sulfate was added, and stirring was continued for 1 h, at which time no bromine was noted in the mixture and a thick yellow suspension was noted. The reaction mixture was poured into 75 mL of cold water and the flask was washed with 15 mL of water. Diethyl ether (100 mL) was added, the resulting two-phase suspension was filtered through a sintered glass funnel to remove silver salts, and the resulting mixture was subjected to a normal workup. Removal of the ether under vacuum left a viscous liquid which was distilled at reduced pressure: bp 119–124 °C (0.6 mm); yield, 4.50 g (66%). The infrared and NMR spectra of this product were virtually identical with those of authentic diethyl *m*-bromophenylphosphonate. However, analysis by means of a Finnigan Model 4000 gas–liquid chromatograph interfaced with a mass spectrometer showed the sample to be contaminated with about 5% diethyl phenylphosphonate and with about 5% of a substance of long retention time with MS characteristic of a dibromo derivative thereof.

Reaction of Iodobenzene with Sodium Diethyl Phosphite and Iodine. Dry ammonia (50 mL) was condensed in a 250-mL, three-neck, round-bottom flask equipped with a polyethylene stir bar and dry ice condenser and under a nitrogen atmosphere. Sodium metal (457 mg, 19.89 mmol) was added to the liquid ammonia. The mixture was stirred and titrated with diethyl phosphonate until no color remained. Then 942 mg (4.62 mmol) of iodobenzene was added. The entire reaction assembly including flask and condenser was covered with aluminum foil to keep light out.

In a vial, 258 mg (1.02 mmol) of iodine was placed and 10 mL of dry tetrahydrofuran (freshly distilled from $LiAlH_4$) was added. The vial was equipped with a stir bar and the solution was stirred until the iodine dissolved. This solution was drawn into a syringe covered with aluminum foil and added dropwise to the stirred liquid ammonia solution. After the addition was complete, the mixture was stirred 3 min and then quenched with 2.1 g of NH_4NO_3 and 50 mL of cold diethyl ether. The aluminum foil was removed and the ammonia was allowed to evaporate. The resulting mixture was subjected to normal workup. GLC analysis showed a 92% recovery of iodobenzene and no trace of diethyl phenylphosphonate.

Reaction of Iodobenzene with Diethyl Phosphonate and Di-*tert*-butyl Peroxide. Iodobenzene (4.08 g, 2.24 mL, 0.02 mol) and diethyl phosphonate (3.16 g, 2.95 mL, 0.0229 mol) were placed in a 25-mL, round-bottom flask equipped with a stir bar and condenser and under a nitrogen atmosphere, Then 1.46 g (1.84 mL, 0.01 mol) of di-*tert*-butyl peroxide was added. The mixture was gently refluxed (at about 111 °C) for 5 h. The reaction mixture was cooled; diethyl ether and water were added and subjected to normal workup. The ether extract was washed with aqueous ferrous ammonium sulfate solution to remove traces of peroxides. GLC analysis of the ether solution showed large quantities of iodobenzene but no trace of diethyl phenylphosphonate.

Solvent Effects. In each of a series of experiments, about 5 mmol of **1a** was allowed to react with about 20 mmol of $(EtO)_2PO^-Na^+$ in 50 mL of ammonia with irradiation by "350 nm" lamps. Three experiments in which 20% tetrahydrofuran was present as cosolvent gave, in irradiation times of 20, 40, and 120 min, respectively, nil, 10, and 15% yields of **3**, with a corresponding amount of unreacted **1a** being present. With 20% dimethyl sulfoxide as cosolvent, a 14% yield of **3** was formed during 20-min irradiation.

Registry No.—**1a**, 108-36-1; **1b**, 591-18-4; **2**, 35125-65-6; **3**, 25944-79-0; sodium diethyl phosphite, 2303-76-6; *m*-bromophenylphosphonic acid, 6959-02-0; *m*-bromobenzenediazonium tetrafluoroborate, 500-25-4; *m*-bromophenylphosphonic dichloride, 65442-15-1; diethyl phenylphosphonate, 1754-49-0; iodobenzene, 591-50-4.

References and Notes

(1) Research supported in part by the National Science Foundation.
(2) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3612 (1974).
(3) J. F. Bunnett, R. G. Scamehorn, and R. P. Traber, *J. Org. Chem.*, **41**, 3677 (1976).
(4) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3611 (1974).
(5) A preliminary experiment mentioned in footnote *b*, Table I, indicated extremely low reactivity for **2**. We suspect that an adventitious impurity may have inhibited that reaction.
(6) A preliminary experiment mentioned in footnote *c*, Table I, indicated much lower reactivity for **2**. This experiment was performed about the same time as that mentioned in footnote *b*, and again interference by an adventitious impurity is suspected.
(7) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951).
(8) J. R. Johnson and C. G. Gauerke, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1941, p 123.
(9) D. H. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 573 (1950).
(10) P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution", Butterworths, London, 1959, p 110.
(11) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463, 7464 (1970).
(12) S. Hoz and J. F. Bunnett, *J. Am. Chem. Soc.*, **99**, 4690 (1977).
(13) M. Anbar and E. J. Hart, *J. Am. Chem. Soc.*, **86**, 5633 (1964).
(14) J. F. Bunnett and R. P. Traber, *J. Org. Chem.*, preceding paper in this issue.
(15) L. Benati, C. M. Camaggi, and G. Zanardi, *J. Chem. Soc., Perkin Trans. 1*, 2817 (1972); J. R. Shelton and A. L. Lipman, Jr., *J. Org. Chem.*, **39**, 2386 (1974); M. Fiorentino, L. Testaferri, M. Tiecco, and L. Troisi, *Chem. Commun.*, 316, 317 (1977); *J. Chem. Soc., Perkin Trans. 2*, 87 (1977).
(16) E. F. Jason and E. K. Fields, *J. Org. Chem.*, **27**, 1402 (1962).
(17) J. M. Denham and R. K. Ingham, *J. Org. Chem.*, **23**, 1298 (1958).

Effect of Substrate Concentration on Partitioning between Mono- and Disubstitution in Photostimulated Reactions of *m*-Haloiodobenzenes with Diethyl Phosphite Ion[1]

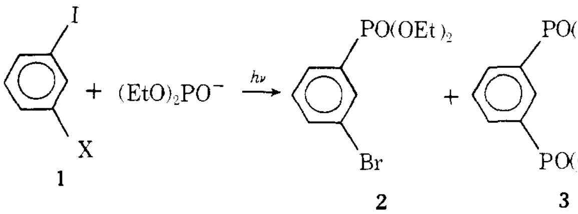
J. F. Bunnett* and Sheldon J. Shafer

University of California, Santa Cruz, California 95064

Received August 16, 1977

The reactions of *m*-bromoiodobenzene (**1a**) and *m*-chloroiodobenzene (**1b**) with diethyl phosphite ion give mixtures of a monosubstitution product, in which only iodine is replaced, and a disubstitution product, in which both halogens are replaced. These products are, respectively, a diethyl *m*-halophenylphosphonate and tetraethyl *m*-phenylenebisphosphonate. Mainly monosubstitution occurs with **1b** and mainly disubstitution with **1a**. As expected from the $S_{RN}1$ radical chain mechanism, the ratio of monosubstitution to disubstitution product from either substrate increases linearly with increasing substrate concentration.

m-Bromoiodobenzene (**1a**) and *m*-chloroiodobenzene (**1b**) react rapidly with diethyl phosphite ion in liquid ammonia under irradiation to form one or both of two products, one representing replacement only of iodine and the other representing replacement of both halogens by the nucleophile;[2–5] see eq 1. These products are, respectively, a diethyl *m*-halophenylphosphonate (**2a** or **2b**) and tetraethyl *m*-phenylenebisphosphonate (**3**).



(1)

1 2 3

a, X = Br; b, X = Cl

Table I. Photostimulated Reactions of *m*-Haloiodobenzenes with Diethyl Phosphite Ion in Liquid Ammonia

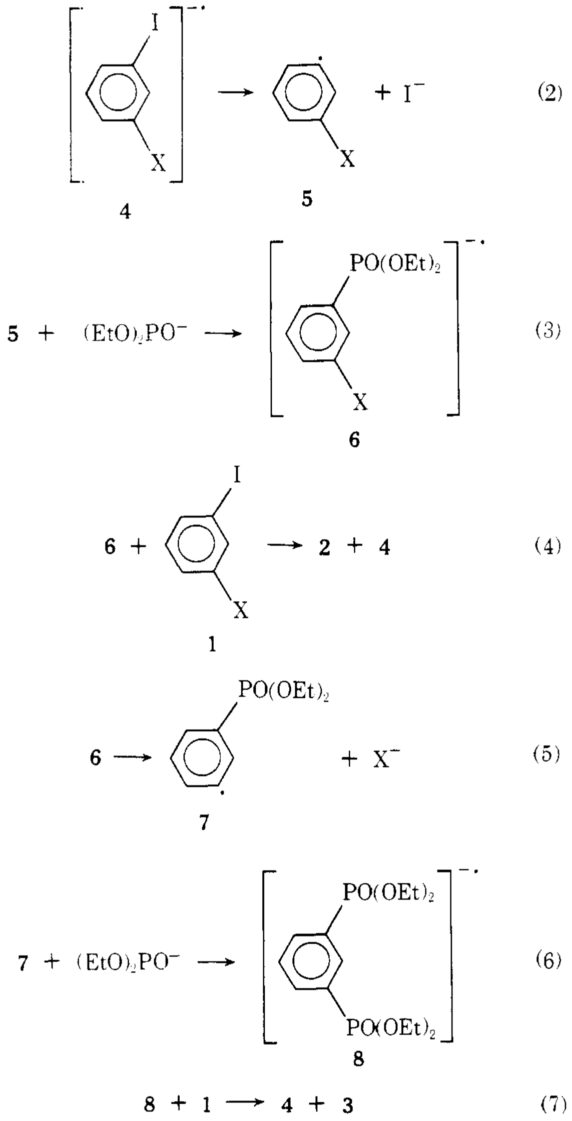
Expt. no.	Substrate	[Substrate], M	Irradiation time, min	Unreacted subtrate, %	Product yields, %	
					2^a	3
1^b	**1a**	0.101	7	28	8	56
2		0.052	5	22	6	58
3		0.027	2	31	3	55
4		0.014	1.0	39	1.5	58
5		0.007	0.8	26	1.0	63
6		0.007	0.7	63	0.6	30
7		0.007	1.0	11	*c*	83
8		0.051	7	14	6	59
9		0.026	7	0	2	96
10	**1b**	0.100	10	7	96	0
11		0.026	2.5	2	91	3
12		0.012	1.2	2	86	7
13		0.008	0.9	2	80	13

[a] Product 2 is **2a** from **1a** or **2b** from **1b**. [b] From ref 5. [c] Present in trace amount but not measured.

From **1a**, the chief product is bisphosphonate ester **3** in about 90% yield, monophosphonate ester **2a** having been reported only to the extent of about 8%. However, from **1b** the principal product is monophosphonate ester **2b** with bisphosphonate ester **3** having been sometimes observed[2] and sometimes not.[3]

These reactions are thought to occur by the $S_{RN}1$ mechanism.[6] This is a radical chain mechanism. The propagation steps relevant to the present reactions are presented in Scheme I. According to this mechanism, the formation of monophosphonate ester **2a** or **2b** is attributed to the cycle of steps 2–4, while the formation of bisphosphonate ester **3** is ascribed to the repeating sequence of steps 2, 3, and 5–7.

Scheme I



In terms of Scheme I, the formation mainly of disubstitution product **3** from *m*-bromoiodobenzene (**1a**) but mainly of monosubstitution product **2b** from *m*-chloroiodobenzene (**1b**) is explicable mainly in terms of the effect of C–X bond strength on the frangibility of radical anion **6** in step 5. Electrochemical studies have shown that the radical anions of aryl bromides fragment, into halide ion and aryl radical, much faster than do the radical anions of aryl chlorides.[7] Fragmentation step 5 is much faster when X is bromine than chlorine, and, therefore, the extended propagation cycle leading from **1a** to **3** is favored over the shorter cycle that leads to **2**.

Strictly speaking, however, it is the relative rates of steps 4 and 5 that determine the relative amounts of mono- and disubstitution products, according to the mechanism of Scheme I. Whereas step 5 is unimolecular, step 4 is bimolecular, for it involves electron transfer from radical anion **6** to substrate molecule. This mechanism would therefore call for the partitioning between mono- and disubstitution products to depend on the concentration of substrate, with a larger percentage of monosubstitution product being obtained at higher substrate concentrations.

We now report an experimental test of this expectation. We have examined the effect of substrate concentration on the partitioning between products for reactions both of **1a** and of **1b**.

Results

Our principal experimental results are summarized in Table I. Experiments 1–5, inclusive, constitute a rational set concerning *m*-bromoiodobenzene (**1a**). The yield of monosubstitution product **2a** drops steadily as the substrate concentration is diminished. Experiments 10–13, inclusive, constitute a corresponding set concerning *m*-chloroiodobenzene (**1b**). Again the yield of monosubstitution product **2b** decreases as the substrate concentration is decreased. There is a corresponding increase in the yield of disubstitution product **3**.

The photostimulated reaction of iodobenzene with potassium diethyl phosphite in dimethyl sulfoxide solution, to form diethyl phenylphosphonate, has been found to proceed at a rate independent of iodobenzene concentration but dependent on about the 0.84 power of light intensity.[8] Those observations were made under conditions such that nearly every incident photon was absorbed. The present reaction mixtures were probably similarly opaque. If a similar rate law obtains for the reactions of eq 1, a shorter time should be necessary at lower substrate concentration to realize a given percentage of conversion of reactants to products.

Because **2a** is known to be capable of reacting under the conditions of these experiments to form **3**, albeit slower than **1a**, it was deemed desirable to terminate each experiment with **1a** at a time at which a substantial amount of **1a** remained unreacted so that conversion of **2a** to **3** could be minimized. It is for this reason that a shorter irradiation time was used with each decrease in substrate concentration, both for the set of experiments 1–5 and for the set of experiments 10–13. Within the former set, in each case about 30% of the substrate remained unreacted.

These concerns were less pressing for reactions of **1b**, for we found that, although **2b** does react with diethyl phosphite ion under photostimulation to form **3**, the reaction is very slow and would have made negligible progress during the very short reaction times involved in our principal experiments. Accordingly, the fact that reactions of **1b** were carried nearly to completion is no cause for worry. Actually, the employment of ever shorter irradiation times within experiments 10–13 was probably unnecessary.

That these concerns were justified in respect to reactions of **1a** is shown by comparison of experiment 9 with experiment 3. The product ratio, **3/2a**, is about 18 when the reaction is conducted only to the extent of about 69% but climbs to 48 when the reaction is conducted for 3.5 times as long, with complete consumption of the substrate. It is probable that in experiment 9 there was some transformation of **2a** to **3** in the later minutes of irradiation.

Experiments 5–7 were conducted with nearly identical reactant concentrations and with irradiation times, respectively, of 48, 40, and 60 s. The percentage of conversion of **1a** to products varies considerably within this set of experiments and is not uniformly related to the measured irradiation times. We suspect that this minor irregularity is to be attributed to short induction periods stemming from the presence of varying amounts of adventitious impurities in ostensibly identical reaction mixtures.

It may be noted in Table I that **1b** appears to be somewhat more reactive than **1a**. Compare especially experiment 11 with experiment 3 or experiment 12 with experiment 4.

Discussion

The $S_{RN}1$ propagation mechanism of Scheme I provides, as we have seen,[5] a straightforward rationalization of the facts that **2a** is not an intermediate on the main route from **1a** to **3** and that **1a** gives mainly disubstitution product **3** while **1b** gives mainly monosubstitution product **2b**.

However, the mechanism of Scheme I also *requires* that the partitioning of reaction between mono- and disubstitution products be related to substrate concentration in the sense that relatively more monosubstitution product should be formed at higher concentrations of substrate. Our results show that requirement to be satisfied both for reactions of **1a** and of **1b**.

Furthermore, the mechanism of Scheme I calls for a quantitative relationship of product ratio to substrate concentration. Inasmuch as product partitioning should be decided by competition between steps 4 and 5

$$d[2]/d[3] = k_4[6][1]/k_5[6] = (k_4/k_5)[1] \qquad (8)$$

Integrating

$$[2]_t/[3]_t = (k_4/k_5) \int [1] \qquad (9)$$

Since substrate concentration did not remain constant within any experiment, one must consider the shape of the integral, $\int$ [1], in eq 9. Providing that each experiment is carried to the same fraction of completion, each integral will have a similar relationship to the original concentration of substrate **1a** or **1b**, and therefore the ratio of mono- to disubstitution product within any such set of experiments should be approximately linearly related to initial substrate concentration.

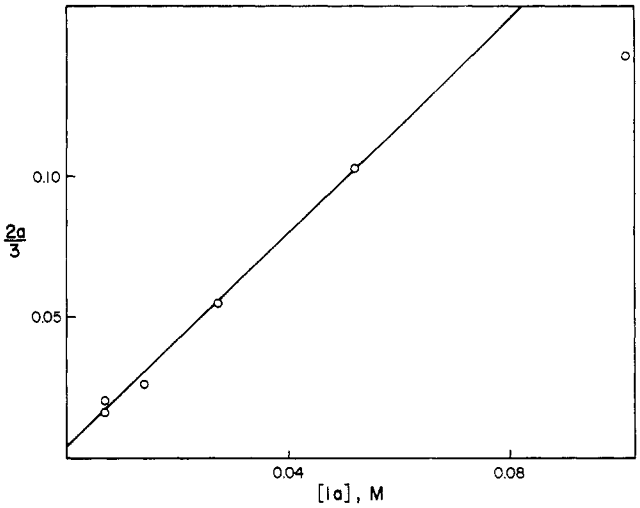


Figure 1. The monosubstitution/disubstitution product ratio (**2a/3**), as a function of **1a** concentration, for reactions of *m*-bromoiodobenzene with diethyl phosphite ion. Data of experiments 1–6, inclusive.

In Figure 1 we present a plot of data from experiments 1–6, inclusive, the product ratio, **2a/3**, against **1a** concentration. The expected linearity is observed except for the point for experiment 1. A similar plot for the data of experiments 11–13 is also linear.

The fact that partitioning between mono- and disubstitution products conforms both qualitatively and quantitatively to the requirements of the mechanism of Scheme I provides further strong support for the $S_{RN}1$ mechanism.

Experimental Section

The experiments summarized in Table I were conducted according to the procedures used in the principal experiments of an accompanying report.[5] The concentration of $(EtO)_2PO^-Na^+$ was throughout about 0.42 M. In a further experiment, 4.96 mmol of diethyl *m*-chlorophenylphosphonate (**2b**) and 21.5 mmol of sodium diethyl phosphite in 50 mL of ammonia under N_2 were irradiated in the Rayonet reactor with "350 nm" lamps for 60 min; by GLC it was determined that 17% of **3** had been formed and that 83% of the **2b** remained unreacted.

Registry No.—**1a**, 591-18-4; **1b**, 625-99-0; **2a**, 35125-65-5; **2b**, 23415-71-6; **3**, 25944-79-0; $(EtO)_2PO^-Na^+$, 2303-76-6.

References and Notes

(1) Research supported in part by the National Science Foundation.
(2) J. F. Bunnett and X. Creary, *J. Org. Chem.*, **39**, 3612 (1974).
(3) J. F. Bunnett and R. P. Traber, *J. Org. Chem.*, first of three papers in this issue.
(4) J. F. Bunnett, R. G. Scamehorn, and R. P. Traber, *J. Org. Chem.*, **41**, 3677 (1976).
(5) J. F. Bunnett and S. J. Shafer, *J. Org. Chem.*, preceding paper in this issue.
(6) J. K. Kim and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 7463 (1970).
(7) L. Nadjo and J. M. Savéant, *J. Electroanal. Chem.*, **30**, 41 (1971); K. Alwair and J. Grimshaw, *J. Chem. Soc., Perkin Trans. 2*, 1150, 1811 (1973); J. Grimshaw and J. Trocha-Grimshaw, *J. Electroanal. Chem.*, **56**, 443 (1974).
(8) S. Hoz and J. F. Bunnett, *J. Am. Chem. Soc.*, **99**, 4690 (1977).
(9) The substantial linearity of five points in Figure 1 is more remarkable than the deviation of one. Experimental uncertainties include the exact volume of solvent employed as well as the usual amount of random error in GLC analysis.