ortho carbons. Since meta substituents are poor at stabilizing the reactant, they do not increase the double bond character of its C-N bond. Therefore the sign of this sensitivity to resonance  $r_m$ due to meta substituents (-3.18) is the same as that of  $f_m$ and  $f_p$  (nonresonance) sensitivities to both meta and para substituents. The  $\Re$  (average relative importance of resonance) is 42.0%, which may be compared with 0% for  $\sigma'$ , 22% for  $\sigma_m$ , 53% for  $\sigma_p$ , and 66% for  $\sigma_p^+$ .<sup>38</sup>

For para substituents, however, resonance with electronsupplying substituents does increase the double-bond character of the C-N bond in the initial reactant diazonium cat-



ion. This effect, which stabilizes the reactant and hinders cleavage of this bond, evidently considerably outweighs the

Table IV. Effect of Substituents on Rate of Dediazoniation of I at 25°a

|                               |             |              | $\sim$ Values of log $(k/k_{\rm H})$ for $\sim$ |               |        |         |  |
|-------------------------------|-------------|--------------|---|---------------|--------|---------|--|
|                               | -Substituen | it constant- | Meta p  | osition       | Para p | osition |  |
| Substituent                   | F           | R            | Obsd  | Calcd         | Obsd   | Calcd   |  |
| Н                             | 0.000       | 0.000        | 0.000   | 0.272         | 0.000  | -0.251  |  |
| CH <sub>3</sub>               | -0.052      | -0.141       | 0.650   | 0.864         | -0.930 | -0.832  |  |
| $C_{2}H_{5}$                  | -0.065      | -0.114       | 0.930   | 0.814         |        |         |  |
| $C(CH_3)_3$                   | -0.104      | -0.138       | 1.250   | 0. <b>997</b> | -0.710 | -0.682  |  |
| C <sub>6</sub> H <sub>5</sub> | 0.139       | 0.088        | 0.398   | 0.171         | -1.252 | -1.060  |  |
| OH                            | 0.487       | -0.643       | 1.088   | 0.981         |        |         |  |
| OCH <sub>3</sub>              | 0.413       | -0.500       | 0.708   | 0.729         | -3.842 | -3.866  |  |
| Cl                            | 0.690       | -0.161       | -1.465  | -1.109        | -2.773 | -2.865  |  |
| Br                            | 0.727       | -0.176       | -1.205  | -1.163        |        |         |  |
| NO <sub>2</sub>               | 1.109       | -0.155       | -3.063  | -3.265        | -2.401 | -2.351  |  |

<sup>a</sup> Chloride salts in 0.1 M HCl (pH 1.7).<sup>2.7e,37</sup>



**Figure 1.** Dual substituent constant  $(f \mathcal{F} + r \mathcal{R} + i)$  plot of para-substituent effects on rate of dediazoniation of I Cl<sup>-</sup> in 0.1 *M* HCl at 25°.

kind of transition-state resonance stabilization exhibited by meta substituents and so causes  $r_p$  to be positive for para substituents (+5.08), in contrast to the otherwise negative fand r constants for these reactions. Para-resonance effects, although in the opposite direction from meta effects, are now an even larger proportion of the total substituent effects (55%). Figure 1 shows the fit for para substituents.

Both correlation coefficients are excellent: 0.984 for ten meta substituents and 0.992 for seven para substituents including hydrogen. The largest deviations calculated from observed log  $(k/k_{\rm H})$  values are for chloro (+0.36) in the meta series and for unsubstituted (-0.25) in the para series. Deviations are relatively negligible for *p*-methoxy (-0.02), *p*-tert-butyl (+0.03), *p*-chloro (-0.09), and *p*-nitro (+0.05).

The most significant aspect of these correlations is the fact that no special set of substituent constants was used to obtain these considerably better than average fits. The substituent constants used are simply the constant  $\mathcal{F}$  and  $\mathcal{R}$  values based on  $\sigma'$ ,  $\sigma_m$ , and  $\sigma_p$  that were used previously<sup>38</sup> to correlate 14 reaction series (average correlation coefficient 0.967), which did not include *any* diazonium ion reactions. There is thus no evidence that substituents can exert any influence on these reactions other than the two influences (field and resonance) measured by  $\mathcal{F}$  and  $\mathcal{R}$ , nor that these two physical modes of interaction, characterized by  $f\mathcal{F}$  and  $r\mathcal{R}$ . A two-term model is therefore quite satisfactory.

The excellent fit illustrated in Figure 1 confirms that



**Figure 2.** Hammett  $(\rho\sigma)$  plot of para-substituent effects on rate of dediazoniation of I Cl<sup>-</sup> in 0.1 *M* HCl at 25°.

only a single mechanism is operating over the whole range of substituents considered, because a constant pair of resonance (r) and nonresonance (f) sensitivity constants accommodates all these data.

Evidently the original reason for proposing<sup>13</sup> that IV is a triplet was not valid, because substituent effects are fully explicable without involving a triplet.

Figure 2, on the other hand, shows that the same data for para substituents give an entirely random Hammett plot [log  $(k/k_{\rm H}) = \rho\sigma + C$ ]. The best line has a slope  $(\rho)$  of -0.7, but its correlation coefficient is so poor as to be quite imaginary  $(-0.16)^{1/2.40}$  No previously published alternative single set of substituent constants fits these data significantly better. Both field and resonance effects are important here. The use of dual substituent constants is always required for successful quantitative correlation whenever resonance contributions become considerable, except when the studied and defining reactions have nearly the *same* ratio of sensitivities (r/f) to these two kinds of substituent influences. Since they do not have the same ratio here, Figure 1 is the proper plot.

## **Experimental Section**

I (Benzenediazonium)  $BF_4^-$  was prepared by diazotization of aniline in HBF<sub>4</sub> solution in an ice-salt bath,<sup>41</sup> recrystallizing twice from saturated 25° solutions in 5% HBF<sub>4</sub> by chilling to 0°, and twice more by dissolving in (CH<sub>3</sub>)<sub>2</sub>CO at 25°, adding CHCl<sub>3</sub> until a few crystals appeared, then chilling to -20°. After being dried at 25° (1 mm) for 2 hr, it could be stored in a vacuum desiccator at 0° in the dark for several months with no sign of decomposition: ir  $\nu_{max}$  (2% in KBr) 3100-3000, 2298, 1570, 1470, 1310, 1200-1000

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 $(BF_4^{-})$ , 770, 760, 665, 535, 523, 512, and 460 cm<sup>-1</sup>; uv  $\lambda_{max}$ (H<sub>2</sub>O) 260 nm ( $\epsilon$  12,000) and 295 (1880); nmr complex multiplet  $\delta_{TMS}$  (20% in CH<sub>3</sub>CN) 7.2-8.8; decomposes slowly above 100° with evolution of BF<sub>3</sub> and melts into boiling C<sub>6</sub>H<sub>5</sub>F at 119-121° (lit.<sup>42</sup> 121-122°).

Anal. Calcd for  $C_6H_5N_2BF_4$ : C, 37.55; H, 2.63; N, 14.60. Found: C, 37.70; H, 2.97; N, 14.68.

**Solvents.** Distilled water was passed through a 2-ft Pyrex column filled with Fisher analytical grade Amberlite MB-1 resin (a mixture of sulfonic acid and quarternary ammonium ion resin) and sealed with a Teflon stopcock. Before use each day, at least 1 l. of water was flushed through the column. The conductivity of the water, measured in a Pyrex conductivity cell with Pt electrodes by a General Radio 1650A impedance bridge, was  $2.5 \times 10^{-7}$  mho cm<sup>-1</sup>. This deionized H<sub>2</sub>O was used to rinse all reaction vessels and as the solvent for all kinetic runs and product studies in aqueous or partially aqueous solutions.

 $H_2SO_4$  used for kinetic runs and syntheses was analytical reagent 96%, diluted with the deionized  $H_2O$ . Fuming  $H_2SO_4$ (Baker and Adamson reagent) showed a uv  $\lambda_{max}$  279-283 nm (absorbance A, 0.8), attributed to  $SO_2$ ,  $\lambda_{max}$  ( $H_2O$ ) 276 nm ( $\epsilon$  525).<sup>43</sup> Fuming  $H_2SO_4$ , 100 ml, and 30%  $H_2O_2$  (1 ml of Baker reagent grade) were refluxed 4 days in an all-glass apparatus sealed with a tube containing Drierite (CaSO<sub>4</sub>). Destruction of SO<sub>2</sub> and  $H_2O_2$ was quantitative: a 1-ml portion of the acid failed to decolorize 100 ml of  $10^{-6}$  M KMnO<sub>4</sub>. The A of the purified acid was 0.030 at 280 nm vs. 96%  $H_2SO_4$ , and its concentration, by titration with standard NaOH, was 105.4  $\pm$  0.2%  $H_2SO_4$  (28% SO<sub>3</sub> by weight).

 $D_2SO_4$  was prepared by Jones<sup>44</sup> by reaction of SO<sub>3</sub> (Baker and Adamson reagent) with 99%  $D_2O$ . Titration with standard NaOH corresponded to 97.0%  $D_2SO_4$ .

Acetic acid (reagent glacial) was titrated with standard NaOH, indicating 99.7  $\pm$  0.3% HOAc. This material was used for most purposes without further purification. The CH<sub>3</sub>CO<sub>2</sub>H used in some of the kinetic runs and for the product studies using LiCl was refluxed for 10 hr over CrO<sub>3</sub> and distilled through a 30-cm Vigreux column. The middle 80% was redistilled from triacetylborate,<sup>45</sup> bp 117°, mp 16.2°.

Cyclohexane (Baker reagent, 2.5 l.) was stirred with four 400ml portions of 96% H<sub>2</sub>SO<sub>4</sub> for at least 2 hr each. The last two portions remained colorless. The cyclohexane was washed with 1 l. of H<sub>2</sub>O, 1 l. of 0.1 *M* NaOH, and three 1-l. portions of H<sub>2</sub>O, dried overnight over Drierite, and distilled through a 30-cm Vigreux column. The middle 80%, bp 80.3°,  $n D^{25}$  1.4232 was used. Methanol (Fisher reagent) was used without further purification.

Methylene chloride (Fisher reagent) was purified by the same procedure as cyclohexane, except that after drying over Drierite, it was dried over Fisher reagent grade molecular sieves (3-mm pellets of a sodium calcium aluminum silicate with a pore size of 4 Å) for at least 30 min, then distilled through a 60-cm column packed with glass helices. The middle 80% of the distillate, bp 40.3°,  $nD^{25}$  1.4209, was stored in the dark and used for kinetic runs within a week.

Sulfolane (tetrahydrothiophene 1,1-dioxide, Shell Development) was distilled through a 60-cm column packed with 3-mm Pyrex beads. The middle 80% was redistilled twice without the fractionating column. Redistilled sulfolane was colorless and odorless, bp 90° (1 mm),  $nD^{25}$  1.4825. Analysis by glc on a 6-ft 20% Apiezon L on Chromosorb W column at 25-300° and 14 psi of He showed 0.1% volatile impurity. Since sulfolane solidifies at 28°, 3.3% Et<sub>2</sub>O (Mallinckrodt reagent) was added to depress the melting point below 25°. 3-Methylsulfolane was purified by the procedure of Alder and Whiting,<sup>46</sup> with the exception that CaO was used instead of  $P_2O_5$  as the drying agent. The purified material, bp 83° (0.2 mm), when analyzed by glc on the Apiezon L column showed less than 0.1% volatile impurities. The A of a 1-cm cell of 3-methylsulfolane vs. air was 0.124 at 315 nm, 0.155 at 295 nm, 0.233 at 270 nm and increased gradually at lower wavelengths.

Determination of Yields of Halobenzenes from Dediazoniation of I BF<sub>4</sub><sup>-</sup>. Three 80-mg samples of I BF<sub>4</sub><sup>-</sup> were dissolved in 10 ml of HBr or HCl solution in 25-ml volumetric flasks. Cyclohexane (10 ml) was added, and the flasks were shaken, sealed, and placed in a constant-temperature bath at 25 or 50° for at least 3 days at 25° or 1-2 hr at 50° (10 half-lives). The acid layer was separated and extracted with two more 5-ml portions of cyclohexane. The combined cyclohexane solutions were extracted thrice with 0.1 M

NaOH and once with 1 M H<sub>2</sub>SO<sub>4</sub>, then diluted to 25 ml. The absorbance A of the C<sub>6</sub>H<sub>5</sub>Br solutions was measured at 265.6 and 261.5 nm. The yields were calculated from the extinction coefficients of C<sub>6</sub>H<sub>5</sub>Br [265.6 nm ( $\epsilon$  211), 261.5 (182)] and C<sub>6</sub>H<sub>5</sub>F [265.6 nm ( $\epsilon$  613), 261.5 (800)]. The yield of C<sub>6</sub>H<sub>5</sub>Cl was calculated from A at 264.6 nm. Since A was measured at only one wavelength, the yield of C<sub>6</sub>H<sub>5</sub>F could not be calculated but was assumed to be 1%, in agreement with the C<sub>6</sub>H<sub>5</sub>Br solutions. The yields of C<sub>6</sub>H<sub>5</sub>F, determined from A at 266 nm ( $\epsilon$  1070), for decomposition of 0.03–0.05 M salt in 1.0 and 7.0 M H<sub>2</sub>SO<sub>4</sub> with no added halide were 1.2–1.4 and 0.8–1.0%, respectively. When solutions, were extracted with cyclohexane immediately after dissolution, the yield was 0.2–0.5%. Part of the C<sub>6</sub>H<sub>5</sub>F therefore arises from decomposition of the salt in the solid phase.

**Products in Methanol.** Solutions containing 0.016–0.028 *M* salt in CH<sub>3</sub>OH were decomposed at 25° in the dark for 42 hr (20 halflives). The solutions showed absorption at 260–400 nm equivalent to formation of 0.01–0.02% of *p*-HOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>C<sub>6</sub>H<sub>5</sub>. The solutions were diluted 25–50-fold and *A* measured at 277.9, 266.5, 260.5, and 254.5 nm. The  $\epsilon$  values for C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub> (1578, 1340, 883, 480) and C<sub>6</sub>H<sub>5</sub>F (2, 800, 900, 600) were measured at these wavelengths. The yields of C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>, 91.5  $\pm$  0.5%, and C<sub>6</sub>H<sub>5</sub>F, 5.5  $\pm$ 1%, were calculated from *A* at 277.9 and 266.5 nm. The values calculated for *A* at 260.5 and 254.5 nm agreed with those observed within 1%. The rate constant was 9.80  $\pm$  0.04  $\times$  10<sup>-5</sup> sec<sup>-1</sup> with 6.8  $\times$  10<sup>-4</sup> *M* 1 BF<sub>4</sub><sup>-</sup> at 25°.

**Products in Acetic Acid.** Solutions containing approximately  $10^{-3}$  M salt and 0, 0.0100, 0.100, and 1.00 M LiCl were decomposed at 25° for 4 days (10 half-lives). The yields of C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>5</sub>Cl, C<sub>6</sub>H<sub>5</sub>F, C<sub>6</sub>H<sub>5</sub>OH, and C<sub>6</sub>H<sub>5</sub>OAc were calculated from A of the solutions and the measured  $\epsilon$  values at 280, 271, 265.8, 263.5, 260.5, and 259.5 nm. As a check, 76 mg (4 × 10<sup>-4</sup> mol) of salt was dissolved in 10 ml of glacial HOAc containing 1.00 M LiCl. After 4 days at 25°, the solution was diluted to 100 ml and shaken with three 10-ml portions of cyclohexane. The cyclohexane solution was analyzed for C<sub>6</sub>H<sub>5</sub>Cl as previously described. The yield of C<sub>6</sub>H<sub>5</sub>Cl was 29 vs. 27% calculated directly from A of the reaction mixture.

**Products in Methylene Chloride.** When 11.6 mg of salt was shaken with 100 ml of  $CH_2Cl_2$  and allowed to stand in a dry box at 25°, the salt dissolved gradually over 2 days as the decomposition progressed. After 7 days (10 half-lives after complete solution), 90 ml of the solution was concentrated to about 1 ml by fractional distillation on a 60-cm Nester-Faust Pt spinning-band column at a reflux ratio of 7:1. The concentrate showed glc peaks for  $C_6H_5Cl$  and  $C_6H_5F$  in a ratio 3/2. The remainder of the original solution was used for spectrophotometric measurements. The products of decomposition of saturated solutions in  $CH_2Cl_2$  were also analyzed spectrophotometrically. The yields of  $C_6H_6$  ( $2 \pm 2\%$ ),  $C_6H_5F$  ( $33 \pm 3\%$ ), and  $C_6H_5Cl$  ( $65 \pm 3\%$ ) were calculated from the A and  $\epsilon$  at 270, 266.5, 264.5, 264, 262.5, 261, 260, 258, and 255 nm. Presumably  $CH_2ClF$  was formed equivalent to the  $C_6H_5Cl$ , but it was not isolated because of its volatility.

**Products in Acetone.** When 0.493 g, in 25 ml reagent  $(CH_3)_2$ -CO was decomposed at 25° for 4 days, the resulting solution was deep purple, with an unpleasant odor. Analysis of the solution by glc on a 6-ft 20% Apiezon L on Chromosorb W S-60-80 column at 130° and 20 psi of He showed 13 ± 2% C<sub>6</sub>H<sub>5</sub>F and 100 ± 15% C<sub>6</sub>H<sub>5</sub>OH. Estimation of the area of the C<sub>6</sub>H<sub>5</sub>OH peak was less accurate because the peak tailed badly. 4-Hydroxy-4-methyl-2-pentanone (2.73 mol per mol of salt) and other higher molecular weight condensation products were also formed.

**Products in 3-Methylsulfolane.** I (0.194 g,  $1.01 \times 10^{-3}$  mol) was decomposed in 10 ml of 3-methylsulfolane at  $25.00 \pm 0.02^{\circ}$  for 11 days (16 half-lives). The solution analyzed by glc showed four peaks, C<sub>6</sub>H<sub>5</sub>F, 0.31, (17% yield); unknown, 0.24; unknown, 0.24; unknown, 0.16; C<sub>6</sub>H<sub>5</sub>OH, 1.0 (57% yield). When 90% of the solvent was distilled at 95° (1 mm), no phenol appeared in the distillate and the residue showed the same peaks by glc. The uv of the solution had  $\lambda_{max}$  266 nm ( $\epsilon$  1.78), 260 (258), and 255 (251) but no peaks for phenol at 280 nm ( $\epsilon$  1500) or 273 (1800). The product was postulated to be a sulfoxonium salt which decomposed to yield phenol during glc analysis. Attempts to isolate the salt were unsuccessful. Chalkley, *et al.*, <sup>47</sup> have subsequently confirmed the existence of the sulfoxonium salt and prepared samples of it by decomposition of 1 in sulfolane at 70-80°.

**Table V.** Yields of Bromobenzene and *p*-Dibromobenzene from Dediazoniation of 0.1 *M* I BF<sub>4</sub><sup>-</sup> in 75% HOAc Containing Br<sub>2</sub> and 0.25 *M* H<sub>2</sub>SO<sub>4</sub> at 25°

| Br <sub>2</sub> , $M$ | C <sub>6</sub> H <sub>5</sub> Br, % | $p-C_6H_4Br_2, \%$ | Total % |
|-----------------------|-------------------------------------|--------------------|---------|
| 0.44                  | 7.7                                 | 0                  | 7.7     |
| 1.1                   | 12.2                                | 0.1                | 12.2    |
| 2.2                   | 12.1                                | 5.9                | 18.0    |
| 3.0                   | 0.8                                 | 21.5               | 22.3    |
| 4.0                   | 0                                   | 28.0               | 28.0    |

**Products in 75% Acetic Acid Containing Bromine.** I BF<sub>4</sub><sup>-</sup> (1.0 g, 0.005 mol) was dissolved in 100 ml of 75% HOAc-25% H<sub>2</sub>O containing 0.50 *M* Br<sub>2</sub> (Mallinckrodt reagent). After 48 hr at 25° in the dark, the solution was filtered, and 0.67 g (30%) of bromanil (tetrabromo-1,4-benzoquinone), mp 291° uncor, was obtained after recrystallization from C<sub>6</sub>H<sub>6</sub>:  $\nu_{max}$  (2% in KBr) 1690, 1560, 1220, 1070, 1030, 710, and 640 cm<sup>-1</sup>. The filtrate was diluted with 200 ml of H<sub>2</sub>O and treated with excess NaHSO<sub>3</sub>. The curdy white precipitate was extracted with CHCl<sub>3</sub> and the CHCl<sub>3</sub> layer with 10% NaOH. Neutralization of the solution gave 0.93 g (54% crude yield) of 2,4,6-tribromophenol, identified by ir, mp 96°, crystallized from EtOH-H<sub>2</sub>O. The CHCl<sub>3</sub> solution was dried over Drierite and analyzed for C<sub>6</sub>H<sub>5</sub>Br (13% yield) and *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> (11% yield) by glc with a 6-ft 20% Apiezon L on Chromosorb W column at 150° and 14 psi of He.

To five 50-ml glass-stoppered erlenmeyer flasks painted black to exclude light were added 25 ml of 75% HOAc-25% H<sub>2</sub>O, 0.25 *M* in H<sub>2</sub>SO<sub>4</sub>, 0.50 g (0.0026 mol) of I BF<sub>4</sub><sup>-</sup>, and Br<sub>2</sub> for 0.44-4.0 *M* Br<sub>2</sub>. The flasks were shaken, sealed tightly, and allowed to stand at 25° for 60-72 hr. The solutions were analyzed for C<sub>6</sub>H<sub>5</sub>Br and *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> by glc (Table V). No *o*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub> was detected, although an authentic sample was cleanly separated from *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>.

In order to determine whether  $C_6H_5Br$  is converted to p- $C_6H_4Br_2$  under these reaction conditions, 29 g (0.18 mol) of  $Br_2$ and 2.0 g (0.013 mol) of  $C_6H_5Br$  were added to 50 ml of 75% HOAc containing 0.25 *M* H<sub>2</sub>SO<sub>4</sub>. The resulting 3.0 *M* Br<sub>2</sub> solution was allowed to stand at 25° in the dark. Analysis of a 10-ml sample withdrawn after 10 hr showed a 98% yield of p- $C_6H_4Br_2$ .

Finally, a solution containing 0.124 *M* I  $BF_4^-$ , 0.24 *M*  $H_2SO_4$ , and 0.95 *M*  $Br_2$  was prepared from 5.00 g of I (0.026 mol), 150 g of glacial HOAc, 50 g of 1.00 *M*  $H_2SO_4$ , and 32.0 g of  $Br_2$  (0.20 mol). The solution was poured into a 250-ml glass-stoppered erlenmeyer flask painted black to exclude light and placed in a constant-temperature bath at 25°. At 1–3 hr intervals, 25-ml samples were withdrawn and analyzed for C<sub>6</sub>H<sub>5</sub>Br and *p*-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>. The half-life for C<sub>6</sub>H<sub>5</sub>Br formation was about 7 hr *vs.* 5 hr for dediazoniation of I in the absence of Br<sub>2</sub>.

If the diradical intermediate had a finite lifetime,  $Br_2$  should readily attack it, forming o- and p-dibromobenzene but no  $C_6H_5Br$ . When I  $BF_4^-$  was decomposed in 75% HOAc containing 0.44-4.0 *M*  $Br_2$  and 0.25 *M*  $H_2SO_4$ , the initial product was  $C_6H_5Br$ . In solutions of  $Br_2$  greater than 1 *M*,  $C_6H_5Br$  is subsequently brominated to p- $C_6H_4Br_2$ . The other products,  $C_6H_5OH$ and  $C_6H_5OAc$ , are converted to a mixture of 2,4,6-tribromophenol and bromanil. Catalysis of dediazoniation by  $Br_2$  does not occur, because the rate of formation of  $C_6H_5Br$  is slower than the rate of dediazoniation in HOAc solutions in the absence of  $Br_2$ . Since  $C_6H_5Br$  rather than p- $C_6H_4Br_2$  is the initial product, the reaction does not proceed through a diradical.

**Products in Concentrated and Fuming Sulfuric Acid.** First, 0.459 g of 1 BF<sub>4</sub><sup>--</sup> was dissolved in 25 ml of 96% H<sub>2</sub>SO<sub>4</sub> (0.096 *M* solution) and kept at 25° for 1 week (16 half-lives). The resulting solution was extracted repeatedly with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solution was dried over Drierite and examined by glc on the Apiezon L column. No volatile products were detected. Next, 0.241 g was dissolved in 25 ml of 105% H<sub>2</sub>SO<sub>4</sub> (0.05 *M* solution) and kept at 25° for 7 days (16 half-lives). The solution was diluted to 250 ml, and three 50-ml aliquots were treated with excess Br<sub>2</sub> for 14 days at 25°, then filtered, average yield 59 mg of a yellow solid, mp 235-240°, 275-280° after recrystallization from benzene. Treatment with more Br<sub>2</sub> for 2 hr at 95° produced an additional 15 mg of yellow crystals, mp 290-295°, total yield 74 mg (70%). The ir spectrum of both fractions was identical with that of bromanil. The formation of bromanil and absence of volatile products confirm

that the original products were sulfonated derivatives of phenol.

Search for a Rearranged Product. To 14.4 g (0.10 mol) of o-toluidine and 60 ml of 4 M HCl in a 1-l. round-bottomed flask at 0°, 6.9 g (0.10 mol) of NaNO<sub>2</sub> in 15 ml of water was added dropwise with stirring. After diazotization was complete, the flask was removed from the ice bath and 100 ml of concentrated H<sub>2</sub>SO<sub>4</sub> was added. The heat of dilution of the H<sub>2</sub>SO<sub>4</sub> was sufficient to cause rapid decomposition. After evolution of N<sub>2</sub> had ceased, the mixture was diluted with 300 ml of water and extracted thrice with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> solution was dried over Drierite and analyzed by glc. Peaks for o- cresol and o- chlorotoluene were observed in a ratio of 5:1, but no peak for *m*- cresol was observed. Tests with a mixture of o- and *m*- cresol showed that as little as 0.5% of either substance could be detected in the presence of the other. *m*-Toluidine was converted to *m*- cresol by the same procedure. No o- cresol was detected by glc of the reaction mixture.

**Deuterium Incorporation into Phenol.** I  $BF_4^-$  (0.001 mol) was dissolved in 20 ml of 0.01 *M* DCl in D<sub>2</sub>O (Columbia Organic Chemicals) or 0.01 *M* HCl in H<sub>2</sub>O and kept at 25° for 16.0 hr (3.8 half-lives). The mixture was extracted with three 10-ml portions of CH<sub>2</sub>Cl<sub>2</sub>, which were then extracted successively with three 20-ml portions of water and one 20-ml portion of saturated NaCl. The CH<sub>2</sub>Cl<sub>2</sub> layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated at low pressure. For investigation of D exchange of C<sub>6</sub>H<sub>5</sub>OH, 0.001 mol of C<sub>6</sub>H<sub>5</sub>OH (Fisher reagent grade) was dissolved in 0.0087 or 0.0434 *M* DCl in D<sub>2</sub>O and maintained at 25° for the designated periods of time, then isolated as described above.

The isotopic composition of the phenol samples was determined on an Atlas CH4 mass spectrometer at 20 eV by scanning the molecular ion peaks repeatedly. The exit slit was 1 mm, which gave flat topped but resolved peaks. The reaction products and corresponding reference samples were introduced at similar ( $\pm$  10%) inlet pressures, and the amplifier attenuator settings were adjusted identically for each sample and such as to give the maximum readable chart value for each m/e value. Because of slow equilibration of the instrument (half-life 1.5 min), it was pumped out for 15 min between samples, and the samples were introduced 15 min before measurements were begun.

**Kinetic Measurements.** Solutions about 0.001 *M* in I were prepared by dissolving 4 mg of salt in 25 ml of solvent. Glass-stoppered 1-cm silica cells containing 3 ml of solution were placed in the water-jacketed cell block of a Zeiss Model PMQ-II spectrophotometer maintained at  $25.00 \pm 0.03^{\circ}$ . The absorbance *A* at 295 nm ( $\epsilon$  1650), or at 315-325 nm if products or solvent absorbed, was measured every 20-30 min for 8-12 hr, then after an 8-10 hr break for another 4-5 hr. An additional measurement was made after at least 10 half-lives. An average of 15-25 measurements was made in each run. The half-lives of the reactions studied varied from 2 to 17 hr.

Experimental data were fitted to  $A_t = A_{\infty} + (A_0 - A_{\infty})e^{-kt}$  by the method of least-squares. Computations were performed on an IBM 7094 computer.<sup>48</sup> The observed values of  $A_0$  and  $A_{\infty}$  and a value of k calculated from the apparent half-life were submitted as initial estimates; the correct values for  $A_0$ ,  $A_{\infty}$ , and k were calculated by repeated iterations of the experimental data. The corrected values of  $A_0$ ,  $A_{\infty}$ , and k after each iteration were used as the estimates for the next iteration. After the fourth iteration, the values of  $A_0$ ,  $A_{\infty}$ , and k, the standard deviations of these values, and ( $A_{calcd} - A_{obsd}$ ) for each point were printed out. Observed  $A_{\infty}$ values were generally less than 1% of  $A_0$  and agreed with calculated  $A_{\infty}$  values within ±0.005 or ±1% of  $A_0$ .

## **References and Notes**

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- For a review of the literature and for further experimental details, *cf.* J.E.S., Ph.D. Thesis, Massachusetts Institute of Technology, December 1965, 198 pp. Deuterium tracer experiments were performed subsequently by K.G.H.
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- (6) We have concentrated our study on the mechanism of the homogeneous, dark, 0-100° thermal decomposition of neutral diazonium salts in aqueous solution when only weakly basic nucleophiles like  $\mathrm{H_2O},\,\mathrm{Br^-}$ Cl<sup>-</sup>, or F<sup>-</sup> are present. There seem to be as many actual mechanisms for denitrogenation (dediazoniation) of diazonium salts as for dehydrogenation of alcohols or decarboxylation of carboxylic acids. However, in this paper, we purposely exclude consideration of mechanisms that may operate with strong bases or with nucleophiles that bond to nitrogen (e.g., in the Gomberg-Bachmann reaction, probably initiated by I + HO<sup>-</sup>  $\rightleftharpoons$  C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>OH  $\rightarrow$  C<sub>6</sub>H<sub>5</sub>· + N<sub>2</sub> + HO·), in reactions with reducing agents (e.g., the Sandmeyer reaction or the Meerwein condensation,  $C_{6H_{S}N_{2}}^{+} + CuCl_{2}^{-} \rightarrow C_{6H_{S}}^{+} + N_{2}^{-} + CuCl_{2}^{-}$ , on metal surfaces (e.g., the Gattermann reaction on powdered Cu), in the solid state, or in photodecompositions. Studies of systems where polar and free radical mechanisms for decomposition coexist (e.g., in methanol or glyme) have been made by D. F. DeTar and T. Kosuge, *J. Amer. Chem. Soc.*, **80**, 6072 (1958), by J. F. Bunnett and H. Takayama, *ibid.*, **90**, 5173 (1968), by T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970), and by L. Friedman and J. F. Chlebowski, ref 9, and personal communication from L. Friedman.
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Most nonaryne nucleophilic aromatic substitution reactions in the abwhich in the indeceptine a complexity of the complexity of the indeceptine and the ant of mechanism 2 involves the rapidly formed but relatively unstable cis adduct of Y to the terminal nitrogen of I as an additional intermediate between I and II. This mechanism is allowed by orbital symmetry, although the one-step rearrangement of this cis azo compound to III [proposed by A. Hantzsch, Chem. Ber., 27, 1702 (1894); 33, 2517 (1900); cited by K. H. Saunders, "Aromatic Diazo Compounds," 2nd ed, Edward Arnold, London, 1949, p 145] is not. (11) W. A. Waters, *J. Chem. Soc.*, 266 (1942).

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