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ABSOLUTE REACTIVITY OF SINGLET PENTAFLUOROPHENYLNITRENE WITH REPRESENTATIVE ALKENES

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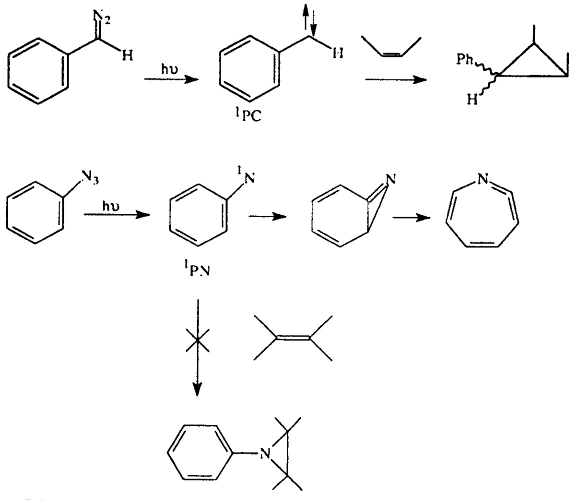
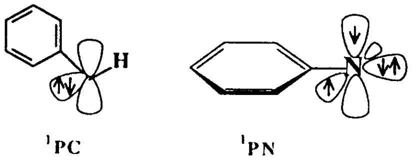
The relative reactivity of singlet pentafluorophenylnitrene with a standard set of alkenes was determined. The singlet nitrene is found to be most reactive towards electron-rich alkenes, as expected, but the selectivity spread is very small. In terms of its selectivity towards alkenes, singlet pentafluorophenylnitrene is analogous in its properties to singlet phenylcarbene.

INTRODUCTION

Cycloaddition reactions of carbenes with alkenes to form cyclopropanes are well known and are of synthetic utility.[1] The corresponding reactions of nitrenes, in contrast, are rare.[2] Whereas singlet phenylcarbene (PC) is readily trapped with alkenes,[3] singlet phenylnitrene (PN) is not.[4] The reaction of PC with alkenes is highly stereospecific.[1,3] Ring expansion of ^{1}PN at ambient temperature is far more rapid than its cycloaddition reactions with alkenes.[4]



The ease with which singlet carbenes in general and phenylcarbene in particular undergo concerted insertion and cycloaddition reactions is due to their closed-shell electron configuration.[5] This allows complexation of an empty p-orbital of ^{1}PC with a pair of electrons. Singlet phenylnitrene (^{1}PN) has an open-shell configuration, however, and consequently is less reactive than ^{1}PC.[6,7]



Abramovitch *et al.*[8a] extended the work of Banks and Sparkes[8b] and discovered that, unlike the parent system, polyfluorinated arylnitrenes will indeed add to alkenes. Our work revealed that fluorine substituents extend the singlet nitrene lifetime by raising the barrier to rearrangement[4,9–11] (Scheme 1), which allows bimolecular processes to compete effectively against the intramolecular rearrangement. These results were obtained using pyridine ylide **2** as a kinetic probe.

We have reported that 2,3-dimethylbut-2-ene [tetramethylethylene (TME)] can trap ^{1}PFPN in 49% isolated yield upon photolysis of azide **1**, to form the azirine **3**. No trace of allylic insertion product **4** was observed in this reaction, despite the fact that photolysis of **1** in cyclohexane produces adduct **5** in 22% isolated yield.[10]

Competitive trapping and laser flash photolysis experiments revealed that TME is about 100-fold better as a trapping agent than is cycloalkane.[10] The missing material balance in these reactions is polymeric tar formed by reaction of photogenerated intermediates with the azide precursor **1**.

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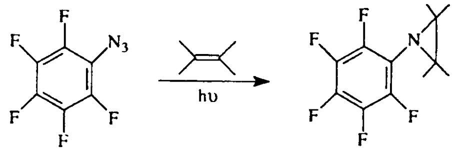

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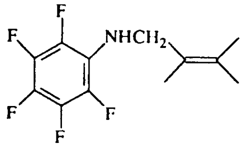

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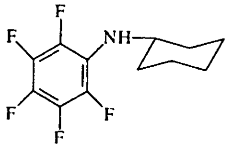

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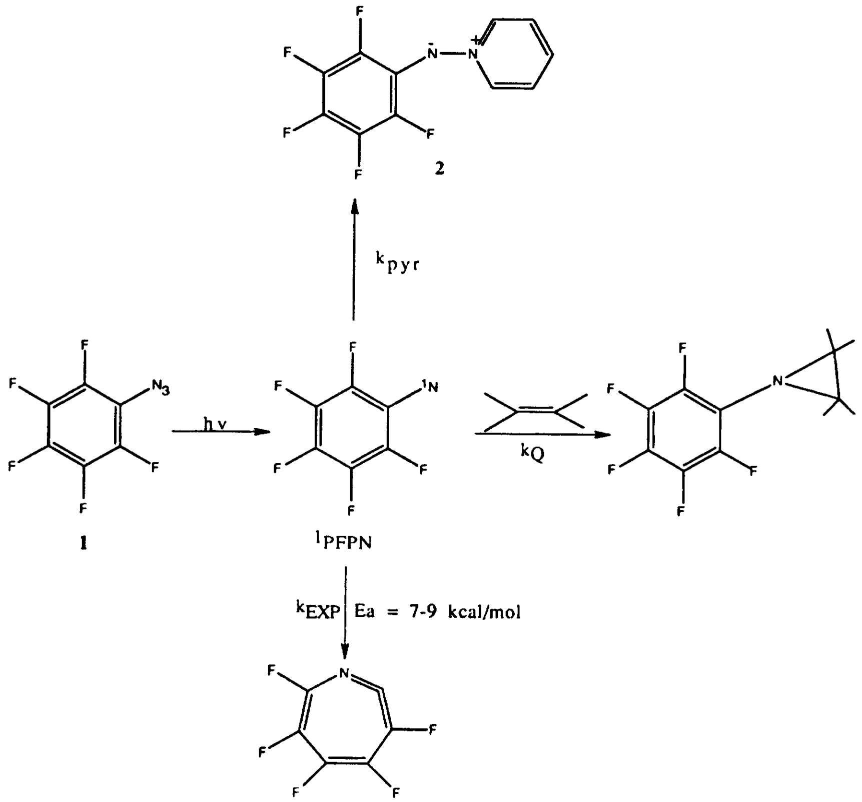
This study encouraged us to determine the absolute reactivity of singlet pentafluorophenylnitrene (^{1}PFPN) towards various alkene substrates. Here we report results of this type which provide an interesting contrast to the more thoroughly studied arylcarbenes.

RESULTS AND DISCUSSION

Laser flash photolysis (LFP) studies of pentafluorophenyl azide **1** have been reported.[9-11] LFP of **1** produces a nitrene which can be trapped with pyridine to form an isolable ylide, **2**, with $\lambda_{max} = 390$ nm (Scheme 1). It was not possible in that study to resolve the formation of ylide **2** by nanosecond spectroscopy because of the short lifetime of ^{1}PNPN (*ca* 20–40 ns) due to its rapid rate of rearrangement. However, it is possible to measure the relative yield, ϕ_y, of ylide. The yield of ylide is zero, of course, in the absence of pyridine, but increases steadily as the concentration of pyridine is raised. Above 0·6–0·7 M pyridine in CH_3CN or CH_2Cl_2 the yield of ylide is saturated, which corresponds to the trapping of every photogenerated nitrene produced in the laser pulse. However, the addition of a second nitrene quencher (Q) reduces the yield of ylide in accord with the equation[12]

$$\frac{\phi_y^0}{\phi_y} = \frac{k_Q[Q]}{k_{pyr}[\text{pyridine}]} \tag{1}$$



Scheme 1

where ϕ_y^0 is the yield of ylide in the pyridine saturation region and in the absence of alkene.[12] Thus, a plot of ϕ_y^0/ϕ_y versus [Q] should be linear at constant [pyridine]. Such a plot is given in Figure 1 with styrene as quencher in acetonitrile at 292 K. The slope of this plot is simply k_Q/k_{pyr}[pyridine]. Values of k_Q/k_{pyr} are listed in Table 1 as a function of alkene, solvent and temperature.[9] The value of k_{pyr} was at first[10] assumed to be $1 \times 10^9\ l\,mol^{-1}\,s^{-1}$. However, in later work[11] k_{pyr} was found to be much slower. Marcinek *et al.* determined that k_{pyr} is $3 \times 10^7\ l\,mol^{-1}\,s^{-1}$ for tetrafluoronitrene ester **6** in CH_2Cl_2 and Gritson *et al.* determined that $k_{pyr} = 6 \times 10^7\ l\,mol^{-1}\,s^{-1}$ for ^{1}PFPN in CH_2Cl_2 at 295K.[11] Thus, absolute rate constants for the trapping of ^{1}PFPN can be deduced for alkenes noting that k_{pyr} of ^{1}PFPN again is $6 \times 10^7\ l\,mol^{-1}\,s^{-1}$ in CH_2Cl_2 and assuming this value in CH_3CN.

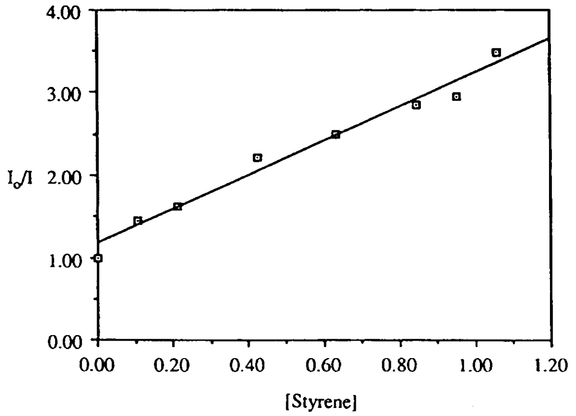
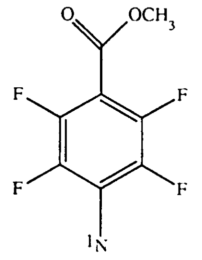


Figure 1. A Stern–Volmer plot of I_0/I versus styrene in CH_3CN at 292 K



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Inspection of Table 1 reveals that increasing alkylation of the alkene moiety raises its absolute reactivity towards ^{1}PFPN. However, this tendency is modest. Tetramethylethylene is only 4–5 times better a trap of ^{1}PFPN than is hex-1-ene. In terms of its selectivity spread, ^{1}PFPN closely resembles ^{1}PC.[3] The selectivity of these two species is much less than that of the halophenylcarbenes which have singlet ground states and show a spread of reactivity, with a similar set of alkenes, by about 100-fold.[13]

The solvent dependence of k_Q is not known for ^{1}PC but is small with halophenylcarbenes.[13] The solvent polarity has only a small effect on k_Q/k_{pyr} for ^{1}PFPN. As k_{pyr} is expected[10,14] to have little solvent dependence, the selectivity spread appears to be independent of solvent. The reactions of ^{1}PFPN appear to be slightly faster in the less polar solvent. This is reminiscent of the results obtained with halophenylcarbenes and alkenes.[13]

Finally, we note that the value of the k_Q/k_{pyr} with TME is independent of temperature between 253 and 308 K. Previously we have deduced that $E_a(\text{pyr}) \approx +1{\cdot}7\text{–}2{\cdot}0\ \text{kcal}\,\text{mol}^{-1}$ and $A_{pyr} = (6\text{–}7) \times 10^8\ l\,mol^{-1}\,s^{-1}$ ($\Delta S^* \approx -20$ e.u.)[9–12] for the reaction of singlet nitrene **6** and ^{1}PFPN with pyridine. Thus, the reaction of ^{1}PFPN with TME and with pyridine must have similar Arrhenius parameters and is dominated by the entropy term.

Table 1. Rate constants for reaction of ^{1}PFPN with alkenes

Quencher	Solvent	T (K)	k_Q/k_{pyr}[a]	k_Q ($l\,mol^{-1}\,s^{-1} \times 10^{-7}$)
Styrene	CH_3CN	292	2·1	12·6
Hex-1-ene	CH_3CN	292	0·5	3·0
Cyclohexene	CH_3CN	292	0·6	3·6
2-Methylbut-2-ene	CH_3CN	292	1·3	7·8
2,3-Dimethylbut-2-ene (TME)	CH_3CN	292	2·1	12·6
Styrene	CH_2Cl_2	292	6·3	37·8
Hex-1-ene	CH_2Cl_2	292	1·5	9·0
Cyclohexene	CH_2Cl_2	292	2·0	12·0
2-Methylbut-2-ene	CH_2Cl_2	292	2·6	15·6
2,3-Dimethylbut-2-ene (TME)	CH_2Cl_2	292	7·0	42·0
2,3-Dimethylbut-2-ene (TME)	CH_2Cl_2	253	7·1	—
2,3-Dimethylbut-2-ene (TME)	CH_2Cl_2	273	7·0	—
2,3-Dimethylbut-2-ene (TME)	CH_2Cl_2	308	7·1	—

[a] Assuming $k_{pyr} = 6 \times 10^7\ l^{-1}\,s^{-10}$ in CH_2Cl_2 and in CH_3CN at 292 K; see text and ref 11.

Unsurprisingly, ^{1}PFPN is found to be an electrophilic species with respect to alkenes but the selectivity spread is modest. The selectivity of ^{1}PFPN to tetramethylethylene/pyridine is 7·0 ± 0·1 and is invariant in CH_2Cl_2 between 253 and 308 K. Hence this selectivity difference must have an entropic origin. We postulate that the reaction of ^{1}PFPN (as per carbenes) with alkenes must have an early transition state. With electron-rich alkenes the transition state (T.S.) must be particularly loose (more positive ΔS^*) relative to a less electron rich alkene with a tighter, later T.S. (more negative ΔS^*).

CONCLUSION

The relative reactivity of singlet pentafluorophenylnitrene (^{1}PFPN) towards representative alkenes was determined. The nitrene reacts faster with more highly substituted alkenes but the selectivity is small. The selectivity of ^{1}PFPN resembles that of singlet phenylcarbene with alkenes. The selectivity of ^{1}PFPN towards alkenes varies only slightly with solvent polarity. The selectivity of ^{1}PFPN towards tetramethylethylene and pyridine does not vary with temperature in methylene chloride. Thus, as with many carbenes,[13] the reactions of ^{1}PFPN must have early transition states and the selectivity differences are due to entropic rather than enthalpic factors.

EXPERIMENTAL

The preparation of azide **1** has been described.[8–10] Alkenes were purified by passing them through a short column of neutral alumina immediately prior to use. The LFP system in use at Ohio State University and the protocols followed have been described elsewhere[9,11,15] and are resummarized.

Sample preparation was the same for all LFP studies. For kinetic studies, stock solutions of the photoabile nitrene precursors were prepared for each system of interest. The concentration of azides **1** in stock solutions was kept constant with an optical density at the selected excitation wavelength (e.g. 308 nm) of *ca* 1·0. Experiments were performed in multiple cells, typically 8–12 for each experiment. A fixed volume (0·5–1·0 ml) of stock solution was mixed with varying volumes of solvent, pyridine, such that the total volume (1·5–2·0 ml) of the sample, and thus the precursor concentration, remained constant. The samples were prepared by adding a fixed amount of stock solution to each of the cells followed by the addition of the quencher of interest and a constant volume of pyridine. Solvent was then added to each cell in order to maintain a constant volume of the sample throughout the experiment. The actual optical yield of the azide at the selected excitation wavelength was approximately 0·5. Samples were prepared by syringe transfer of the various solutions into quartz or Pyrex cells and were deoxygenated by bubbling with dry, oxygen free nitrogen for 5 min.

The LFP apparatus for the determination of kinetics consists of a Lambda Physik LPX-100 excimer laser (308 nm, 150 mJ, 17 ns pulse width). Each of the aforementioned samples was placed in the appropriate sample cell and fitted with a rubber septum. Sample cells were irradiated with excimer laser pulses that impinged on the sample at a right-angle to a 150 W xenon arc lamp fitted with an Oriel Aspherab beam columnator . The monitoring beam was focused on the slit of an Oriel monochromator, selected for the wavelength of interest, with both front and rear slits set at approximately 1 mm width. The detector was an IP 28 photomultiplier tube and the analog signals were digitized by a Tektronix 7912 A/D transient digitizer. The entire apparatus was controlled by Apple Macintosh ITx microcomputer.

Transient absorption spectra were obtained on an EG&G PARC 1460 optical multichannel analyser (OMA) fitted with an EG&G PARC 1304 pulse amplifier, an EG&G PARC 1024 UV detector and a Jarrell-Ash 1234 grating. The excitation sources used for these studies were the same as described above. The concentration of the azide was kept constant with an optical density at the selected excitation wavelength (e.g. 308 nm) of 1·0. Because of the large photochemical conversion of azide to product in each laser pulse, the samples were changed after every laser shot.

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