

Relative Reactivities of Amide, Diphenylphosphide, and Diphenylarsenide Ions toward Aryl Radicals

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Competition experiments have been carried out in liquid ammonia at reflux temperature to determine the relative rate constants for the coupling reactions of amide (NH_2^-), diphenylphosphide (Ph_2P^-), and diphenylarsenide (Ph_2As^-) ions toward aryl radicals. It is proposed that these nucleophiles react under photostimulation with halo aromatic substrates through the $\text{S}_{\text{RN}}1$ mechanism of aromatic substitution. Relative rate constants of NH_2^- vs. Ph_2P^- ions toward 2,4,6-trimethylphenyl radicals and Ph_2P^- vs. Ph_2As^- ions toward 2-quinolyl radicals have been determined. The results here reported indicate that NH_2^- (1.00) < Ph_2P^- (6.4) \approx Ph_2As^- (6.4). The fact that there is not a difference in the rate constants of Ph_2P^- vs. Ph_2As^- suggests that both nucleophiles react at diffusion-controlled rate. In competition experiments of Ph_2P^- vs. Ph_2As^- ions toward phenyl radicals, it was found that Ph_2P^- (1.00) > Ph_2As^- (0.44). The decrease of the Ph_2As^- ion reactivity is attributed to the reversible coupling of this nucleophile with phenyl radicals.

The mechanism of aromatic radical nucleophilic substitution, or $\text{S}_{\text{RN}}1$,² rationalizes the reactions of different nucleophiles with aryl radicals,²⁻⁴ and in some cases the relative reactivities of nucleophiles toward aryl radicals have been determined.^{5,6} We have already reported the relative reactivities of nucleophiles from the VIA group of the periodic table: benzenethiolate, benzeneselenate, and benzenetellurate ions (PhS^- , PhSe^- , and PhTe^-) toward aryl radicals.⁶ We thought it of interest to study the relative reactivities of the VA group toward aryl radicals.

In order to compare reactivities, it is convenient to use nucleophiles with similar structures. For instance, the systems diphenylamide, diphenylphosphide, and diphenylarsenide ions (Ph_2N^- , Ph_2P^- , and Ph_2As^-) seem appropriate to study the relative reactivities of the VA group. However, it is not possible to use Ph_2N^- as the nucleophile because aryl radicals not only react on nitrogen to give triphenylamine, but also on carbon of the benzene rings of the nucleophile to give diphenylphenylamines.⁷

Another possibility would be to use unsubstituted amide ions. The amide ion was the first nucleophile recognized to react with aryl radical; these reactions occur spontaneously with 5- and 6-iodo-1,2,4-trimethylbenzenes,² or with several haloarenes stimulated with alkali metals in liquid ammonia.^{2,8} It is not known whether amide ions react under photostimulation with haloarenes. In order to avoid the competing benzyne mechanism, we decided to study the photostimulated reaction of amide ions with 1-bromo-2,4,6-trimethylbenzene. We found good yields of substitution product in reactions stimulated by light, and we were able to determine the relative reactivity of amide ions vs. diphenylphosphide ions.

Diphenylarsenide ions gave scrambling of aryl rings with halobenzenes, 1-bromonaphthalene, etc, but they gave only the substitution products with 2-chloroquinoline and 4-chlorobenzophenone.^{9,10} The scrambling of aryl rings was attributed to the reversible coupling of diphenylarsenide ion with aryl radicals.¹¹

We have shown that the relative reactivity of two nucleophiles with aryl radicals depends on their irreversible reaction with these radicals; in this case the *actual* relative reactivity is obtained. However, if one of the nucleophiles reacts reversibly with aryl radicals, but the other one reacts in an irreversible reaction, an *apparent* relative reactivity is obtained, being different from the actual one.⁶

We studied the relative reactivity of diphenylphosphide vs. diphenylarsenide ions with 2-chloroquinoline as substrate. In this system both nucleophiles react with 2-quinolyl radicals in an irreversible reaction under our experimental conditions. With iodobenzene as substrate, diphenylphosphide reacts irreversibly with the phenyl radicals, but diphenylarsenide ion does so in a reversible reaction.

It was not possible to study the relative reactivity of diphenylantimonide ion because it reacted reversibly with all the aryl radicals studied.¹⁰⁻¹²

Results

Photostimulated Reaction of Amide Ions and Diphenylphosphide Ions with 1-Bromo-2,4,6-trimethylbenzene. In order to learn whether amide ion reacts by the $\text{S}_{\text{RN}}1$ mechanism stimulated by light, we performed the reaction of amide ion with 1-bromo-2,4,6-trimethylbenzene 1 (eq 1). We found 70% 1-amino-2,4,6-trimethylbenzene 2 and 6% 1,3,5-trimethylbenzene 3 were formed. There is no reaction at all after 120 min (Table I) in complete darkness.

In photostimulated reactions of diphenylphosphide ion with 1 (60 min) we found 20-45% (2,4,6-trimethylphenyl)diphenylphosphine 4 (quantified as its oxide) and

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(7) In the photostimulated reaction of diphenylamide ion with bromobenzene, besides triphenylamine it was found biphenylphenylamines were formed (Alonso, R. A.; Bornancini, E. R.; Rossi, R. A., unpublished results). This result resembles the reaction of anilide ion with iodobenzene and potassium metal which gave diphenylamine and aminobiphenyls.²

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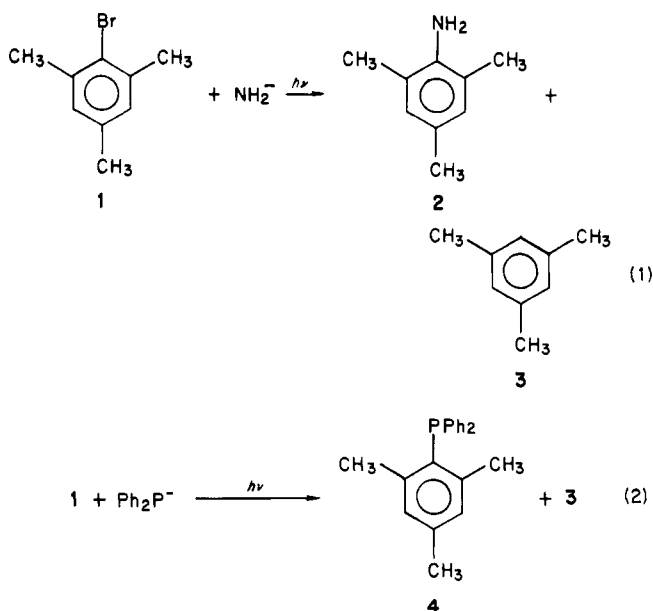
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(12) It was reported that diphenylantimonide ion reacts reversibly with 2-quinolyl and 4-benzoylphenyl radicals.¹⁰ We studied the photostimulated reaction of diphenylantimonide ion with 9-chloroacridine and 2-chloroquinoxaline, but no substitution products were formed (Alonso, R. A.; Bornancini, E. R.; Rossi, R. A., unpublished results).

50–55% yield of 3 (Table I) (eq 2).



Competition Experiments. Amide Ion vs. Diphenylphosphide Ion. Once the yields of the substitution product 2 and 4 (as its oxide) were determined in the photostimulated reaction of 1 with diphenylphosphide and amide ions in excess, it was possible to calculate k_P/k_N as previously reported (Table II).^{5,6,13}

Diphenylphosphide Ion vs. Diphenylarsenide Ion. The relative reactivities of both nucleophiles were determined in photostimulated reactions of diphenylarsenide and diphenylphosphide ions with 2-chloroquinoline and iodobenzene as substrates (Table II).

Discussion

The facts that amide ions react only under photostimulation with 1, and that there is no dark reaction show that amide ions react with haloarenes by the $\text{S}_{\text{RN}}1$ mechanism stimulated by light. We chose 1 as substrate because it is unable to react with amide ion through the benzyne mechanism.

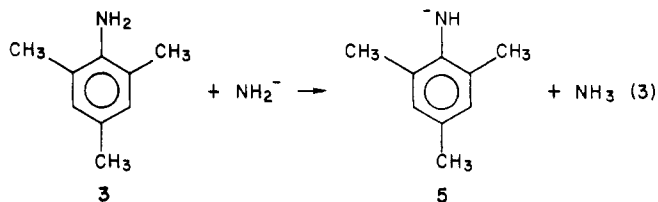
In the photostimulated reaction of 1 with diphenylphosphide we found a substantial amount of the reduction product 1,3,5-trimethylbenzene 3 together with a modest yield of the substitution product 4. This result is quite different from the result of the reaction of this nucleophile with *p*-iodotoluene, in which 90% yield of the substitution product *p*-tolylidiphenylphosphine (quantified as its oxide) was found.¹⁴

1-Iodo-2,4,6-trimethylbenzene reacted with acetone enolate ion to give 10% of the reduction product 3 together with 82% of the substitution product;¹⁵ however it gave 25% of 3 with a 24% of the substitution product¹⁶ with 3-pentanone enolate ion as nucleophile (a more hindered nucleophile). From these and other results,^{4,15,16} it was concluded that when the substrate has a substituent in positions 2 and 6, or when the nucleophile is bulky, the substitution yield decreases and the reduction yield increases. Consequently, diphenylphosphide ion has similar or greater steric requirements than 3-pentanone enolate

ion in the coupling with 2,4,6-trimethylphenyl radicals.

The reduction of 2,4,6-trimethylphenyl radical in the reaction with diphenylphosphide ion might occur because the reaction with this nucleophile is slower than with *p*-tolyl radicals; thus the radical has a greater chance to be reduced. However, in the competition experiments with an excess of amide ion present, there was also a substantial reduction of 1,3,5-trimethylbenzene, and 2,4,6-trimethylphenyl radical was not trapped by amide ions. (In the photostimulated reaction with only amide ion present, 1,3,5-trimethylbenzene was formed in only 6% yield.) These results suggest that 2,4,6-trimethylphenyl radicals are reduced by diphenylphosphide ions in competition with the coupling reaction.

In the competition experiments with a range of ratios of amide to diphenylphosphide from 21 to 8.5 (Table II, experiments 1–4), $k_P/k_N = 6.4 \pm 0.4$, but with a ratio of amide to diphenylphosphide of 5.7–5.1 (Table II, experiments 5 and 6) there is an apparent increase in the reactivity of diphenylphosphide ion (k_P/k_N 9–15). These results suggest that the apparent decrease in the reactivity of amide ion when it is present in a relatively low concentration might be due to the deprotonation of the substitution product 3 by amide ion to form the ion 5 (eq 3).



The consumption of 2 mol of amide ions to form the ion 5 from the radical, as well as the fact that ion 5 can also react with the 2,4,6-trimethylphenyl radical, reduce the yield of the substitution product. Experiments 5 and 6 (Table II) were not taken into account to calculate the k_P/k_N reactivity.

It has been previously reported that amide ions are 2.0 times more reactive than acetone enolate ion toward 2,4,6-trimethylphenyl radical, in reactions stimulated by potassium metal.¹⁷ Diphenylphosphide ion is 5.9 times more reactive than pinacolone enolate ion (photostimulated reactions).⁵ Our results indicate that amide ions have about the same reactivity as ketone enolate ions, and that diphenylphosphide ions are about 6 times more reactive.

In the photostimulated reaction of diphenylphosphide and diphenylarsenide ions with 2-chloroquinoline as substrate, we found the same reactivity of both nucleophiles toward 2-quinolyl radicals. Diphenylphosphide ion is the most reactive nucleophile toward aryl radicals, and it has been suggested that it might react at diffusion-controlled rate.⁵ The fact that diphenylarsenide ion reacts at the same rate suggests that both nucleophiles react at the diffusion-controlled rate with 2-quinolyl radicals.

The trend observed in these competition experiments is similar to that observed with the VIA group⁶ [PhO^- (0.0) < PhS^- (1.0) < PhSe^- (5.6) < PhTe^- (28)]; as the nucleophile becomes softer, it reacts faster with aryl radicals. Similarly for group VA: NH_2^- (1.0) < Ph_2P^- (6.4) \approx Ph_2As^- (6.4). There is no increase when using the diphenylarsenide ion because it is limited by the diffusion rate.

A different result is obtained in competition experiments between diphenylphosphide ion vs. diphenylarsenide ion with iodobenzene as substrate. In this system diphenyl-

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Table I. Photostimulated Reaction of Amide and Diphenylphosphide Ions with 1-Bromo-2,4,6-trimethylbenzene (1)

expt	1 10 ³ M	nucleophile (10 ³ M)	<i>hν</i> , ^a min	products, % yield		
				1 ^b	3	substitution product
1	4.0	NH ₂ ⁻	120	1	6	70 ^c
2	4.0	NH ₂ ⁻	120 ^d	100	0	0 ^c
3	4.0	Ph ₂ P ⁻	60	7	55	20 ^e
4	6.0	Ph ₂ P ⁻	60	3	50	45 ^e

^a Irradiation time. ^b Substrate recovered. ^c 1-Amino-2,4,6-trimethylbenzene. ^d Dark reaction wrapped with aluminum foil. ^e (2,4,6-Tri-methylphenyl)diphenylphosphine (quantified as its oxide).

Table II. Competition Experiments of ArX with Two Nucleophiles^a

expt	ArX	10 ³ M	nucleophile Nu ₁ ⁻		nucleophile Nu ₂ ⁻		Nu ₁ /Nu ₂ ²	yield, %		<i>k</i> _{Nu1} / <i>k</i> _{Nu2}
			identity	10 ³ M	identity	10 ³ M		ArNu ₁	ArNu ₂	
1 ^b	1	1.88	Ph ₂ P ⁻	2.00	NH ₂ ⁻	42.00	21.0	5.0	17.5	6.12
2 ^c	1	4.00	Ph ₂ P ⁻	3.32	NH ₂ ⁻	37.20	11.2	5.4	9.0	6.92
3 ^c	1	1.80	Ph ₂ P ⁻	2.08	NH ₂ ⁻	18.88	10.8	8.0	15.0	5.95
4 ^d	1	4.00	Ph ₂ P ⁻	3.76	NH ₂ ⁻	32.00	8.5	8.0	11.0	6.44
5 ^c	1	3.44	Ph ₂ P ⁻	3.32	NH ₂ ⁻	18.88	5.7	28.0	15.0	12.3
6 ^c	1	3.60	Ph ₂ P ⁻	3.91	NH ₂ ⁻	20.08	5.1	25.0	9.0	15.8
								av expt 1-4		6.4 ± 0.4
7	2-ClQ ^e	7.88	Ph ₂ As ⁻	8.40	Ph ₂ P ⁻	7.80	1.08	43.8	34.6	1.20
8	2-ClQ	4.60	Ph ₂ As ⁻	8.12	Ph ₂ P ⁻	4.08	1.99	77.4	28.3	1.09
9	2-ClQ	2.00	Ph ₂ As ⁻	3.96	Ph ₂ P ⁻	4.28	0.93	42.0	56.0	0.79
10	2-ClQ	2.60	Ph ₂ As ⁻	2.60	Ph ₂ P ⁻	5.24	0.50	26.2	53.8	0.98
										Av 1.0 ± 0.13
11	PhI	3.96	Ph ₂ As ⁻	7.80	Ph ₂ P ⁻	7.84	1.00	26.0	54.5	0.44

^a Photostimulated reactions; expt 1-6: irradiation time, 120 min; expt 7-11: irradiation time, 60 min. ^b 1,3,5-Trimethylbenzene: 66% yield. ^c 1,3,5-Trimethylbenzene detected but not quantified. ^d 1,3,5-Trimethylbenzene: 60% yield. ^e 2-ClQ = 2-chloroquinoline.

phosphide ion reacts irreversibly with phenyl radicals, whereas diphenylarsenide ion does so in a reversible reaction. In these conditions, the apparent reactivity of *k*_{As}/*k*_P is 0.44. The decrease in the reactivity of diphenylarsenide ion is due to the reversible coupling with phenyl radicals.

Experimental Section

General Methods. The general method was as described before.^{6,9,10}

Materials. All the haloaromatic compounds, triphenylphosphine, and triphenylarsine were analytical grade, commercially available products used as received. The nucleophiles diphenylphosphide and diphenylarsenide ions were prepared in situ, following the same procedure as reported.^{9,10} 2-Quinolyldiphenylarsine⁹ was synthesized as reported.

Photostimulated Reactions. These reactions were carried out in a photochemical reactor equipped with four 250-W lamps with maximum emission at 350 nm (Philips, Model HPT, water refrigerated).

Photostimulated Reaction of Amide Ions with 1-Bromo-2,4,6-trimethylbenzene. Approximately 250 mL of ammonia, previously dried over sodium, was distilled into a 500 mL, three-necked, round-bottomed flask equipped with a cold finger, nitrogen inlet, and magnetic stirrer. To the ammonia was added sodium metal (9.9 mol) and a small piece of ferric chloride to catalyze the formation of amide ions. 1-Bromo-2,4,6-trimethylbenzene (1.0 mmol) dissolved in 1 mL of dry diethyl ether was added and then the solution was irradiated (120 min). The reaction was quenched with water and the ammonia was allowed to evaporate. Water was added to the residue and the mixture was then extracted three times with diethyl ether. The ether extracts were analyzed and quantified by GLC. The products 1,3,5-trimethylbenzene and 1-amino-2,4,6-trimethylbenzene were identified by comparing their retention times with those of authentic samples.

Photostimulated Reaction of Diphenylphosphide Ions with 1-Bromo-2,4,6-trimethylbenzene. The procedure was similar to that for the previous reaction. The reaction was quenched by ammonium nitrate and 30 mL of CH₂Cl₂ was added. The ammonia was allowed to evaporate. The residue was washed with 25 mL of CH₂Cl₂. From the dichloromethane extract

(2,4,6-trimethylphenyl)diphenylphosphine was oxidized with 25 mL of aqueous H₂O₂ (20 vol %) for 40 min. The dichloromethane was distilled and the residue was column chromatographed (silica gel) and eluted with petroleum ether. After recrystallization from petroleum ether, a pure sample of (2,4,6-trimethylphenyl)diphenylphosphine oxide was obtained: mp 119-121 °C; mass spectrum, *m/e* (relative intensity) 320 (37), 319 (100), 241 (11), 193 (9), 179 (23), 165 (17), 152 (8), 91 (12), 77 (21), 51 (22); NMR (δ) 1.90 (s, 6 H), 2.11 (s, 3 H), 6.80 (d, 2 H), and 7.1 (s, 10 H).

Photostimulated Competitive Reaction of Amide and Diphenylphosphide Ions. The reaction of these nucleophiles with 1-bromo-2,4,6-trimethylbenzene is representative: to 250 mL of distilled ammonia was added triphenylphosphine (0.5 mmol) and sodium metal (1.0 mmol) to form 0.5 mmol of diphenylphosphide ion and 0.5 mmol of amide ion. After 30 min sodium metal was added (10 mmol) and a small piece of ferric nitrate to form 10 mmol of amide ions (the total of amide ions formed was 10.5 mmol). 1-Bromo-2,4,6-trimethylbenzene (0.47 mmol) dissolved in 1 mL of dry diethyl ether was then added and irradiated for 120 min. The reaction was quenched (NH₄NO₃), 25 mL of CH₂Cl₂ was added, the ammonia was allowed to evaporate, the residue was filtered, and the solid was washed three times with CH₂Cl₂. 1,3,5-Trimethylbenzene and 1-amino-2,4,6-trimethylbenzene were quantified by GLC. The CH₂Cl₂ extract was then oxidized by 15 mL of aqueous H₂O₂ (20 mol %) and then (2,4,6-trimethylphenyl)diphenylphosphine oxide was quantified. It was not possible to quantify (2,4,6-trimethylphenyl)diphenylphosphine because part of it was always oxidized in the workup.

Photostimulated Competitive Reaction of Diphenylphosphide and Diphenylarsenide Ions. The procedure was similar to that for the previous reaction. The dichloromethane extract was oxidized with 15 mL of aqueous H₂O₂ (40 min, 20 vol %); 2-quinolyldiphenylphosphine was quantitatively oxidized to its oxide whereas 2-quinolyldiphenylarsine was not oxidized at all. The oxidation reaction was followed by TLC (silica gel, chloroform:methanol 75:25, 2-quinolyldiphenylarsine *R*_f 0.9, 2-quinolyldiphenylarsine oxide *R*_f 0.4). After oxidation, the reaction mixture was quantified by GLC.

Photostimulated Reaction of Diphenylphosphide Ion with 2-Chloroquinoline. The nucleophile and the procedure was similar to that for the previous reaction. The CH₂Cl₂ extract was oxidized and then evaporated. The residue was column chro-

matographed (silica gel, eluted with petroleum ether) and 2-quinolyldiphenylphosphine oxide was isolated and twice recrystallized from petroleum ether (40% yield): mp 139.5–140 °C; mass spectrum, *m/e* (relative intensity) 329 (13), 328 (17), 252 (52), 204 (47), 201 (23), 183 (17), 128 (63), 101 (43), 77 (100), 51 (53).

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Registry No. 1, 576-83-0; 2, 88-05-1; 3, 108-67-8; 2-ClQ, 612-62-4; NH_2^- , 17655-31-1; Ph_2P^- , 34676-89-6; Ph_2As^- , 14971-22-3; PhI , 591-50-4; (2,4,6-trimethylphenyl)diphenylphosphine oxide, 91239-43-9; 2-quinolyldiphenylphosphine oxide, 91239-45-1; 2-quinolyldiphenylarsine, 91239-44-0.

Perdeuteration and Selective Deuteration of Alkynols by Isomerization of Triple Bonds Using N-Deuterated Reagents

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A novel method for introduction of deuterium into long-chain carbon compounds is described. The procedure is based upon isomerization of a triple bond of an $(n + 1)$ -alkyn-*n*-ol to an ω -alkyn-*n*-ol using N-deuterated reagents and solvent. Isomerization of 2-alkyn-1-ols effects exchange of the protons from C-2 to the terminal carbon, resulting in perdeuteration of all methylene carbons of the chain except C-1. Reaction of $(n + 1)$ -alkyn-*n*-ols ($n > 1$) with deuterated isomerization reagents affords specific, selective deuteration of methylene carbons $> (n + 1)$. The reagents for these transformations are alkali metal amides of the solvent of the reaction, 1,3-diaminopropane-*N,N,N',N'*- d_4 . When the cation is sodium or potassium, isomerization of 2-decyn-1-ol affords 9-decyn-1-ol with 89% deuterium incorporation at C-2 to C-8 in isolated yields of 48–53%. An isomerization reagent prepared by addition of potassium *tert*-butoxide to the lithium salt of 1,3-diaminopropane-*N,N,N',N'*- d_4 affords 93% deuterium incorporation and isolated yields of 52% or better. With this reagent 2-octadecyn-1-ol is rearranged to 17-octadecyn-1-ol with an overall deuterium incorporation of 93% over 31 exchangeable positions in 60% isolated yield.

Perdeuterated fatty acids and their derivatives are employed in studies of biological processes as probes for exploring biosynthetic and metabolic pathways¹ and in NMR and IR studies of the structure and function of micelles and membranes.² Current methods of synthesis of perdeuterated organic compounds are based upon catalytic exchange techniques in which protons are replaced by deuterons under extremely vigorous conditions (high pressures and temperatures and long reaction times).³ Known methods are limited to preparation of compounds stable to the severe reaction conditions. Unsaturated compounds, for instance, are reduced in the course of deuteration.

Alkali metal amides in the diamine solvents such as 1,2-diaminoethane and 1,3-diaminopropane mediate isomerization of internal triple bonds to the terminal position of straight-chain hydrocarbons and alcohols.^{4,5} Overall, during the course of such isomerization reactions, protons in the path of the migrating triple bond are stripped from the carbon skeleton and replaced by protons from the amide or from the solvent. We thought that such a remote functionalization reaction could be used to exchange protons of a methylene chain with deuterons if the solvent of the reaction was replaced by its *N,N,N',N'*-tetra-deuterated analogue. Such a procedure, if successful, would provide ready access to functionalized deuterated long-chain com-

pounds and would have decided advantages over presently available methods. Reaction conditions would be more moderate; unsaturated perdeuterated compounds could be prepared from 2-alkyn-1-ols, and specifically partially deuterated chemicals would be accessible from disubstituted α -acetylenic alcohols. As well, deuterium labeling could be used to study the course of triple-bond migrations.

There have been reports of deuterium exchanges mediated by alkali metal amides. Brown⁶ observed that the potassium salt of 1,3-diaminopropane was sufficiently basic to cause exchange of deuterons of benzene- d_6 by protons. Wotiz et al.⁷ showed that the rate of rearrangement of 3- to 2-hexyne with the lithium salt of 1,2-diaminoethane-*N,N,N',N'*- d_4 paralleled the rate of deuterium incorporation into the latter. Procedures for incorporation of deuterium into alkynes by base-mediated isomerization techniques have been reviewed.⁸ Methods are limited to exchange at the terminal and propargylic positions.

We report our studies on the incorporation of deuterium into a variety of alkynols using an *N,N,N',N'*-tetra-deuterated diamine solvent and some derived alkali metal amide isomerization reagents.

Results and Discussion

In the cases discussed in this work, unless noted, rearrangement reactions proceeded to completion. That is, one isomer, that containing a terminal triple bond, was the exclusive product. Deuterium incorporations of products

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