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Gas-Phase Reactivity of the 2,6- and 3,5-Dimethylenepyridinium Biradicals

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Abstract: The 2,6- and 3,5-dimethylenepyridinium biradical ions were generated and structurally characterized in the gas phase by using Fourier transform ion cyclotron resonance mass spectrometry. Their reactivity was examined toward several commonly used spin traps. Reaction rates and product distributions were determined. The isomeric biradicals were found to possess remarkably different chemical properties. Most importantly, the 2,6-dimethylenepyridinium biradical is highly reactive toward all the reagents studied, while the 3,5-dimethylenepyridinium biradical reacts slowly or not at all. The reaction of the 2,6-dimethylenepyridinium biradical with *tert*-butyl isocyanide occurs via HCN abstraction and addition, the same pathways observed for isomeric closed-shell pyridylmethyl cations. In contrast, the 3,5-dimethylenepyridinium biradical reacts exclusively by slow addition. The same reaction was observed for the analogous 3-methylenepyridinium monoradical ion. The 3,5-dimethylenepyridinium biradical and the 3-methylenepyridinium monoradical also display similar reactivity toward the other reagents studied, while this is not the case for the 2,6-dimethylenepyridinium biradical and the pyridylmethyl cations. Some of the differences observed in the reactivity of the isomeric biradicals are likely explained by their different ground-state multiplicities. Earlier *ab initio* molecular orbital calculations predict a triplet ground state for the 3,5-dimethylenepyridinium biradical (by about 6 kcal/mol) and a closed-shell singlet ground state for the 2,6-dimethylenepyridinium biradical (by about 2 kcal/mol). The different location of the protonated nitrogen relative to the methylene groups probably has a minor influence over the types of reaction products obtained since this is the case for the analogous monoradicals.

Introduction

Biradicals with fully delocalized π-systems have been the subject of numerous recent studies.[1] Knowledge concerning the predisposition of these biradicals toward a singlet or a triplet ground state is important for the rational design and synthesis of organic magnetic materials, *i.e.*, very high spin organic molecules.[2] Hence, many efforts have been dedicated to experimental and computational investigations of the ground-state spin preferences of π-conjugated biradicals.[2,3]

The *m*-xylylene biradical is known to be a ground-state triplet[3,4] ($\Delta E_{ST} = 9.6$ kcal/mol[3f]). The same is thought to be true for its heteroatom-substituted analogues.[4,5] However, recent calculations by West *et al*. predict that protonation of selected dimethylenepyridine biradicals will unequally stabilize the two nearly degenerate nonbonding molecular orbitals that are singly occupied in triplet *m*-xylylene (Scheme 1 shows the Hückel nonbonding molecular orbitals of *m*-xylylene), and thus substantially alter or even reverse the ground-state spin preference of these *m*-xylylene analogues.[5] These predictions are difficult to test via solution experiments.[5] However, charged biradicals are well suited to mass spectrometric studies since the low pressure allows detailed studies of highly reactive species.[6] We report here an experimental investigation of the 2,6-dimethylenepyridinium biradical (**1**), predicted to have a closed-shell singlet ground state ($\Delta E_{ST} = -2.4$ kcal/mol), and the 3,5-dimethylenepyridinium biradical (**2**), calculated to be a ground-state triplet ($\Delta E_{ST} = 6.4$ kcal/mol).[5] The gaseous biradicals were generated and isolated in a mass spectrometer, and their products and reaction rates were determined for reactions with several commonly used spin traps.

Scheme 1

Experimental Section

All experiments were performed by using an Extrel Model 2001 Fourier-transform ion cyclotron resonance mass spectrometer (FT/ICR) described previously.[7] This instrument contains a differentially pumped dual cell that is placed within the magnetic field produced by a 3.0-T superconducting magnet operated at about 2.7 T. The nominal base

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[1] (a) Greenberg, M. M.; Blackstock, S. C.; Stone, K. J.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3671. (b) Gajewski, J. J.; Paul, G. C.; Chang, M. J.; Gortva, A. M. *J. Am. Chem. Soc.* **1994**, *116*, 5150. (c) Stone, K. J.; Greenberg, M. M.; Blackstock, S. C.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 3659. (d) Brook, D. J. R.; Fox, H. H.; Lynch, V.; Fox, M. A. *J. Phys. Chem.* **1996**, *100*, 2066.

[2] (a) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (b) Iwamura, H. I.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (c) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

[3] See for example: (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (b) Li, S.; Ma, J.; Jiang, Y. *J. Phys. Chem.* **1996**, *100*, 4775. (c) Rajca, A.; Rajca, S. *J. Am. Chem. Soc.* **1996**, *118*, 8121. (d) Adam, W.; Finzel, R. *J. Am. Chem. Soc.* **1992**, *114*, 4563. (e) Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 5816. (f) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354.

[4] Inglin, T. A.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 3394.

[5] West, A. P., Jr.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 1452.

[6] (a) Hu, J.; Squires, R. R. *J. Am. Chem. Soc.* **1996**, *118*, 5816. (b) Thoen, K. K.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1997**, *119*, 3832.

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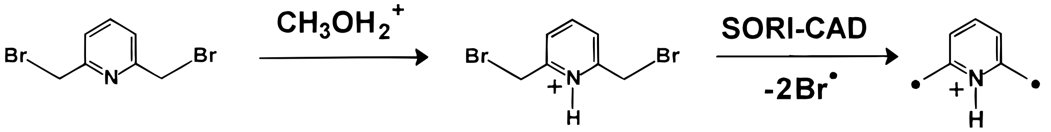
Scheme 2



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pressure is less than 10^{-9} Torr, as maintained by two Balzers turbomolecular pumps (330 L s^{-1}), each backed with an Alcatel mechanical pump. The pressure is measured with two ionization gauges located on each side of the dual cell. The two cells are separated by a common wall (the conductance limit) that contains a 2 mm hole in the center. Ions were transferred from one cell into the other by grounding the conductance limit plate for approximately 150 μs. Unless otherwise noted, this plate and the other two trapping plates were maintained at +2 V.

All compounds were obtained commercially and used as received, with the exception of 3,5-bis(bromomethyl)pyridine, which was synthesized via benzylic bromination of 3,5-lutidine.[8] The identity and purity of all reagents were verified by mass spectrometry. The 2,6- and 3,5-bis(bromomethyl)pyridine precursors were introduced at a nominal pressure of $(1.0-3.0) \times 10^{-7}$ Torr into one side of the dual cell by using a heated solids probe. Methanol (or methanol-d_4) was added at a nominal pressure of $(1.0-2.0) \times 10^{-7}$ Torr into the same cell through a batch inlet system. The mixture was subjected to electron ionization (typically 20 eV electron energy, 8 μA emission current, 70 ms ionization time) and allowed to react for approximately 1 s, which resulted in an abundant signal for the protonated bis(bromomethyl)pyridine.

The protonated precursors were transferred into the other side of the dual cell and kinetically and internally cooled for 1 s by multiple collisions with the neutral molecules present in this cell (the reagent to be used in the final stage of the experiment; the nominal pressure was 6.0×10^{-8} to 2.0×10^{-7} Torr). The ions were isolated by ejecting all unwanted ions from the cell through the application of a stored-waveform inverse Fourier transform (SWIFT)[9] excitation pulse to the excitation plates of the cell (Extrel SWIFT module). After isolation, argon was pulsed into the cell via a pulsed valve assembly (the nominal peak pressure was $(1.0-2.0) \times 10^{-5}$ Torr in the cell) and the carbon−bromine bonds were cleaved via the sustained off-resonance collision-activated dissociation (SORI−CAD)[10] technique for about 1 s at a frequency 0.5−1.0 kHz higher than the cyclotron frequency of the ions. The biradical product ions (**1** and **2**) were cooled for about 0.5 s through multiple collisions with the neutral molecules present in the cell. This approach was also used to generate the methylenepyridinium monoradicals (**7** and **8**) from the appropriate picolyl chloride precursors (carbon−chlorine rather than carbon−bromine bonds were cleaved to form the monoradicals). The 2-(6-methylpyridyl)methyl (**3**) and 3-(5-methylpyridyl)methyl (**4**) cations were produced directly by electron ionization of the corresponding lutidine precursors, transferred into the other side of the dual cell, and cooled.

Ions were isolated by ejecting all unwanted ions from the cell, as described above. The isolated ions were allowed to undergo reactions with a neutral reagent for a variable period of time (typically 0.10−45 s). After reaction, the ions were excited for detection by using "chirp" excitation. All the measured spectra are the average of at least 30 transients and were recorded as 64K data points and subjected to one zero fill *prior* to Fourier transformation.

Since the reactions studied under the conditions described above follow pseudo-first-order kinetics, the second-order rate constant (k_{exp}) of each ion−molecule reaction was derived from a semilogarithmic plot of the relative abundance of the reactant ion versus time. The collision rate constants (k_{coll}) were calculated by using the parametrized trajectory theory.[11] The reaction efficiencies are given as $k_{\mathrm{exp}}/k_{\mathrm{coll}}$. The pressure readings were corrected for the sensitivity of the ion gauge toward each neutral reagent[12] and for the pressure gradient between the dual cell and the ion gauge. The latter correction factor was obtained by measuring the rates of exothermic proton and electron-transfer reactions involving the neutral molecules of interest that occur at the collision rate. Primary products were identified based on their fixed relative abundances at short reaction times. The branching ratios for the primary products are given as the ratio of their relative abundances.

Molecular orbital calculations of the relative energies of some of the possible products formed upon HCN abstraction from *tert*-butyl isocyanide by the biradical **1** were carried out with use of the Gaussian 92 Revision F suite of programs.[13a] The relative energies of one of the biradicals (**2**) and several of its isomers were calculated by using the Gaussian 94 Revision D.2 suite of programs.[13b] The geometries were fully optimized at the Becke3LYP/6-31G(d) level of theory. Zero-point vibrational energies (ZPVE) were calculated from the Becke3LYP/6-31G(d) harmonic frequencies and scaled by a factor of 0.9804 to account for the systematic overestimation of the vibrational frequencies by the density functional method.[13c] The force constant matrices obtained for the stationary points were confirmed to have the correct number of negative eigenvalues (zero for equilibrium structures).

Results and Discussion

Synthesis. A two-step procedure (Scheme 2) was used to generate the 2,6- (**1**) and 3,5-dimethylenepyridinium (**2**) biradicals in a dual-cell Fourier transform ion cyclotron resonance mass spectrometer. The first step involved protonation of the appropriate bis(bromomethyl)pyridine precursors via methanol chemical ionization. The bromine atoms were homolytically cleaved by sustained off-resonance irradiated collision-activated dissociation[10] (SORI−CAD) in the other side of the dual cell (Figure 1a). The biradical ions were isolated (Figure 1b) and allowed to react (Figure 1c) with various neutral reagents for variable periods of time. The linear decrease of the natural logarithm of the relative abundances of the biradical reactant ions as a function of time (see Figure 2 for an example) suggests

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Table 1. The Observed Reactions (Relative Product Abundances Given in Parentheses) and Their Efficiencies (Eff = k_{exp}/k_{coll})

ion no.	*tert*-butyl isocyanide	di-*tert*-butyl nitroxide	dimethyl diselenide	triethylamine	benzeneselenol
1	HCN abstraction (90%) addition (10%) Eff 27%	addition − C_4H_8 (100%) 2×(addition − C_4H_8)[b] Eff ~44%	addition (100%) Eff 15%	H^+ transfer (67%) H-abstraction (33%) Eff 30%	addition (70%) two sequential $H^•$ abstractions[b] (24%) C_6H_6 abstraction (6%) Eff 8%
***d*-1**	HCN abstraction	addition − C_4H_8 (100%) 2×(addition − C_4H_8)[b] Eff ~46%		D^+ transfer (68%) H−abstraction (32%) Eff 30%	
2	addition (100%) Eff 0.8%	C_4H_8 abstraction (100%) Eff 2%	no reaction[a]	H^+ transfer (100%) Eff ~37%	$H^•$ abstraction (100%) Eff 0.1%
3	addition (60%) HCN abstraction (40%) Eff 2%	addition (100%) Eff ~2%	no reaction[a]	H^+ transfer (100%) Eff ~46%	no reaction[a]
4	addition (50%) HCN abstraction (50%) Eff ~1%	addition (100%) Eff ~1%		H^+ transfer (100%) Eff ~38%	
8	addition (55%) $H^•$ abstraction (45%) Eff 0.04%	addition − C_4H_8 (100%) Eff 85%	no reaction[a]	H^+ transfer (100%) Eff 69%	$H^•$ abstraction (100%) Eff 4%
9	addition (100%) Eff 0.09%	addition (44%) addition − C_4H_8 (56%) Eff 56%	no reaction[a]		$H^•$ abstraction (100%) Eff 2%

[a] Not detectable under the experimental conditions. [b] Secondary product.

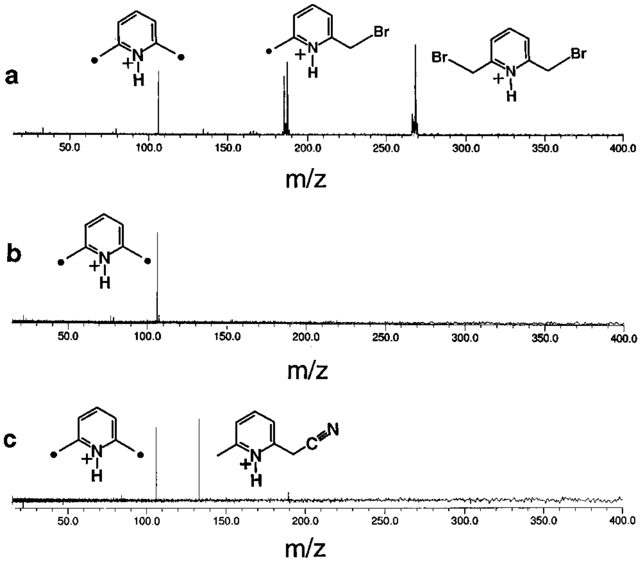

Figure 1. (a) Generation of **1** (*m*/*z* 106) by sustained off-resonance irradiated collision-activated dissociation (SORI−CAD) of the 2,6-bis-(bromomethyl)pyridinium ion (*m*/*z* 264/266/268). (b) Isolation of **1** (*m*/*z* 106). (c) Reaction of **1** for 1.5 s with *tert*-butyl isocyanide (MW 83; nominal pressure 8.0 × 10^{-8} Torr). HCN abstraction (*m*/*z* 133) and addition (*m*/*z* 189) were observed.

that the biradicals were internally and kinetically cooled before each reaction (*i.e.*, hot ions that may react at different rates were not observed at short reaction times). The reaction products, their branching ratios, and the measured reaction efficiencies are summarized in Table 1.

Structural Characterization. Our previous work demonstrates that sustained off-resonance irradiated collision-activated dissociation of carbon−halogen bonds can be used to generate stable aromatic monoradicals. For example, isomeric *m*- and *p*-phenyl radicals with a positively charged substituent were produced from halobenzene precursors by SORI−CAD and demonstrated not to undergo isomerization during generation or upon subsequent collisions with neutral reagent molecules.[14] More recently, SORI−CAD was used to generate a stable derivative of the *m*-benzyne via the cleavage of iodine atoms from a phenyl ring carrying a positively charged substituent.[6b] Hence, it is reasonable to expect that the analogous procedure employed here yields the unisomerized *m*-xylylene derived biradicals **1** and **2**.

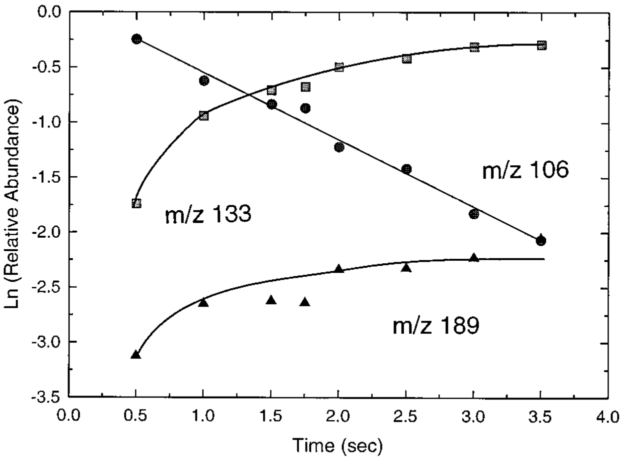

Figure 2. Temporal variation of the ion abundances for the reaction of **1** (*m*/*z* 106; ●) with *tert*-butyl isocyanide (MW 83; nominal pressure 8.0 × 10^{-8} Torr). HCN abstraction (*m*/*z* 133; ■) and addition (*m*/*z* 189; ▲) were observed. The data points measured for the products are connected by arbitrary smooth lines.

Verification of the structures of the reaction products was carried out by examining their reactivity, by deuterium labeling experiments, and by comparison to isomeric ions. The experimental investigation was limited to isomers assessed to be energetically feasible. High-energy pyridinium carbene ions, such as **7**, were not considered (molecular orbital calculations carried out at the Becke3LYP/6-31G(d) + ZPVE level of theory predict **7** to lie 23 kcal mol^{-1} higher in energy than **2**). Further, isomers with a different carbon skeleton, such as **5** and **6**, are highly unlikely since their formation probably requires[15] very

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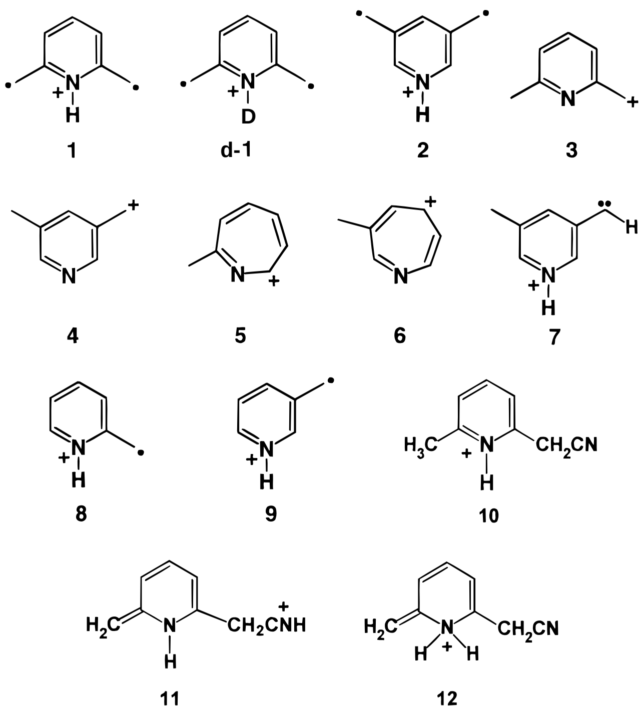
[14] Thoen, K. K.; Smith, R. L.; Nousiainen, J. J.; Nelson, E. D.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1996**, *118*, 8669.

Chart 1



high-energy transition states (however, **6** lies about 8 kcal mol^{-1} lower in energy than **2**).

The low-energy isomers that still remain to be considered are the 2-(6-methylpyridyl)methyl (**3**) and 3-(5-methylpyridyl)-methyl (**4**) cations (**4** was calculated to lie 7 kcal mol^{-1} lower in energy than **2**). Formation of **3** and **4** from the biradical ions **1** and **2,** respectively, either via a unimolecular or bimolecular process, is not only energetically feasible but could be facile since it only involves transfer of a hydrogen atom from the nitrogen to one of the methylenes. To examine whether this process takes place, the pyridylmethyl cations **3** and **4** were generated by electron ionization of the corresponding dimethylpyridines and allowed to react with various neutral reagents. The observed reactivity (Table 1) conclusively demonstrates that **1** and **2** have not rearranged to **3** and **4**. For example, **1** reacts with dimethyl diselenide by addition and with benzeneselenol by benzene and hydrogen atom abstraction and addition (Table 1), while **3** is unreactive toward both reagents (Table 1). On the other hand, **2** abstracts C_4H_8 from di-*tert*-butyl nitroxide and slowly adds to *tert*-butyl isocyanide, while **4** reacts by exclusive addition with the former reagent and by HCN abstraction as well as addition with the latter.

Deuterium labeling experiments provide a final demonstration of the stability of the biradical **1** toward isomerization to **3** (or to **5)**. This isomerization process would necessarily involve migration of the nitrogen-bound proton to a carbon, thus making the acidic proton indistinguishable from the carbon-bound hydrogens. The observation of exclusive deuterium transfer to triethylamine from the nitrogen-deuterated form of **1** (***d*-1**, Table 1; Figure 3) shows that the biradical retains its connectivity. From this and the results described above, it is reasonably concluded that **1** and **2** are produced intact and without subsequent isomerization in our experiments.

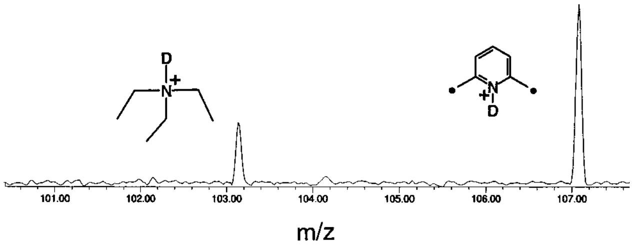


Figure 3. Reaction of ***d*-1** (*m*/*z* 106) for 1 s with triethylamine (MW 101; nominal pressure 4.0 × 10^{-8} Torr). Deuteron transfer (*m*/*z* 103) but no proton transfer (*m*/*z* 102) was observed.

Reactivity. According to West *et al.*,[5] **1** and **2** may provide a rare opportunity to compare the intrinsic reactivity of structurally related biradicals with different ground-state spin preferences. Hence, the chemical properties of the biradicals **1** and **2** were examined toward various spin traps. The reactions of the analogous monoradicals **8** and **9** and the isomeric closed-shell cations **3** and **4** were also examined in order to gain insight into the mechanisms of the reactions.

When considering the results reported below, one may wish to keep in mind the key differences between reactions observable in high vacuum and in solution. Due to the very low pressures employed in the present study, an ion only encounters a neutral reagent molecule approximately once every 100−500 ms. This low encounter rate, together with the submicrosecond lifetime of the collision complex, guarantees that each ion−molecule collision complex is isolated from other molecules, *i.e.*, the reactions occur in a solvent-free environment. Due to the absence of the energy source that the solvent provides, endothermic reactions are rarely observed. Similarly, there is no medium that can act as a heat sink for the excess energy released in exothermic reactions. Accordingly, any vibrationally excited addition products formed in gas-phase reactions generally undergo subsequent fragmentation to release their excess energy.

General Comparison of 1 and 2. The chemical properties of the isomeric biradicals **1** and **2** are different. The most remarkable observation deals with the overall level of reactivity. The biradical **1** is exceedingly reactive toward all the reagents studied while **2** usually reacts slowly or not at all (during the time of observation). For example, **1** abstracts HCN from *tert*-butyl isocyanide at about 30% of the collision rate (every third collision leads to reaction) and adds to dimethyl diselenide at 15% of the collision rate. In contrast, **2** adds to *tert*-butyl isocyanide very slowly (about 1% of the collision rate), and is unreactive toward dimethyl diselenide (Figure 4).

Comparison of the types of products formed upon reactions of the biradical **2** and the monoradicals **8** and **9** reveals an obvious similarity in the chemical properties of these species. All three species slowly add to *tert*-butyl isocyanide (see Figure 4b for the reaction of **2**), slowly abstract a hydrogen atom from benzeneselenol, and are unreactive toward dimethyl diselenide (Table 1). This monoradical-type behavior of biradical **2** conforms to expectations[6a] of triplet biradical reactivity and hence agrees qualitatively with the predicted[5] triplet electronic ground state of **2**.

The biradical **1** is predicted[5] to be a closed-shell singlet. Consideration of its valence bond description (three of its resonance structures are shown in Schemes 3 and 4) suggests that some of its reactions may resemble those of the isomeric, closed-shell pyridylmethyl cations **3** and **4**. Indeed, **1**, **3**, and **4** were found to react with *tert*-butyl isocyanide via the same pathways, HCN abstraction and addition (albeit at very different efficiencies). However, this is the only similarity observed for

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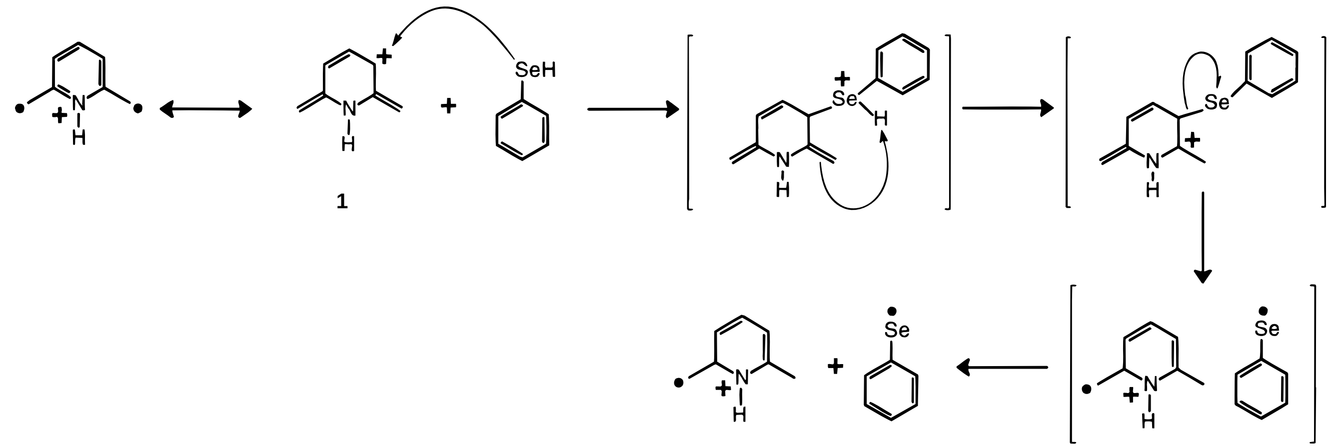
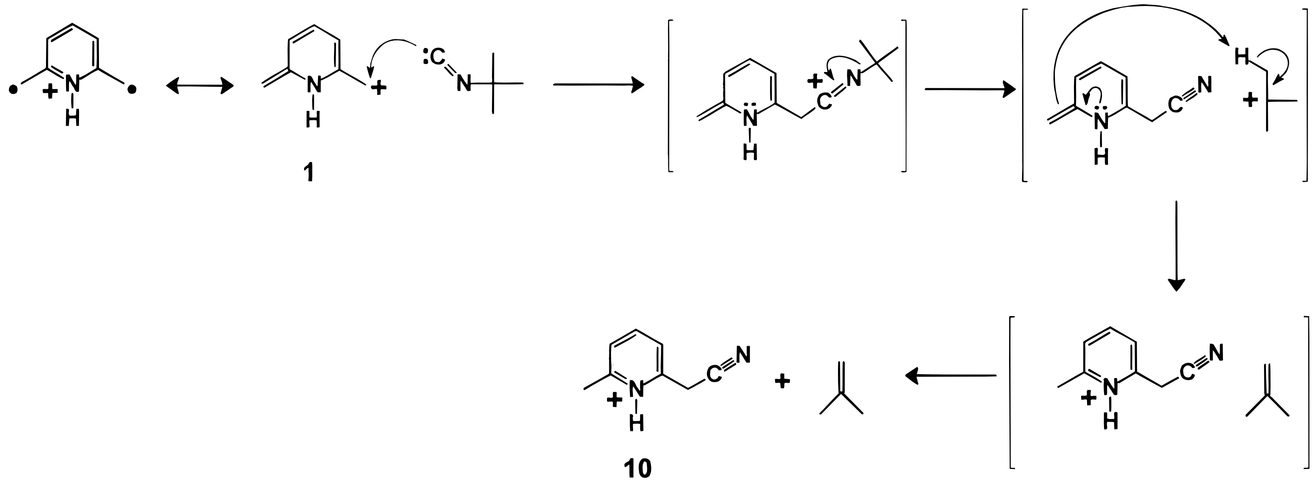
(15) For isomerization of tolyl cations to tropylium ions, see, for example: (a) McLafferty, F. W.; Bockhoff, F. M. *Org. Mass Spectrom.* **1979**, *14*, 181. (b) Ausloos, P. *J. Am. Chem. Soc.* **1982**, *104*, 5259. (c) Olesik, S.; Baer, T.; Morrow, J. C.; Ridal, J. J.; Buschek, J.; Holmes, J. L. *Org. Mass Spectrom.* **1989**, *24*, 1008.

Scheme 3



Scheme 4



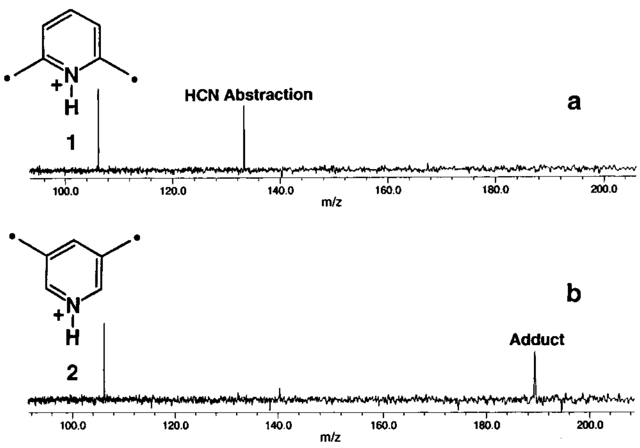


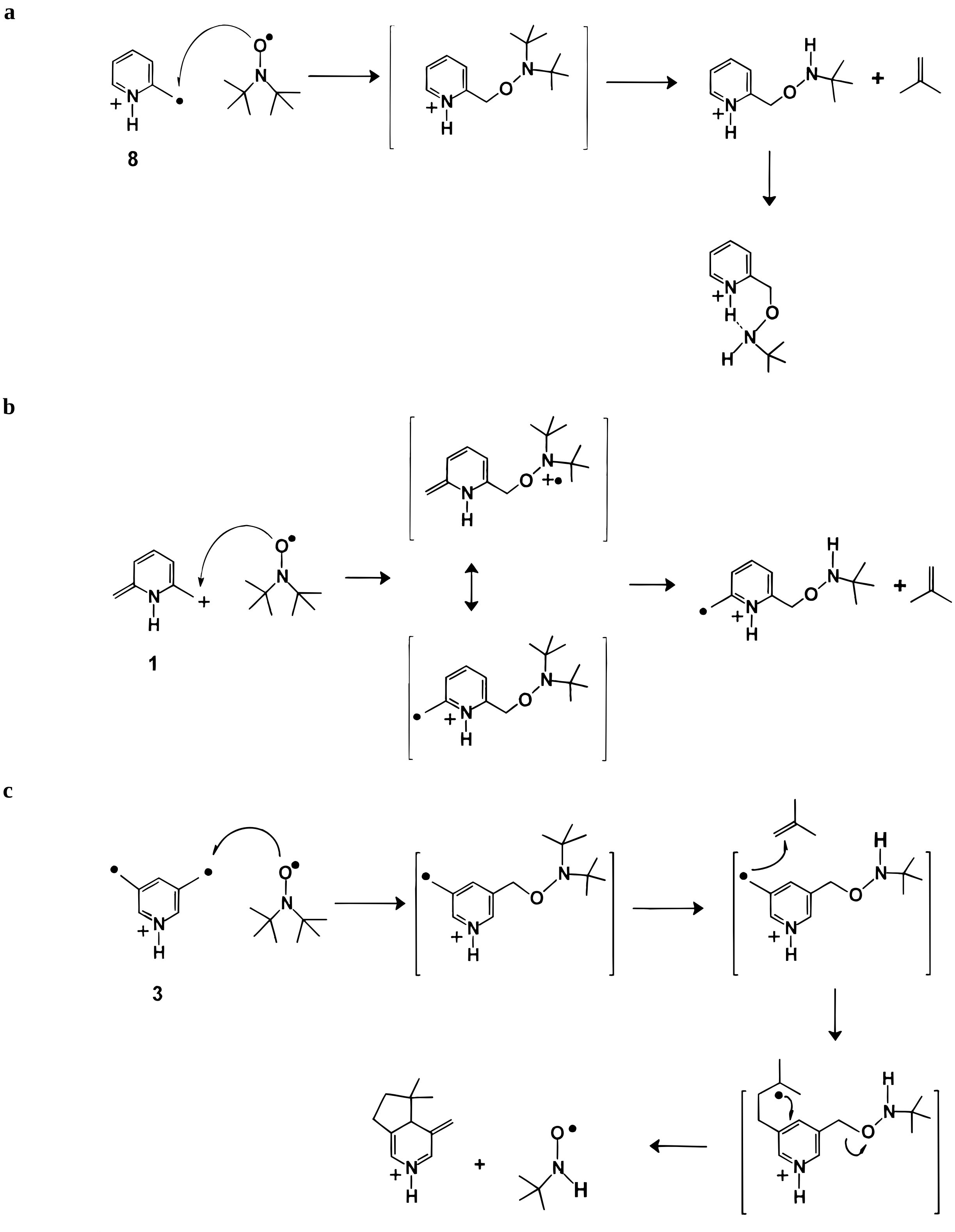
Figure 4. (a) Reaction of **1** (*m*/*z* 106) for 0.5 s with *tert*-butyl isocyanide (MW 83; nominal pressure 2.8 × 10^{-7} Torr). HCN abstraction (*m*/*z* 133) was observed (at longer times, the addition product also becomes visible). (b) Reaction of **2** (*m*/*z*106) for 8 s with *tert*-butyl isocyanide (MW 83; nominal pressure 4.2 × 10^{-7} Torr). Addition (*m*/*z* 189) was observed.

these three species. With the exception of *tert*-butyl isocyanide, the pyridylmethyl cations either are unreactive toward or slowly add to the reagents studied, while the biradical **1** reacts rapidly to yield a variety of products.

In agreement with the predicted[5] singlet electronic state of **1**, this biradical generally reacts through pathways other than those observed for the analogous monoradicals **8** and **9**. For example, **1** rapidly abstracts HCN from *tert*-butyl isocyanide (Figure 4; Table 1) while **8** and **9** react by predominant addition (**8** also reacts by hydrogen atom abstraction; Table 1). On the other hand, addition dominates the reaction of **1** with benzeneselenol while **8** and **9** react with this well-known[6b,7b,d,14,16] hydrogen atom donor by exclusive hydrogen atom abstraction. A minor channel corresponding to hydrogen atom abstraction was also observed for **1** (together with C_6H_6 abstraction; Table 1). This reaction may occur via an ionic mechanism (Scheme 3). The reaction produces a monoradical that abstracts a hydrogen atom from another benzeneselenol molecule via a radical mechanism, like its homologue **8**.

The HCN abstraction reaction observed upon interaction of the biradical **1** with *tert*-butyl isocyanide (Figure 4) almost certainly follows an electrophilic pathway since the same reaction occurs for the pyridylmethyl cations **3** and **4** (albeit at a low efficiency; Table 1). The HCN abstraction is likely to take place in a stepwise manner: cyanide abstraction produces the *tert*-butyl cation that transfers a proton to yield the observed HCN abstraction product. Molecular orbital calculations (Becke3LYP/6-31G(d) + ZPVE) suggest that proton transfer to the methylene group in the cyanide abstraction product of **1** yields the most stable final product ion (**10**). The methylene-protonated molecule **10** lies 56 kcal mol^{-1} lower in energy than the nitrogen-protonated molecule **12** and 62 kcal mol $^{-1}$ lower than the CN-protonated molecule **11**. Some support for the proposed stepwise mechanism is provided by the observation that the unsubstituted benzyl cation (generated by electron

Scheme 5



ionization of benzyl chloride) reacts with *tert*-butyl isocyanide by exclusive cyanide abstraction (26% efficiency).

Radical−Biradical Reactions. Examination of the reactions of the stable free radical di-*tert*-butyl nitroxide produced intriguing results (Table 1). This reagent slowly adds to the pyridylmethyl cations **3** and **4** (Table 1). However, the monoradicals **8** and **9** undergo a very rapid radical−radical recombination that is often followed by spontaneous elimination of C_4H_8 (2-methylpropene). The possibility for internal hydrogen bond formation in the C_4H_8 elimination product of **8** (Scheme 5a; steric crowding prevents this in the initial addition product) may explain why the adduct formed from this radical always undergoes subsequent C_4H_8 elimination, while this is only true for half of the adduct population formed from **9**. Reaction of the biradical **1** yields the analogous primary product ion as is obtained for the monoradical **8** (the reaction of **1** may proceed by an ionic mechanism, as shown in Scheme 5b). However, the product obtained from the biradical is an odd-electron species. As expected, this product ion reacts with another di-*tert*-butyl nitroxide molecule in the same manner as the monoradical **8**, *i.e.*, via exclusive radical−radical recombination followed by C_4H_8 elimination.

In contrast to the behavior of **1**, reaction of the biradical **2** proceeds by slow C_4H_8 abstraction. This reaction likely takes place via the same initial steps as the reaction of the analogous monoradical **9**, *i.e.*, radical−radical recombination followed by C−N bond cleavage to release 2-methylpropene (Scheme 5c). For the monoradical, the product complex has only one exit channel, dissociation to the final products. However, the complex formed from the biradical is composed of a radical ion and an alkene (2-methylpropene) that can react with each other by radical addition. Cleavage of the weakest bond in the adduct (the C−O bond to the nitroxide) yields the final reaction products. The ionic product ion is concluded to be a closed-shell singlet since it is unreactive toward di-*tert*-butyl nitroxide. Hence, radical cyclization likely accompanies the bond cleavage, possibly as shown in Scheme 5c. Analogous reactivity has been reported for the *m*-xylylene upon interaction with alkenes and dienes.[17] The difference in the reaction products obtained for the biradicals **1** and **2** is likely explained by the much greater overall reactivity of the former biradical. The reaction of **1** with di-*tert*-butyl nitroxide is probably highly exothermic since it is very efficient (44%). Consequently, C−N bond cleavage (Scheme 5b) yields a product complex that is too short-lived to react further, and C_4H_8 is released.

Effects of Charges. There are several possible explanations for the marked discrepancies in reactivities of biradicals **1** and **2**. The most obvious source is their predicted different ground-state multiplicity.[5] Another possibility is the differing proximity of the protonated heteroatom and the methylene groups. It is not uncommon for the charge site of an ion to direct and catalyze its reactivity even when the reactivity is of radical type.[18] Comparison of the reactivities of the monoradicals **8** and **9** provides some basis for the evaluation of the importance of these effects.

The reaction efficiencies of the monoradicals **8** and **9** are not markedly different. However, these radicals yield somewhat different product distributions upon reaction with two of the reagents studied. Specifically, **9** (with the protonated heteroatom in the *meta* position as in **2**) reacts with di-*tert*-butyl nitroxide to yield a stable adduct that was not observed for **8** (which has the *ortho* arrangement as in **1**). Further, the reaction with *tert*-butyl isocyanide yields addition and hydrogen atom abstraction products for **8** but only the addition product for **9**. These results suggest that the differing proximities of the protonated heteroatoms and the methylene groups may also affect the types of products obtained for biradicals **1** and **2**. However, this explanation appears insufficient to alone justify the observed different products and reaction rates. Thus, different multiplicities must also play a role in controlling the reactivities of **1** and **2**.

Conclusions

Comparison of the products and reaction rates of the gaseous 2,6- and 3,5-dimethylenepyridinium biradical ions reveals remarkably different chemical properties. Most importantly, the 2,6-dimethylenepyridinium biradical is highly reactive toward all the reagents studied, while the 3,5-dimethylenepyridinium biradical reacts slowly or not at all. Furthermore, the reactions of the latter biradical resemble those observed for analogous monoradicals while the reactions of the former biradical are not typical radical processes. Hence, the reactivity differences of the two biradicals are consistent with the predicted[5] closed-shell singlet electronic ground state for the 2,6-dimethylenepyridinium and triplet for the 3,5-dimethylenepyridinium biradical. The differing proximities of the protonated nitrogen and the methylene groups are likely to have only a minor influence on the reactivity.

This work represents a logical extension of previous efforts to deduce multiplicity from the analysis of radical trapping products formed in solution.[19] The results obtained illustrate the power of mass spectrometry to facilitate the study of biradicals. The ion manipulation abilities allow significant additional flexibility in all stages of the experiment. Elaborate gas-phase synthesis can be used to produce exotic species from commercially available precursors in the mass spectrometer and isolate them before studies. Any radical trap employed in solution can be used in these gas-phase experiments, with the additional advantage that the reaction kinetics can be conveniently monitored. These experiments are limited by the fact that, since all steps take place inside the mass spectrometer, the products can only be probed mass spectrometrically, *i.e.*, via determination of elemental composition and deduction of connectivity from reactivity and fragmentation patterns. On the other hand, the experiments are typically quite rapid. These sorts of experiments can be conveniently applied to the study of any charged as well as neutral intermediate as long as a charge can be added to the latter without substantially affecting its intrinsic reactivity.

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