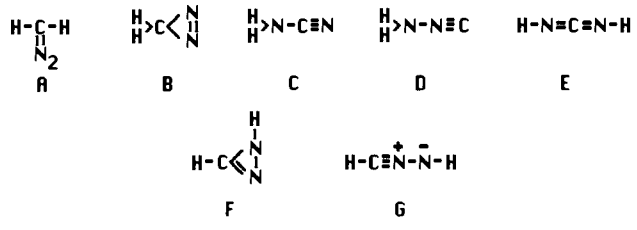
Synthesis and Reactivity of Stable Phosphorus-Substituted Nitrilimines. X-ray Crystal Structure of *C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine

Michel Granier, Antoine Baceiredo, Yves Dartiguenave, Michèle Dartiguenave, Marie-Joelle Menu, and Guy Bertrand*

Contribution from the Laboratoire de Chimie de Coordination du CNRS, 205, route de Narbonne, 31077 Toulouse Cêdex, France. *Received January 8, 1990*

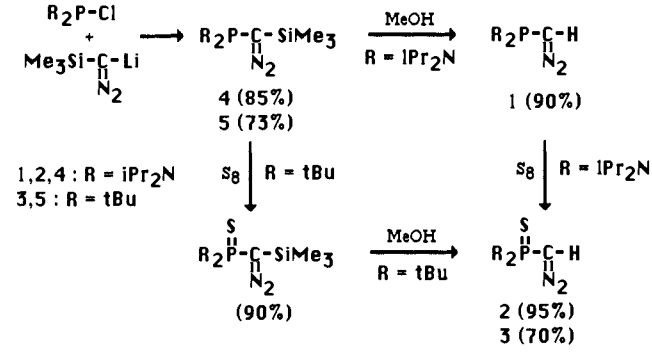
Abstract: Addition of bis(diisopropylamino)chlorophosphane to the lithium salt of [bis(diisopropylamino)phosphanyl]diazomethane (**6**), or of diphenyl- or bis(dimethylamino)chlorophosphane to the lithium salt of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**7**) led to bis[[bis(diisopropylamino)]phosphanyl]diazomethane (**9**), [bis(diisopropylamino)-thioxophosphoranyl](diphenylphosphanyl)diazomethane (**10**), or [bis(diisopropylamino)thioxophosphoranyl][bis(dimethylamino)phosphanyl]diazomethane (**11**), respectively. In contrast, lithium salt **7** reacted with bis(diisopropylamino)chlorophosphane or di-*tert*-butylchlorophosphane, affording *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**12**) or *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[di-*tert*-butylphosphanyl]nitrilimine (**13**). In the same way, the lithium salt of (di-*tert*-butylthioxophosphoranyl)diazomethane (**8**) reacted with bis(diisopropylamino)chlorophosphane, giving *C*-(di-*tert*-butylphosphoranyl)-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**14**). Nitrilimine **12** rearranged by heating into the isomeric diazo derivative **17**, while by photolysis bis(diisopropylamino)thioxophosphoranecarbonitrile (**19**) and tetrakis(diisopropylamino)cyclodiphosphazene (**20**) were obtained. The regio- and stereoselectivity of the reactions of **12** with methyl acrylate, methyl propiolate, dimethyl fumarate, dimethyl maleate, and methyl isocyanate were studied. An X-ray diffraction study of **12**, as a mixture of two enantiomers, is reported, and the geometrical parameters were compared with those predicted by theoretical calculations.

Diazomethane (A) is unique among small molecules in potentially having six structural isomers (B–G).[1] Of these isomers, diazirine (B) and cyanamide (C) are stable at room temperature, and derivatives of isocyanamide (D) and cardodiimide (E) have been reported, but, in contrast, no example of isodiazirine (F) is known. Concerning the last isomer, namely nitrilimine (G), transient derivatives were first prepared by Huisgen et al. in 1959.[2] They have been widely used in organic synthesis, in regioselective 1,3 dipolar cycloadditions.[3] Up to now, they have only been observed by IR and UV in 85 K matrix,[4a-c] by mass,[4c] or real-time photoelectron spectroscopy[5] in the gas phase.



Nitrilimines are commonly prepared, as transient species, by dehydrohalogenation of hydrazonoyl halides, dehydrogenation of aldehyde hydrazones, and thermolysis or photolysis of tetrazoles or related heterocycles such as oxadiazolinones, oxathiadiazolinones and sydnones.[3] Our approach is totally different and lies

Scheme I



on the attack of an electrophile at the terminal nitrogen atom of diazo lithium salts H. Indeed, although it is generally admitted that electrophiles react with salts of type H giving the corresponding substituted diazo derivative I, one can imagine that the first step of this reaction is in fact the formation of nitrilimines J which subsequently rearrange into I. The nitrilimine J–diazo I rearrangement has already been postulated[6] to explain the nature of the products obtained in the thermolysis of potential nitrilimine precursors.

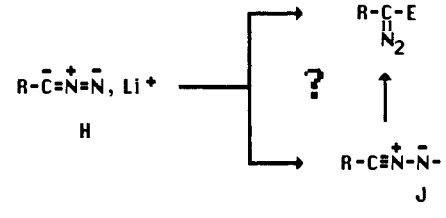


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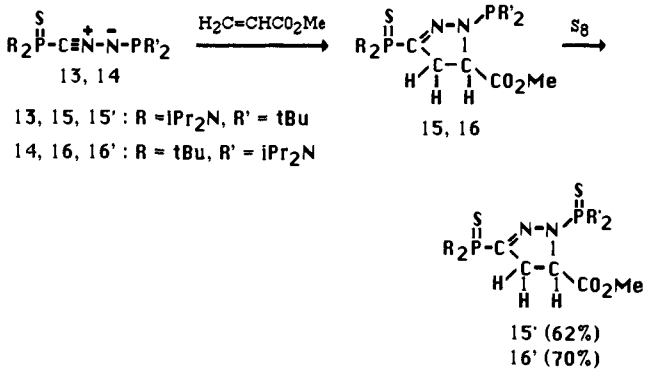
Table I. Reactivity of Diazolithium Salts **6–8** with Various Chlorophosphanes

diazolithium salt	chlorophosphane	product	no.
$(iPr_2N)_2PC(N_2)$-Li (**6**)	$(iPr_2N)_2PCl$	$(iPr_2N)_2PC(N_2)P(NiPr_2)_2$	**9**
$(iPr_2N)_2P(s)C$-$(N_2)Li$ (**7**)	Ph_2PCl	$(iPr_2N)_2P(s)C(N_2)PPh_2$	**10**
	$(Me_2N)_2PCl$	$(iPr_2N)_2P(s)C(N_2)P(NMe_2)_2$	**11**
	$(iPr_2N)_2PCl$	$(iPr_2N)_2P(s)C\equiv N^+-N^--P(NiPr_2)_2$	**12**
	tBu_2PCl	$(iPr_2N)_2P(s)C\equiv N^+-N^--PtBu_2$	**13**
$tBu_2P(s)C(N_2)Li$ (**8**)	$(iPr_2N)_2PCl$	$tBu_2P(s)C\equiv N^+-N^--P(NiPr_2)_2$	**14**

Scheme II



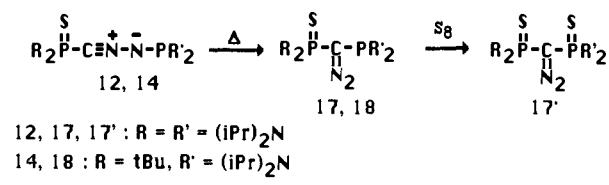
Here we wish to report that, by using this hypothesis, we have been able to synthesize several stable or relatively stable nitrilimines.[7] The influence of the nature of the C- and N-substituents on the stability of these species is discussed. Direct evidence for the isomerization of nitrilimines into diazo derivatives,[8] as well as for the photochemical cleavage into nitrile and nitrene are presented. The regioselectivity and the stereoselectivity of [2 + 3] cycloadditions are studied. The X-ray crystal structure of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine is reported.

Results

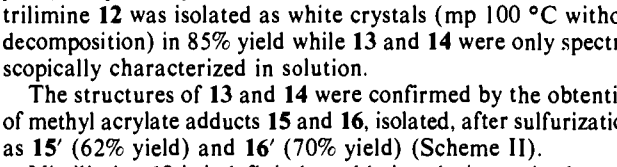
Three phosphorus-substituted diazomethane derivatives were chosen to study the scope and limitation of the synthesis of stable nitrilimine via electrophilic attack on diazo lithium salts: [bis(diisopropylamino)phosphanyl]diazomethane (**1**),[9] [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**2**), and (di-*tert*-butylthioxophosphoranyl)diazomethane (**3**). These compounds were prepared by using similar synthetic pathways, as indicated in Scheme I. In a first step, the lithium salt of the [trimethylsilyl]diazomethane[10] is added to the desired chlorophosphane affording (trimethylsilyl)(phosphanyl)diazomethanes **4** (85% yield)[9] and **5** (73% yield) which are stable enough to be purified by distillation. Then, methanolysis of the carbon–silicon bond of **4** leads to [bis(diisopropylamino)phosphanyl]diazomethane (**1**) (90% yield)[9a] which after treatment with elemental sulfur affords the thioxophosphoranyl analogue **2** (95% yield). To obtain the *tert*-butyl-substituted compound **3** (70% yield), it is necessary to cleave the carbon–silicon bond after oxidation of the phosphane **5** by elemental sulfur.

Various chlorophosphanes were added, at low temperature, to the corresponding lithium salts **6–8**, obtained by addition at −78 °C of BuLi to a THF solution of diazo derivatives **1–3**, and the reactions were monitored by ^{31}P NMR spectroscopy at −50 °C. Depending on the nature of both electrophiles and diazolithium salts, diazo derivatives **9–11** or alternatively nitrilimines **12–14** were obtained. The results are summarized in Table I. Diazo derivative **9**[11] was isolated in 85% yield while **10** and **11** were characterized in solution and isolated as bis(thioxophosphoranyl)diazo derivatives **10'** (50% yield) and **11'** (55% yield), respectively, after treatment with elemental sulfur. Nitrilimine **12** was isolated as white crystals (mp 100 °C without decomposition) in 85% yield while **13** and **14** were only spectroscopically characterized in solution.

Scheme III



Scheme IV



The structures of **13** and **14** were confirmed by the obtention of methyl acrylate adducts **15** and **16**, isolated, after sulfurization, as **15'** (62% yield) and **16'** (70% yield) (Scheme II).

Nitrilimine **12** is indefinitely stable in solution or in the solid state at room temperature. However, by heating, in chloroform solution, at 55 °C for 6 h, **12** rearranged into the isomeric diazo derivative **17** which was isolated as **17'** (80% yield) after treatment with elemental sulfur (Scheme III). Nitrilimine **13** is stable in solution for several weeks at room temperature, but attempted isolation led to a complex mixture of unidentified products. Nitrilimine **14** is completely transformed into the corresponding diazo **18**, after 72 h in solution at room temperature (note that this compound is also quite unstable and can only be characterized in solution).

The ease of handing of nitrilimine **12** has allowed a detailed study of its photolytic behavior and chemical reactivity. Under irradiation at 300 nm, **12** underwent a very clean cleavage leading to bis(diisopropylamino)thioxophosphoranecarbonitrile (**19**)[12] and tetrakis(diisopropylamino)cyclodiphosphazene **20**[13] in 86 and 25% isolated yield, respectively (Scheme IV). The 1,3-dipole **12** reacts at room temperature with methyl acrylate, methyl propiolate, and dimethyl fumarate, affording the corresponding 5-membered rings **21–23**. With dimethyl maleate, the reaction only occurred at 55 °C, and a mixture of trans and cis adducts **23** and **24** (in a 50/50 ratio) was obtained. Note that heating of **24** at 70 °C for 6 h did not lead to **23**. The ability of **12** to give [2 + 3] cycloadditions was not restricted to dipolarophiles featuring a carbon–carbon multiple bond, since it also reacted with 2 equiv of methyl isocyanate affording heterocycle **25**. The use of the stoichiometric amount of methyl isocyanate afforded a mixture of unreacted starting material **12** and five-membered ring **25**. Products **21–25** were characterized in solution and isolated after treatment with elemental sulfur as **21'–25'** (Scheme V). Although nitrilimine **12** is not very sensitive to water, filtration on silica gel afforded [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**2**) (82% yield) and the phosphane oxide **26**[14] (83% yield) (Scheme VI).

(7) For a preliminary account of this work, see: Sicard, G.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 2663.

(8) For a preliminary account of this work see: Granier, M.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1350.

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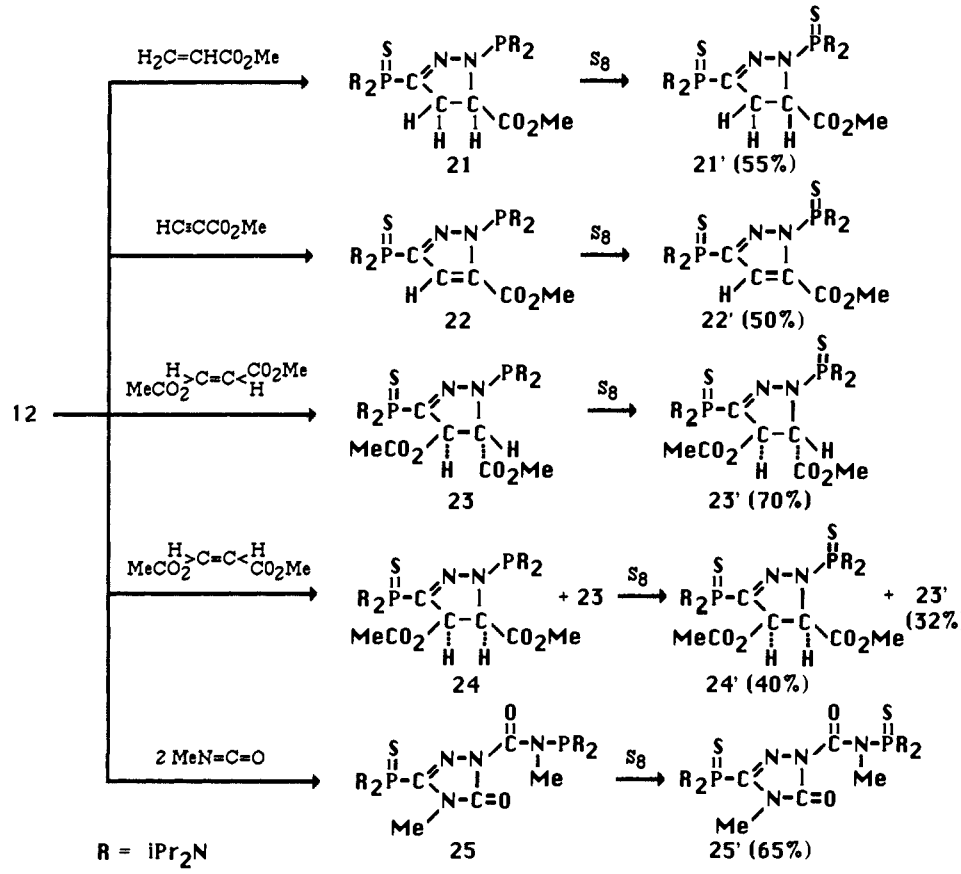
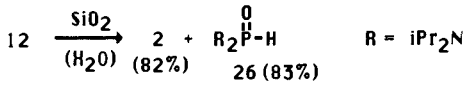
Scheme V



Scheme VI



Experimental Section

All experiments were performed in an atmosphere of dry argon or nitrogen. Melting points are uncorrected. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on Bruker AC80, WM250, or AM300 spectrometers. ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P NMR downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Beckman IR10 and a Perkin-Elmer lattice spectrometer (Mol 598), with a polystyrene film used for calibration. Mass spectra were obtained on a Ribermag R10 10E instrument. Photochemical reactions were performed in quartz tubes with a Rayonnet photochemical reactor. Conventional glassware was used. Liquid chromatography was done on silica gel.

Synthesis of [Bis(diisopropylamino)thioxophosphoranyl]diazomethane (2). To a pentane solution (30 mL) of [bis(diisopropylamino)phosphanyl]diazomethane (**1**)[9] (2.7 g, 10 mmol) was added an excess of elemental sulfur. After stirring overnight, at room temperature, the mixture was filtered, and **2** was isolated by column chromatography (pentane/ether 90/10, R_f = 0.5) as yellow crystals (2.89 g, 95% yield): mp 80–82 °C; ^{31}P NMR ($CDCl_3$) + 57.6; ^1H NMR ($CDCl_3$) 1.20 (d, J(HH) = 6.9 Hz, 12 H, CH_3), 1.31 (d, J(HH) = 6.9 Hz, 12 H, CH_3), 3.62 (sept d, J(HH) = 6.9 Hz, J(HP) = 19.0 Hz, 4 H, CHN), 3.86 (d, J(HP) = 10.6 Hz, 1 H, CHP); ^{13}C NMR ($CDCl_3$) 22.69, 22.72, 23.01, 23.05 (s, CH_3), 40.28 (d, J(CP) = 134.8 Hz, PC), 46.50 (d, J(CP) = 5.6 Hz, CHN); IR (KBr) 2090 cm^{-1} (C=N_2); mass spectrum, m/e 304 (M^+). Anal. Calcd for $C_{13}H_{29}N_4PS$: C, 51.29; H, 9.6; N, 18.40. Found: C, 51.08; H, 9.72; N, 18.31.

Synthesis of (Di-*tert*-butylthioxophosphoranyl)diazomethane (3). To a THF solution (20 mL) of di-*tert*-butylchlorophosphine (1.59 g, 8.8 mmol) was added dropwise, at −78 °C, the lithium salt of the (trimethylsilyl)diazomethane[10] (8.8 mmol) in THF solution (20 mL). After the solution was warmed up to room temperature and the solvent was removed, the residue was treated with pentane and filtered. Distillation gave (di-*tert*-butylphosphanyl)(trimethylsilyl)diazomethane (**5**) (1.66 g, 73% yield) as a red oil: bp 65 °C (10^{-1} mmHg); ^{31}P NMR (C_6D_6) + 19 ppm; ^1H NMR (C_6D_6) 0.15 (s, 9 H, CH_3Si), 1.25 (d, J(HP) = 13 Hz, 18 H, CH_3C); IR (C_6H_6) 2040 cm^{-1} (C=N_2); mass spectrum, m/e 258 (M^+). A benzene solution (20 mL) of phosphanyl diazomethane **5** (1 g, 3.9 mmol) and an excess of sulfur was stirred, at room temperature, for 2 h. After evaporation of the solvent, (di-*tert*-butylthioxophosphoranyl)(trimethylsilyl)diazomethane was isolated by column chromatography (ether) as a yellow oil (1.02 g, 90% yield): ^{31}P NMR (C_6D_6) +74.47 ppm; ^1H NMR (C_6D_6) 0.35 (s, 9 H, CH_3Si); 1.25 (d, J(HP) = 16 Hz, 18 H, CH_3C); IR (KBr) 2040 (C=N_2); 740 cm^{-1} (P=S); mass spectrum, m/e 290 (M^+). A pentane solution of this thioxophosphoranyldiazomethane (1g, 3.4 mmol) and an excess of methanol was stirred, at room temperature, for a week. After removal of the solvent, **3** was isolated by column chromatography (pentane/ether 85/15, R_f = 0.7) as yellow crystals (0.53 g, 70% yield): mp 100 °C; ^{31}P NMR ($CDCl_3$) +76.7 ppm; ^1H NMR ($CDCl_3$) 1.32 (d, J(HP) = 16.2 Hz, 18 H, CH_3C), 3.80 (d, J(HP) = 16.2 Hz, 1 H, CH); ^{13}C NMR ($CDCl_3$) 27.30 (d, J(CP) = 1.7 Hz, CH_3C), 28.99 (d, J(CP) 74 Hz, C=N_2), 39.74 (d, J(CP) = 46.9 Hz, CH_3C); IR ($CDCl_3$): 2100 cm^{-1} (C=N_2). Anal. Calcd for $C_9H_{19}N_2PS$: C, 49.52; H, 8.77; N, 12.83. Found: C, 49.59; H, 8.77; N, 12.78.

Synthesis of Diazolithium Salts 6–8. (General Method) To a THF solution (30 mL) of diazo derivatives **1–3** (2 mmol), at −78 °C, was added dropwise the stoichiometric amount of BuLi in hexane. After the mixtures were stirred for 30 min, at −78 °C, the lithium salts 6–8 were ready to use.

Synthesis of [Bis(diisopropylamino)thioxophosphoranyl](diphenylthioxophosphoranyl)diazomethane (10'). To a solution of diazo lithium salt **7** (2 mmol, 30 ml THF), at −78 °C, was added diphenylchlorophosphane (0.44 g, 2 mmol). After the solution was warmed up to room temperature, the [bis(diisopropylamino)thioxophosphoranyl](diphenylphosphanyl)diazomethane (**10**) was characterized in solution: ^{31}P NMR ($CDCl_3$) +66.20, −12.60 (J(PP) = 113.0 Hz); IR ($CDCl_3$) 2050 cm^{-1} (C=N_2). To this THF solution of **10** was added an excess of sulfur. After the solution was stirred overnight at room temperature, the excess of sulfur was filtered off, and the solvent was evaporated. The diazo **10'** was isolated by column chromatography (pentane/ether 90/10, R_f = 0.25) as yellow crystals (0.52 g, 50% yield): mp 113 °C dec; ^{31}P NMR ($CDCl_3$) +66.10, +43.60 (J(PP) = 28.8 Hz); ^1H NMR ($CDCl_3$) 1.34 (d, J(HH) = 7 Hz, 24 H, CH_3C), 4.02 (sept d, J(HH) = 7 Hz, J(HP) = 14.5 Hz, 4 H, CHN), 7.44–8.01 (m, 10 H, H_{arom}); ^{13}C NMR ($CDCl_3$) 24.20, 24.27, 24.55, 24.58 (s, CH_3), 48.06 (d, J(CP) = 6.04 Hz, CHN), 128.13 (d, J(CP) = 13.58 Hz, C_m), 131.73 (d, J(CP) = 3.02 Hz, C_p), 132.28 (d, J(CP) = 94.34 Hz, C_i), 132.74 (d, J(CP) = 11.32 Hz, C_o);

IR ($CDCl_3$) 2070, 2080 cm^{-1} (C=N_2); mass spectrum, *m/e* 520 (M^+). Anal. Calcd for $C_{25}H_{38}N_4P_2S_2$: C, 57.67; H, 7.36; N, 10.76. Found: C, 57.49; H, 7.42; N, 10.66.

Synthesis of [Bis(diisopropylamino)thioxophosphoranyl][dimethylamino)thioxophosphoranyl]diazomethane (11′). To a THF solution (30 mL) of lithium salt **7** (2 mmol), at −78 °C, was added bis(dimethylamino)chlorophosphane (0.31 g, 2 mmol). After the solution was warmed up to room temperature, the [bis(diisopropylamino)thioxophosphoranyl][bis(dimethylamino)phosphanyl]diazomethane (**11**) was characterized in solution: ^{31}P NMR ($CDCl_3$) +63.7, +106.0 (*J*(PP) = 104.9 Hz); IR ($CDCl_3$) 2040 cm^{-1} (C=N_2). To this THF solution of **11** was added an excess of sulfur. After the solution was stirred overnight, at room temperature, the excess of sulfur was filtered off, and the solvent was evaporated. The diazo **11′** was isolated by column chromatography (pentane/ether 90/10, R_f = 0.4), as yellow crystals (0.50 g, 55% yield); mp 90 °C; ^{31}P NMR ($CDCl_3$) +69.30, +77.66 (*J*(PP) = 47.9 Hz); ^{13}C NMR ($CDCl_3$) 24.23, 24.29, 24.79, 24.82 (s, *C*H_3C), 30.31 (dd, *J*(CP) = 45.7 and 47.1 Hz, C=N_2), 37.42 (d, *J*(CP) = 2.9 Hz, CH_3N), 48.21 (d, *J*(CP) = 6.3 Hz, CH); ^1H NMR ($CDCl_3$) 1.45 (d, *J*(HH) = 7 Hz, 12 H, CH_3C), 1.50 (d, *J*(HH) = 7 Hz, 12 H, CH_3C) 2.70 (d, *J*(HP) = 12.4 Hz, 12 H, CH_3N), 4.00 (sept d, *J*(HH) = 7 Hz, *J*(HP) = 14.7 Hz, CHN); IR ($CDCl_3$) 2070 cm^{-1} (C=N_2); mass spectrum, *m/e* 454 (M^+). Anal. Calcd for $C_{17}H_{40}N_6P_2S_2$: C, 44.91; H, 8.87; N, 18.49. Found: C, 45.04; H, 8.95; N, 18.40.

Synthesis of *C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (12). To a THF solution (30 mL) of **7** (2.6 mmol), at −78 °C, was added dropwise bis(diisopropylamino)chlorophosphane (0.71 g, 2.6 mmol). After the solution was warmed up to room temperature and the solvent was removed, the residue was treated with pentane and filtered. After evaporation, the yellow solid was washed several times with acetonitrile, affording **12** in analytically pure form as white crystals (1.18 g, 85% yield): mp 100 °C, ^{31}P NMR ($CDCl_3$) +35.4, +99.9 (*J*(PP) = 5.25 Hz); ^1H NMR ($CDCl_3$) 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 (sept d, *J*(HH) = 6.7 Hz, *J*(PH) = 11.3 Hz, 4 H, CH), 3.64 (sept d, *J*(HH) = 6.8 Hz, *J*(PH) = 19.7 Hz, 4 H. CH); ^{13}C NMR ($CDCl_3$) 22.53, 22.55, 23.01, 23.03, 24.11, 24.46, 24.58 (s, CH_3), 46.00 (d, *J*(PC) = 12.2 Hz, CHN), 46.46 (d, *J*(PC) = 5.6 Hz, CHN), 61.04 (d, *J*(PC) = 99.4 Hz, PC); IR (KBr) 2040 cm^{-1} (CNN): mass spectrum, (EI) *m/e* calcd for $C_{25}H_{56}N_6P_2S$ 534.7768; found 534.7749.

Synthesis of *C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[di-*tert*-butylphosphanyl]nitrilimine (13) and Obtention of 15′. To a THF solution (30 mL) of **7** (2 mmol), at −78 °C, was added di-*tert*-butylchlorophosphane (0.36 g, 2 mmol). After the solution was warmed up to room temperature, the nitrilimine **13** was characterized in solution: ^{31}P NMR (THF) +31.6, +119.0 ppm (*J*(PP) < 1 Hz); IR (THF) 2060 cm^{-1} (CNN). To this THF solution was added, at room temperature, a stoichiometric amount of methyl acrylate (0.18 g, 2 mmol). After stirring for 1 h at room temperature, the adduct **15** was characterized in solution: ^{31}P NMR (THF) +55.7, +91.0 ppm (*J*(PP) = 2.7 Hz); IR (THF) 1750 (C=O), 1530 (C=N) cm^{-1}. To the THF solution of **24** was added an excess of sulfur. After the solution was stirred overnight, at room temperature, the excess of sulfur was filtered off, and the solvent evaporated. **15′** was isolated by column chromatography (pentane/ether 50/50, R_f = 0.75) as white crystals (0.70 g; 62% yield): mp 108–109 °C; ^{31}P NMR ($CDCl_3$) +54.9, +102.1 (*J*(PP) = 2.9 Hz); ^1H NMR ($CDCl_3$) 1.33 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.33 (d, *J*(HP) = 15.8 Hz, 9 H, CH_3C), 1.36 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.37 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.38 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.44 (d, *J*(HP) = 16.6 Hz, 9 H, CH_3C), 3.14, 3.58, 4.93 (AMXP system, *J*(AM) = 18.4 Hz, *J*(AX) = 13.6 Hz, *J*(MX) = 7.1 Hz, *J*(AP) = 2 Hz, *J*(XP) = 2.4 Hz, 3 H, CH_2CH), 3.68 (s, 3 H, CH_3O), 3.80 (sept d, *J*(HH) = 6.9 Hz, *J*(HP) = 15.8 Hz, 2 H, CHN), 3.92 (sept d, *J*(HH) = 6.9 Hz, *J*(HP) = 15.8 Hz, 2 H, CHN); ^{13}C NMR ($CDCl_3$) 23.54, 23.69, 24.10, 24.18 (s, *C*H_3CH), 27.54 (s, *C*H_3C), 40.89 (d, *J*(PC) = 49.7 Hz, CH_3C), 41.18 (dd, *J*(PC) = 4.5 and 23.0 Hz, CH_2), 42.44 (d, *J*(PC) = 44.6 Hz, CH_3C), 47.32 (d, *J*(PC) = 6.2 Hz, CH_3CH), 47.51 (d, *J*(PC) = 5.6 Hz, CH_3CH), 51.90 (s, OCH_3), 62.07 (dd, *J*(PC) = 3.1 and 5.9 Hz, CH_{ring}), 152.91 (dd, *J*(PC) = 6.0 and 42.4 Hz, C=N), 172.33 (s, C=O); IR ($CDCl_3$) 1745 cm^{-1} (C=O). Anal. Calcd for $C_{25}H_{52}N_4O_2P_2S_2$: C, 52.98; H, 9.25; N, 9.88. Found: C, 53.12; H, 9.32; N, 9.78.

Synthesis of *C*-[Di-*tert*-butylthioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (14) and Obtention of 16′. To a THF solution (20 mL) of **8** (2 mmol), at −78 °C, was added dropwise a solution of bis(diisopropylamino)chlorophosphane (0.53 g, 2 mmol) in THF (10 mL). The nitrilimine **14** was characterized in solution at −60 °C: ^{31}P NMR (THF) +106.8, +80.9 (*J*(PP) = 6.2 Hz); IR (THF) 2030 cm^{-1} (CNN). To this solution of **14**, at −78 °C, was added methyl acrylate (0.18 g, 2 mmol). After the solution was warmed up to room temperature and the solvent was removed, the residue was treated with pentane and filtered. The adduct **16** was characterized in solution: ^{31}P NMR (pentane) +68.1, +79.8 (*J*(PP) = 3.0 Hz); IR (pentane) 1740 cm^{-1} (C=O). To this pentane solution of **16** was added an excess of sulfur. After stirring overnight at room temperature, the mixture was filtered and **16′** was isolated by column chromatography (pentane/ether 70/30, R_f = 0.5) as white crystals (0.80 g, 70% yield); mp 170–171 °C; ^{31}P NMR ($CDCl_3$) +59.4, +69.7 (*J*(PP) = 2.6 Hz); ^1H NMR ($CDCl_3$) 1.28 (d, *J*(HH) = 6.8 Hz, 6 H, C*H*$_3$CH), 1.33 (d, *J*(HH) = 6.8 Hz, 6 H, C*H*$_3$CH) 1.35 (d, *J*(HP) = 15.8 Hz, 9 H, CH_3C) 1.36 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.39 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.41 (d, *J*(HP) = 15.9 Hz, 9 H, CH_3C), 3.24, 3.40, 4.84 (AMXP system, *J*(AM) = 18.8 Hz, *J*(AX) = 12.9 Hz, *J*(MX) = 5.1 Hz, *J*(AP) = 3 Hz, *J*(XP) = 1.9 Hz, 3 H, CH_2CH), 3.68 (s, CH_3O), 3.74 (sept d, (*J*(HH) = 6.8 Hz, *J*(HP) = 16.9 Hz, 2 H, CHN), 4.13 (sept d, *J*(HH) = 6.9 Hz, *J*(HP) = 16.9 Hz, 2 H, CHN); ^{13}C NMR ($CDCl_3$) 22.91, 22.95, 24.28, 24.34, 24.54, 24.58, 24.60, 24.62 (s, *C*H_3CH), 27.19 (d, *J*(CP) = 1.8 Hz, *C*H_3C), 27.58 (d, *J*(CP) = 1.8 Hz, *C*H_3C), 39.40 (d, *J*(CP) = 41.2 Hz, CH_3C) 39.97 (d, *J*(CP) = 41.8 Hz, CH_3C), 44.43 (dd, *J*(CP) = 4.2 and 14.3 Hz, CH_2), 47.63 (d, *J*(CP) = 5.4 Hz, *C*HN), 47.79 (d, *J*(CP) = 6.9 Hz, *C*HN), 52.14 (s, *C*H_3O), 59.90 (dd, *J*(CP) = 3.0 and 11.9 Hz, CH_{ring}), 147.15 (dd, *J*(CP) = 8.5 and 75.5 Hz, C=N), 172.50 (s, C=O); IR ($CDCl_3$) 1750 (C=O), 1615 cm^{-1} (C=N). Anal. Calcd for $C_{25}H_{52}N_4O_2P_2S_2$: C, 52.98; H, 9.25; N, 9.88. Found: C, 53.06; H, 9.28; N, 9.83.

Rearrangement of Nitrilimine 12 into [Bis(diisopropylamino)thioxophosphoranyl][bis(diisopropylamino)phosphanyl]diazomethane (17) and Obtention of 17′. A chloroform solution (10 mL) of nitrilimine **12** (0.5 g, 0.94 mmol) was heated at 55 °C for 6 h. According to ^{31}P NMR, the isomeric diazo derivative **17** was quantitatively formed, and it was used without further purification: ^{31}P NMR ($CDCl_3$) +71.6, +72.4 (*J*(PP) = 140 Hz); ^{13}C NMR ($CDCl_3$) 23.97, 24.05, 24.80, 24.82, 25.82, 25.85 (s, CH_3), 42.76 (dd, *J*(PC) = 36.7 and 74.0 Hz, C=N_2), 47.42 (d, *J*(PC) = 5.1 Hz, CHN), 48.61 (d, *J*(PC) = 14.9 Hz, CHN); IR (toluene) 2028 cm^{-1} (C=N_2). A toluene solution of **17** (0.5 g, 0.94 mmol) and elemental sulfur (0.03 g, 0.94 mmol) was heated for 8 h at 65 °C. After removal of the solvent under vacuum, the residue was recrystallized in pentane affording **17′** (0.42 g, 80% yield), as yellow green crystals: mp 160–162 °C; ^{31}P NMR ($CDCl_3$) +72.2; ^1H NMR (C_6D_6) 1.35 (d, *J*(HH) = 7 Hz, 24 H, CH_3), 1.48 (d, *J*(HH) = 7 Hz, 24 H, CH_3), 4.10 (sept d. *J*(HH) = 7 Hz, *J*(HP) = 14 Hz, 8 H, CHN); ^{13}C NMR ($CDCl_3$) 24.35, 24.92 (s, CH_3), 48.14 (d, *J*(PC) = 2.7 Hz, CHN), 48.18 (d, *J*(PC) = 2.9 Hz, CHN), CN_2 is not observed; IR (KBr) 2051 cm^{-1} (CN_2); mass spectrum, *m/e* 566 (M^+). Anal. Calcd for $C_{25}H_{56}N_6P_2S_2$: C, 52.97; H, 9.96; N, 14.83. Found C, 53.10; H, 10.00; N, 14.80.

Rearrangement of 14 into (Di-*tert*-butylthioxophosphoranyl)[bis(diisopropylamino)phosphanyl]diazomethane (18). Nitrilimine **14** was totally rearranged into the isomeric diazo derivative **18** after a THF solution was stirred for 72 h at room temperature. **18** was characterized in solution: ^{31}P NMR (THF) +71.1, +76.8 (*J*(PP) = 91.8 Hz); IR (THF) 2030 cm^{-1} (C=N_2). Attempted isolation failed.

Photolysis of 12. A benzene solution (10 mL) of nitrilimine **12** (0.6 g, 1.1 mmol) was irradiated at 300 nm. The reaction was monitored by ^{31}P NMR and was complete after 14 h. The solvent was removed under vacuum. Cyclodiphosphazene **20**[13] was purified by crystallization from chloroform as white crystals (0.13 g, 25% yield), while **19**[12] was isolated by column chromatography (pentane/ether 95/5, R_f = 0.4) as white crystals (0.28 g, 86% yield). Their spectroscopic data were compared to those of authentic samples.[12,13]

Reaction of 12 with Methyl Acrylate, Methyl Propiolate, and Dimethyl Fumarate. To a pentane solution (10 ml) of **12** (0.53 g, 1 mmol), was added, at room temperature, a stoichiometric amount of dipolarophile. The reaction was monitored by ^{31}P NMR, and the adducts **21–23** were characterized in solution. Then, to the pentane solutions of **21–23** was added an excess of sulfur. After stirring for 2 h at room temperature, the mixture was filtered, and the corresponding thioxophosphoranyl products **21′–23′** were isolated as indicated below. **21**: ^{31}P NMR ($CDCl_3$) +75.0, +57.9 (*J*(PP) = 3.57 Hz); ^1H NMR ($CDCl_3$) 1.07 (d, *J*(HH) = 6.4 Hz, 6 H, C*H*$_3$CH), 1.13 (d, *J*(HH) = 6.4 Hz, 12 H, C*H*$_3$CH), 1.16 (d, *J*(HH) = 6.4 Hz, 6 H, C*H*$_3$CH), 1.20 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 1.33 (d, *J*(HH) = 7.0 Hz, 12 H, C*H*$_3$CH), 1.72 (d, *J*(HH) = 6.9 Hz, 6 H, C*H*$_3$CH), 3.22 (dddd, *J*(HH) = 15.8 Hz and 9.3 Hz, *J*(PH) = 4.2 and 2.2 Hz, 1 H, CH_2), 3.52 (sept d, *J*(HH) = 6.4 Hz, *J*(PH) = 13.8 Hz, 4 H, CHN), 3.68 (s, 3 H, CH_3O), 3.85 (sept d, *J*(HH) = 6.9 Hz, *J*(PH) = 17.3 Hz, 2 H, CHN), 3.89 (sept d, *J*(HH) = 7.0 Hz, *J*(PH) = 18.1 Hz, 2 H, CHN), 4.34 (ddd, *J*(HH) = 13.7 and 9.3 Hz, *J*(PH) = 9.0 Hz, 1 H, CH_{ring}), one of the CH_2 proton is under the signal at 3.52; ^{13}C NMR ($CDCl_3$) 23.39, 23.44, 23.47, 23.55, 23.83, 23.93, 23.97, 24.05 (s, *C*H_3CH), 42.13 (dd, *J*(CP) = 26.4 and 4.52 Hz, CH_2), 47.05 (d, *J*(CP) = 6.8 Hz, CHN), 47.14 (d, *J*(CP) = 6.8 Hz,

CHN), 51.90 (s, CH_3O), 61.72 (dd, J(CP) = 27.17 and 5.3 Hz, CH_{ring}), 144.20 (d, J(CP) = 151.6 Hz, C=N), 173.36 (s, C=O); IR ($CDCl_3$) 1740 cm^{-1} (C=O); mass spectrum, m/e 621 (M^+). **21'** was purified by crystallization in cold hexane as colorless crystals (0.36 g, 55% yield); mp 119° C; ^{31}P NMR ($CDCl_3$) +61.6, +57.9 (J(PP) = 3.6 Hz); ^1H NMR ($CDCl_3$): 1.46 (d, J(HH) = 6.9 Hz, 6 H, CH_3CH), 1.52 (d, J(HH) = 6.9 Hz, 6 H, CH_3CH), 1.53 (d, J(HH) = 6.7 Hz, 6 H, CH_3CH), 1.56 (d, J(HH) = 6.7 Hz, 6 H, CH_3CH), 1.57 (d, J(HH) = 7.0 Hz, 6 H, CH_3CH), 1.58 (d, J(HH) = 7.0 Hz, 6 H, CH_3CH), 1.59 (d, J(HH) = 6.9 Hz, 6 H, CH_3CH), 1.61 (d, J(HH) = 6.9 Hz, 6 H, CH_3CH), 3.29 (dddd, J(HH) = 6.3 and 18.1 Hz, J(PH) = 1.7 and 3.3 Hz, 1 H, $CH_{2\,ring}$), 3.85 (s, 3 H, CH_3O), 3.93 (m, 4 H, CHN), 4.13 (sept d, J(HH) = 7.0 Hz, J(PH) = 14.2 Hz, 2 H, CHN), 4.35 (sept d, J(HH) = 6.9 Hz, J(PH) = 14.6 Hz, 2 H, CHN), 5.04 (ddd, J(HH) = 13.8 and 6.3 Hz, J(PH) = 3.3 Hz, 1 H, CH_{ring}), one of the CH_2 proton is under the signal at 3.93; ^{13}C NMR ($CDCl_3$) 22.86, 22.90, 23.71, 23.75, 23.95, 23.98, 24.13, 24.18, 24.43, 24.49, 24.54, 24.60, 24.71, 24.74, 24.80, 24.85 (s, CH_3CH), 41.87 (dd, J(CP) = 25 and 4.9 Hz, CH_2), 47.53 (d, J(CP) = 4 Hz, CHN), 47.60 (d, J(CP) = 5.2 Hz, CHN), 47.96 (d, J(CP) = 5.3 Hz, CHN), 48.08 (d, J(CP) = 6.6 Hz, CHN), 52.20 (s, CH_3O), 60.5 (dd, J(CP) = 12 and 4.2 Hz, CH_{ring}), 150.20 (dd, J(CP) = 149.4 and 8.3 Hz, C=N), 173.0 (s, C=O); IR (KBr) 1750 cm^{-1} (C=O). Anal. Calcd for $C_{29}H_{62}N_6O_2P_2S_2$: C, 53.35; H, 9.57; N, 12.87. Found: C, 53.48; H, 9.60; N, 12.82. **22**: ^{31}P NMR ($CDCl_3$) +95.82, +59.52 (J(PP) = 4.34 Hz); ^1H NMR ($CDCl_3$) 1.02 (d, J(HH) = 6.7 Hz, 12 H, CH_3CH), 1.18 (d, J(HH) = 6.9 Hz, 12 H, CH_3CH) 1.20 (d, J(HH) = 6.7 Hz, 12 H, CH_3CH), 1.35 (d, J(HH) = 6.9 Hz, 12 H, CH_3CH), 3.59 (sept d, J(PH) = 12.9 Hz, J(HH) = 6.7 Hz, 4 H, CHN), 3.79 (s, 3 H, CH_3O), 3.94 (sept d, J(PH) = 15.7 Hz, J(HH) = 6.9 Hz, 4 H, CHN), 7.58 (dd, J(HP) = 1.9 Hz, J(HP) = 0.6 Hz, 1 H, CH=); ^{13}C NMR ($CDCl_3$) 22.46, 22.97, 23.32, 24.11, 24.64, 24.96 (s, CH_3CH), 47.09 (d, J(CP) = 4.4 Hz, CHN), 47.30 (d, J(CP) = 5.6 Hz, CHN), 51.64 (s, CH_3O), 120.80 (d, J(CP) = 27.2 Hz, CH=), 136.96 (t like, J(CP) = 10.57 Hz, C=CH), 152.58 (dd, J(CP) = 148.67 and 3.8 Hz, C=N), 160.21 (s, C=O); IR ($CDCl_3$) 1730 cm^{-1} (C=O). **22'** was purified by column chromatography (pentane/ether 90/10, R_f = 0.5) as yellow crystals (0.325 g, 50% yield); mp 112° C; ^{31}P NMR ($CDCl_3$) +64.94, +59.1 (J(PP) = 2.33 Hz); ^1H NMR ($CDCl_3$) 1.22 (d, J(HH) = 6.9 Hz, 12 H, CH_3CH), 1.26 (d, J(HH) = 6.9 Hz, 12 H, CH_3CH), 1.38 (d, J(HH) = 6.9 Hz, 24 H, CH_3CH), 3.86 (s, 3 H, CH_3O), 3.87 (sept d, J(PH) = 15.9 Hz, J(HH) = 6.9 Hz, 8 H, CHN), 7.29 (dd, J(HP) = 2.05 and 0.84 Hz, 1 H, CH=); ^{13}C NMR ($CDCl_3$) 23.43, 23.48, 23.59, 23.62, 23.65, 23.69, 23.79, 23.82 (s, CH_3CH), 47.35 (d, J(CP) = 5.3 Hz, CHN), 48.75 (d, J(CP) = 6 Hz, CHN), 52.30 (s, CH_3O), 115.98 (dd, J(CP) = 23.7 and 3 Hz, CH=), 141.53 (dd, J(CP) = 11.32 and 8.3 Hz, C=) 153.2 (dd, J(CP) = 150 and 7 Hz, C=N), 162.52 (s, C=O); IR ($CDCl_3$) 1600 (C=N), 1730 cm^{-1} (C=O); mass spectrum, m/e 650 (M^+). Anal. Calcd for $C_{29}H_{60}N_6O_2P_2S_2$: C, 53.51; H, 9.29; N, 12.91. Found: C, 53.63; H, 9.30; N, 12.87. **23**: ^{31}P NMR (pentane) +76.07, +56.70 (J(PP) = 3.6 Hz). **23'** was recrystallized from cold hexane (0.50 g, 70% yield) as colorless crystals: mp 140 °C; ^{31}P NMR ($CDCl_3$) +61.15, +57.17; ^1H NMR ($CDCl_3$) 1.36 (d, J(HH) = 6.9 Hz, 24 H, CH_3CH), 1.38 (d, J(HH) = 6.9 Hz, 24 H, CH_3CH), 3.72 (s, 6 H, CH_3O), 4.01 (ddd, (J(HH) = 6.2 Hz, J(HP) = 2.8 and 1.5 Hz, 1 H, CH_{ring}), 4.07 (sept d, J(HH) = 6.9 Hz, J(HP) = 15.6 Hz, 8 H, CHN), 4.97 (dd, J(HH) = 6.2 Hz, J(HP) = 2.5 Hz, 1 H, CH_{ring}); ^{13}C NMR ($CDCl_3$) 23.27, 23.31, 23.57, 23.60, 23.75, 23.80, 23.91, 23.95, 24.01, 24.03, 24.22, 24.27, 24.38, 24.42, 24.56, 24.61 (s, CH_3CH), 47.42 (d, J(CP) = 6.4 Hz, CHN), 47.66 (d, J(CP) = 6.0 Hz, CHN), 47.74 (d, J(CP) = 5.4 Hz, CHN), 47.96 (d, J(CP) = 6.0 Hz, CHN), 52.65, 52.69 (s, CH_3O), 57.82 (dd, J(CP) = 24.5 and 4.2 Hz, CH_{ring}), 66.52 (dd, J(CP) = 3.2 and 12.1 Hz, CH_{ring}), 147.76 (dd, J(CP) = 148.3 and 7.9 Hz, C=N), 170.56, 171.25 (s, C=O); IR ($CDCl_3$) 1740, 1749 (C=O) 690 cm^{-1} (P=S), mass spectrum, m/e 710 (M^+). Anal. Calcd for $C_{31}H_{64}N_6O_4P_2S_2$: C, 52.37; H, 9.07; N, 11.82. Found: C, 52.30; H, 9.09; N, 11.71.

Reaction of 12 with Dimethyl Maleate. A chloroform solution (10 mL) of **12** (0.53 g, 1 mmol) was heated at 55 °C for 2 h. We obtained a mixture of cis adduct **24** (^{31}P NMR +82.33, +59.14 (J(PP) = 2.7 Hz) and trans adduct **23** in a 50/50 ratio (according to ^{31}P NMR). To this chloroform solution was added an excess of sulfur. After the solution was stirred for 2 h, at room temperature, the excess of sulfur was filtered off and the solvent evaporated. The cis adduct **24'** was purified by column chromatography (pentane/ether 70/30, R_f = 0.35), as a colorless oil (0.28 g, 40% yield): ^{31}P NMR ($CDCl_3$) +60.23, 63.43 (J(PP) = 2.4 Hz); ^1H NMR ($CDCl_3$) 1.37 (m, 48 H, CH_3CH), 3.66 (s, 3 H, CH_3O), 3.67 (s, 3 H, CH_3O), 4.11 (sept d, J(HH) = 7.1 Hz, J(HP) = 14.2 Hz, 8 H, CHN), 4.47 (d, J(HH) = 12.5 Hz, 1 H, CH_{ring}), 5.01 (dd, J(HH) = 12.5 Hz, J(HP) = 1.6 Hz, 1 H, CH_{ring}); ^{13}C NMR ($CDCl_3$) 23.24, 23.28, 23.82, 23.88, 23.94, 24.00, 24.20, 24.25, 24.29, 24.33. 24.38, 24.42, 24.45, 24.49, 24.60, 24.62 (s, CH_3), 47.37 (d, J(CP) = 6.3 Hz, CHN), 47.66 (d, J(CP) = 5.7 Hz, CHN), 47.82 (d, J(CP) = 6.3 Hz, CHN), 47.98 (d, J(CP) = 6.5 Hz, CHN), 52.20, 52.38 (s, CH_3O), 58.55 (dd, J(CP) = 4.8 and 23.7 Hz, CH_{ring}), 65.61 (dd, J(CP) = 12.6 and 2.9 Hz, CH_{ring}), 147.53 (dd, J(CP) = 150.9 and 7.5 Hz, C=N), 168.33, 169.11 (s, C=O); IR ($CDCl_3$) 1740 (C=O), 1605 cm^{-1} (C=N); mass spectrum, m/e 710 (M^+). Anal. Calcd for $C_{31}H_{64}N_6O_4P_2S_2$: C, 52.37; H, 9.07; N, 11.82. Found: C, 52.28; H, 9.11; N, 11.79.

Reaction of 12 with Methyl Isocyanate. To a pentane solution (10 mL) of **12** (0.53 g, 1 mmol) was added, at room temperature, 2 equiv of methyl isocyanate (0.12 g). After the solution was stirred overnight at room temperature, heterocycle **25** was characterized in solution: ^{31}P NMR (pentane) +100.9, +47.5. To this pentane solution was added an excess of sulfur. After stirring overnight, at room temperature, the mixture was filtered, and **25'** was isolated by column chromatography (pentane/ether 50/50, R_f = 0.8), as colorless crystals (0.44 g, 65% yield); mp 204 °C; ^{31}P NMR ($CDCl_3$) +70.07, +46.7; ^1H NMR ($CDCl_3$): 1.31 (d, J(HH) = 6.8 Hz, 12 H, CH_3CH), 1.34 (d, J(HH) = 6.8 Hz, 24 H, CH_3CH), 1.39 (d, J(HH) = 6.8 Hz, 12 H, CH_3CH), 3.11 (d, J(HP) = 10.6 Hz, 3 H, CH_3N), 3.61 (s, 3 H, CH_3N), 3.79 (sept d, J(HH) = 6.8 Hz, J(PH) = 16.7 Hz, 4 H, CHN), 4.09 (sept d, J(HH) = 6.8 Hz, J(PH) = 17.0 Hz, 4 H, CHN); ^{13}C NMR ($CDCl_3$) 23.67, 23.72, 23.76, 23.78, 23.84, 23.88, 23.96, 23.98 (s, CH_3CH), 30.95 (s, CH_3N), 37.55 (d, J(CP) = 6.8 Hz, CH_3N), 48.23 (d, J(CP) = 6.8 Hz, CHN), 48.53 (d, J(CP) = 5.3 Hz, CHN), 145.16 (d, J(CP) = 157 Hz, C=N), 149.89 (s, C=O), 153.20 (d, J(CP) = 4.5 Hz, C=O); IR (KBr) 1765 (C=O), 1680 cm^{-1} (C=N); mass spectrum, m/e 680 (M^+). Anal. Calcd for $C_{29}H_{62}N_8O_2P_2S_2$: C, 51.15; H, 9.18; N, 16.46. Found: C, 51.00; H, 9.16; N, 16.45.

Reaction of 12 with Silica Gel. A pentane solution (5 mL) of **12** (0.53 g, 1 mmol) was filtrated on silica gel. **2** (0.25 g, 82% yield) was obtained as yellow crystals (pentane/ether 90/10, R_f = 0.5), and then **26** (0.20 g, 83% yield) was isolated as white crystals (ether, R_f = 0.1). Their spectroscopic data were compared to those of authentic samples.[14]

X-ray Crystallographic Analysis of Nitrilimine 12. Crystals suitable for X-ray analysis were obtained by slow crystallization in pentane, at −20 °C. The data were collected at 20 °C by using an Enraf-Nonius CAD4 Diffractometer, equipped with a graphite-monochromated Mo Kα radiation. The cell parameters were determined from a least-squares fitting of 25 centered reflections with 2θ between 17 and 30°, space-group determination by nonsystematic absences was identified as $P(-1)$. A summary of crystal and intensity collection data is given in Table II. Successful refinement was done in the centrosymmetric space group. Independent reflections (6596) were measured, 5356 with $I > 3\sigma(I)$ measured using $\theta/2\theta$ scans for 2θ from 2 to 44°. Intensities of three reflections measured every hour during data collection varied less than 15%. The data were corrected for the Lorentz effect, polarization, and absorption. Structure solved with SHELX86, refinement done by full-matrix least-squares based on $|F_o|$, by using the SHELX76 package.[15] After an anisotropic refinement for all non-H atoms, hydrogen atoms

Table II. Crystallographic Data for Nitrilimine **12**

formula	$SP_2N_6C_{25}H_{56}$
cryst syst	triclinic
space group	$P(-1)$
a, Å	16.933 (3)
b, Å	17.186 (3)
c, Å	14.048 (2)
α	113.761 (14)
β	113.781 (14)
γ	69.848 (15)
V, Å^3	3342 (2)
Z	4
d calcd, g/cm3	1.0625
μ (Mo Kα), cm^{-1}	1.77
temp, °C	20 ± 2
scan method	$\theta/2\theta$
data collcn range (θ), deg	$1 < \theta < 22.$
no. of reflcns measured	6596
no. of unique data with $(I) > 3\sigma(I)$	5356
no. of params refined	613
R^a	0.0398
$R_w{}^b$	0.0397

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

(14) Scherer, O.; Glabel, W. *Chem. Ztg.* **1975**, *99*, 246.
(15) Sheldrick, G. M. *SHELX76, Program for crystal structure determination*, University of Cambridge, England, 1976.

Table III. Selected Spectral Data for Diazo **10**, **11**, **17**, and **18**, and Nitrilimines **12–14**[a]

	$\delta^{31}P$				
no.	λ^5P	λ^3P	J(PP)	^{13}C (J(PC))	IR
10	+66.2	−12.60	113.0		2050
11	+63.7	+106.0	104.9		2040
12	+35.4	+99.9	5.2	61.04 (99.4)	2040 (br s)
13	+31.6	+119.0	<1		2060 (br s)
14	+80.9	+106.8	6.2		2030 (br s)
17	+72.4	+71.6	140.0	42.76 (74.0, 36.7)	2028
18	+76.8	+71.1	91.8		2030

[a] ^{31}P NMR (121.5 MHz); ^{13}C NMR (75.5 MHz); coupling constants are reported in Hz and infrared frequencies in cm^{-1}.

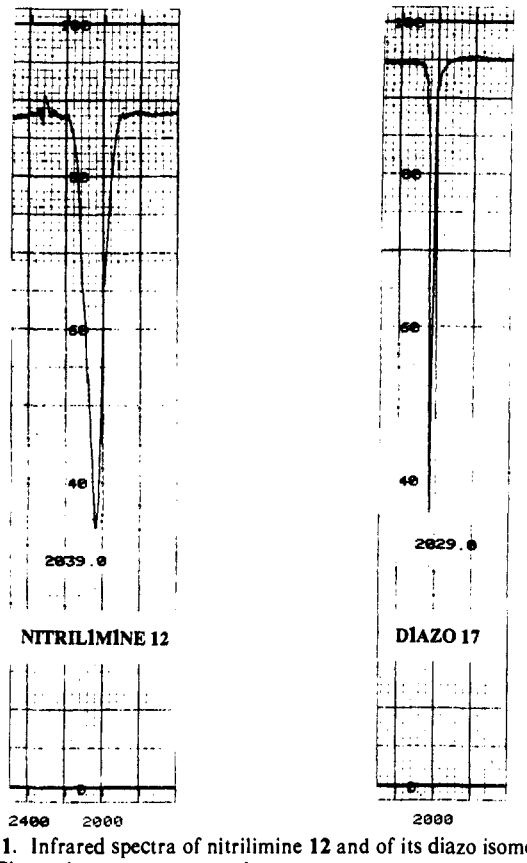


Figure 1. Infrared spectra of nitrilimine **12** and of its diazo isomer **17**, in $CDCl_3$, at the same concentration.

were fixed at idealized positions (C–H = 0.97 Å kept fixed) and repositioned after each least-squares cycle. Final parameters are $R = 0.0398$, $R_w = 0.0397$[16] and $S = 1.129$ for 613 variables, largest residual electron density on final DF map = 0.2 e $Å^{-3}$. Scattering factor, from Cromer and Mann,[17] for P, N, and C and, from Stewart, Davidson, and Simpson,[18] for H were employed.

Discussion

Spectroscopic Characterization of Nitrilimines. Since it is generally known that diazolithium salts react with electrophiles affording substituted diazo derivatives,[1b,19] it was of primary interest to have a quick spectroscopic method to differentiate nitrilimines from diazo derivatives. In this respect, ^{31}P NMR appeared to be a very powerful tool. Indeed, it is quite clear from Table III, that the $^2J(\lambda^5P - \lambda^3P)$ in diazo **10**, **11**, **17**, and **18** are much larger than $^4J(\lambda^5P - \lambda^3P)$ in nitrilimines **12–14**. The ^{31}P chemical shift of the λ^5P is also a good indication when diisopropylamino substituents are used since it is always at higher field for nitrilimine than for diazo. In the infrared, it is important to note that the stretching frequencies of both structural isomers are quite comparable and could be the cause of some misinterpretations in the literature. Both of the absorptions are strong, however the nitrilimine one is much broader as illustrated in Figure 1. The ^{13}C signal of the quaternary carbon would also be characteristic but it is difficult to observe due to the nitrogen quadrupolar moment and to the coupling with the λ^5P. In the case of nitrilimine **12**, only a saturated solution and a phosphorus–carbon decoupling experiment allowed us to find the signal without ambiguity. All attempts to obtain a ^{15}N NMR spectrum failed. Lastly, since most of the structural isomers of diazomethane are interconvertible, it was also necessary to consider the other possibilities. The IR absorptions allowed us to rule out diazirines, isodiazirines, and carbodiimides while the value of the phosphorus–phosphorus coupling constants excluded cyanamides and isocyanamides.

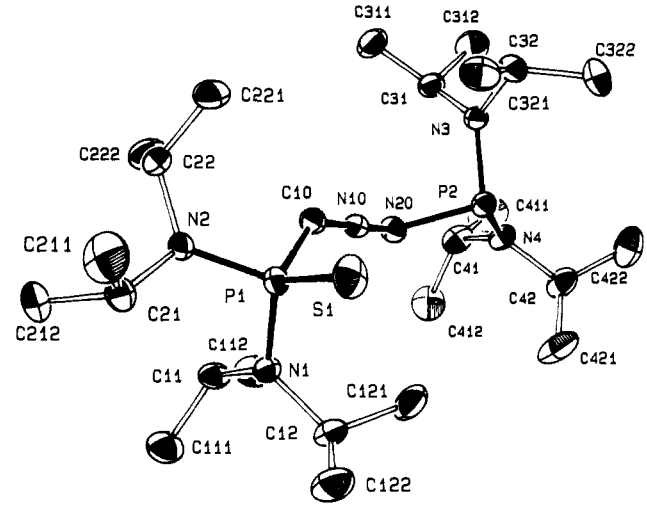


Figure 2. Molecular structure and labeling scheme of one of the enantiomers of nitrilimine **12**.

Table IV. Bond Distances (Å) for Nitrilimine **12**

atom 1	atom 2	distance	atom 1	atom 2	distance
S1	P1	1.931 (1)	N3	C32	1.486 (5)
S1′	P1′	1.935 (1)	N3′	C31′	1.478 (4)
P1	N1	1.658 (3)	N3′	C32′	1.483 (6)
P1	N2	1.646 (3)	N4	C41	1.458 (5)
P1	C10	1.771 (7)	N4	C42	1.479 (5)
P1′	N1′	1.647 (3)	N4′	C41′	1.465 (7)
P1′	N2′	1.650 (3)	N4′	C42′	1.486 (5)
P1′	C10′	1.774 (6)	N10	N20	1.240 (5)
P2	N3	1.661 (4)	N10	C10	1.177 (6)
P2	N4	1.683 (3)	N10′	N20′	1.236 (5)
P2	N20	1.777 (3)	N10′	C10′	1.180 (6)
P2′	N3′	1.664 (3)	C11	C111	1.513 (9)
P2′	N4′	1.673 (4)	C11	C112	1.524 (7)
P2′	N20′	1.776 (3)	C11′	C111′	1.520 (9)
N1	C11	1.486 (4)	C11′	C112′	1.516 (8)
N1	C12	1.494 (5)	C12	C121	1.526 (7)
N1′	C11′	1.488 (5)	C12	C122	1.505 (9)
N1′	C12′	1.490 (5)	C12′	C121′	1.497 (7)
N2	C21	1.480 (7)	C12′	C122′	1.50 (1)
N2	C22	1.493 (7)	C21	C211	1.522 (7)
N2′	C21′	1.484 (8)	C21	C212	1.519 (6)
N2′	C22′	1.492 (7)	C21′	C211′	1.517 (7)
N3	C31	1.475 (6)	C21′	C212′	1.514 (6)
C22′	C221′	1.513 (7)	C32	C321	1.519 (8)
C22′	C222′	1.520 (8)	C32	C322	1.509 (6)
C22	C221	1.520 (6)	C41′	C411′	1.527 (6)
C22	C222	1.507 (7)	C41′	C412′	1.51 (2)
C31′	C311′	1.500 (8)	C41	C411	1.52 (2)
C31′	C312′	1.50 (2)	C41	C412	1.516 (8)
C31	C311	1.508 (5)	C42′	C421′	1.496 (9)
C31	C312	1.51 (1)	C42′	C422′	1.497 (6)
C32′	C321′	1.50 (2)	C42	C421	1.52 (2)
C32′	C322′	1.530 (8)	C42	C422	1.498 (7)

(16) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w|F_o|^2]^{1/2}$; $W = 1/\sigma^2(|F_o|)$.
(17) Cromer, D. T.; Mann, J. B. *Acta Cryst. A.* **1968**, *24*, 3175.
(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(19) Regitz, M.; Maas, G. *Diazo Compounds, Properties and Synthesis*; Academic Press Inc.: Orlando, FL, 1986.

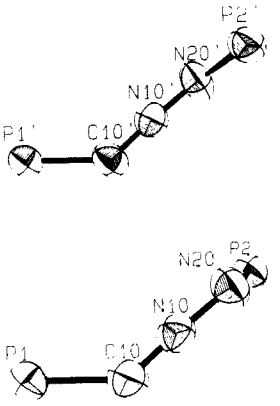


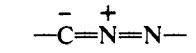
Figure 3. Basic skeletons of the two enantiomers of nitrilimine **12**.

Solid-State Structure of Nitrilimine 12. The unit cell contains four molecules. The basic asymmetric unit contains two different molecules between which there is no correlation, confirming the space group assignment as the centrosymmetric ($P\bar{1}$). In fact, they are two enantiomers as expected because of the chiral axis. The structure of one of the enantiomers of **12** is illustrated in Figure 2 along with the atom numbering scheme. The basic skeleton of the enantiomers are given in Figure 3. Bond lengths and angles are reported in Table IV and V, respectively.

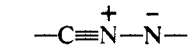
It is of interest to compare these experimental data with the geometries predicted by theoretical works (Table VI).[20] All the calculations concluded that two geometries are possible for nitrilimines: a bent allenyl type and a planar propargyl anion type. The parent nitrilimine was predicted, by non ab initio methods to be bent with a HCN angle ranging from 122° (MINDO/2) to 126° (MINDO/3). The preference over the planar structure was, however, only slight: 2.2 kcal/mol (MINDO/2) and 3.2 kcal/mol (MINDO/3).[20a] Ab initio calculations also predicted similar stabilities for the two forms, the bent being favored by 2.2 kcal/mol at the STO-3G level and the planar being favored by 3.9 kcal/mol at the 4-31G level.[20b] It is clear from Table VI

"Bent" "Planar"

that in the solid state, nitrilimine **12** has a structure at halfway between the "planar" and the "bent". Of special interest, the CNN skeleton is almost linear (173.6°) with rather short C–N (1.18 Å) and N–N (1.24 Å) bond lengths (Note that these bond lengths are in good agreement with those obtained by the geometry-optimized MNDO calculations which correlated satisfactorily with the PE spectroscopic vertical ionization energies observed for N-silylated nitrilimine[5]). In other words, the most important resonance form seems to be



The planar structure would imply a negative charge on the terminal nitrogen atom



which is strongly unfavored in the case of **12** because of the presence of the phosphorus lone pair. The comparison between P(2)–N(20) bond length (1.777 Å) and the other phosphorus–nitrogen bond lengths of the molecule (1.646–1.683 Å) strongly suggest that even with this geometry, there is a repulsion between the phosphorus and nitrogen lone pairs of **12**.

Another noteworthy feature of the geometry of nitrilimine **12** is the arrangement at the termini of the dipole. For the bent structure, the N–Y bond was predicted to bend "inside" by MINDO/2 and MINDO/3 calculations, whereas ab initio gave a small but definite "outside" bending. In **12**, the dihedral angle between PCNN and CNNP is close to 90° (87.5°)!

To summarize, although nitrilimine **12** has a bent structure, it is quite possible that nitrilimines bearing different substituents could have a planar structure.

Stability of Nitrilimines, Their Thermal and Photochemical Rearrangements. The results, summarized in Table I, might indicate that, depending on the nature of diazo lithium salts and chlorophosphanes, N or C substitution occurred.[21] Indeed, it is reasonable to postulate that because of the steric hindrance, bis(diisopropylamino)chlorophosphane and di-*tert*-butylchlorophosphane prefer to react at the nitrogen end of lithium salt **7** affording nitrilimines **12** and **13**, while less hindered chlorophosphanes react at the carbon affording diazo **10** and **11**. However, it is then difficult to explain the formation of diazo **9**, since the lithium salts **6** and **7** are sterically quite similar and the total regiospecificity of all of the reactions would be rather surprising. On the other hand, according to theoretical calculations,[1] the parent nitrilimine would be, along with isodiazirine, the most thermodynamically unstable isomer of diazomethane by about 40 kcal/mol. Thus, another hypothesis would be that the nitrilimines are the kinetic products of electrophilic attack on diazo

Table V. Bond Angles (deg) for Nitrilimine **12**

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
S1	P1	N1	114.5 (1)	C11′	N1′	C12′	114.8 (3)
S1	P1	N2	117.8 (1)	P1	N2	C21	115.9 (3)
S1	P1	C10	109.9 (1)	P1	N2	C22	124.2 (4)
N1	P1	N2	104.8 (2)	C21	N2	C22	115.6 (3)
N1	P1	C10	106.7 (2)	P1′	(I′	C21′	115.9 (4)
N2	P1	C10	102.0 (2)	P1′	N2′	C22′	124.6 (4)
S1′	P1′	N1′	115.1 (1)	C21′	N2′	C22′	115.0 (4)
S1′	P1′	N2′	117.5 (1)	P2	N3	C31	125.5 (2)
S1′	P1′	C10′	109.9 (1)	P2	N3	C32	117.9 (3)
N1′	P1′	N2′	104.8 (2)	C31	N3	C32	116.0 (3)
N1′	P1′	C10′	106.9 (2)	P2′	N3′	C31′	117.6 (3)
N2′	P1′	C10′	101.5 (2)	P2′	N3′	C32′	125.9 (2)
N3	P2	N4	109.8 (3)	C31′	N3′	C32′	114.8 (3)
N3	P2	N20	100.5 (2)	P2	N4	C41	125.8 (2)
N4	P2	N20	94.8 (1)	P2	N4	C42	116.2 (3)
N3′	P2′	N4′	110.3 (3)	C41	N4	C42	115.7 (3)
N3′	P2′	N20′	94.9 (2)	P2′	N4′	C41′	125.3 (2)
N4′	P2′	N20′	100.4 (2)	P2′	N4′	C42′	118.0 (4)
P1	N1	C11	119.0 (3)	C41′	N4′	C42′	116.3 (3)
P1	N1	C12	123.0 (2)	N20	N10	C10	173.6 (3)
C11	N1	C12	114.7 (3)	N20′	N10′	C10′	173.0 (4)
P1′	N1′	C11′	118.4 (3)	P2	N20	N10	115.0 (2)
P1′	N1′	C12′	124.4 (2)	P2′	N20′	N10′	116.7 (2)
P1	C10	N10	138.2 (4)	N2	C22	C221	115.6 (3)
P1′	C10′	N10′	137.0 (4)	N2	C22	C222	111.9 (3)
N1	C11	C111	111.5 (4)	C221	C22	C222	111.9 (6)
N1	C11	C112	113.4 (3)	N3′	C31′	C311′	111.2 (4)
C111	C11	C112	111.4 (4)	N3′	C31′	C312′	113.6 (4)
N1′	C11′	C111′	110.6 (4)	C311′	C31′	C312′	111.5 (4)
N1′	C11′	C112′	113.7 (3)	N3	C31	C311	113.1 (4)
C111′	C11′	C112′	111.3 (4)	C3	C31	C312	112.1 (3)
N1	C12	C121	114.2 (5)	C311	C31	C312	112.0 (4)
N1	C12	C122	112.6 (4)	N3′	C32′	C321′	112.3 (4)
C121	C12	C122	112.9 (4)	N3′	C32′	C322′	112.9 (5)
N1′	C12′	C121′	114.3 (6)	C321′	C32′	C322′	111.2 (4)
N1′	C12′	C122′	112.5 (4)	N3	C32	C321	112.4 (4)
C121′	C12′	C122′	116.1 (4)	N3	C32	C322	112.0 (4)
N2	C21	C211	112.9 (4)	C321	C32	C322	111.7 (5)
N2	C21	C212	111.1 (5)	N4′	C41′	C411′	112.6 (4)
C211	C21	C212	111.1 (4)	N4′	C41′	C412′	112.8 (4)
N2′	C21′	C211′	113.3 (4)	C411′	C41′	C412′	111.0 (4)
N2′	C21′	C212′	111.3 (6)	N4	C41	C411	112.6 (5)
C211′	C21′	C212′	110.9 (4)	N4	C41	C412	113.6 (6)
N2′	C22′	C221′	115.5 (4)	C411	C41	C412	111.2 (4)
N2′	C22′	C222′	112.2 (4)	N4′	C42′	C421′	112.6 (4)
C221′	C22′	C222′	111.7 (5)	N4′	C42′	C422′	112.2 (3)
C421′	C42′	C422′	111.3 (5)	N4	C42	C422	111.7 (4)
N4	C42	C421	113.8 (4)	C421	C42	C422	110.8 (6)

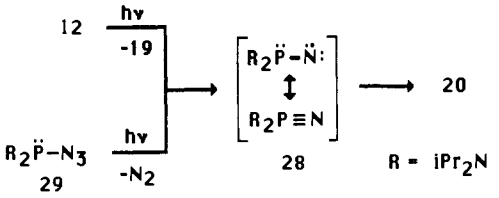
(20) (a) Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 6397. (b) Caramella, P.; Gandour, R. W.; Hall, J. A.; Deville, C. G.; Houk, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 385 and references therein.

(21) Diazolithium salts **6–8** are isoelectronic to nitrile α-carbanions, and it has been shown that depending on the steric requirements of the reagents, C- or N-alkylation occurred. Newman, M. S.; Fukunaga, T.; Miwa, T. *J. Am. Chem. Soc.* **1960**, *82*, 873.

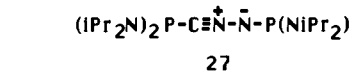
Table VI. Calculated and Experimental Geometries of Nitrilimines

	MINDO/2[20b]		MINDO/3[20b]		STO-3G[20a]		MNDO[5]		RX	
	bent	planar	bent	planar	bent	planar	X = Me Y = tBu	X = Ph Y = tBu	12	12'
∠XCN, deg	122	152	126	159	118	179	176	173	138	137
∠CNN, deg	169	176	167	177	169	170	164	161	174	173
∠NNY, deg	124	123	115	116		100	125	123	115	117
∠XCNN, deg	154	-	141	-	143	-			121	129
∠CNNY, deg	109	-	120	-		-			152	141
r(CN), Å	1.24	1.20	1.20	1.17	1.23	1.16	1.18	1.18	1.18	1.18
r(NN), Å	1.08	1.10	1.19	1.20	1.27	1.36	1.23	1.23	1.24	1.24

Scheme VII



lithium salts, whereas the diazo compounds are the thermodynamic products. The possible existence of a diazomethane–nitrilimine equilibrium was reported in the 1960s,[22] but this finding was later demonstrated to be wrong.[23] Nitrilimine–diazo rearrangement has been postulated[6] to explain the nature of the products obtained in the thermolysis of potential nitrilimine precursors; however, the nitrilimines have never been observed and, apart from one case,[6a] the resulting diazo were also not stable under the experimental conditions used. The obtention of diazo **17** and **18** from nitrilimines **12** and **14**, respectively, strongly support this hypothesis and thus the obtention of nitrilimine versus diazo should depend on the energy barrier of the 1,3 shift from the nitrogen substituent to the carbon center and of the thermodynamic stability of nitrilimine. It is well-known that the larger the substituent is, the higher the energy barrier is, which rationalized the stability of **12–14**. The nonobservation of nitrilimine **27**, while **12** is remarkably stable, might be explained by electronic factors. It is obvious that the push–pull effect of the substituents in **12** is a strong stabilizing factor.

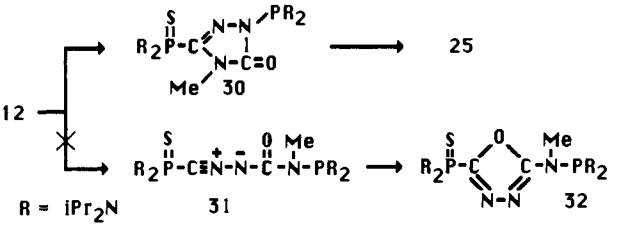


27

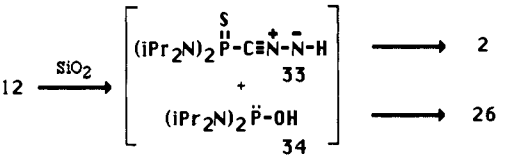
It has been shown by matrix spectroscopy that under irradiation, nitrilimines rearrange into carbodiimides or undergo cleavage of the nitrogen–nitrogen bond.[4] In the case of nitrilimine **12**, we only observed the cleavage of the N–N bond leading to thioxophosphoranyl carbonitrile **19** and to [[bis(diisopropylamino)]-phosphanyl]nitrene (**28**) which dimerized into the cyclodiphosphazene **20**. We have already shown[13] that **28**, generated by photolysis of the corresponding azide **29**, behaved as a phosphonitrile, compound possessing a formal phosphorus–nitrogen triple bond and led to **20** (Scheme VII).

Reactivity of Nitrilimines. This study has mainly been done by using nitrilimine **12** but the 1,3 dipolar character of **13** and **14** has been checked by their reactions with methyl acrylate, leading to heterocycles **15** and **16**. Reactivity of **12** was considerably limited by the steric hindrance of the substituents. Moreover, it appeared that **12** only reacted with electron-poor dipolarophiles. Note, that although transient nitrilimines are known to react with styrene, butadiene, and phenylacetylene.[3] Huisgen has observed a higher reactivity with electron poor olefins (for example, diphenylnitrilimine adds onto dimethyl fumarate 177 times faster than onto styrene).[3]

Scheme VIII



Scheme IX



Concerning the orientation of the addition of unsymmetrically bonded olefins or alkynes, a good regioselectivity, yielding the 5-substituted pyrazolines or pyrazoles was observed with transient nitrilimines. An adequate rationalization was given by Houk[24] using FMO theory. In the same way, **12** added onto methyl acrylate and methyl propiolate in one direction only, affording **21** and **22**, respectively. With methyl isocyanate, as expected for a HOMO (dipole) controlled cycloaddition and in contrast to the results observed with transient nitrilimines, **12** only reacted with the carbon–nitrogen double bond and not to the CO. The regioselectivity fit nicely with FO interactions.[24] It is quite likely that the second molecule of isocyanate involved in this reaction, inserts into the nitrogen–phosphorus bond of the primary form **30**. Indeed, an initial insertion would have led to *N*-amide nitrilimine **31**, which would probably undero 1,5 electrocyclization into **32** (Scheme VIII).[25]

Nitrilimine **12** reacted with dimethyl fumarate, at room temperature, affording the trans adduct **23**, while with dimethyl maleate the reaction occurred only at 55 °C, giving a mixture of cis (**24**) and trans adducts (**23**). Previous studies of the addition of nitrilimine onto geometrically isomeric alkenes concluded that cis addition predominated and the trans isomer was more reactive. When a lack of stereoselectivity was observed, it has been proven to be due to an epimerization of the primary adduct into the thermodynamically more stable isomer.[3] Surprisingly, attempted epimerization of **24**, even by heating in solution at 70 °C for 4 h, failed. Moreover, when the reaction was run with 1.2 equiv of maleic ester, NMR analysis revealed that the unconsumed dipolarophile was not isomerized. Therefore, the nonstereoselectivity observed in the reaction of **12** with dimethyl maleate must be explained by a "non-concerted addition" process.[26]

To explain the formation of thioxophosphoranyldiazomethane **2** along with phosphane oxide **26**, in the reaction of **12** with silica

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(23) (a) Müller, E.; Kastner, P.; Beutler, R.; Rundell, W.; Suhr, H.; Zeeh, B. *Ann. Chem.* **1968**, *713*, 87. (b) Müller, E.; Beutler, R.; Zeeh, B. *Ann. Chem.* **1968**, *719*, 72. (c) Müller, E.; Nespital, V.; Beutler, R. *Tetrahedron Lett.* **1971**, 525.

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

(26) (a) Huisgen, R.; Mloston, G.; Langhals, E. *J. Am. Chem. Soc.* **1986**, *108*, 6401. (b) Huisgen, R.; Mloston, G.; Langhals, E. *J. Org. Chem.* **1986**, *51*, 4085. (c) Mloston, G.; Langhals, E.; Huisgen, R. *Tetrahedron Lett.* **1989**, *30*, 5373.

gel, it seems reasonable to postulate the hydrolysis of the phosphorus-nitrogen bond leading to *N*-hydridonitrilimine **33** and hydroxyphosphane **34**; subsequent rearrangements would give the observed products (Scheme IX).

Conclusion

Thirty years after the discovery by Huisgen of transient nitrilimines, we have shown that these 1,3 dipolar species can be isolated at room temperature. The use of bulky substituents is necessary and push-pull effects also are important. The electrophilic substitution of diazolithium salts is a new and effective synthetic method for nitrilimines. Thermal rearrangement, under mild conditions, leads to the isomeric diazo derivatives, while under irradiation nitrilimine **12** undergoes a nitrogen-nitrogen bond cleavage leading to the nitrile **19** and to the dimer of the phosphanyl nitrene **28**. This is a new route to the only known cyclodiphosphazene **20**. Regioselective [2 + 3] cycloaddition is observed with electron-poor olefins, alkynes, and with isocyanates. The absence of stereoselectivity observed with dimethyl maleate might involve a non-concerted process. The X-ray crystal study of **12** brings some evidence for the nonplanarity of nitrile imines.

Acknowledgment. Thanks are due to Dr. G. Sicard for her participation at the early stages of this work and to Dr. G. Gillette for helpful discussions.

Supplementary Material Available: Tables of fractional atomic coordinates, hydrogen atomic positional and thermal parameters, and final anisotropic thermal parameters (7 pages); listings of structure factor amplitudes (26 pages). Odering information is given on any current masthead page.

Competing Hole Catalyzed Diels-Alder and Cyclobutanation/Vinylcyclobutane Rearrangement Paths. A Mechanistic Dichotomy

Taisun Kim, R. Jerome Pye, and Nathan L. Bauld*

Contribution from the Deparament of Chemistry, The University of Texas, Austin, Texas 78712.
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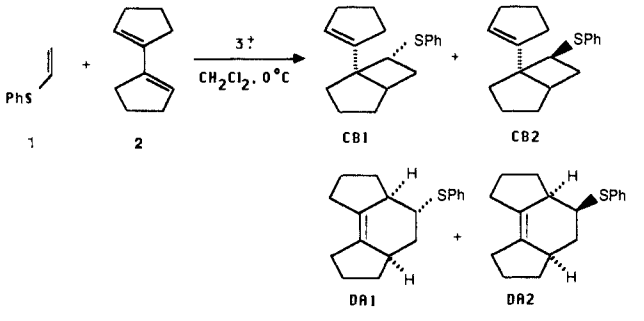
Abstract: Kinetic studies of the tris(4-bromophenyl)aminium hexachloroantimonate catalyzed cycloaddition of phenyl vinyl sulfide (**1**) and 1,1′-bicyclopentenyl (**2**) reveal three discernible stages: (1) a cycloaddition stage in which cyclobutanation predominates over Diels-Alder addition, (2) a syn/anti rearrangement stage in which the initially predominant syn cyclobutane (CB) adduct rearranges to the more stable anti isomer, and (3) a vinylcyclobutane rearrangement stage in which the anti cyclobutane isomer rearranges to the endo Diels-Alder (DA) isomer. At -30 °C, the latter rearrangement is frozen out. The variation of the initial CB/DA ratio with time, relative and absolute substrate concentrations, added triarylamine, and with electron-donating and -withdrawing substituents on the aryl ring of **1** reveals a mechanistic dichotomy in which the reaction $\mathbf{1}^{\bullet+}/\mathbf{2}$ affords primarily DA adducts and the reaction $\mathbf{2}^{\bullet+}/\mathbf{1}$ give CB adducts. Hole transfer in the ion dipole complexes $\mathbf{1}^{\bullet+}/\mathbf{2}$ and $\mathbf{2}^{\bullet+}/\mathbf{1}$ is therefore inferred to be slower than cycloaddition. Finally a competition between a hole transfer chain and a true hole catalytic reaction is inferred.

Hole-catalyzed (cation radical/neutral) cycloadditions of conjugated dienes with electron-rich dienophiles such as vinyl ethers, vinyl sulfides, and *N*-vinyl amides provide an effective strategy for cycloaddition to this normally unreactive class of dienophiles.[1-6] Although Diels-Alder (DA) periselectivity has been observed in cycloadditions of vinyl ethers and vinyl sulfides to 1,3-cyclohexadiene,[2] the addition of *N*-methyl-*N*-vinylacetamice to the latter diene is highly cyclobutane (CB) periselective,[4] and the additions of all three electron-rich dienophiles to conformationally flexible dienes yield CB adducts predominantly.[1,3] In the case of the vinyl ether and *N*-vinyl amide CB adducts, anion assisted vinylcyclobutane rearrangement strategies have been developed which provide efficient indirect synthetic routes to the corresponding Diels-Alder adducts.[3,4] In the case of the phenyl vinyl sulfide CB adducts, a hole-catalyzed vinylcyclobutane rearrangement provides similarly convenient access to net Diels-Alder addition.[5] The hole-catalyzed cycloadditions of phenyl vinyl sulfide (**1**) are especially complex because of the competition between direct and indirect Diels-Alder pathways. The present study of the hole-catalyzed cycloaddition of **1** and 1,1′-bicyclopentenyl (**2**) was undertaken to determine the relative extent of the contributions of the two discrete pathways and to establish and compare their respective stereochemical profiles. In fact the reaction system $[\mathbf{1} + \mathbf{2}]^{\bullet+}$ emerges as significantly more complex than had initially been assumed in that two distinct role-differentiated mechanisms, characterized by distinctly different CB/DA periselectivities, are observed. The results have potentially im-

Scheme I



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(3) Pabon, R. A.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1984**, *106*, 2730-1.
(4) Bauld, N. L.; Harirchian, B.; Reynolds, D. W.; White, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 8111-7.
(5) Reynolds, D. W.; Harirchian, B.; Chiou, H.-S.; Marsh, B. K.; Bauld, N. L. *J. Phys. Org. Chem.* **1989**, *2*, 57-88.
(6) Harirchian, B.; Bauld, N. L. *J. Am. Chem. Soc.* **1989** *111*, 1826-8.

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