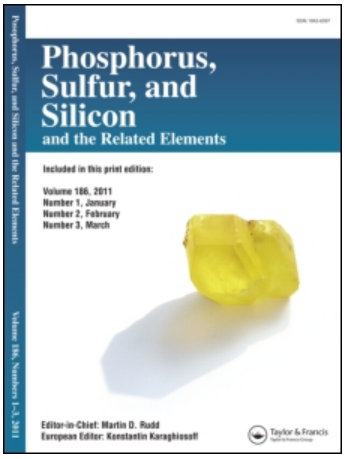

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Use of Phosphorus for Stabilizing Highly Reactive Organic Species: Nitrileimines and Pseudo-Diazoalkenes

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USE OF PHOSPHORUS FOR STABILIZING HIGHLY REACTIVE ORGANIC SPECIES: NITRILEIMINES AND PSEUDO-DIAZOALKENES

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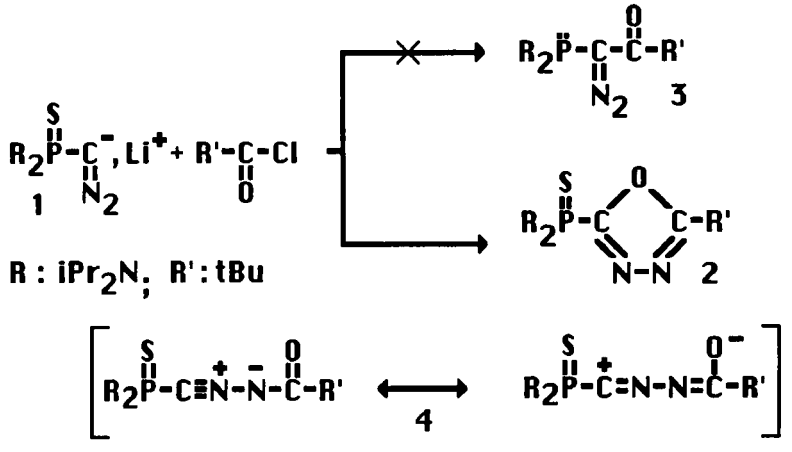
Abstract The synthesis and reactivity of several stable nitrile-imines bearing phosphorus groups are described. The use of stable diazomethylenephosphoranes in heterocyclic chemistry is reported.

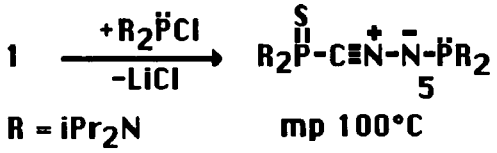
Diazoalkenes and nitrile-imines are two examples of species previously believed to exist only as transient intermediates. Here we report that, these species can be isolated and characterized, using the stabilizing properties of the phosphorus atom.

Nitrileimines, first prepared by Huisgen *et al*,[1] have been widely used in organic synthesis[2]. Up to now, they have only been observed at 85K, in matrix[3a-c], or by mass[3c] and real time photoelectron spectroscopy[4] in the gas phase.

We have shown that the reaction of the lithium salt of bis(diisopropylamino)thiophosphino diazomethane **1**, with an acyl chloride, led to the quantitative formation of 1,3,4-oxadiazole **2** and not to the expected diazoketone **3**[5].In order to rationalize the formation of heterocycle **2**, one can postulate a 1,5 electrocyclization[6] of the first-formed carbonylnitrile-imine **4**. Thus, N-acylation strongly competes with C-acylation in the case of phosphorus-substituted diazo lithium salts.

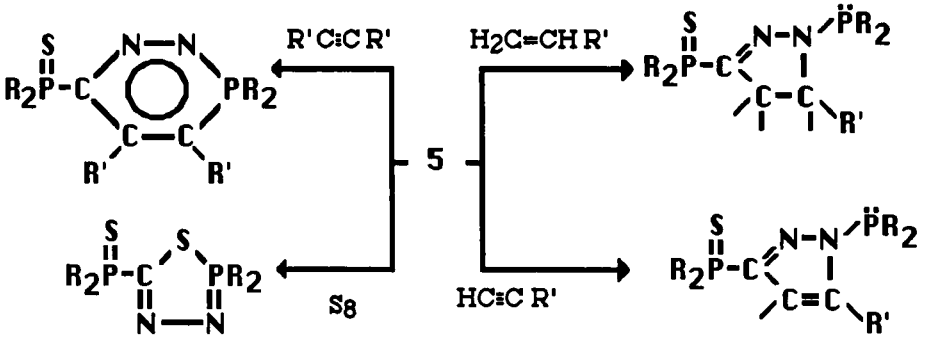


Indeed, the lithium salt **1** reacts with the bis(diisopropylamino)chlorophosphine to give the stable N-thiophosphino C-phosphino nitrileimine **5**, as white crystals, in 85% isolated yield[5].

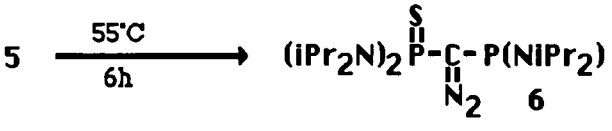


The nitrileimine structure was clearly established by osmometry in benzene, mass, infra-red and NMR spectroscopy as well as by an X-ray crystal structure analysis. As expected the CN and NN bond lengths are very short (1.17 and 1.24 Å respectively), but in contrast to what is generally believed, the -CNN- skeleton has not a zigzag structure but is almost linear (CNN : 173.5°).

Nitrileimine **5** is a very versatile species giving rise to, not only, [3+2] but also [4+2] and [4+1] cycloadditions as illustrated by the following scheme.



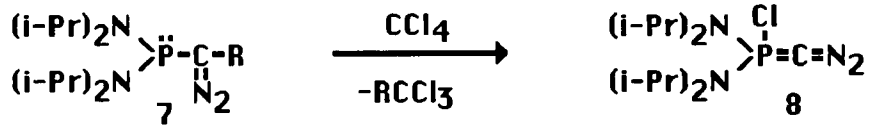
Nitrileimines are known to undergo rearrangements into carbodiimides or azines[3], or fragmentations into nitriles and nitrenes[3a], intramolecular ring closures have also been observed[7]. The possible existence of a diazomethane - nitrileimine equilibrium was reported in the 1960's[8], but was later considered to be highly controversial[9]. Nitrileimine - diazo rearrangements have been postulated[10] to explain the nature of the products obtained in the thermolysis of potential nitrileimine precursors; however, the nitrileimines have never been observed and apart from one case[10a] the resulting diazo derivatives were also not stable under the experimental conditions used.We have obtained the first evidence for this rearrangement, when a chloroform solution of nitrileimine **5** was heated at 55°C for 6 hours. The corresponding (thiophosphino)(phosphino)diazomethane **6** was obtained in near quantitative yield.



This result strongly suggests that in contrast to what is generally admitted, nitrileimines are the kinetic products of the electrophilic attack of diazo lithium salts, the isomeric diazo derivatives being the thermodynamic products.

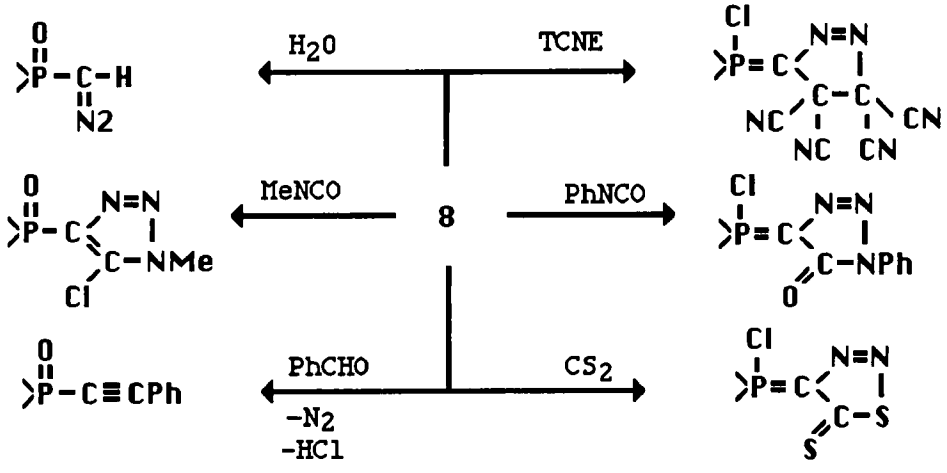
Diazoalkenes (>C=C=N_2) have attracted considerable interest in the last few years as potential generators of unsaturated carbenes[11], however, they have never been spectroscopically characterized. We report the synthesis and reactivity of a new type of phosphacumulene[12] possessing both phosphorus-ylide and diazo moieties. Since a Wittig reagent displays, to some extent, a doubly-bonded character, this is also an approach to unsaturated diazo derivatives.

Addition of a stoichiometric amount of carbon tetrachloride to a benzene solution of bis(diisopropylamino)phosphinodiazomethane **7**, at room temperature, leads, after loss of chloroform (or trimethylsilylchloroform), to the desired cumulene **8** in quantitative yield[13].



R = H, $SiMe_3$

Compound **8** is a water-sensitive, red, oily material. It is stable in solution for several weeks, but slowly decomposes in the absence of solvent. As expected, diazomethylenephosphoranes appear to be extremely versatile derivatives reacting either by the diazo group, or as a functionalized Wittig ylide as illustrated in the following scheme.



All the reactions described here occur in quantitative yield demonstrating the potential synthetic utility of this new type of phosphacumulene ylide.

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