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Synthesis of *P*-Chlorophosphaethene and *N*-Chloromethanimine: Estimation of Cl Substitution on the Electronic Structure of Heteroatomic Double Bonds[1]

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Comparison between the electronic structure of *N*-chloroaldimines and *P*-chlorophosphaethene has been achieved by photoelectron spectroscopy. Whereas *N*-chloroaldimines have been synthetized in the gas phase by a new "one-line" reaction starting from α-cyanoamines (vacuum gas-solid reaction, VGSR), *P*-chlorophosphaethene has been generated by flash vacuum thermolysis (FVT) of dichloromethylphosphine. Chlorine substitution at the heteroatom destabilizes the double bond to a much greater extent for aldimines than for phosphaethene, thus reflecting a greater interaction between chlorine and $\pi_{C=N}$ than between chlorine and $\pi_{C=P}$ and a more diffuse character of the $\pi_{C=P}$ bond than the $\pi_{C=N}$ bond. For both series the heteroatom substitution does not modify the ionization energy of the heteroatom lone pair. This observation is evidence for a counterbalance between a stabilizing inductive effect of chlorine and a destabilizing interaction between the lone pairs. The discrepancy between the experimental results and the theoretical evaluation of the ionization potential is again pointed out for compounds bearing third-row atoms involved in double bonds.

Introduction

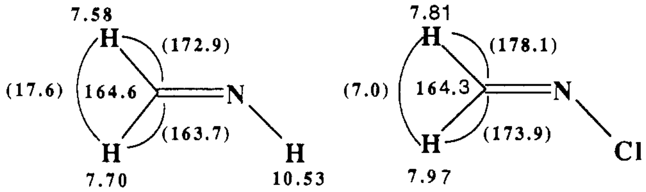
In the course of our investigations on unstable low-coordinated phosphorus species,[2] we studied the generation of the parent compound, phosphaethene[3] ($CH_2=PH$ (1)) by vacuum gas-solid reaction (VGSR) and derived its electronic structure from its photoelectron spectrum (PES).[4] Starting from these results, we carried out similar work on the parent *P*-chlorophosphaethene ($CH_2=PCl$ (2)) to assess the influence of a halogen atom on the carbon-phosphorus double bond. The parallel evaluation of the influence of a chlorine atom of a carbon-nitrogen double bond was also undertaken on the previously unknown *N*-chloroimines to have a comparison with the phosphorus series and to evaluate our conclusions about the electronic structure of these unsaturated heteroatomic systems. Since the corresponding methanimine ($CH_2=NH$ (3)) and its substituted derivatives have been extensively studied by Bock and Dammel[5] and their photoelectron spectra are well-known, we synthesized the parent *N*-chloromethanimine $CH_2=N-Cl$ (4) and a substituted compound, *N*-chloro-2-methyl-2-ethylideneamine $(CH_3)_2-C=N-Cl$ (5). The electronic structures of 4 and 5 and have been investigated through their photoelectron spectra and compared with the results on *P*-chlorophosphaethene.

Results

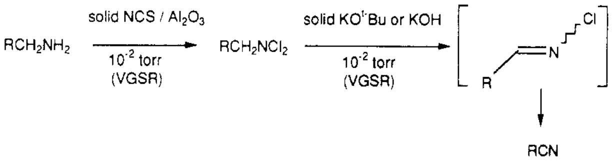
Synthesis of *N*-Chloroimines. While *N*-chloroketimines are easily prepared by a basic dehydrohalogenation of the corresponding *N*,*N*-dichloroamine,[6] only aromatic *N*-chloroaldimines are known;[7] moreover they readily undergo thermal or basic dehydrohalogenation leading to nitriles. The simplest *N*-chloroalkylaldimines have never been synthesized so far.

We have described an efficient synthesis of *N*,*N*-dichloroamines by N-chlorination of the corresponding amines on solid *N*-chlorosuccinimide (NCS) using vacuum gas-solid reaction (VGSR).[8] Attempts to prepare *N*-chloroaldimines by basic HCl elimination on solid base (VGSR) failed, the corresponding nitriles being always observed (eq 1).

Scheme I. Chemical Shifts of 3 and 4 in ppm (Coupling Constants of 3 and 4 in hertz)



3 4



(1)

We recently reported a general approach to the N-unsubstituted aldimines by a vacuum gas-solid dehydrocyanation of α-aminonitriles on a solid base (VGSR).[9] We took advantage of the acidity of the proton bonded to nitrogen to prepare the *N*-chloroaldimines by a gas-solid N-chlorination of the corresponding imine in a "one-line" sequence:[10] α-aminonitriles were vaporized on solid base

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(1) Application of photoelectron spectroscopy to molecular properties, part 40. Part 39: Lacombe, S.; Pfister-Guillouzo, G. *J. Chem. Soc., Faraday Trans. 2*, in press.

(2) Pellerin, B.; Denis, J. M.; Perrocheau, J.; Carrie, R. *Tetrahedron Lett.* **1986**, *27*, 5723.

(3) Pellerin, B.; Guenot, P.; Denis, J. M. *Tetrahedron Lett.* **1987**, *28*, 5811.

(4) Lacombe, S.; Gonbeau, D.; Cabioch, J. L.; Pellerin, B.; Denis, J. M.; Pfister-Guillouzo, G. *J. Am. Chem. Soc.* **1988**, *110*, 6964.

(5) Bock, H.; Dammel, R. *Chem. Ber.* **1987**, *120*, 1961.

(6) Reid, S. L.; Sharp, D. B. *J. Org. Chem.* **1961**, *26*, 2567.

(7) Hauser, C. R.; Gillapsie, A. G.; Le Maistre, J. W. *J. Am. Chem. Soc.* **1935**, *57*, 567.

(8) Guillemin, J. C.; Denis, J. M. *Synthesis* **1985**, *12*, 1131.

(9) Guillemin, J. C.; Denis, J. M. *Tetrahedron* **1988**, *44*, 4431.

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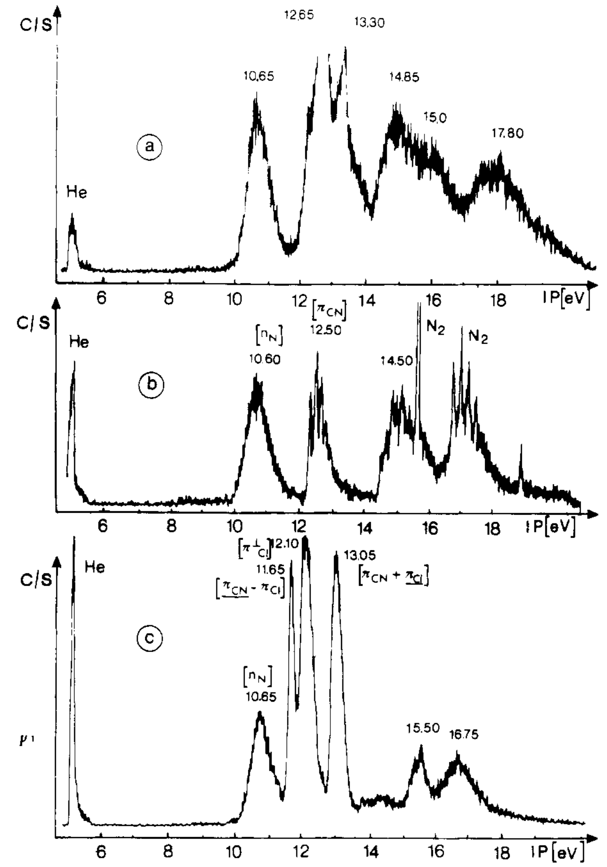
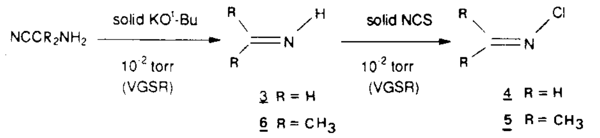


Figure 1. PE spectrum of (a) aminoacetonitrile (6), (b) methanimine (3), (c) *N*-chloromethanimine (4).

(KOᵗBu) and the resulting aldimines were directly N-chlorinated on solid NCS. This technique was extended to the synthesis of N-chloroaldimines 4 and 5[11] (eq 2).



(2)

N-Chloroimines 4 and 5 were characterized by ^{1}H and ^{13}C NMR, IR, and mass spectroscopy.[12] The 300-MHz ^{1}H NMR spectrum and the 75.2-MHz ^{13}C NMR spectrum of 4 were recorded in a 1:2 mixture of $CDCl_3$ and $CFCl_3$ at −40 °C. The ^{1}H NMR spectrum was analyzed as an AB system, and the ^{13}C NMR as the X part of an ABX spectrum. The chemical shifts of the two CH_2 protons and the $^2J_{CH}$ coupling constants were attributed by comparison with methanimine (3, see Scheme I). The protons chemical shifts of 4 are slightly downfield shifted ($\Delta\delta$: 0.2 ppm). The $^2J_{HCH}$ coupling is significantly smaller (respectively 7.0[13] and 17.6 Hz). These data are in good agreement with those reported for alkene and chloroalkene derivatives.[14] In the IR spectrum, a small bathochrome effect (17 cm^{-1}) is observed.

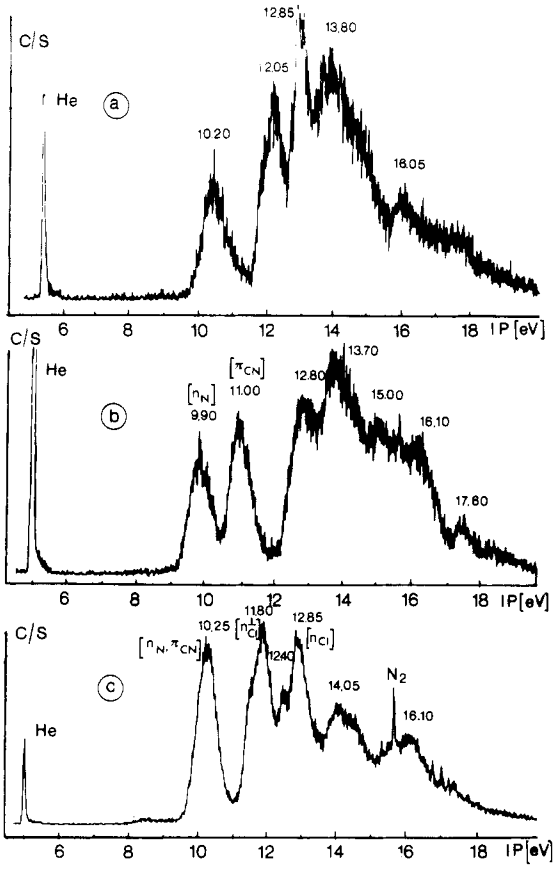


Figure 2. PE spectrum of (a) 2,2-dimethyl-2-aminoacetonitrile, (b) 2-methylethylideneamine (6), (c) *N*-chloro-2-methylethylideneamine (5).

N-Chloroimines are considerably more stable than the corresponding imines.[6,9,15] Decomposition of the parent compound slowly occurs in solution at room temperature to give polymers.

Photoelectron Spectra of *N*-Chloroimines and of *P*-Chlorophosphaethene. Methanimine (3) and 2-methyl-2-ethylideneamine (6) were synthesized by the VGS dehydrocyanation of the corresponding α-aminonitrile on solid base according to the reported method,[8] and their photoelectron spectra (Figures 1b and 2b) proved to be identical with those of Bock and Dammel.[4]

In the spectrum of 3, two first bands are observed at 10.60 and 12.50 eV and have been attributed respectively to the ejection of an electron from the nitrogen lone pair and from the $\pi_{C=N}$ double bond. In the spectrum of the substituted imine 6 the corresponding bands are observed respectively at 9.90 and 11 eV. The following bands in both spectra concern the σ skeleton. The VGS N-chlorination of these imines was then performed as described above, and the spectra obtained for *N*-chloromethanimine (4) and 2-methyl-*N*-chloro-2-ethylideneamine (5) are displayed respectively in Figures 1c and 2c.

In the spectrum of *N*-chloromethanimine (4, Figure 1c) a first broad band is observed at 10.65 eV, the following one at 11.65 eV being much higher and sharper. Two other intense bands at 12.10 and 13.05 eV probably arise from chlorine ionizations, whereas the other bands at 15.50 and 16.75 eV are broad and weak.

In the spectrum of the substituted compound 5 (Figure 2c) the three intense first bands appear at 10.25, 11.80, and 12.85 eV and two smaller and broader ones follow at 14.05 and 16.10 eV.

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(10) For other "one-line" gas-phase sequences: Guillemin, J. C.; Denis, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 690. Guillemin, J. C.; Denis, J. M.; Lasne, M. C.; Ripoll, J. L. *J. Chem. Soc., Chem. Commun.* **1983**, 238.

(11) Other *N*-chloroaldimines or -ketimines were synthetized by this sequence; unpublished results.

(12) Attempts to record mass spectrum of 4 failed.

(13) The coupling constant value was attributed by INDOR.

(14) *Proton and Carbon 13 NMR Spectroscopy*; Abraham, R. J., Lotfus, P., Eds.; Heyden & Sons: Chichester, UK, 1981; p 18. *Carbon 13 NMR Spectroscopy*; Stothers, J. B., Ed.; Academic Press: New York, 1972; pp 183–195.

(15) Findeisen, K.; Heitzer, H. *Synthesis* **1981**, 702.

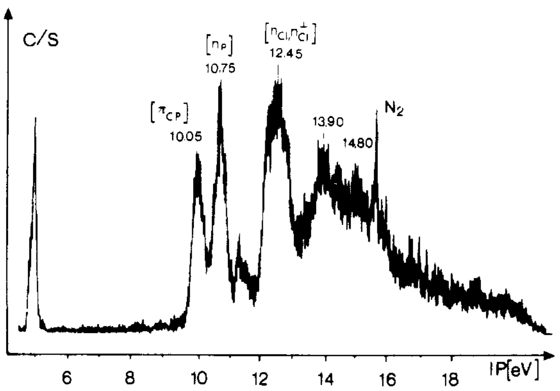
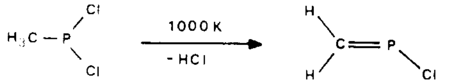


Figure 3. PE spectrum of *P*-chlorophosphaethene.

In both cases the chlorination of the imine proceeds very cleanly as no side product except chlorine is observed in the PE spectra (11.60, 14.40, and 16.10 eV). In the case of *N*-chloromethanimine (4), the reaction works only if *N*-chlorosuccinimide is used in mixture with silica gel; otherwise a lot of products such as, for example, chlorine, ammonia, and unidentified compounds are observed in small amount. With 50/50 NCS/SiO_2 the reaction proceeds smoothly, probably due to adsorption of the imine on silica gel and slow revaporization of the chlorinated compound (the chloroimine 4 may be detected for a long time even when the inlet valve for introduction of the starting cyanoamine has been closed).

The spectrum of *P*-chlorophosphaethene, obtained according to the reported method[2] by the flash vacuum thermolysis (FVT) of dichloromethylphosphine at 1000 K and successive trapping of hydrochloric acid on solid *s*-triazine and of unreacted starting material at 153 K (eq 3) is displayed in Figure 3. We observe two first bands at 10.05 and 10.75 eV, the latter more intense than the former, contrary to the spectrum of phosphaethene (1).[4] Another broad band follows at 12.45 eV, whereas the other ionizations observed at 13.90 and 14.80 eV are only poorly resolved.



(3)

In this case, the reaction course is strongly dependant on the thermolysis temperature. A slight increase may promote the formation of phosphaethyne (10.80 and 12.90 eV) and modify the shape of the spectrum. To confirm the formation of *P*-chlorophosphaethene in these conditions, a finger fitted to an NMR tube was inserted into the device just before the outlet to the photoelectron spectrometer. After the PE spectrum of the gaseous flow was recorded (identical with the spectrum depicted in Figure 3), the pyrolyzate was condensed on the coldfinger at 100 K and analyzed by low-temperature NMR spectroscopy: at 190 K the ^1H NMR spectrum obtained was identical with the reported one.[2]

Interpretation of the Photoelectron Spectra. *P*-Chlorophosphaethene (2). Our previous attribution of the photoelectron spectrum of phosphaethene relies upon alkyl substitution effects: we could thus conclude that the former band observed at 10.30 eV arises from the ejection of an electron from the $\pi_{P=C}$ double bond ($^2A''$ ionic state) and the latter one at 10.70 eV from the ejection of an electron from the phosphorus lone pair ($^2A'$ ionic state).[4]

Table I. Comparison between Calculated and Experimental Ionization Potentials for Phosphaethene (1) and *P*-Chlorophosphaethene (2)

		Koopmans' approx			
	ionic state	MNDO	ab initio[4]	CIPSI[4]	exptl
$H_2C{=}PH$ (1)	$(^2A'')\pi_{P=C}$	10.58	9.63	9.94	10.30
	$(^2A')n_P$	11.22	10.43	9.77	10.70
	σ_{HPCH}	13.82	14.02		13.20
	σ_{CH_2}	15.82	16.51		15.00
$H_2C{=}PCl^a$ (2)	$(^2A'')\pi_{P=C}$	10.61	9.92	9.90	10.05
	$(^2A')n_P$	11.65	10.95	10.20	10.75
	$n_{Cl}{}^{\perp}$	13.21	12.60		12.45
	$n_{Cl}{}^{\parallel}$	13.67	13.02		
	σ_{HCPCl}	14.98	14.90		13.90
	$\sigma_{CH_2,PCl}$	16.39	17.02		14.80

[a] Calculated geometries: MNDO P–C, 1.57 Å; P–Cl, 1.99 Å; C–H, 1.09 Å; CPCl, 108.16°; *cis*-HCP, 128.5°; *trans*-HCP, 118.4°. Ab initio P–C, 1.63 Å; P–Cl, 2.09 Å; C–H, 1.07 Å; CPCl, 103.01°; *cis*-HCP, 126.01°; *trans*-HCP, 117.87°.

Usually experimental ionization potentials may be correlated, within the approximation of Koopmans' theorem, with the calculated orbital eigenvalues. This approximation thus neglects both polarization and correlation effects. More accurate results may be obtained by calculation of the ground- and ionic-state energies through a configuration interaction formalism including polarization and correlation effects (CIPSI algorithm). Nevertheless we have already reported for phosphaethene the strong discrepancy evidenced between experimental results and theoretical calculations, especially for the $^2A'$ ionic state (Table I). It may be seen from this table that the Koopmans' evaluation of this state is unexpectedly underestimated for 1. This observation indicates that the result of the SCF calculation for the ground state is quite inaccurate and probably follows from the inadequacy of the basis set used (4-31G*). Such discrepancies are a common feature for molecules bearing third-row atoms involved in a double bond.[16]

Despite these defects, we may assume from Table I that the same attribution is to be done for phosphaethene (1) and *P*-chlorophosphaethene (2): the first band of 2 at 10.05 eV is concerned with the $^2A''$ ionic state ($\pi_{P=C}$), and the second one at 10.75 eV with the $^2A'$ ionic state (n_P). The following broad band at 12.45 eV arises from two chlorine lone-pair ionizations calculated according to ab initio results at 12.60 eV ($n_{Cl}{}^{\perp}$) and 13.02 eV ($n_{Cl}{}^{\parallel}$) respectively. The poorly resolved following bands at 13.90 and 14.80 eV may be attributed to ejection of electrons from the σ skeleton.

It may be noticed at this stage that for these two compounds the MNDO eigenvalues are overestimated for the two first ionic states, but the obtained results are not much worse than those derived from more elaborated ab initio calculations.

Nevertheless, it is evident from this analysis that whatever the calculation method choosen, neither of them reproduces the experimentally observed destabilization of the double bond upon chlorination (10.30 eV for 1 and 10.05 eV for 2). Moreover the same position of the second ionization potential arising from the ejection of an electron from the phosphorus lone pair (10.70 eV for 1 and 10.75 eV for 2) could not be produced from the results of these different calculations.

For these reasons, it was thus important to ascertain our experimental results by comparison with the corresponding study of *N*-chloroimines.

***N*-Chloroimines.** In the imine series, it is well established from numerous substitution effects that the first

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[16] Von Niessen, W.; Cederbaum, L. S.; Domcke, W.; Dierksen, G. H. F. *J. Chem. Phys.* 1977, *66*, 4894. Goddard, J. D. *J. Comput. Chem.* 1987, *8*, 389.

Table II. Comparison between Calculated and Experimental Ionization Potentials for Methanimine (3)

	Koopmans' approx			
ionic state	MNDO	ab initio[17]	MRD-CI[17]	exptl[5]
$^2A'(n_N)$	11.20	11.61	10.52	10.60
$^2A''(\pi_{N=C})$	12.13	12.34	12.26	12.50

Table III. Comparison between MNDO-Calculated and Experimental Ionization Potentials for Methanimine (3) and *N*-Chloromethanimine (4)

	$H_2C{=}NH$ (3)		$H_2C{=}NCl$ (4)		$(H_3C)_2C{=}NCl$ (5)
ionic state	MNDO	exptl	MNDO[a]	exptl	exptl
$^2A'(n_N)$	11.20	10.60	11.63	10.65	10.25
$^2A''(\pi_{C=N})$	12.13	12.50	11.67	11.65	
$n_{Cl}{}^{\perp}$			13.09	12.10	11.80
$n_{Cl}{}^{\parallel}$			14.45	13.05	12.85
σ_{HCNCl}	15.06	14.80	16.18	15.50	14.05
$\sigma_{CH,NCl}$	17.69	16.90	18.00	16.75	16.10

[a] Calculated geometry: C–N, 1.29 Å; N–Cl, 1.72 Å; C–H, 1.1 Å; CNCl, 117.15°; *cis*-HCN, 128.61°; *trans*-HCN, 116.79°.

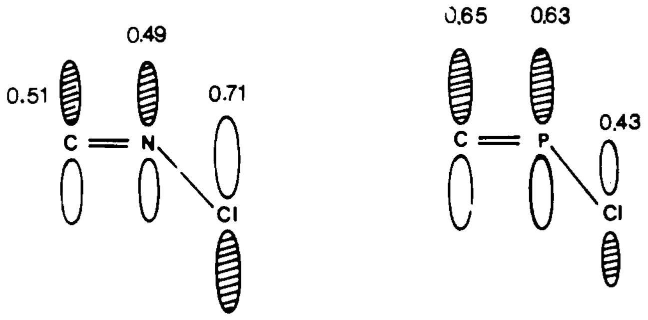
band arises from the ejection of an electron from the nitrogen lone pair ($^2A'$ ionic state) and the second from the ejection of an electron from the $\pi_{C=N}$ double bond ($^2A''$ ionic state).[5] The order is reversed relative to the phosphaalkene series.

It is known from the work of Bruna and Peyerimhoff[17] that the experimental ionization potential observed for the $^2A''$ ionic state ($\pi_{C=N}$) of 3 at 12.50 eV is in good agreement with calculated orbital eigenvalues within Koopmans' limitation (12.34 eV, Table II). This result is not improved when configuration interaction methods (MRD-CI) are used (12.26 eV). For the $^2A'$ ionic state it may be seen that the result of the SCF calculation (i.e., the Koopmans' evaluation) is, as expected from the neglect of polarization effects, overestimated by about 1 eV (11.61 vs 10.60 eV experimentally). In this series, configuration interaction methods give reliable results, lowering to a correct extent the Koopmans' potential (10.52 eV).

In light of these results and our previous conclusions on the phosphorus analogues, it did not seem worthwhile to carry out extensive ab initio calculations on chlorinated derivatives of imines. Our attribution of their spectra is thus based on MNDO calculations (the results of which are of the same type as more elaborate ab initio evaluations for 3 (Table II)) and on substitution effects. Our conclusions are displayed in Table III, from which it may be seen that the first broad band observed for 4 at 10.65 eV is attributed to the ejection of an electron from the nitrogen lone pair ($^2A'$ ionic state) and the second sharp one at 11.65 eV to the ejection of an electron from the $\pi_{N=C}$ double bond in antibonding interaction with the chlorine lone pair ($^2A''$ ionic state). The following two intense and sharp bands at 12.10 and 13.05 eV are attributed respectively to the ejection of an electron from the chlorine lone pair perpendicular to the π system ($n_{Cl}{}^{\perp}$) and parallel to the π system ($n_{Cl}{}^{\parallel}$). The two weak bands at 15.50 and 16.75 eV arise from ejection of electrons from the σ skeleton and are calculated respectively at 16.18 and 18 eV.

It is important to note the sharp shape of the second band at 11.65 eV (attributed to the $^2A''$ ionic state), which is strikingly different from the corresponding band of *P*-chlorophosphaethene (2) observed at 10.05 eV. This is the result of the much stronger interaction of the chlorine lone pair with the N=C π system than with the P=C π system (Scheme II). This stronger interaction is also evident from the position of the second chlorine lone pair observed for 2 at about 12.45 eV and for 4 at 13.05 eV, whereas the perpendicular chlorine lone pair is observed at the same energetic level for both compounds (12.45 eV for 2 and 12.10 eV for 4).

Scheme II



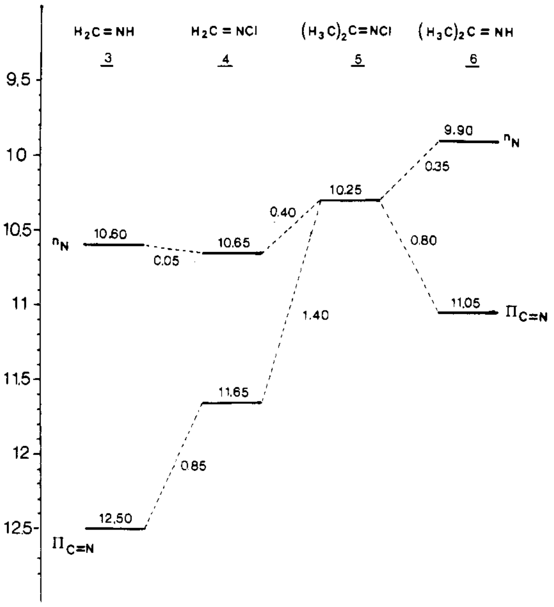


Figure 4. Correlation diagram between the ionization potentials of imines and of their *N*-chloro derivatives.

Our assignment is further corroborated by substitution effects as exemplified in the correlation diagram displayed in Figure 4. By substitution of the double bond with two methyl groups, the ionization potential attributed to the $^2A''$ ionic state is strongly lowered (11.65 eV for 4 and 10.25 eV for 5), while the band associated with the nitrogen lone pair is much less shifted to higher energies (10.65 eV for 4 and 10.25 eV for 5). Chlorine substitution at nitrogen destabilizes the $\pi_{C=N}$ double bond for both compounds (0.85 eV between 3 and 4 and 0.80 eV between 6 and 5) to a much greater extent than for the corresponding P=C double bond (0.25 eV between the first ionization potentials of 1 and 2, respectively; Table I). This observation agrees fairly well with the already mentioned stronger interaction between chlorine and $\pi_{C=N}$ than between chlorine and $\pi_{C=P}$ and with the already reported more pronounced diffuse character of the $\pi_{C=P}$ bond relative to $\pi_{C=N}$.[4]

Concerning the heteroatom lone pair, we may first notice that in either the phosphaalkene or the imine series, it is observed at very close energetic levels (10.70–10.75 eV in the former case and 10.60–10.65 eV in the latter) despite the greater electronegativity of nitrogen. The strong s character of the phosphorus lone pair relative to nitrogen causes its stabilization. The nitrogen lone pair is either unaffected by chlorine substitution (10.60 eV for 3 and

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[17] Bruna, P. J.; Krumbach, V.; Peherimhoff, S. D. *Can. J. Chem.* **1985**, *63*, 1594.

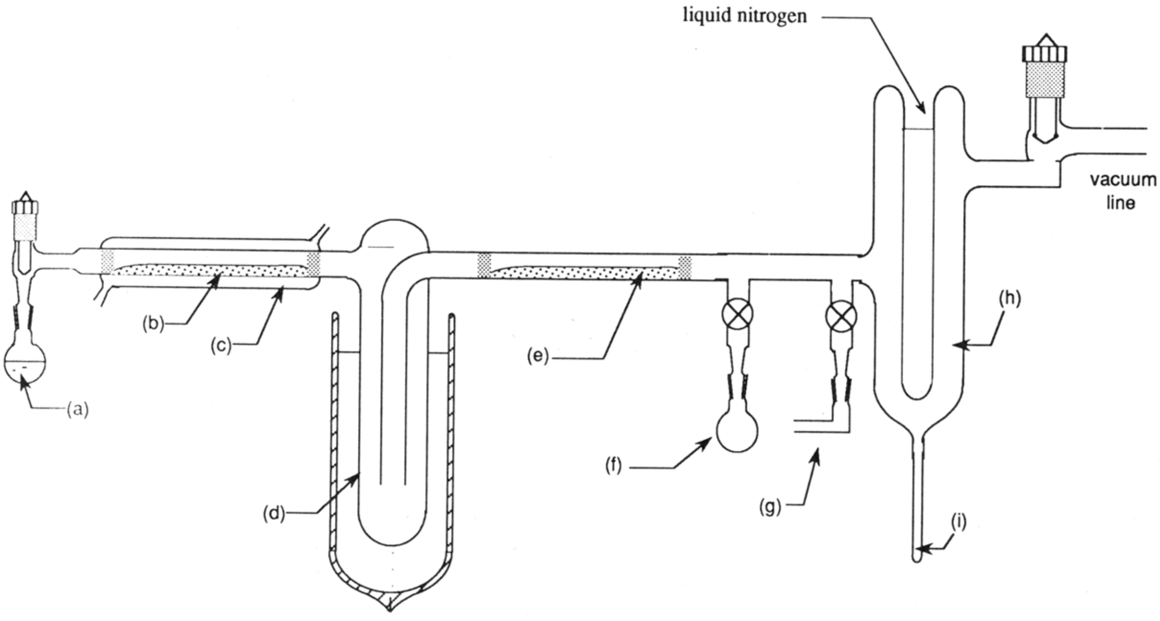

Figure 5. Vacuum device for "one-line" VGSR of α-aminonitriles: (a) α-aminonitrile; (b) KO^tBu; (c) 353 K hot mantle; (d) 183 K cold trap; (e) 1:1 NCS/SiO_2; (f) NMR cosolvent; (g) nitrogen gas inlet; (h) coldfinger (77 K); (i) NMR tube.

10.65 eV for **4** or slightly stabilized (9.90 eV for **6** and 10.25 eV for **5**). It may be remembered that for phosphaalkenes, chlorine substitution at phosphorus did not modify the position of the phosphorus lone pair (10.70 eV for **1** and 10.75 eV for **2**). As a matter of fact, we observe, for either the phosphorus or nitrogen series, a very weak effect of chlorine on the heteroatom lone pair: this observation reflects a counterbalance between the stabilizing inductive effect of chlorine and the destabilizing interaction between the lone pairs of chlorine and the heteroatom. As the localizations of the n_N and n_P orbitals are very close for *N*-chloromethanimine (**4**) and *P*-chlorophosphaethene (**2**) and as the $3p_\pi$–$3p_\pi$ and $2p_\pi$–$3p_\pi$ overlaps calculated respectively for **4** and **2** are found to be of the same order of magnitude, the similar behavior of the heteroatom lone pair in both series is easily accounted for. It is worth noticing that chlorine substitution at phosphorus produces exactly the same type of interactions for saturated phosphines: the differences between ionization potentials of PCl_nR_{3-n} and PH_nR_{3-n} ($R = Me$, $n = 1$–3) never exceed 0.11 eV.[18]

Experimental Section

***N*-Chloromethanimine (4).** Silica gel (Merck, ref 7033) previously dehydrated under vacuum in an oven heated at 800 °C during 5 h, was mixed with NCS at room temperature under nitrogen flow.

The apparatus was assembled as shown in Figure 5. Commercial potassium *tert*-butoxide (33.7 g, 0.3 mol) was introduced in the first reactor (30 cm × 40 mm Pyrex tube) and then horizontally distributed between two pads of glass wool at a distance of 20 cm. The second reactor (40 cm × 40 mm Pyrex tube) is filled with a 1:1 mixture of *N*-chlorosuccinimide (20 g, 0.15 mol) and silica gel (20 g). Reactors and coldtrap are fitted on the vacuum line. The solid base was heated at 350 K under vacuum during 1 h for degassing. Aminoacetonitrile (0.56 g, 10^{-2} mol) was slowly vaporized. *tert*-Butyl alcohol was removed by the coldtrap, and **4** condensed on the coldfinger (77 K). Continuous pumping was maintained for 1 h after the complete vaporization of the precursor. Analysis was performed by ^1H and ^{13}C NMR (coupling constants are in hertz), IR (77 K), and PES; yield 30%; ^1H NMR (1:2 $CDCl_3$ and CCl_3F mixture, 233 K) δ 7.81 (d, part A of an AB system, ^1H, $J = 7.0$), 7.97 (d, part B of an AB system); ^{13}C NMR (1:2 $CDCl_3$ and $CFCl_3$ mixture, 233 K) δ 164.3 ($J_{CH} = 173.9$, $J_{CH} = 178.1$); IR (KBr, 77 K) $\nu_{C=N}$ 1617 cm^{-1}.

***N*-Chloro-2-methyl-2-ethylideneamine (5).** The same experiment was performed starting with 2,2-dimethyl-2-aminoacetonitrile with pure NCS (yield 50%); ^1H NMR δ 2.17 (s, 3 H), 2.19 (s, 3 H); ^{13}C NMR δ 22.6 ($J_{CH} = 129.6$), 26.2 ($J_{CH} = 129.6$), 178.7 ($J_{CCH} = 6.0$); IR $\nu_{C=N}$ 1653 cm^{-1}; high-resolution MS calcd 91.01887, found 91.0192; MS, m/z 31 (17), 41 (16), 42 (25), 49 (2), 56 (2), 76 (3), 91 (4).

***P*-Chlorophosphaethene** was generated according to the reported method by the flash vaccum thermolysis of dichloromethylphosphine at 1000 K.[2] The gaseous thermolyzate was then passed over a solid base (*s*-triazine) to trap the hydrochloric acid formed during the course of the reaction and then through a coldtrap at 153 K for unreacted starting material.

In each case the real-time analysis of the gaseous flow obtained either after the VGSR reactions (for *N*-chloroimines) or after the FVT-VGSR reaction (for *P*-chlorophosphaethene) was performed by PES as the vacuum device where the reactions are proceeding are directly coupled to the spectrometer.[4] The spectra were recorded on an Helectros 008 PE spectrometer monitored by a microcomputer complemented with a digital analogic converter (DAC). The spectra are built with 4000 points and are calibrated on the known ionizations of helium (4.99 eV, autoionization), xenon (12.13 and 13.45 eV), and argon (15.75 and 15.95 eV).

Calculations were performed at the MNDO level with the AMPAC program.[19] Ab initio calculations on *P*-chlorophosphaethene were performed according to the same methods as already reported for phosphaethene.[4]

Conclusion

N-Chloroaldimines have been synthetized from α-aminonitriles by a one-line gas-phase sequence (VGSR) through chlorination of intermediate aldimines on solid *N*-chlorosuccinimide. *P*-Chlorophosphaethene has been generated in the gas phase by the known dehydrochlorination of dichloromethylphosphine.[2] Analysis of these chlorinated heteroatomic double bonds by real-time photoelectron spectroscopy reveals that in both series the double bond is destabilized upon chlorination and that this effect is markedly stronger for aldimines than for phos-

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phorus compounds. This observation may be accounted for by the stronger interaction between chlorine and $\pi_{C=N}$ than between chlorine and $\pi_{C=P}$ and by the pronounced diffuse character of the $\pi_{C=P}$ bond relative to $\pi_{C=N}$. On the other hand, for both type of compounds the heteroatomic lone pair is not sensitive to chlorination, thus reflecting a counterbalance between the stabilizing inductive effect of chlorine and the destabilizing interaction between the lone pairs of chlorine and of the heteroatom.

Note added in proof: During the course of our investigations, the microwave spectrum of *N*-chloromethanimine, generated from the pyrolysis of *N*-chloroazetidine, has been reported.[20]

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Registry No. 4, 32360-82-0; 5, 34508-68-4; $H_2C{=}PCl$, 61183-51-5; $NCCH_2NH_2$, 540-61-4; $NCC(CH_3)_2NH_2$, 19355-69-2; *N*-chlorosuccinimide, 128-09-6.

Supplementary Material Available: 300-MHz ^{1}H and 75.47-MHz ^{13}C NMR spectra of *N*-chloromethanimine and 80-MHz ^{1}H and 20.11-MHz ^{13}C NMR spectra of *N*-chloro-2-methylideneamine (6 pages). Ordering information is given on any current masthead page.

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The Use of Precise Structural Information for the Understanding of the Conformational Behavior of *cis*-5-(*tert*-Butylsulfonyl)- and *cis*-5-(*tert*-Butylsulfinyl)-2-*tert*-butyl-1,3-dioxane[1]

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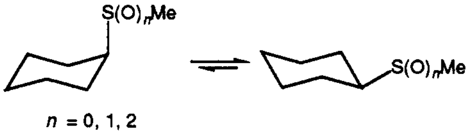
A single-crystal X-ray structure determination of the title sulfoxide (*cis*-2) was carried out and compared with data previously reported for the corresponding sulfone (*cis*-1). Whereas the latter adopts an eclipsed conformation (one S—C/C—H and two S=O/C—C eclipsed bond pairs), both the *tert*-butyl and the S=O group in the sulfinyl function point outside the ring in a staggered rotamer. A substantial difference in length for the endocyclic C–C bonds in *cis*-2 suggests the effect of through-space $\sigma_{C-C}/\sigma^*_{S-O}$ (attractive) and σ_{C-C}/n_S (repulsive) interactions and/or $\sigma_{C-H} \rightarrow \sigma^*_{C-S}$ stereoelectronic mechanisms. The X-ray diffraction study of the cyclohexane analogue (*cis*-4) shows again a staggered conformation for the *tert*-butylsulfinyl group, but confirms the repulsive steric hindrance between the *gauche* *t*-BuS and endocyclic methylene groups. The contrasting behavior between the sulfone and sulfoxide groups points to the existence of an attractive interaction S=O/C—C, which stabilizes the eclipsed conformer in *cis*-1 and overcomes the torsional strain in the eclipsed bond pair S—C/C—H. The nature of the stabilizing S=O/C—C interaction is proposed in the light of recent theoretical calculations.

Introduction

Several years ago, Eliel and Kandasamy described the conformational free energies ($\Delta G°$ values) for the methyl sulfide, methyl sulfoxide, and methyl sulfone groups in the cyclohexane ring.[3] The reported values, −1.00, −1.20, and −2.50 kcal/mol, respectively, clearly reflect the steric requirements of the sulfur functions (eq 1).

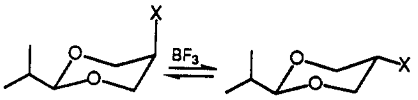


(1)

$n = 0, 1, 2$

Eliel et al.[4] discovered also that the CH_3S group attached at C(5) in a 1,3-dioxane has a stronger preference for the equatorial conformation ($\Delta G° = -1.82$ kcal/mol in solvent cyclohexane) than that measured for (methylthio)cyclohexane, this being the result of a repulsive interaction of the unshared electrons of sulfur with the unshared electrons of the ring oxygens (the so-called "repulsive gauche effect"[5]) (Table I).

Table I



X	$\Delta G°$, kcal/mol
CH_3S	−1.82 ± 0.01
CH_3SO	+0.82 ± 0.11
CH_3SO_2	+1.19 ± 0.10
t-BuS	−1.90 ± 0.11
t-BuSO	+0.10 ± 0.01
t-BuSO$_2$	−1.14 ± 0.01

In strong contrast, similarly placed methylsulfinyl (CH_3SO) and methylsulfonyl (CH_3SO_2) groups prefer the axial conformation.[4] (Table I). This unusual behavior was

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