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Solvents for Aromatic SRN1 Reactions[1a]

J. F. Bunnett,* R. G. Scamehorn,[1b] and Rene P. Traber[1c]

University of California, Santa Cruz, California 95064

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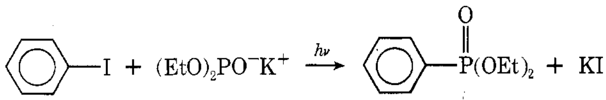
Whereas previously aromatic SRN1 reactions were conducted almost exclusively in ammonia, it is now found that dimethyl sulfoxide is a good solvent for photostimulated reactions of diethyl phosphite ion, thiophenoxide ion, and acetone enolate ion with iodobenzene. Yields in the iodobenzene–diethyl phosphite ion reaction were also high in acetonitrile and dimethylformamide and fairly good in *tert*-butyl alcohol, but poor in hexamethylphosphoric triamide and some other common dipolar, aprotic solvents. In *tert*-butylamine, attempted reactions with thiophenoxide and acetone enolate ions were not very satisfactory, but iodobenzene as well as *m*-bromoiodobenzene underwent rapid photostimulated reaction with diethyl phosphite ion. In water, poor yields were obtained in photostimulated reactions of thiophenoxide ion with two substrates which were the more reactive of several tried.

The SRN1 mechanism of aromatic substitution, first recognized in 1970,[2] involves radical and radical anion intermediates and electron transfer steps but the overall consequence is that of nucleophilic substitution. A representative reaction is that of iodobenzene with potassium diethyl phosphite (eq 1).[3]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Other nucleophiles successfully involved in aromatic SRN1 reactions include arenethiolate ions,[4] the amide ion,[2,5] ketone enolate ions,[6–10] α-cyanoalkyl carbanions,[2,11] picolyl anions,[12] and several carbanions of other sorts.[8] The mechanism tolerates substituents such as alkyl, alkoxy, and carboxylate ($-COO^-$) groups and is remarkably insensitive to the steric effects of groups ortho to the site of substitution. These reactions usually require stimulation, for purposes of chain initiation, by photons or electrons.

The SRN1 mechanism of substitution was initially discerned for certain reactions at aliphatic sites by Kornblum[13] and Russell[14] and their associates and has recently been reviewed as a mechanism of substitution at saturated carbon by Kornblum.[15] As a radical chain mechanism, it involves initiation, propagation, and termination steps but, since the initiation and termination steps are not very well understood and probably vary in character from case to case, we sketch in Scheme I only the probable cycle of propagation steps. In Scheme I, ArX is a generalized aromatic substrate and Y^- a generalized nucleophile.

Liquid ammonia has been the solvent for nearly all the aromatic SRN1 reactions reported from this laboratory. Bunnett and Sundberg[9] did report a few experiments on the use of other solvents for the reaction of bromobenzene with potassium acetone enolate. The investigations of Kornblum and Russell and their co-workers were conducted mainly in dipolar aprotic solvents such as dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), and hexamethylphosphoric triamide (HMPT). In order to assess the utility of diverse solvents for aromatic SRN1 reactions, we carried out the studies now described.

Scheme I

$$[ArX]\cdot^- \rightarrow Ar\cdot + X^- \tag{2}$$

$$Ar\cdot + Y^- \rightarrow [ArY]\cdot^- \tag{3}$$

$$[ArY]\cdot^- + ArX \rightarrow [ArX]\cdot^- + ArY \tag{4}$$

General Considerations. An obvious requirement is that a solvent should dissolve the reactants, usually a nonpolar organic compound and an alkali metal salt of an anionic nucleophile. Another, for photostimulated reactions, is that the solvent be transparent to the light which provokes reaction, which is probably about 300–380 nm.

Most of the nucleophiles that have been successfully involved in aromatic SRN1 reactions are highly basic. The acidity of the solvent must be low enough so that it does not protonate the nucleophile very much under the reaction conditions. Also, a rather acidic solvent might protonate one of the radical anion intermediates, especially $[ArY]\cdot^-$, in the manner of the Birch reduction.[16] Inasmuch as electron transfer steps are involved, solvents which accept electrons readily (e.g., nitrobenzene) or irreversibly (CCl_4) are unlikely to be satisfactory.

Solvents with which aryl radicals can readily react, especially to abstract hydrogen atoms, present a problem inasmuch as the by-product radicals from hydrogen atom abstraction

Table I. Photostimulated Reaction of Iodobenzene with Potassium Diethyl Phosphite in Diverse Solvents

Registry no.	Solvent	Irradiation time, h	Product yields, %		Color after irradiation
			I^- [a]	**2** [b]	
7664-41-7	Ammonia	0.75	99	96	Colorless
75-65-0	*t*-BuOH[c]	2.0	63	31	Nearly colorless
	t-BuOH[d]	4.5	81	74	Nearly colorless
67-68-5	Me_2SO	4.0	100	68	Pale yellow
90-72-2	DMF	4.5	94	63	Pale yellow-brown
680-31-9	HMPT	4.5	30	4	Yellow
75-05-8	CH_3CN	4.0	98	94[e]	Yellow
127-19-5	$CH_3CON(CH_3)_2$	4.5	72	53	Pale gray
872-50-4	*N*-Methyl-2-pyrrolidone	4.5	24	10	Yellow-orange
110-71-4	$CH_3OCH_2CH_2OCH_3$	4.5	73	56	Colorless
	50% Me_2SO–50% *t*-BuOH	4.5	74	48	Pale yellow
126-33-0	Sulfolane[f]	4.5	28	20[g]	Yellow

[a] By titration with $AgNO_3$. [b] By isolation and weighing unless otherwise noted. [c] Mallinckrodt AR grade, without further purification. [d] Specially purified; see Experimental Section. [e] Yield by GLC, with phenanthrene as internal standard. [f] Tetramethylenesulfone. [g] Yield estimated from GLC.

might not lead back into the propagation sequence. Whether hydrogen abstraction from the solvent is a serious complication or not depends on the relative rates of two alternative pathways available to the aryl radical: reaction with nucleophile (step 3) to continue the propagation cycle, or reaction with solvent leading usually to termination. Methanol, which may be taken to represent alcohols with α-hydrogen atoms, is a good hydrogen atom donor to aryl radicals and the methoxide ions present in basic methanol are better yet,[17] but the by-product formaldehyde radical anions ($\cdot CH_2O^-$) can sometimes lead back into the SRN1 propagation cycle.[18]

Finally, important for preparative applications are practical considerations such as cost, ease of purification, and convenience of product isolation.

Results

Reactions of Iodobenzene with Potassium Diethyl Phosphite (eq 1). A series of experiments is summarized in Table I. In these experiments iodobenzene and a twofold excess of the nucleophile in the listed solvent in a Pyrex flask were exposed to the light of "350-nm" fluorescent lamps in a Rayonet photochemical reactor for the times shown. All the yields listed are based on iodobenzene provided at the beginning of the reaction.

It is noteworthy that iodide ion release was in excess of 90% in ammonia, Me_2SO, DMF, and acetonitrile. However, the yields of diethyl phenylphosphonate (**2**) isolated from reactions in Me_2SO and DMF were appreciably lower. The reason, we believe, is that relatively large amounts of water were used when the crude **2** was extracted into diethyl ether causing some losses of **2** because of its appreciable solubility in water.

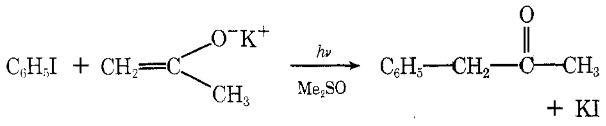
The times of irradiation chosen, mostly 4.0 or 4.5 h, were rather long in order to provide reactions an ample opportunity to occur. They do not represent the results of optimization efforts. In the case of solvent Me_2SO, subsequent quantitative studies[19] show that under typical conditions reaction is complete in 40 min or less.

Small amounts of by-products were detected in some cases, notably in *tert*-butyl alcohol and acetonitrile solvents.

Reactions in Dimethyl Sulfoxide. Iodobenzene was observed to react with a 2.5-fold excess of potassium thiophenoxide during 2-h irradiation to release 66% of iodide ion and form 65% of diphenyl sulfide (eq 5), leaving 34% of the iodobenzene unreacted.[20] No by-products were detectable. An identical reaction mixture kept for 2 h in the dark underwent virtually no reaction. In an experiment of similar design, except that all reagents were used "from the shelf" without further purification, iodide ion release during 2-h irradiation was 51% but the yield of diphenyl sulfide was only 37%.

$$C_6H_5I + C_6H_5S^-K^+ \xrightarrow[Me_2SO]{h\nu} C_6H_5\text{-}S\text{-}C_6H_5 + KI \qquad (5)$$

The reaction of iodobenzene with acetone enolate ion (eq 6) was much faster; it was complete after 1-h irradiation. With a 4:1 ratio of enolate to iodobenzene, the yield of phenylacetone was 81% and of 1,1-diphenyl-2-propanone, 11%. A mere trace of benzene was detectable. When the ratio of enolate reagent to iodobenzene was 8:1, the yield of phenylacetone rose to 88% and only 4% of diphenylation occurred. In a further experiment with a 4:1 reactant ratio, 55% release of iodide ion was observed during only 12-min irradiation, but remarkably a similar sample kept for 12 min in the dark furnished 31% of iodide ion. A significant dark reaction is indicated.



$$C_6H_5I + CH_2{=}C(O^-K^+)CH_3 \xrightarrow[Me_2SO]{h\nu} C_6H_5{-}CH_2{-}C({=}O){-}CH_3 + KI \qquad (6)$$

Reactions in *tert*-Butylamine (*t*-$BuNH_2$). This solvent seemed attractive, a priori, because of its low acidity and its lack of hydrogen atoms readily abstractable by radicals. Its resemblance to ammonia is obvious, but it was expected better to dissolve organic compounds.

Of four nucleophiles that were tried, namely the diethyl phosphite, acetone enolate, thiophenoxide, and *tert*-butylamide ions, only one underwent SRN1 reactions satisfactorily in *t*-$BuNH_2$. Potassium diethyl phosphite reacted with iodobenzene during 60-min irradiation according to eq 1, releasing 94% of iodide ion and affording a 76% isolated yield of **2**. The same nucleophile reacted with *m*-bromoiodobenzene during 60-min irradiation to form tetraethyl *m*-phenylenebisphosphonate[3] in high yield together with a small amount of diethyl *m*-bromophenylphosphonate, liberating bromide and iodide ions to the extents of 89 and 100%, respectively.

Because iodobenzene reacted with $(EtO)_2PO^-K^+$ so attractively in *t*-$BuNH_2$, the reaction was investigated more closely in the hope that it might be suitable for quantitative study. With only eight of the usual 16 lamps in place in the reactor, the reaction was nearly complete in 20 min. A plot of percent iodide ion formed vs. time was nearly linear although there was a slight lag within the first 4 min in the manner of an induction period. Such behavior indicates that the reaction is zero order in iodobenzene.

Nevertheless, there are disadvantages to this system for purposes of meticulous measurements. For one thing, solu-

Table II. Photostimulated Reactions of Nucleophiles with Aromatic Substrates in Water Solution

Registry no.	Substrate	Nucleophile[a]	Irradiation time, min	Halide ion yield, %	Products and yields
98-04-4	$C_6H_5NMe_3^+I^-$	PhS^-(930-69-8[f])	150		Ph_2S, 1%
19095-34-2	p-$IC_6H_4NMe_3^+I^-$	PhS^-	100	100	p-$C_6H_4(SPh)_2$, 12% p-$PhSC_6H_4NMe_3^+I^-$, 38% p-$PhSC_6H_4NMe_2$, trace p-$IC_6H_4NMe_2$, trace PhSSPh, trace
2532-17-4	o-$IC_6H_4COO^-Na^+$	PhS^-	180	11	b
2532-18-5	m-$IC_6H_4COO^-Na^+$	PhS^-	180	12	b
60118-02-7	p-$IC_6H_4CH_2COO^-Na^+$	PhS^-	200	26	b
60118-03-8	p-$IC_6H_4OCH_2COO^-Na^+$	PhS^-	180[c]	43	p-$PhSC_6H_5OCH_2COOH$,[d] 6% $C_6H_5OCH_2COOH$, 4% p-$IC_6H_4OCH_2COOH$, 55%
	p-$IC_6H_4NMe_3^+I^-$	$PhSO_2^-$ (873-55-2)	180	5	b
	p-$IC_6H_4NMe_3^+I^-$	$CH_2NO_2^-$ (25854-38-0)	150	0	b
	$C_6H_5NMe_3^+I^-$	$CH_2NO_2^-$	Na(Hg)[e]		$C_6H_4CH_2NO_2$, nil
	p-$IC_6H_4NMe_3^+I^-$	$CH_2NO_2^-$	Na(Hg)[e]	5	b

[a] Nucleophiles supplied as sodium salts. [b] Not investigated. [c] "300-nm" lamps used. [d] Isolated as the methyl ester. [e] Sodium amalgam, without irradiation. [f] Registry number.

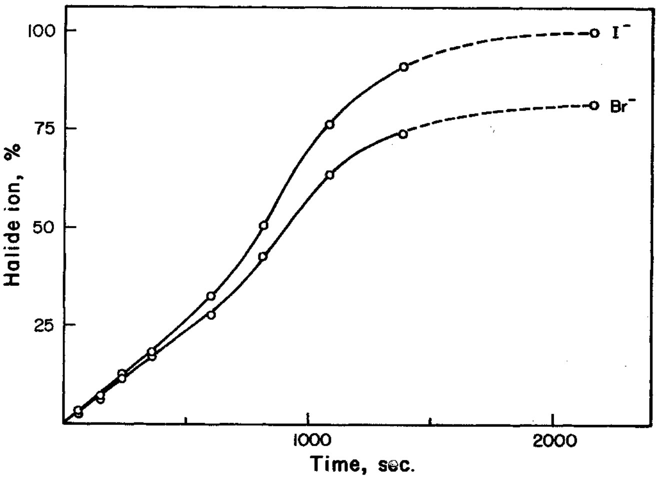


Figure 1. Rates of halide ion release in photostimulated reaction of *m*-bromoiodobenzene with potassium diethyl phosphite in *tert*-butylamine.

tions of $(EtO)_2PO^-K^+$ in t-$BuNH_2$ were somewhat cloudy. Also, potassium iodide began to precipitate after about 15% reaction.

The reaction of *m*-bromoiodobenzene with $(EtO)_2PO^-K^+$ in t-$BuNH_2$ was also observed closely. Samples were taken at intervals, quenched with acid, and analyzed for both bromide and iodide ions by potentiometric titration. The results are presented in Figure 1. It is noteworthy that formation of iodide and bromide ions was closely coupled, rather than sequential, with iodide ion being formed in somewhat greater amount.

It was shown that t-$BuNH_2$ does not react with $(EtO)_2PHO$, $(EtO)_2PO^-K^+$, or 2 under the conditions of our reactions.

Potassium and lithium acetone enolates, formed in t-$BuNH_2$ by reaction of acetone with t-BuOK and butyllithium, respectively, were soluble but reacted very slowly with iodobenzene. During 200-min irradiation, reaction with the potassium enolate formed only 46% of iodide ion together with 31% of phenylacetone. The lithium enolate, during 120-min exposure to light, generated only 29% of iodide ion and 18% of phenylacetone.

Both *tert*-butylammonium thiophenoxide and potassium thiophenoxide were found to be insoluble in t-$BuNH_2$. Irradiation of a mixture of the former with iodobenzene in t-$BuNH_2$ gave only a trace of diphenyl sulfide. The lithium salt of thiophenol is soluble in t-$BuNH_2$ but irradiation of a solution of it and iodobenzene for 120 min gave only 36% of iodide ion and a low yield (about 12%) of diphenyl sulfide.

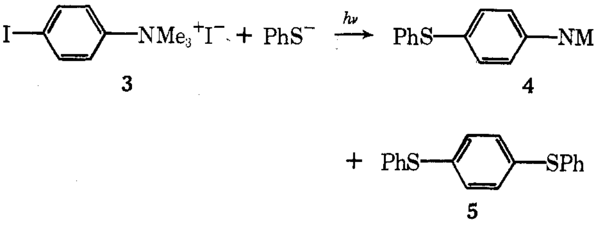
A solution of lithium *tert*-butylamide and iodobenzene in t-$BuNH_2$ was irradiated for 70 min. Iodide ion release was 98% and an 82% isolated yield of *N-tert*-butylaniline was obtained. However, our finding that quantitative release of iodide ion also occurred in the dark suggested that reaction occurred via the intermediacy of benzyne.[21] This interpretation was supported by observation that lithium *tert*-butylamide and bromomesitylene in t-$BuNH_2$, irradiated for 120 min, formed only 5% of bromide ion. Bromomesitylene is structurally unable to afford an aryne intermediate.

Reactions in Water. Investigations in this solvent were limited to substrates soluble in it.

Because water is rather acidic, only a few of the nucleophiles that have been found reactive in aromatic SRN1 reactions can be provided in aqueous solution. Most of our experiments, which are summarized in Table II, concerned thiophenoxide ion as nucleophile. A few concerned the anion of nitromethane, which is reported[22] to react with phenyl radical in aqueous medium to form the radical anion of phenylnitromethane. One experiment was performed with benzenesulfinate ion as nucleophile; its participation in aliphatic SRN1 reactions has been described,[23] although it has never been observed to engage in such substitutions at aromatic carbon.

The first experiment in Table II involves the photostimulated interaction of thiophenoxide with phenyltrimethylammonium ion, which earlier[7] was found to react with acetone enolate ion in ammonia, under irradiation, to form phenylacetone. Scarcely any reaction occurred during 2.5-h illumination, and only 1% of diphenyl sulfide was obtained.

In ammonia, *p*-iodophenyltrimethylammonium ion (3)



(7)

reacts with thiophenoxide ion under irradiation to form bissulfide **5** in 95% yield, both the iodine atom and the trimethylammonio group being replaced.[24] The same reaction in water (Table II) is less straightforward. Although the covalently bound iodine atom was released quantitatively, only 12% of **5** was obtained together with 38% of *p*-thiophenoxyphenyltrimethylammonium ion (**4**), which represents replacement of the iodine atom only, and trace amounts of tertiary amines formed by demethylation of **3** and **4**. Much tar was formed, amounting to about 20% of the mass of the **3** used.

Upon being irradiated in the presence of thiophenoxide ion for 3 h or more, the anions of *o*- and *m*-iodobenzoic acid and of *p*-iodophenylacetic acid released only about a quarter or less of their iodine atoms as iodide ion; other products were not sought. Under irradiation by "300-nm" lamps, the anion of *p*-iodophenoxyacetic acid was somewhat more reactive, 43% of iodide ion being formed, but the yield of the thiophenoxy deiodination product was only 6%. There was also 4% of phenoxyacetic acid, the deiodination product, as well as 55% of recovered starting material and some tar. Also with "300-nm" illumination, sodium *p*-iodophenylacetate behaved very similarly.

A single attempt to observe a photostimulated substitution reaction between benzenesulfinate ion and *p*-iodophenyltrimethylammonium ion was fruitless. Likewise, no evidence of substitution could be found from the interaction of this substrate with the anion of nitromethane, either under stimulation by photons or by electrons from sodium amalgam. Phenyltrimethylammonium ion failed to form phenylnitromethane when exposed to the nitromethane anion in the presence of sodium amalgam.

Discussion

Of solvents for aromatic SRN1 reactions other than ammonia, Me_2SO appears to be the best on the basis of evidence now available. Photostimulated reactions of iodobenzene with the diethyl phosphite, thiophenoxide, and acetone enolate ions, and of bromobenzene with the last of these, all occur in high yield in Me_2SO. In this laboratory Me_2SO has become the solvent of choice for quantitative kinetic or photochemical studies.

There are some disadvantages to Me_2SO. Methods for its purification are laborious and there is evidence[19] that impurities in incompletely purified Me_2SO can significantly affect reaction rates or quantum yields. Also, product isolation from Me_2SO is rather inconvenient.

One of the reasons that Me_2SO is so satisfactory is its low reactivity as a hydrogen atom donor toward aryl radicals. Of more than 100 substances of diverse structure and functional type whose hydrogen donor reactivity toward phenyl radical was measured by Bridger and Russell,[25] Me_2SO was the least reactive but for one. Me_2SO is a good solvent for organic compounds as well as for many salts.

Nevertheless, ammonia is the solvent of choice for preparative work. Its advantages include low cost, ease of purification, and convenience of product isolation, besides its favorable chemical characteristics. The special techniques for handling this low-boiling solvent (−33 °C) are easily learned and do not substantially interfere with its use for preparative purposes.

Although experience with other dipolar, aprotic solvents is limited mainly to reactions with diethyl phosphite ion, we consider the evidence in Table I to be very significant, at least insofar as the less satisfactory solvents are concerned, because SRN1 reactions with this nucleophile are exceptionally fast and clean in ammonia and Me_2SO. In the experiments of Table I, a superb nucleophile was provided and irradiation was conducted for rather a long time; a solvent that fails to support reaction in high yield under such conditions is truly unpromising.

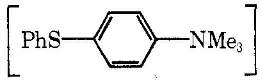
The unsatisfactoriness of HMPT is especially worthy of note. In another study,[9] bromobenzene and potassium acetone enolate failed to react in HMPT during 65 min irradiation.

Acetonitrile and DMF stand out in Table I as rather good solvents, and merit further attention.

In *tert*-butylamine solvent, the main difficulty appears to be the low solubility of many salts. Potassium diethyl phosphite is, however, soluble, and its reactions with iodobenzene and *m*-bromoiodobenzene occurred rapidly and in high yield.

It is unclear why reactions in water (Table II) were so poor. Perhaps the identity of products which escaped isolation would provide a clue.

The fact that **3** afforded mainly **4** in water but mainly **5** in ammonia[24] may be taken to indicate that zwitterionic radical **6** in ammonia almost exclusively expels trimethylamine to yield the *p*-thiophenoxyphenyl radical, which continues to form **5**, whereas **6** in water preferentially transfers an electron to **3**, leaving **4** as a stable product.



6

Experimental Section

Instrumentation. Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. NMR spectra were determined on JEOL Minimar or Varian A-60A instruments. Infrared spectra were taken on a Perkin-Elmer 237B spectrometer. Gas chromatographic analyses were performed using a Hewlett-Packard 5750 flame ionization instrument, and reaction yields were calculated by standard methods using internal standards with peak areas suitably corrected for molar response. Iodide titrations were carried out potentiometrically using a Corning Model 7 pH meter with silver and glass electrodes. Photochemical reactions were carried out in a Rayonet Model RPR-100 reactor equipped normally with 16 "350-nm" lamps.

Materials. Commercially available solvents and most reagents were purified prior to use by distillation or crystallization unless otherwise noted. *tert*-Butyl alcohol was repetitively partially frozen, the remaining liquid discarded each time, then refluxed over sodium and distilled. Me_2SO, DMF, HMPT, and 1,2-dimethoxyethane were dried over calcium hydride and distilled. Acetonitrile was distilled from phosphorus pentoxide. *N,N*-Dimethylacetamide and *N*-methyl-2-pyrrolidone were dried over $CaSO_4$ and distilled. Tetramethylenesulfone was dried over BaO at 140 °C for 8 h and distilled. Commercial anhydrous ammonia was distilled from sodium directly into the reaction flask. *tert*-Butylamine was freshly distilled prior to use.

Iodobenzene was dried and distilled, and stored protected from light. Diethyl phosphonate (Aldrich) was dried over CaH_2 and distilled. Thiophenol was freshly distilled each week. Spectrograde acetone was used without further purification.

Reactions of Iodobenzene with Potassium Diethyl Phosphite. Typical Procedure. A 250-ml, three-neck flask equipped with magnetic stirrer, nitrogen inlet, and dry ice condenser was constantly swept with dry nitrogen. Potassium *tert*-butoxide (3.36 g, 0.03 mol) was placed in the flask and 120 ml of DMF was added. After the solid had dissolved, 4.15 g (0.03 mol) of diethyl phosphite was added, followed by 3.06 g (0.015 mol) of iodobenzene. The resulting clear and nearly colorless solution was irradiated in a Rayonet reactor for 4 h. The solution was concentrated to about 10 ml and taken up in 150 ml of ether and 20 ml of water. The organic layer was separated and the aqueous layer was extracted five more times with ether. The combined ether extracts were washed with 20 ml of saturated NaCl solution and dried (Na_2SO_4). After removal of the ether, the crude product was distilled to give 2.03 g (68%) of diethyl phenylphosphonate as a colorless liquid: NMR δ_{CCl_4} (Me_4Si) 1.3 (t, 6 H), 4.1 (m, 4 H), and 7.4–7.9 (m, 5 H, Ar); ir (film) λ_{max} 1250 (P=O), and 1205 cm^{-1} (P–O–C).

The aqueous layer was acidified with 6 M nitric acid and titrated for iodide ion: 0.936 equiv of iodide ion was found per mole of iodobenzene used.

Reactions in Dimethyl Sulfoxide. Typical Procedure. Potassium *tert*-butoxide (2.30 g, 20.5 mmol) was placed in a nitrogen-flushed three-neck flask fitted with condenser and nitrogen inlet and 50 ml of Me_2SO was added. Acetone (1.16 g, 20 mmol) was added, followed by 500 mg (2.45 mmol) of iodobenzene. The solution turned yellow immediately. After irradiation for 60 min, the brown solution was cooled, diluted with water, and thrice extracted with ether. Analysis of the aqueous phase showed 2.46 mmol of iodide ion. The ether layer was analyzed by GLC (Carbowax 20M column, biphenyl internal standard), and phenylacetone (2.16 mmol, 88%) and 1,1-diphenylacetone (0.086 mmol, 3.5%) were found.

Reaction of Iodobenzene and Potassium Acetone Enolate in *tert*-Butylamine. Typical Procedure. Potassium *tert*-butoxide (2.30 g, 20.5 mmol) was dissolved in 50 ml of *tert*-butylamine, and 1.16 g (20 mmol) of acetone and 1.00 g (4.90 mmol) of iodobenzene were added. The solution, under nitrogen atmosphere, was irradiated with 300-nm lamps for 200 min. Ammonium nitrate (1.8 g) was added and the solvent was evaporated on a warm water bath. The product was taken up in ether and water and the aqueous phase was extracted with two further portions of ether. The combined ether fractions were dried ($MgSO_4$), and analyzed by GLC. The yield of phenylacetone was 1.5 mmol (31%). Titration of the aqueous fraction with silver nitrate solution showed 0.46 equiv of iodide ion.

Kinetic Procedure in *tert*-Butylamine. In a nitrogen flushed flask was placed 1.68 g (15 mmol) of potassium *tert*-butoxide and 125 ml of *tert*-butylamine and 2.00 g of diethyl phosphite was added. After the solid dissolved, aryl halide was added. Aliquots (5 ml) were transferred to screw-cap test tubes which were then flushed with nitrogen and placed in a Rayonet reactor with a merry-go-round apparatus. The reactor was started and tubes were removed at timed intervals, quenched with ammonium nitrate, heated to remove solvent, and titrated for free halide ion.

Reaction of Iodobenzene and Lithium *tert*-Butylamide. To 50 ml of *tert*-butylamine under nitrogen was added 20 mmol of *n*-butyllithium followed by 1.00 g (4.9 mmol) of iodobenzene. A 2.00-ml aliquot was removed and placed in a foil-wrapped screw-cap test tube to check the dark reaction. The solution was irradiated for 70 min and then diluted with water and extracted twice with ether. The combined ether fractions were washed with water (three times), dried, and concentrated. Distillation of the resulting oil gave *N*-*tert*-butylaniline (600 mg, 4.03 mmol, 82%): bp 69 °C (5 mm) [lit.[26] 92.5–93 °C (19.5 mm)]; NMR δ_{CCl_4} (Me_4Si) 1.27 (s, 9 H), 3.23 (s, broad, 1 H), and 6.5–7.2 (m, 5 H); ir (film) λ_{max} 690, 746, 1224, 1500, 1608, 2970, and 3415 cm^{-1}.

Titration of the aqueous layer showed 0.98 equiv of iodide ion.

The aliquot kept in the dark was worked up in a similar manner. Titration showed 1 equiv of iodide ion and GLC analysis showed only *N*-*tert*-butylaniline.

***p*-Iodophenyltrimethylammonium iodide**[27] was prepared from *p*-iodo-*N*,*N*-dimethylaniline[27] and methyl iodide in methanol. After refluxing for 6 h, the precipitated product was filtered and recrystallized twice from hot water: mp 196–198 °C dec; NMR (Me_2SO-d_6) δ (Me_4Si) 3.61 (s, 9 H), 7.78 (AB doublet, J = 9 Hz, 2 H), and 8.07 (AB doublet, 2 H).

Reaction of *p*-Iodophenyltrimethylammonium Iodide (3) with Sodium Thiophenoxide in Water. To a solution of 3 (0.51 g, 1.31 mmol) in 50 ml of doubly distilled water (heat) and 25 ml of 2 M sodium hydroxide, thiophenol (1.25 g, 11.4 mmol) was added and the system was purged with nitrogen. A 2-ml aliquot was removed and wrapped with foil to check the dark reaction, and the remaining solution was irradiated for 180 min at 350 nm. After cooling, the yellow, turbid solution was extracted with ether (three times), and the combined ethereal fractions were dried and concentrated. There remained 220 mg of a dark brown oil which was analyzed by GLC (SE-54 column). At least eight peaks were observed and the following compounds identified: diphenyl sulfide (25 mg), *p*-di(thiophenoxy)benzene (5) (43.3 mg, 0.15 mmol, 12%), and small amounts (10–15 mg) of diphenyl disulfide, and *p*-thiophenoxy-*N*,*N*-dimethylaniline. The latter compound was identified by acid extraction of the ether-soluble material. GLC analysis of the acid-soluble extract also revealed a trace of *p*-iodo-*N*,*N*-dimethylaniline.

The aqueous solution was acidified with acetic acid and extracted with ether (three times) to remove excess thiophenol. A 10-ml aliquot was titrated for iodide ion: 2.00 equiv of iodide was found. Titration of the foil-wrapped aliquot removed before irradiation (dark reaction) showed 1.02 equiv of iodide.

The water-soluble product of another experiment was isolated in two ways. (1) The aqueous solution was concentrated to about half its original volume and sodium iodide was added. A precipitate formed and the solution was filtered. Further concentration yielded two more portions of the water-soluble product. The product so obtained contained a mixture of compounds and was typically about 60% substitution product as judged by comparison of the Ph–S NMR singlet with the trimethylammonio peaks. The product was dissolved in Me_2SO-d_6 and methylene chloride was added as an internal standard. With this method of product isolation being used, 3.55 mmol of 3 reacted to give 1.18 mmol (33%) of 4. The presence of this product was confirmed by comparison of spectra with those of an authentic sample. The other products were not identified. (2) Tetraphenylborate isolation:[28] addition of an aqueous solution of sodium tetraphenylborate to the aqueous solution above gave an immediate precipitate of ammonium tetraphenylborate salts. The product isolated in this way was examined by NMR (Me_2SO-d_6), and the amount of substitution product estimated by comparing the Ph–S singlet to the trimethylammonio peaks. The yield of substitution product observed in several experiments ranged from 23 to 38%.

***p*-Thiophenoxy-*N*,*N*-dimethylaniline.** *N*,*N*-Dimethylaniline (20.0 g, 0.165 mol) was dissolved in 200 ml of anhydrous ether under nitrogen. Benzenesulfenyl chloride (8.0 g, 0.055 mol) in 100 ml of ether was added slowly. After 1–2 min the solution became perceptibly lighter in color and anilinium hydrochloride began to precipitate. After 2-h refluxing, the ether was removed, water was added, and the residue was steam distilled to remove the excess aniline. Upon cooling, the residue remaining solidified. It was taken up in ether, dried, and concentrated. Dilution with petroleum ether gave white crystals (6.8 g, 0.03 mol, 55%): mp 66.5–67 °C (lit.[29] 66–67 °C); δ_{CCl_4} (Me_4Si) 2.97 (s, 6 H), 7.15 (s, PhS, 5 H), 6.68 (AB doublet, 2 H), and 7.42 (AB doublet, J = 9 Hz, 2 H).

***p*-Thiophenoxyphenyltrimethylammonium Iodide (4).** *p*-Thiophenoxy-*N*,*N*-dimethylaniline (2.0 g, 8.73 mmol) in 15 ml of methanol and methyl iodide (1.24 g, 8.73 mmol) were refluxed for 2 h. No precipitate appeared. The solution was cooled in ice water; crystals appeared as a rigid mass filling the liquid volume. NMR analysis of the solid showed only partial conversion to the quaternary ammonium salt. More methyl iodide was added (0.75 g) and the solution was refluxed for an additional 1 h. A few drops of 1 M sodium methoxide in methanol were added until the yellow color was discharged, and the product, which crystallized upon cooling, was filtered, washed with small portions of methanol and with ether, and dried. The yield was 0.95 g (2.56 mmol, 29%): mp 179.5–180.5 °C; NMR $\delta_{Me_2SO\text{-}d_6}$ (Me_4Si) 3.63 (s, 9 H), 7.40 (AB doublet, J = 9 Hz, 2 H), 7.52 (s, PhS, 5 H), and 8.00 (AB doublet, 2 H); ir λ_{max} (KBr) 699, 752, 840, 935, 1015, 1130, 1400, 1445, 1480, 1495, 1590 and 3010 cm^{-1}.

Anal.[30] Calcd for $C_{15}H_{18}INS$: C, 48.53; H, 4.89; S, 8.64. Found: C, 48.25; H, 4.78; S, 8.90.

Reaction of *p*-Iodophenoxyacetic Acid with Sodium Thiophenoxide. 4-Iodophenoxyacetic acid (1.00 g, 3.60 mmol) in 125 ml of 0.8 M sodium hydroxide and thiophenol (2.5 g, 22.7 mmol) were irradiated under nitrogen for 3 h (300 nm). The solution was acidified and the thiophenol was extracted with three portions of ether. The combined ether extracts were dried and concentrated to give 1.04 g of an oily yellow solid. Titration of the aqueous layer indicated 0.433 equiv of iodide (43% reaction). The acidic product was dissolved in methanol, a drop of concentrated sulfuric acid was added, and the solution was refluxed for 1 h, diluted with water, and extracted with ether. Concentration gave 0.97 g of a yellow oil. GLC analysis (SE-54 column, 4 ft × 0.125 in.) showed three peaks: methyl *p*-iodophenoxyacetate (1.98 mmol, 55%), methyl phenoxyacetate (0.14 mmol, 4%), and methyl *p*-thiophenoxyphenoxyacetate (0.23 mmol, 6%). The methyl *p*-thiophenoxyphenoxyacetate was identified by preparative GLC isolation by means of a 3 ft × 0.25 in. 2.5% SE-54 column at 250 °C. The material collected had NMR δ_{CCl_4} (Me_4Si) 3.75 (s, 3 H, OCH_3), 4.55 (s, 2 H, CH_2), 6.97 (AB doublet, J = 9 Hz, 2 H), 7.13 (s, 5 H, PhS), and 7.38 (AB doublet, 2 H); ir λ_{max} (CCl_4) 826, 1080, 1210 (broad), 1435, 1495, 1600, 1751 cm^{-1} (C=O); MS *m/e* 274 (M^+), 201, 184, 109.

Reaction of *p*-Iodophenyltrimethylammonium Iodide with Nitromethane Anion and Sodium Amalgam.[31] The iodide (500 mg, 1.29 mmol) was dissolved in 100 ml of 0.5 M sodium hydroxide. Nitromethane (1.13 g, 18.5 mmol) was added and the system purged with nitrogen. Sodium amalgam (2%, 2.0 g, 1.74 mmol) was added in small portions over about 25 min with vigorous mechanical stirring. After 1 h of additional stirring, the solution was acidified with 10% sulfuric acid and extracted with ether. Analysis of the aqueous layer showed 1.05 equiv of iodide ion.

Registry No.—**1,** 591-50-4; **2,** 1754-49-0; **4,** 60118-04-9; potassium diethyl phosphite, 54058-00-3; lithium *tert*-butylamide, 31828-54-9; *N*-*tert*-butylaniline, 937-33-7; *p*-iodo-*N*,*N*-dimethylaniline, 698-70-4; *p*-thiophenoxy-*N*,*N*-dimethylaniline, 42881-80-1; *N*,*N*-dimethylaniline, 121-69-7; benzenesulfenyl chloride, 931-59-9; *p*-iodophenoxyacetic acid, 1878-94-0; methyl-*p*-thiophenoxyphenoxyacetate, 60118-05-0.

References and Notes

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Chemical Consequences of Hydride Addition to Aromatic Olefins

Itshak Granoth,* Yoffi Segall, Haim Leader, and Rivka Alkabets

Department of Chemistry, Israel Institute for Biological Research, Ness-Ziona, Israel

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The scope and synthetic applications of hydride addition to aromatic olefins have been studied. Many aromatic olefins are reduced by $LiAlH_4$ in tetrahydrofuran (THF), 1,2-dimethoxyethane, *p*-dioxane, or diglyme at 65–150 °C. Hydride addition to 1,1-diarylethylenes is accelerated by THF and other solvents, as compared with diethyl ether, and by electron delocalizing or cyclic, relatively rigid, aromatic groups. Substituents which increase the electron density at the double bond, or form steric hindrance, decelerate the hydride addition. *o*-MeO and especially *o*-Me_2N groups accelerate the reaction, probably by coordination with the lithium ion and displacing solvent molecules in both the transition state and the generated carbanions. 2,2-Diarylpropanes are efficiently obtained from 1,1-diarylethylenes, $LiAlH_4$, and anisole in THF, while 1,1-diarylethanes are produced in diglyme at 140–150 °C. A novel specific carbon–carbon bond formation is utilized for the diarylpropanes synthesis, involving methylation of the intermediate carbanions by anisole. Anthracene and phenanthrene are reduced by $LiAlH_4$ in diglyme, the former giving eventually 9,9,10,10-tetramethyl-9,10-dihydroanthracene. *cis*-Stilbene undergoes competing reduction and isomerization to *trans*-stilbene when heated with $LiAlH_4$ in diglyme; the latter ultimately gives 1,2-diphenylethane.

It has generally been accepted[1,2] that nonfunctionalized aromatic olefins do not react with $LiAlH_4$. The hydride addition to dibenzofulvene[3] has been interpreted as evidence for the high polarity of the exocyclic double bond of this special olefin. Transformation of cinnamyl alcohols to phenylcyclopropanes,[4] 1-phenylpropyne to *n*-propylbenzene,[4f] cinnamaldehyde to dihydrocinnamyl alcohol, and reduction of some unsaturated azabicyclic systems,[5] effected by $LiAlH_4$, have indicated that suitable functionalization of an olefin might enable hydride addition across a carbon–carbon double bond to occur. However, these latter reactions have been shown to be specific examples of intramolecular reactions.[4e] Recently, it has been found that aromatic compounds bearing an exocyclic double bond, such as substituted 9-methylenexanthenes[6] and methylenebenzanthrene,[7] react with $LiAlH_4$ under mild conditions. Furthermore, alternate aromatic olefins, such as 1,1-diphenylethylene,[8,9] are converted by $LiAlH_4$ in THF to the corresponding benzylic carbanions. Possible synthetic applications of these carbanions have briefly been outlined.[8,10] Similar findings have been reported[11] for the reduction of some aromatic olefins with sodium bis(2-methoxyethoxy)aluminum hydride. We now wish to present new data[12] concerning the scope of hydride addition to aromatic olefins, substituent and solvent effects, and some synthetic applications associated with this reaction.

Substituent and Geometry Effects. We have studied the hydride addition to aromatic olefins using $LiAlH_4$ in several ethereal solvents and temperatures. Reaction progress was followed by ^{1}H NMR spectroscopy and final products were isolated, purified, and characterized by standard techniques.

Generally, substituents which increase the electron density at the double bond or cause steric hindrance decelerate the hydride addition to an aromatic olefin. Electron-delocalizing, and cyclic, relatively rigid aromatic groups accelerate the reaction. Half-lives of some representative olefins in the presence of $LiAlH_4$ in refluxing THF (65 °C) are given in Table I. The hydride addition to 1,1-di-*o*-anisylethylene (**2**) is considerably faster than it is to 1,1-di-*p*-anisylethylene (**3**) in refluxing THF. A similar ortho effect is exhibited by 1-(*o*-anisyl)-1-phenylethylene[10] and especially 1-(*o*-dimethylaminophenyl)-1-phenylethylene ($T_{1/2}$ **31**/$T_{1/2}$ **30** = 40).

This rate-enhancing phenomenon exhibited by *o*-MeO[13] and *o*-Me_2N might be associated with the hydride attack (the "activated complex") as well as the stabilization of the generated carbanion (the "product"). The *o*-MeO group, e.g., might replace a solvent molecule[14,18] in the transition state, thus placing the hydride closer to the double bond and consequently enhancing the reaction rate. Similarly, intramolecular stabilization could be extended to the carbanion by