In these experiments the "infinity titers" were about 90% of the theoretical value. Subsequent heating of the solution increased the titer to the calculated value.

C. **Acetolysis of the Rearrangement Product.**—Solutions of 0.05 M II in anhydrous acetic acid were thermostated at 30° for 4 hr. (12 half-lives for the solvolysis). These solutions were neutralized with 0.25 N sodium acetate in acetic acid and the resulting solutions were used for the kinetic experiments. The rate of acetolysis was measured by the ampule technique. The reactions were followed by potentiometric titration of aliquots with 0.01 M sodium acetate in acetic acid. The first-order rate constants calculated in the usual manner showed a downward trend as illustrated by Table VI. Plots of log [ROTs] vs. time, such as Fig. 1, were used after the manner of Brown and Fletcher, for the determination of the inital concentration and acetolysis rate constants (Table III) of the two components (α-tosylate and β-tosylate).[22]

In a control experiment the acetolysis of 0.01 M trans-trans-1-decalyl p-toluenesulfonate in the presence of 0.05 M sodium p-toluenesulfonate was followed by the method described above. The rate constants obtained did not show any trends.

D. **Measurement of k_r/k_s.**—Solutions of 0.1 M II were thermostated at 30° for 10–15 half-lives for the solvolysis.

TABLE VI

ACETOLYSIS OF REARRANGEMENT PRODUCT AT 79.65° IN THE PRESENCE OF 0.0362 N NaOTs AND 0.00812 N NaOAc

Time, 10^3 sec.	ROTs, 10^3 M	$10^6 k$, sec.$^{-1}$	Time, 10^3 sec.	ROTs, 10^3 M	$10^6 k$, sec.$^{-1}$
0	5.56		3.12	2.09	31.4
0.12	5.18	58.7	4.62	1.95	22.6
.42	4.40	55.6	6.12	1.78	18.6
.72	3.78	53.4	7.32	1.59	17.1
1.02	3.34	49.9	9.72	1.29	15.0
1.32	3.08	44.8	12.42	1.06	13.3
1.62	2.82	41.9	15.62	0.88	11.8
1.92	2.64	38.9	19.32	.62	11.4
2.22	2.46	36.6	24.12	.44	10.5

Aliquots were then titrated and the titers compared with those of aliquots that were heated for 15 hours at 90°. The ratio of the difference in titer to the titer after 10–15 half-lives at 30° is k_r/k_s.

MADISON 6, WIS.

Hydrolysis of Diaryliodonium Salts

BY MARJORIE C. CASERIO, DONALD L. GLUSKER AND JOHN D. ROBERTS

The products of hydrolysis of some unsymmetrically substituted diphenyliodonium salts to phenols and aryl iodides have been identified and their distributions determined. The direction of cleavage has been found to be insensitive to the nature of the substituents, the solvent, catalysts, and the nature of the associated anion, fluoride, fluoroborate, p-toluenesulfonate or trifluoroacetate. A rate study has shown that hydrolysis is a complex reaction which is retarded by acid and catalyzed by cuprous copper and also by oxygen when dioxane–water is used as the solvent. Possible mechanisms are discussed.

Introduction

The kinetics of hydrolysis of diazonium salts in acidic aqueous solution has provided substantial evidence that a phenyl cation is an intermediate in the reaction.[1] This is a unique example of aromatic nucleophilic displacement by an SN1-type mechanism. The investigation here described was initially undertaken in the hope that alternative classes of aromatic compounds might be found to undergo nucleophilic displacement by similar mechanisms. At the outset, it was hoped that the hydrolysis of diaryliodonium salts might proceed with intermediate formation of a phenyl cation, by analogy with certain diazonium salt reactions.

$$(C_6H_5)_2I^\oplus \longrightarrow C_6H_5^\oplus + C_6H_5I$$

$$C_6H_5^\oplus + 2H_2O \longrightarrow C_6H_5OH + H_3O^\oplus$$
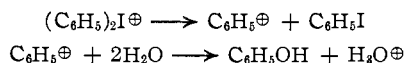
The work of Beringer,[2] Lewis[3] and Nesmeyanov,[4] on the reactions of diphenyliodonium salts has shown clearly how susceptible these salts are to attack by nucleophilic reagents by a variation of the SN2 mechanism. For example, only 6–15%

(1) For leading references see E. S. Lewis, THIS JOURNAL, **80**, 1371 (1958), and also D. F. DeTar and D. I. Relyea, ibid., **76**, 1680 (1954).

(2) (a) F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler and C. C. Lumpkin, ibid., **75**, 2708 (1953); (b) F. M. Beringer and E. M. Gindler, ibid., **77**, 3203 (1955); (c) F. M. Beringer, E. J. Geering, I. Kuntz and M. Mausner, J. Phys. Chem., **60**, 141 (1956).

(3) E. S. Lewis and C. A. Stout, THIS JOURNAL, **76**, 4619 (1954).

(4) A. N. Nesmeyanov, L. G. Makarova and T. P. Tolstaya, Tetrahedron, **1**, 145 (1957), and references cited therein.

hydrolysis occurs on refluxing aqueous solutions of diphenyliodonium chloride; the main reaction is one of attack by chloride ion to give chloro- and iodobenzenes.[2c] Therefore, substantial hydrolysis will not occur by either an SN1 or SN2 mechanism unless the nucleophilic character of the associated anion is negligibly small. It was for this reason that fluoride, fluoroborate, tosylate and trifluoroacetate iodonium salts were selected for investigation, since these anions possess little or no nucleophilic character, and consequently might allow hydrolysis to take place exclusively.

We hoped that a study of the products from hydrolysis of unsymmetrical iodonium salts would indicate the operative mechanism, since it was anticipated that substituents would strongly influence the product distributions in a manner which would allow a distinction to be made between reaction by an SN1 or SN2 mechanism. Thus, the products to be expected for SN2 hydrolysis of the 3-nitrodiphenyliodonium ion are m-nitrophenol and iodobenzene; in contrast, SN1 hydrolysis should give predominantly m-nitroiodobenzene and phenol.

Hydrolysis of Unsymmetrical Iodonium Salts.—In carrying out experiments designed to test some of the preceding hypotheses, the iodonium salts were refluxed with water for periods varying from a few hours to several days. In a few instances, aqueous dioxane and acetonitrile were used as solvents to prevent separation of an organic phase.

The hydrolysis of 4-methoxydiphenyliodonium

TABLE I

PRODUCT DISTRIBUTION IN THE HYDROLYSIS OF DIARYLIODONIUM SALTS, $\overset{\oplus}{Ar}I\overset{\ominus}{C_6H_5}$ X

Expt.	Ar	X	Solvent	Catalyst	Iodo-benzene	p-Iodo-anisole	Phenol	p-Methoxy-phenol
					Mole per cent.(± 5%)			
1	4-CH₃OC₆H₄-	F⊖	H₂O	. . .	42	58	59	41
2	4-CH₃OC₆H₄-	F⊖	H₂O[a]	. . .	38	62	57	43
3	4-CH₃OC₆H₄-	F⊖	H₂O[a]	. . .	37	63	58	42
4	4-CH₃OC₆H₄-	BF₄⊖	H₂O	. . .	29	71	. .	. .
5	4-CH₃OC₆H₄-	CTs⊖	H₂O	. . .	30	70	. .	. .
6	4-CH₃OC₆H₄-	OTs⊖	Aq. dioxane	. . .	25	75	. .	. .
7	4-CH₃OC₆H₄-	F⊖	Aq. dioxane	. . .	28	72	. .	. .
8	4-CH₃OC₆H₄-	OTs⊖	H₂O	Cu⊕⊕[b]	40	60	60	. .
9	4-CH₃OC₆H₄-	CF₃CO₂⊖	H₂O	Cu⊕⊕	40	60	. .	. .
10	4-CH₃OC₆H₄-	OTs⊖	Aq. dioxane	Cu⊕⊕	41	59	. .	. .
11	4-CH₃OC₆H₄-	OTs⊖	Aq. CH₃CN	Cu⊕⊕	35	65	. .	. .
12	4-CH₃OC₆H₄-	OTs⊖	H₂O	Cu⊕	40	60	. .	. .

Expt.	Ar	X	Solvent	Catalyst	Iodo-benzene	m-Iodo-toluene	Phenol	m-Cresol
13	3-CH₃C₆H₄-	OTs⊖	H₂O	Cu⊕⊕	46	54	56	44
14	3-CH₃C₆H₄-	OTs⊖	H₂O	Cu⊕	43	57	. .	. .

[a] Fluoroboric acid present.　[b] 2 × 10⁻⁴ M.

tosylate, fluoride and fluoroborate afforded all four possible products, p-iodoanisole, iodobenzene, phenol and p-methoxyphenol. In material balance, the products isolated accounted for 90–96% of the iodonium salt, and equimolar amounts of phenol and p-iodoanisole were formed. The product distribution slightly favored the formation of p-iodoanisole and phenol, and this distribution did not vary significantly with the nature of the anion or with the composition of the solvent. The results are summarized in expts. 1–7, Table I.

Shortly after this work commenced, Beringer and associates[2c] reported the thermal decomposition of diphenyliodonium halides in various solvents to be strongly catalyzed by trace amounts of cupric and cuprous copper. We have found the hydrolysis of iodonium salts to be similarly catalyzed. Furthermore, the product distribution in the Cu[II] and Cu[I]-catalyzed hydrolyses of 4-methoxydiphenyliodonium tosylate or trifluoroacetate in water, aqueous dioxane and acetonitrile was found to be the same as in the uncatalyzed reaction (cf. expts. 8–12, Table I).

The hydrolysis of 3-methyldiphenyliodonium tosylate, in the presence of micromolar amounts of Cu[II], gave a mixture of the four possible products, iodobenzene, m-iodotoluene, phenol and m-cresol, and the same products in the same distribution resulted from the Cu[I]-catalyzed reaction (cf. expt. 13–14, Table I). The two iodine–carbon bonds of this iodonium salt rupture with almost equal ease.

It is at once apparent that the direction of C–I bond fission is remarkably insensitive to the substituents present. This is strikingly demonstrated in the hydrolysis of 3-nitro-4'-methoxydiphenyliodonium tosylate. The phenyl groups in this salt carry substituents of extreme and opposite polar character, yet the Cu[II]-catalyzed hydrolysis in aqueous solution[5] afforded an astonishingly even split between the two possible directions of C–I fission. The iodonium salt was found to be consumed by four competing reactions as shown in Fig.

(5) Solution was 0.1 M in p-toluenesulfonic acid in order to suppress phenoxide formation (vide infra).

1. The main reaction is one of hydrolysis in which the nitro and methoxyl groups exert no significant directional influence. The phenolic products react further with the iodonium ion to form diaryl ethers, and since these ethers were identified by independent synthesis as 3,3'-dinitro- and 3-nitro-4'-methoxydiphenyl ethers, with no 4,4'-dimethoxydiphenyl ether, it is probable that phenols attack as phenolate ions by an SN2 mechanism.

Similarly, the uncatalyzed hydrolysis of 3-nitrodiphenyliodonium fluoride gave a mixture of iodobenzene, m-nitroiodobenzene, phenol and m-nitrophenol, together with appreciable amounts of diaryl ethers, although no attempt was made in this case to identify the ethers. It was reasoned that ether formation could probably be reduced by the initial addition of strong acid in order to suppress dissociation of the phenols to phenolate ions. In actual fact, hydrolysis of a 0.15 M solution of the iodonium salt in the presence of one equivalent of added fluoroboric acid reduced the extent of ether formation from approximately 39% to 16% of the total isolated product.

The distribution of products from these hydrolyses is surprisingly insensitive to the nature of the phenyl substituents. A plausible reaction mechanism must necessarily account for this lack of substituent effect and the pronounced catalytic effect of cupric copper, and it seems therefore unlikely that reaction proceeds by either an SN1 or SN2 mechanism. The results suggest that some sort of homolytic mechanism is involved, and this possibility will be discussed in greater detail in a later section.

Rate Studies.—It was hoped that a kinetic study of the hydrolysis reaction might serve to clarify the mechanism. However, a preliminary study revealed unexpected complications which made rigorous kinetic investigation far from simple experimentally although a number of significant observations were made.

The compound chosen for most of the kinetic experiments was 4-methoxydiphenyliodonium tosylate. The hydrolyses were carried out at 100° in
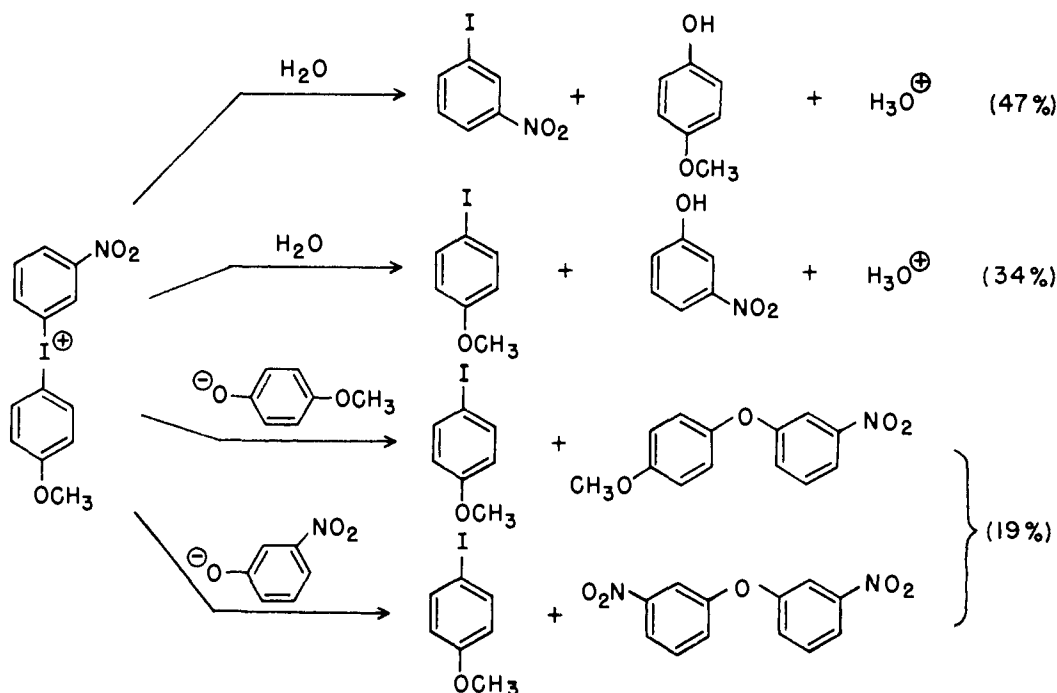
Fig. 1.—Products of the Cu^{II}-catalyzed hydrolysis of 4-methoxy-3'-nitrodiphenyliodonium tosylate.

sealed tubes and the rate was followed by the amount of acid produced with time.

The uncatalyzed reaction of 4-methoxydiphenyliodonium tosylate proceeded very slowly, and the rate was observed to fall off considerably faster than predicted for a strictly first-order process. In one experiment, the hydrolysis of a solution, initially 0.1 M in iodonium salt, virtually halted at only 30% completion after nine days at 100°. The rates of hydrolysis of 4-methoxydiphenyliodonium fluoride and fluoroborate were found to be considerably retarded by the initial addition of an equivalent amount of fluoroboric acid. It is, therefore, the production of acid which has a retarding effect on reaction; but no detailed kinetic measurements were made owing to the poor reproducibility of the rates in water.

An organic phase separates as hydrolysis proceeds in aqueous solution and, to avoid this, reaction was carried out in 1:1 aqueous dioxane. In this solvent, the rate did not follow a simple first-order kinetic law but increased with time in a manner characteristic of an autocatalytic reaction, and seemingly identical runs could not be even approximately reproduced. The discrepancy was traced to the presence of oxygen; when care was taken to degas solutions prior to reaction, only 7% of the tosylate hydrolyzed in 24 hours, whereas solutions sealed in an atmosphere rich in oxygen reacted completely in the same time. Under identical reaction conditions, in the absence of iodonium salt, the aqueous dioxane developed an appreciable acid titer, thus showing solvent decomposition to be considerable. Apparently, the oxygen-induced decomposition of dioxane effectively catalyzes hydrolysis of the iodonium salt. The effect is not restricted to dioxane since similar rate curves were obtained in acetone–water mixtures. In

water alone, the rate of hydrolysis was not noticeably affected by the presence of oxygen or hydrogen peroxide. The combined effect of oxygen and dioxane is all the more remarkable in that the resulting product distribution is essentially the same as in the uncatalyzed reaction in water. Furthermore, analysis by vapor-phase chromatography of the reaction mixture from the hydrolysis of diphenyliodonium tosylate in aqueous dioxane gave no indication of benzene or other volatile products (besides iodobenzene and phenol) which might arise from the attack of free phenyl radicals on the solvent.

The rate studies were extended to include the effect of copper salts on reaction. Micromolar quantities of cupric chloride catalyzed the hydrolysis of 4-methoxydiphenyliodonium tosylate in water and in 50% aqueous dioxane. In marked contrast to the behavior in the absence of copper, the rate in both solvents was first-order, as shown in Fig. 2; and there was no apparent retardation by the acid produced. However, the kinetics within and between runs were not reproducible with any precision, and this also was found to be due to the presence of oxygen. Sealed vials of solution, identical in cupric and iodonium salt concentration but with purposely varied oxygen contents, reacted at appreciably different rates; the higher the oxygen content, the slower the reaction (cf. Fig. 2). The difficulties involved in obtaining reliable kinetic data from oxygen-sensitive systems are manifold, and no attempt was made to rigidly exclude oxygen. This was adjusted to be a constant factor, as far as possible, by sealing reaction tubes under atmospheric conditions. The oxygen content was therefore relatively large, but the effect of small differences became correspondingly less important. No attempt was made to deter-
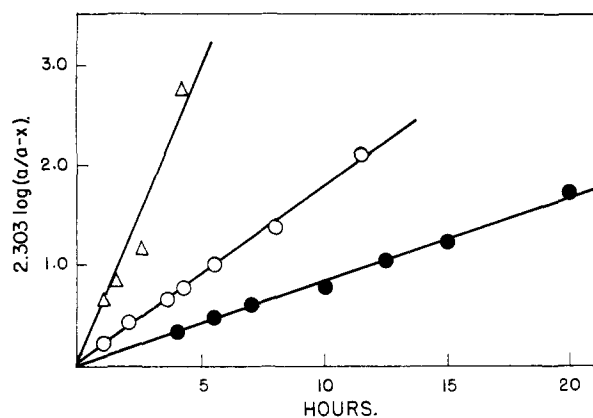
Fig. 2.—First-order plot of rate of hydrolysis of p-methoxydiphenyl-iodonium tosylate in the presence of Cu^{II} (2×10^{-4} M) at 100.1°: ●, in 50% aqueous dioxane under nitrogen, $k_1 = 2.33 \pm 0.05 \times 10^{-5}$ sec.$^{-1}$; O, in water, oxygen present, $k_1 = 4.87 \pm 0.08 \times 10^{-5}$ sec.$^{-1}$; △, in water, oxygen excluded, $k_1 = 1.7 \pm 0.1 \times 10^{-4}$ sec.$^{-1}$; a is the initial concentration of iodonium salt (0.1 M); x is the amount reacted at the indicated times.

mine the order of reaction with respect to copper because of the complicating effects of oxygen.

It was of interest to study the effect of acid on the Cu^{II}-catalyzed reaction in water. The production of acid during reaction was not observed to retard the first-order rate up to 85% completion, but the addition of acid at the start of reaction produced a marked retardation. A solution of 4-methoxydiphenyliodonium tosylate, 2×10^{-4} M in cupric chloride, and containing two equivalents of added p-toluenesulfonic acid, showed 50% reaction after 37 hours at 100°, whereas, in the absence of added acid, the half-life was 4.6 hours. Furthermore, the rate in the presence of added acid was not first order, but increased with time in an auto-catalytic manner. These experiments are reproduced in Fig. 3, which also includes a first-order plot of the rate in the presence of sodium p-toluenesulfonate. Obviously, there is no detectable salt effect.

The retardation produced by acid on the Cu^{II}-catalyzed hydrolysis when initially added, and not as it is formed during reaction, suggests that acid retards, not the hydrolysis reaction, but the formation of an intermediate necessary for hydrolysis to occur. This species we consider to be cuprous copper.[6] Hydrolysis appears to occur subsequent to reduction of Cu^{II} to Cu^{I}, and the effect of oxygen and acid is to retard this reduction. A similar inhibitory effect of oxygen was observed by Kochi[7] in the Cu^{I}-catalyzed Meerwein reaction. Kochi also found reduction of Cu^{II} by acetone to be inhibited by acid.[8]

If Cu^{I} is the effective catalyst, then hydrolysis in its presence should occur rapidly and exhibit no retardation by added acid. The catalytic effects of Cu^{I} and Cu^{II}, with and without added acid, were directly compared by conducting separate experi-

(6) Beringer and co-workers (ref. 2c) consider the effective catalyst in the decomposition of diphenyliodonium halides to be cuprous copper.

(7) J. K. Kochi, THIS JOURNAL, 78, 1228 (1956).
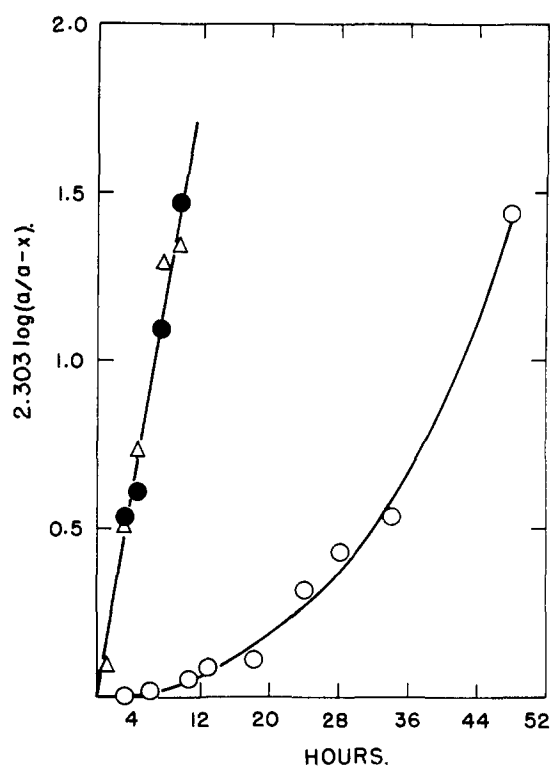
(8) J. K. Kochi, ibid., 77, 5274 (1955).

Fig. 3.—First-order plot of rate of hydrolysis of p-methoxydiphenyl-iodonium tosylate in the presence of Cu^{II} (2×10^{-4} M) in water at 100.1°: O, p-toluenesulfonic acid (0.186 M); △, sodium p-toluenesulfonate (0.1 M); ●, no added salt or acid; best line through points ● and △, $k_1 = 4.2 \pm 0.2 \times 10^{-5}$ sec.$^{-1}$; a is the initial concentrations of iodonium salt (0.1 M) and x is the amount reacted at the indicated times.

ments in the presence of each catalyst and observing the percentage reaction at equal times. The results are shown in Table II, and they illustrate (a) the powerful catalytic effect of cuprous copper which is not measurably diminished by added acid, and (b) the relatively weaker effect of cupric copper which is strongly suppressed by acid.

TABLE II

RELATIVE EFFECTS OF Cu^{I} AND Cu^{II} ON THE HYDROLYSIS OF 4-METHOXYDIPHENYLIODONIUM TOSYLATE[a] AT 90°

$Cu^{I,b}$ $M \times 10^3$	$Cu,^{IIc}$ $M \times 10^3$	HOTs, M	Reaction after 50 min., %
1.8	..	..	100
1.8	..	0.05	100
..	1.8	..	45
..	1.8	0.05	0.6

[a] Initial concentration, 0.1 M. [b] Cuprous solutions were prepared immediately prior to use by the reduction of cupric chloride with acetone (cf. ref. 8) followed by appropriate dilution with water. Owing to the inherent instability of cuprous copper in aqueous solution, the concentrations of Cu^{I} listed above cannot be considered accurate, and the effects produced no more than qualitative. [c] Cupric solutions were prepared as for cuprous, except the reflux period in acetone to reduce Cu^{II} to Cu^{I} was omitted.

That cuprous copper is exclusively the catalyst was demonstrated by effectively inhibiting the reaction with cuproin (2,2'-biquinoline). This reagent is a highly specific chelating agent for cuprous copper, and forms a purple-colored complex of for-

mula Cu^I (cuproin)$_2$.[9] It has been used recently to demonstrate the nature of copper catalysis in the oxidation of ascorbic acid.[10]

Solvolysis of 4-methoxydiphenyliodonium tosylate was carried out in 50% aqueous ethanol, 2×10^{-4} M in cupric chloride and 4×10^{-4} M in cuproin. A control reaction was conducted simultaneously in which all reaction conditions were identical except that cuproin was omitted. The control solvolyzed at a smooth first-order rate, but reaction in the presence of cuproin was almost completely suppressed. These results are shown graphically in Fig. 4. The effect of cuproin identifies
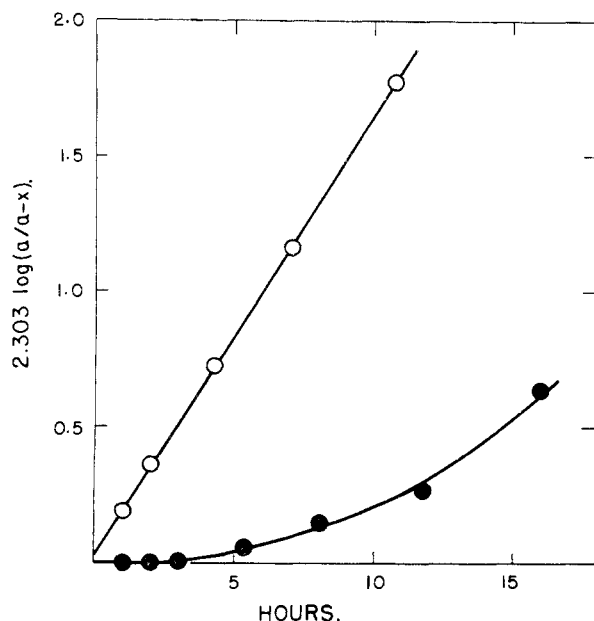

Fig. 4.—Effect of cuproin $(4 \times 10^{-4} M)$ on the first-order rate of solvolysis of 4-methoxydiphenyliodonium tosylate in the presence of Cu^{II} $(2 \times 10^{-4} M)$ in 50% aqueous ethanol at 100.1°: O, control, $k_1 = 4.51 \pm 0.04 \times 10^{-5}$ sec.$^{-1}$; ●, cuproin; a is the initial concentration of iodonium salt $(5 \times 10^{-2} M)$, x is the amount reacted at the indicated times.

cuprous copper as the catalyst. As Cu^I forms, it is removed from the sphere of reaction as the cuprous–cuproin complex, and solvolysis is thereby inhibited.

The reduction $Cu^{II}–Cu^{I}$ [11] is not instantaneous since the purple color of the complex appeared only gradually and intensified perceptibly over a period of several hours. Cupric copper cannot then have any catalytic effect, since, if it had, the solvolysis would have proceeded at a finite but decreasing rate from the start of reaction.

After several hours at 100°, the inhibiting effect of cuproin appeared to diminish, and the rate of solvolysis gradually increased. This is undoubtedly due to dissociation of the cuproin com-

(9) J. Hoste, *Anal. Chim. Acta*, **4**, 23 (1950).

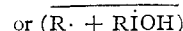(10) R. Flitman and E. Frieden, THIS JOURNAL, **79**, 5198 (1957).
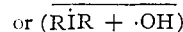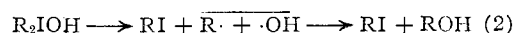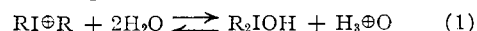
(11) This reduction was observed to take place slowly in 50% aqueous ethanol at 100° in the absence of iodonium salt. Careful purification of the ethanol did not eliminate the reduction, but this does not invalidate any of the arguments presented here. It was necessary to employ aqueous ethanol as the solvent owing to the limited solubility of cuproin in water.

plex as acid is produced by uncatalyzed solvolysis, and the stability of the complex is known to decrease at a pH less than 4.4.[12] Moreover, it was observed that if cuproin is added after 50% solvolysis has taken place (pH $\sim$1.4), the rate is very little suppressed.

Summary and Conclusions.—We summarize the experimental findings as: (1) The direction of bond fission in the hydrolysis of unsymmetrical iodonium salts is little influenced by the polar nature of the substituents present. (2) The product distribution remains unchanged on varying the anion associated with a given iodonium cation or the nature of the aqueous organic solvent. The latter is particularly noteworthy in the case of aqueous dioxane. In this solvent hydrolysis is catalyzed as the result of oxygen- or peroxide-induced decomposition of dioxane, and yet the product distribution remains essentially unchanged. (3) Hydrolysis is catalyzed by micromolar amounts of cupric or cuprous copper. Cupric copper is not in itself an effective catalyst, but becomes so by reduction to the cuprous state. This reduction is retarded by oxygen and acid. The iodonium salt may act as the reducing agent, but the oxidation product has not been identified. Again, no substantial change in the product distribution is effected during copper-catalyzed hydrolysis. (4) The uncatalyzed reaction in water is retarded by acid as it is formed, and by acid when initially added.

These results are not consistent with a mechanism of hydrolysis which involves heterolytic fission of the carbon–iodine bond, either by an S_N1 or S_N2 process. It is more likely that homolytic fission occurs; the literature records several instances of radical decomposition of diaryliodonium salts.[13]

A possible mechanism for uncatalyzed hydrolysis which satisfactorily accounts for retardation by acid and the lack of substituent effects is given by eq. 1 and 2 (in which possible pairs of geminate radicals are designated with a superscript bar).

$$RI^{\oplus}R + 2H_2O \rightleftarrows R_2IOH + H_3^{\oplus}O \qquad (1)$$

$$R_2IOH \longrightarrow \overline{RI + R \cdot + \cdot OH} \longrightarrow RI + ROH \quad (2)$$

$$\text{or } \overline{(RIR + \cdot OH)}$$

$$\text{or } \overline{(R \cdot + RIOH)}$$

The first step, eq. 1, is represented as the equilibrium formation of an unstable covalent iodonium hydroxide, R_2IOH. Such hydroxy compounds have never been isolated, but undissociated diphenyliodonium hydroxide has been suggested as an intermediate in the non-ionic decomposition of diphenyliodonium chloride in aqueous sodium hydroxide with pyridine.[13c] Certain triaryliodine compounds are known,[14] and they readily decom-

(12) R. J. Guest, *Anal. Chem.*, **25**, 1484 (1953).

(13) (a) R. B. Sandin, F. T. McClure and F. Irwin, THIS JOURNAL, **61**, 2944 (1939); (b) R. B. Sandin, R. G. Christiansen, R. K. Brown and S. Kirkwood, *ibid.*, **69**, 1550 (1947); (c) R. B. Sandin and R. K. Brown, *ibid.*, **69**, 2253 (1947); (d) L. G. Markarova and A. N. Nesmeyanov, *Bull. Acad. Sci. U.S.S.R., Classe, Sci. chim.*, 617 (626 in English) (1945); C. A., **40**, 4686 (1946); (e) F. M. Beringer, P. Forgione, M. Winicov and M. D. Yudis, Abstracts of Papers, A.C.S. Meeting, September, 1957, p. 36-P.

(14) (a) G. Wittig and K. Clauss, *Ann.*, **578**, 136 (1952); (b) K. Clauss, *Chem. Ber.*, **88**, 268 (1955).

pose. By analogy, the decomposition of R_2IOH, eq. 2, may give hydrolytic products through intermediate formation of aryl and arylhydroxyiodine ($R\dot{I}OH$), or diaryliodine ($R\dot{I}R$) and hydroxyl radicals. None of these radicals can have more than a transitory existence before coupling to give the final products because no products were detected which would normally arise from free radicals by dimerization or hydrogen abstraction. In effect, then, these are radical reactions with a chain length of one.

Cuprous-catalyzed hydrolysis may take place by a similar mechanism, as shown in eq. 3 and 4.

$$RI \oplus R + Cu^I \longrightarrow \overline{R\dot{I}R} + Cu^{II} \qquad (3)$$

$$\overline{R\dot{I}R} + Cu^{II} + 2H_2O \longrightarrow RI +$$
$$ROH + Cu^I + H_3O\oplus \qquad (4)$$
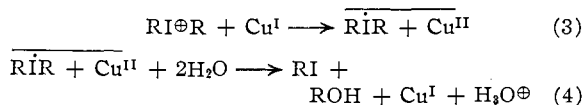
Cuprous ions function to effect an electron transfer to iodine, eq. 3. The diaryliodine, $R\dot{I}R$, may then collapse to give products by a further series of one-electron transfers, eq. 4.[15] This step might be illustrated in more detail as

However, the sequence in time of each electron transfer is a matter of pure speculation.

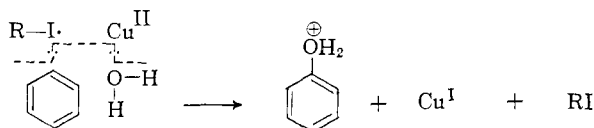**Acknowledgment.**—We are indebted to the John Simon Guggenheim Foundation for support of part of this research. D. L. G. is indebted to the National Science Foundation for a post-doctoral fellowship.

Experimental

Iodoso Compounds.—Chlorination of iodobenzene and m-iodotoluene gave pure iodobenzene dichloride[16a] and m-iodotoluene dichloride, respectively, in 89–95% yields. Iodosobenzene[16b] and m-iodosotoluene were prepared by basic hydrolysis of the corresponding dichlorides[16a] in 54–64% and 64–67% yields, respectively.

m-Nitroiodosobenzene,[17] was prepared in 58% yield by the action of iodyl sulfate on nitrobenzene in cold concentrated sulfuric acid.

4-Methoxydiphenyliodonium Salts.—The bromide was prepared from iodosobenzene[16b] and anisole by the method of Beringer and co-workers.[17b]

A mixture of 15.0 g. (38.4 mmoles) of the bromide and 10.0 g. (44.3 mmoles) of silver oxide in 200 ml. of water was shaken for 3 hr. at room temperature. The solution was filtered and neutralized with 1 N p-toluenesulfonic acid. The water was removed in vacuo at 40–50° and the residue of **4-methoxydiphenyliodonium tosylate** (18.5 g.) was recrystallized from a mixture of ethanol, acetone and ligroin (60–70°) to yield 15.7 g. (85%), m.p. 145–151° dec.

Anal. Calcd. for $C_{20}H_{19}ISO_4$: C, 49.80; H, 3.97; S, 6.65; I, 26.31. Found: C, 49.64; H, 3.82; S, 6.66; I, 26.29.

(15) It is noteworthy that the photochemical oxidation of benzene in aqueous solution to give phenol is markedly assisted by cupric ions and the phenol-forming step has been formulated as Ar· + Cu^{II} + H$_2$O → ArOH + Cu^I + H$\oplus$. See J. H. Baxendale and J. Magee, *Trans. Faraday Soc.*, **51**, 205 (1955).

(16) (a) H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **22**, 69 (1942); (b) H. J. Lucas, E. R. Kennedy and M. W. Formo, *ibid.*, **22**, 70 (1942).

(17) (a) I. Masson and W. E. Hanby, *J. Chem. Soc.*, 1699 (1938); (b) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

By a similar procedure **4-methoxydiphenyliodonium trifluoroacetate** was prepared. A solution of the iodonium hydroxide was neutralized with a 10% solution of trifluoroacetic acid, and the water removed in vacuo at 40–50°. The residue was recrystallized from benzene to give 10.9 g. (67%), m.p. 158–162° dec.

Anal. Calcd. for $C_{15}H_{12}IF_3O_3$: C, 42.47; H, 2.85; I, 29.92. Found: C, 42.58; H, 2.92; I, 29.80.

Neutralization of the iodonium base with fluoroboric acid and evaporation to dryness in vacuo at 40–50° gave colorless crystalline **4-methoxydiphenyliodonium fluoroborate**, m.p. 91–94° dec. This salt could not be recrystallized satisfactorily owing to its thermal instability, but repeated washing with ether removed much soluble impurity.

Anal. Calcd. for $C_{13}H_{12}BIF_4O$: C, 39.23; H, 3.03. Found: C, 38.84; H, 3.02.

Dilute hydrofluoric acid in place of fluoroboric acid gave **4-methoxydiphenyliodonium fluoride**, m.p. 95–97° dec. This salt is hygroscopic and thermally unstable. It was recrystallized from acetone by allowing a saturated solution (prepared at room temperature) to stand at 0° for several days. No elemental analysis for this salt was obtained owing to its hygroscopic, unstable nature.

3-Methyldiphenyliodonium Salts.—The bromide was prepared essentially by the method of Beringer and co-workers.[17b] To a cold, stirred solution of 10.6 g. (45.3 mmoles) of m-iodosotoluene, 40 ml. of benzene, 25 ml. of acetic anhydride and 130 ml of glacial acetic acid, there was added dropwise 10 ml. of concentrated sulfuric acid. Stirring was continued for 9 hr. (negative starch–iodide test). The solution was diluted with 200 ml. of water and extracted twice with 100-ml. portions of ether to remove excess benzene. Addition of 25 g. of sodium bromide in 100 ml. of water to the aqueous extract precipitated 3-methyldiphenyliodonium bromide, 11.2 g. (66%), m.p. 173–174° dec. The crude salt was recrystallized from boiling water (Norite) to give 7.0 g. (41%), m.p. 182.5–183.5° dec.

A mixture of 7.0 g. (18.7 mmoles) of the bromide and 5.0 g. (21.6 mmoles) of silver oxide in 90 ml. of water was shaken for 40 min. The mixture was filtered and neutralized with 20% p-toluenesulfonic acid. On cooling, white crystals of **3-methyldiphenyliodonium tosylate** separated, 7.0 g. (80%), m.p. 175–180° dec. The salt was recrystallized from a mixture of ethanol and acetone to give material of m.p. 169–170° dec.

Anal. Calcd. for $C_{20}H_{19}SIO_3$: C, 51.51; H, 4.11; S, 6.88; I, 27.21. Found: C, 51.74; H, 4.13; S, 6.80; I, 27.46.

3-Nitro-4'-methoxydiphenyliodonium Salts.—To a cold, stirred solution of 23.5 g. (88.0 mmoles) of m-nitroiodosobenzene, 10 ml. of anisole, 600 ml. of acetic acid and 50 ml. of acetic anhydride, there was added dropwise 7 ml. of concentrated sulfuric acid. After 15 min. (negative starch–iodide test), a solution of 25 g. of sodium bromide in 100 ml. of water was added, with stirring. The gelatinous precipitate of **3-nitro-4'-methoxydiphenyliodonium bromide** which formed was filtered and washed repeatedly with water until free of acid, to give 36 g. (94%) m.p. 163–166° dec. The salt was recrystallized from boiling water, treated with Norite, which gave material of m.p. 174–175° dec.

Anal. Calcd. for $C_{13}H_{11}NIBrO_3$: C, 35.81; H, 2.54; N, 3.21; (Br + I), 47.4. Found: C, 35.76; H, 2.62; N, 3.25; (Br + I), 48.9.

To a suspension of 10.0 g. (23 mmoles) of the bromide in 400 ml. of boiling water there was added 5.0 g. (22 mmoles) of silver oxide and 8.0 g. (46 mmoles) of p-toluenesulfonic acid. Immediately, silver bromide precipitated. The hot solution was stirred vigorously for one min., filtered, and the **3-nitro-4'-methoxydiphenyliodonium tosylate** allowed to crystallize. A further recrystallization from boiling water (Norite) gave 8.5 g. (72%) of the tosylate, m.p. 175–180°.

Anal. Calcd. for $C_{20}H_{18}NSIO_6$: C, 45.55; H, 3.44. Found: C, 45.34; H, 3.60.

3-Nitrodiphenyliodonium Salts.—The bromide was prepared from m-nitroiodosobenzene dibisulfate[17a] in sulfuric acid and benzene, according to the procedure described by Beringer and co-workers.[17b]

To 10 g. (24.6 mmoles) of the bromide there was added an equivalent of silver fluoride (prepared by dissolving 2.86 g. (12.3 mmoles) of silver oxide in 5% hydrofluoric acid). The mixture was filtered, treated with Norite, refiltered, and

evaporated to dryness *in vacuo* to yield 6.0 g. (71%) of crude 3-nitrodiphenyliodonium fluoride. This was recrystallized from a mixture of alcohol and ether to give a microcrystalline product, m.p. 120–124° dec. A product of greater purity was obtained by shaking the bromide in aqueous suspension with excess silver oxide for 1–2 hr., followed by filtration and neutralization with 5% hydrofluoric acid. Evaporation to dryness *in vacuo* gave material of m.p. 143–146° dec.

3-Nitro-4'-methoxydiphenyl Ether.—A solution of 1.0 g. of *p*-methoxyphenol in 50 ml. of 0.1 *M* sodium hydroxide was shaken with 1.95 g. (3.80 mmoles) of 3-nitro-4'-methoxydiphenyliodonium tosylate. The oil which formed was extracted with methylene chloride, and shaken with 5% sodium hydroxide and with water. The solvent was evaporated and the residue flash distilled at 1 mm. The fraction collected below 100° was identified as *p*-iodoanisole, 0.74 g. (83%). Above 150°, a yellow oil distilled which solidified on cooling. Recrystallization from aqueous methanol gave 0.53 g. (57%) of 3-nitro-4'-methoxydiphenyl ether, m.p. 73–74°.

Anal. Calcd. for $C_{13}H_{11}NO_4$: C, 63.67; H, 4.52; N, 5.71. Found: C, 63.81; H, 4.61; N, 5.56.

3,3'-Dinitrodiphenyl Ether.—A solution of 1.0 g. of *m*-nitrophenol in 50 ml. of 0.1 *M* sodium hydroxide was shaken with 2.0 g. (3.9 mmoles) of 3-nitro-4'-methoxydiphenyliodonium tosylate. The oil which formed was extracted as described in the preparation of 3-nitro-4'-methoxydiphenyl ether. Distillation at 1 mm. gave 0.85 g. (93%) of *p*-iodoanisole, and at 150–200° there distilled an oil which crystallyzed at room temperature. Recrystallization from aqueous ethanol gave pale yellow needles of 3,3'-dinitrodiphenyl ether, 0.54 g. (50%), m.p. 124–125°.

Anal. Calcd. for $C_{12}H_8N_2O_5$: C, 55.49; H, 3.09; N, 10.77. Found: C, 55.60; H, 3.16; N, 10.71.

Isolation of Products from Hydrolysis.—The products were extracted continuously from aqueous solution with ether. Unreacted iodonium salt was precipitated from aqueous solution as the bromide. Phenols were separated from neutral products by shaking the ether extracts with 5% sodium hydroxide solution. The basic extracts were acidified and continuously extracted with ether. In initial runs, the ether was evaporated and the products in the residue

were separated by fractionation through a Holzmann column and identified as the pure compounds. In subsequent runs, the products were flash distilled at 1 mm., and the composition of the distillate was determined by means of infrared analysis. The ether extracts of neutral products were worked up in the same way as the acidic extracts; the products were similarly identified by separation into the pure compounds and the composition was determined by infrared analysis. In the case of 3-methyldiphenyliodonium tosylate the composition of the neutral products was found by the method of refractive indices. In the hydrolysis of 3-nitrodiphenyliodonium fluoride and 3-nitro-4'-methoxydiphenyliodonium tosylate, the phenols were not equimolar with the iodo compounds. Additional high boiling neutral products were observed which were identified from their infrared spectra as diaryl ethers. Hydrolysis in the presence of fluoroboric or *p*-toluenesulfonic acids considerably reduced the amount of ether formation. The ethers from the hydrolysis of 3-nitro-4'-methoxydiphenyl iodonium tosylate were identified as 3-nitro-4'-methoxy- and 3,3'-dinitrodiphenyl ethers.

Kinetic Experiments.—The water employed in the kinetic runs was doubly-distilled. The dioxane was purified according to Fieser[18]; 95% ethanol was fractionally distilled before use. Reagent grade chemicals, *p*-toluenesulfonic acid, cupric chloride and cuproin were used without further purification. Aqueous solvents were prepared by mixing equal volumes of water and the organic solvent (dioxane or ethanol) at 25°. Sodium *p*-toluenesulfonate solutions were prepared by neutralization of standard *p*-toluenesulfonic acid with standard sodium hydroxide, and then dilution to the required volume.

Ten-milliliter portions of a standard iodonium salt solution were sealed in Pyrex test-tubes and immersed in an oil-bath maintained at $100.1 \pm 0.05°$. Tubes were withdrawn at various intervals and cooled. The contents were titrated with 0.1 *N* sodium hydroxide from a 10-ml. microburet using brom cresol green–methyl red indicator.[19]

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PASADENA, CALIF.

Diaryliodonium Salts. IX. The Synthesis of Substituted Diphenyliodonium Salts[1]

BY F. MARSHALL BERINGER, ROBERT A. FALK, MARILYN KARNIOL, IRVING LILLIEN, GIULIO MASULLO, MARVIN MAUSNER AND ERWIN SOMMER

This paper reports the synthesis of numerous diphenyliodonium salts bearing nitro, halogeno, methanesulfonyl, carboxyl alkyl, cycloalkyl, acetoxyl, acetamido, succinimido and methoxyl substituents.

The first paper[2] of this series surveyed the synthesis of diphenyliodonium salts and reported improved methods. These methods have been used and extended in the present work to prepare diphenyliodonium salts bearing nitro,[3] halogeno,[4–7] methanesulfonyl, carboxyl, alkyl,[8–12] cycloalkyl acetoxy, acetamido,[13,14] succinimido and methoxy[15,16] substituents. The methods are listed below and then discussed in connection with the experimental results.

(A) Coupling of two aromatic compounds with iodyl sulfate in sulfuric acid (Table I)

(1) This paper is taken from the Ph.D. dissertations of Robert A. Falk, Irving Lillien and Marvin Mausner and from the M.S. theses of Marilyn Karniol, Giulio Masullo and Erwin Sommer; see also Acknowledgments. Irving Lillien was an Alfred P. Sloan Foundation Fellow, 1956–1959.

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