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# GENERATION OF PHENYLPHOSPHINIDENE AND GROUP $V_A$ ANALOGUES BY ELECTRON IMPACT

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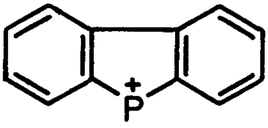
Phosphinidenes ($R-\dot{P}:$), the phosphorus analogues of nitrenes, are considered to be intermediates in a number of phosphine reactions.[1,2] Ionized phenylphosphinidene ($C_6H_5P^+$) occurs to a small extent in the mass spectra of triphenylphosphine[3,4] and some cyclophosphines.[2] We have found that the phenylphosphinidene cation (*m/e* 108) and its analogues with other Group $V_A$ elements account for the base peaks in the mass spectra[5] of phenylphosphine ($\%\Sigma_{40} = 25$), diphenylphosphine ($\%\Sigma_{40} = 40$), triphenylarsine (*m/e* 152, $\%\Sigma_{40} = 40$), and triphenylstibine (*m/e* 198 and 200, $\%\Sigma_{40} = 37$), while the bismuth analogue (*m/e* 286, $\%\Sigma_{40} = 26$) is the second most abundant species in the spectrum of triphenylbismuth. Aniline,[6] diphenylamine,[7] and triphenylamine give rise to the phenylnitrene cation to a very minor extent. Neither phenyldichlorophosphine nor other halogenated phosphines[3] show any significant amount of phenylphosphinidene ion.

The $C_6H_5X^+$ ions (except when X = Bi) lose one hydrogen in a subsequent step, as is indicated (except when X = Sb) by the appropriate metastable ions. Since 2,4,6-$d_3$-$C_6H_5P^+$, from tri(2,4,6-$d_3$-phenyl)phosphine,[4] suffers random loss of H and D, it is not clear whether this species is open chain, bridged, or cyclic.

The mass spectrum of diphenylphosphine shows an M - 3 fragment from which the hydrogen on phosphorus has been lost, since *P*-$d_1$-diphenylphosphine yields the same ion with loss of deuterium. This species is most probably the 9-phosphafluorenylium cation (I), which is abundant in the spectrum of



(I)

triphenylphosphine.[3,4] Analogous fragments are moderately abundant in the spectra of triphenylarsine and triphenylstibine, of low abundance for diphenylamine[7] and triphenylamine, and absent for triphenylbismuth.

Rearrangement ions at m/e 154 ($C_{12}H_{10}$), 153 ($C_{12}H_9$), and 152 ($C_{12}H_8$), previously observed[8] in the mass spectrum of triphenylbismuth, are also seen for diphenylamine[5] and triphenylamine (extremely weak), triphenylphosphine,[3,5] triphenylarsine, and triphenylstibine, but not for diphenylphosphine.

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