Formal Fusion of a Pyrrole Ring onto 2-Pyridyl and 2-Pyrimidyl Cations: One-Step Gas-Phase Synthesis of Indolizine and Its Derivatives

Regina Sparrapan, Maria Anita Mendes, Marcia Carvalho, and Marcos N. Eberlin*[a]

Abstract: Two *ortho*-hetarynium ions, the 2-pyridyl and 2-pyrimidyl cations, react promptly with 1,3-dienes in the gas phase by annulation, formally by fusion, onto the ions of a pyrrole ring. This novel reaction proceeds through an initial polar $[4+2^+]$ cycloaddition across the $C{\equiv}N^+$ bond, followed by fast ring opening, a [1,4-H] shift, and finally a recyclization that results in a contraction of a six- to a five-membered ring and dissociation by the loss of a methyl radical. For the 2-pyridyl cation, this reaction yields ionized indolizines (pyrrolo[1,2-*a*]pyridines), while for the 2-pyrimidyl cation, it gives ionized pyrrolo[1,2-*a*]pyrimidines. The annulation reaction, performed in the rf-only collision quadrupole of a pentaquadrupole (QqQqQ) mass spectrometer, occurs readily with both 1,3-butadiene and isoprene, and is thermodynamically and kinetically favored as predicted by ab initio calculations. *Ortho*-hetarynium ions and 1,3-dienes provide, therefore, the two building blocks for the efficient one-step gas-phase synthesis of ionized bicyclic pyrrolo[1,2-*a*]pyridine (indolizine) and pyrrolo[1,2-*a*]pyrimidine, as well as their analogues and derivatives.

Keywords: cycloadditions · heterocycles · ion–molecule reactions · mass spectrometry

Introduction

The simplest *ortho*-hetarynium ion,[1] the mesomeric 2-pyridyl cation (**1**), and its N-analogue, the 2-pyrimidyl cation (**2**), are isoeletronic with *ortho*-benzyne, the simplest and most common aryne, and like *ortho*-benzyne,[2] they both participate as key and short-lived intermediates in several reactions in the condensed phase.[3]


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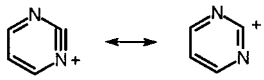
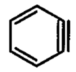
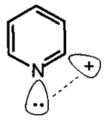

2' **2''**


ortho-benzyne

The fully occupied sp^2 orbital of the ring nitrogen(s) and the empty sp^2 orbital of the neighboring carbon atom of **1** and **2** overlap extensively, which results in extra resonance stabilization of 18–28 kcal mol^{-1} (as compared to the *meta* and *para* isomers); hence the *ortho*-hetarynium ion structures **1'** and **2'** largely dominate.[4] The ions are, however, most often represented in their canonical forms **1''** and **2''**.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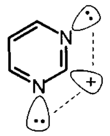
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In the gas phase, particularly in the environment of the mass spectrometer, **1** and **2** are common, stable (long-lived), and easily accessible species;[4] hence, the intrinsic properties and reactivities of these and other gaseous, isolated, and stable ionic species, can be extensively and conveniently studied, free of solvent, ligands, and counterion effects. Recently,[5] we found that **1** and **2** react, in the gas phase, by a novel and structurally diagnostic transacetalization-like[6] annulation with the cyclic acetal 2-methyl-1,3-dioxolane. Formally, a 4,5-dihydrooxazole ring is fused onto the ions, and dihydrooxazolopyridinium and dihydrooxazolopyrimydinium ions are readily formed (Scheme 1).[5] Since the *meta* and *para* isomers fail to react similarly, this novel annulation reaction locates the charge site in the heteroaromatic rings; hence, it provides a general analytical tool to reveal the positions of substituents in pyridine and pyrimidine rings.[5]

We now report that **1** and **2** readily react in the gas phase with neutral 1,3-dienes by annulation, a novel thermodynami-

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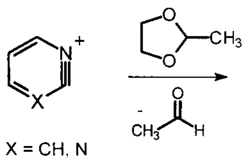


Scheme 1. Gas-phase reaction of **1** and **2** with the cyclic acetal 2-methyl-1,3-dioxolane.[5]

cally and kinetically favored reaction that results formally in fusion onto the ions of a pyrrole ring; thus, *ortho*-hetaryne ions and 1,3-dienes are found to provide the two building blocks for the efficient one-step gas-phase synthesis of the heterocycle indolizine, as well as its analogues and derivatives.

Experimental Section

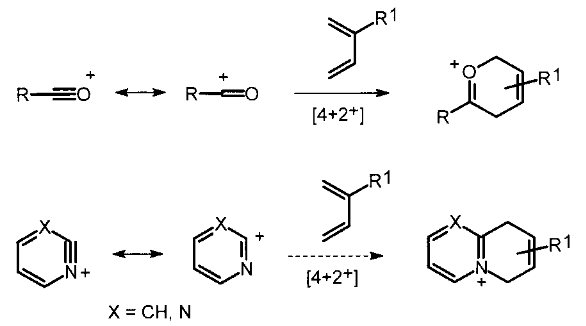
The MS^2 and MS^3 experiments[7] were performed with a pentaquadrupole (QqQqQ) mass spectrometer (Extrel, Pittsburgh, PA), which is described in detail elsewhere.[8] The $Q_1q_2Q_3q_4Q_5$ consists of three mass-analyzing quadrupoles (Q_1, Q_3, Q_5), in which mass-selection and mass-analysis are performed; and two rf-only reaction quadrupoles (q_2, q_4), which are used to perform either low-energy ion–molecule reactions or collision-induced dissociations (CID). Ion–molecule reactions were performed by means of MS^2 experiments in which the ion of interest was generated by dissociative 70 eV electron ionization (EI) of 2-chloropyridine (for **1**) or 2-chloropyrimidine (for **2**), and further purified (mass-selected) by Q_1. After the mass-selected ion reacts in q_2 with the neutral reagent of choice, Q_5 is scanned to record its product ion mass spectrum, while operating Q_3 and q_4 in the non-mass analyzing "full" ion-transmission, rf-only mode. The target gas pressures used in q_2 cause typical beam attenuations of 50–70%, that is, conditions of multiple collision were used.

For the MS^3 experiments, Q_3 was used to mass-select a reaction product of interest, and q_4 to dissociate the mass-selected ion by low-energy collisions with argon, and Q_5 to record the sequential product ion spectrum. For the reactions in q_2, ion-translational energies were set to near 1 eV as calibrated by the m/z 39:41 ratio in neutral ethylene–ionized ethylene reactions.[9] For CID in either q_2 or q_4, 15 eV collision energy was used, as calculated by the voltage difference between the ion source and the collision quadrupole.

Molecular orbital ab initio calculations were performed with GAUSSIAN94 [Gaussian Inc.]. First, the geometries were fully optimized at the HF/6-311G(d,p) level of theory,[10] then improved energies were obtained with single-point calculations at the 6-311G(d,p) level, whereas incorporating valence-electron correlation calculated by second-order Møller–Plesset (MP2) perturbation theory;[11] this procedure is denoted as MP2/6-311G(d,p)//6-311G(d,p).

Results and Discussion

Reactions with the 1,3-dienes: Some years ago,[12] a novel, often efficient and structurally diagnostic[13] gas-phase reaction of acylium ions was reported: polar [4+2$^+$] cycloaddition with 1,3-dienes (Scheme 2, top).[14] Since the structures of *ortho*-hetarynium ions are electronically similar to those of acylium ions, and to test, therefore, their polar [4+2$^+$] cycloaddition reactivity (Scheme 2, bottom) in the solvent and counterion-free gas-phase environment, gaseous, stable[4] and mass-selected **1** and **2** were treated with 1,3-dienes in the collision cell of a pentaquadrupole[7a] mass spectrometer.



Scheme 2. Gas-phase polar [4+2$^+$] cycloadditions of acylium ions with 1,3-dienes (top) and that conceived for **1** and **2** (bottom).

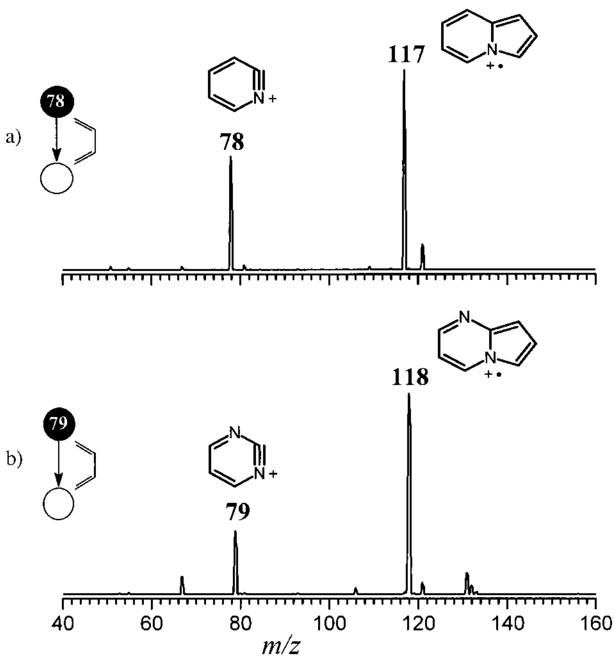


Figure 1. Double-stage (MS^2) mass spectra for the reaction of 1,3-butadiene with a) **1**, and b) **2**. The structures shown for the product ions are those which result from annulation as proposed in Scheme 4.

Figure 1 compares the mass spectra acquired from the reaction of **1** or **2** with 1,3-butadiene. No intact adducts (of m/z 132 and 133, respectively) were formed; hence, the ions were initially assumed to be unreactive towards polar [4+2$^+$] cycloaddition. Both spectra show, however, an intense product ion (those of m/z 117 and 118), which indicates that the ion–molecule adducts dissociate rapidly and completely by the loss of a methyl radical (15 u). This dissociation, of an even-electron ion to an odd-electron ion, is surprising since it contravenes the even-electron rule.[15] The other minor ions constitute the normal set of products formed by a series of reaction/dissociations initiated by proton transfer to 1,3-butadiene; mainly those of m/z 55, 67, 81, 93, 109, 121, and 131.[13]

Figure 2 compares the mass spectra acquired from the reaction of **1** or **2** with isoprene. Again, none of the intact adducts (of m/z 146 and 147, respectively) are observed. Both **1** and **2** form, instead, *two* major product ions: for **1**, those of m/z 131 and 130 (Figure 2a); for **2**, those of m/z 132 and 131 (Figure 2b). As observed for the reactions with 1,3-butadiene, the other minor ions are the products formed by a series of reactions/dissociations initiated by proton transfer to isoprene, mainly those of m/z 69, 81, 95, 117, 135, 137 and 149.[13]

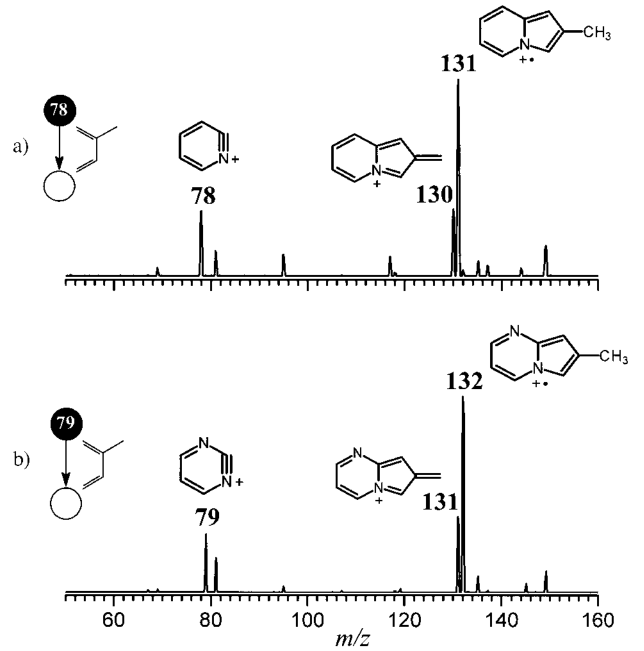
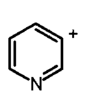


Figure 2. Double-stage (MS^2) product ion mass spectra for the reaction of isoprene with: a) **1**, and b) **2**.

The *meta* and *para* isomers of **1** and **2**: the 3-pyridyl (**3**) and 4-pyridyl (**4**) cations, and the 4-pyrimidyl (**5**)[16] and 5-pyrimidyl (**6**) cations, react with 1,3-butadiene and isoprene predominantly by proton transfer (spectra not shown).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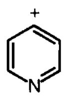
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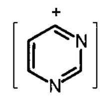
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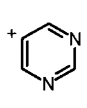
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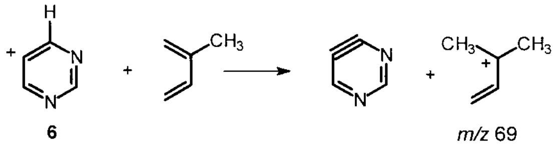
7

Just as the phenyl cation (**7**) can be regarded as a protonated form of *ortho*-benzyne, **3**–**6** can be regarded as protonated forms of neutral hetarynes.[1, 17] Not surprisingly therefore, these "protonated molecules" react with 1,3-dienes predominantly by proton transfer (as rationalized for **6** in Scheme 3), thus displaying an aromatic carbocation-like behavior similar to that of the phenyl cation.[18]



Scheme 3. Proton-transfer reaction from **6** to isoprene.

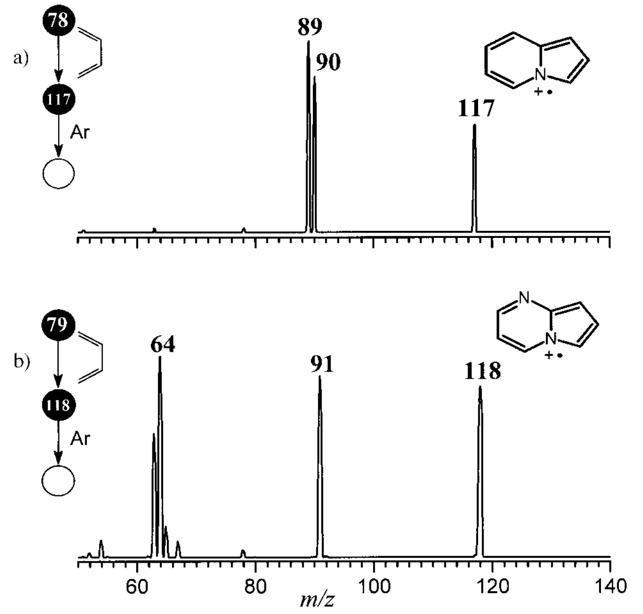


Figure 3. Triple-stage (MS^3) sequential mass spectra for product ions formed in reactions of 1,3-butadiene with: a) **1** (*m*/*z* 117), and b) **2** (*m*/*z* 118).

Dissociation behavior of the product ions: Figures 3 and 4 compare the sequential CID mass spectra for the major reaction products. Upon CID, both product ions of *m*/*z* 117 (Figure 3a) and *m*/*z* 118 (Figure 3b), formed respectively when **1** or **2** reacted with butadiene, lost HCN to form the fragments ions of *m*/*z* 90 and *m*/*z* 91, respectively. The fragment ion of *m*/*z* 90 apparently lost an H atom to form *m*/*z* 89 (Figure 3a), whereas *m*/*z* 91 lost HCN to form *m*/*z* 64 (Figure 3b). The product ions of *m*/*z* 131 (Figure 4a) and *m*/*z* 132 (Figure 4b), formed respectively when **1** or **2** reacted with isoprene, lost mainly a H atom; *m*/*z* 131 forms *m*/*z* 130; and *m*/*z* 132 forms *m*/*z* 131.

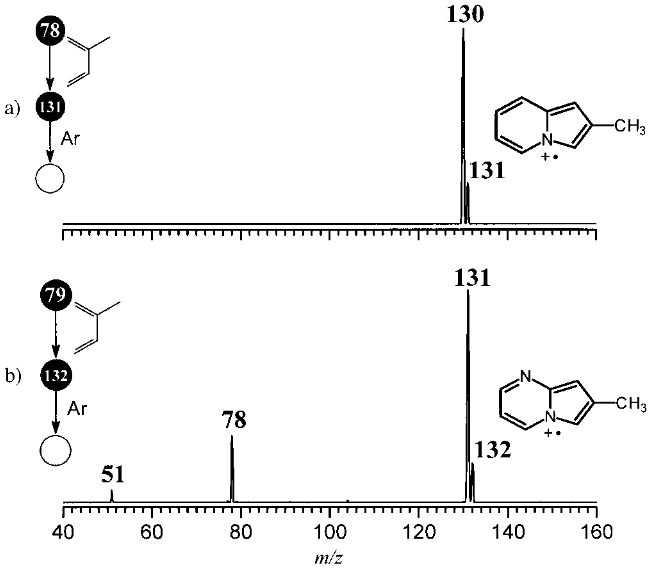


Figure 4. Triple-stage (MS^3) sequential mass spectra for product ions formed in reactions of isoprene with: a) **1** (*m*/*z* 131), and b) **2** (*m*/*z* 132).

Figure 5 compares the CID sequential mass spectra of the product ions for the two additional products formed when **1** (*m*/*z* 130) or **2** (*m*/*z* 131) reacted with isoprene. Upon CID, the *m*/*z* 130 ion yielded mainly two fragment ions of *m*/*z* 78 and *m*/*z* 77 (Figure 5a); however, its *N*-analogue ion of *m*/*z* 131 yielded the *m*/*z* 78 ion exclusively (Figure 5b).

Mechanism of reaction: The present findings suggest that in the gas phase, the *ortho*-hetarynium ions **1** and **2** fail to form

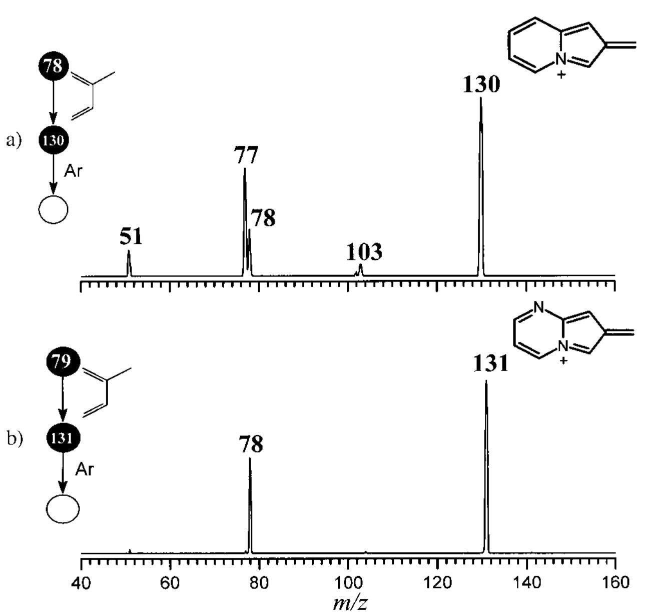
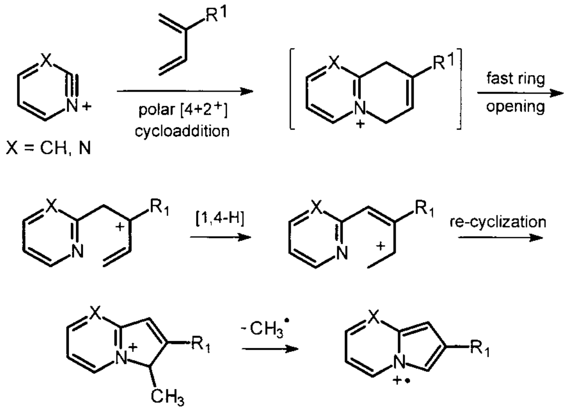


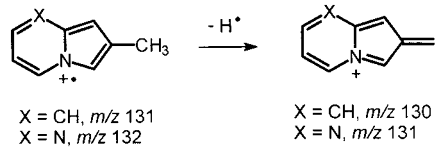
Figure 5. Triple-stage (MS^3) sequential mass spectra for product ions formed in reactions of isoprene with: a) **1** (*m/z* 130), and **2** (*m/z* 131).

stable polar $[4+2^+]$ cycloadducts with 1,3-dienes. Since the ion–molecule adducts most likely dissociate by the loss of a methyl radical from both the isoprene and 1,3-butadiene adducts, a novel annulation reaction is suggested (Scheme 4).[19] Annulation could be initiated either by simple addition or by polar $[4+2^+]$ cycloaddition to the 1,3-diene; however, based on the ab initio calculations (see the following section), it is assumed that polar $[4+2^+]$ cycloaddition dominates. The cycloadduct is unstable and undergoes fast contraction from a six- to a five-membered ring: the new fused six-membered ring opens, a [1,4-H] shift favors recyclization through intramolecular nucleophilic attack of nitrogen, and the nascent bicyclic adduct dissociates by the loss of a methyl radical,[20] to form ionized indolizine (pyrrolo[1,2-*a*]pyridine) (for **1**),[21] and ionized pyrrolo[1,2-*a*]pyrimidine (for **2**). These are both aromatic and therefore relatively stable molecules.



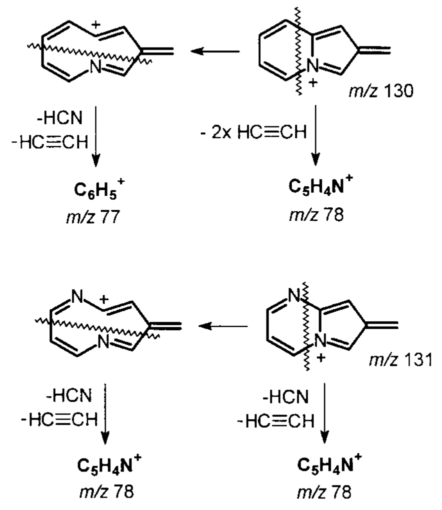
Scheme 4. Proposed mechanism for the annulation reaction between **1** and **2** and 1,3-dienes.

If annulation occurs as proposed in Scheme 4, and if ionized pyrrolo[1,2-*a*]pyridines and pyrrolo[1,2-*a*]pyrimidines are formed, then the dissociation behavior of the product ions (Figures 3 and 4) are adequately rationalized. For the isoprene annulation products, the methyl substituent at the pyrrole ring induces subsequent dissociation by the loss of a H atom (Scheme 5). Such a loss, which yields the *m/z* 130 product for **1** and the *m/z* 131 product for **2**, occurs only moderately under the ion–molecule reaction conditions (Figures 2a and 2b); however, it is extensive under 15 eV collisional activation (Figures 4a and 4b).



Scheme 5. Loss of a H atom from the methyl substituent on the pyrrole ring of the isoprene annulation product.

Upon CID, the *m/z* 130 ion formed when **1** reacted with isoprene (Figure 2a) yielded *two* fragment ions of *m/z* 77 and 78 (Figure 5a), and, as did the phenyl cation, the *m/z* 77 fragment dissociated further by loss of C_2H_2 to produce *m/z* 51. The diaza ion of *m/z* 131 from **2** (Figure 2b) dissociated to a single fragment ion of *m/z* 78 (Figure 5b). Dissociation mechanisms for such bicyclic cations are probably complex; however, it is possible to roughly rationalize their dissociations, as proposed in Scheme 6. The aza ion of *m/z* 130 probably dissociates by two pathways (Scheme 6, top): combined loss of acetylene + HCN and acetylene + acetylene to form *two* fragments of *m/z* 77 and 78 (Figure 5a). Then, if the *diaza* ion of *m/z* 131 dissociates similarly (Scheme 6, bottom), both pathways result in a combined loss of acetylene + HCN; hence, only (either the same or isomeric) $C_5H_4N^+$ ions of *m/z* 78 are formed (Figure 5b).



Scheme 6. Proposed dissociation mechanisms for the bicyclic aza (top) and diaza (bottom) cations.

Authentic ion: Additional evidence that annulation (a formal pyrrole ring fusion) occurs when *ortho*-hetarynium ions react with 1,3-dienes is obtained by the dissociation of the authentic ion, that is, ionized indolizine[22] (Figure 6). Upon CID, ionized indolizine behaves identically[23] to the product ion of *m*/*z* 117 (Figure 3a) which is formed when **1** reacted with 1,3-butadiene (Figure 1a).

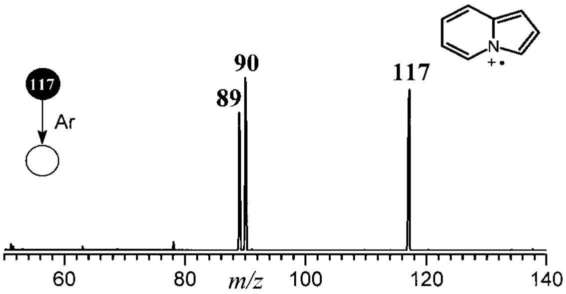


Figure 6. Double-stage (MS^2) 15 eV CID mass spectrum of ionized indolizine of *m*/*z* 117.

Ab initio calculations: Figure 7 shows a potential energy surface diagram for the reaction of **1** with butadiene. The initial reaction step could involve either simple addition to, or polar $[4+2^+]$ cycloaddition across the $C{\equiv}N^+$ bond, or both; however, the calculations predict polar $[4+2^+]$ cycloaddition to be far more exothermic (by -113.2 kcal mol^{-1}), and hence, far more thermodynamically favored. For the cycloadduct to undergo contraction from a six- to a five-membered ring, two considerably endothermic steps should occur: ring-opening of the new six-membered fused ring, which is hampered by a $+51.0$ kcal mol^{-1} energy threshold;[24] and [1,4-H] shift connected by a TS lying $+34.2$ kcal mol^{-1} higher in energy. However, these energy barriers should be easily surpassed since the highly exothermic (-113.2 kcal mol^{-1}) first step of polar $[4+2^+]$ cycloaddition provides a great excess of internal energy to the nascent cycloadduct. Intramolecular N-nucleophilic attack then rapidly completes ring-contraction since this attack proceeds "downhill" in an overall -125.9 kcal mol^{-1} exothermic process, even more exothermic than the initial polar $[4+2^+]$ cycloaddition. As expected for an even–odd-electron ion dissociation, the final reaction step, that of methyl loss, is rather energy demanding: endothermic by $+80.9$ kcal mol^{-1}. Yet, and again, the overall great exothermicity of the preceding reaction steps provides more than enough internal energy to the bicyclic cation to surpass such an energy barrier. Overall, annulation is kinetically and thermodynamically favored; it is exothermic by -45.0 kcal mol^{-1}.

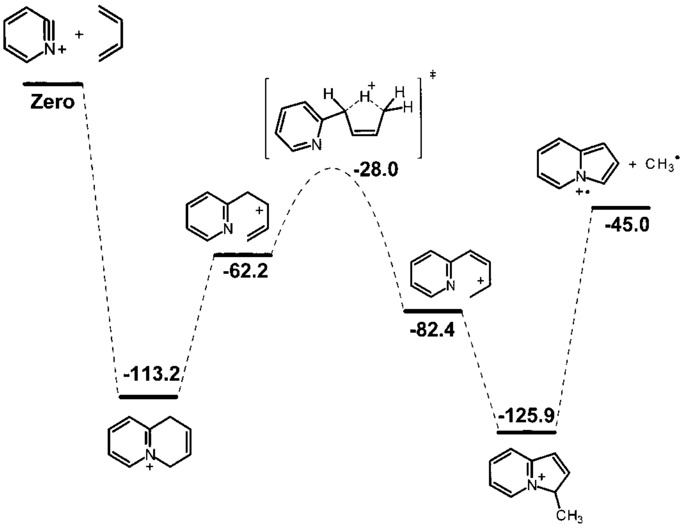


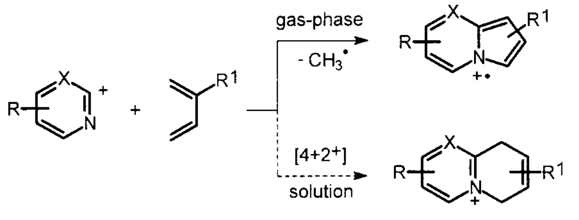
Figure 7. Ab initio MP2/6-311G(d,p)//6-311G(d,p) potential energy diagram for the reaction of **1** with 1,3-butadiene. Energies are given in kcal mol^{-1}. The final electronic energies are (in hartrees): **1** (-246.64910), 1,3-butadiene (-155.52086), the $[4+2^+]$ cycloaddition product (-402.35036), acyclic $C_5H_4NCH_2CHCHCH_2^+$ (-402.26904), TS (-402.21456), acyclic $C_5H_4NCHCHCHCH_3^+$ (-402.301332), cyclic $C_5H_4NCHCHCHCH_3^+$ (-402.37066), ionized pyrrolo[1,2-*a*]pyridine (-362.53267), and $CH_3^{\cdot}$ (-39.70908). The TS energy, and the barrier for the [1,4-H] shift, decreases from 34.2 kcal mol^{-1} to 27.3 kcal mol^{-1} when the structure optimization is performed at the MP2/6-311G(d,p) level.

The potential energy diagram of Figure 7 corroborates, therefore, the proposed reaction sequence as outlined in Scheme 4. Initially, polar $[4+2^+]$ cycloadditon occurs predominantly as the more favorable exothermic process. However, the nascent cycloadducts, owing to their high internal energy, easily surpass the energy barriers for the contraction from a six- to a five-membered ring to form even more stable bicyclic adducts, the methyl pyrrolo[1,2-*a*]pyridyl cation intermediates. These ions then shed their even greater excess of internal energy by releasing a methyl radical to form the final observed products: ionized indolizines (pyrrolo[1,2-*a*]pyridines) or pyrrolo[1,2-*a*]pyrimidines.

Conclusions

Ortho-hetarynium ions react with 1,3-dienes by a highly exothermic, thermodynamically and kinetically favored annulation, formally a fusion reaction onto the ions of a pyrrole ring. This novel and efficient gas-phase reaction occurs through several steps: initial polar $[4+2^+]$ cycloaddition, ring-opening, [1,4-H] shift, and recyclization to result in the contraction from a six- to a five-membered ring; and dissociation by the loss of a methyl radical. The 2-pyridyl cation (**1**) gives the ionized pyrrolo[1,2-*a*]pyridines (indolizines), while the 2-pyrimidyl cation (**2**) gives ionized pyrrolo[1,2-*a*]pyrimidines.

Ortho-hetarynium ions and 1,3-dienes provide, therefore, the two building blocks for the straightforward, *one-step* synthesis of indolizines (pyrrolo[1,2-*a*]pyridines) and pyrrolo[1,2-*a*]pyrimidines, and their analogues (Scheme 7) and derivatives. This gas-phase reaction has potential analytical and synthetic use. As *ortho*-hetarynium ions are also common



Scheme 7. Activation of *ortho*-hetarynium ions with 1,3-dienes in the gas phase and cycloaddition to 1,3-dienes that may be favored in solution.

condensed-phase intermediates,[3] and can be generated chemically or electrochemically in solution, this novel annulation reaction should be tested for its potential use in analogous condensed-phase synthesis, or more likely, owing to solvent quenching, in the synthesis of the intact polar $[4+2^+]$ cycloadducts (Scheme 7) in solution by another interesting annulation reaction.

Acknowledgments

This work was supported by the Research Support Foundation of the State of São Paulo (FAPESP) and the Brazilian National Research Council (CNPq).

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Received: April 16, 1999
Revised version: August 23, 1999 [F 1730]

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0947-6539/00/0602-0326 $ 17.50+.50/0