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## The Synthesis and Study of the Enolate Monoanion of 2, 4-Di-p-anisylbicyclo(3.2.1)oct-6-en-3-one

Phillip D. Reynhout

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THE SYNTHESIS AND STUDY OF  
THE ENOLATE MONOANION OF  
2,4-DI-P-ANISYLBICYCLO(3.2.1)OCT-6-EN-3-ONE

by

Phillip D. Reynhout

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment  
of the  
Degree of Master of Arts

Western Michigan University  
Kalamazoo, Michigan  
April 1977

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Phillip D. Reynhout

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THE SYNTHESIS AND STUDY OF THE ENOLATE  
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## I. INTRODUCTION

For many years it has been known that carbanions can be stabilized by certain unsaturated substituents such as vinyl and aryl groups when the latter are directly attached to the carbon bearing the charge. In more recent times it has been shown that certain anions can be stabilized by an unsaturated group even when this moiety is not directly attached to the carbon carrying the negative charge.

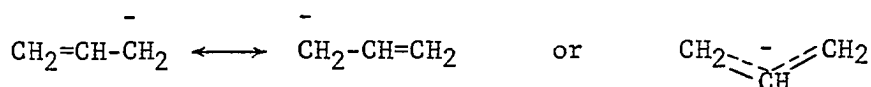
This investigation was initiated in order to examine the possibility of charge delocalization from C<sub>2</sub> in enolate anion 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one to the remote carbon-carbon double bond at C<sub>6,7</sub>. Furthermore, the effect of three different alkaline earth cations on the charge delocalization of the anion was to be examined.



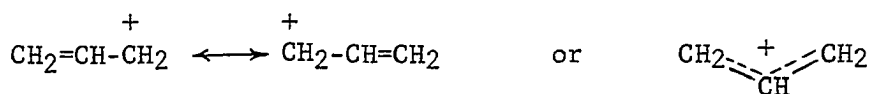
## II. HISTORICAL

### A. Homoconjugative and Homoaromatic Stabilization Effects.

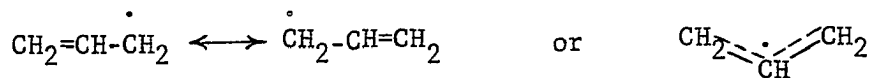
It has been established that carbanions,<sup>1</sup> carbonium ions,<sup>2</sup> and free radicals<sup>3</sup> can be stabilized by certain unsaturated substituents such as vinyl and aryl groups. The stabilization is the result of interaction of the p-orbitals bearing the charge or unpaired electron with the p-orbitals of the adjacent unsaturated group. This stabilization is represented by structures 1, 2, and 3, using the vinyl group as an example.



1



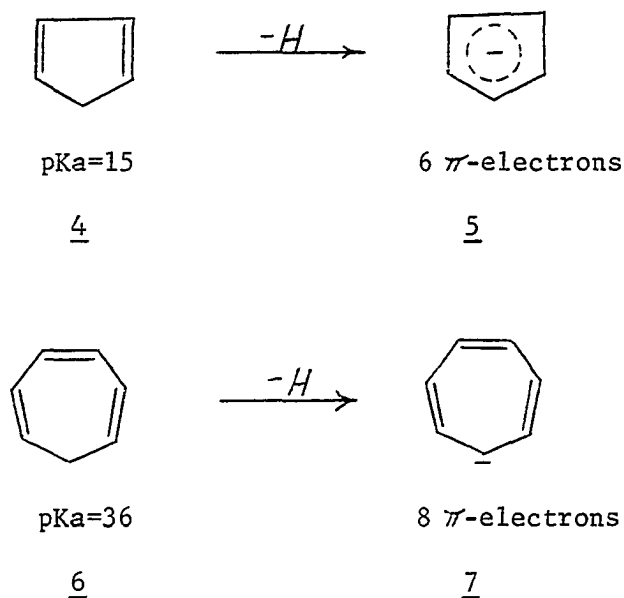
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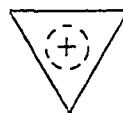
In addition to the type of stabilization described above, charge stabilization can also be achieved by aromaticity.

Aromaticity refers to a completely conjugated planar cyclic hydrocarbon with the sum of the  $\pi$ -electrons in the system complying with Huckel's<sup>4</sup>  $4n+2$  rule. The difference in acidity between cyclopentadiene<sup>5</sup> 4 and cycloheptatriene<sup>6</sup> 6, (21 pKa units), is a good example of aromatic stabilization. This large difference is

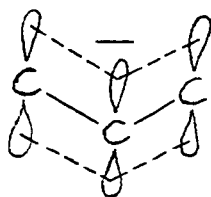
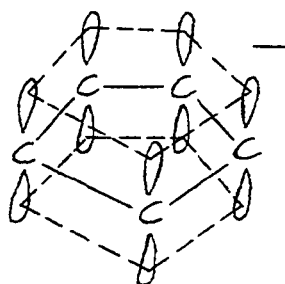


attributed to the fact that the cyclopentadienyl anion 5 has a 6  $\pi$ -electron aromatic system. Other well known unusually stable systems such as the tropylium cation<sup>7</sup> 8, and the cyclopropenyl cation<sup>8</sup> 9, are believed to achieve their stability by the attainment of a favorable number of electrons leading to aromatic stabilization.

It is important to note that in all of the above systems delocalization of charge has occurred by way of p-orbitals on adjacent carbon atoms between which there is an additional

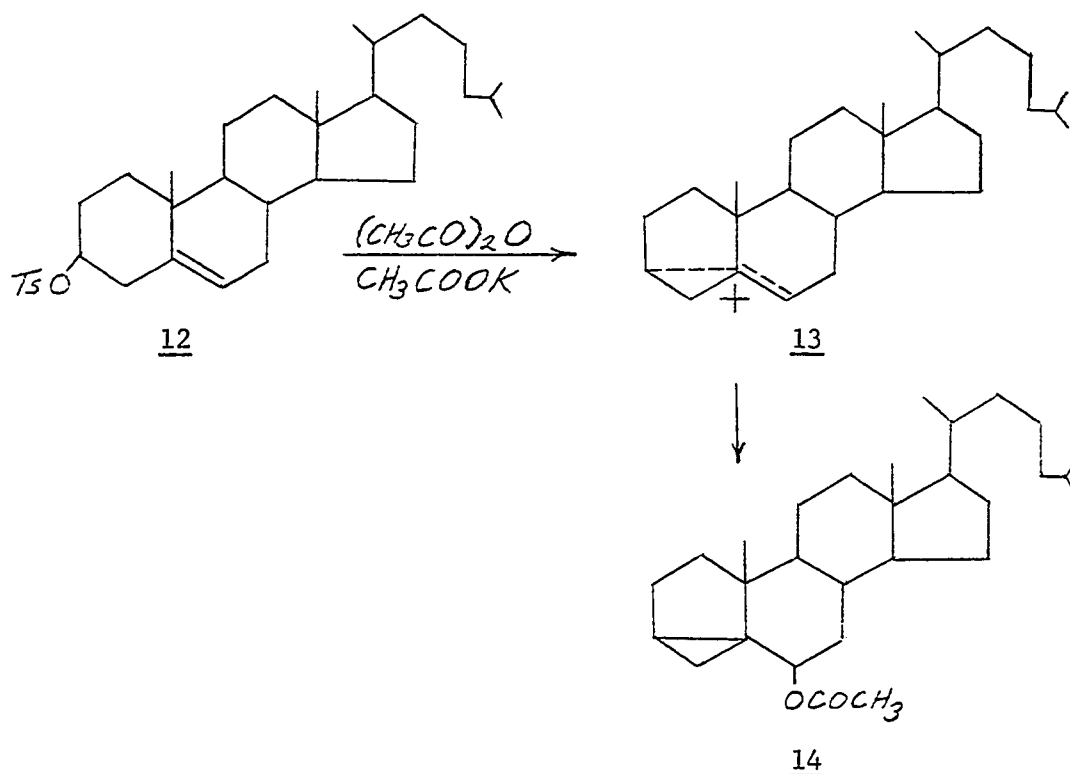
6  $\pi$ -electrons82  $\pi$ -electrons9

$\sigma$ -bond. This is shown in structures 10 and 11 for the allylic and cyclopentadienyl anions.

1011

As a result of studies by a number of workers<sup>9</sup>, but especially by Winstein<sup>10</sup>, a new concept has developed. It was determined that under conditions of favorable geometry, charge stabilization could take place even if the carbon bearing the charge is not directly attached to the unsaturated group. In this type of stabilization carbonium ions and carbanions can conjugate and therefore be stabilized by certain unsaturated groups even when a directly connecting  $\sigma$ -bond is not present.

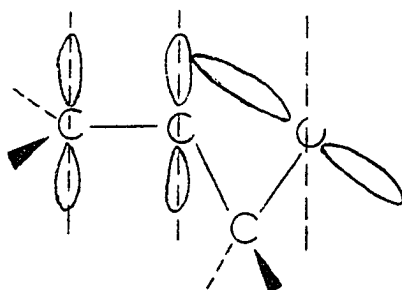
An example of this type of interaction is that of the cholesteryl carbonium ion 13<sup>11</sup>, obtained from cholesteryl-p-toluenesulfonate 12, as shown. Reaction of the carbonium ion 13 with acetic anhydride led to the formation of the rearranged acetate 14.



The interaction of the positive charge with the C<sub>5,6</sub> olefinic group in intermediate 13 was termed homoconjugation by Winstein<sup>12</sup>, and the cation a homoallylic cation by analogy to allylic conjugation and allylic carbonium ions. This designation was used in order to show that carbonium ion 13 may be considered a homolog of the allylic carbonium ion 2.

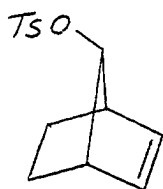
The important difference between allylic conjugation and homoconjugation is the geometry of the interacting p-orbitals. While allylic conjugation achieves maximum stabilization when the p-orbitals associated with the charge are parallel to the p-orbitals of the olefinic group (structure 10), a homoallylic system achieves maximum stabilization when the orbital associated with the charge

is arranged perpendicularly to the orbitals of the olefinic group<sup>12</sup>, as shown in structure 15.

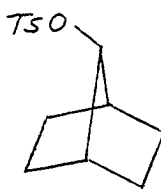


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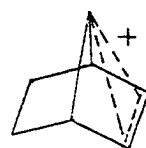
Homoconjugation can also lead to cyclic delocalization<sup>13</sup> with suitably chosen substrates. For example, the acceleration ( $10^{11}$ ) in the solvolysis rate of anti-norbornen-7-yl-p-toluene-sulfonate 16, compared to its saturated analog 17 was attributed by Winstein<sup>14</sup> to the interaction of the developing positive charge with the C<sub>6,7</sub> olefinic group, leading to a cyclically delocalized system 18.



16



17



18

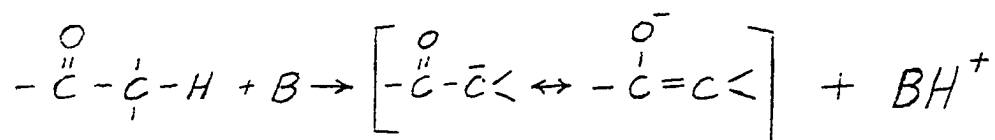
This type of conjugation was termed homoaromaticity<sup>10</sup>, and carbonium ion 18 was considered to be a homoaromatic analog of the aromatic cyclopropenyl cation 9.

The above studies are concerned with the homoconjugation and homoaromatic stabilization effects of positive charges. It is also

possible for negative charges to be stabilized by homoconjugation and/or homoaromaticity. The first studies exploring nonclassical interactions in carbanion chemistry were concerned with carbanions stabilized by the carbonyl group.

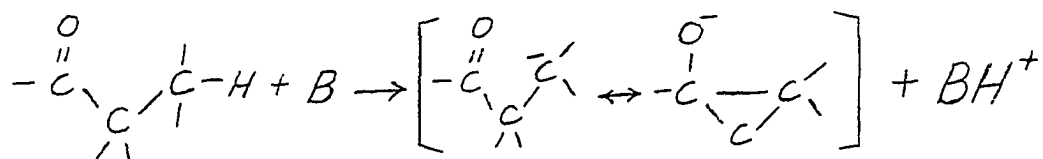
The interaction between carbonyl and a negatively charged alpha carbon, which results in a resonance stabilized enolate anion, is responsible for the ease of alpha proton abstraction from carbonyl compounds as shown in Scheme 1. By analogy with homoallylic

Scheme 1



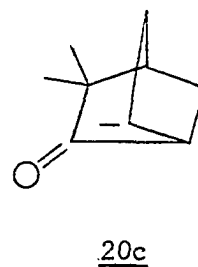
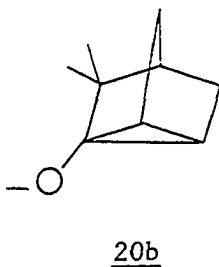
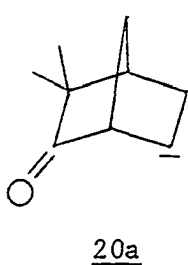
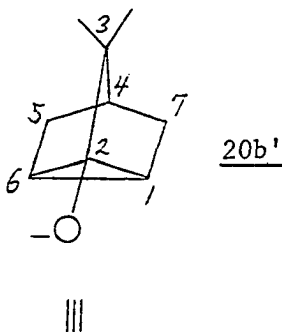
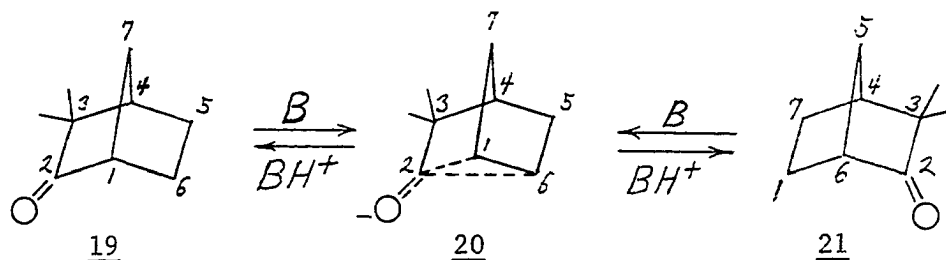
conjugation a carbonyl group could conceivably activate a more distant hydrogen, (on a  $\beta$ -carbon), sufficiently to allow conversion to an anion stabilized by homoconjugation, or a homoenolate anion, as shown in Scheme 2.

Scheme 2



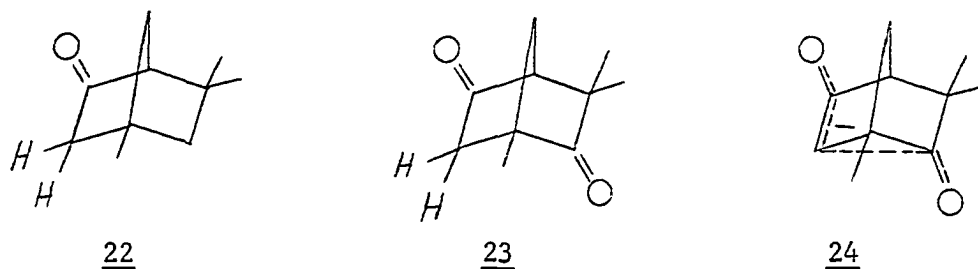
The first studies of this type were reported by Nickon and Lambert.<sup>15</sup> They observed that when optically active camphenilone 19 was heated with potassium t-butoxide in t-butyl alcohol at 165-185° a gradual racemization occurred. The loss in optical

activity is consistent with formation of a bridged nonclassical ion 20 (limiting classical structures 20a,b,c) upon proton abstraction from C<sub>6</sub>. Since structure 20b has a plane of symmetry, which is shown more clearly in 20b', capture of a proton at C<sub>6</sub> by the ion regenerates the starting ketone whereas capture at the equivalent site C<sub>1</sub> produces the enantiomer 21.



In a related study<sup>16</sup> it was found that hydrogen exchange, with sodium deuterioxide in aqueous dioxane, occurs much faster with the diketone compound 23 than with 22. This rate enhancement is in accord

with formation of a homodienolate ion 24 on proton abstraction from 23.



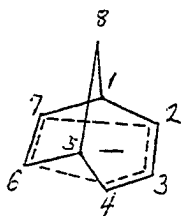
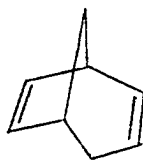
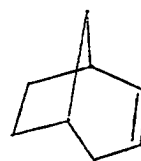
The above study<sup>16</sup> also provided one answer to the question of whether a carbanion formed alpha to carbonyl would be further stabilized by a more distant double bond. The results show that

relative rates of H/D exchange:	<u>22</u>	<u>25</u>	<u>23</u>
endo	1	3	1,800
exo	380	2,700	80,000

the hydrogen-deuterium exchange is increased only a moderate amount by the olefinic group in 25. This contrasts with the situation in 23, where a homoenolate interaction is clearly indicated by the large rate enhancement of hydrogen exchange.

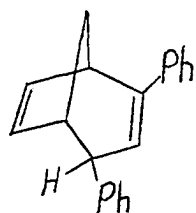
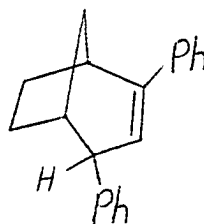


There is also evidence for carbanion stabilization by homoconjugative and homoaromatic mechanisms in systems which do not contain heteroatom functions capable of acting as carbanion stabilizing sites. The homoaromatically stabilized carbanion 26 was proposed as an intermediate by Brown<sup>17</sup> to explain the large ( $10^{4.5}$ ) acceleration in the rate of base catalyzed hydrogen-deuterium exchange at C<sub>4</sub> of bicyclo(3.2.1)octa-2,6-diene 27 compared to its more saturated analog 28. Anion 26 was produced in large enough

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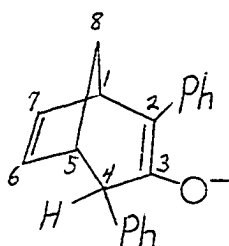
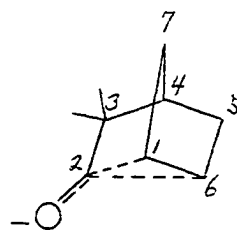
amounts by Winstein<sup>18</sup> to study its nuclear magnetic resonance (nmr) spectrum. It was found that vinylic protons H<sub>6</sub> and H<sub>7</sub> had moved upfield 2.3 ppm relative to the starting diene 27, clearly establishing that delocalization of charge to the double bond at C<sub>6,7</sub> had taken place.

Trimitsis and Tuncay<sup>19</sup> have shown that replacement of hydrogens at C<sub>2</sub> and C<sub>4</sub> of compounds 27 and 28 by phenyl groups to produce structures 29 and 30 results in greatly reducing the large difference in the base catalyzed hydrogen-deuterium exchange rate. These results are interesting because they demonstrate that the homoaromatic character of an anion can be destroyed by certain stabilizing groups. The elimination of the

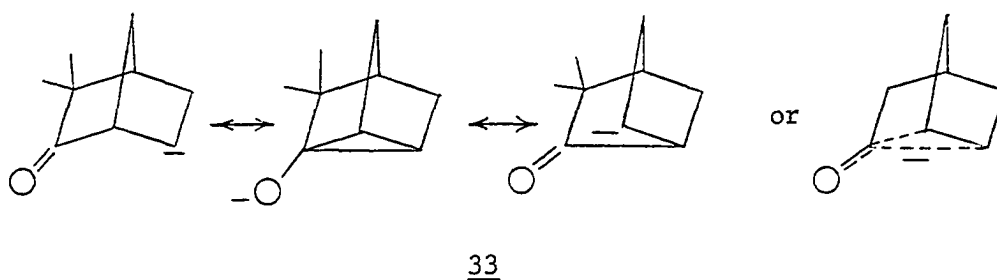
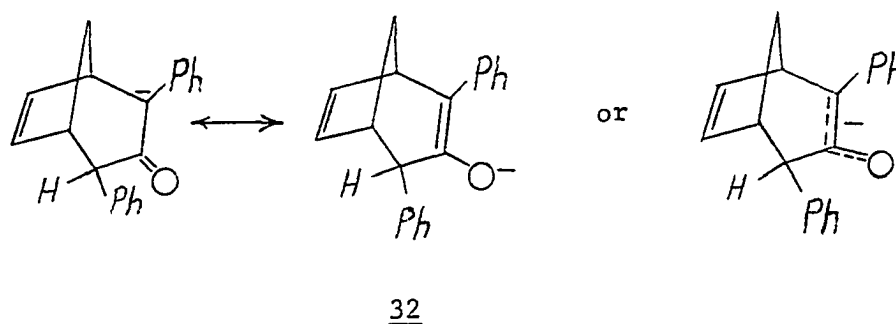
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homoaromatic delocalization effect in compound 29 was explained by the stabilization rendered the negative charge by the phenyl groups. This was the first study demonstrating that the extent of charge delocalization in carbanions has an inverse relationship to the stability given to the developing negative charge by groups directly attached to the carbanionic center.

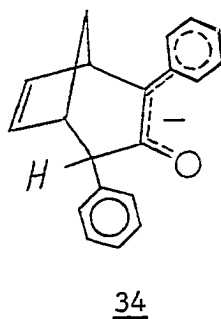
In other experiments aimed at studying the effects of stabilizing groups Trimitsis and Crowe<sup>20</sup> have found that the enolate anion of 2,4-diphenylbicyclo(3.2.1)oct-6-en-3-one 31 did not homoconjugate with the olefinic double bond. This is in contrast to anion 20, mentioned earlier, which was shown to homoconjugate and

3120

therefore form a homoenolate anion. It is important to note that although both form enolate anions, anion 20 must homoconjugate to be stabilized by the carbonyl group upon proton abstraction from C<sub>6</sub>, while anion 31 does not have to homoconjugate to be stabilized by the carbonyl. The interactions between carbonyls and negatively charged carbons are shown in the structures 32 and 33 below. It



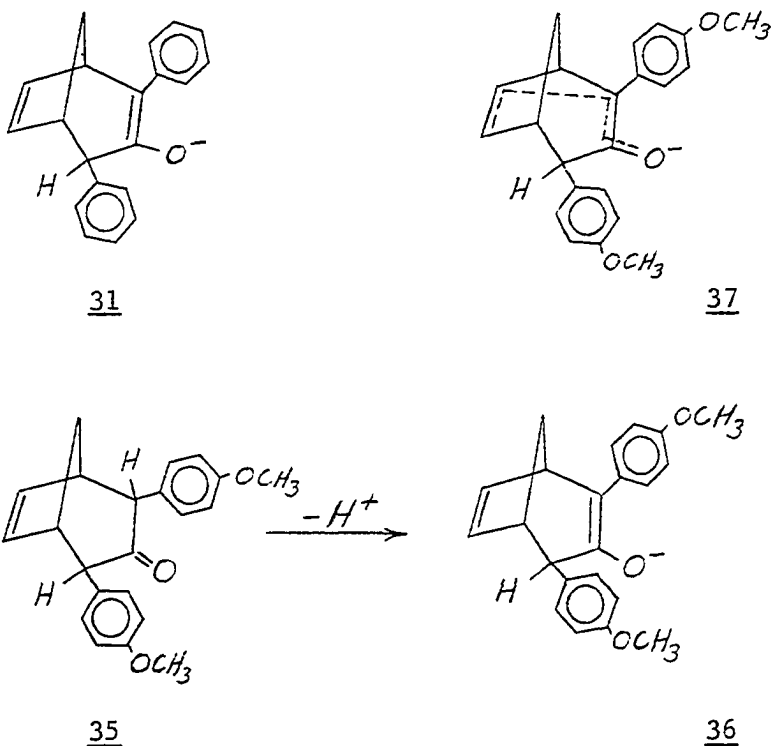
is also possible that the negative charge in compound 31 was also stabilized by the phenyl group at C<sub>2</sub> as shown in structure 34.



### III. RESULTS AND DISCUSSION

#### A. The Formation and Study of 2,4-Di-p-anisylbicyclo-(3.2.1)oct-6-en-3-one Monoanion 36

It was stated in the previous section that enolate anion 31 did not homoconjugate with the double bond at C<sub>6,7</sub>. This is because the negative charge was sufficiently stabilized by the carbonyl group at C<sub>3</sub> and phenyl group at C<sub>2</sub>. The present study was undertaken in order to determine if enolate anion 36 would



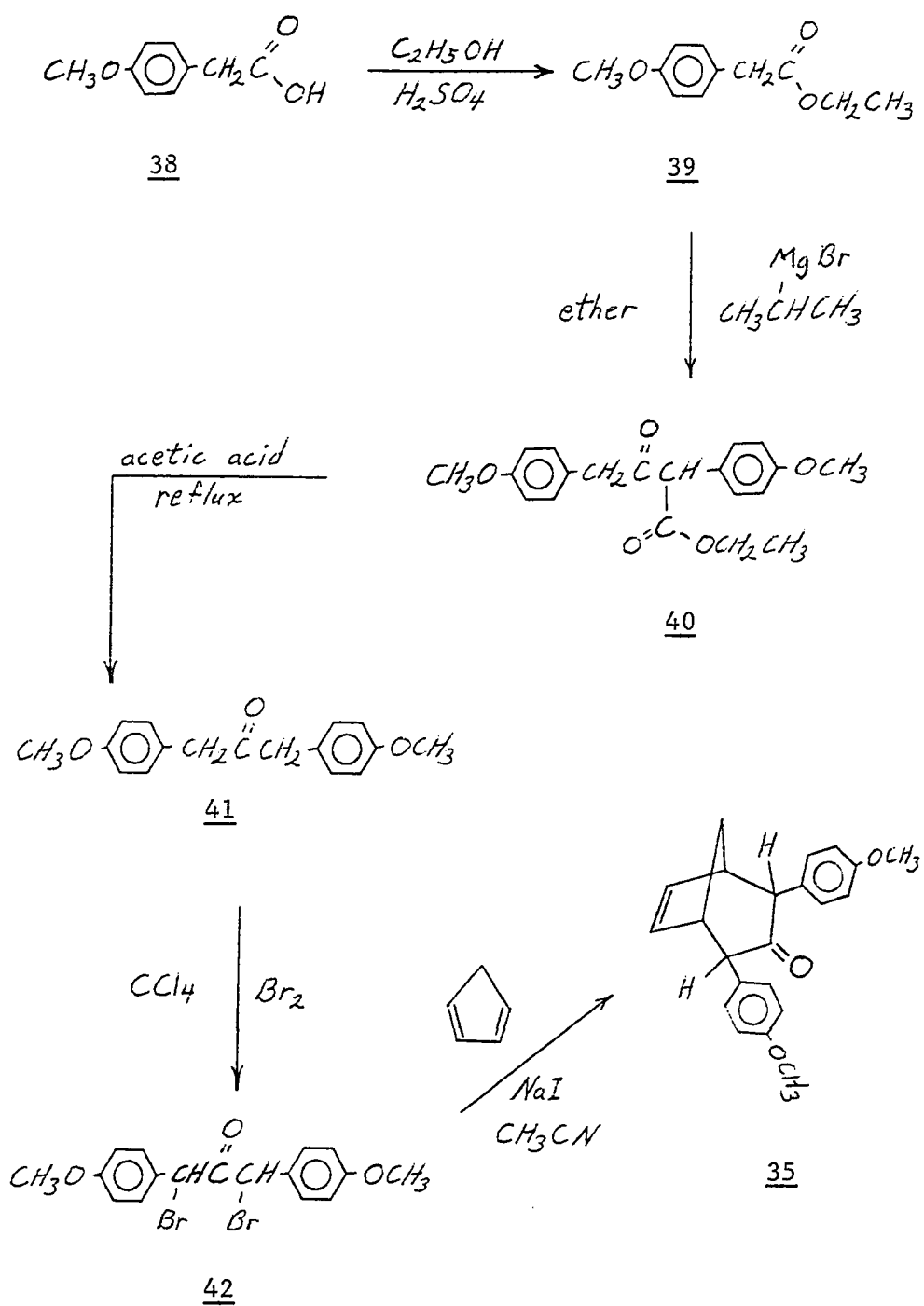
homoconjugate with the olefinic double bond thus forming a homo-enolate anion 37. The sodium, lithium, and potassium salts of enolate monoanion 36 would also be formed to compare the effect

of the metal cation on the anion.

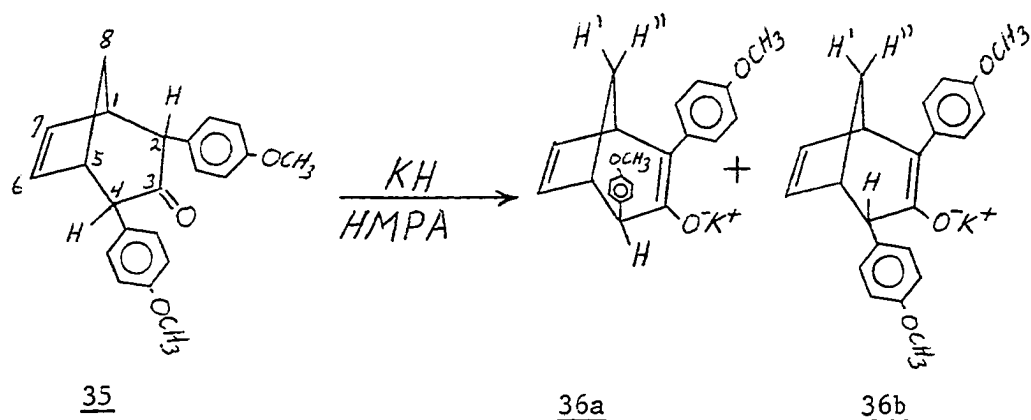
The synthesis of the ketone, 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one 35 was accomplished as illustrated in Scheme 3. Thus p-methoxyphenylacetic acid 38 was converted to ethyl-p-methoxyphenylacetate 39 with an excess of 95% ethanol, and in the presence of sulfuric acid. Reaction of the ester 39 with a Grignard reagent formed from 2-bromopropane and magnesium in ether, produced the  $\beta$ -ketoester 40. As in the procedure of Coan<sup>21</sup>, the  $\beta$ -ketoester was not isolated, but instead immediately refluxed with acetic acid to produce 1,3-di-p-anisyl-2-propanone 41. Ketone 41 was brominated in carbon tetrachloride essentially by the method of Breslow<sup>22</sup>, with certain modifications, to produce 1,3-dibromo-1,3-di-p-anisyl-2-propanone 42. Reaction of the dibromoketone 42 with cyclopentadiene and sodium iodide in acetonitrile following the procedure of Cookson<sup>23</sup> with some modification afforded 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one 35.

Enolate monoanion 36 was prepared by the treatment of ketone 35 with potassium hydride in the aprotic solvent hexamethylphosphoric triamide (HMPA). Thus ketone 35 was rapidly added to 1.5 equivalents of potassium hydride in HMPA at room temperature as illustrated in Scheme 4. This resulted in effervescence, a change in color from gray to dark red-brown, and the evolution of one equivalent of hydrogen gas which was taken to indicate complete monoionization. Although HMPA is not a common aprotic solvent, attempts to dissolve ketone 35 in the more common solvents such as THF and DMSO were not successful. Subsequent quenching of the enolate solution with

Scheme 3



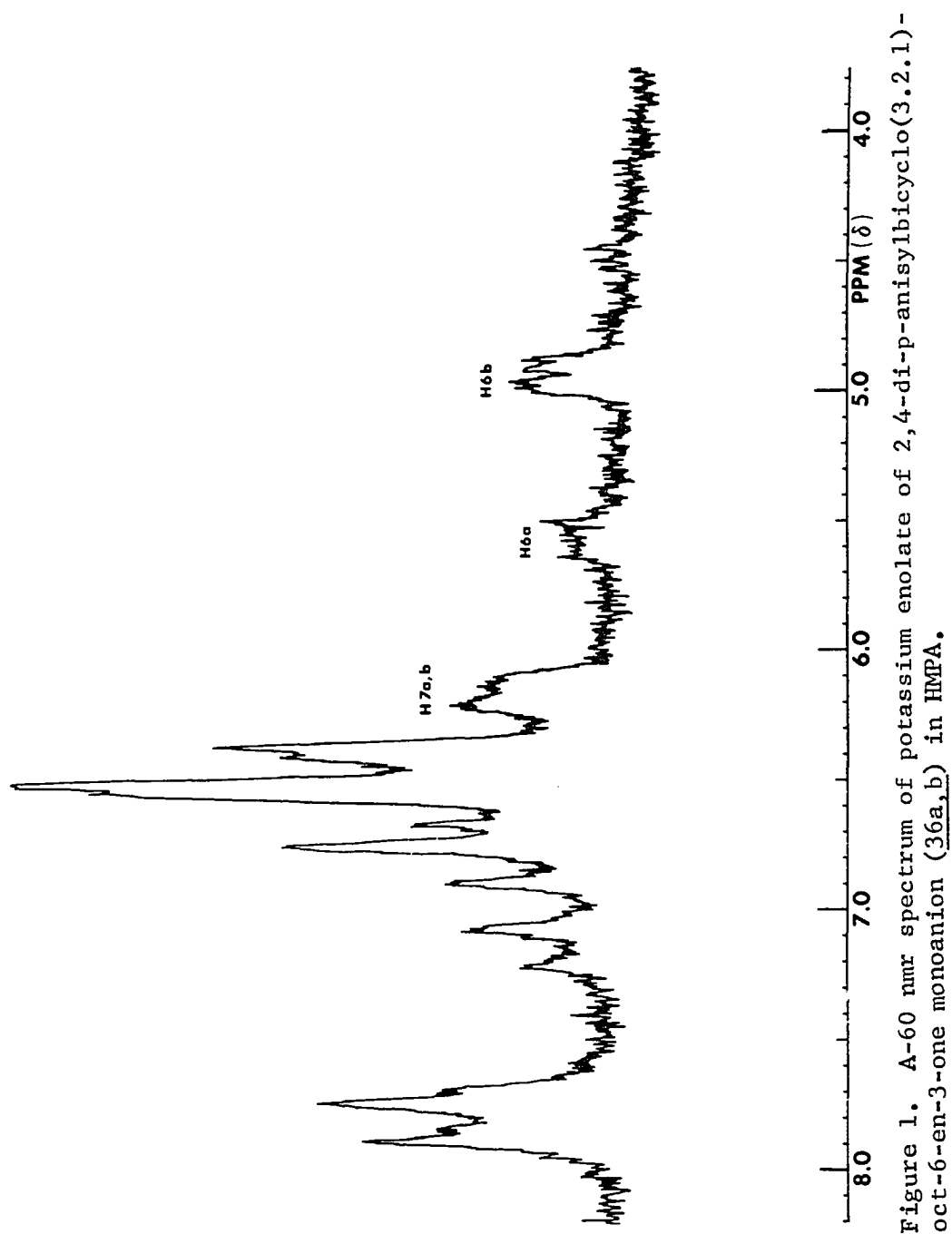
Scheme 4



water or deuterium oxide afforded the starting ketone, as shown by ir and nmr analysis of the reaction mixture.

The nmr spectrum of enolate anion 36 was recorded on a Varian A-60 instrument in HMPA with an external TMS standard and is shown in figure 1. From inspection of this nmr spectrum and earlier experimental results<sup>20,24</sup> it was concluded that enolate anion 36 actually consisted of two isomers 36a and 36b. The following resonances were assigned to the nmr spectrum shown in figure 1; protons H<sub>6a</sub> and H<sub>6b</sub> appear at 5.58 and 4.92 ppm respectively as multiplets due to coupling with H<sub>7a</sub>, H<sub>7b</sub> and H<sub>5a</sub>, H<sub>5b</sub>. Protons H<sub>7a,b</sub> appear as a multiplet at 6.18 ppm due to coupling with H<sub>6a</sub>, H<sub>6b</sub> and H<sub>1a</sub>, H<sub>1b</sub>. The aromatic protons appear as a wide multiplet between 6.2 and 8.0 ppm. All other upfield protons were covered by solvent peaks and could not be identified.

Enolate anion 36 was also prepared in HMPA-d<sub>18</sub>. Ketone 35 was added to potassium hydride in HMPA-d<sub>18</sub> exactly as described earlier. The nmr spectrum of enolate anion 36 in HMPA-d<sub>18</sub> was





taken on a Varian XL-100 spectrometer and is shown in figure 2. The following resonances were assigned to the spectrum; protons  $H_{1a,b}$  appeared as poorly resolved multiplet at 3.22 ppm due to coupling with  $H_{7a,b}$ . The signal for endo proton  $H_{4a}$  of isomer 36a appeared as a sharp singlet at 2.70 ppm while proton  $H_{4b}$  of isomer 36b appeared as a partially covered doublet at 3.30 ppm due to coupling with  $H_{5b}$ . This is because the  $H_{5a}$ - $H_{4a}$  dihedral angle is near  $90^\circ$ , and the  $H_{5b}$ - $H_{4b}$  dihedral angle is approximately  $40^\circ$ , thus accounting for the lack of spin-spin coupling between  $H_{5a}$  and  $H_{4a}$ . The fact that the endo proton  $H_{4a}$  was found to absorb upfield from exo proton  $H_{4b}$  is in good agreement with the nmr spectrum of the closely related bicyclic enolate monoanion 31.<sup>20,24</sup>

Proton  $H_{5a}$  was covered by HMPA peaks, but proton  $H_{5b}$  occurred as a multiplet at 2.57 ppm due to coupling with  $H_{4b}$ ,  $H_{6b}$ , and  $H_{8b}'$ . No coupling was observed between  $H_{5b}$  and  $H_{8b}''$  because their dihedral angle is about  $85^\circ$ . Vinylic protons  $H_{6a}$  and  $H_{6b}$  resonate at 5.56 and 4.94 ppm respectively as pairs of doublets arising from coupling with  $H_{7a}$ ,  $H_{7b}$  and  $H_{5a}$ ,  $H_{5b}$ . Irradiation at  $H_{5a,b}$  reduced both patterns to doublets. The other vinylic protons  $H_{7a}$  and  $H_{7b}$  occurred each as a pair of doublets partially overlapping at 6.18 ppm due to coupling with  $H_{6a}$ ,  $H_{6b}$  and  $H_{1a}$ ,  $H_{1b}$ . Simultaneous irradiation at  $H_{1a,b}$  reduced the multiplet to two doublets with their inner peaks overlapping thus appearing as a triplet. Protons  $H_{8a,b}'$  and  $H_{8a,b}''$  appear as a multiplet centered at 1.73 ppm.

The methoxy protons appeared as three partially overlapping singlets due to the two different para-methoxy groups of isomers

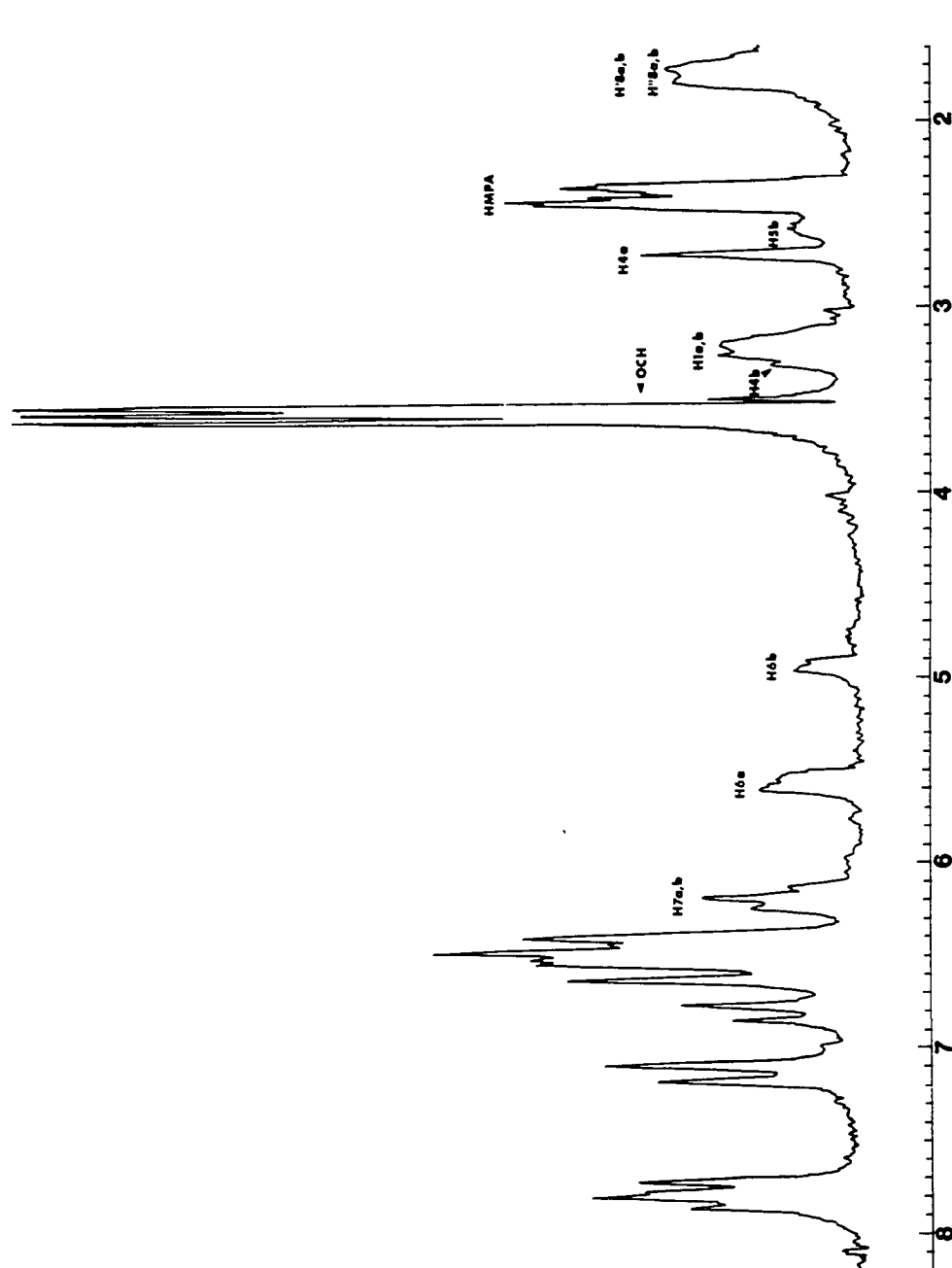
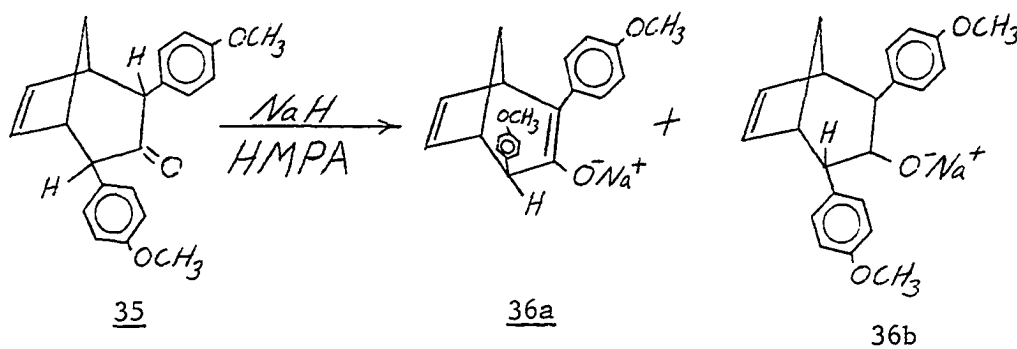


Figure 2. XL-100 spectrum of potassium enolate of 2,4-di-p-anisylbicyclo(3.2.1)-oct-6-en-1-one monoanion (36a,b) in HMPA-d<sub>18</sub>.

36a and 36b at C<sub>4</sub>, and the para-methoxy group at C<sub>2</sub>. The absorption pattern is centered at 3.56 ppm. The aromatic protons appeared as a wide multiplet from 6.3 to 8.0 ppm. In the similar system 31<sup>20</sup> the ortho protons resonated downfield from meta protons at C<sub>2</sub>, and all of the aromatic protons at C<sub>4</sub> appeared as a multiplet, however this system (36) did not follow such an integration pattern.

The enolate monoanion 36 was also prepared in HMPA with sodium hydride. In this procedure ketone 35 was rapidly added to two equivalents of sodium hydride in HMPA at room temperature as shown in Scheme 5. This resulted in a dark red-brown reaction mixture

Scheme 5

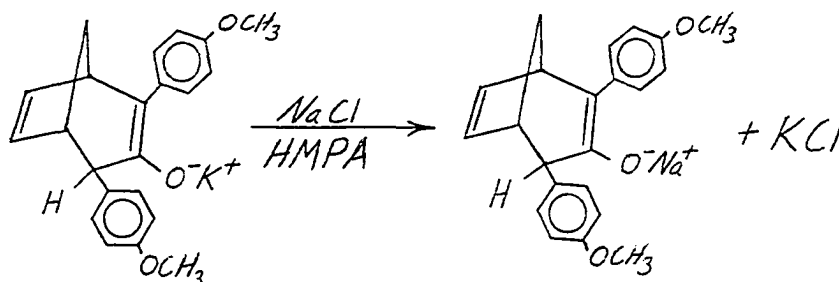


and the evolution of one equivalent of hydrogen gas. The nmr spectrum was recorded on a Varian A-60 instrument and it appears in figure 3. The nmr absorption pattern for the sodium salt of enolate anion 36 in HMPA (figure 3) was found to be identical to that of the potassium salt (figure 1).

The sodium salt of enolate anion 36 was next formed by a metal-metal exchange reaction in HMPA. After first forming a

potassium salt of anion 36 as described earlier, and shown in Scheme 4, one equivalent of sodium chloride was added to the reaction mixture as shown in Scheme 6. In this process the transfer of the

Scheme 6



organic group to another metal only works if the metal of the metal halide is more electronegative than that of the organometallic compound.<sup>25</sup> Thus sodium (EN=0.9) will replace potassium (EN=0.8). In general, when an organometallic compound and metal halide are reacted the effect is to combine the halogen with more electropositive metal and the organic anion with the more electronegative element of the pair.<sup>26</sup> The nmr spectrum of the sodium salt of enolate monoanion 36 formed by a metal-metal exchange reaction is shown in figure 4, and is also identical to that of the potassium salt (figure 1).

The sodium salt of enolate monoanion 36 was also formed by a metal exchange reaction in HMPA-d<sub>18</sub>. Thus the potassium salt of anion 36 was first formed in HMPA-d<sub>18</sub> and then one equivalent of sodium chloride was added to the reaction mixture. The nmr

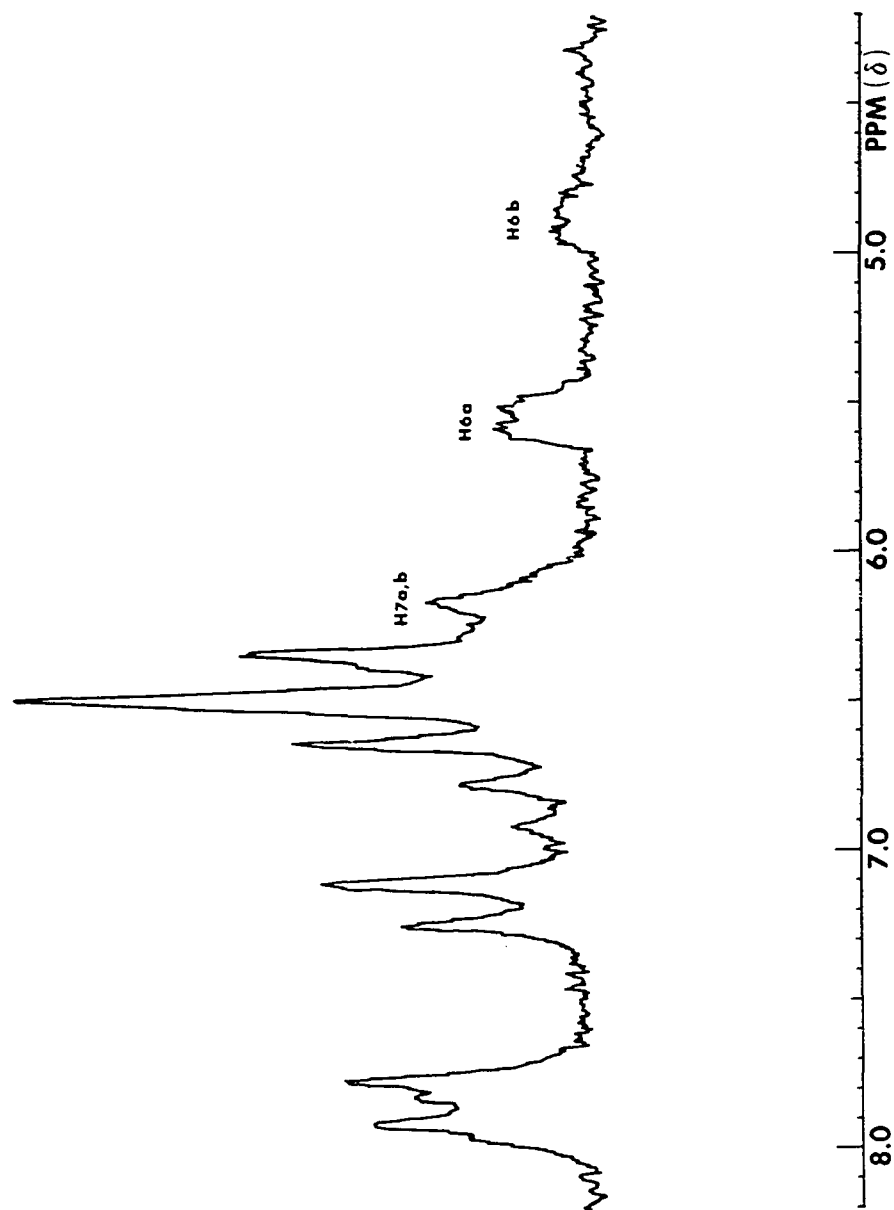


Figure 3. A-60 nmr spectrum of sodium enolate of 2,4-di-p-anisylbicyclo-(3.2.1)oct-6-en-3-one monoanion (36a,b) in HMPA.

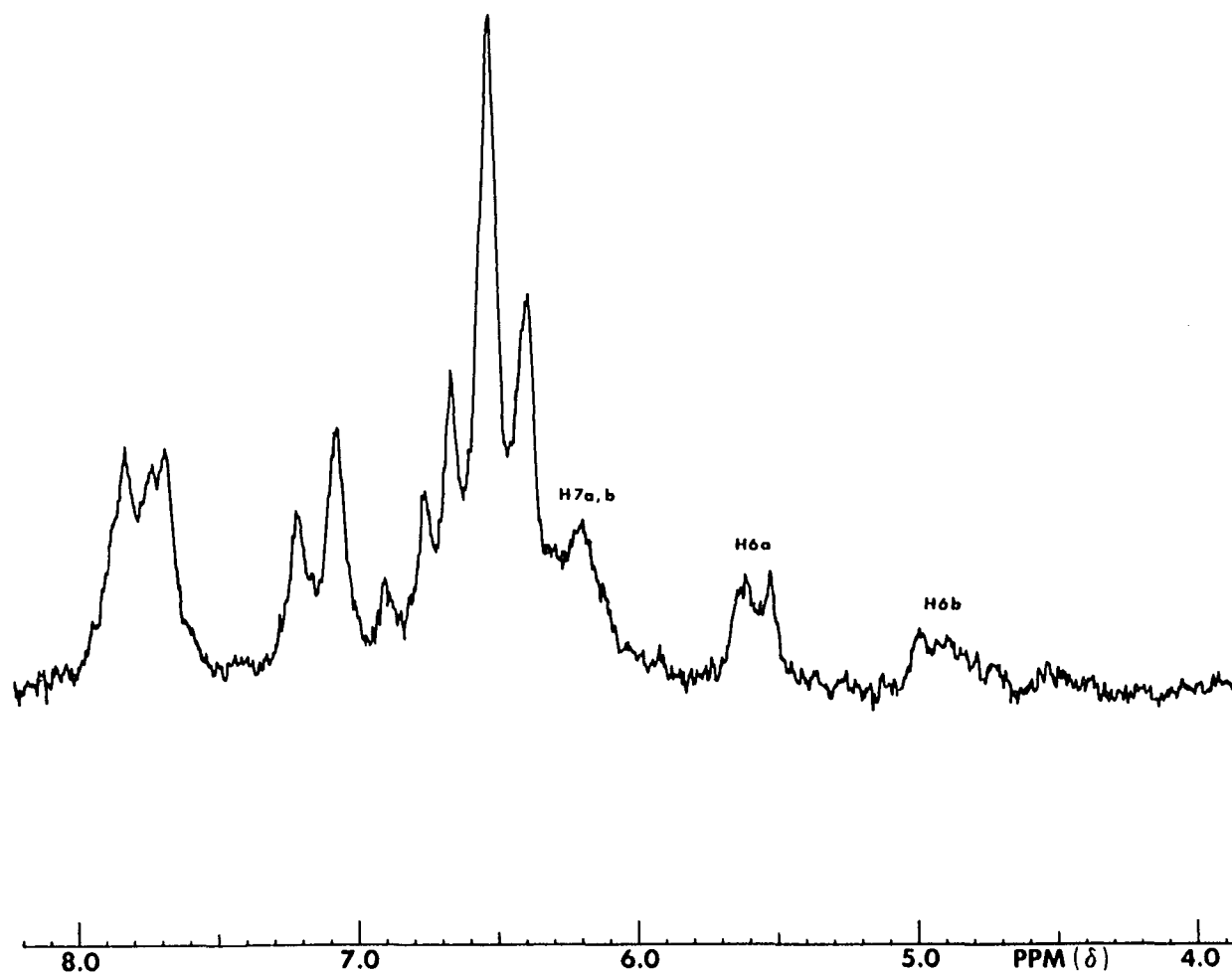


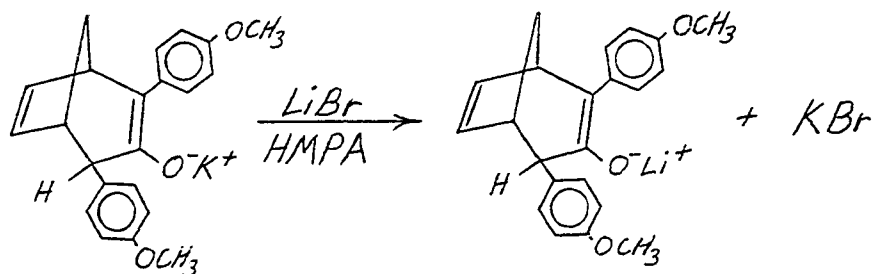
Figure 4. A-60 nmr spectrum of sodium enolate of 2,4-di-p-anisylbicyclo-(3.2.1)oct-6-en-3-one monoanion (36a,b) in HMPA formed by sodium potassium exchange.

spectrum was taken on a Varian XL-100 instrument and is shown in figure 5. The spectrum is identical to that of the potassium salt of anion 36 described earlier and shown in figure 2.

Finally the lithium salt of anion 36 was formed by a metal-metal exchange reaction. Although there was no difference in the nmr's between the potassium and sodium salts of anion 36, it was thought that some difference might be seen in the nmr of an organolithium compound. This difference might be because of the more covalent character of the organolithium compounds compared to those of sodium and potassium.<sup>26</sup>

Therefore the lithium salt of anion 36 was formed in HMPA by adding one equivalent of lithium bromide to the potassium salt as shown in Scheme 7. The nmr spectrum of the organolithium compound

Scheme 7



was taken on a Varian A-60 instrument and was found to be identical to the organopotassium and organosodium compounds (figures 1, 3 and 4). The spectrum is shown in figure 6. The lithium salt of anion 36 was also formed in  $\text{HMPA-d}_{18}$  by a metal-metal exchange

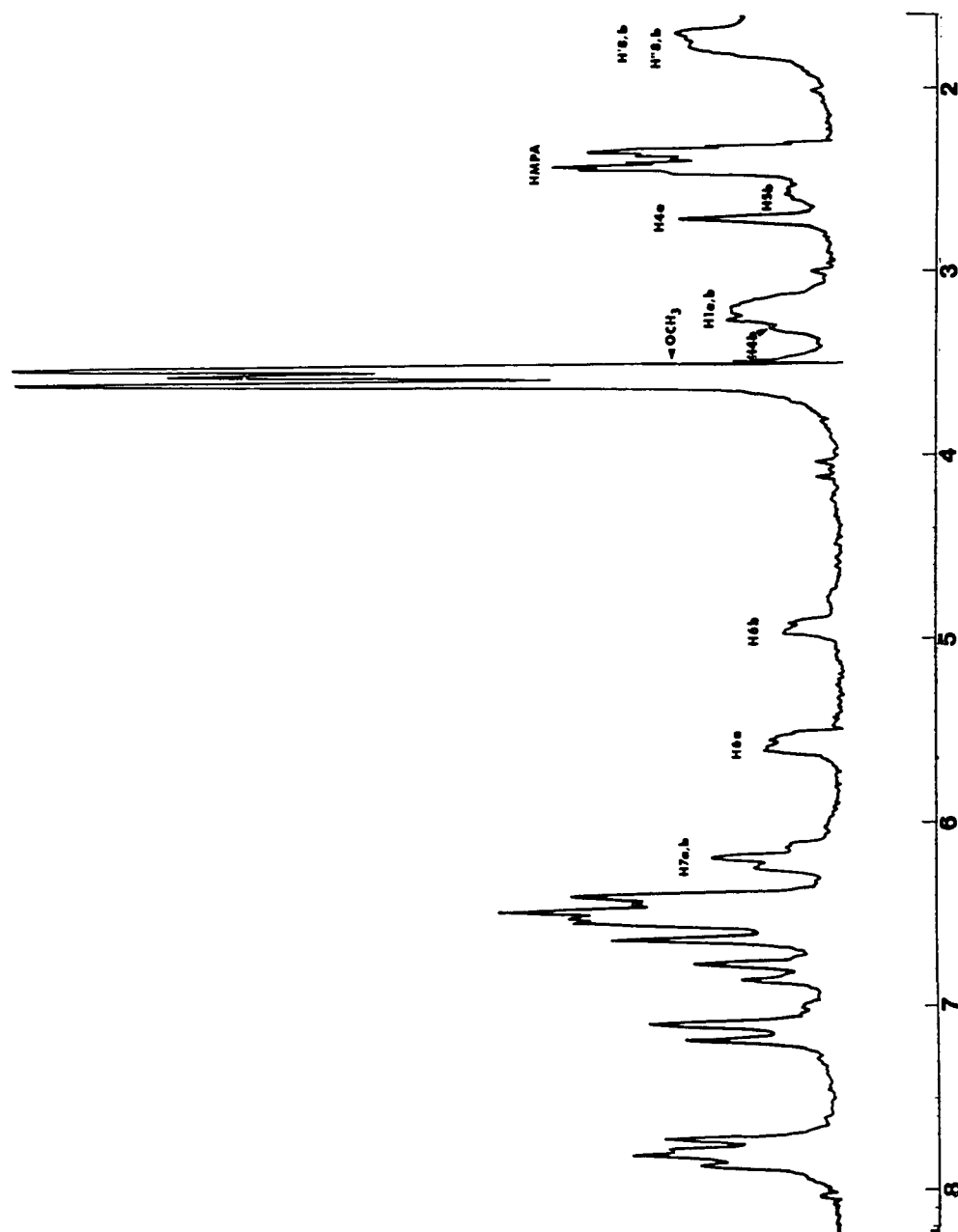


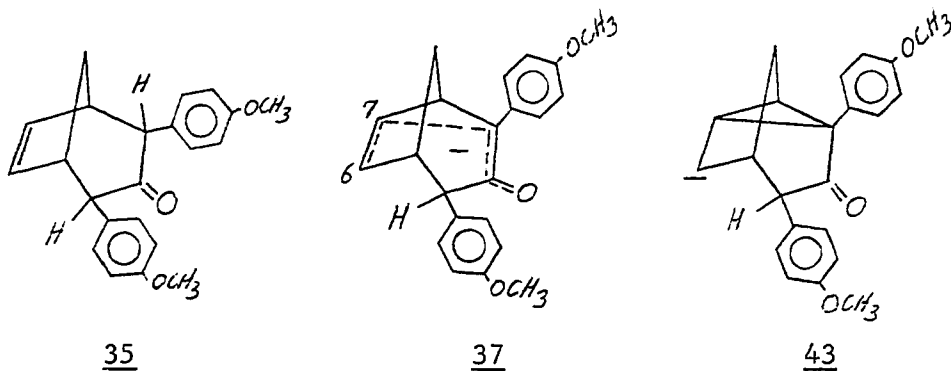
Figure 5. XL-100 spectrum of sodium enolate of 2,4-di-p-anisylbicyclo(3.2.1)-oct-6-en-3-one monoanion (36a,b) in HMPA- $d_{18}$  formed by sodium-potassium exchange.



reaction and its nmr spectrum was recorded on a Varian XL-100 instrument. The spectrum is identical to the potassium and sodium salts formed in HMPA- $d_{18}$  and is shown in figure 7.

From inspection of all earlier discussed nmr spectrums it was concluded that all of the alkali metal salts of enolate anion 36 display the same pattern and therefore different cations do not produce different effects in the anion. Although the lithium salt had been expected to produce a different nmr spectrum because of its more covalent character, it should be noted that the carbon-metal bond becomes more ionic in this case due to the stabilization of the enolate anion<sup>26</sup>.

The question of whether or not homoconjugation had occurred in anion 36 was next examined. To determine if the negative charge at  $C_2$  had interacted with the double bond at  $C_{6,7}$  to give a homoallylic enolate anion such as 37, the chemical shifts of  $H_{6a}$  and  $H_{6b}$  were compared to the chemical shifts of  $H_6$  in the starting ketone 35. If charge delocalization had taken place across the carbon-carbon double bond to form structure 43 the electron density around  $C_6$  should increase causing protons  $H_{6a,b}$  to undergo an upfield shift in the nmr.



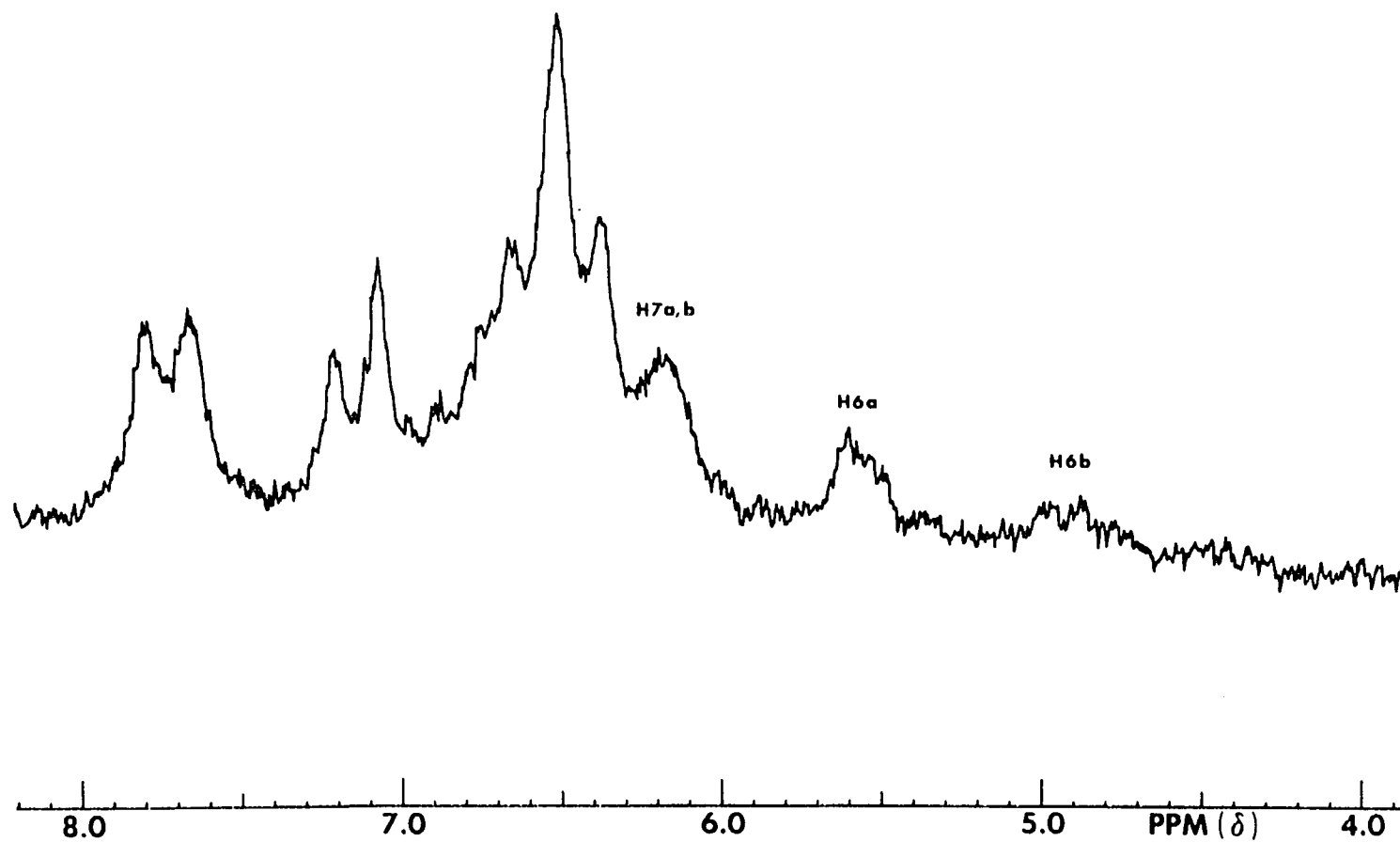


Figure 6. A-60 nmr spectrum of lithium enolate of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one monoanion (36a,b) in HMPA formed by lithium-potassium exchange.

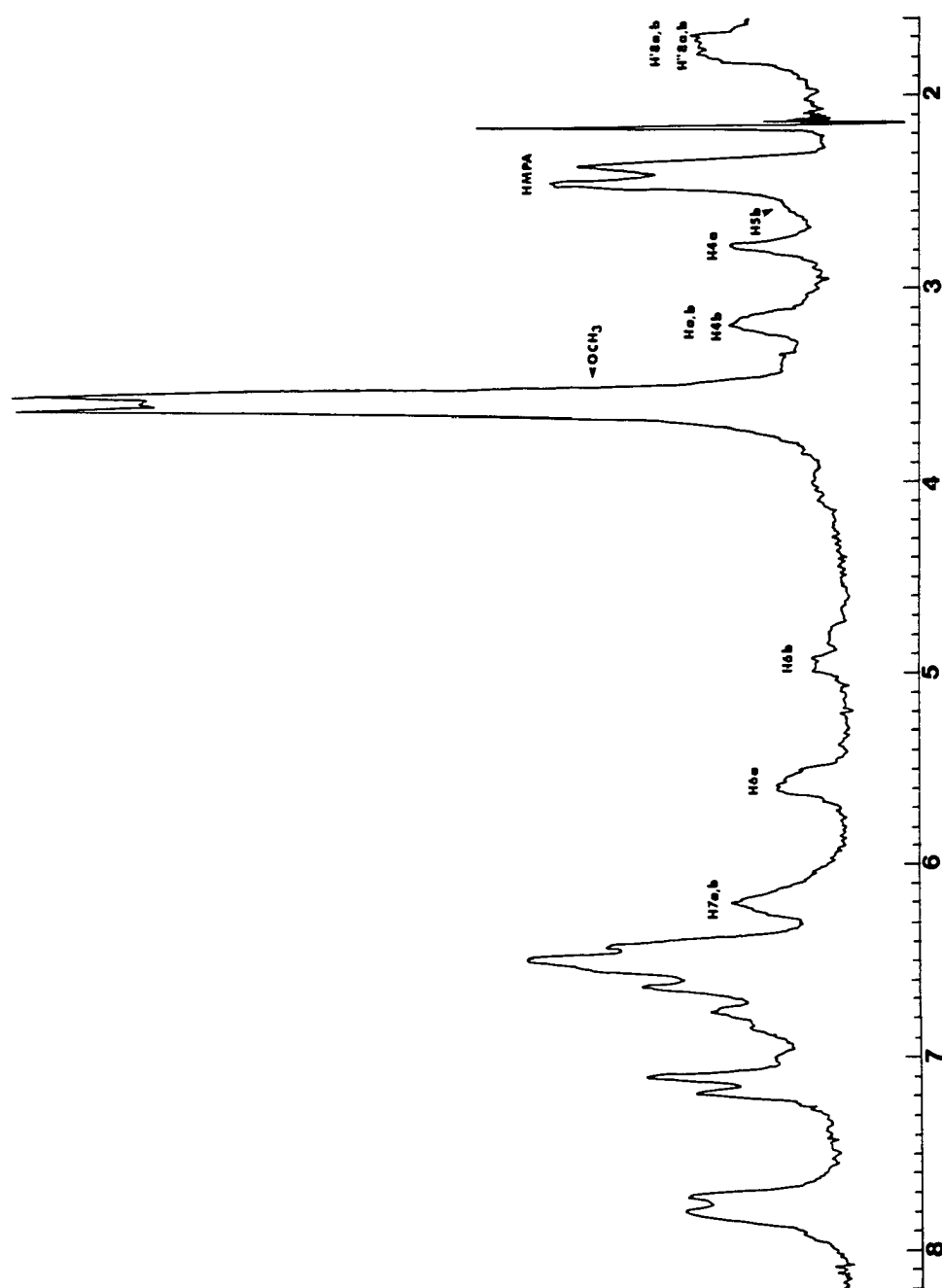
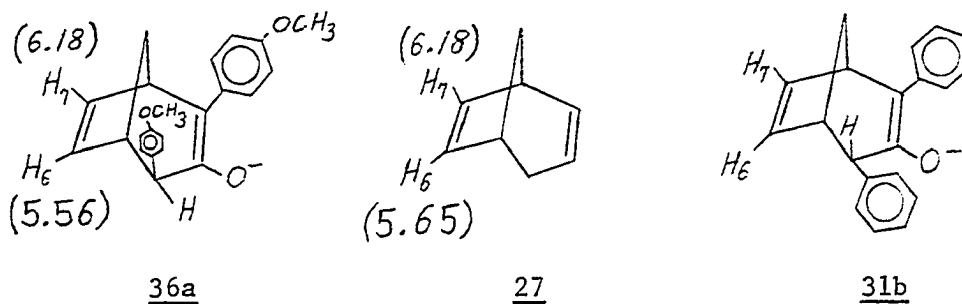


Figure 7. XL-100 nmr spectrum of lithium enolate of 2,4-di-p-anisylbicyclo(3.2.1)-oct-6-en-3-one monoanion (36a,b) in HMPA- $d_{18}$  formed by lithium-potassium exchange.

Examination of the nmr spectrum of enolate monoanion 36 shows that protons  $H_{6a}$  and  $H_{6b}$  had undergone an upfield shift of 0.56 and 1.18 ppm respectively, relative to the starting ketone 35 in HMPA with an external TMS standard. Although these upfield shifts at first seem substantial, it should be pointed out that they are slightly smaller than those of protons  $H_{6a,b}$  in anion 31 which has previously been shown<sup>24</sup> not to homoconjugate. The upfield shift of proton  $H_{6a}$  is quite small and can be accounted for on the basis of anisotropic effects due to the carbon-carbon double bond at  $C_{2,3}$ . The chemical shifts of both vinylic hydrogens  $H_{6a}$  and  $H_{7a}$  are in fact very similar to the closely related system 27<sup>18</sup> as shown in the following figures.

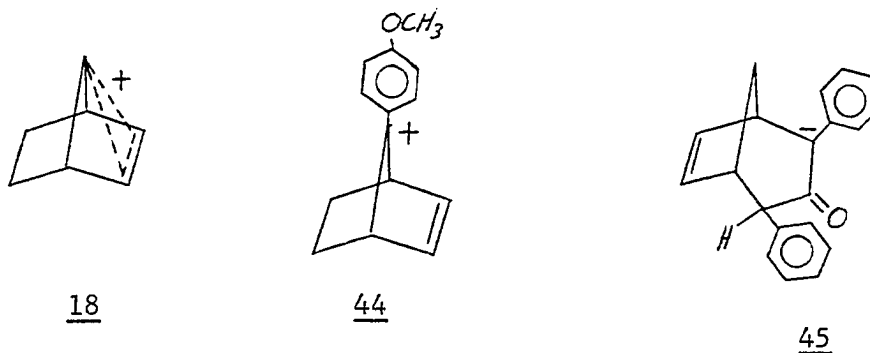


The upfield shift of proton  $H_{6b}$  relative to the starting ketone 35 is much larger than that of  $H_{6a}$ . In this isomer the anisyl group at  $C_4$  is in the endo position and the larger upfield shift of proton  $H_{6b}$  relative to  $H_{6a}$  can be attributed to the shielding ring current effect of the  $C_4$  benzene ring. This shielding ring current effect may also affect proton  $H_{6b}$  of system 31b in the same way.<sup>18</sup>

As stated earlier the H<sub>6a,b</sub> protons of isomers 36a,b have undergone a slightly smaller upfield shift than that of protons H<sub>6a,b</sub> in the closely related isomers 31a,b. In system 31 the vinylic protons H<sub>6a,b</sub> had moved upfield by 0.68 and 1.35 ppm respectively<sup>24</sup>, compared to the 0.56 and 1.18 ppm upfield shift of protons H<sub>6a,b</sub> in system 36. These small differences can be attributed to the two different solvents used, THF for system 31 and HMPA for system 36.

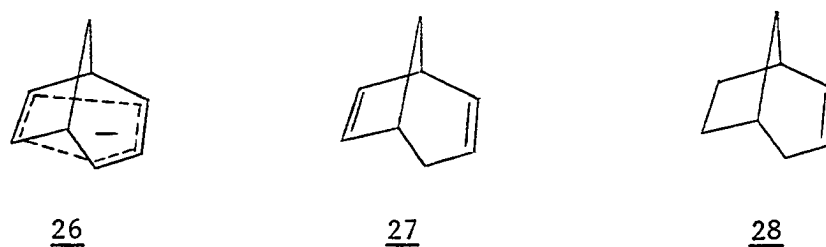
In view of the results and explanations to the small upfield shifts in their nmr spectrum, it is concluded that no homoallylic conjugation has taken place in either of the isomeric enolates 36a,b. The lack of charge delocalization to the C<sub>6,7</sub> carbon-carbon double bond is explained by the fact that the negative charge at C<sub>2</sub> can be stabilized through classical conjugation with both the carbonyl group and with one of the phenyl rings. Therefore classical conjugation has eliminated the tendency for the negative charge at C<sub>2</sub> in system 36 to engage in nonclassical interactions.

Classical stabilization has previously been shown to eliminate nonclassical interactions. Gassman<sup>27</sup> has shown that the tendency of the C<sub>7</sub> positive charge to interact with the carbon-carbon double bond as in structure 18 was eliminated by an anisyl group as in structure 44. Trimitsis and Crowe<sup>20</sup> have also shown that the negative charge at C<sub>2</sub> of enolate anion 31 (as shown in structure 45) does not interact with the carbon-carbon double bond at C<sub>6,7</sub> but instead is stabilized through classical conjugation with the carbonyl group and one of the phenyl rings.

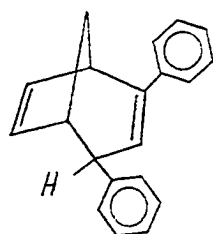
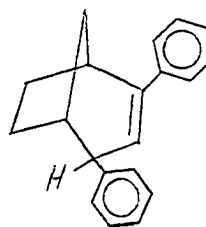


B. The Attempted Formation of  
2,4-Di-p-anisylbicyclo(3.2.1)octa-2,6-diene 46

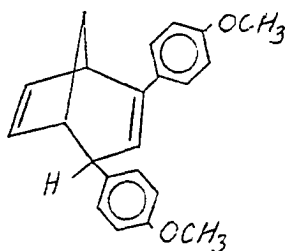
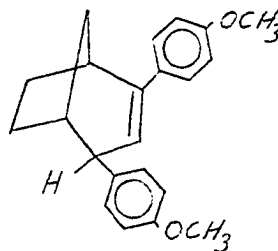
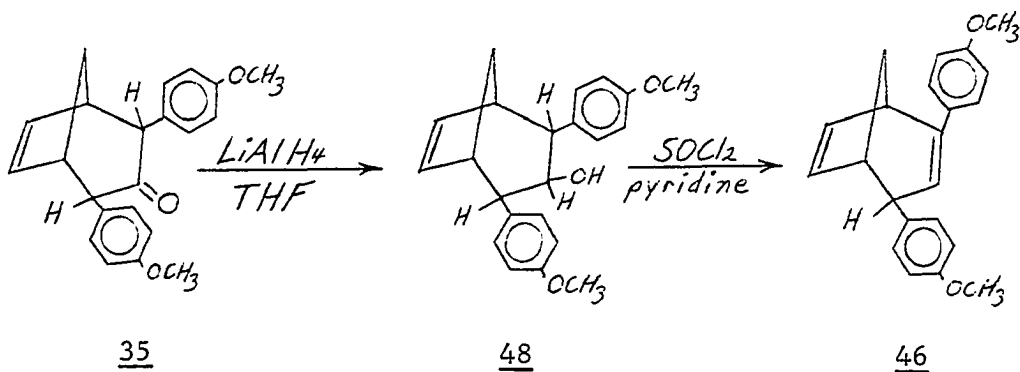
As explained earlier in the historical discussion, compound 27 was found to undergo base catalyzed hydrogen-deuterium exchange at a much faster rate than compound 28. The homoaromatically stabilized carbanion 26 was proposed and finally proven as an intermediate to



27 to explain the large rate difference. Compounds 29 and 30 were then found to undergo base catalyzed hydrogen-deuterium exchange at the same rate.

2930

Another interesting study would be the formation of compounds 46 and 47, and the measurement of their base catalyzed hydrogen-deuterium exchange rates. This study was begun by the synthesis of 46 as shown in Scheme 8.

4647Scheme 8354846

Treatment of the ketone 35 with lithium aluminum hydride in tetrahydrofuran (THF) resulted in the formation of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-ol 48. As expected the ir spectrum of the bicyclic alcohol 48 displayed OH absorption at  $3580\text{ cm}^{-1}$  while the nmr spectrum still displayed vinylic hydrogen absorption at 6.56 ppm.

The desired product, 2,4-di-p-anisylbicyclo(3.2.1)octa-2,6-diene 46 could be obtained by simple dehydration of alcohol 48. The related diene 29 was prepared from its corresponding alcohol by using thionyl chloride in pyridine, therefore this method was used for the attempted preparation of 46. Therefore alcohol 48 was treated with purified thionyl chloride in dry pyridine to yield white crystals in the rotary evaporator which immediately decomposed to a reddish oil. A nmr analysis of the decomposed product showed that it was not the desired diene. Subsequent tries and other purification techniques proved futile and the diene 46 was never isolated.



## IV. EXPERIMENTAL

### A. General

Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes and are not corrected.

Infrared spectra were taken on a Beckman IR-8 infrared spectrophotometer.

Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60 and/or XL-100 spectrometer. All chemical shifts are reported in ppm relative to tetramethylsilane and were measured to the center of a singlet or multiplet. Data are recorded in the order; chemical shift, multiplicity (where s=singlet, d=doublet, t=triplet, q=quartet, and m=multiplet), integration and interpretation. Samples were run in ordinary 5mm nmr tubes.

Mass spectra were taken on a Dupont 21-490B spectrometer.

4-Methoxyphenylacetic acid (99%) was obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin. The sodium hydride was in a 50% mineral oil dispersion and the potassium hydride was 23.4% in mineral oil. Both hydrides were purchased from Alfa Products, Beverly, Massachusetts. Cyclopentadiene was obtained by fractional distillation of 3a,4,7,7a-tetrahydro-4,7-methanoindene and was obtained from Matheson Coleman and Bell, East Rutherford, New Jersey. Hexamethylphosphoric triamide (HMPA) was a gift from Dow Chemical Company, Midland, Michigan. HMPA-d<sub>18</sub> was obtained

from Aldrich Chemical Company, Milwaukee, Wisconsin.

The yields of the products reported are the best yields from each reaction.

## B. Preparation of Starting Material

### 1. Preparation of ethyl-4-methoxyphenylacetate

4-Methoxyphenylacetic acid (100 g, 0.6 moles) was placed in a one liter-one-necked round bottom flask and dissolved in 300 ml (5.1 moles) of 95% ethanol. Concentrated sulfuric acid (10 ml) and a stirring bar were added and the mixture was refluxed with good stirring for 2 hours. The reaction mixture was cooled and poured into a 2 liter separatory funnel containing 400 ml of a 1% aqueous salt solution. The ester was extracted from the mixture with 3x100 ml portions of ether. The extracts were combined, washed with 50 ml of 5% aqueous sodium bicarbonate, 50 ml of water, and then dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtering and the ether was fractionally distilled using a column packed with glass beads. The remaining liquid was distilled under vacuum to give 99.3 g (85%) of ethyl-4-methoxyphenylacetate, bp  $104^{\circ}$  @ 1mm Hg, lit<sup>28</sup> bp  $141-143^{\circ}$  @ 12 mm Hg; nmr ( $\text{CCl}_4$ ) 1.19 (t, 3H,  $\text{CH}_2\text{-CH}_3$ ), 3.43 (s, 2H,  $\text{Ph-CH}_2\text{-C=O}$ ), 3.67 (s, 3H,  $\text{O-CH}_3$ ), 4.05 (q, 2H,  $\text{-CH}_2\text{-CH}_3$ ), 6.92 (d of d, 4H, aromatic).

### 2. Preparation of 1,3-dianisyl-2-propanone

The method used for the preparation of this compound was essentially that of Coan, et al<sup>21</sup>, with certain modifications. A one liter three-necked round bottom flask equipped with a

mechanical stirrer, a condenser, an addition funnel, and under nitrogen atmosphere was charged with 12.5 g (0.52 moles) of magnesium turnings and 300 ml of dry ether. In the addition funnel was placed 64 g (49 ml, 0.52 moles) of 2-bromopropane, and one-third of it was added to the reaction mixture. The reaction was started by gently warming the round bottom flask, and the refluxing was sustained by addition of the 2-bromopropane dropwise. After the addition was complete the reaction mixture was refluxed with a heating mantle for 40 minutes.

After cooling, 100 g (0.52 moles) of ethyl-4-methoxyphenylacetate in 100 ml of dry ether was added dropwise with constant stirring. After the addition was complete the reaction mixture was refluxed for 15 min and allowed to stir for 18 hrs under nitrogen. A 200 ml portion of 10% aqueous sulfuric acid solution was then added carefully and the two layers were separated. The water layer was extracted with 3x50 ml portions of ether. The ether layers were combined and washed with 50 ml of 5% aqueous sodium bicarbonate, 50 ml of water, and dried over anhydrous magnesium sulfate. The ether was fractionally distilled leaving a yellow-red residue of ca 100 ml. This  $\beta$ -ketoester (40) was not further identified or purified.

The residue was placed in a one liter one-necked round bottom flask, 400 ml of glacial acetic acid and 40 ml of 18% aqueous hydrochloric acid were added, and the mixture was refluxed for 5 hours. The acid was then distilled off leaving a red-brown residue which crystallized upon standing. This was recrystallized

from ethanol (95%) to yield 39.3 g (56%) of 1,3-dianisyl-2-propanone, mp  $84^{\circ}$ , lit<sup>21</sup> mp  $86^{\circ}$ ; nmr ( $\text{CDCl}_3$ ) 3.65 (s, 4H,  $\overset{\text{O}}{\underset{\text{||}}{\text{C}}}\text{-CH}_2$ ), 3.78 (s, 6H, O-CH<sub>3</sub>), 6.97 (d of d, 8H, aromatic).

### 3. Preparation of 1,3-dibromo-1,3-dianisyl-2-propanone

This compound was prepared by the method of Breslow, et al<sup>28</sup>, with certain modifications. In a two liter three-necked round bottom flask equipped with a condenser, an addition funnel, and an egg shaped stirring bar was placed 25 g (0.093 moles) of 1,3-di-p-anisyl-2-propanone dissolved in 800 ml of carbon tetrachloride. Bromine (29.8 g, 0.186 moles) in 150 ml of carbon tetrachloride was placed in the addition funnel and added dropwise with good stirring over a period of 3 hrs. After the addition of bromine was complete the reaction mixture was stirred an additional 45 min. A 400 ml portion of aqueous sodium sulfite solution was added and the solution was stirred for 15 min. The gray solid product was filtered, the layers separated, and the carbon tetrachloride layer reduced by evaporation to ca 200 ml by means of a rotary evaporator. The carbon tetrachloride was cooled, any solid product filtered, combined with the earlier solid and recrystallized from acetone to yield 30 g (75%) of 1,3-dibromo-1,3-di-p-anisyl-2-propanone, mp  $155^{\circ}$  (decomposes); ir,  $1700\text{ cm}^{-1}$ ,  $2300\text{ cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ ) 3.82 (s, 6H, -O-CH<sub>3</sub>), 5.78 (s, 2H, -CH-Br), 7.13 (d of d, 8H, aromatic).

Mass spectrum (relative intensity) 428 (1,  $\text{M}^+$ ), 268 (75), 240 (90), 209 (87), 121 (100).

Analysis; Calcd. for  $\text{C}_{17}\text{H}_{16}\text{Br}_2\text{O}_3$ ; C, 47.69; H, 3.77

Found; C, 47.79; H, 3.80

#### 4. Preparation of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one

This compound was prepared by the method of Cookson, et al<sup>23</sup>, with certain modifications as described below. A 2 liter three-necked round bottom flask was charged with 13.5 g (0.032 moles) of 1,3-dibromo-1,3-di-p-anisyl-2-propanone, 120 ml (1.46 moles) of cyclopentadiene, and 600 ml of acetonitrile. The solution was stirred with a magnetic stirring bar while 60 g (0.41 moles) of sodium iodide was added. After the addition was complete the mixture was refluxed for 45 min with good stirring. The brown solution was cooled to room temperature and 300 ml of chloroform was added and the solution was washed with 240 ml of 15% aqueous sodium thiosulfate until the brown color disappeared. The solution was filtered through sintered glass, the layers separated, and the yellow organic layer flash evaporated until only a small amount of solvent was left. The white crystals which appeared were filtered, combined with the earlier solid product, and recrystallized from acetone to give 8.3 g (75%) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one, mp 210<sup>0</sup>; ir, 1690 cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>), 2.30 (m, 2H, C<sub>8</sub>-H<sub>2</sub>), 3.07 (m, 2H, C<sub>1</sub>-H, C<sub>5</sub>-H), 3.81 (s, 8H, O-CH<sub>3</sub>, C<sub>2</sub>-H, C<sub>4</sub>-H), 6.29 (t, 2H, H-C<sub>6</sub>-C<sub>7</sub>-H), 6.99 (d of d, 8H, aromatic).

Mass spectrum (relative intensity) 334 (50, M<sup>+</sup>), 240 (100), 180 (40), 121 (45).

Analysis; Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>3</sub>; C, 79.02; H, 6.63

Found; C, 78.96; H, 6.63

#### C. Attempted Preparation of 2,4-Di-p-anisylbicyclo(3.2.1)octa-2,6-diene

1. Preparation of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-ol

A solution of 4.2 g (0.013 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one in 700 ml of dry THF was introduced dropwise into a 2 liter three-necked round bottom flask containing 1.5 g (0.04 moles) of lithium aluminum hydride in 200 ml of dry THF and equipped with an egg-shaped stirring bar, a reflux condenser connected to a nitrogen tank, and a heating mantle. The mixture was refluxed for 22 hrs under nitrogen with good stirring. The reaction mixture was then cooled and 1.5 ml of water, 1.5 ml of 15% aqueous sodium hydroxide, and 4.5 ml of water were added in that order. The solids were filtered using a Buchner funnel and celite. The filtered solution was dried over anhydrous magnesium sulfate, and was freed of solvent on the flash evaporator to give white flakes which were recrystallized from 95% ethanol to yield 3.1 g (74%) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-ol, mp 123<sup>0</sup>; ir, 3580 cm<sup>-1</sup> (OH); nmr (CDCl<sub>3</sub>) 1.68 (m, 2H, C<sub>8</sub>-H<sub>2</sub>), 2.56 (m, 1H, C<sub>3</sub>-H<sub>OH</sub>), 2.97 (m, 2H, C<sub>1</sub>-H, C<sub>5</sub>-H), 3.35 (m, 2H, C<sub>2</sub>-H, C<sub>4</sub>-H), 3.79 (s, 6H, OCH<sub>3</sub>), 4.39 (m, 1H, C<sub>3</sub>-H<sub>OH</sub>), 6.56 (s, 2H, H-C<sub>6</sub>=C<sub>7</sub>-H), 7.08 (d of d, 8H, aromatic).

Analysis; Calcd. for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>; C, 78.54; H, 7.19

Found; C, 78.78; H, 7.23

2. Attempted preparation of 2,4-di-p-anisylbicyclo(3.2.1)octa-2,6-diene

To a well stirred ice cooled solution of 2 g (0.006 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-ol in 40 ml dry pyridine in a 100 ml three-necked round bottom flask equipped with a condenser connected to a nitrogen tank, and a septum, was added dropwise by

syringe 1.3 g (0.01 moles) of purified thionyl chloride. The temperature was not allowed to rise above 10° during the addition. After the addition the ice bath was removed and the mixture was allowed to stir for 6 hrs. The orange solution was then poured into 150 ml of ice water and extracted with 3x100 ml portions of pentane. The extracts were combined, washed with 50 ml of 3N hydrochloric acid, 50 ml of aqueous saturated sodium bicarbonate, and 50 ml of water, then dried over anhydrous magnesium sulfate. After filtering the clear solution was flash evaporated to a volume of about 15 ml. A white oil appeared which turned yellow and finally yellow-red in the freezer. A nmr analysis showed the presence of a new product which was not identified.

D. Formation and Study of the 2,4-Di-p-anisylbicyclo(3.2.1)oct-6-en-3-one Enolate Monoanion

1. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using potassium hydride in HMPA

This reaction, as well as the following reactions except where otherwise specified were each carried out in 15, 25, or 50 ml three-necked round bottom flasks equipped with a magnetic stirrer, a septum, and a condenser connected to a simple gas collection apparatus consisting of an inverted 250 ml graduated cylinder filled with water. The flask was charged with 0.092 g (0.0023 moles) of potassium hydride, connected to a nitrogen stream and closed to the atmosphere. HMPA (3 ml) dried immediately before use by distilling under vacuum from anhydrous barium oxide was added through the septum by syringe, and the potassium hydride was allowed to

settle to the bottom. Quickly 0.5 g (0.0015 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was added, and the nitrogen stream was replaced by the gas collection apparatus. The stirrer was then turned on and reaction occurred quickly as evidenced by the evolution of gas. After 30 min the color had turned from gray to dark red-brown and 1 eq of hydrogen gas had been collected. About 2 ml of the liquid was then drawn out by means of a syringe and placed in a small test tube with a nitrogen atmosphere through a septum. The test tube was centrifuged for 2 min, then the liquid was transferred into a nmr tube containing a nitrogen atmosphere and an external TMS standard. The nmr spectrum was then recorded on a Varian A-60 instrument. The following resonances were observed; 4.92 (m, H<sub>6b</sub>), 5.58 (m, H<sub>6a</sub>), 6.18 (m, H<sub>7a,b</sub>), and a multiplet at 6.50-8.0 due to the aromatic protons. All resonances below 4.0 ppm were hidden because of the solvent peaks.

## 2. Formation of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate using potassium hydride in HMPA-d<sub>18</sub>

A 15 ml three-necked round bottom flask equipped with a magnetic stirrer, a septum, and a condenser connected to a nitrogen stream was charged with 0.06 g (0.0015 moles) of potassium hydride and flushed with nitrogen. Then 2 ml of HMPA-d<sub>18</sub> was added as described earlier. After the potassium hydride had been allowed to settle 0.334 g (0.001 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was added and the mixture was stirred for 30 min. The liquid was then extracted, centrifuged, and transferred to a nmr tube. The nmr spectrum was obtained on a Varian XL-100 instrument and the following resonances were observed; 1.73 (m, 2H, C<sub>8</sub>-H<sub>2</sub> protons of both isomers), 2.40



(C-H<sub>5a</sub> proton covered by HMPA signal), 2.57 (m,  $\frac{1}{2}$ H, C-H<sub>5b</sub>), 2.70 (s,  $\frac{1}{2}$ H, C-H<sub>4a</sub>), 3.22 (m, 1H, C-H<sub>1a,b</sub>), 3.30 (d,  $\frac{1}{2}$ H, C-H<sub>4b</sub>), 3.56 (three sharp s, 6H, OCH<sub>3</sub>), 4.94 (d of d,  $\frac{1}{2}$ H, C-H<sub>6b</sub>), 5.56 (d of d,  $\frac{1}{2}$ H, C-H<sub>6a</sub>), 6.18 (four sets of d, 1H, C-H<sub>7a,b</sub>), 6.3-8.0 (m, 8H, aromatic).

### 3. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using sodium hydride in HMPA

A 15 ml three-necked round bottom flask equipped with a stirrer, septum, condenser, and gas collection apparatus was charged with 0.144 g (0.006 moles) of sodium hydride. The flask was then connected to nitrogen stream, 6 ml of dry HMPA was added and after the sodium hydride had settled 1 g (0.003 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was added as described earlier. The nitrogen stream was replaced by the gas collection apparatus and the mixture was stirred for 1 hr. After 1 hr the color had turned from gray to dark red-brown and 1 eq of hydrogen gas had been collected. About 2 ml of the liquid was drawn out by syringe, centrifuged, and placed into a nmr tube containing an external TMS standard. The nmr spectrum was recorded on a Varian A-60 instrument and the resonances observed were exactly the same as those described for the potassium salt (part 1. above).

### 4. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using potassium hydride and sodium-potassium exchange in HMPA

A 15 ml three-necked round bottom flask equipped with a magnetic stirrer, a septum, and a condenser connected to a nitrogen tank was charged with 0.06 g (0.0015 moles) of potassium hydride. Then 2 ml of dry HMPA was added and the potassium hydride was allowed to settle

to the bottom, after which time 0.334 g (0.001 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was added and the solution was stirred for 30 min under nitrogen. After 30 min 0.0643 g (0.0011 moles) of sodium chloride was added and the solution was stirred for another 30 min under nitrogen. The solution was then extracted, centrifuged, and placed into a nmr tube containing an external TMS standard. The nmr spectrum was recorded on a Varian A-60 instrument and the resonances were exactly those as described earlier for the potassium and sodium salts (parts 1. and 3.).

5. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using potassium hydride and sodium-potassium exchange in HMPA-d<sub>18</sub>

A 25 ml three-necked round bottom flask was charged with 0.06 g (0.0015 moles) of potassium hydride, and 2 ml of HMPA-d<sub>18</sub> was added as described earlier. After the addition of 0.334 g (0.001 moles) of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one the mixture was stirred for 30 min. After 30 min 0.0643 g (0.0011 moles) of sodium chloride was added, and the solution was stirred an additional 30 min. The liquid was then extracted by syringe, centrifuged, and transferred to a nmr tube containing an external TMS standard. The nmr spectrum was obtained on a Varian XL-100 instrument and is identical to that of the potassium salt in HMPA-d<sub>18</sub> (part 2.).

6. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using potassium hydride and lithium-potassium exchange in HMPA

A 50 ml three-necked round bottom flask was charged with 0.06 g (0.0015 moles) of potassium hydride and 2 ml of HMPA was added as described earlier. After the addition of 0.334 g (0.001 moles) of

2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one the mixture was stirred for 30 min. After 30 min 0.0957 g (0.0011 moles) of lithium bromide was added and the solution was stirred for another 30 min. The liquid was then extracted by syringe, centrifuged, and transferred to a nmr tube as described earlier. The nmr spectrum was obtained on a Varian A-60 instrument and was identical to those spectra of the sodium and potassium salts in HMPA (parts 1., 3., and 4.).

7. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using potassium hydride and lithium-potassium exchange in HMPA-d<sub>18</sub>

A 50 ml three-necked round bottom flask was charged with 0.06 g (0.0015 moles) of potassium hydride and 2 ml of HMPA-d<sub>18</sub> was added as described earlier. A 0.334 g (0.001 moles) portion of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was added and the solution was stirred for 30 min. Lithium bromide (0.0957 g, 0.0011 moles) was then added and the solution stirred an additional 30 min. The liquid was extracted by syringe, centrifuged, and transferred to a nmr tube as described earlier. The nmr spectrum was obtained on a Varian XL-100 instrument and is identical to the spectra of the sodium and potassium salts in HMPA-d<sub>18</sub> (parts 2. and 5.).

8. Formation of the 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one enolate monoanion using potassium hydride and subsequent quenching with water

In a 15 ml three-necked round bottom flask was placed 1 g (0.0025 moles) of potassium hydride and 3 ml of dry HMPA as described earlier. A 0.334 g (0.001 moles) portion of 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was added and stirred for 30 min, after which time one equivalent of hydrogen gas had been collected.

A 5 ml portion of water was then added by syringe through the septum while the reaction mixture was being cooled in an ice bath. After the addition was complete and the reaction mixture was at room temperature the solid was filtered and dried. A nmr analysis showed that 2,4-di-p-anisylbicyclo(3.2.1)oct-6-en-3-one was obtained in quantitative yield.

## V. SUMMARY

2,4-Di-p-anisylbicyclo(3.2.1)oct-6-en-3-one (35) was synthesized and converted to its potassium and sodium enolate monoanions (36a,b) by reaction with metal hydrides in HMPA. The nmr spectra of both the potassium and sodium enolate anions looked identical. 2,4-Di-p-anisylbicyclo(3.2.1)oct-6-en-3-one (35) was then converted to its sodium and lithium enolate monoanions by reacting the potassium enolate with sodium chloride and lithium bromide respectively, in HMPA. The nmr spectrum of the sodium and lithium enolates formed in this manner also looked identical to each other and to the enolates formed earlier. 2,4-Di-p-anisylbicyclo(3.2.1)oct-6-en-3-one (35) was then converted to its potassium enolate with potassium hydride, its sodium enolate by reacting a potassium enolate with sodium chloride, and its lithium enolate by reacting a potassium enolate with lithium bromide all in HMPA-d<sub>18</sub>. These nmr spectra also exhibited identical patterns.

It was concluded that the alkaline earth metal cation had no effect on the organic anion.

It was also shown that there was no interaction between the negative charge at C<sub>2</sub>, on enolate monoanion 36, and the olefinic group at C<sub>6,7</sub>. Therefore it was concluded that classical stabilization of the charge at C<sub>2</sub> eliminated the possibility that it might engage in nonclassical interactions.

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