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Reactions of Two-Coordinate Phosphines with Allenes[1]

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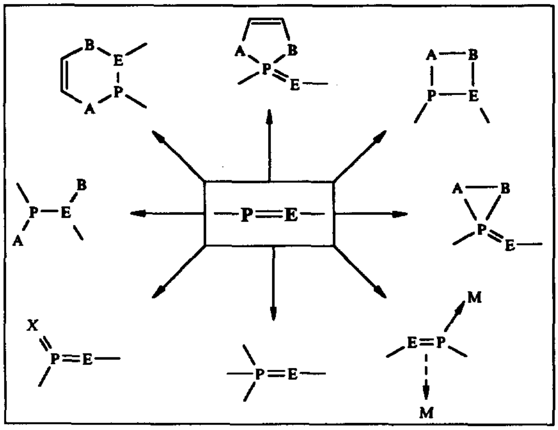
Abstract: The two-coordinate phosphines, $(Me_3Si)_2NP{=}ESiMe_3$ (E = N, CH) react smoothly with 1,1-dimethylallene, or with allenic phosphonates, via an *ene* process to afford novel 2-phospha- or 1,2-diphosphabutadienes.

Introduction

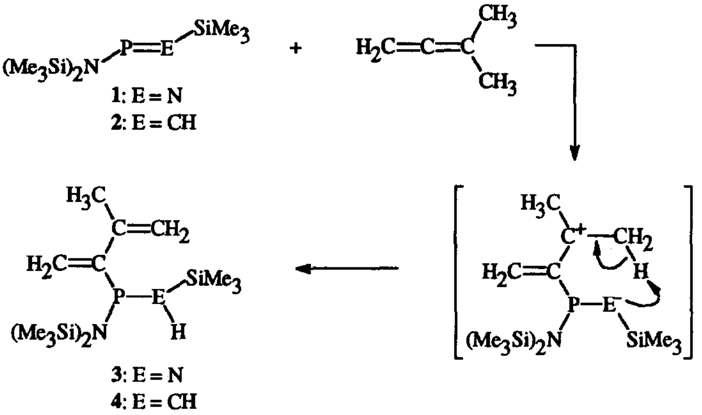
The extensive development of phosphorus chemistry is largely due to the great variety of different valence states and coordination numbers that the element phosphorus exhibits. Until recently, the chemistry of phosphorus compounds included mainly the well known P^{III} and P^{V} valence states with their common coordination numbers of three, four, and five. In the past two decades, however, many different examples of (p-p)π-bonded, one- and two-coordinate, trivalent phosphorus compounds have been synthesized and isolated as thermally stable, but highly reactive, products.[2] In particular, the two-coordinate derivatives (-P=E-) have been found to undergo a variety of interesting and synthetically useful transformations, including 1,2-addition, cycloaddition, oxidation, and metal-coordination reactions. Nevertheless, the full synthetic potential of these new reagents has not yet been realized.



Within this context, part of our research program in organophosphorus chemistry deals with the study of new chemical reactions of two such low-coordinate phosphines: the iminophosphine[3], $(Me_3Si)_2NP{=}NSiMe_3$ (**1**) and the analogous, isoelectronic methylenephosphine,[4] $(Me_3Si)_2NP{=}CHSiMe_3$ (**2**). The heteroatomic (p-p)π bond in these two-coordinate phosphines is highly polar in nature with a partial positive charge on phosphorus, thus making it an electrophilic center. The sp^2 hybridized phosphorus atom also carries a lone pair of electrons and, accordingly, might be expected to exhibit nucleophilic character as well. While the nucleophilic nature of the two-coordinate phosphorus is important in some metal complexation reactions, it is of secondary importance in most additions and cycloadditions involving organic reagents. We report here some new results related to the *electrophilic* properties of the two-coordinate, trivalent phosphorus atoms in **1** and **2**. In particular, the novel reactions of these compounds with 1,1-dimethylallene and some allenic phosphonates[5] are described in this paper.

Results and Discussion

A recent aspect of our ongoing study of the reactivity of two-coordinate phosphines involved the interaction of these P=E derivatives with allenes. This work provided some very interesting, unexpected results that may well be of use in synthetic organophosphorus chemistry. For example, in attempting to study the (2+2)-cycloadditions of the P=E bonds in the iminophosphine **1** and the methylenephosphine **2** with the C=C bonds in 1,1-dimethylallene, we established that the reaction takes a much different and more interesting course -- that of an "ene" process (eq 1). Apparently, the electrophilic phosphorus center initially attacks the nucleophilic central carbon of the allene system. Instead of then undergoing nucleophilic attack on the incipient carbonium ion, the anionic center (E^-) abstracts a proton from the terminal C-H bond, leading to the formation of a new double bond in the phosphorus-substituted 1,3-butadiene derivatives **3** and **4**. This process, therefore, represents a novel and efficient synthetic route to phosphorus-substituted dienes.

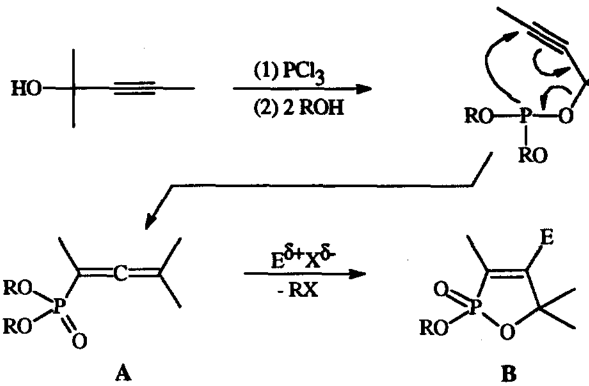


(1)

Compounds **3** and **4** were obtained in 82 and 55% yields, respectively, as colorless, thermally stable, distillable liquids that were fully characterized by NMR spectroscopy (^1H, ^{13}C, and ^{31}P) and elemental analysis. The ^1H and ^{13}C NMR spectral data (Table 1) provide strong evidence for the phosphadiene structure. Four distinct signals in the ^{13}C NMR spectra, each a doublet due to P-C coupling, are observed for the vinylic carbons. The ^1H NMR spectra contain signals for two sets of vinylic $=CH_2$ groups, one of which exhibits coupling to phosphorus. Other expected resonances due to the allylic CH_3 group, the two types of $SiMe_3$ groups, as well as the N-H proton in **3** and the P-CH_2-Si moiety in **4** are also clearly seen.

Interestingly, the relative rates of these reactions illustrate the considerable difference in polarity and, hence, reactivity between the P=N and P=C bonds. While the reaction with the P=N compound **1** was complete at room temperature in ca. 24 hours, the methylenephosphine **2** required ca. 40 days to completely react with the allene. In both cases, the reactions were highly chemoselective as indicated by NMR analysis of the crude reaction mixtures which showed that only a single product was produced in each case.

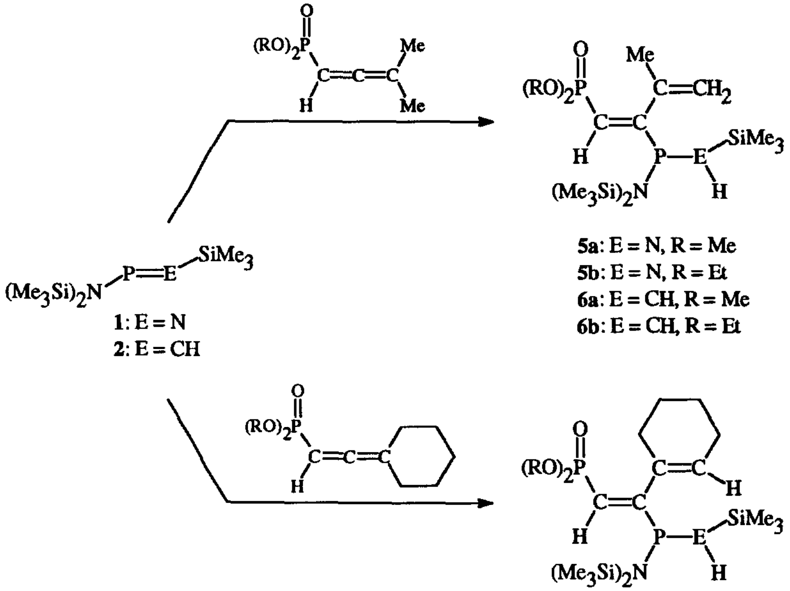
In order to assess the generality of this process, the reactivity of **1** and **2** toward some phosphorus-substituted allenes was also investigated. Specifically, a series of allenic phosphonates (**A**) were selected for this aspect of the study for two reasons. First, they are readily prepared from acetylenic alcohols by a known variation of the Arbusov rearrangement that involves an acetylene-allene transformation[5] (eq 2). Second, they readily undergo cyclization reactions with simple electrophiles (EX) to afford various phosphorus heterocycles (e.g., **B**).[6]



A **B**

(2)

Upon treatment with the two-coordinate phosphines **1** and **2**, these allenic phosphonates (**A**) underwent the same type of "ene" reaction as we observed for 1,1-dimethylallene. This process was found to be quite general and afforded a series of novel 1,2-diphosphabutadienes (**5** - **7**) that contain *two phosphorus substituents in different oxidation states*. Products derived from both acyclic (eq 3) and cyclic (eq 4) precursors were obtained with equal facility. Generally, these reactions required somewhat harsher conditions than in the case of 1,1-dimethylallene. It was necessary to reflux the reaction mixtures in benzene (4 - 6 hr) for the iminophosphine **1** and in toluene (6 - 8 hr) for the methylenephosphine **2**.



(3)

5a: E = N, R = Me
5b: E = N, R = Et
6a: E = CH, R = Me
6b: E = CH, R = Et

1: E = N
2: E = CH

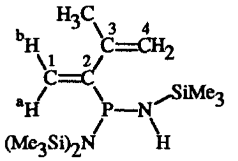
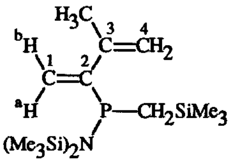
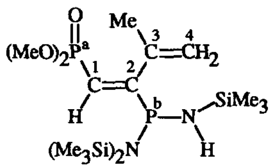
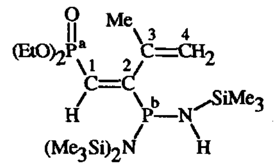
(4)

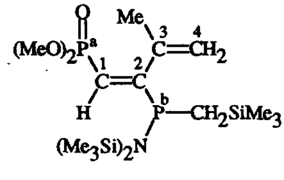
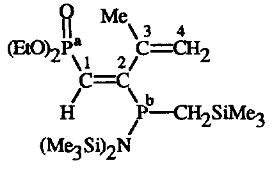
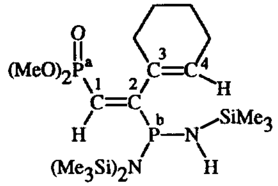
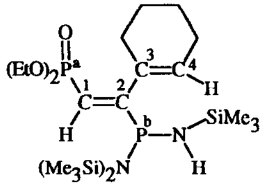
7a: E = N, R = Me
7b: E = N, R = Et

The 1,2-diphosphabutadienes **5** - **7** were obtained in yields of 45 - 76% as high-boiling, but distillable, liquids. Their structures were completely confirmed by NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopy. Some of the more informative features of the NMR spectral data include: (1) two doublets, at ca. 50 - 68 ppm (P^{III}) and ca. 15 - 20 ppm (P^V) with $^3J_{PP}$ values of 8 - 14 Hz, in the ^{31}P NMR spectra; (2) distinct signals for each of the four different vinylic carbons with coupling to one or both phosphorus centers; (3) doublet of doublets for the HC= (i.e., C^1) moiety in both the ^{1}H and the ^{13}C NMR spectra due to coupling with both phosphorus centers; and (4) a one-bond P-C coupling of C-1 to the P^V center (ca. 185 Hz) that is characteristically[7] much larger than that of C-2 to the P^{III} center (ca. 30 - 50 Hz).

In summary, the reactions of two-coordinate phosphines with dimethylallene and with allenic phosphonates occur cleanly via an "ene" process, thus providing an efficient, one-step synthesis of new 2-phospha- and 1,2-diphosphabutadienes. Related studies of the interaction of the two-coordinate phosphines with other unsaturated organic reagents as well as possible addition polymerization reactions of the phosphabutadienes are ongoing in our laboratory.

NMR Spectroscopic Data (CDCl$_3$ solution)

 3 δP 64.9	^{1}H δ 0.06 (Me$_3$SiN); 0.12 [*d*, (Me$_3$Si)$_2$N, J_{PH} = 0.7]; 1.82 (CH$_3$); 1.93 (*d*, NH, J_{PH} = 4.0); 4.76, 4.89 (=CH$_2$); 5.18 (*dd*, ^{a}H, J_{PH} = 5.2, J_{HH} = 2.4); 5.38 (*dd*, ^{b}H, J_{PH} = 13.6, J_{HH} = 2.3) ^{13}C δ 1.44 (*d*, Me$_3$SiN, J_{PC} = 5.5); 4.87 [*d*, (Me$_3$Si)$_2$N, J_{PC} = 7.3]; 23.50 (*d*, CH$_3$, J_{PC} = 4.4); 117.96 (*d*, ^{1}C, J_{PC} = 14.3); 160.65 (*d*, ^{2}C, J_{PC} = 28.7); 146.07 (*d*, ^{3}C, J_{PC} = 17.6); 112.75 (*d*, ^{4}C, J_{PC} = 7.7)
 4 δP 42.3	^{1}H δ 0.01 (*d*, Me$_3$SiN, J_{PH} = 0.8); 0.13 [*d*, (Me$_3$Si)$_2$N, J_{PH} = 1.0]; 0.92 (*dd*, PCH$_2$, J_{HH} = 14.4, J_{PH} = 2.5); 1.23 (*d*, PCH$_2$, J_{HH} = 14.4); 1.84 (CH$_3$); 4.84, 4.97 (=CH$_2$); 5.00 (*dd*, ^{a}H, J_{PH} = 4.0, J_{HH} = 1.5); 5.36 (*dd*, ^{b}H, J_{PH} = 11.5, J_{HH} = 1.6) ^{13}C δ 0.25 (*d*, Me$_3$SiN, J_{PC} = 5.5); 5.00 [*d*, (Me$_3$Si)$_2$N, J_{PC} = 7.3]; 18.90 (*d*, PCH$_2$, J_{PC} = 45.8); 23.90 (*d*, CH$_3$, J_{PC} = 4.4); 116.33 (*d*, ^{1}C, J_{PC} = 10.5); 158.22 (*d*, ^{2}C, J_{PC} = 36.1); 145.40 (*d*, ^{3}C, J_{PC} = 20.1); 113.49 (*d*, ^{4}C, J_{PC} = 11.9)
 5a δP^a 18.8 δP^b 67.1 J_{PP} = 12.7 Hz	^{1}H δ -0.04 (Me$_3$SiN); 0.04 [(Me$_3$Si)$_2$N]; 1.76 (*d*, CH$_3$, J_{PH} = 0.8 Hz); 1.90 (*d*, NH, J_{PH} = 6.5); 3.51 (*dd*, MeO, J_{PH} = 11.1, 2.0); 4.61, 4.79 (=CH$_2$); 5.61 (*dd*, ^{1}CH, J_{PH} = 22.2, 5.0) ^{13}C δ 1.07 (*d*, Me$_3$SiN, J_{PC} = 5.5); 3.55 [*d*, (Me$_3$Si)$_2$N, J_{PC} = 6.6]; 23.97 (*d*, CH$_3$, J_{PC} = 4.4); 52.11 (*dd*, MeO, J_{PC} = 28.5, 6.0); 116.07 (*dd*, ^{1}C, J_{PC} = 185.5, 18.3); 177.56 (*d*, ^{2}C, J_{PC} = 41.0); 144.13 (*dd*, ^{3}C, J_{PC} = 15.4, 10.0); 112.76 (*d*, ^{4}C, J_{PC} = 5.0)
 5b δP^a 15.7 δP^b 66.9 J_{PP} = 11.7 Hz	^{1}H δ 0.00 (Me$_3$SiN); 0.08 [(Me$_3$Si)$_2$N]; 1.2 (*m*, *Me*C); 1.80 (*d*, CH$_3$, J_{PH} = 0.8 Hz); 1.94 (*d*, NH, J_{PH} = 6.5); 3.9 (*m*, CH$_2$O); 4.65, 4.82 (=CH$_2$); 5.66 (*dd*, ^{1}CH, J_{PH} = 21.7, 5.2) ^{13}C δ 0.92 (*d*, Me$_3$SiN, J_{PC} = 5.5); 3.41 [(Me$_3$Si)$_2$N]; 16.30 (*d*, *Me*C, J_{PC} = 4.1); 23.95 (*d*, CH$_3$, J_{PC} = 4.4); 61.06 (*dd*, CH$_2$O, J_{PC} = 19.5, 6.0); 117.27 (*dd*, ^{1}C, J_{PC} = 185.0, 18.0); 176.04 (*d*, ^{2}C, J_{PC} = 40.7); 143.86 (*dd*, ^{3}C, J_{PC} = 15.9, 9.8); 112.59 (*d*, ^{4}C, J_{PC} = 5.5)

 **6a** δ P^a 18.5 δ P^b 50.0 J_{PP} = 8.8 Hz	^1H δ 0.03 (*d*, Me_3SiN, J_{PH} = 0.8); 0.11 [*d*, $(Me_3Si)_2N$, J_{PH} = 1.0]; 0.9 - 1.1 (*m*, PCH_2); 1.76 (CH_3); 3.4 - 3.5 (*m*, MeO); 4.59, 4.78 (=CH_2); 5.45 (*dd*, ^1CH, J_{PH} = 20.5, 4.4) ^{13}C δ -0.22 (*d*, Me_3SiN, J_{PC} = 5.6); 5.70 [$(Me_3Si)_2N$]; 16.34 (*d*, PCH_2, J_{PC} = 48.5); 24.31 (*d*, CH_3, J_{PC} = 4.2); 52.92 (*dd*, MeO, J_{PC} = 19.2, 6.0); 113.45 (*dd*, ^1C, J_{PC} = 187.1, 16.0); 177.42 (*d*, ^2C, J_{PC} = 50.5); 143.16 (*dd*, ^3C, J_{PC} = 17.3, 10.2); 113.50 (*dd*, ^4C, J_{PC} = 7.6, 2.2)
 **6b** δ P^a 15.5 δ P^b 49.8 J_{PP} = 9.8 Hz	^1H δ -0.09 (Me_3SiN); 0.03 [$(Me_3Si)_2N$]; 0.9 (*m*, PCH_2); 1.1 (*m*, *Me*C); 1.79 (CH_3); 3.8 (*m*, CH_2O); 4.61, 4.80 (=CH_2); 5.49 (*dd*, ^1CH, J_{PH} = 19.8, 4.7) ^{13}C δ -0.15 (*d*, Me_3SiN, J_{PC} = 5.5); 5.76 [$(Me_3Si)_2N$]; 16.40 (*dd*, *Me*C, J_{PC} = 6.5, 3.0); 16.44 (*d*, PCH_2, J_{PC} = 49.1); 24.31 (*d*, CH_3, J_{PC} = 4.2); 61.20 (*dd*, CH_2O, J_{PC} = 16.8, 5.8); 114.92 (*dd*, ^1C, J_{PC} = 186.7, 15.7); 176.08 (*d*, ^2C, J_{PC} = 49.6); 143.12 (*dd*, ^3C, J_{PC} = 17.5, 9.9); 113.53 (*d*, ^4C, J_{PC} = 7.5)
 **7a** δ P^a 19.7 δ P^b 67.4 J_{PP} = 12.7 Hz	^1H δ -0.13 (Me_3SiN); -0.05 [$(Me_3Si)_2N$]; 1.37, 1.85 [*m*, $(CH_2)_4$]; 1.97 (*d*, NH, J_{PH} = 1.2); 3.38 (*dd*, MeO, J_{PH} = 11.1, 2.8); 5.3 (*br, m* ^4CH); 5.52 (*dd*, ^1CH, J_{PH} = 22.7, 5.0) ^{13}C δ 1.00 (*br*, Me_3SiN); 3.55 [*br*, $(Me_3Si)_2N$]; 21.70, 22.46, 25.09, 29.50 [$(CH_2)_4$]; 51.70 (*dd*, MeO, J_{PC} = 22.3, 6.0); 115.72 (*dd*, ^1C, J_{PC} = 185.5, 18.8); 177.33 (*d*, ^2C, J_{PC} = 39.4); 136.90 (*dd*, ^3C, J_{PC} = 15.2, 9.9); 123.75 (^4C)
 **7b** δ P^a 16.4 δ P^b 67.2 J_{PP} = 13.6 Hz	^1H δ -0.08 (Me_3SiN); 0.00 [$(Me_3Si)_2N$]; 1.1 (*m*, *Me*C); 1.4, 1.8 [*m*, $(CH_2)_4$]; 2.01 (*d*, NH, J_{PH} = 1.4); 3.8 (*m*, CH_2O); 5.3 (*br, m* ^4CH); 5.59 (*dd*, ^1CH, J_{PH} = 22.3, 5.4) ^{13}C δ 1.16 (*d*, Me_3SiN, J_{PC} = 5.6); 3.51 [*br*, $(Me_3Si)_2N$]; 16.46 (*d*, *Me*C, J_{PC} = 6.6); 21.83, 22.59, 25.19, 29.60 [$(CH_2)_4$]; 61.08 (*dd*, CH_2O, J_{PC} = 18.5, 6.0); 117.21 (*dd*, ^1C, J_{PC} = 184.7, 18.7); 176.30 (*d*, ^2C, J_{PC} = 38.9); 136.92 (*dd*, ^3C, J_{PC} = 15.2, 9.8); 123.80 (*d*, ^4C, J_{PC} = 3.2)

Experimental

Materials and General Procedures. 1,1-Dimethylallene was obtained commercially and used without further purification. Benzene, toluene, and CH_2Cl_2 were distilled from CaH_2 prior to use. The two-coordinate phosphines, $(Me_3Si)_2N$-P=E-$SiMe_3$ (**1**: E = N;[3] **2**: E = CH[4]), and the allenic phosphonates[5] were prepared according to published procedures. Proton and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer and ^{31}P NMR spectra were obtained on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. 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.

Reactions of 1 and 2 with 1,1-dimethylallene. The iminophosphine **1** (5.7 g, 20 mmol) was added via syringe to a stirred solution of 1,1-dimethylallene (2.5 mL, 25 mmol) in CH_2Cl_2 (ca. 10 mL) at room temperature. The mixture was stirred for 24 hours. NMR spectroscopy indicated that the reaction was complete at this point. Solvent removal and fractional distillation afforded the 1-phosphabutadiene **3** as a colorless liquid. The same procedure was used to prepare **4** from the methylenephosphine except that a much longer time (ca. 40 days) was required for complete reaction. **3**: 82% yield; bp 58-59 (0.02 mm). *Anal.* Calcd: C 48.36; H 10.44. Found: C 48.50; H 10.18. **4**: 55% yield; bp 63-64 (0.02 mm). *Anal.* Calcd: C 52.12; H 10.50. Found: C 52.48; H 10.62.

Reactions of 1 and 2 with allenic phosphonates. The iminophosphine **1** (30 mmol) was added via syringe to a stirred solution of the phosphonate $(MeO)_2P(O)$-CH=C=CMe$_2$ (30 mmol) in benzene (ca. 15 mL) at room temperature. The mixture was refluxed for 4-6 hours. NMR spectroscopy indicated that the reaction was complete at this point. Solvent removal and fractional distillation afforded the 1,2-diphosphabutadiene **5a** as a colorless liquid. The same procedure was used to prepare compounds **5b**, **6a-b**, and **7a-b** except that toluene (reflux) was used in the synthesis of the methylenephosphine derivatives **6a-b**. In each case, NMR spectroscopy was used to monitor the progress of the reaction which generally required 4 - 8 hours for complete conversion. **5a**: 61% yield; bp 115-116 (0.01 mm). *Anal.* Calcd: C 42.26; H 8.87. Found: C 42.02; H 8.98. **5b**: 51% yield; bp 114-115 (0.01 mm). *Anal.* Calcd: C 44.78; H 9.19. Found: C 44.60; H 9.12. **6a**: 45% yield; bp 116-117 (0.01 mm). *Anal.* Calcd: C 45.00; H 9.11. Found: C 44.70; H 9.05. **6b**: 50% yield; bp 111-112 (0.01 mm). *Anal.* Calcd: C 47.37; H 9.47. Found: C 47.20; H 9.53. **7a**: 62% yield; bp 130-131 (0.01 mm). *Anal.* Calcd: C 46.12; H 8.96. Found: C 46.07; H 9.16. **7b**: 76% yield; bp 134-135 (0.01 mm). *Anal.* Calcd: C 48.24; H 9.24. Found: C 48.01; H 9.35.

Acknowledgment

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