MS that could be attributed to bis(1-naphthyl) telluride: MS, *m/e* (rel intensity) 384 (36), 382 (32), 380 (21), 379 (17), 257 (12), 255 (19), 254 (100), 253 (92), 252 (57), 127 (10).

p-Bis(phenyltelluryl)benzene. The residue obtained in reaction 4, Table III, was column chromatographed, and the pure product was isolated in 30% yield: mp 88–90 °C; MS, *m/e* (rel intensity) 490 (25), 488 (47), 486 (49), 485 (17), 484 (35), 483 (14), 482 (21), 360 (10), 358 (12), 283 (42), 281 (40), 279 (26), 278 (18), 230 (100), 207 (44), 205 (43), 203 (23), 202 (11).

By GC–MS there were also Ph$_2$Te and *p*-bromophenyl phenyl telluride: MS, *m/e* (rel intensity) 364 (36), 362 (47), 360 (34), 358 (26), 287 (6), 285 (13), 283 (11), 234 (99), 232 (100), 207 (11), 205 (10), 203 (16), 202 (14), 77 (58).

Photostimulated Reaction of *p*-Iodoanisole with 7. The procedure was the same as that used before, except that the reaction was quenched with methyl iodide to avoid the oxidation products, diaryl ditellurides. By GC of the ether extract three peaks were detected, the first one with the same retention time as Ph$_2$Te. The diethyl ether was distilled and the residue column chromatographed, obtaining 15% yield of Ph$_2$Te, 73% yield of *p*-anisyl phenyl telluride, and 11% yield of bis(*p*-anisyl) telluride. *p*-Anisyl phenyl telluride: mp 59–60 °C (lit.[22a] mp 60.5–61.5 °C); NMR δ 3.70 (3 H, s), 6.6–6.8 (2 H, m), 7.04–7.20 (3 H, m), 7.40–7.77 (4 H, m); MS, *m/e* (rel intensity) 315 (2), 314 (13), 313 (3), 312 (12), 311 (3), 310 (7), 309 (3), 308 (2), 307 (1), 306 (1), 237 (3), 236 (4), 235 (3), 234 (4), 221 (8), 219 (7), 217 (4), 206 (4), 204 (4), 193 (6), 191 (6), 189 (4), 184 (28), 183 (45), 169 (10), 168 (18), 142 (9), 141 (65), 140 (4), 139 (8), 130 (6), 128 (5), 115 (33), 92 (23), 79 (5), 78 (11), 77 (94), 76 (17), 75 (10), 65 (8), 64 (32), 63 (41), 62 (10), 51 (100), 50 (48). Bis(*p*-anisyl) telluride: mp 52–54 °C (lit.[34] mp 56–57 °C), this compound gave NMR and MS spectra in agreement with those previously reported.[34,27]

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Registry No. **1**, 1666-13-3; **2**, 14971-39-2; **3**, 1132-39-4; **4**, 65490-21-3; **5**, 134-85-0; **6**, 65081-67-6; **7**, 1202-36-4; **8**, 70838-54-9; **9**, 4537-22-8; 1-chloronaphthalene, 90-13-1; benzeneselenol, 645-96-5; Ph$_2$SeBr$_2$, 4190-46-9; *p*-biphenylyl phenyl selenide, 65490-22-4; 9-phenanthryl phenyl selenide, 65490-23-5; 2-quinolyl phenyl selenide, 71672-71-4; *p*-bis(phenylselenyl)benzene, 71672-72-5; diphenyl ditelluride, 32294-60-3; Ph$_2$TeBr$_2$, 29135-65-7; *p*-bis(phenyltelluryl)benzene, 71672-73-6; *p*-iodoanisole, 696-62-8; *p*-anisyl phenyl telluride, 56949-99-6; bis(*p*-anisyl) telluride, 4456-34-2; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; iodobenzene, 591-50-4; 4-chlorobiphenyl, 2051-62-9; 9-bromophenanthrene, 573-17-1; 2-chloroquinoline, 612-62-4; 1-bromonaphthalene, 90-11-9; *p*-dibromobenzene, 106-37-6; *p*-bromoiodobenzene, 589-87-7.

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S$_{RN}$1 Reactions of Some Phosphorus Nucleophiles with Iodo- and Bromobenzene[1]

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Four phosphanion nucleophiles, PhP(OBu)O$^-$, Ph$_2$PO$^-$, (EtO)$_2$PS$^-$, and (Me$_2$N)$_2$PO$^-$, react with iodo- or bromobenzene in ammonia under brief irradiation to form substitution products Ph$_2$PO(OBu), Ph$_3$PO, PhPS(OEt)$_2$, and PhPO(NMe$_2$)$_2$, respectively. Reactions of the first three nucleophiles with iodobenzene occur in nearly quantitative yield. Iodobenzene/bromobenzene reactivity ratios, measured in competition experiments, are 1 × 10^3 for PhP(OBu)O$^-$, 5 × 10^2 for (Me$_2$N)$_2$PO$^-$, and 45 for (EtO)$_2$PS$^-$. These reactions are believed to occur by the radical chain S$_{RN}$1 mechanism.

Dialkyl phosphite ions (eq 1) and diphenylphosphide ion (eq 2) react with halobenzenes and like substrates to replace the halogen atom by a phosphorus moiety.[2,3] The former reaction requires photostimulation.[2] The latter occurs in the dark at room temperature or below but more rapidly under irradiation.[3] Both reactions are much faster with iodobenzene than with bromobenzene.

$$(\mathrm{RO})_2\mathrm{PO}^- + \mathrm{PhX} \rightarrow \mathrm{PhPO(OR)}_2 + \mathrm{X}^- \qquad (1)$$

$$\mathrm{Ph}_2\mathrm{P}^- + \mathrm{ArX} \rightarrow \mathrm{ArPPh}_2 + \mathrm{X}^- \qquad (2)$$

These reactions are believed on good evidence to occur by the radical chain S$_{RN}$1 mechanism.[4]

Both these reactions occur in high yield and serve to establish aryl carbon–phosphorus bonds. Inasmuch as other methods for attaching phosphorus to aromatic sites, including Friedel–Crafts, Grignard, and diazonium salt reactions,[5] are subject to limitations of various kinds,[5] these S$_{RN}$1 reactions have actual or potential value for synthetic purposes.

Furthermore, there is the possibility that additional types of phosphanion nucleophiles may react similarly with aryl halides, so as to install various types of phosphorus functionality on aromatic rings. It is this possibility that we now explore.

Results

Descriptive Studies. Our principal experiments are summarized in Table I. They concern four phosphanion nucleophiles not previously involved in S$_{RN}$1 reactions, namely, PhP(OBu)O$^-$, Ph$_2$PO$^-$, (EtO)$_2$PS$^-$, and (Me$_2$N)$_2$PO$^-$. These can be regarded as analogues of the much-studied[2,5-11] (EtO)$_2$PO$^-$. Whereas diethyl phosphite

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Table I. Reactions of Phosphanions with Phenyl Halides in Liquid Ammonia

expt no.	PhX	nucleophile	irradiation time, min	products
1	PhI	$PhP(OBu)O^-K^+$	15	$Ph_2P(O)OBu$, 95%
2	PhBr	$PhP(OBu)O^-K^+$	75	$Ph_2P(O)OBu$, 72%
3	PhI	$PhP(OBu)O^-K^+$	60[a]	I^-, 45%; $Ph_2P(O)OBu$[b]
4	PhI	$PhP(OBu)O^-K^+$	dark[c]	I^-, 15%; $Ph_2P(O)OBu$[b]
5	PhI[d]	$PhP(OBu)O^-K^+$	60[d]	I^-, 61%; $Ph_2P(O)OBu$, 42%
6	PhI	$Ph_2PO^-K^+$	20	Ph_3PO, 95%
7	PhBr	$Ph_2PO^-K^+$	80	Br^-, nil; Ph_3PO, nil
8	PhI	$(EtO)_2PS^-K^+$	15	$PhP(S)(OEt)_2$, 95%
9	PhBr	$(EtO)_2PS^-K^+$	60	Br^-, 50%; $PhP(S)(OEt)_2$[b]
10	PhI	$(Me_2N)_2PO^-K^+$	30	I^-, 93%; $PhP(O)(NMe_2)_2$, 64%;[e] PhH, 7.8%[e]
11	PhBr	$(Me_2N)_2PO^-K^+$	90	Br^-, 66%; $PhP(O)(NMe_2)_2$, 65%;[e] PhH, 4%[e]

[a] Irradiation was conducted with two 22-W "cool white" circular fluorescent lamps. [b] Characterized, but not quantified. [c] Reaction vessel wrapped in foil and allowed to remain in the dark for 240 min. [d] Reaction conducted in dimethyl sulfoxide solvent. [e] Determined by quantitative gas chromatography.

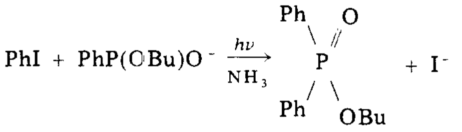
Table II. Reactivity of Iodobenzene vs. Bromobenzene with Phosphanion Nucleophiles

expt no.	nucleophile	vol of NH_3, mL	moles of nucleophile × 10^4	moles of PhI × 10^4	moles of PhBr × 10^4	irradiation time, min	moles of I^- × 10^4	moles of Br^- × 10^4	k_{PhI}/k_{PhBr}
12	$PhP(OBu)O^-K^+$	250	100	10.0	100	15[a]	4.67	0.039	1600
13		100	22.0	2.00		15[a]	0.472		
14		100	22.0		20.0	15[a]		0.0009	
15		100	22.0	2.00	20.0	15[a]	0.602	0.0075	950
16	$(Me_2N)_2PO^-K^+$	50	40.0	3.07	33.5	0.75[b]	1.32	0.039	480
17		50	40.0	3.32	33.0	0.75[b]	1.73	0.043	560
18		50	40.0	3.11		0.75[b]	0.64		
19		50	40.0		33.4	0.75[b]		0.055	
20	$(EtO)_2PS^-K^+$	50	30.0	5.00	20.4	2.0[a]	3.36	0.525	43
21		50	30.0	5.22	20.3	2.0[a]	4.59	0.875	48
22		50	30.0	5.08		2.0[a]	3.73		
23		50	30.0		20.0	2.0[a]		0.049	

[a] With 16 lamps in the photochemical reactor. [b] With 4 lamps in the photochemical reactor.

ion has two alkoxy groups and an oxygen atom attached to phosphorus, $PhP(OBu)O^-$ has one alkoxy group and one phenyl group, Ph_2PO^- has two phenyl groups, and $(Me_2N)_2PO^-$ has two dimethylamino groups attached to phosphorus, as well as an oxygen atom. $(EtO)_2PS^-$ is a thio analogue of $(EtO)_2PO^-$.

The potassium salt of butyl phenylphosphinate, $PhP(OCH_2CH_2CH_2CH_3)O^-K^+$, reacted rapidly with iodobenzene in refluxing ammonia under 15-min irradiation in a laboratory photochemical reactor, furnishing a 95% yield of butyl diphenylphosphinate (expt 1); see eq 3.



$$PhI + PhP(OBu)O^- \xrightarrow[NH_3]{h\nu} Ph_2P(O)OBu + I^- \quad (3)$$

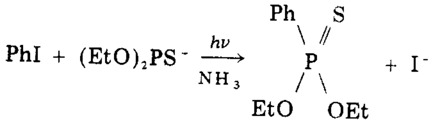
Reaction also occurred, though less rapidly, under the weaker irradiation provided by two household-type circular fluorescent lamps (expt 3). In the photochemical reactor, reaction was much slower in Me_2SO solution (expt 5) than in ammonia. In refluxing ammonia in the dark (expt 4), only 15% of iodide ion was released in 4 h.

Bromobenzene reacted with $PhP(OBu)O^-$ in like fashion but more slowly, furnishing the same product in 72% yield after 75-min irradiation in the laboratory photochemical reactor (expt 2).

The potassium salt of diphenylphosphine oxide, $Ph_2PO^-K^+$, reacted rapidly under photostimulation (expt 6) to form triphenylphosphine oxide in high yield (eq 4). However, analogous reaction with bromobenzene failed to occur detectably during 80-min irradiation (expt 7).

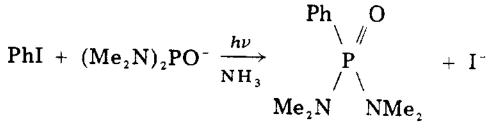
$$Ph_2PO^- + PhI \xrightarrow[NH_3]{h\nu} Ph_3PO + I^- \quad (4)$$

Potassium *O,O*-diethyl thiophosphite, $(EtO)_2PS^-K^+$, reacted quickly with iodobenzene under irradiation (expt 8) to form *O,O*-diethyl phenylthiophosphonate in nearly quantitative yield (eq 5). The analogous reaction with bromobenzene (expt 9) was much slower.



$$PhI + (EtO)_2PS^- \xrightarrow[NH_3]{h\nu} PhP(S)(OEt)_2 + I^- \quad (5)$$

The potassium salt of *N,N,N′,N′*-tetramethylphosphonamide, $(Me_2N)_2PO^-K^+$, reacted with iodobenzene during 30 min of irradiation (expt 10) to release 93% of iodide ion and form 64% of *N,N,N′,N′*-tetramethylphenylphosphonamide (eq 6). Benzene (8%) was also formed, but some of the iodobenzene consumed is unaccounted for. Bromobenzene underwent similar reaction (expt 11) but more slowly; in this case the material balance is better.



$$PhI + (Me_2N)_2PO^- \xrightarrow[NH_3]{h\nu} PhP(O)(NMe_2)_2 + I^- \quad (6)$$

Halogen Mobility Studies. Several experiments are summarized in Table II. We compared the reactivities

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of iodo- and bromobenzene in two ways: in competition with each other and in separate experiments under conditions for each halobenzene similar to those of the competition experiment.

In competitive reactions with $PhP(OBu)O^-K^+$ (expts 12 and 15), iodobenzene is about 10^3 times more reactive than bromobenzene. The measured values of k_{PhI}/k_{PhBr} are 1600 and 950, respectively. Such estimates are very sensitive to experimental titration errors in measurement of the very small amounts of bromide ion released. For that reason we do not regard these two estimates as being significantly different from each other. We express k_{PhI}/k_{PhBr} as ca. 1×10^3.

In separate reactions with $PhP(OBu)O^-K^+$, iodobenzene (expt 13) has about the same reactivity as in comparable competition expt 15, but bromobenzene (expt 14) is much less reactive than in experiment 15. This phenomenon is a further manifestation of entrainment effects previously observed in $S_{RN}1$ reactions of these two halobenzenes with pinacolone enolate ion[12] and in reactions of *p*-iodo- and *p*-bromotoluene with diphenylphosphide ion.[3] Bromobenzene reacts much faster in the presence of iodobenzene reacting with the same nucleophile than it does when reacting separately.

In competitive reactions with $(EtO)_2PS^-K^+$ (expts 20 and 21), iodobenzene is about 45 times more reactive than bromobenzene. Again, in separate reaction (expt 22), iodobenzene has about the same reactivity as in competition experiments under comparable conditions, but bromobenzene (expt 23) is much less reactive. Enhancement of bromobenzene reactivity in the presence of iodobenzene reacting with the same nucleophile is again evident.

In competitive reactions with $(Me_2N)_2PO^-K^+$ (expts 16 and 17), iodobenzene is about 500 times more reactive than bromobenzene. However, with this nucleophile, bromobenzene reacting separately (expt 19) has about the same reactivity as in competition experiments, and iodobenzene (expt 18) is perhaps a little less reactive than in competition with bromobenzene. (Small variations in iodide ion yield among separate experiments conducted for only 45 s each are of uncertain significance, owing to the large relative difference in exposure time resulting from random exposure time error and to the possible appearance in some reaction mixtures of adventitious inhibitor impurities.)

Discussion

Utility in Synthesis. Three phosphanion nucleophiles, namely, $PhP(OBu)O^-$, Ph_2PO^-, and $(EtO)_2PS^-$, have been found to react exceedingly well with iodobenzene, as shown in eq 3, 4, and 5, forming the products shown in nearly quantitative yield within an irradiation time for 15 or 20 min. Experiments listed in Table II suggest that shorter irradiation times would in some cases suffice. These three nucleophiles resemble the extensively studied[2,5-11] $(EtO)_2PO^-$ in speed of reaction and excellence of yield. Reaction of $(Me_2N)_2PO^-$ with iodobenzene (eq 6) occurred in similar fashion but gave only 64% of the expected product.

Generalizing from these results, one anticipates that other aryl iodides and bromides would react analogously with $PhP(OBu)O^-$, Ph_2PO^-, and $(EtO)_2PS^-$, and thus that a wide variety of alkyl diarylphosphinates, triarylphosphine oxides, and *O,O*-dialkyl arylthiophosphonates may be readily obtained via these substitution reactions. Studies with other nucleophiles have shown alkyl, phenyl, alkoxyl, benzoyl, and carboxylate (COO^-) groups to have a benign influence on $S_{RN}1$ reactions and that such reactions occur with halogen derivatives of polycyclic aromatic hydrocarbons and of pyridine and quinoline.[4] Also, the trimethylammonio and phenylthio groups are satisfactory nucleofugal groups in $S_{RN}1$ reactions with other nucleophiles[4] and possibly would be readily replaced by the nucleophiles of the present investigation. Furthermore, one anticipates that other nucleophiles of types G_2PO^- and G_2PS^-, where G represents any of several substituent groups, may undergo similar reactions.

Scheme I

$$[ArX]^{-\cdot} \longrightarrow Ar\cdot + X^- \qquad (M1)$$

$$Ar\cdot + Y^- \longrightarrow [ArY]^{-\cdot} \qquad (M2)$$

$$[ArY]^{-\cdot} + ArX \longrightarrow ArY + [ArX]^{-\cdot} \qquad (M3)$$

These reactions are convenient to run, requiring no specialized equipment other than a source of low-intensity ultraviolet light (white-light fluorescent lamps can be used). Strongly basic but otherwise mild reaction conditions are employed, and the reaction times are quite short (a few minutes). No excess of any reactant is required. Thus the reactions are relatively inexpensive to conduct, and products are easily isolable from the reaction mixtures in pure form and high yield. Due to its generality, convenience, and resultant high yields, we believe that aryl phosphorus bond formation by the $S_{RN}1$ reaction offers important opportunities for the synthesis of organophosphorus compounds.

Reaction Mechanism. These reactions are believed to occur by the radical chain $S_{RN}1$ mechanism,[4] the propagation cycle of which is presented in Scheme I. In Scheme I, Y^- represents an anionic nucleophile.

The fact that reaction of iodobenzene with $(EtO)_2PS^-$ occurs as shown in eq 5 warrants comment. Whereas alkoxide and phenoxide ions are unreactive in aromatic $S_{RN}1$ reactions, alkane- and arenethiolate ions react very well.[13-16] It was therefore conceivable that one might observe a change from P-arylation of $(EtO)_2PO^-$ in $S_{RN}1$ reactions to S-arylation of $(EtO)_2PS^-$. The fact that again only P-arylation occurs is consistent with the pattern of reactivity of $(EtO)_2PS^-$ with other electrophilic reagents.[17]

It is noteworthy that the yield of $PhPO(NMe_2)_2$ in reaction 6 was significantly less than quantitative, namely, 64%. A small amount of benzene was also formed, presumably owing to hydrogen atom abstraction from the nucleophile by the intermediate phenyl radical. An analogous hydrogen atom abstraction from hexamethylphosphorotriamide appears to occur during the hydrodediazoniation of benzenediazonium ion in that solvent.[18]

From our work and earlier observations,[3,8] the iodobenzene/bromobenzene reactivity ratio in competition experiments with various phosphanion nucleophiles may be summarized as follows: $(EtO)_2PO^-$, ca. 1×10^3; $PhP(OBu)O^-$, ca. 1×10^3; $(Me_2N)_2PO^-$, 5×10^2; Ph_2P^-, 4×10^2; $(EtO)_2PS^-$, 4.5×10^1. We eschew detailed discussion of these interesting variations until we have better information as to the step or steps within the propagation sequence (Scheme I) in which the relative reactivity of two aryl halides is determined and until more physical data, especially redox potentials, for the nucleophiles and sub-

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stitution products are available. Some of the relevant considerations have been mentioned previously.[8]

The entrainment effect noted above, whereby bromobenzene reacts much faster in the presence of iodobenzene reacting with the same nucleophile than it does separately, is readily understood in terms of the $S_{RN}1$ mechanism but is incompatible with conceivable nonchain ionic mechanism alternatives. This radical chain mechanism involves not only the propagation steps shown in Scheme I but also initiation and termination steps. If the iodobenzene/bromobenzene reactivity ratio is higher in initiation than in propagation, the observed entrainment effect is intelligible. Separately, the bromobenzene overall reactivity is severely limited by the low initiation rate, but in competition bromobenzene can take advantage of initiation involving iodobenzene so that its relative reactivity is limited only by its capacity to react in propagation.

The lack of observable entrainment effect in reactions with $(Me_2N)_2PO^-$ perhaps indicates that with this nucleophile the iodobenzene/bromobenzene reactivity ratio in initiation is similar to that in propagation, or even lower. If so, why should that be?

There is much yet to be learned about reactions of this type.

Experimental Section

General Methods. Gas chromatography was conducted on a Hewlett-Packard Model 5751B chromatograph equipped with a flame-ionization detector. Analyses were done by using a 5% SE-30 on 60/80-mesh Chromosorb W, 5 ft × $^1/_8$ in. column operating at 40–140 °C. Yields of products were determined with reference to biphenyl and toluene as internal standards. In all cases, the areas were corrected for molar response as determined from standard solutions of the products and the internal standard.

Irradiations were conducted in a Rayonet Model RPR-100 photochemical reactor equipped with 16 lamps emitting maximally at 350 nm.

Infrared spectra were recorded on a Perkin-Elmer Model 237 or 337 grating spectrophotometer, NMR spectra on a Jeolco Minimar (60 MHz) instrument, and mass spectra on a Hitachi RMU-6E mass spectrometer or Finnigan Model 4000 GC/MS system.

Most of our experimental results are summarized in Tables I and II.

Materials. Ammonia was distilled from sodium prior to use. Dimethyl sulfoxide was distilled from calcium hydride immediately prior to use. Potassium *tert*-butoxide (Alfa Inorganics) was sublimed immediately prior to use, quickly weighed, and transferred to the reaction vessel. Bromobenzene and iodobenzene were purchased from commercial sources, distilled from calcium hydride, and stored in foil-wrapped bottles. Butyl phenylphosphinate was prepared by butanolysis of phenyldichlorophosphine.[19] Diphenylphosphine was prepared as previously described[20] and oxidized to diphenylphosphine oxide.[21] Reaction of hydrogen sulfide with diethyl chlorophosphite, formed by action of 2 equivalents of ethanol on phosphorus trichloride,[22] gave *O,O*-diethyl thiophosphonate.[23] Conproportionation of phosphorus acid and hexamethylphosphorotriamide[24] gives *N,N,-N',N'*-tetramethylphosphonamide.[25]

Photostimulated Reaction of Potassium *n*-Butyl Phenylphosphonite with Iodobenzene in Ammonia (Eq 3). Into a three-necked, 500-mL round-bottom flask equipped with dry ice and 2-propanol-charged cold finger condenser, nitrogen inlet, and magnetic stirrer was condensed ca. 250 mL of liquid ammonia. To the ammonia was added 2.38 g (0.012 mol) of butyl phosphinate and 1.34 g (0.012 mol) of potassium *tert*-butoxide. The resulting solution was light green. Iodobenzene (2.04 g, 0.01 mol) was then added and the flask placed in the photochemical reactor and irradiated for 15 min (with one interruption to wash frost from the flask exterior with acetone). The green color had almost completely faded. Excess ammonium nitrate and ca. 200 mL of diethyl ether were added, and the ammonia was allowed to evaporate.

To the ether solution was added 100 mL of water, and the layers were separated. The water layer was extracted with diethyl ether (3 × 150 mL), and the combined organic layers were washed with 100 mL of water. The organic phase was dried over anhydrous sodium sulfate, and the ether was removed on a rotary evaporator. The resulting crude white crystalline butyl diphenyl phosphinate (2.57 g, 95%, mp 78–85 °C) was recrystallized from diethyl ether; 1.95 g (71%), mp 88.5–89 °C. After three more recrystallizations from diethyl ether–petroleum ether mixture, the melting point was found to be 93–94 °C. The aqueous phase was diluted to 250 mL. Titration of a 10-mL fraction with 0.0700 M silver nitrate indicated 0.0095 mol of iodide ion to have been released.

Butyl diphenylphosphinate: NMR ($CDCl_3$) δ 8.08–7.28 (m, 10 H), 4.06 (q, 2 H, J = 7 Hz), 1.93–0.72 (m, 7 H); IR (KBr) 3060, 2960 (CH), 1215 (P=O), 980 (P—O—C) cm^{-1}; MS ($m/e > 170$) m/e (rel intensity) 275 (27), 274 (47), 245 (35), 231 (71), 219 (100), 201 (97), 173 (84). Anal. Calcd for $C_{16}H_{19}O_2P$: C, 70.07; H, 6.93 Found: C, 70.36; H, 6.90.

Butyl diphenylphosphinate was also synthesized by the reaction of diphenyl phosphinic chloride with 1-butanol. Melting point and spectral data were identical.

Photostimulated Reaction of Potassium Diphenylphosphinite with Iodobenzene in Ammonia (Eq 4). The scale and procedure were virtually identical with those above. The residue from evaporation of the dried diethyl ether extract was triphenylphosphine oxide (2.64 g, 95%, mp 150–151 °C). After recrystallization 2.42 g of product was obtained, mp 153–153.5 °C (lit.[26] mp 156 °C). Titration of an aliquot of the aqueous phase indicated 0.0098 mol of iodide ion had been released. The triphenylphosphine oxide NMR and IR spectra were in good agreement with the literature.[27]

Photostimulated Reaction of Potassium *O,O*-Diethyl Thiophosphite with Iodobenzene in Ammonia (Eq 5). The scale and procedure were virtually identical with those above. The residue from evaporation of the dried diethyl ether extract was distilled; bp 87 °C (0.4 mm) [lit.[28] bp 94–96 °C (0.3 mm)]. *O,O*-Diethyl phenylthiophosphonate: NMR ($CDCl_3$) δ 7.4–8.3 (m, 5 H), 4.14 (d of q, J_{H-H} = 6.5 Hz, J_{P-H} = 9 Hz, 4 H), 1.25 (t, J = 6.5 Hz, 6 H); IR (neat) 3090, 3000 (CH), 1450 (P—O—C), 1040 (P—O—C), 800 (P=S) cm^{-1}; MS ($m/e > 150$) m/e (rel intensity), 230 (100), 186 (52), 169 (74), 158 (29), 157 (43).

A sample of *O,O*-diethyl phenylthiophosphonate was prepared by refluxing phenylphosphonothioic dichloride in absolute ethanol overnight. NMR, IR, and mass spectra were identical with those of the compound prepared above.

Titration of an aliquot of the aqueous layer indicated 95.5% iodide ion release.

Photostimulated Reaction of Potassium *N,N,N',N'*-Tetramethyl Phosphorodiamidite (Eq 6). The scale and procedure were virtually identical with those above. The residue from evaporation of the dried diethyl ether extract was a yellow oil which crystallized on cooling and was recrystallized once from diethyl ether. *N,N,N',N'*-Tetramethylphenylphosphonamide: mp 84.5–85 °C (lit.[29] mp 82–84 °C); 1.0 g (47%); NMR ($CDCl_3$) 7.97–7.32 (m, 5 H), 2.63 (d, J = 10 Hz, 12 H); IR (KBr) 3100, 2940

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(CH), 1200 (P=O), 1280, 975, 735 cm^{-1}; MS *m/e* 212, 168, 92.

Titration of an aliquot of the aqueous layer indicated 93.4% iodide ion release.

An authentic sample of *N,N,N',N'*-tetramethylphenylphosphonamide, mp 82.5–84 °C, with NMR, IR, and mass spectra identical with those for the product just described, was prepared by condensation of phenylphosphonic dichloride with dimethylamine in diethyl ether solution at temperature below 15 °C.

Competitions between Iodo- and Bromobenzene. The following procedure is representative. Into a three-necked, 125-mL round-bottom flask equipped with a cold finger condenser charged with solid CO_2 and 2-propanol, nitrogen inlet, and magnetic stirrer, was condensed ca. 50 mL of ammonia distilled from sodium. To the ammonia were added freshly resublimed potassium *tert*-butoxide (0.47 g, 4.2 × 10^{-3} mol), *N,N,N',N'*-tetramethylphosphonamide (0.54 g, 4.0 × 10^{-3} mol), iodobenzene (0.0626 g, 3.07 × 10^{-4} mol), and bromobenzene (0.526 g, 3.35 × 10^{-3} mol), and the mixture was stirred briefly. (The iodo- and bromobenzene were previously weighed and mixed in a small vial, and it was shown by weighing that no appreciable residue remained in the vial or in the pipet used to transfer the mixture.) The flask was placed in the photochemical reactor equipped with only four lamps symmetrically disposed, and the lamps were turned on for 45 s. The mixture was quickly acidified with ammonium nitrate, and 50 mL of diethyl ether was added. The entire process, from addition of the phenyl halides to acidification, took about 60 s. The ammonia was allowed to evaporate, 25 mL of water was added, the phases were separated, and the water phase was extracted with diethyl ether (2 × 50 mL). The aqueous phase was diluted to 100 mL, and 25 mL aliquots were titrated with 0.07 M $AgNO_3$ potentiometrically. The iodide and bromide ion end points were easily identified; in a representative run, 4.71 mL of $AgNO_3$ solution was required to attain the iodide ion end point and a further 0.14 mL for the bromide ion end point.

Rate constant ratios were reckoned by means of eq 7.[30]

$$k_{PhI}/k_{PhBr} = ([ArBr]_0/[Br^-]_t)\ \ln\ ([PhI]_0/([PhI]_0 - [I^-]_t)) \qquad (7)$$

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Registry No. $PhP(OBu)O^-K^+$, 71774-84-0; $Ph_2PO^-K^+$, 19115-01-6; $(EtO)_2PS^-K^+$, 71774-85-1; $(Me_2N)_2PO^-K^+$, 71774-86-2; PhI, 591-50-4; PhBr, 108-86-1; $Ph_2P(O)OBu$, 20610-34-8; Ph_3PO, 791-28-6; $PhP(S)(OEt)_2$, 6231-03-4; $PhP(O)(NMe_2)_2$, 3732-83-0; PhH, 71-43-2.

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Occurrence of an S_N(ANRORC) Mechanism in the Chichibabin Amination of 4-Phenylpyrimidine[1]

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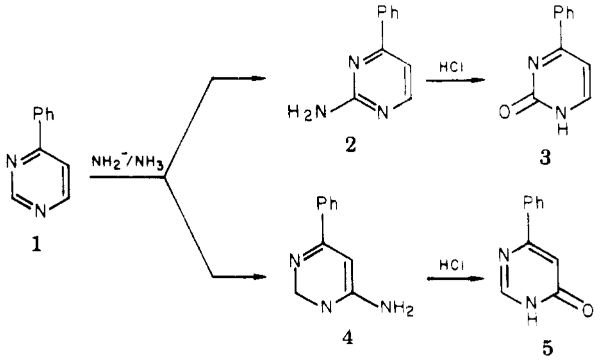
On treatment of 4-phenylpyrimidine with potassium amide in liquid ammonia, a mixture of 6-amino-4-phenylpyrimidine and 2-amino-4-phenylpyrimidine is obtained. It was proven that in the formation of the 2-amino compound the pyrimidine ring is opened but that in the formation of the 6-amino compound *no* ring opening is involved. ^1H and ^{13}C NMR spectroscopy gave evidence for formation of two σ adducts between the amide ion and 4-phenylpyrimidine, i.e., the 6-amino-1(or 3),6-dihydropyrimidinide ion and the 2-amino-1(or 3),2-dihydropyrimidinide ion.

During the last decade the amination of aza aromatics containing groups with considerable leaving character has been a subject of continuous interest; special attention is paid to the use of potassium amide in liquid ammonia as an aminating reagent. Sound proof is obtained—on the basis of application of ^{15}N-labeled compounds and NMR spectroscopy—that in an overwhelming number of cases the replacement of the leaving group by the amino group takes place for the greater part according to a so-called S_N(ANRORC) mechanism, describing a reaction sequence involving an *A*ddition of the *N*ucleophile to the heterocycle, *R*ing *O*pening, and *R*ing *C*losure reaction.[2]

Scheme I



In order to extend these studies we became interested as to whether the Chichibabin amination of aza aromatics by potassium amide (i.e., the replacement of a hydrogen by an amino group) would also occur according to an S_N(ANRORC) mechanism. Up to now only one example of a Chichibabin reaction has been reported in which the

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[1] (a) Part 78 on pyrimidines from this laboratory. For part 77 see: N. J. Kos, H. C. van der Plas, and A. van Veldhuizen, *J. Org. Chem.*, 44, 3140 (1979). (b) Part 25 on the S_N(ANRORC) mechanism. For part 24 see: H. C. van der Plas, *Acc. Chem. Res.*, 11, 462 (1978). For part 23 see: C. A. H. Rasmussen and H. C. van der Plas, *Tetrahedron Lett.*, 3841 (1978). (c) Part 23 on σ adducts. For part 22 see: A. Nagel, H. C. van der Plas, G. Geurtsen, and A. van Veldhuizen, *J. Heterocycl. Chem.*, 16, 301 (1979).

[2] For a review, see the first reference in 1b.

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