

water and recrystallized from methanol: yield 4.86 g of pure 4-toluidine (90% yield), mp 47 °C.

Registry No. Pd, 7440-05-3; D₂, 7782-39-0; HCOOH, 64-18-6; HCOONa, 141-53-7; HCOOK, 590-29-4; hydrogen, 1333-74-0; 4-toluidine, 106-49-0; 3-nitrotoluidine, 99-08-1; 1-ethyl-3-nitrobenzene, 7369-50-8; 2-nitroanisole, 91-23-6; 4-nitroanisole, 100-17-4;

4-fluoronitrobenzene, 350-46-9; 4-nitrobenzaldehyde, 555-16-8; 4-iodonitrobenzene, 636-98-6; 4-nitrobenzotrile, 619-72-7; chloronitrobenzene, 25167-93-5; bromonitrobenzene, 61878-56-6; benzonitrile, 100-47-0; iodobenzene, 591-50-4; styrene, 100-42-5; bromobenzene, 108-86-1; 4-nitrotoluene, 99-99-0; 2-nitrotoluene, 88-72-2; 4-nitrophenetole, 100-29-8; nitrobenzene, 98-95-3; 1-ethyl-4-nitrobenzene, 100-12-9; 1-ethyl-2-nitrobenzene, 612-22-6.

Aromatic Radical Nucleophilic Substitution Reactions Initiated by Sodium Amalgam in Liquid Ammonia

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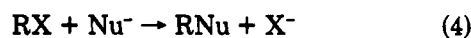
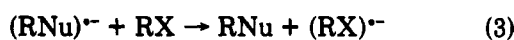
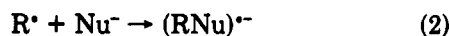
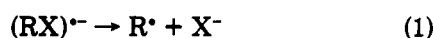
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Neither 1-chloronaphthalene nor 2-chloroquinoline reacted with Ph₂P⁻ ions in liquid ammonia. However, in the presence of sodium amalgam [Na(Hg)], reaction did occur, and the substitution products 1-naphthylidiphenylphosphine and 2-quinolyldiphenylphosphine (isolated as the *P*-oxides), respectively, were obtained in good yield. *p*-Bromoanisole reacted with Na(Hg) amalgam in the presence of Ph₂P⁻ ions in liquid ammonia to give anisole as the only product, but when benzonitrile was used as a redox catalyst, a good yield of the substitution product *p*-anisylidiphenylphosphine (isolated as the *P*-oxide) was obtained. It is believed that Na(Hg) amalgam initiated these S_{RN1} reactions. Preparative-scale reactions gave good yields of the substitution products.

First-order radical nucleophilic substitution (S_{RN1}) has been shown to be an excellent means of effecting the nucleophilic substitution of unactivated aromatic compounds possessing suitable leaving groups. Many different types of nucleophiles can be employed.¹

The mechanism of the reaction is a chain process. The propagation steps are shown in Scheme I,¹ in which eq 4 summarizes eqs 1-3.

Scheme I



Overall, Scheme I depicts a nucleophilic substitution in which radicals and radical anions are intermediates. However, this chain process requires an initiation step. In a few systems, spontaneous electron transfer (ET) from the nucleophile to the substrate has been observed and the radical anion (RX)^{•-} that is formed initiates the chain propagation steps.² When electron transfer does not occur spontaneously, it can be induced by light,³ by solvated electrons in liquid ammonia,⁴ by cathodically generated electrons,⁵ or by certain inorganic salts.⁶

All these methods of initiation have some disadvantages from a preparative point of view. For instance, light-initiated or electrochemically initiated reactions can be performed only in dilute solutions. Solvated electrons are very strong reducing agents, and in certain systems, reduction of the substitution products can take place.⁷

We believed it would be of interest to find an alternative method for initiating aromatic S_{RN1} reactions, one that could be used on a preparative scale, and one in which the disadvantages of the other methods of initiation were absent.

We recently reported⁸ that sodium amalgam [Na(Hg)] selectively dehalogenated haloarenes in liquid ammonia. We believed that Na(Hg) amalgam could also be used as a catalyst in synthetic-scale S_{RN1} reactions. We used the diphenylphosphide (Ph₂P⁻) ion as the model nucleophile because it is especially reactive in aromatic S_{RN1} reactions.⁹

Results and Discussion

When 3% Na(Hg) amalgam was added to dry liquid ammonia, a heterogeneous mixture was formed. The supernatant liquid remained colorless, which suggested that no solvated electrons were present. Moreover, that *p*-chloroanisole (*p*-ClAn) and naphthalene did not react under these conditions⁸ also suggested that no electrons were present in the solution. Because *p*-ClAn and naphthalene did not react with the amalgam, their reduction potentials must be more negative than that of Na(Hg) amalgam in liquid ammonia. (The reduction potential of Na(Hg) amalgam in DMF is $E_{1/2} = -2.0$ vs SCE.¹⁰)

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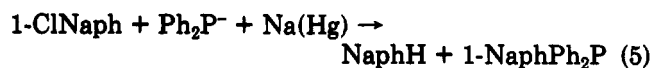
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Table I. Reactions of Haloarenes with Ph_2P^- Ion in Liquid Ammonia Catalyzed by $\text{Na}(\text{Hg})$ Amalgam^a

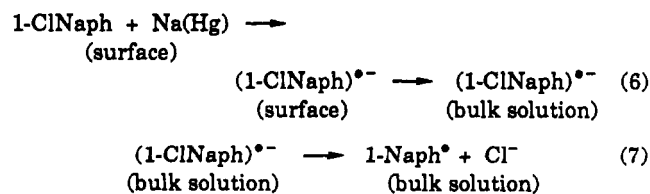
expt	haloarene ArX^b	Na(Hg) (mmol)	PhCN (mmol)	product yields (%)		
				X^-	redn product ^c	substn product ^c
1	1-CIN	0	0	≤ 10	<i>d</i>	<i>d</i>
2	1-CIN	4.5	0	100	20	71
3	1-CIN	0.30	4.5	51	20	31
4	1-CIN	0.75	4.5	79	10	57
5	1-CIN	1.1	4.5	90	13	74
6	1-CIN	1.5	4.5	99	10	81
7 ^e	1-CIN	4.5	4.5	100	19	83
8	1-CIN	15.2	4.5	100	22	72
9	1-CIN	4.5	1.5	100	19	83
10	1-CIN	4.5	15.2	100	25	73
11	1-CIN ^f	37.6	12.5	100	14	82 (54) ^g
12	2-ClQ	3.0	0	100	0	91
13	2-ClQ	3.0	4.5	100	0	94
14	2-ClQ ^h	28	0	100	0	96 (75) ^g
15	<i>p</i> -BrAn	3.0	0	78	78	0
16	<i>p</i> -BrAn	1.5	1.5	57	18	32
17	<i>p</i> -BrAn	3.0	1.5	98	43	49
18	<i>p</i> -BrAn	3.0	6.0	99	37	72
19	<i>p</i> -BrAn	3.0	12.0	100	17	85
20	<i>p</i> -BrAn	3.0	22.5	100	17	83
21	<i>p</i> -BrAn	3.0	1.5 ⁱ	33	18	2
22	<i>p</i> -BrAn	3.0	1.5 ^j	67	18	36
23	<i>p</i> -BrAn	3.0	6.0 ^k	83	32	32
24	<i>p</i> -BrAn	3.0	6.0 ^l	46	23	10
25	<i>p</i> -BrAn	3.0	6.0 ^l	48	32	10
26	<i>p</i> -BrAn	3.0	1.5 ^m	35	0	0
27	<i>p</i> -BrAn ⁿ	25.1	63	100	6	78 (50) ^g
28	<i>p</i> -IAN	0	0	34	0	27
29	<i>p</i> -IAN	3.0	0	86	61	27
30	<i>p</i> -IAN	3.0	1.5	94	63	40
31	<i>p</i> -IAN	3.0	1.5 ⁱ	45	41	10

^a Substrate, 1.5 mmol; Ph_2P^- ion, 3.0 mmol; liquid ammonia, ca. 300 mL; reaction time, 2 h. ^b 1-CIN = 1-chloronaphthalene; 2-ClQ = 2-chloroquinoline. ^c Determined by GLC by the internal standard method. Unless otherwise indicated, the substitution products were quantified as the *P*-oxides. ^d Not quantified. ^e Reaction time, 15 min. ^f Substrate, 12.5 mmol. ^g Isolated yield. ^h Substrate, 14.0 mmol. ⁱ *p*-Dicyanobenzene. ^j Quinoline. ^k Biphenyl. ^l Naphthalene. ^m Methyl benzoate. ⁿ Substrate, 12.5 mmol.

1-Chloronaphthalene (1-ClNaph) did not react with Ph_2P^- ions in liquid ammonia (Table I, experiment 1). However, in the presence of $\text{Na}(\text{Hg})$ amalgam, reaction did occur and gave a 71% yield of the substitution product 1-naphthyldiphenylphosphine (quantified as the *P*-oxide) and a 20% yield of naphthalene (Table I, experiment 2) (eq 5).



This result suggested that 1-ClNaph received an electron from $\text{Na}(\text{Hg})$ amalgam to form the radical anion (1-ClNaph)^{•-}, which diffused from the surface of the amalgam to the bulk solution before it fragmented (eq 6). (It was determined electrochemically that the fragmentation was first order with $k = 1.6 \times 10^7 \text{ s}^{-1}$ in DMF).¹¹ Fragmentation yielded the 1-naphthyl radical, which then entered the propagation steps of the $\text{S}_{\text{RN}}1$ reaction (eq 7).



The presence of PhCN (used as "redox catalyst", vide infra) did not produce an increase in the yield of the substitution product (70–83% yield) (Table I, experiments 5–7).

The effect of varying the amount of $\text{Na}(\text{Hg})$ amalgam used in these reactions was also studied. With 20 mol % of $\text{Na}(\text{Hg})$, a 31% yield of the substitution product and a 20% yield of naphthalene (overall yield of 51%) (Table I, experiment 3) were produced. If the reaction were not a chain process, the overall reaction yield should be only 20%. Thus, these results suggested that $\text{Na}(\text{Hg})$ amalgam initiated the chain propagation steps.

With 50, 70, and 100 mol % of $\text{Na}(\text{Hg})$ amalgam, the yields of substitution product were 57, 74, and 81%, respectively (Table I, experiments 4–6). With 1000 mol % of $\text{Na}(\text{Hg})$ amalgam, no noticeable increase in yield was obtained (Table I, experiment 8).

Varying the PhCN:1-ClNaph ratio from 1 to 10 gave comparable results (Table I, experiments 9 and 10). From a preparative-scale reaction of 1-ClNaph, 2.3 g (54% yield) of the pure substitution product (Table I, experiment 11) was isolated.

With 2-chloroquinoline as the substrate, a 91% yield of the substitution product 2-quinolyldiphenylphosphine (isolated as the *P*-oxide) (Table I, experiment 12) was obtained. The same result was obtained from the same reaction in the presence of PhCN (Table I, experiment 13). This enhancement of yield could be the result of a slower rate of fragmentation of the 2-chloroquinoline radical anion (the first-order rate constant is $6.3 \times 10^5 \text{ s}^{-1}$ in DMF).¹¹ From a preparative-scale reaction, 4.6 g (75% yield) of pure 2-quinolyldiphenylphosphine oxide (Table I, experiment 14) was isolated.

The reaction of *p*-bromoanisole (*p*-BrAn) (An = anisyl = methoxyphenyl) with $\text{Na}(\text{Hg})$ amalgam in liquid ammonia gave anisole.⁸ When the reaction was performed in the presence of Ph_2P^- ions (to trap *p*-anisyl radicals),

(11) Andrieux, C. P.; Savéant, J. M.; Zann, D. *Nouv. J. Chim.* 1984, 8, 107.

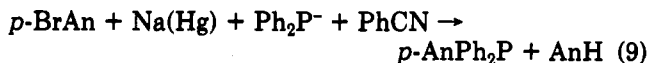
again only anisole was detected (Table I, experiment 15) (eq 8).



That no substitution product was formed in this reaction could be ascribed to the fact that the *p*-bromoanisole radical anion that was formed by electron transfer from the amalgam to *p*-BrAn fragmented faster than it diffused into the bulk solution. Thus, the *p*-anisyl radical was formed very close to the surface of the Na(Hg) amalgam, where it was further reduced to *p*-anisyl anion. This, in turn, was protonated by liquid ammonia to form anisole. Haloarene radical anions are known to fragment very rapidly, at or near the diffusion-controlled limit.¹²

It is well-known from electrochemical studies that a "redox catalyst", a compound that displays a more positive reduction potential than that of the haloarene that is to be reduced, can be used to catalyze the electrochemical reduction of haloarenes. Such a catalyst forms a relatively stable radical anion which can diffuse from the surface of the electrode into the bulk solution. It then transfers its unpaired electron to the haloarene under homogeneous reaction conditions.^{8,13,14} By employment of a redox catalyst, haloarene radical anions thus can be formed far from the surface of the electrode. After the radical anion fragments into halide ion and aryl radical, the latter is able to react with a nucleophile. For instance, PhBr, which is reduced in a single two-electron wave at ca. -2.70 V (DMSO vs Ag/AgCl), is reduced to benzene and, consequently, does not react with nucleophiles.¹⁴ However, benzonitrile (PhCN), which undergoes a reversible one-electron reduction at -2.25 V (DMSO vs Ag/AgCl), has been used as a redox catalyst in the electrochemically stimulated $S_{RN}1$ reaction of PhBr with PhS^- ion.¹⁴ It was believed that PhCN would also act as a redox catalyst in the reaction of *p*-BrAn with Na(Hg) amalgam and Ph_2P^- ion in liquid ammonia.

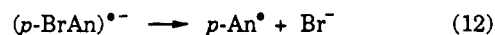
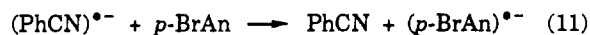
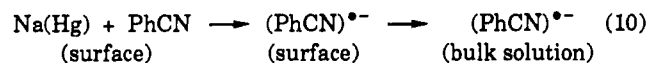
When the reaction shown in eq 8 was performed, in the presence of PhCN (*p*-BrAn:PhCN = 1:1) and 1 equiv of Na(Hg) amalgam, a 57% yield of Br^- ions was produced along with the substitution product *p*-anisyl-diphenylphosphine (*p*-AnPh₂P) (quantified as the *P*-oxide, 32% yield) and anisole (18% yield) (Table I, experiment 16). With 2 equiv of Na(Hg) amalgam, the substitution product *p*-AnPh₂P (quantified as the *P*-oxide, 49% yield) and anisole (43% yield) (Table I, experiment 17) (eq 9 vs eq 8) were formed.



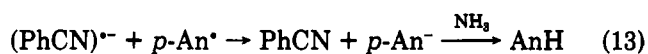
When *p*-BrAn:PhCN = 1:4, a 72% yield of *p*-AnPh₂P was obtained. When *p*-BrAn:PhCN = 1:8, the yield of *p*-AnPh₂P increased to 85%. When *p*-BrAn:PhCN = 1:15, almost the same yield of *p*-AnPh₂P (83%) (Table I, experiments 18–20) was obtained. It should be noted that, as the concentration of PhCN rose, the yield of the substitution product increased, to a limiting value beyond which no additional substitution product was formed.

These results suggested that PhCN competed with *p*-BrAn in the reaction with Na(Hg) amalgam and that

PhCN received an electron to form the corresponding radical anion. The radical anion then diffused into the bulk solution (eq 10). Then it transferred its unpaired electron to *p*-BrAn, far from the surface of the amalgam, to form the radical anion (*p*-BrAn)^{•-} (eq 11). This radical anion then fragmented into Br^- ion and *p*-anisyl radical (eq 12). The latter entered the chain propagation steps of the reaction (Scheme I).



That anisole was formed (15–17% yield) even in the presence of a high concentration of PhCN suggested that either some *p*-BrAn reacted with Na(Hg) amalgam and was reduced or *p*-anisyl radical was also reduced by the benzonitrile radical anion (eq 13).¹⁵



The 83–85% yield of substitution product so obtained could be the maximum yield that is possible under these experimental conditions.

On a preparative scale, 1.9 g (50% yield) of pure *p*-anisyl-diphenylphosphine oxide was obtained (Table I, experiment 27).

Other substances, like quinoline, biphenyl, and naphthalene, were tested as redox catalysts. Most of these compounds also catalyzed the reactions. However, lower yields (10–30%) of the substitution products were found (Table I, experiments 22–25). *p*-Dicyanobenzene (2% of substitution product) (Table I, experiment 21) and methyl benzoate (no reaction at all in the case of *p*-BrAn) (Table I, experiment 26) were ineffective catalysts.

p-Iodoanisole (*p*-IAN) reacted with Ph_2P^- ion in the absence of catalyst (a case of spontaneous ET from the nucleophile) to give a 27% yield of the substitution product after 1 h (Table I, experiment 28).¹⁶ The same reaction in the presence of Na(Hg) amalgam gave the same yield of substitution product, but along with an increased yield of anisole (Table I, experiment 29). Reaction in the presence of Na(Hg) amalgam and PhCN resulted in a slight increase in the yield of substitution product (Table I, experiment 30). Because *p*-IAN displays a more positive reduction potential than PhCN, there was only slight catalysis of the reaction. With *p*-dicyanobenzene as the catalyst, the yield of substitution product was lower still (Table I, experiment 31).

Conclusions. The experimental results showed that Na(Hg) amalgam was able to initiate the $S_{RN}1$ reaction of aryl halides with Ph_2P^- ions. Those haloarenes that formed radical anions which fragmented very fast and very close to the surface of the amalgam were further reduced to arenes. Thus, in order to induce an $S_{RN}1$ substitution reaction, a redox catalyst was used. In the system studied, PhCN fulfilled this function. Preparative-scale reactions

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(13) (a) Andrieux, C. P.; Blocman, C.; Dumas-Bouchiat, J. M.; Savéant, J. M. *J. Am. Chem. Soc.* 1979, 101, 3431. (b) Andrieux, C. P.; Blockman, C.; Dumas-Bouchiat, J. M.; M'Halla, F.; Savéant, J. M. *J. Am. Chem. Soc.* 1980, 102, 3806. (c) Savéant, J. M. *J. Am. Chem. Soc.* 1987, 109, 6788. (d) Andrieux, C. P.; Hapiot, P.; Savéant, J. M. *Chem. Rev.* 1990, 90, 723 and references cited therein.

(14) Swartz, J. E.; Stenzel, T. T. *J. Am. Chem. Soc.* 1984, 106, 2520.

(15) Electrochemical studies in liquid ammonia showed that the most important process by which aryl radicals in $S_{RN}1$ reactions were reduced was by homogeneous ET from radical anion intermediates. See: (a) Amatore, C.; Oturan, M. A.; Pinson, J.; Savéant, J. M.; Thiebault, A. *J. Am. Chem. Soc.* 1984, 106, 6318. (b) Savéant, J. M. *Bull. Soc. Chim. Fr.* 1988, 226.

(16) It was reported that *p*-iodotoluene reacted with Ph_2P^- ion in liquid ammonia in the dark in 5.5 h to give an 89% yield of the substitution product. See: Swartz, J. E.; Bunnett, J. F. *J. Org. Chem.* 1979, 44, 340.

gave good yields of the substitution products.

Experimental Section

General Method. ^1H NMR spectra of CD_2Cl_2 solutions were recorded with a Varian T-60 nuclear magnetic resonance spectrometer. The positions of the signals are reported in parts per million relative to Me_4Si (δ). Mass spectra were recorded with a Finnigan 3300 f-100 mass spectrometer. Gas chromatographic analyses were performed with either a Shimadzu GC8A gas chromatograph equipped with a Shimadzu CR-3A data system or a Spectra Physics SP-2400 gas chromatograph equipped with a flame ionization detector. A 3 mm \times 1.5 m column packed with 5% OV 17 on Chromosorb P was used. Quantitative analysis was done by the internal standard method. The potentiometric titration of halide ions was performed with a pH meter (Seybold Wien) equipped with a Ag/Ag^+ electrode and AgNO_3 standard. Melting points were measured with a Büchi 510 apparatus and are uncorrected.

Materials. Triphenylphosphine (Aldrich), *p*-IAN (Fluka), *p*-BrAn (Fluka), 1-chloronaphthalene (Fluka), 2-chloroquinoline (Fluka), and benzonitrile (BDH) were commercially available and were used as received. Diphenylphosphide ions were generated by the reaction of triphenylphosphine and Na metal in liquid ammonia.^{1b} Na(Hg) amalgam was prepared from Na metal (Mallinckrodt) and mercury.¹⁷ The activity of the amalgam was determined by measuring the hydrogen evolved during reaction of the amalgam with water with a modified Haldane respirometer.¹⁸

Reaction of Na(Hg) Amalgam with 1-Chloronaphthalene and Ph_2P^- Ion in Liquid Ammonia. The following procedure is representative. Liquid ammonia (300 mL, previously dried under nitrogen with Na metal), triphenylphosphine (3.0 mmol), and Na metal (6.1 mmol) were mixed under dry N_2 to form diphenylphosphide ions. *t*-BuOH (3.1 mmol) was then added to neutralize the amide ions formed. The reaction vessel was wrapped with aluminum foil to exclude light. Na(Hg) (4.5 mmol), *t*-BuOH (4.5 mmol), and 1-ClNaph (1.5 mmol) were then added in the dark. The reaction was quenched by addition of excess NH_4NO_3 , and the ammonia was allowed to evaporate. The residue was dissolved in water, and the solution was extracted with CH_2Cl_2 . The extract was treated with 40% H_2O_2 ¹⁹ to give 1-naphthyl-di-

phenylphosphine oxide (71% yield) and naphthalene (20% yield), as determined by GLC. In a preparative experiment, after oxidation the solution was evaporated to dryness. Flash chromatography of the residue on silica gel (Et_2O /acetone, 1:1) gave pure 1-naphthylidiphenylphosphine oxide (2.3 g, 54% yield): mp 177–179 °C (lit.²⁰ mp 178–179 °C); ^1H NMR δ 7.4 (16 H, m), 8.4 (1 H, m); MS *m/e* (%) 329 (8), 328 (100), 202 (9), 77 (4); MS *m/e* (relative intensity) 308 (49), 307 (100), 231 (22), 215 (19), 183 (12), 77 (5).

Reaction of Na(Hg) Amalgam with 2-Chloroquinoline and Ph_2P^- Ion in Liquid Ammonia. In the preparative experiment, after oxidation the solution was evaporated, and the residue was recrystallized (hexane) to give 4.6 g (75% yield) of pure 2-quinolyldiphenylphosphine oxide: mp 138–139 °C (lit.^{9b} mp 139.5–140 °C); MS *m/e* (relative intensity) 329 (15), 328 (20), 252 (59), 204 (51), 201 (25), 183 (20), 128 (69), 101 (45), 77 (100), 51 (55).

Reaction of Na(Hg) Amalgam with *p*-BrAn and Ph_2P^- Ion in Liquid Ammonia Catalyzed by PhCN. Ph_2P^- (3.0 mmol, prepared as described above), Na(Hg) (3.0 mmol), *t*-BuOH (3.0 mmol), *p*-BrAn (1.5 mmol), and PhCN (12.0 mmol) were added to 300 mL of liquid ammonia. The subsequent procedure was the same as that of the previous reaction. The residue was dissolved in water, and the solution was extracted with CH_2Cl_2 . Oxidation of the products with 40% H_2O_2 gave *p*-anisylidiphenylphosphine oxide (85% yield) and anisole (17% yield), as determined by GLC. In a preparative experiment, after oxidation the solution was evaporated under reduced pressure. The residue was recrystallized (hexane/ CH_2Cl_2 , 9:1) to give 1.9 g (50% yield) of pure *p*-anisylidiphenylphosphine oxide: mp 104–105 °C (lit.²¹ mp 103–104 °C); ^1H NMR δ 3.8 (3 H, s), 7.8 (14 H, m); MS *m/e* (%) 308 (49), 307 (100), 231 (22), 215 (19), 183 (12), 77 (5).

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