Role of Monosubstitution Product in the Reactions of *m*-Dihalobenzenes with Diethyl Phosphite Ion to Form Tetraethyl *m*-Phenylenebisphosphonate. Strong Evidence of Mechanism from Simple Observations[1]

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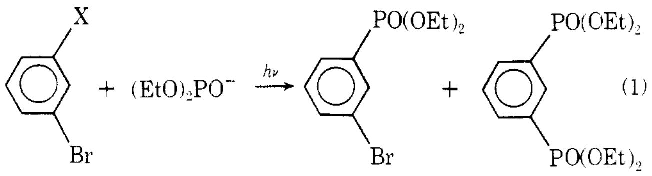
Interrupted photostimulated reaction of diethyl phosphite ion with *m*-bromoiodobenzene (**1b**) in liquid ammonia gives much tetraethyl *m*-phenylenebisphosphonate (**3**), much unreacted **1b**, and a little diethyl *m*-bromophenylphosphonate (**2**). Inasmuch as **2** is less reactive than **1b** with diethyl phosphite ion under these conditions, **2** cannot be an intermediate on the main route from **1b** to **3**. This result is compatible with the $S_{RN}1$ mechanism but excludes all conceivable alternative mechanisms. Interrupted reaction with *m*-dibromobenzene (**1a**) affords a similar product mixture but, since **2** is more reactive than **1a** under the more strenuous conditions necessary to get **1a** to react, the failure of **2** to appear as a product of interrupted reaction is of uncertain significance. Experiments specifically to probe one alternative radical chain mechanism offer no support for it.

Under photostimulation, diethyl phosphite ion reacts readily[2] with iodobenzene and more slowly with bromobenzene to form diethyl phenylphosphonate, $C_6H_5PO(OEt)_2$. The same reagent converts *m*-bromoiodobenzene mainly into tetraethyl *m*-phenylenebisphosphonate (3) (87% yield), only a small amount of monosubstitution product 2 being formed.[2] Titration of samples taken in the course of a reaction showed that the ratio of iodide ion to bromide ion release was virtually constant throughout the process and, thus, that there was no accumulation of 2 at early stages of the reaction.[3]



1a, X = Br
b, X = I

2

3

Analogous behavior has been observed for reactions of certain dihalobenzenes with thiophenoxide ion.[4] In the case of the thiophenoxide reaction with *m*-chloroiodobenzene, not only is the disubstitution product, *m*-$C_6H_4(SPh)_2$, formed preferentially to *m*-chlorophenyl phenyl sulfide, but the latter reacts demonstrably slower than *m*-chloroiodobenzene with thiophenoxide ion. The conclusion that *m*-chlorophenyl phenyl sulfide is not an intermediate on the main route to the disubstitution product is of great significance in regard to reaction mechanism.[4]

We now report an inquiry into the role that 2 may play as an intermediate or by-product in the photostimulated conversion of 1a and 1b into 3. We have also performed some other experiments concerning the mechanism of reaction of aryl halides with diethyl phosphite ion.

Results

Reactions of *m*-bromoiodobenzene (1b). In the presence of a fourfold excess of sodium diethyl phosphite under irradiation at about 350 nm for 7 min, **1b** reacted incompletely, forming **2** in about 7% yield and **3** in about 60% yield, with about 28% of unreacted **1b** remaining (experiments 1 and 2, Table I). Under the same conditions, **2** reacted only to the extent of 40% (experiment 3), and thus **2** is less reactive than **1b**.

The lesser reactivity of **2** is demonstrated also by the behavior of mixtures of **1b** and **2** under conditions of the same type (experiments 4 and 5). While all or nearly all of the **1b** reacts, virtually all of the **2** introduced is recovered as such, and there is extensive formation of **3**. Undoubtedly some of the **2** was a minor by-product from the reaction of **1b**, but nevertheless experiments 4 and 5 show that while **1b** reacts extensively **2** reacts only to a small extent.[5]

There was negligible reaction of **1b** with $(EtO)_2PO^-Na^+$ in the dark (experiments 16 and 17).

These experiments constitute compelling evidence that **2** is not an intermediate except perhaps to a minor extent in the transformation of **1b** into **3**. They do not exclude the possibility of an alternative stepwise reaction involving first the replacement of bromine to form diethyl *m*-iodophenylphosphonate and then the replacement of iodine, but strong arguments against such a possibility can be marshaled on other grounds.

Reactions of *m*-Dibromobenzene (1a). If both halogens in a *m*-dihalobenzene are the same, uncertainties as to which would be replaced first in a stepwise mechanism disappear.

1a is much less reactive than **1b** with diethyl phosphite ion. Compare experiment 6 with experiment 1 or 2. Under identical conditions, **1a** reacts (forming **3** exclusively) only to the extent of 15% while **1b** is about 70% consumed. In no case did the reaction of **1a** with sodium diethyl phosphite form any detectable amount of **2**.

In experiments 7 and 8, the reactivities of **1a** and **2**, separately, are compared under identical conditions. Whereas **1a** reacts only to the extent of about 30%, **2** is almost wholly consumed.[6] In experiments 9 and 10, which are nearly identical in design, the reactivities of **1a** and **2**, admixed, are compared. In both experiments there was almost total reaction by **2** and scarcely any consumption of **1a**.

The comparative reactivities of **1a** and **2** were also examined under irradiation with lamps that emit maximally at 300 nm. Experiments 12 and 13 show that, separately, **2** is more reactive than **1a**. Experiment 14 shows that, admixed, **2** is again more reactive than **1a**. Experiment 15 demonstrates that extended irradiation of **2** in the absence of the nucleophile causes little change.

It is thus evident that, for reactions of **1a** with diethyl phosphite ion, the monosubstitution product **2** is *more* reactive than the original substrate. One cannot tell from the present data whether or not the absence of **2** as a detectable product from the reaction of **1a** is due to its never being formed or to its rapid transformation, after being formed, to disubstitution product **3**. A more detailed kinetic and product study might, however, enable the question to be answered definitively.

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Table I. Photostimulated Reactions of *m*-Dihalobenzenes with Sodium Diethyl Phosphite in Liquid Ammonia

Expt no.	Dihalobenzene, mmol	**2**, mmol	$(EtO)_2PO^-Na^+$, mmol	λ, nm[a]	Irradiation time, min	Materials present after reaction, mmol: Dihalobenzene	**2**	**3**
1	**1b**, 5.1		19.4	350	7	1.4	0.3	3.2
2	**1b**, 5.0		22.0	350	7	1.4	0.4	2.8
3[b]		4.8	22.1	350	7		3.0	1.9
4	**1b**, 3.1	2.4	22.0	350	7	0.12	2.7	2.5
5	**1b**, 2.6	2.5	21.3	350	7	0	2.4	2.2
6	**1a**, 5.3		21.0	350	7	4.5	0	0.8
7	**1a**, 5.1		21.9	350	20	3.6	0	1.6
8[c]		4.8	21.8	350	20		0.1	4.3
9	**1a**, 2.7	2.4	22.3	350	20	2.7	0.5	1.9
10	**1a**, 2.5	2.4	22.2	350	20	2.5	0	2.2
11	**1a**, 5.2		21.9	350	120	1.3	0	3.6
12	**1a**, 5.0		20.7	300	20	2.1	0	2.6
13		4.7	21.7	300	20		*d*	4.7
14	**1a**, 2.5	2.4	22.0	300	20	2.1	0	2.9
15		4.6	Nil	300	120		4.3	
16[e]	**1b**, 4.6		20.3	Dark	7.5[f]		*g*	*g*
17[e]	**1b**, 4.6		20.2	Dark	122[f]		*h*	*j*

[a] Broad-bd radiation from fluorescent lamps rated emit maximally at the wavelength listed. [b] In a preliminary experiment, 4.6 mmol of **2** and 20.9 mmol of $(EtO)_2PONa$ scarcely reacted in 7 min, and 94% of unreacted **2** was determined. [c] In a preliminary experiment, 4.9 mmol of **2** and 22.1 mmol of $(EtO)_2PONa$ during 20-min irradiation afforded 9% of **3**, and 92% of unreacted **2** was determined. [d] A trace at the appropriate GLC retention time. [e] Experiment by Raymond R. Bard. [f] Time in dark. [g] No detectable formation of halide ion. [h] Iodide ion (1.9%) and bromide ion (1.4%) were determined as products.

Comparison of experiments 7 and 12, Table I, suggests that light of shorter wavelength is more effective for stimulation of the reaction of **1a** with diethyl phosphite ion. However, inasmuch as both sets of fluorescent lamps furnish broad-band radiation and no actinometry was performed, these experiments cannot be regarded as an adequate test of the dependence of quantum yield on wavelength.

Probes of an Alternative Mechanism. For reasons discussed below, we exposed iodobenzene to two sets of conditions under which we thought that diethyl phosphonyl radicals, $(EtO)_2PO\cdot$, might exist transiently. In one experiment, a mixture of iodobenzene, diethyl phosphonate [$(EtO)_2PHO$], and di-*tert*-butyl peroxide was heated at reflux for 5 h. A large amount of unreacted iodobenzene was found by GLC analysis, but no diethyl phenylphosphonate could be detected. In the other, a solution of diiodine, I_2, in tetrahydrofuran was added slowly with stirring to a solution of iodobenzene and sodium diethyl phosphite in liquid ammonia carefully shielded from external illumination, and the solution was stirred a few minutes longer. Again there was extensive recovery (94%) of iodobenzene, and no trace of diethyl phenylphosphonate could be found.

Preparation of Diethyl *m*-Bromophenylphosphonate (2). Because little or no **2** is formed in the reactions of **1a** and **1b** with diethyl phosphite ion, we were obliged to use another approach in order to obtain quantities sufficient for our studies. The Doak–Freedman synthesis[7] of *m*-bromophenylphosphonic acid (from *m*-bromobenzenediazonium fluoroborate and PCl_3 in ethyl acetate with catalysis by CuBr) served us dependably although the yield was modest (32%). In some cases we experienced difficulty in converting the acid to the acid chloride, m-$BrC_6H_4POCl_2$. For reasons not well understood, successful conversion to the acid chloride seemed to depend on fastidious recrystallization of the phosphonic acid. Transformation of the acid chloride to **2** was straightforward. The **2** used in the studies reported above was prepared by this route.

Despite its serviceability, the route described was somewhat objectionable because of the difficulties mentioned, the many steps involved, and the low overall yield. We therefore attempted the direct bromination of diethyl phenylphosphonate, a reaction of which we found no mention in the literature. Attempted bromination by means of the *Organic Syntheses* procedure for bromination of nitrobenzene[8] afforded no bromination product. The method of Derbyshire and Waters,[9,10] which employs bromine and silver sulfate in concentrated sulfuric acid, was, however, successful, giving **2** in 66% yield in a short reaction time. The **2** so obtained was, however, not pure. GLC analysis showed the presence of some unbrominated diethyl phenylphosphonate and of some dibrominated material, each to the extent of about 5%. In working with small quantities, we were able to effect a partial separation by distillation, and we believe that a larger quantity could be purified successfully by this means.

Solvent Effects. A problem with use of liquid ammonia as a solvent for $S_{RN}1$ reactions is the limited solubility of some substrates in it. We did a few experiments concerning photostimulated reaction of **1a** with sodium diethyl phosphite in ammonia containing 20% of tetrahydrofuran or dimethyl sulfoxide as cosolvent. Whereas a 32% yield of **3** was obtained in neat ammonia (experiment 7, Table I), three experiments with tetrahydrofuran cosolvent for the same or longer irradiation time gave **3** in yields ranging from 0 to 15%, and one experiment with dimethyl sulfoxide cosolvent gave **3** in 14% yield.

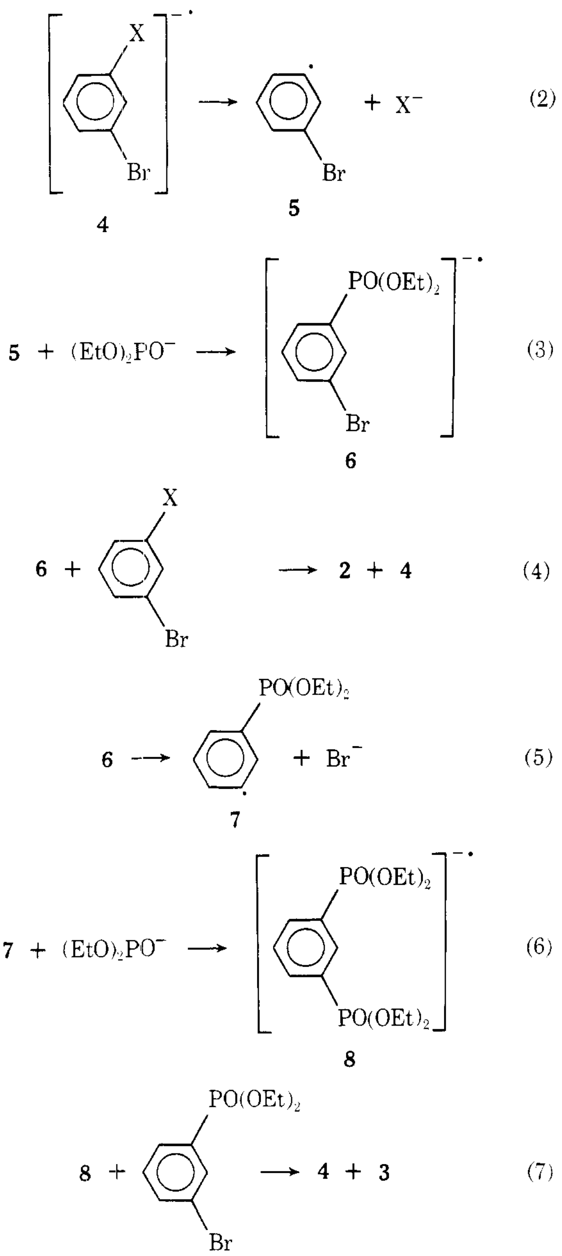
Discussion

We have observed that both **1a** and **1b**, in interrupted photostimulated reactions with excess diethyl phosphite ion according to eq 1, give mainly or entirely disubstitution product **3** with little or none of monosubstitution product **2**, even as substantial amounts of **1a** and **1b** remain unreacted.

In the case of **1b**, we have shown that **1b** reacts with diethyl phosphite ion faster than does **2**. The fact that little **2** is formed compels the conclusion that **2** is not an intermediate on the main route from **1b** to **3**.

In the case of **1a**, we have found that **2** does react faster than **1a**. That experiment is therefore inconclusive as to whether or not **2** is an intermediate on the pathway from **1a** to **3**. Because of the close analogy between **1a** and **1b** and because of

Scheme I

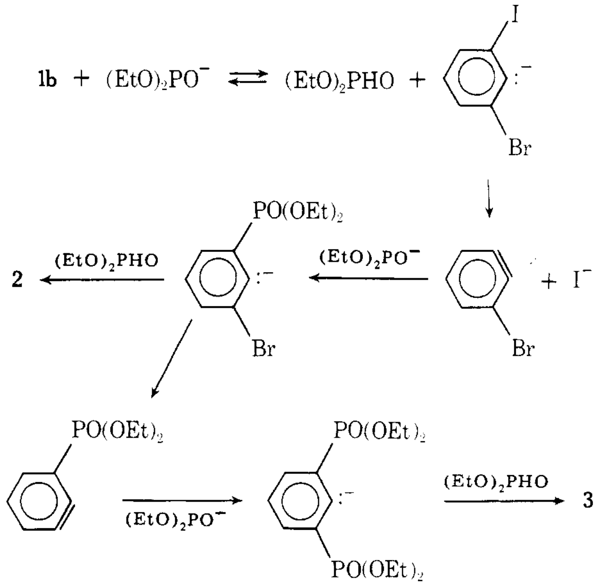


mechanistic considerations discussed below, we believe that **2** is not an intermediate in this reaction either.

These reactions are presumed to occur by the $S_{RN}1$ mechanism.[11] When that mechanism is applied straightforwardly to the present case, two alternative propagation cycles result, as sketched in Scheme I. One cycle, which leads to monosubstitution product **2**, comprises steps 2–4. The other, leading to disubstitution product **3**, consists of steps 2, 3, and 5–7. This radical chain mechanism must, of course, also involve initiation and termination steps, but they are of little immediate interest. Other work[12] gives some insight into what their nature may be.

The mechanism of Scheme I accommodates naturally the experimental conclusion that **2** is not an intermediate on the main route from **1b** to **3**. The intermediate which represents replacement of iodine but not of bromine is not **2** but **6**, which is the radical anion of **2**. Scheme I provides two pathways for **6** to tread, namely, electron transfer to **1b** (step 4) with formation of **2** and fragmentation to expel bromide ion (step 5) and ultimately to form **3**. Under the conditions employed, the latter pathway was selected about ten times as often as the former.

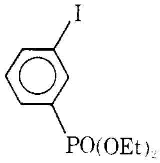
Scheme II



The reaction of **1a** with diethyl phosphite ion is presumed to occur via the same mechanism. The same crucial intermediate, **6**, is involved regardless of the identity of halogen X. In the partitioning between steps 4 and 5, somewhat less use of step 4 would be anticipated because electron transfer from the hydrated electron to bromobenzene is slower than to iodobenzene.[13] One would therefore expect less formation of **2** than in the reaction of **1b**, but one cannot tell whether this is the reason no **2** could be detected as a product because **2** itself is transformed comparatively rapidly to **3** under the conditions of the reaction with **1a**.

Although the mechanism of Scheme I gives a fine account of the present observations and of others regarding the photostimulated reactions of *m*-dihalobenzenes with dialkyl phosphite ions and is the only conceivable mechanism compatible with the evidence, we must invoke the universal caveat that the evidence may also be consistent with some mechanism as yet unconceived, that is, with a mechanism that no one has thought of or that at least has not come to our attention.

Our finding that **2** is not an intermediate on the main route from **1b** to **3** serves to exclude a great many mechanisms, some rational, some ridiculous, some conceivable, and maybe some as yet unconceived, that would involve **2** as an intermediate. However, the significance of this exclusion is considerably reduced unless stepwise replacement first of bromine, to form intermediate **9**, and then of iodine can also be excluded. We did not investigate the reactivity of **9** with diethyl phosphite ion but, taking note of the greater reactivity of **2** than of **1a**, we suppose that **9** would be more reactive than **1b**. There is, however, a strong argument against any mechanism that would replace the bromine of **1b** before the iodine, namely, that iodobenzene is enormously more reactive than bromobenzene in photostimulated reaction with diethyl phosphite ion.[14] The greater reactivity of **1b** than of **1a** is a further expression of the same characteristic. The exclusion of reaction via the intermediacy of **9** is therefore strongly supported.



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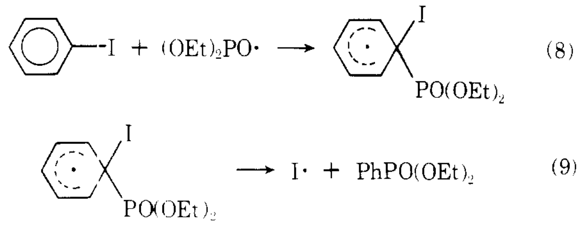
A mechanism of wholly different character that provides for conversion of **1b** to **3** without the intermediacy of **2** is

Scheme III



$$\text{I}\cdot + (\text{EtO})_2\text{PO}^- \longrightarrow \text{I}^- + (\text{EtO})_2\text{PO}\cdot \qquad (10)$$

sketched in Scheme II. It is an aryne mechanism, and a central intermediate is the conjugate base of **2** rather than **2**. Arguments against it can be made, but it is definitively disqualified by the fact (experiment 16) that **1b** does not react detectably with $(\text{EtO})_2\text{PO}^-\text{Na}^+$ in the dark under the conditions of experiments 1, 2, 4, or 5.

Exclusion of an Alternative Radical Mechanism. Among the many mechanisms excluded by the predominance of a pathway that avoids **2** as an intermediate is a radical chain mechanism, the propagation cycle of which is sketched (for reaction of iodobenzene) in Scheme III. This mechanism finds precedent in mechanisms suggested for substitution reactions in which, it appears, other types of radicals react with aryl halides.[15]

Although a mechanism analogous to that of Scheme III could be written for an aryl bromide, the far greater reactivity of iodo- than of bromobenzene with diethyl phosphite ion would dictate that as applied to **1b** it should involve replacement first of iodine to form **2** and then of bromine. Such a mechanism provides no way for involvement of iodine in the process to trigger the involvement of bromine, as does the mechanism of Scheme I. For that reason alone a mechanism of the type in Scheme III can be rejected.

As mentioned above, we did nevertheless perform further experiments to test the mechanism of Scheme III. The experiment with iodobenzene, diethyl phosphonate, and di-*tert*-butyl peroxide was fashioned after experiments of Jason and Fields[16] who achieved the phosphonation of naphthalene, anthracene, and other polynuclear aromatic hydrocarbons in good yields by refluxing them with diethyl phosphonate and di-*tert*-butyl peroxide. They proposed a radical mechanism involving the attachment of $(\text{EtO})_2\text{PO}\cdot$ radicals to ring carbon atoms and then removal of hydrogen atoms. The failure of iodobenzene to react appreciably if at all under those conditions inveighs against the mechanism of Scheme III.

The experiment with iodobenzene, sodium diethyl phosphite, and diiodine in liquid ammonia in the dark was performed with the thought that diiodine might bring about one-electron oxidation of the diethyl phosphite ion, somewhat as in step 10, Scheme III. If diethyl phosphonyl radicals were thereby generated, reaction to form diethyl phenylphosphonate should occur readily if Scheme III were valid, for the conditions are (except for the mode of stimulation) identical with those under which reaction occurs in high yield under illumination. Again, little reaction of the iodobenzene was detected.

Experimental Section

Instrumentation. NMR spectra were determined on a JEOL Minimar 60-MHz instrument. GLC analyses were performed by means of a Hewlett-Packard Model 5750 flame ionization instrument equipped with a 183 cm × 3.2 mm, 10% silicone rubber (UC-W98) on 80–100 mesh WAW DMCS column. Reaction yields were esitmated from peak areas with respect to those of an internal standard, suitable molar response corrections being applied. Photostimulated reactions were carried out in a Rayonet Model RPR-100 reactor equipped with 16 lamps, usually a set rated to emit maximally at 350 nm but sometimes a set rated to emit maximally at 300 nm, as noted in Table I.

Reactions of Substrates with Sodium Diethyl Phosphite. In a three-neck 250-mL round-bottom flask equipped with a dry ice condenser and polyethylene stir bar, and under a dry nitrogen atmosphere, dry ammonia was condensed to the level of 50 mL as marked on the outside of the flask. Then 20–22 mmol of clean sodium metal was added and stirred until dissolved. This solution was then titrated dropwise with diethyl phosphonate, until no blue color remained. Then the substrate or substrates were added, in amounts as noted in Table I. The solution was placed in the photolysis apparatus and stirred gently, and the frost was washed off the flask with acetone. The photolysis was then started. If photolysis was longer than 20 min, it was stopped every 20 min and the frost removed from the outside of the flask by rinsing with acetone. After the photolysis was complete, 1.7 g (21 mmol) of ammonium nitrate and 50 mL of chilled diethyl ether were added. The ammonia was allowed to evaporate, and water was added and then a measured amount of diphenylmethane as internal standard. The crude reaction mixture was subjected to a normal workup. A portion of the resulting ether extract was analyzed by GLC.

Modified Doak-Freedman Synthesis of *m*-Bromophenylphosphonic Acid. *m*-Bromobenzenediazonium tetrafluoroborate (48.59 g, 0.179 mol) was placed in a 1-L, three-neck, round-bottom flask and 279 mL of ethyl acetate was added. The flask was equipped with a mechanical stirrer, thermometer, and a gas outlet into a water trap. After stirring was begun, 15.84 mL (24.93 g, 0.182 mol) of phosphorus trichloride and 4.0 g of copper(I) bromide were added. After some 30 min, a slight darkening of the reaction mixture was noted but no gas evolved. The reaction mixture was then heated with a water bath to 50 °C; then the bath was removed. Gas started to evolve slowly and then rapidly, and the reaction mixture was cooled with an ice bath to prevent foaming. After about 30 min, no more gas could be observed. The reaction was stirred 1 h, and then the heating started again, this time without cooling as gas was evolved slowly. After 30 min more of stirring, the now black solution was quenched carefully with water. The reaction mixture was subjected to steam distillation to remove volatile materials. The remaining solution was concentrated on a rotary evaporator until the solid–aqueous suspension contained only about 50 mL of liquid. The solid was removed by filtration. The crude solid was dissolved in a minimum of 10% sodium hydroxide and an insoluble tar removed by filtration. The solution was again concentrated to about 50 mL and titrated dropwise with concentrated hydrochloric acid until the pH was 4–4.5, as indicated by means of pH 3–5 indicator paper. The resulting crude solid was removed by filtration and added to 60 mL of 6 M hydrochloric acid which was then brought to boiling. The solution of phosphonic acid was then separated from insoluble diarylphosphinic acid, placed in a warm beaker, and allowed to cool slowly. Initially, some granular crystals formed. The hydrochloric acid solution was decanted from this granular solid and allowed to cool. The crystals that formed slowly (plates) were collected on a sintered glass funnel. These crude crystals were recrystallized from 40 mL of 6 M hydrochloric aicd, again with separation of the initial granular crystals from the acid solution. The acid solution was allowed to cool slowly and the resulting crystals (plates) were collected by glass frit filtration and then dried for 15 h under a vacuum (~0.5 mm) at room temperature: yield, 13.48 g (32%); mp 149–151 °C (lit.[7] mp 149–151 °C).

m-Bromophenylphosphonic dichloride was prepared from the phosphonic acid after Denham and Ingham.[17]

Preparation of Diethyl *m*-Bromophenylphosphonate. To a mixture of 2.83 g (3.6 mL, 0.0614 mol) of absolute ethanol and 2.04 g (2.1 mL, 0.0257 mol) of pyridine under a nitrogen atmosphere at 0 °C was added dropwise 3.36 g (0.0123 mol) of *m*-bromophenylphosphonic dichloride. After the addition was complete, the mixture was allowed to warm to room temperature, stirred for 15 min at room temperature, and heated to 50 °C for 30 min. The mixture was cooled, 30 mL of cold diethyl ether was added, and the solution was filtered to remove pyridine hydrochloride. The resulting solution was evaporated until all the ether and ethanol were gone. The resulting viscous liquid was redissolved in cold diethyl ether, and the additional pyridine hydrochloride which separated was removed by filtration. The ether solution was washed with water and the ether removed under vacuum. The crude liquid was distilled at reduced pressure: yield, 2.876 g (79%); bp 110–114 °C (0.2 mm); NMR (CDCl_3) δ 1.33 (t, 6 H), 4.18 (quintet, ^{31}P coupling, 4 H), 7.18–8.27 (m, 4 H).

Bromination of Diethyl Phenylphosphonate. In a 100-mL three-neck, round-bottom flask equipped with a Teflon stir bar and a condenser was placed 22.5 mL of 98% sulfuric acid and 2.5 mL of distilled water. To this mixture was added 5.00 g (0.0233 mol) of diethyl phenylphosphonate and then 1.3 mL (4.0 g, 0.0253 mol) of bromine. The reaction mixture was stirred, 4.25 g (0.0136 mol) of silver 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.

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(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.

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

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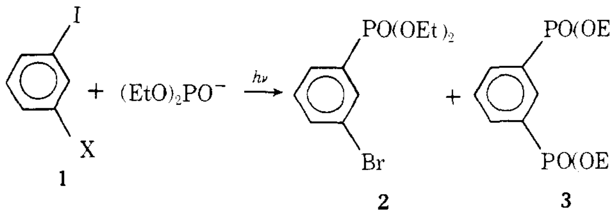
The reactions of *m*-bromoiodobenzene (**1a**) and *m*-chloroiodobenzene (**1b**) with diethyl phosphite ion give mixtures of a monosubstitution product, in which only iodine is replaced, and a disubstitution product, in which both halogens are replaced. These products are, respectively, a diethyl *m*-halophenylphosphonate 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)

a, X = Br; b, X = Cl

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