Rearrangement and Cleavage of 2-Aryliodoniobenzoates. Trapping Agents for Benzyne[1-3]

F. Marshall Beringer and Samuel J. Huang[4]

The Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn 1, New York

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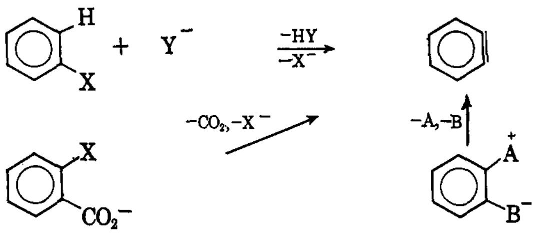
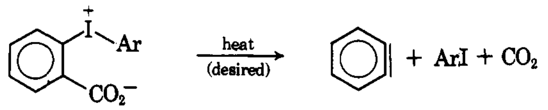
Acid-catalyzed condensation of 2-iodosobenzoic acid with benzene, mesitylene, and cyclohexylbenzene has given 2-carboxydiphenyliodonium salts, which were converted by base to the corresponding betaines, 2-aryliodoniobenzoates. On heating, these betaines rearrange in part to aryl 2-iodobenzoates. A competitive thermal reaction of the betaines, favored at higher temperatures, is cleavage to aryl iodides, carbon dioxide, benzyne, and other reactive intermediates, whose structure and further reactions are discussed. The efficiency of benzyne-trapping reagents increases in the order: anthracene < 1,3-diphenylisobenzofuran < 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) < 2,5-bis(p-dimethylaminophenyl)-3,4-diphenylcyclopentadienone < 2,5-di-p-anisyl-3,4-diphenylcyclopentadienone.

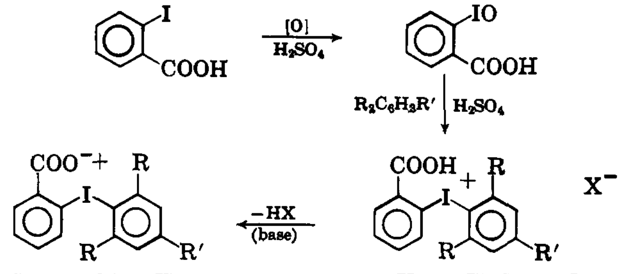
The reactive, highly unsaturated benzyne[5] is prepared by the removal of two *ortho* substituents from substituted benzenes in three ways: removal of hydrogen and an *ortho* substituent by strong base,[5] loss of carbon dioxide and halide ion (pyrolysis of an *o*-halobenzoate ion[6]), and loss of two *ortho* substituents as stable molecules.[5,7,8]



In previous examples of the third method $-A^+$ has been the diazonio group ($-N_2^+$) while $-B^-$ has been the carboxylate ion[7] ($-CO_2^-$) or the sulfinate ion[8] ($-SO_2^-$). An aim of the present work was to investigate the possibility that the decomposition of the stable betaine 2-phenyliodoniobenzoate[3] (diphenyliodonium-2-carboxylate) might provide an additional route to benzyne.



Preparation of Betaines.—Previously, 2-phenyliodoniobenzoate was prepared by the oxidation of 2-iodobenzoic acid to 2-iodosobenzoic acid in sulfuric acid, followed by addition of benzene to allow condensation to an iodonium salt.[3] In the present work it was found preferable to isolate 2-iodosobenzoic acid[9] and effect separately its condensation with benzene, mesitylene, and cyclohexylbenzene.



I, $R = R' = H$
II, $R = R' = CH_3$
III, $R = H$; R' = cyclohexyl

$X^- = HSO_4^-$ or I^-

In aprotic solvents the solubilities of the betaines, formed by treatment of the iodonium salts with base, increased with alkylation of the phenyl group. The importance of such solubility lies in the fact that reaction of betaines in solution is more rapid than those of betaines in the solid state.[10]

Thermal Reactions of Betaines.—Exploratory work showed that betaine I and II dissolved in halobenzenes and γ-butyrolactone at about 100° and in diglyme (β-methoxyethyl ether) at about 120°; betaine III, from cyclohexylbenzene, was more soluble. Slow carbon dioxide evolution began above 130° and increased in rate and total amount with temperature.

Table I

Products from 2-Aryliodoniobenzoates on Heating in the Absence of Benzyne-Trapping Reagents

Betaine	Solvent	Temp., °C.	Hours	Yield, % IV	V	VI	VII
I	C_6H_5I	100	150	*a*	100[b]		
		130	20	*a*	54	10	*a*
		150	4	*a*	30	12	15
	Diglyme	162	2	42	20	13	10
	Lactone[c]	204	2	44	6	30	6
II	Triglyme	175	2	72	5	4	*a*
III	Xylene	138	2	33	25	4	*a*
	C_6H_5Br	155	2	29	20	10	*a*

[a] Not determined. [b] In 5% conversion. [c] γ-Butyrolactone.

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[1] This article is taken from the dissertation of Samuel J. Huang, submitted in partial fulfillment of the requirement of the degree of Doctor of Philosophy (Chemistry).

[2] Diaryliodonium Salts. XX. Preceding article: F. M. Beringer and P. S. Forgione, *Tetrahedron*, **19**, 739 (1963).

[3] The synthesis of 2-, 3-, and 4-phenyliodoniobenzoates and their conjugate acids has been reported and their electronic structure discussed: F. M. Beringer and I. Lillien, *J. Am. Chem. Soc.*, **82**, 725 and 5141 (1960).

[4] U. S. Rubber Co. Fellow, 1960-1963.

[5] Review articles on benzyne: (a) H. Heaney, *Chem. Rev.*, **62**, 81 (1962); (b) J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); (c) R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Co., New York, N. Y., 1960, pp. 36-87; (d) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); **74**, 479 (1962).

[6] E. McNelis, *J. Org. Chem.*, **28**, 3188 (1963). This work makes unlikely the formation of xanthone by decomposition of halobenzoate through a disalicylide intermediate.

[7] (a) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); M. S. Barry, G. N. Spokes, and M. Stiles, *ibid.*, **82**, 5240 (1960); M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, **85**, 1792 (1963); R. G. Miller and M. Stiles, *ibid.*, **85**, 1798 (1963); (b) L. Friedman and F. M. Loguilo, *ibid.*, **85**, 1549 (1963).

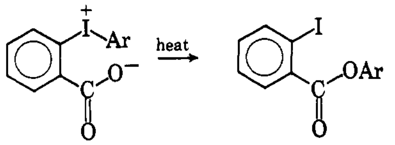
[8] G. Wittig and R. W. Hoffmann, *Angew. Chem.*, **73**, 435 (1961).

[9] (a) V. Meyer and W. Wachter, *Ber.*, **25**, 2632 (1892); P. Askenasy and V. Meyer, *ibid.*, **26**, 1354 (1893); (b) D. Twiss and R. V. Heinzelmann, *J. Org. Chem.*, **15**, 496 (1950).

[10] It has long been known that diphenyliodonium iodide dissolved in iodobenzene decomposes faster than the same salt in the solid state: C. J. Fletcher and C. N. Hinshelwood, *J. Chem. Soc.*, 596 (1935).

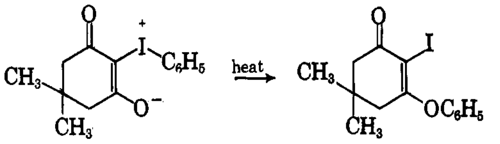
In the absence of added benzyne-trapping reagents the other main products were aryl iodides (IV), aryl 2-iodobenzoates (V), xanthone (VI), and 3,4-benzocoumarin (VII), as summarized in Table I.

Rearrangement.—At the low end of the temperature range for thermal reaction of the betaines the predominant path is rearrangement to aryl 2-iodobenzoates (V), possibly by intramolecular nucleophilic displacement. Indeed when betaine I was heated in iodobenzene at 100° for 7 days, the only product found was phenyl 2-iodobenzoate, in 5% conversion.

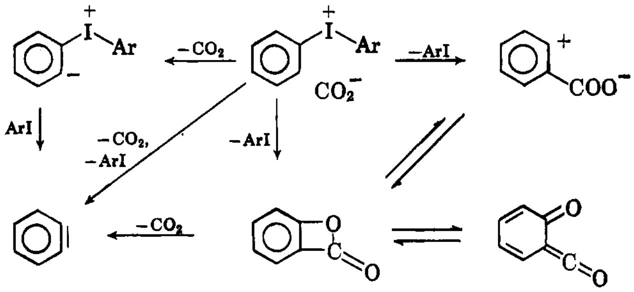


I–III V

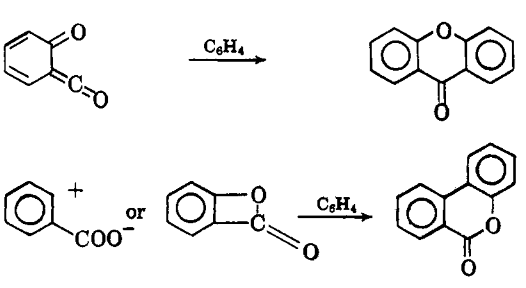
Such a rearrangement is closely relately to that of a betaine from dimedone.[11]



Thermal Cleavage Reactions.—To facilitate discussion, a schematic chart is now given to summarize other possible competitive modes of "decomposition" proceeding by cleavage of the betaines. In the absence of benzyne-trapping reagents these intermediates



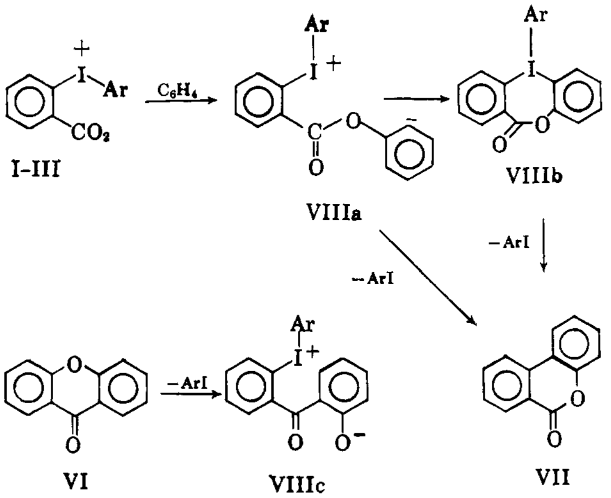
may react to give xanthone (VI) and the isomeric lactone 3,4-benzocoumarin (VII). The structures of the products suggest the natures of the intermediates.



VI

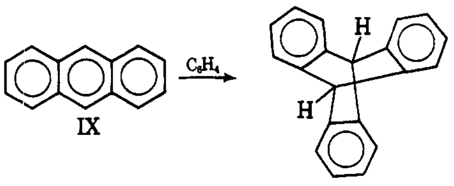
VII

The formation of xanthone[6] and 3,4-benzocoumarin also can be rationalized as arising from the addition of benzyne to betaine,[5] giving intermediates VIIIa[6] and/or VIIIb[12] which undergo ring closure with loss of iodobenzene to give 3,4-benzocoumarin (VII). The intermediate VIIIa also may rearrange to VIIIc which undergoes ring closure with loss of iodobenzene to give xanthone (VI).



While the intermediacy of benzyne seems highly probable (and is confirmed by trapping experiments, which follow), a choice between the various reaction paths for forming or utilizing benzyne is not now possible.

Trapping of Benzyne with Anthracene.—When analytically pure betaine I was heated at 222° with an equivalent of anthracene (IX) in triglyme, 22% of triptycene (X) was formed.[13] When the reaction was run with four equivalents of I, 90% of triptycene was isolated. However, when the same reaction was run in diglyme at 162°, no triptycene was isolated. Rather, the main products were phenyl 2-iodobenzoate, iodobenzene, carbon dioxide, xanthone, and a compound of unknown structure, $C_{28}H_{18}O_4$, m.p. 270–272°. Subsequently, it was found that catalytic amounts of cupric sulfate, silver acetate, molecular iodine, or the unknown impurities in crude betaine[14] allow the formation of 16–30% of triptycene under the same conditions (Table II). The origin of the catalytic effects is not known.



IX X

Other Trapping Reagents for Benzyne.—When betaine I was heated at 162° in diglyme containing 1,3-diphenylisobenzofuran (XI), 21% of 9,10-diphenylanthracene (XIII) was formed. The intermediate 9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene[15] (XII) was isolated when the reaction was run in triglyme

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[11] O. Neilands, G. Vanags, and E. Gudriniece, *J. Gen. Chem., USSR*, **28**, 1258 (1958).

[12] (a) F. M. Beringer, J. W. Dehn, Jr., and M. Winicov, *J. Am. Chem. Soc.*, **82**, 2948 (1960); (b) K. Clauss, *Ber.*, **88**, 268 (1955).

[13] (a) The isolation of triptycene from the thermal decomposition of 2-phenyliodoniobenzoate in the presence of anthracene, carried out in this laboratory, has been reported by F. A. Weinstein (B. S. thesis, Polytechnic Institute of Brooklyn, 1961). (b) While the present work was in progress, a communication was published reporting the same reaction: E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962).

[14] Betaine prepared according to the procedures of 13a and 13b was found to contain 1–2% of uncombustible impurities.

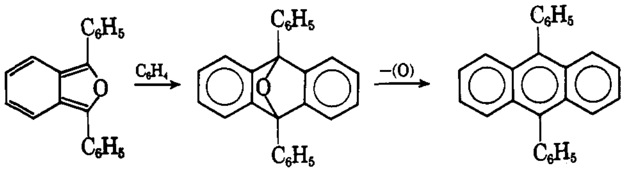
[15] G. Wittig, E. Knauss, and K. Niethammer, *Ann.*, **630**, 16 (1960).

TABLE II

TRIPTYCENE FORMED BY HEATING BETAINE I IN THE PRESENCE OF ANTHRACENE[a]

Solvent	Temp., °C.	Hours	Catalyst[b]	Yield triptycene, %
Diglyme	162	2	None	0
			I_2	30
			$CuSO_4$	24
			AgOAc	16
			c	18
			Others[d]	0
C_6H_5X[e]	132	3	I_2	Trace
C_6H_5Br	155	3	I_2	14
C_6H_5I	189	3	I_2	23
Triglyme	222	2	None	22, 90[f]

[a] One equivalent of anthracene. [b] One-tenth equivalent of catalyst. [c] Unidentified impurities in crude betaine. [d] Copper powder, potassium *t*-butoxide, potassium persulfate, and sodium hydroxide. [e] Chlorobenzene and iodobenzene, separately. [f] One-fourth equivalent of anthracene.


XI XII XIII

at 222° for 15 min. The conversion of XII to XIII could be achieved by heating in diglyme at 162° for 2 hr. or by reduction with zinc dust in acetic acid.

Decomposition of betaine I in the presence of tetracyclone[16] (XIVa) gave 1,2,3,4-tetraphenylnaphthalene (XVa) in 36–57% yield depending on solvent and reaction temperature (Table III).

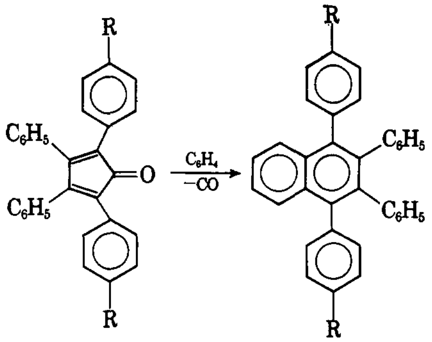
TABLE III

DECOMPOSITION OF BETAINE I IN THE PRESENCE OF VARIOUS BENZYNE-TRAPPING REAGENTS[a]

Reagent	Solvent	Temp., °C.	Hours	Yield product, %
IX	Diglyme	162	2	0 (X)
	Triglyme	222	2	22
XI	Diglyme	162	2	21 (XIII)
XIVa	Diglyme	162	2	36 (XVa)
	Lactone[b]	204	0.25	56
	Triglyme	222	0.25	57
XIVb	Lactone[b]	204	0.5	79 (XVb)
XIVc	Lactone[b]	204	0.5	65 (XVc)

[a] Equivalent amounts of reagent and betaine I. [b] γ-Butyrolactone.

2,5-Di-*p*-anisyl-3,4-diphenylcyclopentadienone (XIVb) was found to be the most effective benzyne-trapping reagent among those studied. In a reaction of betaine I with XIVb (1:1 molar ratio) in γ-butyrolactone at 204°, 79% of 1,4-di-*p*-anisyl-2,3-diphenylnaphthalene (XVb) was isolated. This suggests that addition reactions of benzyne are favored by increased electron density in the diene. These results are in agreement with the observation of Romanelli and Becker[17] that the reaction of methyl phenylpropiolate with substituted tetracylones is speeded by high electron density in the tetracyclone.



XIVa, R = H
b, R = OCH_3
c, R = $N(CH_3)_2$

XVa, R = H
b, R = OCH_3
c, R = $N(CH_3)_2$

Experimental[18]

Starting Materials.—Solvents were purified by passage through alumina columns and distillation. Reagent grade chemicals were distilled or recrystallized before used.

2-Iodosobenzoic Acid.—2-Iodobenzoic acid (148.8 g., 0.6 mole) in 200 ml. of concentrated sulfuric acid and 100 ml. of fuming nitric acid was heated at 100° for 1 hr. The mixture after cooling was poured into ice–water, and the resulting yellow precipitate was filtered, washed with water, and dried to give 144 g. (0.55 mole, 92%) of 2-iodosobenzoic acid. Recrystallization from water gave white crystals, m.p. 200° dec., lit.[9] m.p. 200° dec.

2-Phenyliodoniobenzoate (I).—To a solution of 26.4 g. (0.1 mole) of 2-iodosobenzoic acid in 100 ml. of concentrated sulfuric acid at 0–5° there was added 100 ml. of benzene. The mixture was stirred for 4 hr. at room temperature and then poured into ice–water. Crystalline 2-carboxydiphenyliodonium bisulfate was collected. Addition to the filtrate of 40 ml. of saturated potassium iodide solution gave pale yellow crystals of 2-carboxydiphenyliodonium iodide, which were also collected. The combined iodonium salts were stirred vigorously with 100 ml. of 5 *N* sodium hydroxide to give a tan precipitate. This was collected, washed with water, and dried to give 29.2 g. (0.09 mole, 90%) of 2-phenyliodoniobenzoate (I). Recrystallization from chloroform–methanol (30/70 by volume) gave colorless crystals, m.p. 205° dec.; ultraviolet absorption maxima, $\lambda_{\max}^{H_2O}$ 205 mμ (log ε 4.43), 266 (4.02); principal bands in infrared spectrum (potassium bromide), 3005 (w), 1630 (s), 1524 (s), 1400 (m), 1335 (s), 1005 (w), 995 (w), 817 (m), 738 (s), 720 (s), and 685 cm.$^{-1}$ (m). The n.m.r. spectrum showed absorption bands with fine structures for ring hydrogens from τ 1.46 to 3.28.

Anal. Calcd. for $C_{13}H_9IO_2$: C, 48.14; H, 2.78; I, 39.19. Found: C, 48.13; H, 2.92; I, 39.58.

Recrystallization from methanol-water (50/50 by volume) gave colorless crystals of **2-phenyliodoniobenzoate monohydrate,** m.p. 220° dec.

Anal. Calcd. for $C_{13}H_{11}IO_3$: C, 45.61; H, 3.21; I, 37.13. Found: C, 45.87; H, 3.35; I, 37.37.

2-Mesityliodoniobenzoate (II).—To a solution of 105.6 g. (0.4 mole) of 2-iodosobenzoic acid and 150 ml. of mesitylene in 300 ml. of acetic anhydride at 0–5° there was added slowly 50 ml. of concentrated sulfuric acid. After the dark blue mixture had been stirred at room temperature for 6 hr. and cooled to 0°, 100 ml. of 30% ammonia was added. The ammonium sulfate that formed was filtered, and the filtrate was evaporated to dryness *in vacuo*. Trituration of the solid with 250 ml. of ether gave tan crystals which were washed with water and dried to give 117.1 g. (0.32 mole, 80%) of 2-mesityliodoniobenzoate (II). Recrystallization from chloroform–methanol (30/70 by volume) gave colorless crystals, m.p. 213–214° dec.

Anal. Calcd. for $C_{16}H_{15}IO_2$: C, 52.48; H, 4.13; I, 34.66. Found: C, 52.70; H, 4.10; I, 34.88.

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(16) This reaction, mentioned in ref. 13b, also has been studied by Professor L. F. Fieser (private communication).

(17) M. G. Romanelli and E. I. Becker, *J. Org. Chem.*, **27**, 662 (1960).

(18) Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Infrared spectra were taken on a Perkin-Elmer double beam recording spectrophotometer, Model 21, and a Perkin-Elmer Infracord spectrophotometer, Model 137. Ultraviolet spectra were taken on a Cary Model 14 recording spectrophotometer. N.m.r. spectra were taken on a Varian A-60 high resolution n.m.r. spectrometer by Mr. H. Talts. Melting points were taken in capillary tubes and were corrected.

2-(*p*-Cyclohexylphenyl)iodoniobenzoate (III).—Compound III was prepared as before in 82% yield. Recrystallization from chloroform–methanol gave colorless crystals, m.p. 208° dec.

Anal. Calcd. for $C_{19}H_{19}IO_2$: C, 56.17; H, 4.69; I, 31.24. Found: C, 56.00; H, 4.51; I, 30.90.

Reactions of Betaines.—Typical procedures are described below. Products are listed in Tables I–III. Known compounds were identified by ultraviolet and infrared spectra, melting points and mixture melting points, and refractive indices. Only the properties of the previously unknown compounds are given below.

Decomposition of Betaines (**Table I**).—Solutions of betaines I–III were heated under nitrogen until the carbon dioxide evolution ceased. The solvent was removed by distillation *in vacuo* or by extraction with water. The residue was chromatographed on a Florisil column (substance–absorbent, $^1/_{40}$ to $^1/_{30}$ by weight) prepared in hexane. The column was eluted successively with hexane, benzene, methylene chloride, acetone, and methanol. Products were obtained from the column in the following order: **aryl iodides, xanthone, 3,4-benzocoumarin**, and then **aryl 2-iodobenzoates**. The esters were hydrolyzed to 2-iodobenzoic acid and the corresponding phenols by acid or base.

2-Phenyliodoniobenzoate (I) **with Anthracene** (**IX**) (**Table II**).—One equivalent of 2-phenyliodoniobenzoate was added to a solution of one equivalent of anthracene (and in some cases one-tenth equivalent of catalyst) at the desired temperature. The mixture was heated under nitrogen for 2–3 hr., and the solvent was removed by distillation *in vacuo* or by extraction with water. The residue and 3 equiv. of maleic anhydride were heated at reflux in xylene for 30 min. After cooling, the anthracene–maleic anhydride adduct was collected, and the filtrate was hydrolyzed with 1 *N* sodium hydroxide at 100° for 1 hr. The organic layer was separated, washed with water, and concentrated *in vacuo*. Trituration of the residue with methanol gave pale yellow crystals of **triptycene** (**X**). Recrystallization from ethanol gave colorless crystals, m.p. 254°, lit.[19] m.p. 255–256°; principal bands of infrared spectrum, 3040 (w), 2960 (w), 1470 (s), 1195 (doublet, w); 1165 (w), 1120 (doublet, w), 795 (m), 755 (w), 748 (m), and 740 cm.$^{-1}$ (s). The n.m.r. spectrum showed ring hydrogen absorption bands at τ 2.75 to 3.52 and bridgehead hydrogen absorption, band at τ 4.82.

Anal. Calcd. for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.70; H, 5.52.

When the reaction of 2-phenyliodoniobenzoate with anthracene was run in diglyme at 162° for 2 hr., no triptycene was isolated. A compound which melted at 270–272°, with an empirical formula of $C_{28}H_{18}O_4$, was found, but its structure has not been established.

2-Phenyliodoniobenzoate (I) **with 1,3-Diphenylisobenzofuran** (**XI**).—To a solution of 2.70 g. (10 mmoles) of 1,3-diphenylisobenzofuran in 75 ml. of diglyme at 162° there was added 3.24 g. (10 mmoles) of 2-phenyliodoniobenzoate. After the mixture had been heated to reflux (nitrogen) for 2 hr., the mixture was concentrated *in vacuo*. The residue was chromatographed on a 200-g. Florisil column prepared in hexane and was eluted successively with hexane and carbon tetrachloride.

The hexane eluate after evaporation of solvent gave 0.69 g. (2.1 mmoles, 21%) of **9,10-diphenylanthracene** (**XIII**) as fluorescent crystals, m.p. 246–247°, after recrystallization from ethanol, lit.[15] m.p. 245–247°. The n.m.r. spectrum showed anthracene ring hydrogen absorption bands at τ 2.38 and 2.97 and a single band for hydrogens on the phenyl rings at τ 2.59.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.59; H, 5.41. Found: C, 94.34; H, 5.38.

When the above reaction was run with three equivalents of I in triglyme at 222° for 15 min., **9,10-epoxy-9,10-diphenyl-9,10-dihydroanthracene** (**XII**) was isolated. Recrystallization from ether–methanol gave white crystals, m.p. 188–188.5°, lit.[15] m.p. 188–188.5°.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.89; H, 5.18.

2-Phenyliodoniobenzoate (I) **with 2,3,4,5-Tetraphenylcyclopentadienone** (**XIVa**) (**Table III**).—To a refluxing solution of 1.92 g. (5 mmoles) of 2,3,4,5-tetraphenylcyclopentadienone in 15 ml. of solvent (diglyme, γ-butyrolactone, and triglyme, separately) there was added 1.62 g. (5 mmoles) of 2-phenyliodoniobenzoate. The mixture was heated to reflux (nitrogen) until the evolution of carbon dioxide ceased and concentrated *in vacuo*. The residue was chromatographed on a 200-g. Florisil column prepared in hexane and was eluted successively with hexane and carbon tetrachloride.

The hexane eluate after evaporation of solvent gave 36 to 57% of **1,2,3,4-tetraphenylnaphthalene** (**XVa**). A sample was recrystallized from ethanol and distilled at 225° (0.05 mm.), m.p. 204°, lit.[16] m.p. 203–204°. The n.m.r. spectrum showed naphthalene ring hydrogen absorption bands at τ 2.49 and 2.68 and phenyl ring hydrogen absorption bands at τ 2.83 and 3.22.

Anal. Calcd. for $C_{34}H_{24}$: C, 94.43; H, 5.57. Found: C, 94.14; H, 5.59.

2-Phenyliodoniobenzoate (I) **with 2,5-Di-*p*-anisyl-3,4-diphenylcyclopentadienone**[17] (**XIVb**).—Reaction of 2.5 mmoles each of I and XIVb in 7.5 ml. of γ-butyrolactone at 204° for 30 min. was followed by removal of solvent and chromatographing largely as described before. The hexane eluate gave 0.97 g. (1.97 mmoles, 79%) of **1,4-di-*p*-anisyl-2,3-diphenylnaphthalene** (**XVb**), m.p. 221.5–222°, unchanged by recrystallization from ethanol–carbon tetrachloride.

Anal. Calcd. for $C_{36}H_{28}O_2$: C, 87.77; H, 5.73. Found: C, 87.67; H, 5.67.

2-Phenyliodoniobenzoate (I) **with 2,5-Bis(*p*-dimethylaminophenyl)-3,4-diphenylcyclopentadienone**[18] (**XIVc**).—The reaction was run and worked up as before to give 65% of **1,4-bis(*p*-dimethylaminophenyl)-2,3-diphenylnaphthalene** (**XVc**), m.p. 246–248°, raised to 247–248° by recrystallization from acetone.

Anal. Calcd. for $C_{38}H_{34}N_2$: C, 87.99; H, 6.59; N, 5.42. Found: C, 87.91; H, 6.47; N, 5.42.

Acknowledgment.—Samples of tetracyclones provided by Mr. M. Ogliaruso and Mr. M. Romanelli are gratefully acknowledged.

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(19) G. Wittig, *Org. Syn.*, **39**, 75 (1959).