form then was added, the aqueous layer was saturated with salt, and the mixture was shaken during addition of potassium hydroxide (4.5 g.) in water. The aqueous layer was extracted six times with chloroform, the extracts being filtered directly into concentrated hydrochloric acid (4.5 ml.) in methanol (55 ml.). Evaporation of the chloroform–methanol–acid mixture below 30° gave an oil, which was dissolved in 2-propanol; the solution was diluted with cyclohexane and scratched. The disulfide **10** separated as hard crystals, 3.9 g. (84%), m.p. 171–172°.

Anal. Calcd. for $C_8H_{20}Cl_2N_2O_2S_2$: C, 30.86; H, 6.48; Cl, 22.78; N, 9.00; S, 20.60; neut. equiv., 311. Found: C, 31.01; H, 6.66; Cl, 22.54; N, 8.82; S, 20.63; neut. equiv., 313 (potentiometric titration of the **10** with alkali showed two distinct end points corresponding to consumption of 1 and then 2 moles of alkali per mole of **10**).

2-Pyridyl 2′-Aminoethyl Disulfide Dihydrochloride (11).—2-Pyridinethiol (11.1 g.)[13] in 40 ml. of alcohol was added to 25.7 g. of the thiolsulfonate **2** in water (30 ml.) and concentrated hydrochloric acid (*ca.* 0.12 mole) with stirring. A small amount of precipitate which separated was dissolved by adding a little more water. After 20 hr. of stirring, the solvent was evaporated, and the residue was dissolved in water. Extraction with chloroform removed 4.4 g. of 2-pyridyl disulfide (infrared spectrum identical with that of authentic 2-pyridyl disulfide). The aqueous solution then was shaken with chloroform while an iced aqueous solution of potassium hydroxide (28 g.) was added. The water layer was extracted twice more with chloroform. Each chloroform layer was immediately extracted with hydrochloric acid (the total amount was 60 ml. of 12 *N*, of which half was used for the first extraction). The combined acid extracts were evaporated to a thick oil, which crystallized completely upon addition of anhydrous ethanol and scratching. After an overnight period at 5°, 15.5 g. of crude **11** was collected. Repeated recrystallizations from absolute alcohol, with use of decolorizing carbon, gave 2-pyridyl 2′-aminoethyl disulfide dihydrochloride (**11**) as colorless prisms, 12.8 g. (82%; conversion, 49%), m.p. 144–145° (sealed capillary); **11** was deliquescent at high relative humidity.

Anal. Calcd. for $C_7H_{12}Cl_2N_2S_2$: C, 32.42; H, 4.66; N, 10.81; S, 24.74. Found: C, 32.27; H, 4.46; N, 10.90; S, 24.74.

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[13] M. A. Phillips and H. Shapiro, *J. Chem. Soc.*, 584 (1942).

Some Anomalous Results in the Bimolecular Displacement Reaction

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Recently[1] a new factor affecting reactivity in the bimolecular nucleophilic displacement reactions was observed by Bunnett.[2,3] Bunnett tentatively identifies this new factor as London interactions between nucleophile and polarizable substituent at or near the reaction site. He concludes that due to London forces there is a lowering of the transition state energy when the transition state structure is such as to bring highly polarizable atoms close to one another with a resultant increase in reaction rate. After allowances for steric and electrical effects, a change to a substituent of higher polarizability will cause more acceleration, or less deceleration, the greater the effective polarizability of the nucleophile.

The *ortho*- and *para*-methyl- and *ortho*- and *para*-bromo-substituted benzyl halides afford an excellent opportunity to observe indications of London forces in rate ratios with minimum considerations for electrical effects. The total polar effects will be nearly identical for the corresponding *para* and *ortho* substituents and will cancel in the ratios, $o\text{-}CH_3/p\text{-}CH_3$ and $o\text{-Br}/p\text{-Br}$, if the susceptibility constants ρ and ρ^* are nearly identical.[4] This has been observed to be generally true.[5] Similar reasoning for minimization of the total polar effects in the benzyl system has been offered by Bunnett.[3] Table II, composed from the kinetic data given in Table I, presents the values for the ratio $k_{o\text{-R}}/k_{p\text{-R}}$ (R = Me and Br) for each of the three nucleophiles. It is apparent that the aforementioned ratio nearly cancels the total polar effects of the substituents (ref. 4).

Table II also presents values for the adjusted rate ratios given by the expression

$$\frac{\left(\dfrac{k_{o-\text{R}}}{k_{p-\text{R}}}\right)_{\text{y}}}{\left(\dfrac{k_{o-\text{R}}}{k_{p-\text{R}}}\right)_{\text{MeO}^-}} \equiv \frac{\left(\dfrac{k_{\text{y}}}{k_{\text{MeO}}}\right)_{o-\text{R}}}{\left(\dfrac{k_{\text{y}}}{k_{\text{MeO}^-}}\right)_{p-\text{R}}} \qquad (1)$$

$$\begin{aligned} \text{y} &= \text{MeO}^-,\ C_6H_5S^-,\ \text{and I}^- \\ \text{R} &= \text{H, Me, and Br} \end{aligned}$$

in which differences in nucleophilicities are cancelled. This expression also cancels conformational differences, since the conformational changes accompanying a change of site, $p \rightarrow o$, for a given substituent should be constant and independent of the attacking reagent. Solvent effects would obviously cancel in the adjusted rate ratios if all the data were available in the same solvent. Since this is not the case, one must consider what change would occur in the value of the ratio

$$\left[\frac{\dfrac{k_{o-\text{R}}}{k_{\text{H}}}}{\dfrac{k_{p-\text{R}}}{k_{\text{H}}}}\right]_{\text{I}^-}$$

with a change of solvent (acetone to methanol). The changes in a given absolute reaction rate which accompany a change in the dipole moment of the solvent are known to be small for this charge type (charged nucleophile with neutral substrate).[6] Since the resultant small changes in absolute reaction rates are incorporated in numerator and denominator of the preceeding ratio, the value of the ratio should remain unchanged. The adjusted rate ratios only should indicate interactions arising between the nucleophile and the *ortho* substituent (London, steric, or other may be significant).

The polarizabilities for the three nucleophiles employed are suggested by the ions OH^-, 1.89; SH^-, 5.28; and I^-, 7.10 (all units $cm.^3 \times 10^{-24}$); the polarizabilities of the *ortho* substituents are H, 0.42; CH_3, 2.19; and Br, 3.34 (units the same as above).[7]

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[1] The work herein was taken in part from the Ph.D. thesis of S. Lowell, Adelphi University, 1963.

[2] J. F. Bunnett, *J. Am. Chem. Soc.*, **79**, 5969 (1957).

[3] J. F. Bunnett and J. D. Reinheimer, *ibid.*, **84**, 3284 (1962).

[4] A plot of $\log (k/k_0)$ *vs.* σ for *p*-substituted benzyl chlorides and a plot of $\log (k/k_0)$ *vs.* σ^* for *o*-substituted benzyl chlorides for I^- in acetone at 20° produces parallel lines for substituents -F, -Cl, -Br, -I, $-NO_2$, and $-CH_3$. The ρ- and ρ^*-values are, therefore, nearly identical. It is interesting to note only the *o*-methyl falls well off the line.

[5] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 649.

[6] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 347–9.

[7] Values taken from, Landolt-Bornstein and J. A. A. Ketelaar, "Chemical Constitution," 2nd Ed., Elsevier Publishing Co., New York, N. Y., 1958, p. 91.

TABLE I

REACTION RATES[a] FOR BENZYL AND SUBSTITUTED BENZYL HALIDES

Reagent and leaving group (X)	Solvent	$C_6H_5CH_2$-X, k	p-$CH_3C_6H_4CH_2$-X, k	p-$BrC_6H_4CH_2$-X, k	o-$CH_3C_6H_4CH_2$-X, k	o-$BrC_6H_4CH_2$-X, k
MeO^-, X = Cl[b]	Methanol	1.31×10^{-5}			3.76×10^{-5}	1.37×10^{-5}
MeO^-, X = Br[c]	Methanol	5.54×10^{-4}	7.33×10^{-4}	7.83×10^{-4}		
$C_6H_5S^-$, X = Cl[b]	Methanol	14.1×10^{-3}			74.2×10^{-3}	40.1×10^{-3}
$C_6H_5S^-$, X = Br[c]	Methanol	1.08	1.62	2.57		
I^-, X = Cl	Acetone	3.35×10^{-4}[d]	5.00×10^{-4}[e]	8.66×10^{-4}[f]	3.37×10^{-3}[c]	1.46×10^{-3}[f]

[a] Rate coefficients in l. mole^{-1} sec.$^{-1}$ at 20°. [b] J. F. Bunnett and J. D. Reinheimer, *J. Am. Chem. Soc.*, **84**, 3284 (1962). [c] G. K. Klopman and R. F. Hudson, *Helv. Chim. Acta*, **44**, 1914 (1961). [d] Average of three constants given by G. M. Bennett and B. Jones [*J. Chem. Soc.*, 1815 (1935)], A. G. Evans and S. D. Hamman [*Trans. Faraday Soc.*, **47**, 25 (1951)], and P. J. C. Fierens, *et al.* [*Helv. Chim. Acta*, **38**, 2009 (1955)]. [e] A. G. Evans and S. D. Hamman, *Trans. Faraday Soc.*, **47**, 25 (1951). [f] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935).

TABLE II

RATE RATIOS OF BENZYL HALIDES WITH VARIOUS NUCLEOPHILES[a,b]

Nucleophile	Solvent	$\frac{k_{o\text{-Br}}}{k_{H}}$	$\frac{k_{o\text{-Me}}}{k_{H}}$	$\frac{k_{p\text{-Br}}}{k_{H}}$	$\frac{k_{p\text{-Me}}}{k_{H}}$	$\frac{k_{o\text{-Br}}}{k_{p\text{-Br}}}$[c]	$\frac{k_{o\text{-Me}}}{k_{p\text{-Me}}}$[c]	$\left(\frac{k_{o\text{-R}}}{k_{p\text{-R}}}\right)_y \Big/ \left(\frac{k_{o\text{-R}}}{k_{p\text{-R}}}\right)_{MeO^-}$		
								-H	-Me	-Br
MeO^-	Methanol	1.05	2.87	1.41	1.32	0.74	2.17	1.00	1.00	1.00
$C_6H_5S^-$	Methanol	2.84	5.26	2.38	1.50	1.19	3.50	1.00	1.60	1.61
I^-	Acetone	4.35	10.00	2.58	1.49	1.68	6.70[d]	1.00	3.11	2.30

[a] Ratios at 20°. [b] It is assumed that the ratio $\frac{p\text{-X-}C_6H_4\text{-}CH_2\text{-Cl}}{C_6H_5CH_2\text{-Cl}}$ is equal to $\frac{p\text{-X-}C_6H_4\text{-}CH_2\text{-Br}}{C_6H_5\text{-}CH_2\text{-Br}}$ for MeO^- and C_6H_5-S^-; the following data is offered as justification: EtO^- at 25° $\frac{p\text{-}CH_3C_6H_4\text{-}CH_2\text{-Cl}/C_6H_5\text{-}CH_2\text{-Cl}}{p\text{-}CH_3\text{-}C_6H_4CH_2\text{-Br}/C_6H_5CH_2\text{-Br}} = \frac{1.57}{1.48}$; the same ratio for I^- at 0° $\frac{1.55}{1.46}$ [data from C. Bevin, E. Hughes, and C. Ingold, *Nature*, **171**, 301 (1953); G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935); A. G. Evans and S. D. Hamman, *Trans. Faraday Soc.*, **47**, 25 (1951); J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 855 (1956)]. [c] Numerators and denominators are relative to benzyl halide. [d] The value of 7.30 was obtained at 0° by J. C. Charlton and E. D. Hughes [*J. Chem. Soc.*, 855 (1956)].

Inspection of the adjusted rate ratios (Table II) show that the thiophenoxide and iodide entries, relative to methoxide, present the trends expected from London interactions when considering only a *given substituent.*[8] However, examination of the hydrogen, methyl, and bromine adjusted rate ratios with a *given nucleophile* does not show the trends expected from London interactions; *i.e.*, nucleophiles of relatively high polarizabilities do not give higher values for the most polarizable substituent (bromo group).

Since the latter observation differs sharply from the expected trends evident in the adjusted rate ratios presented by Bunnett,[3] the following discussion is offered as an explanation for this difference. Bunnett[2] employed the expression

$$\frac{\left(\frac{k_{o\text{-R}}}{k_H}\right)_y}{\left(\frac{k_{o\text{-R}}}{k_H}\right)_{MeO^-}} \equiv \frac{\left(\frac{k_y}{k_{MeO^-}}\right)_{o\text{-R}}}{\left(\frac{k_y}{k_{MeO^-}}\right)_H} \tag{2}$$

R = H, Me, and Br
y = MeO^-, $C_6H_5S^-$, and I^-

for the cancellation of nucleophilicity differences. Although inherent nucleophilic differences are reflected in the ratio $(k_y/k_{MeO^-})_H$, Bunnett assumed that these differences are the same in the ratio $(k_y/k_{MeO^-})_{o\text{-R}}$; in other words, the susceptibility of methoxide to the polar changes H → o-R is the same as the susceptibility of iodide and thiophenoxide given the same polar changes. The apparent justification is that the ρ for the reaction is small ($\rho = +0.78$, I^- in acetone at 20°),[9] and it should not change with different nucleophiles and different solvents (I^- in acetone, $C_6H_5S^-$ and MeO^- in methanol). These assumptions are highly suspect.[10] However, the treatment presented herein more nearly cancels nucleophilicity differences. Inherent nucleophilic differences reflected in $(k_y/k_{MeO^-})_{p\text{-R}}$ are the same in $(k_y/k_{MeO^-})_{o\text{-R}}$ since $\rho \cong \rho^*$ (see ref. 4); in other words, it is the difference in response or susceptibility of methoxide, iodide, and thiophenoxide to a much smaller electrical difference, p-R → o-R. Therefore, the division (eq. 1) should more nearly cancel nucleophilicity differences.

The treatment presented and that of Bunnett[3] yield the expected trends *only* when considering a *given substituent* with nucleophiles of increasing polarizabilities, $MeO^- \rightarrow C_6H_5S^- \rightarrow I^-$ (Table II). These trends are still manifest in view of a possible increasing adverse steric effect with the three nucleophiles (see ref. 8). However, the results for a given nucleophile with *ortho* substituents of increasing polarizabilities (H → Me → Br) are anomalous. It is, therefore, apparent that, if dispersion forces are obtained in the anomalous results, some offsetting or adverse factor(s) must be considered. Possible steric dissimilarities (Me and Br), variation of distance between a given nucleophile and the *ortho* substituents,[11] conformational differences, or a combination of the three may account for the anomalous behavior. Unpublished results from this laboratory indicate that the different inductive field

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[8] These trends are also consistent with a decreasing steric interaction between the nucleophiles, MeO^-, $C_6H_5S^-$, and I^-, and the given *ortho* substituent, since highly polarizable nucleophiles can easily distort their bonding electrons without bringing the rest of the molecule close enough to cause excessive repulsive forces [see R. G. Pearson, *et al.*, *J. Am. Chem. Soc.*, **74**, 5131 (1953); R. G. Pearson and J. O. Edwards, *ibid.*, **84**, 16 (1962)].

[9] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 190.

[10] Ref. 5, p. 571, 572; H. H. Jaffe, *Chem. Rev.*, **53**, 217 (1953).

[11] The benzene carbon to methyl carbon bond distance is 1.51 Å.; the benzene carbon to bromine bond distance 1.85 Å. Since dispersion forces vary inversely with the sixth power of the distance, this may be an important consideration.

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]

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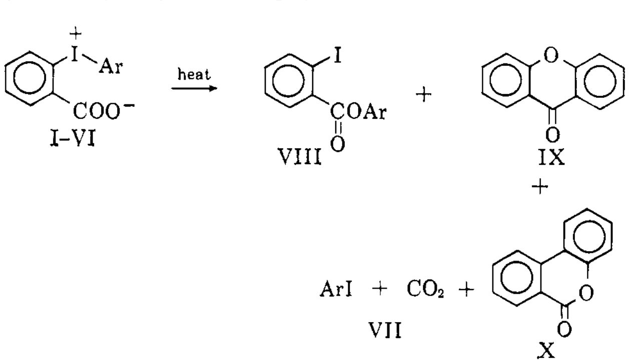
A previous article[3] reported that, on heating, 2-aryl iodoniobenzoates I–III rearrange in part to aryl 2-iodobenzoates (VIII). A competitive reaction, favored at higher temperatures, is cleavage to aryl iodides (VII), carbon dioxide, benzyne,[3,4] and perhaps other reactive intermediates.[3] In the 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

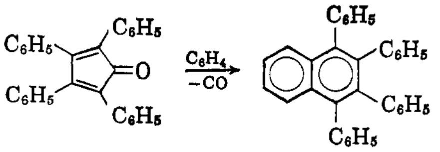
PRODUCTS FROM 2-ARYL IODONIOBENZOATES ON HEATING IN THE ABSENCE OF BENZYNE-TRAPPING REAGENTS[a]

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.



XI **XII**

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.