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The Decomposition of Iodonium Compounds. Reaction with Pyridine

BY REUBEN B. SANDIN AND ROBERT K. BROWN

In a previous communication from this Laboratory[1] it was suggested that the decomposition of iodonium salts might to some extent at least, be a non-ionic one and might proceed through the intermediate formation of free radicals. The assumption was made that in the iodonium salt the central iodine was able, by expanding its valence shell, to act as an acceptor for the chloride or sulfide ion and so form a covalent bond. Subsequent transformations of this complex would then result from a tendency of the central atom to revert to an octet. Working on this assumption, the decomposition of some iodonium salts was carried out in the presence of mercury, tellurium and antimony. In all cases, reactions occurred which suggested the formation of free radicals. In the present paper this work has been continued and an attempt has been made to accumulate more evidence in favor of a possible free radical mechanism for certain iodonium salt decompositions.

In a large number of reactions in which it seems certain that free phenyl radicals are produced in solution, it has been shown that the radicals react with the solvent and never with each other.[2] For that reason a great variety of solvents such as benzene, nitrobenzene, methyl benzoate, thiophene and pyridine have been used in connection with the diazo and nitrosoacetylamine reactions for the preparation of biaryls. Haworth, Heilbron and Hey[3] for example, have prepared arylpyridines by the addition of an aqueous solution of a diazonium salt to an excess of pyridine at temperatures varying from 20 to 70°. Available evidence favors a free radical mechanism, since all three isomeric arylpyridines are produced. This indicates that the normal directive influences of the pyridine nucleus are not in operation.

The authors of the present paper have carried out the decomposition of diphenyliodonium chloride in the presence of pyridine and sodium hydroxide solution. When pyridine was added to a boiling aqueous solution of the iodonium salt there was no indication of any appreciable decomposition. However, when sodium hydroxide was added there was a vigorous reaction which was always indicated by the rapid formation of an almost black color. The reaction mixture afforded α-, β- and γ-phenylpyridines which were separated by fractional crystallization of their picrates from acetone and alcohol. It appears probable that the active agent is diphenyliodonium hydroxide and that the underlying mechanism is

$$(C_6H_5)_2\overset{+}{I}\overset{-}{O}H \longrightarrow (C_6H_5)_2I{-}OH$$

$$(C_6H_5)_2I{-}OH \longrightarrow C_6H_5I + C_6H_5\cdot + \cdot OH$$

$$C_6H_5\cdot + \text{pyridine} \longrightarrow \alpha\text{-, }\beta\text{- and }\gamma\text{-pyridine}$$

In this connection it is interesting to point out that Masson and Race[4] have called attention to the fact that bis-(*p*-chlorophenyl)-iodonium hydrogen sulfate can exist as an oily form and is partly soluble in chloroform, in which it undergoes decomposition to some extent, producing the aromatic iodo compound. Masson and Race have made the observation that it "points to marked polarizability of the anion by the cation. This interpretation is in no way inconsistent . . . with the evidence from X-rays, by which Medlin showed that the distance between the two iodine atoms in the crystals (of diphenyliodonium iodide) is compatible with an ionic structure, not with a covalent link." Also they remark that "it seems clear that any strong interionic polarization, the effects of which are to induce, as has been mentioned, properties tending toward those of covalent compounds must play an important part in in-

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(1) Sandin, McClure and Irwin, THIS JOURNAL, **61**, 2944 (1939).

(2) For excellent reviews see: Hey and Waters, *Chem. Rev.*, **21**, 169 (1937); Hey, *Ann. Repts.*, **37**, 278 (1940). An excellent review of the preparation of unsymmetrical biaryls has been published by Bachmann and Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., pp. 224–261.

(3) Haworth, Heilbron and Hey, *J. Chem. Soc.*, 349 (1940).

(4) Masson and Race, *ibid.*, 1718 (1937).

itiating the wholly irreversible fission which all iodonium salts undergo when they are heated."

The present authors wish to point out that their work in no way contradicts the ionic mechanism which the careful work of Lucas and co-workers[5] has shown to be the case in the decomposition of di-*o*-tolyliodonium iodide. The authors also believe that their work is not at variance with the fact that the iodine–iodine bond in diphenyliodonium iodide is an ionic, not a covalent, bond.[6]

Experimental

Materials.—Diphenyliodonium chloride was prepared readily by a standard procedure[5,7] and was purified by crystallization from water. It was shown to be pure by analysis. "Eastman" grade pyridine obtained from the Eastman Kodak Co. was used. For purposes of characterization, the known picrates of α- and β- and γ-phenylpyridine were made by the procedure of Haworth, Heilbron and Hey.[3]

Reaction with Pyridine.—Diphenyliodonium chloride (25 g.) was dissolved in 300 ml. of boiling water. To this was added 200 ml. of pyridine and the mixture was refluxed for one hour. A slight coloration was produced but there was no evidence of any appreciable reaction. The solution was cooled and sodium hydroxide (32 g.) was added. A separation of two layers occurred and the top organic layer became almost black. After refluxing for one hour the mixture was steam distilled until 6 liters of distillate had been collected. A considerable amount of tar remained in the distilling flask. The distillate was extracted with benzene, the benzene solution was washed repeatedly with water and then dried over anhydrous sodium sulfate. After removal of the benzene the residue which consisted of the isomeric phenylpyridines and phenyl iodide was taken up in 75 ml. of boiling alcohol. To the hot solution was added picric acid (1 g.) dissolved in 10 ml. of boiling alcohol. On cooling the pure picrate of γ-phenylpyridine separated as orange needles; m. p. 195–196°. A mixed melting point with an authentic specimen of the γ-phenylpyridine picrate prepared by the method of Haworth, *et al.*, showed no depression. Enough picric acid was now added to the alcohol solution to precipitate all of the phenylpyridine. In this way there was isolated a total yield of 6 g. of combined α-, β- and γ-phenylpyridine picrates. By fractional crystallization from acetone and alcohol there was obtained 1.5 g. of γ-phenylpyridine picrate, m. p. 195–196°; 0.8 g. of β-phenylpyridine picrate, silky, yellow needles, m. p. 161–162°; and 1.2 g. of α-phenylpyridine picrate, yellow, rhombic prisms, m. p. 175–176°. These picrates showed no depression of the melting points when mixed with authentic specimens. Also, since pyridine picrate (m. p. 165–166°) might be an impurity, an equal-part mixture of it and the picrate of β-phenylpyridine was made. In this case there was a very marked depression of the melting point. When the picrate of γ-phenylpyridine was treated with cold dilute sodium hydroxide, γ-phenylpyridine separated and solidified, m. p. 75–76°.

A considerable amount of phenyl iodide was obtained from the original reaction mixture. However, no phenyl chloride or phenol could be detected.

Summary

The decomposition of diphenyliodonium chloride in the presence of pyridine and sodium hydroxide solution has afforded a mixture of α-, β- and γ-phenylpyridine. A free radical mechanism has been suggested.

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[5] Lucas, Kennedy and Wilmot, THIS JOURNAL, **58**, 157 (1936).

[6] (a) Juliusburger, Topley and Weiss, *J. Chem. Soc.*, 1295 (1935); (b) Medlin, THIS JOURNAL, **57**, 1026 (1935).

[7] Lucas and Kennedy, "Organic Syntheses," Vol. XXII, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 52.

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The Rates of Dissociation of Some Tetraphenylxylylethanes

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The hydrocarbon 1,2,9,10-tetramethylanthracene has been synthesized[3] and has been found to be very sensitive to air. It becomes oxygenated after brief periods of storage in the solid state. It is also known that 1,2,9,10-tetramethylanthracene cannot be prepared by some of the procedures which are useful for the preparation of other similar hydrocarbons. Badger, Cook and Goulden[4] following the excellent method developed by Bachmann and Chemerda[5] succeeded in adding methyl Grignard reagent to 1,2-dimethylanthraquinone. However, they found the dimethyl ether of the resulting diol resistant to normal reductive cleavage with sodium, even after the ether had been shaken for six days with the powdered metal. It was because of these interesting properties which involve the stability of the dihydride structure of 1,2,9,10-tetramethylanthracene that the work in the present paper was carried out.

The authors have considered that a plausible explanation for the behavior of 1,2,9,10-tetramethylanthracene might be found in the steric effect of the 1,2-dimethyl group.[6] For this reason it was decided to examine the effect of the 1,2-dimethyl group and related groups on the dissociation of some pentaarylethanes. Bachmann and

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[3] Sandin, Kitchen and Fieser, THIS JOURNAL, **65**, 2018 (1943). The compound is of interest as a model of the highly active carcinogen 9,10-dimethyl-1,2-benzanthracene.

[4] Badger, Cook and Goulden, *J. Chem. Soc.*, 16 (1940).

[5] Bachmann and Chemerda, THIS JOURNAL, **60**, 1023 (1938).

[6] The possibility of describing this effect in terms of an increased tendency to form a "biradical" structure is a tempting one. For excellent discussions on biradical structure see Fieser, THIS JOURNAL, **53**, 2329 (1931); Bachmann in Gilman's "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 602-604; Branch and Calvin, "Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 333-339.