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Conformational Effects on the Excited State 1,2-Hydrogen Migration in Alkyldiazomethanes

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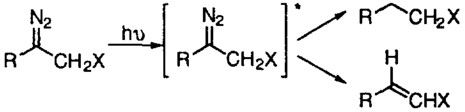
Abstract: Excited state rearrangements of alkyldiazo compounds are well-known. In particular, 1,2-hydrogen migrations to give carbene products are common. In this communication we provide evidence showing the migration in the diazo excited state is dependent upon the dihedral angle formed between the migrating hydrogen and the diazo carbon.

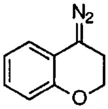
The involvement of the excited state in diazo compounds and diazirines has recently been implicated in many reactions previously thought to proceed by a carbene intermediate.[1] In particular, the recent efforts of Platz and co-workers have extensively documented the effects of bond strength on the excited state migration of hydrogen concurrent with nitrogen loss in arylalkyldiazo[2] compounds (i.e., Scheme 1) and alkyldiazirines.[3]

Scheme 1



These workers have found that the amount of excited state migration linearly tracks the α C-H bond strength of model systems. Inspired by their work on this rearrangement, and work showing a relationship between the rate of migration in alkylcarbenes as a function of the dihedral angle between the empty p-orbital of a singlet carbene and the migrating hydrogen,[4] we decided to study conformational effects on the excited state 1,2-H rearrangement.[5] Herein, we report evidence that the rate of hydrogen migration in the excited state is dependent on the dihedral angle between the α C-H bond and the diazo group in alkyldiazo precursors.

Laser flash photolysis experiments utilizing the pyridine-ylide probe technique[6] at saturating concentrations of pyridine (A_y^{Sat}) reveals diazo compound **1** to have the highest yield of ylide (Table 1),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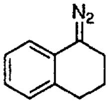
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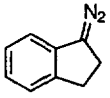
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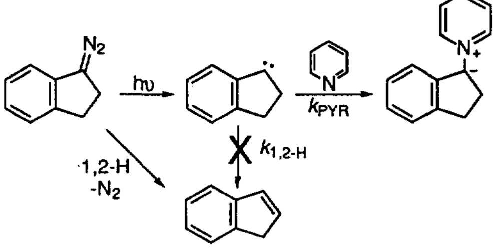
with **2** having 10% less and **3** yielding nearly 50% less. At these concentrations of pyridine, every carbene generated within the laser pulse is captured by pyridine (Scheme 2). Thus, any differences in yield must result from formation of olefin by way of the excited state migration, and we can conclude that twice as much carbene is generated from **1** (and 36% from **2**) than from **3**. Product studies confirm these results (Table 1).[7] When **3** is photolyzed in a static reactor at 300 nm in methanol, more than twice as much olefin is formed than for diazo compounds **1** or **2**. Since neat methanol is 24.7 M and the reaction of alkylcarbenes with methanol is quite rapid

Scheme 2



to form methyl ethers,[8] we are confident that in this experiment every carbene produced during photolysis has been trapped by methanol. Any olefin produced must therefore result from the diazo excited state. Assuming

Table 1. Yields of Pyridine Ylides[9] and Methyl Ethers Derived from Diazo Compounds **1-3** as a Function of the Orientation of the Migrating Hydrogen to the Diazo Group.

Diazo Compound	Dihedral Angles[10]	A_y^{Sat}	Relative Intensity (Carbene, %Yield)	% Ether[a] (Carbene, %Yield)[7]
1	$H_a = 96°, H_e = 24°$	181	100	100[b]
2	$H_a = 92°, H_e = 26°$	161	89	65
3	$H_a = 61°, H_e = 60°$	96	53	38

[a] The ether/olefin ratio was computed using the relative GC responses of the compounds, as identified by co-injection with known compounds or from mass spectral data.

[b] No olefin was formed during photolysis in methanol.

the C-H bond strengths are similar in each diazo compound[2,3] and that the quantum yield of excited state diazo compound from photolysis of each precursor is similar, we conclude that nearly twice as much excited state migration results from **3** as from **1** or **2**.

These results are significant when one examines the geometries of each of the diazo compounds used in this study (Figure 1).[10] Both **1** and **2** have larger dihedral angles between the axial α hydrogen and the

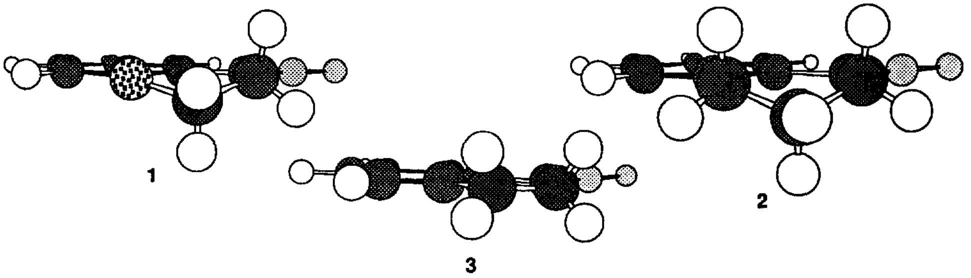


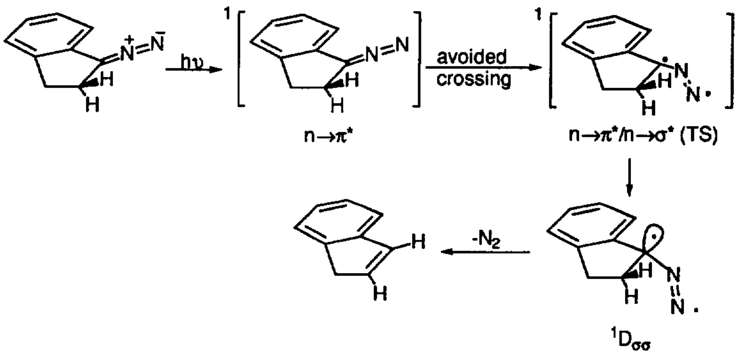
Figure 1. Calculated structures (RHF/6-31g*) of ground state diazo compounds **1-3**; the view shown is along the CH_2-CN_2 bond axis showing the relationship between the diazo group and the α hydrogens.[10]

plane formed by the diazo group and the α-carbons than does **3**, corresponding to more orbital overlap with the p-orbitals of the diazo group. We initially expected **1** and **2** to have *more* migration from the excited state than **3**, in analogy to the ground state carbene migration where better overlap between the migrating hydrogen and the empty p-orbital on the singlet carbene correlates to a more facile migration.[4] However, this trend is not observed. Surprisingly, the diazo compound with *smaller* dihedral angle results in formation of the *greater* amount of rearranged product.

Examination of the theoretical studies by Olivucci and Robb[11] provides a ready explanation for these seemingly contradictory results. MCSCF calculations[11] on the excited state energy surface of diazirine/diazo photolysis indicate the lowest excited state minimum on the energy surface to be an $n \rightarrow \pi^*$ state. From this state the excited compound follows one of two paths. The first path passes through a transition state ($n \rightarrow \pi^*/n \rightarrow \sigma^*$) toward a conical intersection resembling a diradicaloid (designated as $D_{\sigma,\pi}$) having a planar geometry, which is 66 kcal/mol below the $n \rightarrow \pi^*$ state. The $D_{\sigma,\pi}$ state can either lose N_2 and form the carbene, or return to the GS. The second path passes through the transition state and then a second intersection ($D_{\sigma,\sigma}$) which is also a diradicaloid, but has a pyramidalized geometry at the diazo carbon and is ~42 kcal/mol below the $n \rightarrow \pi^*$ state.

We believe the diazo compound (like the diazirine) partitions between these two pathways and that the $D_{\sigma,\sigma}$ state is responsible for excited state migration. The pyramidalized geometry enables the migrating hydrogen to achieve favorable overlap with the singly filled orbital of the carbon in the excited state. The reaction then proceeds as per a 1,2-hydrogen shift in a biradical (Scheme 3), with the driving force being the thermodynamically favored loss of N_2 and the formation of a carbon-carbon double bond. Thus, the diazo compound having the greatest amount of overlap in the excited state[12] is not the same one that would have large overlap in the ground state. In other words, because of pyramidalization at the diazo carbon in the excited state, one of the hydrogens in **3** becomes better aligned *in the excited state* and therefore results in a higher yield of olefin than is found for diazo compounds **1** or **2**. We are currently performing MCSCF calculations to probe the exact nature of the excited state migration energy surface.

Scheme 3



In conclusion we find that the 1,2-H migration from an alkyldiazomethane is not only dependent upon the α C-H bond strength, but also upon the dihedral angle the migrating hydrogen orbital makes with the singly occupied orbital in the excited state of the diazo compound.

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5. Nickon *et al.*[4i] have found that thermal generation of brexanylidene leads to a 138:1 ratio of exo/endo hydrogen migration, while photochemical generation of the carbene was found to yield a 4:1 ratio. Our data indicates the excited state migration may be responsible for the change in selectivity in the photochemical reaction. The endo hydrogen, which in the ground state carbene is not well aligned, becomes better aligned upon photoexcitation and presumably then undergoes a more favorable migration.

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7. Product studies were performed by photolyzing the appropriate diazo compound (A_{300nm} ~1.0) in neat methanol at 25°C; the only products from these photolysis were the corresponding olefins and methyl ethers formed from O-H insertion which were identified in a GC/MS by co-injection with known compounds or by mass spectral data.

8. Platz *et al.* have reported $k_{MeOH} = 1\text{-}2 \times 10^9$ $M^{-1}s^{-1}$ for several alkylarylcarbenes (ref. 2).

9. Solutions for use in LFP experiments were prepared by diluting the diazo compounds **1-3** to within ±0.001 absorbance units at 308 nm in acetonitrile and saturating concentrations of pyridine (typically >2.5 mol/L). These solutions were then flashed five times, with the absorbance at λ_{max} averaged and reported (A_y^{Sat}). This process was repeated for each diazo compound three separate times.

10. Diazo geometries were optimized on a Silicon Graphics Indigo2 workstation at the *ab initio* level of theory (RHF/6-31G*) using the SPARTAN computational package (SPARTAN version 4.0, Wavefunction, Inc.; 18401 Von Karman Ave., #370; Irvine, CA 92715). Dihedral angles are quoted as the difference between 90° and the angle between the α hydrogen and the plane formed by the diazo carbon and the two adjacent α carbons.

11. Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M.A.; Wilsey, S. *J. Am. Chem. Soc.* **1994**, *116*, 2064.

12. Calculations of the excited state geometries of diazo compounds and reaction coordinate surface are currently in progress, Ichimura, A.S.; Modarelli, D.A.

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