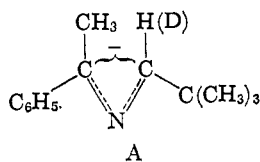


rate constants a number of interesting rate ratios and values were determined: $(k_e/k_a)_{OD}^{CH} \sim 28$; $(k_e/k_a)_{OH}^{CD} \sim 34$; $(k_i^H/k_i^D)_{OH} = 3.3$; ratio of rate of collapse of azaallylic anion to starting material to that to product, 4.9–6.0; intramolecularity when proton is transferred in deuterated solvent, $\sim 13\%$; intramolecularity when deuterium is transferred in protonated solvent, $\sim 13\%$.

These data provide the following interesting conclusions. (1) The proton transfer in this base-catalyzed transamination is essentially completely stereospecific and involves only a single face of an azaallylic anion. (2) This result could only have been obtained had the reaction occurred essentially exclusively through one of the four possible azaallylic anions, undoubtedly the one least strained (A). (3) Collapse of azaallylic anion favors starting material over product, although the product is the more thermodynamically stable isomer. (4) Starting material undergoes isotopic exchange with high retention. (5) While a proton or deuteron is being transferred, extensive isotopic exchange with solvent occurs. (6) Stereospecificity in this proton transfer does not depend on intramolecularity. (7) In spite of the fact that isotopic exchange of starting material occurs faster than isomerization, a substantial kinetic isotope effect for isomerization is observed. (8) This method provides a useful means of preparing optically active deuterated primary amines.



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Protonation of Monohomocyclooctatetraene Dianion^{1,2}

Sir:

Reactions of the aromatic ten- π -electron cyclooctatetraene dianion^{3a} as a nucleophile^{3b} are both interesting and useful. Similar interest attaches to the chemistry of the homoaromatic counterpart of cyclooctatetraene dianion, namely monohomocyclooctatetraene dianion (I). The latter species was recently reported,^{4a} and we now describe the first information on

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(2) Reported in part by S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967, p 5.

(3) (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) e.g., T. J. Katz and P. J. Garratt, *ibid.*, **86**, 4876, 5194 (1964); W. R. Roth, *Ann.*, **671**, 25 (1964); D. A. Bak and K. Conrow, *J. Org. Chem.*, **31**, 3958 (1966).

(4) (a) M. Ogliaruso, R. Rieke, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 4731 (1966); (b) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *ibid.*, **88**, 4729 (1966); (c) T. J. Katz and C. Talcott, *ibid.*, **88**, 4732 (1966).

its chemical behavior, specifically its behavior on protonation with methanol.

A priori, assuming stepwise protonation of I, it is not easy to predict whether the first protonation should lead to monocyclic anions, such as IIa–d, or to bicyclic ones containing a cyclopropane ring (III).⁵ It is also not clear to what extent the initial protonation would be governed by relative charge densities at C₁–C₈ or by relative stabilities of the monoanions. Further, in a product of diprotonation of I containing a cyclopropane ring it would not be clear without a labeling study whether the cyclopropane methylene group in the final product is the same as the original methylene group of the homocyclooctatetraene (IV) from which the dianion I was derived. For this and other reasons, the 9,9-dideuterio dianion I-D, generated from IV-D,^{4a,b} was also quenched in MeOH, and the protio-I was protonated with MeOD.

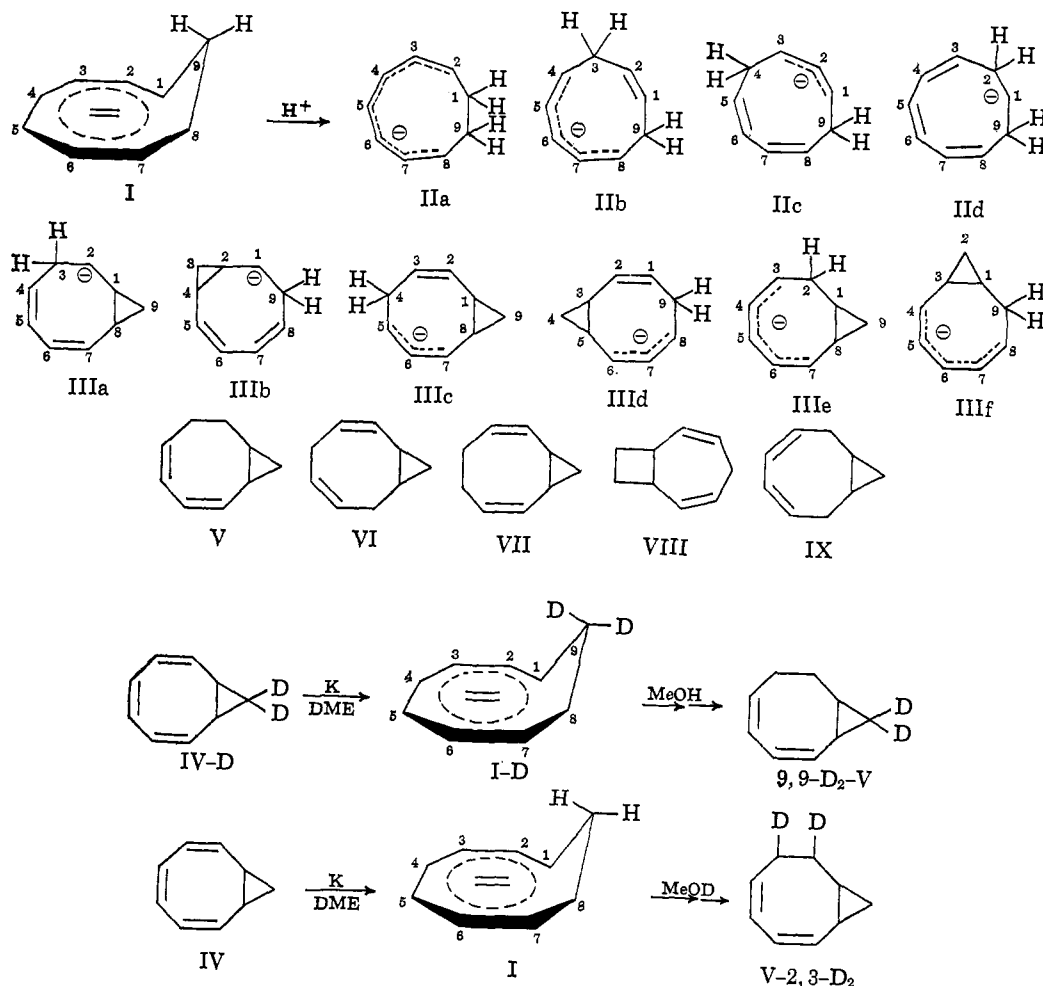
The potassium salt of I was generated as before^{4a} by allowing a solution of ca. 25 mg of monohomocyclooctatetraene IV in ca. 1.5 ml of 1,2-dimethoxyethane (DME) to stand at -80° over a mirror of excess K. The reaction mixture was prepared in one leg of a two-legged vacuum line apparatus equipped with a small side arm into which some of the solution could be diverted for the detection of an esr signal. Complete conversion of IV to the dianion was checked by the absence of such a signal for the monohomocyclooctatetraene anion radical.^{4b,c} A 1-ml quantity of anhydrous MeOH was degassed on the vacuum line and then distilled under vacuum into the DME anion solution which had been transferred to the other leg of the apparatus and thus was no longer in contact with the excess K mirror but was still at -80° . Addition of the MeOH produced an immediate color change from deep orange-brown to a light straw yellow with essentially no further change as the solution was allowed to come to room temperature. Only one main product⁶ was detected by vpc and this, obtained in over 85% yield, was collected by preparative vpc. The retention time of the product was identical with that of bicyclo-[6.1.0]octa-2,4-diene^{7a-e} (V) and its infrared, nmr, and ultraviolet spectra were identical with those of authentic material (Table I).

When the dianion I-D from IV-9,9-D₂ was quenched with MeOH the final product was pure V-9,9-D₂ with infrared, nmr, ultraviolet, and mass spectra identical with those of authentic material prepared from 1,3,5-cyclooctatriene and CD₂I₂. When CH₃OD was employed in the quench of the protio dianion I the bicyclooctadiene product contained two D atoms as judged by the mass spectrum, and the nmr spectrum showed that

(5) Monocyclic anions IIa–d may be visualized as arising from 1-, 3-, 4-, and 2-protonation, respectively. Bicyclic anions may be visualized as arising from monocyclic ones, IIIa and IIIb from IIb, IIIc and IIId from IIc, and IIIe and IIIf from IId. Alternatively, bicyclic anions IIIa, IIIc, and IIIe may be visualized as arising directly from protonation of I.

(6) Two very small additional vpc peaks were observed, but these were shown to arise in blank experiments involving all manipulations except inclusion of hydrocarbon IV.

(7) (a) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); (b) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963); (c) W. R. Roth, *Ann.*, **671**, 10 (1964); (d) P. Radlick, Ph.D. Thesis, University of California at Los Angeles, 1964; (e) J. Zirner, unpublished work; (f) D. S. Glass, Ph.D. Thesis, University of California at Los Angeles, 1966; (g) J. W. H. Watthey and S. Winstein, *J. Am. Chem. Soc.*, **85**, 3715 (1963); D. S. Glass, J. W. H. Watthey, and S. Winstein, *Tetrahedron Letters*, 377 (1965).



these were located at least very largely as in V-2,3-D₂. With regard to possible stereospecificity of the protonations at C₂ and C₃, we do not as yet have any precise information.

Table I. Ultraviolet Spectra and Deuterium Contents of I

Source of V	λ_{max} , $m\mu^a$	$\log \epsilon$	% of 2D
1,3,5-Triene ^b + CH ₂ I ₂	234	3.79 ^c	
I + CH ₃ OH	234	3.78	
1,3,5-Triene ^b + CD ₂ I ₂	235	3.78	95.4
I-D + CH ₃ OH	235	3.77	96.1
I + CH ₃ OD	234	3.78	94.7

^a Cyclohexane solvent. ^b 1,3,5-Cyclooctatriene. ^c Lit.^{7c} λ_{max} 234 $m\mu$ ($\log \epsilon$ 3.81); lit.^{7b,e} λ_{max} 234 ($\log \epsilon$ 3.78).

Not only do the present results provide information as to mechanism of protonation of I, but they confirm the absence of rearrangement with major skeletal reorganization in the formation of the anion radical^{4b} and dianion^{4a} from hydrocarbon IV. With regard to bicyclic product V, it cannot come from fully formed monocyclic trienes, since the known 1,4,7-, 1,3,6-, and 1,3,5-cyclononatrienes do not yield V under any conditions resembling those employed in the present work.^{7e,f} Also, V cannot be derived through a monocyclic monoanion. This is clear on two scores: (i) no such ring closure is observed in base-catalyzed isomerization of the cyclononatrienes,^{7e,f} e.g., with KOBu-*t* in DMSO; (ii) formation of a bicyclic from a monocyclic anion

permits the cyclopropane methylene group in V to be different from the one in the original IV, and this type of scrambling is not observed. This leaves bicyclic monoanions IIIa, IIIc, and IIIe, formed directly from monoprotection of I, as the only permissible main intermediates. Of these, anion IIIc from C₄ protonation cannot be important since it would be visualized to lead to bicyclic hydrocarbons VI and VII. If these were to equilibrate to V under the conditions for the CH₃OD quench, then one would expect inclusion of substantially more than two D atoms in product V, and this is not observed. Further, the equilibrium ratios of bicyclic olefins V:VI:IX are known^{7e} to be 94.6:1.6:3.8, and thus significant amounts of isomers of V would be expected in the final product, and this is not observed. Finally, VII, one of the products visualized from IIIc, has been observed by Roth^{7c} to undergo very ready valency isomerization to VIII, and yet none of this latter isomer was observed in the product from the MeOH quench of I.

The present data do not provide a clear choice between intermediates IIIa and IIIe. Formation of the former is favored by the expected greater negative charge⁴ at C₃ than at C₂ of I, while the latter is favored by greater anion stability.

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