(3) The result with **14b** (Table I, entry iii) indicates that of the three acetals (benzylic, α-ethoxyethyl, and glycosidic) present in the molecule, only the last was removed during brominolysis. By contrast, upon treatment of **14b** with mild acid, the last was the only acetal to survive—as expected.

(4) Pursuant to the survival of the acid labile protecting groups, the result with the silyl ether **14c** (entry iv) should be noted.

In general, the results with **14b** → **14g** reveal that under the deglycosidation conditions, the benzylidene ring does not undergo the well-known Hanessian–Hullar[13,14] reaction with NBS, a procedure widely used to cleave a benzylidene acetal while leaving a glycosidic center intact The formation of **15b** → **15g** allows that pattern of chemoselectivity to be reversed.

(5) In view of the reactions in entry i, survival of the *O*-benzyl ethers in entry v (**14d** → **15d**) is not surprising. However, the oxidative conditions proved to be so mild that even the activated methoxybenzyl ether survived (**14e** → **15e**) to a substantial degree (entry vi).

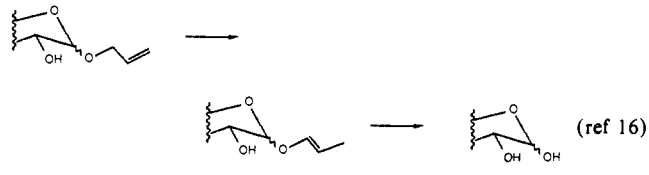
(6) The results with the diacetate **14f** (entry vii) were complicated by acetyl migration to give **16**. (In this context, it should be noted that silyl migration[15] was not observed with **15c**.)

An obvious question relates to the formation of bromohydrins **10** from intermediate **5** (Scheme Ib). Such substances were indeed encountered, particularly when the proportion of water in the solvent was higher than prescribed.[12] Indeed, there is enough adventitious water in "dry" acetonitrile to accomplish the hydrolysis step but at an appreciably slower rate.

The foregoing observation had seminal overtones, since it implied that double bonds, which do not lead to intermediates such as **6**, would not compete significantly for NBS. This postulate was tested by use of allyl protecting groups.[16]

(7) Indeed, the result in entry viii shows that substantive glycosidic cleavage can be achieved in the presence of *O*-allyl ethers.

The specificity of the deglycosidation is particularly noteworthy in light of the result in (7). Thus, while it is true that an allyl protecting group can also be removed from the glycosidic center under nonacidic conditions,[16] the process is not chemoselective, being operational for other allyloxy groups. The same holds true for the cleavage of benzyl glycosides.[17]



(ref 16)

The apparent driving force of the ready formation of the oxonium ion species **6** is of added interest in view of the timely report from the laboratories of Liotta and Maryanoff on the reversibility of bromonium ion catalyzed RO5 participation.[18] That aspect as well as other mechanistic details is currently being probed and will be reported in due course.[19]

(12) *N*-Bromosuccinimide (2.5 equiv) was added to a solution of the pentenyl glycosides in 1% aqueous acetonitrile (20 mL/mmol of glycoside). The progress of the reaction was monitored by TLC and quenched by addition of 10% aqueous sodium thiosulfate solution. Most of the solvent was removed in vacuo, and the residue was diluted with water and extracted with ether. The ethereal extract was dried (Na_2SO_4), filtered, and evaporated in vacuo. Column chromatography of the resulting residue afforded the respective pyranose.

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(19) An invention disclosure has been filed for the process described in this communication.

Synthesis and Reactivity of a Stable Nitrile Imine

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Nitrile imines, first prepared by Huisgen et al.,[1] have been widely used in organic synthesis and in regioselective 1,3-dipolar cycloadditions.[2] Up to now, they have only been observed by IR and UV in 85 K matrix[3a–c] or by mass[3c] and real time photoelectron spectroscopy[4] in the gas phase. Hydrolysis of alkali metal salts of diazomethane A,A′ (R = H), at −15 °C, with a concentrated weakly acidic buffer solution, leads to a colorless diazomethane isomer, which was originally considered to possess the nitrile imine structure B (R = E = H),[5] but which is now identified as the amino isocyanide C.[6] However, one can imagine that substituted salts of type A or A′ are suitable candidates for an electrophilic addition leading to B or B′ (Scheme I), and here we wish to report that, by using this hypothesis, we have been able to synthesize the first stable nitrile imine.

We have already shown that the reaction of the lithium salt of bis(diisopropylamino)phosphinodiazomethane (**1a**), with an acyl chloride, led to the formation of 1,3,4-oxadiazole **2a**, in addition to the expected diazoketone **3**.[7] Interestingly, the thiophosphine analogue **1b** quantitatively affords the five-membered ring heterocycle **2b**.[8] In order to rationalize the formation of products 2, one can postulate a 1,5-electrocyclization[9] of the first-formed carbonylnitrile imine **4** (Scheme II). In other words, N-acylation strongly competes with C-acylation in the case of phosphorus-substituted diazo lithium salts.

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(8) All new compounds afforded satisfactory elemental analysis. Selected spectroscopic data are the following. **2b**: ^{31}P NMR (C_6D_6) +45.5 ppm; ^1H NMR (C_6D_6) 1.55 (d, *J*(HH) = 6 Hz, 12 H, $CHCH_3$), 1.58 (s, 9 H, CCH_3), 1.70 (d, *J*(HH) = 6 Hz, 12 H, $CHCH_3$), 3.90 (d of sept, *J*(PH) = 17.8 Hz, *J*(HH) = 6 Hz, 4 H, CH); mass spectrum *m/e* 388 (M^+). **5a**: ^{31}P NMR ($CDCl_3$) +60.6 ppm; IR (C_6H_6) 2020 cm^{-1}. **5b**: ^{31}P NMR ($CDCl_3$) +68.8 ppm; IR (C_6H_6) 2040 cm^{-1}. **6a**.[11] **6b**: ^{31}P NMR (C_6D_6) +65.7 ppm; IR (C_6H_6) 2050 cm^{-1}. **7b**: ^{31}P NMR ($CDCl_3$) +68.5 ppm; IR (C_6H_6) 2020 cm^{-1}. **14**: ^{31}P NMR ($CDCl_3$) +75.0, +57.9, *J*(PP) = 3.6 Hz; ^{13}C NMR ($CDCl_3$) 42.13 (dd, *J*(PC) = 26.4 and 4.5 Hz, CH_2), 51.9 (s, CH_3O), 61.7 (dd, *J*(PC) = 27.1 and 5.3 Hz, CHring), 144.2 (d, *J*(PC) = 151.6 Hz, C=N), 173.4 (s, C=O); IR (KBr) 1740 cm^{-1} (CO), mass spectrum *m/e* 620 (M^+). **15**: ^{31}P NMR ($CDCl_3$) +95.8, +59.5, *J*(PP) = 4.34 Hz; ^{13}C NMR ($CDCl_3$) 51.6 (s, CH_3O), 120.8 (d, *J*(PC) = 27.2 Hz, =CH), 136.9 (t-like, *J*(PC) = 10.56 Hz, =C), 152.6 (dd, *J*(PC) = 148.7 and 3.0 Hz, C=N), 162.2 (s, CO); IR ($CDCl_3$) 1730 (CO), 1590 (C=N) cm^{-1}; mass spectrum *m/e* 618 (M^+).

(9) For a review see, for example: Taylor, E. C.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181.

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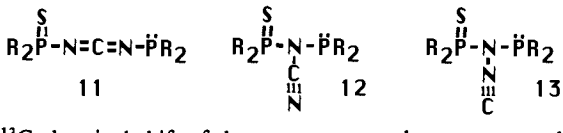
Table I. Selected Spectral Data for **9** and **10**[a]

		9	10
^{31}P NMR		+35.4 +99.9 (5.25)	+74.5 +72.8 (140.10)
^{13}C NMR	CH_3	22.53, 22.55, 23.01, 23.03, 24.03, 24.11, 24.46, 24.58	23.97, 24.05, 24.80, 24.82, 25.82, 25.85
	CH	46.00 (12.10), 46.46 (5.58)	47.34 (5.28), 48.52 (14.82)
	C	61.04 (99.00)	42.61 (36.71 and 74.03)
IR		2040 cm^{-1}	2028 cm^{-1}

[a] ^{31}P (121.5 MHz); ^{13}C (75.5 MHz); coupling constants with phosphorus, reported in hertz, are in parentheses.

It was of interest to study the reactivity of lithium salts **1** with various electrophiles. C-substitution was observed in the reaction of methyl iodide, trimethylchlorosilane, and triethylchlorogermane with **1a** and **1b** affording the diazo derivatives **5–7**.[8] Although the phosphinodiazolithium salt **1a** also reacts with the bis(diisopropylamino)chlorophosphine to give the bis(phosphino)diazomethane **8** (orange crystals, 85% yield, characterized by a single X-ray diffraction study),[7] the thiophosphino analogue **1b**, under the same experimental conditions, gives rise to the stable nitrile imine **9**, as white crystals, in 85% isolated yield.[10] The isomeric (thiophosphino)(phosphino)diazomethane structure **10** was readily ruled out by comparing spectral data of **9** with those of an authentic sample of **10** (Table I), prepared by the action of a stoichiometric amount of elemental sulfur on **8** (Scheme III).

Mass spectrum (EI; *m/e* calcd for $C_{25}H_{56}N_6P_2S$ 534.7768, found 534.7749, absence of $M^+ - N_2$ fragment) and osmometry in benzene (M = 525) were consistent with a monomeric structure. The ^{1}H NMR spectrum [1.08 (d, J(HH) = 6.8 Hz, 12 H, CH_3), 1.14 (d, J(HH) = 6.7 Hz, 12 H, CH_3), 1.27 (d, J(HH) = 6.8 Hz, 12 H, CH_3), 1.32 (d, J(HH) = 6.7 Hz, 12 H, CH_3), 3.46 (d of sept, J(PH) = 11.3 Hz, J(HH) = 6.7 Hz, 4 H, CH), 3.64 (d of sept, J(PH) = 19.73, J(HH) = 6.8 Hz, 4 H, CH)] clearly demonstrated that no diisopropylamino group migration occurred. A strong and broad absorption in the IR spectrum, at 2040 cm^{-1}, was in the range observed for nitrile imine in matrix.[3] Three other potential isomers **11**, **12**, and **13** need to be considered. However,



the ^{13}C chemical shift of the quaternary carbon was at too high a field position by far for all of these compounds, the phosphorus–carbon coupling constant was much too large for a ^3J as in **13**, and this signal would probably have been a doublet of a doublet in the case of **11** and **12**. Moreover, the phosphorus–phosphorus coupling constant was not at all in the range expected for a $^2J(\lambda^5P\text{-}\lambda^3P)$ (compounds **12** and **13**) as illustrated by derivative **10**.

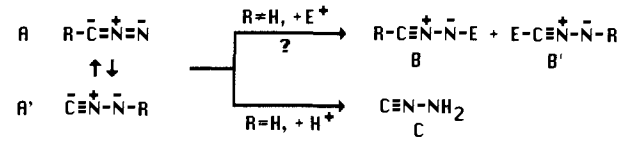
Lastly, the reactivity of **9** is quite usual for a nitrile imine since regioselective 1,3-dipolar cycloaddition takes place, at room temperature, with methyl acrylate and methyl propiolate leading to heterocycles **14** and **15**,[8] respectively, in near quantitative yield (Scheme IV).

The surprising thermal stability of nitrile imine **9** (mp 100 °C without decomposition) is probably due to steric factors and to the delocalization of the charges on the two phosphorus substituents as shown by the ^{31}P chemical shifts.

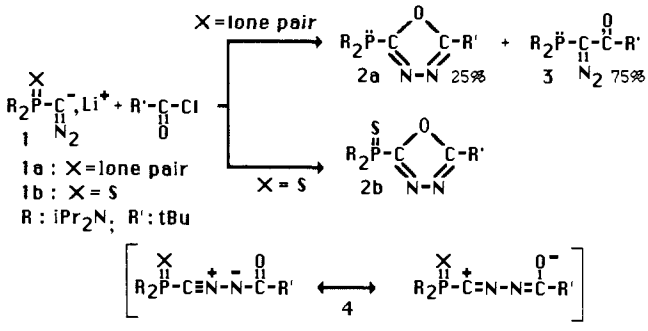
(10) In a typical experiment to a THF solution (30 mL) of thiophosphinodiazomethane **1b** (0.81 g, 2.6 mmol), at −78 °C, was added dropwise a stoichiometric amount of BuLi in hexane. After stirring for 30 min, at −78 °C, bis(diisopropylamino)chlorophosphine (0.71 g, 2.6 mmol), in THF (20 mL) was added. After warmup to room temperature and removal of the solvent, the residue was treated with pentane and filtrated. After evaporation, the yellow solid is washed several times with acetonitrile affording **9**, in analytically pure form, as white crystals (1.18 g, 85%, mp 100 °C).

(11) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781.

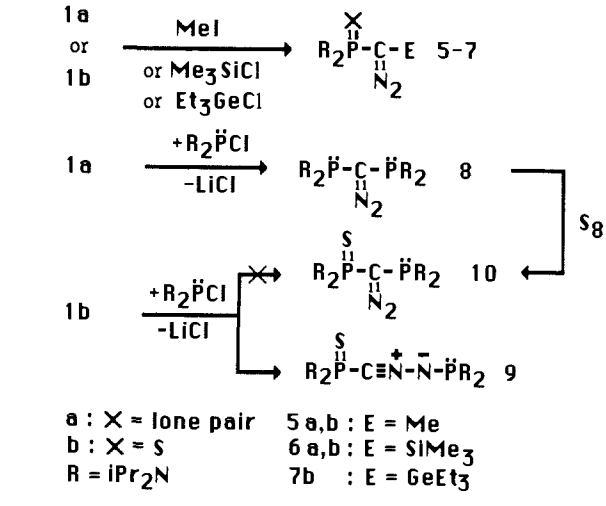
Scheme I



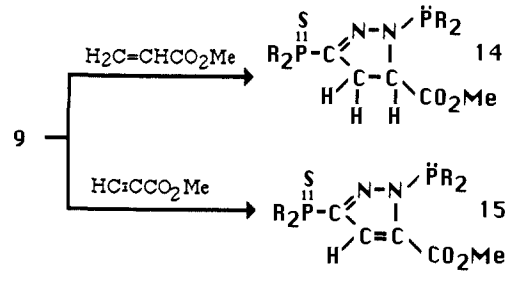
Scheme II



Scheme III



Scheme IV



Work is in progress concerning the use of phosphorus substituents to stabilize other species, hitherto believed to be only short-lived intermediates.

Acknowledgment. Thanks are due to Drs. I. Tkatchenko, Y. Dartiguenave, and M. Dartiguenave (Laboratoire de Chimie de Coordination du CNRS at Toulouse) for providing us with laboratory facilities after the destruction, on March 25, 1987, of the chemistry building of the University Paul Sabatier and to the CNRS (GRECO basses coordinences) for financial support of this work.

Registry No. 1a, 113533-26-9; **1b**, 113548-06-4; **2b**, 113533-19-0; **5a**, 107394-77-4; **5b**, 113533-20-3; **6a**, 97135-48-3; **6b**, 112550-05-7; **7b**, 113533-21-4; **8**, 105309-80-6; **9**, 113533-22-5; **10**, 113533-23-6; **14**, 113533-24-7; **15**, 113533-25-8; *t*-BuCOCl, 3282-30-2; $(i\text{-}Pr_2N)_2PCl$, 56183-63-2; $H_2C{=}CHCO_2Me$, 96-33-3; $HC{\equiv}CCO_2Me$, 922-67-8.