test for fluoride ion.[24] This method was successful when applied to small amounts of 1-fluoronaphthalene. All of the isolated organic fractions failed to show the presence of a fluoride.

Perylene and its 3,10-quinone were isolated from attempted reaction with AgF (97%, 46%); AgF, HF (gas) (90%, 47%); and KF (97%, 50%). The figures in parentheses refer to products formed in reaction with unremoved water according to the stoichiometry of eq 1. The use of HF (gas), KF, HF (gas), KF, HF (liquid), and $(n\text{-}C_4H_9)_4NF$ failed to discharge the color of the cation radical during a 36-hr period.

Iodimetric Assay.—In a typical iodimetric analysis, 124.8 mg of $P\cdot^+ClO_4$, AgI (2.13×10^{-4} equiv) was placed in 150 ml of deaerated, dry acetonitrile and 200 mg (5.42×10^{-4} equiv) of tetra-n-butylammonium iodide was added. The purple reaction mixture *immediately* turned yellow. The reaction mixture was then titrated potentiometrically using a 0.0566 N sodium thiosulfate solution. An end point corresponding to 2.13×10^{-4} equiv of I_2 was obtained. The titrated solution was then poured into water and extracted with benzene. The benzene extract was chromatographed on silica gel giving 48 mg of perylene (89.6% of theory).

Registry No. 1, 12576-62-4; 1 perchlorate, 12576-63-5: 9, 32174-97-3; 10, 32174-98-4; 11, 32174-99-5.

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Electrophilic and Homolytic Cleavage of 5-Aryl-5H-dibenziodoles[1]

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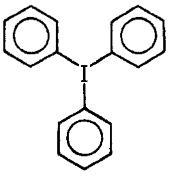
The organometallic character of triaryliodine compounds has been demonstrated by the reactivity of 5-phenyl-5H-dibenziodole toward water, protonic acids, and Lewis acids. Cleavage of 5-phenyl-5H-dibenziodole by electrophilic reagents is rapid and gives both cyclic dibenziodolium and acyclic 2-biphenylylphenyliodonium salts. The product ratio was found to be dependent on the electrophile used. Thermal decomposition and rearrangement of 5-phenyl-5H-dibenziodole have also been studied. A free-radical mechanism is suggested to account for the complexity of the products in the presence of alkyl and acyl halides. In contract, heating in hexane gives 2-iodo-o-terphenyl in good yield and suggests a molecular rearrangement. Various new 5H-dibenziodoles have been prepared with aryl groups attached to iodine: p-tolyl, m- and p-chlorophenyl, and 1-naphthyl. Cleavage of these species with ethereal hydrogen chloride has also been studied.

Since the first isolation of triphenyliodine (**1**) by Wittig[2] in 1952, little work has been reported on the relatively unstable triorganoiodine compounds. In 1955, Clauss[3] prepared from dibenziodolium iodide and phenyllithium the first triaryliodine, 5-phenyl-5H-dibenziodole (**2**) that is stable at room temperature.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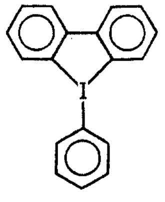
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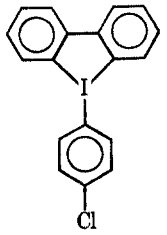
Using the method of Clauss, we have successfully prepared three previously unknown 5-aryl-5H-dibenziodoles, *i.e.*, 5-(p-chlorophenyl)-5H-dibenziodole (**3**), 5-(p-tolyl)-5H-dibenziodole (**4**), and 5-(1-naphthyl)-5H-dibenziodole (**5**), in 75–85% yield. Attempts to isolate 5-(m-chlorophenyl)-5H-dibenziodole (**6**) from the reaction mixture of dibenziodolium chloride and m-chlorophenyllithium solution were unsuccessful because of its high solubility in the reaction medium. Therefore, **6** was often used immediately without isolation for further reaction. 5-Phenyl-5H-dibenziodole was also successfully prepared by the present authors from dibenziodolium chloride and phenylmagnesium bromide in 90% yield.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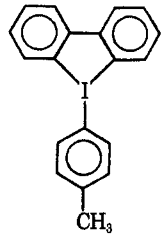
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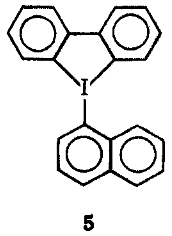
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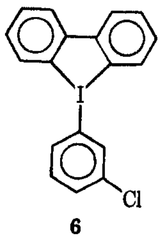
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Thermal Decomposition and Rearrangement.—It has been long known that trisubstituted organoiodine compounds on heating decompose homolytically to complex products.[4–6] When a suspension of 5-phenyl-5H-dibenziodole (**2**) in hexane was decomposed gradually at room temperature, the products were benzene, iodobenzene, biphenyl, 2-iodobiphenyl, and 2,2′-diiodobiphenyl, all in 10–15% yield, and 2-iodo-o-terphenyl in about 10% yield. At higher temperature (refluxing hexane), 2-iodo-o-terphenyl was formed as the major product (*ca.* 80%). Adapting the radical mechanism proposed previously[4,5] for the thermal cleavage of Ph_2IR[6] and Ph_2ISR, one can envision free-radical sequences initiated by homolysis to account for the complexity of the products from **2**. Path L, in-

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(1) (a) Taken from the dissertation of L. L. Chang submitted to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry), 1971. (b) Supported by National Institutes of Health, 1968–1969, through Grant No. 5-SO5-FR-07063-04.

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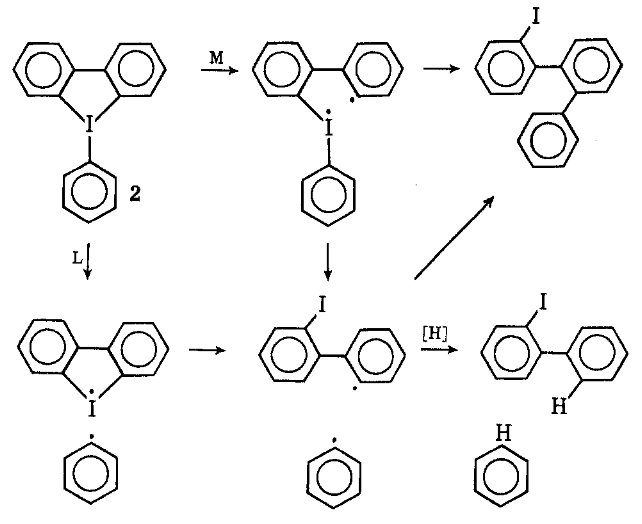
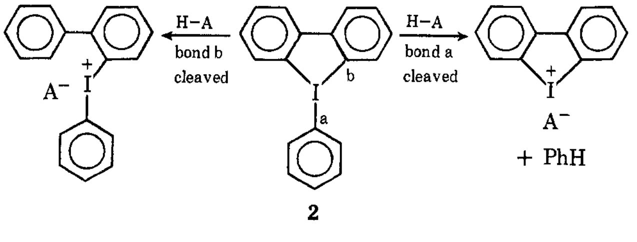


volving the cleavage of the phenyl–iodine bond, is probably the process of the lowest activation energy and is therefore favored at low temperature. Path M, involving a ring opening, seemed to compete better at high temperature with a statistical limit of 67%. However, it seems unlikely that the high yield of 2-iodo-*o*-terphenyl arises from homolysis followed by coupling; a direct migration of the phenyl group from iodine to carbon seems more likely.

Heterolytic Cleavage.—The first example[2] of the heterolytic cleavage of a triaryliodine was the regeneration of the starting diphenyliodonium salt from triphenyliodine (1) by cleavage with hydrogen chloride. Similarly, Clauss[3] reported the recovery of dibenziodolium salts from 5-phenyl-5*H*-dibenziodole (2) by cleavage with a number of electrophilic reagents. However, contrary to the findings of Clauss, we have found that the cleavage of 2 with electrophiles gave



two iodonium salts. The cyclic dibenziodolium salt from the cleavage of bond a (the phenyl–iodine bond) and the previously unknown acyclic 2-biphenylylphenyliodonium salt from the cleavage of bond b (the biphenylene–iodine bond) were both formed. A fully random cleavage of both types of bonds would give 66.7% of the cyclic salt and 33.3% of the acyclic salt.

Reaction of 2 with cold water was very slow. Only when the suspension of 2 in degassed water was heated at 60–70° under argon for 3 hr did reaction occur, giving iodonium hydroxides which contained only traces of acyclic iodonium ions. A solution of 2 in tetrahydrofuran under fully anhydrous condition was essentially inert to carbon dioxide gas.

Cleavage of 2 with protonic and Lewis acids (Table I) was fast and gave both cyclic and acyclic iodonium salt, with product distribution dependent on the acid used. The weak carboxylic acids (acetic and benzoic) reacted predominantly with the phenyl group. The stronger inorganic acids showed low selectivity in the cleavage of bonds to iodine. As for Lewis acids, the large triphenylboron cleaved the carbon–phenyl bond slowly and selectively to form dibenziodolium tetraphenylborate. At the other end of the scale, the strong electrophile aluminum chloride cleaved 5-phenyl-5*H*-dibenziodole in a completely random manner. Finally, molecular iodine cleaved both bond a and b; however, the former cleavage was favored.

Table I

Reaction[a] of 5-Phenyl-5*H*-dibenziodole with Protonic and Lewis Acids

Acid	Solvent	Reaction[b] time, hr	% of iodonium ions Cyclic[c]	Acyclic[d]	Total –I⁺– yield, %
CH_3CO_2H	THF	0.1	89.5[e]	10.5	87
$C_6H_5CO_2H$	THF	0.5	78.5[e]	21.5	98
HF	THF	0.5	79.5[e]	20.5	104
HCl	THF	0.5	50.0[e]	50.0	96
HNO_3	THF	0.5	37.0[e]	63.0	101
CH_3SO_3H	THF	0.5	42.5[e]	57.5	93
HBF_4	THF	0.5	44.6[e]	55.4	92
I_2[e]	THF	0.5	62.0[e]	38.0	94
Ph_3B	PhH	3.0	100.0	0.0	77
$AlCl_3$	PhH	0.5	31.5	68.5	80

[a] Inverse addition of a solution of 2 to the acids. [b] The reaction was completed at the end of addition of 2. However, the mixture was stirred totally for 0.5 hr before work-up. [c] Percentage of 2,2′-diiodobiphenyl based on the number of millimoles in the pyrolysate of the iodonium salt mixture. While benzene was identified as a reaction product, quantitative determination by vpc was not successful because of overlapping with solvent (THF). [d] Percentage of iodobenzene based on the number of millimoles in the pyrolysate of the iodonium salt mixture. [e] Two equivalents of iodine to 1 equiv of 2 was used.

The reaction of 5-phenyl-5*H*-dibenziodole with borane in tetrahydrofuran gave not iodonium salts but reduced products such as biphenyl and 2-iodobiphenyl.

Concerning the relative stability of the carbon–iodine bonds in the molecule of 5-phenyl-5*H*-dibenziodole, one might suggest that the iodine–phenyl bond is the most labile bond in the molecule. Bearing in mind that solid 5-phenyl-5*H*-dibenziodole is stable to around 100° while triphenyliodine decomposes at −10°, one sees that the joining of the two phenyl rings contributes some special stability to the molecule. It has also been found that the dibenziodolium ion is much less reactive than the diphenyliodonium ion.[7]

Cleavage of other 5-aryl-5*H*-dibenziodoles with hydrogen chloride in tetrahydrofuran has also been studied (Table II). Both 5-(*p*-chlorophenyl)-5*H*-dibenziodole (3) and 5-(*m*-chlorophenyl)-5*H*-dibenziodole (6) have yielded only cyclic dibenziodolium cation with benzoic acid and with hydrogen chloride. In other words, both a weak and a strong acid cleaved off the chlorophenyl group exclusively. A comparison of the results of acid cleavage of 2, 5-(*p*-tolyl)-5*H*-dibenziodole (4), and 5-(1-naphthyl)-5*H*-dibenziodole (5), has suggested that the *p*-tolyl group was cleaved with about the same ease as the phenyl group, while the 1-naphthyl group was cleaved with greater ease than a phenyl group.

The effect of substituents on the benzene nucleus in the protodemetalation of organometallic compounds has been most exhaustively explored in the group IV elements. Accumulated results have been excellently

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[7] J. Nachtigal, Ph.D. Dissertation, Polytechnic Institute of Brooklyn, 1967.

TABLE II

REACTION[a] OF 5-ARYL-5*H*-DIBENZIODOLES WITH HYDROGEN CHLORIDE IN TETRAHYDROFURAN

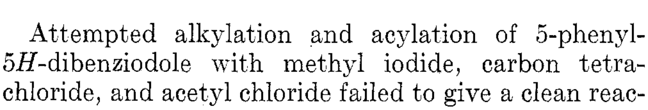
Ar	% of iodonium salts Cyclic	 Acyclic	Total $-I^{+}-$ yield, %	Other product
Ph	50	50	96	PhH (Table I)
p-ClPh	100[b]	0	85–97[c]	PhCl[d]
m-ClPh	100[e]	0	70	PhCl[f]
p-Tolyl	52[g]	48[h]	100	$PhCH_3$[i]
1-Naphthyl	76[g]	24[j]	93	Naphthalene[k]

[a] Inverse addition of triaryliodine to the acid. [b] Results from three identical experiments with hydrogen chloride and two with benzoic acid. [c] Range of the yield in five experiments. [d] The yield was 95 ± 5%. [e] Results from duplicate runs. [f] The yield was 61%. [g] Based on 2,2′-diiodobiphenyl in the pyrolysate of the mixture of iodonium iodides. [h] Based on 4-iodotoluene in the pyrolysate of the mixture of the iodonium iodides. [i] The yield was 47%. [j] Based on 1-iodonaphthalene in the pyrolysate of the mixture of iodonium iodides. [k] The yield was 67%.

organized by Dessy and Kitching,[8] Reutov and Beletskaya,[9] and MacDiarmid.[10] In general, the mechanism proposed for the cleavage of metal–carbon bonds is electrophilic attack at carbon with or without nucleophilic participation at metal; often the latter is an important factor. In the cases where nucleophile and electrophile are combined in the same molecule, a multicenter pathway is available. The effect of substituents in the aryl groups usually can be correlated with those in electrophilic aromatic substitution; *i.e.*, electron-releasing substituents increase the ease of cleavage and electron-withdrawing substituents decrease it.

However, according to Table II, a *p*-methyl group seems to exert only a slight influence on the ease of the cleavage of phenyl–iodine bonds. Most striking is the observation that both *m*- and *p*-chlorophenyl groups were cleaved exclusively. Exclusive cleavage of a *p*-chlorophenyl group from an acyclic triaryliodine has been also observed.[1]

The authors do not have any fully satisfactory rationalization of the enhancement of reactivity by *m*- or *p*-chlorine in the heterolysis of the phenyl–iodine bond by acids. The transition state might be pictured as involving a weakened carbon–iodine bond with partial charge separation. If the leaving phenyl group has a partial negative charge, a *m*- or *p*-chlorine might favor this process.



Attempted alkylation and acylation of 5-phenyl-5*H*-dibenziodole with methyl iodide, carbon tetrachloride, and acetyl chloride failed to give a clean reaction yielding alkylated or acylated product. Even though in each case a good yield (70–80%) of dibenziodolium salt was obtained, the organic phase was always a very complex mixture. With acetyl chloride, a low yield (13%) of acetophenone was detected among products derived from homolytic decomposition. With methyl iodide, the formation of toluene was either in trace amount or in question. With carbon tetrachloride, chlorobenzene and 2-chloro-2′-iodobiphenyl were identified among other products. In summary, reaction of 5-phenyl-5*H*-dibenziodole with organic halides probably went largely by a homolytic process. The small yield of acetophenone may have arisen from a competitive electrophilic attack by acetyl chloride. Similarly, reactions of diphenylmercury with an excess of acetyl or benzoyl chloride led to complex organic mixtures in which only small amounts of acetophenone or benzophenone were found.[11]

Experimental Section

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Chemalytics, Tempe, Ariz. Gas chromatography was done on 6-ft columns, packed with 20% OV-1 on 60–80 Chromosorb W with an Aerograph 1520-A gas chromatograph. Melting points were taken in capillary tubes on a Thomas–Hoover apparatus and corrected. The technique involved in taking the melting points of iodonium salts has previously been discussed.[12] All reactions involving the handling of organometallic reagent and triorganoiodine compounds were performed under argon atmosphere unless otherwise stated.

Organometallic Reagents.—*n*-Butyllithium in hexane, phenyllithium in 70:30 benzene–ether, phenylmagnesium bromide, and triphenylboron were purchased from Alfa Inorganics. *trans*-Chlorovinylmercuric chloride was prepared by the addition of mercuric chloride to acetylene.[13-16]

Concentrations of *n*-butyllithium and phenyllithium solution were frequently checked by the double titration method[17] using benzal chloride and water.

p-Tolyllithium,[4] 3-chlorophenyllithium,[18] 4-chlorophenyllithium,[19] 1-naphthyllithium,[20] *p*-dimethylaminophenyllithium,[21] and 2-lithiobiphenyl were prepared by the exchange reactions of corresponding aryl bromides or iodides with *n*-butyllithium. 2,2′-Dilithiobiphenyl[20] was prepared by the action of *n*-butyllithium on 2,2′-diiodobiphenyl, obtained in turn from the thermal decomposition of dibenziodolium iodide.[22]

Iodonium Salts.—Phenyl(*trans*-chlorovinyl)iodonium chloride[23] and dibenziodolium chloride[24] were prepared by known procedures.

5-Aryl-5*H*-dibenziodoles.—Because of their instability, 5-aryl-5*H*-dibenziodoles can be kept at room temperature even under vacuum for only a few days; decomposition is more rapid in the presence of air. Recrystallization from anhydrous tetrahydrofuran was accomplished by preparing and filtering a solution of the sample under argon at room temperature and partially removing the solvent under vacuum at Dry Ice–acetone temperature. The crystals were collected by rapid filtration under air. Analytical samples were shipped in sealed tubes, degassed, then filled with argon and covered with aluminum foil.

5-Phenyl-5*H*-dibenziodole (2).—The procedure described by Clauss[3] was modified as follows. To a suspension of 3.14 g (10

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mmol) of dibenziodolium chloride in 100 ml of anhydrous ether held at 0° under argon, 12 mmol of phenyllithium solution was added dropwise. The resulting citrus-yellow suspension was further stirred at 0° under argon for 3 hr. The yellow solid was quickly collected, washed with a small amount of ether once, with water a few times, and finally with hexane, and dried under vacuum over P_2O_5 overnight. The yield of the crude product was 3.2 g (90%).

An analytical sample was prepared by recrystallization from anhydrous tetrahydrofuran under argon. The bright yellow crystals decomposed vigorously at around 100°. Reported[3] decomposition range was 105–115°.

Anal. Calcd for $C_{18}H_{13}I$: C, 60.70; H, 3.68; I, 35.63. Found: C, 60.49; H, 3.95; I, 35.37.

This compound was also successfully prepared by treating a suspension of 3.14 g (10 mmol) of dibenziodolium chloride in anhydrous ether at 0° with 12 mmol of phenylmagnesium bromide solution. The yellow solid collected was washed first with 10 ml of anhydrous ether, then a few times with water, and finally with dilute aqueous ammonium chloride. After drying, 3.0 g (85%) of the lemon-yellow 5-phenyl-5*H*-dibenziodole, mp 105° dec, was obtained.

5-(*p*-Chlorophenyl)-5*H*-dibenziodole (3).—A suspension of 3.14 g (10 mmol) of dibenziodolium chloride was treated with 13 mmol of freshly prepared *p*-chlorophenyllithium solution. The resulting yellow solid was collected and worked up as described above to give 2.6 g (66.5%) of 5-(4-chlorophenyl)-5*H*-dibenziodole, mp 85–90° dec.

Anal. Calcd for $C_{19}H_{12}ICl$: C, 55.10; H, 3.06. Found: C, 55.37; H, 3.12.

The bright yellow color of the filtrate indicated some solubility of 5-(*p*-chlorophenyl)-5*H*-dibenziodole in benzene–ether mixture. Titration with standard hydrochloric acid, using the disappearance of the yellow color as the end point, showed that approximately 10% of the product remained in the filtrate. The crude iodonium salts weighed 0.29 g.

5-(*m*-Chlorophenyl)-5*H*-dibenziodole (6).—When the suspension of dibenziodolium chloride was treated, as above, with *m*-chlorophenyllithium solution, a bright yellow, semitransparent solution resulted. By filtration, 0.04 g (1.2%) of unreacted dibenziodolium chloride was recovered. The yellow filtrate, presumably containing the triaryliodine, was used immediately for further reactions. Reaction with hydrogen chloride etherate gave 2.2 g (7.0 mmol, 71%) of dibenziodolium chloride, mp 280° dec; its iodide decomposed at 225° to give only 2,2′-diiodobiphenyl.

5-(*p*-Tolyl)- and 5-(1-Naphthyl)-5*H*-dibenziodole (4 and 5).—These compounds were prepared in 70–80% yield as described above for compound 2 and decompose vigorously at about 100 and 90°, respectively.

Anal. Calcd for $C_{19}H_{15}I$: C, 61.62; H, 4.05; I, 34.33. Found: C, 61.95; H, 4.10; I, 34.10. Calcd for $C_{22}H_{15}I$: C, 65.02; H, 3.69; I, 31.29. Found: C, 64.96; H, 3.72; I, 31.59.

Thermal Rearrangement of 2 in Hexane.—A suspension of 3.2 g (9 mmol) of 2 in 150 ml of hexane was heated under reflux with stirring under argon for 6 hr. The bright citrus-yellow color of 2 faded completely. After a trace of insoluble material was removed by filtration, the filtrate was condensed and by vpc analysis was shown to contain iodobenzene (0.2 mmol, 2.2%), biphenyl (0.35 mmol, 3.9%), 2-iodobiphenyl (0.48 mmol, 5.7%), 2,2′-diiodobiphenyl (0.31 mmol, 3.4%), and a high-boiling material (*ca.* 80% by peak height). Purification of this high-boiling product was accomplished by chromotography of the mixture of neutral alumina with hexane and cyclohexane. The cyclohexane fraction that contained more than 95% of this material (detected by vpc) was condensed to a colorless oil which was then triturated with cyclohexane and slowly crystallized to give a white solid. The mass spectrum of this solid gave a molecular ion at 356; isotopic analysis was in good agreement with the formula $C_{18}H_{13}I$; and fragmentation was consistent with that expected of an iodoterphenyl. The melting point of 53–54° agrees with that of 2-iodo-*o*-terphenyl (lit.[25] mp 55–57°).

Anal. Calcd for $C_{18}H_{13}I$: C, 60.69; H, 3.68; I, 35.63. Found: C, 60.79; H, 3.53; I, 35.69.

Repeated attempts at synthesis of an authentic sample by the reported procedure[25] from fluorobenzene and phenyllithium were unsuccessful.

Cleavage of 5-Aryl-5*H*-dibenziodole with Electrophilic Reagents. Determination of Concentration of Triaryliodine Compounds.—Because of the instability of triaryliodine compounds in solution, their concentration was best established by dissolving a weighed amount of sample in anhydrous tetrahydrofuran and filtering through a sintered-glass funnel into a three-necked round-bottomed flask containing a weighed amount of benzoic acid in tetrahydrofuran under argon. The color of triaryliodine solution was usually immediately discharged by the acid solution. After the reaction, the excess benzoic acid was titrated with dilute standard sodium hydroxide solution. The difference between the concentrations of the starting acid and the unreacted acid gave the number of millimoles of the weighed sample of triaryliodine. Then another solution of the identical batch of the sample was prepared and allowed to react with other electrophilic reagents in the same fashion as described above.

General Reaction Procedure.—A solution of triaryliodine compound of known concentration was prepared and added dropwise with stirring and gentle cooling under argon to a solution of the electrophilic reagent. In cases where the resulting iodonium salts were insoluble in the reaction media, an appropriate solvent such as acetone, methanol, or water was added, and the reaction mixture was treated with a concentrated solution of potassium iodide. The iodonium iodides were collected, washed with dilute aqueous sodium thiosulfate, water, and ether, and dried over P_2O_5. The composition of the iodonium iodide mixture was determined as described in the following section. The filtrate was extracted a few times with ether, and the combined organic layers were washed with dilute sodium hydroxide solution, dried over $MgSO_4$, and analyzed by vpc.

In order to obtain samples of iodonium salts from the above reactions, duplicates were run. After removal of tetrahydrofuran, the mixed salts were separated by fractional recrystallization from appropriate solvents.

Analysis of the Mixture of Iodonium Salts.—On heating, iodonium iodides are known to give high yields of aryl iodides.[12,22,26,27] Therefore, the amounts of aryl iodides determined by vpc were used to calculate the composition of two-component mixtures of iodonium salts. The mixture of iodonium iodides from the reaction of triaryliodine with electrophiles was heated at decomposition temperature under argon in a round-bottomed flask equipped with a condenser. After cooling, the contents were transferred with methylene chloride into a flask, and a weighed amount of dibenzofuran was added as internal standard. The mixtures were analyzed by vpc. The area under each peak was read by a planimeter. Calibration factors were determined using standard mixtures of authentic samples with dibenzofuran, and averaged calibration factors were used to determine the weights in grams of all products obtained from the reactions.

An authentic sample of **2-biphenylylphenyliodonium iodide** was prepared by application of a newly developed synthesis.[20] To a cooled (−78°) stirred suspension of 3.01 g (10 mmol) of phenyl(*trans*-chlorovinyl)iodonium chloride, a solution of 12 mmol of 2-lithiobiphenyl was added dropwise. The lemon-yellow suspension was stirred at −78° for 2 hr and allowed to warm slowly. At −40° the bright yellow color began to fade. The mixture was further stirred at room temperature overnight. The pale yellow solid was collected, washed with ether and water, and dried to give 1.233 g of crude salt. Metathesis of the crude salt with potassium iodide gave 0.97 g (2 mmol, 20%) of 2-biphenylylphenyliodonium iodide, mp 148–149° dec. Recrystallization from ethanol gave an analytically pure sample, mp 148–149° dec.

Anal. Calcd for $C_{18}H_{10}I_2$: C, 44.64; H, 2.90; I, 52.46. Found: C, 44.29; H, 2.85; I, 52.80.

Pyrolysis of the iodide gave 1 mol of iodobenzene with 0.95 mol of 2-iodobiphenyl.

Pyrolysis of a mixture of 0.8 g (1.94 mmol) of dibenziodolium iodide and 0.1 g (0.203 mmol) of 2-biphenylylphenyliodonium iodide, after work-up and vpc analysis, gave iodobenzene (0.202 mmol, 99%), 2-iodobiphenyl (0.253 mmol), and 2,2′-diiodobiphenyl (1.8 mmol, 93%).

Reaction of 2 with Hot Water.—A suspension of 3.2 g (9 mmol) of 2 in 200 ml of degassed distilled water was heated at 65–70° under argon with stirring for 3 hr. The yellow color of 2

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gradually disappeared, giving a colorless solution. This hot, strongly basic solution was neutralized with 7.02 ml of 1 *N* hydrochloric acid (7.02 mequiv, 78% of hydroxide ion). The white precipitate that formed immediately in the hot solution was collected after the mixture was cooled to room temperature to give 2.3 g (6.75 mmol, 75%) of dibenziodolium chloride, mp 290–291° dec (lit.[24] mp 293–294° dec).

Treatment of this hot basic solution with aqueous potassium iodide solution yielded iodonium iodides which thermally decomposed to 94% of 2,2′-diiodobiphenyl, 2% of iodobenzene, and 1.7% of 2-iodobiphenyl.

Crude dibenziodolium hydroxide was obtained by cooling of the hot basic solution. It has a melting point between 165 and 220° with decomposition and its infrared spectrum showed strong, broad peaks at 3600–3200, 1700–1550, and 1450–1200 cm^{-1}, indicative of hydroxide and bicarbonate ions. The filtrate was extracted three times with 20 ml of ether. The combined organic layers were analyzed by vpc and shown to contain approximately 55% of benzene (based on **2**).

Reaction of 2 with Carbon Dioxide.—Through a bright citrus-yellow solution of 2.15 mmol of **2** in THF, which was carefully dried and freshly distilled over lithium aluminum hydride, a stream of dry carbon dioxide gas was passed with stirring. The yellow color of **2** persisted for 2 hr. Quenching of **2** with ethereal hydrogen chloride gave approximately 70% of iodonium salts.

Cleavage by Protic Acids.—A solution of 5-phenyl-5*H*-dibenziodole of known concentration in tetrahydrofuran was prepared and added immediately with stirring to a tetrahydrofuran solution of glacial acetic acid, benzoic acid, hydrofluoric acid, hydrogen chloride, nitric acid, methanesulfonic acid, or hydrofluoroboric acid. Stirring with gentle cooling was continued for a half hour except with acetic acid, where the product was worked up immediately (5 min). Analysis of product distribution were performed according to the general procedure described above.

In parallel runs, removal of the solvent gave crude iodonium salt mixtures. The following salts were obtained in pure form from the mixtures by repeated recrystallizations.

Dibenziodolium acetate (one recrystallization from water) turned dark at 185° and decomposed at 195–196° [lit.[28] 187° (darkens), mp 195.5° dec].

Anal. Calcd for $C_{14}H_{11}IO_2$: C, 49.70; H, 3.25; I, 37.57. Found: C, 49.81; H, 3.32; I, 37.29.

Dibenziodolium benzoate (two recrystallizations from water) darkens at 190° and decomposes at 198–199° (lit.[28] turns dark at 177°, mp 184° dec). This salt is soluble in organic solvents such as tetrahydrofuran and methanol and partially soluble in cold water.

Anal. Calcd for $C_{19}H_{13}IO_2$: C, 57.00; H, 3.25; I, 31.75. Found: C, 56.98; H, 3.25; I, 31.71.

Dibenziodolium fluoride (two recrystallizations from water) is very soluble in water, mp 269° dec (lit.[28] mp 166°). Because of the large discrepancy in the melting point with the reported value, the identity of this compound was carefully established by an independent synthesis from dibenziodolium chloride and silver fluoride to give, after careful recrystallization, pure dibenziodolium fluoride.[29] Samples obtained both ways have identical melting points and satisfactory elementary analysis.

Anal. Calcd for $C_{12}H_{18}IF$: C, 48.33; H, 2.69; I, 42.62; F, 6.36. Found: C, 48.67; H, 2.81; I, 42.27; F, 6.29 (from acidic cleavage of **2**); C, 48.30; H, 2.76; I, 42.31; F, 6.37 (from metathesis with AgF).

Dibenziodolium nitrate was obtained after three recrystallizations from water, mp 243.5–244° dec (lit.[28] mp 230°).

Anal. Calcd for $C_{12}H_8INO_3$: C, 42.24; H, 2.35; N, 4.11; I, 37.22. Found: C, 42.62; H, 2.35; N, 4.25; I, 36.94.

2-Biphenylylphenyliodonium fluoroborate was obtained after six recrystallizations from water as colorless, crystalline needles, mp 200–201°.

Anal. Calcd for $C_{18}H_{14}IBF_4$: C, 48.68; H, 3.15; I, 28.59; F, 17.13. Found: C, 49.00; H, 3.24; I, 28.92; F, 16.94.

Dibenziodolium fluoroborate was isolated, after condensation of the mother liquor of the recrystallizations of 2-biphenylylphenyliodonium fluoroborate, in crude form. Three recrystallizations of the crude salt from water gave crystalline needles of dibenziodolium fluoroborate, mp 247–248°.

Anal. Calcd for $C_{12}H_8IBF_4$: C, 39.35; H, 2.18; I, 34.70; F, 20.78. Found: C, 39.18; H, 2.12; I, 35.69; F, 20.45.

Another sample has also been prepared by metathesis of dibenziodolium chloride with $AgBF_4$ in 20% H_2O–80% MeOH. The infrared spectrum was identical with that of the sample prepared above.

Dibenziodolium Methanesulfonate.—The white gummy material obtained from the reaction of **2** with methanesulfonic acid was dissolved in methanol and filtered. The filtrate was condensed to give a viscous oil, which, upon standing, gave colorless crystals. Trituration with acetone of the crude crystals yielded pure dibenziodolium methanesulfonate, mp 231–232°, decomposition point 285°.

Anal. Calcd for $C_{13}H_{11}ISO_3$: I, 32.55; S, 8.56. Found: I, 32.78; S, 8.75.

Reactions with Lewis Acids. A. With Iodine.—Addition of a solution of **2** (3.08 mmol) in tetrahydrofuran to a solution of 1.58 g (6.2 mmol) of iodine in tetrahydrofuran gave a dark brown suspension, from which a brown solid was separated and stirred with dilute aqueous $Na_2S_2O_3$ for a few hours to give 0.93 g (2.33 mmol, 61.3%) of crude dibenziodolium iodide. One recrystallization from dimethylformamide gave pure iodide, mp 220° dec (lit.[22] mp 210–215°). Condensation of the filtrate to 15 ml yielded a brown residue, which was redissolved in methylene chloride. After shaking with aqueous $Na_2S_2O_3$, the methylene chloride layer was condensed slowly to 20 ml, giving pale yellow crystalline 2-iodo-2′-biphenylylphenyliodonium iodide (0.67 g, 1.1 mmol, 29%), mp 165–170° dec. Pyrolysis of this salt gave 1 equiv of iodobenzene for each 0.95 equiv of 2,2′-diiodobiphenyl. Recrystallization of the salt from hot ethanol did not raise the melting point and sometimes caused decomposition of the salt.

Anal. Calcd for $C_{18}H_{13}I_3$: C, 35.42; H, 2.15; I, 62.43. Found: C, 35.47; H, 1.97; I, 62.55.

The filtrate contained 1.54 mmol (66.6%) of iodobenzene according to vpc analysis.

B. With Triphenylboron.—After a solution of **2** (2.43 mmol) and triphenylboron (0.726 g, 3 mmol) in benzene had been stirred at room temperature for a few hours, the yellow precipitate was collected, washed with benzene, and dried to give 1.21 g (2.03 mmol, 83.7%) of dibenziodolium tetraphenylborate, mp 196–197° (lit.[3] mp 195–196°). Recrystallization from 50% aqueous DMF produced yellow, crystalline, analytically pure salt, mp 196° dec. There was no depression of melting point on admixture with an authentic sample prepared by treating dibenziodolium hydroxide solution[28] with sodium tetraphenylborate. Their infrared spectra were identical.

C. With Aluminum Chloride.—A solution of 2.7 mmol of **2** in benzene was prepared and added under argon with gentle cooling to a suspension of 0.8 g (6 mmol) of aluminum chloride in 50 ml of benzene. The light brown solution was stirred at room temperature under argon for 0.5 hr and hydrolyzed by pouring into cold dilute hydrochloric acid. The white precipitate was collected, dissolved in hot water, and treated with KI to give iodonium iodides. The aqueous layer of the filtrate was also treated with KI. The combined mixture of iodonium iodides (0.85 g) was decomposed by heating to 1.25 mmol of iodobenzene, 1.13 mmol of 2-iodobiphenyl, and 0.83 mmol of 2,2′-diiodobiphenyl. Total yield of iodonium salt was 2.08 mmol (76%), in which there were 68.5% of 2-biphenylylphenyliodonium salt and 31.5% of dibenziodolium salt. In the organic phase, 0.14 mmol of iodobenzene, 0.59 mmol of biphenyl, 0.19 mmol of 2-iodobiphenyl, and 0.05 mmol of 2,2′-diiodobiphenyl were found. The total recovery of iodine atom was 2.51 mg-atoms (93.5%).

D. With Borane.—After a solution of 2.8 mmol of **2** in tetrahydrofuran was added to 4 mmol of borane in tetrahydrofuran, the pale yellow mixture was stirred for 0.5 hr and hydrolyzed with cold dilute hydrochloric acid (gas evolution). After concentration by solvent removal, the reaction mixture was extracted a few times with ether. The aqueous layer gave no iodonium iodide when treated with KI solution. Vpc analysis of the ether layer showed iodobenzene (0.074 mmol, 2.6%), biphenyl (0.52 mmol, 18.6%), 2-iodobiphenyl (1.72 mmol, 61.5%), and 2,2′-diiodobiphenyl (0.046 mmol, 1.6%). The total recovery of iodine atom was 68% (1.9 mg-atoms)

Reactions with Acyl and Alkyl Halides. A. With Acetyl Chloride.—Pure dibenziodolium chloride (0.62 g, 1.96 mmol, 72%) was isolated from the mixture of 2.73 mmol of **2** and 4 mmol of freshly distilled acetyl chloride in benzene and stirred for 12 hrs under argon at room temperature. Infrared spectrum and thermal decomposition product of this salt were completely in accord with those of an authentic sample. The organic phase showed iodobenzene (0.30 mmol, 11%), acetophenone (0.35

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(28) L. Mascarelli, D. Gatti, E. Jona, and V. Leoncini, *Gazz. Chim. Ital.*, **59**, 867 (1929).

(29) Unpublished work by S. Messing in this laboratory.

mmol, 12.8%), biphenyl (0.6 mmol, 22.2%), 2-iodobiphenyl (0.07 mmol, 2.55%), 2,2′-diiodobiphenyl (0.5 mmol, 1.8%), 2-iodo-*o*-terphenyl (0.125 mmol, 4.25%), and small amounts of unidentified high-boiling products.

B. With Carbon Tetrachloride.—A yellow suspension of 0.86 (2.24 mmol) of 2 in 30 ml of carbon tetrachloride was stirred under Ar at room temperature in the dark for 6 hr. The white precipitate was collected, washed with carbon tetrachloride, and dried to give 0.563 g (1.8 mmol, 80%) of dibenziodolium chloride, mp 295° dec. The mother liquor was shown by peak enhancement with authentic samples to be a complex mixture of chlorobenzene, iodobenzene, benzotrichloride, biphenyl, 2-iodobiphenyl, 2-chloro-2′-iodobiphenyl, 2,2′-diiodobiphenyl, and traces of unidentified high-boiling products.

C. With Methyl Iodide.—A suspension of 1 g (2.08 mmol) of 2 in 50 ml of methyl iodide was stirred for 12 hr to yield 0.83 g (1.97 mmol, 70%) of dibenziodolium iodide, mp 220° dec. In the complex organic phase, benzene, toluene, iodobenzene, biphenyl, 2-iodobiphenyl, and 2,2′-diiodobiphenyl have been identified.

Cleavage of 5-Aryl-5*H*-dibenziodole with Hydrogen Chloride.—5-(*p*-Tolyl)-, 5-(*p*-chlorophenyl)-, 5-(*m*-chlorophenyl)-, and 5-(1-naphthyl)-5*H*-dibenziodole have been cleaved by benzoic acid and by hydrogen chloride in tetrahydrofuran. The mixtures of iodonium salts formed were all precipitated as iodides and analyzed as described previously.

Iodonium iodides obtained from 5-(*p*-tolyl)-5*H*-dibenzoidole decomposed to 4-iodotoluene (48%), 2-iodobiphenyl (45%), and 2,2′-diiodobiphenyl (52%). From 5-(1-naphthyl)-5*H*-dibenziodole, the iodides were pyrolyzed to 1-iodonaphthalene (23.8%), 2-iodobiphenyl (21.0%), and 2,2′-diiodobiphenyl (76.3%). 5-(*p*-Chlorophenyl)- and 5-(*m*-chlorophenyl)-5*H*-dibenziodole were cleaved by hydrogen chloride to form pure dibenziodolium chloride and with benzoic acid to give pure dibenziodolium benzoate.

Registry No.—2, 32174-73-5; 3, 32174-74-6; 4, 32174-75-7; 5, 32174-76-8; 6, 32174-77-9; 2-biphenylylphenyliodonium iodide, 32174-78-0; 2-biphenylylphenyliodonium fluoroborate, 32174-79-1; dibenziodolium fluoroborate, 18116-06-8; dibenziodolium methanesulfonate, 6478-21-8; 2-iodo-2′-biphenylylphenyliodonium iodide, 32174-81-5; dibenziodolium chloride, 4673-26-1; dibenziodolium iodide, 1010-76-0.

Transannular Interactions of the Silyl Center with Distant Keto Groups in the Mass Spectra of Medium-Sized Organosilicon Heterocycles. Improved Synthetic Routes to Six-, Seven-, and Eight-Membered Silicon Ring Systems

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The mass spectra of 4,4-dimethylsilacyclohexanone (I), 4,4-dimethylsilacycloheptanone (II), and 5,5-dimethylsilacyclooctanone (III) are discussed. I was prepared by a modified Dieckmann cyclization. II and III were prepared by use of a modified acyloin reaction. Significantly improved yields over previous synthetic routes were obtained.

Only a limited amount of work has been done so far on the mass spectra of functionally substituted organosilicon compounds. Significant differences from the behavior of analogous organic molecules in which silicon is replaced by carbon have been observed. These differences may arise due to strong interaction of the silyl center with electron-rich functional groups. Such interaction often leads to rearranged ions, in which the silyl center and the previously distant electron-rich functional group become directly bonded.[2,3] Two major types of rearrangements involving silyl centers have been observed. The first involves the direct transfer of an intact trimethylsilyl group from one part of the ion to another with concurrent fragmentation in a manner similar to certain types of specific hydrogen migrations frequently observed in mass spectrometry.[3,4] The second involves interaction of a siliconium ion center formed by loss of a methyl group from the quaternary silyl center with a distant electron-rich center in the molecule.[3]

We were interested in the mass spectral behavior of medium-sized organosilicon heterocyclic ketones, since it is well known that strong transannular interactions often play a dominant role in the carbonium ion chemistry of analogous medium-sized organic compounds.[5-7] We propose to discuss the mass spectra of three compounds in which transannular interaction of a silyl center with a remote keto functionality appears to play a dominant role. The compounds are 4,4-dimethylsilacyclohexanone (I),[8] 4,4-dimethylsilacycloheptanone (II),[9] and 5,5-dimethylsilacyclooctanone (III).[9]

Most of the major ions in the mass spectrum of I are probably formed by interaction of the silyl center with the carbonyl functionality. The fragmentation pattern of I is outlined in Figure 1. Metastable peaks at appropriate masses $m^* = (m_2)^2/m_1$ were observed for all fragmentation rearrangement processes discussed (see Table I).

The peak at mass 142 is the parent ion. Loss of a methyl radical from the parent leads to a siliconium ion at mass 127. Cleavage at a quaternary silyl center

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