

THE DIRECTION OF THE DIPOLE MOMENTS OF PHOSPHABENZENE AND ARSABENZENE

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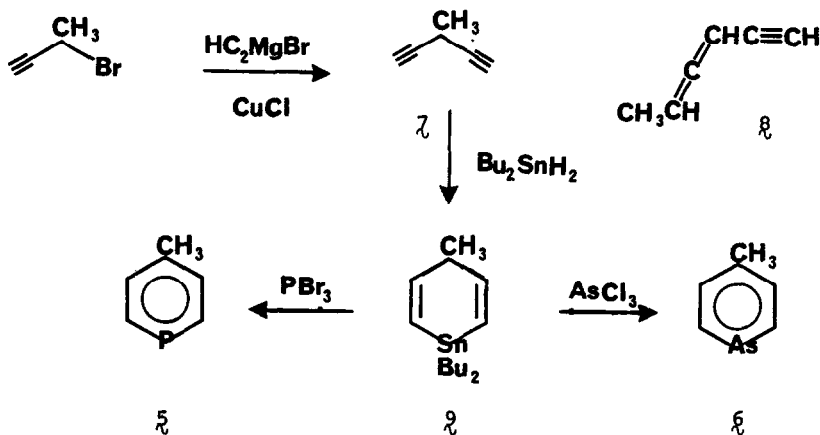
Preliminary studies of the spectral properties of phosphabenzene (phosphorin) $\mathfrak{2}$ and arsabenzene (arsenin) $\mathfrak{3}$ have emphasized their similarities to pyridine²⁻⁶. Recently we reported the gas phase dipole moment of phosphabenzene as 1.54D⁵ and that of arsabenzene as 1.10D⁶. The magnitude is considerably less than that for pyridine $\mathfrak{4}$ (2.215D)⁷. The direction of the dipole was not determined. Since the difference in electronegativity⁸ between nitrogen (3.04) and carbon (2.55) relative to phosphorus (2.19) and carbon (2.55) and to arsenic (2.18) and carbon (2.55) changes sign, one might naively expect a change in the dipole moment direction as well. On the other hand both CNDO/2^{9,10} and ab initio¹¹ MO calculations have predicted that all three heterobenzenes have the same direction of polarization.

It was felt desirable to test this prediction. A comparison of the dipole moments of 4-substituted heterobenzenes with those of the parents should unambiguously define the direction of the moments. We now wish to report on the synthesis of 4-methylphosphabenzene $\mathfrak{5}$ and 4-methylarsabenzene $\mathfrak{6}$ ¹² and their use in determining the direction of the dipole moments of the ring systems.

The cuprous chloride catalyzed coupling of 3-bromobutyne with ethynyl magnesium bromide in tetrahydrofuran gave a 40% yield of a 4:1 mixture of isomeric hydrocarbons which could be separated by g.l.p.c. The major component was assigned as 3-methyl-1,4-pentadiyne $\mathfrak{7}$ on the basis of its ¹H-NMR spectrum: (CDCl₃) τ 6.52qt (J, 7, 2.5Hz) (1H); 7.90d (J, 2.5Hz) (2H); 8.50d (J, 7Hz) (3H). The

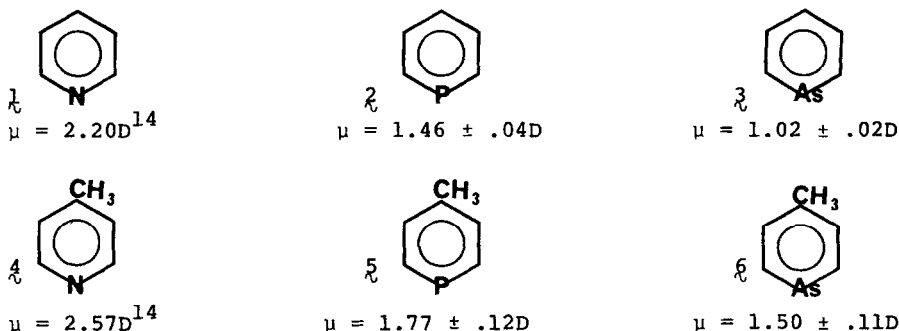
minor isomer was 3,4-hexadienyne δ . $^1\text{H-NMR}(\text{CCl}_4)$: τ 4.50-4.80m(2H); 7.20t(J, 1.5Hz)(1H); 8.30dd(J,7,4Hz)(3H). The more reactive allene could be removed by heating with an equivalent of dibutyltin hydride, followed by distillation of the diyne. Stannohydration of λ with dibutyltin dihydride in refluxing heptane gave 42% of 1,1-dibutyl-1,4-dihydro-4-methylstannabenzene ρ . $^1\text{H-NMR}(\text{CDCl}_3)$: τ 3.49dd(J,14,4Hz)(2H); 4.00dd(J,14,2Hz)(2H); 7.00m(1H); 8.92d(J, 8Hz)(3H); 8.3-9.3bm(18H).

Heating ρ with phosphorus tribromide in carbon tetrachloride gave 34% of 4-methylphosphabenzene. $^1\text{H-NMR}(\text{CDCl}_3)$: 1.45dd(J,37.5,10Hz)(2H); 2.33.t(J,10Hz)(2H); 7.62d(J,3Hz)(3H). MS : M^+ , 110. A 65% yield of 4-methylarsabenzene was obtained from arsenic trichloride and ρ . $^1\text{H-NMR}(\text{CCl}_4)$: τ 0.62d(J,11Hz)(2H); 2.40d(J,11Hz)(2H); 7.60s(3H). MS : M^+ , 154. Final purification was effected by g.l.p.c.



The dipole moments of λ , ρ , δ and ξ were determined in cyclohexane from standard measurements of dielectric constants and calculations of polarization at infinite dilution.¹³ Data are summarized in figure 1. Agreement with the more precise gas phase data is acceptable.^{5,6} The dipole moment of each 4-methylheterobenzene exceeds its parent. Thus the electron donating methyl group reinforces the ring dipole. In all three heterobenzenes the negative end of the dipole is at the hetero atom.¹⁵

Figure 1. Solution Dipole Moments of the Heterobenzenes and the 4-Methylheterobenzenes.



Although the MO calculations predict that pyridine and its two homologs have the same direction of polarization, the charge distributions of \mathfrak{z} and \mathfrak{z} are predicted to be dramatically different from \mathfrak{z} .^{9,10,11} The major contribution to the pyridine dipole is the difference between the very electropositive α -carbon atoms and the electronegative nitrogen. For phosphabenzene and arsabenzene the major contribution is apparently a difference between a relatively large negative charge on the α -carbon atoms and a large positive charge on the β -carbon atoms. While the observed direction of polarization of \mathfrak{z} and \mathfrak{z} is consistent with this charge distribution, we believe that a further experimental verification would be desirable.

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