

THE REACTION OF PHOSPHABENZENE, ARSABENZENE AND STIBABENZENE
WITH METHYLLITHIUM

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As a part of our general study of the Group V heteroaromatic compounds pyridine 1a, phosphabenzene 1b,² arsabenzene 1c,² stibabenzene 1d³ and bismabenzene 1e,⁴ we have examined their reactions with methyllithium. It is well known that alkyllithium reagents attack pyridine 1a at the most electro-positive atom, the α -carbon, to give the charge delocalized anion 2a.⁵ On the other hand it has been reported that 2,4,6-triphenylphosphabenzene is attacked at phosphorus.⁶ Since the three phenyl rings must greatly stabilize this anionic product, one cannot confidently predict that the parent phosphabenzene will behave similarly. No reactions of strong bases with the heavier heterobenzenes have appeared. We now wish to report that methyllithium does add to the electropositive heteroatom of phosphabenzene (1b), arsabenzene (1c) and stibabenzene (1d) to give the corresponding lithium 1-methyl-heterocyclohexadienides 3 b,c,d.⁷

The addition of methyllithium to an ether-THF solution of arsabenzene (1c) gave a dark green solution of anion 3c. Quenching with water afforded 1-methyl-2,4-arsacyclohexadiene 4c: ¹H nmr (CCl₄) δ 6.2 (m, 2 H), 5.7 (m, 2 H), 2.2 (m, 2 H), 0.9 (s, 3 H). Mass spectral m/e, 156 (M⁺). This anion may be regenerated by treating 4c with *t*-butyllithium in THF-pentane or more conveniently with dimsyl anion in DMSO. The proton nmr spectral parameters of 3c are listed in Table I, while ¹³C nmr spectral data are summarized in Table II. These first-order spectra are completely consistent with the assigned structure for 3c. In order to independently prepare 3c, 1-methyl-2,5-arsacyclohexadiene 6c was prepared from the exchange reaction of methylarsenic dichloride with 1,1-dibutyl-1,4-dihydrostannabenzene (5). ¹H nmr (CDCl₃) δ 6.1 (s, 4 H), 2.8

(m, 2 H), 1.0 (s, 3 H). ^{13}C nmr (CDCl_3) δ 128.2, 124.2, 27.8, 8.0. Mass spectral m/e , 156 (M^+). Deprotonation of 6c with t-butyllithium in THF-pentane or dimethyl anion in DMSO gave solutions of 3c which were identical in all respects with those prepared from 1c or 4c.

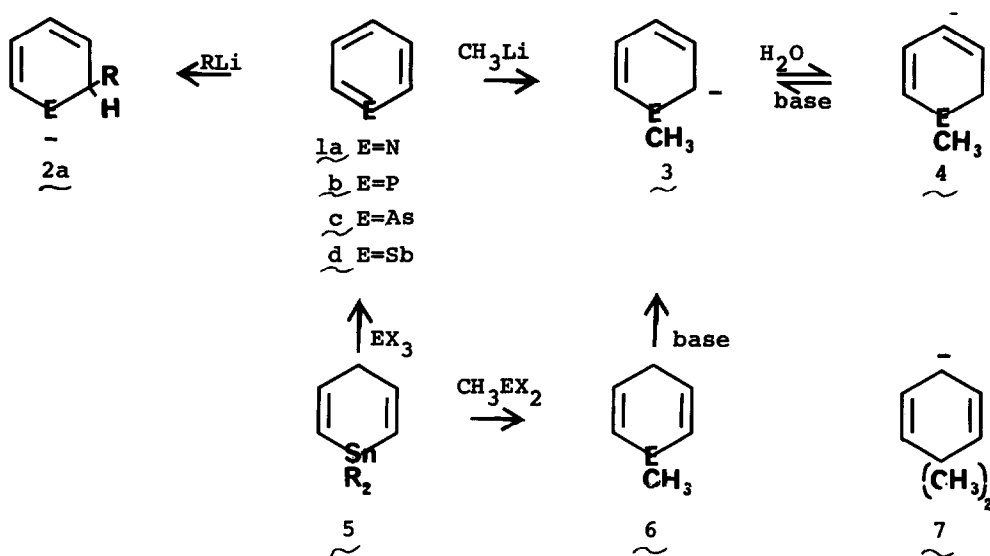


Table I. ^1H NMR Spectral Parameters of the Heterocyclohexadienide Anions.

Compound	$\delta\text{C}_2(\text{C}_6)$	$\delta\text{C}_3(\text{C}_5)$	δC_4	$J_{\text{H}_2-\text{H}_3}^3$	$J_{\text{H}_3-\text{H}_4}^3$	Others
<u>3b</u> ^a	3.3	6.1	4.3	9 Hz	7	$J_{\text{PH}}^2 = 53$ Hz $J_{\text{PH}}^3 \sim 8$
<u>3c</u> ^a	3.6	6.1	4.0	10 Hz	7.5	
<u>3d</u> ^a	4.0	6.2	4.0	10.5 Hz	8	
<u>7</u> ^{b,c,d}	3.4	5.9	3.9	7.5 Hz	6.4	

^aIn DMSO. ^bIn THF-pentane. ^cR. B. Bates, D. W. Grosselink and J. A. Kaczywsk *Tetrahedron Lett.*, 205 (1967). ^dFor consistency in this table, the carbon bearing the gem-methyl groups is numbered 1.

Table II. ^{13}C NMR Chemical Shifts of the Heterocyclohexadienide Anions.

Compound	$\delta\text{C}_2(\text{C}_6)$	$\delta\text{C}_3(\text{C}_5)$	δC_4	
<u>3b</u> ^a	71.8	133.0	96.5	$J_{\text{PC}}^1 = 3 \text{ Hz}$, $J_{\text{PC}}^2 = 8 \text{ Hz}$, $J_{\text{PC}}^3 = 9 \text{ Hz}$
<u>3c</u> ^a	72.9	132.1	92.6	
<u>3d</u> ^a	69.8	134.2	95.3	
<u>7</u> ^{b,c,d}	91.7	127.9	78.1	

^aIn THF-ether, the lower field THF signal was taken as δ 68.6. Chemical shift values of 3b in DMSO are very similar. ^bIn THF-pentane. ^cR. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs and A. S. Roth, *J. Am. Chem. Soc.*, **95**, 926 (1973). ^dFor consistency in this table, the carbon bearing the gem-methyl groups is numbered 1.

The behavior of phosphabenzene 1b is completely analogous to that of arsa-benzene. Methyl lithium converted phosphabenzene to anion 3b which could be quenched to 1-methyl-2,4-phosphacyclohexadiene 4b. ^1H nmr (CDCl_3) δ 6.6-5.6 (m, 4 H), 2.3 (m, 2 H), 1.0 (d, $J = 4 \text{ Hz}$, 3 H). ^{13}C nmr (CDCl_3) δ 124.6 (d, $J = 7 \text{ Hz}$), 131.8 (d, $J = 5 \text{ Hz}$), 124.9 (d, $J = 3 \text{ Hz}$), 121.8 (s), 20.9 (d, $J = 12 \text{ Hz}$), 7.8 (d, $J = 16 \text{ Hz}$). Mass spectral m/e , 112 (M^+). The anion may be regenerated by base. Similarly treating stibabenzene 1d with methyl lithium yields anion 3d, which may be reversibly quenched to a mixture of 4d and 6d. Anion 3d may also be conveniently prepared from pure 6d, itself available from the reaction of one equivalent of methyl lithium with 1-chloro-1,4-dihydro-stibabenzene.³ The proton and carbon nmr spectra of 3b and 3d are very similar to those of 3c. These data are summarized in Tables I and II.

It is interesting to consider the possible bonding available to anions 3. To the extent the heteroatom electron pair interacts with the ring, the anions may be regarded as 8 π -electron "antiaromatic" systems⁸ and consequently might show a paramagnetic ring current.⁹ On the other hand possible π -electron donation by the α -carbon atoms to the vacant ultimate d-orbitals of the heteroatom¹⁰ might diminish the negative charge at carbon.

Ring current and charge density effects can be probed by examining chemical shift values in the proton¹¹ and carbon¹² nmr spectra. The most striking feature of nmr spectra of anions 3b,c,d is the especially great shielding of the protons and carbon atoms at C_2 , C_4 and C_6 relative to those at C_3 and C_5 . The upfield shift of the protons at C_2 and C_6 is approximately three ppm, while the corresponding carbon atoms are close to 50 ppm upfield from those at C_3 and C_5 . These spectra are similar to those of their carbocyclic analog 7^{13,14} and strongly suggest that both 3 and 7 have a similar electronic structure in which the negative charge is largely localized on C_2 , C_4 and C_6 .¹⁵ Furthermore, the observation that the protons at C_3 and C_5 of 3 have nearly identical chemical shift values to those of their conjugate acids 4 indicates that there are no

important ring current effects in the anions. Apparently the heteroatoms of 3 do not strongly interact with the carbanionic pentadienyl system which forms the remainder of the ring.

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References and Notes

1. A. P. Sloan Fellow 1972-1976.
2. A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 3293 (1971).
3. A. J. Ashe, III, *J. Am. Chem. Soc.*, **93**, 6690 (1971).
4. A. J. Ashe, III and M. D. Gordon, *J. Am. Chem. Soc.*, **94**, 7596 (1972); A. J. Ashe, III, *Tetrahedron Lett.*, **415** (1976).
5. K. Ziegler and H. Zeiser, *Ber.*, **63**, 1847 (1930); K. Ziegler and H. Zeiser, *Ann.*, **485**, 174 (1931).
6. G. Märkl, F. Lieb and A. Merz, *Angew. Chem. Int. Ed. Engl.*, **6**, 87 (1967).
7. The H-nmr spectra were taken in CDCl_3 or CCl_4 using TMS as an internal standard, while those in DMSO-d_6 use the residual proton peak at δ 2.50. Spectra were recorded on either a Varian T-60 or a JEOL NMR-PFT/100 instrument.
8. For examples of other electronically destabilized, hence antiaromatic, 8 π -electron heterocyclic anions see: R. R. Schmidt, *Angew. Chem. Int. Ed. Engl.*, **14**, 581 (1975).
9. R. C. Haddon, V. R. Haddon and L. M. Jackman, *Top. Current Chem.*, **16**, 103 (1971).
10. For a discussion of the d-orbitals which might be available, see: M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N.Y., 1969, pp. 430-436.
11. G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); T. Shaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).
12. For example see: T. Tokuhiro and G. Fraenkel, *J. Am. Chem. Soc.*, **91**, 5005 (1969).
13. R. B. Bates, D. W. Gosselink and J. A. Kaczynski, *Tetrahedron Lett.*, 205 (1967).
14. R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs and A. S. Roth, *J. Am. Chem. Soc.*, **95**, 926 (1973).
15. That the signals for C_4 of 3 are not shifted as far upfield as those of C_2 and C_6 is a likely consequence of the polarization of the system by the electropositive heteroatom. In contrast the signal for the terminal carbon atoms of 7 is downfield from the central carbon. Both anions 3b,c,d and 7 protonate at the higher field carbon, again suggesting a larger electron density at that carbon.