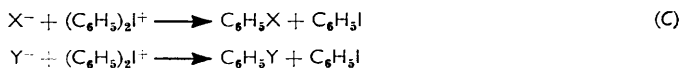




competition when two reagents compete for an insufficiency of a symmetrical iodonium salt, either  $(C_6H_5)_2I^+$  or  $(RC_6H_4)_2I^+$ , where R is 4-nitro or 4-methoxy.



*Reactions Studied.*—A study of competing reactions, such as those outlined above, necessarily involves analysis of the products, which are present as mixtures of three or four components. Since the products were formed in pairs, phenylated product and an iodobenzene, it was not generally necessary to determine independently all products. In many cases analysis was simplified by choosing reagents such that the iodobenzenes were volatile with steam and the phenylated products were not. This was the case when the phenylated product contained a sulphonate group, as resulted from the use of sulphite,<sup>4</sup> 4-sulphophenoxide,<sup>5</sup> or sulphanilate<sup>4,11</sup> ions, or when the product was high-boiling, as resulted from the use of dimedone<sup>6a</sup> in the presence of base. The steam-volatile compounds were a mixture of iodobenzene and 4-nitroiodobenzene or 4-iodoanisole. The ratio of these iodo-compounds, determined by infrared analysis, is also the ratio of attachment to the different rings. For example, reaction of the *p*-sulphophenoxide ion with 4-nitrodiphenyliodonium ion gave iodobenzene and 4-nitroiodobenzene in the ratio 5 : 1, reflecting a five-fold preference by the reagent for attachment to the nitrophenyl group.

In some of the reactions in which anions competed for an insufficiency of a symmetrical iodonium salt, one or both of the products were steam-volatile along with the iodobenzene. Such products included nitrobenzenes and benzonitriles, formed by nitrite and cyanide ions,<sup>4</sup> and diphenyl ethers, formed from phenoxide ions.<sup>4,5</sup> Phenols<sup>4,7,8</sup> (formed with hydroxide or carbonate ions, or water in the presence of copper catalysts) were not carried over appreciably under the conditions of the steam-distillation. Some three-component systems (*e.g.*, benzonitrile–nitrobenzene–iodobenzene) were analysed by infrared spectrophotometry.

*Intramolecular Competition.*—In Table I data are given on the cleavage (equations A)

TABLE I.

Cleavage of 4-substituted diphenyliodonium ions  $(RC_6H_4I^+Ph)$  in water at 100°.

R	$[X^-]/[-I^-]$	$[CuSO_4]/[-I^-]$	Reagent X	$[C_6H_5I]/[RC_6H_4I]^a$
4-NO <sub>2</sub> .....	4.0		SO <sub>3</sub> <sup>2-</sup>	> 10 <sup>b</sup>
	3.4		HO·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup> + HO <sup>-</sup>	5.0
	4.0	0.1	SO <sub>3</sub> <sup>2-</sup> + CuSO <sub>4</sub>	1.9
	4.0		H <sub>2</sub> N·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	1.5
	3.3		Dimedone + HO <sup>-</sup>	1.0
	4.0	0.9	SO <sub>3</sub> <sup>2-</sup> + CuSO <sub>4</sub>	0.5
	—	0.1	H <sub>2</sub> O + CuSO <sub>4</sub>	0.3
4-CH <sub>3</sub> O .....	3.4		HO·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup> + HO <sup>-</sup>	1.4 <sup>c</sup>
	8.0		H <sub>2</sub> N·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	1.1
	3.3		Dimedone + HO <sup>-</sup>	1.0
	4.0	0.9	SO <sub>3</sub> <sup>2-</sup> + CuSO <sub>4</sub>	0.9
	—	0.1	H <sub>2</sub> O + CuSO <sub>4</sub>	0.5 <sup>d</sup>
	4.0		H <sub>2</sub> O + CO <sub>3</sub> <sup>2-</sup>	0.4
	4.0		SO <sub>3</sub> <sup>2-</sup>	< 0.1 <sup>b,e</sup>

<sup>a</sup> The values given are believed to be accurate within  $\pm 10\%$ . <sup>b</sup> The notations > 10 and < 0.1 mean that  $RC_6H_4I$  and  $C_6H_5I$ , respectively, were not detectable by infrared spectrophotometry.

<sup>c</sup> Duplicate experiments gave values agreeing to  $\pm 0.1$ . <sup>d</sup> A value of  $0.43 \pm 0.1$  has been reported for this cleavage in the absence of copper catalyst along with a value of  $0.67 \pm 0.15$  in the presence of  $2 \times 10^{-4}$  molar cupric sulphate (*ref. 8*). <sup>e</sup> Earlier results from ultraviolet spectrophotometry had given a value of 0.07 (*E. Sommer, M. S. Thesis, Polytechnic Institute of Brooklyn, 1953*).

of the 4-nitrodiphenyliodonium ion, introduced as the tosylate,<sup>8</sup> and the 4-methoxydiphenyliodonium ion, introduced as the trifluoroacetate.<sup>1</sup> These salts not only were quite

<sup>11</sup> Makarova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1951, 741 (*Chem. Abs.*, 1952, 46, 7532).

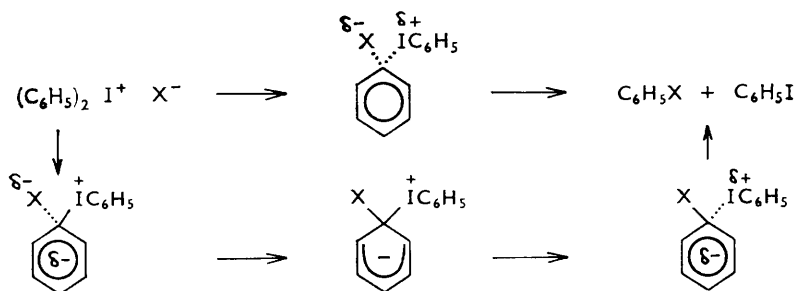
soluble in water but have anions of low nucleophilicity. In these reactions the concentration of the reagent effecting the cleavage (X) was several times that of the iodonium ion to speed the reaction and to minimize reaction with water. Results are given by the ratio  $[\text{C}_6\text{H}_5\text{I}]/[\text{RC}_6\text{H}_4\text{I}]$ , which is also the ratio of nitrophenylation or methoxyphenylation to phenylation.

Discussion of the results in Table I might start with the observation that most selectivity in the intramolecular competition between the unsubstituted and substituted rings of the iodonium ion was shown when sulphite ion effected the cleavage: the 4-nitrophenyl group was much more reactive and the 4-methoxyphenyl group was much less reactive than the unsubstituted phenyl group. This is the behaviour to be expected if the product-determining step involves nucleophilic attack. At this point no choice seems possible between one-step and two-step nucleophilic displacements.

Next, it should be noted that with all other reagents the selectivity between the two rings was much less than with sulphite ion, and the selectivity was generally less with the 4-methoxydiphenyliodonium ion than with the 4-nitrodiphenyliodonium ion.

SCHEME 1.

One-step and two-step nucleophilic displacements.

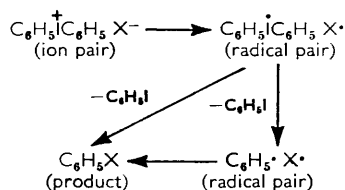


(The structures with the broken lines represent transition states. Charges written in the ring are distributed over *o*- and *p*-positions.)

The explanation tentatively suggested now and discussed more fully in later sections involves an alternative reaction path in which the product-determining steps are relatively insensitive to substituents. This alternative sequence (Scheme 2) is now<sup>6b,9</sup> thought to begin with electron transfer from anion to cation within ion-pairs to give radical-pairs, which yield products in one or two steps.

If, then, the reaction may be initiated by nucleophilic attack of  $\text{X}^-$  (Scheme 1) or electron transfer from  $\text{X}^-$  (Scheme 2), the former should be favoured by the nucleophilicity

SCHEME 2.

Formation and reaction of radical-pairs.<sup>a</sup>

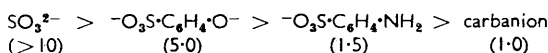
<sup>a</sup> For a more complete formulation of possible reactions of the free radicals see ref. 6d.

of  $\text{X}^-$  and by the electron-accepting ability of the substituent (R), while the latter should be favoured by the high reducing potential of  $\text{X}^-$ . Since the electron-releasing methoxyl group will inhibit nucleophilic attack, and since it does not appreciably change the potential

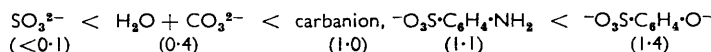
at which the iodonium cation accepts an electron,<sup>12</sup> it is to be expected that in the reaction of a given reagent with substituted or unsubstituted diphenyliodonium ions the ratio of nucleophilic attack to electron transfer will be influenced by substituents and will decrease with variation of substituents in the following order:



Having now formulated two alternative and potentially competitive reaction paths, we may return our attention to the data for the reactions of the two unsymmetrically substituted diphenyliodonium ions in Table 1. We see that the ratio of nitrophenylation to phenylation decreased in the following order:



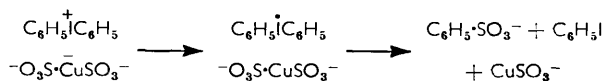
while the ratio of methoxyphenylation to phenylation increased in the following order:



The two sequences are similar but not identical, the major difference being that the sulphophenoxide ion shows a decided preference for the nitrophenyl ring (indicating nucleophilic attack) and a weak preference for the methoxyphenyl ring (indicating electron transfer, with slight discrimination in the cleavage of the unsymmetrical 4-methoxydiphenyliodine). For the other reagents the sequence is that of decreasing ratio of nucleophilic attack to electron transfer. The only carbanion tested, the anion from dimedone,<sup>6a</sup> showed no discrimination between substituted and unsubstituted rings in both cases, indicating reaction by electron transfer, as has been suggested on the basis of other evidence for other carbanions.<sup>6b-d</sup>

Another pattern evident in the data of Table 1 is that the presence of added cupric sulphate strongly influences the ratio of attack on the substituted and unsubstituted rings, the direction being that of decrease of selectivity. Thus the sulphite ion, strongly selective in the absence of copper, is only weakly selective in its presence. Since in the presence of a small amount of copper catalyst ( $[\text{CuSO}_4]/[\text{I}^{\ddagger}] = 0.1$ ) the cleavage ratio is intermediate between that in its absence and that in the presence of a larger amount ( $[\text{CuSO}_4]/[\text{I}^{\ddagger}] = 0.9$ ), it seems that, in the presence of a small amount of copper, catalysed and uncatalysed reactions occur to comparable extents.

It has previously been shown<sup>7a</sup> that a copper(I) species is the effective reagent in the decomposition of diphenyliodonium chloride in diethylene glycol, and it has been suggested<sup>9</sup> that this reaction proceeds by electron transfer from the dichlorocuprate(I) ion,  $\text{CuCl}_2^-$ , to the diphenyliodonium ion within an ion-pair to form diphenyliodine and cupric chloride, whose further reaction gives chlorobenzene, iodobenzene, and cuprous chloride. A similar formulation in the present case would involve reduction by sulphite ion of Cu(II) to Cu(I), formation of a complex such as  $\text{Cu}(\text{SO}_3)_2^{2-}$ , and its transfer of an electron to the diphenyliodonium ion. The diphenyliodine and the Cu(II) complex might then react in one or two steps (cf. Reaction Scheme 2) to form the final products.



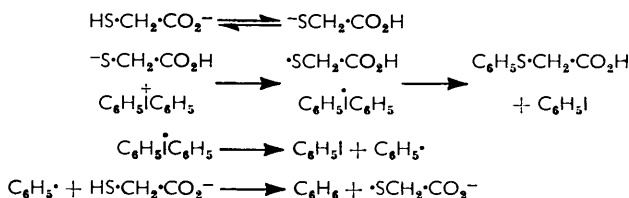
While reaction of the diphenyliodonium ion with water is slow, it is accelerated by base.<sup>4,7,8</sup> In the present study the 4-methoxydiphenyliodonium ion was hydrolysed in the presence of carbonate ion, with approximately 30% of new bonds to oxygen being formed

<sup>12</sup> Bachofner, Beringer, and Meites, *J. Amer. Chem. Soc.*, 1958, **80**, 4274.

by the substituted ring. However, it is not known whether carbonate or hydroxide ion was the effective reagent.

Finally, it might be noted that when hydrolysis occurred in the presence of added cupric sulphate, the bond from the phenyl group was broken about twice as often as that from the methoxyphenyl group<sup>8</sup> and about three times as often as that from the nitrophenyl group. This is taken as indicating that cleavage of the unsymmetrical diphenyliodonium gave more substituted iodobenzene ( $R \cdot C_6H_4I$ ) than iodobenzene; such cleavage might occur unimolecularly or under attack by a copper species.

*Benzene as a By-Product of the Phenylation of the Mercaptoacetate Ion.*—If, as suggested in Scheme 2, phenyl radicals are produced as members of radical-pairs, the majority should react within the solvent cage to form phenylated product while the minority should escape from the cage to give free phenyl radicals.<sup>6d</sup> In the case of the reaction of diphenyliodonium ions with mercaptoacetate ions, such free phenyl radicals might be expected to abstract hydrogen from sulphhydryl groups to give benzene.



Some years ago Sandin and his co-workers<sup>13</sup> reported the phenylation of the mercaptoacetate ion, forming phenylmercaptoacetic acid. Repetition of this work with analysis of the neutral fraction by vapour-phase chromatography showed, in addition, an 18% yield of benzene.

*Intermolecular Competition.*—To supplement the experiments just discussed involving intramolecular competition, some others were run in which an unsubstituted and a symmetrically-disubstituted diphenyliodonium cation competed for a small amount of reagent, between 29 and 33 mole-% of the available iodonium ions, according to equations (B). Reagents, mode of reaction, work-up, and analysis were similar to those described in the preceding sections, and the data obtained are summarized in Table 2.

TABLE 2.

Intermolecular competition between an equimolar mixture of  $(C_6H_5)_2I^+$  and  $(RC_6H_4)_2I^+$  for an insufficiency of reagent X in water at 100°.<sup>a</sup>

R	Reagent X	$[RC_6H_4I]/[C_6H_5I]^b$
4-NO <sub>2</sub>	SO <sub>3</sub> <sup>2-</sup>	> 10 <sup>b</sup>
	HO·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup> + HO <sup>-</sup>	> 10 <sup>b</sup>
	H <sub>2</sub> N·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	> 10 <sup>b</sup>
	Dimedone + HO <sup>-</sup>	5.0
4-CH <sub>3</sub> O	H <sub>2</sub> N·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	1.3 <sup>c</sup>
	SO <sub>3</sub> <sup>2-</sup> + CuSO <sub>4</sub> <sup>d</sup>	1.2
	H <sub>2</sub> O + CO <sub>3</sub> <sup>2-</sup>	1.1
	HO·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup> + HO <sup>-</sup>	1.0 <sup>c</sup>
	Dimedone + HO <sup>-</sup>	0.8
	SO <sub>3</sub> <sup>2-</sup>	0.7 <sup>c,e</sup>

• The iodonium salts used were: diphenyliodonium nitrate, 4,4'-dinitrodiphenyliodonium tosylate and 4,4'-dimethoxydiphenyliodonium trifluoroacetate. The initial ratio of reagent to iodonium salt,  $[X]/[-I^+]$ , was 0.29 to 0.33. <sup>b</sup> See Table 1, footnotes *a* and *b*. <sup>c</sup> Duplicate experiments show deviation of  $\pm 0.1$ . <sup>d</sup> Molar ratio of cupric sulphate to iodonium ion was 0.001. <sup>e</sup> A molar ratio,  $[SO_3^{2-}]/[-I^+]$ , of 0.14 gave an identical result.

<sup>13</sup> Sandin, Christiansen, Brown, and Kirkwood, *J. Amer. Chem. Soc.*, 1947, **69**, 1550.

The first point to be noticed is that intermolecular discrimination between  $(4\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4)_2\text{I}^+$  and  $(\text{C}_6\text{H}_5)_2\text{I}^+$  (Table 2) is greater for all four reagents tested than intramolecular discrimination between the two rings of  $4\text{-O}_2\text{N}\cdot\text{C}_6\text{H}_4\overset{\ddagger}{\text{I}}\text{C}_6\text{H}_5$  (Table 1). This is most easily understood as suggesting that nucleophilic displacement occurs by a one-step mechanism (upper line of Scheme 1), 4-nitroiodobenzene being a "better" leaving group than iodobenzene. As nucleophilic displacement is facilitated, even the anion of dimedone reacts largely by this path rather than by electron transfer.

By way of contrast, there is little discrimination between  $(4\text{-CH}_3\text{O}\cdot\text{C}_6\text{H}_4)_2\text{I}^+$  and  $(\text{C}_6\text{H}_5)_2\text{I}^+$ , as the cleavage ratios fall between 1.3 and 0.7, also expressed as  $1.0 \pm 0.3$ . It would seem that in these systems reaction proceeded largely by electron transfer. No interpretation will be attempted of the small variations from unity of the cleavage ratios.

*Competitions Between Nucleophiles.*—In these systems two reagents competed for an insufficiency of a symmetrical iodonium ion (equations C). Relevant data are collected in Table 3.

If first consideration is given to competitions between reagents in the absence of copper, it is seen that the five reagents can be placed in two groups, with sulphite and sulphophenoxide ions competing more than ten times as effectively for iodonium ions as cyanide, chloride, and nitrite ions (which had similar reactivities). It may be recalled that in the cleavage of the 4-nitrodiphenyliodonium ion, sulphite and sulphophenoxide ions were the most selective, and were judged to act by nucleophilic attack rather than by electron transfer.

In the presence of copper, sulphite and sulphophenoxide ions are still the most effective ions. More interestingly, the apparent reactivities of cyanide, chloride, and nitrite ions

TABLE 3.

Intermolecular competition of reagents X and Y for an insufficiency of  $(4\text{-RC}_6\text{H}_4)_2\text{I}^+$  in water at  $100^\circ\text{a}$

R	Initial [X] : [Y]	X	Y	E <sup>b,c</sup>	
				No Cu	Cu <sup>d</sup>
H	1 : 7	SO <sub>3</sub> <sup>2-</sup>	NO <sub>2</sub> <sup>-</sup>	>10	7
	1 : 7	SO <sub>3</sub> <sup>2-</sup>	CN <sup>-</sup>	>10	—
	1 : 4	SO <sub>3</sub> <sup>2-</sup>	Cl <sup>-</sup>	>10	5.5
	1 : 8	-C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	>10	>10
	1 : 8	-O·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	CN <sup>-</sup>	7	3
	1 : 1	CN <sup>-</sup>	Cl <sup>-</sup>	1.7	2.7
4-CH <sub>3</sub> O	1 : 1	CN <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	1 <sup>e</sup>	>10 <sup>g</sup>
	1 : 4	SO <sub>3</sub> <sup>2-</sup>	CN <sup>-</sup>	>10	>10
	1 : 1	CN <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	0.3	9
4-NO <sub>2</sub>	1 : 4	SO <sub>3</sub> <sup>2-</sup>	CN <sup>-</sup>	>10	>10
	1 : 1	-O·C <sub>6</sub> H <sub>4</sub> ·SO <sub>3</sub> <sup>-</sup>	CN <sup>-</sup>	>10	>10

<sup>a</sup> The salts used were those of Table 2, footnote a. <sup>b</sup> For calculation of E, the relative effectiveness of X and Y, see Experimental section. <sup>c</sup> When E is given as >10, no ArY was found. <sup>d</sup> One tenth mole of CuSO<sub>4</sub> was added per mole of iodonium salt. <sup>e</sup> See Table 4 and related text.

now decrease in that order (whereas in the absence of copper they were similar); this new sequence of reactivities is also that of the tendencies to complex with cuprous or cupric ions. It is evident that the tendency of X<sup>-</sup> and Y<sup>-</sup> to complex with cuprous ion would help determine the relative amounts of CuX<sub>2</sub><sup>-</sup> and CuY<sub>2</sub><sup>-</sup>, which are suggested as the effective reagents in electron-transfer processes.

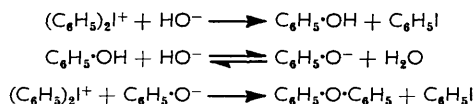
It cannot yet be said whether the high effectiveness of sulphite and sulphophenoxide ions in the presence of copper, as in its absence, involves a high tendency of these ions to form complexes with copper ions. Alternatively, the uncatalysed reactions of these ions may be faster than the catalysed reactions of cyanide, chloride, and nitrite ions. If these cation-anion reactions are formulated as proceeding by way of ion-pairs,<sup>5,7a</sup> the presence



of two negative charges on the sulphite and sulphophenoxide ions would be expected to increase the concentration of ion-pairs and hence increase the rates of both the uncatalysed and the catalysed reactions.

*Effect of Catalyst Concentration: Hydrolysis as a Competitive Reaction.*—As an extension of the results reported in Table 3 it was of interest to determine the effect of varying the concentration of copper. To a solution containing one equivalent of iodonium salt there was added a solution containing four equivalents of cyanide ion, four equivalents of nitrite ion, and various concentrations of cupric sulphate. The molar ratio of cupric ion to iodonium ion was varied from zero to one. Here both phenylation products (nitrobenzene and benzonitrile) and the iodobenzene were steam-distillable, and the distillate was analysed directly by infrared spectrophotometry for all these compounds.

In all reactions of iodonium salts in water a competing reaction was the hydrolytic cleavage of the iodonium salt to form phenol, present largely as the phenoxide ion, diphenyl



ether, and iodobenzene. Such hydrolysis was most extensive when the solution contained strong bases, such as cyanide and sulphophenoxide ions. A measure of these competing reactions can be obtained by measuring the amount of iodobenzene formed and comparing it with the sum of the nitrobenzene and benzonitrile formed.

The relative effectiveness of cyanide and nitrite ions in the competition for diphenyliodonium ions, the percentage of concurrent hydrolysis of the diphenyliodonium ion, and the dependence of these quantities on the concentration of copper sulphate are shown in Table 4.

The results indicate that copper ions strongly catalysed the reaction of cyanide but not of nitrite ions. Further, copper-catalysed reaction with cyanide ion was somewhat faster

TABLE 4.

Effect of catalyst concentration on cyanide–nitrite competition for  $(\text{C}_6\text{H}_5)_2\text{I}^+$  and competitive hydrolysis of cation.

$[\text{Cu}^{++}]/[-\text{I}^-]^a$ .....	0.00	0.01	0.05	0.50	1.00
$[\text{C}_6\text{H}_5\cdot\text{CN}]/[\text{C}_6\text{H}_5\cdot\text{NO}_2]^b, c$ .....	1.1	4.0	18	>20	>20
Hydrolysis (%) <sup>d</sup> .....	51	55	37	25	14

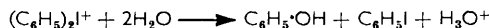
<sup>a</sup> The molar ratio of cupric sulphate to diphenyliodonium nitrate. <sup>b</sup> The relative effectiveness of  $\text{CN}^-$  and  $\text{NO}_2^-$  is approximated by the molar ratio of benzonitrile and nitrobenzene. Four moles of each ion were initially present per mole of diphenyliodonium nitrate. <sup>c</sup> The value >20 means that no nitrobenzene could be detected within the limits of this determination (see Table 5, footnote c).

<sup>d</sup> Calculated as:  $100\{1 - ([\text{C}_6\text{H}_5\text{CN}] + [\text{C}_6\text{H}_5\text{NO}_2])/[\text{C}_6\text{H}_5\text{I}]\}$ .

than copper-catalysed hydrolysis. Both facts may reflect the predominant formation by the copper of cyanide complexes such as  $\text{Cu}(\text{CN})_2^-$  and  $\text{HO}\cdot\text{CuCN}^-$ .

From Table 4 it can also be seen that the presence of small amounts of copper did not completely change the reaction path. If it is assumed that the reaction of nitrite ion was not affected by the presence of copper, then it seems that in the presence of 0.01 equivalent of copper the catalysed reaction of cyanide ion was about three times faster than the uncatalysed. The reaction catalysed by 0.05 equivalent of copper was about 17 times as fast as the uncatalysed reaction. Thus, the ratio of rate constants for the catalysed and uncatalysed reactions of cyanide ion with diphenyliodonium ion is at least 300, if one assumes the kinetic orders of the reactions to be the same. If there is also some catalysed reaction of nitrite ion, then the ratio must be greater than 300.

It had been previously reported<sup>7a</sup> that the uncatalysed reaction of the chloride ion and the diphenyliodonium cation proceeded fairly completely to yield 85—90% of chloride reaction products and 10—15% of hydrolysis products. The effect of a cupric chloride catalyst was to catalyse the chloride reaction more than the hydrolysis reaction so that 93.6% chloride reaction and 6.4% hydrolysis occurred. Under the conditions of these experiments the solutions were initially neutral and became acidic as the reaction progressed, as a result of the hydrolysis:



In order to assess further the contribution of hydrolysis to the reaction of iodonium salts with various nucleophiles in water, several isolation experiments were run. The carbonate ion in water was found to react fairly completely with the diphenyliodonium ion to yield diphenyl ether, iodobenzene, and a trace of phenol. The nitrite ion in water reacted only partially with the diphenyliodonium cation even under prolonged reflux, the products consisting of nitrobenzene, iodobenzene, and a trace of phenol. Cyanide ion in water reacted with the diphenyliodonium ion to yield a mixture about equally divided between phenylation and hydrolysis products. The characteristic odour of phenyl isocyanide was apparent, but this product was not further identified.

It is interesting that both carbonate and cyanide ions, to a lesser degree, permitted further phenylation of phenol. This is in accord with the higher basicity of their solutions than those of the nitrite ion. Indeed, virtually no hydrolysis occurred in the very slow reaction with aqueous nitrite ion.

*Summary of Mechanistic Conclusions.*—In the foregoing sections the results of numerous intramolecular and intermolecular competition reactions have been interpreted in terms of two alternative reaction paths: nucleophilic attack by an anion on a 1-carbon of the diphenyliodonium ion (Scheme 1), and electron transfer from anion to cation in an ion-pair to form a radical-pair, followed by coupling or diffusion (Scheme 2). The results also suggest the following conclusions:

(1) The presence of nitro groups enhances, and that of methoxyl groups decreases, the susceptibility of diphenyliodonium ions to nucleophilic attack.

(2) The greater susceptibility of a 4,4'-dinitro- than of a 4-nitro-diphenyliodonium ion to nucleophilic attack suggests that the former may undergo direct one-step nucleophilic displacement, 4-iodonitrobenzene leaving as the nucleophile enters.

(3) The electron-transfer mechanism is not strongly affected by substituents; when nucleophilic displacement is repressed, electron transfer becomes the dominant mode of reaction.

(4) The tendency toward nucleophilic attack is greatest, among the reagents studied, with sulphite ion and least with the anion of dimedone. The sulphophenoxide ion acts predominantly as a nucleophile toward the 4-nitrodiphenyliodonium ion and as a reducing agent toward the 4-methoxydiphenyliodonium ion.

(5) Added cupric ion functions as catalyst in the reactions of anions ( $\text{X}^-$ ) by virtue of the reducing power of the Cu(I) species, such as  $\text{CuX}_2^-$ .

(6) It is not yet clear in which cases the diphenyliodonium free radical cleaves unimolecularly and in which cases cleavage occurs upon attack by another free radical ( $\text{X}\cdot$ ) or by a copper species ( $\text{CuX}_2$ ).

(7) To explain the present results, it has not been necessary to invoke mechanisms other than nucleophilic attack and electron transfer. It is possible that other mechanisms (see introduction) are operative under other conditions.<sup>10</sup>

#### EXPERIMENTAL

*Iodonium Salts.*—Diphenyliodonium nitrate,<sup>5</sup> 4-nitrodiphenyliodonium bromide,<sup>1</sup> 4-methoxydiphenyliodonium trifluoroacetate<sup>1</sup> and 4,4'-dimethoxydiphenyliodonium trifluoroacetate<sup>1</sup> were prepared by known procedures. 4-Nitrodiphenyliodonium tosylate was prepared



in 78% yield from the less-soluble bromide<sup>1</sup> by metathesis with lead tosylate in methanol, removal of lead bromide, concentration, and crystallization from ethanol-water: colourless crystals, m. p. 190—193° (Found: C, 45.7; H, 3.5; I, 25.3. C<sub>19</sub>H<sub>16</sub>INO<sub>3</sub>S requires C, 45.9; H, 3.2; I, 25.5%).

**4,4'-Diacetamidodiphenyliodonium Iodide.**—The previously reported<sup>14</sup> yield of 48% was increased to 72% by an improved work-up, as follows. The reaction mixture was stirred at room temperature for 1.5 days and set aside for 2 days. After addition of 500 ml. of ice-water below 20°, removal of insoluble material and destruction of residual oxidizing power with aqueous sodium sulphite, an aqueous solution of 150 g. of potassium iodide was added, and the solution was diluted with an equal volume of methanol. After chilling, the precipitate was washed with methanol and ether, and dried, giving 4,4'-diacetamidodiphenyliodonium iodide (116 g., 0.22 mole; 72%), m. p. 180—183° (decomp.) after insertion in the Kofler hot-stage apparatus at 165°; reported m. p. 173°,<sup>14</sup> 176.5°.<sup>15</sup>

**4,4'-Diaminodiphenyliodonium Tosylate.**—The hydrolysis of this amide in 36% yield by hot 10:1 methanol-concentrated hydrochloric acid has been described.<sup>3b</sup> 4,4'-Diaminodiphenyliodonium iodide (9.5 g., 21.7 mmole) and lead tosylate (6.3 g., 23 mmole) in 200 ml. of methanol were heated under reflux with stirring for 2 hr. and then stirred for several additional hours at room temperature. After removal of lead iodide the solution was diluted with an equal volume of ether. The resulting precipitate was collected and dried to yield 8.0 g. (16.6 mmole; 77%) of 4,4'-diaminodiphenyliodonium tosylate. This salt was recrystallized from water to yield pale green needles of m. p. 177—180° (decomp.) after insertion in the Kofler hot-stage apparatus at 168°.

**4,4'-Dinitrodiphenyliodonium Tosylate.**—After 4,4'-diaminodiphenyliodonium tosylate (11.5 g., 23.9 mmole) had been dissolved in 100 ml. of trifluoroacetic acid, 55 ml. of 90% hydrogen peroxide was added in 5—10-ml. portions.<sup>16</sup> After each addition the mixture was allowed to warm to 75°, when there was additional exothermic reaction, and then cooled. Another 50 ml. of trifluoroacetic acid was added, and another 55 ml. of peroxide (stepwise). To ensure complete decomposition of the peroxide, the mixture was gradually heated to 85°. Removal of solvent below 45° gave a reddish oil, which on trituration with anhydrous ether yielded 9.1 g. (16.8 mmole; 70%) of 4,4'-dinitrodiphenyliodonium tosylate. The product, which was readily soluble in warm water, was crystallized from ethanol-ether to yield 7.5 g. (13.8 mmole; 58%) of fine crystals of m. p. 180—183° (decomp.) after insertion in the Kofler hot-stage apparatus at 150° (Found: C, 42.2; H, 3.0. C<sub>18</sub>H<sub>15</sub>IN<sub>2</sub>O<sub>7</sub>S requires C, 42.1; H, 2.8%).

**Analyses.**—Suitable infrared absorption peaks were chosen for the products of the competition reactions so that mixtures could be analysed quantitatively. Standards and unknowns were run in carbon disulphide. The results are given in Table 5. Each compound is numbered, and the particular mixtures which were actually analysed are indicated. The following compounds were studied: (1) iodobenzene, (2) 4-iodoanisole, (3) 4-nitroiodobenzene, (4) benzonitrile, (5) nitrobenzene, (6) chlorobenzene, (7) 4-methoxybenzonitrile, (8) 4-nitroanisole, and (9) 4-nitrobenzonitrile.

The spectra were run in a double-beam Perkin-Elmer infrared spectrophotometer using a 0.994-mm. fixed cell. The absorbances were determined at the wavelength minimum and were corrected for the background. The analytical results, obtained by plotting concentration against absorbance, followed Beer's law in the desired concentration range for all compounds studied. The molar extinction coefficient  $\epsilon_{\max}$  was calculated as follows:

$$\epsilon_{\max} = \frac{\text{Mean absorbance} \times M \times 50}{\text{Mean } C \text{ (in mg./ml.)} \times 0.0994} \text{ in l. mole}^{-1} \text{ cm}^{-1}$$

The average absorbance (mg./50 ml.) was given by the slope of the plots of absorbance against concentration. The data are summarized in Table 5.

**Competition Reactions.**—For each of the three different types of competition reaction one general procedure was followed, which is described below.

The iodonium salt (or salts) and reagent (or reagents) were heated under reflux in water, and the iodobenzenes were collected in a Dean-Stark trap. When distillation was complete

<sup>14</sup> Beringer, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2705.

<sup>15</sup> Willgerodt and Nagel, *Ber.*, 1907, **40**, 4070.

<sup>16</sup> Emmons, Pagano, and Freeman, *J. Amer. Chem. Soc.*, 1954, **76**, 3472.

the distillate was extracted with ether, the extract dried over sodium carbonate, and the solvent removed by evaporation. The mixture of iodobenzenes was redissolved in a small quantity of ether, and an aliquot portion transferred to a weighed 50-ml. volumetric flask. The solution was then made up to volume with carbon disulphide and analysed quantitatively by infrared

TABLE 5.

Infrared spectral parameters used in the analysis of substituted benzenes.<sup>c</sup>

Compound <sup>a</sup>	Analysed in presence of	$\lambda_{\max.}$ (microns)	Concentration (mg./50 ml. CS <sub>2</sub> )	(l. mole <sup>-1</sup> cm. <sup>-1</sup> )
1 <sup>b</sup>	2, 3	14.63	120 to 600	68
2	1	7.77	120 to 550	177
2	7, 8	10.00	210 to 390	69
3	1	7.42	25 to 250	397
3	9	13.58	70 to 280	204
4	1, 5, 6	13.23	30 to 170	85
5	1, 4	7.44	25 to 100	413
6	1, 4	14.24	70 to 540	84
7	2, 8	12.00	20 to 115	360
8	2, 7	7.48	30 to 115	513
9	3	13.37	80 to 230	113

<sup>a</sup> The compounds identified by numbers are those listed under "Analyses." <sup>b</sup> A  $\lambda_{\max.}$  of 9.45  $\mu$  was used in the presence of compound 6, and a  $\lambda_{\max.}$  of 13.74  $\mu$  was used when compounds 4 and 5 were present. <sup>c</sup> When the molar ratio of the two components was more than 1 : 10, accurate determination of the minor component was not generally possible. When nitrobenzene (compd. 5) was determined in the presence of benzonitrile (compd. 4), its concentration could be determined in the ratio of 1 : 20 because of its comparatively high  $\epsilon_{\max.}$

spectrophotometry. The concentrations of the iodobenzenes in the mixture were determined from the absorbance at the appropriate wavelengths.

It was determined by a separate experiment that phenol does not steam-distil under these conditions but is isolated from the reaction mixture as 2,4,6-tribromophenol.

When a base was used to generate the effective reagent, there was no reaction in the absence of base. The effective reagent was then considered equivalent to the base added.

The relative effectiveness,  $E$ , of X and Y in the competition for an insufficiency of iodonium ion (Table 3) was calculated as follows:

$$E = \frac{[\text{ArX}]/[\text{X}]}{[\text{ArY}]/[\text{Y}]} = \frac{[\text{ArX}]}{[\text{ArY}]} \cdot \frac{[\text{Y}]}{[\text{X}]}$$

The ratio of reagents used in these calculations was that of the initial quantities, since the reagents were in sufficient excess to prevent large changes in the ratio during the reaction.

When both ArX and ArY were steam-volatile, their ratio was determined by infrared analysis of the distillate. When ArX was non-volatile, [ArX] was taken as the difference between [ArI] and [ArY]. Since ArI is also formed by hydrolysis reactions, along with phenol and diphenyl ether, [ArX] calculated by difference includes products formed by X, HO<sup>-</sup>, and ArO<sup>-</sup>.

Permission to use the research facilities of the Colgate-Palmolive Co. and of the Sperry Gyroscope Co. is acknowledged. One of us (R. A. F.) thanks the Sperry Gyroscope Co. for tuition support. Constructive criticism from Dr. Suzanne A. Galton and Mr. Milton D. Yudis was most helpful.