°C. The red-brown solution was then heated at 55 °C for 1 h. After being cooled, the solution was poured into 150 mL of ice-cold water and carefully basified with excess sodium carbonate. The aqueous mixture was extracted with methylene chloride (3 × 100 mL). The methylene chloride solution was dried with magnesium sulfate and evaporated to give 1.215 g (64%) of crude **20**, a viscous, red-brown oil: $[\alpha]^{20}_D$ (*c* 0.413, methylene chloride); picrate, mp 187–192 °C; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, 1, *J* = 3 Hz), 7.71 (d, 1, *J* = 3 Hz), 3.51 (t, 1, *J* = 8 Hz), 3.20 (m, 1), 1.25–2.63 (m, 5), 2.31 (s, 3), 2.24 (s, 3); EI mass spectrum, *m/e* 256, 254 (M^+), 84 (1-methylpyrrolidinyl). The crude material was utilized directly in the next step.

Anal. Calcd. for $C_{17}H_{18}BrN_5O_7$ (picrate): C, 42.16, H, 3.72; N, 14.47. Found: C, 42.64; H, 3.87; N, 14.66.

Compound **19**, prepared from Shioiri's compound **4**,[18] was also converted as above to **20**; $[\alpha]^{20}_D$ −66° (*c* 0.435, methylene chloride).

(*S*)-(−)-5-Methylnicotine (2). A mixture of 1.177 g (4.62 mmol) of crude **20**, 0.327 g (0.4 equiv, 1.85 mmol) of palladium chloride, 1.52 g (4 equiv, 18.5 mmol) of sodium acetate, and 25 mL of absolute ethanol was shaken under hydrogen at 50 psi in a Parr apparatus for 8 h. The mixture was filtered through Celite and evaporated to a small volume which was basified with 15 mL of 10% aqueous sodium hydroxide. The aqueous mixture was extracted with methylene chloride (3 × 25 mL). The combined methylene chloride solution was dried with magnesium sulfate and evaporated to a mobile, red-brown oil. Bulb-to-bulb distillation of the oil [oven temperature 70–90 °C (0.15 torr)] yielded 0.421 g (52%) of **2**, a clear, colorless oil: $[\alpha]^{20}_D$ −41° (*c* 0.504, methylene chloride); dipicrate, mp 202–205 °C; ^{1}H NMR ($CDCl_3$) δ 8.35, (br s, 1), 8.33 (br s, 1), 7.53 (s (v br, approximating a t), 1), 3.13 (m, 1), 3.06 (t, *J* = 6.5 Hz, 1), 2.34 (s, 3), 2.19 (s, 3), 1.5–2.5 (m, 5); EI mass spectrum, *m/e* 176 (M^+), 84 (1-methylpyrrolidinyl).

Nicotinoid **2** was also prepared by the same sequence starting with Shioiri's compound **4**.[18] Optical rotation of **2**: $[\alpha]^{20}_D$ −90° (*c* 0.5075, methylene chloride).

Anal. Calcd for $C_{23}H_{22}N_8O_{14}$ (dipicrate): C, 43.53; H, 3.47; N, 17.67. Found: C, 43.27; H, 3.55, N, 17.38.

Acknowledgment. We thank Dr. Jeffrey I. Seeman for helpful discussions, Dr. Richard Kornfeld for mass spectral analyses, Mrs. Anne Donathan for secretarial assistance, and Mr. James Day for preparing the figures.

Registry No. 1, 54-11-5; 2, 77629-31-3; 2 dipicrate, 80294-08-2; 4, 67824-39-9; 4 picrate, 80294-09-3; 6, 34381-71-0; 8, 67824-38-8; 14, 80301-18-4; 15, 80294-10-6; 19, 80294-11-7; 20, 80294-12-8; 20 picrate, 80294-13-9; 3-ethoxyacrolein, 19060-08-3; 3-ethoxy-2-methylacrolein, 42588-57-8.

Nitrones. 6.[1] Reactions of Nitrones with Cyclic Phosphonates. Influence of the Phosphonate Ring Size upon the Course of the Reaction[2]

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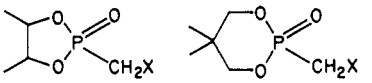
Received September 15, 1981

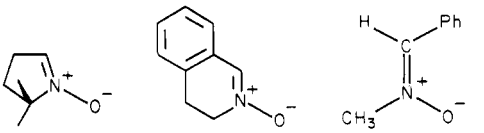
Nitrones, 5,5-dimethyl-Δ^1-pyrroline *N*-oxide (**5**), and 3,4-dihydroisoquinoline *N*-oxide (**6**) were reacted with the five-membered cyclic phosphonates 2-[(ethoxycarbonyl)methyl]-2-oxo-4,5-dimethyl-1,3,2-dioxaphospholane (**1**) and 2-(cyanomethyl)-2-oxo-4,5-dimethyl-1,3,2-dioxaphospholane (**2**) and with the six-membered cyclic phosphonates 2-[(ethoxycarbonyl)methyl]-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (**3**) and 2-(cyanomethyl)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (**4**). The reactions of the five-membered phosphonates gave aziridines as products, except that of **6** and **2**. The reactions of the six-membered phosphonates gave exclusively or predominantly enamines. The reactions of *C*-phenyl-*N*-methylnitrone (**7**) with **2** gave only *trans*-1-methyl-2-cyano-3-phenylaziridine (**22**). Cyclic phosphates 2-hydroxy-2-oxo-4,5-dimethyl-1,3,2-dioxaphospholane (**20**) and 2-hydroxy-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (**21**) were isolated as byproducts from the reactions of the corresponding phosphonates.

Previously, we reported that the aziridines formed in the reactions of nitrones with phosphonates or phosphine oxides are exclusively of trans stereochemistry.[1-5] This appears to be reminiscent of the phosphonate or phosphine oxide modification of the Wittig reaction,[6] which also leads predominantly to trans products (olefins).[7] Consequently, some time ago we expressed the assumption[5] that, similarly to the olefin synthesis, the stereoselectivity of the aziridine formation is a result of thermodynamic control upon the reversible formation and interconversion of the two possible diastereoisomeric erythro and threo reaction intermediates. Recently we succeeded in changing the steric course of the phosphonate modification of the Wittig reaction by the use of cyclic phosphonates (**1–4**), achieving



1, X = CO_2Et 3, X = CO_2Et
2, X = CN 4, X = CN

in some cases predominant formation of cis olefins.[8] Consequently, it was of interest to examine the reactions of representative nitrones with our cyclic phosphonates. In this paper we describe the results obtained from the reactions of the cyclic phosphonates with the representative nitrones 5,5-dimethyl-Δ^1-pyrroline *N*-oxide (**5**), 3,4-dihydroisoquinoline *N*-oxide (**6**), and *C*-phenyl-*N*-methylnitrone (**7**).



5 6 7

(1) Part 5: Zbaida, S.; Breuer, E. *Tetrahedron* **1978**, *34*, 1241.
(2) Part of this work was reported in a preliminary communication: Zbaida, S.; Breuer, E., *J. Chem. Soc., Chem. Commun.* **1978**, 6.
(3) Breuer, E.; Ronen-Braunstein, I. *J. Chem. Soc., Chem. Commun.* **1974**, 949.
(4) Breuer, E.; Zbaida, S.; Pesso, J.; Ronen-Braunstein, I. *Tetrahedron* **1977**, *33*, 1145.
(5) Breuer, E.; Zbaida, S. *J. Org. Chem.* **1977**, *42*, 1904.
(6) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87. Wadsworth, W. S., Jr. *Org. React.* **1977**, *25*, 73.
(7) Schlosser, M., Top. *Stereochem.* **1970**, *5*, 1.
(8) Breuer, E.; Bannet, D. M. *Tetrahedron Lett.* **1977**, 1141; *Tetrahedron* **1978**, *34*, 997.

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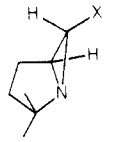
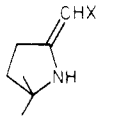
Table I. Results from the Reactions of 5,5-Dimethyl-Δ^1-pyrroline *N*-Oxide (%) with Phsophonates

expt	phosphonate	base	solvent	temp, °C	time, h	products: aziridine	yield, %	enamine	yield, %
1[5]	18	NaH	DME	82	24	8	35	10	0
2	1	NaH	DME	82	24	8	37	10	0
3	3	NaH	DME	82	24	8	23	10	33
4	3	BuLi	THF	64	24	8	10	10	52
5[5]	19	NaH	DME	25	3	9	32	11	0
6	2	NaH	DME	25	4	9	30	11	0
7	4	NaH	DME	25	3.5	9	0	11	40

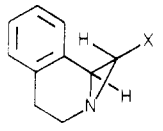
In previous papers we have shown that, depending upon the conditions, reactions of phosphonates with nitrone **5** may result in the formation of aziridines **8** or **9** and/or



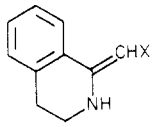
8, X = X = CO_2Et
9, X = CN



10, X = CO_2Et
11, X = CN

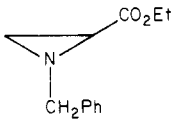


12, X = CO_2Et
13, X = CN



14, X = CO_2Et
15, X = CN

enamines **10** or **11**.[1,5] Nitrone **6** may give aziridine **12** and enamines **14** or **15**, but we never observed the formation of **13**.[1,4] Reaction of nitrone **7** with triethyl phosphonoacetate (**18**) gave ethyl 1-benzylaziridinecarboxylate (**16**) and ethyl *trans*-1-methyl-3-phenylaziridine-2-carboxylate (**17**).[3]



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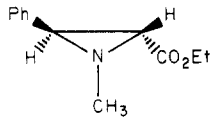

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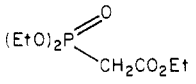
The results of the reactions of nitrones **5** and **6**, along with some of the results of the reactions of acyclic phosphonates **18** and **19**, are listed in Tables I and II. The



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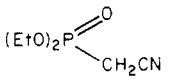
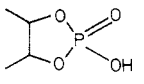


19

reactions were carried out by following the general procedure developed for the acyclic phosphonates and described previously.[4,5] The progress of reactions was monitored by thin-layer chromatography. In all reactions the isolation of products and unreacted starting materials was followed by the isolation of the byproduct of the reaction, namely, the cyclic phosphate **20** or **21**. This was done to



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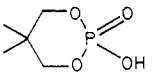


21

ascertain that no ring opening of the phosphorus-containing ring occurred during the reaction. Aziridine and enamine products were identified by comparison with authentic samples obtained in our previously described work.[4,5] No additional products were detected in the reaction mixtures. In no case was *cis*-aziridine formed.

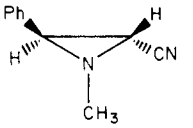
Table II. Results from the Reactions of 3,4-Dihydroisoquinoline *N*-Oxide (6) with Phosphonates[a]

expt	phosphonate	time, h	products: aziridine	yield, %	enamine	yield, %
1[4]	18	9	12	57	14	23
2	1	16	12	50	14	0
3	3	16	12	0	14	63
4[4]	19	4	13	0	15	85
5	2	3	13	0	15	25

[a] All reactions were carried out in DME at ambient temperature by using NaH as base.

Examination of the tables reveals that the course of the reactions is determined by the ring size of the phosphonate employed. In Table I it can be seen that while the results of the reactions of the five-membered phosphonates are identical with those of the open-chain phosphonates (compare entries 2 and 6 to 1 and 5), the reactions of the six-membered phosphonate **3** give an appreciable proportion of enamine **10** on using sodium hydride (entry 3). The proportion of **10** can further be increased by using lithium as the countercation.[5] In the cyano series the six-membered cyclic phosphonate **4** gives enamine **11** as the exclusive product.

From Table II it is apparent that while the reaction of 3,4-dihydroisoquinoline *N*-oxide (**6**) with the open-chain phosphonate **18** gives a mixture of **12** and **14**, by use of the cyclic phosphonates the reaction can be directed to the exclusive formation of either **12** (by use of the five-membered **1**, entry 2) or **14** (by use of the six-membered **3**, entry 3). In the cyano series only formation of enamine **15** was observed (entries 4 and 5). Phosphonate **1** was not sufficiently reactive toward **7**. However, we were able to react this nitrone with **2** by refluxing it for 48 h in 1,2-dimethoxyethane. This reaction gave a low yield of *trans*-1-methyl-2-cyano-3-phenylaziridine (**22**). In this reaction also, no *cis*-aziridine was detected.



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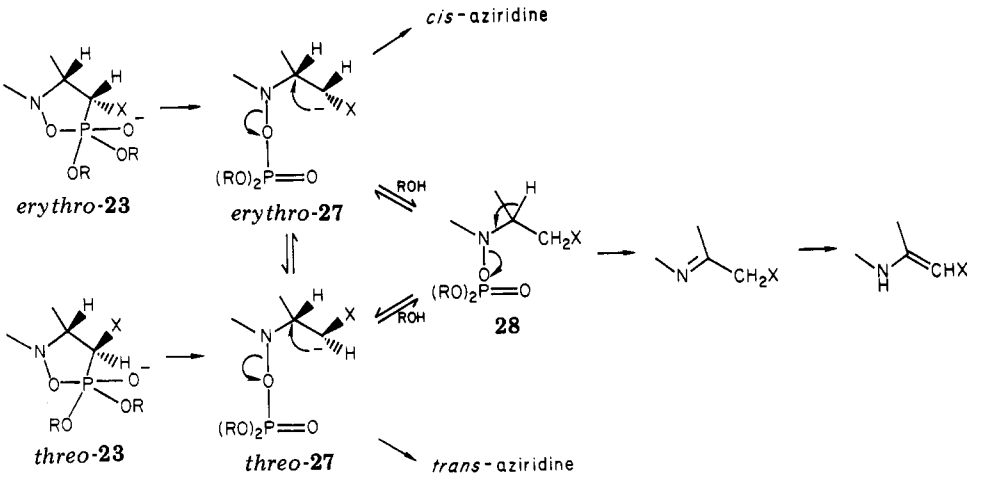
Discussion

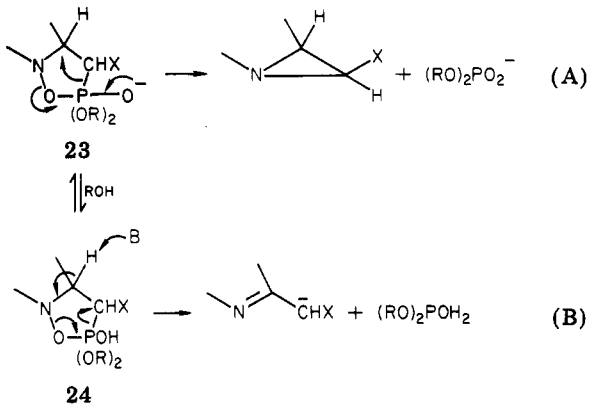
Previously we postulated that the reactions of nitrones with phosphonates[2-5] and oxides proceed via oxazaphospholidine intermediates. Recently we also reported the observation of such intermediates in the reactions of **2** and **5** and with **6**.[9] We have also shown that when the reactions are conducted in aprotic solvents they lead predom-

(9) Zbaida, S.; Breuer, E. *Experimentia* **1979**, *35*, 851. Subsequent to the publication of this paper we were also able to observe a high-field signal at −34.7 ppm in 1,2-dimethoxyethane at ambient temperature in the reaction of **5** with **1**.

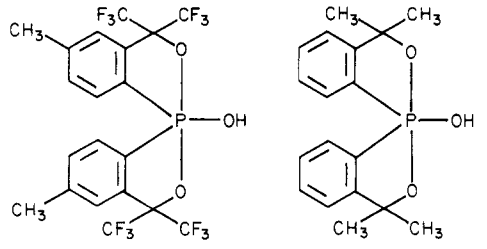
Scheme I



inantly or exclusively to aziridines, while in protic solvents (alcohols) the same reactions lead to enamines, the proportion of which increases with increasing acidity of the solvent.[4,5] This phenomenon was interpreted in terms of an oxazaphospholidine derivatives **23**, which may undergo fragmentation to an aziridine by path A. Such fragmentation was assumed to be facilitated by back-donation from the negatively charged exocyclic oxygen.[4,5] It was further assumed that in protic solvents the negatively charged oxygen in **23** is protonated, resulting in the formation of **24**. This intermediate may undergo a different type of base-catalyzed fragmentation to yield the corresponding enamine derivative (path B).



Recently the acidity of some pentacoordinated phosphorus acids was determined.[10] Granoth and Martin reported the values of 5.3 and 10–11 for the pK_a's of the phosphoranes **25** and **26**.[10a] On consideration of the



25 (pK_a = 5.3) **26** (pK_a ≈ 10-11)

structural features of phosphorane **24** in comparison with those of **26**, it may be assumed reasonably that **24** would be no less, and perhaps even slightly more, acidic than **26**.

In view of this, our previous assumption regarding the protonation of anions of type **23** by alcohols of pK_a's of 15–18 no longer seems reasonable. Instead, it may be assumed that the decomposition of **23** to products occurs in a stepwise manner. Thus, the first step, in the decomposition of **23** leads to carbanion **27** (Scheme I). The pK_a's of the analogues of the conjugate acid of **27** fall in the range of 20–22;[11] therefore, it is reasonable to assume that such carbanions will be protonated by alcohols to **28**, which cannot give aziridine but can undergo 1,2-elimination via an imine to an enamine. The relative amounts of aziridine and enamine formed will thus depend on the position of the **27** ⇌ **28** equilibrium, which in turn will depend upon the acidity of the solvent. We have discussed previously, in terms of perturbation theory, the influence of X upon the aptitude of an intermediate of type **27** to undergo the two possible reactions, namely, S_Ni type reaction leading to aziridine vs. protonation leading via **28** to enamine.[4]

As to the question of the stereoselectivity of the aziridine formation, it is pertinent to this subject that *trans*-1-alkyl-2,3-diaroylaziridines[12-14] and *trans*-1-alkyl-2-aryl-3-aroylaziridines[12,14] have been shown to undergo base-catalyzed isomerization to the more stable[15] cis isomer. Therefore, it is reasonable to assume that **17** and **22** that have been obtained from nitrone **7** are also the thermodynamically less stable products. The same conclusion, however, does not ncecessarily apply to the fused bicyclic aziridines **8**, **9**, and **12**. An attempted isomerization of **9** by sodium trideuteriomethoxide in tetradeuteriomethanol gave only the methyl ester analogue of **8** but no detectable cis product. This consistent trans stereoselectivity of the reaction regardless of the stability of the products can be accounted for either by assuming that the *threo*-**23** is formed with the exclusion of *erythro*-**23** and that the former collapses directly to a *trans*-aziridine or by assuming the formation of both diastereoisomers of **23** and their ring opening to the carbanions **27**, which can equilibrate and lead to the kinetic trans product. The latter reaction path seems more probable because it agrees with the previously presented stepwise decomposition mechanism. It also resembles the mechanism of the formation of cy-

(10) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618. (b) Segall, Y., and Granoth, I., *Ibid* **1979**, *101*, 3687.

(11) Gordon, A. J.; Ford, R. A. "The chemists Companion"; Wiley-Interscience: New York, 1972; pp 62, 63.

(12) Lutz, R. E.; Amacker, T.; King, S. M.; Shearer, N. H. *J. Org. Chem.* **1950**, *15*, 181.

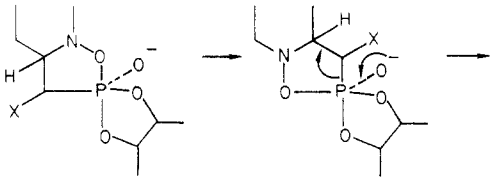
(13) Turner, A. B.; Heine, H. W.; Irving, J.; Bush, J. B., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1050.

(14) Lutz, R. E.; Turner, A. B. *J. Org. Chem.* **1968**, *33*, 516.

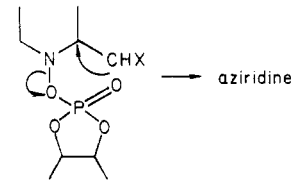
(15) Anet, F. A. L.; Osyany, J. M. *J. Amer. Chem. Soc.* **1967**, *89*, 352, footnote 6.

clopropanes by the reactions of epoxides with phosphonate anions.[16]

For discussion of the influence of the phosphonate ring size upon the course of the reaction, it is necessary to consider the structures of the intermediates in these cases. We have reported ^{31}P NMR data that indicate the existance of phosphoranes as intermediates in the reactions of nitrones with five-membered phosphonates.[9] Phosphoranes (e.g., **29**) resulting from five-membered phosphonates are expected to be relatively stable due to the favorable apical–equatorial orientation of both five-membered rings[17-19] and the equatorial orientation of the oxide ion[18-20] in a trigonal bipyramide (TBP).[21] Formation of the aziridine occurring by P–C bond cleavage requries bringing the carbon atom to an apical position, which can be attained by permutational isomerization of **29** to **30** (by Berry pseudorotation or turnstile rotation of **29**).



29 **30**



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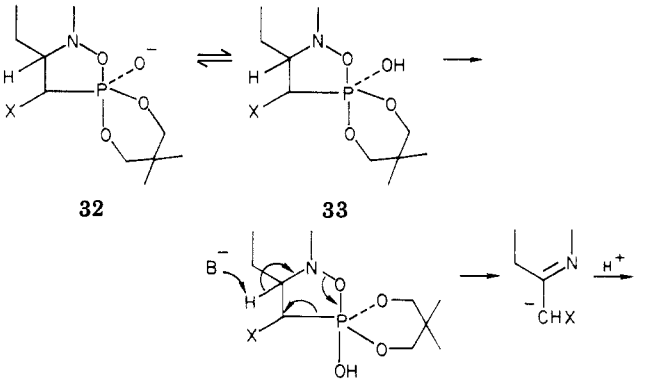
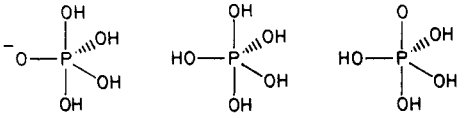
In contrast, phosphoranes formed as intermediates in the reactions of six-membered phosponates are expected to be less stable. Calculations have indicated a preference of the six-membered phosphorinane ring for a diequatorial position in a TBP.[26] However, when the six-membered ring contains heteroatoms attached to the phosphorus, lone-pair orientation effects have to be taken into account. The preference for the oxygen lone-pairs to be oriented in the equatorial plane[27] makes an apical equatorial orientation of a boat conformer more favored than either a diequatorial or an apical equatorial chair. Recently this was demonstrated by the X-ray analysis of an apical equatorial oxazaphosphorinane in a TBP.[28] The intermediate in the reaction of the six-membered phosphonate would thus have structure **32**. Our results can be rationalized by assuming that in the 5,5-dimethyl-1,3,2-dioxaphosphorinane boat ring of **32** nonbonded interactions between the *gem*-dimethyl groups and the phosphorus substituents will cause the phosphorane with an apical equatorial six-membered ring to have relatively high energy. One reasonable way that the energy of such an intermediate can be lowered is by protonation followed by permutational isomerization to **34**, which is unlikely to undergo reionization since this would lead to an apically oriented oxide ion. Such orientation is strongly disfavored as demonstrated both by experimental evidence[20] and by calculations that indicate that the equatorial anion, **35**, of



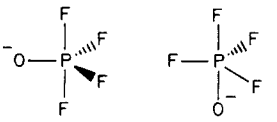
32 **33**

34



35 **36** **37**

pentahydroxyphosphorane **36** is more stable by 28 kcal/mol than the apical **37**.[29] In another case the equatorial anion **38** was calculated to be more stable by about 13 kcal/mol than the apical **39**.[18] These differences in stabilities of the anion correspond to about 10–20 pK_a units between the acidities of the apical and equatorial POH groups. Consequently, if we accept the pK_a value for the equatorially oriented OH group in a phosphorane such as **29** to be in the neighborhood of 10, the pK_a of **34** would be between 20 and 30. Since it is too weak an acid to undergo ionization to the anion which was assumed to be the required precursor of the aziridine, it will undergo fragmentation to enamine.



38 **39**

Experimental Section

^1H and ^{31}P NMR spectra were measured on a Bruker WP-60 (FT) instrument. Proton chemical shifts are given in parts per million downfield from Me_4Si. Negative phosphorus chemical shifts are given upfield from an external standard of 85% orthophosphoric acid.

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General Procedure for the Reactions of Nitrones with Phosphonates. A 50% dispersion of sodium hydride in mineral oil (0.5 g, 0.01 mol) was washed with petroleum ether (bp 40–60 °C, 3 × 10 mL) in an inert atmosphere. After evaporation of the residual petroleum ether, 10 mL of DME (freshly distilled from lithium aluminum hydride) was injected, followed by 0.01 mol of phosphonate dissolved in 5 mL of DME with cooling. After the liberation of hydrogen ceased, 0.01 mol of the nitrone dissolved in 5 mL of DME was introduced. The reaction mixture was stirred under the conditions (time and temperature) indicated in the tables. DME was evaporated in vacuo, and the residue was placed on a short alumina column. Elution of the column by chloroform gave mixtures of starting nitrone with aziridine and enamine products. These mixtures were separated by preparative thin-layer chromatography (alumina GF_{254}, 1 mm) by development with mixtures of chloroform–petroleum (bp 40–60 °C). The physical constants of products **8–15** were reported previously.[4,5] The yields are given in the tables. Further elution of the columns by methanol gave the cyclic phosphates **20** or **21** which were isolated by the evaporation of the solvent.

***trans*-1-Methyl-2-cyano-3-phenylaziridine (22).** This compound was obtained from the reaction of nitrone **7** with phosphonate **2** in refluxing DME for 48 h. The product was isolated in the usual manner: IR (neat film) 2220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43 (5 H, m), 2.86 (1 H, d, J = 3 Hz), 2.73 (3 H, br s), 2.51 (1 H, d, J = 3 Hz, lit.[20]).

4,5-Dimethyl-2-hydroxy-2-oxo-1,3,2-dioxaphospholane (20): IR (Nujol) 3300, 1640, 1210, 1120, 1080, 975 cm^{-1}; ^1H NMR (D_2O) δ 4.33–3.66 (2 H, m), 1.38–1.30 (6 H, singlets); ^{31}P NMR (D_2O) 15.6 ppm.[21]

5,5-Dimethyl-2-hydroxy-2-oxo-1,3,2-dioxaphosphorinane (21): IR (Nujol) 3300, 2400, 1680, 1620, 1200, 1075, 1060, 1000, 940, 900 cm^{-1}; ^1H NMR (D_2O) δ 3.93 (4 H, d, J = 12 Hz), 0.97 (6 H, s); ^{31}P NMR (D_2O) −2.1 ppm; ^{31}P NMR (pyridine) −5.15 ppm.[22,23]

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Registry No. **1**, 72258-75-4; **2**, 67920-85-8; **3**, 67889-05-8; **4**, 66934-40-5; **5**, 3317-61-1; **6**, 24423-87-8; **7**, 3376-23-6; **8**, 57740-49-5; **9**, 57740-50-8; **10**, 61650-07-5; **11**, 66934-41-6; **12**, 64890-49-9; **13**, 80387-05-9; **14**, 5019-07-8; **15**, 64890-46-6; **18**, 867-13-0; **19**, 2537-48-6; **20**, 50577-87-2; **21**, 873-99-4; **22**, 80375-47-9.

Ring Transformations in Reactions of Heterocyclic Compounds with Nucleophiles.[1] Conversion of 5-Nitropyrimidine into 2-Substituted 5-Nitropyrimidine and 2-Amino-5-nitropyridines by Amidines[2]

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The reaction of 5-nitropyrimidine (1) with benzamidine, pivalamidine, acetamidine, propionamidine, α-phenylacetamidine, *O*-methylisourea hydrochlorides, and cyanamide in ethanolic solution in the presence of triethylamine has been investigated. It was found that reaction of 1 with alkyl(aryl) amidines, having no active methylene groups attached to the amidine moiety (pivalamidine, benzamidine), *exclusively* formed the corresponding 2-substituted 5-nitropyrimidines in good yields. With acetamidine and propionamidine, in addition to the formation of the 2-substituted 5-nitropyrimidines, the formation of 2-amino-5-nitropyridines also was observed; with α-phenylacetamidine a 2-amino-5-nitropyridine derivative *exclusively* was obtained. The reaction of 1 with both *O*-methylisourea and cyanamide leads to 2-amino-5-nitropyrimidine. These reactions provide new examples of degenerate ring transformations of the pyrimidine ring system and of the ring transformatin of pyrimidines into pyridines.

It has been firmly established that pyrimidine an its C- and N-substituted derivatives are appropriate systems to undergo transformations to other heterocyclic ring systems by reaction with various nucleophilic reagents.[3-4] Ring transformations occurring with 1,3-ambident nucleophiles are of special interest since displacement of the N(1)–C-(2)–N(2) portion of the pyrimidine ring by either the N–C–N, C–C–N, or C–C–C fragment of the employed nucleophile (forming pyrimidine, pyridine, or benzene ring systems, respectively) has been observed.

Conversion of a pyrimidine ring into a benzene ring has been reported for the first time in the reaction of 5-nitropyrimidine with ketonic reagents[5] and very recently in the treatment of uracil derivatives with various active methylene compounds[6a] and 5-nitro-2(1*H*)-pyrimidinone with acetone.[6b]

The ring conversion of the pyrimidine system into the pyridine system through replacement of the N(1)–C(2) fragment of the pyrimidine ring by the C–C part of the reacting species has been well-established,[5,7-9] but displacement of the N(1)–C(2)–N(3) portion of the pyrimidine by a C–C–N fragment has only recently been observed in the conversion of 1,3-dimethyluracils into the corresponding 5-substituted 2,6-dihydroxypyridines[10] by α-substituted acetamide derivatives in ethanolic sodium ethoxide.

An interesting series of transformations of the pyrimidines are the so-called degenerate ring transformations.[11,12] In these reactions atom N(1) or the fragments N(1)–C(2) or N(1)–C(2)–n(3) of the pyrimidine ring are replaced by the N, N–C or N–C–N moiety of the nucleophile, respectively, thus leading in all three cases to the same pyri-

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