

the interpretations. Also, the CNDO/2 method predicts that the preferred conformation of the phenyl group is perpendicular to the plane of the diene moiety for all dienes except 1-phenylthio-2-methoxy-1,3-butadiene. Consequently, this conformation of the phenyl group was used in those calculations.

Conclusion

The regioselectivity in the Diels–Alder reactions of disubstituted butadienes cannot be predicted from the primary orbital interactions. However, by including the secondary orbital interactions in the theory the preferred regioisomer can be predicted in all these cases.¹⁶ Furthermore, we have applied our approach to approximately 100 examples of the Diels–Alder reaction including 1-substituted, 2-substituted, 1,3-disubstituted, and 1,4-disubstituted butadienes as well as the reactions in this paper. In all these other cases, the preferred regioisomer was correctly predicted using CNDO/2 FMO energies and coefficients.

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Registry No.—3-Acetamido-2-methyl-3-cyclohexene-1-carboxaldehyde, 65415-14-7; 4-acetamido-5-methyl-3-cyclohexene-1-carboxaldehyde, 65415-15-8; methyl 3-methoxy-2-methyl-3-cyclohexene-1-carboxylate, 65415-16-9; methyl 4-methoxy-5-methyl-3-cyclohexene-1-carboxylate, 65415-17-0; 2,3-dimethyl-3-cyclohexene-1-carbonitrile, 65415-18-1; 4,5-dimethyl-3-cyclohexene-1-carbonitrile, 65415-19-2; methyl 2,3-dimethyl-3-cyclohexene-1-carboxylate, 65415-20-5; methyl 4,5-dimethyl-3-cyclohexene-1-carboxylate, 65484-18-6; 2,3-diphenyl-3-cyclohexene-1-carboxylic acid, 65415-21-6; 4,5-diphenyl-3-cyclohexene-1-carboxylic acid, 65415-22-7; 3-phenyl-2-methyl-3-cyclohexene-1-carboxylic acid, 65415-23-8; 4-phenyl-5-methyl-3-cyclohexene-1-carboxylic acid, 65415-24-9; 2-methoxy-3-phenylthio-4-acetylcyclohexene, 65415-25-0; 1-methoxy-6-phenylthio-4-acetylcyclohexene, 65415-07-8; 1-methoxy-2-phenylthio-5-acetylcyclohexene, 60603-21-6; 1-methoxy-2-phenylthio-4-acetylcyclohexene, 60603-33-0; 3-methoxy-4-phenylthio-3-cyclohexene-1-carbonitrile, 60603-20-5; 4-methoxy-3-phenylthio-3-cyclohexene-1-carbonitrile, 65415-08-9; 3-methyl-4-chloro-3-cyclohexene-1-carboxylic acid, 35563-73-6; 4-methyl-3-chloro-3-cyclohexene-1-carboxylic acid, 65415-09-0; 3-methyl-4-phenyl-3-cyclohexene-1-carboxylic acid, 65415-10-3; 4-methyl-3-phenyl-3-cyclohexene-1-carboxylic acid, 65415-11-4.

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Observations Concerning the Scope and Mechanism of Photostimulated Reactions of Aryl Iodides with Diethyl Phosphite Ion. A Remarkable Difference in Behavior between *m*- and *p*-Chloriodobenzene¹

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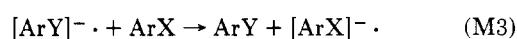
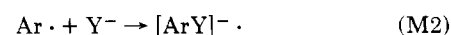
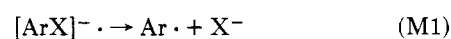
Extending studies of the photostimulated reactions of diethyl phosphite ion with aryl halides to form diethyl arylphosphonates, we find that sodium and potassium diethyl phosphite serve equally well, that the reaction is suitable for use on a preparative scale, that the ortho, meta, and para isomers of the iodoanisoles and iodotoluenes all react satisfactorily, and that the iodobenzene/bromobenzene reactivity ratio is about 1×10^3 . In $S_{RN}1$ reactions of dihalobenzenes with nucleophiles, whether one or two halogen atoms are replaced depends on the nucleophiles and the halogens involved and on their orientation (meta or para in this study); reactions of the chloriodobenzenes are about the borderline between mono- and disubstitution.

Under photostimulation, aryl iodides react smoothly and quickly with diethyl phosphite ion to form diethyl arylphosphonate esters;^{3,4} see eq 1. The reaction occurs in a number of solvents, although ammonia or dimethyl sulfoxide is preferred. Observed quantum yields in Me_2SO greatly exceed unity;⁵ that and other facts indicate a chain mechanism, and the radical chain $S_{RN}1$ mechanism⁶ is believed to obtain.



The propagation cycle for the $S_{RN}1$ mechanism, which was first proposed (though without symbolization) by Kornblum⁷ and Russell⁸ and their associates for some substitutions at rather specialized aliphatic centers, is sketched in Scheme I.

Scheme I



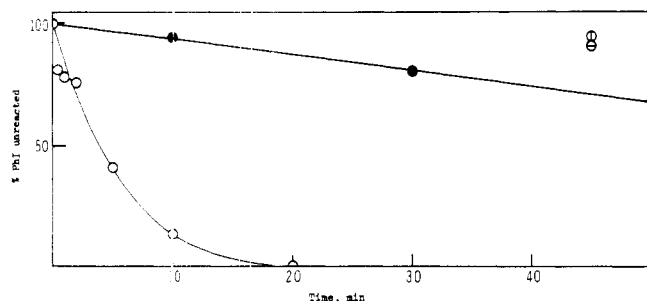


Figure 1. Reactivity of iodobenzene with diethyl phosphite ion in liquid ammonia at reflux: open circles, irradiation without additives; closed circles, irradiation with 0.5 mol % of *p*-dinitrobenzene added; circle with horizontal bar, irradiation with 5 mol % of *p*-dinitrobenzene added; circle with vertical bar, without additives in the dark.

The sum of the three steps of this cycle is, after cancellation of like terms that appear on both sides, merely a substitution ($\text{ArX} + \text{Y}^- \rightarrow \text{ArY} + \text{X}^-$) in which nucleophile Y^- replaces nucleofuge X^- . A complete radical chain mechanism also comprises initiation and termination steps. The probable character of these for the reaction of eq 1 is discussed in detail elsewhere.⁵

We now report observations relevant to the scope and mechanism of this reaction.

Results

Preparative Scale Reaction. Inasmuch as previous reactions according to eq 1 had all been conducted on a small scale, about 0.01 mol, an experiment was conducted in which 0.1 mol of iodobenzene and 0.2 mol of $(\text{EtO})_2\text{PO}^- \text{K}^+$ in 1 L of ammonia were irradiated for 45 min in the Rayonet photochemical reactor. All the iodobenzene was consumed, and 20 g (94%) of pure diethyl phenylphosphonate was obtained. The reaction is thus shown to be useful on a preparative scale. An *Organic Syntheses* procedure on an even larger scale was developed on the basis of this experiment.⁹

Use of Sodium Diethyl Phosphite. In all previous experiments concerning the reaction of eq 1, *potassium* salts of diethyl phosphite or other dialkyl phosphites had been employed. We prepared *sodium* diethyl phosphite in the usual way by reaction of sodium metal with diethyl phosphonate, $(\text{EtO})_2\text{PHO}$, in liquid ammonia and found that it reacted with iodobenzene during 45-min irradiation to give diethyl phenylphosphonate in 88% yield. Because this is satisfactory and because sodium metal is easier to handle, sodium diethyl phosphite is the reagent employed in most of the present work.

Behavior of Bromobenzene. The reaction of bromobenzene with diethyl phosphite ion, under photostimulation, is much slower than of iodobenzene. During 4-h irradiation, only 61% of bromide ion was released. GLC examination of the organic products indicated the presence of 59% of diethyl phenylphosphonate as well as residual bromobenzene.

Reactivity of Iodobenzene. A mixture of iodobenzene (0.0455 M) and $(\text{EtO})_2\text{PO}^- \text{K}^+$ (0.0909 M) in ammonia at reflux was irradiated in the Rayonet reactor with "350 nm" lamps, and samples taken at various times were analyzed by GLC. After 21 min, more than 99% of the iodobenzene had reacted. From experience with the same reaction in Me_2SO solution,⁵ one would expect the rate to be independent of iodobenzene concentration but dependent on the first power of $(\text{EtO})_2\text{PO}^- \text{K}^+$ concentration and, therefore, that a plot of $\ln(b-x)$ vs. time, where b is the initial nucleophile concentration and x is the diethyl phenylphosphonate concentration, would be linear. Such a plot (not shown) was linear from time 2 to 12 min (31–86% reaction) but had a steeper slope for the first 2 min. A second-order kinetic plot, of $\ln(a-x)/(b-x)$

vs. time, where a is the initial iodobenzene concentration, was linear from time 0 to 10 min (to 74% reaction) but was steeper thereafter. We judge this experiment not to be definitive of kinetic order.

The outcome of a group of experiments at similar but not identical concentration levels is shown in Figure 1. Under irradiation, the reaction of iodobenzene with $(\text{EtO})_2\text{PO}^- \text{K}^+$ was finished in 20 min. In the dark, only 5% of iodide ion was released in 45 min. When 5 mol % of *p*-dinitrobenzene (an efficient inhibitor of many $\text{S}_{\text{RN}}1$ reactions⁷) was present, an irradiated reaction released only 9% of iodide ion in 45 min. When the *p*-dinitrobenzene presence was reduced to a mere 0.5 mol %, reaction under irradiation was somewhat faster; it went to the extent of 32% in 50 min, but that nevertheless represents strong retardation.

Interpretation of the retarding effect of *p*-dinitrobenzene is not straightforward. On the one hand, it may be acting as a scavenger of electrons or radicals and thereby interfering with perpetuation of the propagation cycle of Scheme I. Alternatively, it or something derived from it may be absorbing photons necessary for initiation. The reaction solutions containing *p*-dinitrobenzene were observed to have yellow to brown-red color.

The influence of dioxygen, a familiar radical scavenger, was assessed by preparing a mixture of $(\text{EtO})_2\text{PO}^- \text{K}^+$ and iodobenzene in ammonia in the usual way, under N_2 , and then bubbling air briskly through it before and during irradiation for 45 min. The usual products were obtained in virtually quantitative yield: iodide ion (98.4%) and diethyl phenylphosphonate (99%). Clearly dioxygen has little, if any, effect.

Reaction in the Presence of Bromide Ion. The reaction of iodobenzene with $(\text{EtO})_2\text{PO}^- \text{Na}^+$ in ammonia was conducted in the presence of excess KBr in order to see if any incorporation of bromide ion occurred to form bromobenzene. After 5-min irradiation, 81% of iodide ion had been released, 77% of diethyl phenylphosphonate had been formed, but no bromobenzene could be detected.

Reactions of Substituted Iodobenzenes with Diethyl Phosphite Ion. Reactions of *o*- and *m*-iodotoluene and of *o*- and *m*-iodoanisole with $(\text{EtO})_2\text{PO}^- \text{Na}^+$ in ammonia under irradiation for 60–75 min afforded the corresponding diethyl arylphosphonates according to eq 1 in yields of 71, 91, 85, and 86%, respectively. The corresponding para isomers have already been reported to undergo the same type of reaction, in both cases in 95% yield.³ Reaction of *o*-iodotoluene with sodium dimethyl phosphite in ammonia during 2-h irradiation afforded dimethyl *o*-tolylphosphonate in 82% yield. These conversions are all straightforward.

Reactions of Dihalobenzenes with Diethyl Phosphite Ion. Experiments concerning photostimulated reactions of all eight *m*- and *p*-haloiodobenzenes with diethyl phosphite ion are summarized in Table I. About half the data are due to Bunnett and Creary,³ and about half stem from the present work. Except for two substrates that have low solubility in ammonia and which reacted incompletely despite prolonged irradiation, all these compounds afforded high yields of arylphosphonate esters. In the cases of the diiodobenzenes and the bromiodobenzenes, both halogen atoms were replaced to afford bis(phosphonate esters); only from *m*-bromiodobenzene was any monophosphonate ester obtained, and it was a minor by-product. The two fluoroiodobenzenes displayed opposite behavior, giving only the corresponding diethyl fluorophenylphosphonates which represent replacement of iodine but not fluorine.

As for the chloriodobenzenes, there is a remarkable difference in the behavior of the meta and para isomers. *p*-Chloriodobenzene affords mainly the corresponding bis(phosphonate ester) accompanied by a mere trace of mono-

Table I. Photostimulated Reactions of Haloiodobenzenes with Diethyl Phosphite Ion ^f in Ammonia

Expt no.	XC ₆ H ₄ I	Registry no.	Irradiation time, min ^a	Products, ^b %		Recovered XC ₆ H ₄ I, %
				C ₆ H ₄ [PO(OEt) ₂] ₂	XC ₆ H ₄ PO(OEt) ₂	
1 ^c	<i>p</i> -C ₆ H ₄ I ₂	624-38-4	205 ^d	87	0	
2 ^c	<i>m</i> -C ₆ H ₄ I ₂	626-00-6	90	94	0	
3	<i>p</i> -BrC ₆ H ₄ I	589-87-7	240 ^d	56	0	24
4 ^c	<i>m</i> -BrC ₆ H ₄ I	591-18-4	60	87	Trace	
5	<i>p</i> -ClC ₆ H ₄ I	637-87-6	90	59	Trace	^e
6a ^c	<i>m</i> -ClC ₆ H ₄ I	625-99-0	40	4	89	
6b	<i>m</i> -ClC ₆ H ₄ I		60	Trace	91	
7	<i>p</i> -FC ₆ H ₄ I	352-34-1	90	0	91	
8 ^c	<i>m</i> -FC ₆ H ₄ I	1121-86-4	50	0	96	

^a In the Rayonet photochemical reactor, with 16 "350 nm" lamps. ^b No cine substitution was detectable. ^c Experiments 1, 2, 4, 6a, and 8 are from ref 3. ^d Irradiation prolonged because of low substrate solubility. ^e Detected but not determined. ^f Registry no.: 29800-93-9.

Table II. Competition between Bromo- and Iodobenzene in Photostimulated Reaction with Diethyl Phosphite Ion in Ammonia

Expt no.	PhI, ^e mmol	PhBr, ^f mmol	(EtO) ₂ PO ⁻ K ⁺ , mmol	PhPO(OEt) ₂ , mmol	Irradiation time, s	% I ⁻	% Br ⁻	<i>k</i> _{PhI} / <i>k</i> _{PhBr} ^a
11 ^b	10	29	29		55 ^c	30	0.089	400
12	5	25	18		55 ^c	42	0.094	580
13	1	25	20		60	69	0.076	1520
14	1	50	20		60	63	0.056	1770
15	1	75	20		60	77	0.060	2230
16	1	25	20	0.1	30	40	0.044	1160
17	1	25	20	1	30	59	0.056	1590
18	1	25	20	3	60	99	0.094	^d
19	1	25	20	5	60	69	0.064	1830
20	1	25	20	10	60	98	0.064	^d
21	1	25	20	10	30	34	0.040	1040
22	1	25	20	10	45	55	0.048	1660

^a Experimental uncertainty due to titration error estimated as $\pm 10\%$ in the rate ratio. ^b Experiment by Creary. ^c Ammonia volume: 160 mL. ^d Not calculated (too much I⁻). ^e Registry no.: 591-50-4. ^f Registry no.: 108-86-1.

phosphonate product. However, *m*-chloriodobenzene gives a high yield of the monophosphonate ester, diethyl *m*-chlorophenylphosphonate, but very little bisphosphonate. This striking difference is susceptible to rational interpretation, as discussed below.

Iodobenzene/Bromobenzene Reactivity Ratio. By means of a direct competition experiment,^{10a} Creary¹¹ estimated the relative reactivity of iodobenzene with respect to bromobenzene to be 400. We have performed several further experiments of the same sort; they are summarized, with Creary's experiment, in Table II. They show iodobenzene to be several hundredfold more reactive than bromobenzene.

In these experiments, the amounts of bromide and iodide ion formed were determined by potentiometric titration with AgNO₃. In a typical experiment (experiment 17), 12.42 mL of titrant was required to attain the iodide end point and a further 0.28 mL to the bromide end point. One may ask whether the end points were well enough defined for such small differences to be accurately measurable. The answer is that the end points were indeed sharp and clearly separated. The estimated uncertainty of each end point is ± 0.02 mL. Taking this uncertainty into account leads to an estimated uncertainty in the *k*_{PhI}/*k*_{PhBr} ratios of about $\pm 10\%$.

In experiments 11–15, the initial iodobenzene/bromobenzene concentration ratio varied from about 1:3 to 1:75, and the measured reactivity ratio rises steadily from 400 to 2230. We believe the effect to be real, not an experimental artifact.

We thought of the possibility that the reaction product, diethyl phenylphosphonate, might influence the reactivity ratio. In experiments 13 and 16–22, varying amounts of this product were present along with constant amounts of the

reactants. Although the measured reactivity ratio varied somewhat among these experiments, there is no correlation of it with the amount of diethyl phenylphosphonate present.

Discussion

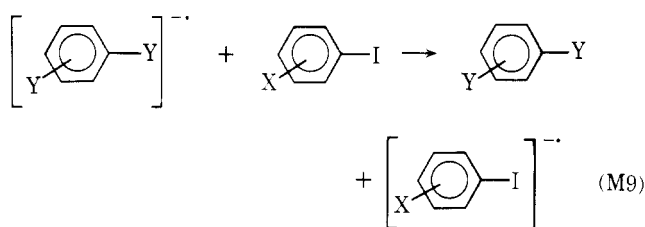
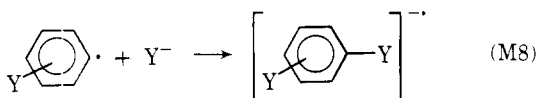
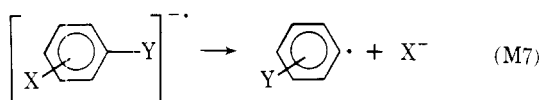
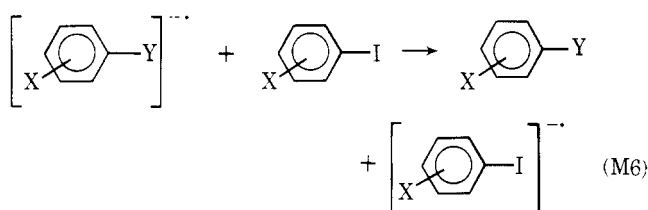
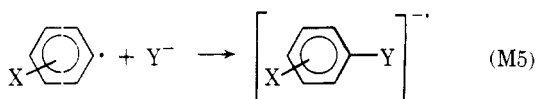
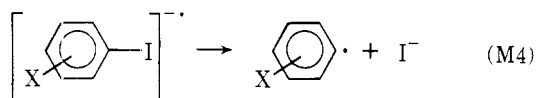
Utility as a Preparative Method. Our work shows that the reaction of eq 1 serves excellently for the preparation of diethyl phenylphosphonate on a 0.1 mol scale. It also shows, extending the experience of Bunnett and Creary,³ that the method works well with the ortho, meta, and para isomers of the iodoanisoles and the iodotoluenes. It appears to be a method of choice for the preparation of dialkyl arylphosphonates, being experimentally convenient, having wide applicability, and giving excellent yields.

Remarkable Behavior of *m*-Chloriodobenzene. In its reaction with (EtO)₂PO⁻K⁺, this dihalobenzene for the most part suffers replacement of iodine but not chlorine, furnishing diethyl *m*-chlorophenylphosphonate. What makes this reaction remarkable is comparison of it with the reaction of the para isomer with the same reagent and with the photostimulated reaction of *m*-chloriodobenzene with thiophenoxide ion in ammonia. In the latter, both halogen atoms are replaced to form mainly *m*-bis(phenylthio)benzene with very little *m*-chlorophenyl phenyl sulfide.¹⁶

In Scheme II, the general S_{RN}1 mechanism of Scheme I is elaborated for the somewhat more complex case of an iodo-halobenzene reacting with nucleophile Y⁻.

Scheme II comprises two parts. Steps M4, M5, and M6 are exactly analogous to the three steps of Scheme I; these constitute a propagation cycle for the replacement of iodine but

Scheme II



not of halogen atom X by nucleophile Y^- . Steps M7, M8, and M9, together with steps M4 and M5, constitute a propagation cycle for the replacement both of iodine and the other halogen by the nucleophile. Steps M7, M8, and M9 are of the same character as steps M4, M5, and M6, respectively, dealing with the involvement of halogen X instead of the depicted iodine atom.

According to the model of Scheme II, the relative rates of steps M6 and M7 determine whether one or both halogens are replaced. (In some cases, the product of monosubstitution, $\text{XC}_6\text{H}_4\text{Y}$, may, of course, be able to react further with the nucleophile under the reaction conditions.) A major factor determining whether step M6 or M7 is the faster is the rate of the fragmentation that occurs in step M7.

Electrochemical studies have provided some information about factors affecting the frangibility of aryl halide radical anions.¹²⁻¹⁴ They show the fragility of carbon-halogen bonds to decrease in the order: $\text{C-I} > \text{C-Br} > \text{C-Cl} > \text{C-F}$. They show the order of frangibility among isomers, $[\text{p-RC}_6\text{H}_4\text{X}]^{--} > [\text{m-RC}_6\text{H}_4\text{X}]^{--}$, where R is a group with capability to accept electrons mesomerically, such as the benzoyl or the (β -4-pyridyl)vinyl group, $\text{NC}_5\text{H}_4\text{CH}=\text{CH}$.

Consider now the behavior of *m*-chloriodobenzene, with respect to the other *m*-haloiodobenzenes, in their photostimulated reactions with diethyl phosphite ion in ammonia. As listed in Table I, *m*-diiodobenzene suffers replacement of both iodines without any monosubstitution product being detectable. *m*-Bromiodobenzene gives mainly disubstitution but a little monosubstitution product is formed. *m*-Chloriodobenzene gives some disubstitution product but mainly monosubstitution. From *m*-fluoriodobenzene, only the product of replacement of iodine could be obtained. With respect to the mechanism of Scheme II, the product pattern

correlates very well with the indicated order of the fragility of C-X bonds in aryl halide radical anions.

Consider next the behavior of *m*-chloriodobenzene as compared to *p*-chloriodobenzene. In photostimulated reaction with diethyl phosphite ion, the para isomer affords mainly the disubstitution product with a mere trace of the monosubstitution product. But the meta isomer gives mainly mono- and little disubstitution product. This is a manifestation of the orientational effect on radical anion frangibility indicated by electrochemical studies. Although to our knowledge *m*- and *p*-chlorophenylphosphonate esters have not been examined by cyclic voltammetry, it would be expected from studies on analogous compounds^{12,14} that the radical anion of the para isomer would fragment perhaps two orders of magnitude faster than that of the meta isomer. Observed behavior again finds interpretation in the model of Scheme II. The further implication that the product ratio should depend on the concentration of *m*-chloriodobenzene, which should affect the absolute rate of step M6 but not M7, has recently been confirmed in experiments of Bunnett and Shafer.¹⁵

Consider finally the behavior of *m*-chloriodobenzene with diethyl phosphite ion as compared to that with thiophenoxide ion. With the phosphorus nucleophile, monosubstitution predominates whereas mainly disubstitution occurs with thiophenoxide ion.¹⁶ Bunnett and Creary³ pointed out that this difference could be understood if step M7 were slower when group -Y were the diethoxyphosphinyl group, $(\text{EtO})_2\text{P}(\text{O})^-$, than the phenylthio group. They suggested that because the former is more strongly electron attracting the $[\text{m-ClC}_6\text{H}_4\text{PO}(\text{OEt})_2]^{--}$ radical anion could be expected to be less frangible than $[\text{m-ClC}_6\text{H}_4\text{SPh}]^{--}$. That seems a reasonable proposition.

A complete argument should also take into account the effect of group -Y on the rate of step M6. We have no information about substituent effects on such processes, but we suspect that when -Y is more strongly electron attracting the rate of electron transfer in the indicated sense should be lower. On the other hand, it is conceivable that the rate constant is at or close to the encounter-controlled limit, irrespective of whether -Y is the diethoxyphosphinyl or the phenylthio group.¹⁷

Iodobenzene/Bromobenzene Reactivity Ratio. In competition experiments, iodobenzene reacts about 1000 times faster than bromobenzene with diethyl phosphite ion. This huge difference contrasts with the approximately eightfold difference observed in the photostimulated reactions of these compounds with acetone enolate ion in ammonia¹¹ or the 5.6-fold difference in the dark or photostimulated reaction with pinacolone enolate ion in dimethyl sulfoxide solution.¹⁸

We suppose, in terms of the $\text{S}_{\text{RN}}1$ mechanism, that the measured reactivity ratios report the relative rate constants for the involvement of iodo- and bromobenzene in step M3, Scheme I. That is an electron-transfer step.

The rate of electronation of iodobenzene by means of the hydrated electron is about thrice as great as for bromobenzene;¹⁹ k_{PHI} is $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, essentially at the encounter-controlled limit, and k_{PHBr} is $4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. In tetrahydrofuran solution, rate constants for electron transfer from (ion-paired) sodium naphthalenide to butyl iodide and hexyl bromide²⁰ are, respectively, 4.6×10^7 and $7.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. Rate constants for electron transfer from aromatic hydrocarbon radical anions to other aromatic hydrocarbons are about $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, essentially at the encounter-controlled limit, when the standard free energy change is negative, but one or two powers of ten slower when it is positive.¹⁷

An hypothesis warranting consideration²¹ is that step M3 shows selectivity similar to that in reactions of the hydrated

Table III. Preparation and Physical Properties of Phosphonate Esters

Substrate	Registry no.	Mol of irradiation reactant used	Halide ion yields, %	Formula	Registry no.	Yield, %	Mp or bp (°C)	Phosphonate ester product		MS	Ref
								IR, cm ⁻¹	¹ H NMR, δ (CCl ₄)		
<i>o</i> -CH ₃ C ₆ H ₄ I ^a	615-37-2	0.023	60	<i>o</i> -CH ₃ C ₆ H ₄ PO(OEt) ₂	15286-11-0	71	94-95 (0.2)	1600, 1480, 1450, 1250, 1025, 965, 820, 760	1.33 (t, 6 H), 2.6 (t, 3 H), 4.1 (m, 4 H), 7.3- 8.1 (m, 4 H)	228 (M ⁺), 227, 226 212, 199, 184, 183	c
<i>o</i> -CH ₃ C ₆ H ₄ I ^{a,b}		0.023	120	<i>o</i> -CH ₃ C ₆ H ₄ PO(OMe) ₂	6840-23-9	82	72-74 (0.09)	1600, 1460, 1245, 1020, 825, 755	2.6 (d, J = 1.5 Hz, 3 H), 3.75 and 3.95 (2 s, 6 H), 7.6-8.3 (m, 4 H)	201, 200, 186	c
<i>m</i> -CH ₃ C ₆ H ₄ I	625-95-6	0.025	75	<i>m</i> -CH ₃ C ₆ H ₄ PO(OEt) ₂	15286-13-2	91	92-93 (0.02)	1610, 1580, 1250, 1025, 960, 785, 700	1.31 (t, 6 H), 2.45 (s, 3 H), 4.13 (m, 4 H), 7.3-8.0 (m, 4 H)	228 (M ⁺), 200, 199, c 184, 183, 172, 171, 156, 155, 154	c
<i>o</i> -CH ₃ OC ₆ H ₄ I	529-28-2	0.015	75	<i>o</i> -CH ₃ OC ₆ H ₄ PO(OEt) ₂	15286-17-6	85	122-124 (0.14)	1275, 1250, 1050, 1025, 760	1.30 (t, 6 H), 3.88 (s, 3 H), 3.8-4.3 (m, 4 H), 6.8-8.1 (m, 4 H)	244 (M ⁺), 215, 213 187	c
<i>m</i> -CH ₃ OC ₆ H ₄ I ^a	766-85-8	0.021	75	<i>m</i> -CH ₃ OC ₆ H ₄ PO(OEt) ₂	65442-22-0	86	143 (1.5)	1600, 1580, 1470, 1430, 1250, 1240, 1040, 1025, 965, 790, 695	1.32 (t, 6 H), 3.88 (s, 3 H), 4.1 (m, 4 H), 7.0-7.6 (m, 4 H)	244 (M ⁺), 216, 215, 200, 188, 187	
<i>p</i> -BrC ₆ H ₄ I ^d		0.015	240	<i>p</i> -C ₆ H ₄ [PO(OEt) ₂] ₂	21267-14-1	56	70-71.5				e
<i>p</i> -ClC ₆ H ₄ I ^d		0.015	90	<i>p</i> -C ₆ H ₄ [PO(OEt) ₂] ₂		59	70.5-72	1480, 1450, 1390, 1375, 1250, 1145, 1025, 960, 805, 760, 620	1.37 (t, 12 H), 4.2 (m, 8 H), 7.8- 8.2 (dd, 4 H)		e
<i>m</i> -ClC ₆ H ₄ I ^d		0.015	60	<i>m</i> -ClC ₆ H ₄ PO(OEt) ₂	23415-71-6	91	107-109 (0.09)	1250, 1145, 1050, 1025, 970, 790, 690, 670		250/248 (M ⁺), 235/ 233, 222/220	f
<i>p</i> -FC ₆ H ₄ I ^d		0.022	90	<i>p</i> -FC ₆ H ₄ PO(OEt) ₂	310-40-7	91	105 (0.65)	1600, 1500, 1445, 1250, 1160, 1130, 1025, 960, 835	1.35 (t, 6 H), 4.1 (m, 4 H), 7.0- 7.5 and 7.7- 8.2 (2 m, 4 H)	232 (M ⁺), 204, 188, h 187, 176, 160, 159	h

^a Experiment performed with the technical assistance of E. W. Bouldin. ^b (MeO)₂PHO used instead of (EtO)₂PHO. ^c Reference 26. ^d See also Table I. ^e P. Tavs, *Chem. Ber.*, **103**, 2428 (1970). ^f D. I. Lobanov, E. N. Tsvelkov, and M. I. Kabachnik, *Zh. Obshch. Khim.*, **39**, 841 (1969). ^g Negative qualitative test with CaCl₂. ^h H. Schindlbauer, *Chem. Ber.*, **100**, 3432 (1967).

electron with phenyl halides when the associated free energy change is significantly negative but that selectivity is much greater when the free energy change is near zero or positive. That would amount to postulating a selectivity-reactivity relationship,²² and whether such relationships exist is a matter of controversy.^{10b} An alternative hypothesis is that when the free energy change for step M3 is positive this step may be a quasi-equilibrium within the encounter complex, with step M1 then entering into determination of the apparent electron-transfer rate.

Available polarographic data do not, however, support such interpretations. For polarographic reduction of diethyl phenylphosphonate in dimethylformamide solution with tetraethylammonium iodide supporting electrolyte, $E_{1/2}$ is reported to be -2.04 V vs. the mercury pool,²³ which amounts to about -2.54 V vs. the standard calomel electrode.²⁴ Inasmuch as $E_{1/2}$ values for reduction of iodo- and bromobenzene are higher (less negative),²⁵ electron transfer from $[\text{PhPO}(\text{OEt})_2]^-$ to either halobenzene should be exoenergetic.

Interpretation of the remarkable difference in iodobenzene/bromobenzene reactivity ratios is a challenge.

Experimental Section

Large-Scale Preparation. To a solution of potassium metal (7.8 g, 0.2 mol) in 1000 mL of liquid ammonia in a 3-L round-bottom flask provided with a well-type condenser and swept by a slow stream of dry N_2 , about 27.7 g (0.2 mol) of diethyl phosphonate was added during a period of 5 min. The last increments were added dropwise, and addition was stopped when the blue color was discharged. Iodobenzene (20.4 g, 0.1 mol) was added, and the flask with condenser and stirrer was placed within a Rayonet Model RPR-100 photochemical reactor equipped with fluorescent lamps emitting maximally at 350 nm. Irradiation was conducted for 45 min, with interruption at ca. 15-min intervals to spray the flask exterior with a little 2-propanol and wipe away the frost with a towel. Ammonium nitrate (10 g) and 250 mL of diethyl ether were added, the ammonia was allowed to evaporate, 100 mL of water was added, the ether layer was separated, and the water layer was thrice extracted with 200-mL portions of ether. The combined ether extracts were dried over anhydrous Na_2SO_4 , the ether was evaporated, and the residue was distilled; 20.0 g (94%) of diethyl phenylphosphonate, bp 85–87 °C (0.05 Torr), was obtained. The IR spectrum was identical with that of an authentic sample.

Reactions of Substituted Iodobenzenes with Diethyl Phosphite Ion. These reactions were conducted as described above, but on a smaller scale. In general, 250 mL of ammonia was used, in a 500-mL flask, and the molar amount of sodium or potassium diethyl phosphite was about double that of the substrate. Details about the experiments and the properties of the products obtained are set forth in Table III. The observed ^1H NMR spectra are in agreement with the observations of Obrycki and Griffin.²⁶ Iodide, bromide, or chloride ion in the

aqueous layer from product workup was determined by titration with AgNO_3 .

Competition Experiments (Table II). Reactions were performed in the manner described, with 250 mL of ammonia being used unless otherwise stated. After evaporation of the ammonia and addition of water, the aqueous phase was separated, acidified with HNO_3 , and titrated with standard AgNO_3 solution. $k_{\text{PhI}}/k_{\text{PhBr}}$ values were reckoned by means of the expression^{10a}

$$k_{\text{PhI}}/k_{\text{PhBr}} = \ln ([\text{PhI}]_0/[\text{PhI}]_t) / \ln ([\text{PhBr}]_0/[\text{PhBr}]_t)$$

Experiments on the Reactivity of Iodobenzene. Reactions were carried out in the manner described. Samples (ca. 1 mL) were removed at measured times by means of a J tube²⁷ and added to 1 mL of water, and the mixture was extracted with 1 mL of ether. The ether layer was examined by GLC on a column of 2.5% SE-54 on Chromosorb GAW/DMCS. The peaks for iodobenzene and diethyl phenylphosphonate were corrected for molar response, and the progress of the reaction was judged from their relative magnitudes.

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