Intramolecular Organometal–Acetylene Interactions. A New Route to Acenaphthylene Derivatives

Raymond E. Dessy and S. A. Kandil

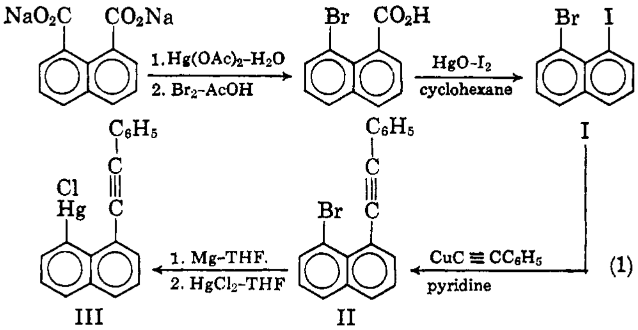
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

Received May 4, 1965

The synthesis of 1-phenylethynyl-8-bromonaphthalene has permitted the synthesis of the 8-magnesio and -lithio derivatives. The former reacts with water to generate phenylethynylnaphthalene and with $HgCl_2$ to yield 1-phenylethynyl-8-chloromercurinaphthalene, thus permitting an evaluation of mercury–acetylene interactions. The lithio derivative rapidly adds intramolecularly to the adjacent acetylenic linkage, yielding 1-phenylacenaphthylenylithium which reacts with water or $HgCl_2$ to give the expected products. This intramolecular organometallic addition reaction opens up an easy route to acenaphthylene derivatives.

Metal–acetylene interactions are well known.[1-5] It would be of interest to investigate such interactions in a system in which a σ-bonded metal atom of an organometallic can be geometrically situated with respect to an intramolecular triple bond so as to enhance their interactions. Models show that the 1- and 8-positions in naphthalene are admirably suited for such an investigation.

Mercury–Acetylene Interactions.—The initial synthetic problem was successfully pursued by the following sequence of transformations.[6]



(1)

III II

m.p. 155–156°

The interactions were evaluated by comparison of the ultraviolet spectra and polarographic data of the related compounds. All spectra showed a main band attributable to the naphthalene ring. In naphthalene itself the most intense absorption occurs at 35,900 cm.$^{-1}$ (THF). Compounds containing acetylene linkages showed still another characteristic band. In phenylethynylnaphthalene this absorption occurs at 37,313 cm.$^{-1}$ (THF). The results are shown in Tables I and II. Spectra in THF, 95% aqueous ethanol, and benzene gave similar results.

Table I illustrates that there are excessive bathochromic shifts for II and IV, but an excess hypsochromic shift for III. Results in Table II show bathochromic shifts for the acetylene bond in both disubstituted cases.

Table I

Shifts in the 35,900-cm.$^{-1}$ Band in the Spectra of the Naphthalenes[a]

Compd.	ν, cm.$^{-1}$	$\Delta\nu_{obsd}$, cm.$^{-1}$	$\Delta\nu_{obsd} - \Sigma\Delta\nu_{obsd}^{mono}$ [b]
Naphthalene	35,900		
1-Bromonaphthalene	34,970	−930	
1-Chloromercurinaphthalene	35,210	−690	
1-Phenylethynylnaphthalene	31,550	−4350	
1-Phenylethynyl-8-bromonaphthalene (II)	29,850	−6050	−770
1-Chloromercuri-8-bromonaphthalene (IV)	33,930	−1970	−350
1-Phenylethynyl-8-chloromercurinaphthalene (III)	31,060	−4840	+200

[a] All spectra in THF. [b] $\Sigma\Delta\nu_{obsd}^{mono}$ refers to the observed shifts due to monosubstituents in the 1-position summed over the two substituents in question.

Table II

Shifts in the 37,313-cm.$^{-1}$ Band in the Spectra of the Naphthalenes[a]

Compd.	ν, cm.$^{-1}$	$\Delta\nu_{obsd}$, cm.$^{-1}$
1-Phenylethynylnaphthalene	37,310	
1-Phenylethynyl-8-bromonaphthalene (II)	36,360	−950
1-Phenylethynyl-8-chloromercurinaphthalene (III)	35,970	−1340

[a] All spectra in THF.

Compound III is of immediate interest. The experimental data for this compound III in comparison to II and IV might be expected to show large shifts due to metal–acetylene interactions. The effects are, however, relatively small. Interestingly, *formation of the perchlorate of III does not alter the ultraviolet spectrum.*

Further attempts to probe the interactions involved have made use of polarography in 1,2-dimethoxyethane using tetrabutylammonium perchlorate as a supporting electrolyte (*vs.* 0.1 *M* $AgClO_4$–Ag reference). Three-electrode geometry was employed to compensate for *iR* loss. *n* values were determined by controlled potential electrolysis in an H cell with cathode and anode compartment separated by a glass frit. The exact techniques and equipment will be discussed elsewhere.[7] Table III shows the results.

The more cathodic reduction potential of the acetylenic linkage in compound III in comparison with the models diphenylacetylene and 1-phenylethynylnaphthalene is to be noted. The reduction of the naphthalene ring system in III is that expected from averaging the half-wave potentials of the models 1-phenylethynylnaphthalene and 1-chloromercurinaphthalene.

---

(1) G. E. Coates, "Organo-Metallic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960.

(2) W. L. Budde and R. E. Dessy, *J. Am. Chem. Soc.*, **84**, 1172 (1962).

(3) M. K. Kal'fus and D. V. Sokol'skii, *Vestn. Akad. Nauk Kaz. SSR*, **13**, No. 9, 74 (1957); *Chem. Abstr.*, **52**, 2510c (1958).

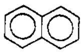
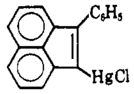
(4) K. Schwabe and H. Berg, *Z. physik. Chem.*, **203**, 383 (1954); *Chem. Abstr.*, **49**, 5091*f* (1953).

(5) H. J. Lucas, *et al.*, *J. Am. Chem. Soc.*, **77**, 939 (1955).

(6) All compounds showed the correct analyses for C, H (Br, I, Hg) and possessed experimental molecular weights within 5% of that expected (Mechrolab osmometer) in THF or benzene.

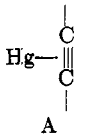
(7) R. E. Dessy, T. Chivers, and W. Kitching, *J. Am. Chem. Soc.*, in press.

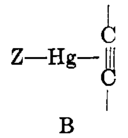
TABLE III
POLAROGRAPHIC DATA (*vs.* 0.1 *M* $AgClO_4$–Ag ELECTRODE)

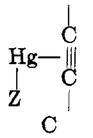
Compound	$E_{1/2}$, v. —Linkage or moiety being reduced— -Hg-Cl (n = 1)	>C-Hg (n = 1)	 (n = 1)	-C≡C- (n = 2)
III	−1.38	−2.76	−2.94	−3.27
1-($C_6H_5C\equiv C$)$C_{10}H_7$	...	...	−2.46	−2.88
1-$ClHgC_{10}H_7$	−1.30	−2.86	−3.46	...
$C_{10}H_8$	...	...	−3.34	...
$C_6H_5C\equiv CC_6H_5$	...	...	...	−3.14
$C_6H_5C\equiv CH$	...	...	...	−3.44
	−1.20	−2.37	...	...
$C_6H_5CH_2HgCl$	−1.21	−2.20	...	...
C_6H_5HgCl	−1.32	−3.04	...	...
$CH_2{=}CHHgBr$	−1.34	−3.10	...	...

The perturbing point appears to be that the interactions are not so strong as might be anticipated, particularly in the perchlorate case. Space-filling models, constructed on the basis of van der Waals radii and covalent radii adapted from Pauling indicate that the mercury should be deeply embedded in the π-system of the acetylene, leading one to expect severe perturbations. Orgel[8] has pointed out the tendency for mercury to form a linear system within HgZ_2 compounds, probably because of the low separation energy between the d and s levels.

It is possible that strong interactions of type A can occur only when a geometrical array B is possible, not when the array is C. Attempts to detect interactions between $MeHg^+ClO_4^-$ and PhC≡CPh in dioxane *via* n.m.r. spectroscopy have thus far failed, but in methanol $MeO_2CHg^+ClO_4^-$ is instantly destroyed by the addition of $C_4H_9C\equiv CH$, leading to CO, $C_4H_9C(OCH_3){=}CH_2$, and the diadduct, presumably *via* a MeO_2CHg^+-acetylene adduct. Further attempts to detect this type of interaction and extensions into the realm of other metals, where such specificity may not be involved, are being made.


A

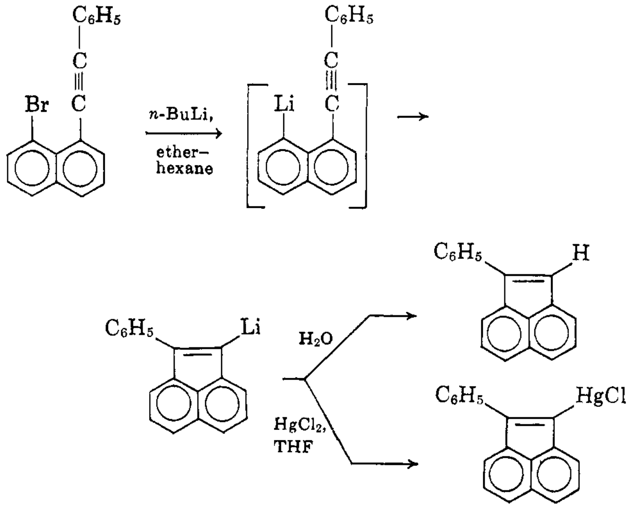

B


C

Lithium–Acetylene Interactions.—Organolithium compounds and the corresponding Grignard reagents are known to react in much the same way to give identical products. Cases where both reagents give different results, however, are found in the literature.[9]

We would like to report the first case of intramolecular addition of an organolithium to a triple bond. When an ethereal solution of 1-phenylethynyl-8-bromonaphthalene was treated with a solution of *n*-butyllithium in hexane at room temperature followed by hydrolysis, 1-phenylacenaphthylene was obtained as the only product identifiable (*via* picrate,[10] ultraviolet and n.m.r. data). Again when the exchange was allowed to occur and a solution of mercuric chloride in THF was added, 1-phenyl-2-chloromercuriacenaphthylene (m.p. 233–235°), an isomer of 1-phenylethynyl-8-chloromercurinaphthalene, was obtained as the only product identified (ultraviolet and n.m.r. data, molecular weight determination, and elemental analysis).

The fact that in both reactions neither 1-phenylethynylnaphthalene nor 1-phenylethynyl-8-chloromercurinaphthalene, respectively, could be detected strongly suggests that the metal–halogen exchange product, once formed, irreversibly adds intramolecularly to the triple bond. These findings may be summarized as follows.



V

Mulvaney and co-workers working with *n*-butyllithium and diphenylacetylene have reported that both *ortho*-metalation and addition to the triple bond can occur.[11] Related open chain-ring isomerizations in the cyclobutylcarbinyl and cyclopentylcarbinyl case have been reported by Roberts, Hill, and Landsbury.[12–14] The present reaction opens up a relatively simple route to the synthesis of acenaphthylene derivatives and suggests a general route to fused ring systems containing a member having four, five, or six carbon atoms. This area is being examined in detail. Added to the recent report of Castro and Letsinger on heterocyclic ring closures involving intramolecular additions of acetylenes and amines or oxyfunctions,[15] it would complete the spectrum of this synthetic route, allowing carbocyclic synthesis.

Some insight into the ring closure process can be obtained from the electrochemistry of the isomers III and V. The reduction potentials of organomercury halides at the second wave have been related to our primitive

$$\begin{tikzcd} RHgX \arrow[r, "e", "E_{1/2}^{1}"'] & RHg \arrow[r, "e", "E_{1/2}^{2}"'] \arrow[d] & R:^- + Hg \\ & R_2Hg + Hg & \end{tikzcd}$$

sequence of carbanion stabilities.[7] The more anodic the reduction potential, the more stable the incipient

---

[8] L. Orgel, "An Introduction to Transition Metal Ligand Field Theory," John Wiley and Sons, Inc., New York, N. Y., 1960.

[9] J. Yoshimura, *et al.*, *J. Am. Chem. Soc.*, **86**, 3858 (1964).

[10] W. A. Bonner, *et al.*, *ibid.*, **75**, 3831 (1953).

[11] J. E. Mulvaney, *et al.*, *ibid.*, **85**, 3898 (1963).

[12] M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

[13] H. G. Richey and E. A. Hill, *J. Org. Chem.*, **29**, 421 (1964).

[14] P. T. Landsbury, V. A. Pattison, W. A. Clement, and J. D. Sidler, *J. Am. Chem. Soc.*, **86**, 2247 (1964).

[15] (a) C. E. Castro and R. D. Stephens, *J. Org. Chem.*, **28**, 2163 (1963); (b) R. L. Letsinger, E. N. Oftedahl, and J. R. Nazy, *J. Am. Chem. Soc.*, **87**, 742 (1965).

carbanion is. The data suggest that here the phenylacenaphthylenyl anion is more stable than the corresponding 1-phenylethynylnaphthyl anion, and that the driving force for the ring closure is this enhanced stability.[16] For comparison purposes the corresponding values of benzyl-, phenyl-, and vinylmercuric halides are included in Table III.

As the above equation indicates, the chemical fate of RHg produced at a mercury or platinum electrode is conversion to R_2Hg. The exact structure of the RHg species is as yet unknown.[17] Unpublished data[7] indicate that alkyl and aryl groups do not have free-radical character, since the conversion to R_2Hg is quantitative, no RH *via* hydrogen abstraction being detected. If R is optically active, complete racemization occurs at some state during or prior to formation of R_2Hg, and, if $RHg^{203}X$ is reduced at Hg electrode, the resulting R_2Hg has little activity in it, indicating that the R group in RHg rapidly exchanges onto and from pool Hg atoms, prior to discharge into R_2Hg. In the present system, controlled potential electrolysis of isomers III and IV at the first wave yields solutions containing halide ion and R_2Hg having ultraviolet spectra almost identical with that of the starting RHgX. No interconversion between the phenylethynylnaphthalene and phenylacenaphthylene systems occurred.

Finally, the ring-closure reaction must occur at finite speeds, since controlled potential electrolysis at the second wave (where a carbanion is generated) of III gave predominantly phenylethynylnaphthalene *via* reaction of the carbanion with small traces of water in the system. Alternatively, the different gegenions involved in ring closure (Li) and this case (Bu_4N) may point to the importance of considering the role of gegenion as an electrophile which can distort the acetylenic link and permit ring closure by subsequent carbanion attack.[18]

Experimental Section

8-Bromonaphthoic acid was prepared from naphthalic acid. Details and yields are to be found elsewhere.[19]

1-Bromo-8-iodonaphthalene.—8-Bromonaphthoic acid (40 g.), red mercuric oxide (20 g.), and iodine (40 g.) were mixed together in 500 ml. of cyclohexane. The stirred mixture, protected from direct light, was refluxed for 8 hr. The reaction mixture was then cooled and the mercuric iodide which had formed together with unreacted starting material was filtered off. The filtrate was evaporated to give a dark brown oil. This was dissolved in ether and treated with a solution of sodium bisulfite followed by a solution of sodium bicarbonate until no further carbon dioxide evolution was observed. The ether layer was then separated, dried, decolorized, and evaporated to give a pale brown solid. The solid was recrystallized from absolute methanol to give white crystals of 1-bromo-8-iodonaphthalene (15 g., 28.31 yield), m.p. 91–92°.

Anal. Calcd. for $C_{10}H_6BrI$: C, 36.04; H, 1.80; Br, 24; I, 38.13. Found: C, 36.21; H, 1.77; Br, 23.82; I, 37.70.

Copper(I) phenylacetylide was prepared from the reaction of phenylacetylene and copper(I) chloride in ammonium hydroxide.[20]

1-Phenylethynyl-8-bromonaphthalene.—1-Bromo-8-iodonaphthalene (12.3 g., 0.037 mole) and copper(I) phenylacetylide[20b] (6.1 g., 0.037 mole) were mixed together in 400 ml. of pyridine that had been purged thoroughly with nitrogen. The mixture was refluxed for a period of 10 hr. The mixture was then cooled, poured into 1500 ml. of water, and extracted with ether. The ether layer was then separated, dried, and filtered. The filtrate was then evaporated to give a dark red oil. This was dissolved in 10 ml. of benzene and chromatographed on activated neutral alumina using petroleum ether (b.p. 40–60°) as the eluent. Two fractions were collected: fraction I, which on evaporation gave starting material (1.5 g.); and fraction II, which on evaporation gave a reddish yellow oil. The oil was chromatographed to give a pale yellow oil, 1-phenylethynyl-8-bromonaphthalene (8.5 g., 75% yield). The ultraviolet spectrum showed two main bands at 334 and 274 mμ with relative intensities of 7:4.

Anal. Calcd. for $C_{18}H_{11}Br$: C, 70.3; H, 3.59; Br, 26.1. Found: C, 68.04; H, 3.56; Br, 26.14.

1-Phenylacenaphthylene.—A solution of 1-phenylethynyl-8-bromonaphthalene (5 g.) in 20 ml. of ether was added dropwise to a solution of *n*-butyllithium in hexane (12 ml., 15% solution) kept at room temperature and under a dry nitrogen atmosphere. The pale yellow color of the original solution changed to greenish red then to red. Stirring was continued for 17 hr., at the end of which an orange-yellow solid formed. The reaction mixture was hydrolyzed and extracted with ether. The orange ethereal solution was separated, dried, decolorized, and filtered. The ether, evaporated under suction, left an orange oil residue. This was chromatographed on neutral alumina with petroleum ether. The eluted solution was evaporated to give an orange oil which readily crystallized to give orange needles of 1-phenylacenaphthylene (3 g., 82% yield), m.p. 54–55°. The picrate derivative was prepared and recrystallized from alcohol to give crimson red crystals, m.p. 122° (lit.[10] m.p. 122–123°).

1-Chloromercuri-2-phenylacenaphthylene.—The above reaction was carried out and, after stirring for 17 hr., a solution of mercuric chloride (4 g.) in THF was added; stirring was continued for another hour. The solid which had formed was filtered and recrystallized from benzene to give a yellow-orange solid of 1-chloromercuri-2-phenylacenaphthylene (33 g., 50% yield), m.p. 234–235°. The n.m.r. spectrum showed a complex pattern centered at τ 2 with no other bands in the spectrum.

Anal. Calcd. for $C_{18}H_{11}ClHg$: C, 46.64; H, 2.35; Cl, 7.67. Found: C, 46.42; H, 2.38; Cl, 7.66.

1-Phenylethynylnaphthalene.—1-Iodonaphthalene (17.8 g.) and Cu(I) phenylacetylide (11.5 g.) were mixed together in 400 ml. of pyridine that was thoroughly purged with dry nitrogen. The mixture was refluxed for a period of 10 hr. The reaction was cooled and worked up in the same manner as before to give two fractions on the column: fraction I, which on evaporation gave starting material (3 g.); and fraction II, which on evaporation gave a colorless oil of 1-phenylethynylnaphthalene (12 g., 75% yield). The ultraviolet spectrum showed two main bands at 315 and 266 mμ with relative intensities of 3.4:1.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.8; H, 5.2. Found: C, 92.71; H, 5.49.

The dibromo derivative was prepared and recrystallized from alcohol to give white crystalline solid, m.p. 159–160°.

Anal. Calcd. for $C_{18}H_{12}Br_2$: C, 55.67; H, 3.09; Br, 41.24. Found: C, 55.37; H, 3.16; Br, 41.04.

1-Phenylethynylnaphthalene.—The Grignard reagent of 1-phenylethynyl-8-bromonaphthalene (5 g.) in 50 ml. of THF was prepared in the usual manner. This was hydrolyzed and extracted with ether. The ether layer was separated, dried, decolorized, and evaporated to give 1-phenylethynylnaphthalene (3 g., 80% yield), identified by comparison of its ultraviolet spectrum with that of an authentic sample.

1-Phenylethynyl-8-chloromercurinaphthalene.—To the Grignard reagent prepared as above was added a solution of mercuric chloride (4.5 g.) in THF. Heat was evolved and the reaction mixture was stirred for 1 hr. The solid which had formed was filtered. The pale brown solid was recrystallized from a benzene–ether mixture by allowing the solution to evaporate slowly at room temperature. Colorless silklike needles of 1-phenylethynyl-8-chloromercurinaphthalene separated (4.8 g., 62.3% yield), m.p. 155–157°. When exposed to air, some discoloration occurred.

Anal. Calcd. for $C_{18}H_{11}ClHg$: C, 46.64; H, 2.35; Cl, 7.67; mol. wt., 463. Found: C, 44.79; H, 2.23; Cl, 6.95; mol. wt., 464.

---

(16) A referee has pointed out that the formation of a new C–C σ-bond at the expense of an acetylenic π-bond and the additional delocalization of the acenaphthylene system *vs.* the ethynylnaphthalene nucleus may be important factors in providing driving force for the process.

(17) G. Coates, "Organometallic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960.

(18) The authors wish to thank a referee for this perceptive observation.

(19) F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **51**, 1831, 3363 (1929).

(20) (a) T. D. Blake, G. Calvin, and G. E. Coates, *Proc. Chem. Soc.*, 396 (1959); (b) *cf.* C. E. Castro and R. D. Stephens, *J. Org. Chem.*, **28**, 2163 (1963), for experimental details on other related compounds.

1-Chloromercurinaphthalene.—To the Grignard reagent of 1-bromonaphthalene (10 g.) prepared in the usual way in THF was added a solution of mercuric chloride (7 g.) in THF. Yellowish solid formed and the reaction was left to stir for 1 hr. The solid was filtered, dissolved in acetone, and reprecipitated by adding water. This was recrystallized from an acetone–water mixture to give a white crystalline solid of 1-chloromercurinaphthalene (9 g., 55.6% yield), m.p. 190–192 (lit.[21] m.p. 190–191).

1-Bromo-8-chloromercurinaphthalene.—An ethereal solution of 1-bromo-8-iodonaphthalene (2.3 g.) was added dropwise to a solution of *n*-butyllithium in hexane (4 ml., 15% soln.). The reaction was stirred for 5 hr. at room temperature. A solution of mercuric chloride (1.8 g.) in THF was then added and the solution stirred for another 0.5 hr. The reaction mixture was hydrolyzed and extracted with ether. The ether layer was separated, dried, decolorized, and evaporated to give a white solid. The solid was recrystallized from benzene to give white needles of 1-bromo-8-chloromercurinaphthalene (0.9 g., 30% yield), m.p. 219–220.

Anal. Calcd.: mol. wt., 442.1. Found: mol. wt., 447.

Acknowledgments.—The authors wish to thank Professor H. H. Jaffé and M. Orchin for their helpful comments and suggestions and to acknowledge support in the form of mission grant from the United Arab Republic Government, under which this work was pursued, and grants from the Petroleum Research Fund of the American Chemical Society (PRF 1086-A4) and the National Science Foundation (NSF-GP-1984).

---

[21] K. Torssell, *Acta. Chem. Scand.*, **13**, 115 (1959).

Organometallic Azides. I. Preparation and Reactions of Diarylphosphinic Azides[1a]

ROGER A. BALDWIN AND ROBERT M. WASHBURN

Whittier Research Laboratory, American Potash and Chemical Corporation, Whittier, California

Received April 28, 1965

A series of new diarylphosphinic azides, $Ar_2P(O)N_3$, having surprising thermal stability, has been prepared in high yield. Reaction of these phosphinic azides with tertiary phosphines provides a new series of compounds, the N-(diarylphosphinyl)iminophosphoranes, $Ar_2P(O)N{=}PR_3$, some of which have exceptional thermal and chemical stabilities. The synthesis of several bis tertiary phosphines is also described.

Prior to the initial communication[2] on the synthesis of diarylphosphinic azides and their reactions, only a few reports concerning group IV (noncarbon), V, and VI azides had been published. The arylsulfonyl azides,[3,4] triphenyllead azide,[5] and dimesitylboron azide[6] were reported to be relatively stable. Less stable were silicon tetraazide[7] and the trivalent phosphorus azides.[8,9] Since then a number of papers describing thermally stable organosilyl,[10] organotin,[11] organoarsenic,[12] and phosphonyl azides[13] has appeared.

Diarylphosphinic Azides.—As part of a program to study reactions leading to thermally stable materials, it was found that diarylphosphinic chlorides would react with sodium azide in pyridine or acetonitrile under anhydrous conditions to give high yields of the corresponding diarylphosphinic azides (I). Although pyridine solutions of the diarylphosphinic azides were readily hydrolyzed, pure samples of the azides were only slowly hydrolyzed in 0.5 *N* sodium hydroxide. This hydrolytic sensitivity is similar to that reported for the organosilyl azides[10a] but in contrast to that of the organotin,[11] lead,[5] and arylsulfonyl azides[3,4] which may be readily prepared *via* aqueous sodium azide. Although the phosphinic azides were initially prepared by refluxing the reactants in pyridine for 18–24 hr., further investigation has shown that these azides may be prepared in 75–100% yield by stirring the reactants at room temperature for 6–8 hr. In contrast to the recently reported isolation of a diphenylphosphinic azide–lithium chloride complex from acetonitrile,[14] no analogous complex with sodium chloride was observed in any of these preparations. Analytical samples were obtained by distillation at low pressures in a simple bulb-to-bulb apparatus. Larger quantities of diphenylphosphinic azide were distilled with some decomposition through a short Vigreux column or without decomposition through a molecular still apparatus to give a water-white product. In a similar manner, sodium azide reacted with diphenylthiophosphinic chloride to yield diphenylthiophosphinic azide (II), $(C_6H_5)_2P(S)N_3$. Attempts to purify crude yellow II by distillation at 10^{-4} mm. resulted in dark red products which gave erratic azide analytical values. Table I reports the pertinent data for the phosphinic azides prepared. None of these diarylphosphinic azides exhibited any shock sensitivity and burned only sluggishly when placed in a bunsen flame.

$$Ar_2P(O)Cl + NaN_3 \xrightarrow{\text{pyridine}} Ar_2P(O)N_3 + NaCl \qquad (1)$$

Ia, Ar = C_6H_5
b, Ar = p-$CH_3C_6H_4$
c, Ar = p-ClC_6H_4

---

[1] (a) Presented in part at the 1961 Pacific Southwest Regional Meeting of the American Chemical Society, San Diego, Calif., Dec. 1961. (b) This investigation was supported by the Materials Laboratory, Wright Air Development Command, Wright-Patterson Air Force Base, Ohio, under Contracts AF 33(616)-6913, -7810, and 33(657)-11129.

[2] R. A. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961).

[3] T. Curtius, *J. prakt. Chem.*, **125**, 303 (1930).

[4] J. Goerdler and H. Ullmann, *Ber.*, **94**, 1067 (1961).

[5] E. Lieber and F. M. Keane, *Chem. Ind.* (London), 747 (1961).

[6] J. E. Leffler and L. J. Todd, *ibid.*, 512 (1961).

[7] E. Wiberg and H. Michaud, *Z. Naturforsch.*, **9b**, 500 (1954).

[8] D. L. Herring, *Chem. Ind.* (London), 717 (1960).

[9] G. Tesi, C. P. Haber, and C. M. Douglas, *Proc. Chem. Soc.*, 219 (1960).

[10] (a) R. West and J. S. Thayer, *J. Am. Chem. Soc.*, **84**, 1763 (1962); J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 406 (1964); (b) N. Wieberg, F. Raschig, and R. Sustman, *Angew. Chem.*, **74**, 388, 716 (1962); (c) W. Sundermeyer, *ibid.*, **74**, 717, 875 (1962); (d) W. T. Reichle, *Inorg. Chem.*, **3**, 402 (1964).

[11] J. G. A. Luijten, M. J. Janssen, and G. J. M. van der Kerk, *Rec. trav. chim.*, **81**, 202 (1962).

[12] W. T. Reichle, *Tetrahedron Letters*, 51 (1962).

[13] F. L. Scott, R. Riordan, and P. D. Morton, *J. Org. Chem.*, **27**, 4255 (1962).

[14] K. L. Paciorek, *Inorg. Chem.*, **3**, 96 (1964).