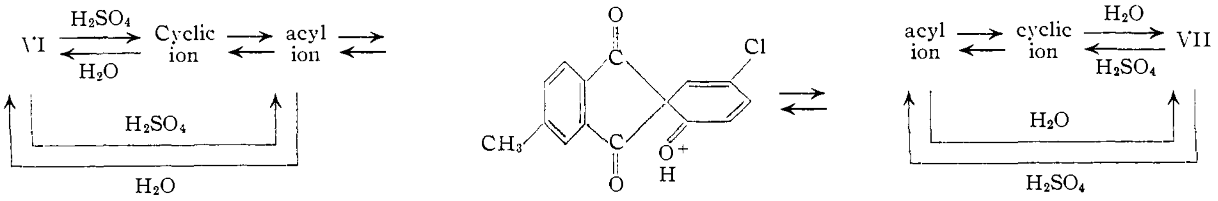
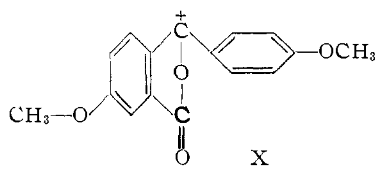


IV

(300 ml.). After refluxing for 3 hr., the reaction mixture was decomposed with 150 ml. of saturated ammonium chloride and 10 ml. of dilute hydrochloric acid. The ether-benzene solution of hydrolyzed reaction products was shaken with carbonate. The carbonate extract was acidified with acetic acid and yielded 11.5 g. of keto acid, m.p. 198–206°. After crystallization from benzene and from alcohol, it melted at 210–211°.



X

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 67.05; H, 4.90.

The keto acid was characterized by heating with basic copper carbonate for 1 hr. at 260°. This afforded the dimethoxy compound which was refluxed with 55% hydriodic acid. The demethylated material was crystallized twice from water and yielded yellow crystals of 3',4-dihydroxybenzophenone, m.p. 196–198°.

2-(4-Methoxybenzoyl)-5-methoxybenzoic Acid (IX).—The acetic acid acidified filtrate from the above keto acid was treated with hydrochloric acid. This afforded 3.5 g. of keto acid, m.p. 165–173°. The acid was crystallized from benzene and alcohol and melted at 174–175°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.1; H, 4.9. Found: C, 66.82; H, 4.96.

It was characterized by heating with basic copper carbonate which yielded 4,4'-dimethoxybenzophenone, m.p. 144–145°.

Reactions of Keto Acids with Concentrated Sulfuric Acid.—The acid (1 g.) was dissolved in concentrated sulfuric acid (6 ml.) and heated at 65° for 1 hr., at which time it was cooled and diluted with ice and water. The reaction mixture was made basic with sodium hydroxide and any cyclized material was separated. The filtrate was acidified to yield unchanged or rearranged keto acid. Under these conditions 2-benzoyl-4-methoxybenzoic acid afforded 0.8 g. of unchanged acid and 0.2 g. of 2-methoxyanthraquinone, m.p. 195°. Compound VIII (0.5 g.) in 3 ml. of concentrated sulfuric acid at 65° for 6 hr. gave 0.5 g. of IX, m.p. 170–172°, and after crystallization from dilute alcohol afforded 0.45 g. of keto acid, m.p. 173–175°.

The following acids were found not to rearrange under the above conditions: 2-benzoyl-4-hydroxybenzoic, 2-benzoyl-5-hydroxybenzoic and 2-benzoyl-5-methoxybenzoic.

Acknowledgment.—The authors wish to express their appreciation to Dr. John D. Roberts of the California Institute of Technology for his kindly interest and the excellent suggestions which he has made in connection with this work.

EDMONTON, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ALBERTA]

Synthesis of Some Cyclic Iodonium Salts

BY JOHN COLLETTE, DONALD MCGREER, ROBERT CRAWFORD, FRANCIS CHUBB AND REUBEN B. SANDIN

RECEIVED MARCH 12, 1956

The facile ring closure of the iodoso compounds from 2-iodobiphenyl, (*o*-iodophenyl)-phenylmethane, 1-(*o*-iodophenyl)-2-phenylethane and 1-(*o*-iodophenyl)-3-phenylpropane to yield the corresponding iodonium salts has been carried out.

In order to find a convenient method for the preparation of cyclic iodonium compounds such as the diphenyleneiodonium salts, which in turn might prove useful for bringing about a carbon-to-carbon ring closure, the elegant method of Beringer, Drexler, Gindler and Lumpkin[1] was investigated.

Beringer and co-workers have shown that an iodoso compound will condense with an aromatic compound in the presence of sulfuric acid to yield an iodonium salt. Unsymmetrical as well as symmetrical diaryliodonium compounds have thus been made available. According to Beringer, *et al.*, it seems likely that the reaction mechanism involves electrophilic substitution by the conjugate acid formed by the action of sulfuric acid on the iodoso compound.

Diphenyleneiodonium iodide has been made by the tetrazotization of 2,2'-diaminobiphenyl and subsequent treatment with potassium iodide.[2] Lothrop[2b] was the first to use diphenyleneiodonium iodide for the purpose of bringing about a carbon-to-carbon ring closure and so was the first to prepare the interesting hydrocarbon biphenylene. In the present work it has been found that diphenyleneiodonium salts can be made in high yield (99%) from 2-iodosobiphenyl by the reaction of Beringer, *et al.* The starting material is the available 2-aminobiphenyl (Eastman Kodak Co.) which is readily converted into 2-iodobiphenyl. The latter compound is oxidized with peracetic acid to the iodoso compound without difficulty.[3] The addition of concentrated sulfuric acid to the iodoso com-

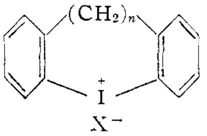
---

(1) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, THIS JOURNAL, **75**, 2705 (1953).

(2 (a) L. Mascarelli and G. Benati, *Gazz. chim. ital,* **38**, 627 (1908); (b) W. C. Lothrop, THIS JOURNAL, **63**, 1187 (1941); (c) W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954); Baker and co-workers report a 69% yield.

(3) (a) J. Böeseken and G. C. Schneider, *Proc. Acad. Sci. Amsterdam*, **33**, 827 (1930); (b) J. Böeseken and E. Wicherlink, *Rec. trav. chim.*, **55**, 930 (1936).

pound in acetic anhydride solution brings about a facile ring closure to give a high yield of the iodonium salt. In the same manner (*o*-iodosophenyl)-phenylmethane has been cyclized in high yield (95%) to the iodonium salt of structure I where n = 1.[4]



I, n = 0, 1, 2 or 3
X^- = HSO_4^-, $SO_4^-/2$, Cl^-, Br^-, I^-

Also it has been possible to bring about the ring closure of 1-(*o*-iodosophenyl)-2-phenylethane and 1-(*o*-iodosophenyl)-3-phenylpropane to the iodonium chlorides in yields of 60 and 70%, respectively, (n = 2 and 3, respectively). It is interesting that the ring closure of compound II to yield a seven-membered ring was the lowest in percentage yield. Also, the iodonium salts from compound II had the lowest melting points and the lowest decomposition temperatures.

Experimental

Iodine Compounds.—2-Iodobiphenyl was prepared without difficulty from 2-aminobiphenyl (Eastman Kodak Co.) by diazotization and subsequent treatment with potassium iodide. In a similar manner (*o*-iodophenyl)-phenylmethane (I) was prepared in 65% yield, b.p. 182° (11 mm.), from the corresponding amine.[5] 1-(*o*-Iodophenyl)-2-phenylethane (II) was prepared from the corresponding amine[6] in 50% yield, b.p. 175° at 0.5 mm.

Anal. Calcd. for $C_{14}H_{13}I$: I, 41.20. Found: I, 40.96, 40.84.

1-(*o*-Aminophenyl)-3-phenylpropane was prepared by the procedure of v. Braun and Deutsch.[7] Diazotization of the amine and treatment with potassium iodide afforded 1-(*o*-iodophenyl)-3-phenylpropane (III) in 75% yield, b.p. 210° at 2 mm.

Anal. Calcd. for $C_{15}H_{15}I$: I, 39.4. Found: I, 38.9, 38.8.

Peracetic Acid Oxidation and Cyclization.—*All preparations and reactions with organic peracids should be carried out behind a safety shield.*[8] A solution of peracetic acid was made by the slow addition of 25 ml. of 25–30% hydrogen peroxide to 100 ml. of *cold* acetic anhydride. The mixture was kept cold in an ice–water-bath until it became homogeneous, at which time the solution was allowed to stand overnight at room temperature. A solution of the iodine compound (5 g.) dissolved in acetic anhydride (10 ml.) was added to 25 ml. of the peracetic acid solution and allowed to stand at room temperature for 12 hr. The reaction mixture which now contained the iodoso compound was cooled in an ice–water-bath, and to the cold stirred solution there was added dropwise 5.0 ml. of sulfuric acid. The reaction mixture became dark and after standing for 6 hr. at room temperature was diluted with 100 ml. of cold water,[9] extracted with benzene,[10] shaken with 5 g. of activated carbon and filtered. The filtrate was saturated with sodium chloride and yielded the iodonium chloride as a white solid.

Iodonium Salts.—The solubilities of the iodonium salts decrease with increasing atomic weight of halide ion. For that reason the chloride was made, crystallized from water and a solution of the pure chloride was then treated with potassium bromide or iodide. This afforded the pure iodonium bromide or iodide. **Diphenyleneiodonium bisulfate** (n = 0) was analyzed without purification.

Anal. Calcd. for $C_{12}H_9SIO_4$: S, 8.52. Found: S, 7.55, 8.25.

When the bisulfate was crystallized from water it separated as the **sulfate**. *Anal.* Calcd. for $C_{24}H_{16}SI_2O_4$: S, 4.90. Found: S, 4.63, 4.66.

The iodonium chloride from compound I (n = 1) was crystallized from water (yield 95%), m.p. 244–245° dec. *Anal.* Calcd. for $C_{13}H_{10}ClI$: Cl, 10.80. Found: Cl, 10.80, 10.80.

The bromide melted at 222–224° dec. *Anal.* Calcd. for $C_{13}H_{10}BrI$: Br, 21.44. Found: Br, 21.35, 21.59.

The iodide melted at 184.5–185.5° dec. *Anal.* Calcd. for $C_{13}H_{10}I_2$: I^-, 30.23. Found: I^-, 30.37, 30.01.

The iodonium chloride from compound II (n = 2), yield 60%, was crystallized from water, m.p. 148–149° dec. *Anal.* Calcd. for $C_{14}H_{12}ClI$: Cl, 10.30. Found: Cl, 10.40, 10.47.

The bromide melted at 150° dec. *Anal.* Calcd. for $C_{14}H_{12}BrI$: Br, 20.67. Found: Br, 21.19.

The iodide melted at 144° dec. *Anal.* Calcd. for $C_{14}H_{12}I_2$: I^-, 29.02. Found: I^-, 29.08.

The iodonium chloride from compound III (n = 3), yield 70%, was crystallized from water, m.p. 180–181.5° dec. *Anal.* Calcd. for $C_{15}H_{14}ClI$: Cl, 9.87. Found: Cl, 9.83, 9.97.

The bromide melted at 170–175° dec. *Anal.* Calcd. for $C_{15}H_{14}BrI$: Br, 19.95. Found: Br, 19.73, 20.28.

The iodide melted at 145–150° dec. *Anal.* Calcd. for $C_{15}H_{14}I_2$: I^-, 28.34. Found: I^-, 28.09.

EDMONTON, CANADA

---

[4] The authors have no rigid proof for the cyclic monomeric structure of these salts. The analytical results seem to rule out the possibility of a linear polymer. There is the possibility of a cyclic polymeric structure. However, a molecular weight determination was carried out on the iodonium chloride from compound II (n = 2), in which a 0.500% solution of the salt in water was used. On the assumption that there is complete ionization (0.055° depression, found) a molecular weight of 339 was obtained; calcd. for $C_{14}H_{12}ClI$: mol. wt., 343.

[5] The amine was prepared by the Huang-Minlon (THIS JOURNAL, **68**, 2487 (1946)) modification of the Wolff–Kishner reduction of 2-aminobenzophenone, yield 80%, b.p. 175° at 10 mm. The acetyl derivative is reported to melt at 135° (O. Fischer and H. Schütte, *Ber.*, **26**, 3085 (1893)). Our acetyl derivative melted consistently at 128°. *Anal.* Calcd. for $C_{15}H_{15}NO$: C, 80.00; H, 6.66. Found: C, 79.96; H, 6.75.

[6] D. N. Kursanov and A. S. Kichkina, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 1342 (1935); *C. A.*, **30**, 2188 (1936).

[7] J. v. Braun and H. Deutsch, *Ber.*, **45**, 2171 (1912).

[8] For an excellent review which contains valuable information on the preparation of organic peracids and *precautions* necessary in their use, see D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

[9] At this point the iodonium salt from 2-iodobiphenyl usually precipitated as the relatively insoluble diphenyleneiodonium bisulfate.

[10] In the case of the iodonium salt from compound II, a dark tarry material separated. For that reason it was found best not to do a benzene extraction. Instead, decantation and filtration were sufficient.