Light and Dark Reactions of *o*-Haloiodobenzenes with Diethyl Phosphite Ion

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Received June 25, 1979

o-Haloiodobenzenes react with diethyl phosphite ion in the dark in a manner wholly different from their reactions under irradiation. The photostimulated reactions afford *o*-phenylenebisphosphonic esters, except that *o*-fluoroiodobenzene (**1f**) undergoes replacement of iodine only, and are believed to occur by the $S_{RN}1$ radical chain mechanism. The dark reactions afford respectively fluoro- and chlorobenzene, as well as iodide ion, from **1f** and *o*-chloroiodobenzene (**1c**). The probable mechanism is nucleophilic attack on iodine to displace an *o*-halophenyl anion which then takes a proton from the solvent. Some of the products from *o*-bromoiodobenzene (**1b**) and *o*-diiodobenzene (**1i**) appear to derive from benzyne arising from the *o*-halophenyl anions by halide ion loss. A minor product from **1b** or **1i**, diethyl *o*-iodophenylphosphonate, appears to have its genesis in a novel ionic chain mechanism.

Iodobenzene reacts readily with diethyl phosphite ion under irradiation to form diethyl phenylphosphonate[2] (eq 1). The analogous reactions with *m*- and *p*-haloiodobenzenes sometimes bring about replacement of both halogens, to form a bisphosphonate ester, but sometimes of iodine only to form a halophenylphosphonic ester.[2,3] Whether both halogens or iodine only are replaced depends on the identity of the second halogen and its orientation with respect to iodine.

$$\mathrm{PhI + (EtO)_2PO^- \xrightarrow{h\nu} PhPO(OEt)_2 + I^-} \qquad (1)$$

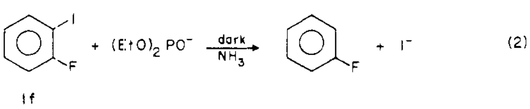
In the case of *m*-bromoiodobenzene, strong evidence was found[4,5] that the main reaction pathway does not involve ordinary replacement first of iodine and then of bromine. Rather, the involvement of iodine triggers the involvement of bromine. The main reaction forms disubstitution product without the intermediacy of monosubstitution product.

This and other facts find interpretation in the $S_{RN}1$ radical chain mechanism.[6] For reaction of a haloiodobenzene with diethyl phosphite ion, the cycle of propagation steps for this mechanism can be written as in Scheme I, in which "–Q–" represents a phenylene moiety. A short cycle comprising steps M1, M2, and M3 forms a diethyl halophenylphosphonate, while a longer cycle of steps M1, M2, and M4–6 leads to disubstitution product.

We now report an investigation of reactions of *o*-haloiodobenzenes with sodium diethyl phosphite in ammonia solution. A new feature enters the scene in the ortho series, namely, facile dark reactions of a character wholly different from the reactions of the same species under irradiation.

Results

***o*-Fluoroiodobenzene (1f).** The dark reaction with $(EtO)_2PO^-$ proceeds readily in liquid ammonia at ca. −33 °C to release iodide ion and form fluorobenzene (expt 1, Table I); see eq 2.



1f

Scheme I[a]

$$\mathrm{[X\text{–}Q\text{–}I]^-\cdot \longrightarrow X\text{–}Q\cdot + I^-} \qquad (M1)$$

$$\mathrm{X\text{–}Q\cdot + (EtO)_2PO^- \longrightarrow [X\text{–}Q\text{–}PO(OEt)_2]^-\cdot} \qquad (M2)$$

$$\mathrm{[X\text{–}Q\text{–}PO(OEt)_2]^-\cdot + X\text{–}Q\text{–}I \longrightarrow X\text{–}Q\text{–}PO(OEt)_2 + [X\text{–}Q\text{–}I]^-\cdot} \qquad (M3)$$

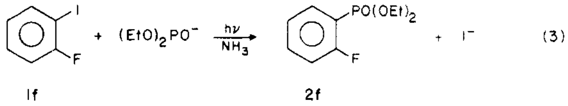
$$\mathrm{[X\text{–}Q\text{–}PO(OEt)_2]^-\cdot \longrightarrow X^- + (EtO)_2PO\text{–}Q\cdot} \qquad (M4)$$

$$\mathrm{(EtO)_2PO\text{–}Q\cdot + (EtO)_2PO^- \longrightarrow [(EtO)_2PO\text{–}Q\text{–}PO(OEt)_2]^-\cdot} \qquad (M5)$$

$$\mathrm{[(EtO)_2PO\text{–}Q\text{–}PO(OEt)_2]^-\cdot + X\text{–}Q\text{–}I \longrightarrow (EtO)_2PO\text{–}Q\text{–}PO(OEt)_2 + [X\text{–}Q\text{–}I]^-\cdot} \qquad (M6)$$

[a] Q represents C_6H_4.

In conducting photostimulated reactions, we strove to start irradiation as soon as possible after mixing of the reactants. Nevertheless, some dark reaction occurred during the short period preceding illumination, and doubtless also during illumination, for it is improbable that light inhibited the dark reaction. Of the products obtained (expt 11, Table II), which were fluorobenzene (19%), diethyl *o*-fluorophenylphosphonate (**2f**, 80%), and iodide ion (98%), the fluorobenzene and some of the iodide ion are undoubtedly to be attributed to the background dark reaction. The photostimulated reaction is then a substitution, named (diethoxyphosphinyl)deiodination,[7] as represented in eq 3.



1f 2f

***o*-Chloroiodobenzene (1c).** The dark reaction is of the same character as that for the fluoro compound. It forms chlorobenzene and iodide ion (expt 2 and 3, Table I). For expt 4, a lower concentration of $(EtO)_2PO^-$ was employed, as well as a rather short reaction time, and only half the substrate was consumed. In this experiment a search was made for phosphorus-containing products, and 18% of diethyl phosphoramidate, $(EtO)_2PONH_2$, was found. The same byproduct was observed from other substrates (cf. expt 7 and 8) but never in molar amounts approximating the aromatic products. Presumably it was also formed in expt 1.

The solvent for expt 5 (Table I) was tetraglyme instead of ammonia, and the concentrations of reactants were

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[2] Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3612.

[3] Bunnett, J. F.; Traber, R. P. *J. Org. Chem.* **1978**, *43*, 1867.

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[5] Bunnett, J. F.; Shafer, S. J. *J. Org. Chem.* **1978**, *43*, 1877.

[6] Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

[7] We call attention to a misprint in ref 6, p 418. Reactions of *m*- and *p*-fluoroiodobenzenes with $(EtO)_2PO^-$ or PhS^- under photostimulation were erroneously stated to bring about replacement only of fluorine. Actually, only iodine is replaced.

0022-3263/79/1944-4918$01.00/0

Table I. Dark Reactions of *o*-Haloiodobenzenes with Sodium Diethyl Phosphite in Ammonia

expt no.	ortho halogen	[substrate], M	$[(EtO)_2PO^-Na^+]$, M	time, min	substrate remaining, %	products, % I^-	X^-	PhX	$H_2NPO(OEt)_2$	$PhPO(OEt)_2$	$PhNH_2$	o-$IC_6H_4PO(OEt)_2$
1	F	0.020	0.080	120	13	82	0	72[a]				
2	Cl	0.052	0.237	70	[b]	81	0	70[c]				
3	Cl	0.068	0.239	93	[b]	87	0	80[c]				
4	Cl	0.020	0.083	56	50	48	0	46[c]	18			
5	Cl	0.574[d]	0.589[d]	130	61	38	0	38[c]				
6	Br	0.073	0.231	100	[b]	97	8[e]	93[f]		2.5		1.0
7	Br	0.021	0.078	120	12	87	14[e]	70[f]	18	1.9	10	2.2
8	I	0.021	0.078	60	24	111[g]		38[h]	15	3.2	24	6.7

[a] PhF. [b] Not determined. [c] PhCl. [d] In tetraglyme. [e] Br^-. [f] PhBr. [g] Reckoned on the basis of one iodide ion per molecule of **1i**. [h] PhI.

Table II. Photostimulated Reactions of *o*-Haloiodobenzenes with Sodium Diethyl Phosphite in Ammonia[a]

expt no.	ortho halogen	[substrate], M	$[(EtO)_2PO^-Na^+]$, M	time, min	products, % I^-	X^-	PhX	$H_2NPO(OEt)_2$	$PhPO(OEt)_2$	$PhNH_2$	o-$C_6H_4[PO(OEt)_2]_2$	o-$XC_6H_4PO(OEt)_2$
11	F	0.020	0.081	50	98	0	19[b]					80[b]
12	Cl	0.019	0.080	50	96	78[c]	6[c]		3		82	1[c]
13	Cl	0.020	0.079	50[d]	82	69[c]	10[c]		3		74	2[c]
14	Br	0.019	0.080	50	100	75[e]	20[e]	4	5	5	72	
15	I	0.022	0.079	50	199[f]		0	6	15	12	70	

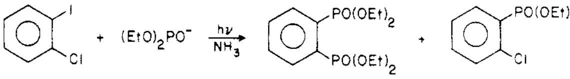
[a] Reactions at reflux (ca. −33 °C) unless otherwise noted. [b] X = F. [c] X = Cl. [d] Reaction at −55 °C. [e] X = Br. [f] On the basis of one iodide ion per substrate molecule.

relatively high. Under these conditions reaction was somewhat slower than in ammonia, but the products were of the same character as formed in ammonia.

The photostimulated reaction of *o*-chloroiodobenzene with $(EtO)_2PO^-$ (expt 12 and 13, Table II) differs from that of its fluoro analogue. The principal product is tetraethyl *o*-phenylenebisphosphonate (**3**). Of the lesser products, chlorobenzene is ascribed to the background dark reaction and diethyl *o*-chlorophenylphosphonate (**2c**) to the photostimulated process.

A conceivable genesis for diethyl phenylphosphonate (**2h**), another minor product, would be photostimulated reaction with chlorobenzene formed in the dark reaction, analogous to eq 1. Whether such reaction would occur was tested experimentally. During 50 min of irradiation of PhCl with $(EtO)_2PO^-Na^+$, 9% of **2h** was formed, and 9% of chloride ion was released. The small amounts of **2h** formed in expt 12 and 13 can thereby be accounted for.

The photostimulated reaction of *o*-chloroiodobenzene proper can thus be represented as in eq 4.

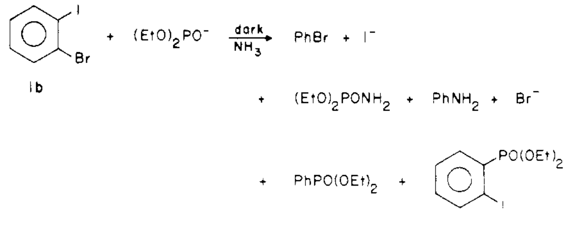


(4)

1c 3 major 2c minor

One photostimulated experiment (expt 13, Table II) was conducted at −55 °C in the hope that the background dark reaction might be disadvantaged by a 22 °C decrease in temperature. The outcome was, however, similar to that from expt 12 at −33 °C.

***o*-Bromoiodobenzene (1b).** The principal products from the dark reaction are analogous to those obtained from *o*-fluoro- and *o*-chloroiodobenzene, namely, bromobenzene and iodide ion; see expt 6 and 7, Table I. In expt 7, as previously in expt 4, 18% of $H_2NPO(OEt)_2$ was formed. However, four new minor products appear, to wit, bromide ion (8–14%), aniline (10%), **2h** (2%), and diethyl *o*-iodophenylphosphonate (**2i**, 2%). Products of the dark reaction are shown in eq 5. With regard to the origin of these products, we note that bromobenzene is unreactive with $(EtO)_2PO^-$ under the dark-reaction conditions.



(5)

1b 2h 2i

The photostimulated reaction of *o*-bromoiodobenzene (expt 14, Table II) is similar to that of its chloro but different from that of its fluoro analogue. Formed in greatest amount was **3**. Most of the minor products can be attributed to the background dark reaction. It is noteworthy that no *o*-halophenylphosphinic ester product could be detected.

Again concerning the dark reaction, we determined the I^-/Br^- product ratio as a function of time by potentiometric titration. This ratio was initially about 3 but increased with time to about 5, as displayed in Figure 1.

***o*-Diiodobenzene (1i).** The dark reaction (see expt 8, Table I) somewhat resembles that with *o*-bromoiodobenzene. The yield of iodobenzene is, however, relatively low, and the yields of the minor products, especially aniline (24%) and **2i** (7%), are higher.

The ratio of two dark-reaction products, of diethyl *o*-iodophenylphosphonate (**2i**) to diethyl phenylphosphonate

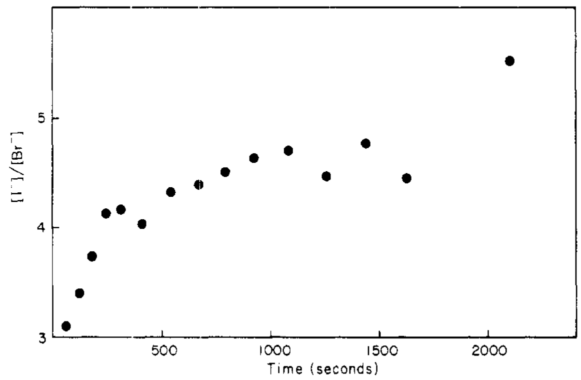


Figure 1. Reaction of *o*-bromoiodobenzene (**1b**) with sodium diethyl phosphite in the dark. The iodide ion/bromide ion product ratio as a function of time.

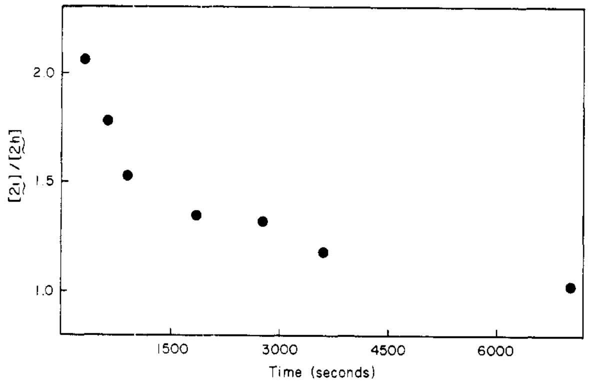


Figure 2. Reaction of *o*-diiodobenzene (**1i**) with sodium diethyl phosphite in the dark. The **2i**/**2h** product ratio as a function of time.

(**2h**), was in one experiment determined as a function of time. This ratio declined from an initial value of about 2 to a final value of about 1, as shown in Figure 2.

The photostimulated reaction of *o*-diiodobenzene (expt 15, Table II) resembles that of its bromo and chloro analogues in that **3** is the predominant product. Again, products of the background dark reaction are formed to some extent. It is to be noted, however, that the main product of the dark reaction, iodobenzene, fails to appear. The obvious reason is that iodobenzene reacts rapidly with $(EtO)_2PO^-$ to form **2h** (eq 1), and the yield of the latter is correspondingly higher.

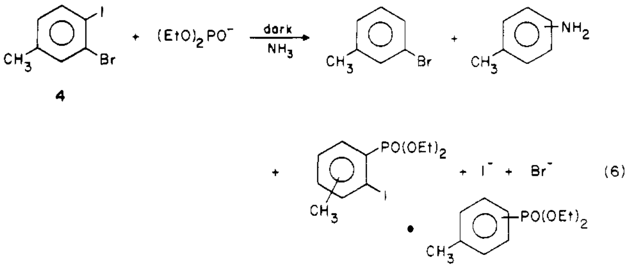
We return to the dark reaction to describe how we established the identity of **2i** as a product. That it is a diethyl iodophenylphosphonate was evident from its mass spectrum, but conceivably it might have been the meta or para isomer. Further evidence was obtained by allowing *o*-diiodobenzene to react with excess $(EtO)_2PO^-$ in the dark for the rather long time of 188 min and then irradiating the reaction solution for 52 min. It was presumed that irradiation after prolonged dark reaction would convert any iodophenylphosphonic ester into the corresponding bisphosphonate ester. That evidently occurred, for no diethyl iodophenylphosphonate was present after irradiation. The tetraethyl phenylenebisphosphonate which was formed, in 7.3% yield, was identified as the ortho isomer (**3**) by its characteristic GLC retention time and mass spectrum. Other products were **1h** (38%), aniline (44%), and iodide ion (200%).

In evaluating this experiment, one must consider first the possibility that some *o*-diiodobenzene remained unreacted even after 188 min of dark reaction and, second, the likelihood that the iodophenylphosphonic ester formed in the dark reaction underwent some photostimulated reaction other than (diethoxyphosphinyl)deiodination. As to the first possibility, if one extrapolates from expt 8 (Table I) on the assumption of pseudo-first-order kinetics, one estimates that about 1% of *o*-diiodobenzene should have remained unreacted after 188 min. This is quantitatively insufficient to account for the **3** formed in the dark-then-light experiment. As to the second, we do know that numerous aryl iodides react readily with $(EtO)_2PO^-$ under photostimulation to form phosphonic esters[2] and that diethyl *m*-bromophenylphosphonate undergoes a similar reaction.[4] Our expectation that **2i** and its meta and para isomers would also undergo (diethoxyphosphinyl)deiodination is amply supported by precedent.

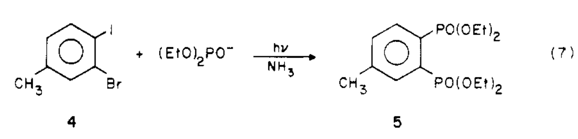
If either the meta or para isomer of **2i** were present after 188 min of dark reaction, it ought to have been converted into the meta or para isomer of **3**, but neither of those familiar compounds[2,3] appeared in the GLC tracing. We conclude that the diethyl iodophenylphosphonate formed from **1i** is the ortho isomer, **2i**.

This experiment also serves to identify the diethyl iodophenylphosphonate formed from **1b** (expt 6 and 7) as **2i**, for it has the same GLC retention time and mass spectrum as that formed in expt 8.

3-Bromo-4-iodotoluene (4). Reaction in the dark for 125 min left 37% of **4** unreacted and formed many products: *m*-bromotoluene (47%), I^- (61%), Br^- (10%), a mixture of *m*- and *p*-toluidine (7.7%), a mixture of diethyl *m*- and *p*-tolylphosphonates (1.3%), and a mixture of diethyl 2-iodo-5-methyl- and 2-iodo-4-methylphenylphosphonates (0.6%); see eq 6.



The photostimulated reaction formed, besides the products of the dark reaction (except that toluidines were not sought and no diethyl iodotolylphosphonate was detected), tetraethyl 4-methyl-1,2-phenylenebisphosphonate (**5**). These can be accounted for by a combination of background dark reaction plus the photostimulated process represented in eq 7.



Rate Measurements. In a few experiments, mostly with **1c**, we determined the amount of iodide ion formed as a function of time by titration with silver nitrate with respect to the amount of bromide ion present as an internal standard. In order to avoid the problems of pipetting aliquots of liquid ammonia, we removed samples by means of a small glass ladle. Such a procedure gives no assurance of equality of volumes, but titration against an internal standard allows the iodide ion concentration to be determined rigorously.

Plots of the resulting data according to integrated rate equations for kinetics first order in aryl iodide and for second-order kinetics (first order in aryl iodide, first order in nucleophile) were in neither case truly linear. The slopes decreased with time. Plots for second-order kinetics were perhaps better than those for first order. We list the

Table III. Kinetics of Reactions of *o*-Haloiodobenzenes with Sodium Diethyl Phosphite in Ammonia in the Dark

expt no.	ortho halogen	temp,[a] °C	$[C_6H_4XI]$, M	$[(EtO)_2PONa]$, M	10^3k, M^{-1} s^{-1}
16	Cl	−33	0.088	0.016	32.0
17	Cl	−33	0.019	0.041	4.1
18	Cl	−33	0.019	0.080	4.0
19	Cl	−33	0.066	0.113	7.7
20	Cl	−33	0.052	0.121	5.2
21	Cl	−33	0.014	0.121	2.8
22	Cl	−33	0.056	0.238	2.7
23	Cl	−33	0.065	0.240	3.2
24	Cl	−52	0.047	0.103	2.3
25	F	−33	0.021	0.078	6.4

[a] Runs at "−33 °C" were conducted at reflux; run 24 was at −52 ± 2 °C.

resulting very approximate rate constants in Table III.

Of the approximate rate constants obtained, those for expt 17, 18, 21, 22, and 23 are somewhat concordant, but those for expt 19 and 20 are distinctly higher, and that for expt 16 is nearly tenfold greater. Experiment 16 differs from the rest in that the aryl halide was in excess over the nucleophile, but it is unclear why that should cause such an increase in rate constant.

The rate constant at −52 °C (expt 24) was not much lower than that in a comparable run (expt 18) at −33 °C. The reactivity of *o*-fluoroiodobenzene (expt 25) was similar to that of its chloro analogue.

Because of the approximate character of these rate measurements, they are of little value as evidence of mechanism. We used them mainly as a guide as to the order of magnitude of reactivity in dark reactions.

Discussion

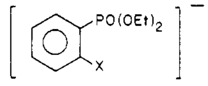
Photostimulated Reactions. Though some products of the background dark reactions always accompanied those from the photostimulated reaction, the products from the photostimulated reaction are easily identified because they are of different character. *o*-Fluoroiodobenzene (**1f**) suffers replacement of iodine only, affording monosubstitution product **2f** (eq 3). Parallel behavior has been observed for *m*- and *p*-fluoroiodobenzene.[2,3]

o-Diiodobenzene (**1i**) and *o*-bromoiodobenzene (**1b**) give, on photostimulated reaction, disubstitution product **3** without any trace of monosubstitution product. Their behavior also resembles that of their meta and para isomers.[2,3] 3-Bromo-4-iodotoluene similarly gives a bisphosphonate ester.

o-Chloroiodobenzene (**1c**) gives mainly disubstitution product **3** but also 1% of monophosphonate ester **2c** (eq 4). It behaves much like its para isomer,[3] but *m*-chloroiodobenzene under the same conditions affords predominantly a monosubstitution product.[2,3,5]

These photostimulated reactions are believed to occur by the $S_{RN}1$ mechanism.[6] The pattern of products formed finds interpretation in the mechanism for the propagation cycle(s) presented as Scheme I. As previously discussed,[3-6] a crucial feature of this mechanism is competition between steps M3 and M4. Step M3 forms monosubstitution product, symbolized by $X-Q-PO(OEt)_2$ in Scheme I. Step M4 leads on to step M6 in which disubstitution product is formed.

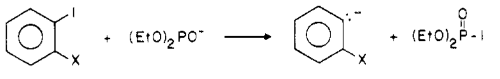
One of the principal factors determining whether step M3 is slower or faster than step M4 is the kinetic fragility of the radical anion formed in step M2. That radical anion has structure **6** in the cases we now consider. If **6** fragments rapidly, disubstitution predominates, but if its fragmentation is slow compared with electron transfer in step M3, mainly monosubstitution occurs. Inasmuch as the order of frangibility of C–X bonds in aryl halide radical anions is C–I > C–Br > C–Cl > C–F, one readily comprehends why only disubstitution is observed with **1b** and **1i** and only monosubstitution with **1f**.



6

In this series, reactions of **1c** are close to the borderline; although disubstitution is predominant, a little monosubstitution is observed, and change to the meta isomer alters the balance between steps M3 and M4 so that monosubstitution comes strongly to the fore.[2,3,5]

Dark Reactions. A consistent interpretation involves three levels of sophistication. *First*, diethyl phosphite ion mounts nucleophilic attack on iodine in an *o*-haloiodobenzene, effecting nucleophilic displacement on iodine with release of an *o*-halophenyl anion as nucleofuge. This step (eq 8) might also be described as a positive iodine transfer reaction, analogous to proton transfer. Nucleophilic displacements on halogen are well-known, and phosphorus nucleophiles are noteworthy for their proclivity to engage in such processes.[8] That such a reaction occurs with



(8)

1 7 8

f, X = F b, X = Br
c, X = Cl i, X = I

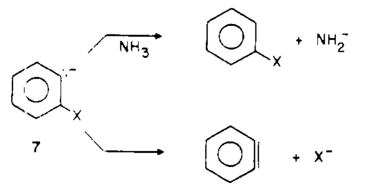
Table IV. Physical Properties of Phosphonate Esters

ester	bp (torr), °C	IR, cm^{-1}	^1H NMR (CCl_4), δ	MS, *m/e*
2f	90–92 (0.02)	1600, 1575, 1480, 1440, 1250, 1025, 830, 770, 690	1.35 (t, 6 H), 4.2 (m, 4 H), 7.0–8.3 (m, 4 H)	232 (M^+), 212, 205, 187, 184, 123,
2i[a,b]				340 (M^+), 312, 295, 284, 267, 213, 185, 157, 141, 125
2c[a]				250 (M^{37+}), 248 (M^{35+}), 223, 221, 213, 113, 111
3	138–140 (0.05)	1250, 1160, 1135, 1025, 965, 770, 670	1.35 (t, 12 H), 4.12 (M, 8 H), 7.3–8.3 (m, 4 H)	350 (M^+), 349, 335, 323, 305, 277, 249
5	144–145 (0.05)	1600, 1480, 1440, 1250, 1025, 880, 795, 750, 690, 655	1.4 (t, 12 H), 2.53 (s, 3 H), 4.3 (m, 8 H), 7.5–8.5 (m, 3 H)	364 (M^+), 349, 319, 291, 263

[a] Identified by mass spectrum (as determined on the Finnigan GC/MS equipment). [b] See text.

o-haloiodobenzene but was not observed for *m*- or *p*-iodohalobenzenes, despite efforts to find a dark reaction, is readily understood as a consequence of the very high stabilizing effect of ortho halogen substituents on phenyl anions.[9] The stabilizing effect of ortho halogens is orders of magnitude greater than that of meta or para halogens. It is manifested in numerous reactions that have been discussed elsewhere.[9]

Products 7 and 8 from the attack of diethyl phosphite ion on iodine are not stable in the environment in which they are formed. One reaction pathway available to aryl anion 7 is proton capture from solvent ammonia to afford halobenzene and amide ion (eq 9a). The formation of halobenzenes in the dark reactions is thus comprehensible.



(9a)

(9b)

As for the phosphoryl iodide, 8, it is doubtless very reactive with the nucleophiles present which include ammonia, amide ion (cf. eq 9a), and diethyl phosphite ion. Reaction with ammonia and/or amide ion forms diethyl phosphoramidate, a product obtained in modest yields, as in eq 10. However, the fact that the yields of

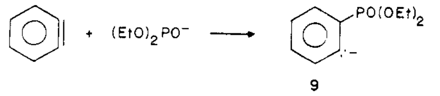
$$(EtO)_2POI + NH_2^- \rightarrow (EtO)_2PONH_2 + I^- \quad (10)$$

$(EtO)_2PONH_2$ detected are less than 20% while iodide ion yields are high suggests that something else happens to the phosphoryl iodide formed in eq 8. One possibility is a second step of diethoxyphosphinylation at nitrogen, as in eq 11. A related product, $Ph_2PNHPPh_2$, has been obtained from the action of $Ph_2P^-Na^+$ on 1,2,4,5-tetrabromobenzene in ammonia,[10] and its genesis has been similarly interpreted.[11]

$$(EtO)_2P(O)I + (EtO)_2PONH^- \rightarrow (EtO)_2P(O)NHP(O)(OEt)_2 + I^- \quad (11)$$

The dark reactions with *o*-bromoiodobenzene and *o*-diiodobenzene require a *second* level of interpretation to be invoked, namely, breakup of the *o*-halophenyl anion to form benzyne, as in eq 9b. Such fragmentation is well recognized.[12] Indeed, what is remarkable in the present work is that high yields of bromobenzene and substantial yields of iodobenzene are obtained by proton-capture process 9a. Most previous work has given the impression that **7b** and **7i** react exclusively via step 9b, eclipsing step 9a entirely. Indeed, in a pioneering report it was suggested that the reaction of bromobenzene with amide ion to form benzyne is a concerted elimination.[12] We note that independent evidence that *o*-bromophenyl anions may react significantly by route 9a has been found.[13]

The benzyne formed in step 9b may add ammonia and amide ion to form aniline, formed in 10% yield from **1b** and in 24% yield from **1i**. That more aniline is formed from *o*-diiodobenzene is attributed to a larger fraction of reaction by step 9b in the case of **7i**. Evidently benzyne may also add diethyl phosphite ion to form ultimately diethyl phenylphosphonate (**2h**), as in eq 12a and 12b.



(12a)

$$9 + NH_3 \longrightarrow 2h \quad (12b)$$

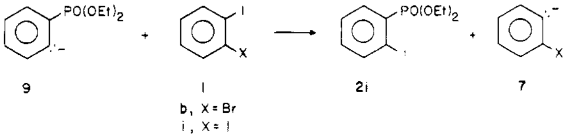
However, this reaction is slow, for the yields of **2h** from **1b** and **1i** are at the level of 2–3%.

It was conceivable that some readdition of halide ion(s) to benzyne occurred.[14] This was tested by allowing **1i** to react with diethyl phosphite ion in the dark in the presence of a 19-fold excess of KBr. Less than 1% of bromobenzene was formed; it was detected by GC/MS. Addition of halide ions to benzyne appears to be of little significance under the conditions of these experiments.

A *third* level of interpretation is needed to account for the formation of diethyl *o*-iodophenylphosphonate (**2i**) from **1b** and **1i** and for the variation of product ratios with time shown in Figures 1 and 2.

The possibility of ipso substitution of the halogen ortho to iodine by diethyl phosphite ion, perhaps by the S_NAr mechanism,[15] is rejected. That there is no precedent for such a process in a system so weakly activated for S_NAr is one consideration. An argument based on experiment is that it would be inconsistent for such ipso substitution to replace bromine to the exclusion of iodine from **1b** but then be of enhanced prominence in reaction with **1i** in which iodine necessarily would be replaced. The most telling argument is that such ipso substitution would give no account of the time variation of the product ratios of Figures 1 and 2.

We propose that **2i** is formed by attack of anion 9 on the iodine of **1b** or **1i** to effect positive iodine capture, as in eq 13. Such a step is centrally involved in the base-catalyzed halogen dance of oligohalobenzenes.[9] It would necessarily play its largest role early in the dark reactions of **1b** and **1i** with $(EtO)_2PO^-$ when the substrate concentration is highest, for the rate of step 13 should depend on **1b** or **1i** concentration, while the competing reaction with the solvent (step 12b) should not. Accordingly, the product ratio **2i**/**2h** should diminish with time, as it does (Figure 2).



(13)

For the dark reaction of **1b**, one can visualize an ionic chain mechanism for conversion of **1b** to **2i** with release of bromide ion. The propagation cycle comprises steps 9b, 12a, and 13. Evidently this is not a very efficient chain, but clearly it is most effective early in any reaction when the concentration of **1b** is high. It has the consequence of producing bromide ion without iodide ion, and therefore should cause the product ratio I^-/Br^- to be relatively low early in the reaction and to increase with time. That is exactly the behavior observed, as shown in Figure 1.

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The observed dark reactions of 3-bromo-4-iodotoluene with $(EtO)_2PO^-$ offer further support for the above interpretations. The aryne formed in this case should be 4-methylbenzyne, and nucleophilic addition to it should give mixtures of *m*- and *p*-toluidine, of diethyl *m*- and *p*-tolylphosphonate, and of isomeric diethyl iodotolylphosphonates. Such mixtures were observed to be formed. Furthermore, it would be expected that a sequence of steps like 8 and 9a should form *m*-bromotoluene not contaminated with its para isomer, and that also was observed.

The postulated interpretation for the formation of **2i** and especially the step suggested in eq 13 raise an interesting question. Inasmuch as *o*-aminophenyl and *o*-ammoniophenyl anions were intermediates in the addition, respectively, of amide ion and ammonia to benzyne to form aniline,[16] why did they not capture positive iodine from **1** analogously to eq 13 so as to form *o*-iodoaniline, of which we found no indication? The probable answer is that these intermediates, having a moderately or highly acidic group close to a highly basic carbanion site, shift protons intramolecularly or via solvent molecules to form anilide ion or aniline before they have a chance to attack **1**.

Reaction of 1c with Diethyl Phosphite Ion in Tetraglyme Solvent. We were motivated to perform expt 5 (Table I) by the report of Wursthorn, Kuivila, and Smith[17] that bromobenzene reacts with (trimethylstannyl)sodium in tetraglyme to form phenyltrimethylstannane in high yield but in ammonia to form only 4% of that product with 96% of benzene. The first step of the mechanism that they propose is a halogen–metal interchange somewhat analogous to reaction 8 above. It seemed conceivable in view of their results that if we changed our solvent from ammonia to tetraglyme, we might change the course of the dark reaction of **1c** with $(EtO)_2PO^-$ from dehalogenation forming chlorobenzene to substitution forming **2c**. However, the products we observed in tetraglyme solvent were chlorobenzene and iodide ion, just as in ammonia.

Experimental Section

Preparation of 3-Bromo-4-iodotoluene. 3-Bromo-4-aminotoluene (45.9 g, 0.247 mol) was dissolved in a mixture of 63 mL of concentrated HCl and 63 mL of water. After the mixture was cooled to 0 °C, $NaNO_2$ (18.4 g, 0.267 mol) in 85 mL of water was added. The rate of addition was regulated so as to maintain the temperature between 0 and 5 °C. To the almost clear solution was added slowly KI (41.5 g, 0.250 mol) in 46 mL water. The dark-colored reaction mixture was stirred for 1.5 h at room temperature and then heated to 80 °C for an additional hour. After the mixture was cooled, a heavy oil settled to the bottom of the flask. The solution was rendered alkaline with 10% NaOH, much of the water layer was poured off, and the remaining water–organic mixture was steam distilled. Redistillation of the crude product gave 39.5 g (54%) 3-bromo-4-iodotoluene as a slightly yellow oil, bp 82–83 °C (0.20 mm). The purity was checked by GLC. The infrared spectrum matched that reported in the literature.[18]

Photostimulated Reaction of *o*-Haloiodobenzenes and Diethyl Phosphite Ion in Liquid Ammonia. A three-necked, 500-mL flask was equipped with a serum cap, dry ice condenser, stir bar, and gas-inlet adapter. The apparatus was continually flushed with nitrogen as ammonia (250 mL) was distilled into the flask. A weighed amount of sodium was added to the stirred ammonia, and enough diethyl phosphite was added via a syringe so as to quench the blue color of the solvated electrons. After the ice was removed from the outside of the flask, the apparatus was placed into the photochemical reactor. The *o*-haloiodobenzene was added to the vigorously stirred solution and irradiation started within seconds. The photolysis was interrupted every 20 min for removal of ice from the surface of the flask. After 50 min, the mixture was quenched by the addition of ammonia nitrate and diethyl ether. The ammonia was evaporated, 20 mL of distilled water was added, and the ether layer was separated. The water layer was extracted with 60-mL portions of ether, and the halide ions in the aqueous layer were determined by potentiometric titration with silver nitrate. The combined ether extracts were dried over anhydrous sodium sulfate. GLC analyses of the ether layers 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-98) on 80–100 mesh WAW DMCS column. Reaction yields were determined from peak areas with respect to internal standards and with molar response corrections. The ether solutions were analyzed qualitatively by use of a Finnigan Model 4000 GC/MS unit. The mass spectra of the compounds in the reaction mixture were compared with those of authentic specimens (when available). The products of certain experiments were isolated by distillation, and their NMR and IR spectra were determined.

Dark Reaction of *o*-Haloiodobenzenes and Diethyl Phosphite Ion in Liquid Ammonia. The setup was the same as that for the photostimulated reactions. After the addition of the sodium and diethyl phosphite to the distilled ammonia, the flask was covered with black tape and the whole apparatus encased in aluminum foil and placed in the dark photochemical reactor. The stirring was adjusted, the *o*-haloiodobenzene added via a syringe, and the (dark) reactor covered with a black cloth. The reaction was quenched with ammonium nitrate and diethyl ether. Workup and analyses were the same as those for the photostimulated reactions.

Reaction of *o*-Diiodobenzene and Diethyl Phosphite Anion in the Dark with Subsequent Irradiation. A solution of 5.43 mmol of *o*-diiodobenzene and 20.3 mmol of diethyl phosphite anion in 250 mL of ammonia was allowed to react at reflux in a flask shielded from all light. After 188 min, the opaque covering was removed from the flask, and the solution was irradiated for 52 min. The workup was as usual: quenching with ammonium nitrate and addition of ether and water followed by separation and drying of the ether layer. Gas chromatographic analysis of the ether layer indicated the absence of any peak having a retention time similar to that for diethyl *o*-iodophenylphosphonate. A single peak having a retention time similar to those of the isomeric tetraethyl phenylenebisphosphonates was present in the spectrum. Comparison of the retention time of this peak with the retention times of authentic specimens of tetraethyl *o*-, *m*-, and *p*-phenylenebisphosphonates, which were distinctly different, showed that only the ortho isomer was formed. Also, the compound exhibited a mass spectrum identical with that of tetraethyl *o*-phenylenebisphosphonate. Quantitative GLC analysis showed that the bisphosphonate was formed in 7.3% yield.

Dark Reaction of *o*-Chloroiodobenzene and Sodium Diethyl Phosphite in Tetraglyme. Dry ammonia (25 mL) was distilled into a three-necked, 50-mL flask equipped with a dry ice condenser, serum cap, gas inlet adapter and stir bar. Sodium (0.117 g, 5.07 mmol) and diethyl phosphite (0.69 g, 5.01 mmol) were added to the ammonia, and the ammonia was evaporated. To the remaining white residue was added tetraglyme (8.5 mL) and the resulting solution stirred vigorously. The flask was covered with black tape and cooled to 0 °C. *o*-Chloroiodobenzene (1.17 g, 4.88 mmol) was added, and after 130 min, the reaction was quenched with ammonium nitrate, ether, and water. GLC analysis showed that 1.85 mmol (37.9%) of chlorobenzene was formed and that 2.96 mmol (60.7%) *o*-chloroiodobenzene remained unreacted.

Dark Reaction of 3-Bromo-4-iodotoluene and Sodium Diethyl Phosphite in Liquid Ammonia. The reaction was performed as previously described. The observed products (with yield and mass spectrum) are as follows: I^- (61.3%), Br^- (10.5%), *m*-bromotoluene (47.1%; *m/e* 172, 170, 91), *m*-toluidine (4.4% *m/e* 107, 106), *p*-toluidine (3.3%), diethyl *m*-tolylphosphonate (0.65%; *m/e* 228, 200, 172, 156, 155), diethyl *p*-tolylphosphonate (0.65%), diethyl 2-iodo-4-methylphenylphosphonate (0.3%), diethyl 2-iodo-5-methylphenylphosphonate (0.3%). The last two compounds were recognized by the mass spectrum of their unseparated peak on the Finnigan GC/MS instrument: MS *m/e*

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354, 326, 298, 281, 227, 199, 171, 155, 139. On the Hewlett-Packard instrument, two peaks of equal area appeared; molar responses equal to that of **3** were assumed.

Kinetics Experiments. A weighed amount of KBr was added to the ammonia containing the nucleophile (formed in the usual manner). The flask was covered with tape and foil, and all lights in the laboratory were extinguished. The dihalobenzene was then added. Samples were removed by means of a small glass ladle at measured times and quenched by addition to a beaker containing water, ether, and a crystal of ammonium nitrate. The water layer was titrated potentiometrically with silver nitrate, and the amounts of iodide and bromide ions were estimated from the respective end points. Since the bromide ion concentration was known, this procedure amounted to a determination of the iodide ion concentration. The slopes of the lines in the plotted graphs of $\ln [(b - 2x)/(a - x)]$, $\ln [(b - x)/(a - x)]$, $\ln (a_\infty - a_t)$, or $\ln (b_\infty - b_t)$ vs. time where $a = [XC_6H_4I]_0$ and $b = [(EtO)_2PO^-Na^+]_0$ were determined by linear-regression analysis. The rate constants were calculated from the slopes. Only rate constants derived from plots of $\ln [(b - x)/(a - x)]$ vs. time are listed in Table III.

Acknowledgment. This research was supported in part by the National Science Foundation. Acquisition of the Finnigan Model 4000 GC/MS equipment was assisted by the NSF Chemical Instrumentation Program.

Registry No. 1b, 583-55-1; **1c**, 615-41-8; **1f**, 348-52-7; **1i**, 615-42-9; **2c**, 28036-18-2; **2f**, 312-05-0; **2h**, 1754-49-0; **2i**, 71838-14-7; **3**, 71838-15-8; **4**, 71838-16-9; **5**, 71838-17-0; 3-bromo-4-aminotoluene, 583-68-6; diethyl phosphite anion, 29800-93-9; I^-, 20461-54-5; Br^-, 24959-67-9; *m*-bromotoluene, 591-17-3; *m*-toluidine, 108-44-1; *p*-toluidine, 106-49-0; diethyl *p*-tolylphosphonate, 1754-46-7; diethyl *m*-tolylphosphonate, 15286-13-2; diethyl 2-iodo-4-methylphenylphosphonate, 71838-18-1; diethyl 2-iodo-5-methylphenylphosphonate, 71838-19-2; PhF, 462-06-6; PhCl, 108-90-7; PhBr, 108-86-1; PhI, 591-50-4; $H_2NPO(OEt)_2$, 1068-21-9; $PhNH_2$, 62-53-3; Cl^-, 16887-00-6.

Some New Reactions of Perfluorinated Sulfonic Acids

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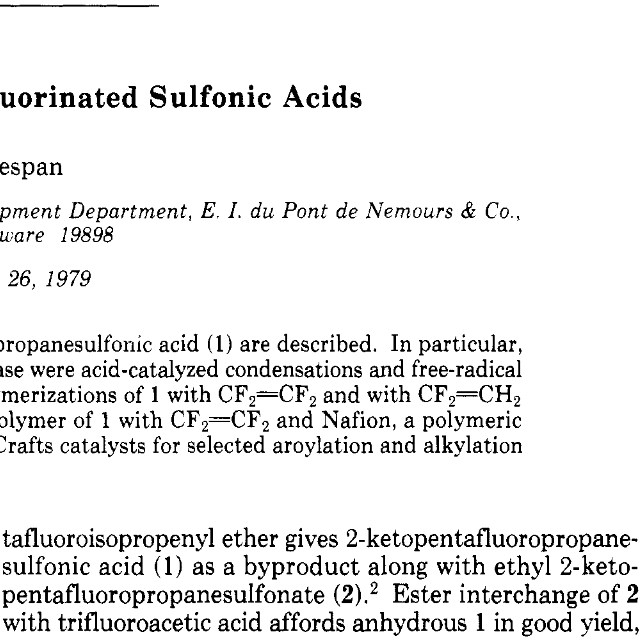
Received April 26, 1979

The synthesis and some chemistry of 2-ketopentafluoropropanesulfonic acid (1) are described. In particular, reactions at the carbonyl group of 1 found to proceed with ease were acid-catalyzed condensations and free-radical additions. The latter reaction was adapted to vinyl copolymerizations of 1 with $CF_2{=}CF_2$ and with $CF_2{=}CH_2$ to prepare new sulfonated fluoro polymers. Both the copolymer of 1 with $CF_2{=}CF_2$ and Nafion, a polymeric perfluorosulfonic acid, are shown to be promising Friedel–Crafts catalysts for selected aroylation and alkylation reactions.

Perfluoroalkylsulfonic acids are exceptionally strong acids and function as Friedel–Crafts catalysts. A striking example of the latter is the demonstration by Effenburger and Epple[1] that aroylation of aromatic nuclei with aroyl chlorides is effectively catalyzed by trifluoromethanesulfonic acid. Our recent synthesis of 2-ketopentafluoropropanesulfonic acid (1)[2] prompted a study of the chemistry of 1 with the aim of incorporating this readily available sulfonic acid into fluoro polymers by reaction at its carbonyl group. The sulfonated fluoro polymers so obtained might be valuable catalysts for reactions known to be promoted by trifluoromethanesulfonic acid or by conventional catalysts such as aluminum chloride. Among the advantages possible with insoluble polymeric catalysts are the use of truly catalytic rather than molar amounts of catalyst, ease of product workup, and reuse of catalyst on a continuous or batchwise basis. Results in the test cases detailed below indicate that such advantages can be realized with sulfonated fluoro polymers of sufficiently low equivalent weight.[3]

Results and Discussion

Synthesis of 2-Ketopentafluoropropanesulfonic Acid (1). The reaction of sulfur trioxide with ethyl pentafluoroisopropenyl ether gives 2-ketopentafluoropropanesulfonic acid (**1**) as a byproduct along with ethyl 2-ketopentafluoropropanesulfonate (**2**).[2] Ester interchange of **2** with trifluoroacetic acid affords anhydrous 1 in good yield, so that 1 is obtained in 67% overall yield from ethyl pentafluoroisopropenyl ether.



An attempt to convert ester **2** directly to the sulfonic anhydride by heating in the presence of phosphoric anhydride resulted in loss of sulfur dioxide as well as ethylene. No sulfonic anhydride was detected, and the volatile product obtained was the perfluorinated sulfonic ester **3**.[4]

Derivatization of 1. As a very strong acid, 1 is capable of adding to vinylidene fluoride, even at temperatures well below 0 °C. Protonation occurs readily to give a polar intermediate with well-stabilized charges; subsequent

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[1] F. Effenberger and G. Epple, *Angew. Chem., Int. Ed. Engl.*, 11, 300 (1972).

[2] C. G. Krespan, B. E. Smart, and E. G. Howard, *J. Am. Chem. Soc.*, 99, 1214 (1977).

[3] A recent paper by Olah et al. (G. A. Olah, R. Malhotra, S. C. Narang, and J. A. Olah, *Synthesis*, 672 (1978)) reports similar conclusions.

[4] F. Effenberger and K. Huthmacher, *Angew. Chem., Int. Ed. Engl.*, 13, 409 (1974), describe thermolyses of fluorinated sulfonic anhydrides which appear to proceed by heterolytic fission, loss of SO_2, and recombination to give esters.