by near-UV light,[7] or by electrons from a cathode[8] in liquid ammonia.

Besides, other nucleophiles such as the anion of anthrone, the dianion of hydroquinone, 9,10-dihydroanthracene, and 1,5-diamino-9,10-dihydroxyanthracene were unreactives toward 1-chloronaphthalene in photostimulated reactions in liquid ammonia.[7] Contrary to the PhO^- ion, most of these anions are soluble in liquid ammonia; the only slightly soluble one is the hydroquinone dianion; thus the lack of reactivity cannot be ascribed to their poor solubility.

On the other hand the report that halobenzenes react with PhO^- in 50% aqueous *tert*-butyl alcohol under stimulation by solvated electrons from dissolution of sodium amalgam, giving good yields of diphenyl ether,[9] prompts us to reinvestigate this reaction with the hope that under these reaction conditions we could study the relative reactivity of PhZ^- nucleophiles (Z = O, S, Se, and Te).

Unfortunately we were unable to reproduce those results, and the PhO^- ion was totally unreactive in our hands.

The experiments were conducted with bromobenzene as substrate and PhO^- ion in excess in 50% v/v aqueous *tert*-butyl alcohol with sodium amalgam as a source of electrons. All the reactions were conducted at 25 °C at concentrations of reactants identical with those reported and at two different ratios of substrate and sodium amalgam.

The reaction products were analyzed by GC, and the halide ion released was quantified by potentiometric titrations. In every case the reaction time which was required for the total dissolution of the sodium amalgam was the same. In reactions carried out with a bromobenzene–sodium amalgam ratio of 1:2 we could not find diphenyl ether or benzene by GC. In reactions with a ratio of 1:3 and in the presence of toluene as internal standard, benzene (6%) and bromide ion (7.5%) were found, but no traces of diphenyl ether (<0.5%) could be detected. Under the same experimental conditions, but with 10% external diphenyl ether added, the same results were obtained, with the diphenyl ether recovered unchanged, showing that it survives under our reaction conditions.

It is known that sodium amalgam dissolved in water generates hydrated electrons[10] which could produce phenyl radicals by reaction with bromobenzene (eq 1, Scheme I). The results reported in this paper show that PhO^- ion is unable to react with phenyl radical by the $S_{RN}1$ mechanism; instead it is reduced to benzene. This statement is reinforced by the fact that 5-chloro- and 5-bromo-2*H*,3*H*-benzo[*b*]thiophene-2,3-dione react with PhS^- in Me_2SO by the $S_{RN}1$ mechanism, but PhO^- gave only the reduction product.[11]

Experimental Section

General Methods. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with a flame-ionization detector, using a column packed with 4% silicon rubber SE-30 on Chromosorb G 80-100. Potentiometric titrations were carried out with a Seybold digital pH meter, Model GTE, using a combined silver–calomel electrode. Reagents were all commercially available materials and were purified by standard procedures.

Reaction of PhO^- ion with Bromobenzene and Sodium Amalgam. To a solution of phenol (2.688 g, 28.6 mmol) in 100 mL of 50% *tert*-butyl alcohol–doubly distilled water was added sodium hydroxide (1.517 g, 38 mmol), and the system was degassed and then constantly swept with nitrogen free of oxygen, under magnetic stirring. This was followed by the addition of bromobenzene (1 mL, 9.5 mmol) and toluene (0.5 mL) as internal standard. A 2-mL aliquot was removed at different reaction times to check the toluene/bromobenzene ratio, while sodium amalgam (containing 0.625 g, 27.2 mmol, of sodium) was added in small portions to the remaining solution. The total dissolution of the sodium amalgam took approximately 24 h. The toluene/bromobenzene ratio remained unchanged by GC in samples taken at 0.5, 1, and 2 h, and only one new peak, identified as benzene, was observed at a 24-h reaction time. The solution was then extracted with ether, and the aqueous layer was titrated for bromide ion.

Registry No. Phenoxide ion, 3229-70-7; bromobenzene, 108-86-1.

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Preparation and Synthetic Utility of Phase-Transfer Catalysts Anchored to Polystyrene[1]

Margaret Shea Chiles, Donald D. Jackson, and
Perry C. Reeves*

Department of Chemistry, Southern Methodist University,
Dallas, Texas 75275

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Phase-transfer catalysts[2] facilitate reactions between water-soluble reagents and water-insoluble organic compounds. The catalysts are generally not recovered and this becomes a problem when the relatively expensive cryptands and crown ethers are used. On the other hand, the inexpensive ammonium and phosphonium salts sometimes form stable emulsions. Development of polymer-supported, phase-transfer catalysts[3] allowed for greater ease in separation of the catalyst and isolation of the product. This paper describes the catalytic activity of several new polystyrene-immobilized tetraalkylphosphonium and ammonium salts and explores the extent to which they have synthetic utility.

Results and Discussion

For the determination of the most effective catalyst, different parameters such as the type of polystyrene used, the length of the spacer chain, the type of salt, and the degree of substitution on the polystyrene backbone were varied (Table I). Microporous polystyrene (cross-linked with 2% divinylbenzene, 200–400 mesh) was found to be superior to either macroporous or noncross-linked polystyrene. Regen[4] and Brown[5] studied catalysts similar to 1 and found them to possess much lower activity than nonimmobilized catalysts. Other investigators[5–8] reported increased activity when the catalytic center was attached to the polystyrene matrix by long (8–39 atoms) spacer

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Table I. Polymer-Supported, Phase-Transfer Catalysts $[P]\text{-}(CH_2)_n\text{-}^{+}ABu_3$ [b]

catalyst	A	n	mequiv of A[a]	$T_{1/2}$, min
1a	P	1	2.46	20
1b	P	1	1.30	60
2a	P	2	1.69	17
2b	P	2	1.00	32
3a	P	3	2.07	15
3b	P	3	1.07	20
4	N	2	1.66	32
5	N	3	1.52	18

[a] Per gram of polymeric catalyst. [b] [P] represents the polymer support.

Table II. Bromide Displacement from 1-Bromooctane by Cyanide

catalyst[a]	solvent	T, °C	t, h	yield, %	ref
$[P]\text{-}CH_2OC(O)(CH_2)_{11}\text{-}^{+}NMe_3$	none	100	4	100	5
$[P]\text{-}CH_2NHC(O)(CH_2)_{10}\text{-}^{+}PBu_3$	none	90	9	100	8
$[P]\text{-}CH_2NHP(O)(NMe_2)_2$	none	80	1	95	10
$[P]\text{-}CH_2NEt(CH_2)_9\text{-}$18-crown-6	toluene	90	7	95	6
$[P]\text{-}(CH_2)_6\text{-}^{+}PBu_3$	toluene	90	1.6	98	11
$[P]\text{-}CH_2\text{-}^{+}NMe_2Bu$	benzene	110	4	92	3
$[P]\text{-}CH_2\text{-}^{+}NMe_3$	benzene	110	15	95	12
$[P]\text{-}CH_2\text{-}^{+}PBu_3$	toluene	90	1	86	4
3a	none	110	0.7	95	

[a] [P] represents the polymer support.

chains. This study shows that the use of short (2 or 3 atoms) spacer chains also produces highly active catalysts.

The reaction between an aqueous solution of potassium cyanide and 1-bromopentane was chosen as a standard reaction to compare the catalytic activity of compounds **1**–**5**. Table I lists the time required to achieve 50% conversion of 1-bromopentane to hexanenitrile. A comparison with other reported polystyrene-anchored, phase-transfer catalysts (Table II) reveals that **3a** is very active and that its catalytic activity compares favorably with hexadecyltributylphosphonium bromide.[9] Some of this increased activity may be due to solvent effects. Compounds **1**–**5** catalyze displacement reactions in a variety of solvents such as benzene, toluene, and cyclohexane, but the activity can be increased dramatically by removing the organic solvent from the reaction mixture. Some investigators[8] have reported the need for conditioning the resin prior to addition of the organic substrate; however, preconditioning of compounds **1**–**5** did not increase their catalytic activity.

The effect on catalytic activity as the distance increases between the polystyrene backbone and the catalytic center can be seen in Table I. The phosphonium salts are more active than the related ammonium salts and in this system tributyl salts are more active than triethyl, trihexyl, or trioctyl salts. There is also an increase in catalytic activity as the percent ring substitution increases from 15 to 65%.

The most detailed study of the synthetic applications of polymer-immobilized, phase-transfer catalysts was reported by Regen[12] but utilized catalysts which have since been shown to be of rather low activity. Thus a wide range of nucleophilic displacement reactions have been studied with a variety of organic halides in order to ascertain the synthetic utility of the very active catalysts **3a** and **5** (Tables III–VII). In all cases, reported yields represent quantities of purified products. The observed order of reactivity of the alkyl halides is bromides > iodides > chlorides. When iodides are used, the catalyst is gradually "poisoned". This is caused by the affinity of the iodide ion[2] for the quaternary cation and is more pronounced when the phosphonium salts are utilized. Thus the ammonium catalyst **5** is the catalyst of choice whenever iodide ions are used or produced.

Table III. Displacement by Cyanide Ions

halide	product	reaction time, h	yield, %
1-bromopentane	hexanenitrile	0.5	79
1-chloropentane	hexanenitrile	5	84
1-iodopentane[a]	hexanenitrile	1.5	85
1-bromooctane	nonanenitrile	1	99
1-chlorooctane	nonanenitrile	6	70
benzyl chloride	phenylacetonitrile	0.5	85
1-bromo-3-methylbutane	4-methylpentanenitrile	0.5	75
1-bromo-3,3-dimethylbutane	4,4-dimethylpentanenitrile	1.1	82
1,4-dibromobutane	hexanedinitrile	0.5	74
2-bromopentane	2-methylpentanenitrile	5.5	51
3-bromopropene	3-butenenitrile	2	0
ethyl bromoacetate	ethyl cyanoacetate	2	0

[a] Catalyst **5** used.

Table IV. Displacements by Sulfur Nucleophiles

alkyl halide	nucleophile	product	t, h	yield, %
1-bromopentane	$C_6H_5S^-$	pentyl phenyl sulfide	0.2	83
	S^{2-}	dipentyl sulfide	1.5	98
	SCN^-	pentyl thiocyanate	2	94
1-chloropentane	$C_6H_5S^-$	pentyl phenyl sulfide	0.3	85
1-iodopentane	$C_6H_5S^-$	pentyl phenyl sulfide	0.5	87
benzyl chloride	S^{2-}	dibenzyl sulfide	0.5	98
	SCN^-	benzyl thiocyanate	1	95

These substitution reactions are governed by the same structural considerations as typical S_N2 reactions, but elimination becomes a significant pathway when secondary halides are used. As expected, the strength of the nucleophile is also important in determining the rate of reaction. Thus strong nucleophiles react rapidly while weaker nucleophiles such as carboxylate ions react slowly and chloride or bromide ions produce equilibrium mixtures.[13] Alkylation of phenoxides occurs exclusively at oxygen,[5] and the rate and degree of alkylation is influenced by substituents present on the ring.

A major advantage of polymeric, phase-transfer catalysis is the recoverability of the catalyst. After removal by filtration, the catalyst is available for use in another reaction. It was found that **3a** could be recycled a minimum of five times without an appreciable decrease in catalytic ability. The corresponding ammonium catalyst, resin **5**, showed only a slight loss of activity in five cycles of iodide

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Table V. Nucleophilic Displacement by Halide Ion

alkyl halide	nucleophile	product	t, h	yield, %
1-bromopentane	I^-	1-iodopentane	1	82
	Cl^-	1-chloropentane	48	90[a]
1-chloropentane	Br^-	1-bromopentane	100	69[a]
1-iodopentane	Br^-	1-bromopentane	24	59[a]
	Cl^-	1-chloropentane	100	35[a]
1-bromooctane	I^-	1-iodooctane	1.5	81
1-chlorooctane	I^-	1-iodooctane	24	47[a]
2-bromopentane	I^-	2-iodopentane	5.5	38
1-bromo-3-methylbutane	I^-	1-iodo-3-methylbutane	0.9	85
1-bromo-3,3-dimethylbutane	I^-	1-iodo-3,3-dimethylbutane	8	55
1,4-dibromobutane	I^-	1,4-diiodobutane	1	92
benzyl chloride	I^-	benzyl iodide	1	90

[a] Remainder consists of starting material.

Table VI. Displacement by Azide Ions

alkyl halide	product	t, h	yield, %
1-bromopentane	1-azidopentane	0.5	62
1-chloropentane	1-azidopentane	12	50
1-iodopentane	1-azidopentane	3	62
2-bromopentane	2-azidopentane	2	17
benzyl chloride	benzyl azide	1	92

Table VII. Displacements by Oxygen Nucleophiles

Phenoxide as Nucleophile

alkyl halide	nucleophile, (Na salt)	product	t, h	yield, %
1-bromopentane	phenol	pentyl phenyl ether	1	81
1-chloropentane	phenol	pentyl phenyl ether	12	70
1-iodopentane	phenol	pentyl phenyl ether	4.5	90
benzyl chloride	phenol	benzyl phenyl ether	1	72
1-bromo-3-methylbutane	phenol	3-methylbutyl phenyl ether	2.2	75
1-bromopentane	catechol	catechol dipentyl ether	1	58
1-bromopentane	*o*-isopropylphenol	1-pentoxy-2-isopropylbenzene	3	86
1-bromopentane	2,6-di-*tert*-butyl-4-methylphenol	1-pentoxy-2,6-di-*tert*-butyl-4-methylbenzene	3	0
dibromomethane	catechol	1,3-benzodioxole	2	10

Acetate as Nucleophile

alkyl halide	product	t, h	yield, %
1-bromopentane	pentyl acetate	8	70
benzyl chloride	benzyl acetate	8	81

transfer. For example, there was a 96% conversion of 1-bromopentane to 1-iodopentane in 1 h for cycle 1 and a 79% conversion in cycle 5.

Experimental Section

Chloromethylated polystyrenes (2% divinylbenzene, 200–400 mesh) used to prepare the catalysts were purchased from Bio-Rad Laboratories, Polysciences, Inc., or were prepared according to literature procedures.[14] The catalysts were analyzed for nitrogen or phosphorus by Chemalytics, Inc. Catalyst 1 was prepared according to the method of Tundo.[11] The preparations of the other catalysts are given below.

Preparation of Catalysts 2 and 4. A stirred mixture of 5 g of chloromethylated polystyrene (4.06 mequiv of Cl/g for **2a** and **4**, 1.06 mequiv of Cl/g for **2b**), 2.02 g of KCN (0.03 mol), and 30 mL of Me_2SO was refluxed overnight. The filtered resin was washed with 100 mL each of Me_2SO, H_2O, acetone, and ether. This nitrile was combined with 50 mL of 70% H_2SO_4 and the mixture refluxed for 3 h. When the hydrolysis was complete, the acid was collected, washed with H_2O (3 × 100 mL), acetone (100 mL), and CCl_4 (100 mL) and dried in vacuo overnight.

A mixture of the acid, 30 mL of anhydrous THF, and 16 mL of 1 M $BH_3\cdot THF$ complex was stirred vigorously at room temperature for 3 h. The resultant alcohol was collected and washed with 100 mL each of H_2O and acetone and dried. A suspension of the alcohol in 175 mL of anhydrous ethyl ether was cooled to 0 °C. Phosphorus tribromide (25 g, 0.09 mol) was added and the mixture stirred overnight. The reaction mixture was quenched by the dropwise addition of 25 mL of methanol. The collected resin was washed with H_2O and saturated $NaHCO_3$ solution and dried. This polystyrene-bound alkyl bromide was converted into the ammonium or phosphonium salt by the method of Tundo.[11]

Preparation of Catalysts 3 and 5. A solution of diethyl sodiomalonate was prepared from 50 mL of absolute EtOH, sodium metal (0.24 g, 0.010 mol), and diethyl malonate (2.12 g, 0.013 mol). Two grams of chloromethylated polystyrene (containing 4.06 mequiv of Cl/g for **3a** and **5** and 1.06 mequiv of Cl/g for **3b**) was added and the stirred suspension refluxed for 4 h. The resin was collected and washed with 100 mL each of EtOH and H_2O. The malonic ester was saponified by refluxing it for 2 h with a solution of 50 mL of H_2O and 30 g of KOH. The resin was filtered and added to 25 mL of 10 N H_2SO_4, and this mixture was refluxed for 3 h in order to complete the decarboxylation of the malonic acid. The collected acid was reacted with $BH_3\cdot THF$, PBr_3, and Bu_3P (or Bu_3N) as described in the preparation of catalysts **2** and **4**.

Nucleophilic Substitution Reactions. All reactions were carried out by stirring (magnetic, >1000 rpm) a mixture of the alkyl halide, catalyst **3a** (catalyst **5** is used when iodide ions are used or produced), and an aqueous solution of the nucleophile ($\sim$5 M) in an oil bath heated to 110 °C. Reactions were followed by GC and allowed to proceed until less than 5% of the halide remained. The catalyst was removed by filtration and the product isolated by extraction and distillation. The molar ratios of nucleophile, halide, and catalyst used are listed for each nucleophile as follows: nucleophile (Nuc/RX/Cat), cyanide (5/1/0.01), halide (5/1/0.01), phenoxide (3/1/0.01), thiophenoxide (1.5/1/0.01), azide (2/1/0.01), thiocyanate (2/1/0.01), sulfide (1.2/1/0.01), acetate (2/1/0.01).

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Registry No. 1-Bromopentane, 110-53-2; 1-chloropentane, 543-59-9; 1-iodopentane, 628-17-1; 1-bromooctane, 111-83-1; 1-chlorooctane, 111-85-3; benzyl chloride, 100-44-7; 1-bromo-3-methylbutane, 107-82-4; 1-bromo-3,3-dimethylbutane, 1647-23-0; 1,4-dibromobutane, 110-52-1; 2-bromopentane, 107-81-3; 3-bromopentane, 1809-10-5; ethyl bromoacetate, 105-36-2; hexanenitrile, 628-73-9; nonanenitrile, 2243-27-8; phenylacetonitrile, 140-29-4; 4-methylpentanenitrile, 542-54-1; 4,4-dimethylpentanenitrile, 15673-05-9; hexanedinitrile, 628-73-9; 2-methylpentanenitrile, 6339-13-5; pentyl phenyl sulfide, 1129-70-0; dipentyl sulfide, 872-10-6; pentyl thiocyanate, 32446-40-5; dibenzyl sulfide, 538-74-9; benzyl thiocyanate, 3012-37-1; 1-iodooctane, 629-27-6; 2-iodooctane, 557-36-8; 1-iodo-3-methylbutane, 541-28-6; 1-iodo-3,3-dimethylbutane, 15672-88-5; 1,4-diiodobutane, 628-21-7; benzyl iodide, 620-05-3; 1-azidopentane, 26330-06-3; 2-azidopentane, 73746-39-1; benzyl azide, 622-79-7; dibromomethane, 74-95-3; pentyl phenyl ether, 2050-04-6; 3-methylbutyl phenyl ether, 1129-64-2; catechol diphenyl ether, 3379-37-1; 1-pentoxy-2-isopropylbenzene, 73746-40-4; 1,3-benzodioxole, 274-09-9; pentyl acetate, 628-63-7; benzyl acetate, 140-11-4; polystyrene, 9003-53-6; diethyl sodiomalonate, 996-82-7.

Communications

Estimation of Electron-Transfer Contributions in Reactions of Alkyl Bromides with (Trimethyltin)sodium

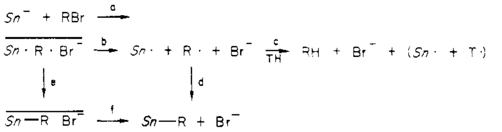
Summary: Estimates of the minimum degrees of electron-transfer contributions to the mechanisms of reaction of primary, secondary, and tertiary alkyl bromides with (trimethyltin)sodium have been obtained by the use of dicyclohexylphosphine as a free-radical trap.

Sir: Several mechanisms have been proposed[1] for the reactions of organic halides with organotinalkalis. These proposals have been based on stereochemical observations,[2-4] anion trapping,[5,8] kinetics,[6] and the formation of rearranged products.[4b,7] Because ionic or radical[5] intermediates are indicated in certain cases, we have sought to apply simple trapping techniques for their identification.

In the case of free radicals, successful trapping would have an advantage over CIDNP and ESR in providing a measure of the extent of their involvement, which would be quantitative if the trapping occurred with unit efficiency. A simple electron-transfer mechanism is shown in Scheme I, where *Sn* = Me_3Sn, the cation is omitted, and the electron transfer is assumed to be dissociative.

Previous stereochemical studies on substituted bromocyclohexanes suggest predominant or exclusive reaction by an electron-transfer mechanism.[5] We now have observed that cyclohexane (10%), cyclohexene (9%), dicyclohexyl (trace), and trimethylcyclohexyltin (73%) were the products from reaction of bromocyclohexane and (trimethyltin)sodium in THF at 0 °C. These results also support an electron-transfer mechanism. Because Sn^- is a good base,[9] a powerful nucleophile,[10] and good reducing agent,[11] the choice of a suitable radical trap is severely restricted. However, the commercially available dicyclohexylphosphine (DCPH) was selected because the P–H bond dissociation energy in PH_3 is about 77 kcal/mol, so hydrogen abstraction from the phosphine by R· should be exothermic and rapid. In Figure 1 are shown the results obtained with bromocyclohexane from a series of reactions in which the DCPH concentration was varied. It is seen that the cyclohexane yield increases and the cyclohexyltrimethyltin yield decreases as the DCPH concentration is increased.

Scheme I



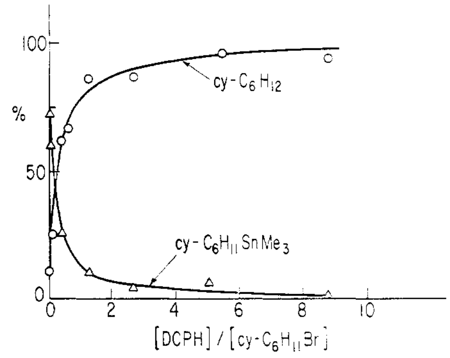


Figure 1. Effect of dicyclohexylphosphine on the yields of cyclohexane and cyclohexyltrimethyltin: THF solvent at 0 °C, cyclohexyl bromide, 0.54 M for first four points, 0.20 M for last two.

Concomitantly the yields of cyclohexene and dicyclohexyl fall to undetectable values. At the highest $[DCPH]/[Sn^-]_0$ value (8.81), the only product observed is cyclohexane, indicating negligible geminate or direct displacement reaction under these conditions. The results

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