Reactions of Two-Coordinate Phosphines with Acetylenes: Synthesis of New Allenic and Acetylenic Phosphines[1]

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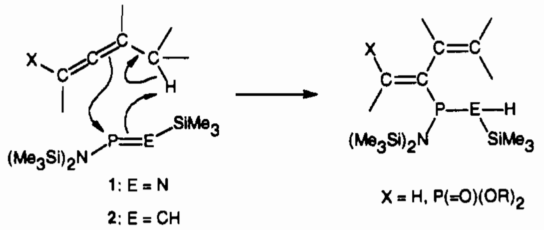
The two-coordinate phosphines $(Me_3Si)_2NP{=}ESiMe_3$ (**1**, E = N; **2**, E = CH) reacted smoothly with 2-butyne via an *ene* process (instead of the expected cycloaddition reaction) to give the novel allenic phosphines $H_2C{=}C{=}C(CH_3)P[E(H)SiMe_3]N(SiMe_3)_2$ (**3**, E = N; **4**, E = CH). Similarly, treatment of the iminophosphine **1** with 1-hexyne (in benzene solution at 80 °C) afforded the analogous allene derivative $CH_3CH_2CH_2CH{=}C{=}CHP[N(H)SiMe_3]N(SiMe_3)_2$ (**5**). Under different conditions (no solvent, 25 °C), however, the reaction of **1** with 1-hexyne occurred via a unique 1,2-addition of the terminal H–C bond to the P═N linkage, thus affording the acetylene isomer $CH_3CH_2CH_2CH_2C{\equiv}CP[N(H)SiMe_3]N(SiMe_3)_2$ (**6**). Other terminal acetylenes, $PhC{\equiv}CH$ and $Me_3SiC{\equiv}CH$, reacted with **1** via this 1,2-addition pathway to give the acetylenic phosphines $RC{\equiv}CP[N(H)SiMe_3]N(SiMe_3)_2$ (**7**, R = Ph; **8**, R = $SiMe_3$). These new allenic (**3–5**) and acetylenic (**6–8**) phosphines were obtained in good yields (50–82%) as thermally stable liquids and were fully characterized by NMR (^1H, ^{13}C, ^{31}P) spectroscopy and elemental analysis.

Introduction

In recent years, the chemistry of low-coordinate, multiply-bonded phosphorus compounds has been extensively studied.[3] The reactions of one- or two-coordinate phosphines (e.g., $P{\equiv}CR$, $RP{=}CR_2$, and $RP{=}NR$) often involve addition or cycloaddition of polar reagents to the heteroatomic multiple bond.[4] For example, some (1 + 2) and (2 + 4) cycloaddition reactions of diphenylacetylene and 2,3-dimethylbutadiene with the iminophosphine $^tBuP{=}NAr$ (Ar = 2,4,6-$^tBu_3C_6H_2$) have been reported.[5] In contrast, we recently found that dimethyl*allene* and several *allenic* phosphonates react with the 2-coordinate phosphines $(Me_3Si)_2NP{=}ESiMe_3$ (**1**, E = N; **2**, E = CH) via an unexpected "ene" process (eq 1), rather than cycloaddition, to afford a series of new 1-phospha- and 1,2-diphosphabutadienes.[6]



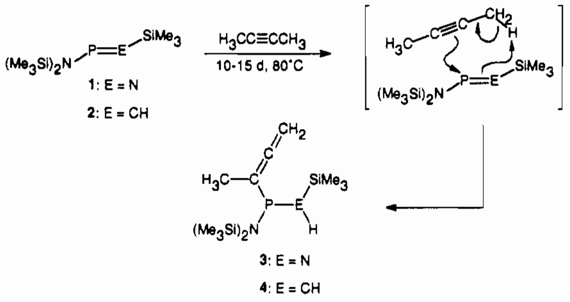
(1)

The present study represents an extension of our general survey of the reactivity of low-coordinate phosphorus compounds toward unsaturated organic substrates. Specifically, we report here the one-step synthesis of several novel allenic and acetylenic phosphines via the reactions of **1** and **2** with acetylenes including 2-butyne, 1-hexyne, phenylacetylene, and (trimethylsilyl)acetylene.

Results and Discussion

Synthesis. In view of the above results, the reactions of acetylenes with 2-coordinate phosphines could reasonably involve any of three possible routes: (a) a cycloaddition, probably a (2 + 2) process; (b) an *ene* reaction analogous to that with allenes (eq 1); (c) an unprecedented 1,2-addition of a terminal acetylenic H–C bond to the P═E moiety. This study, therefore, was mainly intended to determine which reaction pathway(s) would be operative for a variety of different acetylenes. In fact, all three modes of reactivity were observed depending on the nature of the acetylene reagent.

We first investigated the reaction of the simplest dialkylacetylene, 2-butyne, with the 2-coordinate phosphines (eq 2). Initially, we found that this reaction was extremely slow at room temperature. Due to the high volatility of 2-butyne, we then carried out the reactions in sealed glass ampules at 80 °C without a solvent. Under these conditions, the reactions were completed after 10–15 days and the novel allenic phosphines **3** and **4** were isolated in good yields as distillable liquids (Tables I and II). The overall simplicity of this reaction makes it a very useful method for the synthesis of here-to-fore unknown allene-substituted phosphines.[7]



(2)

Similarly, when the phosphinimine **1** was heated with 1-hexyne in benzene, the analogous allenic phosphine **5** (eq 3) was produced. Under milder conditions (25 °C, neat), however, the same reaction took a different and more surprising course (eq 4). In this case,

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(1) Presented in part at the 202nd National Meeting of the American Chemical Society, New York, NY, 1991. For a brief summary, see: Neilson, R. H.; Angelov, C. M. *ACS Symp. Ser.* **1992,** *No. 486,* 76.

(2) Permanent address: Department of Chemistry, University of Shoumen, 9700 Shoumen, Bulgaria.

(3) For some general reviews of the field of low-coordinate phosphorus compounds, see for example: (a) Niecke, E.; Gudat, D. *Angew. Chem., Intl. Ed. Engl.* **1991,** *30,* 217. (b) Appel, R.; Knoll, F. *Adv. Inorg. Chem.* **1989,** *33,* 259. (c) Regitz, M. *Chem. Rev.* **1990,** *90,* 191. (d) Cowley, A. H. *Polyhedron* **1984,** *3,* 389.

(4) Markovski, L. N.; Romanenko, V. D. *Tetrahedron* **1989,** *45,* 6019.

(5) Niecke, E.; Lysek, M. *Tetrahedron Lett.* **1988,** *29,* 605.

(6) Angelov, C. M.; Neilson, R. H. *Tetrahedron,* in press. For a general review of *ene* reactions, see: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969,** *8,* 556.

(7) Phosphorus(V) compounds containing allene functional groups are readily prepared by a variation of the Arbusov reaction. See, for example: Ignatiev, V. M.; Ionin, B. I.; Petrov, A. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1967,** *37,* 1807.

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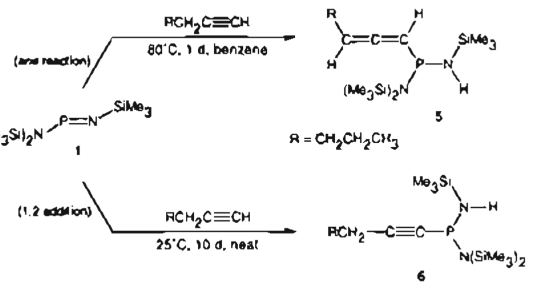
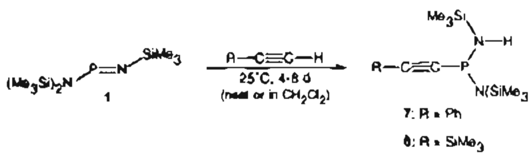


(3)

(4)

simple 1,2-addition of the terminal C–H bond of the acetylene to the polar P═N double bond occurred to give the acetylenic phosphine **6**. The isomeric compounds **5** and **6** were easily distinguished and structurally characterized by their NMR spectra (Table I) as discussed below.

In similar fashion, we obtained the new acetylenic phosphines **7** and **8** (eq 5) when this reaction was carried out with other



(5)

monosubstituted acetylenes, HC≡C—R (R = Ph, SiMe$_3$). The methylenephosphine **2**, however, did not react with acetylenes in this manner even when the mixtures were heated in benzene for several days. All of these 1,2-addition reactions afforded high yields of a single product. The reaction mechanism probably involves electrophilic addition of the relatively acidic C–H proton to the very polar P═N double bond.

NMR Spectra. All of the new allenic and acetylenic phosphines described here were structurally characterized by NMR spectroscopy (Table I). In addition to the expected peak multiplicities and relative intensities, the NMR spectra reveal a number of noteworthy features. First, the ^{13}C NMR spectra of the allene derivatives **3–5** contain the characteristic low-field signal (at ca. δ 205)[8] for the central carbon of the allene moiety. Second, all of the allene and the acetylene derivatives exhibit relatively small (ca. 30 Hz) one-bond P–C coupling constants, indicative of the 3-coordinate, P^{III} environment.[9] Third, the protons of the α-CH$_3$ group in allenes **3** and **4** appear as a doublet of triplets due to spin coupling with both phosphorus ($^3J_{PH} \approx 9$ Hz) and the two *equivalent* protons ($^5J_{HH} \approx 3$ Hz) of the terminal ═CH$_2$ moiety. Finally, the NMR spectra of compound **5** clearly show the presence of two diastereomers (of approximately equal intensity) resulting from chirality at both phosphorus and the unsymmetrical allene functionality.

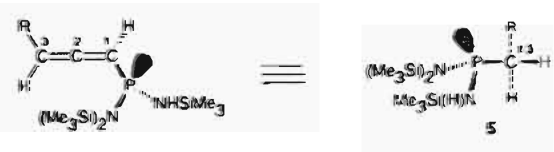
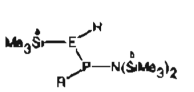
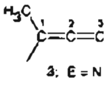
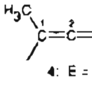
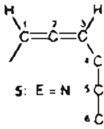
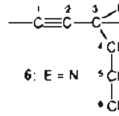
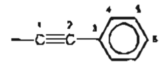
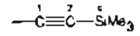


Table I. NMR Spectroscopic Data[a] for Allenic and Acetylenic Phosphines



E = N (3, 5-8); CH (4)

R	signal	^{1}H NMR^b		^{13}C NMR		^{31}P NMR
		δ	J_{PH} (Hz)	δ	J_{PC} (Hz)	δ
 3: E = N	^{a}Me$_3$Si	0.35	0.7	1.51	6.2	56.6
	^{b}Me$_3$Si	0.11	0.5	4.67	8.1	
	NH	2.07				
	H$_3$C	1.69	8.8 (3.3)	16.46	30.2	
	^{3}CH$_2$	4.47	5.2 (3.2)	73.50		
	^{2}C			205.21	8.7	
	^{1}C			102.15	26.8	
 4: E = CH	^{a}Me$_3$Si	−0.05	1.0	0.06	5.0	35.4
	^{b}Me$_3$Si	0.11	1.1	4.57	7.5	
	PCH$_2$	0.66^c	4.2 (13.8)	20.12	42.3	
		1.43^c	1.2 (13.8)			
	H$_3$C	1.77	8.9 (3.0)	17.56	31.4	
	^{3}CH$_2$	4.3–4.5^d		73.03		
	^{2}C			204.80	6.9	
	^{1}C			98.90	30.3	
 5: E = N	^{a}Me$_3$Si	0.03		1.44^e	5.5	52.3^e
				1.55	4.9	57.2
	^{b}Me$_3$Si	0.11^e	1.2	4.55	5.1	
		0.12	1.3	4.66	5.2	
	NH	2.07				
	^{1}CH	5.2–5.4^d		97.22	28.7	
				98.13	27.8	
	^{2}C			204.07	5.5	
				204.51	8.6	
	^{3}CH	4.9–5.0^d		90.51		
				90.66		
	^{4}CH$_2$	1.8–2.0^d		30.63		
				30.67		
	^{5}CH$_2$	1.2–1.4^d		23.04		
				23.62		
	^{6}CH$_3$	0.83	(7.4)	13.98		
		0.85	(7.4)			
 6: E = N	^{a}Me$_3$Si	0.04		1.51	6.4	49.0
	^{b}Me$_3$Si	0.17	1.2	4.22	8.2	
	NH	2.49				
	^{1}C			86.71	25.1	
	^{2}C			104.97	5.4	
	^{3}CH$_2$	2.20	(7.0)	22.21		
	^{4}CH$_2$	1.2–1.4^d		30.74		
	^{5}CH$_2$	1.2–1.4^d		19.95		
	^{6}CH$_3$	0.81	(7.2)	13.78		
 7: E = N	^{a}Me$_3$Si	0.12		1.54	6.5	40.3
	^{b}Me$_3$Si	0.25	1.2	4.26	8.2	
	NH	2.66				
	^{1}C			96.17	31.8	
	^{2}C			102.83	5.5	
	^{3}C			123.63		
	$^{4-6}$CH	7.2–7.4^d		128.49, 131.44, 131.47		
 8: E = N	^{a}Me$_3$Si	0.04	0.9	1.51	6.1	39.6
	^{b}Me$_3$Si	0.17	1.1	4.21	7.9	
	^{c}Me$_3$Si	0.07		−0.05		
	NH	2.53				
	^{1}C			114.21	36.0	
	^{2}C			110.13		

[a] Proton and ^{13}C chemical shifts downfield from Me$_4$Si; ^{31}P shifts downfield from H$_3$PO$_4$; CDCl$_3$ solvent. [b] J_{HH} values in parentheses. [c] Diastereotopic protons in PCH$_2$ group. [d] Complex multiplet. [e] Distinct signals observed for two diastereomers.

Conclusion. The work described here, especially when combined with other recent results,[6] demonstrates that the reactions of 2-coordinate phosphines with unsaturated organic reagents such as allenes (eq 1)[6] and acetylenes (eqs 3–5) leads to the facile synthesis of a variety of previously inaccessible organophosphorus compounds. Details of the related reactions of these 2-coordinate phosphines with acetylenic alcohols, propargyl halides, and diketones as well as some reactivity studies of the new compounds reported here will be presented in forthcoming papers.

Experimental Section

Materials and General Procedures. The acetylene reagents (2-butyne, 1-hexyne, phenylacetylene, (trimethylsilyl)acetylene) were obtained from commercial sources and used without further purification. The 2-coordinate phosphines, (Me$_3$Si)$_2$NP═ESiMe$_3$ (**1**, E = N; **2**, E = CH), were prepared according to published procedures.[10,11] Benzene and CH$_2$Cl$_2$ were distilled from CaH$_2$ and stored over molecular sieves prior to use. Proton and ^{13}C NMR spectra were recorded on a Varian XL-300

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[8] Silverstien, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Characterization of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 289.

[9] Quin, L. D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Deerfield Beach, FL, 1987; Chapter 12.

Table II. Preparative and Analytical Data

compd	yield (%)	bp (°C)/(mm Hg)	anal.[a]	
			% C	% H
3	50	58–59/0.03	46.98 (46.94)	10.23 (10.00)
4	76	64–65/0.02	50.85 (50.70)	10.44 (10.33)
5	55	66–67/0.01	49.74 (49.95)	9.82 (10.34)
6	74	84–85/0.05	49.78 (49.95)	10.07 (10.34)
7	82	99–100/0.01	53.45 (53.64)	8.60 (8.74)
8	71	64–65/0.01	44.40 (44.63)	9.63 (9.90)

[a] Calculated values in parentheses.

spectrometer. A JEOL FX-60 instrument was used for ^{31}P NMR spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are typical of those used for the preparation of the new compounds in this study.

Preparation of Allenic Phosphines 3 and 4. A heavy-walled, nitrogen-filled glass ampule was charged with the iminophosphine **1** (5.6 g, 20 mmol) and an excess of 2-butyne (30 mmol). The contents of the ampule were degassed by the freeze–pump–thaw technique, and the ampule was sealed under vacuum. The ampule was heated in an oil bath at 75–80 °C for 10 days. After cooling, the ampule was opened under nitrogen and the contents were transferred to a small round-bottomed flask. Fractional distillation gave **3** as a colorless liquid (Tables I and II). Compound **4** was prepared from **2** and 2-butyne in the same manner except that the mixture was heated for 15 days to ensure complete reaction.

Preparation of Allenic Phosphine 5. The iminophosphine **1** (4.2 g, 15 mmol) was added via syringe to a stirred solution of 1-hexyne (2 mL, 16 mmol) in benzene (ca. 10 mL) at room temperature. The mixture was then refluxed for 24 h. Following solvent removal, distillation afforded **5** as a colorless liquid (Tables I and II). The distillate contained a small amount (ca. 5–10%) of the isomeric acetylene **6**.

Preparation of Acetylenic Phosphines 6–8. The iminophosphine **1** (4.2 g, 15 mmol) was added via syringe to 1-hexyne (2 mL, 16 mmol) without a solvent. The mixture was stirred at room temperature for 10 days. Fractional distillation gave **6** as a colorless liquid (Tables I and II). Compounds **7** and **8** were prepared by the same procedure except that CH_2Cl_2 (ca. 1 M) was used as a solvent in the synthesis of **7** and the mixture was stirred for 4 days at room temperature.

Acknowledgment. We thank the Robert A. Welch Foundation and the Texas Christian University Research Fund for financial support of this research.

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(10) Niecke, E.; Flick, W. *Angew Chem., Intl. Ed. Engl.* **1973**, *12*, 585.

(11) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1969.