Synthesis and Characterization of a Distonic Nitrene Ion: Gas-Phase Reactivity of Singlet and Triplet *N*-Phenyl-3-Nitrenopyridinium Ion

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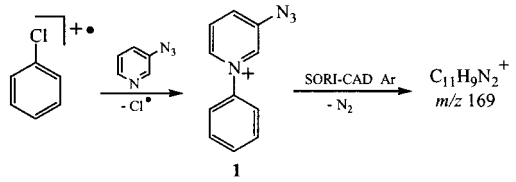
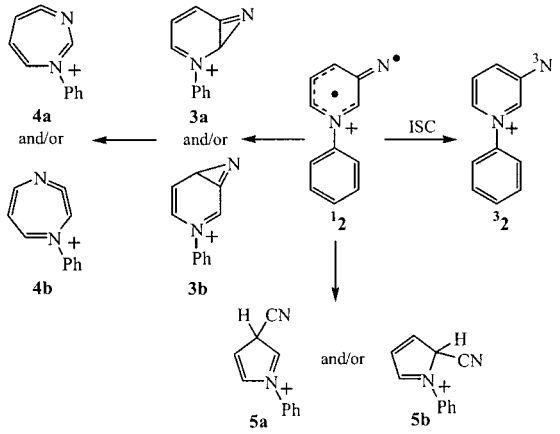
The intermediates produced upon photolysis and thermolysis of phenyl azide have been studied extensively by a variety of experimental techniques.[1] Photolysis of phenyl azide in solution produces open-shell singlet phenylnitrene whose lifetime (∼1 ns) depends on the temperature at which it is generated. At ambient temperature, singlet phenylnitrene rapidly ring-expands to azacycloheptatetraene via the intermediacy of azabicyclo[4.1.0]-heptatriene. The ring-expanded species is responsible for the observed bimolecular reactivity.[2] However, at lower temperatures (<123 K), singlet phenylnitrene undergoes rapid intersystem crossing (ISC) to the triplet ground state (ca. −18 kcal/mol).[3,4] The reactions reported for triplet phenylnitrene in solution are dimerization to form azobenzene, polymerization, H-atom abstraction from trapping reagents to form aniline,[5a−c] and reactions with oxygen to form nitrosobenzene, nitrobenzene, and azoxybenzene.[5d,e] No kinetic reactivity studies have been reported. Gas-phase experiments sometimes allow in-depth studies of highly reactive intermediates that are not accessible to condensed phase studies. However, photolysis or thermolysis of phenyl azide in the gas phase produces vibrationally excited singlet phenylnitrene that rearranges over a large barrier (∼40 kcal/mol) to cyanocyclopentadiene, the global minimum (ca. −30 kcal/mol) on the C_6H_5N surface.[6]

This communication details an elaborate experimental approach that allows the study of the gas-phase reactivity and reaction kinetics of pure triplet aryl nitrenes by using mass spectrometry. The approach employs distonic ions that contain a reactive nitrene moiety and a chemically inert charged group for mass spectrometric manipulation. Other reactive intermediates that have been studied using this approach include phenyl radicals,[7] phenylcarbene,[8] and *o*- and *m*-benzynes.[9]

Scheme 1



Scheme 2



All experiments were carried out using an Extrel Model FTMS 2001 dual cell Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR).[10] The synthetic methodology is analogous to that used to generate nitrenes in solution, employing an aryl azide as the direct precursor to the nitrene intermediate. In a typical experiment, chlorobenzene was ionized by electron ionization in the source side of the dual cell. 3-Azidopyridine was allowed to react with the radical cation of chlorobenzene to produce *N*-phenyl-3-azidopyridinium ion **1** (Scheme 1). The pyridinium ion was transferred into the other side of the dual cell, where it was subjected to sustained off-resonance irradiation for collision-activated dissociation (SORI-CAD)[11] using Ar as a target gas to induce nitrogen extrusion from the azide moiety (*m*/*z* 169).

Examination of the reactivity of the product ion of *m*/*z* 169 revealed that a mixture of isomers was present (see below). Based on the findings made in solution,[12] we postulate that the mixture of isomeric ions of *m*/*z* 169 in our experiments is composed of the charged analogue of the triplet phenylnitrene (**^{3}2**), as well as the ring-expanded (**4a/b**) and ring-contracted (**5a/b**) isomers (Scheme 2).

The most abundant of the isomeric ions exhibited radical-type reactivity toward 1,4-cyclohexadiene by sequentially (and exclusively) abstracting two H-atoms. This observation is consistent with a molecule having an open-shell, high-spin state, such as **^{3}2**. We believe that **^{3}2** is formed upon ISC of the initially generated open-shell singlet phenylnitrene analogue, **^{1}2**. At the completion of the H-atom abstraction reaction, 10% of the *m*/*z* 169 ions remained unreacted, indicating that another isomeric ion was present that did not exhibit radical-type reactivity.

A portion of the remaining unreactive isomeric ions reacted by exclusive adduct formation with the nucleophiles diethyl ether, tetrahydrofuran, and dimethylamine. In solution experiments, adduct formation was ascribed to the bicyclic azirine (7-

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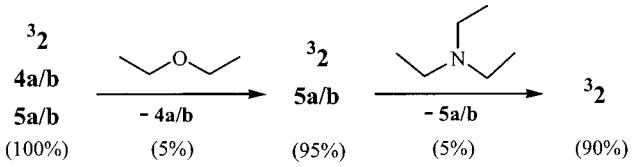
Scheme 3



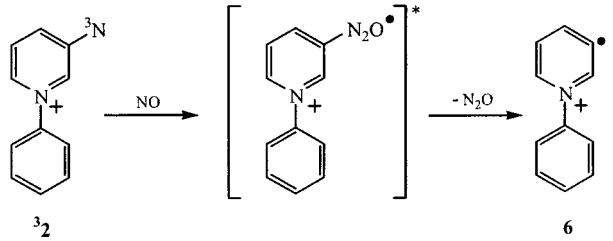
azabicyclo[4.1.0]hepta-2,4,6-triene) and ring-expanded dehydroazepine (1-aza-1,2,4,6-cycloheptatetraene),[13] the analogues of **3a/b** and **4a/b**. We postulate that a small amount of analogous ring-expanded *m*/*z* 169 ion, **4a/b,** is formed by isomerization of ^{1}**2** (Scheme 2) and that it exhibits similar reactivity to the analogue studied in solution. Interestingly, only 50% of the ions that were unreactive toward 1,4-cyclohexadiene reacted away to form adducts.

The remaining isomeric ions were completely quenched by proton transfer to triethylamine. A plausible structure for this ion is **5a/b**, whose conjugate base is a stable pentadiene. Calculations at the BPW91/AUG-cc-pVDZ + ZPVE level of theory predict proton transfer from **5a/b** to triethylamine to be exothermic by 10 kcal/mol. Further support for this structural assignment can be found in the literature.[6] Singlet phenylnitrene formed with excess internal energy has been reported to rapidly rearrange to the global minimum cyanocyclopentadiene that sometimes loses a hydrogen atom. On the basis of all the results presented above, we conclude that the product ion population of *m*/*z* 169 likely consists of three isomers: ^{3}**2**, **4a/b**, and **5a/b**, of which ^{3}**2** is the most abundant.

The reactions attributed to the triplet ^{3}**2** were examined in the absence of the isomers **4a/b** and **5a/b** by selectively quenching the other isomers without affecting the population of ^{3}**2** (Scheme 3). This was carried out by using diethyl ether and triethylamine in one side of the dual cell to remove **4a/b** and **5a/b** from the mixture of ^{3}**2**, **4a/b**, and **5a/b**, which reduced the total abundance of *m*/*z* 169 by 10%. ^{3}**2** was isolated by ejecting all unwanted ions from the cell through the application of a stored waveform inverse Fourier transform (SWIFT)[14] excitation pulse to the excite plates of the cell.

The pure triplet ^{3}**2** was allowed to react with various reagents in the other (clean) side of the dual cell to verify the proposed structure. For example, ^{3}**2** undergoes two sequential H-atom abstractions from benzeneselenol (adduct corresponds to 95% of primary products). Energy-resolved CAD studies on this ion revealed similar fragment ion distributions and appearance energies as those measured for the authentic *N*-phenyl-3-aminopyridinium ion, thus indicating that the ions are identical. Further structural proof comes from examination of the sole product formed upon reaction of ^{3}**2** with doublet NO. This product corresponds to addition of NO with concomitant loss of N_2O. The product was demonstrated to have the structure of *N*-phenyl-3-dehydropyridinium ion, **6** (Scheme 4), by comparison of its reactivity toward H-atom donors to that of an independently generated[15] **6** (same reaction efficiencies, same products).

Scheme 4



Reactivity characteristic of a triplet ground state is evident from the above examples wherein ^{3}**2** reacts with the free radical NO, and undergoes radical-type hydrogen atom abstraction reactions with commonly used H-donors. The efficiency measured for the reaction of ^{3}**2** with NO corresponds to near collision rate[16,17] (efficiency = k_{exp}/k_{coll} = 81%). The first H-atom abstraction by ^{3}**2** from benzeneselenol also occurs readily (26%) whereas the second H-atom abstraction is much slower (8%).

Further radical reactions observed for ^{3}**2** include CH_3S- and CH_3SH-abstraction (1:1) from dimethyl disulfide (efficiency = 0.45%) and a simple adduct formation with O_2 (the sole product; efficiency = 0.001%). Interestingly, a secondary CH_3S-abstraction was not observed during the reaction of ^{3}**2** with dimethyl disulfide, thus demonstrating higher reactivity for ^{3}**2** than its monoradical counterpart. Calculations at the BPW91/AUG-cc-pVDZ + ZPVE level of theory predict the first CH_3S-abstraction to be exothermic by 24.2 kcal/mol. However, calculations at the same level of theory predict the second thiomethyl abstraction to be endothermic by 17.6 kcal/mol.

To support our observations on ^{3}**2**, we carried out calculations on an analogous but more computationally feasible system wherein the phenyl ring is replaced with a proton (3-nitrenopyridinium). At the CASSCF(8,8)/6-31G(d) + ZPVE level of theory, the triplet state, ^{3}A″, of this nitrene is predicted to be the electronic ground state, with the lowest open-shell singlet, ^{1}A″, lying 19.8 kcal/mol higher in energy. The singlet−triplet splitting is therefore estimated to be within 1 kcal/mol of that calculated for phenylnitrene.[3] The ring-expansion of ^{1}A″ is calculated to be 1.6 kcal/mol exothermic overall. The first step of this two-step process, the formation of the bicyclic intermediate, is predicted to be the rate-determining step for the phenylnitrene.[3] In the case of 3-nitrenopyridinium, the corresponding transition state is calculated to lie 7.2 kcal/mol above ^{1}A″. This value is comparable to that calculated for phenylnitrene at the CASSCF(8,8)/6-31G(d) + ZPVE level of theory (8.5 kcal/mol).[3]

In conclusion, a new experimental approach has been described for the study of an aryl nitrene in the gas phase. This approach allowed the first detailed examination of reaction products and kinetics of a triplet aryl nitrene.

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