Nitrilimines: Evidence for the Allenic Structure in Solution, Experimental and *Ab Initio* Studies of the Barrier to Racemization, and First Diastereoselective [3 + 2]-Cycloaddition

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Abstract: The lithium salts of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**2**) and [(diisopropylamino)-(dicyclohexylamino)thioxophosphoranyl]diazomethane (**5**) react with the (diisopropylamino)(dicyclohexylamino)-chlorophosphine (**3**) and bis(diisopropylamino)chlorophosphine (**6**), leading to the nitrilimines **4** (63% yield) and **7** (69% yield), respectively. The lithium salt of **2** also reacts with the bis(dicyclohexylamino)phosphenium ion, affording nitrilimine **9** in 51% yield. Using the presence of a chiral substituent either at the carbon or at the nitrogen terminus of the CNN skeleton, variable-temperature solution NMR studies of nitrilimines **4** and **7** demonstrate that they possess a bent allenic structure. The free energy of activation for racemization is ca. 30 kJ mol^{-1}. *Ab initio*/DFT studies performed on nitrilimine with *C*-P(S)H_2 and *N*-PH_2 substituents **10** show that the most likely pathway for the racemization process is inversion at the carbon atom, followed by rotation of the PSR_2 fragment. Bis(trityl)nitrilimine **17** reacts with (*R*)-α-(acryloxy)-*β*,*β*-dimethyl-*γ*-butyrolactone, leading to diastereomeric pyrazolines **18a**,**b** (3/1 ratio) in 60% total yield; this is the first example of a diastereoselective [3 + 2]-cycloaddition reaction involving a nitrilimine.

Introduction

Nitrilimines are important building blocks in organic synthesis, particularly in regio- and stereoselective 1,3-dipolar cycloadditions.[1] However, until recently,[2] these 1,3-dipoles were considered reactive intermediates,[3] and as a consequence there has been very little experimental evidence concerning their actual structures. *Ab initio* calculations revealed that the lowest energy conformations of the parent molecule, formonitrilimine (HCNNH), were the planar propargylic structure **A** and the bent allenic form **B** (Figure 1).[4] Depending on the basis set employed, form **A** or form **B** can be the lowest point on the energy surface. In any case, the energy difference between **A** and **B** was very small, and thus the unsubstituted nitrilimine was described as a "floppy" molecule.[4f] More recently, calculations at much higher levels of theory predicted that the allenic geometry **B** is favored over the propargylic one **A** by 14 kJ mol^{-1},[5] and in a very elegant paper, Maier et al. reported the first matrix-IR spectrum of the parent nitrilimine, which fits nicely with this prediction.[6]

Figure 1. Lowest energy structures of nitrilimine.

We have shown that, using the right set of substituents, nitrilimines can be obtained as stable compounds.[2,7] X-ray analyses[7a−e] revealed that, in the solid state, they featured an allenic structure (form **B**), and as expected, two enantiomers were present in the unit cell. However, almost no information on the structure of nitrilimines in solution is available, even though most of their 1,3-dipolar reactions are performed in this phase.

Here, using low-temperature NMR studies, we show that nitrilimines retain the allenic structure in solution, and we

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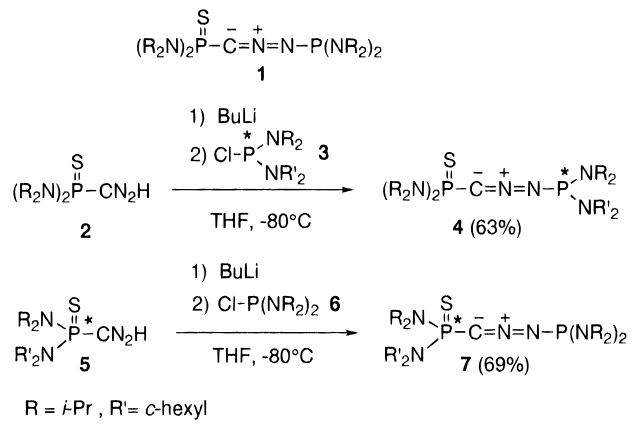
Scheme 1



estimate the barrier to racemization and perform an *ab initio*/DFT study in order to understand the mechanism of this process. Lastly, we report the first diastereoselective [3 + 2]-cycloaddition reaction involving a nitrilimine.

Results and Discussion

In order to reveal the chiral axis which is only present in the allenic form **B**, our strategy was based on the preparation of nitrilimines possessing a chiral substituent either at the carbon or at the nitrogen terminus. For this purpose, *C*-(thioxophosphoranyl)-*N*-phosphinonitrilimines offer several advantages. These derivatives are easily accessible, and they are stable at room temperature.[7a] Moreover, the X-ray data for the nitrilimine **1**[7a] (Scheme 1) are in excellent agreement with the calculated MP2/6-311G(2df,2p) geometry of HCNNH,[5a] showing that for these phosphorus-substituted nitrilimines, no major electronic or steric effects are operating. Last but not least, the presence of the phosphorus nuclei is crucial since ^{31}P NMR spectroscopy allows a rapid and convenient observation of nitrilimines.[8a]

The lithium salt of [bis(diisopropylamino)thioxophosphoranyl]-diazomethane[7a] (**2**) reacted in THF, at −80 °C, with the chiral chlorophosphine **3**, leading to the nitrilimine **4** as a yellow oil in 63% yield. In the same way, nitrilimine **7** was obtained as a yellow oil in 69% yield, by reacting the lithium salt of the chiral (thioxophosphoranyl)diazomethane **5** with the bis(diisopropylamino)chlorophosphine **6**.

Nitrilimines **4** and **7** were characterized by spectroscopy in solution. At room temperature, in THF, the ^{31}P NMR spectrum of **4** and **7** consisted of two doublets typical of (thioxophosphoranyl)(phosphino)nitrilimines[7a,8a] [**4**, +35.3 and +103.0, J_{PP} = 5 Hz; **7**, +35.8 and +100.2, J_{PP} = 5.1 Hz]. Since at 25 °C no evidence for the presence of diastereomers was apparent, low-temperature ^{31}P NMR spectra of nitrilimines **4** and **7** were recorded in a 95/5 solution of 2-methylpentane and CD_2Cl_2 (Figures 2 and 3). For both compounds, below 220 K the J_{PP} coupling constant was no longer observable, and a shielding of the two signals occurred on decreasing the temperature. The temperature-dependent chemical shift is a well-known phenomenon;[8b] furthermore, the initial chemical shifts were restored when the solutions were allowed to warm to room temperature. For nitrilimine **4**, at 150 K, the signal corresponding to the chiral (low-field) σ^3-phosphorus atom split into two signals with a chemical shift difference of 200 Hz; this phenomenon was less pronounced for the σ^4-phosphorus atom, where two broad, overlapping signals about 50 Hz apart were observed. The coalescence temperature can be estimated to be 160 K (Figure 2).

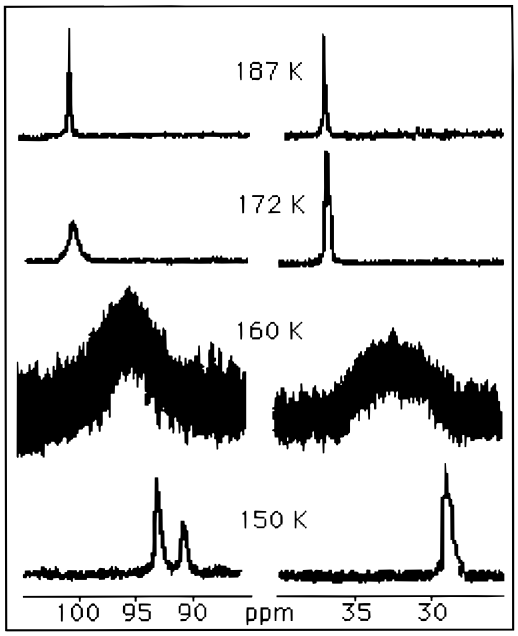


Figure 2. ^{31}P NMR spectra of nitrilimine **4** at various temperatures in a 95/5 solution of 2-methylpentane and CD_2Cl_2.

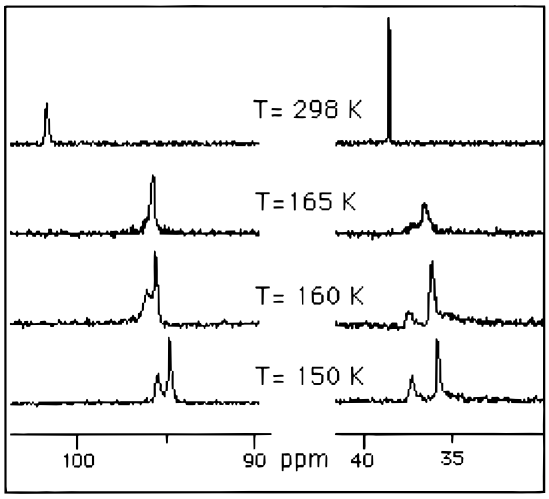


Figure 3. ^{31}P NMR spectra of nitrilimine **7** at various temperatures in a 95/5 solution of 2-methylpentane and CD_2Cl_2.

The same trend was found for nitrilimine **7**, featuring the chiral substituent at the carbon terminus. At 150 K, two sets of two doublets were observed, and the splitting was again more pronounced for the chiral phosphorus atom, which is now the high-field σ^4-one. Here too, the coalescence temperature was ca. 160−165 K (Figure 3).

In order to address possible interpretations of these low-temperature measurements in terms of restricted rotation due to the bulky substituents at the phosphorus atoms, we recorded the ^{31}P NMR spectra of the nitrilimine **1**[7a] and of the *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(dicyclohexylamino)phosphino]nitrilimine **9** at low temperature. Note that nitrilimine **9** is not accessible through the addition of the lithium salt of **2** to the bis(dicyclohexylamino)chlorophosphine (**8**), probably because of the considerable steric hindrance; the corresponding bis(dicyclohexylamino)phosphenium ion has to be used and in this way nitrilimine **9** was isolated as yellow crystals (mp 92 °C) in 51% yield (Scheme 2).

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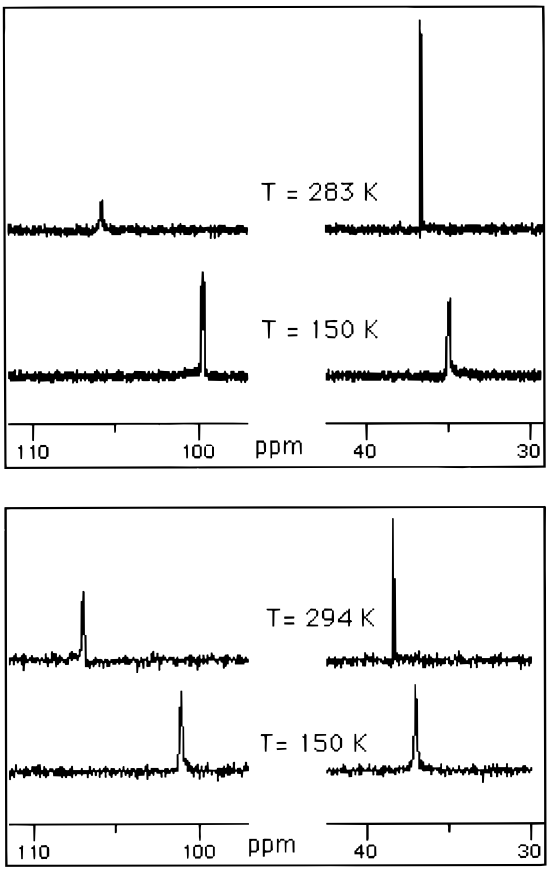
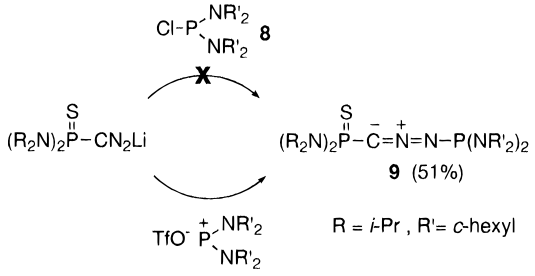


Figure 4. ^{31}P NMR spectra of nitrilimines **1** (top) and **9** (bottom) at various temperatures in a 95/5 solution of 2-methylpentane and CD_2Cl_2.

Scheme 2



In analogy with nitrilimines **4** and **7**, a temperature-dependent shielding of the two signals was also observed for derivatives **1** and **9**. However, of primary importance, no broadening or separation of the lines occurred, even at 150 K (Figure 4).

Therefore, the signal separation occurring for nitrilimines **4** and **7** (Figures 1 and 2), featuring a chiral substituent, is due to the presence of two diastereoisomers which rapidly interconvert at temperatures above 160 K. This implies that these nitrilimines possess a bent allenic structure in solution. The free energy of activation for racemization as estimated at the coalescence temperature is ca. 30 kJ mol^{-1}. This value is at the lower limit of the range found for cumulenes such as ketenimines[9] (60−80 kJ mol^{-1}) and carbodiimides[10] (28−73 kJ mol^{-1}). The trend is confirmed by theoretical calculations (*vide infra*), which predict a lower energy pathway for nitrilimines than for ketenimine (54 kJ mol^{-1})[9b] and carbodiimide (33−44 kJ mol^{-1}).[10c]

Table 1. Calculated Structural Parameters[a] of Nitrilimine $H_2P(S)CNNPH_2$ (**10**)

parameter	MP2/ 6-31G*	B3-LYP/6-31G* $\epsilon = 1$[c]	B3-LYP/6-31G* $\epsilon = 40$[d]	B3-LYP/ 6-311+G**	expt[b]
r(P−C)	1.771	1.796	1.790	1.796	1.771
r(C−N)	1.199	1.200	1.199	1.196	1.177
r(N−N)	1.246	1.230	1.231	1.224	1.236
r(N−P)	1.769	1.787	1.793	1.783	1.777
∠PCN	145.9	135.6	136.4	135.4	138.2
∠CNN	173.2	173.0	173.0	173.5	173.6
∠NNP	116.4	117.0	116.6	118.2	115.0
τPCNN	128.9	133.3	135.3	132.1	
τCNNP	130.5	132.4	131.2	132.0	

[a] Bond lengths in angstroms and bond angles in degrees. [b] Crystal structure of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**1**).[7a] [c] $\epsilon = 1$ corresponds to the gas phase. [d] SCIPCM calculations.

Several mechanisms of isomerization of nitrilimines can be envisaged: inversion at the carbon, nitrogen, or phosphorus atom and rotation about the C−P or N−P bonds. In order to model the nitrilimines **4** and **7**, we have examined the structure of nitrilimine with *C*-P(S)H_2 and *N*-PH_2 substituents, i.e. $H_2P(S)$−*CNN*−PH_2 (**10**). A previous study has shown that inclusion of electron correlation is essential for the proper description of the structure of formonitrilimine.[5a] Here, we have optimized compound **10** with three correlated levels of theory: MP2/6-31G*, B3-LYP/6-31G*, and B3-LYP/6-311+G** (Table 1). The MP2/6-31G* and B3-LYP/6-31G* methods lead to similar results. Expanding the basis set from 6-31G* to 6-311+G** has little effect on the optimized geometry. As with the parent molecule, formonitrilimine (HCNNH), **10** is calculated to have an allenic structure. The rather short NN bond length (1.230 Å) and long CN bond length (1.199 Å) reflect the $-C^{-}{=}N^{+}{=}N-$ cumulenic skeleton in **10**. This is confirmed by the value of the PCN angle which is close to the value calculated for the optimized structure of the allenic form of formonitrilimine (144.6°; for the propargylic form the value is 181.4°).[5a] Note that the C−P bond in **10** is almost perpendicular to the N−P moiety (dihedral angle = 98.5°, B3-LYP/6-31G*). **10** is a chiral molecule, and **10′** (Figure 5) represents its enantiomer (mirror image), with identical energy (Table 2). In fact, the propargylic structure **11** (Figure 5) corresponds to the transition structure for inversion at the carbon atom. The calculated structural parameters of **10** at the B3-LYP/6-31G* level are in very good accord with those obtained from the X-ray crystal structure[7a] of *C*-[bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphanyl]nitrilimine (**1**). The calculated bond lengths are within 0.02 Å and bond angles within 3° of the experimental values, reiterating that the diisopropylamino substitutions have no major electronic or steric effects on the structure. We have also investigated the effects of solvent on the structure of **10** using the SCIPCM solvation theory.[11] As seen in Table 1, the introduction of a reaction field, in a polar dielectric medium of $\epsilon = 40$, has only a small influence on the structure of **10** (Table 1). This result is in accord with the fact that **10** has a modest dipole moment of 2.55 Debye (B3-LYP/6-31G*).

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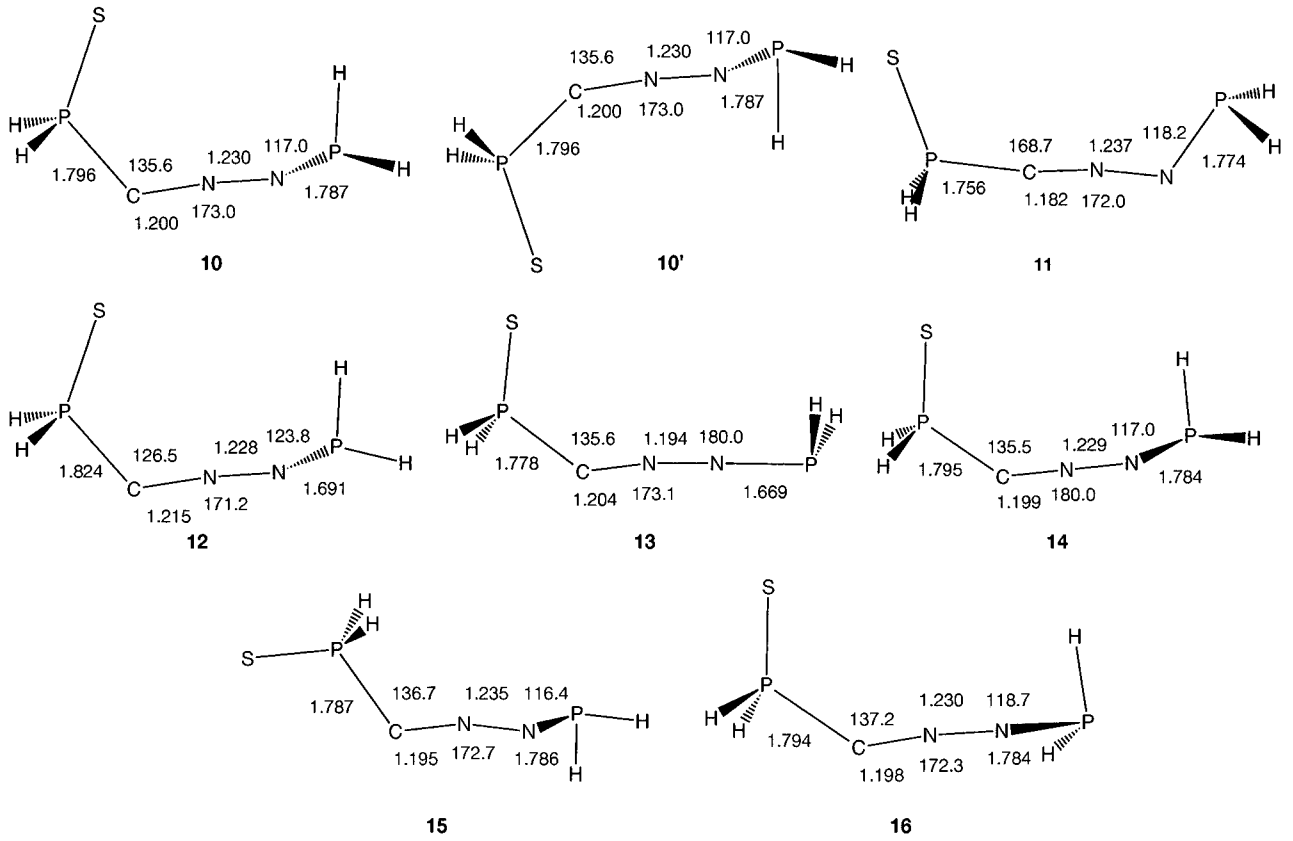

Figure 5. Optimized geometries (B3-LYP/6-31G*) for the equilibrium structures (**10** and **10′**) and transition structures (**11**−**16**) of $H_2P(S)CNNPH_2$. Bond lengths in angstroms and bond angles in degrees.

Table 2. Calculated Total Energies[a] (hartrees), Relative Energies[b] (kJ mol^{-1}) and Zero-Point Vibrational Energies[c] (ZPVE, kJ mol^{-1}) of Nitrilimine $H_2P(S)CNNPH_2$ (**10**) and Transition Structures **11**−**16**

species	total energy	N_i[d]	ZPVE	relative energy
10	−1230.927 61	0	138.9	0.0
10′	−1230.927 61	0	138.9	0.0
11	−1230.922 57	1	137.5	11.9
12	−1230.866 41	1	134.0	155.8
13	−1230.906 18	2	137.4	54.8
14	−1230.926 81	0	138.9	2.2
15	−1230.924 31	1	137.8	7.6
16	−1230.925 31	1	137.7	4.9

[a] B3-LYP/6-311+G**//B3-LYP/6-31G* values. [b] Based on the total energies together with zero-point vibrational contribution. [c] B3-LYP/6-31G* values, scaled by 0.9804.[19] [d] Number of imaginary frequencies (B3-LYP/6-31G* level).

The calculated barriers for the various isomerization processes, at the B3-LYP/6-311+G(3df,2p)//B3-LYP/6-31G* + ZPVE level, are summarized in Table 2. Inversion at the phosphorus atom of the PH_2 group, via transition structure **12** (Figure 5), is calculated to require a high activation energy of 156 kJ mol^{-1} (making this process too slow under our experimental conditions). In contrast, inversion at carbon, via the propargylic transition structure **11** (Figure 5), requires a barrier of ca. 12 kJ mol^{-1} (thus making this process fast, even at the lowest temperatures accessed in this study). Higher-level G2(MP2) theory[12] predicts a similar barrier height, 15 kJ mol^{-1}. The linear NNP structure (**13**) corresponds to the transition structure for inversion at the terminal nitrogen atom. However, **13** is a second-order saddle point which has two imaginary frequencies. Both of the displacement vectors of the normal modes for the imaginary frequencies correspond to inversion of the nitrogen atom, but in mutually perpendicular directions. **13** lies 55 kJ mol^{-1} higher in energy than the equilibrium structures **10**. A similar activation barrier (54 kJ mol^{-1}) was calculated for the nitrogen inversion in ketenimine.[9b] Nitrilimines **10**/**10′** have a slightly bent CNN framework (173°). Attempts to locate the transition structure for inversion on the central nitrogen atom were not successful. Constraining the CNN skeleton to be linear (**14**) increases the energy by just 2 kJ mol^{-1}. This result clearly indicates that the CNN bending potential is extremely flat, and this moiety is best considered to be quasi-linear. Note that small barriers (Table 2) are calculated for the rotations about the C−P and N−P bonds via transition structures **15** and **16**, respectively.

It is conceivable that the stereoisomerization between **10** and **10′** can occur via a combination of inversion and rotation. The two most likely pathways for the racemization process are (a) inversion of the carbon atom followed by rotation of the PSH_2 moiety and (b) inversion of the (terminal) nitrogen atom followed by the rotation of the PH_2 fragment. Pathway (b) is a high-energy process because of the involvement of an inversion at nitrogen (55 kJ mol^{-1}). Hence, (a) is the preferred pathway for racemization in **10** and the associated barrier is predicted to be in the order of 15 kJ mol^{-1}. Inclusion of a solvent reaction field is predicted to have little effect on the calculated racemization barrier (change by less than 1 kJ mol^{-1}).

The calculated racemization barrier for **10** is significantly smaller than the observed value (30 kJ mol^{-1}) for compounds **4** and **7**.[13] How do we account for this discrepancy between theory and experiment? Since the racemization of **10** (**4** or **7**) has a low activation barrier, the racemization rate will depend on the rate at which the $P(S)R_2$ group can move through the solvent cage, and such movement becomes the slowest step for

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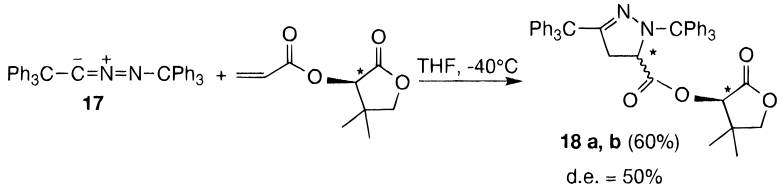
(13) Semiempirical calculations at the PM3 level give similar racemization barriers for **10** and **7**.

Scheme 3



a diffusion-controlled reaction.[14] In other words, the rate of racemization of **10** (**4** or **7**) depends on the bulkiness of the substituents R and the viscosity of the solvent used. For compounds **4** and **7**, one would expect a larger barrier for the movement of the bulky substituents in solution and hence a relatively large racemization barrier in a low-temperature (viscous) solvent.

Of special interest for heterocyclic synthesis, a diastereoselective [3 + 2]-cycloaddition reaction has been observed by addition at −40 °C of (*R*)-α-(acryloxy)-*β*,*β*-dimethyl-*γ*-butyrolactone to bis(trityl)nitrilimine[7c] **17**. Indeed, diastereomeric pyrazolines **18a**,**b** were obtained in 60% total yield in a 3/1 ratio according to the integrated AB sections of the pyrazoline ABX system in the ^{1}H NMR spectra (Scheme 3). Considering the low energetic barrier between the enantiomerics nitrilimines in solution, it is quite likely that in this case a Curtin−Hammett situation prevails.

Conclusion

We have shown that in solution nitrilimines possess a bent allenic-type structure **B**, the energetic barriers between the enantiomers being experimentally estimated at about 30 kJ mol^{-1}. *Ab initio*/DFT studies show that the most likely pathway for the racemization process is inversion at the carbon atom of the nitrilimine moiety, followed by rotation of the PSR_2 fragment. For the first time, a diastereoselective [3 + 2]-cycloaddition reaction involving a nitrilimine has been performed. Considering the wide utility of these readily available 1,3-dipoles, this first example opens new perspectives in heterocyclic synthesis.

Experimental Section

All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Brucker AC80, AC200, WM250, or AMX400 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4-Si as external standard, and ^{31}P NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Infrared spectra were recorded on a Perkin-Elmer FT-IR spectrometer 1725 X. Conventional glassware was used. The (*R*)-α-(acryloxy)-*β*,*β*-dimethyl-*γ*-butyrolactone was purchased from Aldrich Chemical Co. and used as received.

Computational Methods. *Ab initio*[15] and density functional[16] calculations were carried out using the GAUSSIAN 92/DFT series of programs.[17] The equilibrium and transition structures of nitrilimine $H_2P(S)CNNPH_2$ were optimized with the 6-31G* basis set[15] using the B3-LYP formulation[18] of density functional theory, i.e. Becke's 3-parameter exchange functional[18a] and the Lee−Yang−Parr correctional functional.[18b] Harmonic vibrational frequencies were calculated at the B3-LYP/6-31G* level in order to characterize the stationary points as minima and saddle points and to evaluate zero-point vibrational energies (ZPVEs). The directly calculated ZPVEs were scaled by 0.9804 to account for the overestimation of ZPVEs at this level of theory.[19] Improved relative energies were obtained through B3-LYP calculations with the larger 6-311+G** basis set,[15] based on the B3-LYP/6-31G* optimized geometries. Our best relative energies discussed in the text correspond to the B3-LYP/6-311+G** values together with zero-point vibrational contributions. The carbon inversion barrier in **10** was also investigated using the Gaussian-2 [G2(MP2)] theory.[12] The G2(MP2) method, described in detail elsewhere,[12] is a composite procedure based effectively on QCISD(T)/6-311+G(3df,-2p)//MP2/6-31G* energies (evaluated by making certain additivity assumptions) together with zero-point vibrational and isogyric corrections. The effects of solvent on the racemization of nitrilimine **10** were studied using the self-consistent isodensity polarizable continuum model (SCIPCM)[11] of solvation. In this model the solute is taken to occupy a cavity which is determined self-consistently from an isodensity surface (0.0004 au), and the solvent is represented by a continuous dielectric, characterized by a given dielectric constant (ϵ).

(Dicyclohexylamino)(diisopropylamino)chlorophosphine (3). To a THF solution (250 mL) of (dicyclohexylamino)dichlorophosphine[20] (36.65 g, 0.130 mol), at −78 °C, was added dropwise a THF solution (30 mL) of freshly prepared LDA (13.91 g, 0.130 mol). The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. Derivative **3** was obtained as an orange solid from an ether solution at room temperature (34.43 g, 76% yield): mp 240 °C; ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 1.06 (d, J_{HH} = 6.9 Hz, 6 H, CH_3), 1.11 (d, J_{HH} = 6.9 Hz, 6H, CH_3), 1.61 (m, 20 H, CH_2), 3.10 (m, 2 H, NC*H*CH_2), 3.55 (sept d, J_{HH} = 6.9 Hz, J_{PH} = 12.7 Hz, 2 H, NC*H*CH_3); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 22.74 (d, J_{PC} = 11.3 Hz, CH_3), 23.93 (d, J_{PC} = 5.6 Hz, CH_3), 25.59 (s, CH_2), 26.54 (d, J_{PC} = 11.5 Hz, CH_2), 33.90 (d, J_{PC} = 12.3 Hz, CH_2), 34.44 (d, J_{PC} = 5.6 Hz, CH_2), 47.41 (d, J_{PC} = 13.8 Hz, NC*H*CH_3), 56.57 (d, J_{PC}= 9.9 Hz, N*C*HCH_2); ^{31}P NMR (32.438 MHz, $CDCl_3$) δ +134.88. Anal. Calcd for $C_{18}H_{36}N_2ClP$: C, 62.32; H, 10.46; N, 8.07. Found: C, 62.41; H, 10.52; N, 8.01.

***C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[(dicyclohexylamino)(diisopropylamino)phosphino]nitrilimine (4).** To a THF solution (10 mL) of [bis(diisopropylamino)thiophosphoranyl]diazomethane (**2**)[7a] (0.40 g, 1.315 mmol), at −78 °C, was added dropwise a stoichiometric amount of BuLi in hexanes. After the mixture was stirred for 30 min at −78 °C, a THF solution (3 mL) of chlorophosphine **3** (0.455 g, 1.315 mmol) was added. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. Nitrilimine **4** was obtained as a yellow oil (0.484 g, 63%): ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 1.12 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.23 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.31 (d, J_{HH} = 6.9 Hz, 12 H, CH_3), 1.37 (d, J_{HH} = 6.8 Hz, 12 H, CH_3), 1.66 (m, 20 H, CH_2), 2.92 (m, 2 H, NC*H*CH_2), 3.71 (m, 6 H,

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NC*H*CH_3); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 22.50 (d, J_{PC} = 13.0 Hz, CH_3), 22.93 (broad s, CH_3), 24.06, 24.15, 24.21, 24.36 (s, CH_3), 26.06 (s, CH_2), 27.0 (d, J_{PC} = 5.5 Hz, CH_2), 34.99 (d, J_{PC} = 5.5 Hz, CH_2), 36.14 (d, J_{PC} = 9.6 Hz, CH_2), 46.29 (d, J_{PC} = 12.4 Hz, PN*C*HCH$_3$), 46.62 (d, J_{PC} = 5.2 Hz, P(S)N*C*HCH$_3$), 55.52 (d, J_{PC} = 9.6 Hz, N*C*HCH$_2$) the CNN carbon atom is not observed; ^{31}P NMR (32.438 MHz, C_6D_6) δ +103.0, +35.3 (d, J_{PP} = 5.0 Hz); IR (THF) 2039 cm^{-1} (CNN). Anal. Calcd for $C_{31}H_{64}N_6P_2S$: C, 60.55; H, 10.49; N, 13.67. Found: C, 60.61; H, 10.55; N, 13.71.

[(Dicyclohexylamino)(diisopropylamino)phosphino](trimethylsilyl)-diazomethane. To a THF solution (10 mL) of (trimethylsilyl)-diazomethane[21] (3.2 g, 28 mmol), at −78 °C, was added the stoichiometric amount of BuLi in hexanes. After the solution was stirred at this temperature for 30 min, a THF solution (20 mL) of chlorophosphine **3** (9.7 g, 28 mmol) was added dropwise. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. [(Dicyclohexylamino)(diisopropylamino)phosphino](trimethylsilyl)diazomethane was obtained as a deep red oil (9.75 g, 82% yield): ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 0.18 (s, 9 H, $SiCH_3$), 1.12 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.18 (d, J_{HH} = 6.8 Hz, 6 H, CH_3), 1.55 (m, 20 H, CH_2), 2.87 (m, 2 H, NC*H*CH_2), 3.44 (sept d, J_{HH} = 6.8 Hz, J_{PH} = 11.7 Hz, 2 H, NC*H*CH_3); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 1.17 (d, J_{PC} = 5.1 Hz, $SiCH_3$), 23.45, 23.57, 24.29, 24.45 (s, CH_3), 25.64, 26.33, 26.67 (s, CH_2), 28.23 (d, J_{PC} = 91.2 Hz, PC), 34.19 (d, J_{PC} = 6.5 Hz, CH_2), 35.80 (d, J_{PC} = 7.6 Hz, CH_2), 47.62 (d, J_{PC} = 12.7 Hz, N*C*HCH$_3$), 57.53 (d, J_{PC} = 10.2 Hz, N*C*HCH$_2$); ^{31}P NMR (32.438 MHz, C_6D_6) δ +58.6; IR (THF) 2018 cm^{-1} (CN_2). Anal. Calcd for $C_{22}H_{45}N_4SiP$: C, 62.22; H, 10.68; N, 13.19. Found: C, 62.41; H, 10.78; N, 13.11.

[(Dicyclohexylamino)(diisopropylamino)phosphino]diazomethane. To a THF solution (25 mL) of [(dicyclohexylamino)-(diisopropylamino)phosphino](trimethylsilyl)diazomethane (9.75 g, 23 mmol) was added neat methanol (1.85 mL, 46 mmol). The solution was stirred for 8 h, the solvent and excess methanol were removed under vacuum, and the residue treated with pentane. [(Dicyclohexylamino)(diisopropylamino)phosphino]diazomethane was obtained as an orange liquid and used without further purification (6.69 g, 85% yield): ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 1.08 (d, J_{HH} = 6.6 Hz, 6 H, CH_3), 1.19 (d, J_{HH} = 6.6 Hz, 6 H, CH_3), 1.65 (m, 20 H, CH_2), 2.85 (m, 2 H, NC*H*CH_2), 3.12 (d, J_{PH} = 20.2 Hz, 1 H, CN_2H), 3.46 (sept d, J_{HH} = 6.6 Hz, J_{PH} = 11.1 Hz, 2 H, NC*H*CH_3); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 23.77, 23.88, 23.91, 24.04 (s, CH_3), 25.12, 25.50 (s, CH_2), 31.07 (d, J_{PC} = 10.5 Hz, PC), 34.61 (d, J_{PC} = 7.2 Hz, CH_2), 35.00 (d, J_{PC} = 7.6 Hz, CH_2), 46.87 (d, J_{PC} = 11.6 Hz, N*C*HCH$_3$), 56.38 (d, J_{PC} = 9.4 Hz, N*C*HCH$_2$); ^{31}P NMR (32.438 MHz, C_6D_6) δ +50.3; IR (THF) 2047 cm^{-1} (CN_2).

[(Dicyclohexylamino)(diisopropylamino)thioxophosphoranyl]-diazomethane (5). To a pentane solution (20 mL) of [(dicyclohexylamino)(diisopropylamino)phosphino]diazomethane (6.69 g, 19 mmol) was added, at 0 °C, an excess of elemental sulfur (0.7 g, 21 mmol). After the solution was stirred overnight at room temperature, the excess of sulfur was filtered off and the solvent was removed under vacuum. Derivative **5** was isolated by column chromatography (pentane/ether, 90/10, R_f = 0.7) as yellow crystals (5.30 g, 72% yield): mp 103−104 °C; ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 1.26 (d, J_{HH} = 6.7 Hz, 6 H, CH_3), 1.35 (d, J_{HH} = 6.7 Hz, 6 H, CH_3), 1.77 (m, 20 H, CH_2), 3.2 (m, 2 H, NC*H*CH_2), 3.67 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 19.4 Hz, 2 H, NC*H*CH_3), 3.88 (d, J_{PH} = 10.6 Hz, 1 H, CN_2H); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 22.34, 22.38, 22.89, 22.94 (s, CH_3), 25.48, 26.76 (s, CH_2), 33.15 (d, J_{PC} = 7.3 Hz, CH_2), 33.19 (d, J_{PC} = 7.9 Hz, CH_2), 40.47 (d, J_{PC} = 134.4 Hz, PC), 46.39 (d, J_{PC} = 5.4 Hz, N*C*HCH$_3$), 56.51 (d, J_{PC} = 4.7 Hz, N*C*HCH$_2$); ^{31}P NMR (32.438 MHz, C_6D_6) δ +58.2; IR (THF) 2095 cm^{-1} (CN_2). Anal. Calcd for $C_{19}H_{37}N_4PS$: C, 59.34; H, 9.70; N, 14.57. Found: C, 59.41; H, 9.73; N, 14.61.

***C*-[(Dicyclohexylamino)(diisopropylamino)thioxophosphoranyl]-*N*-[bis(diisopropylamino)phosphino]nitrilimine (7).** To a THF solution (5 mL) of diazo derivative **5** (0.54 g, 1.40 mmol), at −78 °C, was added the stoichiometric amount of BuLi in hexanes. After the solution was stirred for 30 min at −78 °C, a THF solution (10 mL) of bis-(diisopropylamino)chlorophosphine (0.38 g, 1.40 mmol) was added. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. Nitrilimine **7** was isolated as a yellow oil (0.59 g, 69%): ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 1.13 (d, J_{HH} = 6.7 Hz, 12 H, CH_3), 1.18 (d, J_{HH} = 6.6 Hz, 12 H, CH_3), 1.31 (d, J_{HH} = 6.7 Hz, 6 H, CH_3), 1.37 (d, J_{HH} = 6.7 Hz, 6 H, CH_3), 1.75 (m, 20 H, CH_2), 3.26 (m, 2 H, NC*H*CH_2), 3.51 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 11.2 Hz, 2 H, NC*H*CH_3), 3.71 (sept d, J_{HH} = 6.7 Hz, J_{PH} = 19.9 Hz, 4 H, NC*H*CH_3); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 22.22, 22.27, 22.32, 22.37, 22.61, 22.64, 23.73, 23.85, 24.10, 24.23, 24.29, 24.42 (s, CH_3), 25.30, 26.64, 32.42, 33.16 (s, CH_2), 45.68 (d, J_{PC} = 12.3 Hz, PN*C*HCH$_3$), 45.71 (d, J_{PC} = 12.3 Hz, PN*C*HCH$_3$), 46.22 (d, J_{PC} = 5.7 Hz, PSN*C*HCH$_3$), 56.0 (d, J_{PC} = 7.8 Hz, N*C*HCH$_2$), 61.25 (d, J_{PC} = 99.6 Hz, PC); ^{31}P NMR (32.438 MHz, C_6D_6) δ +100.2, +35.8 (d, J_{PP} = 5.1 Hz); IR (THF) 2040 cm^{-1} (CNN). Anal. Calcd for $C_{31}H_{64}N_6P_2S$: C, 60.55; H, 10.49; N, 13.67. Found: C, 60.58; H, 10.52; N, 13.71.

***C*-[Bis(diisopropylamino)thioxophosphoranyl]-*N*-[bis(dicyclohexylamino)phosphino]nitrilimine (9).** To a THF solution (5 mL) of [bis(diisopropylamino)thioxophosphoranyl]diazomethane (**2**) (0.265 g, 0.871 mmol), at −78 °C, was added the stoichiometric amount of BuLi in hexanes. After the solution was stirred for 30 min at −78 °C, a THF solution (5 mL) of bis(dicyclohexylamino)phosphenium cation (0.47 g, 1.20 mmol) was added at −78 °C. The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was treated with pentane and filtered. Nitrilimine **9** was purified by crystallization from acetonitrile at −20 °C as pale yellow crystals (1.12 g, 51%): mp 92 °C; ^{1}H NMR (200.132 MHz, $CDCl_3$) δ 1.33 (d, J_{HH} = 6.5 Hz, 12 H, CH_3), 1.38 (d, J_{HH} = 6.5 Hz, 12 H, CH_3), 1.65 (m, 40 H, CH_2), 2.97 (m, 4 H, NC*H*CH_2), 3.68 (sept d, J_{HH} = 6.5 Hz, J_{PH} = 19.4 Hz, 4 H, NC*H*CH_3); ^{13}C NMR (62.896 MHz, $CDCl_3$) δ 22.46, 22.97 (s, CH_3), 25.80, 26.85, 26.77, 26.94 (s, CH_2), 34.87 (d, J_{PC} = 5.9 Hz, CH_2), 35.80 (d, J_{PC} = 8.8 Hz, CH_2), 46.39 (d, J_{PC} = 5.9 Hz, N*C*HCH$_3$), 55.23 (d, J_{PC} = 9.8 Hz, N*C*HCH$_2$), the CNN carbon atom was not observed; ^{31}P NMR (32.438 MHz, C_6D_6) δ +101.7, +37.2 (d, J_{PP}= 5.1 Hz); IR (THF) 2040 cm^{-1} (CNN). Anal. Calcd for $C_{37}H_{72}N_6P_2S$: C, 63.94; H, 10.44; N, 12.09. Found: C, 63.88; H, 10.42; N, 12.01.

Cycloadducts 18a and 18b. To a THF solution (10 mL) of freshly prepared bis(triphenylmethyl)nitrilimine **17**[7c] (0.282 g, 0.536 mmol), at −40 °C, was added the stoichiometric amount of (*R*)-α-(acryloxy)-*β*,*β*-dimethyl-*γ*-butyrolactone (0.098 g, 0.536 mmol). The solution was allowed to warm to room temperature, and the solvent was removed under vacuum. The residue was washed with pentane (2 × 5 mL). Diastereomers **18a** and **18b** (in a 3:1 ratio according to ^{1}H NMR spectroscopy) were obtained as a yellow powder (0.228 g, 60%). **18a** (75%)/**18b** (25%): ^{1}H NMR (250.133 MHz, $CDCl_3$) δ 1.22, 1.29 (s, 6 H, CH_3, **18a** and **18b**), 2.26 (dd, 0.75 H, J_{HaHb} = 17.8 Hz, J_{HHx} = 12.9 Hz, $CH_aH_bCH_xCOO$, Ha or b, **18a**), 2.33 (dd, 0.25 H, J_{HaHb} = 17.7 Hz, J_{HHx} = 12.8 Hz, $CH_aH_bCH_xCOO$, Ha or b, **18b**), 2.57 (dd, 0.75 H, J_{HaHb} = 17.8 Hz, J_{HHx} = 7.5 Hz, $CH_aH_bCH_xCOO$, Ha or b, **18a**), 2.61 (dd, 0.25 H, J_{HaHb} = 17.8 Hz, J_{HHx} = 7.4 Hz, $CH_aH_bCH_xCOO$, Ha or b, **18b**), 3.93 (s, 2 H, CH_2O), 4.06 (dd, 0.75 H, J_{HHx} = 7.5 Hz, J_{HHx} = 12.9 Hz, $CH_aH_bCH_xCOO$, **18a**), 4.19 (dd, 0.25H, J_{HHx}= 7.5 Hz, J_{HHx} = 12.8 Hz, $CH_aH_bCH_xCOO$, **18b**), 5.39 (s, 0.75H, OCH, **18a**), 5.44 (s, 0.25 H, OCH, **18b**), 7.20 (m, 30 H, H aromatiques, **18a** and **18b**); ^{13}C NMR ($CDCl_3$) **18a** δ 19.97 (s, CH_3); 22.98 (s, CH_3), 39.95 (s, *C*$(CH_3)_2$), 42.75 (s, CH_2 pyrazoline), 60.93 (s, NCH), 61.83 (s, Ph_3CC), 75.14 (s, CH_2 lactone), 75.81 (s, OCH), 78.64 (s, N*C*Ph_3), 126.05 (s, C_{arom}), 126.83 (s, C_{arom}), 127.08 (s, C_{arom}), 127.54 (s, C_{arom}), 129.34 (s, C_{arom}), 130.15 (s, C_{arom}), 143.42 (s, C_{arom}), 143.83 (s, C_{arom}), 157.29 (s, CNN), 171.34 (s, CO lactone), 172.14 (s, CO ester). **18b** δ 19.73 (s, CH_3), 22.72 (s, CH_3), 39.78 (s, *C*$(CH_3)_2$), 42.96 (s, CH_2 pyrazoline), 60.80 (s, NCH), 61.83 (s, Ph_3CC), 75.20 (s, CH_2 lactone), 75.87 (s, OCH), 78.66 (s, N*C*Ph_3), 126.18 (s, C_{arom}), 126.91 (s, C_{arom}), 127.34 (s, C_{arom}), 127.78 (s, C_{arom}), 129.55 (s, C_{arom}), 143.26 (s, C_{arom}), 143.69 (s, C_{arom}), 157.08 (s, CNN), 171.60 (s, CO lactone), 172.93 (s, CO ester).

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