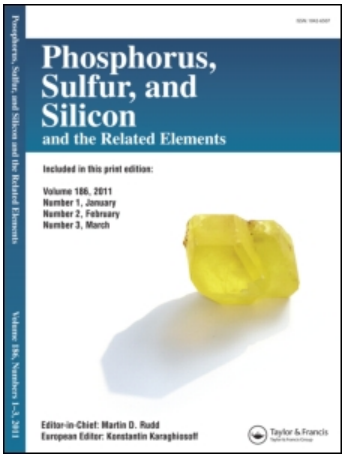

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SYNTHESIS OF THE 8-PHOSPHABICYCLO[3.2.1]OCTA-2,6-DIENE RING SYSTEM

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SYNTHESIS OF THE 8-PHOSPHABICYCLO[3.2.1]OCTA-2,6-DIENE RING SYSTEM

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The 8-phosphabicyclo[3.2.1]octa-2,6-diene ring system is conveniently synthesized by the addition of chloro(diisopropylamino)phosphenium ion ((Cl)(*i*-Pr_2N)P^+, **1**) to cycloheptatriene. Hydrolysis of the primary adduct yields the corresponding phosphinamide (**3**). The NMR of **3** is discussed in terms of its structure, and the orientation at P is assigned by a combination of 2-D NMR techniques. The structure of **3** is also probed by model calculations at the MNDO level.

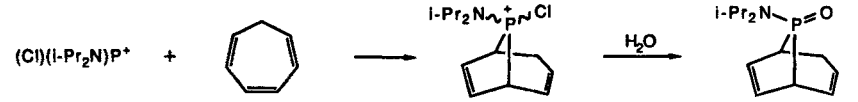
Key Words: Phosphinamide; 2D-NMR; cycloaddition; MNDO calculation; 7-phosphanorbornene; 8-phosphabicyclo[3.2.1]octa-2,6-diene; phosphenium ions.

INTRODUCTION

The chemistry of the 7-phosphanorbornene skeleton has been reported in great detail.[1] These compounds are usually synthesized by the dimerization of phosphole derivatives and often display unusual chemical and physical properties. In comparison, relatively little is known about the 7-phosphanorbornadiene system. Stille has synthesized a phosphine oxide derivative which has served as a source of phenylphosphinidene oxide,[2] and Mathey has prepared a series of transition-metal complexes.[3] On the basis of the exceptional ^{31}P deshielding in the transition-metal complexes, 7-phosphanorbornadienes are predicted to exhibit ^{31}P chemical shifts far downfield of normal phosphines.[3]

We expect the 8-phosphabicyclo[3.2.1]octa-2,6-diene skeleton to represent an interesting intermediate case. The five-membered ring portion of the molecule should possess essentially the same geometry as those for the norbornene and norbornadiene derivatives, and the angle strain at P is also expected to be similar. In addition, the 2,3-double bond should have at least some interaction with P. Although there have been a few reports on the synthesis and chemistry of the 8-phosphabicyclo[3.2.1]octane and -oct-6-ene skeletons,[1g,4] none of these synthetic approaches seemed well suited for the synthesis of the 2,6-diene system. In the past, we and others have noted the facile synthesis of phosphorus-containing heterocycles by the addition of phosphenium ions (R_2P^+)[5] to unsaturated organic compounds.[6] We now report the addition of chloro(diisopropylamino)phosphenium ion ((Cl)(*i*-Pr_2N)P^+, **1**) to cycloheptatriene (CHT) to yield 8-chloro-8-diisopropylamino-8-phosphoniabicyclo[3.2.1]octa-2,6-diene tetrachloro-aluminate (**2**), which on hydrolysis yields 8-diisopropylamino-8-phosphabicyclo[3.2.1]octa-2,6-diene oxide (**3**). The NMR spectra and the configuration at P for **3** are

assigned by a combination of 2-D NMR techniques, and the geometry of **3** is discussed in terms of model calculations at the MNDO level.[7,8]



1 2 3

RESULTS AND DISCUSSION

Dropwise addition of CHT to a solution of **1** in CH_2Cl_2 yields a crude reaction mixture which when examined by ^{31}P NMR spectroscopy exhibits a major absorption (about 60% by ^{31}P NMR intensities) at 80.7 ppm. This peak is in the range commonly observed for the oxidative addition products of aminophosphenium ions with unsaturated hydrocarbons, and we assign it to **2**. The ^{31}P NMR spectrum of the $CHCl_3$ extract of the hydrolyzed reaction mixture shows one major signal (~95%) at 63.6 ppm, which we assign to **3**. Pure **3** is obtained in 35% yield by vacuum sublimation. The fact that the isolated percent yield of **3** is greater than the percentage of any of the other peaks in the initial reaction mixture supports our assignment of **2**. For comparison, we also examined the reaction of bis(diethylamino)phosphenium ion, $(Et_2N)_2P^+$, with CHT. In contrast to the addition of **1**, which is fairly clean and is complete within two hours, the addition of $(Et_2N)_2P^+$ yields a complicated mixture and proceeds much more slowly (~70% of $(Et_2N)_2P^+$ remains after stirring for four days). That the reaction of **1** is faster than that of $(Et_2N)_2P^+$ is in accord with our previous observation that substitution of a chlorine atom for a dialkylamino group in R_2P^+ results in increased reactivity.

The ^1H and $^{13}C\{^1H\}$ NMR data for **3** are given in Table I, and the olefinic region of the projection of the ^1H J-resolved[9] spectrum is shown in Figure 1.

TABLE I

^1H and ^{13}C NMR data for compound **3** (δ in ppm, J in Hz)

Assignment	^1H (J_{PH})	^{13}C (J_{PC})
i-Pr-CH_3	1.24 (<2)	22.9 (<2)
	1.23 (<2)	23.0 (<2)
i-Pr-CH	3.37 (14.7)	48.1 (<2)
1	2.73 (14.1)	37.3 (74.4)
2	6.00 (14.1)	128.3 (3.8)
3	5.52 (5.9)	127.7 (13.9)
4	2.86 (4.7)	28.8 (<2)
4′	2.34 (22.9)	
5	2.50 (14.1)	36.7 (75.8)
6	6.08 (21.1)	129.1 (12.5)
7	6.58 (18.8)	138.9 (11.3)

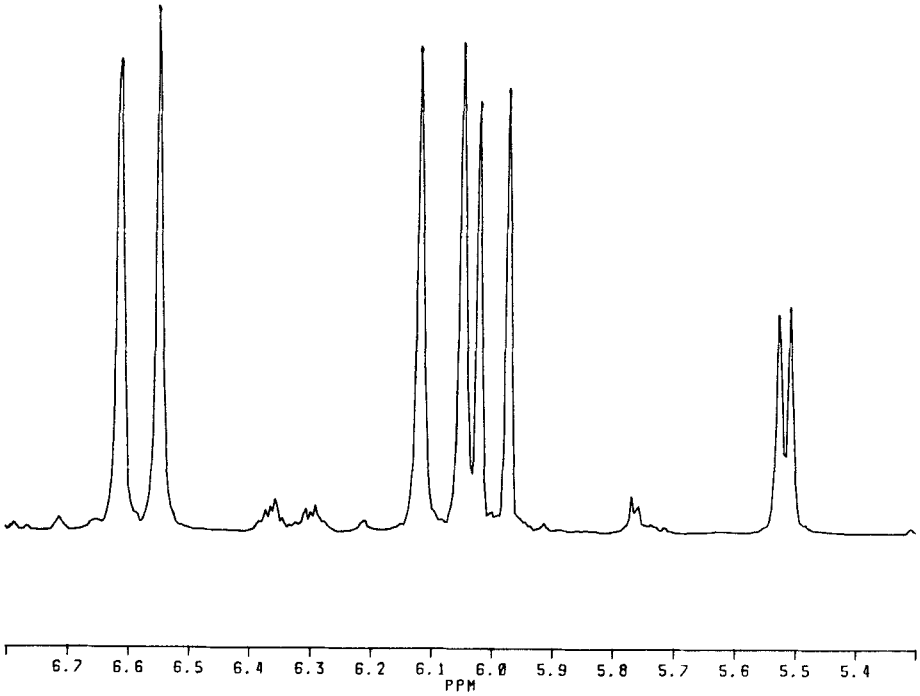


FIGURE 1 The olefinic region of the projection of the ^1H J-resolved 2-D NMR spectrum of **3**.

Based on its reduced J_{PH} value, we assign the resonance at 5.52δ to that of H_3. Examination of the ^1H shift correlated 2-D NMR (COSY)[10] spectrum (Figure 2) indicates coupling between the resonances at 5.52δ and 6.00δ and again at 6.08δ and 6.58δ. Thus, we make the following assignments: H_2, 6.00δ; H_6, 6.08δ; and H_7, 6.58δ. Distinction between H_6 and H_7 is possible by observing that H_2 and H_7 are coupled to the same upfield resonance (H_1, 2.73δ). Similarly, we are able to assign the 2.50δ absorption to H_5. The peak at 2.86δ is assigned to H_4 based on our expectation that its proximity to the P=O moiety (vide infra) would result in a downfield shift relative to $H_{4'}$ (2.34δ). The J_{PH} values for H_4 and $H_{4'}$ (4.7 and 22.9 Hz, respectively) are consistent with the MNDO calculated torsion angles (for 5s: P—C_5—C_4—H_4 = 77.0° and P—C_5—C_4—$H_{4'}$ = 167.8°). Once the ^1H assignments are complete, the ^{13}C signals are easily assigned by inspection of the ^1H-^{13}C shift correlated 2-D NMR[11] spectrum.

The large chemical shift differences between H_6 and H_7 (0.50 ppm) and C_6 and C_7 (9.8 ppm) are nearly identical to those observed in the hydrocarbon analogue, bicyclo[3.2.1]octa-2,6-diene, (0.52[12] and 9.8 ppm,[12d] respectively). These differences may be at least partially attributed to H_6 and C_6 residing in a more crowded region of the molecule. Evidence for the C_5, C_6 side of the molecule being more crowded than the C_1, C_7 side can be found in the MNDO calculations which are in turn supported by the NOESY spectrum (vide infra).

The phosphorus in **3** could, in principle, adopt two orientations, leading to two diastereomeric pairs of enantiomers (Scheme I). Thus, if the diisopropylamino group is syn to C_6 and C_7 (**3s**), the compound is (1R, 5S, 8S) and (1S, 5R, 8R),

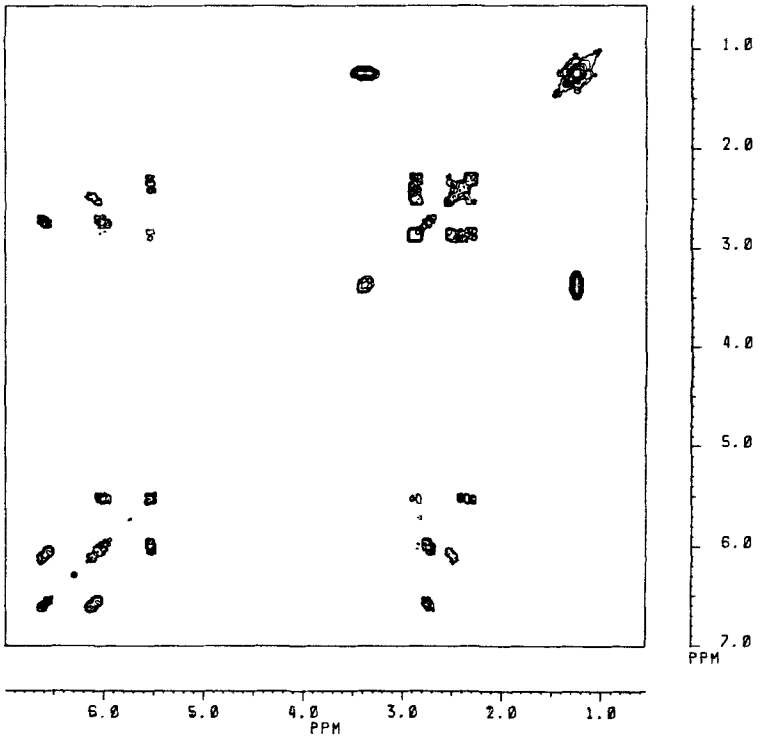
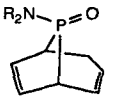


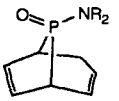
FIGURE 2 The ^1H shift-correlated 2-D NMR (COSY) spectrum of **3**. The diagonal peak at 6.3 ppm arises from foldover of the residual $CHCl_3$ absorption.

but, if it is anti to C_6 and C_7 (**3a**), the compound is (1R, 5S, 8R) and (1S, 5R, 8S). Obviously, **3** can be only one of these diastereomers. Since the ^1H NMR spectrum had been assigned, the orientation at P could in principle be determined by obtaining the NOESY[13] spectrum (Figure 3). The most important feature is the cross peak connecting the resonances for R_{CH_3} and H_7. Thus, the diisopropylamino group is syn to C_6 and C_7, while the P=O bond is syn to C_2, C_3, and C_4, and the structure **3s** is assigned.

It is interesting to compare the ^{31}P chemical shift of **3** to those of phosphinamides with the 7-phosphanorbornene skeleton. At first glance, the value for **3** (63.6 ppm) would appear to more closely resemble that of a simple 3-



3s-5s



3a-5a

3 R = i-Pr
4 R = Me
5 R = t-Bu

Scheme I

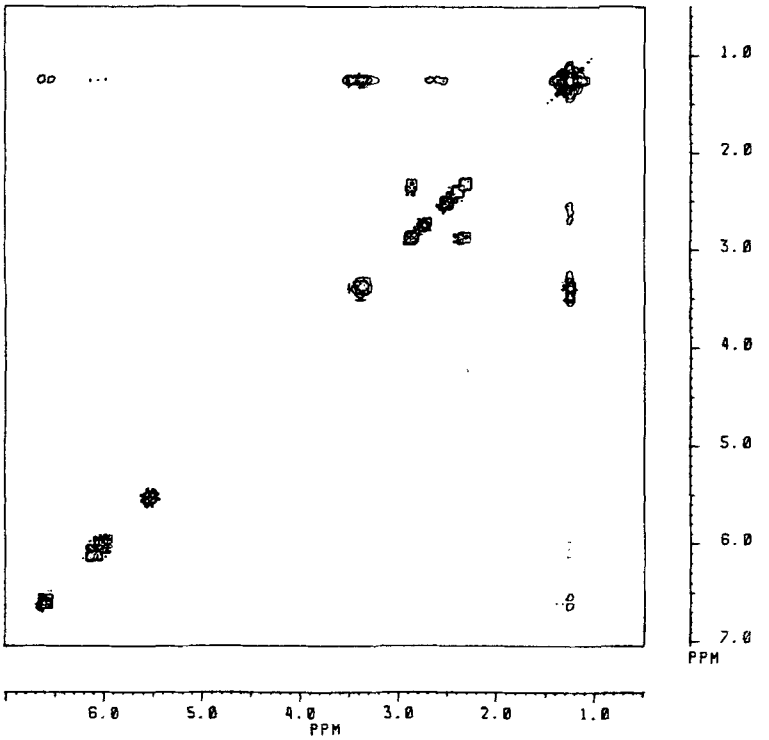


FIGURE 3 The NOESY spectrum of **3**.

phospholene amide (63.2 ppm)[1k] than those of the bridging P in the 7-phosphanorbornene system (*ca.* 83 ppm).[1k] However, we have noted that substitution of *i*-Pr_2N– for Me_2N– in a polycyclic phosphinamide results in an upfield shift of 6 ppm,[6g] and that substitution of Et_2N– for Me_2N– produces an upfield shift of from ~0.5 to ~5 ppm for a variety of cyclic phosphinamides.[1i,1k] Thus, a corrected value of ~70 ppm for the Me_2N– derivative of **3** would appear to be more appropriate for comparison with the examples cited in ref. 1k. Use of the corrected value indicates that the 8-phosphabicyclo[3.2.1]octa-2,6-diene skeleton represents an intermediate case between the 7-phosphanorbornene and 3-phospholene skeletons.

In order to test our assignment of the orientation at P and to assess the structural similarities between **3** and the 7-phosphanorbornene skeleton, we wished to calculate the geometry of **3** at the MNDO level.[7,8] However, the hypersurface of **3** is exceedingly complex. Due to the lack of any local symmetry about the C—N bonds and the overall $\mathbf{C_1}$ symmetry of **3**, one would need to examine nine input structures for both **3a** and **3s**. Thus, a thorough study of **3** is prohibitively time consuming. Introduction of more symmetrical substituents on N would simplify matters greatly. We choose to calculate the syn and anti isomers of the dimethylamino and di-*t*-butylamino derivatives (**4s,a** and **5s,a**, respectively) with the assumption that the steric demands of Me_2N– and *t*-Bu_2N– would bracket those of *i*-Pr_2N– and that the structure and syn-anti energy difference of **3** would be intermediate to those of **4** and **5**.

TABLE II

ΔH_f's for compounds **4s**, **4a**, **5s**, and **5a** as calculated by MNDO (in kcal/mol)

Compound	ΔH_f	Relative Energy
4s	8.52	0.00
4a	8.76	0.24
5s	45.87	0.00
5a	47.89	2.02

The ΔH_f's and some selected structural parameters for the fully optimized structures are given in Tables II and III, respectively. Although the syn-anti energy difference for **4** is small, **5s** is calculated to be significantly more stable than **5a**. Thus, the calculated preferred orientation at P is in agreement with that assigned to **3**.

For the most part the geometries of **4** and **5** are very similar. Both compounds

TABLE III

Selected structural parameters of **4s**, **4a**, **5s**, and **5a** as calculated at the MNDO level

Parameter	Compound			
Bond lengths (Å)	**4s**	**4a**	**5s**	**5a**
C_1—C_2	1.505	1.502	1.505	1.501
C_2—C_3	1.352	1.351	1.351	1.350
C_3—C_4	1.512	1.511	1.510	1.507
C_4—C_5	1.546	1.543	1.547	1.539
C_5—C_6	1.506	1.507	1.500	1.502
C_6—C_7	1.356	1.358	1.354	1.357
C_1—C_7	1.507	1.508	1.501	1.503
C_1—P	1.861	1.863	1.899	1.903
C_5—P	1.857	1.859	1.883	1.893
P—O	1.500	1.502	1.502	1.504
P—N	1.705	1.702	1.740	1.743
Bond Angles (°)				
C_1—C_2—C_3	122.8	122.8	123.1	123.3
C_2—C_3—C_4	124.8	124.9	124.3	124.2
C_3—C_4—C_5	114.2	114.3	114.2	114.4
C_4—C_5—C_6	112.9	112.5	112.7	114.4
C_5—C_6—C_7	114.3	114.3	114.2	114.5
C_1—C_7—C_6	113.9	114.1	113.8	113.6
C_2—C_1—C_7	112.0	112.1	111.4	109.9
C_2—C_1—P	103.6	106.9	103.1	110.6
C_7—C_1—P	99.5	96.5	101.0	96.0
C_4—C_5—P	106.4	110.1	106.3	110.5
C_6—C_5—P	99.3	96.5	100.9	96.5
C_1—P—O	118.1	115.5	110.4	109.3
C_5—P—O	118.6	115.2	117.2	111.7
C_1—P—N	112.0	114.1	122.8	123.2
C_5—P—N	108.9	113.2	112.0	118.3
C_1—P—C_5	88.2	88.3	85.8	85.7
P—N—C_{11}	115.7	116.1	115.6	115.0
P—N—C_{12}	116.5	115.7	115.3	115.6
C_{11}—N—C_{12}	115.0	114.7	122.0	121.4

manifest the steric demand of the R_2N group by expanding the P—C—C angles that are syn to R_2N and contracting those that are anti to R_2N. In **4** the C—P—N and C—P—O angles depend greatly on the orientation at P. Thus, C—P—N and C—P—O are expanded when N and O point toward C_2, C_3, and C_4 and contracted when N and O point toward C_6 and C_7. We interpret this as an indication of the steric congestion of the C_2, C_3, C_4 side of the molecule. In the more crowded **5**, the effect survives in only the C_5—P—N and C_5—P—O angles. The structural differences between **4** and **5** can be explained in terms of the greater steric bulk of the *t*-Bu_2N group in **5**. The P—C and P—N bonds are all significantly longer in **5** than in **4**, and the C_1—P—C_5 angle in **5** is smaller than that in **4**, probably as a result of N—P—X angle expansion.

There are only a few structures of 7-phosphanorbornenes and -norbornadienes available for comparison. Lipscomb[1c] and Quin[1k] have reported X-ray structures of some phosphole oxide dimers, and Mathey[3] has published the structure of a $Cr(CO)_5$ complex of a 7-phosphanorbornadiene. All of these compounds exhibit contracted C—P—C angles. The norbornadiene derivative shows the smallest (79.0°), while the values for the norbornenes range from 82.3° to 86.9°. If we assume that the C—P—C angle in **3** is intermediate to those of **4** and **5**, we can conclude that the strain in the 7-phosphabicyclo[3.2.1]octa-2,6-diene skeleton approaches that of the 7-phosphanorbornene. On the other hand, the 7-phosphanorbornadiene is even more strained.

Interestingly, the nitrogens in both **4s** and **5s** are pyramidal as indicated by the sums of their valence angles (Table III). This stands in contrast to the phosphole dimer structure reported by Quin[1k] which exhibits a nearly planar phosphinamide nitrogen. In order to convince ourselves that the pyramidality in **4s** and **5s** was not simply the result of incomplete energy minimization, we have examined the effect of imposing nitrogen planarity while relaxing all other parameters. The resulting structures (**4sP** and **5sP**) are 2.0 and 3.3 kcal/mole more strained than their fully relaxed counterparts. The discrepancy between the experimental and calculated structures may be ascribed to an inadequacy of the MNDO method, crystal packing forces, or differences in the two skeletons.

Perhaps the most surprising aspect of the calculated structures is the twist about the P—N bonds in **4s** and **5s**. As depicted in the Newman projections in Figure 4, the P—N bonds are twisted in such a way as to move one N—R group toward C_7 and the other away from C_6. The effect is magnified in **5s**. The result is a significantly shorter closest approach of the *t*-Bu group to H_7 (2.66 Å) than to H_6 (3.48 Å). The presence of an intense cross peak connecting R_{CH_3} with H_7 but none with H_6 in the NOESY spectrum of **3** suggests that such a twist is also present in **3**.

FIGURE 4 The Newman projections along the P—N bonds of **4s** and **5s**.

The net [4 + 2] cycloaddition of **1** to CHT is surprising in at least one respect. Although there is ample precedent for such additions of R_2P^+ to 1,3-dienes,[6] CHT rarely participates as a diene. Instead, it is the norcaradiene tautomer that reacts with typical dienophiles to yield tricyclo[3.2.2.$0^{2,4}$]non-6-enes.[14] The only precedent for direct [4 + 2] cycloaddition to CHT is its reaction with maleic anhydride which gives ~1% of the bicyclic product in addition to tricyclic compounds.[15] Initial addition of **1** to CHT to form a tricyclic product which rearranges to **3** is unlikely, since such rearrangements usually require high temperatures.[16]

EXPERIMENTAL

CH_2Cl_2 was freshly distilled (under N_2) from P_2O_5. $[(Cl)(i\text{-}Pr_2N)P]^+[AlCl_4]^-$ was prepared as in the literature[5e] with triply sublimed $AlCl_3$. Cycloheptatriene (Aldrich) was used without further purification. Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. NMR spectra were obtained on a Bruker AM-300 spectrometer in $CDCl_3$ solution. Chemical shifts are reported relative to internal TMS for the ^1H and ^{13}C spectra and external 85% H_3PO_4 for the ^{31}P spectra. Positive δ values represent downfield shifts. The 2-D NMR programs used were those found in the Bruker Pulse Programmer Library.

8-Diisopropylamino-8-phosphabicyclo[3.2.1]octa-2,6-diene oxide (**3**). Cycloheptatriene (8.9 mmol, ~6M in CH_2Cl_2) was added dropwise to a stirred solution of $[(Cl)(i\text{-}Pr_2N)P]^+[AlCl_4]^-$ (8.9 mmole, ~0.4 M in CH_2Cl_2) which was cooled by an ice-water bath. After the addition was complete, the bath was removed, and the mixture was stirred for two hours at room temperature. The resulting mixture was then pipetted into an ice-water $NaHCO_3$ solution and stirred for ten minutes. The mixture was filtered through celite and extracted three times with $CHCl_3$. The organic layers were combined and dried over $MgSO_4$. Rotary evaporation of the solvent yielded a crude orange oil which solidified upon standing. Vacuum sublimation gave 0.74 g (3.1 mmol, 35%) of **3** as hygroscopic white crystals; m.p. 84–86°C. Calcd: C, 65.25; H, 9.27; N, 5.85. Found: C, 65.15: H, 9.60; N, 5.61.

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