Efforts toward the Synthesis of Aliphatic Iodonium Salts[1]

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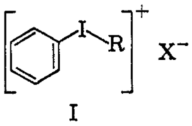
Although diaryliodonium salts have been known for almost 74 years,[2] salts in which one or both of the ligands are not aromatic are quite rare. Some years ago, Lachman tried unsuccessfully to prepare phenylethyliodonium chloride from diethylzinc and iodobenzene dichloride.[3] Neilands and coworkers have prepared some interesting iodonium betaines derived from the enolate anions of dimedone, methyl acetoacetate, 5-phenyl-1,3-cyclohexanedione, and dibenzoylmethane.[4] Recently, Beringer and Galton have synthesized some acetylenic iodonium salts by the reaction between a lithium acetylide and iodobenzene dichloride.[5]

Our incentive to synthesize iodonium salts (I) where R is not aromatic was derived from a study of the mechanism of hydrolysis of diaryliodonium salts



I

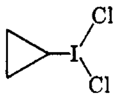
possessing weakly nucleophilic anions.[6] We report here the results of some attempts to prepare partially aliphatic iodonium salts in which the central iodine atom possesses an alicyclic group (R) of types known to be sluggish in both SN1 and SN2 reactions. It was hoped thereby to achieve a measure of kinetic stability toward nucleophilic reagents. The choices of R included cyclopropyl, 7,7-dimethyl-1-norbornyl,[7] and 9-triptycyl[7] radicals.

Two general synthetic approaches were considered: coupling between an appropriate iodoso derivative and an aromatic hydrocarbon[8] (eq 1) and coupling between an appropriate organometallic reagent and an iodo dichloride (eq 2).[9] For the first method, the requisite iodocyclopropane was obtained in 38% yield by treatment of the diacyl peroxide with iodine. A modified Hunsdiecker reaction[10] performed on apocamphane-1-carboxylic acid gave a 52% yield of 1-iodoapocamphane. A convenient synthesis of 9-iodotriptycene was achieved by means of a photochemical iodinative decarboxylation of triptoic acid.[11]

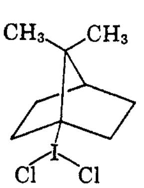
$$\begin{tikzcd}\mathrm{R{-}I} \arrow[r, "\mathrm{Cl_2}"] \arrow[rr, bend right, "\mathrm{[O]}"'] & \mathrm{R{-}ICl_2} \arrow[r, "^{-}\mathrm{OH}"] & \mathrm{R{-}IO} \arrow[r, "\mathrm{H^+, ArH}"] & \mathrm{Ar{-}\overset{+}{I}{-}R}\end{tikzcd} \quad (1)$$

$$\begin{array}{l}\mathrm{R{-}M + Ar{-}ICl_2 \longrightarrow [Ar{-}\overset{+}{I}{-}R]Cl^- + MCl} \\ \qquad\qquad\quad \text{or} \\ \mathrm{Ar{-}M + R{-}ICl_2 \longrightarrow [Ar{-}\overset{+}{I}{-}R]Cl^- + MCl}\end{array} \quad (2)$$

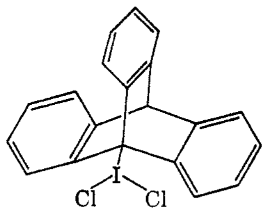
Treatment of iodocyclopropane and 1-iodoapocamphane with chlorine at low temperature gave what appeared to be the expected iodo dichlorides (II and III). These substances were much less stable than corresponding aromatic iodo dichlorides, and had to be stored below 0°.[12] It was not possible to obtain dichloride IV from 9-iodotriptycene, presumably because of steric crowding about the iodine. Dichlorides II and III reacted vigorously with cold, aqueous base[13] with formation of considerable amounts of elemental iodine, but no iodoso derivative could be isolated. Exner, who recently was able to convert a series of iodomethylsulfones to their respective dichlorides, found that these substances also did not hydrolyze to the expected iodoso derivatives.[14] The only reported nonaromatic iodoso compounds are those derived from 1,2-diiodoethylene and 1-chloro-2-iodoethylene (geometry not specified).[15] It is possible that conjugation with a double bond or with an aromatic ring is essential to the stability of the I–O bond.[2b]



II

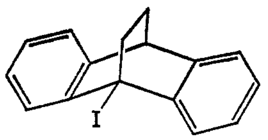


III



IV

In view of the failure of 9-iodotriptycene to add chlorine, 9,10-dihydro-9,10-ethano-9-iodoanthracene (V) was prepared in 63% yield by the modified Hunsdiecker reaction on the carboxylic acid. Treatment of V with chlorine at −25°, however, failed to produce the iodo dichloride.



V

Diaryliodonium salts may also be prepared by *in situ* oxidation of the appropriate iodide to the iodoso derivative in the presence of an aromatic hydrocarbon.[16] In the present cases, this reaction was unsuccessful. For example, starting material was recovered when oxidation was attempted on 9-iodotriptycene with either ammonium persulfate or peracetic acid as the oxidant.

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(1) Supported by the National Science Foundation.

(2) (a) See C. Hartman and V. Meyer, *Ber. Deutsch. Chem. Ges.*, **27**, 426 (1894). (b) For a recent review of organic polyvalent iodine compounds, see D. F. Banks, *Chem. Rev.*, **66**, 243 (1966).

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(4) O. Neilands and G. Vanags, *Proc. Acad. Sci., USSR*, **129**, 983 (1959); **131**, 425 (1960); **141**, 1232 (1961); O. Neilands and B. Karele, *J. Org. Chem., USSR*, **2**, 491 (1966).

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(12) Iodomethane dichloride is reported to decompose above −28°; J. Thiele and W. Peter, *Ber. Deutsch. Chem. Ges.*, **38**, 2842 (1905).

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(15) C. Willgerodt, "Die organischen Verbindungen mit mehrwertigem Jod," F. Enke Verlag, Stuttgart, Ger., 1914, pp 250–251.

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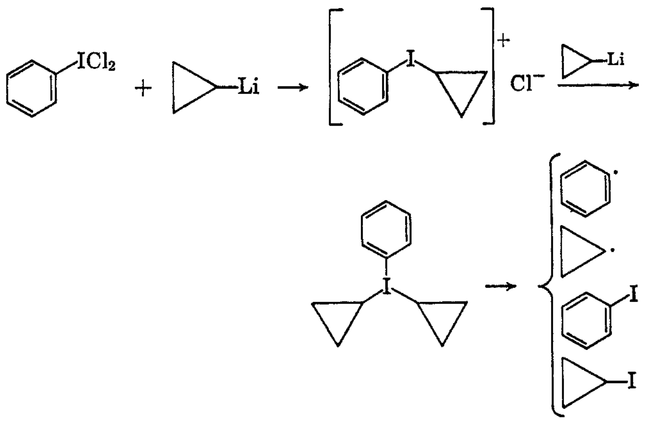
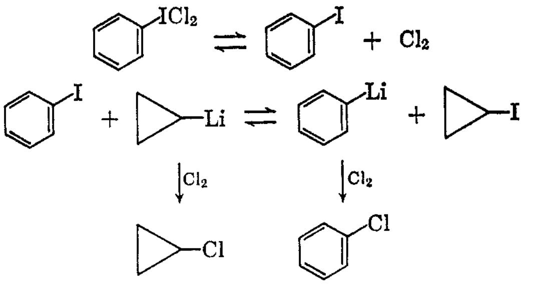
The second general method involves organolithium reagents, but when either iodocyclopropane dichloride (II) or 1-(dichloroiodo)apocamphane (III) was treated with phenyllithium in ether at −75°, or when cyclopropyllithium was similarly treated with iodobenzene dichloride, no iodonium salt could be isolated. Vapor phase chromatographic examination of the etherates generally showed that mixtures of halides were present. Thus, starting with cyclopropyllithium and iodobenzene dichloride, chlorocyclopropane, iodocyclopropane, chlorobenzene, and iodobenzene were all present. The presence of these four constituents could be taken as presumptive evidence for the transient formation of cyclopropylphenyliodonium chloride which subsequently is converted to an unstable trisubstituted iodine that decomposes to phenyl and cyclopropyl radicals.[9a]



However, none of the expected phenylcyclopropane was formed. An alternative explanation for the various products is dissociation of iodobenzene dichloride to chlorine and iodobenzene followed by a series of halogen-metal exchanges.



Addition of benzyne to 9-bromoanthracene gave 9-bromotriptycene in 30–44% yield. Triptycyllithium was then prepared at −70° in ether–benzene and treated with iodobenzene dichloride. No triptycyliodonium salt could be isolated although a small amount of diphenyliodonium salt was isolated, indicative of a halogen–metal exchange followed by coupling of two benzene moieties.

The failure to obtain either aliphatic iodoso derivatives or aliphatic iodonium salts by conventional means may reflect an inherent reactivity or thermodynamic instability of these systems that is not obvious in the aromatic series. Some other possible lines of approach such as electrochemical means,[17] a carbonium ion salt with an appropriate iodide, decomposition of a bridgehead diazonium salt in the presence of an aromatic iodide,[18] etc., were not investigated.

Experimental Section

Iodocyclopropane.—Cyclopropanecarboxylic acid was converted to the acid chloride, which was treated with a urea–hydrogen peroxide complex[19] to give dicyclopropanoyl peroxide. To a suspension of 50.8 g (0.200 mole) of powdered iodine in 20 ml of bromobenzene at 105° was added slowly a solution of 22.5 g (0.132 mole) of dicyclopropanoyl peroxide in 80 ml of bromobenzene. Gas evolution was complete after 3 hr. The mixture was then diluted with 100 ml of pentane, treated successively with sodium bisulfite and sodium carbonate solutions, and dried. Distillation through a spinning-band column gave 17.0 g (38%) of liquid: bp 97–98° (lit.[20] 92–93°); δ ($CHCl_3$) 1.0 (multiplet, 4 H), 2.3 (multiplet, 1 H).

1-Iodoapocamphane.—Camphor-10-sulfonic acid was converted in two steps to ketopinic acid.[21] The Huang-Minlon modification of Wolff-Kishner reduction of this acid proceeded in 80% yield to give apocamphane-1-carboxylic acid. A mixture of 18.3 g (0.080 mole) of red mercuric oxide and 200 ml of cyclohexane was stirred and heated under reflux while 25.9 g (0.154 mole) of apocamphane-1-carboxylic acid in 175 ml of cyclohexane was added dropwise. The apparatus was then covered with toweling and 40.0 g (0.158 mole) of iodine added over 1.5 hr. After being heated under reflux for 3.5 hr more, the suspension was filtered, the filtrate shaken successively with sodium bisulfite and 2 *M* sodium hydroxide solutions, and dried. Evaporation of the solvent gave 23.3 g of crude material which was chromatographed on neutral alumina (pentane as eluent) to give 20.0 g (52%) of white solid: mp 129–131° (lit.[11] 130–132°); ν ($CHCl_3$) 2935, 2850, 1465, 1380, 1255, 965, 905, 880 cm^{-1}; δ ($CHCl_3$) 1.0 (s, 6 H), 1.1–2.2 (complex, 9 H).

9-Iodotriptycene.—Triptoic acid was available either by the addition of benzyne to methyl 9-anthroate followed by saponification or commercially from the Eastman Co. To a stirred and refluxed suspension of 6.7 g (0.0225 mole) of triptoic acid and 30.0 g (0.0677 mole) of lead tetraacetate in 300 ml of dry benzene there was added in portions a 0.408 *M* solution of iodine in benzene. As each portion was added, the flask was irradiated with 100-w tungsten lamp. Addition was stopped when a purple color persisted (*ca.* 145 ml, 0.059 mole). After being heated under reflux for another 1.5 hr, the suspension was filtered, the filtrate washed with sodium bisulfite and sodium hydroxide solutions and water and brine, then dried. Evaporation of the solvent left 2.29 g of a solid which was sublimed to give 1.97 g (23%) of white material: mp 259–265° (lit.[22] 262–265°); ν ($CHCl_3$) 3045, 2975, 1610, 1450 (doublet), 1285, 1145, 1035, 920, 830 cm^{-1}; δ ($CDCl_3$) 5.4 (s, 1 H), 6.8–7.1 (complex, 6 H), 7.2–7.4 (complex, 3 H), 7.5–7.9 (complex, 3 H).

Anal. Calcd for $C_{20}H_{13}I$ (380.0): C, 63.16; H, 3.45; I, 33.39. Found: C, 63.29; H, 3.49; I, 33.50.

9,10-Dihydro-9,10-ethano-9-iodoanthracene (V).—The modified Hunsdiecker reaction previously described for the preparation of 1-iodoapocamphane was applied to 6.0 g (0.024 mole) of 9,10-dihydro-9,10-ethanoanthracene-9-carboxylic acid.[23] There resulted 5.0 g (63%) of white solid: mp 136–138°; ν ($CHCl_3$) 3040, 2985, 2925, 1605, 1450, 1290, 1140 (doublet), 1035, 915, 820 cm^{-1}; δ ($CDCl_3$) 1.4–1.9 and 2.1–2.5 (complex, 4 H), 4.2 (t, J = 2.6 Hz, 1 H), 6.9–7.2 (complex, 6 H), 7.5–7.8 (complex, 2 H).

Anal. Calcd for $C_{16}H_{13}I$ (332.0): C, 57.83; H, 3.95; I, 38.22. Found: C, 57.66; H, 3.97; I, 38.19.

Chlorination of 1-Iodoapocamphane.—The following procedure is illustrative of conditions used in the chlorination experiments. A solution of 13 g (0.052 mole) of 1-iodoapocamphane in 45 ml of dry chloroform was stirred and cooled to −20°. Chlorine, scrubbed by passage through two towers of concentrated sulfuric acid and passage through glass wool, was admitted for 1.5 hours.

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(23) The authors are indebted to Professor J. S. Meek for a generous sample of this acid.

The precipitated brick-orange dichloride (III) was removed by filtration and transferred quickly to a container for immediate storage in a refrigerator; the yield was 13–16 g (78–95%). At room temperature, spontaneous evolution of chlorine from the solid occurred. When a chloroform solution of the dichloride is allowed to sit exposed to the air at room temperature for a day, starting material can be recovered in good yield.

Attempted Hydrolysis of 1-(Dichloroiodo)apocamphane.—Approximately 1.2 g (3.7 mmoles) of 1-(dichloroiodo)apocamphane (III) was placed in a mortar at −5°, covered with 2 g of anhydrous sodium carbonate, and then ground with a pestle. With trituration there was added 0.5 ml of 5 M sodium hydroxide; a black paste resulted. When additional 2.5 ml of base was added, the color of the suspension changed to white. Water (20 ml) was added and grinding continued until all solid matter had gone into solution. Tests for iodide and chloride ions were positive; when the solution was extracted with ether and the ether evaporated, no residue of iodoso compound was obtained. The fate of the carbon skeleton was not pursued further.

9-Bromotriptycene.—Benzyne, generated by the method of Friedman and Logullo[24] from 3.7 g (0.026 mole) of anthranilic acid and 3.5 g (0.030 mole) of isoamyl nitrite, was added to 6.2 g (0.024 mole) of 9-bromoanthracene in 80 ml of methylene chloride. A chromatographic separation yielded 3.5 g (44%) of crude, yellow product which was recrystallized from methylcyclohexane to give nearly white crystals: mp 250–254° (lit.[25] 246–248°); ν ($CHCl_3$) 3045, 2980, 1605, 1450 (doublet), 1285, 1155, 1035, 935, 840 (doublet) cm^{-1}.

Anal. Calcd for $C_{20}H_{13}Br$ (333.0): C, 72.07; H, 3.94; Br, 23.99. Found: C, 72.30; H, 4.00; Br, 23.88.

Iodobenzene Dichloride and Triptycyllithium.—A solution of 4.00 g (12 mmole) of 9-bromotriptycene in a mixture of 95 ml of benzene and 225 ml of ether was cooled to −50°. Over a period of 0.75 hr there was added with stirring under argon 9.5 ml (15.2 mmole) of 1.6 M *n*-butyllithium in hexane. The mixture was stirred for 0.5 hr at −50°, then for 1 hr at −70° and 3.25 g (11.8 mmole) of iodobenzene dichloride was added portionwise. The resulting mixture was stirred at −70° for 10 hr and then the reaction flask was allowed to stand in a refrigerator for 2 days. A suspended white solid (0.47 g) which was removed by filtration and washed with water proved to be 9-bromotriptycene, mp 253–255°. Addition of potassium iodide solution to the above aqueous filtrate precipitated 0.1 g of diphenyliodonium iodide, mp 178°, and nmr spectrum identical with that of an authentic sample. The ethereal residue which contained chlorobenzene and iodobenzene in roughly equal amounts on evaporation gave 2.1 g of a mixture of 9-bromotriptycene and 9-iodotriptycene. No unreacted iodobenzene dichloride could be isolated.

Registry No.—1-Iodoapocamphane, 933-27-7; 9-iodotriptycene, 15364-53-1; V, 15364-54-2; 9-bromotriptycene, 15364-55-3.

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[25] P. D. Bartlett, *et al.*, *ibid.*, **72**, 1003 (1950).

The Synthesis of Chlorobenzene-d_5 in a Radiofrequency Discharge

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Studies conducted in this laboratory dealing with the reactions of halobenzenes in an electrodeless radiofrequency (RF) discharge required the use of isotopically pure chlorobenzene-d_5. This material is not available commercially and a survey of the literature failed to uncover a method for its preparation. The synthesis of bromobenzene-d_5 has, however, been reported[1,2] and this material is commercially available[3] in 99.5% isotopic purity. Hence, a method for efficiently converting bromobenzene-d_5 into chlorobenzene-d_5 would be desirable.

Walling and Miller[4] had converted bromobenzene into chlorobenzene by photolytic chlorination, and it seemed that this procedure might be suitable for the synthesis of chlorobenzene-d_5. However, the original procedure afforded low yields of chlorobenzene based on the amount of bromobenzene reacted. In an attempt to maximize the conversion of bromobenzene into chlorobenzene by this reaction, a wide range of chlorine to bromobenzene ratios were investigated in this laboratory. Repeated attempts to obtain chlorobenzene by this route afforded a maximum of 20% conversion based on the amount of bromobenzene used.

Work performed elsewhere,[5] as well as in this laboratory, has demonstrated that aromatic carbon–halogen bonds can be broken with facility in an electrodeless RF discharge. Thus, it seemed reasonable that bromobenzene might be efficiently converted to chlorobenzene if it were passed through an RF discharge in the presence of chlorine. An attempt to effect this conversion by passing an equal mole ratio of chlorine gas and bromobenzene vapor through a 28-Mc electrodeless discharge afforded an approximately 1:1 mixture of chlorobenzene and bromobenzene together with trace amounts of benzene and higher boiling materials. The recovered products represented about 87% of the bromobenzene exposed to the discharge; the remainder undergoes complex competing reactions to give polymeric products and noncondensable gases. The over-all yield of chlorobenzene, based on the amount of bromobenzene reacted, is therefore approximately 45%.

The maximum conversion to chlorobenzene seems to occur with a 1:1 mole ratio of bromobenzene to chlorine. An investigation disclosed that higher chlorine–bromobenzene ratios resulted in the formation of a greater proportion of nonrecoverable products and a sharply increased percentage of benzene in the recovered material. For example, when a 7:1 ratio of chlorine to bromobenzene was used, only 43% of the reacted bromobenzene was converted to condensable materials; the remainder reacted to form polymeric materials and noncondensable gases. The condensable product was found to be a mixture of chlorobenzene and bromobenzene, together with a substantial amount of benzene. The over-all yield of chlorobenzene, based on the amount of bromobenzene reacted, was greatly reduced. These data are summarized in Table I.

Experiments in which bromobenzene-d_5 was used and the product mixture separated by preparative gas chromatography afforded chlorobenzene which was shown to be fully deuterated by mass spectrometry. Additionally, the recovered bromobenzene and benzene were also found to be fully deuterated.

The mechanism by which the presence of excess chlorine results in the formation of increased amounts

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