Synthesis and Reactivity of Stable Silyl-Substituted Nitrilimines

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The reaction of chlorophosphanes and chlorosilanes with the lithium salts of the (bis(diisopropylamino)-thiophosphoranyl)-, bis(diisopropylamino)phosphanyl)-, (trimethylsilyl)-, and (triisopropylsilyl)diazomethane (1, 4, 5, 6) has been studied. Four isolable nitrilimines XCNNY (X = $(iPr_2N)_2P(S)$, Y = $SiiPr_3$, **10a**; X = $(iPr_2N)_2P$, Y = $SiPh_3$, **14a**; X = $(iPr_2N)_2P$, Y = $SiiPr_3$, **15a**; X = Y = $SiiPr_3$, **18a**) and three observable nitrilimines (X = $(iPr_2N)_2P(S)$, Y = $SiMe_3$, **8a**; X = $(iPr_2N)_2P(S)$, Y = $SiPh_3$, **9a**; X = $(iPr_2N)_2P$, Y = $SiMe_3$, **13a**) have been obtained. The factors influencing the stability of nitrilimines are analyzed. Several examples of thermal nitrilimine–diazo rearrangements and photochemical nitrilimine–carbodiimide rearrangements are described. The regioselectivity of the reaction of the observable nitrilimines with methyl acrylate and methyl propiolate is compared to that reported for transient nitrilimines. An example of 1,3-addition of butyllithium to a nitrilimine is given.

The intermediacy of nitrilimines was postulated for the first time in 1948.[1] However, it was only in the 1960s, with the development of the concept of 1,3-dipolar cycloadditions, mainly by Huisgen,[2] that these nitrilium betaines attracted considerable interest. Until recently, they had only been observed by IR and UV in 85 K matrix[3a,c] or by mass[3c] and real time electron spectroscopy[4] in the gas phase. Dehydrohalogenation of hydrazonoyl halides, and thermolysis or photolysis of tetrazoles or related 5-membered heterocycles, were the most widely used routes for the generation of nitrilimines.[5]

Although, it is generally admitted that the reaction of an electrophile with a diazo lithium salt leads to the corresponding substituted diazo derivative,[6] we have shown that in the case of phosphorus-substituted diazo lithium salts, both diazo compounds and nitrilimines can be obtained, depending on the nature of the electrophile. Indeed, using the (bis(diisopropylamino)thiophosphoranyl)diazo lithium salt **1** and the bis(diisopropylamino)chlorophosphane **2** as electrophile, we have synthesized the first stable nitrilimine **3a** (Scheme I).[7]

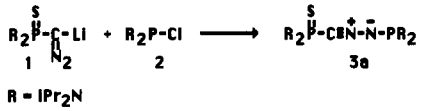
We now report that this new route to nitrilimines is not restricted to phosphorus electrophiles nor to phosphorus-substituted diazo lithium salts but is quite general. The influence of the N- and C-substituents on the stability of the nitrilimine is discussed, and four new isolable nitrilimines are described. Their reactivity and photochemical behavior are presented.

Results

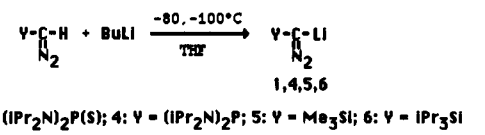
Four different diazo lithium salts **1**, **4**, **5**, and **6** have been prepared by addition of a stoichiometric amount of BuLi to a cold (−80, −100 °C) THF solution of the corresponding monosubstituted diazomethane (Scheme II).

Since **1** was a demonstrated nitrilimine precursor,[7] we first studied its reactivity with non-phosphorus derivatives in order to explore the influence of the electrophile on the course of the reaction and/or on the stability of the nitrilimine. With methyl iodide, trimethylchlorosilane, and triphenylchlorosilane, we isolated the corresponding diazo compounds **7b**, **8b**, and **9b**, respectively, after workup. When the reactions were monitored by IR and ^{31}P NMR at −78 °C, nitrilimines **8a** and **9a** were observed but we were unable to observe the hypothetical formation of the *C*-thiophosphoranyl-*N*-methylnitrilimine (**7a**). In the same fashion *C*-[bis(diisopropylamino)thiophosphoranyl]-*N*-(trimethylsilyl)nitrilimine (**8a**) is only stable for a few hours at 0 °C in solution whereas the *N*-triphenylsilyl derivative **9a** is still observable after several hours at room temperature.[8] When triisopropylsilyl chloride was used, the

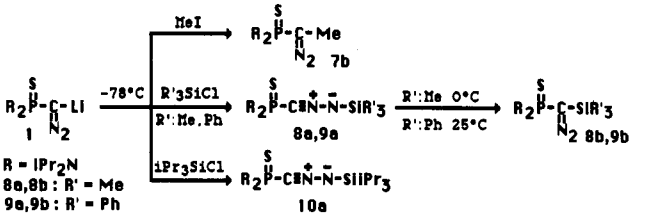
Scheme I



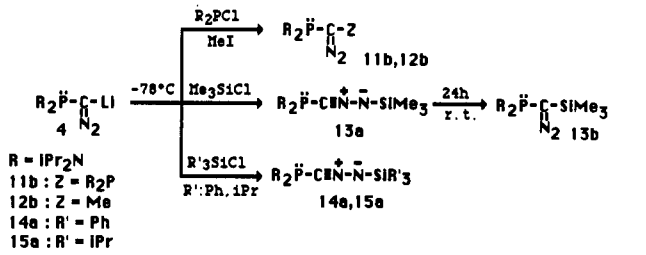
Scheme II



Scheme III



Scheme IV



(1) Fusco, R.; Romani, R. *Gazz. Chim. Ital.* **1948**, *78*, 342.
(2) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565 and 633.
(3) (a) Toubro, H.; Holm, A. *J. Am. Chem. Soc.* **1980**, *102*, 2093. (b) Meier, H.; Heinzelmann, W.; Heimgartner, H. *Chimia* **1980**, *34*, 504 and 506. (c) Wentrup, C.; Fisher, S.; Maquestiau, A.; Flammang, R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 56.
(4) Bock, H.; Dammel, R.; Fisher, S.; Wentrup, C. *Tetrahedron Lett.* **1987**, *28*, 617.
(5) Caramella, P.; Grünanger, P. *1,3 Dipolar Cycloaddition Chemistry*; Wiley: New York, 1984.
(6) (a) Patai, S. *The chemistry of diazonium and diazo groups*; Wiley: New York, 1978. (b) Regitz, M. *Diazoalkanes*; Georg Thieme Verlag: Stuttgart, 1977. (c) Regitz, M.; Maas, G. *Diazo Compounds, Properties and Synthesis*; Academic Press Inc.: Orlando, 1986.
(7) (a) Sicard, G.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 2663. (b) Granier, M.; Baceiredo, A.; Dartiguenave, Y.; Dartiguenave, M.; Menu, M. J.; Bertrand, G. *J. Am. Chem. Soc.* **1990**, *112*, 6277.

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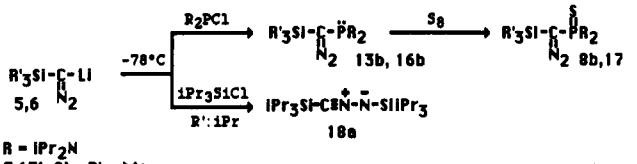
Table I. Selected Spectroscopic Data for Nitrilimines (XCNNY), Diazos (XC(N_2)Y), and Carbodiimides (XN=C=NY)[a]

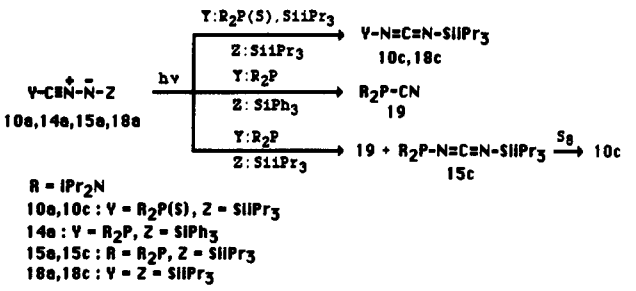
		diazo			nitrilimine			carbodiimide		
X	Y	^{31}P	IR	^{29}Si	^{31}P	IR	^{29}Si	^{31}P	IR	^{29}Si
$R_2P(S)$	PR_2	72.4	2028		35.4	2040				
$R_2P(S)$	$SiMe_3$	65.8	2050	+0.9 (13)	32.5	2010				
$R_2P(S)$	$SiPh_3$	59.4	2100		31.1	2120				
$R_2P(S)$	$SiiPr_3$	76.9	2040	+6.6 (11)	33.2	2050	+12.2	55.2	2200	+0.3
R_2P	$SiMe_3$	56.0	2010	+1.7 (43)	44.1	2100				
R_2P	$SiPh_3$				42.2	2140	-10.4			
R_2P	$SiiPr_3$	54.0	2010		45.7	2110	+6.6 (3)	83.0	2160	
iPr_3Si	$SiiPr_3$					2120	+0.7, +6.4		2200	+3.8

[a] ^{31}P and ^{29}Si chemical shifts are expressed in ppm; the J_{PSi} in hertz are in brackets; infrared frequencies are in cm^{-1}.

Scheme V



Scheme VI

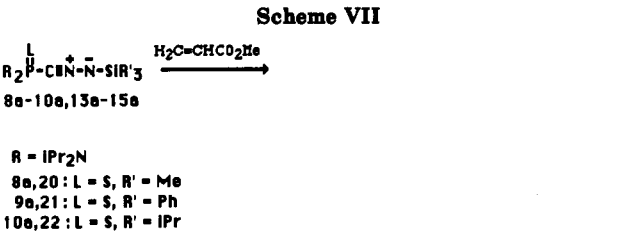


corresponding nitrilimine **10a** was isolated in 96% yield (Scheme III).

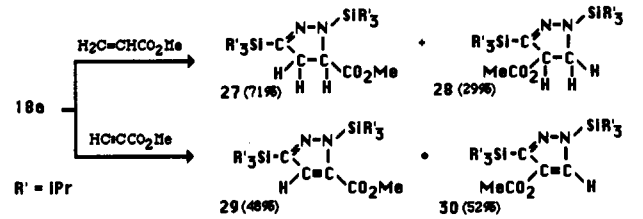
The diazo lithium salt **4** reacted with chlorophosphane **2** and methyl iodide affording the corresponding diazo compounds **11b**[9] and **12b**. In marked contrast, silyl electrophiles gave observable (IR, ^{31}P NMR) nitrilimine **13a** and nitrilimines **14a** and **15a** which were isolated in good yields. Although **13a** rearranged into diazo **13b** after 24 h at 25 °C, nitrilimines **14a** and **15a** were perfectly stable for weeks at ambient temperature (Scheme IV).

In our hands, the reactions of different chlorosilanes (trimethyl, triphenyl, and triisopropyl) with the diazo lithium salt **5** were not clean.[10] However, the bis(diisopropylamino)chlorophosphane (**2**) reacted with **5** giving rise to the diazo derivative **13b**[11] in 95% yield. In the same way, the (triisopropylsilyl)diazo lithium salt **6** reacted with chlorophosphane **2** quantitatively (according to ^{31}P NMR) affording diazo compound **16b**, isolated after sulfuration as **17** in 60% yield, whereas with triisopropylchlorosilane as electrophile the bis(triisopropylsilyl)nitrilimine **18a** was isolated by distillation in 80% yield (Scheme V).

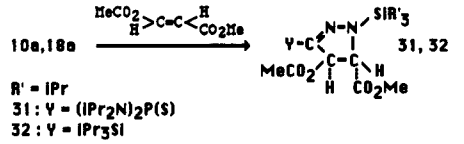
Scheme VII



Scheme VIII



Scheme IX



The photochemical behavior, at 254 and 300 nm, of the four stable nitrilimines has been studied. Irradiation of nitrilimines **10a** and **18a** cleanly led to the isomeric carbodiimides **10c** (72% yield) and **18c** (quantitative). On the other hand, photolysis of *N*-(triphenylsilyl)nitrilimine **14a** gave rise to phosphanylnitrile **19** in 85% yield along with several silylated products which were not isolated. Lastly, irradiation of *C*-phosphanyl-*N*-(triisopropylsilyl)-nitrilimine **15a** produced both phosphanylnitrile **19** (10% yield) and carbodiimide **15c** which was isolated as **10c** in 25% yield after treatment with elemental sulfur (Scheme VI).

C-Thiophosphoranyl- and *C*-phosphanylnitrilimines, **8a–10a** and **13a–15a**, reacted at room temperature with methyl acrylate regiospecifically yielding 5-substituted pyrazolines **20–25** (40–75% yield). When *C*-phosphanyl adducts **23–25** were sulfurized with elemental sulfur the λ^5-phosphorus derivatives **20–22** were obtained. Although **21** and **22** can be isolated by chromatography on silica gel, the trimethylsilyl group of derivative **20** is cleaved under the same experimental conditions leading to the N-un-

(8) For preliminary accounts of this work, see: (a) Granier, M.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1350. (b) Castan, F.; Baceiredo, A.; Bertrand, G. *Angew, Chem., Int. Ed. Engl.* **1989**, *28*, 1250.

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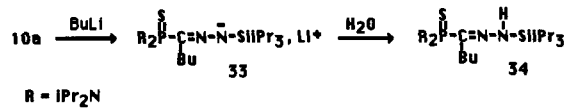
(10) The reaction of the lithium salt of (trimethylsilyl)diazomethane with trimethylchlorosilane was reported to give the bis(trimethylsilyl)-diazomethane. Seyferth, D.; Flood, T. C. *J. Organomet. Chem.* **1971**, *29*, C25.

(11) (a) Baceiredo, A.; Bertrand, G.; Sicard, G. *J. Am. Chem. Soc.* **1985**, *107*, 4781. (b) Igau, A.; Grützmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6363.

Scheme X



substituted pyrazoline **26** (Scheme VII).

On the other hand, the addition of methyl acrylate or methyl propiolate to the fully silylated nitrilimine **18a** led to a mixture of 4- and 5-substituted pyrazolines **27** and **28** (30% yield) or pyrazoles **29** and **30** (40% yield) in 29/71 and 52/48 ratios (according to ^{1}H NMR of the crude reaction mixture), respectively (Scheme VIII).

The reactions of dimethyl fumarate with the 1,3-dipoles **10a** and **18a** are stereospecific and lead to pyrazolines **31** (40% yield) and **32** (30% yield), respectively (Scheme IX).

Lastly addition of BuLi to **10a** led to the 1,3-addition product **33**, which was characterized in solution. Mild hydrolysis gave rise to hydrazone **34** (63% yield) (Scheme X). No clean reactions were observed with the other nitrilimines.

Discussion

The characterization of nitrilimines versus their diazo isomers was made spectroscopically. Selected data are given in Table I. In the case of C-phosphorus-substituted nitrilimines, ^{31}P NMR proved highly useful. The ^{31}P chemical shift was always at higher field for the nitrilimine than for the diazo compound; this is particularly dramatic in the case of thiophosphoranyl substituents (27 to 43 ppm) but also appeared for phosphanyl substituents (9 to 12 ppm). The ^{29}Si NMR signals were somewhat difficult to observe and were not indicative of the structure except in the case of C-phosphorus nitrilimines where, as expected, the phosphorus–silicon coupling constants were much smaller than in the corresponding diazo compounds. The ^{13}C NMR signal of the quaternary carbon (+46.7 ppm in the case of **18a**) would be characteristic, since they are (in all the known examples[7,8]) at lower field than the diazo carbon but are extremely difficult to observe due to the nitrogen quadripolar moment. All attempts to obtain a ^{15}N NMR spectrum failed. Infrared was the most general and useful spectroscopic technique although the stretching frequencies of one structural isomer compared to the other were unpredictable. However, the shape of the signal was characteristic: both of the absorptions were strong but the nitrilimine ones were much broader as illustrated in Figure 1.

In previous papers,[7,8] we discussed the two mechanistic possibilities to rationalize the formation of diazo compounds when the nitrilimines were not observed: either a direct C-substitution in the diazolithium salt, or a N-substitution giving a transient nitrilimine followed by 1,3-migration. The results reported here support the hypothesis that the nitrilimines are the kinetic products of electrophilic attack on diazo lithium salts whereas the diazo compounds are the thermodynamic products.

The next question is to understand which factors influence the stability of the nitrilimines, or, in other words, what prevents the rearrangement into the diazo isomer. Table II summarizes the results concerning the stability of nitrilimines. Comparing nitrilimines **8a**, **9a**, and **10a** or **13a**, **14a**, and **15a** where the C-substituent is unchanged and where the electronic factors at nitrogen are identical, it is clear that the steric factors at the nitrogen end play an important role. Since the rearrangement to diazo involves the migration of the N-substituent, this is in good agreement with the decreased migratory ability of bulky substituents. Assuming that bis(diisopropylamino)phosphanyl, bis(diisopropylamino)thiophosphoranyl and triisopropylsilyl groups have comparable steric hindrance, we can try to analyze the electronic effects on the stability of nitrilimines. The phosphanyl group can be considered as an electron-donating group (D), the thiophosphoranyl group as an electron-withdrawing group by resonance (W), and the silyl group as a π-acceptor σ-donor (A). From **15a** and **18a**, it seems that the combination of an A substituent at nitrogen and an A or D substituent at carbon leads to comparable stability. The comparison of nitrilimines **8a** and **13a**, or **9a** and **14a**, or **10a** and **15a** indicates that when an A substituent is present at nitrogen, it is slightly better to have a D substituent at carbon rather than a W substituent. Comparing **3a** and **10a**, it seems that when there is a W substituent at carbon, an A substituent at nitrogen is prefered over a D substituent. The comparison of nitrilimines **3a**, **11a**, and **16'a** indicates that when the nitrogen is D substituted, a W group is better than an A or a D group at carbon. Thus, from these results, the order of stability of nitrilimines, depending on the electronic effects of the substituents, is the following:

D-CNN-A ≈ A-CNN-A > W-CNN-A > W-CNN-D > A-CNN-D ≈ D-CNN-D

Among all the mesomeric structures, theoretical calcula-

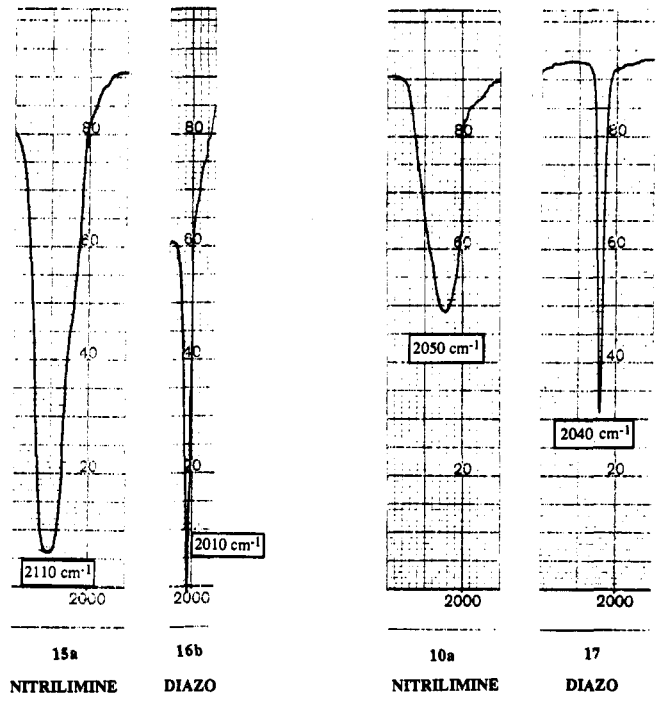


Figure 1. Infrared spectra of nitrilimines **15a** and **10a** and of its diazo isomers **16b** and **17**, respectively, in $CDCl_3$ at the same concentration.

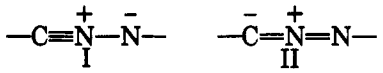
Table II. Rearrangement of Nitrilimines into the Isomeric Diazo Derivatives

XCNNY			
X	Y	no.	*T*, °C (time, h)
$R_2P(S)$	PR_2	**3a**	55 (6)
$R_2P(S)$	$SiMe_3$	**8a**	0 (4)
$R_2P(S)$	$SiPh_3$	**9a**	25 (6)
$R_2P(S)$	$SiiPr_3$	**10a**	no
R_2P	PR_2	**11a**	<−78
R_2P	$SiMe_3$	**13a**	25 (24)
R_2P	$SiPh_3$	**14a**	no
R_2P	$SiiPr_3$	**15a**	no
Me_3Si	PR_2	**13'a**	<−78
iPr_3Si	PR_2	**16'a**	<−78
iPr_3Si	$SiiPr_3$	**18a**	no

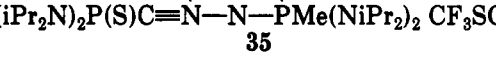
Table III. Regioisomer Ratios (5-Substituted/4-Substituted) for the Cycloaddition of Various Nitrilimines to Methyl Acrylate and Methyl Propiolate

	PhCNNPh	MeCNNPh	PhCNNMe	18a	8a–10a, 13a–15a
methyl acrylate	100/0	97.5/2.5	88/12	71/29	100/0
methyl propiolate	78/22	84/16	75/25	48/52	

tions[12] performed on the parent nitrilimine predicted that the heteropropargylic form I and the heteroallenic form II should be the most stable forms. To stabilize form I,



it is necessary to have an electron-withdrawing group at nitrogen, while the substituent at carbon is of lesser importance, confirming experimental observations. If there is a donor at nitrogen, form II becomes more important and thus it seems necessary to have a strong electron-withdrawing group at carbon (because of its σ-donating effect, a silyl group is not sufficient). The X-ray crystal structures of **3a**[7b] and **35**[13] corroborate these conclusions: **3a** has a heteroallenic geometry while **35** presents an heteropropargylic structure.



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Thus, it is possible to synthesize a variety of stable, or relatively stable, nitrilimines provided that the substituents are bulky, and that at least one substituent has a strong electron-withdrawing effect.

The photolytic behavior of nitrilimines is difficult to rationalize. Toubro and Holm,[3a] have shown that irradiation of diphenylnitrilimine at 370 nm (85K), led to a mixture of diphenylcarbodiimide along with products resulting from nitrogen-nitrogen bond cleavage. A similar result is observed when the *C*-phosphanyl-*N*-(triisopropylsilyl)nitrilimine **15a** was photolyzed (Scheme VI). However, the reactions observed with the three other nitrilimines selectively give either the carbodiimides **10c** and **18c** from **10a** and **18a**, respectively, or the nitrile **19** from **14a**.

It is clear that the regioselectivity of nitrilimine, 1,3-dipolar cycloaddition is dependent of the nature of the dipole substituents (Table III). Bastide[14] and Houk[15] have previously applied frontier molecular orbital theory to the regioselectivity question in 1,3-dipolar cycloadditions and Sustmann[16] has proposed a simple interaction scheme. Acceptor substituents on the nitrilimine increase the LUMO (dipole) control leading to the 5-substituted pyrazolines which is observed for **8a–10a** and **13a–15a**. On the other hand, the presence of two silyl substituents in **18a** raises the FMO energies and thus the reaction can be either LUMO (dipole) or HOMO (dipole) controlled giving rise to a mixture of 5- and 4-substituted heterocycles **27** and **28**. Not surprisingly, in the case of methyl propiolate which has lower lying MOs (IP, 11.15 eV) than methyl acrylate (IP, 10.72 eV), the percentage of 4-substituted heterocycles becomes more important and 4-pyrazole **30** is even the major isomer in the case of the fully silylated nitrilimine **18a** (Scheme VIII).

The study of the stereoselectivity of the 2 + 3 cycloadditions involving stable nitrilimines **10a** and **18a** was more difficult (Scheme VIII). Indeed, **10a** and **18a** reacted with dimethyl fumarate stereospecifically leading to trans pyrazolines **31** and **32** but they did not react with dimethyl maleate. Previous studies of the cycloaddition of transient nitrilimines[5] to geometrically isomeric alkenes concluded that cis-addition predominated and that the trans dipolarophile was more reactive (we have shown that dimethyl fumarate reacted stereospecifically with **3a** at room temperature while dimethyl maleate only reacted with **3a** at 55 °C nonstereospecifically[7]).

Although 3 + 2 cycoadditions are the most important aspect of the chemistry of nitrilimines, a few examples of 1,3-addition have been reported.[17] In this respect nitrilimine **10a** reacted regioselectively with butyllithium affording the lithium salt **33**. It should be noted that only this very strong nucleophile reacted with **10a**.

Conclusions

The reaction of a diazo lithium salt with an electrophile is a quite general method for the synthesis of nitrilimines. A variety of stable 1,3-dipoles of this type can be prepared providing there is at least one electron-withdrawing substituent present. Most of the nitrilimines thermally rearrange into the isomeric diazo derivatives. Under irradiation, these nitrilium betaines can either rearrange to the corresponding carbodiimides or undergo a nitrogen–nitrogen cleavage. The stable nitrilimines described here seem less reactive than the transient nitrilimines reported in the literature and are strongly nucleophilic. The regioselectivity observed for the 2 + 3 cycloadditions fits nicely with the predictions based on frontier molecular orbital theory.

Experimental Section

All experiments were performed in an atmosphere of dry nitrogen. ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded on Bruker AC80, AC200, WM250, or AM300 spectrometers. ^{1}H, ^{13}C, and ^{29}Si chemical shifts are reported in ppm relative to Me_4Si as external standard. ^{31}P downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. IR spectra were recorded in a Perkin–Elmer 597 spectrometer and UV spectra on a Varian Cary 219 spectrophotometer. Mass spectra were obtained on a Ribermag R10 10E instrument. Photolysis was performed in glass and quartz tubes at 300 and 254 nm with a rayonnet photochemical reactor. Liquid chromatography was done on silica gel or neutral alumina. Melting points are uncorrected.

Synthesis of (Triisopropylsilyl)diazomethane. An ether solution (200 mL) of diazomethane (4.62 g, 110 mmol) was transferred by canule under nitrogen to neat diisopropylethylamine (12.92 g, 100 mmol). Triisopropylsilyl triflate (30.64 g, 100 mmol) was then added dropwise to the mixture at −20 °C. A white precipitate was formed. After one night, at room temperature,

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(17) See for example: Huisgen, R.; Sauer, J. *Chem. Ber.* **1961**, *94*, 2503.

the mixture was washed with water. The yellow organic phase was dried over anhydrous sodium sulfate, filtered, and ether was removed under reduced pressure. The residue was then passed as a hexanyl solution through neutral alumina (hexane, R_f = 0.90) and the (triisopropylsilyl)diazomethane was obtained after distillation as a yellow oil (9.80 g, 45% yield): bp 39 °C/ (0.15 mmHg); IR ($CDCl_3$) 2060 cm^{-1} (C=N_2); ^1H NMR ($CDCl_3$) 1.04, 1.06 (s-like, 21 H, $(CH_3)_2CH$), 2.54 (s, 1 H, C(N_2)H); ^{13}C NMR ($CDCl_3$) 11.52 (s, CH_3CHSi), 14.99 (s, C(N_2)), 18.21 (s, CH_3CHSi); ^{29}Si NMR ($CDCl_3$) +6.13; mass spectrum, m/e 199 (M + 1). Anal. Calcd for $C_{10}H_{22}N_2Si$: C, 60.54; H, 11.18; N, 14.12. Found: C, 60.85; H, 11.35, N, 14.00.

Synthesis of Nitrilimines and Diazo Compounds. A stoichiometric amount of *n*-BuLi (1.6 M in hexane) was added to a solution of [bis(diisopropylamino)thiophosphoranyl]-, [bis(diisopropylamino)phosphanyl]-, (trimethylsilyl)-, or (triisopropylsilyl)diazomethane [dibenzo(18)crown-6 ether was added in the synthesis of **18a**] in THF (20 mL), at −78 °C (−90 °C in the case of **18a**), to give the corresponding diazo lithium salts **1**, **4**, **5**, or **6**. After the mixture was stirred for 10 min at this temperature the desired chloride was added to the mixture. The reaction was monitored by IR and ^{31}P NMR. After warming to room temperature, the solvent was removed under vacuum. The residue was treated with pentane and after filtration of the solvent, the nitrilimine or the diazo compound was obtained.

Amounts of starting materials are given for each compound.

***C*-[Bis(diisopropylamino)thiophosphoranyl]methyldiazomethane (7b).** [Bis(diisopropylamino)thiophosphoranyl]diazomethane (0.61 g, 2 mmol), methyl iodide (0.28 g, 2 mmol). After purification on silica gel (pentane/ether, 50/50, R_f = 0.60), diazo **7b** was obtained as a yellow oil (0.32 g, 70% yield): IR (C_6H_6) 2040 cm^{-1} (C=N_2); ^{31}P NMR ($CDCl_3$) +68.80; ^1H NMR (C_6D_6) 1.21 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 1.37 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CH), 1.82 (d, J_{PH} = 10.0 Hz, 3 H, CH_3C), 3.68 (d sept, J_{PH} = 17.0 Hz, J_{HH} = 7.0 Hz, 4 H, CH). Anal. Calcd for $C_{14}H_{31}N_4PS$: C, 52.80; H, 9.82; N, 17.60. Found: C, 52.98; H, 9.88; N, 17.48.

***C*-[Bis(diisopropylamino)thiophosphoranyl]-*N*-(trimethylsilyl)nitrilimine (8a).** [Bis(diisopropylamino)thiophosphoranyl]diazomethane (0.61 g, 2 mmol), trimethylsilyl chloride (0.22 g, 2 mmol): IR (THF) 2010 cm^{-1} (br, s) (C=N—N); ^{31}P (THF) +32.50. After warming to room temperature the rearrangement to the diazo isomer **8b** was observed.

[Bis(diisopropylamino)thiophosphoranyl](trimethylsilyl)diazomethane (8b). After purification on silica gel (hexane/ether, 90/10, R_f = 0.90), the diazo compound **8b**[7b] was obtained as a yellow oil (0.49 g, 65% yield).

***C*-[Bis(diisopropylamino)thiophosphoranyl]-*N*-(triphenylsilyl)nitrilimine (9a).** [Bis(diisopropylamino)thiophosphoranyl]diazomethane (0.61 g, 2 mmol), triphenylsilyl chloride (0.59 g, 2 mmol): IR (THF) 2120 cm^{-1} (br, s) (C=N—N); ^{31}P NMR (THF) +31.10. This compound rearranged to the diazo isomer **9b** after a few hours at room temperature.

[Bis(diisopropylamino)thiophosphoranyl](triphenylsilyl)diazomethane (9b). This compound can only be characterized in solution; decomposition was observed on silica gel: IR (THF) 2100 cm^{-1} (C=N_2); ^{31}P NMR (THF) +59.40.

***C*-[Bis(diisopropylamino)thiophosphoranyl]-*N*-(triisopropylsilyl)nitrilimine (10a).** [Bis(diisopropylamino)thiophosphoranyl]diazomethane (0.61 g, 2 mmol), triisopropylsilyl chloride (0.39 g, 2 mmol). Compound **10a** was obtained as a white solid after recrystallization in acetonitrile (0.88 g, 96% yield): mp 54 °C; IR (pentane) 2050 cm^{-1} (br, s) (C=N—N); ^{31}P NMR (C_6D_6) +33.17; ^1H NMR (C_6D_6) 1.27 (s-like, 21 H, CH_3CHSi), 1.30 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CH), 1.40 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CH), 3.59 (d sept, J_{PH} = 19.7 Hz, J_{HH} = 6.8 Hz, 4 H, CHN); ^{13}C NMR (C_6D_6) 12.02 (s, CH_3CHSi), 17.88 (s, CH_3CHSi), 22.32, 22.69 (s, CH_3CHN), 46.55 (d, J_{PC} = 5.4 Hz, CH_3CHN), C=N is not observable; ^{29}Si NMR (C_6D_6) +12.18; UV (pentane) λ_{max} = 275 nm. Anal. Calcd for $C_{22}H_{49}N_4PSSi$: C, 57.35; H, 10.72; N, 12.16. Found: C, 57.60; H, 10.73; N, 12.02.

[Bis(diisopropylamino)phosphanyl]methyldiazomethane (12b). [Bis(diisopropylamino)phosphanyl]diazomethane (0.54 g, 2 mmol), methyl iodide (0.28 g, 2 mmol). **12b** was obtained as a red oil by distillation (0.33 g, 57% yield): bp 95–100 °C (10^{-2} mmHg); IR (C_6H_6) 2020 cm^{-1} (C=N_2); ^{31}P NMR (C_6D_6) +60.60; ^1H NMR (C_6D_6) 1.18 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CHN), 1.25 (d, J_{HH} = 7.0 Hz, 12 H, CH_3CHN), 1.60 (d, J_{PH} = 7.0 Hz, 3 H, CH_3), 3.40 (d sept, J_{PH} = 14.0 Hz, J_{HH} = 7.0 Hz, 4 H, CHN).

***C*-[Bis(diisopropylamino)phosphanyl]-*N*-(trimethylsilyl)nitrilimine (13a).** [Bis(diisopropylamino)phosphanyl]diazomethane (0.54 g, 2 mmol), trimethylsilyl chloride (0.22 g, 2 mmol). **13a** was characterized in solution: IR (THF) 2100 cm^{-1} (br, s) (C=N—N); ^{31}P NMR (THF) +44.15. This compound rearranged to the diazo isomer **13b**[11] (0.41 g, 60% yield) after 1 day at room temperature.

***C*-[Bis(diisopropylamino)phosphanyl]-*N*-(triphenylsilyl)nitrilimine (14a).** [Bis(diisopropylamino)phosphanyl]diazomethane (0.54 g, 2 mmol), triphenylsilyl chloride (0.59 g, 2 mmol). Nitrilimine **14a** was obtained as a yellow oil (0.85 g, 80% yield): IR (pentane) 2140 cm^{-1} (br, s) (C=N—N); ^{31}P NMR ($CDCl_3$) +42.25; ^1H NMR ($CDCl_3$) 1.06 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 1.13 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 3.35 (d sept, J_{PH} = 12.1 Hz, J_{HH} = 6.6 Hz, 4 H, CHN), 7.36–7.72 (m, 15 H, H arom); ^{13}C NMR ($CDCl_3$) 23.36, 23.49, 23.86, 23.93, (s, CH_3CHN), 49.15 (d, J_{PC} = 12.0 Hz, CH_3CHN), 127.91, 129.36, 135.77 (s, C arom), C=N not observable; ^{29}Si NMR ($CDCl_3$) −10.44; UV (pentane) λ_{max} = 256, 292 nm.

***C*-[Bis(diisopropylamino)phosphanyl]-*N*-(triisopropylsilyl)nitrilimine (15a).** [Bis(diisopropylamino)phosphanyl]diazomethane (0.54 g, 2 mmol), triisopropylsilyl chloride (0.39 g, 2 mmol). Nitrilimine **15a** was obtained as an orange oil (0.77 g, 90% yield): IR (pentane) 2110 cm^{-1} (br, s) (C=N—N); ^{31}P NMR (C_6D_6) +45.74; ^1H NMR (C_6D_6) 1.04 (d, J_{HH} = 6.6 Hz, 12 H, CH_3CHN), 1.16 (d, J_{HH} = 6.6 Hz, 12 H, CH_3CHN), 1.25 (s-like, 21 H, CH_3CHSi), 3.33 (d sept, J_{PH} = 11.9 Hz, J_{HH} = 6.6 Hz, 4 H, CHN); ^{13}C NMR (C_6D_6) 12.99 (s, CH_3CHSi), 18.61 (s, CH_3CHSi), 23.61, 23.74, 23.97, 24.04, (s, CH_3CHN), 49.07 (d, J_{PC} = 11.7 Hz, CH_3CHN), C=N not observable; ^{29}Si NMR (C_6D_6) +6.59 (d, J_{SiP} = 3.6 Hz); UV (pentane) λ_{max} = 244, 273 nm.

[Bis(diisopropylamino)phosphanyl](triisopropylsilyl)diazomethane (16b). Triisopropylsilyl diazomethane (0.40 g, 2 mmol), bis(diisopropylamino)phosphanyl chloride (0.53 g, 2 mmol). After warming up to room temperature, treatment with dry degazed pentane, and filtration, the product **16b** was obtained as a very sensitive orange oil (0.67 g, 78% yield): IR (THF) 2010 cm^{-1} (C=N_2); ^{31}P NMR (THF) +54.02.

[Bis(diisopropylamino)thiophosphoranyl](triisopropylsilyl)diazomethane (17). A stoichiometric amount of sulfur was added to the solution of **16b** in dry and degazed pentane (20 mL). After the mixture was stirred for 3 h at room temperature and purified by column chromatography on silica gel (hexane/ether, 98/2, R_f = 0.72), the product was obtained as an orange solid (0.55 g, 60% yield): mp 100 °C; IR ($CDCl_3$) 2040 cm^{-1} (C=N_2); ^{31}P NMR ($CDCl_3$) +76.93; ^1H NMR ($CDCl_3$) 1.15 (d, J_{HH} = 7.4 Hz, 18 H, CH_3CHSi), 1.38 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHN), 1.39 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHN), 1.59 (sept, J_{HH} = 7.4 Hz, CH_3CHSi), 4.16 (d sept, J_{PH} = 13.3 Hz, J_{HH} = 6.9 Hz, 4 H, CHN); ^{13}C NMR ($CDCl_3$) 12.81 (s, CH_3CHSi), 18.81 (s, CH_3CHSi), 24.26, 24.37, 24.55, 24.61 (s, CH_3CHN), 33.04 (d, J_{PC} = 87.2 Hz, C=N_2), 47.68 (d, J_{PC} = 5.3 Hz, CH_3CHN); ^{29}Si NMR ($CDCl_3$) 6.59 (d, J_{SiP} = 11.1 Hz); mass spectrum, m/e 460 (M^+). Anal. Calcd for $C_{22}H_{49}N_4PSSi$: C, 57.35, H, 10.72; N, 12.16. Found: C, 57.55; H, 10.78; N, 12.10.

***C*,*N*-Bis(triisopropylsilyl)nitrilimine (18a).** (Triisopropylsilyl)diazomethane (0.40 g, 2 mmol), dibenzo(18)crown-6 ether (0.80 g, 2 mmol), triisopropylsilyl chloride (0.39 g, 2 mmol). **18a** was obtained as a pale yellow oil by distillation (0.57 g, 80% yield): bp 90–100 °C (5×10^{-2} mmHg); IR (pentane) 2120 cm^{-1} (br, s) (C=N—N); ^1H NMR (C_6D_6) 1.08–1.13 (m, 18 H, CH_3), 1.00–1.48 (m, 6 H, CH), 1.36–1.39 (m, 18 H, CH_3); ^{13}C NMR (C_6D_6) 12.52, 12.57 (s, CH_3CHSi), 18.07, 18.75 (s, CH_3CHSi), 46.73 (s, C=N); ^{29}Si NMR (C_6D_6) +0.71, +6.40; UV (pentane) λ_{max} = 272 nm. Anal. Calcd for $C_{19}H_{42}N_2Si_2$: C, 64.33; H, 11.93; N, 7.90. Found: C, 64.50; H, 12.00; N, 7.80.

Irradiation of *C*-[bis(diisopropylamino)thiophosphoranyl]-*N*-(triisopropylsilyl)nitrilimine (10a) (0.46 g, 1 mmol) in pentane or benzene solution at 254 or 300 nm gave after evaporation of the solvent and purification on silica gel (hexane/ether, 95/5, R_f = 0.80) carbodiimide **10c** as a pale yellow oil (0.33 g, 72% yield): IR ($CDCl_3$) 2200 cm^{-1} (br, s) (N=C=N); ^{31}P NMR ($CDCl_3$) +55.21; ^1H NMR ($CDCl_3$) 1.03 (s-like, 21 H,

CH_3CHSi), 1.26 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CHN), 1.32 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CHN), 3.64 (d sept, J_{PH} = 19.4 Hz, J_{HH} = 6.8 Hz, 4 H, CHN); ^{13}C NMR ($CDCl_3$) 11.85 (s, CH_3CHSi), 17.57 (s, CH_3CHSi), 21.97, 22.49 (s, CH_3CHN), 46.02 (d, J_{PC} = 5.9 Hz, CH_3CHN), 124.90 (d, J_{PC} = 8.5 Hz, N=C=N); ^{29}Si NMR ($CDCl_3$) +0.32; mass spectrum, *m/e* 469 (M^+). Anal. Calcd for $C_{22}H_{49}N_4PSSi$: C, 57.35; H, 10.72; N, 12.16. Found: C, 57.38; H, 10.74; N, 12.08.

Irradiation of *C,N*-bis(triisopropylsilyl)nitrilimine (18a) (0.57 g, 1.6 mmol) in a pentane solution (20 mL), at 254 (20 H) or 300 nm (48 h), gave carbodiimide **18c** as a pink oil in quantitative yield: IR (pentane) 2200 cm^{-1} (br, s) (N=C=N); ^1H NMR (C_6D_6) 1.00–1.22 (m, 42 H, $(CH_3)_2CH$); ^{13}C NMR (C_6D_6) 12.89 (s, CH_3CHSi), 18.15 (s, CH_3CHSi), 124.25 (s, N=C=N); ^{29}Si NMR (C_6D_6) +3.80; mass spectrum, *m/e* 354 (M^+).

Irradiation of *C*-[bis(diisopropylamino)phosphanyl]-*N*-(triphenylsilyl)nitrilimine (14a) (0.85 g, 1.6 mmol) at 254 nm (15 h) in pentane (10 mL) led to the bis(diisopropylamino)phosphanylnitrile **19**[11b] (0.35 g, 85% yield). The silylated products were not characterized.

Irradiation of *C*-[bis(diisopropylamino)phosphanyl]-*N*-(triisopropylsilyl)nitrilimine (15a) (0.77 g, 1.8 mmol), at 254 nm (20 h), in pentane led to a mixture of nitrile **19** (0.05 g, 10% yield) and carbodiimide **15c**, which was characterized in solution: IR (pentane) 2160 cm^{-1} (br, s) (N=C=N); ^{31}P NMR (pentane) +82.97. A large excess of elemental sulfur was added to this solution. After removal of the solvent and purification on silica gel (hexane/ether, 95/5, R_f = 0.80), [bis(diisopropylamino)thiophosphoranyl](triisopropylsilyl)carbodiimide **10c** (0.21 g, 25% yield) was obtained.

Synthesis of Cycloadducts. A large excess of dipolarophile was added dropwise to a solution of nitrilimine in dry benzene at room temperature (**10a**, **14a**, **15a**, **18a**) or in THF at −78 °C (**8a**, **9a**, **13a**). The reaction was monitored by IR. Then the solvent was removed under vacuum and the adduct was purified by column chromatography on silica gel. In the case of *C*-phosphanylnitrilimines **13a–15a**, the adducts were purified after treatment with elemental sulfur.

23. This product was characterized in solution: IR (THF) 1730 cm^{-1} (C=O); ^{31}P NMR (THF) +41.35. The corresponding thiophosphoranyl adduct **20** was also only characterized in solution: ^{31}P NMR (THF) +55.00; ^{29}Si NMR (THF) +17.97. Attempted purification on silica gel gave the desilylated derivative **26** (pentane/ether, 50/50, R_f = 0.60) as a white solid (74% yield from **8a** and 50% yield from **13a**): mp 75–76 °C; IR (pentane) 1740 cm^{-1} (C=O); ^{31}P NMR ($CDCl_3$) +53.30; ^1H NMR ($CDCl_3$) 1.20 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.24 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.31 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.33 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), AMX system 3.29 (dd, J_{HAHM} = 17.8 Hz, J_{HAHX} = 11.8 Hz, 1 H, CH_A), 3.56 (dd, J_{HAHM} = 17.8 Hz, J_{HMHX} = 4.0 Hz, 1 H, CH_M), 3.71 (s, 3 H, OCH_3), 3.76 (d sept, J_{PH} = 16.9 Hz, J_{HH} = 6.8 Hz, 2 H, CHN), 3.77 (d sept, J_{PH} = 17.2 Hz, J_{HH} = 6.8 Hz, 2 H, CHN), 4.23 (dd, J_{HAHX} = 11.8 Hz, J_{HMHX} = 4.0 Hz, 1 H, CH_X), 6.67 (s, 1 H, NH); ^{13}C NMR ($CDCl_3$) 23.23, 23.41, 23.44 (s, CH_3CHN), 41.25 (d, J_{PC} = 24.9 Hz, CH_2 ring), 47.06 (d, J_{PC} = 2.3 Hz, CH_3CHN), 52.70 (s, OCH_3), 59.70 (d, J_{PC} = 4.5 Hz, CH ring), 152.53 (d, J_{PC} = 144.9 Hz, C=N), 173.58 (s, C=O). Anal. Calcd for $C_{17}H_{35}N_4O_2PS$: C, 52.29; H, 9.03; N, 14.35. Found: C, 52.46; H, 8.94 N, 14.10.

24: ^{31}P NMR ($CDCl_3$) +39.60. **21** (70% yield from **9a** and 55% yield from **14a**) was obtained after purification (pentane/ether, 70/30, R_f = 0.50) as a white solid: mp 98–99 °C; IR (pentane) 1760 (C=O), 1595 cm^{-1} (C=N); ^{31}P NMR ($CDCl_3$) +55.78; ^1H NMR ($CDCl_3$) 1.09 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.23 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.31 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 3.28 (s, 3 H, OCH_3) AMX system 3.37 (dd, J_{HAHM} = 18.0 Hz, J_{HAHX} = 6.8 Hz, 1 H, CH_A), 3.64 (dd, J_{HAHM} = 18.0 Hz, J_{HMHX} = 13.5 Hz, 1 H, CH_M), 3.76 (d sept, J_{PH} = 16.8 Hz, J_{HH} = 6.8 Hz, 2 H, CHN), 3.79 (d sept, J_{PH} = 16.8 Hz, J_{HH} = 6.8 Hz, 2 H, CHN), 4.43 (dd, J_{HMHX} = 13.5 Hz, J_{HAHX} = 6.8 Hz, 1 H, CH_X), 7.30–7.70 (m, 15 H, H arom); ^{13}C NMR ($CDCl_3$) 23.27, 23.55, 23.68 (s, CH_3CHN), 43.04 (d, J_{PC} = 25.6 Hz, CH_2 ring), 47.20 (d, J_{PC} = 5.3 Hz, CH_3CHN), 47.28 (d, J_{PC} = 6.0 Hz, CH_3CHN), 51.71 (s, OCH_3), 61.25 (d, J_{PC} = 4.5 Hz, CH ring), 127.69, 130.06, 134.99, 136.15 (s, C arom), 148.44 (d, J_{PC} = 149.4 Hz, C=N), 173.43 (s, C=O); ^{29}Si NMR ($CDCl_3$) −15.44; mass spectrum, *m/e* 648 (M^+). Anal. Calcd for $C_{35}H_{49}N_4O_2PSSi$: C, 64.78; H, 7.61; N, 8.63. Found: C, 64.92; H, 7.84; N, 8.57.

25: IR (pentane) 1737 cm^{-1} (C=O); ^{31}P NMR (pentane) +40.41. **22** (75% yield from **10a** and 40% from **15a**) was obtained after purification (hexane/ether, 90/10, R_f = 0.26) as an orange oil: IR ($CDCl_3$) 1730 cm^{-1} (C=O); ^{31}P NMR ($CDCl_3$) +56.51; ^1H NMR ($CDCl_3$) 1.01–1.08 (m, 21 H, CH_3CHSi), 1.26 (d, J_{HH} = 6.9 Hz, 6 H, CH_3CHN), 1.28 (d, J_{HH} = 6.9 Hz, 6 H, CH_3CHN), 1.32 (d, J_{HH} = 6.9 Hz, 12 H, CH_3CHN), AMX system 3.31 (dd, J_{HAHB} = 17.8 Hz, J_{HAHX} = 13.2 Hz, 1 H, CH_A), 3.63 (s, 3 H, OCH_3), 3.79 (d sept, J_{PH} = 17.3 Hz, J_{HH} = 6.9 Hz, 2 H, CHN), 3.81 (d sept, J_{PH} = 16.0 Hz, J_{HH} = 6.9 Hz, 2 H, CHN), 4.41 (dd, J_{HAHX} = 5.9 Hz, J_{HBHX} = 13.2 Hz, 1 H, CH_X); ^{13}C NMR ($CDCl_3$) 12.14 (s, CH_3CHSi), 17.90, 18.06 (s, CH_3CHSi), 23.39, 23.65 (s, CH_3CHN), 43.30 (d, J_{PC} = 26.2 Hz, CH_2 ring), 47.02 (d, J_{PC} = 5.4 Hz, CH_3CHN), 51.76 (s, OCH_3), 61.13 (d, J_{PC} = 4.4 Hz, CH ring), 145.93 (d, J_{PC} = 152.2 Hz, C=N), 173.45 (s, C=O); ^{29}Si NMR ($CDCl_3$) +10.33; mass spectrum, *m/e* 546 (M^+). Anal. Calcd for $C_{26}H_{55}N_4O_2PSSi$: C, 57.10; H, 10.14; N, 10.24. Found: C, 56.98; H, 10.10; N, 10.10.

27 and 28. A mixture of **27**:**28** = 71:29 (30% yield) was obtained as a pale yellow oil after purification (hexane/ether, 90/10, R_f = 0.80): IR (pentane) 1735 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 1.01–1.08 (m, CH_3CHSi), 1.07–1.27 (m, CHSi); regioisomer **27** ABX system 2.96 (J_{HAHX} = 16.0 Hz, J_{HAHB} = 16.7 Hz, 1 H, CH_A), 2.99 (J_{HBHX} = 1.4 Hz, J_{HAHB} = 16.7 Hz, 1 H, CH_B), 3.63 (s, 3 H, OCH_3), 4.29 (dd, J_{HXHA} = 16.0 Hz, J_{HXHB} = 1.4 Hz, 1 H, CH_X); regioisomer **28** 3.65 (s, 3 H, OCH_3), ABX system between 3.53 and 3.84; ^{13}C NMR ($CDCl_3$) regioisomer **27** 11.34, 12.38 (s, CH_3CHSi), 18.16, 18.58 (s, CH_3CHSi), 45.60 (s, CH_2 ring), 51.62 (s, OCH_3), 59.42 (s, CH ring), 147.16 (s, C=N ring), 174.48 (s, C=O); regioisomer **28** 11.74, 12.21 (s, CH_3CHSi), 18.33, 18.65 (s, CH_3CHSi), 45.60 (s, CH_2 ring), 51.68 (s, OCH_3), 56.63 (s, CH ring), 142.66 (s, C=N ring), 172.84 (s, C=O); ^{29}Si NMR ($CDCl_3$) regioisomer **27** −1.02, +8.12; regioisomer **28** −0.05, +7.40; mass spectrum, *m/e* 440 (M^+).

29. This compound was isolated (20% yield) as a pale yellow oil (hexane/ether, 95/5, R_f 0.80): IR (pentane) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 1.07 (d, J_{HH} = 6.8 Hz, 18 H, CH_3), 1.08 (d, J_{HH} = 7.5 Hz, 18 H, CH_3), 1.32 (sept-like, J_{HH} = 6.8 Hz, 3 H, CH), 1.76 (sept, J_{HH} = 7.5 Hz, 3 H, CH), 3.84 (s, 3 H, OCH_3), 7.04 (s, 1 H, CH ring); ^{13}C NMR ($CDCl_3$) 11.24, 13.34 (s, CH_3CHSi), 18.27, 18.68 (s, CH_3CHSi), 51.65 (s, OCH_3), 120.59 (s, CH ring), 139.79 (s, C ring), 151.33 (s, C=N ring), 161.61 (s, C=O); ^{29}Si NMR ($CDCl_3$) −0.92, +20.28; mass spectrum, *m/e* 438 (M^+). Anal. Calcd for $C_{23}H_{46}N_2O_2Si_2$: C, 62.96; H, 10.57; N, 6.38. Found: C, 62.86; H, 10.54; N, 6.30.

30. After purification (hexane/ether, 95/5, R_f = 0.60) this compound was obtained as a white oil (20% yield): IR (pentane) 1725 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 1.06 (d, J_{HH} = 7.3 Hz, 18 H, CH_3), 1.08 (d, J_{HH} = 7.3 Hz, 18 H, CH_3), 1.52 (sept like, J_{HH} = 7.3 Hz, 6 H, CH), 3.77 (s, 3 H, OCH_3), 8.16 (s, 1 H, CH ring); ^{13}C NMR ($CDCl_3$) 11.68 12.03 (s, CH_3CHSi), 17.76, 19.00 (s, CH_3CHSi), 50.85 (s, OCH_3), 121.42 (s, C ring), 140.17 (s, CH ring), 154.11 (s, C=N ring), 164.82 (s, C=O); ^{29}Si NMR ($CDCl_3$) +1.70, +15.96. Anal. Calcd for $C_{23}H_{46}N_2O_2Si_2$: C, 62.96; H, 10.57; N, 6.38. Found: C, 62.83; H, 10.51; N, 6.31.

31. This compound was obtained (40% yield) as a pale orange oil (hexane/ether, 90/10, R_f = 0.37); IR (pentane) 1735 cm^{-1} (C=O); ^{31}P NMR ($CDCl_3$) +56.88; ^1H NMR ($CDCl_3$) 1.06 (d, J_{HH} = 7.2 Hz, 9 H, CH_3CHSi), 1.10 (d, J_{HH} = 7.2 Hz, 9 H, CH_3CHSi), 1.27 (d, J_{HH} = 6.9 Hz, 6 H, CH_3CHN), 1.34 (d, J_{HH} = 6.8 Hz, 6 H, CH_3CHN), 1.35 (d, J_{HH} = 7.1 Hz, 6 H, CH_3CHN), 1.37 (d, J_{HH} = 7.0 Hz, 6 H, CH_3CHN), the CHSi protons were not observed, 3.69, 3.71 (s, 3 H, OCH_3), 3.73–3.87 (m, 2 H, CHN), 4.08 (d sept, J_{PH} = 16.1 Hz, J_{HH} = 6.9 Hz, 2 H, CHN), 4.31 (dd, J_{PH} = 0.6 Hz, J_{HAHB} = 4.7 Hz, 1 H, CH_A), 4.48 (d, J_{HAHB} = 4.7 Hz, 1 H, CH_B); ^{13}C NMR ($CDCl_3$) 12.28 (s, CH_3CHSi), 17.89, 18.13 (s, CH_3CHSi), 23.60, 23.62, 23.65, 24.18, 24.23, 24.42, 24.46 (s, CH_3CHN), 47.12 (d, J_{PC} = 5.5 Hz, CH_3CHN), 47.26 (d, J_{PC} = 6.8 Hz, CH_3CHN), 52.40, 52.42 (s, OCH_3), 59.57 (d, J_{PC} = 26.0 Hz, CH ring), 66.46 (s, CH ring), 143.94 (d, J_{PC} = 154.5 Hz, C=N), 171.03, 171.67, (s, C=O); ^{29}Si NMR ($CDCl_3$) +11.34. Anal. Calcd for $C_{28}H_{57}N_4O_4PSSi$: C, 55.60; H, 9.50; N, 9.26. Found: C, 55.41; H, 9.58; N, 9.20.

32. This compound was obtained as a pale yellow oil (30% yield) after purification (hexane/ether, 90/10, R_f = 0.46): IR

(pentane) 1747 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) 1.02 (d, J_{HH} = 6.8 Hz, 9 H, CH_3CHSi), 1.03 (d, J_{HH} = 7.1 Hz, 9 H, CH_3CHSi), 1.08 (d, J_{HH} = 6.6 Hz, 9 H, CH_3CHSi), 1.09 (d, J_{HH} = 6.9 Hz, 9 H, CH_3CHSi), 1.16–1.31 (m, 6 H, CHSi), 3.65 and 3.66 (s, 3 H, OCH_3), 4.30 (AB system, J_{HAHB} = 3.9 Hz, 2 H, CH ring); ^{13}C NMR ($CDCl_3$) 11.54, 12.09 (s, CH_3CHSi), 17.80, 17.95, 18.37 (s, CH_3CHSi), 51.77, 51.81 (s, OCH_3), 61.55 (s, CH_A), 63.92 (s, CH_B), 142.75 (s, C=N ring), 170.44, 172.30 (s, C=O); ^{29}Si NMR ($CDCl_3$) +0.11, +9.39; mass spectrum, m/e 498 (M^+). Anal. Calcd for $C_{25}H_{50}N_2O_4Si_2$: C, 60.19; H, 10.10; N, 5.62. Found: C, 60.40; H, 10.21; N, 5.55.

33 and 34. A stoichiometric amount of *n*-BuLi (1.6 M in hexane) was added dropwise to a solution of nitrilimine **10a** (0.92 g, 2 mmol) in dry THF at −78 °C. After the mixture was warmed to room temperature the lithium salt **33** was characterized in solution: IR (THF) 1605 cm^{-1} (C=N); ^{31}P NMR (THF) +75.42. After slow hydrolysis and purification on silica gel (hexane/ether, 95/5, R_f = 0.67) **34** was isolated as a pale yellow oil (0.65 g, 63% yield): IR (pentane) 1530 cm^{-1} (C=N); ^{31}P NMR ($CDCl_3$) +68.57; ^{1}H NMR ($CDCl_3$) 0.94 (t, J_{HH} = 7.2 Hz, 3 H, CH_2CH_3), 1.06 (d, J_{HH} = 6.9 Hz, 18 H, CH_3CHSi), 1.26 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CHN), 1.33 (d, J_{HH} = 6.8 Hz, 12 H, CH_3CHN), 1.60 (m, 2 H, CH_2), 2.55 (m, 2 H, CH_2), 3.85 (d sept, J_{PH} = 15.0 Hz, J_{HH} = 6.8 Hz, 4 H, CHN), 5.64 (s, 1 H, NH), CHSi and a CH_2 group from Bu were not observed; ^{13}C NMR ($CDCl_3$) 11.34 (s, CH_3CHSi), 13.89 (s, $CH_3(CH_2)_3$), 18.13 (s, CH_3CHSi), 23.40 (s, CH_2), 24.07, 24.11, 24.16, 24.18 (s, CH_3CHN), 26.79 (d, J_{PC} = 27.4 Hz, $CH_3(CH_2)_2CH_2$), 27.40 (s, CH_2CN), 47.22 (d, J_{PC} = 5.4 Hz, CH_3CHN), 146.58 (d, J_{PC} = 155.3 Hz, C=N); ^{29}Si NMR ($CDCl_3$) +6.71; mass spectrum, m/e 518 (M^+). Anal. Calcd for $C_{26}H_{59}N_4PSSi$: C, 60.18; H, 11.46; N, 10.80. Found: C, 60.35; H, 11.40; N, 10.70.

Intramolecular Diels–Alder Reactions of 1,2,4-Triazines. Synthesis of 2,3-Cyclopentenopyridines and 5,6,7,8-Tetrahydroquinolines

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2,3-Cyclopentenopyridines and 5,6,7,8-tetrahydroquinolines are prepared by intramolecular Diels–Alder reactions of appropriately substituted 1,2,4-triazines. Two general routes to the requisite triazine precursors are described.

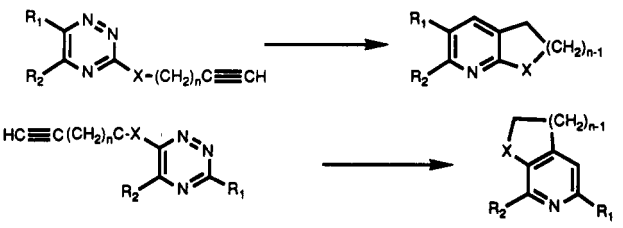
Introduction

Intramolecular inverse-electron-demand Diels–Alder reactions of 1,2,4-triazines constitute a versatile method for the preparation of a variety of functionalized, fused heterocycles.[2] Application of this method to the preparation of fused pyridines requires an alkyne or alkene (or their equivalents) as the dienophilic component which, when tethered to C-3 of the 1,2,4-triazine, leads to fused [2,3-*b*]pyridines following cycloaddition and nitrogen extrusion. The analogous reaction of C-6 tethered dienophiles gives fused [2,3-*c*]pyridines (Scheme I). Our previous efforts in this area employed heteroatoms (X = S, O, and N) to join the dienophile to the diene (1,2,4-triazine). Terminal acetylenes tethered through a carbon atom at position 3 (Scheme I, X = C) with n = 2 would afford 2,3-cycloalkenopyridines,[3] which are of interest as C-3′ quaternizing groups for cephalosporins; alternative synthetic approaches to these compounds have been reviewed.[4] The homologous 5,6,7,8-tetrahydroquinoline synthesis outlined in Scheme I (n = 3) is complimentary to the reduction of quinolines, which leads to the isomeric 1,2,3,4-tetrahydro derivatives through selective reduction of the electron-deficient pyridine ring.

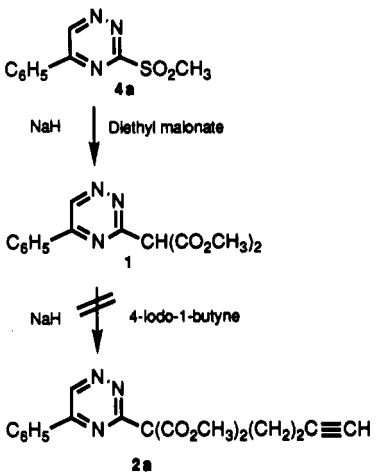
Results and Discussion

Displacement of methyl sulfinate from 3-(methylsulfonyl)-5,6-diphenyl-1,2,4-triazine with anions of active methylene compounds has been reported to occur readily.[5]

Scheme I



Scheme II



Alkylation of the anions of such displacement products (e.g., 1, Scheme II) with 4-iodo-1-butyne would provide access to a carbon-linked dienophilic substituent at C-3 of the 1,2,4-triazine ring. However, since attempts to carry out this alkylation of the displacement product prepared from 3-(methylsulfonyl)-5-phenyl-1,2,4-triazine (**4a**) proved

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