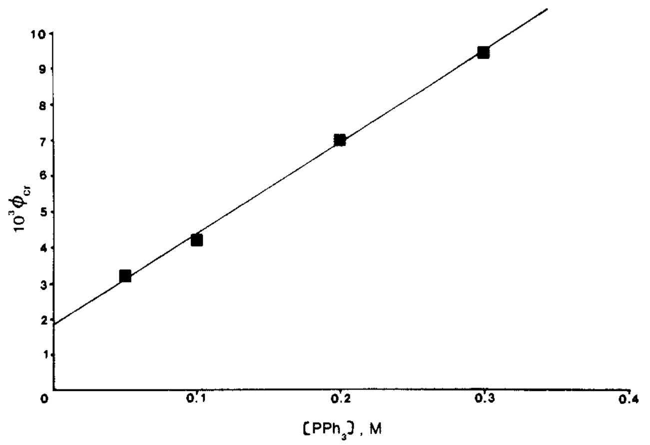

Figure 2. Plot of ϕ_{cr} vs PPh$_3$ ligand concentration for the 458-nm photochemical conversion of 2.5×10^{-3} M $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ to $(\eta^5\text{-}C_5H_5)Rh(CO)PPh_3$ in deoxygenated decalin solution at 10 °C. Each ϕ_{cr} value represents a mean of at least three readings; estimated uncertainties on ϕ_{cr} are within ±5%.

Spectral changes recorded during a typical photolysis experiment are depicted in Figure 1. These FTIR absorption changes are entirely in accordance with simple ligand photosubstitution (eq 1), which is the same as the thermal reaction characterized by Basolo.[7a-c] The photochemistry here appears to be excep-

$$(\eta^5\text{-}C_5H_5)Rh(CO)_2 \xrightarrow[PPh_3]{h\nu} (\eta^5\text{-}C_5H_5)Rh(CO)PPh_3 + CO \quad (1)$$

tionally clean as demonstrated by the retention of sharp isosbestic points throughout the reaction to completion; in addition, the $(\eta^5\text{-}C_5H_5)Rh(CO)PPh_3$ photoproduct is both thermally and photochemically stable under the conditions of the experiment. Moreover, there was no indication that other complexes are produced, such as the bridged $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ species formed during excitations of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in the absence of scavenging ligands.[8] Photochemical quantum efficiencies (ϕ_{cr}) were calculated by monitoring the disappearance of the reactant's ν(CO) bands (over at least 60% of reaction) and application of eq 2, which accounts for the changing degree of light absorption and inner-filter effects. Here, [R] is the concentration of the $(\eta^5\text{-}C_5H_5)$-

$$d[R]/dt = -\phi_{cr}I_0(1 - 10^{-D})\epsilon_R b[R]/D \quad (2)$$

$Rh(CO)_2$ complex at varying photolysis time t, I_0 is the incident light intensity per unit solution volume, b is the cell path length, D and ϵ_R are the optical density of the solution and molar absorptivity of the reactant complex at the irradiation wavelength, respectively, and ϕ_{cr} is the reaction quantum efficiency. Plots of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ versus $\int_{t_0}^{t_i}[(1 - 10^{-D})/D]dt$, where A_0, A_t, and A_∞ are the infrared absorbance readings of the reactant's ν(CO) bands throughout photolysis, were observed to yield straight lines of slope α to reaction completion, where $\alpha = -\phi_{cr}\epsilon_R I_0 b$. In accordance with these photochemical conversions being complete and uncomplicated by side or subsequent reactions, the plots showed linearity when $A_\infty = 0$ and yielded coincident α values at both ν(CO) bands. Moreover, α values obtained by monitoring the increasing ν(CO) absorbance due to photoproduct formation were concordant. Determined ϕ_{cr} values were corrected for the small contribution (typically 4–8%) from the thermal process. Quantum efficiencies have been obtained for various concentrations of PPh$_3$ and are shown in Figure 2. Significantly, when the solutions were prior saturated with CO, there was no change in the observed spectral progressions or the measured quantum efficiency results.[9]

The observed linear dependence of ϕ_{cr} with [PPh$_3$] and lack of an observed effect with added CO clearly implicate that the photosubstitutional chemistry of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ in PPh$_3$ solutions proceeds via an associative process. This knowledge is pertinent for developing a further understanding of reaction pathways in C–H activation chemistry. Although the current results do not yield specific information on the nature of the associative mechanism, a reasonable rationale is that the excited $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ complex undergoes a $\eta^5 \rightarrow \eta^3$ ring slippage which then reacts with the phosphine ligand, analogous to the thermal process[7a-c] and to a photochemical mechanism suggested for hydrocarbon activation by $(\eta^5\text{-}C_5H_5)Ir(CO)_2$.[4] Alternatively, a $\eta^5 \rightarrow \eta^1$ ring slippage or another type of complex deformation (such as a bending of the Rh–CO bonds) could be involved. It is also possible that there could be a direct reaction of the photoexcited complex with the incoming nucleophile, although our attempts to record luminescence from $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ have, to date, been unsuccessful (even at 77 K), implying that the excited state is very short-lived.[10] Finally, more complicated mechanisms such as bimolecular reaction of PPh$_3$ with initially photoproduced $(\eta^5\text{-}C_5H_5)Rh(CO)(R)H$ cannot be excluded at this time.

Presently, we are investigating whether associative photochemical mechanisms are more widespread in organometallic systems undergoing intermolecular C–H bond activation.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society and the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy (Grant DE-FG02-89ER14039), for support of this research. We also thank Prof. Arthur W. Adamson for useful discussions.

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Infrared Spectrum of Triplet Phenylnitrene. On the Origin of Didehydroazepine in Low-Temperature Matrices

James C. Hayes and Robert S. Sheridan*,[1]

Department of Chemistry, University of Nevada
Reno, Nevada 89557

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Despite years of scrutiny,[2] the complete picture of the photochemistry of phenyl azide (**1**) has only recently begun to unfold. Beyond offering mechanistic novelty, this compound is an archetype for many photoaffinity labeling approaches[2,3] and photoresist[2,4] technologies. Early ESR investigations revealed that triplet phenylnitrene (**2**) is formed on irradiation of **1** in low-temperature glasses,[5] and UV/vis spectra were consequently attributed to this intermediate.[6] In a landmark observation in 1978, however, Chapman and LeRoux reported that photolysis of **1** in argon matrices at 10 K gave 1-aza-1,2,4,6-cycloheptatetraene (**3**), which was characterized by IR.[7] This unusual,

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(1) Fellow of the Alfred P. Sloan Foundation, 1986–1990.

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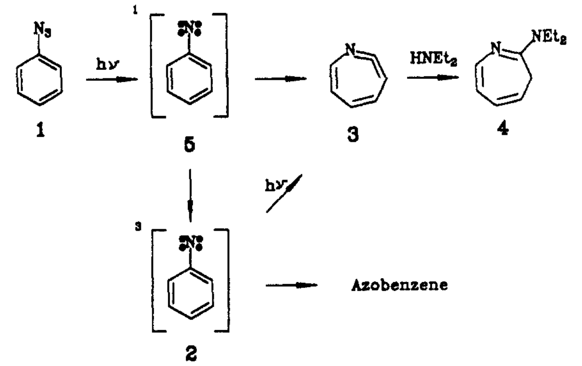
highly strained intermediate accounted for solution trapping results, giving, for example, 2-(diethylamino)-3*H*-azepine (**4**) in the presence of diethylamine.[8] These matrix results have been confirmed by others.[9] The didehydroazepine **3** has also been shown to be a major photoproduct of **1** in solution by both IR and UV spectroscopy, in laser flash photolysis experiments by Schuster and co-workers.[10] Recently, however, Platz and co-workers[11] have presented elegant spectroscopic and trapping studies indicating that irradiation of **1** at 77 K in organic glasses produces mainly triplet phenylnitrene (**2**). They have proposed singlet phenylnitrene (**5**) as the primary photoproduct of **1**, which undergoes either thermally activated ring expansion to give **3** (favored at room temperature) or intersystem crossing to give **2** (favored at low temperatures).



Although the results of Platz and co-workers[11] nicely explain most of the known photochemistry of **1**, they raise another critical question: what is the difference between their low-temperature results, giving **2**, and Chapman and LeRoux's, giving **3**? These authors have proposed two possible explanations.[11] First, inert gas matrices might not cool an initially formed vibrationally excited **5** as rapidly as organic matrices. Hence, in argon, intersystem crossing to **2** might not compete with chemically activated ring expansion to **3**. Such matrix effects have precedent.[12] Second, **2** is photolabile. Trapping experiments[11] suggest that **3** is a photoproduct of **2**, and it is possible that previous workers[7,9] were observing the product of secondary photolysis of the nitrene. We now describe results supporting the latter explanation. Moreover, we report the first measurement of the IR spectrum of phenylnitrene (**2**).

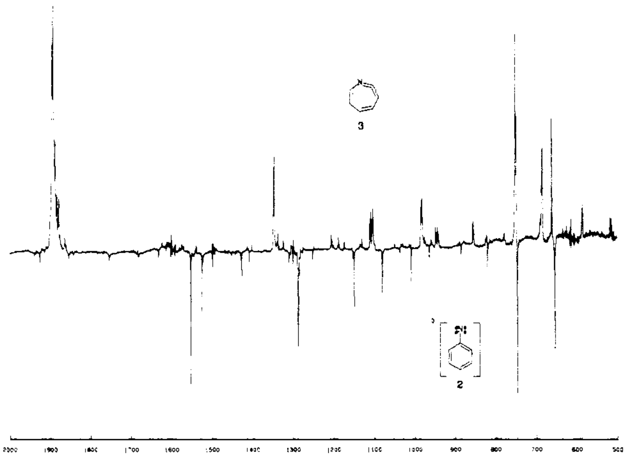


Figure 1. Difference spectrum obtained by subtracting IR spectra of 12 K Ar matrix containing phenylnitrene (3) before and after irradiation at >450 nm. The matrix was initially prepared by irradiation of **1** (1:800 in Ar, 334 nm) for 40 h. The small amount of **1** also formed on irradiation of **2** has been subtracted out of the spectrum. Positive peaks are assigned to didehydroazepine **3**, and negative peaks to phenylnitrene (**2**).

Irradiation[13] of N_2 or Ar matrix isolated azide **1** (1:800, 12 K) at 334 nm produced only a small amount of didehydroazepine **3**, judged by the low intensity of the characteristic[7,9] IR band at 1895 cm^{-1}. Instead, mainly a different species was observed whose IR we assign to triplet phenylnitrene (**2**).[15] The distinctive absorptions[11b] of **2** appeared in the UV/vis spectrum of the matrix simultaneously with the IR spectrum. Subsequent irradiation of the matrix at 485 nm (or with broad-band irradiation >450 nm) concurrently destroyed the IR and the UV/vis absorptions of **2** and considerably increased the IR and UV spectra of **3** (Figure 1). Consistent with its UV/vis spectrum, **2** was stable to irradiation at wavelengths >500 nm. Interestingly, the photoreaction of **2** was reversible. Irradiation at 334 nm of the matrix containing mainly didehydroazepine **3** (λ_{max} 330 nm) produced a decrease in the IR and UV absorptions of **3** and reappearance of those of **2**. (IR bands of phenyl azide were also observed to grow a small amount on irradiation of **2** or **3**.)

Trapping experiments gave additional support to the assignment of the IR spectrum to **2**. A 2-methylbutane (2-MB) matrix containing **1** (ca. 1:20, 45 K) was irradiated at 334 nm until most of the phenyl azide had been converted to nitrene **2** (by IR). Warming the matrix to 80 K caused the disappearance of the bands of **2** and the appearance of IR absorptions of dimerization product azobenzene (confirmed by comparison to authentic material).

We also searched for matrix effects on the initial ratio of **2** to **3**. Ar, N_2, and 2-MB matrices containing azide **1** were irradiated for very short periods of time (5 s up to 30 m, depending on the amount of starting material) and were interrogated with a large number of FTIR scans to increase sensitivity to a maximum. Under all conditions, even over a 10^2-fold increase in concentration of **2**, the ratio of **2** to **3** remained approximately constant. This ratio was estimated to be ca. 4:1 by measurement of the increase of the IR absorptions of **3** on photodestruction of **2**.

The above trapping results confirm the previous assignments[11b] of the UV/vis spectrum of **2** and confirm that didehydroazepine **3** is formed on photolysis of **2**.[11] Finally, they resolve the differences between the earlier work reporting **3** as the major photoproduct of phenyl azide in Ar matrices[7,9] and the more recent investigations favoring **2** in organic glasses.[11] *Triplet phenylnitrene (**2**) is the major primary photoproduct of **1** at low temperatures in all matrices.* We estimate (vide supra) that **1** gives 80% **2** and 20% **3** under these conditions. The discrepancy between our matrix IR results and those of previous workers[7,9] can plainly be traced to differing irradiation wavelengths. The UV/vis spectrum of nitrene **2** has a minimum at ca. 330 nm, and hence irradiation of starting material at 334 nm minimizes secondary photolysis of **2**. On the other hand, the broad-band irradiation conditions of earlier investigators[7,9] (>210 nm) would readily convert **2** to **3**. Close scrutiny of the previously published IR spectrum[7] of matrix-isolated **3**, however, reveals the presence of trace amounts of **2**.

A final issue to be resolved is the origin of the minor amounts of **3** observed in all of our photolyses, under conditions designed

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(13) The apparatus for the low-temperature matrix isolation experiments has been previously described.[14] Irradiations were performed with either a PTI 100-W high-pressure Hg lamp/monochromator apparatus or a 300-W high-pressure Xe lamp with appropriate cut-off filters for broad-band irradiations. FTIR spectra were obtained on a Perkin-Elmer 1800 spectrometer, and UV/vis spectra were obtained on a Perkin-Elmer Lambda-4 spectrometer.

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(15) Major IR bands for phenylnitrene (**2**) at 12 K in Ar (relative intensity): 1552 (0.68), 1524 (0.33), 1497 (0.09), 1426 (0.13), 1408 (0.06), 1309 (0.05), 1299 (0.07), 1287 (0.47), 1286 (0.49), 1250 (0.05), 1148 (0.32), 1079 (0.22), 1008 (0.17), 964 (0.06), 885 (0.05), 820 (0.12), 746 (1.00), and 654 (0.55) cm^{-1}.

to minimize irradiation of **2**. From the shortest irradiation times, where the minute concentrations of photoproducts are at the limit of our detection, to the point where much of the starting azide is destroyed, the ratio of **2** to **3** remains constant. This is most consistent with **3** also being a primary photoproduct of **1**. The absence of a matrix effect[12] on the product ratio weakens, but does not eliminate, the possibility that **3** arises from rearrangement of vibrationally hot singlet nitrene **5**. An alternative is that an electronically excited state of **5** (or **2**) directly produces **3**. The facile photochemical conversion of the triplet nitrene **2** to **3** suggests that there may be a readily accessible excited state of the nitrene with a proclivity toward rearrangement.[16,17]

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High-Resolution ^{13}C Nuclear Magnetic Resonance Observations of Two Crystalline Model Compounds for Syndiotactic Polystyrene

M. A. Gomez,† B. Jasse,‡ M. H. Cozine,§ and A. E. Tonelli*

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

Received April 2, 1990

Recently synthesized[1,2] syndiotactic polystyrene (s-PS) has been observed[1-8] to crystallize into two distinct polymorphs. Melt crystallization produces form I crystals (T_m = 270 °C) with an X-ray diffraction fiber repeat of 5.1 Å, which is consistent with a planar-zigzag, all-trans chain conformation. Form II crystals, with an X-ray fiber repeat of 7.5 Å, are obtained by casting films from dilute solutions or by exposure of amorphous, melt-quenched films to certain organic solvent vapors. At ca. 190 °C, form II crystals are transformed into form I crystals via a solid-solid phase transition. The 7.5-Å fiber repeat found for the form II crystals is consistent with a 2_1-helical, ...*ttggttgg*... chain conformation, as was found previously[9] for syndiotactic polypropylene. High-resolution, solid-state ^{13}C NMR spectra[10] of forms I and II s-PS are consistent with the proposed ...*tttttttt*... and ...*ttggttgg*... chain conformations.

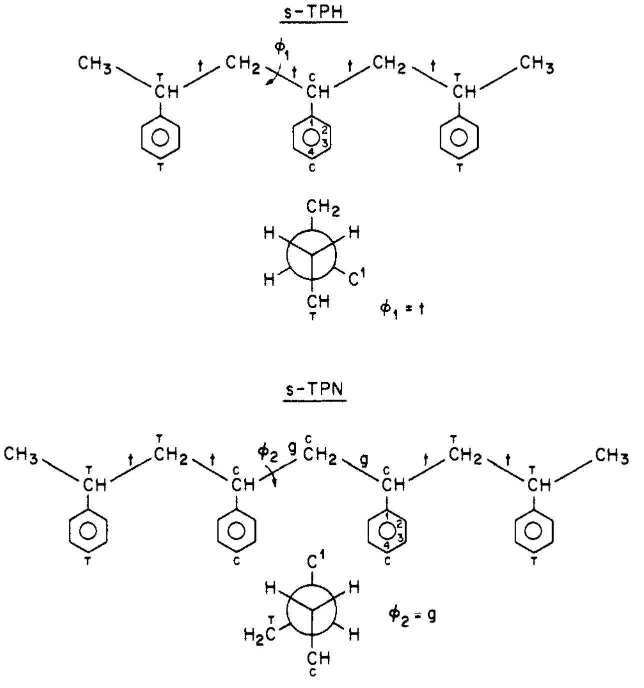

Figure 1. The molecular structure and labeling scheme for s-TPH and s-TPN. Below each structural drawing is a Newman projection illustrating a trans (s-TPH) or a gauche (s-TPN) backbone bond conformation.

Table I. Relative $\delta(^{13}C)$'s Expected for Crystalline s-TPH and s-TPN on the Basis of γ-Gauche Shielding Effects

Methylene Carbons[a]
$\delta^{C}_{CH_2}$(s-TPN) and δ_{CH_2}(s-TPH) should be downfield from $\delta^{T}_{CH_2}$(s-TPN) by $\gamma_{CH_2,CH} \approx 5$ ppm
Quaternary Aromatic Carbon[a]
$\delta^{C,T}_{C^1}$(s-TPN) and $\delta^{T}_{C^1}$(s-TPH) should be downfield from $\delta^{C}_{C^1}$(s-TPH) by $\gamma_{C^1,CH} \approx 2.5$ ppm

[a] See Figure 1 for labeling of carbons and Newman projections of s-TPH and s-TPN.

Well before the synthesis of s-PS, Jasse et al.[11,12] reported the X-ray-derived structure of the single crystals of the syndiotactic isomers of 2,4,6-triphenylheptane (s-TPH) and 2,4,6,8-tetraphenylnonane (s-TPN). s-TPH was found to crystallize in the planar-zigzag, all-trans, *tttt* conformation, while the *ttggtt* conformation was adopted by s-TPN in its crystals. In this communication we report the preliminary high-resolution, solid-state ^{13}C NMR spectra of both s-PS model compounds and compare their ^{13}C chemical shifts to those observed for forms I and II s-PS. The conformationally sensitive γ-gauche shielding effects[13] on ^{13}C chemical shifts [$\delta(^{13}C)$] are utilized to discuss the crystalline conformations of forms I and II s-PS by way of comparison to the ^{13}C NMR spectra observed for crystalline s-TPH and s-TPN.

The structures and labeling scheme used to describe s-TPH and s-TPN are presented in Figure 1 together with Newman projections along backbone bonds in the *t* and *g* conformations. On the basis of the demonstrated[13] sensitivity of ^{13}C chemical shifts

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[†] Permanent address: Instituto de Ciencia y Tecnologia de Polimeros, Calle Juan de la Cierva, 3, 28006, Madrid, Spain.

[‡] Address: Laboratoire de Physiochimie Structurale et Macromoleculaire, ESPCI, 10 rue Vauquelin, 75231, Paris, Cedex 05, France.

[§] Address: Robert Wood Johnson Pharmaceutical Research Institute, Rt. 202, P.O. Box 300, Raritan, NJ 08869.

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