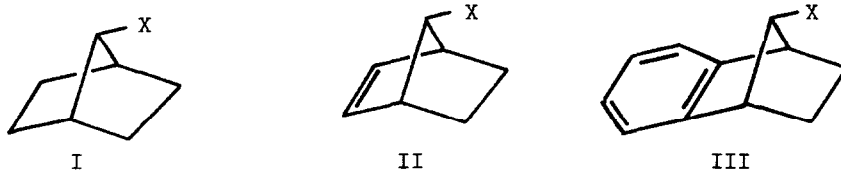


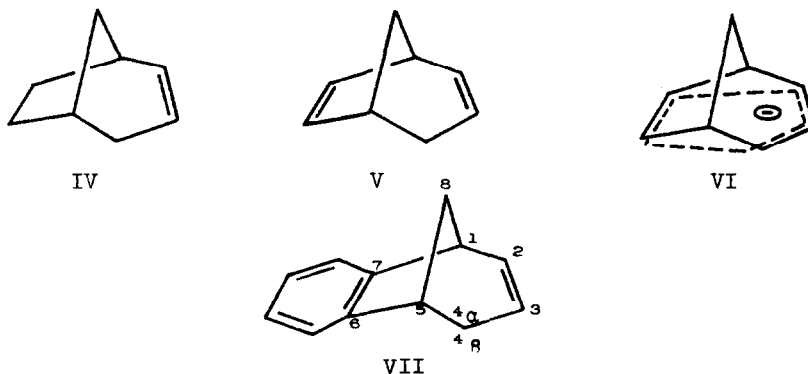
A BISHOMOINDENYL ANION
Joel W. Rosenthal (1)
Chevron Research Company, Richmond, California 94802
S. Winstein (2)
Department of Chemistry, University of California,
Los Angeles, California 90024

(Received in USA 26 May 1970; received in UK for publication 8 June 1970)

A large number of homoaromatic species formed by the interaction of a carbon-carbon double bond with a charged moiety have been studied (3). In certain carbonium ions the double bond has been part of an aromatic system and as a consequence the ΔE_{π} due to cyclic delocalization was diminished in comparison to that in the parent system. Thus one found relative rates of solvolysis for I, II and III to be 1, 10^{11} and 10^6 , respectively (4,5).

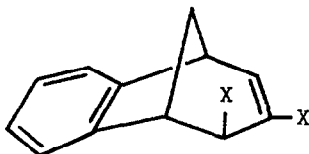


We now report the results of our investigation of a series of carbanions analogous to I, II and III. The bicyclo[3.2.1]octane system was chosen since a number of anions in this series have already been studied (6,7,8,9). Brown and Occolowitz found that V exchanged protons $10^{4.5}$ times faster than IV in potassium



t-butoxide(KO t-Bu)/ d_6 -dimethylsulfoxide(d_6 -DMSO) and that there was extensive delocalization in the anion (VI) derived from V (6). We have prepared benzo[6,7]-bicycloocta-2,6-diene (VII), a benzo analog of V, and studied its exchange properties.

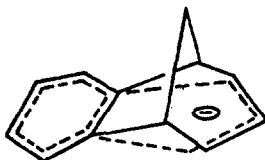
Tanida and his coworkers have prepared VIII (X = Cl), a suitable precursor to VII, in ca. 5% of th. via chloroform decomposition (10). In vain we attempted several variations of this method in an effort to improve the yield. However, the application of Seyferth's reagent ($\text{C}_6\text{H}_5\text{HgCBr}_3$) to benzonorbomadiene produced VIII (X = Br) in 60% of th. (11,12). Debromination of VIII with Li/t-butanol/THF gave VII (89%), bp 115-117 (18 mmHg) (14).



VIII

The kinetics of deprotonation of VII were determined by p.m.r. and, more accurately, by mass spectrometry. By the former method the half-life for exchange of the allylic protons ($4_{\alpha,\beta}$) was found to be less than 35 min. at 75.0°. However, the 2-proton had a half-life of 110 min. under the same conditions (15). This result is similar to that observed by Brown and Occolowitz (6) and points toward significant ion-pairing and lack of symmetrization in the exchange process.

The reactivity of VII compared to that of V was determined by exchanging each in 0.96 N KOt-Bu in d_6 -DMSO (0.1 M in hydrocarbon) at 50.0°. The first order rate constant for exchange in VII was found to be $(1.3 \pm 0.1) \times 10^{-4} \text{ sec}^{-1}$ while that for V under these conditions was $(2.4 \pm 0.2) \times 10^{-5} \text{ sec}^{-1}$ (16). This rate factor of 18 indicates the homodelocalization in IX is significant, but somewhat damped compared to VI. Further, it is interesting to note that in the



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carbonium ion series (II and III) the fused benzene ring provides only half (on an energy scale) (5) the assistance that a double bond donates whereas in the carbanion series (V and VII) the corresponding number is about eight-tenths.

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12. All attempts to purify VIII (X = Br) resulted in substantial decomposition. The proof of its structure rests on the p.m.r. of a mixture of VIII and benzo-norbornadiene. In particular, the doublet ($J = 2.3$ Hz) at 5.36 τ due to H_4 is characteristic of the 3,4-dihalobicyclooctadienes. (9,10,13).
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14. Satisfactory elemental analysis, i.r. and p.m.r. spectra were obtained.
15. As determined by this method not more than 0.5% deuterium was incorporated into any position other than 2 and 4.

16. Deuterium incorporation was followed mass spectrometrically with appropriate corrections for natural abundance of isotopes.