the peroxide was extracted (throughout this and subsequent operations the solutions were *not allowed to warm to above 0°*). The aqueous solution was extracted further with pentane. The ether and pentane extracts were combined and washed with chilled dilute sulfuric acid, sodium carbonate solution, and water and dried over sodium sulfate. The pentane–ether extract was concentrated on a rotary evaporator first at aspirator pressures and then the final traces of solvent were removed on a vacuum pump. (The flask was kept chilled throughout this operation by rotating it in an ice bath.) The yield of peroxide was 90–95%.

n-**Valeryl chloride**, Eastman Kodak Co. White Label, was partially converted to the methyl ester. Gas chromatography showed less than 0.3% isomeric (isovaleryl and 2-methylbutyryl) impurities.

Isovaleryl chloride was usually contaminated with 2-methylbutyryl chloride. Eastman Kodak White Label isovaleric acid was converted to the acid chloride with thionyl chloride. Less than 0.4% isomeric impurities were present.

Phenylacetyl chloride, Trubek Laboratories, was redistilled before use.

Pivaloyl Chloride (Enjay Chemical Co.).—Pivalic acid was converted to acid chloride with thionyl chloride (>99.7% isomerically pure).

2-Methylbutyryl chloride, Eastman Kodak Co. White Label, after conversion to the methyl ester showed 1.5% isovaleryl chloride as adulterant. It was corrected for in the final analysis. The peroxide is thermally unstable neat.[47]

t-**Butylacetyl chloride** was prepared by carbonation of Grignard reagent from neopentyl chloride (Aldrich Chemical Co.), followed by thionyl chloride. Analysis of methyl ester indicated it to be greater than 99.7% pure. The melting point of peroxide[47] was 43.5–44.0°.

Cyclopropanecarbonyl chloride was prepared from cyclopropane carboxylic acid (K and K Laboratories) with thionyl chloride. The melting point of peroxide[60] was 80.0–80.5°.

Cyclopropylacetyl Chloride.—The acid was prepared[61] from ethyl vinylacetate and methylene iodide by the Simmons–Smith procedure, followed by distillation and saponification. The peroxide melted at approximately 5°.[62] It is thermally quite unstable neat.

Cyclobutanecarbonyl chloride (Kaplop Laboratories) was shown by gas chromatography of the methyl ester to be 99.5% pure. The peroxide is described elsewhere.[61]

Allylacetyl chloride was prepared from allylacetic acid (Peninsular Chemical Co.) and thionyl chloride. The peroxide is described elsewhere.[61]

Methylene iodide (National Biochemical Co.), **methylene bromide, 1,1-dibromomethane, 1,3-dibromobutane**, and **1,3-dibromopropane** (Eastman Kodak Co.), and **1,3-diiodopropane** (City Chemical Co.) were commercially available samples used as such.

Diacyl peroxides were reduced with chromous sulfate in a 200-ml. round-bottom flask to which was added an aqueous alcohol solution of the peroxide. The free volume to solution ratio was at least 10. It was cooled in ice, and the solution was swept with oxygen-free nitrogen for 15 min. by inserting hypodermic needles through the rubber septum. It was finally evacuated to approximately 10-mm. pressure and the chromous solution was added with a syringe. The flask was put on a mechanical shaker to ensure complete mixing. The reaction was analyzed by adding a known quantity of marker (isobutane for *n*-butane) with a gas-tight syringe, shaking until homogeneous, and sampling the gas mixture for gas chromatographic analysis. Calibration curves (straight lines) were constructed for each gas marker–carbon dioxide combination obtained from a given solvent mixture. Marker gas was chosen so that its solubility characteristics would be as close as possible to the component to be identified (*e.g.*, *n*-butane–isobutane, butene-1–isobutylene, methylcyclopropane–cyclobutane, neopentane–butane, and cyclopropane–*n*-butane). Results obtained in this manner were reproducible and accurate to 3%. Gas chromatography was conducted with both a 50-ft. dimethyl sulfolane on firebrick and a 15-ft. silver nitrate–benzyl cyanide on Chromosorb W column which have sufficiently different characteristics to enable positive identification of the components in the gas mixtures.

After gas analysis, an aliquot was removed with a hypodermic syringe and added to excess ferric chloride solution, which was titrated with standard ceric sulfate. The carboxylatochromium(III) was analyzed by ion-exchange chromatography on a Dowex-50 sulfonic acid resin (60–100 mesh). Excess chromous ion was destroyed with bromine or oxygen and the carboxylatochromium(III) was eluted with 1.5 *M* perchloric acid after first washing with 0.4 *M* perchloric acid to remove anions and other easily eluted species. The dipositive chromium ions were analyzed by oxidation with alkaline hydrogen peroxide for total chromium. Another aliquot was hydrolyzed, and the liberated acid continuously was extracted with ether and analyzed by gas chromatography (6-ft. Carbowax–didecylphthalate on Chromosorb W treated with hexamethyldisilazane) with a homologous acid as marker.

Acknowledgment.—We wish to thank Dr. G. R. McMillan for helpful discussions concerning alkoxy radicals with one of us (J. K. K.), and the National Science Foundation for financial support of this work.

[60] H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).

[61] H. Mains, unpublished results.

[62] H. Hart and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

Iodonium Salts Containing Heterocyclic Iodine[1-3]

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New or improved syntheses are reported for iodonium cations with heterocyclic iodine in five-, six-, and seven-membered rings and for cations with both iodine and oxygen, sulfur, or nitrogen in six-membered rings. Pyrolytic decomposition of the iodonium iodides gave 2,2'-diiododiphenyl compounds in which the rings are attached either directly or by carbon, oxygen, sulfur, or nitrogen.

Prior synthetic methods in the preparation of cyclic iodonium salts have involved replacement of a diazonio group with iodine,[4,5] acid-catalyzed condensation of an iodoso group with a benzene ring,[6] and the reaction of iodyl sulfate with an appropriate aromatic substrate in strong acid.[7] Only methylene-bridged salts, where n = 0, 1, 2, or 3, have been prepared by these methods.

The present work is concerned with an extension of the above methods to produce cyclic iodonium salts with nitrogen, oxygen, and sulfur in six-membered

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[1] This article is taken from M.S. Theses of G. B. T., 1960, and L. K., 1963.

[2] Diaryliodonium Salts. XXIV. Preceding article: F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, 4442 (1964).

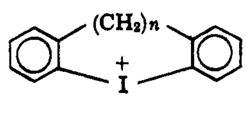
[3] Previously reported ring systems are named according to A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960.

[4] L. Mascarelli and G. Benati, *Gazz. chim. ital.*, **38**, 624 (1908).

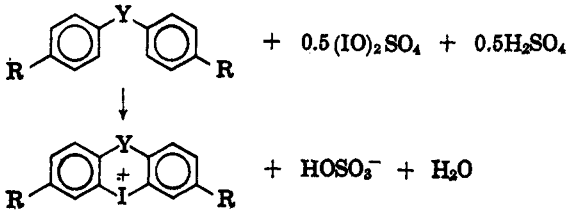
[5] N. E. Searle and R. Adams, *J. Am. Chem. Soc.*, **55**, 1649 (1933).

[6] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *ibid.*, **78**, 3819 (1956).

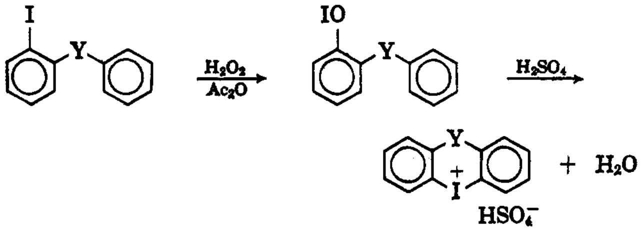
[7] W-K. Hwang, *Sci. Sinica* (Peking), **6**, 123 (1957); *Chem. Abstr.*, **51**, 16476 (1957).



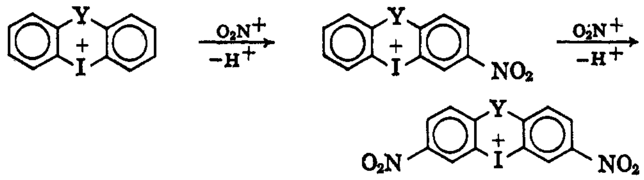
rings, and substituted salts with methylene bridges in five-, six- and seven-membered rings. The following general methods were utilized: (A) reaction of a 4,4′-disubstituted diphenyl compound with iodyl sulfate in the presence of sulfuric acid[8]; (B) oxidation of an iodo compound with hydrogen peroxide or potassium persulfate to an iodoso compound, followed by cyclization *in situ* using sulfuric acid[9-11]; and (C) nitration of a heterocyclic iodonium cation followed by metathesis of the halide salt.[12-14]



Method A



Method B



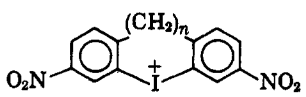
Method C

Syntheses of *o*-iodo compounds began with appropriately substituted *o*-nitrohalobenzenes which were treated with arylamines, arylmercaptans, or potassium phenolates. Dimethylformamide, recently discovered by Randall and co-workers[15] to be an effective solvent in such substitutions, was often utilized in this first step. Reduction of the nitrophenyl compound gave the amine which was converted to the iodo compound by a Sandmeyer reaction.

Standard methods were used in preparing symmetrical 4,4′-dinitrodiarylalkanes. 4,4′-Dimethyldiphenyl ether was formed by the reaction of potassium *p*-cresoxide with 4,4′-dimethyldiphenyliodonium bromide.[16]

TABLE I

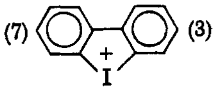
CYCLIC SALTS WITH IODINE AS THE ONLY HETERO ATOM PREPARED BY CONDENSATION METHOD A[a,b]



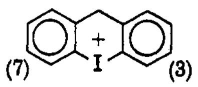
Cation	n	Anion	Conditions, temp, °C. (time, hr.)	M.p., °C.	% yield
I	0	SO_4^{-2}[c]	5 (1), 25–30 (17)	317	93
II	1	$HOSO_3^-$	0–5 (4), 25–30 (16)	216[d]	87
III[e]	2	$HOSO_3^-$	5 (1.5), 25 (17)	180	38

[a] Headings of Tables I–IV: "Conditions" refer to the condensation step; melting points were all accompanied by decomposition, the single number indicating the point at which effervescence occurred. [b] See method A in text and details in Experimental section. [c] In this case the sulfate rather than the bisulfate was isolated. This sometimes occurred upon crystallization; *e.g.*, see ref. 6. [d] Lit.[7] m.p. 217.5°. [e] 1,2-Bis(2-iodo-4-nitrophenyl)ethane was also isolated as a by-product of this reaction; see Chart I and accompanying text.

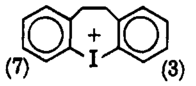
Cations with Heterocyclic Iodine Only (Table I).—When method A (described above) was applied to 4,4′-dinitrobiphenyl and to 4,4′-dinitrodiphenylmethane, high yields of the 3,7-dinitrodibenziodolium (I) and 3,7-dinitro-10H-dibenz[*b,e*]iodinonium (II)[7] cations, respectively, were obtained. When applied to 1,2-bis(4-nitrophenyl)ethane, method A produced only a 35% yield of the cyclic 3,7-dinitro-10,11-dihydrodibenz[*b,f*]iodeponium (III) cation. A yield of 42% of III was obtained in a run in which iodyl sulfate was slowly added (during 1 hr.) to a mixture of 1,2-bis(2-nitrophenyl)ethane in sulfuric acid, rather than the inverse addition. The lower yield as well as the unexpected isolation of 1,2-bis(2-iodo-4-nitrophenyl)ethane as a by-product of this reaction may be rationalized by the scheme depicted in Chart I. Here, it it is proposed that in the first formed monoiodoso compound the protonated iodoso group may attack the other ring to form the cyclic salt. Alternatively, iodyl sulfate may form the diiodoso compound, which is reduced to the diiodo compound. Reductions of iodoso groups to iodo groups by a yet unknown mechanism have previously been reported.[8b]



dibenziodolium cation



10H-dibenz[*b,e*]iodinonium cation



10,11-dihydrodibenz[*b,f*]iodeponium cation

The smaller fraction of closure to a seven-membered ring presumably arises from small additional strains in the ring and/or proximity effects. Sandin and coworkers obtained almost quantitative yields of cyclic iodonium salts from 2-iodobiphenyl and 2-iododiphenyl-

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[8] Formation of iodonium cations by iodyl sulfate has been suggested to involve electrophilic attack of IO^+ on an aromatic substrate to give an iodoso compound, followed by attack of the conjugate acid on another molecule of ArH: (a) I. Masson and E. Race, *J. Chem. Soc.*, 1718 (1937); (b) F. M. Beringer, M. Drexler, E. M. Gindler and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2705 (1953).

[9] F. M. Beringer, R. A. Falk, M. Karniol, I. Lillien, G. Masullo, M. Mausner, and E. Sommer, *ibid.*, **81**, 342 (1959).

[10] K. H. Pausacker, *J. Chem. Soc.*, 107 (1953).

[11] R. B. Sandin and A. S. Hay, *J. Am. Chem. Soc.*, **74**, 274 (1952).

[12] D. Vorlander, *Ber.*, **58**, 1893 (1925).

[13] F. Challenger and E. Rothstein, *J. Chem. Soc.*, 1258 (1934).

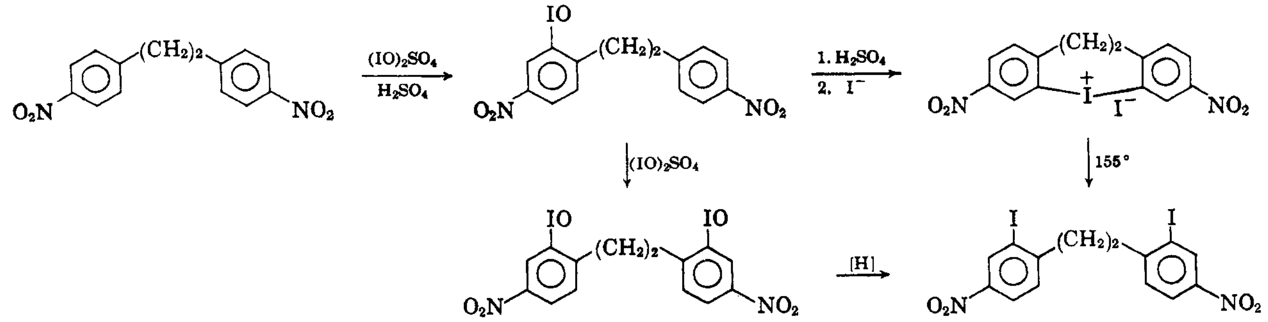
[14] R. B. Sandin, F. T. McClure, and F. Irwin, *J. Am. Chem. Soc.*, **61**, 3061 (1939).

[15] J. J. Randall, C. E. Lewis, and P. M. Slagan, *J. Org. Chem.*, **27**, 4098 (1962).

[16] F. M. Beringer, A. Brierley, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *J. Am. Chem. Soc.*, **75**, 2707 (1953).

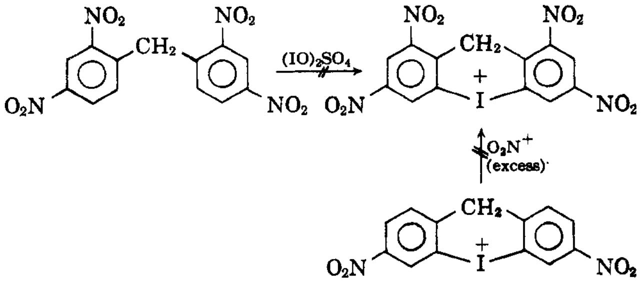
Chart I

The Reaction of 1,2-Bis(4-nitrophenyl)ethane with Iodyl Sulfate

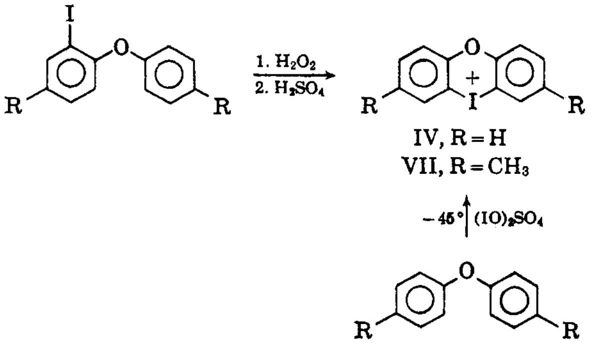


methane but only a 60% yield from 1-phenyl-2-(*o*-iodophenyl)ethane.[6]

Attempts to form the 1,3,7,9-tetranitro-10H-dibenz[*b,e*]iodinonium cation by applying method A to 2,4,2′,4′-tetranitrodiphenylmethane resulted in recovery of starting material.[17] Starting material was also obtained when the nitration of 3,7-dinitro-10H-dibenz[*b,e*]iodinonium bisulfate (II) was attempted. Both electronic and steric factors would seem to operate against the success of this reaction.



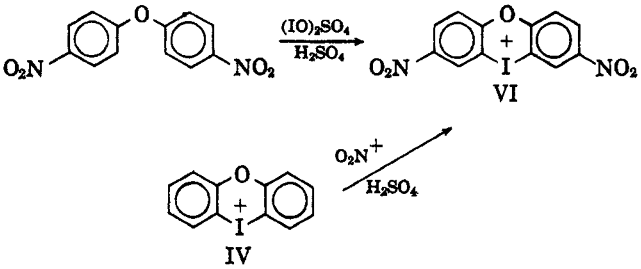
Cations with Heterocyclic Iodine and Oxygen (Tables II and III).—The phenoxiodonium cation (IV) was obtained from 2-iododiphenyl ether by modifying method B: a lower temperature (−45°) and a large excess of sulfuric acid. However, even these conditions when



applied to 2-iodo-4,4′-dimethyldiphenyl ether produced only a 17% yield of the 3,7-dimethylphenoxiodonium cation (VII). Attempted utilization of method A produced only a 4% yield of cation VII from 4,4′-dimethyldiphenyl ether.

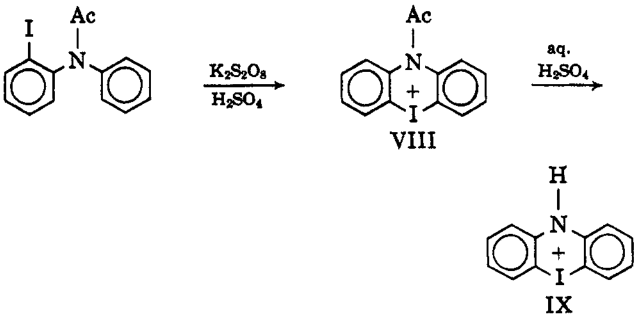
When method B was used, starting iodo rather than iodoso compounds were also recovered from the reaction mixtures, indicating a competing reduction of the iodoso compound to the iodo compound before cyclization.

When method A was applied to 4,4′-dinitrodiphenyl ether, the 3,7-dinitrophenoxiodonium cation (VI) produced was found to be identical with that made by dinitration of phenoxiodonium nitrate.



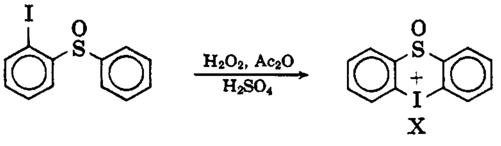
A comparison of the infrared spectra of the bromide salts produced by these two methods showed superposition except for a small peak at 733 cm.⁻¹ in the case of the compound synthesized from phenoxiodonium nitrate. This extraneous peak may arise from small amounts of nitration *ortho* to oxygen.

Cations with Heterocyclic Iodine and Nitrogen (Table II).—The 10-acetylphenaziodonium cation (VIII) was obtained in 50% yield from N-acetyl-2-iododiphenylamine by method B using potassium persulfate.



No iodinium salt was obtained by method B when hydrogen peroxide in acetic acid was the oxidizing medium. Hydrolysis of the amide VIII with 20% sulfuric acid produced the phenaziodonium cation (IX).

Cations with Heterocyclic Iodine and Sulfur (Table II).—Method B with 2-iodiphenyl sulfoxide produced the 10-oxidophenothiiodonium cation (X). Attempted variations of this cyclization failed because 2-iodoso-



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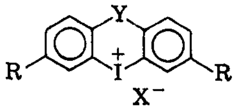
[17] There was isolated, however, approximately a 2% yield of iodonium salt containing catio n II.

TABLE II

CYCLIC SALTS WITH IODINE AND ANOTHER HETERO ATOM PREPARED BY CONDENSATION METHOD B[a,b]

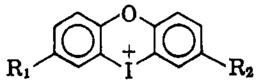


Cation	Anion	Y	R	M.p., °C.	Conditions, temp., °C. (time, hr.)	% yield
IV	Br$^-$	–O–	H	206	−45 (0.5), 0 (0.5)	56
VII[c]	I$^-$	–O–	CH_3	179	−45 (0.5), 0 (0.5)	17
VIII[d]	Br$^-$	>N—Ac	H	230	−10 (1), 0 (3)	43
X	Br$^-$	>SO	H	225	25 (96)	17

[a] See Table I, footnote *a* for explanations of column headings. [b] See method B in text and details in Experimental section. [c] Also prepared in 4% yield by applying method A to 4,4′-dimethyldiphenyl ether; compounds prepared by both methods showed no depression in melting point when admixed and superposition of infrared spectra. [d] Hydrolysis of the nitrate of VIII (See Table IV) produced the phenaziodonium cation (IX) in 30% yield.

TABLE III

NITROPHENOXIODONIUM SALTS PREPARED BY METHOD C STARTING WITH PHENOXIODONIUM NITRATE[a,b]



Cation	R_1	R_2	Anion	M.p., °C.	Conditions, temp., °C. (time, min.)	% yield
V	NO_2	H	Br$^-$	246	25 (30)	80
			I$^-$	126		18
VI[c]	NO_2	NO_2	HSO_4^-	255	25 (30)	64

[a] Column headings are explained in footnote *a* of Table I. Salts paired with braces were isolated from the same reaction mixture; yields are additive. [b] See method C in text and details in Experimental section. [c] Also prepared by applying method A to 4,4′-dinitrodiphenyl ether; yield was 89%; compounds prepared by both methods showed no depression in melting point when admixed and the infrared spectra were superimposable except for a small peak at 733 cm.$^{-1}$ in the case of the salt prepared by method C.

TABLE IV

CYCLIC SALTS PREPARED BY METATHESIS[a,b]

Cation	Anion	Other salt[c]	M.p., °C.	% yield	Reaction solvent	Crystn. solvent
I	Cl$^-$	K_2SO_4	317	37	9:1 HCO_2H–H_2O	9:1 HCO_2H–H_2O
	I$^-$	K_2SO_4	211	44	9:1 HCO_2H–H_2O	
II	Cl$^-$	$KHSO_4$	252[d]	90	9:1 HCO_2H–H_2O	
	I$^-$	$KHSO_4$	174[e]	3[f]	3:2 H_2O–H_2SO_4	9:1 HCO_2H–H_2O
	NO_3^-	AgCl	176	84	Methanol	Methanol
III	Cl$^-$	$NaHSO_4$	195	45	Glacial HOAc	
	I$^-$	$NaHSO_4$	147	49	Glacial HOAc	
	NO_3^-	AgCl	202	80	Methanol	Methanol
IV	NO_3^-	AgBr	190	52	Methanol	Methanol
	Cl$^-$	NH_4NO_3	254	12	5:1 methanol–H_2O	
	I$^-$	$NaNO_3$	165	19	5:1 methanol–H_2O	
VI	Br$^-$	$NaHSO_4$	255	98	9:1 HCO_2H–H_2O	
	NO_3^-	AgBr	215	80	Methanol	Methanol
VIII	NO_3^-	AgBr	219	83	Methanol	Methanol
	I$^-$	$NaNO_3$	187	97	Water	
IX	Br$^-$	$NaNO_3$	253	30	5:1 H_2O–H_2SO_4	
X	NO_3^-	AgBr	215	96	Methanol	Ethyl acetate
	Cl$^-$	$NaNO_3$	240	84	Water	Methanol
	I$^-$	$NaNO_3$	176	87	Water	

[a] Column headings are explained by footnote *a* of Table I. The appropriate cation may be found in Tables I, II, or III. Salts paired with braces were obtained from the same metathetical reaction mixture; the yields are additive. [b] Details may be found in the Experimental section and the discussion in the text. [c] "Other salt" is that resulting from metathesis along with the iodonium salt. [d] Lit.[7] m.p. 211.5°. [e] Lit.[7] m.p. 164°. [f] Based on starting aromatic compound; here the iodide was precipitated from the aqueous filtrate after the bisulfate or bromide had been removed.

diphenyl sulfide could not be prepared and because 2-iodosodiphenyl sulfone could not be cyclized.

Metathetical Reactions (Table IV).—Iodonium halides were isolated after addition of aqueous alkali halide to a solution of the bisulfate or sulfate salt in the reaction mixture. In those cases where the bisulfate or sulfate salt had precipitated from the reaction mixture, the alkali halide in water was added to the salt dissolved in hot 90% formic acid.

Iodonium nitrates were obtained by stirring for several hours a suspension of the iodonium halides in a large volume of methanol containing 1 equiv. of silver nitrate, collecting the silver halide formed, and concentrating the solution.

Structure Proof of Iodonium Salts (Chart II).—Thermal decomposition of the iodides of salts I–IV, VIII, and X produced the 2,2′-diiodoaromatic compounds (Table V).

CHART II

DIIODO COMPOUNDS FROM CYCLIC SALTS AND FROM DIAMINES

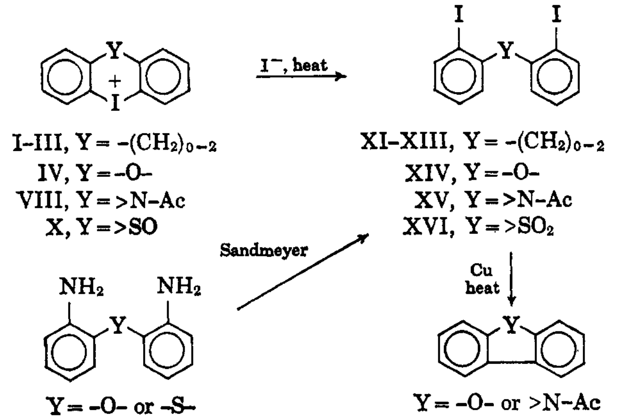
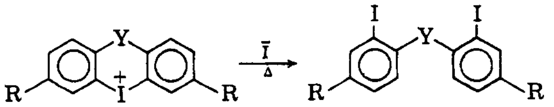


TABLE V

DECOMPOSITION PRODUCTS OF IODONIUM IODIDES[a,b]



Decompn. product[c]	Reactant	M.p., °C.	Crystn. solvent	% yield
2,2′-Diiodo-4,4′-dinitrobiphenyl (XI)	I	146–148	Ether	30
2,2′-Diiodo-4,4′-dinitrodiphenylmethane (XII)	II	156–158[d]	Ethanol–H_2O	50
1,2-Bis(2 iodo-4-nitrophenyl)ethane (XIII)	III	246–247	Acetone	50
2,2′-Diiododiphenyl ether (XIV)[e,f]	IV	64–65[g]	Pentane	47
N-Acetyl-2,2′-diiododiphenylamine (XV)[h]	VIII	187–188	Ether	52
Bis-2-iodophenyl sulfone (XVI)[i]	X	195	Methanol	45

[a] Reactant may be found by referring to appropriately numbered iodides in Tables I–IV. [b] See discussion in text and Experimental section for details. [c] For other possible decomposition products, see discussion in text under "Structure Proof of Iodonium Salts." Compounds XI, XIII, XV, and XVI are new. [d] Lit.[7] m.p. 158–159°. [e] Independently synthesized from 2,2′-diaminodiphenyl ether using Sandmeyer reaction. [f] An Ullmann reaction produced dibenzofuran. [g] Lit.[29] m.p. 66°. [h] An Ullmann reaction produced N-acetylcarbazole which was independently made from carbazole. [i] A mixture of sulfoxide and sulfone from the decomposition yielded, upon oxidation, pure sulfone which was independently synthesized from bis-2-iodophenyl sulfide by oxidation with peracetic acid.

The compounds whose aromatic moieties were bridged by sulfur or oxygen were independently synthesized by Sandmeyer reactions of the 2,2′-diamino or 2-iodo-2′-amino compounds. An attempt to synthesize N-acetyl-2,2′-diiodiphenylamine by a Sandmeyer reaction of N-acetyl-2,2′-diaminodiphenylamine failed. However, Ullmann reactions performed on the diiodo compounds obtained from the pyrolyses of those cyclic salts containing nitrogen and oxygen produced, respectively, N-acetylcarbazole and dibenzofuran. Although the corresponding 2,2′-diiodo compounds were also produced from the pyrolyses of those cyclic iodonium salts whose aromatic nuclei were bridged by polymethylene groups, independent syntheses were not performed since no alternate routes were readily available.

In all the pyrolyses of iodonium iodides, decomposition was accompanied by formation of at least 10% of iodine, as determined by thiosulfate titration. When the diiodo compound, isolated as a product of the decomposition, was heated at the same temperature for the same length of time as the iodonium iodide, no iodine was detected, indicating that the iodine was formed in a decomposition step which took place prior to formation of the diiodo compound. While a vapor phase chromatogram of the reaction mixture obtained from decomposition of phenoxiodonium iodide indicated a small peak in the region where dibenzofuran appeared in an authentic sample, it was not found possible to isolate dibenzofuran from the reaction mixture.

Experimental[18,19]

Starting Materials.—Phenol, o-nitrophenol, thiophenol, o-aminothiophenol, o-chloronitrobenzene, p-nitrotoluene, diphenylmethane, 2-nitrodiphenyl ether, 4,4′-dinitrodiphenyl ether, 4,4′-dinitrobiphenyl, 2-nitrodiphenylamine, dibenzofuran, and carbazole were obtained from Distillation Products Industries. Aldrich Chemical Co. was the source of 4-chloro-3-nitrotoluene, while Matheson Coleman and Bell supplied p-cresol. Unless otherwise stated these intermediates were not further purified.

Iodo Compounds and Precursors.—4,4′-Dinitrodiphenylmethane,[20] 1,2-bis(4-nitrophenyl)-ethane,[21] 2-aminodiphenyl ether,[22] 2-iododiphenyl ether,[23] 2-nitrodiphenyl sulfide,[24] 2-aminodiphenyl sulfide,[25] N-acetyl-2-nitrodiphenylamine,[26] and N-acetyl-2-aminodiphenylamine[27] were prepared by known methods.

The following general methods were used to prepare the iodo compounds and their precursors (new compounds) listed in Table VI.

Method 1.—2-Nitro-4,4′-dimethyldiphenyl ether was prepared, using the method of Randall and co-workers,[15] by refluxing a mixture of potassium p-cresoxide and 4-chloro-3-nitrotoluene in dimethylformamide.

Method 2.—Nitro compounds were reduced in methanol to amines by hydrogen in a Parr apparatus, using platinum oxide monohydrate as the catalyst.

Method 3.—Amines were diazotized at −10° in 18% hydrochloric acid. Aqueous potassium iodide in twofold excess was added dropwise with vigorous stirring, and the mixture was warmed to 50° over 1 hr. Ether extracts were then washed with sodium bisulfite solution, dried, and concentrated; the iodo compounds were distilled or crystallized.

Method 4.—To prepare sulfoxides, sulfides in acetic acid were treated for 2 days with 1 equiv. of 30% hydrogen peroxide. If the sulfone was the desired product, 2 equiv. of 30% hydrogen peroxide were used.

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(18) Microanalyses were performed in the analytical laboratories of Burroughs Wellcome, Inc., and The Schering Corp. Infrared spectra were obtained on a Beckman IR-4 using sodium chloride prisms and on a Perkin-Elmer Infracord 137. Vapor phase chromatograms were obtained on a Perkin-Elmer vapor fractometer 154. Capillary melting points are corrected and in the case of iodonium salts were obtained by inserting the sample 5–10° below the roughly determined decomposition point and allowing the temperature to rise at 4–6°/min. The decomposition point was considered to be the temperature at which explosion or effervescence occurred and could be reproduced to the nearest 0.5°.

(19) Bromide ion was determined in the following manner: after dissolving the iodonium bromide in aqueous dimethyl sulfoxide or acetonitrile, an excess of 0.1 *N* silver nitrate was added, and the excess was titrated with 0.1 *N* potassium thiocyanate using ferric ammonium sulfate as indicator. Chloride ion in phenoxiodonium chloride was determined, after dissolving the salt in 3:1 acetic acid–water, by the use of an Aminco automatic chloride titrator, while, in the case of 10-oxidophenothiiodonium chloride, that ion was determined by potentiometric titration with 0.1 *N* silver nitrate in 1:2 acetonitrile–water.

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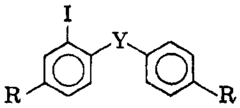
TABLE VI

IODO COMPOUNDS AND PRECURSORS

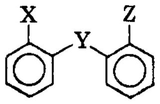


X	Y	R	Method	Yield, %	Crystn. solvent	M.p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
NO_2	–O–	CH_3	1	50	Pentane	54–55[a]	69.14	5.35	69.36	5.65
NH_2HCl	–O–	CH_3	2	93	*b*	172–175	. . .	. . .	. . .	. . .
I	–O–	CH_3	3	41	*c*	. . .	51.85	4.01	52.13	3.75
I	–S–	H	3	22	Ether	55–56	46.12	2.89	46.16	2.74
I	$>S\rightarrow O$	H	4	58	Methanol	73–75	43.90	2.74	44.20	2.70
I	$>S\overset{\nearrow O}{\underset{\searrow O}{}}$	H	4	75	Methanol	119–120	41.86	2.62	41.98	2.78
I	>N–Ac	H	3	19	Methanol[d]	120–121	49.85	3.56	50.02	3.73

[a] B.p. 148–152 (0.25 mm.). [b] Characterized by conversion to the *p*-nitrobenzamido derivative, m.p. 130–131°. *Anal.* Calcd. for $C_{21}H_{19}N_2O_4$: C, 69.42; H, 5.23; N, 7.71. Found: C, 69.19; H, 4.88; N, 7.34. [c] B.p. 125–127 (0.35 mm.). [d] Crystallization from methanol followed by chromatography of mother liquors over Florisil in benzene.

TABLE VII

DIIODO COMPOUNDS AND PRECURSORS



X	Y	Z	Method	Yield %	Crystn. solvent	M.p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
I	S	NO_2	3	32	Methanol	90–92	40.34	2.24	40.44	2.33
I	S	NH_2	*a*	82	Methanol	92–93	44.04	3.06	44.30	3.05
I	S	I	3	28	Methanol	49–50	32.88	1.83	33.12	1.98
I	SO_2	I	4	46	Methanol	195	30.63	1.70	30.83	1.89

[a] Reduction with zinc in acetic acid by the method of Yale.[24]

4,4′-Dimethyldiphenyl Ether.—A procedure similar to that of Beringer and co-workers[16] was used, except that dimethylformamide was the reaction solvent. To a suspension of 72 g. (185 mmoles) of 4,4′-dimethyldiphenyliodonium bromide[8b] in 220 ml. of dimethylformamide at about 70° there was added a solution of 43.8 g. (300 mmoles) of potassium *p*-cresoxide in 110 ml. of dimethylformamide. After stirring for 22 hr. at 120–125°, the red reaction mixture was cooled and poured onto 400 g. of ice. The ether extracts were washed with 1 *N* sodium hydroxide and with water, treated with activated carbon, and dried over calcium chloride. Removal of the ether and distillation of the yellow-orange residue yielded 20 g. of water-white liquid, b.p. 99–101° (0.65 mm.). The liquid on standing formed a white oily solid, which was crystallized from ether to yield 15 g. (75 mmoles, 40%) of 4,4′-dimethyldiphenyl ether, m.p. 47–49°, lit.[28] m.p. 50°.

Diiodo Compounds and Precursors.—2,2′-Dinitrodiphenyl ether,[15] 2,2′-diaminodiphenyl ether,[15] 2,2′-diiododiphenyl ether,[29] and 2-amino-2′-nitrodiphenyl sulfide[30] were prepared by known methods. Table VII lists the previously unknown diiodo compounds and precursors. The methods were essentially those used to prepare the compounds in Table VI.

General Procedures for Preparing Cyclic Iodonium Salts. A.—Iodyl sulfate was prepared according to the method of Beringer and co-workers[8b] by stirring stoichiometric quantities of potassium iodate and iodine in concentrated sulfuric acid for about 6 hr., at which point yellow crystals of iodyl sulfate had formed. The biaryl compound was then added; the reaction mixture was stirred at about 25° for 17 hr. and then poured onto ice. If the resulting iodinium bisulfate was soluble, dilute sodium bisulfite solution was carefully added, if necessary, until the solution tested negative to potassium starch–iodide paper. After treatment of the solution with activated carbon, the appropriate alkali halide in water was added to precipitate the iodonium halide.

If the iodonium bisulfate was found to be insoluble after the reaction mixture had been poured onto ice, it was collected, and the filtrate was treated for soluble iodonium bisulfate as above. The insoluble bisulfate was triturated with boiling benzene, filtered hot, and washed with several further quantities of boiling benzene. It was then dissolved in hot 90% formic acid, treated with activated carbon, and allowed to crystallize after addition of an equal volume of hot water. Iodonium halides were precipitated from 90% formic acid solutions of the bisulfates by addition of the appropriate alkali halide in water.

Metathesis to the nitrate was accomplished as described below.

B-1.—To a 10% solution of the iodobiaryl in acetic anhydride there was added dropwise first a tenfold excess of 30% hydrogen peroxide and then, at −45°, 10 ml. of concentrated sulfuric acid. At this point a vigorous exothermic reaction occurred, but quickly subsided. Concentrated sulfuric acid equal in volume to the acetic anhydride was added rapidly, with only small evolution of heat. After further stirring at 0° for 30 min., the reaction mixture was poured onto ice and the resulting solution was extracted with ether to remove any starting material. After the aqueous portion had been treated with activated carbon, the appropriate alkali halide was added and the resulting iodonium halide was collected, washed with water and ethanol, and dried. Metathesis to the nitrate was then accomplished as in procedure D below.

B-2.—To a 10% solution of the iodobiaryl in concentrated sulfuric acid at −10° there was added slowly with stirring a 100% excess of potassium persulfate. After 1 hr. at −10° and 3 hr. at 0°, the solution was poured onto enough ice to quadruple the volume of the solution. After extraction with ether, the aqueous portion was worked up as in method B-1 above.

C-1.—The iodonium nitrate was stirred with concentrated sulfuric acid at room temperature for 1 hr. The solution was poured on ice and the bisulfate was worked up as in procedure A.

C-2.—The iodinium nitrate was stirred at room temperature for 1 hr. with concentrated sulfuric acid to which 1 equiv. of potassium nitrate had been added. The mixture was then poured on ice and the bisulfate was worked up as in procedure A.

D.—To a suspension of the iodonium halide in methanol approximately equal to 700 times its weight there was added 1 equiv. of powdered silver nitrate. After 5 hr. of stirring, the silver halide was filtered; the iodonium nitrate was obtained by concentration of the filtrate and precipitation with ether. The pre-

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TABLE VIII

ANALYTICAL DATA[a]

Compd. No.	Anion	Calcd., %				Found, %			
		C	H	N	X[b]	C	H	N	X
I	SO_4^{-2}	34.53	1.44	...	...	34.63	1.58	...	...
	Cl^-	35.60	1.48	6.92	...	35.25	1.31	6.92	...
	I^-	29.03	1.21	5.65	...	29.25	1.50	5.64	...
XI[b]		29.03	1.21	5.85	...	29.36	1.36	5.47	...
II	NO_3^-	35.06	1.80	...	...	35.06	2.10	...	...
	Cl^-	37.28	1.91	6.69	...	37.41	2.11	6.62	...
	I^-	30.58	1.56	5.49	...	30.40	1.90	5.41	...
III	NO_3^-	36.60	2.18	...	...	36.97	2.11	...	...
	Cl^-	38.84	2.31	6.47	...	38.92	2.30	6.45	...
	I^-	32.06	1.91	5.36	...	31.91	1.93	5.36	...
XIII[c]		32.06	1.96	5.36	...	32.19	1.96	5.53	...
IV	Br^-	...	...	...	21.2	...	...	...	19.8
	NO_3^-	40.34	2.24	3.92	...	40.24	2.24	4.52	...
	Cl^-	43.57	2.42	...	10.74	43.57	2.42	...	10.75
	I^-	34.12	1.90	...	...	33.86	1.83	...	...
V	I^-	30.83	1.50	2.99	...	31.06	1.76	2.60	...
VI	Br^-	30.96	1.29	6.02	17.2	30.84	1.22	5.89	16.9
	NO_3^-	32.21	1.34	...	...	31.81	1.61	...	...
VII	I^-	37.33	2.67	...	...	37.43	3.16	...	...
VIII	Br^-	...	...	...	19.2	...	...	...	19.4
	NO_3^-	42.21	2.76	7.28	...	42.50	2.94	6.96	...
XV[b]		36.29	2.36	3.07	...	36.32	2.56	2.88	...
IX	Br^-	...	...	...	21.4	...	...	...	21.1
X	Br^-	...	...	...	19.7	...	...	...	18.3
	NO_3^-	37.02	2.06	3.60	8.23[d]	37.12	2.12	3.68	8.03[d]
	Cl^-	...	...	...	9.79	...	...	...	9.39

[a] Other data may be found by referring to the appropriate table in text. [b] Unless otherwise noted, X is the halide ion of the anion. [c] Decomposition product of preceding iodonium iodide in Table VIII. Other decomposition products mentioned in this research had been previously prepared by other workers (XIV, Table V) or may be found in Table VII. [d] Sulfur.

cipitated iodonium nitrates were recrystallized from methanol or methanol–ether. Further metathesis to different halides was accomplished by addition of the appropriate alkali halide to a water solution of the iodonium nitrate.

Cyclic Iodonium Salts Bridged by Polymethylene Groups.—Cations I, II, and III were prepared from 4,4′-dinitrobiphenyl, 4,4′-dinitrodiphenylmethane, and 1,2-bis(4-nitrophenyl)ethane, respectively, according to procedure A.

The combined benzene filtrate and washings from the preparation of cation III yielded, after concentration, 16% of 1,2-bis(2-iodo-4-nitrophenyl)ethane (XIII), which after two recrystallizations from acetone melted at 244–246°.

The bisulfate of the iodonium cation III was converted to the iodide which was then decomposed to XIII (see procedure below). The melting point was undepressed when admixed with XIII obtained as a by-product above, and the infrared spectra were superimposable.

Cyclic Salts with Heterocyclic Oxygen and Iodine.—Phenoxiodonium bromide (IV) was prepared from 2-iododiphenyl ether according to procedure B-1. The bromide was then metathesized to the nitrate which was subsequently converted to the chloride and iodide using procedure D.

Phenoxiodonium nitrate was also nitrated to 3-nitro- and 3,7-dinitrophenoxidonium salts (V and VI) according to procedures C-1 and C-2, respectively.

3,7-Dinitrophenoxiodonium salts were also prepared from 4,4′-dinitrodiphenyl ether by procedure A. The melting point of the bromides of VI, obtained by these two procedures, did not depress when admixed, and their infrared spectra were superimposable.

3,7-Dimethylphenoxiodonium salts (VII) were prepared according to procedure A from 4,4′-dimethyldiphenyl ether and by procedure B-1 from 2-iodo-4,4′-dimethyldiphenyl ether. The iodides of the cations produced by both these methods showed no depression in melting point upon admixture and their infrared spectra were superimposable.

Cyclic Salts with Heterocyclic Nitrogen and Iodine.—10-Acetylphenaziodonium bromide (VIII) was prepared according to procedure B-2 from N-acetyl-2-iododiphenylamine. The bromide was metathesized to the nitrate, which was then converted to the iodide using procedure D.

Phenaziodonium bromide (IX) was prepared as follows. A solution of 0.15 g. (0.37 mmole) of 10-acetylphenaziodonium nitrate (VIII) in 20% sulfuric acid was refluxed for 1.5 hr. After cooling, some tar was removed by filtration and the salt was precipitated by addition of an excess of aqueous sodium bromide. The product was collected and washed with water and acetone to give 0.46 g. (0.11 mmole, 30%) of phenaziodonium bromide, m.p. 253° dec.

Salts with Heterocyclic Sulfur and Iodine.—The following modification of procedure B-1 was used. At 5–10° 175 ml. of vigorously stirred concentrated sulfuric acid was treated slowly with 66.6 ml. of glacial acetic acid and with 8.0 g. (24.4 mmoles) of 2-iododiphenyl sulfoxide. With the temperature held below 10°, 24.4 ml. of 30% hydrogen peroxide was added dropwise, and the solution was stirred for 96 hr. Dilution with 1.5 l. of ice–water gave a colorless precipitate which was collected, recrystallized from ethyl acetate, and identified as **2-iododiphenyl sulfone** (Table VI). The aqueous filtrate was treated as in procedure B-1 to give 1.68 g. (4.1 mmoles, 17%) of **10-oxidophenothiiodonium bromide (X)**, m.p. 225° dec. The bromide was metathesized to the nitrate, which was then converted to the chloride and iodide using procedure D.

Decomposition of Iodonium Iodides (Table V).—The iodonium iodides were heated in a sealed tube for 5 min. in a silicone oil bath at approximately 10° above their decomposition points. After cooling, the tube was opened, and the contents were extracted with hot acetone. After removal of the acetone, the residue was recrystallized from the solvent indicated in Table V.

Decomposition of 10-Oxidophenothiiodonium Iodide (X).—The iodide of cation X (153 mg., 0.34 mmole) was decomposed at 185° according to the above general procedure; the residue was dissolved in methanol, treated with activated carbon, and crystallized to yield 120 mg. of a product which was assumed from its infrared spectrum to be a mixture of bis-2-iodophenyl sulfoxide and the corresponding sulfone.

The 120 mg. of mixture in 2.5 ml. of acetic anhydride was treated with 2.5 ml. of a cooled (10°) solution prepared by adding 1 ml. of sulfuric acid and 2.9 ml. of acetic acid to 11.3 ml. of 30% hydrogen peroxide. After 48 hr. standing at room temperature, the product, which had crystallized out of solution, was collected and washed with water. The filtrate was then diluted with 25 ml. of ice–water and the resulting suspended solid was collected, washed with water, and recrystallized once from methanol to a melting point of 190°. Combination of the two precipitates and recrystallization from methanol yielded 72 mg. (0.14 mmole, 45%) of **bis-2-iodophenyl sulfone (XVI)**, m.p. 195°. The melting point was not depressed upon admixture with an independently synthesized sample (Table V) and the infrared spectra were superimposable.

Dibenzofuran from 2,2′-Diiododiphenyl Ether.—A mixture of 2 g. of purified copper powder and 0.25 g. (0.59 mmole) of 2,2′-diiododiphenyl ether (XIV, from the decomposition of phenoxiodonium iodide) in a sealed tube was immersed in a silicone oil bath at 255° for 5 hr. The tube was cooled and opened, and the contents were dissolved in ether. Upon concentration to dryness the residue was recrystallized from methanol–water to yield 0.05 g. (0.3 mmole, 50%) of **dibenzofuran**, m.p. 82–84°; there was no depression of the melting point upon admixture with an authentic sample and the infrared spectra were superimposable.

N-Acetyl Carbazole from N-Acetyl-2,2′-Diiododiphenylamine.—A mixture of 100 mg. (0.22 mmole) of N-acetyl-2,2′-diiododiphenylamine (XV) (from the decomposition of N-acetylphenazidonium iodide) and 1 g. of purified copper powder was heated according to the above procedure at 230°. The residue was taken up in ether, filtered, and concentrated; the resulting residue was crystallized from hexane to yield 27 mg. (0.13 mmole, 59%) of N-acetylcarbazole. The melting point (62–64°) was not depressed upon admixture with a sample prepared by acetylation of carbazole and the infrared spectra were superimposable.

Attempted Preparations of 1,3,7,9-Tetranitro-10H-dibenz[*b,e*]iodinonium Salts. A. 2,2′,4,4′-Tetranitrodiphenylmethane with Iodyl Sulfate.—When 8.7 g. (25 mmoles) of 2,2′,4,4′-tetranitrodiphenylmethane[31] was treated with iodylsulfate according to procedure A and the resulting mixture was poured onto ice, a large amount of iodine was formed along with a solid. The iodine was removed by washing the collected solid with ether. Recrystallization of the solid from glacial acetic acid gave 8.1 g. (23 mmoles, 93%) of starting tetranitro aromatic compound, m.p. 171–173°, undepressed when admixed with an authentic sample. The aqueous filtrate was treated with sodium bisulfite until no more oxidizing power was observed with potassium starch–iodide paper. Clarification with activated carbon, followed by addition of aqueous potassium iodide, gave a yellow precipitate which was filtered to yield 0.4 g. (0.67 mmole, 3%) of **3,7-dinitro-10H-dibenz[*b,e*]iodinonium iodide**, identified by lack of depression of the melting point with an authentic sample of the iodide of cation II and by superposition of their infrared spectra.

B. 3,7-Dinitro-10H-dibenz[*b,e*]iodinonium Bisulfate with Potassium Nitrate in Sulfuric Acid.—An attempt to nitrate the bisulfate of cation II using procedure C-2 with a large excess of potassium nitrate resulted only in recovery of starting material.

Analytical data for the above preparations may be found in Table VIII.

Acknowledgment.—We are pleased to acknowledge the contribution of Mr. Fred Gruen who did exploratory work in the syntheses employing iodyl sulfate (1953–1957). Thanks are due also to the companies in whose laboratories this work was performed: Burroughs Wellcome and Company, Inc. (L.K.), and The Schering Corporation (G.B.T.).

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Organometallic Studies. X.[1a] Reductive Dimerization of α-Metallocenylcarbonium Ions. I[1b]

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Solvolysis of ferrocenylcarbinols followed by reduction with zinc leads to the formation of 1,2-diferrocenylethanes in yields of 60% and better. The reaction sequence is envisaged to consist of reduction by zinc of the initially formed α-ferrocenylcarbonium ion to the ferrocenylcarbinyl radical which upon coupling yields the dimer.

In the course of our studies on the synthesis of metal π-complexes of the pentalene and benzopentalene systems[2-5] the key step in the envisaged reaction sequence involved the formation of an α-metallocenylcarbonium ion. This prompted us to look into some pertinent aspects of the reactions involving such carbonium ions.

Both qualitative and quantitative evidence has been presented to show that carbonium ions adjacent to metallocene systems possess an unusual stability. Thus, ferrocenecarboxaldehyde is soluble in dilute hydrochloric acid.[6] Ferrocenylmethylcarbinol can be dehydrated to vinylferrocene under very mild conditions[7] and the latter adds very readily, across the double bond, weak acids such as hydrogen azide and acetic acid.[8] Ferrocenylphenylcarbinol forms ethers with great ease.[9] The formation of the rearranged product 1,1-diferrocenylethane on alkylation of ferrocene with 1,2-dichloroethane has been ascribed to the rearrangement of the initially formed primary carbonium ion to the more stable α-ferrocenylcarbonium ion.[10]

Quantitative evidence for the stabilization of α-metallocenylcarbonium ions has been obtained from studies on the solvolysis of metallocenylcarbinyl acetates.[11-14] The latter have been shown to solvolyze with rates somewhat greater than that of trityl acetate and this has been taken to indicate stabilization of the α-metallocenylcarbonium ion. A similar conclusion was drawn from the results obtained in a kinetic study of the solvolysis of α-ferrocenylethyl chloride.[15]

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