THE REACTION OF PHOSPHABENZENE, ARSABENZENE AND STIBABENZENE
WITH METHYLLITHIUM

Arthur J. Ashe, III* and Timothy W. Smith

Department of Chemistry, The University of Michigan,
Ann Arbor, Michigan 48109

(Received in USA 4 October 1976; received in UK for publication 6 January 1977)

As a part of our general study of the Group V heteroaromatic compounds pyridine 1a, phosphabenzene 1b, arsabenzene 1c, stibabenzene 1d and bisma-
benzene 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 hetero-
benzenes 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-heterocyclohexa-
dienides 2 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 regener-
ated 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$_3$) $\delta$ 128.2, 124.2, 27.8, 8.0. Mass spectral m/e, 156 ($M^+$). Deprotonation of 6c with t-butyllithium in THF-pentane or dimsyl anion in DMSO gave solutions of $\sim$ 3c which were identical in all respects with those prepared from $\sim$ 1c or 4c.

![Chemical structures](image)

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{C_2}$</th>
<th>$\delta_{C_3}$</th>
<th>$\delta_4$</th>
<th>$J_{H_2-H_3}$</th>
<th>$J_{H_3-H_4}$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sim$ 3b</td>
<td>3.3</td>
<td>6.1</td>
<td>4.3</td>
<td>9 Hz</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>$\sim$ 3c</td>
<td>3.6</td>
<td>6.1</td>
<td>4.0</td>
<td>10 Hz</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>$\sim$ 3d</td>
<td>4.0</td>
<td>6.2</td>
<td>4.0</td>
<td>10.5 Hz</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>$\sim$ 7b,c,d</td>
<td>3.4</td>
<td>5.9</td>
<td>3.9</td>
<td>7.5 Hz</td>
<td>6.4</td>
<td></td>
</tr>
</tbody>
</table>

Table II. $^1$C NMR Chemical Shifts of the Heterocyclohexadienide Anions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$C$_2$(C$_6$)</th>
<th>$\delta$C$_3$(C$_5$)</th>
<th>$\delta$C$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b$^a$</td>
<td>71.8</td>
<td>133.0</td>
<td>96.5</td>
</tr>
<tr>
<td>3c$^a$</td>
<td>72.9</td>
<td>132.1</td>
<td>92.6</td>
</tr>
<tr>
<td>3d$^a$</td>
<td>69.8</td>
<td>134.2</td>
<td>95.3</td>
</tr>
<tr>
<td>3b$^{b,c,d}$</td>
<td>91.7</td>
<td>127.9</td>
<td>78.1</td>
</tr>
</tbody>
</table>

$^a$In THF-ether, the lower field THF signal was taken as $\delta$ 68.6. Chemical shift values of 3b in DMSO are very similar. $^b$In THF-pentane. $^c$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). $^d$For 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 arsabenzene. Methyllithium converted phosphabenzene to anion 3b which could be quenched to 1-methyl-2,4-phosphacyclohexadiene 4b. $^1$H nmr (CDCl$_3$) $\delta$ 6.6-5.6 (m, 4 H), 2.3 (m, 2 H), 1.0 (d, J = 4 Hz, 3 H). $^{13}$C nmr (CDCl$_3$) $\delta$ 124.6 (d, J = 7 Hz), 131.8 (d, J = 5 Hz), 124.9 (d, J = 3 Hz), 121.8 (s), 20.9 (d, J = 12 Hz), 7.8 (d, J = 16 Hz). Mass spectral m/e, 112 (M$^+$). The anion may be regenerated by base. Similarly treating stibabenzene 1d with methyllithium 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 methyllithium with 1-chloro-1,4-dihydrostibabenzene. $^3$ 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 $\pi$-electron "antiaromatic" systems $^8$ and consequently might show a paramagnetic ring current. $^9$ On the other hand possible $\pi$-electron donation by the $\alpha$-carbon atoms to the vacant ultimate d-orbitals of the heteroatom $^{10}$ might diminish the negative charge at carbon.

Ring current and charge density effects can be probed by examining chemical shift values in the proton $^{11}$ and carbon $^{12}$ 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.

Acknowledgment. We wish to thank the National Science Foundation for partial support of this work under grant (#MSP-74-17594). Thanks are also due to Mr. Bruce Garner for help with some preliminary experiments.

References and Notes

7. The H-nmr spectra were taken in CDCl₃ or CCl₄ using TMS as an internal standard, while those in DMSO-d₆ 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.
15. That the signals for C₄ of 3 are not shifted as far upfield as those of C₂ and C₆ 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.