treated with hexamethyldisilazane and programmed from 50 to 300 °C at 30 °C/min.

All mass spectra were recorded with an AEI MS-30 dual beam mass spectrometer interfaced to an AEI DX-50 data system.

**Procedures.** All experiments were done with sealed containers. Large-scale experiments were done with a 1.4-l. 316 stainless steel autoclave. Others were done in sealed Pyrex glass tubes. A typical example for expt 1 and 3 in Table I follows.

The autoclave was charged with I (707.9 g, 1.9 mol) and trimethylamine (265 g, 4.5 mol) was added from a small steel sampling bottle. The mixture was heated to 130 °C for 129 h and cooled to room temperature. Trimethylamine was then permitted to escape into a trap filled with dilute hydrochloric acid. The products were vacuum filtered to yield 223.6 g of crystalline solids. These were washed with hexane, dried under vacuum, and titrated potentiometrically in water for chloride ion. Found: 109.5 mg/mequiv (calcd for $Me_4N^+Cl^-$, 109.60 mg/mequiv). The filtrate was >98 area % of one compound. The filtrate was distilled to obtain 641.1 g (88% yield), bp 106–107 °C (3 mmHg), $n^{25}D$ 1.4086, neut equiv 382.2 mg/mequiv (calcd for $(Me_3SiO)_3Si(CH_2)_3NMe_2$ (II),[7] $Si_4C_{14}H_{39}O_3N$, 381.8).[7] The distilled product was one sharp peak on GLC and was taken as a standard for subsequent analyses.

The analysis of example 4 of Table I illustrates how mixtures were analyzed when they contained I, II, and III at the end of the experiment.

The product was filtered and the crystalline material was washed with dry hexane, dried, weighed, and titrated for $Cl^-$ with $AgNO_3$. The $Cl^-$ equivalent weight was 269.6 mg/mequiv (calcd for a 1:1 molar mixture of III and $Me_4N^+Cl^-$ 270.61 mg/mequiv). The filtrate and hexane washes were stripped of solvent under vacuum to obtain 14.5 g of a liquid residue, which by GLC was 65.25 wt % I, 0.025 mol, 0.5 of initial charges of I, and 34.7 wt % II. The liquid residue had a base neutral equivalent weight of 1097.1 mg/mequiv which independently indicated ~34.75% II or about 0.013 mol.

**Analysis of Examples 7 and 8 (Table I).** Various standard solutions of III decomposed in a very reproducible way when injected into our GLC column. III → I + $Me_3N$ + II + MeCl. The ratio of the peak areas of I/II was very close to 1:3.125.

The composition of mixtures that contained both II and III was determined from peak areas measured for I and II. For example, a solution of 1 equiv of I, 2.2 equiv of $Me_3N$, and 2-propanol, 30% by volume, was heated to 100 °C for 69 h. The tube was then cooled and opened and a sample was injected on the GLC column. The peak areas of I/II were 1/14.9 corresponding to that calculated to result from a mixture of 21% III and 79% II.

The alcohol was stripped from the sample under vacuum. The salts that precipitated were removed by filtration. The filtrate contained no I detectable by GLC. Thus, I observed above in solution had its origin in the thermal decomposition of III.

**Analysis of Examples in Table II.** Concentrated aqueous NaOH was added to the mixtures to free amines from their hydrochlorides. The mixtures were shaken with a weighed quantity of heptane.

The amount of each amine in the heptane was determined by GLC with heptane as an internal standard.

**Registry No.**—I, 18077-31-1; II, 29346-33-6; III, 29394-88-5; $Me_3N$, 75-50-3; $NH_4^+Cl^-$, 12125-02-9; $PhCH_2NC_5H_5^+Cl^-$, 2876-13-3.

## References and Notes

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(3) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).
(4) R. E. J. Hutchinson and D. S. Tarbell, *J. Org. Chem.*, **34**, 67 (1969).
(5) O. Westphal and D. Jerchel, *Ber.*, **73B**, 1002 (1940).
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# Nuclear Magnetic Resonance Studies. 6. Properties of Phosphorus–Nitrogen Ylides[1]

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The electronic distribution and conformation of triphenylphosphinimines and phosphinazines are discussed in the context of their $^{13}C$ and $^{31}P$ NMR parameters. CNDO/2 molecular orbital calculations on model phosphorus–nitrogen ylides are substantially in agreement with these NMR properties. It is found that the barriers of rotation about the N–C and N–N bond in *N*-vinylphosphinimine (**17**) and formylphosphazine (**18**), respectively, are small. The lone pairs of electrons on the nitrogen adjacent to phosphorus are delocalized to the methylene carbon in **17** but not in **18**. Direct evidence is found for the dissociation of a phosphinazine into triphenylphosphine and the parent diazo compound.

Phosphinimines and phosphazines have been known since 1919[3] and their synthetic utility has been extensively explored.[4] Little, however, is known about the physical properties, conformation, and electron distribution in these phosphorus–nitrogen ylides. In the present work[5] we have examined the $^{13}C$ and $^{31}P$ NMR of these ylides and by the use of CNDO/2 molecular orbital calculations[6] information concerning the conformation and electronic nature of these compounds is discussed. The $^{31}P$ and $^{13}C$ NMR parameters for a series of *N*-trimethylsilyltrialkylphosphinimines has recently been reported[7] and Hückel $\pi$-type calculations have been published with regard to the uv properties of phosphinimines and phosphazines.[8]

**NMR Results.** The $^{31}P$, $^{13}C$ chemical shifts and $^{13}C$–$^{31}P$ couplings are given in Tables I–III, respectively. The $^{31}P$ chemical shift in Table I of *N*-phenyltriphenylphosphinimine (**1**) is shielded by 29.0 ppm from its phosphonium salt, **2**. Likewise, the phosphazines are shielded by approximately 20 ppm from their corresponding salts, i.e., compare **9** with **10**. These $\Delta\delta P$ values are somewhat larger than for the isoelectronic benzylidene or allylidenetriphenylphosphoranes (16.2 and 10.1 ppm, respectively).[1] The $^{31}P$ chemical shift of **1** where the excess negative charge on the nitrogen can be delocalized into the phenyl ring is not much different from that of *N*-trimethylsilyltriphenylphosphinimine (**4**). However, phosphinimines containing a strong electron-withdrawing group adjacent to the nitrogen, i.e., **5** and **6**, are deshielded by 11.6 to 17.6 ppm, respectively, from **1**. The phosphazines in Table I have $^{31}P$ chemical shifts that are deshielded from **1** by 15.4 to 19.4 ppm. *N*-Tosyltriphenylphosphazide (**14**) is deshielded from its phosphinimine counterpart, **6**, by 14.2 ppm.

The $^{31}P$ chemical shift of *N*-trityltriphenylphosphinimine (**3**) is shielded with respect to the other phosphinimines. This is presumably a result of steric interactions between the two sets of phenyl rings.[9]

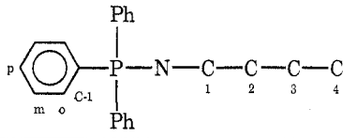
The $^{13}C$ chemical shift for carbon 4 in *N*-phenyltriphenyl-

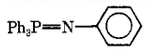
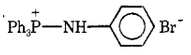
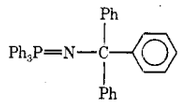
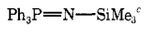
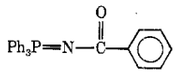
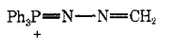
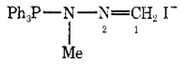
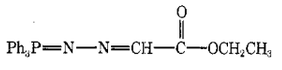
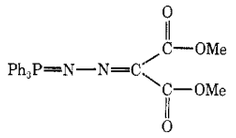
Table I. $^{31}P$ Chemical Shifts of Phosphinimines, Phosphazines, and Related Compounds

| Compd | No. | $\delta P^a$ | Registry no. | Compd | No. | $\delta P^a$ | Registry no. |
|---|---|---|---|---|---|---|---|
| $Ph_3P{=}N{-}Ph$ | 1 | 3.0 | 2325-27-1 | $Ph_3P{=}N{-}N{=}CH_2$ | 7 | 21.4 | 15990-54-2 |
| $Ph_3\overset{+}{P}{-}NH{-}Ph\ Br^-$ | 2 | 32.0 | 59230-96-5<br>17490-46-9[c] | $Ph_3\overset{+}{P}{-}N(Me){-}N{=}CH_2\ I^-$ | 8 | 47.0 | 55009-66-0<br>59230-97-6[c] |
| $Ph_3P{=}N{-}CPh_3$ | 3 | −10.3 | 56956-92-4 | $Ph_3P{=}N{-}N{=}CPh_2$ | 9 | 18.4 | 1109-01-9 |
| $Ph_3P{=}N{-}SiMe_3$ | 4 | −1.8[b] | 13892-06-3 | $Ph_3\overset{+}{P}{-}NH{-}N{=}CPh_2\ Br^-$ | 10 | 39.3 | 1109-00-8<br>59230-98-7[c] |
| $Ph_3P{=}N{-}C(O)Ph$ | 5 | 20.6 | 17436-52-1 | $Ph_3\overset{+}{P}{-}N(Me){-}N{=}CPh_2\ I^-$ | 11 | 48.3 | 1109-43-9<br>59230-99-8[c] |
| $Ph_3P{=}N{-}Tos$ | 6 | 14.6 | 1058-14-6 | $Ph_3P{=}N{-}N{=}CH{-}CO_2Et$ | 12 | 22.4 | 22610-15-7 |
| | | | | $Ph_3P{=}N{-}N{=}C(CO_2Me)_2$ | 13 | 20.9 | 6085-22-9 |
| | | | | $Ph_3P{=}N{-}N{=}N{-}Tos$ | 14 | 28.8 | 13378-67-1 |

[a] The $^{31}P$ chemical shifts are reported in parts per million downfield from external 85% $H_3PO_4$. The values correspond to those obtained in $CDCl_3$. [b] Value taken from ref 7. [c] Uncharged form.

Table II. $^{13}C$ Chemical Shifts of Phosphinimines and Phosphazines




| Compd | No. | Carbon, ppm[a] 1 | 2 | 3 | 4 | 5 | C-1 | o | m | p |
|---|---|---|---|---|---|---|---|---|---|---|
|  | 1 | 151.0 | 123.4 | 128.5 | 117.3 | | 131.2 | 132.4 | 128.4 | 131.5 |
|  | 2 | 137.8 | 123.5 | 129.2 | 121.8 | | 119.8 | 135.5 | 130.0 | 135.2 |
|  | 3 | *b* | 151.7 | 126.9 | 129.2 | 125.2 | 135.0 | 132.4 | 127.8 | 130.1 |
|  | 4 | 6.1 | | | | | 136.4 | 132.6 | 128.7 | 131.3 |
|  | 5 | 176.6 | 139.5 | 130.6 | 127.6 | 129.5 | 128.4 | 133.1 | 128.6 | 132.2 |
|  | 7 | 137.7 | | | | | 129.4 | 133.2 | 128.6 | 132.0 |
|  | 8 | 136.6 | 34.1 | | | | 118.6 | 134.1 | 130.4 | 135.7 |
|  | 12 | 137.8 | 165.2 | 59.5 | 14.4 | | 127.8 | 133.3 | 128.7 | 132.4 |
|  | 13 | 139.5 | 166.6<br>(163.1) | 51.8<br>(51.5)[d] | | | *b* | 133.4 | 128.8 | 132.7 |

[a] The $^{13}C$ chemical shifts are reported in parts per million from internal $Me_4Si$. [b] The resonances were too weak to be observed or obscured by another peak. [c] Values taken from ref 7. [d] Two sets of resonances were observed for carbons 2 and 3.

phosphinimine (1) (Table II) suggest some delocalization of charge onto this carbon by comparison with its amino-substituted phosphonium salt, **2**. Thus, carbon 4 in **1** is shielded by 4.5 ppm from that in **2**. This is a relatively small effect compared to benzylidenetriphenylphosphorane where the value for the corresponding position is 14.5 ppm.[1] The $^{13}C$ chemical shift of the methylene carbon in formyltriphenylphosphazine (**7**) is slightly deshielded from its phosphonium salt analogue, **8**, and therefore there is little, if any, delocalization of negative charge onto this carbon. This is contrasted by the fact that the analogous carbon in the isoelectronic allylidenetriphenylphosphorane is shielded by 32.4 ppm from its phosphonium salt.[1]

The $^{13}C$ chemical shifts for the C-1 phenyl carbons in the phosphinimines and phosphazines are similar to those found for the phosphorus–carbon ylides.[1,10] Note that the C-1 phenyl carbons for the phosphorus–nitrogen ylides are deshielded with respect to their phosphonium salt analogues, i.e., compare **1** with **2** and **7** with **8**. The $^{13}C$ chemical shift of alkyl carbon 1 in **1** is also deshielded in comparison to that found for **2**. This effect which is present for phosphorus–carbon ylides[1] and phosphine oxides may be due, in part, to an electric field effect of the P=X bond.[11]

The $^{13}C$ chemical shifts of the meta and para carbons are shielded by 1.6 and 3.7 ppm for **1** compared to its phosphonium salt protomer, **2**. A similar situation occurs for **7** and

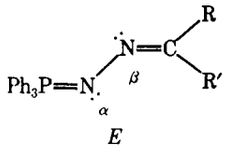
Table III. $^{13}C-^{31}P$ Couplings of Phosphinimines and Phosphazines

| Compd | No. | Carbon, Hz[a] | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | C-1 | o | m | p |
| $Ph_3P{=}N-C_6H_5$ | 1 | 2.4 | 17.5 | 98.7 | 9.6 | 11.9 | 2.8 |
| $Ph_3\overset{+}{P}-NH-C_6H_5\ Br^-$ | 2[b] | 2.4 | 18.3 | 102.5 | 11.6 | 13.4 | * |
| $Ph_3P{=}N-\overset{Ph}{\underset{Ph}{C}}-C_6H_5$ | 3 | c | 8.7 | 101.5 | 9.9 | 12.0 | 2.7 |
| $Ph_3P{=}N-SiMe_3$ | 4[d] | 3.2 | | 101.6 | 10.2 | 12.0 | 2.8 |
| $Ph_3P{=}N-\overset{O}{\overset{\|}{C}}-C_6H_5$ | 5 | 2.4 | 20.8 | 99.3 | 10.1 | 12.2 | 2.9 |
| $Ph_3P{=}N-N{=}CH_2$ | 7 | 45.9 | | 93.6 | 8.3 | 11.4 | 2.7 |
| $Ph_3\overset{+}{P}-\underset{Me}{\overset{\|}{N}}-N{=}CH_2\ I^-$ | 8 | 6.7 | 12.2 | 103.3 | 11.0 | 13.4 | 2.7 |
| $Ph_3P{=}N-N{=}CH-CO_2Et$ | 12 | 48.8 | * | 94.0 | 8.5 | 11.0 | 2.4 |
| $Ph_3P{=}N-N{=}C(CO_2Me)_2$ | 13 | 47.6 | * | c | 8.6 | 11.0 | * |

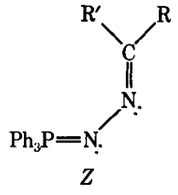
[a] The numbering system used is described in Table II. The digital resolution used was ±0.1 Hz. An asterisk indicates unresolved coupling. [b] The P–C coupling to carbon 4 was 6.7 Hz. [c] The resonances were too weak to be observed or observed by another peak. [d] Values taken from ref 7.

phosphorus–carbon ylides.[1] This may be taken as evidence that some charge is being transferred from nitrogen to phosphorus if it is assumed that $^{13}C$ chemical shifts of meta and para phenyl carbons reflect changes in the inductive and resonance properties of substituents.[12]

That only one set of resonances for carbon 2 and 3 were observed for 1 implies rapid rotation about the N–C bond. The phosphazines can also have cisoid (*Z*) or transoid (*E*)




*E*




*Z*

geometries. The fact that two carbonyl and methoxy carbon resonances are observed for **13** implies that inversion of the $\beta$ nitrogen or C–N$_\beta$ rotation is slow on the NMR time scale at 38 °C. The two methoxyl groups are also nonequivalent by ~10 Hz in the $^1H$ NMR of **13** up to 65 °C. There is, however, only one methylene carbon for all of the phosphazines reported in Table II. Discounting accidental isochrony,[13] this result implies that interconversion of the *E* and *Z* conformers in the phosphazines is rapid or that one conformer is strongly preferred over the other. There is also only one $^{31}P$ resonance for **7** and **9** up to 100 °C. Examination of molecular models for **7** reveals that there are steric interactions between the methylene protons and the phenyl rings; however, this is not severe.[15] CNDO/2 molecular orbital calculations on formylphosphazine indicate a low barrier of rotation about the N–N bond with neither conformer strongly favored (vide infra). Molecular orbital calculations on azines and hydrazones also indicate low N–N barriers of rotation.[16] That only one set of ethyl and carbonyl resonances was observed for **12** can be taken to imply that the carboethoxy group is favored in either a syn or anti relationship with respect to the N$_\beta$=C bond.

The $^{31}P-^{13}C$ couplings are quite similar to those found for phosphorus–carbon ylides,[1] with the exception of an extraordinarily large $^3J_{P-C}$ found for alkyl carbon in the phosphazines, **7**, **12**, and **13**. It was previously suggested[5] that part of this difference is due to the substitution of an additional nitrogen atom. However, phosphonium salt, **8**, has a $^3J_{P-C}$ which is typical for that found in other ylides and phosphonium salts.[1,9a] Finite perturbation calculations of $^3J_{P-C}$ for model phosphinimines and phosphazines suggest essentially no difference for this coupling.[17]

**Molecular Orbital Calculations.** In order to ascertain why the phosphazines, and to a smaller extent the phosphinimines, show little delocalization of charge throughout the $\pi$ framework of the molecules, a series of molecular orbital calculations was carried out on model compounds.[18]

Calculations on *N*-vinylphosphinimine (**17**) were carried out using the geometry reported for *p*-bromo-*N*-phenyltriphenylphosphinimine.[19a] Both CNDO/2 methods (spd and sp) showed the transoid (*E*) geometry of **17** to be more stable than the cisoid (*Z*) by 0.8 and 7.2 kcal/mol, respectively. The barriers of rotation about the N–C bond from the transoid geometry are 1.3 and 7.7 kcal/mol for the CNDO/2 (spd and sp) methods, respectively. Likewise, formylphosphazine (**18**), using the same P–N bond length as **17**,[20] gives barriers of rotation about the N–N bond of 3.7 and 3.6 kcal/mol; with CNDO/2 (spd and sp) starting from the cisoid conformer, CNDO/2 (spd) predicts the cisoid geometry of **18** to be more stable than the transoid by 4.2 kcal/mol, while the CNDO/2 (sp) results favor the transoid geometry by 1.0 kcal/mol. These barriers of rotation are much smaller than those found by allylidene or formylmethylenephosphorane using the same basis sets.[18] These low barriers are consistent with the NMR data and the discussion in the previous section.

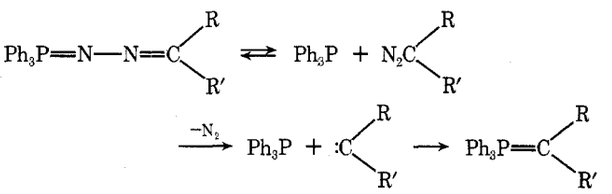
If $^{31}P$ chemical shifts can be related in a qualitative fashion to the electron density on phosphorus, then the shielding of the $^{31}P$ chemical shifts of the ylides **1**, **7**, and **9** compared to their respective phosphonium salts[21] is adequately treated by the CNDO/2 (spd) method. It must be emphasized that this technique overestimates the importance of d orbitals.[1,22] However, the fact that the ylides (Table I) are shielded in the $^{31}P$ NMR from their salts may be partly a consequence of $d_\pi-p_\pi$ overlap.[23] For $H_3P{=}N-CH{=}CH_2$ (**17**) and $H_3P{=}N-N{=}CH_2$ (**18**) the charges found for phosphorus are essentially identical by CNDO/2 (spd). With CNDO/2 (sp), **18** has greater electron density on phosphorus than that in **17**. Both of these results are not in accord with a comparison of the $^{31}P$ chemical shifts of **1** and **7**.

Both CNDO/2 methods predict the methylene carbon in $H_3P{=}N-CH{=}CH_2$ (**17**) to accommodate some electron density due to delocalization of negative charge from the nitrogen. Rotation of the N–C bond by 90°, however, does not

alter the charge distribution significantly, since the other lone pair on nitrogen can mix almost as effectively with the $\pi$ orbital of the vinyl group. In **17**, it is found that the charges from phosphorus to the terminal carbon alternate in sign. However, the introduction of an electronegative nitrogen atom $\beta$ to the phosphorus causes a major redistribution of the electron density in $H_3P{=}N{-}N{=}CH_2$ in **18**. The $\beta$ nitrogen withdraws electron density in the $\sigma$ framework from both the $\alpha$ nitrogen and the methylene group, whereas in **17**, a very different situation exists due to the fact that the $\beta$ atom is carbon. Therefore, CNDO/2 (spd and sp) and Hückel calculations[7b] suggest that there should be significantly less electron density on the methylene carbon in **18** than that in **17**. This is consistent with the $^{13}C$ chemical shifts of **1**, **2**, **7**, and **8** as discussed in the previous section.

If delocalization of electrons from the $\alpha$ nitrogen to the methylene carbon in **18** were important, then this would serve to decrease the negative charge on the $\alpha$ nitrogen and, thereby, diminish the electrostatic interaction with the positively charged phosphorus. This should serve to weaken the P–N bond, and in fact effects of this type are important for compounds such as **12** and **13** (vide infra). Similar effects have been noted for other highly charged groups.[24]

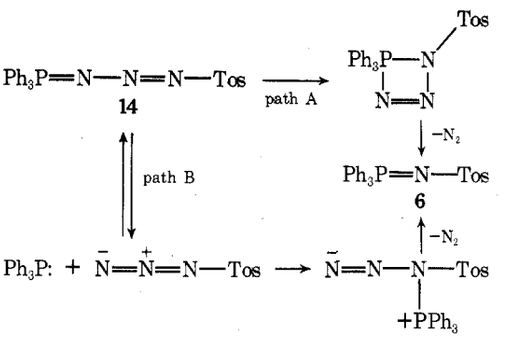
**Decomposition of Phosphazines and Phosphazides.** The decomposition of a phosphazine to a phosphorane and nitrogen has warranted considerable attention in the literature.[25] The proposed mechanism[25a] for this reaction is as follows:



The evidence for a prior dissociation of the phosphazine to triphenylphosphine and the diazo compound, rather than attack of the methylene carbon on phosphorus and extrusion of nitrogen from the resulting four-center intermediate, is primarily based on the fact that decomposition of a mixture of triphenylphosphine and the diazo compound gives essentially the same product distribution as with the parent phosphazine.[27] We have directly observed the dissociation of phosphazine **12** and **13** by NMR techniques. The $^{31}P$ NMR spectra of **12** and **13** both show an additional peak at $-5.4$ ppm, which is assigned to triphenylphosphine. When the temperature in the NMR probe is raised, the peak at $-5.4$ ppm becomes larger at the expense of the peak attributed to the phosphazine. Cooling the solution restores the original integral ratio of this peak compared to the phosphazine. The addition of triphenylphosphine to solutions of **12** and **13** increases the intensity of the peak at $-5.4$ ppm, while the addition of the parent diazo compound for **12** and **13** causes it to disappear. Likewise the $^1H$ NMR spectrum of **13** shows two nonequivalent methoxy resonances for the phosphazine and another single resonance which is identical with that found for authentic dimethyl diazomalonate. This single peak also increases when the temperature is raised at the expense of the two methoxy resonances for **13**.

At 39 °C, a solution of **12** in $C_6D_6$ contained 7 mol % of triphenylphosphine, based on the total areas of the phosphorus resonances. However, a solution of **13** at the same temperature showed a greater tendency to dissociate as it contained 56 mol % of triphenylphosphine. Similar values, within experimental error, were obtained from the $^1H$ NMR. No peak for triphenylphosphine was observed when **7** or **9** was heated to 100 °C in benzene or $Me_2SO$. Therefore, our results indicate that replacement of hydrogen atoms with carbonyl groups on the methylene carbon favors the dissociated products of the phosphazine. This is consistent with the theoretical analysis in the preceding section, in that strong electron withdrawing groups on the methylene carbon will weaken the P–N bond.

*N*-Tosyltriphenylphosphazide (**14**) and other phosphazides also decompose with loss of nitrogen to form phosphinimines.[4] Two mechanisms can be considered for this reaction:



Path A has been favored by kinetic and nitrogen labeling studies.[27] Our $^{31}P$ results seem to be in agreement with this since at $-10$ to 39 °C no triphenylphosphine was observed, although at the latter temperature decomposition of **14** was extremely rapid as evidenced by nitrogen evolution and the increase in intensity of a $^{31}P$ resonance corresponding to authentic *N*-tosyltriphenylphosphinimine (**6**).

## Experimental Section

The phosphinimines, phosphinazines, and phosphonium salts used in this study were prepared by standard routes.[4] The $^{13}C$ and $^{31}P$ data were taken at operating frequencies of 22.63 and 36.43 MHz, respectively, on a Bruker HFX-90 spectrometer. All samples were run as 0.1–0.05 M solutions in $CDCl_3$, except **2** in which $Me_2SO$-$d_6$ was used as the solvent. Assignment of peaks was accomplished by the use of off-resonance decoupling and model compounds[12] as appropriate.

All calculations were carried out on a Burroughs B6700 computer using the standard CNDO/2 program.

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(13) A similar situation occurs for alkyl- and alkoxycarbonylmethylenephosphoranes. Here the barrier to rotation about the $Ph_3PC$–C(O)R bond is slow producing different $^{13}C$, $^1H$, and $^{31}P$ resonances for the two conformers.[9,14]
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# Quinazolines and 1,4-Benzodiazepines. 74.[1] Phosphorylation[2] of Ambident Anions. Preparation of Some Di-4-morpholinylphosphinyloxy Imines via O-Phosphorylation of Anions of Lactams

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The reaction of ambident anions of amide type with di-4-morpholinylphosphinic chloride (1) has been investigated. O-Phosphorylations predominate in the cases of the lactams 1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-ones (**2**), 7-chloro-3,4-dihydro-2-methylamino-5*H*-1,4-benzodiazepin-5-one (**4**), and 2-phenyl-4-quinazolone. The novel dimorpholinylphosphinyloxy imines **3, 5,** and **11** formed are crystalline and readily isolable. In contrast, reaction of **1** with the anions of anthranilamides **7,** 8-chloro-2,4-dihydro-6-phenyl-1*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepin-1-one, 2-hydroxybenzimidazole, and 2-benzoxazolinone afforded good yields of the N-phosphorylated products **8, 13, 14,** and **15,** respectively. A thermal isomerization of the O-phosphorylated compound **5** to the N-phosphorylated isomer **6** is also observed. Compound **6** was prepared independently from the anthranilamide derivative **8.**

Although the reaction of phosphorylating agents[3-5] with enolate anions[6,7] has been studied extensively, there is a paucity of information on the reaction of these agents with ambident anions containing nitrogen and oxygen sites. Enolate anions phosphorylate almost exclusively on oxygen. In contrast, the site of phosphorylation of nitrogen-containing ambident anions seems less predictable. 2-Hydroxypyridine and 4-hydroxypyridine with phosphoryl chloride in aqueous alkali were reported to yield *O*-phosphoryl and *N*-phosphoryl derivatives, respectively.[8]

We now wish to report the results of some investigations carried out on the ambident anions of amides using di-4-morpholinylphosphinic chloride (**1**)[9,10] as the phosphorylating agent. Compound **1** is a crystalline (mp 80–82 °C) and readily available[14] reagent useful in the preparation of phosphate monoesters.[9a,15] Both O-phosphorylation and N-phosphorylation reactions were observed, with selectivity depending on the amide used. The preference for the oxygen site of the anions of cyclic secondary amides has permitted the isolation, in good yields, of the novel[11] and synthetically useful[13] dimorpholinylphosphinyloxy imines **3** and **5** in the 1,4-benzodiazepine series. When a slight excess of **1** was allowed to react with anions derived from 1,3-dihydro-2*H*-1,4-benzodiazepin-2-ones (**2**) in tetrahydrofuran at room temperature, the predominant products formed, as evident by TLC, were the O-phosphorylated products **3,** which could be isolated in 43–66% yields. Although crystalline and readily isolable, these dimorpholinyloxy imines are quite reactive toward nucleophiles to give 2-substituted benzodiazepines.[13] The infrared spectra of **3** indicate the absence of lactam carbonyl signals (typically strong bands at about 1680 $cm^{-1}$). When 7-chloro-3,4-dihydro-2-methylamino-5*H*-1,4-benzodiazepin-5-one[16] compound **4** was treated with sodium hydride followed by **1,** the O-phosphorylated product **5** crystallized in 48% yield. The N-phosphorylated product **6** was eventually also isolated (9% yield) from the same reaction mixture. However, owing to the complexity of the mixture, this isolation was not achieved until a reference sample of **6** was synthesized from compound **8b** by an alternate process as described below. In contrast to the cyclic amides **2** and **5,** it was found that the anthranilamides **7,** under the same conditions, afforded the N-phosphorylated products **8** in yields of 58–62%. Chloroacetylation of 2-amino-5-chloro-*N*-(di-4-morpholinylphosphinyl)benzamide (**8b**) led to the chloroacetanilide **9** (95%) which was cyclized in the presence of triethylamine to 7-chloro-4-(di-4-morpholinyl)phosphinyl-1,2,3,4-tetrahydro-5*H*-1,4-benzodiazepine-2,5-dione (**10,** 65%). The *N*-dimorpholinylphosphinylamide group in **10** survived a titanium tetrachloride–methylamine treatment[17] leading to the amidine **6** in 57% yield. While compound **6** was relatively thermally stable (as a melt at 220 °C for 2 min), the O-phosphorylated isomer compound **5** was not. In refluxing mesitylene (bp 163–166 °C), **5** isomerized in 80% yield, to the N isomer **6.** This observation suggests that the predominance of O-phosphorylation leading to **3** and **5** is kinetic in nature, and that N-phosphorylation is thermodynamically preferred.

To extend our observations to ambident anions of aromatic cyclic amide, cyclic urea, and cyclic carbamate types, we chose the following compounds purely on the basis of their potential usefulness as intermediates leading to new derivatives of potential medicinal utility: 2-phenyl-4-quinazolone,[18] 3-amino-6-chloro-4-phenylcarbostyril,[19] 8-chloro-2,4-dihy-