

# Bicycloaromaticity. Stability and Rearrangements of the Bicyclo[3.2.2]nonatrienyl Anion and Cation<sup>1a,b</sup>

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**Abstract:** The question of bicycloaromatic stabilization and destabilization is examined. A revised reference point for determining bicycloaromatic character is proposed, and the relative importance of homoaromaticity and bicycloaromaticity is considered. The chemistry of the bicyclo[3.2.2]nona-2,6,8-trienyl anion and cation has been studied to provide a test of these concepts. The anion is shown to be a stable delocalized ion which undergoes a degenerate scrambling. The cation has probably not been prepared under the solvolytic procedures employed because of a facile rearrangement to barbaralyl products. The barbaralyl cations undergo a specific rearrangement, which results in asymmetric labeling in a formally symmetric system. Mechanisms for these rearrangements are proposed. It is concluded that the homoaromatic character of these ions is the major factor governing their behavior and that destabilization in antihomoaromatic and antibicycloaromatic systems will be small.

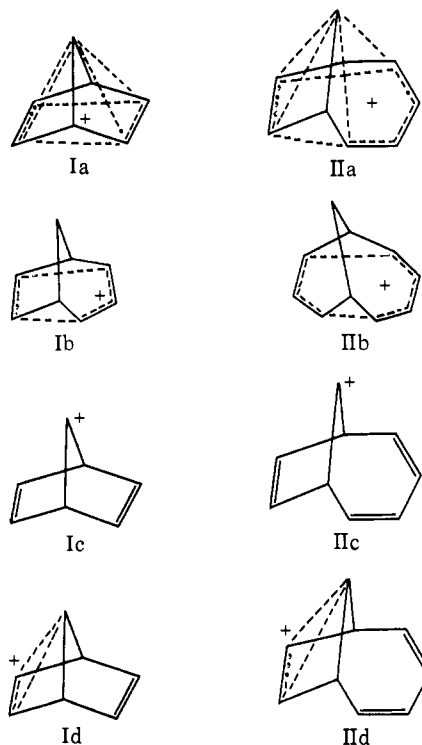
Since the early work on the solvolysis of cholesteryl chloride,<sup>2</sup> Winstein and coworkers have been concerned about the long-range stabilization of ionic centers by remote carbon. One of the most fascinating concepts to develop from this interest was the theory of homoaromaticity.<sup>3</sup> Experimental verification of these ideas has been built up over the last decade.

In 1967, Goldstein<sup>4</sup> used MO symmetry arguments to extend the concept of homoaromatic ions ( $2\pi$  bridges) to bicycloaromatic ions ( $3\pi$  bridges). At the same time, Goldstein<sup>5</sup> provided some preliminary experimental indications in support of his ideas based on the chemistry of the bicyclo[3.2.2]nonatrienyl system which he had synthesized. Because of our long-standing interest in the question of long-range stabilization, we undertook a study of the preparation, stability, and rearrangements of the bicyclo[3.2.2]nonatrienyl cation and anion. The results should provide a test of the importance of bicycloaromatic stabilization or destabilization since the anion is predicted<sup>4</sup> to be bicycloaromatic while the cation is antibicycloaromatic.

### Possible Reference Systems for Bicycloaromaticity.

In order to determine whether a system has bicycloaromatic character, a suitable reference system must be available. In his original definition,<sup>4a</sup> Goldstein stated that "an appropriate reference compound (was) one that possesses the same number of trigonal carbons and  $\pi$  electrons." We agree with this definition but differ with his choice for the configuration of these trigonal carbons and  $\pi$  electrons. Goldstein selected the series of bishomoconjugated ions (*i.e.*, bishomoaromatic and antibishomoaromatic) as suitable reference compounds. That this choice is inappropriate is shown by the following argument. For a compound to be bicycloaromatic it must gain stability by interaction between the  $\pi$  bridges and this additional stabilization must be discernible (either from calculations

or experiment) by comparison with the chosen reference. Consider the cations Ia and IIa and their corresponding bishomo reference compounds Ib and IIb as defined by Goldstein. Even if there were no interaction between the bridges in Ia, comparison with the antihomoaromatic reference Ib would lead to the conclusion that Ia was bicycloaromatic. Similarly, com-



parison of IIa (no interaction between bridges) with its homoaromatic reference IIb would require that IIa be antibicycloaromatic. Comparison of Ia with IIa shows that by simply converting a monoene in one bridge to a diene, *without change in the interaction between the bridges*, we have changed a bicycloaromatic system to an antibicycloaromatic one.

A reference system for bicyclic ions requires comparison between the ion under consideration and a (hypothetical) ion of the same general geometry in which some or all of the interaction between the bridges

(1) (a) Supported by the National Science Foundation. (b) Preliminary reports of this work have been published: J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968); **92**, 3186 (1970). (c) Address correspondence to this author at the Department of Chemistry, Purdue University, Lafayette, Ind. 47907.

(2) S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948).

(3) S. Winstein, *Chem. Soc., Spec. Publ.*, No. 21, 5 (1967).

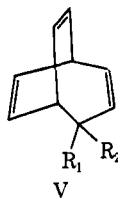
(4) (a) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967); (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971). We thank Professor Goldstein for a preprint of this paper.

(5) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

has been eliminated. One alternative is to reference the ion to an ion containing completely isolated  $\pi$  bridges. The other is to reference the ion to one in which overlap is allowed between two bridges, but the third one is isolated from both the interacting bridges. The two interacting bridges would be the odd-membered bridge bearing the formal charge and that even-membered bridge which, in combination with the odd bridge, yielded the most stable homoaromatic or antihomoaromatic ion. Thus for Ia and IIa the choice of reference systems would be Ic or Id, and IIc or IID, respectively. (The dotted lines in these structures represent interaction between  $\pi$  systems and do not imply equal bonding between all the centers.)

The definition of bicycloaromaticity in terms of isolated  $\pi$  bridges is attractive on the grounds of simplicity and the theoretical procedures used to derive the concept of bicycloaromaticity. However, it does not take account of the fact that the "bicycloaromatic" 7-norbornadienyl cation, Ia, is an unsymmetrical ion rather than a symmetrical one.<sup>6</sup> In this case much of the stabilization due to interaction between the bridges is already present in the homoaromatic 7-norbornenyl cation, and the bicycloaromatic character of Ia must be limited to the additional stabilization generated by interaction with the third bridge. For this reason, we prefer to define bicycloaromaticity in terms of homoaromatic (or antihomoaromatic) reference ions, involving interaction between two bridges insulated from the third, *i.e.*, Id and IID.

**Preparation of Bicyclo[3.2.2]nona-3,6,8-trien-2-one (III) and Its Derivatives.** The preparation of the [3.2.2] ketone III followed the scheme outlined by Goldstein and Odell.<sup>5</sup> Alternative procedures employing intermolecular cycloaddition reactions have yielded the bicyclo[3.2.2]nonatrienyl skeleton.<sup>7-12</sup> However, Goldstein's procedure remains the best route to the parent ketone. Yields of 30-35% of III were obtained. Indanone (IV) is formed in equal amounts with III, but we have not observed the 8,9-dihydroindenone reported by Goldstein. Preparation and properties of derivatives Va-g is reported in the Experimental Section.



	R <sub>1</sub>	R <sub>2</sub>		R <sub>1</sub>	R <sub>2</sub>
a	OH	H	e	OH	D
b	OCH <sub>3</sub>	H	f	OCH <sub>3</sub>	D
c	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COO	H	g	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COO	D
d	H	H			

(6) (a) S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, **82**, 2084 (1960); (b) P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962); (c) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

(7) M. Jones and S. D. Reich, *ibid.*, **89**, 3935 (1967).

(8) J. Ciabottoni, J. E. Crowley, and A. S. Kende, *ibid.*, **89**, 2778 (1967).

(9) J. Daub and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **7**, 468 (1968).

(10) S. W. Staley and D. W. Reichard, *J. Amer. Chem. Soc.*, **91**, 3998 (1969).

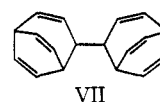
(11) T. H. Kinstle and P. H. Carpenter, *Tetrahedron Lett.*, 3943 (1969).

(12) T. Ueyehara, M. Funamizu, and Y. Kitahara, *Chem. Ind. (London)*, 1500 (1970).

**Preparation, Stability, and Quench of the Bicyclo[3.2.2]nonatrienyl Anion VI.** The [3.2.2] anion VI was prepared under vacuum line conditions by subjecting the [3.2.2] methyl ether Vb to the sodium-potassium alloy cleavage procedure previously employed in these laboratories.<sup>13</sup> The cleavage was completed cleanly in about 15 min at  $-10^\circ$  to yield a deep green solution which deposited orange needles on concentration. The [3.2.2] anion was the only species detectable in solution by nmr spectroscopy. The anion was only slightly soluble in ether solvents at room temperature, but the solubility (THF,  $\sim 0.2$  mg/ml; DME,  $\sim 1$  mg/ml; diglyme,  $\sim 4$  mg/ml) could be increased at higher temperatures. The <sup>13</sup>C satellites of the solvent provided a convenient internal standard to check these concentrations. All the anion solutions used in this investigation contained solid anion.

The [3.2.2] anion was quite stable under anaerobic conditions but slowly decomposed on long standing in ether solution to yield the [3.2.2] hydrocarbon as the only product detectable by nmr spectroscopy. Storage of a sample of the anion in diglyme for 18 days at room temperature resulted in a 30% change in the ratio of anion to hydrocarbon as determined by nmr. Heating the anion at  $100^\circ$  in diglyme resulted in formation of the [3.2.2] hydrocarbon Vd as sole product. The half-life of the anion was 10 min which corresponds to an activation free energy of  $27 \pm 1$  kcal/mol. These values should be treated with a little caution as anion lost from solution, by conversion to the hydrocarbon, may have been replenished by the dissolution of solid anion.

The quench of the anion VI-H with methanol yielded bicyclo[3.2.2]nonatriene and the [3.2.2] dimer VII as



the only detectable products by vpc and nmr. Barbalane and indane were shown to be absent from the quench by vpc comparison with authentic samples (0.5% could have been detected). The hydrocarbon VId was identified by its nmr, ir,<sup>7</sup> and mass spectra and by vpc comparison with the hydrocarbon obtained from the lithium aluminum hydride-aluminum trichloride reduction of the [3.2.2] ketone III. The white solid dimer VII was identified by analysis and nmr and mass spectra. Although this solid gave a satisfactory analysis, it had a  $30^\circ$  melting range. Since this dimer may exist as two possible diastereomers, this broad melting range is not unexpected. The ratio of monomer to dimer varied from quench to quench, but preliminary experiments suggest that the dimer is formed in an oxidative reaction with dissolved oxygen. Combined yields of Vd and VII were about 80% based on starting ether Vb.

**Nmr Spectrum of the [3.2.2] Anion.** Apart from the quenching experiments described above, the major evidence for the existence of the [3.2.2] anion is the nmr spectrum. Unfortunately, this spectrum is difficult to obtain because of the limited solubility of the anion and the masking of anion absorptions by ether

(13) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).

solvent peaks. However, by using DME- $d_{10}$  as solvent and utilizing spectral accumulation, satisfactory spectra can be obtained.<sup>14</sup> The considerable amount of long-range coupling, confirmed by decoupling experiments, uniquely defines the sequence of protons in the system and helps to verify that all the absorptions arise from a single species.

The bridgehead protons, H<sub>1</sub> and H<sub>5</sub>, appear at  $\delta$  2.29 as a septet which arises from a symmetrical quintet (corresponding to the A portion of an A<sub>2</sub>X<sub>4</sub> pattern<sup>15</sup> with a spacing of 3.8 Hz, each line of which is further split into a doublet ( $J_{12} = 7.6$  Hz) because of coupling with H<sub>2</sub> (H<sub>4</sub>). The outermost lines of this multiplet are weak and of comparable intensity to the noise. Each of the lines is broadened by long-range coupling to H<sub>3</sub> ( $J_{13} \sim 1.0$  Hz). Irradiation at the H<sub>6</sub> frequency collapses the multiplet to a broadened doublet ( $J_{12} = 7.6$  Hz).

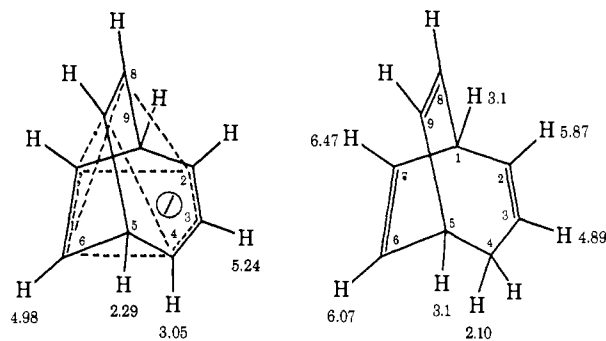
The allylic protons, H<sub>2</sub> and H<sub>4</sub>, absorb at  $\delta$  3.05 as a triplet arising from equal coupling with H<sub>1</sub> and H<sub>3</sub> ( $J_{12} = J_{23} = 7.6$  Hz). Irradiation at either H<sub>1</sub> or H<sub>3</sub> collapses this triplet to a doublet. The presence of a small coupling with H<sub>7</sub> ( $J_{27} = 1.5$  Hz) was indicated by decoupling experiments.

The central proton, H<sub>3</sub>, occurs as a simple triplet at  $\delta$  5.24 coupled to H<sub>2</sub> and H<sub>4</sub> ( $J_{23} = 7.6$  Hz) with broadening due to long-range coupling with H<sub>1</sub>. Irradiation at H<sub>2</sub> reduces this triplet to a broad singlet while irradiation at H<sub>1</sub> sharpens the triplet.

The vinyl protons, H<sub>6-9</sub>, appear at  $\delta$  4.98 as a symmetrical six-line pattern corresponding to the X portion of the A<sub>2</sub>X<sub>4</sub> pattern.<sup>15</sup> Irradiation at the H<sub>1</sub> frequency collapses the multiplet to a triplet ( $J_{27} = 1.5$  Hz).

The anion spectrum is unchanged from  $-35$  to  $100^\circ$ . Integration of the multiplets yields ratios which are consistent with the proposed structure. These chemical shifts, multiplicities, and coupling patterns are only consistent with a symmetrical (on the nmr time scale)

$\delta$  values in DME- $d_{10}$



VI					Vd						
$J$	1,2	1,3	1,6	1,7	2,3	$J$	1,2	1,3	1,5	1,6	
Hz	8.0 ~ 1.0	1.6	6.7	10.5		Hz	7.6 ~ 1.0	~ 0.7	1.8		
$J$	2,4	3,4	4,5	5,6	5,7	6,7	$J$	1,7	2,3	2,7	6,7
Hz	< 1	3.0	2.5	6.3	1.6	7.8	Hz	6.4	7.6 ~ 1.5	7.5	

(14) M. V. Moncur and J. B. Grutzner, unpublished observations. Spectra showing greatly improved sensitivity have recently been obtained using larger sample tubes.

(15) The H<sub>1</sub> and H<sub>6</sub> patterns were satisfactorily simulated by the spin-spin coupling program of Bothner-By<sup>16</sup> (LOACN3). The calculation assumed that these six protons formed an AA'XX'X''X''' system with the chemical shifts and coupling constants given in the figure.

(16) A. A. Bothner-By and S. Castellano, *J. Chem. Phys.*, **41**, 3863 (1964).

[3.2.2] anion system. In particular the sequence H<sub>1</sub> to H<sub>5</sub> combined with the chemical shift equivalence of H<sub>6-9</sub> cannot be accommodated by alternative C<sub>9</sub>H<sub>9</sub> anion structures such as barbaralyl, [4.2.1]nonatrienyl, dihydroindenyl, or their time average. Variable-temperature studies over the range  $-35$ – $100^\circ$  showed no new species and that line broadening attributable to exchange processes was absent.

**Deuterium Labeling Studies.** The 2-deuteriobicyclo[3.2.2]nonatrienyl anion (VI-d) was prepared by the same procedure from 2-methoxy-2-deuteriobicyclo[3.2.2]nonatriene (Vf). After storage at room temperature for 2 days the deuterated anion was quenched with methanol. The mass spectrum of the hydrocarbon showed that less than 1% deuterium had been lost from the anion. The nmr spectrum and integration showed that the deuterium was essentially completely scrambled ( $\pm 10\%$ ). A second preparation was carried out in DME at  $-15^\circ$ . The nmr spectrum of the H<sub>3</sub> and H<sub>6</sub> multiplets were recorded at  $-20^\circ$ . H<sub>3</sub> appeared as a broadened doublet (vicinal coupling to one H and one D) whereas H<sub>6</sub> was unchanged from the normal spectrum. On warming to  $25^\circ$ , the H<sub>3</sub> doublet diminished and the normal triplet grew in, until the statistical equilibrium was attained. At the same time two new lines were detected in the H<sub>6</sub> multiplet which intensified at approximately the same rate as the H<sub>3</sub> triplet. These results are consistent with a mechanism involving initial generation of the anion, specifically deuterated at position 2, followed by scrambling of the deuterium into the other positions as the temperature was raised. An approximate rate for the deuterium scrambling in the anion at  $28^\circ$  was determined by following the doublet to triplet ratio within the H<sub>3</sub> multiplet. Similar results were obtained using the H<sub>6</sub> multiplet changes. The half-life for the rearrangement was found to be 10 min at  $28^\circ$  corresponding to an activation energy of 22.5 kcal/mol (assuming a transmission coefficient of 1). Methanol quenches of these samples and nmr integration of the resulting hydrocarbons confirmed the random scrambling of the deuterium. A detailed study of the sites of deuterium incorporation in partially scrambled samples is currently being undertaken.<sup>14</sup>

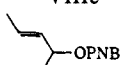
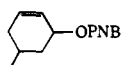
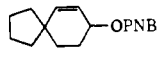
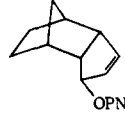
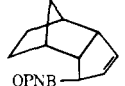
**Solvolysis of 4-Bicyclo[3.2.2]nonatrienyl *p*-Nitrobenzoate (Vc).** Solvolyses were carried out with 0.01 *M* solutions of the *p*-nitrobenzoate Vc in 80% aqueous acetone at 100.0 and 125.0°. The reaction was followed by titration of the resultant *p*-nitrobenzoic acid. A drifting rate and  $77 \pm 1\%$  infinity titer were observed at both temperatures. Product analyses (see below) revealed that isomerization of Vc to barbaralyl *p*-nitrobenzoate (VIIIc) was competing with the solvolysis reaction and accounted for the diminished titer and drifting rate. After correcting for this competing process, good first-order kinetic plots were obtained for at least the first 50% of the reaction. The rates are given in Table I together with results for several related systems.

The solvolysis products were identified as barbaralol (VIIIb) and barbaralyl *p*-nitrobenzoate (VIIIc) by comparison with an authentic sample of barbaralol<sup>17,18</sup>

(17) W. von E. Doering, B. M. Ferrier, E. D. Fossel, J. H. Hartenstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(18) We thank Dr. M. Sakai for providing a sample of this material.

**Table I.** Solvolysis Data for Allyl *p*-Nitrobenzoates<sup>a</sup>

Compound	Temp, °C	Rate × 10 <sup>6</sup> sec <sup>-1</sup>	E <sub>a</sub> , kcal/mol
VIIIc	100	11.8 ± 1.0	
VIIIc	125	98 ± 5	24.9
 -OPNB	100	12 <sup>b</sup>	
 -OPNB	100	3.7 <sup>b</sup>	
 -OPNB	100	3.8 <sup>b</sup>	
 -OPNB	100	51 <sup>c</sup>	
	125	430	25.1
 -OPNB	100	21 <sup>c</sup>	
	125	170	25.6

<sup>a</sup> In 80% aqueous acetone. <sup>b</sup> E. C. Friedrich, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1961. <sup>c</sup> H. C. Brown and H. M. Hess, unpublished observations; H. M. Hess, Ph.D. Thesis, Purdue University, 1969.

and by their characteristic nmr spectra. Isolated yields of 21% barbaralyl *p*-nitrobenzoate and 46% alcohol were obtained. The 21% recovery of *p*-nitrobenzoate is in close agreement with the proportion expected from the titration results. Previously,<sup>1b</sup> we reported that the [3.2.2] alcohol Va was a product of this solvolysis. Further work has shown that Va was derived from unreacted [3.2.2] *p*-nitrobenzoate Vc during the work-up. Thus our product analyses are now in accord with those reported by Barborak and Schleyer.<sup>19</sup> Control experiments have shown that [3.2.2] alcohol may rearrange to barbaralol under solvolytic, but not work-up, conditions. However, the rate of this isomerization is an order of magnitude too slow to account for the absence of [3.2.2] alcohol in the product. Less than 2% of Va could be detected by nmr spectroscopy in those solvolysis products where [3.2.2] *p*-nitrobenzoate was absent. Additional control experiments have shown that barbaralyl *p*-nitrobenzoate is stable to the conditions of solvolysis and product isolation.

**Solvolysis of Deuterium Labeled [3.2.2] *p*-Nitrobenzoate Vg.** 4-Deuterio-4-bicyclo[3.2.2]nonatrienyl *p*-nitrobenzoate (Vg) was obtained from the deuterated alcohol Ve, and the position and extent of deuteration were confirmed by nmr spectroscopy. The solvolysis and product analysis procedures were the same as those discussed above, although accurate rate data were not obtained. The distribution of the deuterium label in the products was established by nmr integration. The aromatic protons provided a convenient internal standard for the ester, and H<sub>3</sub> and H<sub>7</sub> were used as standard for the alcohol. The results for the alcohol agree with those reported by Barborak, *et al.*,<sup>19,20</sup> within experimental error. The ester behaves similarly except for

(19) J. C. Barborak and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 3184 (1970).

(20) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *ibid.*, **91**, 7760 (1969).

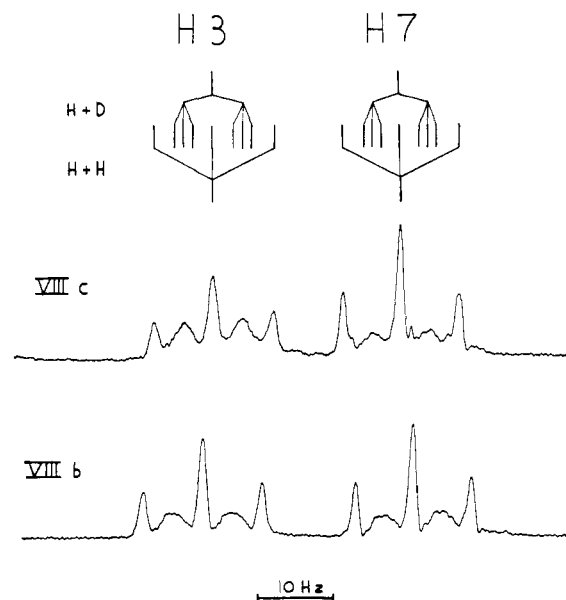


Figure 1. The  $\delta$  5-6 region of nmr spectrum of (A) barbaralyl *p*-nitrobenzoate (VIIIb) and (B) barbaralol (VIIIc), both obtained from solvolysis of 4-deuteriobicyclo[3.2.2]nonatrienyl *p*-nitrobenzoate. The coupling patterns expected for two vicinal hydrogens and for one hydrogen and one deuterium are shown. Note the intensity differences in spectrum A.

one fascinating detail. Examination of the multiplets assigned to H<sub>3</sub> and H<sub>7</sub> in the nmr spectrum of VIIIc revealed a triplet (for molecules containing two vicinal hydrogens) superimposed on a doublet (for molecules containing one vicinal hydrogen and one vicinal deuterium) as expected. However, the intensity of the doublet peaks in H<sub>3</sub> and H<sub>7</sub> differed by a factor of at least 2, clearly showing that the isomerization of the [3.2.2] *p*-nitrobenzoate to barbaralyl *p*-nitrobenzoate was an asymmetric process. There was no evidence of similar asymmetry in the deuterated barbaralol. The spectra of these multiplets are shown in Figure 1. The down-field multiplet has been assigned to H<sub>3</sub> on the basis of additional broadening due to long-range coupling (<0.3 Hz) with H<sub>9</sub>. Similar coupling has been observed in a number of related systems.<sup>21</sup>

**Reduction of Bicyclo[3.2.2]nonatrienone with LiAlH<sub>4</sub>-AlCl<sub>3</sub>.** In the original work on this reduction,<sup>5</sup> it was reported (without experimental detail) that the [3.2.2] hydrocarbon could not be detected. In our hands this reduction produced small yields of the [3.2.2] hydrocarbon. This reaction has little bearing on the question of the stability of the [3.2.2] cation. Reduction of the [3.2.2] ketone III with a 250-fold excess of LiAlH<sub>4</sub> in the presence of AlCl<sub>3</sub> in ether at -78° gave a range of products: barbaralol, barbaralane, [3.2.2] alcohol, and [3.2.2] hydrocarbon together with trace amounts of 1-indanol and indane. The hydrocarbons were analyzed by vpc and nmr; the alcohols were analyzed by nmr alone because these materials decompose under vpc conditions. Product yields are shown in Table II, and these results demonstrate the importance of aluminum trichloride in controlling the course of this reduction.

(21) D. L. Harris, unpublished observations.

**Table II.** Reduction of III with  $\text{LiAlH}_4\text{-AlCl}_3^a$ 

$\text{AlCl}_3/\text{LiAlH}_4$	% yields			
	Alcohols Va	VIIIb	Hydrocarbons Vd	VIIIa
1.2	30	30	1.5	21.5
0.28	0.5	62	5	6

<sup>a</sup> See Experimental Section for details.

## Discussion

**Bicycloaromaticity and the Stability of the Bicyclo[3.2.2]nonatrienyl Cation and Anion.** Goldstein<sup>4</sup> has predicted that the bicyclo[3.2.2]nonatrienyl anion should be stabilized, and hence bicycloaromatic and the bicyclo[3.2.2]nonatrienyl cation should be destabilized and thus antibicycloaromatic. At first sight, the results reported here might be taken as support for these predictions. However, the *same* predictions regarding the stability of these ions would have been made if we had considered them as (a) bishomoaromatic systems containing an additional (noninteracting) double bond; bicycloaromatic ((b) longicyclic ions,<sup>4b</sup> (c) laticyclic ions<sup>4b</sup>); or (d) Mobius stabilized ions.<sup>22</sup> Each of these descriptions differ in the degree and nature of the interaction between the  $\pi$  bridges.

Whatever the interpretation of the results, it must first be established that (a) the [3.2.2] anion is stabilized, (b) the [3.2.2] cation is destabilized, and (c) there is interaction and charge delocalization between the  $\pi$  bridges. In the case of the anion the results are consistent with delocalization and stabilization, but the cation results are equivocal (see below).

Staley<sup>10</sup> has shown that 3-methylbicyclo[3.2.2]nonatriene undergoes base-catalyzed deuterium exchange  $7.5 \times 10^2$  times faster than 3-methylbicyclo[3.2.2]nona-2,6-diene. According to our definition, this rate difference can be attributed to bicycloaromatic stabilization of the trienyl anion. It is interesting to note that this is approximately the same degree of bicycloaromatic stabilization which can be ascribed to the norbornadienyl cation.

The degree of interaction between the two vinyl bridges and the allylic bridge in the anion can be derived from the chemical shifts in the nmr spectrum. The difference in chemical shift between the central allylic proton ( $\text{H}_3$ ) and the outer protons ( $\text{H}_2$  and  $\text{H}_4$ ) provides a convenient guide which is independent of any assumptions used to relate  $\pi$  charge densities to proton chemical shifts. The chemical shift difference for these protons in the [3.2.2] anion is 2.19 ppm, and this value can be compared with allyllithium (4.17 ppm),<sup>23</sup> bis-homo[3.2.1]cyclopentadienide<sup>13</sup> (2.55 ppm), and cyclopentadienide (0.0 ppm). These results suggest that there is a more even charge distribution in the [3.2.2] anion than in the simple allylic models; hence delocalization between the  $\pi$  bridges must be important. Strong support for this conclusion comes from the observation that the upfield shift of 1.3 ppm of the vinyl protons in the [3.2.2] anion relative to the [3.2.2] hydrocarbon Vd is the same magnitude as the downfield

(22) (a) H. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971). (b) The Mobius descriptions of these ions is equivalent to the longicyclic designation. These terms should be used interchangeably in the following discussion.

(23) G. Frankel, D. E. Adams, and J. Williams, *Tetrahedron Lett.*, 767 (1963).

shift of 0.8 ppm of the "bound" vinyl protons in the norbornadienyl cation.<sup>6</sup> A Buckingham-type formula,<sup>24</sup> which had proved satisfactory for estimation of charge density effects on proton chemical shifts in aromatic ions,<sup>25</sup> was employed to estimate the excess  $\pi$  charge density at C-6-C-9. A value of  $0.24 \pm 0.1$  electron was obtained for the four vinyl carbons which further supports a delocalized structure for the [3.2.2] anion.

The question of the destabilization of the bicyclo[3.2.2]nonatrienyl cation cannot be answered simply. The solvolysis rates for the *p*-nitrobenzoate Vc are quite similar to those obtained for other allylic systems (see Table I). However, the absence of bicyclo[3.2.2]nonatrienyl derivatives in the solvolysis product and the facile rearrangement to the barbaralyl system raise the question whether the [3.2.2] cation is formed at any stage during the solvolysis. The results obtained here cannot answer this question directly, and no firm conclusion can be reached regarding destabilization of the [3.2.2] cation. However, an estimate can be made of the difference in energy between the barbaralyl and [3.2.2] cations. Combining this energy difference with the solvolysis rate data provides an upper limit for the destabilization of the [3.2.2] cation.

The fact that barbaralol is the product of the solvolysis of the [3.2.2] *p*-nitrobenzoate and barbaralyl tosylate, combined with the deuterium scrambling pattern in barbaralol (see below), indicate that both these solvolyses are proceeding through the same intermediate (or transition state), presumably the barbaralyl cation. The single-line nmr spectrum of the barbaralyl cation observed at  $-125^\circ$ <sup>26</sup> is consistent with an activation energy difference of  $<6$  kcal/mol between the barbaralyl cation and the [3.2.2] cation in this strong acid medium. Comparison of Barborak and Schleyer's results for the rates of solvolysis of barbaralyl tosylate to yield barbaralol with the deuterium label specifically rearranged with the rate for degenerate scrambling of deuterium<sup>20</sup> (assumed to be *via* the [3.2.2] cation) provide an estimate for the free energy difference between the [3.2.2] cation and barbaralyl cation of 2.2 kcal/mol in acetic acid. Analysis of the solvolysis product data provides another estimate of the difference between these cations of  $\geq 2.5$  kcal/mol. As the solvolysis of the [3.2.2] *p*-nitrobenzoate takes place at about the same rate as simple allylic *p*-nitrobenzoates (see Table I), the antihomoaromatic and antibicycloaromatic destabilization of the bicyclo [3.2.2] cation can be estimated to be between 2.2 and 6 kcal/mol.

Comparison with other systems suggests that the antihomoaromatic character of the ion will provide the major portion of the observed destabilization, and thus we conclude that antibicycloaromatic destabilization has very little significance.

**Bridge Flipping in the [3.2.2] Anion.** The [3.2.2] anion is the first member of the anionic series where there is a possibility of a bridge flipping process akin to that observed for the norbornadienyl cation.<sup>6c</sup>

Spectra of the anion taken at  $-35^\circ$  showed a symmetrical pattern for  $\text{H}_6\text{-H}_9$  with no additional broadening attributable to exchange processes. Thus, no

(24) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(25) J. B. Grutzner, Ph.D. Thesis, University of Melbourne, 1967.

(26) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4454 (1970).

choice can be made between the symmetrical ion and two bridged ions equilibrating rapidly on the nmr time scale. An upper limit of 11.8 kcal/mol can be set for the barrier to bridge flipping between bridged ions. This value contrasts with the barrier of  $>19.6$  kcal/mol observed for the norbornadienyl cation.<sup>6c</sup> This substantial difference can be understood since the activation energy for bridge flipping depends on the degree of stabilization of the unsymmetrical ion relative to the symmetrical form. Stabilization of unit charge on a single carbon by delocalization over a vinyl bridge in the cation will be greater than the stabilization obtained from delocalization of the charge on the three carbon allylic segment of the anion. Furthermore, it has been shown that a cyclopropenyl system should have a larger stabilization energy than a cyclopentadienide system.<sup>27</sup>

**Homoaromatic, Laticyclic, Longicyclic, or Mobius Ions?** In each of the theoretical discussions of bicyclic ions,<sup>4,22</sup> little attention has been paid to the question of how much of the stabilization is due to homoaromatic character (interaction between two bridges) and how much to bicycloaromatic character (interaction between the three  $\pi$  bridges). The Mobius description of these ions is equivalent to the longicyclic description and the longicyclic terminology will be used here. The series of cations, 7-norbornyl, 7-norbornenyl, and 7-norbornadienyl, provides a useful guide to the relative importance of homoaromatic *vs.* bicycloaromatic stabilization. The homoaromatic stabilization gained in the norbornenyl system relative to the norbornyl<sup>28</sup> leads to a rate enhancement of  $10^{11}$ . The addition of the second double bond in the norbornadienyl system<sup>6a</sup> only causes a rate enhancement by  $10^3$ . Thus, homoaromatic stabilization is the major factor involved in the stability of the "bicycloaromatic" 7-norbornadienyl cation.

The experimental results<sup>6</sup> show that the norbornadienyl cation is a laticyclic system, enhancing its homoaromatic character by distortion. Furthermore, the stabilization energy of the 7-norbornadienyl cation relative to the 7-norbornyl cation can be calculated to be 19.2 kcal/mol at 25 $^\circ$  from their relative rates of solvolysis. The barrier to bridge flipping in the norbornadienyl cation has been determined to be  $>19.6$  kcal/mol at 45 $^\circ$ .<sup>6c</sup> Thus, the stabilization of a *symmetrical* 7-norbornadienyl cation must be quite small and may even be zero. Since the norbornadienyl system should be the ion providing the greatest possibility for longicyclic stabilization (stabilization of a localized charge, closest separation between  $\pi$  bridges for best overlap), this raises the serious question whether longicyclic stabilization is important in any practical molecule. It is obviously important to establish whether the [3.2.2] anion is symmetrical or not, and attempts to observe the ion at lower temperatures are in progress. The reasons for the lower barrier to bridge flipping in this ion were discussed above.

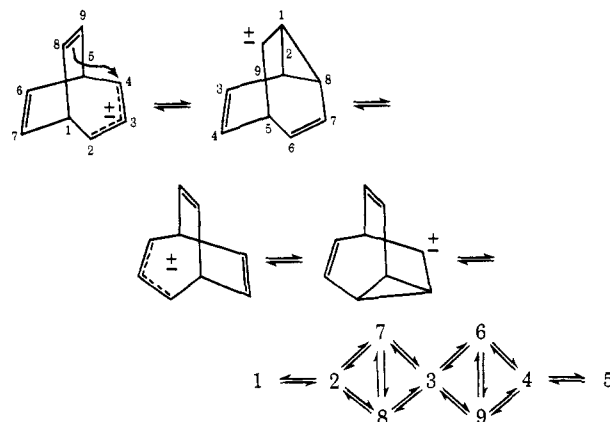
The arguments regarding the relative destabilization of antihomoaromatic and antibicycloaromatic ions are similar to those given above. There is one additional feature that diminishes the importance of destabilization: antiaromatic systems will distort to

decrease the destabilizing interaction. This point has been illustrated and discussed by Breslow.<sup>29</sup>

**Rearrangements of the [3.2.2] Anion and Cation.** The present results do not provide definitive evidence as to the mechanism of the rearrangement in either the [3.2.2] anion or cation. However, it is clear that the cation and anion must be rearranging through different skeletal modifications. Orbital symmetry rules provide a useful guideline in attempting to understand these results.

The interconversion of barbaralyl ions with [3.2.2] ions by a series of symmetry-allowed disrotatory cyclopropane openings and closures provides a potential mechanism for completely degenerate scrambling of a deuterium label in both of these ions (Scheme I). This

Scheme I



process can be expressed in the form of a flow sheet using the [3.2.2] numbering scheme. A more complex scheme must be written if the barbaralyl ion undergoes a Cope rearrangement before it reopens to the [3.2.2] ion. The relatively slow rearrangement of protonated barbaralone<sup>30</sup> suggests that this additional feature does not play a role in the cation rearrangement but may be quite significant in the anion.

The completely degenerate scrambling in the [3.2.2] anion shown by the deuterium labeling experiments can be interpreted in terms of Scheme I. The ring closure of this anion to yield the barbaralyl ion and its subsequent reopening are allowed six-electron processes. The fact that the H<sub>3</sub> and H<sub>6</sub> multiplets show incorporation of deuterium into the adjacent positions at essentially the same rate is also consistent with this mechanism. Further support for the intermediacy of the barbaralyl anion in this interconversion comes from Staley's observation<sup>10</sup> that treatment of 3-methylbicyclo[3.2.2]nonatriene with potassium amide in liquid ammonia yields 3-methylbarbaralane as product. The similarity in the rate of the rearrangement reported by Staley (complete in 3 hr at 50 $^\circ$ ) and that observed here by deuterium labeling (complete in 90 min at 28 $^\circ$ ) lends further credence to this postulate. Several other mechanisms could account for these results, and we are currently engaged in an analysis of the deuterium scrambling results in order to provide additional proof for Scheme I.

For the [3.2.2] cation, it is clear that the specific deuterium reorganization observed in the conversion

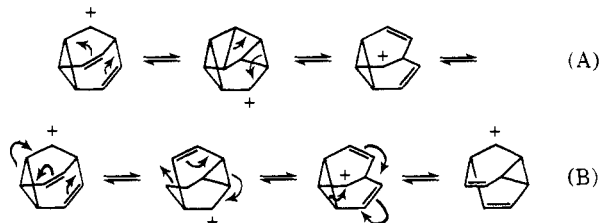
(29) R. Breslow, R. Pagni, and W. N. Washburn, *Tetrahedron Lett.*, 547 (1970).

(30) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, 92, 3478 (1970).

(27) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc., B*, 411 (1968).  
(28) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).

of the [3.2.2] *p*-nitrobenzoate to barbaralyl derivatives under solvolytic conditions requires an alternative mechanism to that given above. The absence of deuterium in the 3, 7, and 9 positions in the barbaralyl products rules out any process involving 1,2 shifts. However a 1,2-shift mechanism may be used to explain the degenerate rearrangement which eventually equilibrates all of the positions in the barbaralyl cation.<sup>20,26</sup> Since it has been shown that the energy barrier for the degenerate rearrangement is <6 kcal/mol, the stereospecific mechanism must be a very facile process and, presumably, orbital symmetry allowed. Schleyer<sup>20,31</sup> has outlined the possible mechanisms for this interconversion (mechanisms A and B, Scheme II). Mech-

Scheme II



anism A is equivalent to the reverse of a Story-Richey<sup>32</sup> rearrangement of the quadricyclyl cation to the norbornadienyl cation. While the Story-Richey rearrangement is known to be a facile reaction, it has been shown that this rearrangement cannot compete with the 1,2 shift mechanism in the norbornadienyl cation.<sup>6c,33</sup> Therefore it seems reasonable to eliminate this alternative for the barbaralyl rearrangement.

The preferred mechanism for the barbaralyl rearrangement is shown in mechanism B. This is an allowed six-electron process requiring a disrotatory 4-6 closure, a disrotatory 1-8 opening, and the double bond shift, with the additional feature that C-6 and C-8 rotate in the same sense. This is a straightforward valence isomerization and presumably may proceed with a low activation barrier.

The asymmetric labeling observed in the barbaralyl *p*-nitrobenzoate can be explained in two possible ways. Either ion pair collapse to give the stable (to solvolysis conditions) barbaralyl *p*-nitrobenzoate occurs at about the same rate as the scrambling discussed above, or the presence of the counterion restricts the scrambling to the first reversible step of mechanism B, *i.e.*, maintaining the positive charge on the same side of the molecule. We cannot distinguish these possibilities on the basis of our results. It should be noted that the 4:1 preference for return of the *p*-nitrobenzoate to the same face of the C<sub>9</sub>H<sub>9</sub> cation from which it ionized, is comparable to the ratio of racemization to solvolysis and rearrangement observed by Goering for allylic *p*-nitrobenzoates.<sup>34</sup> The fact that Schleyer<sup>19</sup> did not observe this asymmetric labeling in the solvolysis of the dinitrobenzoate can be explained by the difference in solvolytic conditions which would favor a longer lived ion pair in his system.

(31) R. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

(32) (a) H. G. Richey and N. C. Buckley, *J. Amer. Chem. Soc.*, **85**, 3057 (1963); (b) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).

(33) R. K. Lustgarten, M. S. Brookhart, and S. Winstein, *ibid.*, **90**, 7364 (1968).

(34) H. L. Goering, G. S. Koermer, and E. C. Linsay, *ibid.*, **93**, 1230 (1971), and references cited therein.

## Experimental Section

Nmr spectra were obtained with Varian A-60 and HA-100 instruments; ir spectra with Perkin-Elmer 421 and Infracord; mass spectra with the AEI-MS9. The analyses were performed by Miss Heather King (UCLA). Gas chromatographic analyses were carried out on an Aerograph HyFi instrument using a 1/8 in. × 2 m column of XF-1150.

**Preparation of Cycloheptatrienylacetic Acid.** Cycloheptatrienylacetic acid was prepared by the method of Jurch and Traylor<sup>35</sup> except that tropylium tetrafluoroborate was prepared by the method of Conrow.<sup>36</sup> The reaction is complete in 2 hr as indicated by cessation of gas evolution and nmr.

**Preparation of Bicyclo[3.2.2]nona-3,6,8-trien-2-one (III).** Cycloheptatrienylacetic acid (74 g) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (500 ml dried over molecular sieves) plus five drops of pyridine in a 1-l. flask fitted with drying tube and magnetic stirrer. Oxalyl chloride (100 g of fresh material) was added in one lot and the solution stirred for 2 hr until gas evolution ceased. The solvent was removed at water pump pressure, and then the hydrochloric acid on an oil pump to give the acid chloride as a brown oil (ir 1800 cm<sup>-1</sup>). The oil was dissolved in hexane (900 ml technical, but dried over molecular sieves) and placed in a 1-l. bypass dropping funnel. A solution of triethylamine (160 ml, redistilled and stored over BaO) in hexane (4 l.) was refluxed in a 5-l. three-neck flask fitted with a condenser and drying tube, the bypass dropping funnel, and a strong magnetic stirrer. The acid chloride solution was dropped slowly into the stirred refluxing solution over 3 days. The triethylamine hydrochloride precipitate was filtered and the hexane removed on the evaporator. The yield was 62.5 g of an approximately 50:50 mixture of 1-indanone and [3.2.2] ketone. This oil was carefully distilled through a good helix-packed, vacuum-jacketed column at 1.5 mm pressure (Caution: On one occasion a small amount of a strong lachrymatory and irritant material was present in the first few drops of this distillation; it has not been identified at this stage.) The first fractions, bp 75-77° (16 g), crystallized on seeding with [3.2.2] ketone. The next fraction, bp 77-79° (8 g), was shown to be a mixture of [3.2.2] ketone (60%) and 1-indanone. The residue in the flask crystallized on seeding with 1-indanone. The oily mixture can be separated by preparative vpc on a 0.75 in. × 2 m 25% XF1150 column (150°, 10 psi) to give the [3.2.2] ketone (retention time 18 min). This product was recrystallized twice from pentane to give pure ketone (13.5 g, mp 41-42° (lit.<sup>5</sup> 44°). The overall yield based on starting acid was 23%. The spectral properties agree well with those reported by Goldstein.<sup>5</sup>

A variety of alternative procedures was tried but the yield of [3.2.2] ketone was diminished (often drastically). If the dehydrohalogenation is carried out in pentane at 0° by addition of the triethylamine to the cycloheptatrienylacetyl chloride, a 60% yield of the ketene dimer<sup>5</sup> may be obtained. Replacement of hexane by diethyl ether in the preferred procedure at 25° gave a 50% yield of cycloheptatrienyl-*N*-ethylacetamide: nmr (CS<sub>2</sub>) δ 7.55 (broad 1.0) removed by shaking with D<sub>2</sub>O, 6.49 (t, 1.9), 6.04 (m, 2.0), 5.02 (q, 2.0), 3.05 (quintet *J* = 7 Hz, 2.0) collapses to quartet treatment with D<sub>2</sub>O, 2.38 (sharp multiplet, 2.0) (broad multiplet, 1.0), 1.0 (t, *J* = 7 Hz, 3.0); ir 3440, 3322 (broad), 3000 (s), 2924, 2864, 1648 (s), 1500 (s), 1440, 1408, 1388, 1370, 1284, 1220, 1196, 1152, 696 (s), 655 cm<sup>-1</sup>; mass spectrum parent 177, 106, 105, 104, 91 (base), 78, 77, 72, 44, 32, 28, metastables 79.2, 63.5.

*Anal.* Calcd for C<sub>11</sub>H<sub>10</sub>NO: C, 74.54; H, 8.53; N, 7.90. Found: C, 74.67; H, 8.57; N, 8.03.

**Preparation of [3.2.2] Alcohol Va.**<sup>5</sup> The [3.2.2] ketone (2 g) was dissolved in dry ether (40 ml) in a 100-ml flask fitted with drying tube and magnetic stirrer and cooled to -78°. LiAlH<sub>4</sub> (300 mg) was added in small lots to the cold stirred solution over 0.5 hr. The mixture was stirred for 2 hr until all the ketone had been reduced. Sodium potassium tartrate solution (5 ml, 20% soln) was added dropwise to the cold solution which was then allowed to warm to room temperature with stirring. The reaction mixture was poured into ether-water (20 ml/20 ml) and the aqueous layer extracted with fresh lots of ether (two 20-ml portions). The ether extracts were combined, dried over potassium carbonate, and evaporated to yield white semisolid material. Two recrystallizations from pentane gave 1.38 g of white needles, mp 51-52° (lit.<sup>5</sup> 54-56). Recrystallization of the mother liquor material afforded a further 0.18 g of product, mp 49-51°, overall yield 72%.

(35) G. R. Jurch and T. G. Traylor, *ibid.*, **88**, 5228 (1966).

(36) K. Conrow, *Org. Syn.*, **43**, 101 (1963).



**Preparation of [3.2.2] Methyl Ether Vg.** The [3.2.2] alcohol was methylated according to the procedure of Diner, *et al.*<sup>37</sup> The resultant oil was distilled at 31–32° (0.5 mm) with a bath temperature below 45° and the receiver cooled in a Dry Ice–acetone bath: nmr (CS<sub>2</sub>)  $\delta$  6.52 (m, 2), 5.78–6.18 (m, 3), 4.85 (doublet of triplets  $J = 11, 2.5$  Hz), 3.46 (broad singlet, 2), 3.24 (s, 3), 3.05 (broad quartet  $J = 6.5$  Hz, 1).

Anal: Calcd for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16. Found: C, 81.21; H, 8.13.

**Preparation of [3.2.2] *p*-Nitrobenzoate Vc.** The [3.2.2] alcohol was esterified by conventional techniques using recrystallized *p*-nitrobenzoyl chloride in cold pyridine. Extraction and recrystallization twice from ether gave the desired [3.2.2] *p*-nitrobenzoate (70% yield), mp 94.5–95.5°: nmr (acetone-*d*<sub>6</sub>)  $\delta$  1.75 (m, 4), 3.19 (t,  $J = 7$  Hz, 2), 3.48–3.87 (m, 3), 4.55 (broad triplet,  $J = 3.5$  Hz, 1), 4.97 (doublet of triplets,  $J = 11, 3.5$  Hz, 1), 6.33 (m, 1), 6.60 (q,  $J = 7$  Hz, 1).

Anal: Calcd for C<sub>16</sub>H<sub>13</sub>NO<sub>4</sub>: C, 67.84; H, 4.63; N, 4.95. Found: C, 68.03; H, 4.67; N, 4.76.

**Preparation of 4-Deuterio [3.2.2] Compounds.** The 4-deuterio [3.2.2] alcohol, methoxy ether, and *p*-nitrobenzoate were made in identical fashion to the methods described above except that Li-<sup>2</sup>D<sub>4</sub> (99% D) was used for the reduction of the ketone to the alcohol and deuterated alcohol was used in place of the fully protonated material. The nmr spectra are consistent with the replacement of H<sub>4</sub> by deuterium; *e.g.*, methoxy ether Vg now shows peak  $\delta$  5.15 as doublet of doublets and that at  $\delta$  6.54 becomes multiplet of area 1.

**Preparation of the [3.2.2] Anion VI.** The preparation was carried out under vacuum line conditions. The H-shaped reaction vessel was equipped with sealable entry port for sodium–potassium alloy, break-seal chamber containing [3.2.2] methyl ether Vb under vacuum, nmr tubes, magnetic stirrer, and a coarse fritted disk separating the two arms of the H vessel. Sodium–potassium alloy (1 g, 78%) (MSA Corp) was added to the vessel which was evacuated to a pressure below 1  $\mu$ . The ether solvent<sup>38</sup> (*ca.* 5 ml redistilled under nitrogen, degassed, and stored over sodium–potassium alloy) was transferred onto the alloy by cooling the reaction vessel. The evacuated vessel was closed and removed from the line. The break-seal to the methyl ether chamber was broken and the mixture of alloy, anion precursor, and solvent was vigorously stirred in an ice bath for 30 min. A green color developed on contact and intensified as reaction proceeded. The solution was filtered and concentrated in the nmr tubes which were then sealed off. The filtration and concentration steps were usually performed at 5°. Solid samples of the anion may also be prepared in this manner if all the solvent is removed before sealing the sample. Preparation of the monodeuterio anion VI-*d* followed the same procedure except that the solution was filtered and concentrated at –10°.

**Quench of the [3.2.2] Anion.** Nmr samples were quenched with methanol (1 ml) as rapidly as possible after opening and then rapidly stirred. Samples contained in break-seal tubes were quenched by covering the seal with MeOH (2–3 ml) and then opening the tube, followed by rapid stirring. Material remaining in the reaction vessel was more difficult to quench satisfactorily because of the excess Na–K alloy. As much of the solution as possible was poured into MeOH (5 ml), the Na–K alloy then poured into *tert*-BuOH (caution), and then the vessel rinsed out with a little more MeOH. The MeOH solution was then poured into water–pentane (10 ml/10 ml) and the aqueous layer extracted with pentane (10 ml) again. The pentane layers were washed with water (10 ml), dried over potassium carbonate, and then analyzed by vpc.

The yield of bicyclo[3.2.2]nonatriene (Vd) was determined by vpc analysis using a known weight of ethylbenzene as internal standard. Careful distillation separated Vd from pentane and the structure was established by nmr, mass spectrum, and ir.<sup>7</sup> Analytical vpc showed that Vd was the only volatile product obtained from the quench. Coinjection with authentic samples of barbaralane and indane showed that  $\leq 0.5\%$  of these hydrocarbons was present. Sublimation (80°, 1 mm) of the solid remaining after distillation yielded the [3.2.2] hydrocarbon dimer VII, mp 88–120°. Structure proof was given by analysis, mass spectrum, nmr, and ir. Preparation of the anion from [3.2.2] methyl ether (100 mg) followed by the quench described above yielded Vd (40.2 mg) and VII (24 mg);

(37) U. E. Diner, F. Sweet, and R. K. Brown, *Can. J. Chem.*, **44**, 1591 (1966).

(38) Tetrahydrofuran (Baker), 1,2, dimethoxyethane (Ansul), 1,2-dimethoxyethane-*d*<sub>10</sub> (Merck Sharp and Dohme), diglyme (Ansul).

overall yield 80%. In a later quench, oxygen was excluded and no dimer was detected.

**Spectral properties of Vd** were as follows: nmr  $\delta$  6.47 (“triplet”  $J = 7$  Hz, 1.9), 6.06 (“triplet”  $J = 7$  Hz, 2.2), 5.86 (multiplet, 1.05), 4.89 (doublet of multiplets  $J = 10.5$  Hz, 1.0), 3.1 (multiplet, 2.0), 2.09 (“quartet”  $J = 3.5$  Hz, 1.75); mass spectrum 118, 117 (base), 116, 115, 103, 91, 78, 77, 65, 51, 39.

**Properties of VII.** The [3.2.2] hydrocarbon dimer showed nmr (CS<sub>2</sub>)  $\delta$  5.85–6.75 (broad multiplet, 5.35), 4.86 (broad doublet,  $J = 11.5$  Hz, 1.0), 3.00 (multiplet, 2.15), 2.10 (broad singlet, 1.35); mass spectrum 234, 232, 230, 229, 228, 217, 215, 204, 203, 202, 178, 165, 155, 153, 152, 144, 143, 142, 141, 130, 129, 138 (base), 127, 117, 116, 115, 105, 104, 103, 92, 91, 89, 78, 65, 63, 51, 44, 41, 39, 32; ir (see Table III).

Table III. Infrared Spectra of [3.2.2] Hydrocarbons ( $\nu$ , cm<sup>-1</sup>)

Ref 7	Present work (CS <sub>2</sub> )	Dimer CS <sub>2</sub>	Ref 7	Present work (CS <sub>2</sub> )	Dimer CS <sub>2</sub>
	3060			1210	1222
	3035	3042	1195	1200	1206
	3005	3002			1153
	2945	2958		1140	1137
	2910	2920			
	2860	2880		1110	1090
		2870	1040	1046	1062
	2800	2825			1027
		2400	980	980	988
		1765	959	960	960
		1730			949
	1630	1664		913	929
		1628	886	878	887
	1610	1610	870	868	862
	1422	1427		820	829
	1378	1383		770	919
	1366	1370		738	
	1325	1325		730	
		1309	715	722	712
	1276	1265	688	698	692
	1249	1250			663
					609

Anal: Calcd for C<sub>18</sub>H<sub>18</sub>: C, 92.26; H, 7.74. Found: C, 92.30; H, 7.81.

The monodeuterated anion preparation was quenched after 2 days at room temperature, and both monomer and dimer hydrocarbons were isolated. The mass spectra showed the parent peak in monomer at 119 (*i.e.*, 1 D) and in dimer at 236 (*i.e.*, 2 D). Low eV scans of the parent ion in the monomer gave the ratios of parent peak to parent – 1 shown in Table IV.

Table IV

Anion quenched	<i>m/e</i>	8 eV	10 eV	12 eV
VI-H	118/117	9.45	5.57	2.2
VI-D	119/118	8.2	7.65	3.2

Integration of the nmr spectra for protonated and deuterated hydrocarbons are shown in Table V using H<sub>3</sub> as standard. Integrations are accurate to  $\pm 10\%$ .

Table V. Integration of Anion Quench

Hydrocarbon	H <sub>6,9</sub>	H <sub>2,7,8</sub>	H <sub>3</sub>	H <sub>1,5</sub>	H <sub>4</sub>
Vd	1.90	3.25	1.0	2.0	1.75
Vd- <i>d</i> <sub>1</sub>	1.90	3.30	1.0	2.15	2.35
VII		5.35	1.0	2.15	1.35
VII- <i>d</i> <sub>1</sub>		5.95	1.0	2.1	1.05



**Solvolysis of [3.2.2] *p*-Nitrobenzoate Vc.** Kinetic studies were carried out using the ampoule technique at 100 and 125°. Solutions (0.01 *M*) of Vc were prepared at 25° in 80% aqueous acetone. Rates were followed by titration of the released *p*-nitrobenzoic acid with 0.01 *M* sodium methoxide solution to the Bromthymol Blue end point. Infinity titers ( $77 \pm 2\%$ ) were obtained in all runs. Product analyses were performed at both temperatures and gave essentially the same results using 25-ml ampoules and work-up after 10 half-lives: 24 hr at 125°, 1 week at 100°. Solvolysis in the presence of 20% excess of sodium acetate did not alter the product analysis.

The solvolysis products were poured into 10% sodium bicarbonate-ether (30 ml/30 ml) and the ether layer washed with bicarbonate (30 ml) and water (30 ml), dried over potassium carbonate, and evaporated. The yellow semisolid material was dissolved in the minimum volume of ether-pentane and chromatographed on silica gel. Elution with 10% ether in pentane (four 25-ml portions) gave barbaralyl *p*-nitrobenzoate. The eluent was changed to 50% ether in pentane (two 100-ml portions) and gave barbaralol as shown by comparison with authentic samples.<sup>17,18</sup> A check showed that the [3.2.2] alcohol was unaffected by the chromatography.<sup>39</sup> The effect of acid generated during the solvolysis of the [3.2.2] alcohol was checked as follows: [3.2.2] alcohol (10 mg) was dissolved in 80% aqueous acetone (7 ml) together with *p*-nitrobenzoic acid (12.5 mg, 1 equiv) and heated at 125° for 3 hr (70% reaction). The solution was worked up as described above but not titrated. Nmr showed the formation of 20% barbaralol. The nmr of barbaralol has been given by Doering<sup>17</sup> and that of barbaralyl *p*-nitrobenzoate is given here: nmr (acetone-*d*<sub>6</sub>  $\delta$  8.24 ("quartet," 4.0), 5.83 (triplet  $J = 8$  Hz, 1), 5.59 (triplet  $J = 8$  Hz, 1), 4.93 (triplet  $J = 3$  Hz, 1), 3.88-4.38 (multiplet, 4), 2.76 (multiplet, 2).

Quantitative analysis was performed starting with [3.2.2] *p*-nitrobenzoate Vc (102 mg), employing the above procedure. Barbaralol (VIIIb, 17 mg, 46%) and barbaralyl *p*-nitrobenzoate (VIIc, 21 mg, 21%) were isolated. Control experiments have shown only a 50-70% recovery of barbaralol from chromatography of pure barbaralol.<sup>39</sup> Barbaralyl *p*-nitrobenzoate may be recovered essentially quantitatively. The loss of barbaralol has not been accounted for.

The analysis for [3.2.2] alcohol was carried out on alcohol mixtures by nmr spectroscopy. Attempts to separate [3.2.2] alcohol from barbaralol by a variety of chromatographic techniques (both column and vpc) were unsuccessful either because of lack of separation or rearrangement on the column. Using nmr, less than 2% of [3.2.2] alcohol was detected in any of the products after complete solvolysis. In the product studies reported previously,<sup>1b</sup> analyses were performed on the products obtained from kinetic runs which contained unreacted [3.2.2] *p*-nitrobenzoate Vc. Control experiments have since shown that Vc may be cleaved to [3.2.2] alcohol under the basic work-up procedures used (barbaralyl *p*-nitrobenzoate is stable to work-up).

Solvolysis and product analysis of the deuterated [3.2.2] *p*-nitrobenzoate Vg were carried out with the procedures described above. The position of the deuterium label was determined by integration of the nmr spectra for each of the products (Table VI).

(39) If chromatography is carried out on alumina, the [3.2.2] alcohol partially rearranges to barbaralol with a small amount of additional unidentified material.

**Table VI.** Integration of Deuterated Solvolysis Products<sup>a</sup>

	H <sub>3,7</sub>	H <sub>2,4,6,8</sub>	H <sub>9</sub>	H <sub>1,5</sub>	Aromatic
Va- <i>d</i> <sub>1</sub>					
Exptl <sup>b</sup>	2.0	3.45	0.9	1.6	
Calcd for complete scrambling	2.0	4.0	1.0	2.0	
Calcd for mechanism B	2.0	3.33	1.0	1.67	
Vc- <i>d</i> <sub>1</sub>					
Exptl	1.83	3.33	0.95	(1.7) <sup>c</sup>	4.0
Calcd for complete scrambling	1.78	3.56	0.89	1.78	4.0
Calcd for mechanism B <sup>d</sup>	2.0	3.40	1.0	1.60	4.0

<sup>a</sup> Values are accurate to  $\pm 0.1$  unit. <sup>b</sup> H<sub>3,7</sub> protons were used as standard for the alcohol and the aromatic protons were used for the ester. <sup>c</sup> Uncertain owing to overlap with solvent impurity. <sup>d</sup> Assuming 80% of product arises from attack on same face of cation that *p*-nitrobenzoate departed from.

Expansion of the H<sub>3</sub> and H<sub>7</sub> multiplets on a 100-Hz sweep width and integration yielded the following H:D ratios for the adjacent positions H<sub>2</sub> and H<sub>4</sub> for H<sub>3</sub>, and H<sub>6</sub> and H<sub>8</sub> for H<sub>7</sub>. These ratios are accurate to  $\pm 0.1$ .

	H <sub>3</sub>	H <sub>7</sub>
Va- <i>d</i> <sub>1</sub>	1.8	1.8
Vc- <i>d</i> <sub>1</sub>	1.2	2.5

**Reduction of [3.2.2] Ketone with LiAlH<sub>4</sub>-AlCl<sub>3</sub>.** Two simultaneous reductions were carried out which only differed in the proportion of AlCl<sub>3</sub> used. The two experiments are reported together; where quantities differ, the more concentrated AlCl<sub>3</sub> reaction is given first. Lithium aluminum hydride (1.5 g) was dissolved in ether (25 ml) and refluxed; aluminum trichloride (5, 1 g) was added and the slurry refluxed for 1 hr and cooled to -78°. The [3.2.2] ketone (41.2, 39.5 mg) in ether (10 ml) was added slowly to the cold solution and stirred for 2 hr until no more ketone remained (tlc). The mixture was allowed to warm to room temperature; ethyl acetate (2 ml) was added and then water (20 ml). The ether was separated, washed twice with water, and dried over potassium carbonate. Vpc (103°, 10 psi) showed [3.2.2] hydrocarbon (retention time 11 min) and barbaralane (12.5 min). The alcohols decompose under these conditions and are not detected. The reduction gave the mixture of hydrocarbons (8.5, 4 mg) which was mainly barbaralane (94, 53%). Nmr confirmed these results and in addition showed the presence of a small amount of indane which could not be separated from barbaralane under the vpc conditions used. The volatile components were removed on the evaporator and a colorless oil (25 mg) remained. Nmr showed the following: the [3.2.2] alcohol, barbaralol, and 1-indanol; and the [3.2.2] alcohol.

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