effects of various substituents may be an important additional factor. A kinetic investigation is presently being undertaken with a variety of *ortho* substituents and various nucleophiles in an attempt to verify the above considerations.

Acknowledgment.—We wish to express our sincere appreciation to Dr. S. Windwer and Dr. S. Moon for their fruitful suggestions.

Effects of Substituents on the Rearrangement of 2-Aryl Iodoniobenzoates and Their Cleavage to Benzyne[1,2]

F. MARSHALL BERINGER AND SAMUEL J. HUANG

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

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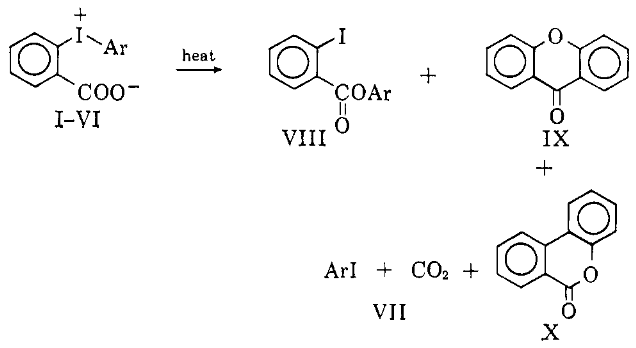
A previous article[3] reported that, on heating, 2-aryl iodoniobenzoates I–III rearrange in part to aryl 2-iodobenzoates (VIII). A competitive reaction, favored at higher temperatures, is cleavage to aryl iodides (VII), carbon dioxide, benzyne,[3,4] and perhaps other reactive intermediates.[3] In the absence of benzyne-trapping reagents, these intermediates react to give xanthone[3] (IX) and 3,4-benzocoumarin[3] (X). As the rearrangement of betaines to esters may involve intramolecular nucleophilic displacement, the effects of substituents on the rearrangement and cleavage reactions of 2-aryl iodoniobenzoates I–VI have now been studied, and the results are listed in Table I.



I, Ar = phenyl
II, Ar = mesityl
III, Ar = *p*-cyclohexylphenyl
IV, Ar = 2,4-dimethoxyphenyl
V, Ar = *m*-nitrophenyl
VI, Ar = 2-methyl-5-nitrophenyl

As expected, introduction of the electron-withdrawing nitro group facilitated the formation of ester *via* intramolecular nucleophilic substitution. A similar effect on intermolecular nucleophilic substitution reactions of diaryliodonium salts has been reported.[5,6]

TABLE I

PRODUCTS FROM 2-ARYL IODONIOBENZOATES ON HEATING IN THE ABSENCE OF BENZYNE-TRAPPING REAGENTS[a]

Betaine	Solvent	Temp., °C.	Time, hr.	% yield VII	VIII	IX	X
I	C_6H_5I	100	150	*b*	100[c]		
		130	20	*b*	54	10	*b*
		150	4	*b*	30	12	15
	Diglyme	162	2	42	20	13	16
	Lactone[d]	204	2	44	6	30	6
II	Triglyme	175	2	72	5	4	*b*
III	Xylene	138	2	33	25	4	*b*
	C_6H_5Br	155	2	29	20	10	*b*
IV	C_6H_5Cl	132	15	63		20	51
	Triglyme	222	0.5	57		30	40
V	C_6H_5Cl	132	15	13	77		
VI	C_6H_5Cl	132	15	17	75		
	Triglyme	222	0.5	34	40	Trace	Trace

[a] Data on betaines I–III from ref. 3. [b] Not determined. [c] In 5% conversion. [d] γ-Butyrolactone.

In contrast, the fact that no 2′,4′-dimethoxyphenyl 2-iodobenzoate was found in the thermal reaction of 2-(2′,4′-dimethoxyphenyl) iodoniobenzoate (IV) indicates that intramolecular nucleophilic substitution was depressed by the electron-donating methoxyl groups.[5,6] The low yield of mesityl 2-iodobenzoate may be due to both steric and electronic effects. Introduction of a cyclohexyl group at the *para* position has little effect on ester formation as compared to the unsubstituted betaine.

Decomposition of betaines I–VI in the presence of 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone, XI)[3,4] gave 1,2,3,4-tetraphenylnaphthalene (XII) in yields of 23–60% (Table II). The formation of benzyne was not repressed by electron-donating substituents on the phenyl group of the betaines, as was shown by the fact that reactions of betaines I–IV with tetracyclone gave comparable yields of 1,2,3,4-tetraphenylnaphthalene. The yield of benzyne from betaines bearing the electron-withdrawing nitro group (V and VI) was lowered by competitive formation of ester.

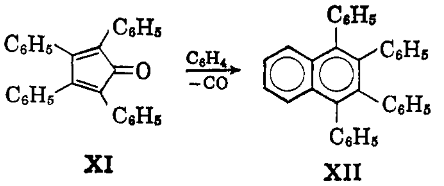


TABLE II

1,2,3,4-TETRAPHENYLNAPHTHALENE FROM THE REACTIONS OF 2-ARYL IODONIOBENZOATES WITH TETRACYCLONE[a]

Betaine	I	II	III	IV	V	VI
% yield	56	55	57	60	23	25

[a] Reactions were run with equivalent amounts of reagent and betaine in γ-butyrolactone at 204° for 15 min.

In summary, it is concluded that the thermal rearrangement of 2-aryl iodoniobenzoates to aryl 2-iodobenzoates proceeds by intramolecular nucleophilic aromatic substitution. The formation of benzyne is af-

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(1) This article is taken from the dissertation of S. J. Huang submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (chemistry), 1964. It is publication XXIII in the series on diaryliodonium salts.

(2) Preceding article in this series: F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **28**, 3417 (1963).

(3) F.M. Beringer and S. J. Huang, *ibid.*, **29**, 445 (1964).

(4) E. LeGoff, *J. Am. Chem. Soc.*, **84**, 3786 (1962).

(5) F. M. Beringer, A. Brierly, M. Drexler, E. M. Gindler, and C. C. Lumpkin, *ibid.*, **75**, 2708 (1953); F. M. Beringer and M. Mausner, *ibid.*, **80**, 4535 (1958).

(6) F. M. Beringer and R. A. Falk, *J. Chem. Soc.*, in press; R. A. Falk, Ph.D. dissertation, Polytechnic Institute of Brooklyn, 1961.

TABLE III

SUBSTITUTED PHENYL 2-IODOBENZOATES

From betaine	Substituents[a]	M.p., °C. Ester	M.p., °C. Phenol[b] (lit.)	Analyses of esters, % Calcd. C	Calcd. H	Found C	Found H
V	3-NO_2	136–138	95 (95[b])	40.25	2.18	40.50	2.35
VI	2-CH_3-5-NO_2	173–174	116–117 (117[d])	43.86	2.61	43.67	2.90

[a] Substituents in phenyl group of ester and in the phenol derived from it. [b] Ref. 8. [c] Ref. 5. [d] Ref. 11.

fected indirectly as ester formation provides a competitive mode of reaction of the betaines.

Experimental[7]

2-Phenyl Iodoniobenzoate (I), 2-Mesityl Iodoniobenzoate (II), and 2-(*p*-Cyclohexylphenyl) Iodoniobenzoate (III).—Betaines I, II, and III were prepared as described in ref. 3.

2-(2′,4′-Dimethoxyphenyl) Iodoniobenzoate (IV).—To a solution held at 0–5° of 26.4 g. (0.1 mole) of 2-iodosobenzoic acid[3] and 20.7 g. (0.15 mole) of *m*-dimethoxybenzene in 100 ml. of acetic anhydride, there was added slowly 10 ml. of trifluoroacetic acid. After the dark green solution had been stirred at room temperature for 24 hr., there was added with stirring 600 ml. of ether. The iodonium salt was collected as tan crystals and stirred vigorously with 200 ml. of 5 *N* sodium hydroxide solution to give a tan precipitate. This was collected, washed with water, and dried to give 31 g. (81 mmoles, 81%) of **2-(2′,4′-dimethoxyphenyl) iodoniobenzoate** (IV). Recrystallization from methanol gave colorless crystals, m.p. 234–235° dec. The infrared spectrum showed a carboxylate group absorption band at 1620 cm.$^{-1}$. The nuclear magnetic resonance spectrum showed ring hydrogen absorption bands at τ 1.30 to 3.31 and methoxyl hydrogen absorption bands at τ 6.09 and 6.18.

Anal. Calcd. for $C_{15}H_{13}IO_4$: C, 46.89; H, 3.38; I, 33.03. Found: C, 46.87; H, 3.33; I, 33.16.

The structure of IV was proved by thermal decomposition, which gave as one product 2,4-dimethoxyiodobenzene,[8] m.p. 40° (from hexane), lit.[9] m.p. 40°.

2-(*m*-Nitrophenyl) Iodoniobenzoate (V).—To a solution of 74.4 g. (0.3 mole) of 2-iodobenzoic acid in 300 ml. of concentrated sulfuric acid at 0–5°, there was added over 1 hr. 81 g. (0.3 mole) of potassium persulfate. After the mixture had been stirred at 0–5° for 1 hr., 49.2 g. (0.4 mole) of nitrobenzene was added, and the mixture was stirred at 100° for 3 hr. The cooled mixture was poured into ice–water, and the unchanged nitrobenzene was removed by extraction with benzene. Addition to the aqueous layer of 100 ml. of saturated potassium iodide solution gave pale yellow crystals of crude 2-carboxy-3′-nitrodiphenyliodonium iodide, which were collected. The iodonium salt was stirred vigorously with 200 ml. of 5 *N* sodium hydroxide solution to give a yellow precipitate. This was collected, washed with water, and dried to give 31 g. (80 mmoles, 28%) of **2-(*m*-nitrophenyl) iodoniobenzoate** (V), m.p. 222–224° dec. Two recrystallizations from ethanol followed by two recrystallizations from chloroform gave colorless crystals, m.p. 229° dec. The infrared spectrum showed a carboxylate group absorption band at 1600 cm.$^{-1}$ and nitro group absorption bands at 1520 and 1340 cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_8INO_4$: C, 40.25; H, 2.18; I, 34.42; N, 3.79. Found: C, 40.59; H, 2.24; I, 34.31; N, 3.83.

The structure of V was proved by thermal decomposition, which gave as one product **m-nitroiodobenzene**,[8] m.p. 36–38° (from hexane), lit.[10] m.p. 38–39°.

2-(2′-Methyl-5′-nitrophenyl) Iodoniobenzoate (VI).—A mixture of 52.8 g. (0.2 mole) of 2-iodosobenzoic acid,[3] 27.4 g. (0.2 mole) of *p*-nitrotoluene, and 300 ml. of concentrated sulfuric acid was stirred at 100° for 2 hr. After cooling, the mixture was poured into ice–water, and the unchanged *p*-nitrotoluene was removed by extraction with benzene. Addition of 100 ml. of saturated potassium iodide solution to the aqueous layer gave pale yellow crystals of 2-carboxy-2′-methyl-5′-nitrodiphenyliodonium iodide, which were collected. The iodonium salt was stirred vigorously with 200 ml. of 5 *N* sodium hydroxide solution to give a yellow precipitate. This was collected, washed with water, and dried to give 30 g. (78 mmoles, 39%) of **2-(2′-methyl-5′-nitrophenyl) iodoniobenzoate** (VI), m.p. 207–209° dec. The infrared spectrum showed a carboxylate group absorption band at 1600 cm.$^{-1}$ and nitro group absorption bands at 1520 and 1340 cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{10}INO_4$: C, 43.86; H, 2.61; I, 33.19; N, 3.66. Found: C, 43.53; H, 2.64; I, 33.30; N, 3.38.

The structure of VI was proved by thermal decomposition, which gave as one product **2-iodo-4-nitrotoluene**,[8] m.p. 53–54° (from hexane), lit.[11] m.p. 54°.

Reactions of 2-Aryl Iodoniobenzoates.—Thermal reactions of 2-aryl iodoniobenzoates and the reactions of 2-aryl iodoniobenzoates with tetracyclone were run and worked up according to the procedures described in ref. 3. The results are listed in Tables I and II. Esters were hydrolyzed with acid or base to the corresponding known phenols and 2-iodobenzoic acid (Table III).

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(7) 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. Nuclear magnetic resonance spectrum was taken on a Varian A-60 high resolution n.m.r. spectrometer. Melting points were taken in capillary tubes and are corrected. Solvents were purified by passage through alumina column and distillation. Reagent grade chemicals were redistilled or recrystallized before used.

(8) The infrared spectrum was identical with that of an authentic sample.

(9) H. Kauffmann and F. Kieser, *Ber.*, **45**, 2333 (1912).

(10) I. R. L. Barker and W. A. Waters, *J. Chem. Soc.*, 150 (1951).

(11) I. Keimatsu and E. Yamazuchi, *J. Pharm. Soc. Japan*, **57**, 992 (1937); *Chem. Abstr.*, **32**, 2519 (1938).

The Infrared Spectra of 1,1-Dinitrocarbanion Salts

LLOYD A. KAPLAN

Organic Chemistry Division,
U. S. Naval Ordnance Laboratory, Silver Spring, Maryland 20910

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Brown[1] has given assignments to the principal infrared absorption bands for the nitro group in various classes of nitro compounds. However, with the exception of the bands at 1151 and 1241 cm.$^{-1}$ reported for the symmetrical and asymmetrical stretching modes, respectively, of the nitro groups in the potassium salt of 1,1-dinitroethane[1] and a report[2] that the anions $H(CH_2)_nC(NO_2)_2^-$, where $n = 0$ to 5 and 9, absorb in the range 1090 to 1157 cm.$^{-1}$ and 1201 to 1251 cm.$^{-1}$ for the symmetrical and asymmetrical stretching modes of the nitro group, there are no assignments given to this functionality in more highly substituted compounds.[3]

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(1) J. F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955).

(2) V. I. Slovetski, S. A. Shevelev, V. I. Erashko, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1126 (1962); 57 (1963).

(3) In one other isolated case [L. W. Kissinger and H. E. Ungnade, *J. Org. Chem.*, **25**, 1471 (1960)], the hydrazine salts of ethyl dinitroacetate and dinitroacetohydrazide are reported to absorb at 1133 and 1269 cm.$^{-1}$ and 1124 and 1259 cm.$^{-1}$, respectively.