

THE SYNTHESIS OF SUBSTITUTED PHOSPHABENZENES AND ARSABENZENES.

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Although pyridine has been known for well over 100 years, its phosphorus and arsenic analogs, phosphabenzene $1a$ and arsabenzene $2a$, have only recently been synthesized.² Studies of their spectra and chemical properties have revealed similarities to benzene and pyridine.^{3,4,5} However to some extent these studies have been limited by the absence of a general method for synthesizing simple substituted phospho- and arsabenzene.

Very highly substituted phosphabenzene⁴ and arsabenzene^{5,6} are available. We have reported the synthesis of the totally unsubstituted phosphabenzene and arsabenzene.² 1,4-Pentadiyne $3a$ reacts with dibutyltin dihydride to give 1,4-dihydro-1,1-dibutyl stannabenzene $5a$.⁷ Phosphorus tribromide converted $5a$ to phosphabenzene, while treatment with arsenic trichloride gave arsabenzene.² We now wish to report on the extension of this method to the synthesis of substituted heterobenzenes.

1,4-Hexadiyne $3b$ reacts with dibutyltin dihydride in refluxing heptane to give a 65% yield of two 1:1 adducts in the ratio of 1:5. Treating these adducts with acetic acid liberated a nearly quantitative yield of trans-1,4-hexadiene. The adducts could be separated by glpc⁸ and structural assignment was made from the H-NMR spectrum (see Tables I and II). In particular the methyl peak of the minor adduct occurred as a doublet (J,6Hz) due to coupling by the geminal hydrogen. This allowed assignment as $4b$. Spectra of the major product were consistent with assignment as $5b$.

Heating the unseparated mixture of tin isomers $4b$ and $5b$ with phosphorus tribromide in carbon tetrachloride gave a 45% yield of 2-methylphosphabenzene $1b$. H-nmr (CDCl₃): tau 7.40d (J, 15Hz) (3H), 2.4-2.9m(3H), 1.50dd(J,38,10Hz) (1H). MS:M⁺,110. Similarly heating with arsenic trichloride gave 43% of 2-methylarsabenzene $2b$. H-nmr (CCl₄): tau 7.31s(3H), 2.3-2.7m(3H), 0.45d(J,10Hz) (1H). MS:M⁺,154.

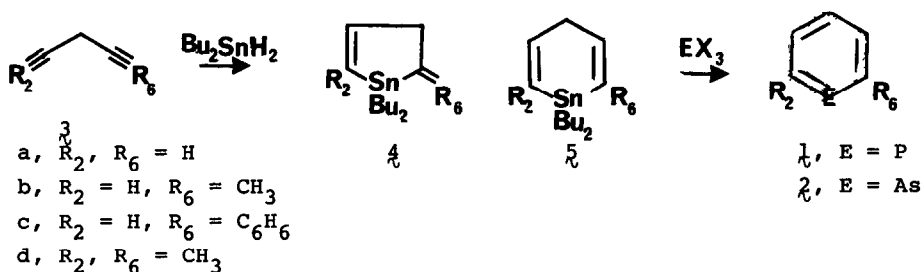


Table I. 100 MHz H-NMR Spectra of the 9
 1,1-Dibutyl-1,4-dihydro-stannabenzenes in CCl_4 .

Compound	R_2	H_3	H_4	H_5	R_6
5a, $R_2=R_6=H$	3.91 dt (14, 1.5Hz)	3.41 dt (14, 3.5Hz)	6.94m		
5b, $R_2=H$ $R_6=CH_3$	4.0m	3.41 dt (13, 4Hz)	6.95m	4.0m	8.05d (2Hz)
5d, $R_2=R_6=CH_3$	8.1s	3.9m	7.0m		

Table II. 100 MHz H-NMR Spectra of the 9
 5-Methylene-stannacyclopent-2-enes in CCl_4 .

Compound	R_2	H_3	H_4	H_6	R_6
4b, $R_2=H$, $R_6=CH_3$	3.62dt (10Hz, 2Hz)	3.14 dt (10, 3Hz)	6.85m	3.80d (6Hz)	8.22d (6Hz)
4c, $R_2=H$, $R_6=C_6H_5$	3.56 dt (10, 2.5Hz)	3.06 dt (10, 3Hz)	6.66m	2.77m	2.77m
4d, $R_2=R_6=CH_3$	8.00m	3.70m	6.89m	3.83dt (6, 2Hz)	8.25dt (6, 2Hz)

1-Phenyl-1,4-pentadiyne reacts with dibutyltin dihydride in a similar manner to give a 41% yield of a single 1:1 adduct. The adduct gave a quantitative yield of 1-phenyl-1,4-pentadiene on treatment with acetic acid.¹⁰ H-NMR spectrum did not allow distinction to be made between the possible five-membered ring adduct 4c and the six-membered ring adduct 5c. Heating this adduct with arsenic trichloride in the usual manner produced no arsabenzene, suggesting that adduct 5c is not present. This suggestion was confirmed by the reaction with acetic acid

d_1 , which gave 1-phenyl-1,4-pentadiene-2,5- d_2 . (H-nmr(CCl_4): tau 7.12d(J,6Hz) (2H), 5.03d(J,10Hz) (1H), 4.27m(1H), 3.67br.s(1H), 2.87m(5H); (MS: M^+ ,146).

In order to prepare disubstituted heterobenzenes 2,5-hexadiyne was synthesized by the cuprous chloride catalyzed coupling reaction of 1-bromo-2-butyne with propyne magnesium bromide. This diacetylene reacted with dibutyltin dihydride to give a 58% yield of a mixture of adducts in the ratio of 3:1. Acetic acid converted the mixture into a single olefin, identified as trans, trans-2,5-hexadiene (IR(CS_2): $960cm^{-1}$) (H-nmr($CDCl_3$):tau 8.33m(6H), 7.33m(2H), 4.59m(4H)); (C-nmr($CDCl_3$): delta 17.9 (CH_3), 35.7(CH_2), 125.3, 129.9(CH)).

The adducts could be separated by glpc. The major product was assigned structure $4d$ on the basis of its H-NMR spectrum. In particular it showed two non-equivalent allylic methyl peaks, one of which was split into a doublet (J,6Hz) by the adjacent hydrogen. The two methyl groups of $5d$ were equivalent.

Refluxing a mixture of $4d$ and $5d$ with phosphorus tribromide in carbon tetrachloride gave a low yield of 2,6-dimethylphosphabenzene $1d$ (H-nmr(CCl_4):tau 7.37d(J,15Hz) (6H), 2.62m(3H) (MS: M^+ ,124). Heating with arsenic trichloride in carbon tetrachloride gave 15% of 2,6-dimethylarsabenzene $2d$ (H-nmr($CDCl_3$):tau 7.28s (6H); 2.62s(3H)) (MS, M^+ ,168).

Formation of the five-membered ring adduct, useless for conversion to the heterobenzenes, had not been observed in the reaction of 1,4-pentadiyne with dibutyltin dihydride.¹¹ However this type of product increases relative to the six-membered ring adduct as methyl substitution increases on the 1,4-diacetylene, and becomes the exclusive product with a single phenyl substitution. Certainly the major portion of this difference can be explained by the increasing stability of intermediate radicals which lead to five membered ring product.

Synthetically only very modest yields of 2,6-disubstituted heterobenzenes were obtained, although the conversion to 2-methyl-heterobenzenes was quite satisfactory. Very likely a variety of 2-substituted heterobenzenes can be obtained by this method, although the results with the phenyl group emphasize its limitations.

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References and Footnotes

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8. Glpc analyses and separations were performed on a Varian 90P instrument using a 10' x 1/4" column packed with 20% Apiezon L on Chromosorb W. Satisfactory combustion analyses have been obtained on all new compounds.
9. In all cases the signal for the 18 butyl protons occurred as a complex envelop tau 8.4-9.3.
10. The H-nmr spectrum was identical to that reported: V. Speziale and A. Lattes, Bull. Soc. Chim. Fr., **1971**, 3057.
11. It is estimated that greater than 5% of 4a would have been detected by nmr.