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THE FORMATION AND STUDY
OF CERTAIN BICYCLIC ENOLATE
MONOANIONS AND DIANIONS

by

Ernest William Crowe

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
August 1972

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Ernest William Crowe

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I. INTRODUCTION

It has been known for many years that negatively charged intermediates, i.e., carbanions, can be stabilized by certain unsaturated substituents such as the vinyl, ethynyl, and aryl groups when the latter are directly attached to the carbon bearing the charge.

As a result of very recent studies it became apparent that under conditions of favorable geometry certain allylic anions could also be stabilized by an olefinic group even when the latter is not directly attached to the negatively charged carbon.

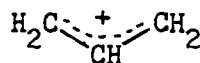
The present investigation was initiated in order to examine whether carbanions stabilized by functional groups more effective than a carbon-carbon double bond would also be subject to long-range stabilization effects. More specifically we wished to investigate the extent to which negative charge in the 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one enolate monoanion (26) and dianion (28) would interact with the olefinic group at C_{6,7}.

II. HISTORICAL

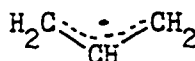
It has long been known that carbanions¹, carbonium ions², and free radicals³ can be stabilized by certain unsaturated substituents such as the vinyl, ethynyl, and aryl groups; and that this stabilization is the result of interaction of the p-orbitals bearing the charge or the unpaired electron with the p-orbitals of the adjacent unsaturated group. This is graphically represented by structures 1, 2, and 3, utilizing the vinyl group as an example.



1

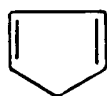


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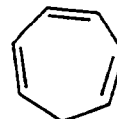
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In addition to the allylic-type stabilization described above, charged species may also be stabilized by means of aromaticity, if the charge is part of a completely conjugated monocyclic hydrocarbon with the sum of the π -electrons in the system complying



4

pKa=15



5

pKa=36

with Huckel's $4n+2$ rule.^{4,5} For example, the enormous difference (21 pKa units) between the acidity of cyclopentadiene^{6a,b} (4) and cycloheptatriene⁷ (5), has been attributed to the fact that deprotonation of the former hydrocarbon leads to the cyclopentadienyl anion 6, a six π -electron aromatic system.

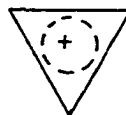


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Similarly, the unusually high stability of such systems as the tropylium ion⁸ 7, and the cyclopropenyl cation^{9a,b} 8, is likewise thought to be due to their favorable number of π -electrons leading to stabilization through resonance.



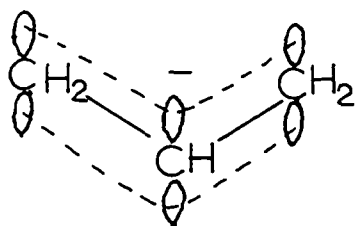
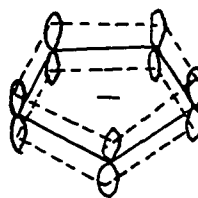
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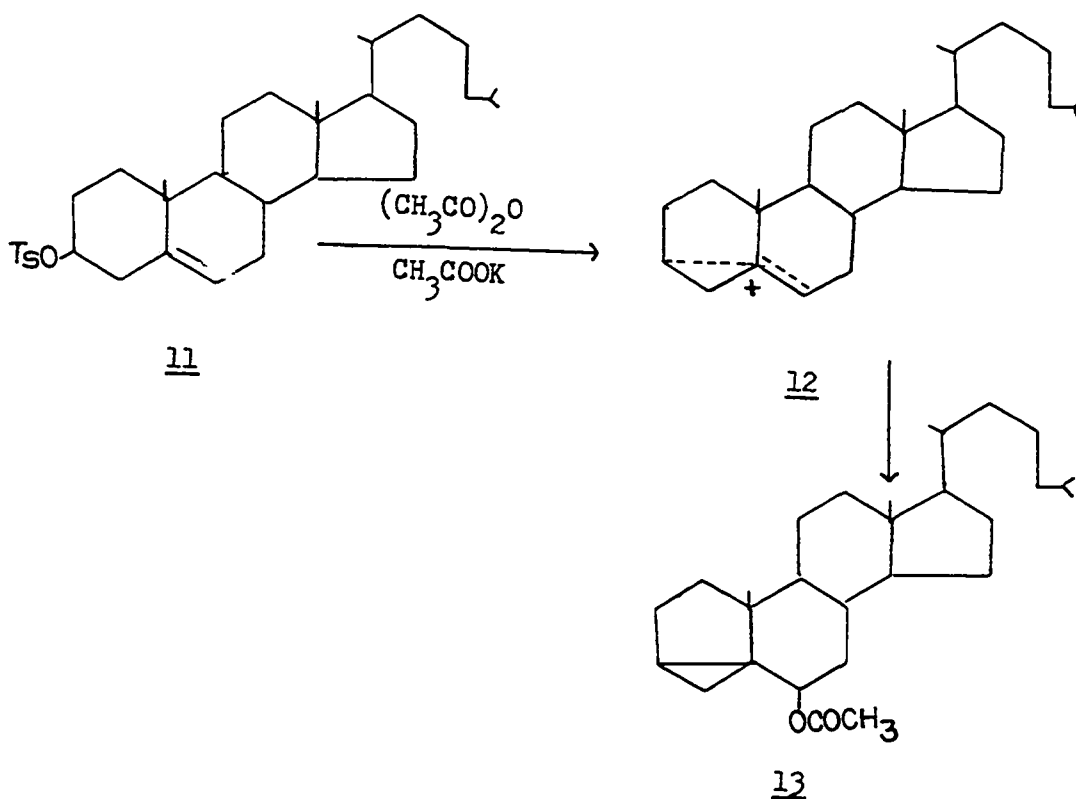
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It should be emphasized that in all of the above cases, delocalization of charge occurred by way of p-orbitals on adjacent carbon atoms, between which there is an additional σ -bond, as exemplified by structures 9 and 10, for the allylic and cyclopentadienyl anions.

As a result of extensive studies during the last forty years by a number of workers^{10a-e}, but especially by Winstein and his group¹¹,

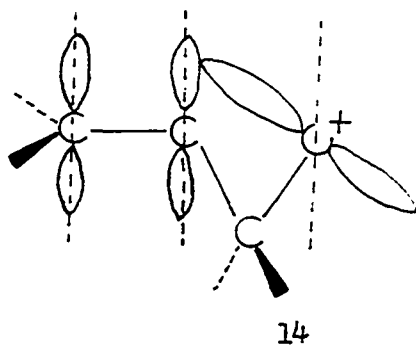
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it became apparent that under conditions of favorable geometry, carbonium ions and carbanions could conjugate and therefore, be stabilized by certain unsaturated groups, even when the latter were not directly attached to the carbon bearing the charge. The first, and by now classic, example¹² of this type of interaction was that of the cholesteryl carbonium ion 12, obtained from cholesteryl p-toluene-sulfonate 11, as shown below. Reaction of carbonium ion 12 with acetic anhydride led to the rearranged acetate 13.



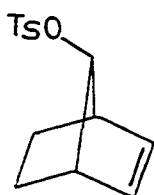
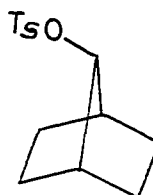
By analogy to allylic carbonium ions and allylic conjugation, Winstein¹³ termed intermediate 12 a homoallylic cation, and the interaction of the positive charge with the C_{5,6} olefinic group homoconjugation. The "homo" designation was used in order to emphasize that carbonium ion 12 may be regarded as a homolog of the more familiar allylic carbonium ion 2.

The most important difference between allylic and homoallylic conjugation is that while in the former case maximum conjugation occurs only when the p-orbital bearing the charge is parallel to the p-orbitals of the olefinic group (Structure 9), in the latter case interaction is at its maximum when the orbital bearing the charge is disposed perpendicularly to the orbitals of the carbon-carbon double bond¹³, as shown in structure 14.

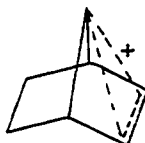


With certain suitably chosen hydrocarbons, homoconjugation was found to lead to cyclic delocalization^{14a-c} similar to that observed in resonance stabilized species such as the cyclopentadienyl anion 6 and the cyclopropenyl cation 8. For example, the tremendous acceleration (10^{11}) in the solvolysis rate of anti-norbornen-7-yl toluene-p-sulfonate (15) compared to its saturated analog 16, was

B

1516

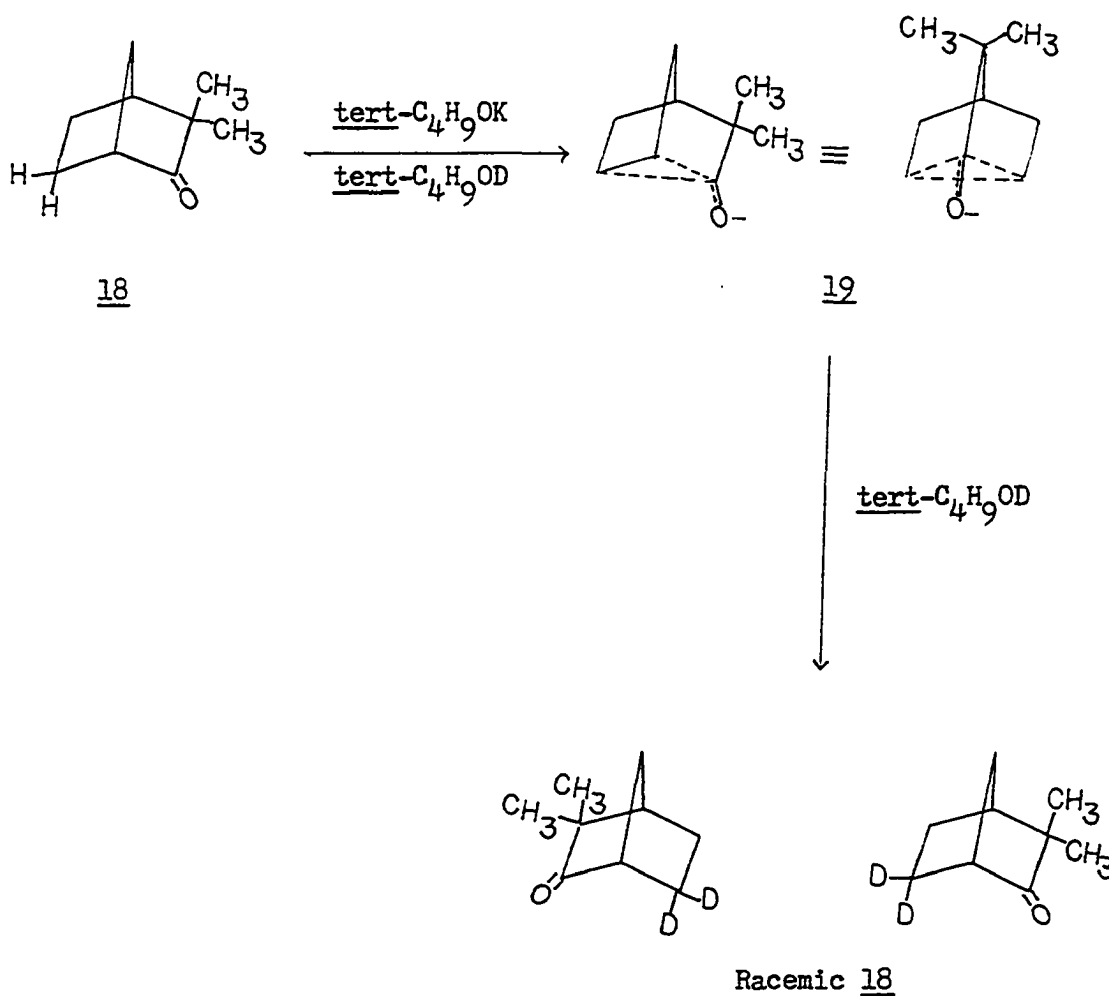
attributed by Winstein and his coworkers^{15a-c} to the interaction of the developing positive charge with the C_{5,6} olefinic group, leading to the cyclically delocalized intermediate 17.

17

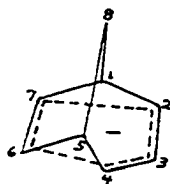
By analogy to the phenomenon of aromaticity, the above delocalization was called homoaromaticity¹¹, and carbonium ion 17 was considered to be a homoaromatic analog¹¹ of the aromatic cyclopropenyl cation 8.

The possibility of homoconjugation and/or homoaromaticity in systems bearing a negative charge, i.e., carbanions, has not been studied until very recently. The first authentic example of homoconjugation involving carbanions was reported in 1962 by Nickon and

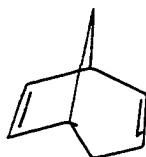
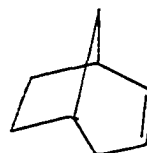
Lambert.¹⁶ They observed that when optically active camphenilone 18 was treated with potassium-tert-butoxide in tert-butyl alcohol-O-d at 185°, the system underwent hydrogen-deuterium exchange (at C₆) and racemization at about the same rate. These results were explained on the basis of a symmetrical homoenolate anion such as 19.



The homoaromatically stabilized carbanionic intermediate 20, was proposed by Brown and his group¹⁷ in 1965, in order to explain the unusually high ($10^{4.5}$) acceleration in the rate of base catalyzed

20

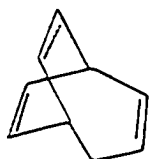
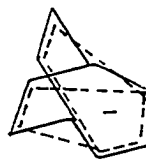
hydrogen-deuterium exchange at C₄ of bicyclo[3.2.1]oct-2,6-diene (21) compared to the rate of exchange of the allylic hydrogens of bicyclo[3.2.1]oct-2-ene (22) or cyclohexene.

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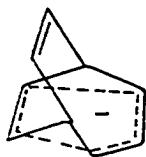
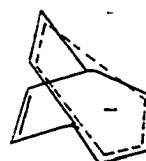
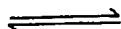
Winstein¹⁸ was subsequently able to generate the anion 20 in sufficiently large quantities to study its nuclear magnetic resonance (nmr) spectrum. He observed that vinylic protons H₆ and H₇ of the monoanion had undergone a substantial upfield shift (2.3 ppm) relative to the starting diene 21, clearly establishing that delocalization of charge to the olefinic bond at C_{6,7} had indeed taken place.

Very recently^{19a-c}, the monoanions of a number of systems closely related to bicyclic diene 21 were generated and studied kinetically and/or spectroscopically. Thus, bicyclo[3.2.1]nona-2,6,8-

triene (23) was converted to its monoanion 24, whose nmr spectrum clearly showed that charge delocalization occurred across both vinylic bridges.

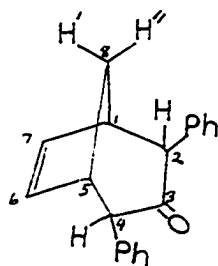
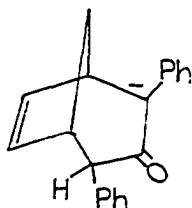
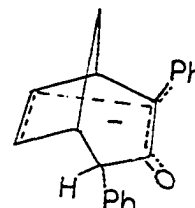
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The question of whether carbanion 24 existed as a symmetrical species with delocalization occurring simultaneously to both vinylic bridges (as implied by structure 24) or whether it was undergoing a rapid (on the nmr time scale) bridge flipping (24a \rightleftharpoons 24b) has not been adequately answered.

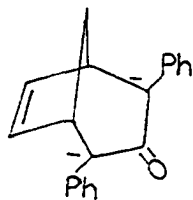
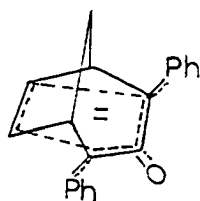
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The literature review presented above shows that all of the carbanions studied which displayed homoconjugation or homoaromaticity were either completely unstabilized (camphenilone 18), or

stabilized by an olefinic group (systems 20 and 24). The present study was initiated in order to investigate to what extent carbanions stabilized by functional groups, more effective than a carbon-carbon double bond, would undergo homoconjugation and/or homoaromaticity. 2,4-Diphenyl-bicyclo[3.2.1]oct-6-en-3-one (25) was recommended as an ideal substrate for the present study, because

252627

of the following reasons: (a) Compound 25 could be easily prepared by known methods.²⁰ (b) Its geometry was closely related to that of bicyclo[3.2.1]octa-2,6-diene (21), and therefore, interaction of the negative charge at C₂ in its monoanion 26 with the β -olefinic group to give a homoconjugatively stabilized enolate such as 27, was expected to be quite possible. (c) While interaction of the negative charge at the α -position in monoanion 26 with the olefinic group may lead to homoconjugation, interaction of the α, α' -charges in the dianion 28 of bicyclic ketone 25, is anticipated to afford the six π -electron homoaromatic intermediate 29, a homolog of the cyclopentenone dianion 30.

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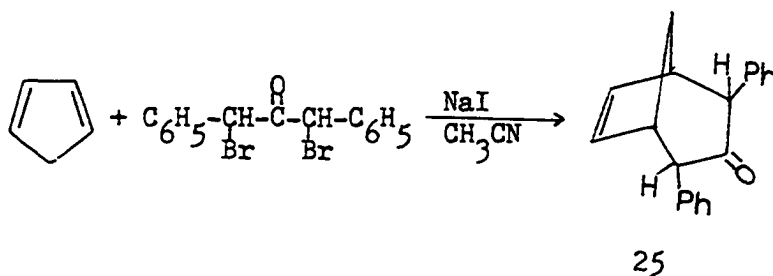
Thus, it can be clearly seen that substrate 25 can adequately serve as a model compound for the study of both homoconjugation and homoaromaticity in bicyclic ketones.

III. RESULTS AND DISCUSSION

A. The Formation and Study of 2,4-Diphenylbicyclo-[3.2.1]oct-6-en-3-one Monoanion (26)

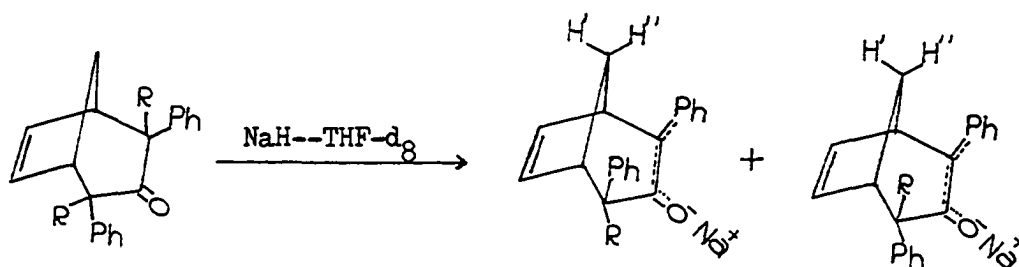
In order to obtain direct information concerning possible long-range interactions in bicyclic enolate monoanion 26, we have generated the sodium salt of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (25) and that of its 2,4-dideuterated analog 31, and have examined their nmr spectra. Bicyclic ketone 25 was prepared essentially by the method of Cookson²⁰, as illustrated in Scheme 1, while dideuterated ketone 31 was obtained from 25 by treatment with sodium deuterioxide in deuterium oxide--dioxane.

Scheme 1



Enolate anions 25a,b and 32a,b were easily formed by treatment of the respective ketones 25 and 31 with sodium hydride in THF-d₈ under equilibrating conditions (Scheme 2). Thus, ketone 25 or 31 was rapidly added to slightly more than one equivalent of sodium hydride in THF at room temperature. This resulted in vigorous

Scheme 2

25 R=H31 R=D26 a R=H32 a R=D26 b R=H32 b R=D

effervescence and the evolution of precisely one equivalent of hydrogen gas, indicating complete monoionization. Subsequent quenching of the enolate solutions with water or deuterium oxide afforded the starting ketone, as shown by ir, nmr, and vapor phase chromatographic (vpc) analysis of the crude reaction mixtures.

The nmr spectra of the anions 26 and 32 were recorded in THF- d_8 as the solvent and are shown in Figures 1 and 2, respectively. In the nmr spectrum of enolate anion 26 (Figure 1), the signal for the endo proton H_{4a} of isomer 26a appears as a sharp singlet at 2.96 ppm, while the signal for the exo proton H_{4b} of isomer 26b, appears as a doublet ($J=5$ Hz) at 3.53 ppm, due to coupling with H_{5b} . Dreiding models indicate that the $H_{5a}-H_{4a}$ dihedral angle is near 80° , while the $H_{5b}-H_{4b}$ dihedral angle is approximately 40° , thus accounting for the lack of spin-spin coupling between H_{4a} and H_{5a} , as compared to the large coupling between H_{4b} and H_{5b} .

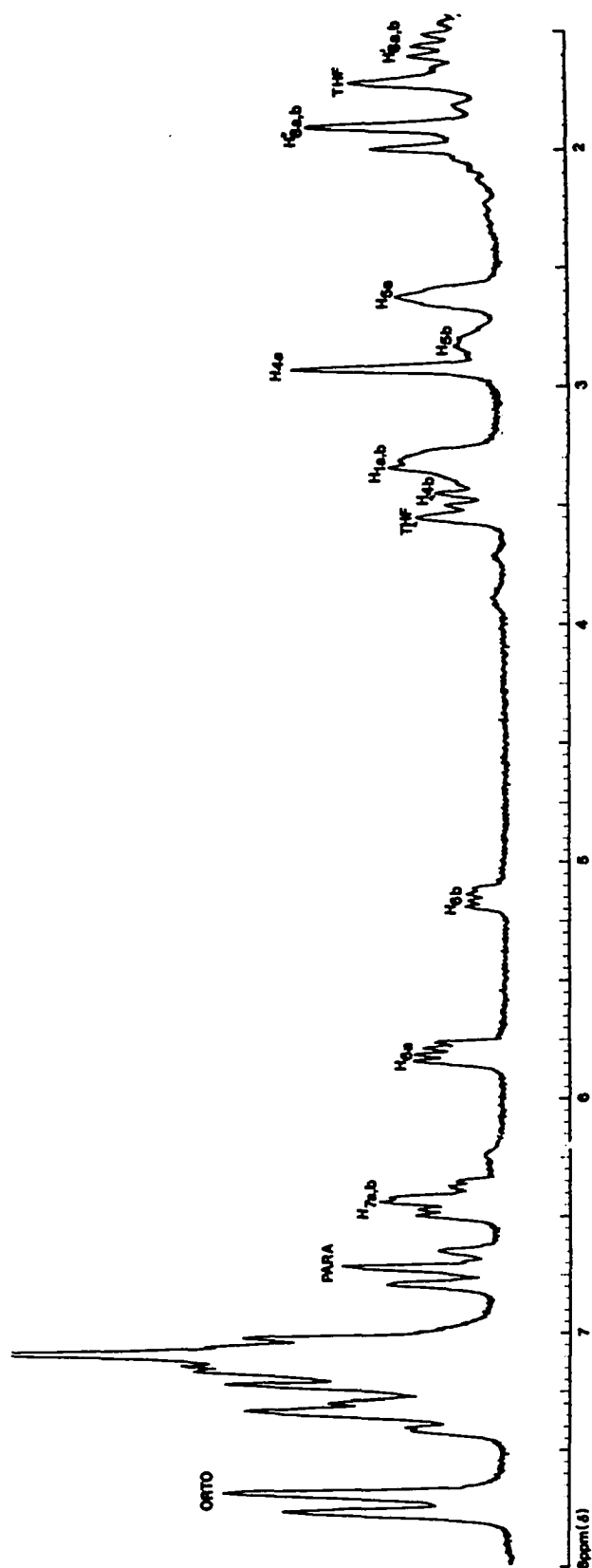
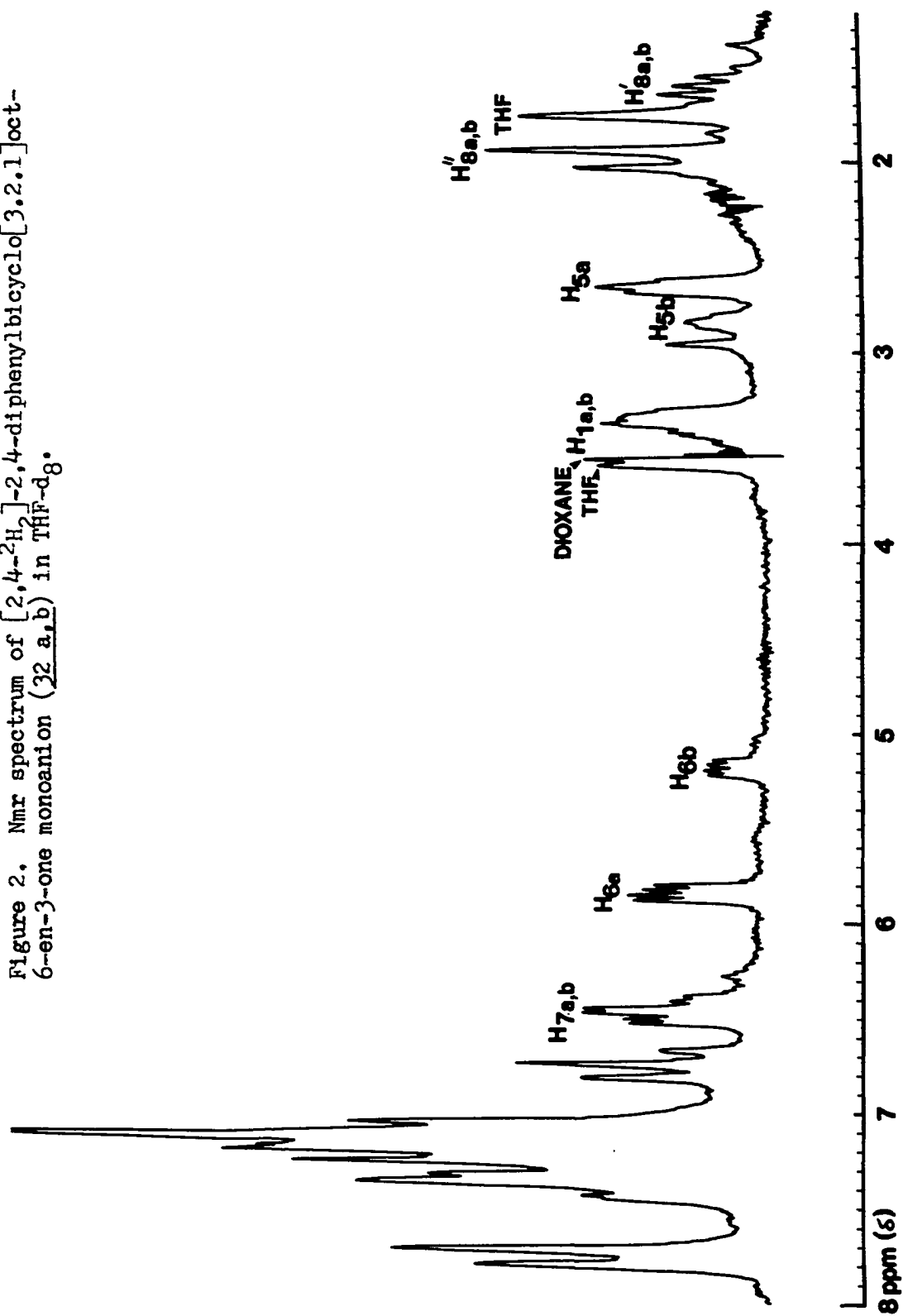


Figure 1. Nmr spectrum of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one monoanion (26 a,b) in THF-d₈.

Figure 2. Nmr spectrum of $[2,4\text{-}^2\text{H}_2]\text{-}2,4\text{-diphenylbicyclo}[3,2,1]\text{oct-6-en-3-one monoanion (32 a,b)}$ in THF-d_8 .



It should be pointed out that the fact that the endo proton H_{4a} was found to absorb upfield from the exo proton H_{4b} is in good agreement with literature reports concerning the assignment of endo-exo protons in a number of closely related bicyclic systems.²¹

As expected, the nmr spectrum of enolate anion 32 (Figure 2), showed only residual signals for protons $H_{4a,b}$. This fact unequivocally established the position of these two protons and helped in the assignment of the remaining protons. Proton H_{5a} appears as a triplet ($J=1.8$ Hz) in both spectra at 2.63 ppm, due to coupling with H_{6a} and H_{8a} . Irradiation at H_{6a} reduced the triplet to a doublet. No coupling is observed between protons H_{5a} and H_{8a} since their dihedral angle is about 85° . The signal for proton H_{5b} , which appears as a broad, unresolved multiplet in the spectrum of enolate 25 (Figure 1), due to coupling with H_{4b} , H_{6b} , and H_{8b} is much better resolved in the spectrum of enolate 31 (Figure 2) and appears as a triplet at 2.82 ppm due to coupling with H_{6b} and H_{8b} . As expected, irradiation at H_{6b} reduced the triplet to a doublet.

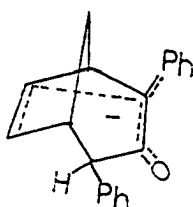
The resonances for the rest of the protons were practically identical in both nmr spectra. Thus, protons $H_{1a,b}$ appear as two overlapping triplets (only poorly resolved) centered at 3.35 ppm. The vinylic protons H_{7a} and H_{7b} occurred each as a pair of doublet (partially overlapping) at 6.50 and 6.42 ppm, respectively, due to coupling with the protons at C_1 ($J_{1,7}=J_{1a,7a}=3$ Hz) and C_6 ($J_{6,7}=J_{6a,7a}=6$ Hz). Irradiation at H_{6a} simplified the left side of the pattern at 6.42-6.50 ppm, while irradiation at H_{6b} simplified the right side of the above pattern. In addition, simultaneous

irradiation at $H_{1a,b}$ reduced the multiplet due to $H_{7a,b}$ to two doublets ($J=6$ Hz) with their inner peaks overlapping, thus appearing as a leaning triplet. Vinylic protons H_{6a} and H_{6b} resonate at 5.84 and 5.17 ppm, respectively, as pairs of doublets arising from coupling with H_{7a} and H_{7b} ($J_{6,7}=J_{6a,7a}=6$ Hz) and H_{5a} and H_{5b} ($J_{5,6}=J_{5a,6a}=3$ Hz). Irradiation at H_{5a} reduced the four-line pattern at 5.84 ppm to just a doublet with the wide coupling ($J=6$ Hz) retained, while irradiation at H_{7a} reduced the above pattern to a doublet with the narrow coupling ($J=3$ Hz) retained. Similar decoupling experiments were satisfactorily performed with H_{5b} and H_{7b} . The signal for protons $H_{8a,b}'$ appear as a multiplet at 1.65 ppm, while that for $H_{8a,b}''$ appear as a doublet at 1.98 ppm.

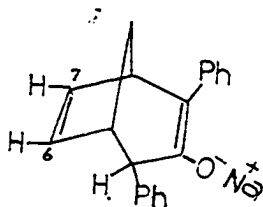
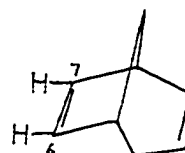
Finally, the aromatic protons appear as a triplet at 6.75 ppm, assigned to the para proton of the phenyl ring at C_2 ; a multiplet centered at 7.30 ppm attributed to the meta protons of the benzene ring at C_2 and all of the protons of the aromatic ring at C_4 ; and a doublet at 7.77 ppm due to the ortho protons of the phenyl group at C_2 . Although the fact that the ortho protons of the phenyl ring at C_2 appear downfield from its meta protons is quite interesting, it is by no means unprecedented. Thus, Freedman²² in 1963 and more recently Okamoto and his coworkers²³, have observed similar trends with benzylic-type carbanions.

The question of homoconjugation in isomeric enolates 26a and 26b was next examined. In order to determine whether the negative charge at C_2 actually interacted with the $C_{6,7}$ olefinic bond to give a homoallylic enolate anion such as 27, the chemical shifts of vinylic protons H_{6a} and H_{6b} were compared with the chemical shift of H_6 in

the starting ketone 25. As mentioned earlier charge delocalization across the carbon-carbon double bond as in 27 should increase the electron density around C_6 , thereby causing protons $H_{6a,b}$ to undergo a significant upfield chemical shift in the nmr. Examination of the nmr spectrum of isomeric enolates 26a and 26b showed that protons H_{6a} and H_{6b} had undergone an upfield shift of 0.68 and 1.35 ppm,

27

respectively, relative to the starting ketone 25 in the THF with an external TMS standard. It can be seen that the upfield shift of H_{6a} is quite small and it is most unlikely that homoconjugation occurred in isomeric enolate 26a. Instead, the small upfield shift of proton H_{6a} can be best accounted for on the basis of anisotropic effects due to the carbon-carbon double bond at $C_{2,3}$ (Structure 33). Indeed the chemical shifts of both vinylic hydrogens H_{6a} and H_{7a} are quite similar to those of $H_{6,7}$ in the closely related system 34²⁴.

3334

On the other hand, the upfield shift of proton H_{6b} relative to the starting ketone 25, is much larger than that of H_{6a} and homoconjugation may be thought to have occurred in this case. However, it should be pointed out that in isomeric enolate 26 the phenyl group at C_4 is in the endo position, and the larger upfield shift of proton H_{6b} relative to H_{6a} may well be due to the shielding ring current effect of the C_4 benzene ring²⁵ (Figure 3).

The above experimental results thus indicate that no homoallylic conjugation occurred in either of the isomeric enolates 26a,b. The lack of charge delocalization at the $C_{6,7}$ carbon-carbon double bond may be explained by taking into account the fact that the negative charge at C_2 can be stabilized through classical conjugation not only with the carbonyl group but also with one of the phenyl rings. Classical stabilization has been previously shown to greatly reduce and sometimes completely eliminate the tendency of a charge to engage in nonclassical interactions. For example, Gassman and his group²⁶ showed that the unusually high tendency of the C_7 positive charge in 35 to interact with the carbon-carbon double bond (Structure 17) was greatly reduced

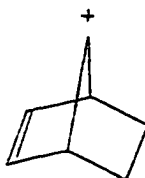
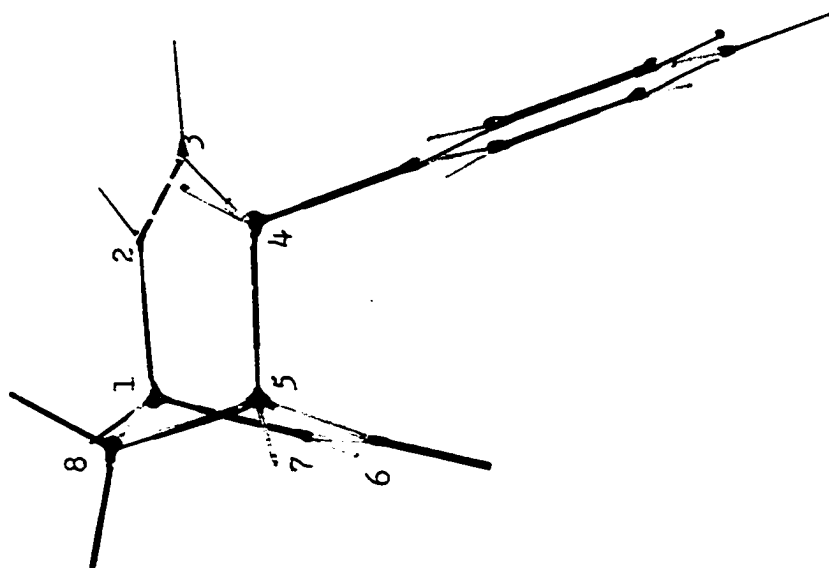
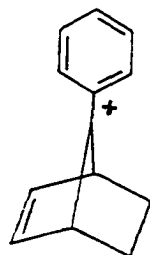
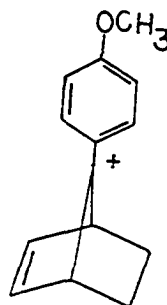


Figure 3. Model exhibiting position of phenyl ring at C_4 so that its ring current can cause a shielding effect on H_{6a} .



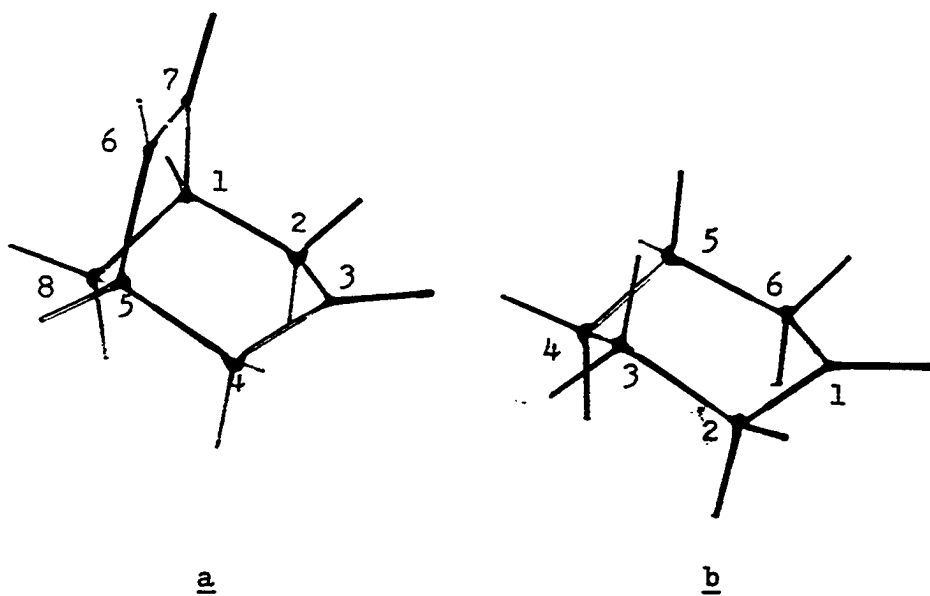
when a phenyl group was placed at C₇ (Structure 36), and completely eliminated by an anisyl group (Structure 37).

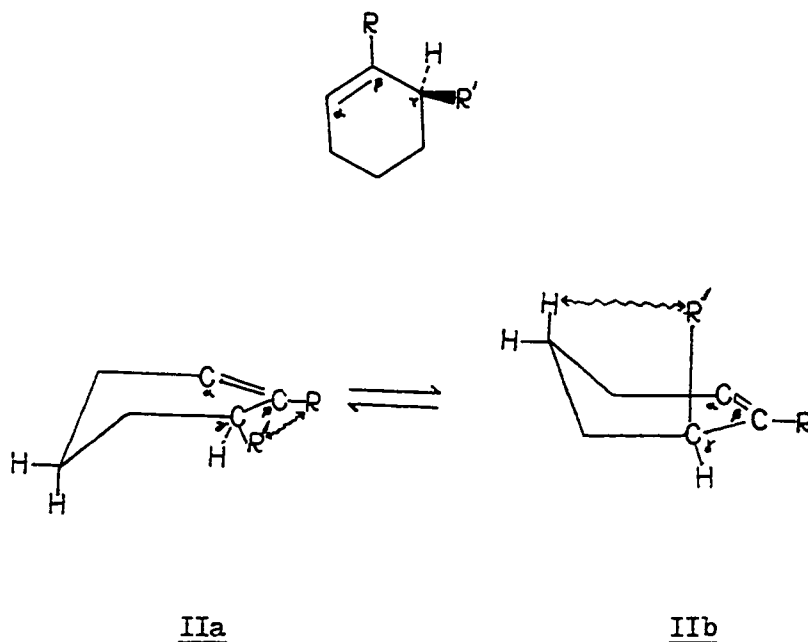
3637

Another conclusion which may be reached by examining the nmr spectrum of isomeric enolates 26a and 26b, is that the two isomers were not produced in equal amounts. Instead, isomer 26a predominated over 26b by a ratio of 2:1. The fact that the two isomeric enolates were not formed in equal amounts is most interesting and deserves further discussion. Two points of particular importance are (a) the question of why enolate 26a predominated over 26b, and (b) whether the isomer distribution is solvent dependent. In addition, since the parent ketone 25 may be regarded as a 2,6-disubstituted cyclohexanone with a vinylic bridge joining carbons C₃ and C₅ (Figure 4), it was of interest to compare and contrast the behavior of the present system with that of simple 2,6-disubstituted cyclohexanones.

In 1965, Johnson and his coworkers²⁷ proposed a theory to account for the conformational preferences of certain 1,6-disubstituted cyclohexene derivatives of the general type II. The following is a statement of the proposal taken from a review by Johnson:²⁸

Figure 4. Models showing comparison between (a) 2,4-diphenylbicyclo-[3.2.1]oct-6-en-3-one (25) and (b) cyclohexanone.





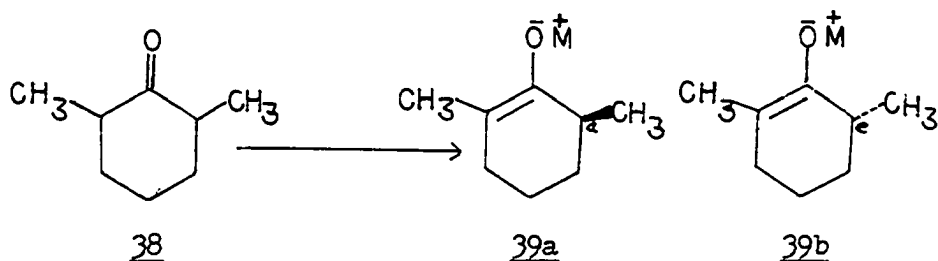
"...in a cyclohexene such as II, if R and R' are moderately large, they will interfere with each other sterically to such an extent that conformer, IIb, having the axial substituent will be the favored form."

The theory was based on the observation that in a system such as II the dihedral angle between RC and R'C is smaller in IIa (R' "equatorial") than in IIb (R' "axial") and therefore, in some cases (R,R' relatively large) the energy of interaction of R with R' in IIa would be greater than the combined energy of interaction of R' with the "axial" hydrogen at C₄ and R with the "equatorial" hydrogen at C₆, in IIb.

Johnson designated this type of interaction as A^(1,2) strain to denote the fact that the groups involved are substituted on the 1 and 2 positions of an allylic system.

One of the most outstanding examples of the manifestation of A^(1,2) strain was found in connection with the conformational composition of certain substituted cyclohexanone enolates (R=O⁻). For

example, it was found that enolization of 2,6-dimethylcyclohexanone (38) affords a mixture of isomeric enolates 39a and 39b, the exact ratio



depending critically on the solvent used²⁸. As shown in Table 1, the bulkier the solvent the greater the amount of isomer 39a, with the methyl group in the axial position. These results were explained on the basis of the interaction of the solvated ion pair O^-M^+ with the methyl group at C_6 . The greater this interaction the greater the amount of 39a.

Table 1²⁸

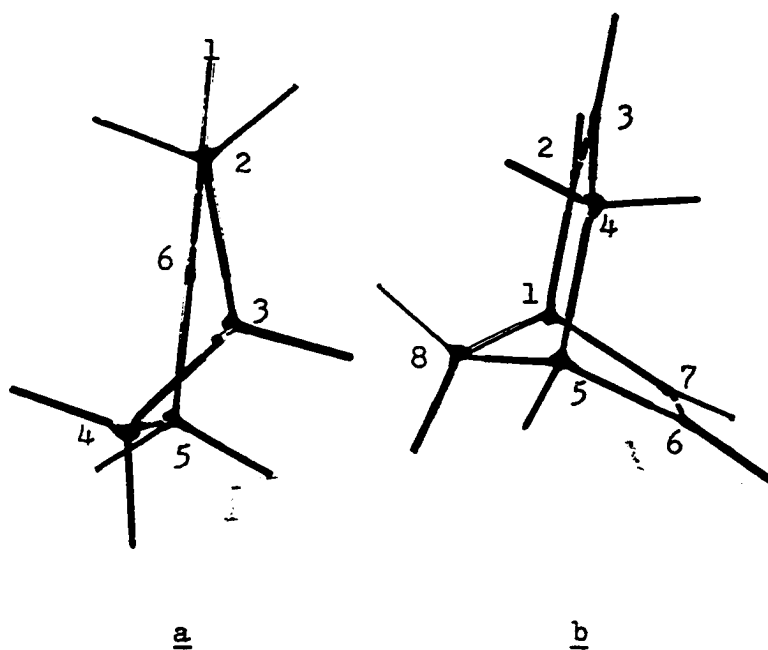
<u>Solvent</u>	<u>Percent of 39a</u>	<u>Percent of 39b</u>
Tetrahydrofuran	36.3	63.7
N,N-Dimethylformamide	38.3	61.7
Benzene	38.4	61.6
Ether	40.9	59.1
Monoglyme	43.8	56.2
Diglyme	45.0	55.0
Dioxane	47.6	52.4
Hexamethylphosphoramide	49.2	50.8
Dimethylformamide	52.2	47.8
Dimethyl sulfoxide	55.1	44.9
Triglyme	61.4	38.6

With these caveat in mind we proceeded to investigate whether the ratio of the isomeric enolates 26a and 26b produced from 2,4-diphenyl-

bicyclo[3.2.1]oct-6-en-3-one (25) was solvent dependent. For this purpose bicyclic ketone 25 was enolized with sodium hydride in dimethyl sulfoxide (DMSO) and hexamethylphosphoramide (HMPA) under conditions identical to those employed when THF was used as a solvent. Most interestingly, nmr examination of the reaction mixtures revealed that, unlike 2,6-dimethylcyclohexanone (38), the ratio of the two isomeric enolates of bicyclic ketone 25 was identical in all three solvents. These observations were accounted for by observing (from Dreiding Stereomodels) that the dihedral angles between the oxygen of the carbonyl group and either the "axial" or "equatorial" bonds at C₄ were equal, thereby, making the interaction of the solvated ion pair O⁻ M⁺ with the phenyl group to be the same regardless of whether the latter is in an axial or equatorial position (Figure 5).

Had the A^(1,2) strain been the only factor controlling the conformational composition of the enolates derived from ketone 25, a 1:1 mixture of the two isomers would be expected to result. As mentioned earlier, however, isomer 26a, with the C₄ phenyl in the "axial" (exo) position, predominated by a ratio of 2:1. It is believed that this particular isomer distribution is a reflection of steric interactions between the ortho hydrogens of the C₄ phenyl ring and the hydrogens at C₆ and C₈. Apparently, the interaction between H₆ and the ortho hydrogen atoms of the benzene ring occupying an equatorial position is more severe than that between proton H₈ and the ortho hydrogen atoms when the ring is in an "axial" position. Dreiding stereomodels do indeed show that the minimum distance between an ortho hydrogen of an "equatorial" (endo) phenyl ring and H₆ is shorter than the minimum

Figure 5. Comparison of dihedral angles between carbonyl group and "axial" or "equatorial" substituents, (a) in cyclohexanone enolate, and (b) in 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one enolate.



distance between H_8'' and an ortho hydrogen of an "axial" (exo) benzene ring (Figures 6 and 7).

Unlike the plethora of studies reported in the literature concerning the isomer distribution of enolates derived from open chain and cyclic ketones, the present study is the first as yet reported dealing with the nature of enolates derived from bicyclic ketones, and our results appear to indicate that subtle differences exist between the former and latter types of ketones.

Figure 6. Model of the 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one monoanion (26a) with phenyl ring at the C_4 position "axial".

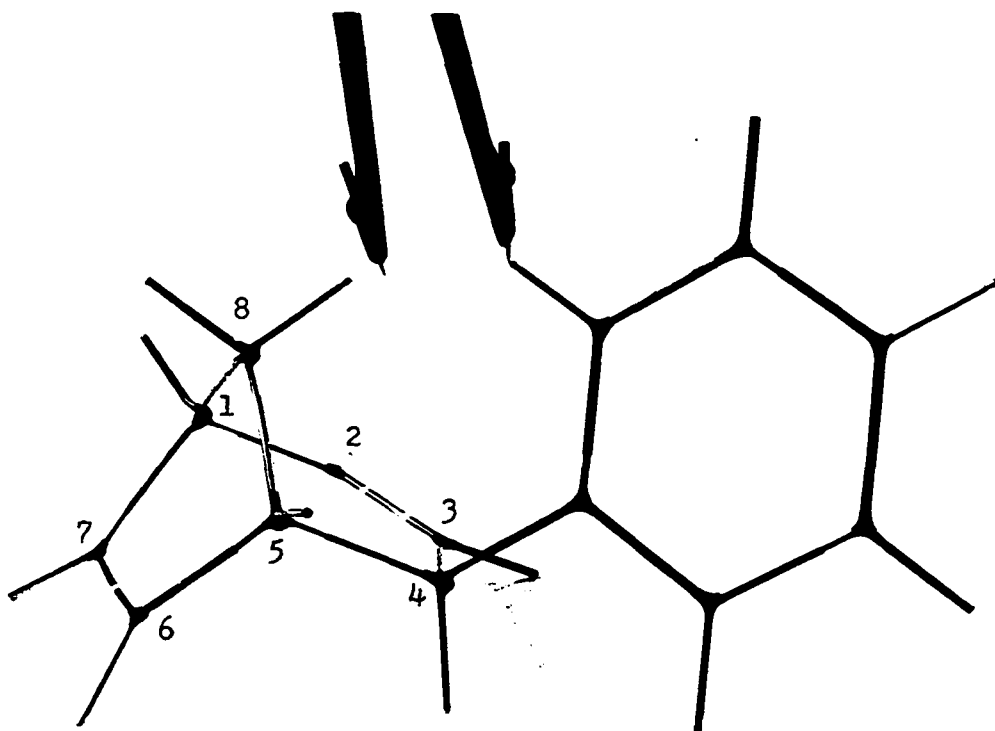
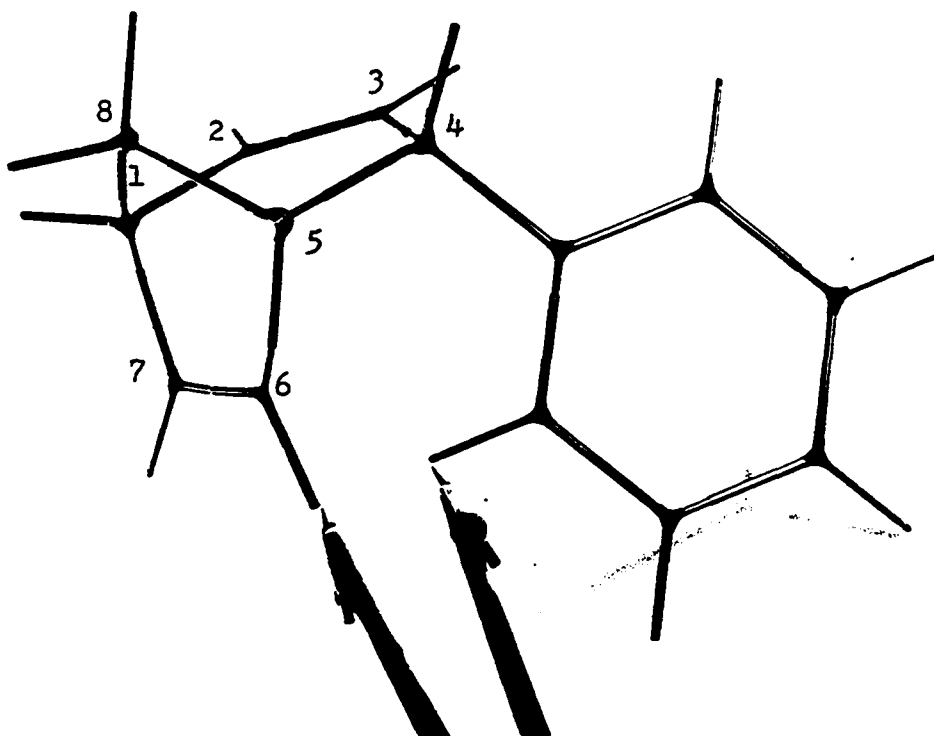


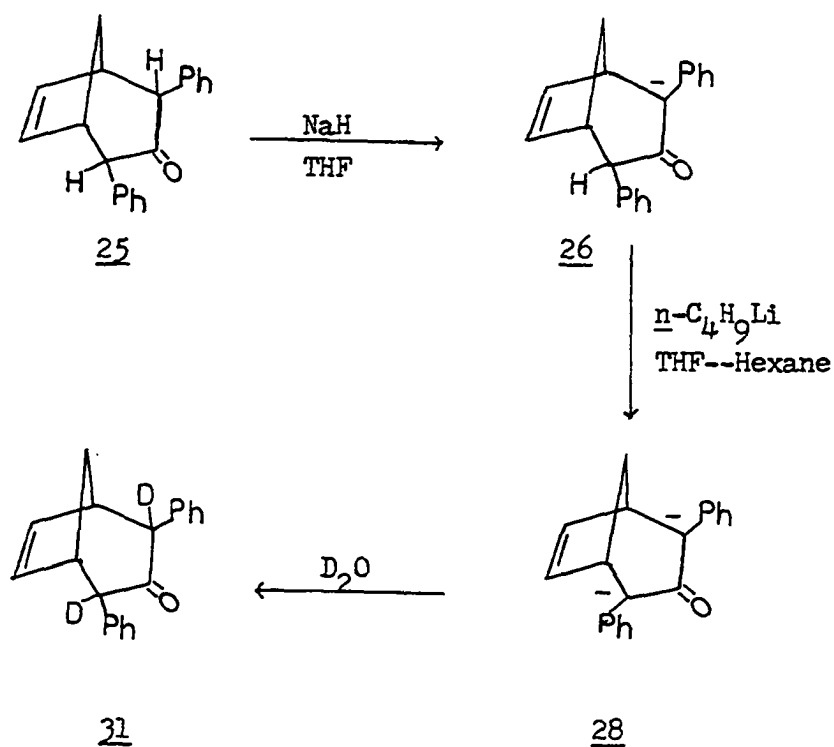
Figure 7. Model of the 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one monoanion (26b) with phenyl ring at C₄ position "equatorial".



B. The Formation and Study of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Dianion (28)

In the previous section the question of long-range interactions in 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one enolates 26a,b was considered. Careful examination of their nmr spectra showed that homoconjugation did not occur in either of these systems. This was attributed to the considerable stabilization rendered to the negative charge by the carbonyl and the phenyl ring at C₂. We next wish to investigate whether long-range interactions can occur in the case of the 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one dianion 28.

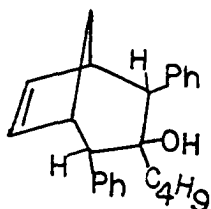
Scheme 3



It was thought that this system would be much more susceptible to long-range interactions than the monoanion for several reasons. First, there is twice as much charge in the dianion as there is in the monoanion. Second, while interaction between the negative charge at C₂ and the olefinic double bond at C_{6,7} in the case of the monoanion would lead only to homoconjugation, long-range interactions in the case of the dianion would lead to cyclic delocalization and homoaromaticity, since a 6 π -electron system would result.

Initial attempts to generate dianion 28 by treating the parent ketone with excess sodium hydride in THF were not successful. Apparently, sodium hydride was not a sufficiently strong base for the diionization of the bicyclic ketone 25.

Although *n*-butyllithium, a base much stronger than sodium hydride, was found to be capable of converting ketone 25 to its dianion, secondary products were also formed, most probably as a result of the addition of the organometallic reagent to the carbonyl to form carbinol 40 after hydrolysis of the salt.



40

Dianion 28 was finally obtained in nearly quantitative yield by means of a two-step process first used by Hauser and Mao²⁹ in 1967. Thus, bicyclic ketone 25 was first treated with one equiva-

lent of sodium hydride in THF to give the monoanion 26 as described earlier and the latter was then reacted with *n*-butyllithium to afford dianion 28 in almost quantitative yield. The sequence of steps leading to the dianion 28 is shown in Scheme 3. The advantage of the two-step process over the direct treatment of the ketone with *n*-butyllithium lies in the fact that initial monoanion formation by means of sodium hydride deactivates the carbonyl, thereby, nullifying its subsequent attack by the organolithium reagent.

Quenching the dianion 28 with deuterium oxide afforded the 2,4-dideuterated ketone 31 in high yield, as shown by vpc, ir, and nmr.

The nmr spectrum of dianion 28 was recorded in THF- d_8 -hexane* on a Varian XL-100 instrument and is displayed in Figure 8.

The most striking difference between the nmr spectrum of the dianion and that of the monoanion is the simplicity of the former compared to the latter. This was expected in view of the completely symmetrical nature of the dianion (Figure 9). The presence of two different cations (sodium and lithium) did not seem to disturb the symmetry of species 28.

As shown in Figure 8, the nmr spectrum of the dianion 28, showed three principal groups of signals. The first group consisted of a doublet ($J=4$ Hz) centered at 3.64 ppm attributed to protons H_1 and H_5 due to coupling with H_8 . Protons H_1 and H_5 were only

*Hexane was introduced into the reaction mixture during the addition of *n*-butyllithium, which was handled as a 1.58 M solution in this solvent.

weakly coupled to H_6 and H_7 as shown by spin-spin decoupling experiments, discussed below.

The second group of signals consisted of a sharp singlet centered at 5.41 ppm attributed to the vinylic protons H_6 and H_7 . Irradiation at the $H_{6,7}$ doublet sharpened the singlet at 5.41 ppm, while irradiation of the singlet resulted in considerable sharpening of the $H_{1,5}$ doublet.

The third group of signals consisted of three different sets of peaks. The first set, a triplet centered at 6.19 ppm, was assigned to the para protons of the two phenyl rings; the second set of peaks was a triplet centered at 7.01 ppm and was assigned to the meta protons of the phenyl rings. Finally, the third set of peaks was a doublet centered at 7.59 ppm and was assigned to the ortho protons of the phenyl rings. The nmr signals corresponding to protons H_8' and H_8'' were obscured by the hexane absorptions and could not be observed.

The most important information obtained from the nmr spectrum of the dianion 42 was the large (1.09 ppm) upfield shift of the vinylic protons $H_{6,7}$ compared to the starting ketone in THF with an external TMS standard. This clearly indicates that charge delocalization to the olefinic carbon-carbon double bond has occurred in this case and that dianion 28 can be best represented by structure 29, which graphically demonstrates the participation of the carbon-carbon double bond in the dispersal of the negative charge, and accentuates its homoaromatic nature.

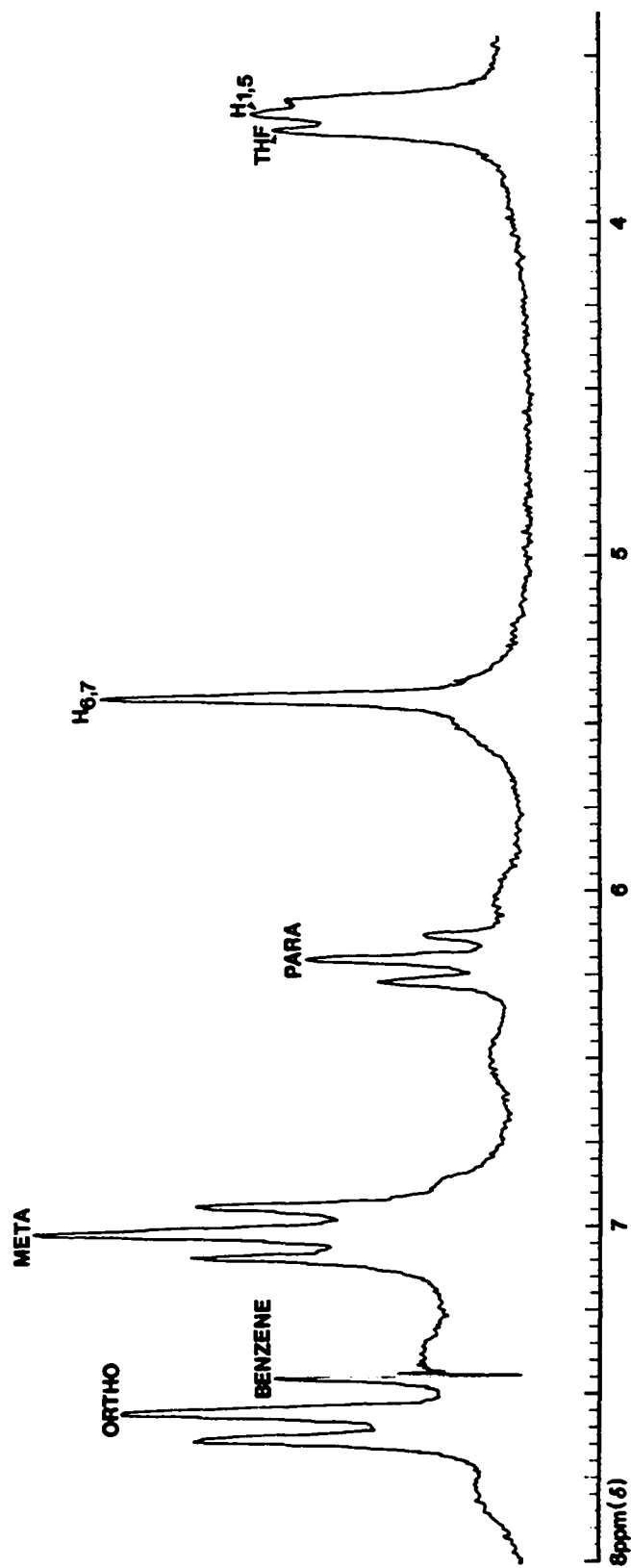
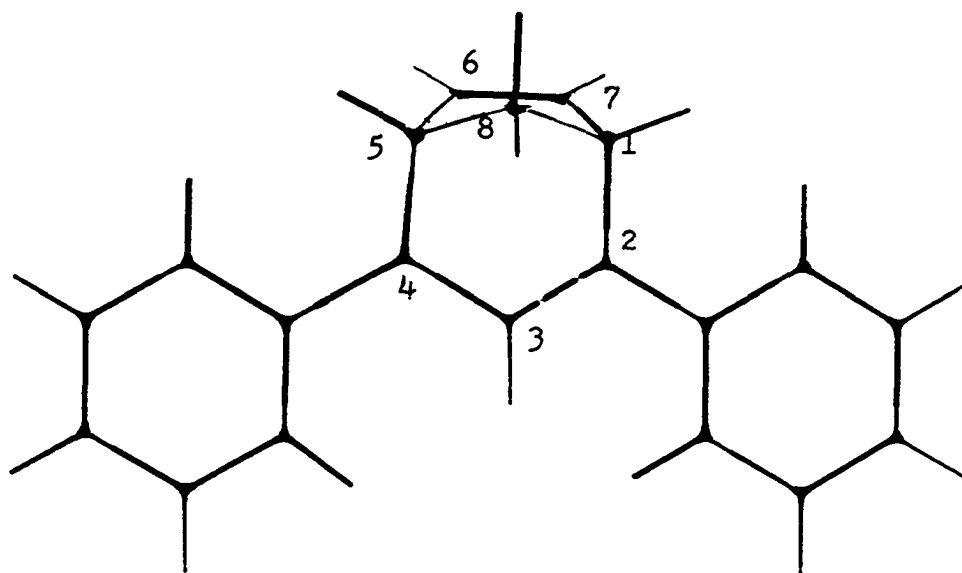
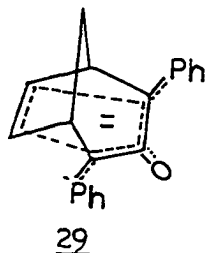


Figure 8. Nmr spectrum of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one dianion (28) in THF-d₈.

Figure 9. Model showing symmetry of the 2,4-diphenylbicyclo[3.2.1]-oct-6-en-3-one dianion (42).





In direct contrast to the large upfield shift experienced by the vinylic protons $H_{6,7}$, the bridgehead protons $H_{1,5}$ of dianion 28 actually moved downfield by 0.37 ppm, relative to the starting ketone 25 in the THF with an external TMS standard. In line with the proposed homoaromatic nature of dianion 29 the downfield shift of protons $H_{1,5}$ can be ascribed to the deshielding ring current effect of the homoaromatic cyclopentenone system which apparently offsets the shielding which protons $H_{1,5}$ are expected to experience due to field effects.³⁰

The fact that deuteration of dianion 28 occurred exclusively at the C_2 and C_4 positions, despite the proposed delocalization of the negative charge at positions C_6 and C_7 is in line with previous reports concerning protonation of homoaromatic carbanion, and it is considered to be due to the fact that positions $C_{2,4}$ are kinetically much more favored than positions $C_{6,7}$.

IV. EXPERIMENTAL

A. General

All melting points were taken on a Thomas Hoover apparatus in open capillary tubes.

Ir spectra for the compounds were recorded on a Beckman IR-8 spectrophotometer.

Nmr spectra were recorded on a Varian Associates Model A-60, HA-100, or XL-100 spectrometer. All chemical shifts are reported in ppm and all coupling constants are in hertz (Hz). Nmr data are recorded in the order: chemical shift, multiplicity (where l=singlet, 2=doublet, 3=triplet, 4=quartet, and m=multiplet), integration, coupling constant, interpretation. Samples were run in ordinary 5 mm nmr tubes.

Gas chromatography was performed on a Varian Aerograph, Series 2700 gas chromatograph equipped with a thermal conductivity detector and 5 ft x 1/4 in SE-30 (silicone gum rubber) columns. The carrier gas was helium.

An IEC International, Size 2, Model K centrifuge was used.

The 1,3-diphenyl-2-propanone was of practical grade and was procured from Eastman Kodak Company, Rochester, New York. The sodium hydride was in a 57% mineral oil dispersion and was a product of Alfa Inorganics, Beverly, Massachusetts. Cyclopentadiene was obtained by fractional distillation of 3 α ,4,7,7 α -tetrahydro-4,7-methanoindene procured from Matheson, Coleman and Bell; East Ruther-

ford, New Jersey. The n-butyllithium was in a 1.58 M solution of hexane and was procured from Foote Mineral Company, Exton, Pennsylvania. THF- d_8 was obtained from Columbia Organic Chemicals Company, Incorporated, Columbia, South Carolina. N,N,N',N' -Tetramethylethylenediamine (TMEDA) was obtained from Eastman Kodak Company, Rochester, New York.

B. Preparation of Starting Materials

1. Preparation of 1,3-dibromo-1,3-diphenyl-2-propanone

This compound was prepared by the method of Cookson,³¹ with certain modifications. Bromine (0.2 mole, 10 ml) was added dropwise over a 1 hr period to a stirred solution of 1,3-diphenyl-2-propanone (0.1 mole, 21 g) in carbon disulfide (100ml). After the addition of bromine was completed the reaction mixture was stirred for a further hour. The reaction mixture was washed with a 15% aqueous sodium thiosulfate solution (100 ml), twice with water (100 ml), dried ($MgSO_4$), and the solvent evaporated under reduced pressure. The product was crystallized from ethanol (95%) and then benzene to yield needles (13g); mp 109-114°C; ir (KBr) 700, 750 and 1715 cm^{-1} ; nmr ($CDCl_3$) 5.69 ppm (2,2H, \underline{H} -CBrCOCBr- \underline{H}), 7.34 ppm (m, 10H, 2 Ph- $\overset{d}{C}$ -Br).

2. Preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (25)

The method used for the preparation of this compound was essentially that of Cookson,²⁰ with certain modifications. 1,3-Dibromo-1,3-diphenyl-2-propanone (0.024 mole, 5 g), sodium iodide (0.17 mole,

25 g), cyclopentadiene (0.61 mole, 50 ml), and acetonitrile (150 ml) were boiled for 15 min. It was important that the sodium iodide be added to the reaction mixture last. Chloroform (100 ml) was added and the reaction mixture was washed with 15% aqueous sodium thiosulfate (100 ml), dried (MgSO_4), and the solvent evaporated under reduced pressure. The product was crystallized from ethanol (95%) or a benzene--petroleum ether solution to give about 4 g of product; mp $149.5^\circ\text{--}151.5^\circ\text{C}$; ir (KBr) 705, 740, 755, and 1700 cm^{-1} ; nmr (CDCl_3) 2.24 ppm (m, 2 H, $\text{C}_8\text{-H}_2$), 3.80 ppm (2, 2 H, $\text{Ph-C}_2\text{-H}$, $\text{Ph-C}_4\text{-H}$), 3.31 ppm (m, 2 H, $\text{-C}_1\text{-H}$ and $\text{-C}_5\text{-H}$) 6.23 ppm (3, 2 H, $\text{H-C}_6=\text{C}_7\text{-H}$), 7.2 ppm (m, 10 H, 2 phenyl rings). The following resonances were found in THF using an external TMS standard: 7.48 ppm (m, 10 H, 2 phenyl rings), 6.52 ppm (3, 2 H, $\text{H-C}_6=\text{C}_7\text{-H}$), 3.36 ppm (m, 2 H, $\text{-C}_1\text{-H}$ and $\text{-C}_5\text{-H}$).

3. Preparation of $[2,4\text{-H}_2]^2\text{-2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one}$ (32)

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (0.0055 mole, 1.5 g), deuterium oxide (20 ml), sodium hydride (0.0006 mole, 0.0144 g), and dioxane (100 ml) were stirred for three days at room temperature in a closed flask. The reaction mixture was extracted with chloroform, dried (MgSO_4), and the solvent evaporated under reduced pressure. The crude product (1.2 g) was dried in vacuo; nmr (CDCl_3) 2.18 ppm (m, 2 H, $\text{C}_8\text{-H}_2$), 2.98 ppm (m, 2 H, $\text{-C}_1\text{-H}$, $\text{-C}_5\text{-H}$), 6.23 ppm (3, 2 H, $\text{H-C}_6=\text{C}_7\text{-H}$), 7.23 ppm (m, 10 H, 2 phenyl rings).

C. Formation and Study of the 2,4-Diphenylbicyclo[3.2.1]-oct-6-en-3-one Monoanion 26 a,b and 32 a,b

1. Formation of the monoanion 26a,b from 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (25) in THF-d₈

This reaction, as well as each of the subsequently described monoanion formations, was carried out in a 15 ml three-necked round bottom flask 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 0.0037 mole (0.09 g) of sodium hydride, flushed with nitrogen and closed to the atmosphere. A solution of (0.0018 mole, 0.5 g) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one in 2 ml of THF-d₈ was introduced into the reaction flask through the septum by means of a syringe. Reaction occurred quite rapidly as shown by the evolution of hydrogen, and was completed within 10 min. Stirring was then discontinued, the excess sodium hydride was allowed to settle to the bottom of the flask and the supernatant brown liquid was drawn out by means of a syringe and placed in a nmr tube with a nitrogen atmosphere through a septum. The nmr tube was then centrifuged for 3-4 min, the liquid transferred into a second nmr tube with nitrogen atmosphere, and spectrum recorded on a Varian A-60 instrument. The following resonances were observed:

1.65 ppm (m, 2 H, $\text{>C}_{8',b}\text{-H}_2$), 1.98 ppm (2, 2H, $\text{>C}_{8''a,b}\text{-H}_2$), 2.96 ppm (1, 1 H, $\text{Ph-C}_{14a}\text{-H}$), 3.53 ppm (2, 1 H, $J=5$ Hz, $\text{Ph-C}_{14b}\text{-H}$), 2.63 ppm (3, 1 H, $J=1.8$ Hz, $\text{-C}_{15a}\text{-H}$), 2.82 ppm (m, 1 H, $\text{-C}_{15b}\text{-H}$), 5.84 ppm (4, 1 H, $J_{6a,5a}=3.0$ Hz, $J_{6a,7a}=6.0$ Hz, $\text{-C}_{7a}=\text{C}_{6a}\text{-H}$), 5.17 ppm (4, 1 H, $J_{6b,5b}=3.0$ Hz, $J_{6b,7b}=6.0$ Hz, $\text{-C}_{7b}=\text{C}_{6b}\text{-H}$), 6.47 ppm (6, 2 H, $J_{7a,b;1a,b}=6.0$ Hz, $\text{H-C}_{7a,b}=\text{C}_{6a,b}\text{-}$), 6.75 ppm (3, 1 H, para H), 7.30 ppm

(m, 7 H, 2 meta H and all H of phenyl at C₄), 7.77 ppm (2, 2 H, 2 ortho H). Integration of the peaks corresponding to protons H_{6a} and H_{6b} showed that isomeric enolates 26 a and 26 b were present in a ratio of 2:1.

2. Formation of the monoanion 32 a,b from [2,4-²H₂]-2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (31) in THF-d₈

2,4-Dideuterated ketone (31) (0.0018 mole, 0.5 g) in 2 ml of THF-d₈ was treated with sodium hydride (0.0037 mole, 0.09 g) as described above and the nmr spectrum was recorded on a Varian HA-100 instrument. The following resonances were observed: 1.65 ppm (m, 2 H, >C₈'_{a,b}-H₂), 1.98 ppm (2, 2 H, >C₈'_{a,b}-H₂), 2.63 ppm (3, 1 H, J=1.8 Hz, -C_{5a}-H), 2.82 ppm (m, 1 H, -C_{5b}-H), 5.84 ppm (4, 1 H, J_{6a,5a}=3.0 Hz, J_{6a,7a}=6.0 Hz, -C_{7a}=C_{6a}-H), 5.17 ppm (4, 1 H, J_{6b,5b}=3.0 Hz, J_{6b,7b}=6.0 Hz, -C_{7b}=C_{6b}-H), 6.47 ppm (6, 2 H, J_{7a,b;1a,b}=6.0 Hz, H-C_{7a,b}=C_{6a,b}-), 6.75 ppm (3, 1 H, para H), 7.30 ppm (m, 7 H, 2 meta H and all H of phenyl at C₄), 7.77 ppm (2, 2 H, 2 ortho H).

3. Formation of the monoanion 26 a,b from 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (25) in DMSO

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (25) (0.0018 mole, 0.5 g) in 2 ml of DMSO was treated with (0.0037 mole, 0.09 g) of sodium hydride as described above and the nmr spectrum of the resulting monoanion was taken on a Varian A-60 instrument. The resonances observed were the same as those found for the monoanion in THF. The signals below 4.5 ppm were obscured by the solvent. The ratio of the peaks corresponding to protons H_{6a} and H_{6b} was again 2:1.

After the nmr spectrum was obtained the liquid was removed from the nmr tube by syringe and placed in 5 ml of distilled water. The resulting solid was collected by filtration, dried and its nmr recorded. The resulting spectrum was that of the bicyclic ketone 25.

4. Formation of the monoanion 26 a,b from 2,4-diphenylbicyclo-[3.2.1]oct-6-en-3-one (25) in HMPA

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (0.0018 mole, 0.5 g) in 2 ml of HMPA was treated with (0.0037 mole, 0.09 g) of sodium hydride as described above and the nmr spectrum taken on a Varian A-60 instrument. The resonances were the same as those of the monoanion in THF. Integration showed that the ratio of protons H_{6a} and H_{6b} was again 2:1. The signals below 4.5 ppm were obscured by the solvent. The liquid was removed from the nmr tube and placed in 5 ml of distilled water. The resulting solid was collected by filtration and a nmr spectrum was obtained. The spectrum was that of the starting ketone 25.

D. Formation and Study of 2,4-Diphenylbicyclo-[3.2.1]oct-6-en-3-one Dianion 28

1. Formation of Dianion 28 in THF by means of sodium hydride followed by n-butyllithium

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (25) (0.0018 mole, 0.5 g) in 2 ml of dry THF was treated with 0.153 g of sodium hydride as a 57% dispersion in mineral oil to afford monoanion 26, as described earlier. To the reaction mixture was then added 2 ml (0.00316 mole) of a 1.58 M solution of n-butyllithium in hexane and stirring was

continued for 4 hr. The blood red solution was then syringed into a nmr tube equipped with a septum and nitrogen atmosphere. The nmr tube was centrifuged for 3-4 min and the nmr spectrum taken on a Varian A-60 instrument. The following resonances were obtained: 3.64 ppm (2, 2 H, $J=4.0$ Hz, $-\overset{|}{\underset{|}{\text{C}}}_1-\text{H}$ and $-\overset{|}{\underset{|}{\text{C}}}_5-\text{H}$), 5.41 ppm (1, 2 H, $\text{H}-\overset{|}{\underset{|}{\text{C}}}_6=\overset{|}{\underset{|}{\text{C}}}_7-\text{H}$), 6.19 ppm (3, 2 H, 2 para H), 7.01 ppm (3, 4 H, 4 meta H), 7.59 ppm (2, 4 H, 4 ortho H). The signals below 4.5 ppm were obscured by solvent.

2. Attempted preparation of dianion 28 by means of n-butyllithium alone in the presence of TMEDA as a catalyst

A mixture of n-butyllithium--TMEDA was prepared by adding 2 ml (0.00316 mole) of a 1.58 M solution of n-butyllithium in hexane to (0.0021 mole, 0.34 g) of TMEDA in a cooled, nitrogen flushed 50 ml three-necked round bottom flask fitted with a septum, magnetic stirrer, and a nitrogen atmosphere. The solution was stirred for a few minutes and then syringed into a solution of (0.0018 mole, 0.5 g) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one in 3 ml of dry THF. The reaction was stirred for 1 hr and 20 min and was then quenched with 5 ml of deuterium oxide. The reaction mixture was dried (MgSO_4) and the solvent evaporated under reduced pressure. A nmr spectrum of the crude solid product was obtained. It showed the presence of the dideutero-bicyclic ketone 31 and a new product. The gc analysis of the product also showed the presence of a new product. The new product was not isolated.

3. Formation of dianion 28 in THF- d_6 by means of sodium hydride followed by n-butyllithium

Bicyclic ketone 25 (0.0018 mole, 0.5 g) in 2 ml of THF-d₈ was treated with 0.153 g of sodium hydride as a 57% dispersion in mineral oil to afford monoanion 26, as described earlier. The reaction mixture was then treated with 2 ml (0.00316 mole) of a 1.58 M solution of *n*-butyllithium in hexane and stirred for 4 hr. The nmr spectrum was then recorded on a Varian XL-100 instrument. The resonances were as follows: 3.64 ppm (2, 2 H, $J=4.0$ Hz, $-\overset{|}{\underset{|}{\text{C}}}_1-\text{H}$ and $-\overset{|}{\underset{|}{\text{C}}}_5-\text{H}$), 5.41 ppm (1, 2 H, $\text{H}-\overset{|}{\underset{|}{\text{C}}}_6=\overset{|}{\underset{|}{\text{C}}}_7-\text{H}$), 6.19 ppm (3, 2 H, 2 para H), 7.01 ppm (3, 4 H, 4 meta H), 7.59 ppm (2, 4 H, 4 ortho H). The signals below 2.4 ppm were obscured by hexane.

4. Deuteration of the dianion 28

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (0.0018 mole, 0.5 g) in 2 ml of dry THF was treated with 0.153 g. of sodium hydride as a 57% mineral oil dispersion to afford monoanion 26. The reaction mixture was then treated with 2 ml (0.00316 mole) of a 1.58 M solution of *n*-butyllithium in hexane and allowed to stir for 3 hr. Deuterium oxide (5 ml) was then added and stirring was continued for a few min. The layers were separated and the THF layer dried (MgSO₄). The solvent was evaporated under reduced pressure. The residue was identified by nmr and gc analysis as the dideuterated bicyclic ketone 31.

5. Attempted preparation of dianion 28 using an excess of sodium hydride

Bicyclic ketone 25 (0.005 mole, 1.37 g) in 15 ml of dry THF was added to 0.632 g of sodium hydride as a 57% mineral oil dis-

persion and the reaction carried out as described above. Only one equivalent of hydrogen was collected. It was, therefore, concluded that the dianion could not be formed using only sodium hydride as the base.

V. SUMMARY

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (25) was converted to its monoanion 26 by means of sodium hydride in a suitable aprotic solvent. Examination of the nmr spectrum of the monoanion showed that this intermediate existed in two isomeric forms 26a and 26b in a 2:1 ratio, and that their ratio was independent of solvent.

It was also shown that interaction of the negative charge at C₂ with the β -olefinic group did not occur in either of the above monoanions.

The dianion of the 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (25) system was prepared by forming the monoanion and then reacting it with *n*-butyllithium in THF. The nmr spectrum of the dianion 28 was recorded and the protons assigned. It was concluded that the negative charge at C₂ and C₄ did interact with the C_{6,7} carbon-carbon double bond to give the bishomoaromatic cyclopentenone dianion, as shown by structure 29.

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