The Effect of Stabilizing Groups on the Extent of Long-Range Π Electron Participation and the Effect of the Negative Charge on the Chemical Shift of Neighboring Protons in Carbanions

Atilla Tuncay
Western Michigan University

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LONG-RANGE $\pi$ ELECTRON PARTICIPATION
AND THE EFFECT OF THE NEGATIVE CHARGE ON THE
CHEMICAL SHIFT OF NEIGHBORING PROTONS IN CARBANIONS

by

Atilla Tuncay

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Faculty of the Graduate College
in partial fulfillment
of the
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Western Michigan University
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August 1976
THE EFFECT OF STABILIZING GROUPS ON THE EXTENT OF
LONG-RANGE \( \pi \) ELECTRON PARTICIPATION
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CHEMICAL SHIFT OF NEIGHBORING PROTONS IN CARBANIONS

Atilla Tuncay, Ph.D.
Western Michigan University, 1976

2,4-Diphenylbicyclo \([3.2.1]\) octa-2,6-diene, 2,4-diphenylbicyclo
\([3.2.1]\) oct-2-ene and \textit{trans}-1,3-diphenylpropene were synthesized
and their base-catalyzed hydrogen-deuterium exchange rates were
measured. Examination of the rate data showed that all three hydrocarbons underwent exchange at essentially the same rate. It was
thus concluded that the extent of long-range \( \pi \) participation in
delocalizing a negative charge is a function of the stability of
the developing carbanion.

2,4-Diphenylbicyclo \([3.2.1]\) octa-2,6-diene was converted to
its anion by means of n-butyllithium in THF-d\(_8\)-hexane. Examination
of the nmr spectrum of carbanion showed a close similarity to that
of the completely delocalized homoaromatic bicyclo \([3.2.1]\) octa-
2,6-dienyl anion. It was thus concluded that anisotropic effects
due to charge delocalization at \( C_2,3,4 \) must play a much more important
role in influencing changes in the chemical shifts of carbanions, than
previously anticipated. Therefore, conclusions regarding long-range
\( \pi \) interactions, homoaromaticity and homoaromatic ring current effects
must be arrived at by examining not only the proton nmr spectrum of
the anion under consideration but also its stability relative to a
suitably chosen reference system.

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I am deeply indebted to my research advisor, Dr. G.B. Trimitsis, for his untiring assistance and understanding during the course of this work. I am also grateful to Dr. D.C. Iffland, Dr. R.E. Harmon and Dr. M.E. McCarville for their help. Special thanks are due to Dr. G. Slomp, T. Schahil and S. Mízsak of the Upjohn Company for their assistance in obtaining the nmr spectra.

Finally, I wish to acknowledge the financial assistance received from the Chemistry Department in the form of teaching assistantships and the Graduate School for associateships.

Atilla Tuncay
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I. INTRODUCTION

It has been recently realized that allylic and related anions can in many cases interact with one or more suitably placed remote carbon-carbon double bonds to produce cyclically delocalized systems as shown by equation (1).

In a limited number of cases the presence of $\pi$ interaction in carbanions was ascertained by comparing the stability of the carbanion under investigation with that of a suitably chosen reference system.

In the majority of cases, however, long-range $\pi$ interactions have been detected by means of proton nmr spectroscopy.

The present study was initiated in order to study the following two aspects of the chemistry of carbanions involving long-range $\pi$ interactions:

(a) The effect of stabilizing groups on the tendency of these carbanions to undergo such interactions, and

(b) The effect of the negative charge on the chemical shifts of the vinylic and other neighboring protons in systems where long-range $\pi$ interaction has been suppressed.
II. HISTORICAL

It has been known for years that a carbon-carbon double bond directly attached to a carbanion\(^1\), carbonium ion\(^2\), or free radical\(^3\) greatly stabilizes these intermediates by allowing delocalization of the charge or odd electron over more carbon atoms as shown graphically by structures 1, 2, and 3.

\[
\begin{align*}
\text{1} & \quad \text{H}_2\text{C} - \text{CH}_2 \\
\text{2} & \quad \text{H}_2\text{C} + \text{CH}_2 \\
\text{3} & \quad \text{H}_2\text{C} \cdot \text{CH}_2
\end{align*}
\]

Delocalization in the above systems is achieved by interaction of the p-orbital bearing the charge or the odd electron with the neighboring p-orbitals of the unsaturated group as shown below for the allylic anion\(^4\). In order for maximum overlap and subsequent stabilization

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to take place in such systems, the p-orbitals involved must be parallel to each other.

Systems such as 1, 2, and 3 are called conjugated systems and their stabilization has been described as conjugative stabilization.

When conjugation leads to cyclic delocalization of $4n + 2 \pi$ electrons, the resulting stabilization is even more pronounced. For example, the unusually high acidity of the methylene hydrogens of cyclopentadiene $^6a,b (5)$ relative to those of 1,4-pentadiene (7) is attributed to the fact that the cyclopentadienyl anion 6 is a six $\pi$-electron cyclically delocalized system with all of its $\pi$ electrons occupying bonding molecular orbitals.

\[
\begin{align*}
5 & \quad \text{pKa} = 15 \\
6 & \quad \text{6 $\pi$ electrons} \\
CH_2=CHCH_2CH=CH_2 & \quad \rightarrow \quad CH_2CH=CHCHCH_2 \\
7 & \quad \text{pKa} = 27
\end{align*}
\]
In the pentadienyl anion 8, two of the six \( \pi \) electrons occupy a non-bonding orbital thereby causing a delocalization energy difference of 1.01 \( \beta \) between this open chain anion 8 and cyclopentadienyl anion 6.

Similarly, the unusually high stability of the well-known tropylium cation 8, and the cyclopropenyl\(^a,b\) cation 10, is likewise thought to be due to all \( \pi \) electrons occupying bonding molecular orbitals in these systems. The type of stabilization derived from
cyclic delocalization of $4n + 2 \pi$ electrons has been called aromaticity and systems displaying this kind of stabilization have been described as aromatic. Thus, the cyclopentadienyl anion $6$, the cycloheptatrienyl cation $9$ and the cyclopropenyl cation $10$ are all examples of aromatic systems.

Whereas cyclic delocalization of $4n + 2 \pi$ -electrons results in stabilization, cyclic conjugation of $4n \pi$ -electrons gives rise to destabilization. This is called antiaromaticity and systems displaying this kind of destabilization have been described as antiaromatic. The cyclopropenyl carbanion $11$ provides a very good example for the concept of antiaromaticity in a cyclic system containing $4n \pi$ -electrons in conjugation. This cyclic $4 \pi$ electron anion has two $\pi$ electrons in its antibonding orbitals and is therefore destabilized relative to its open chain analog, the allyl anion $1$ which has
none of its \( \pi \) electrons in its antibonding orbitals.

\[
\begin{array}{c}
-2\beta \\
-\beta \\
\alpha \\
+\beta \\
+2\beta \\
\end{array}
\begin{array}{c}
-1.41 \\
1.000 \\
1.41 \\
+2.000 \\
\end{array}
\]

Figure 3. HMO energy levels for cyclopropenyl anion \( \text{11} \) and allyl anion \( \text{1} \), respectively.

Similarly, the unusually high pKa of cycloheptatriene (\( \text{12} \)) is attributed to the formation of the 8 \( \pi \) electron antiaromatic cycloheptatrienyl anion \( \text{13} \) which has two of its eight \( \pi \) electrons in

\[
\begin{array}{c}
\text{12} \\
pKa = 36 \\
\end{array}
\begin{array}{c}
\xrightarrow{\text{13}} \\
8 \pi \text{ electrons} \\
\text{Anti-Aromatic} \\
\end{array}
\]

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its antibonding orbitals and is therefore destabilized.

\begin{align*}
-2\beta & \quad -1.802 \\
-\beta & \quad -0.445 \\
\alpha & \quad 1.247 \\
+\beta & \quad 2.000 \\
+2\beta & \quad -2.000
\end{align*}

Figure 4. HMO energy levels for cycloheptatrienyl anion.\textsuperscript{7,13}

The substituted cyclopropenyl anion,\textsuperscript{14} the cyclopentadienyl cation,\textsuperscript{15} and the cyclobutadienocyclopentadienyl anion\textsuperscript{16} are all other examples of antiaromatic systems.

\begin{align*}
& \quad \text{Structure 14} & \quad \text{Cyclopentadiene} & \quad \text{Structure 15} \\
& \quad \text{Structure 16}
\end{align*}

It should be emphasized that in all of the cases mentioned so far, delocalization of charge occurred by way of overlap of p-orbitals on adjacent carbon atoms as exemplified by structures \textsuperscript{17} and \textsuperscript{18}, for the allyllic and cyclopentadienyl anions.

As a result of extensive studies during the last forty years by a number of workers\textsuperscript{17a-e}, but especially by Winstein and his group\textsuperscript{18}, a new stabilization mechanism has emerged. It was found that under
conditions of favorable geometry, carbonium ions and carbanions could interact and therefore, be stabilized by certain unsaturated groups, even when the latter were not directly connected to the carbon bearing the positive or negative charge. The first, and by now classic example of this type of interaction was that of the cholesteryl carbonium ion \( 21 \), obtained in the solvolysis of cholesteryl chloride \( (19, X = \text{Cl}) \). Reaction of carbonium ion \( 21 \) with acetic acid led to the cholesteryl acetate\(^{17a} \) \( (19, X = \text{OAc}) \) with retained configuration at \( \text{C}_3 \). This was very unexpected in view of the fact that solvolytic processes lead to racemization or partial inversion of configuration. The solvolysis of cholesteryl tosylate \( (19, X = \text{OTs}) \) in methanol containing acetate ions, afforded the rearranged ether\(^{17a} \) \( (20, Y = \text{OMe}) \). The cholesteryl tosylate \( (19, X = \text{OTs}) \) also underwent acetolysis with a rate enhancement of 100 compared to that of cyclohexyl tosylate and gave rise to the rearranged acetate\(^{20} \) \( (20, Y = \text{OAc}) \). Similarly, cholesteryl tosylate reacted with ethanol 40 times faster than cholestanyl tosylate, the saturated derivative corresponding to \( 19 \).

These observations were interpreted on the basis of an intermediate nonclassical carbonium ion as represented by structure \( 21 \).
The interaction of the positive charge with the C₅₋₆ olefinic group in 21 was called homoconjugation and the intermediate carbonium ion 21 was termed a homoallylic cation by Winstein by analogy to allylic conjugation and allylic carbonium ions. The "homo" designation was used to show that cation 21 could be considered as a homolog of the more familiar allylic carbonium ion 1.

There is an important difference between allylic and homoallylic conjugation. While in allylic conjugation maximum stabilization occurs only when the p-orbital bearing the charge is parallel to the
p-orbitals of the olefinic group (structure 17), in homoallylic conjugation maximum interaction is achieved when the orbital bearing the charge is disposed perpendicularly to the orbitals of the carbon-carbon double bond\textsuperscript{21}, as shown in 22. This type of overlap is intermediate between \( \sigma \) and \( \gamma \) bonding.

With suitably chosen hydrocarbons, homoconjugation can also lead to cyclic delocalization\textsuperscript{22a-c} similar to that observed in aromatic systems such as the cyclopentadienyl anion 6 and the cyclopropenyl cation 10. This causes greatly enhanced stability in systems where such delocalization is possible. For example, the tremendous rate acceleration (10\textsuperscript{11}) in the solvolysis of anti-norbornen-7-yl p-toluene-sulfonate (23) compared to its saturated analog 24 was attributed by Winstein\textsuperscript{23a-c} to the interaction of the developing positive charge with the \( C_5 \),\( C_6 \) olefinic group, leading to the cyclically delocalized intermediate 25.

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The above delocalization was called homoaromaticity since it was quite analogous to the phenomenon of aromaticity, and carbonium ion \(^{25}\) was considered to be a homoaromatic analog of the aromatic cyclopropenyl cation \(^{10}\).

Related to the norbornen-7-yl cation \(^{25}\) is the norbornadien-7-yl species \(^{28}\) which is another example of a homoaromatic carbonium ion. Winstein \(^{24}\) has found that norbornadien-7-yl chloride \(^{26}\) solvolyzed \(10^{14}\) times faster than its saturated analog, norborn-7-yl chloride \(^{27}\).

In all the cases two methods were used to establish the presence of homoconjugation and/or homoaromaticity in carbonium ions: (a) The stability of the carbonium ion under examination was compared with that of a suitably chosen reference system. (b) Proton nuclear magnetic resonance (nmr) spectroscopy was employed as an important tool in detecting long-range \(\pi\) interactions. Sizable downfield shifts in the resonance of the protons directly attached to the remote carbon-

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carbon double bond have been interpreted as evidence indicating considerable charge delocalization in such carbonium ions. Either or both of these methods were used to ascertain the presence of long-range $\pi$ interactions.

The possibility of homoconjugation and/or homoaromaticity in systems bearing a negative charge, (i.e., carbanions) has not been investigated until very recently. The first example of a nonclassical interaction in carbanion chemistry, analogous to the interactions discussed for carbonium ions, was found with enolate ions. The relative ease of $\alpha$-proton abstraction from carbonyl compounds is explained by the resonance stabilized enolate ion 29 which results from the interaction between a carbonyl and the negatively charged alpha carbon.

\[ \begin{align*}
\text{O} & \quad \text{B} \\
\text{-C-C-H} & \quad \rightarrow \\
\text{O}^{-} & \quad \text{C=C} + \text{BH}^{+}
\end{align*} \]

29

By analogy with homoallylic resonance, one can conceive of an interaction between a carbonyl and a negatively charged alpha carbon as taking place across an intervening methylene group to afford a homoenolate ion 30.

\[ \begin{align*}
\text{O} & \quad \text{B} \\
\text{-C-C-H} & \quad \rightarrow \\
\text{O}^{-} & \quad \text{C=C} + \text{BH}^{+}
\end{align*} \]

30

Charge delocalization in the enolate and homoenolate ions is shown in diagrams 31 and 32, respectively.
Since the orientation of atoms relative to one another is largely fixed in ring compounds, the most favorable structural environment for orbital overlap between non-continuous atomic centers should be found in such systems. Thus, just as in the case of carbonium ions, most of the evidence for nonclassical interactions in carbanions has been gathered from studies with suitably chosen cyclic systems. The first authentic example of homoconjugation involving carbanions was reported in 1962 by Nickon and Lambert with the camphenilone system. They observed that when optically active camphenilone (33a) was treated with potassium t-butoxide in t-butyl alcohol at 165-185°, a gradual racemization occurred. The loss in optical activity can only be explained by the formation of the symmetrical homoenolate anion 34 on proton abstraction from C₆. Since structure 34 has a plane of symmetry, protonation will regenerate 33a and its enantiomer 33b in equal amounts.

It was also found that with potassium t-butoxide in t-butyl alcohol-0-d, the system underwent hydrogen-deuterium exchange at C₆ resulting in a racemic mixture of 33c and 33d and the rate of exchange was about equal to the rate of racemization. These results provided strong evidence for a homoenolization process in the camphenilone system.
Evidence for carbanion stabilization by the homoallylic or homo-conjugative mechanism in systems which do not contain heteroatom functions capable of acting as carbanion stabilizing sites has only recently been obtained. The norbornenyl system, which has yielded valuable information concerning nonclassical interactions in carbonium ion processes, was studied by Stille and his coworkers as to the possibility of homoallylic carbanion stabilization. These workers were able to produce the norbornenyl carbanionic species by basic oxidative cleavage of the norbornenylhydrazine derivative 35 and the nortricyclyl derivative 36.
It was found that the reaction of either 35 or 36 in water or in t-butyl alcohol yielded a 43:57 mixture of norbornene (37) to nortricyclene (38).

This result could be explained either by the postulate that a nonclassical ion such as 39 is the intermediate or that the classical ions 40a and 40b are in equilibrium and that this process is rapid compared to proton capture from the solvent.

The possibility of stabilization due to charge delocalization in the interaction of an allylic carbanion with a remote olefinic double bond (as depicted by structure 41) has only recently been examined. For such a case, HMO calculations indicate a significant delocalization.
energy even with small overlap of the remote \( \pi \)-orbitals as seen below:

\[
\text{Delocalization energy (8-units) as function of overlap}
\]

\[
\begin{array}{c|ccccc}
\beta_1,3/\beta_0 & 0 & 0.3 & 0.5 & 1.0 \\
\hline
DE & 0.828 & 1.032 & 1.346 & 2.472 \\
\end{array}
\]

In structure 41, six \( \pi \) electrons are delocalized over a pseudo five-membered ring system. Thus 41 is a homoaromatic analog of the aromatic cyclopentadienide anion 6 and may be called a bishomocyclopentadienide nonclassical anion 28.

The first experimental support for this type of long-range \( \pi \) -interaction was obtained in hydrogen-deuterium exchange studies with the bicyclooctadiene 42 by J.M. Brown and his coworkers 29 in 1965. These workers observed that bicyclo [3.2.1] octa-2,6-diene (42) underwent hydrogen-deuterium exchange in \( t\)-BuO\(^-\)K\(^+\)/DMSO-d\(_6\) at the allylic 4-position at a rate which was \( 10^{4.5} \) times greater than that of bicyclo [3.2.1] oct-2-ene (43). The latter exchanged at a rate comparable with that of cyclohexene. The observed rate enhancement was rationalized

\[
42 \quad k_{\text{rel}} 10^{4.5}
\]

\[
43 \quad 1
\]
in terms of participation by the C₆,₇ double bond and the incipient allylic carbanion, with the formation of the homoaromatically stabilized carbanionic intermediate 44.

\[ \text{44} \]

Subsequently, Winstein and his coworkers were able to generate the anion 44 in sufficiently large quantities to study its nuclear magnetic resonance (nmr) spectrum. They observed that the vinylic protons H₆ and H₇ of anion 44 had undergone a substantial upfield shift (2.3 ppm) relative to the starting diene 42. This was interpreted as evidence indicating considerable charge delocalization to the olefinic bond at C₆,₇ in anion 44.

Recently, the anions of a number of related systems were generated and studied in order to determine the presence and the extent of homoaromaticity in these species. Thus the monoanion 45 of bicyclo[3.2.2]nona-2,6,8-triene (46) was formed and its nmr spectrum seemed to indicate that charge delocalization occurred across both vinylic
bridges. In this case the original report based its conclusions entirely on $^1\text{H}$ nmr. Later Staley and his coworkers presented kinetic evidence for the closely related 3-methylbicyclo[3.2.2]nonatriene supporting charge delocalization in the anion derived from this system. The question of whether carbanion existed as a symmetrical species with simultaneous delocalization to both vinylic bridges (as implied by structure 45) or whether there was a rapid (on the nmr time scale) bridge flipping ($45a \rightleftharpoons 45b$) has not been answered. Later Grutzner and Goldstein independently presented kinetic evidence for charge delocalization in the bicyclo-[3.2.2]nona-2,6,8-trienyl anion 45.

In 1973 Grutzner was able to generate the anion of bicyclo-[3.2.2]nona-2,6-diene (49) and study its nmr spectrum. He observed that the chemical shifts of $\text{H}_6$ and $\text{H}_7$ of anion 48 were comparable to those of anions 44 and 45 and concluded that 48 was a delocalized homoaromatic anion.
Recently, Goldstein used molecular orbital symmetry arguments to extend the concept of homoaromaticity to bicycloaromaticity. He predicted that conjugation between three interrupted bridges in systems which contain $4n$ electrons would give rise to stabilization in excess of homoaromatic stabilization (interaction between two bridges) and called such systems bicycloaromatic. According to his definition the bicyclo[3.2.2]nona-2,6,8-trienyl anion $45$ would be termed bicycloaromatic and would be more stable than the homoaromatic bicyclo[3.2.2]nona-2,6-dienyl anion $48$.

In trying to verify these theoretical predictions experimentally, Grutzner obtained an energy of activation difference between anions $45$ and $48$ by measuring the rate of deprotonation of the ether solvent used by the carbanions $45$ and $48$ at different temperatures. This difference which is an estimation of relative kinetic carbanion stabilities was 2.5 kcal/mol additional stabilization of $45$ as compared with the anion $48$. Grutzner argues that although there might be extensive delocalization between the three bridges in the bicyclo[3.2.2]nona-2,6,8-trienyl carbanion $45$ (as depicted in structure $45$), such interaction would not lead to significant stabilization energy, in contrast to homoaromatic interaction between two bridges. He then concluded, as he did in his earlier report that homoaromatic stabili-
zation is the major factor involved in the stability of "bicycloaromatic" bicyclo $[3.2.2]$ nona-2,6,8-trienyl anion $45$.

Simultaneously, Goldstein$^{33}$ reported that stabilization of the bicyclo $[3.2.2]$ nona-2,6,8-trienyl anion $45$ exceeds that of the bicyclo $[3.2.2]$ nona-2,6-dienyl anion $48$ by 4.0 kcal/mol as measured by base-catalyzed detritiation of $50$ and $51$. He therefore argued that this 4.0 kcal/mol stabilization in excess of the homoaromatic stabilization is significant and can only be attributed to $\pi$-electron delocalization throughout all three $\pi$ bridges of the trienyl anion $45$. This result was considered by Goldstein to be a confirmation of his theoretical predictions.

Recently, Stille and his coworkers$^{36}$ presented the first evidence for a bishomocyclopropenyl anion, in this case 7-norbornenyl anion $54$. They were able to produce the anion $54$ by basic oxidative cleavage of anti- and syn-7-norbornenylhydrazine (52) and (55). Capture of the anion $54$ by deuterium oxide afforded anti-(56) and syn-7-deuterio norbornene (57), in approximately a 94:6 ratio as the only products. They suggested that the preference for anti capture can be explained in
terms of an equilibrated mixture of anti-(53) and syn-7-norbornenyl anion (54) intermediates which contain predominantly the anti anion 53. They concluded that the predominance of 53 over 54 is the result of a destabilizing effect experienced by the latter anion. The syn anion 54 has a significant amount of antiaromatic character since the interaction of the negative charge at the 7-position with the double bond at C5,6 will result in the bishomoantiaromatic analog of the cyclopropenyl anion (11) as shown in structure 54a.
Very recently, Trimitsis and his coworkers were able to generate both the monoanion 58 and the dianion 59 of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (60) in order to investigate to what extent carbanions stabilized by functional groups other than a carbon-carbon double bond would undergo homoconjugation and/or homoaromaticity. The nmr spectrum of the monoanion 58 indicated that the negative charge at C2 did not interact with the double bond at C6,7 (as implied by structure 58). The nmr spectrum of dianion 59 showed that the H6 and H7 vinylic protons moved upfield by 1.1 ppm relative to the starting ketone 60. These workers interpreted this upfield shift as evidence indicating considerable charge delocalization to the olefinic bond at C6,7 in dianion 59. They then concluded that dianion 59 was a six \( \pi \) electron bishomoaromatic system as shown by structure 59. The results were based on nmr alone. The dianion 59 is the first bishomoaromatic analog of the aromatic cyclopentenone dianion 61.
In 1974 Goldstein was able to prepare the bicyclo[3.3.2]decatrienyl anion (62) and study its NMR spectrum which indicated that delocalization of ten \( \pi \) electrons over eight trigonal carbons had occurred resulting in the homoaromatic analog 63 of the aromatic cyclooctatetraenyl dianion (64). Again the results were based on NMR alone.
III. STATEMENT OF PROBLEM

The literature review presented in the previous section clearly shows that allylic and related anions can in many cases interact with one or more suitably placed remote carbon-carbon double bonds to produce cyclically delocalized systems as shown by equation (1).

\[ \text{Base} \quad \text{(1)} \]

In a limited number of cases the presence of \( \mathcal{J} \) interaction in carbanions was ascertained by comparing the stability of the carbanion under investigation with that of a suitably chosen reference system.

In the majority of cases, however, long-range \( \mathcal{J} \) interactions have been detected by means of proton nmr spectroscopy. Most significantly, sizable upfield shifts in the resonance of the protons directly attached to the remote carbon-carbon double bond have been interpreted as evidence indicating considerable charge delocalization in such species.

The present study was initiated in order to study the following two aspects of the chemistry of carbanions involving long-range \( \mathcal{J} \) interactions:

(a) The effect of stabilizing groups on the tendency of carbanions to undergo such interactions, and

(b) The effect of the negative charge on the chemical shifts of
the vinylic and other neighboring protons in systems where long-range \[\pi\] interaction has been supressed.
IV. RESULTS AND DISCUSSION

A. Preparation of Starting Materials

The present study required the synthesis of the following three systems: 2,4-diphenylbicyclo [3.2.1] octa-2,6-diene (65), 2,4-diphenylbicyclo [3.2.1] oct-2-ene (66), and trans-1,3-diphenylpropene (67).

The synthesis of 2,4-diphenylbicyclo [3.2.1] octa-2,6-diene (65) was accomplished as illustrated in Scheme I. Thus 1,3-diphenyl-2-propanone was converted into 1,3-dibromo-1,3-diphenyl-2-propanone (68) essentially as described by Breslow.\textsuperscript{39} Reaction of the ketone 68 with cyclopentadiene and sodium iodide in acetonitrile following the procedure of Cookson\textsuperscript{40} with some modifications afforded cis-endo-2,4-diphenylbicyclo [3.2.1] oct-6-en-3-one (69). Treatment of the latter compound with LiAlH\textsubscript{4} in ether resulted in the formation of 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-ol (70), mp 78-83°. As expected the ir spectrum of the bicyclic alcohol 70 displayed OH absorption at 3570 cm\textsuperscript{-1}; the nmr spectrum of 70 exhibited a vinylic hydrogen absorption at 6.49 ppm indicating that these hydrogens survived the
Scheme I

\[
\begin{align*}
\text{C}_6\text{H}_5-\text{CH}_{2}-\text{C}-\text{CH}_{2}-\text{C}_6\text{H}_5 & \quad \text{Br}_2 \quad \text{Acetic Acid} \quad \text{C}_6\text{H}_5-\text{CH}-\text{C}-\text{CH}-\text{C}_6\text{H}_5 \\
& \quad \text{Br} \quad \text{Br} \quad \underline{68} \\
& \quad \text{NaI} \quad \text{Acetonitrile} \\
& \quad \text{LiAlH}_4 \quad \text{Ether} \\
& \quad \underline{70} \\
& \quad \text{SOCl}_2 \quad \text{Pyridine} \\
& \quad \underline{65}
\end{align*}
\]

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LiAlH₄ reaction and the mass spectrum of 70 showed a molecular ion peak at 276 mass units. The desired product, namely 2,4-diphenyl-bicyclo [3.2.1] octa-2,6-diene (65) could be obtained by simple dehydration of alcohol 70. Dehydration of the bicyclic alcohol 70 by a number of standard procedures failed since attempts to convert 70 to the required p-toluenesulfonate ester, methanesulfonate ester and acetate were not successful. Thus treatment of the bicyclic alcohol 70 with p-toluenesulfonyl chloride in the presence of various bases such as sodium, sodium hydride, sodium amide or pyridine failed to afford the p-toluenesulfonate ester 71. Similarly, reaction of the bicyclic alcohol 70 with methanesulfonyl chloride in the presence of pyridine or triethylamine did not afford the expected methanesulfonate ester 72 even after prolonged reaction times and heating. In the same manner, treatment of the bicyclic alcohol 70 with acetic anhydride in the presence of pyridine failed to yield the acetate 73, whereas
treatment of the alcohol 70 with acetyl chloride in the presence of pyridine resulted after a long period of heating, in a 60:40 mixture of the acetate 73 and the alcohol 70 as determined by gas chromatographic analysis of the crude product. However, treatment of the bicyclic alcohol 70 with p-toluenesulfinyl chloride 74, which was prepared essentially as described in the literature69, in the presence of pyridine afforded the 2,4-diphenylbicyclo[3.2.1]oct-6-eny1-3-p-toluenesulfinate (75), mp 159-62°. As expected, the ir spectrum of the p-toluenesulfinate ester 75 displayed S = O absorption at 1120 cm⁻¹; the nmr spectrum of 75 exhibited a vinylic hydrogen absorption at 6.30 ppm and a methyl absorption at 2.38 ppm, whereas the mass spectrum of 75 showed a molecular ion peak at 414 mass units. Reaction of sulfinate ester 75 with m-chloroperbenzoic acid in methylene chloride afforded a new product instead of the expected 2,4-diphenylbicyclo[3.2.1]oct-6-eny1-3-toluene sulfonate (71). This new product was not identified. Bicyclic alcohol 70 was finally successfully dehydrated to produce the desired product by treatment of the alcohol 70 with purified thionyl chloride in dry pyridine to afford 2,4-diphenylbicyclo[3.2.1]octa 2,6-diene (65), mp 43-45°. The
nmr spectrum of the bicyclic alkene 65 expectedly displayed three vinylic hydrogen absorptions at 5.32, 5.72 and 6.47 ppm, for H₆, H₃ and H₇ hydrogens respectively, indicating that a new double bond was formed. The mass spectrum of 65 exhibited a molecular ion peak at 258 mass units. Proton assignments in the nmr of compound 65 were established by spin-decoupling and by Internuclear Double Resonance (INDOR) experiments using a Varian XL-100 instrument. Thus, irradiation at the H₁ frequency simplified the multiplet at 5.72 ppm to a doublet and also reduced the doublet of doublets at 6.47 ppm to a doublet with the large coupling retained. Irradiation at the H₃ frequency reduced the doublet of doublets at 5.32 ppm to a doublet with the large coupling retained. Irradiation at the H₄ frequency simplified the multiplet at 3.05 ppm and also reduced the multiplet at 5.72 ppm to a broad singlet. In the INDOR experiments, observation at the H₁ frequency showed that only H₇ proton appeared. Observation at the H₄ frequency indicated that the H₃ and H₅ protons appeared, whereas observation at the H₅ frequency showed that only the H₄ and H₆ protons appeared.

2,4-Diphenylbicyclo[3.2.1]oct-2-ene (66), the saturated analog of the bicyclic diene 65, was synthesized by a very similar route as depicted in Scheme II. Thus, cis-endo-2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (69) was prepared as described above and then hydrogenated by treatment with p-toluenesulfonylhydrazine in acidic methanol to afford 2,4-diphenylbicyclo[3.2.1]octan-3-one (76), mp 114-116°C. The ir spectrum of the bicyclic ketone 76 expectedly displayed C = O absorption at 1700 cm⁻¹; the nmr spectrum of 76 exhibited an absorption at 2.02 ppm corresponding to H₆ and H₇ hydrogens indicating that C₆,7...
Scheme II

\[
\begin{align*}
\text{C}_6\text{H}_5-\text{CH}_2-\text{C-CH}_2-\text{C}_6\text{H}_5 & \xrightarrow{\text{Br}_2} \text{C}_6\text{H}_5-\text{CH-C-CH-C}_6\text{H}_5 \\
& \text{Acetic Acid} \\
\text{C}_6\text{H}_3-\text{CH-C-CH-C}_6\text{H}_3 & \xrightarrow{68} \text{NaI} \\
& \text{Acetonitrile} \\
& \text{Br} \quad \text{Br} \\
\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2, \text{H}^+ & \xrightarrow{\text{Methanol}} \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHNH}_2, \text{H}^+ \\
\text{LiAlH}_4 & \xrightarrow{\text{Ether}} \\
\text{C}_6\text{H}_5 & \xrightarrow{77} \text{C}_6\text{H}_5 \\
\text{SOCl}_2 & \xrightarrow{\text{Pyridine}} \\
\text{C}_6\text{H}_5 & \xrightarrow{66}
\end{align*}
\]
double bond had been hydrogenated and the mass spectrum of 76 showed a molecular ion peak at 276 mass units. Bicyclooctanone 76 was then reduced by means of LiAlH₄ in ether to 2,4-diphenylbicyclo[3.2.1]octan-3-ol (77), mp 103.5-106.5°. As expected, the ir spectrum of the bicyclic alcohol 77 displayed OH absorption at 3420 cm⁻¹; the nmr spectrum showed an OH absorption at 1.09 ppm indicating that the ketone was reduced and the mass spectrum exhibited a molecular ion peak at 278 mass units. Finally, treatment of bicycloalcohol 77 with purified thionyl chloride in dry pyridine produced 2,4-diphenylbicyclo[3.2.1]oct-2-ene (66), mp 53-55°. The nmr spectrum of the bicyclic alkene 66 expectedly displayed a vinylic hydrogen absorption at 5.90 ppm indicating that a double bond was formed; the mass spectrum of 66 showed a molecular ion peak at 260 mass units.

The preparation of trans-1,3-diphenylpropene (67) was accomplished by aldol condensation of phenylacetaldehyde in the presence of potassium hydroxide following the procedure of Bonner.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_2\text{CH} & \quad \text{KOH} \quad \text{Ethanol} \quad \text{H} \\
\text{O} & \quad \text{H} \\
\text{C}_6\text{H}_5\text{CH}_2\text{CH} & \quad \text{C}_6\text{H}_5\text{CH}_2\text{CH} \\
\text{C}_6\text{H}_5 & \quad \text{C}_6\text{H}_5
\end{align*}
\]

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B. The Effect of Stabilizing Groups
on the Extent of Long-Range \( \pi \)-Electron Participation in Carbanions

In the past few years it was shown that allylic and related anions
can interact with one or more suitably placed remote carbon-carbon
double bonds to produce cyclically delocalized systems as \( 44_{30} \), \( 45_{31} \),
\( 59_{37} \) and others (see Historical). It has been realized that these

\[ \text{long-range } \pi \text{ interactions greatly enhance the stability of such car­banions.} \]

A number of reports have appeared in the literature indicating
qualitatively that the more stable a carbanion becomes the less prone
it is to undergo long-range \( \pi \) interactions. For example, the negative
charge at \( C_2 \) in the 2,4-diphenylbicyclo \( [3.2.1] \) oct-6-en-3-one mono­
anion \( 37_{58} \) did not interact with the carbon-carbon double bond at \( C_6 \).
However, no quantitative studies have been reported. Thus the present
study was initiated in order to determine quantitatively the effect of
stabilizing groups on the extent of long-range \( \pi \) interactions.

A system suitable for investigating such interactions would have
three requirements: (a) the molecule should possess structural rigidity,
so that the interaction would be geometrically defined; (b) the inter­
acting centers, that is the negative charge and the remote double bond should be in close proximity; and (c) it should be possible to convert the model under study into a similar system in which only the allylic anion is present.

Thermodynamic stabilities would be best to obtain since the question is one of relative energy. This would mean a measurement of relative pKa values of the conjugate acids. However, these values are very difficult to obtain. There is now considerable evidence that in several systems such as cyclohexylamine, aqueous dioxane and in methanolic dimethyl sulphoxide, the kinetic acidity (the rate of proton abstraction by base from a hydrocarbon) is proportional to the equilibrium acidity of that hydrocarbon if the site of ionization is very similar in the substrates under comparison. Therefore, kinetic acidities have been reported in the literature instead of the equilibrium acidities due to the fact that these values are more accessible. The rate of proton abstraction is usually not obtainable directly. Thus, more rapid reactions such as hydrogen isotope exchange, racemization at an optically active site, or double bond isomerizations have been used to obtain information about the rate of proton abstraction.

2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (65) was recommended as an ideal substrate for the present study because of the following reasons: (a) Bicyclic diene 65 was thought to be easily accessible from 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (60) which could be prepared by known methods. (b) It fulfills the previously mentioned criteria. (c) It is ideally suited for the study of long-range \(\pi\) interactions in stabilized carbanions. Its geometry is
closely related to that of bicyclo[3.2.1]octa-2,6-diene (42) whose unusually high hydrogen-deuterium exchange rate could only be explained by the homoaromatically stabilized carbanionic intermediate 44 (Historical, p. 17). Replacement of hydrogens at C₂ and C₆ in bicyclic hydrocarbon 42 by phenyl groups would be expected to reduce the extent of long-range π interactions between the negative charge and the double bond at C₆ in carbanionic intermediate 78, since this anion is now stabilized by both phenyl substituents.

Thus, in order to obtain information concerning the effect of stabilizing groups on the tendency of bicyclic carbanions to undergo

long-range π electron interactions, the base-catalyzed hydrogen-deuterium exchange rates of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65), 2,4-diphenylbicyclo[3.2.1]oct-2-ene (66) and trans-1,3-diphenyl-propene (67) were measured. The latter compound was included as a reference system. The exchange experiments were carried out in 87:13 DMSO-d₆-CH₃OD (by volume) containing CH₃ONa as the base at 25°, and the deuterium uptake was monitored by mass spectrometry. In these experiments aliquots were withdrawn at varying time intervals, quenched and worked up to afford the partially deuterated products. The extent

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of deuterium incorporation was determined by low voltage mass spectrometry with appropriate correction for $^{13}$C in natural abundance. Mass spectrometric measurements at low ionizing voltage have been found very useful for determining the deuterium content of compounds quantitatively\textsuperscript{46}.

Experimental data were treated by the method of least squares using a Wang calculator. In all of the exchange reactions, pseudo-first order kinetics with respect to the alkene were observed. Pseudo-first order rate constants were obtained from a plot of log H remaining vs time. Division of the first order rate constants by the base concentration gave the second order rate constants.

The data obtained are recorded in Table I. A representative graph, with a computer plotted least squares line, is shown for each of the compounds studied.

As mentioned earlier (Historical p. 17) Brown and his coworkers\textsuperscript{29} recently reported that bicyclo $[3.2.1]$ octa-2,6-diene (42) undergoes base-catalyzed hydrogen-deuterium exchange at $C_a$ $10^{4.5}$ times faster than its saturated analog, bicyclo $[3.2.1]$ oct-2-ene (43). The increased reactivity of bicyclooctadiene 42 was attributed to the greater stability of its incipient carbanion intermediate during hydrogen-
### Table I

Second-Order Rate Constants of Hydrogen-Deuterium Exchange of Hydrocarbons

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>( k ) (M(^{-1})sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Diphenylbicyclo [3.2.1] octa-2,6-diene (65)</td>
<td>( 0.50 \times 10^{-2} )(^{a,b} )</td>
</tr>
<tr>
<td>2,4-Diphenylbicyclo [3.2.1] oct-2-ene (66)</td>
<td>( 0.15 \times 10^{-2} )(^{a,c} )</td>
</tr>
<tr>
<td>trans-1,3-diphenylpropene (67)</td>
<td>( 0.33 \times 10^{-2} )(^{a,b,d} )</td>
</tr>
<tr>
<td>Bicyclo [3.2.1] octa-2,6-diene (42)</td>
<td>( 2.0 \times 10^{-3} )(^{d,e} )</td>
</tr>
<tr>
<td>Bicyclo [3.2.1] oct-2-ene (43)</td>
<td>( 0.7 \times 10^{-7} )(^{d,e} )</td>
</tr>
</tbody>
</table>

---

**Explanations:**

- **a.** Experiments were carried out at 25.0° in 87:13 DMSO-d\(_6\)-CH\(_3\)OD with CH\(_3\)ONa as the base. Rates are reproducible to less than ±10%.
- **b.** Average of two runs.
- **c.** Average of three runs.
- **d.** The reported rate has been corrected for statistical factors.
- **e.** The second-order rate constant for this compound has been computed on the basis of the data reported in ref. 29b. Experiments were carried out at 60.0° in DMSO-d\(_6\) with tert-C\(_4\)H\(_9\)K as the base\(^{29b}\).
Figure 5. Typical first order plot of the base-catalyzed hydrogen-deuterium exchange in 2,4-diphenylbicyclo[3.2.1] oct-2,6-diene (65).
Figure 6. Typical first order plot of the base-catalyzed hydrogen-deuterium exchange in 2,4-diphenyl bicyclo[3.2.1] oct-2-ene (66).
Figure 7. Typical first order plot of the base-catalyzed hydrogen deuterium exchange in *trans*-1,3-diphenylpropene (67).
deuterium exchange, in which the negative charge could interact not only with the carbon-carbon double bond at $C_2$, but also with the carbon-carbon double bond at $C_6$, thereby producing a bishomocyclopentadiene anion as depicted by structure 44. Whereas such a homoaromatic interaction leading to anion 44 is possible in the deuterium exchange reaction of diene 42, no such stabilization can be visualized in the case of monoene 43. The participation of the $C_6$ double bond in delocalizing the negative charge in 44 was subsequently confirmed by Winstein and his coworkers who studied its $^1$H nmr spectrum (see Historical p. 17).

In the present study it was found that replacement of the hydrogens at $C_2$ and $C_6$ in bicyclic diene 42 by phenyl groups resulted in totally eliminating the charge delocalization from $C_6$ to the carbon-carbon double bond at $C_6$. This conclusion was reached on the basis of the fact that 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65) and its saturated analog 66 were found to undergo base-catalyzed hydrogen-deuterium exchange at $C_6$ at essentially the same rate as shown in Table I.

In the accepted theory for the base catalyzed hydrogen-deuterium exchange reactions, the mechanism on the following page is considered to be valid showing bicyclic diene 65 as the example.

The proton removal by base yields a carbanion in proximity of the OH proton of a solvent molecule. Thus the internal return ($k_-$) reaction is often faster than further dissociation ($k_2$) to a carbanion capable of reacting with a deuterated solvent molecule especially when the developing charge remains localized, for example with aryl car-
banions. Therefore aromatic hydrocarbons are usually inert to base-catalyzed isotope exchange\textsuperscript{47,48}. However, when the charge of the developing carbanion can be delocalized, $k_2$ will become important, and more important relative to $k_{-1}$ as the strength of conjugation increases. Consequently in the base-catalyzed hydrogen-deuterium exchange reactions involving stabilized carbanions, the assumption is made that formation of the carbanion is the slowest and thus the rate-determining step, that is $k_2 \gg k_{-1}$. This assumption is well documented for delocalized carbanions\textsuperscript{29b,49}. Anything that will stabilize carbanion 78 can be assumed to stabilize the transition state leading to it and thus enhance the rate of formation of that species\textsuperscript{50}. Therefore, if anion 78 has any homoaromatic stabilization (which will arise by delocalization of charge from C$_4$ to the C$_6$,7

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olefinic bond affording the 6 \( \pi \) electron homoaromatic species 80), the parent hydrocarbon 65 should exhibit a faster rate of hydrogen-deuterium exchange than its saturated analog 66 since the latter cannot be expected to afford a homoaromatically stabilized anionic intermediate. (Ground state energies of compounds 65 and 66 are assumed to be about the same since these substrates are very similar). Both anions 78 and 81 are allylically and benzylically stabilized by classical conjugation, but in addition carbanion 78 has non-classical long-range \( \pi \) electron stabilization available to it as depicted in structure 80.

Examination of Table I shows that both 2,4-diphenylbicyclo [3.2.1] octa-2,6-diene (65) and 2,4-diphenylbicyclo [3.2.1] oct-2-ene (66) underwent hydrogen-deuterium exchange at essentially the same rate. Thus replacement of the hydrogens at C2 and C4 in bicyclic hydrocarbons 42 and 43 by phenyl groups has eliminated the large rate difference of deuterium exchange between the two systems. While bicyclooctadiene 42 was found to exchange its allylic hydrogens 10^4.5 times faster than monoene 43, diphenylbicyclooctadiene 65 underwent deuterium exchange only 3.3 times faster than its saturated analog, diphenylbicyclooctene 66, clearly indicating that there is no remote \( \pi \) electron participation in hydrocarbon 65. The tremendous neighboring group effect of the C6,7 double bond in bicyclooctadiene 42 has thus been eliminated.

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and is non-existent in diphenylbicyclooctadiene 65. The slightly larger rate of bicyclic diene 65 relative to monoene 66 is that which would be expected on the basis of purely inductive effects.\textsuperscript{51} A remote double bond will aid the development of a carbanionic center and thus stabilize it by an inductive mechanism. For example, the rate of vinyl hydrogen exchange in norbornadiene (82) is twenty times faster than in norbornene (83) when the exchange reaction is run in cyclohexylamine with cesium cyclohexylamine as the base\textsuperscript{52}.

Additional evidence against any long-range Π electron participation in carbanion 78 is derived from Table I. A comparison of the kinetic data in this table shows that the rates of both hydrocarbons 65 and 66 are in very close proximity to the exchange rate of trans-1,3-diphenylpropene (67), a system in which stabilization by means of neighboring group effects is not possible. Therefore, the present study clearly indicates that there is no neighboring group effect from the C6\textsubscript{7} olefinic bond in diphenylbicyclooctadiene 65 and thus the carbanion 78 derived from this hydrocarbon is a classical anion with no homoaromatic stabilization associated with it. Thus, the 2,4-diphenylbicyclo[3.2.1]octa-2,6-dienyl anion 78 can be best represented by structure 78a where the negative charge is delocalized into the C2\textsubscript{3}, double bond and the two phenyl rings as shown below.
The lack of charge delocalization from C₄ to the C₆₋₇ carbon-carbon double bond in 7₈ may be explained by taking into account the fact that the negative charge at C₄ can interact not only with the C₂₋₃ carbon-carbon double bond but also with the two phenyl rings. Classical stabilization has been previously shown to greatly reduce and sometimes completely eliminate the tendency of the positive charge in a carbonium ion to engage in nonclassical interactions. A number of reports have appeared in the recent literature indicating that the more stable the carbonium ion center is, the less demand that center will make upon neighboring groups for additional stabilization through long-range participation. For example, Gassman and his coworkers⁵³,⁵⁴ showed that the unusually high tendency of the positive charge at C₇ in 7-norbornenyl cation 8₄ to interact with the C₂₋₃ carbon-carbon double bond (structure 2₅) was somewhat reduced by a p-trifluoromethyl-phenyl group at C₇ (structure 8₅), greatly reduced by a phenyl group (structure 8₆), and completely eliminated by an anisyl group (structure 8₇).
As shown in Table II, the original reactivity difference of $10^{11}$ between 7-anti-norbornenyl p-nitrobenzoate 88 and 7-anti-norbornyl p-nitrobenzoate 89 gradually disappears as the carbonium ions derived from the respective hydrocarbons become progressively more stable.
Table II

Relative Rates of Solvolysis of 7-Norbornenyl and 7-Norbornyl p-Nitrobenzoates in Dioxane-Water at 25\(^\circ\)C

<table>
<thead>
<tr>
<th>X</th>
<th>7-Norbornenyl</th>
<th>7-Norbornyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CF(_3)</td>
<td>1.0</td>
<td>34,500</td>
</tr>
<tr>
<td>p-H</td>
<td>1.0</td>
<td>41.5</td>
</tr>
<tr>
<td>p-CH(_3)O</td>
<td>1.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>
A recent NMR study also confirmed the classical nature of 7-p-anisyl-7-norbornenyl cation 87, and the non-classical nature of 7-trifluoromethylphenyl-7-norbornenyl cation 85a.

Thus, the stabilizing effect of a neighboring group seems to be a function of the electron demand of the incipient carbonium ion over a wide range of reactivity. This postulate has also been shown to be true in the case of long-range \( \sigma \) participation by H.C. Brown and his coworkers. For example, it was observed that with increasing electron demand at the cationic center, the rates of solvolysis of 1-aryl-1-cyclopropyl-1-ethyl p-nitrobenzoates increase tremendously relative to 2-aryl-3-methyl-2-butyl p-nitrobenzoates as shown in Table III. Thus \( \sigma \) electrons from the carbon-carbon bonds of the cyclopropane ring participate more and more in stabilizing the incipient carbonium ions as these ions become stabilized less and less by the corresponding aryl groups.

Very recently the relationship between neighboring group participation and stability of the incipient carbonium ion has been used as a very effective tool in determining the extent of \( \gamma \) and \( \sigma \) participation in a large variety of carbonium ions. For instance,
Table III

Relative Rates of Solvolysis of 1-Aryl-1-cyclopropyl-1-ethyl and 2-Aryl-3-methyl-2-butyl p-Nitrobenzoates in 80% Acetone at 25° °° 57a

<table>
<thead>
<tr>
<th>X</th>
<th>Structure</th>
<th>Relative Rate</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CH₃O</td>
<td><img src="image" alt="Structure" /></td>
<td>1.0</td>
<td>505</td>
</tr>
<tr>
<td>p-H</td>
<td><img src="image" alt="Structure" /></td>
<td>1.0</td>
<td>25,300</td>
</tr>
<tr>
<td>p-CF₃</td>
<td><img src="image" alt="Structure" /></td>
<td>1.0</td>
<td>285,000</td>
</tr>
</tbody>
</table>
the application of this tool revealed the absence of \( \pi \) -participation in the solvolysis of 2-aryl-2-norbornenyl p-nitrobenzoates\(^{57b} \) \(^90\) and \(^91\) and the presence of such participation in the solvolysis of 2-aryl-5-methyl-2-norbornenyl p-nitrobenzoates\(^{57c} \) \(^92\) and \(^93\) as shown in Tables IV and V respectively.

On the basis of our experimental findings which clearly showed that 2,4-diphenylbicyclo [3.2.1] octa-2,6-diene (65), 2,4-diphenylbicyclo [3.2.1] oct-2-ene (66) and trans-1,3-diphenylpropene (67) all underwent base-catalyzed hydrogen-deuterium exchange at about the same rate, it can be concluded that just as in the case of carbonium

\[
\begin{align*}
\text{90} & \quad \text{OPNB} \\
\text{91} & \quad \text{OPNB} \\
\text{92} & \quad \text{OPNB} \\
\text{93} & \quad \text{OPNB}
\end{align*}
\]

\[ X = p-\text{CH}_3\text{O}, \ p-H \text{ and } p-\text{CF}_3 \]

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Table IV

Relative Rates of Solvolysis of 2-Aryl-2-norbornenyl p-Nitrobenzoates in 80% Acetone at 25°

<table>
<thead>
<tr>
<th>X</th>
<th>OPNB</th>
<th>OPNB</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CH₃O</td>
<td>1.0</td>
<td>312</td>
</tr>
<tr>
<td>p-H</td>
<td>1.0</td>
<td>202</td>
</tr>
<tr>
<td>p-CF₃</td>
<td>1.0</td>
<td>283</td>
</tr>
</tbody>
</table>

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Table V

Relative Rates of Solvolysis of 5-Methyl-2-aryl-2-norbornenyl p-Nitrobenzoates in 80% Acetone at 25°elsius

<table>
<thead>
<tr>
<th>X</th>
<th>![Chemical Structure 1]</th>
<th>![Chemical Structure 2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-CH₃O</td>
<td>1.0</td>
<td>354</td>
</tr>
<tr>
<td>p-H</td>
<td>1.0</td>
<td>1260</td>
</tr>
<tr>
<td>p-CF₃</td>
<td>1.0</td>
<td>6700</td>
</tr>
</tbody>
</table>
ions, the extent of charge delocalization in carbanions has an inverse relationship to the stability rendered to the developing negative charge by groups directly attached to the carbanionic center.

The present findings constitute the first study demonstrating that the extent of long-range $\pi$ participation in delocalizing a negative charge is a function of the stability of the developing carbanion center. It is also apparent from this study that remote $\pi$ electron participation and classical stabilization are competitive rather than cooperative. With this principle now firmly established for carbanions as well, its use as a tool in detecting the presence of long-range $\pi$ electron participation in these and similar intermediates should prove very valuable.

Whether both phenyl groups are necessary for the elimination of $\pi$ electron participation in the carbanion $\text{78}$ derived from hydrocarbon $\text{65}$ is not clear from the present study. The synthesis of a number of bicyclic systems whose exchange rates could help determine the minimum stabilization necessary to eliminate charge delocalization in anion $\text{78}$ would be a very interesting and worthwhile extension of the present study.

In carbonium ions, the neighboring group participation is a linear function of the electron demand of the incipient carbonium ion. There is a linear relationship between long-range $\pi$ participation and substitution over a wide range of reactivity$^{55}$. Would such a relationship exist in carbanions as well?
C. Effect of the Negative Charge on the Chemical Shift of Neighboring Protons in Carbanions Devoid of Long Range Interactions

In the past few years a number of reports have appeared in the literature describing long range $\pi$ interactions between a carbanionic center and a suitably placed carbon-carbon double bond, to produce such species as $44^{30, 45^{31, 59^{37}}}$ and others $^{32, 38, 59}$ (see Historical).

![Chemical Structures]

44  45  59

In the majority of cases $^{31c, 37, 59}$ the experimental evidence in support of $\pi$ electron participation in these anions was based exclusively on their proton nmr spectra. Most significantly, sizable upfield shifts (ca. 1-2.5 ppm) in the resonance of the protons directly attached to the remote carbon-carbon double bond has been interpreted as evidence indicating considerable charge delocalization in these species.

Very recently, the aza analogue of carbanion $44$, 2-aza-2-N-methyl-bicyclo $[3.2.1]$ octa-3,6-diene ($94$) has been classified as a hetero-homoconjugated system again on the basis of its proton nmr spectrum. Anastassiou and his coworkers $^{60}$ interpreted the upfield chemical shift (0.7 ppm) of $H_7$ in going from monoene $96$ to diene $94$ and the downfield chemical shift (0.2 ppm) of the $2-CH_3$ resonance in going from monoene $95$
to diene 94 as direct evidence showing considerable interaction of the N-lone pair with the remote C₆,₇ carbon-carbon double bond in 94. The same group of workers also detected the closely related anion 97 by means of nmr and classified it as a completely delocalized species as depicted by structure 97a exclusively on the basis of the upfield shift of the H₆ and H₇ vinylic hydrogens (0.98 and 0.78 ppm respectively) relative to diene 94.

However, despite the strong reliance on proton nmr as a tool for detecting the presence and/or extent of remote \( \pi \) electron participation in carbanions and other closely related anions, the effect of the negative charge on the chemical shift of the vinylic and other neighboring protons in the absence of \( \pi \) participation has received very little\(^{31c} \), if any, consideration.
As mentioned earlier (Results and Discussion, Part B) we have found that replacement of the hydrogens at $C_2$ and $C_4$ in the bicyclic hydrocarbons 42 and 43 by phenyl groups reduces the rate difference of the base-catalyzed hydrogen-deuterium exchange of their allylic hydrogens from $10^{4.5}$ to 3.3, clearly indicating that the stabilization rendered by the phenyl groups to the incipient carbanion $78$ has totally eliminated the charge delocalization from the allylic part of the system to the $C_6$-$C_7$ carbon-carbon double bond.

![Diagram of molecules 42 and 43](image)

$k_{rel} \quad 10^{4.5}$

$k_{rel} \quad 1$

It occurred to us that a study of the proton nmr spectrum of carbanion $78$, and especially a comparison of this spectrum with that of anion $44$, previously reported by Winstead and his coworkers\textsuperscript{30} (Historical, p. 17), would be ideally suited in providing information con-
cerning the effect of the negative charge on the chemical shift of neighboring protons in the absence of long-range interactions. More generally, it was thought that the present study would adequately test the appropriateness of using proton nmr alone as a tool in detecting long-range interactions and homoaromaticity in carbanions.

Scheme III

We therefore proceeded to prepare the 2,4-diphenylbicyclo[3.2.1]octadienyl anion (78) and study its proton nmr spectrum. Initial attempts to form this anion by treating the parent bicyclic diene 65 with excess dimethyl anion in THF were not successful. However, carbanion 78 was successfully generated by treatment of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65) with n-butyllithium in THF-d₈-hexane.
(Scheme III). Thus bicyclic diene 65 was reacted with 1.3 equivalents of n-butyllithium (as a 2.2 M solution in hexane) in THF-d$_6$ at -5° and the reaction mixture was allowed to stir at 0-5° for 30 minutes, and at room temperature for 1.5 hours to produce a dark red solution of the anion 78. Subsequent quenching of the anion solution with deuterium oxide afforded the deuterated diene 79 quantitatively, as shown by nmr and vapor phase chromatographic (vpc) analysis of the crude reaction mixture.

The proton nmr spectrum of carbanion 78 in THF-d$_6$-hexane was recorded on a Varian XL-100 instrument using tetramethylsilane (TMS) as an external reference and is displayed in Figure 8.

The multiplet centered at 1.30 ppm and partly overlapped by the signals due to the hexane protons and the residual β-protons of the THF was attributed to protons H$_{8a,b}$. This multiplet arises from the geminal coupling between H$_{8a}$ and H$_{8b}$ as well as from coupling between H$_{8a}$ and H$_{1,5}$. No coupling between H$_{8b}$ and H$_{1,5}$ is observed since their dihedral angle is close to 90°.

The doublet (J = 4.5 Hz) centered at 3.02 ppm was attributed to

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Figure 8. Nmr spectrum of 2,4-diphenylbicyclo[3.2.1]oct-2,6-diene anion (78) in THF-d$_6$-hexane.
protons $H_{1,5}$. This doublet arises from coupling of $H_{1,5}$ with $H_{8a}$. Irradiation at the $H_{8a,b}$ frequency reduced the doublet to a sharp singlet and irradiation at the $H_{1,5}$ frequency simplified the multiplet at 1.30 ppm.

The singlet appearing at 4.53 ppm and integrating for two protons was assigned to the vinylic hydrogens $H_6$ and $H_7$. Irradiation at the $H_{1,5}$ frequency sharpened the singlet at 4.53 ppm.

The triplet centered at 5.66 ppm was assigned to the para protons of the phenyl rings at $C_{2,4}$, while the multiplet centered at 6.45 ppm and integrating for nine protons was attributed to the four ortho and four meta protons of the aromatic rings and to the $H_3$ proton of the bicyclic ring. Irradiation at the para proton frequency simplified the multiplet at 6.45 ppm whereas irradiation at the ortho-meta proton frequency resulted in considerable sharpening of the triplet at 5.66 ppm.

The nmr spectrum of anion 78 exhibits a number of interesting and in many respects unexpected features which merit further discussion. The most outstanding and interesting feature is the close similarity of this spectrum to that of the bicyclooctadienyl anion 44 (compare chemical shift values in Tables VI and VII). Thus, just as in the case of anion 44 (Table VII), the vinylic hydrogens $H_6$ and $H_7$ in anion 78 have experienced a substantial upfield shift (an average of 1.01 ppm; 44% as large as that observed in 44) relative to the parent hydrocarbon 65 (Table VI). Similarly, the protons at $C_8$ have undergone a 0.62 ppm upfield shift (60% as large as that observed in 44), while the proton at $C_3$ moved 1.10 ppm downfield. On the basis
Table VI

Summary of NMR Data for Hydrocarbon 65 and its Corresponding Anion 78

<table>
<thead>
<tr>
<th>Proton</th>
<th>Hydrocarbon 65</th>
<th>Carbanion 78</th>
<th>( \Delta \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_{1,5} )</td>
<td>2.79</td>
<td>3.02</td>
<td>0.23</td>
</tr>
<tr>
<td>( H_3 )</td>
<td>5.38</td>
<td>6.45</td>
<td>1.07</td>
</tr>
<tr>
<td>( H_{6,7} )</td>
<td>5.54 (av)(^a)</td>
<td>4.53</td>
<td>1.01</td>
</tr>
<tr>
<td>( H_{8a,b} )</td>
<td>1.92</td>
<td>1.30</td>
<td>0.62</td>
</tr>
<tr>
<td>( H_o )</td>
<td>6.45 (av)(^a)</td>
<td>6.45 (av)(^a)</td>
<td>0.51</td>
</tr>
<tr>
<td>( H_m )</td>
<td>6.96 (av)(^a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( H_p )</td>
<td>5.66</td>
<td>1.30</td>
<td></td>
</tr>
</tbody>
</table>

a. av = Average value.
b. \( H_o \) = ortho protons of the aromatic ring.
c. \( H_m \) = meta protons of the aromatic ring.
d. \( H_p \) = para protons of the aromatic ring.
Table VII

Summary of NMR Data for Hydrocarbon 42 and its Corresponding Anion 44

<table>
<thead>
<tr>
<th>Proton</th>
<th>Hydrocarbon 42</th>
<th>Carbanion 44</th>
<th>( \Delta \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_{1,5} )</td>
<td>2.57</td>
<td>2.45</td>
<td>0.12</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>5.92</td>
<td>2.84</td>
<td>3.08</td>
</tr>
<tr>
<td>( \text{H}_4^{\text{exo,endo}} )</td>
<td>1.98 (av)(^a)</td>
<td>2.84</td>
<td>0.86</td>
</tr>
<tr>
<td>( \text{H}_3 )</td>
<td>5.15</td>
<td>5.39</td>
<td>0.24</td>
</tr>
<tr>
<td>( \text{H}_{6,7} )</td>
<td>5.92 (av)(^a)</td>
<td>3.67</td>
<td>2.25</td>
</tr>
<tr>
<td>( \text{H}_{8a,b} )</td>
<td>1.78</td>
<td>0.64</td>
<td>1.14</td>
</tr>
</tbody>
</table>

\(^a\) av = Average value.

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of these observations and in the absence of other evidence to the contrary, it may be concluded that charge delocalization to the $C_6^\bullet$, $C_7$ olefinic carbon-carbon double bond has occurred in the diphenylbicyclo-octadienyl carbanion $\text{78}$ to produce a completely delocalized, 6 $\pi$ electron homoaromatic species as represented by structure $\text{80}$. However anion $\text{78}$ has been shown earlier to display no charge delocalization from $C_2^\bullet$, $C_3^\bullet$, $C_4^\bullet$ to the $C_6^\bullet$, $C_7$ double bond (see Results and Discussion, Part B). It is therefore evident from the present study that anisotropic effects$^{61}$ due to charge delocalization at $C_2^\bullet$, $C_3^\bullet$, $C_4^\bullet$ must play

![Diagram](image.png)

a much more important role in influencing changes in the chemical shifts of carbanions such as $\text{44}$, $\text{78}$, and probably many others, than previously anticipated. Thus, the upfield shift of the vinylic protons $H_6^\bullet$, $C_8$, and that of the protons on $C_8$ in anion $\text{78}$ is almost certainly the result of an anisotropic shielding effect due to charge delocalization over $C_2^\bullet$, $C_3^\bullet$, $C_4^\bullet$.

Interestingly enough, the proton at $C_3$ experienced a large downfield shift (1.07 ppm) in anion $\text{78}$. This is quite reminiscent of the large downfield shift (0.90 ppm) of proton $H_2$ in the 1,3-diphenylallyl anion$^{62}$ $\text{98}$, and can be similarly attributed to deshielding aniso-
tropic effects of the delocalized charge at C₂,₃,₄ and to the diamagnetic deshielding effect of the phenyl rings⁴¹,⁶². That the anisotropic deshielding effect of the negative charge at C₂,₃,₄ contributes significantly to the downfield shift of protons H₃ and H₂ in carbanions 78 and 98, respectively, is strongly supported by the fact that sizable downfield shifts are also experienced by the H₂ protons in the phenyl-allyl anion⁶³,⁶⁴ 99 and in the allyl anion⁶⁵,⁶⁶ 100.

Further evidence in support of lack of charge delocalization from C₂,₃,₄ to the C₆,₇ double bond in anion 78 is that the para and ortho-meta protons of the phenyl rings in this anion experienced upfield shifts of 1.30 ppm and 0.51 ppm, respectively. These upfield shifts are almost the same in magnitude as those experienced by the aromatic protons of the 1,3-diphenylallyl anion⁶² 98, and can be
similarly attributed to the extensive charge delocalization into the phenyl rings and especially to the para position.

A final point of interest in connection with carbanion 78 is that unlike anion 44, its $H_1,3$ protons underwent a small downfield shift (ca. 0.23 ppm) relative to the parent hydrocarbon 65. This is most likely due to the diamagnetic deshielding effect of the phenyl rings which is apparently sufficiently strong to offset the shielding effect of the neighboring negative charge delocalized over $C_2,3,4$.

In conclusion, the above results serve to indicate that while proton nmr spectroscopy is certainly a powerful tool in detecting the presence and extent of the effect of the negative charge on the chemical shift of neighboring protons in a carbanionic system, the exact mechanism by which the effect is transmitted cannot be accurately predicted. Therefore, conclusions regarding long-range $\pi$ interactions, homoaromaticity, and homoaromatic ring current effects are best and most safely arrived at by examining not only the proton nmr spectrum of the anion under consideration but also its stability.
relative to a suitably chosen reference system.
V. EXPERIMENTAL

A. General

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

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

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

Gas chromatograms were run on a Varian Aerograph, series 2700 gas chromatograph equipped with a thermal conductivity detector, and using helium as a carrier gas. A 5' x 1/4'' SE-30 on Varaport 30 column was used.

Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60 and/or XL-100 spectrometer. Chemical shifts relative to tetramethylsilane, were measured to the center of a singlet or multiplet.

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

The mass spectra of the deuterated samples were taken at an ionizing voltage of 7eV and at a source block temperature of 180-200°. All samples were introduced into the ion source by a direct insertion probe.

The yields of the products reported are the best yields obtained in each reaction.

Unless otherwise noted the starting materials were used as obtained.
B. Preparation of Starting Materials

1. Preparation of 1,3-dibromo-1,3-diphenyl-2-propanone (68)

This compound was prepared essentially by the method of Breslow, et al., with certain slight modifications. 1,3-Diphenyl-2-propanone (70.0 g; 0.333 moles) dissolved in 250 ml glacial acetic acid was placed in a 1 l. Erlenmeyer flask. To this solution, 110 g (0.666 moles) of bromine in 500 ml acetic acid was added with stirring over a period of 30 min. After the addition was complete, the mixture was stirred for an additional 5 min. and then poured into 1 l. of water. Solid sodium sulfite was added in small portions until the initial yellow color of the solution was discharged and the reaction mixture was allowed to stand for 1 hr. The yellow solid product obtained at the end of this period was filtered and recrystallized from ethanol (95%) to afford 98 g (80%) of 1,3-dibromo-1,3-diphenyl-2-propanone (68), mp 103-108°, lit. mp 79-97°; nmr (CDCl₃) δ 5.69 (d, 2H, H-CBrCOCBr-H), 7.34 (m, 10H, aromatic).

2. Preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (69)

The method used for the preparation of this compound was that of Cookson, et al., with certain modifications as described below.

A 2 l. one-necked round bottom flask was charged with 20 g (0.0544 moles) of 1,3-dibromo-1,3-diphenyl-2-propanone (68), 200 ml (2.44 moles) of cyclopentadiene (which was obtained by fractional

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distillation of 3α,4,7α-tetrahydro-4,7-methanoindene immediately before use), 100 g (0.68 moles) of sodium iodide and 600 ml of acetonitrile. It was important that the sodium iodide be added to the reaction mixture last. The resulting brown solution was refluxed for 45 min. with good stirring. Chloroform (400 ml) was added and the reaction mixture was washed with 400 ml of 15% aqueous sodium thiosulfate. The layers were separated, the organic layer was washed gently with 200 ml of water, dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. It was important that the reaction mixture be worked up immediately. The resulting yellow solid was recrystallized from ethanol (95%) to give 11 g (74%) of 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-one (69), mp 149.5-151.5°, lit. mp 149.5-151.5°; nmr (CDCl₃) 2.24 (m, 2H, C₈-H₂), 3.05 (m, 2H, C₁-H, C₅-H), 6.23 (t, 2H, H-C₆=C₇-H), 7.20 (m, 10H, aromatic).

3. Preparation of 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-ol (70)

A solution of 11 g (0.040 moles) of 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-one (69) in 1400 ml of dry ether was introduced dropwise into a 2 l. three-necked round bottom flask containing 2.50 g (0.066 moles) of LiAlH₄ in 200 ml of dry ether and equipped with an egg-shaped stirring bar, a reflux condenser connected to a nitrogen tank through a T-tube, and a heating mantle. The resulting slurry was allowed to reflux for 48 hrs. with good stirring. The reaction mixture was cooled and 2.50 ml of water, 2.50 ml of 15% sodium hydroxide solution and then 7.50 ml of water was added successively. This
work-up procedure is described by Fieser and Fieser. The solid hydroxides were filtered by means of a Buchner funnel with the aid of Celite. The clear filtrate was dried over anhydrous magnesium sulfate. The filtered solution was freed of solvent on the flash evaporator and a viscous oil which solidified gradually was obtained. Recrystallization of this oil from ethanol (95%) afforded 8 g (73%) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70), mp 78-83°; ir 3570 cm⁻¹ (OH); nmr (DMSO-d₆) δ 2.12 (m, 2H, C8-H₂), 2.80 (m, 2H, -C₁-H, -C₃-H), 3.05 (s, 1H, C₅H₀H), 3.32 (m, 2H, Ph-C₂-H, Ph-C₄-H), 4.22 (m, 1H, C₅H₀H), 6.49 (s, 2H, H-C₆=C₇-H), 7.27 (m, 10H, aromatic).

Mass spectrum (relative intensity) 276 (12, M⁺), 258 (19, M-H₂O), 157 (53), 120 (30), 91 (100).

Found:  C, 87.03; H, 7.02.

4. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluenesulfonate (71) using metallic sodium and p-toluene sulfonyl chloride

Sodium (0.20 g; 0.009 moles) with 20 ml of dry ether was placed in a 250 ml three-necked round bottom flask under nitrogen. A solution of 2.4 g (0.008 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) in 60 ml of dry ether was added dropwise. After the addition was completed, the reaction mixture was allowed to stir at room temperature for 2 hrs. and then refluxed for 1 hr. At the end of this period, a solution of 1.53 g (0.008 moles) of p-toluenesulfonyl chloride in 50 ml of dry ether was added dropwise and the reaction
mixture was allowed to stir at room temperature for 2 hrs. Water (80 ml) was added carefully and the layers were separated. The organic layer was washed once with 50 ml of water, dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. Nmr, ir, and gc analysis of the crude solid product indicated that unreacted starting material, 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) was obtained.

5. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluenesulfonate (71) using sodium hydride and p-toluenesulfonyl chloride

Sodium hydride (0.526 g; 0.0125 moles) in 40 ml of dry ether was placed in a 250 ml three-necked round bottom flask under nitrogen. To this mixture, a solution of 1.38 g (0.005 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) in 40 ml of dry ether was added dropwise. After the addition was completed, the reaction mixture was allowed to stir at room temperature for 2 hrs. At the end of this period, a solution of 1.53 g (0.008 moles) of p-toluenesulfonyl chloride in 50 ml of dry ether was added dropwise and the reaction mixture was allowed to stir at room temperature for 3 hrs. Water (80 ml) was added carefully and the layers were separated. The organic layer was washed once with 50 ml of water, dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. Nmr, ir and gc analysis of the crude solid product indicated that unreacted starting material, 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-
ol (70) was obtained.

6. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluenesulfonate (71) using sodium amide and p-toluenesulfonyl chloride

Sodium amide (0.01 mole) was freshly prepared by reacting 0.23 g (0.01 moles) of sodium with 200 ml of liquid ammonia as described in Organic Reactions. The excess ammonia was evaporated on the steam bath while dry ether was added to the reaction mixture to keep the volume constant. To the stirred dark gray suspension of sodium amide in dry ether was added dropwise 1.38 g (0.005 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) in 40 ml of dry ether. The reaction mixture was allowed to stir at room temperature for 2 hrs. At the end of this period, a solution of 1.53 g (0.008 moles) of p-toluenesulfonyl chloride in 50 ml of dry ether was added dropwise and the reaction mixture was allowed to stir at room temperature for 2 hrs. The mixture was then poured into 200 ml of cold 3N HCl and the layers were separated. The organic layer was washed with 50 ml of aqueous saturated NaHCO₃ and 50 ml of water, dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The crude solid product was identified by gas chromatographic analysis to be 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70).
7. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-yl-3-p-toluenesulfonate (71) using pyridine and p-toluenesulfonyl chloride

To a stirred and ice-cooled solution of 0.993 g (0.0036 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) in 6 ml of dry pyridine in a 35 ml three-necked round bottom flask was added dropwise a solution of 1.04 g (0.0055 moles) of p-toluenesulfonyl chloride in 7 ml of dry pyridine. After the addition was completed, the reaction mixture was allowed to stir at 0-5° for 1 hr. and then it was left to stand in the refrigerator overnight. The mixture was poured onto ice and the product was extracted with two 100 ml portions of ether-pentane. The extracts were combined and washed with 20 ml of cold dilute sulfuric acid, 30 ml of water, 30 ml of aqueous saturated NaHCO₃ and 50 ml of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The crude solid product was identified by gas chromatographic analysis to be 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70).

Attempts to prepare the p-toluenesulfonate ester 71 by refluxing a solution of 0.50 g (0.0018 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) and 0.57 g (0.0030 moles) of p-toluenesulfonyl chloride in 13 ml of dry pyridine for 42 hrs. following the procedure described above again failed to yield the desired product.
8. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-
3-methanesulfonate (72) using pyridine and methanesulfonyl chloride

To a stirred solution of 0.50 g (0.0018 moles) of 2,4-diphenyl-
bicyclo[3.2.1]oct-6-en-3-ol (70) in 12 ml of dry pyridine in a 25 ml
three-necked round bottom flask was added dropwise 0.34 g (0.0030
moles) of methanesulfonyl chloride in 5 ml of dry pyridine. The reac-
tion mixture was allowed to stir at room temperature for 42 hrs.; the
mixture was then poured onto ice and the product was extracted with
two 50 ml portions of ether. The extracts were combined and washed
with 20 ml of cold dilute sulfuric acid, 30 ml of water, 30 ml of
aqueous saturated NaHCO₃, and 50 ml of water. The organic layer was
dried over anhydrous magnesium sulfate and freed of solvent on the
flash evaporator. The residue was identified by gas chromatogrpahic
analysis to be 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70).

Attempts to prepare the methanesulfonate ester 72 by refluxing
a solution of 0.50 g (0.0018 moles) of 2,4-diphenylbicyclo[3.2.1]
oct-6-en-3-ol (70) and 0.34 g (0.0030 moles) of methanesulfonyl chlor-
ride in 17 ml of dry pyridine for 71 hrs. following the procedure
described above again failed to yield the desired product.

9. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-
3-methanesulfonate (72) using triethylamine and methanesulfonyl
chloride
To a stirred solution of 0.40 g (0.0015 moles) of 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-ol (70) in 9 ml of dry triethylamine in a 25 ml three-necked round bottom flask was added dropwise 0.34 g (0.0030 moles) of methanesulfonyl chloride in 5 ml of dry triethylamine. After the addition was completed, the reaction mixture was allowed to stir at room temperature for 20 hrs. The mixture was then poured onto ice and the product was extracted with two 50 ml portions of ether. The extracts were combined and washed with 20 ml of 3N HCl, 30 ml of aqueous saturated NaHCO₃, and 50 ml of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The crude solid product was identified by gas chromatographic analysis to be 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-ol (70).

10. Attempted preparation of 2,4-diphenylbicyclo [3.2.1] oct-6-enyl-3-acetate (73) using pyridine and acetyl chloride

Acetyl chloride (0.22 g; 0.0027 moles) was added dropwise to a stirred solution of 0.50 g (0.0018 moles) of 2,4-diphenylbicyclo [3.2.1] oct-6-en-3-ol (70) in 10 ml of dry pyridine in a 25 ml three-necked round bottom flask. After the addition was completed, the reaction mixture was allowed to stir at room temperature for 20 hrs. The mixture was then poured onto ice and the product was extracted with two 50 ml portions of ether. The extracts were combined and washed with 20 ml of 3N HCl, 30 ml of aqueous saturated NaHCO₃, and 50 ml of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The crude solid product was identified by gas chromatographic analysis to be 2,4-diphenylbicyclo [3.2.1] oct-6-enyl-3-acetate (73).

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sulfate and freed of solvent on the flash evaporator. The residue was identified by gas chromatographic analysis to be 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70).

An attempt to prepare the bicyclic acetate 73 by refluxing a solution of 0.50 g (0.0018 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) and 0.22 g (0.0027 moles) of acetyl chloride in 10 ml of dry pyridine for 24 hrs. following the procedure described above resulted in a 60:40 mixture of acetate 73 to alcohol 70 as determined by gas chromatographic analysis of the crude reaction mixture.

11. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-acetate (73) using pyridine and acetic anhydride

To a stirred solution of 0.50 g (0.0018 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) in 10 ml of dry pyridine in a 25 ml three-necked round bottom flask was added dropwise 0.28 g (0.0027 moles) of acetic anhydride. The reaction mixture was allowed to stir at room temperature for 3 days. The mixture was then poured onto ice and the product was extracted with two 50 ml portions of ether. The extracts were combined and washed with 20 ml of 3N HCl, 30 ml of aqueous saturated NaHCO₃, and 50 ml of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The residue was identified by gas chromatographic analysis to be 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70).

Attempts to prepare the bicyclic acetate 73 by refluxing a solution of 0.50 g (0.0018 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-
en-3-ol (70) and 0.28 g (0.0027 moles) of acetic anhydride in 10 ml of dry pyridine for 24 hrs. following the procedure described above again failed to yield the desired product.

12. Preparation of p-toluenesulfinyl chloride (74)

This compound was prepared essentially by the method described in Organic Syntheses. To 109 ml (1.5 moles) of thionyl chloride in a 250 ml round-bottom flask, 35.6 g (0.2 moles) of powdered sodium p-toluenesulfinate was added in portions at room temperature over a 10 to 15 minute period. A vigorous reaction occurred with the evolution of hydrogen chloride and sulfur dioxide. As the first portions of the sulfinate were added, the temperature of the reaction mixture rose, but it soon dropped to 0° as the addition proceeded. The resulting clear yellow liquid containing a white opaque solid was protected from moisture by means of a calcium chloride drying tube and was left to stand at room temperature for 2 hrs. Most of the excess thionyl chloride was evaporated under a reduced pressure of 20 mm on the water aspirator. Dry ether (50 ml) was added and the solvent was evaporated under reduced pressure to remove the last traces of thionyl chloride. The crude product was dissolved by successive treatments of 50, 30 and 30 ml portions of dry ether and was filtered off from the inorganic residue very quickly. Evaporation of the solvent on the flash evaporator afforded 7.0 g (20%) of pale yellow p-toluenesulfinyl chloride (74); nmr (CCl₄) δ 2.43 (s, 3H, CH₃), 7.50 (m, 4H, aromatic).
13. Preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluene sulfinate (75)

To a well stirred and ice-cooled solution of 2.0 g (0.0072 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70), 0.60 g (0.0072 moles) of dry pyridine in 25 ml of dry ether in a 50 ml three-necked round bottom flask was added dropwise 1.28 g (0.0072 moles) of p-toluenesulfinyl chloride (74). After the addition was completed, the reaction mixture was allowed to stir at 0-5° for 3 hrs. The white solid product obtained at the end of this period was dissolved in 50 ml of dry ether and the ether layer was washed with 25 ml of 3N HCl, 25 ml of water, 25 ml of aqueous saturated NaHCO₃ and 25 ml of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The resulting white solid was recrystallized from ethanol (95%) to give 2.1 g (70%) of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluenesulfinate (75), mp 159-162°; ir 1120 cm⁻¹ (S = O); nmr (CDCl₃) δ 2.38 (s, 3H, CH₃), 2.90 (m, 2H, -C₆-H, -C₇-H), 3.50 (dd, 2H, Ph-C₂-H, Ph-C₃-H), 5.00 (t, 1H, -C₃-H), 6.30 (t, 2H, H-C₆ = C₇-H), 7.20 (m, 14H, aromatic).

Anal. Calcd for C₂₇H₂₆O₂S: C, 78.20; H, 6.28; S, 7.72.

Found: C, 77.93; H, 6.32; S, 7.93.

14. Attempted preparation of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluenesulfonate (71) using m-chloroperbenzoic acid

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To a stirred and ice-cooled solution of 0.414 g (0.0010 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-enyl-3-p-toluenesulfinate (75) in 10 ml of methylene chloride in a 50 ml three-necked round bottom flask was added dropwise a solution of 0.26 g (0.0015 moles) of m-chloroperbenzoic acid in 10 ml of methylene chloride. After the addition was completed, the reaction mixture was allowed to stir at 0-5° for 2.5 hrs. The mixture was then washed with 10 ml of 5% aqueous K₂CO₃ and 10 ml of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent on the flash evaporator. The gc and nmr analysis of the residue showed the presence of a new product. This new product was not identified.

15. Preparation of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65)

To a well stirred and ice-cooled solution of 8.2 g (0.0297 moles) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-ol (70) in 85 ml dry pyridine in a 250 ml three-necked round bottom flask was added dropwise 5.3 g (0.446 moles) of purified thionyl chloride. The temperature was not allowed to exceed 20° during the addition. After the addition was completed, the ice-bath was removed and the reaction mixture was allowed to stir at room temperature for 6 hrs. The mixture was then filtered onto 25 g of ice, leaving the pyridine salt behind. The product was then extracted with three 125 ml portions of hexane and the extracts were combined and washed with 90 ml of 3N HCl, 90 ml of aqueous saturated NaHCO₃, and 90 ml of water. The hexane layer was subsequently boiled for 10 min. in the presence of 1 g of decolorizing carbon. The solution was then filtered through a Buchner funnel with

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the aid of Celite and the clear filtrate was dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded a highly viscous oil. This was recrystallized from methanol to give 6.2 g (80%) of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65), mp 43-45°; nmr (CDCl₃) Δ 2.27 (m, 2H, -C₈-H₂), 3.05 (m, 1H, -C₅-H), 3.21 (m, 1H, -C₁⁻H), 3.83 (m, 1H, Ph-C₄⁻H), 5.32 (dofd, 1H, H-C₆=C₇⁻H), 5.72 (m, 1H, -C₃⁻H), 6.47 (dofd, 1H, H-C₆ = C₇⁻H), 7.31 (m, 10H, aromatic).

Mass spectrum (relative intensity) 258 (71, M⁺), 230 (40), 154 (40), 105 (100), 91 (82).


Found: C, 92.63; H, 7.23.

The following resonances were found in THF-d₈-hexane using an external TMS standard: Δ 1.92 (m, 2H, -C₈⁻H₂), 2.70 (m, 1H, -C₅⁻H), 2.87 (m, 1H, -C₁⁻H), 3.48 (m, 1H, Ph-C₄⁻H), 4.95 (dofd, 1H, H-C₆ = C₇⁻H), 5.38 (m, 1H, -C₃⁻H), 6.13 (dofd, 1H, H-C₆ = C₇⁻H), 6.96 (m, 10H, aromatic).

Proton assignments in the nmr of compound 65 were established by spin-decoupling and INDORe41 (Internuclear Double Resonance) experiments on a Varian XL-100 instrument. Irradiation at the H₁ frequency simplified the multiplet at 5.72 ppm to a doublet and also reduced the doublet of doublets at 6.47 ppm to a doublet with large coupling retained. Irradiation at the H₅ frequency reduced the doublet of doublets at 5.32 ppm to a doublet with large coupling retained. Irradiation at the H₄ frequency simplified the multiplet at 3.05 ppm and also reduced the multiplet at 5.72 ppm to a broad singlet. In

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the INDOR\textsuperscript{41} (Internuclear Double Resonance) experiments, observation at the $H_1$ frequency showed that only $H_7$ proton appeared. Observation at the $H_4$ frequency indicated that $H_3$ and $H_5$ protons appeared whereas observation at the $H_5$ frequency showed that only $H_4$ and $H_6$ protons appeared.

16. Preparation of 2,4-diphenylbicyclo \{3.2.1\} octan-3-one (76)

To a solution of 10.5 g (0.0383 moles) of 2,4-diphenylbicyclo \{3.2.1\} oct-6-en-3-one (69) in 700 ml of absolute methanol in a one-necked 1000 ml round bottom flask was added 10.5 g (0.0564 moles) of p-toluenesulfonyl hydrazine and 16 drops of concentrated hydrochloric acid and the mixture was refluxed for 23 hrs. with good stirring under nitrogen. The resulting yellow solution was concentrated by evaporation of the solvent on the flash evaporator and the product was recrystallized from methanol to give 8.25 g (78\%) of 2,4-diphenylbicyclo \{3.2.1\} octan-3-one (76), mp 114-116°; ir 1700 cm\textsuperscript{-1} (C=O); nmr (CDCl\textsubscript{3}) $\delta$ 2.02 (m, 6H, $\text{C}_8$-$\text{H}_2$, $\text{C}_7$-$\text{H}_2$, $\text{C}_6$-$\text{H}_2$), 2.78 (m, 2H, $\text{C}_1$-$\text{H}$, $\text{C}_5$-$\text{H}$), 3.93 (d, 2H, Ph-$\text{C}_2$-$\text{H}$, Ph-$\text{C}_4$-$\text{H}$), 7.30 (m, 10H, aromatic).

\textbf{Anal.} Calcd for C\textsubscript{20}H\textsubscript{20}O: C, 86.96; H, 7.24.

Found: C, 86.93; H, 7.24.

17. Preparation of 2,4-diphenylbicyclo \{3.2.1\} octan-3-ol (77)

A solution of 9.34 g (0.0338 moles) of 2,4-diphenylbicyclo \{3.2.1\} octan-3-one (76) in 1400 ml of dry ether was introduced
dropwise into a 2 l. three-necked round bottom flask containing 2.50 g (0.006 moles) of LiAlH₄ in 200 ml of dry ether and equipped with an egg-shaped stirring bar, a reflux condenser connected to a nitrogen tank through a T-tube, and a heating mantle. The resulting slurry was allowed to reflux for 48 hrs. with good stirring. The reaction mixture was cooled and 2.50 ml of water, 2.50 ml of 15% sodium hydroxide solution, and then 7.50 ml of water was added successively. This work-up procedure is described by Fieser and Fieser. The solid hydroxides were filtered through a Buchner funnel with the aid of Celite and the clear filtrate was dried over anhydrous magnesium sulfate. The filtered solution was freed of solvent on the flash evaporator to afford a viscous oil which solidified upon standing. Recrystallization of this oil from methanol afforded 7.50 g (80%) of 2,4-diphenylbicyclo[3.2.1] octan-3-ol (77), mp 103.5-106.5°; ir 3420 cm⁻¹ (OH); nmr (CDCl₃) 1.09 (s, 1H, CH₃), 2.04 (m, 6H, C₆-H₂, C₇-H₂, C₈-H₂), 2.73 (m, 2H, -C₁-H, -C₅-H), 3.21 (m, 2H, Ph-C₂-H, Ph-C₄-H), 4.69 (m, 1H, OCH₃), 7.42, m, 10H, aromatic).

Mass spectrum (relative intensity) 278 (57, M⁺), 260 (3, M-H₂O), 171 (39), 117 (41), 91 (100).

**Anal.** Calcd for C₂₀H₂₂O: C, 86.33; H, 7.91.
Found: C, 86.58; H, 7.86.

18. Preparation of 2,4-diphenylbicyclo[3.2.1] oct-2-ene (66)

To a well-stirred and ice-cooled solution of 13.0 g (0.0470 moles) of 2,4-diphenylbicyclo[3.2.1] octan-3-ol (77) in 140 ml dry pyridine in a 250 ml three-necked round bottom flask was added drop-
wise 8.39 g (0.0705 moles) of purified thionyl chloride. The temperature was not allowed to exceed 20° during the addition. After the addition was completed, the ice-bath was removed and the reaction mixture was allowed to stir at room temperature for 6 hrs. The mixture was then filtered onto 25 g of ice, leaving the pyridine salt behind. The product was then extracted with three portions of 150 ml of hexane and the combined extracts were washed with 90 ml of 3N HCl, 90 ml of aqueous saturated NaHCO₃, and 90 ml of water. The hexane layer was boiled for 10 min. in the presence of 1 g of decolorizing carbon. The solution was then filtered through a Buchner funnel with the aid of Celite and the clear filtrate was dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure afforded a highly viscous oil. This was recrystallized from methanol to give 10.0 g (82%) of 2,4-diphenylbicyclo [3.2.1] oct-2-ene (66), mp 53-55°; nmr (CDCl₃)  δ 1.73 (m, 6H, SCB-H₂, 'c7-H₂, 'c6-H₂), 2.72 (m, 2H, -C₃-H, -C₄-H), 4.03 (m, 1H, Ph-C-H), 5.90 (m, 1H, -C₃-H), 7.33 (m, 10H, aromatic).

Mass spectrum (relative intensity) 260 (27, M⁺), 219 (18), 141 (39), 130 (42), 91 (100).

Found: C, 92.08; H, 7.56.

19. Preparation of trans-1,3-diphenylpropene (67)

trans-1,3-Diphenylpropene was prepared by the method of Bonner, et al., with slight modifications. Phenylacetaldehyde, (30 g, 0.249 moles) 105 ml of ethanol and 15 g (0.267 moles) of potassium...
hydroxide were placed in a 300 ml one-necked round bottom flask equipped
with a reflux condenser. Most of the potassium hydroxide pellets
dissolved immediately and the resulting red solution was refluxed
for 4 hrs. The reaction mixture was cooled and diluted with 500 ml
of water. The product was then extracted with two portions of 250 ml
of ether. The ether extracts were combined and washed first with
100 ml of 10% aqueous sodium hydroxide solution and then with 100 ml
of water. The ether layer was dried over anhydrous magnesium sulfate.
The filtered solution was freed of solvent on the flash evaporator
to afford a yellow thin oil. This oil was chromatographed on a 40 x
600 mm neutral alumina column. Elution with hexane, followed by
evaporation of the solvent gave a colorless oil which was further
purified by recrystallization from hexane. Precipitation of the pro-
duct was induced by cooling the solution in a dry-ice-2-propanol bath.
There was obtained 15.6 g (33%) of trans-1,3-diphenylpropene (67),
mp 18-19°, lit.42 mp 18°; nmr (CCl₄) 3.50 (m, 2H, Ph-C₃-H₂), 6.30
(d, 1H, H-C≡C₂-H), 6.38 (d, 1H, H-C₁=C₂-H), 7.22 (m, 10H, aromatic).

20. Preparation of sodium methoxide solution

Deuterio methanol (CH₃OD; 15 ml) was placed in a 25 ml three-necked
flask under nitrogen. Sodium (1.06 g; 0.046 moles) was weighed out in
dry hexane and was carefully added to the CH₃OD at room temperature over
a period of 8 hrs. The mixture was allowed to stir until all the
sodium had reacted. The resulting sodium methoxide solution was then
transferred into a clean, dry, nitrogen flushed volumetric flask and
was standardized by titration against standard hydrochloric acid.
using phenolphthalein as the indicator. Appropriate amounts of this stock base solution were then used in the rate experiments.

C. Preparation of the 2,4-diphenylbicyclo
\[3.2.1\] octa-2,6-diene Anion (78)

1. Preparation of 2,4-diphenylbicyclo \[3.2.1\] octa-2,6-diene anion (78) in THF-\(d_8\)

This reaction 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 nitrogen tank through a T-tube. The flask was charged with 0.50 g (0.0019 moles) of 2,4-diphenylbicyclo \[3.2.1\] octa-2,6-diene (65), flushed with nitrogen and closed to the atmosphere. Per-deuterio THF (2.5 ml) was introduced into the reaction flask through the septum by means of a syringe. The clear solution was cooled to -5° with a sodium chloride-ice-water mixture and then 1.13 ml (0.0025 moles) of a 2.2 M solution of n-butyllithium in hexane was added through the septum. The reaction mixture was allowed to stir for 10 min., the salt-ice-water bath was replaced by an ice-water solution and stirring was continued for 20 min. at 0-5°. The ice-water bath was then removed and the reaction mixture was stirred for an additional 1.5 hrs. at room temperature. The dark red solution was then syringed into a nmr tube equipped with a septum and a nitrogen atmosphere. The nmr tube was centrifuged for 3-4 min. and the spectrum of the solution was recorded on a Varian XL-100 instrument. The following resonances were obtained using an external TMS standard: \(\delta 1.30\)

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(m, 2H, C8-H2), 3.02 (d, 2H, -C1-H and -C3-H), 4.53 (s, 2H, H-C6=C7-H), 5.66 (t, 2H, para H), 6.45 (m, 9H, 4 ortho H, 4 meta H and C3-H). Spin-decoupling experiments were done to establish the proton assignments in the nmr of anion 76: Irradiation at the H8a,b frequency reduced the doublet at 3.02 ppm to a sharp singlet. Irradiation at the H1,s frequency simplified the multiplet at 1.30 ppm and also sharpened the singlet at 4.53 ppm. Irradiation at the para proton frequency simplified the multiplet at 6.45 ppm whereas irradiation at the ortho-meta proton frequency resulted in considerable sharpening of the triplet at 5.66 ppm. After the nmr spectrum was obtained the solution was removed from the nmr tube by means of a syringe and discharged in 5 ml of water. The layers were separated; the organic layer was washed with 5 ml of water, dried over anhydrous magnesium sulfate, filtered, and the solvent evaporated under reduced pressure. The residue was identified by nmr and gas chromatographic analysis as the 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65).

2. Deuteration of the anion 78

2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (10.5 g, 0.0019 moles) in 2.5 ml of dry THF was treated with 1.04 ml (0.0025 moles) of a 2.4 M solution of n-butyllithium in hexane to afford the anion as described above. Deuterium oxide (5 ml) was then added and stirring was continued for 10 min. 10 ml of water was added and the layers were separated. The organic layer was washed with 5 ml of water, dried over anhydrous magnesium sulfate and freed of most of the solvent under reduced pressure to give 2,4-diphenylbicyclo[3.2.1]
octa-2,6-diene-d$_1$, (79) as shown by nmr analysis; nmr (CDCl$_3$) \( \delta \)

- 2.28 (m, 2H, C$_8$-H$_2$),
- 3.12 (m, 2H, -C$_1$-H, -C$_5$-H),
- 5.32 (m, 1H, H-C$_6$=C$_7$-H),
- 5.72 (t, 1H, -C$_3$-H),
- 6.47 (m, 1H, H-C$_6$=C$_7$-H),
- 7.31 (m, 10H, aromatic).

D. Kinetic Procedure

The base catalyzed hydrogen-deuterium exchange rates of 2,4-
diphenylbicyclo[3.2.1] octa-2,6-diene (65), 2,4-diphenylbicyclo-

[3.2.1] oct-2-ene (66) and trans-1,3-diphenylpropene (67) were

measured in 87:13 DMSO-d$_6$-CH$_3$OD containing CH$_3$ONa as the base at 25°,

and the deuterium uptake was monitored by mass spectrometry.$^46$

Mass spectra were run on a Dupont 21-490B spectrometer operating

at 70 eV. The mass spectra of the deuterated samples were taken at

an ionizing voltage of 7 eV where very little or no fragmentation

has occurred. Several scans of each cluster of molecular ion peaks

were made at different detector sensitivities. Peak heights were

taken as proportional to ion concentrations (peak areas at expanded

scale settings were found to be proportional to peak heights). The

relative height of each peak in the molecular ion cluster was calcu-

lated as a fraction of the total cluster. These values were averaged

and corrected for natural abundance intensities by measuring the

peak heights in the unlabeled standard and subtracting the contributions

of the unlabeled species from each isotope peak height in the

molecular ion cluster.

In all of the exchange reactions, pseudo-first order kinetics

with respect to the alkene were observed. The base was acting as

the catalyst. Plots of log H remaining vs. time gave straight lines.
A change in the initial alkene concentration did not affect the rate constant. Six points were taken in each experiment over a period of 1.5 hrs. The data were treated in a least squares analysis on a Wang calculator program for log H remaining vs. time. The pseudo-first order rate constants obtained in this fashion were divided by the appropriate base concentration to afford the second order rate constants, \( K_2 = \frac{K_{\text{obs}}}{[B]} \) shown in Table I. Three experiments were run and the resulting second order rate constants were averaged to get the individual rate constants for each of the three compounds studied.

In a typical run, 1.0 g (0.00386 moles) of 2,4-diphenylbicyclo[3.2.1]octa-2,6-diene (65) was weighed in a clean, dry, nitrogen flushed 5 ml volumetric flask. Perdeuterio DMSO (3.5 ml) and 0.51 ml of methanol-0-d was added into the flask by means of pipettes under a large inverted funnel connected to a nitrogen tank. The mixture was shaken well to dissolve the alkene. The clear solution was then diluted up to the mark with 0.03 ml of CH$_3$ONa/CH$_3$OD stock solution under nitrogen atmosphere and mixed well. The final base concentration after mixing was 1.83 x 10$^{-2}$M. The flask cap was replaced quickly by a septum and the volumetric flask was immediately transferred to a constant-temperature bath at 25$^\circ \pm$ 0.1. After thermal equilibration (30 sec) the timer was started. Aliquots (0.8 ml) were withdrawn by syringe at intervals over a period of approximately 1.5 hrs. The flask was constantly flushed with nitrogen during this period. The aliquots were quenched immediately with a solution containing 10 ml of water and 1 ml of 3N HCl and extracted with 30 ml of pentane. The layers were separated, the organic layer was dried over anhydrous
magnesium sulfate and the filtered solution was freed of solvent on the flash evaporator to afford the partially deuterated alkene.

The extent of deuterium incorporation as a function of time is shown in Table VIII for each of the compounds studied.
### Table VIII

**Extent of Deuterium Incorporation as a Function of Time**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temp.</th>
<th>Time (sec)</th>
<th>Percent Unlabeled</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>trans-1,3-Diphenylpropene</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25°</td>
<td>137</td>
<td>90.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>348</td>
<td>86.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>956</td>
<td>80.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1660</td>
<td>77.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2926</td>
<td>67.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4868</td>
<td>57.84</td>
</tr>
<tr>
<td><strong>2,4-Diphenylbicyclo[3.2.1] octa-2,6-diene</strong></td>
<td>25°</td>
<td>192</td>
<td>95.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>389</td>
<td>90.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>899</td>
<td>87.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1460</td>
<td>82.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2037</td>
<td>78.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2862</td>
<td>73.29</td>
</tr>
<tr>
<td><strong>2,4-Diphenylbicyclo[3.2.1] oct-2-ene</strong></td>
<td>25°</td>
<td>204</td>
<td>98.91</td>
</tr>
<tr>
<td></td>
<td></td>
<td>796</td>
<td>96.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1597</td>
<td>91.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2763</td>
<td>90.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4176</td>
<td>81.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6167</td>
<td>74.69</td>
</tr>
</tbody>
</table>
VI. SUMMARY

2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (65), 2,4-diphenylbicyclo[3.2.1]oct-2-ene (66) and trans-1,3-diphenylpropene (67) were synthesized and their base-catalyzed hydrogen-deuterium exchange rates were measured. Examination of the rate data showed that all three hydrocarbons underwent hydrogen-deuterium exchange at essentially the same rate. It was thus concluded that the 2,4-diphenylbicyclo[3.2.1]octa-2,6-dienyl anion (78) derived from hydrocarbon 65 is a classical anion with no homoaromatic stabilization associated with it and that just as in the case of carbonium ions, the extent of long-range participation in delocalizing a negative charge is a function of the stability of the developing carbanion.

2,4-Diphenylbicyclo[3.2.1]octa-2,6-diene (65) was converted to its anion \(78\) by means of n-butyllithium in THF-d\(6\)-hexane. Examination of the nmr spectrum of carbanion \(78\) showed a close similarity to that of the completely delocalized, homoaromatic bicyclo[3.2.1]octa-2,6-dienyl anion 44. Since anion \(78\) has been shown earlier to display no charge delocalization from C\(_2\), C\(_3\), C\(_4\) to the C\(_6\), C\(_7\) double bond, it was concluded that anisotropic effects due to charge delocalization at C\(_2\), C\(_3\), C\(_4\) must play a much more important role in influencing changes in the chemical shifts of carbanions such as 44, 78 and probably many others, than previously anticipated.

While proton nmr spectroscopy is certainly a powerful tool in detecting the presence and extent of the effect of the negative charge on the chemical shift of neighboring protons in a carbanionic...
system, the exact mechanism by which the charge is transmitted cannot be accurately predicted. Therefore, conclusions regarding long-range \( \pi \) interactions, homoaromaticity and homoaromatic ring current effects are best and most safely arrived at by examining not only the proton nmr spectrum of the anion under consideration but also its stability relative to a suitably chosen reference system.
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