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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### $^{15}\text{N}$ , $^{31}\text{P}$ , and $^{13}\text{C}$ NMR Spectroscopy of N-Arylsulfonyl- and N-Arylcarbonyl-P,P,P-triphenylphospha- $\lambda$ -Azenes. Substituent Effects and Electronic Structure

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# **$^{15}\text{N}$ , $^{31}\text{P}$ , and $^{13}\text{C}$ NMR Spectroscopy of N-Arylsulfonyl- and N-Arylcarbonyl-P,P,P-triphenylphospha- $\lambda^5$ -Azenes. Substituent Effects and Electronic Structure**

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The  $^{15}\text{N}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$  NMR spectra of several series of phospha- $\lambda^5$ -azenes are reported. For the N-arylsulfonyl-P,P,P-triphenylphospha- $\lambda^5$ -azene series ( $\text{R}-\text{C}_6\text{H}_4-\text{SO}_2-\text{N}=\text{PPh}_3$ ), the  $^{31}\text{P}$  chemical shifts, various  $^{13}\text{C}$  chemical shifts and  $^1\text{J}_{\text{PN}}$  were observed to correlate linearly with the Hammett  $\sigma$  constants. Interestingly, the  $^{15}\text{N}$  chemical shifts did not correlate acceptably with any  $\sigma$  or with the Taft dual substituent parameter equation, and  $^1\text{J}_{\text{PC}}$  was invariant with substituent. For the N-arylcarbonyl-P,P,P-triphenylphospha- $\lambda^5$ -azene series ( $\text{R}-\text{C}_6\text{H}_4-\text{CO}-\text{N}=\text{PPh}_3$ ),  $\delta_{31\text{P}}$  and various  $\delta_{13\text{C}}$ 's were observed to linearly correlate with the  $\sigma$  constants, while  $\delta_{15\text{N}}$ ,  $^1\text{J}_{\text{PN}}$  and  $^1\text{J}_{\text{PC}}$  correlated with both the  $\sigma$  and  $\sigma^-$  constants. For the N-phenyl-P,P,P-triarylphospha- $\lambda^5$ -azene series [ $\text{Ph}-\text{N}=\text{P}(\text{C}_6\text{H}_4-\text{R})_3$ ] the best correlations were observed between  $^{31}\text{P}$ ,  $^{15}\text{N}$  and several  $^{13}\text{C}$  chemical shifts and the  $\sigma$  constants. However,  $^1\text{J}_{\text{PN}}$  correlated with both  $\sigma^-$  and  $\sigma$  while  $^1\text{J}_{\text{PC}}$  correlated with  $\sigma_{\text{R}}$  and, interestingly, the slope of these correlations had the same sign. These data will be discussed in terms of inductive and resonance effects and the contribution of  $\text{p}\pi\text{-d}\pi$  and  $\text{p}\pi\text{-}\sigma^*$  bonding to the phosphazene system. These results will be compared to those in the N-aryl-P,P,P-triphenylphospha- $\lambda^5$ -azene series ( $\text{R}-\text{C}_6\text{H}_4-\text{N}=\text{PPh}_3$ ) where the chemical shifts ( $^{15}\text{N}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ ) and  $^1\text{J}_{\text{PC}}$  were observed to correlate with  $\sigma^-$  while  $^1\text{J}_{\text{PN}}$  correlated with  $\sigma_{\text{R}}$  and  $\sigma_{\text{R}}^+$ . In this case it was suggested that the chemical shifts were sensitive to electron density rather than to  $\text{p}\pi\text{-d}\pi$  bonding and that the coupling constant changes could be understood in terms of both  $\text{p}\pi\text{-d}\pi$  PN bonding and competitive  $\text{p}\pi\text{-}\sigma^*$  bonding.