

slightly with higher levels of theory.

From the internuclear distance, a qualitative description of a bond can be determined. For example, the C₁-C₂ and C₃-C₄ distances are predicted to be 1.291 and 1.295 Å, respectively, at the TZ2P/CCSD level of theory. Although slightly shorter than the prototypical C-C double bond length of ethylene, $r_e = 1.330$ Å,¹⁵ each is characterized as a double bond. The distance between the C₁ and C₃ nuclei is determined to be 1.488 Å at this level of theory. Since this is close to the typical value of the C-C single bond length for cyclopropane, $r_0 = 1.510$ Å,¹⁶ the C₁-C₃ linkage is considered to be a single bond.

The harmonic vibrational frequencies shown in Table I are consistent throughout the levels of theory investigated. However, the CH out-of-plane a₂ bend (ω_6) becomes lower in frequency than the C-C a₁ stretch (ω_5) when electron correlation is included. According to the normal coordinate analysis, the C₁-C₂ and C₃-C₄ double bond stretchings are found to couple strongly (almost 50/50 mixing) with each other. The values of 1899 and 1621 cm⁻¹ (DZP/CISD) for the combinations of these stretches fall within the range of double bond harmonic stretching vibrational frequencies.

The infrared intensities remain reasonably consistent as well, with the exception of the C₁C₂ + C₃C₄ a₁ stretch (ω_3). While the SCF wavefunctions predict moderate intensities for the ω_3 mode, correlated methods indicate that this mode exhibits the strongest intensity. In addition, the CH out-of-plane b₁ bend (ω_7) has a relatively strong intensity.

An encouraging sequence of events occurred in the mid 1980s when ab initio studies¹⁷ aided the laboratory identification¹⁸ and, subsequently, the astronomical observation¹⁹ of cyclopropenylidene (:C=C₂H₂). In the experimental study several band frequencies, including the CH out-of-plane b₁ bend ($\nu = 789$ cm⁻¹), were matched with theoretical frequencies (b₁ bend, $\omega = 854$ cm⁻¹ and

$I = 53$ km mol⁻¹, DZP/SCF) to identify this molecule. The success of this search supports our prediction that the CH out-of-plane b₁ bend (ω_7) may be used to identify cyclopropenylidene (:C=C₂H₂). Theoretical investigations of a related structure, silacyclopropenylidene (:SiC₂H₂),^{20,21} indicate that it has several detectable modes. The CH out-of-plane b₁ bend of :SiC₂H₂ is particularly intense (740 cm⁻¹ and 67 kcal mol⁻¹, TZ2P/CISD),²⁰ a finding that is similar to our results for :C=C₂H₂. Due to its large IR intensity, the previously mentioned C₁C₂ + C₃C₄ stretch ω_3 at 1621 cm⁻¹ (DZP/CISD) is another attractive choice.

The theoretical estimates given in Table II indicate that the dipole moment is approximately 5 D, a value significantly higher than that of either cyclopropenylidene (3.3 D)²² or silacyclopropenylidene (1 D).²⁰ In cyclopropenylidene, the distance (along the C₂ axis) between the hydrogens and the lone pair is much greater than in the other two systems, contributing to these differences. The values of each rotational constant remain within a range of 0.041 cm⁻¹ throughout the levels of theory. Our recommended equilibrium rotational constants are those from the highest level of theory, namely, $A_e = 1.110$, $B_e = 0.273$, and $C_e = 0.219$ cm⁻¹ (TZ2P/CCSD).

Conclusions

With large basis sets and high-level theoretical methods, the structure and physical properties of the exocyclic ring isomer of diacetylene, cyclopropenylidene (:C=C₂H₂), are predicted. Several of the vibrational frequencies appear to have IR intensities strong enough for detection. Moreover, cyclopropenylidene has a large dipole moment, raising the hope that experimental and astronomical investigations will soon meet with success.

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Communications to the Editor

Palladium-Catalyzed Tandem Cyclization of 4,6- and 5,7-Diene Amides. A New Route toward the Pyrrolizidine and Indolizidine Alkaloids

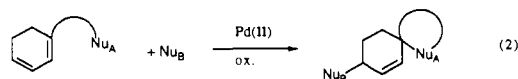
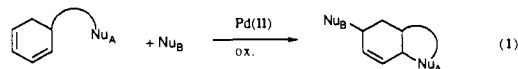
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A few years ago we developed several palladium-catalyzed 1,4-oxidations of conjugated dienes which allow the regio- and stereoselective addition of nucleophiles to the 1- and 4-positions of the 1,3-diene.^{1,2} These reactions, which proceed via (π -al-

lyl)palladium intermediates, were recently extended to intramolecular variants which give access to a number of heterocyclic systems (eqs 1 and 2).^{3,4}



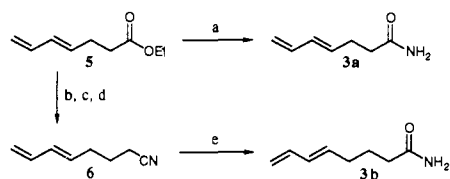
A further extension of the intramolecular reaction would be to use a nucleophile with the ability of making a 2-fold attack

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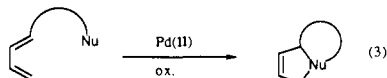
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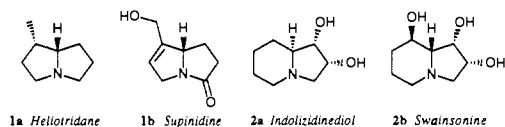
Scheme I^a

^a (a) NH₃, NaCN, MeOH, 85%; (b) DIBAL-H, CH₂Cl₂, 95%; (c) MsCl, Et₃N, THF, 96%; (d) NaCN, THF/DMSO, 95%; (e) KOH, *t*-BuOH, 67%.

and direct it to the 1- and 4-positions of the 1,3-diene. This would lead to a bicyclic system and would constitute a synthetically useful formal [4 + 1] intramolecular cycloaddition (eq 3). In this communication, we report results on palladium-catalyzed cyclization of diene amides to pyrrolizidine and indolizidine systems on the basis of this approach.



In the approach according to eq 3, primary amides were chosen as nucleophiles. By varying the length of the tether between the conjugated diene and the amide it would be possible to produce either 5,5- or 5,6-bicyclic systems. These structural units are of great interest since they are found in the naturally occurring pyrrolizidine (1) and indolizidine (2) alkaloids. Recently, considerable effort⁵ has been directed toward the synthesis of these compounds because of their interesting pharmacological properties⁶ (cytotoxic, antimetabolic immunostimulatory, and anticancer). However, in the great majority of recently published methods, the bicyclic compounds are synthesized in two separate operations. Only a few of the papers⁷ describe syntheses based on the more efficient strategy in which both rings are constructed in the same step.



The syntheses of the two diene amides, 4,6-heptadienoic acid amide (3a)⁸ and 5,7-octadienoic acid amide (3b) used as substrates in the palladium-catalyzed tandem cyclization are outlined in Scheme I. The synthesis starts with ethyl 4,6-heptadienoate, which is readily available from a Johnson-Claisen rearrangement

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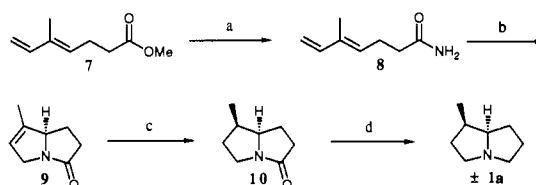
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Table I. Effect of Various Oxidants on the Cyclization of 3a into Pyrrolizidinone 4a^a

oxidant	solvent	temp/°C	time/h	% yield ^b
1,4-benzoquinone	AcOH	20	24	0
LiNO ₃	AcOH	20	24	3
isoamyl nitrite	AcOH	20	24	5
urea hydroperoxide	AcOH	20	24	7
CuCl ₂	AcOH	20	24	28
CuCl ₂	THF	20	24	35
CuCl ₂ /O ₂ ^c	THF	20	24	54
CuCl ₂ /O ₂ ^c	THF	60	24	90

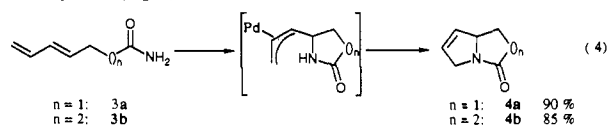
^a The reaction was performed on a 1-mmol scale using 0.1 mmol of Pd(OAc)₂ (10 mol %) and 2 mmol of the oxidant. ^b Entries 4–8 refer to isolated yield after flash chromatography. ^c The reaction was performed under an atmospheric pressure of O₂ using 10 mol % of Pd(OAc)₂ and 2 equiv of CuCl₂.

Scheme II^a

^a (a) NH₃, NaCN, MeOH, 75%; (b) Pd(OAc)₂, CuCl₂/O₂, THF, 60 °C, 85%; (c) PtO₂, H₂, EtOH, 95%; (d) LiAlH₄, ether, 89%.

of divinylcarbinol and triethyl orthoacetate.⁹ Subsequent cyanide-catalyzed aminolysis¹⁰ afforded the diene amide 3a in good yield. The one-carbon elongation of 5 was performed via reduction, mesylation, and nucleophilic displacement with sodium cyanide in DMSO to give 6¹¹ in 87% overall yield from 5. Hydrolysis of 6 with KOH in *t*-BuOH¹² afforded diene amide 3b.

Preliminary attempts to cyclize 3a with Pd(OAc)₂ using 1,4-benzoquinone as a reoxidant for palladium(0) resulted in the exclusive formation of the Diels–Alder adduct between the diene and 1,4-benzoquinone. To circumvent this undesired reaction, several other oxidants were tried (Table I), and the best results were obtained using a system consisting of CuCl₂/O₂ in tetrahydrofuran (THF) at 60 °C.¹³ With the latter reaction conditions, pyrrolizidinone 4a was obtained in 90% isolated yield. Application of the same conditions (Pd(OAc)₂-CuCl₂/O₂) to diene amide 3b resulted in the formation of the expected indolizidinone 4b in 85% isolated yield (eq 4).¹⁴



To further demonstrate the synthetic utility of the reaction, a short synthesis of (±)-heliotridane was carried out (Scheme II). The synthesis starts with the diene ester 7,¹⁵ which was converted into the amide in the same manner as described for 3a. Palladium-catalyzed cyclization of 8 with CuCl₂/O₂ as the oxidant afforded the pyrrolizidinone 9¹⁶ in 85% isolated yield. Subsequent

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hydrogenation of the double bond with PtO₂/H₂ takes place exclusively from the sterically least hindered side and gave the *cis*-pyrrolizidinone **10**.¹⁶ Reduction of **10** with LiAlH₄ afforded (\pm)-heliotridane (**1a**) in 54% overall yield from **7**. The preparation of pyrrolizidinone **9** also constitutes a formal total synthesis of (\pm)-supinidine (**1b**) since **9** has previously been converted into **1b**.¹⁷

Acknowledgment. Financial support from the Swedish Natural Science Research Council and the Swedish Board of Technical Development is gratefully acknowledged.

Supplementary Material Available: Description of general procedure for the palladium-catalyzed tandem cyclization reaction and listings of spectral data for **3b**, **4a,b**, and **8** (2 pages). Ordering information is given on any current masthead page.

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Ab Initio Calculations of the Singlet-Triplet Energy Difference in Phenylnitrene

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Depending on the conditions under which phenylnitrene (PhN) is generated, chemistry can be observed from either the singlet or the triplet state.¹ EPR studies by Wasserman and co-workers established that the triplet is the ground state.² Photodetachment measurements of phenylnitrene radical anion were interpreted by Drzagic and Brauman in terms of energy differences of 4.3 and 8.8 kcal/mol between the triplet and the two low-lying singlet states.³ These values, when compared to the energy difference of 36.0 kcal/mol measured between the ³ Σ^- ground state and the degenerate ¹ Δ state of HN,⁴ indicate a tremendous stabilization of both singlet states, relative to the triplet, by the phenyl group in PhN.

In order to understand how a phenyl substituent exerts such a large stabilizing effect on both singlet states, we have performed ab initio MCSCF and CI calculations on PhN. Our calculations find that only one of the two degenerate singlet states of HN is significantly stabilized, relative to the triplet, by the phenyl group in PhN. Moreover, the selective stabilization of this singlet is computed to be considerably less than the 32 kcal/mol indicated by the original interpretation of the radical anion photodetachment spectrum.³

The geometries of the ³A₂, ¹A₂, and ¹A₁ states of PhN were optimized with the 3-21G basis set,⁵ using an MCSCF wave function that included all configurations in which the six benzene π electrons and the two, highest energy, nonbonding nitrogen electrons were distributed among seven π orbitals and the σ -p orbital that is largely localized on nitrogen.⁶ The optimized C-C

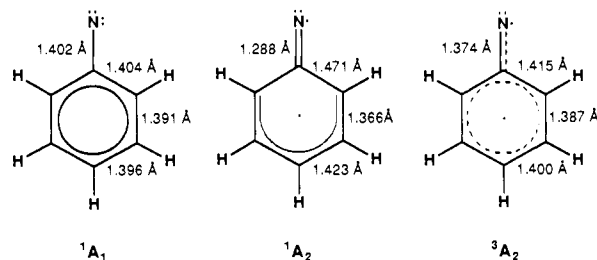


Figure 1. (8/8) MCSCF/3-21G bond lengths in the three lowest states of phenylnitrene.

Table I. Triplet Energies (hartrees) and Singlet-Triplet Energy Differences (kcal/mol) for PhN at (8/8) MCSCF/3-21G Optimized Geometries and for HN at ROHF/3-21G Optimized Geometries

state	(8/8) MCSCF/3-21G	(8/8) CI/6-31G*	π -SDCI/6-31G*	σ -S, π -SDCI/6-31G*
³ A ₂	-283.0106	-284.5734	-284.6070	-284.7959
¹ A ₂	21.5	17.3	19.5	18.3
¹ A ₁	43.3	39.0	39.8	38.7
³ Σ^-	-54.6550 ^a	-54.9517 ^a		-55.0778 ^b
¹ Δ	44.6	43.2		42.7

^a ROHF calculation on HN. ^b SDCI calculation on HN.

bond lengths in each state are shown in Figure 1.⁷ Vibrational analyses showed the optimized geometries to be minima.⁸

Using the 6-31G* basis set,⁹ 8-electron/8-orbital full CI calculations¹⁰ were performed with K orbitals¹¹ at the 3-21G optimized geometries. The (8/8) MCSCF and CI energies with both basis sets are given in Table I. In order to assess the effect of additional configurations containing all the virtual π orbitals, π -SDCI calculations were performed, using one reference configuration for the two A₂ states and two for ¹A₁.¹⁰ Correlation between σ and π electrons was also provided by addition of all single σ excitations (σ -S, π -SDCI). The CI results are also given in Table I. For comparison, the results of comparable calculations on HN are also given in Table I.¹²

The results contained in Table I clearly show that the phenyl group provides the most stabilization for ¹A₂, the state in which one nonbonding nitrogen electron occupies a σ -p orbital and another occupies a π orbital. On going from HN to PhN, this singlet state is stabilized by about 25 kcal/mol, relative to the triplet ground state, resulting in a predicted energy difference between ¹A₂ and ³A₂ in PhN of 18.3 kcal/mol at the σ -S, π -SDCI level. In contrast, ¹A₁, which consists of two dominant configurations in which the σ -p orbital is either doubly occupied or empty,¹³ is stabilized, relative to the triplet, by only about 4 kcal/mol on going from HN to PhN.

The origin of the selective stabilization of ¹A₂ is indicated by the C-C bond lengths shown in Figure 1. Unlike the case in either ³A₂ or ¹A₁, in ¹A₂ there is a strong π bond formed between nitrogen and the phenyl group; and an open-shell π electron, which is localized on nitrogen in HN, is highly delocalized into the phenyl

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