

NONATETRAENYL ANION AND HOMOCYCLOOCTATETRAENE DIANION

by

Bruce Ian Mayall

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SIGNED: Bruce S. Mayall

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

R. Bates

ROBERT B. BATES  
Professor of Chemistry

6-4-'75

Date

To LMK

in commiseration

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## TABLE OF CONTENTS

	Page
LIST OF ILLUSTRATIONS . . . . .	vi
ABSTRACT . . . . .	vii
INTRODUCTION . . . . .	1
EXPERIMENTAL . . . . .	2
1,3,6,8-Nonatetraene [6] . . . . .	2
1,3,6-Cyclononatriene . . . . .	3
1,3,5,8-Undecatetraene . . . . .	3
Nonatetraenyl Anion (IVa) . . . . .	3
Anion from 1,3,6-Cyclononatriene . . . . .	3
DISCUSSION . . . . .	5
REFERENCES . . . . .	14

LIST OF ILLUSTRATIONS

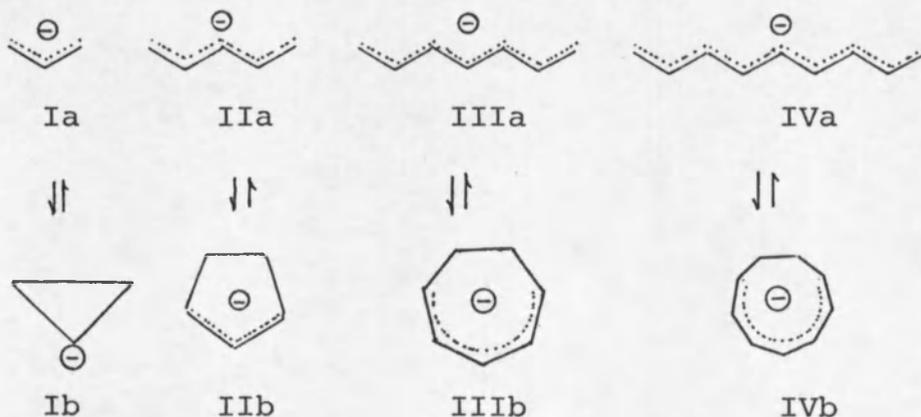
Figure	Page
1. Nonatetraenyl Anion--HA-100 . . . . .	6
2. 1,3,6-Cyclononatriene--T-60 . . . . .	9
3. Initial Homocyclooctatetraene Dianion-- T-60 . . . . .	11
4. Later Homocyclooctatetraene Dianion--T-60 . . .	12

## ABSTRACT

Nonatetraenyl and undecatetraenyl anions were prepared, the former by metalation of a 1,3,6,8-tetraene and the latter by metalation of a 1,3,5,8-tetraene. The latter method is inferior because an appreciable amount of addition of butyllithium to the conjugated triene system accompanies metalation. The nmr and visible spectral parameters fit for an extension of the series allyl, pentadienyl, heptatrienyl. Unlike heptatrienyl anions, these tetraenyl anions show no tendency to cyclize. An attempt to prepare cyclononatrienyl anion to see if it would open to nonatetraenyl anion failed, apparently because of over-metalation to the homoaromatic dianion.

## INTRODUCTION

The linear delocalized anions allyl (Ia), pentadienyl (IIa), and heptatrienyl (IIIa) have been successfully prepared and the chemical shifts of similar protons in their nmr spectra have been found to follow a pattern indicating increasing delocalization as the series progresses [1, 2]. The electrocyclization reactions  $Ia \rightleftharpoons Ib$ ,  $IIa \rightleftharpoons IIb$ , and  $IIIa \rightleftharpoons IIIb$  have been studied, with equilibrium probably favoring the open form in the first two cases and the cyclic form in the last [3-5]. The major goal of this work was to prepare nonatetraenyl anion (IVa) and study its nmr parameters and electrocyclization ( $IVa \rightleftharpoons IVb$ ).



## EXPERIMENTAL

All products were isolated by glc on a Varian Aerograph gas chromatograph under the following conditions: Column--1/4 inch by 10 ft. copper tubing packed with 30% DEGS on base-washed Chromosorb W, 60/80 mesh; injector, column, and detector temperatures of 205, 118, and 210 degrees, respectively; helium flow rate of 60 ml/minute.

All spectra were recorded on the Varian HA-100 or T-60 nmr spectrometers, as indicated in the figures.

### 1,3,6,8-Nonatetraene [6]

The bisphosphonium salt of 1,3-dibromopropane was prepared from 1,3-dibromopropane and triphenylphosphine in DMF. The well defined, crystalline product was separated, washed several times with petroleum ether, and dried overnight in a vacuum oven at 80°. This bisphosphonium salt was dissolved in DMSO and two moles of dimethyl sodium per mole of salt were added dropwise, under nitrogen, and with constant stirring to form the dark, reddish orange ylide. A twofold excess of freshly distilled acrolein in a 1:4 (v:v) dilution with DMSO was added dropwise to the reaction mixture at 0-10°. The resulting reaction mixture was allowed to warm to room temperature and stand overnight under nitrogen. The reaction mixture was then poured over

ice and the product separated by repeated extraction with pentane (technical grade, sulfuric acid washed). Final yield was consistently about 5%.

#### 1,3,6-Cyclononatriene

The procedure followed was that of Okamura, Ito, and Kellett [7] and the overall yield from cyclooctatetraene was approximately 30%.

#### 1,3,5,8-Undecatetraene

This substance was isolated by glc from a sample of Dictyopteris oil kindly furnished by Dr. Richard E. Moore, University of Hawaii.

#### Nonatetraenyl Anion (IVa)

To 50-100 mg of 1,3,6,8-nonatetraene in an nmr tube were added two volumes of dry  $d_8$ -THF and an excess of 1.6M n-butyllithium in hexane (Foote Chemical Co.) at dry ice temperature and under nitrogen. As the reaction mixture warmed to room temperature a yellow color developed which slowly separated into a reddish-orange lower layer. This layer became progressively darker until a deep blue-black color was produced and then solidified into a plastic material. Spectra were obtained before the solid formed.

#### Anion from 1,3,6-Cyclononatriene

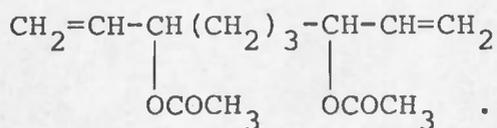
To one volume of 1,3,6-cyclononatriene in an nmr tube was added a mixture of three volumes of dry

N,N,N',N'-tetramethylethylenediamine (TMEDA) and 6-8 volumes of n-butyllithium. All reactants were kept under argon and mixed at room temperature. The initial light yellow color became orange and finally deep red. After 20-30 minutes a tan solid formed. The mixture was shaken rapidly and centrifuged briefly to separate the solid cyclonatrienyllithium. The supernatant was removed and the product washed under argon three times with dry pentane. After the last washing argon was gently blown through the product to remove residual pentane. The cyclonatrienyllithium was dissolved in  $d_8$ -THF for spectral analysis. (A substantial amount of TMEDA occluded with the solid and could not be washed out.)

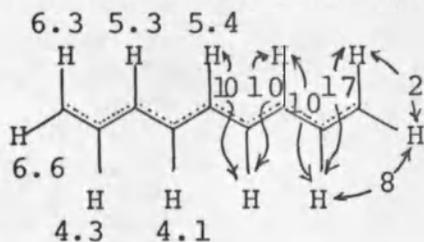
Each anion was quenched by adding  $D_2O$  or water dropwise to the iced nmr tube containing the anion. The quenched product of each anion was then extracted with pentane and hydrogenated at ambient pressure over a platinum catalyst.

## DISCUSSION

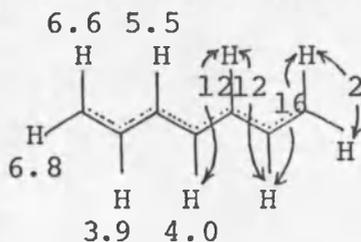
An unsuccessful attempt was made to prepare 1,3,6,8-nonatetraene, the prospective starting material for nonatetraenyl anion (IVa), by pyrolysis of the allylic diacetate of 1,8-nonadiene,



It was then prepared in low yield by a Wittig reaction [6]. Its nmr parameters were in accord with the proposed structure and it apparently (nmr) was quantitatively metalated by *n*-butyllithium in THF at  $-40^\circ$  to produce nonatetraenyl anion (IVa, Fig. 1). This anion (IVa) exhibits nmr parameters closely paralleling those determined for heptatrienyl anion (IIIa) [4], as shown below.



Nonatetraenyl anion  
(IVa)



Heptatrienyl anion  
(IIIa)

The negative charge is maximal on the odd numbered carbons and minimal on the even numbered ones, but the

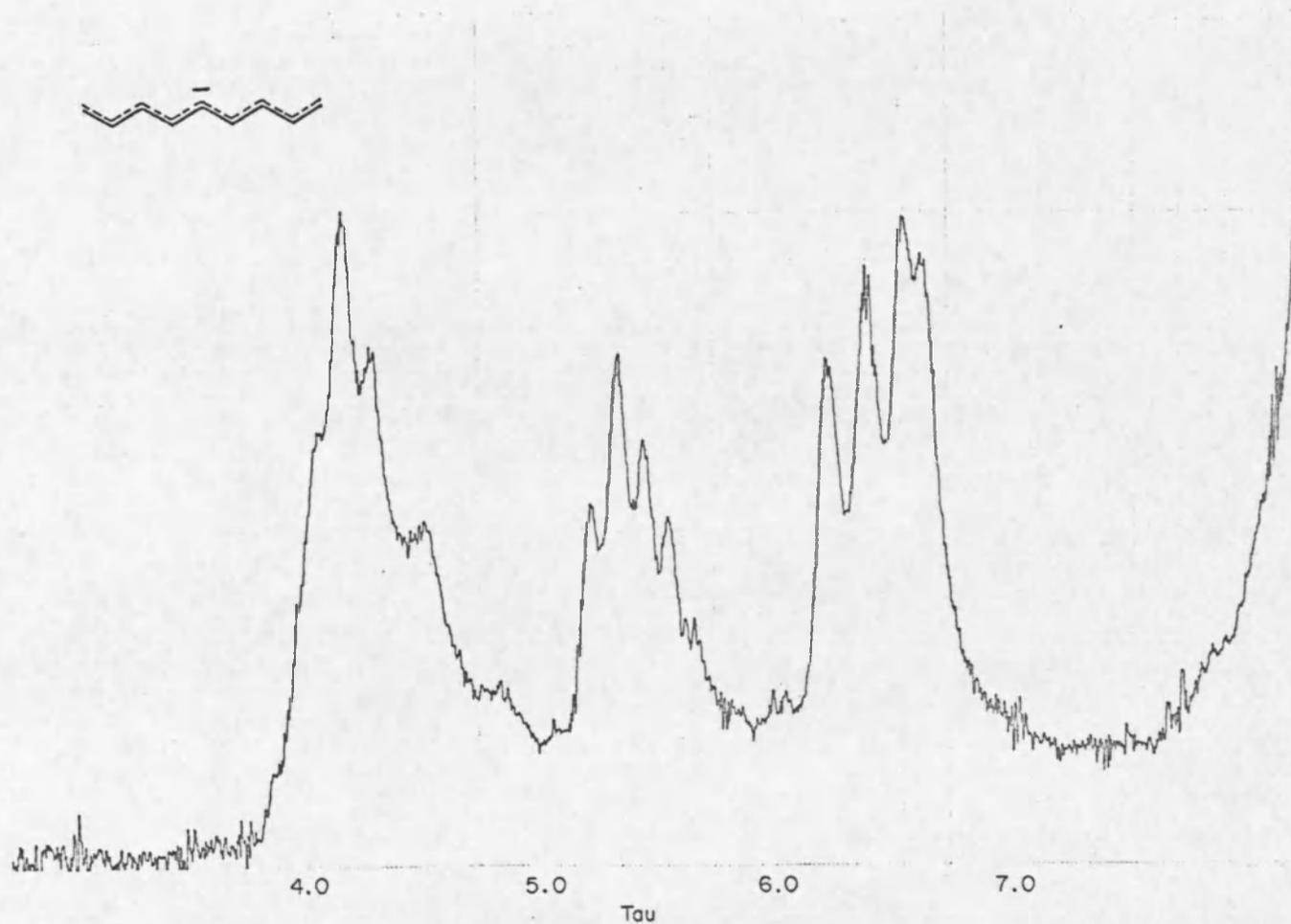


Fig. 1. Nonatetraenyl Anion--HA-100

greater degree of delocalization (across nine carbons instead of seven) diminishes both effects relative to heptatrienyl anion; hence, the greater chemical shifts from TMS (lower  $\tau$  values) for protons on the odd numbered carbons and the lesser shifts for the even ones are to be expected.

After IVa was produced, it was quenched with  $D_2O$  and hydrogenated over Pt. The product of hydrogenation had the same glc retention time as an authentic sample of nonane and its mass spectrum gave the parent ion at  $m/e$  129, corresponding to a monodeuterated, acyclic product of a mono-anion, thus affording conclusive proof that the anion did not cyclize. Heating the anion to  $70^\circ$  before quenching and hydrogenation gave identical results; hence, either the barrier to cyclization is appreciable or equilibrium favors the open form.

A recurring problem in obtaining the spectrum of IVa was the fact that this anion solidified as a dark, plastic substance shortly after metalation, thus precluding double resonance studies to better prove the assignments, particularly in the poorly resolved vinyl region of the spectrum. Consequently, the assignments should be considered fairly certain but not conclusive.

The 1,3,5,8-undecatetraene formed a black precipitate too soon after metalation to obtain an nmr spectrum sufficiently well resolved for interpretation. Quenching with  $H_2O$  followed by hydrogenation gave two glc peaks, one

corresponding to authentic undecane and one with a longer retention time. Mass spectral analysis of the mixture of these products showed a parent ion at  $m/e$  212, corresponding to pentadecane, and a peak of approximately equal height at  $m/e$  156, corresponding to undecane. Quenching with  $D_2O$  followed by hydrogenation showed a parent ion at  $m/e$  213 and another peak, about equally high, at  $m/e$  157. Thus, metalation provides approximately equal competition for proton abstraction from, and addition to the triene system, both resulting in a monoanion. This indicates that if proton abstraction is preferred, conjugation should (1) be limited to no more than two double bonds on either side of the bisallylic hydrogens, or (2) be symmetrical about these hydrogens.

Since cyclization of these tetraenyl anions did not occur, it was thought that the cyclononatrienyl anion (IVb) might open to give IVa. The spectrum for 1,3,6-cyclononatriene (Fig. 2) is well resolved and straightforward: the four allylic hydrogens, very nearly equivalent, give a pair of doublets almost superimposed at  $\tau 8.2$  (the central line almost completely obscures the downfield portion of the higher field doublet), the triplet for the two bisallylic protons is centered at  $\tau 7.6$ , and the six vinyl protons appear in a complex pattern between  $\tau 4.3$  and  $\tau 5.1$ . (The peaks at  $\tau 6.6$  and  $\tau 8.6$  are due to  $d_7$ -THF.) Integration gives vinyl:bisallylic:allylic as 3:1:2, corresponding

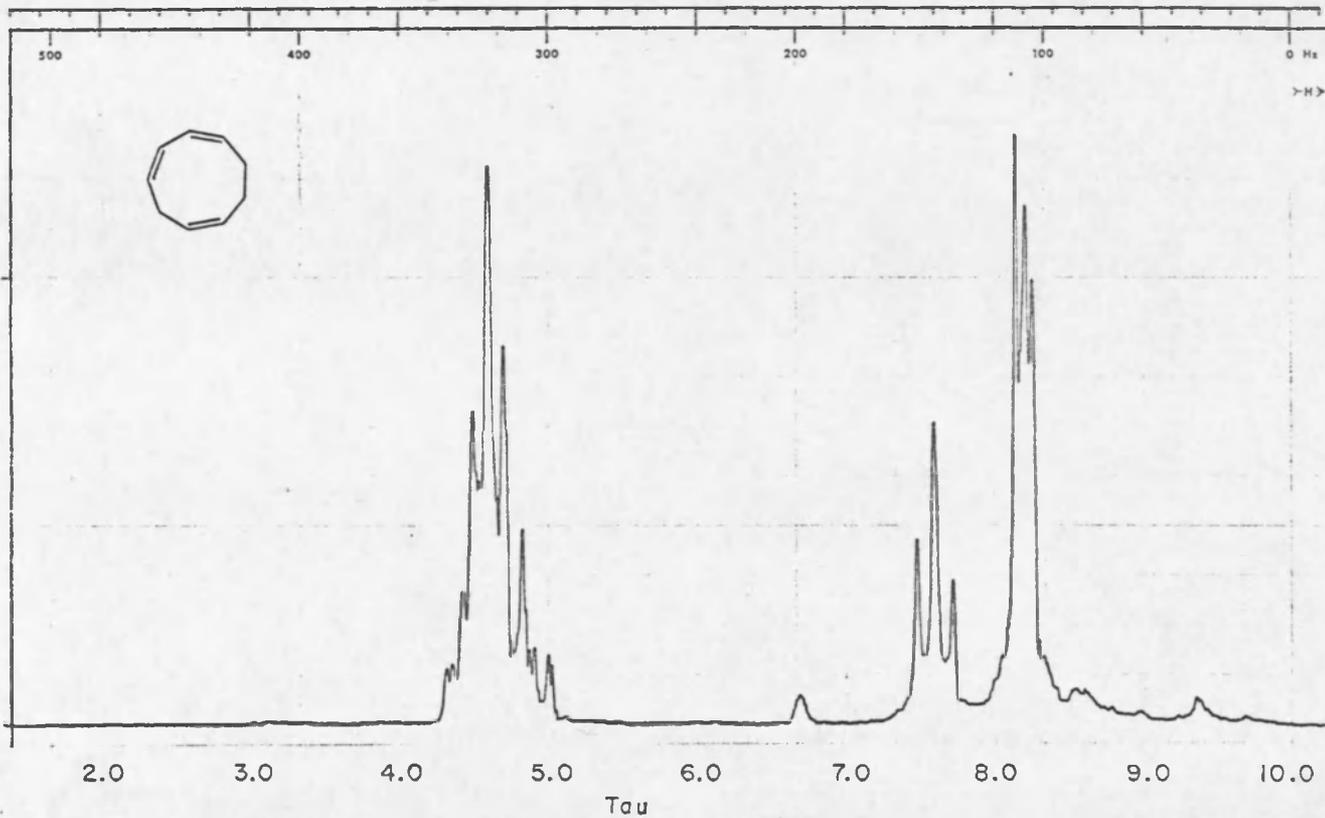


Fig. 2. 1,3,6-Cyclononatriene--T-60

to the structure given. Models indicate that no trans isomer is likely. Mass spectral analysis of the hydrogenated product of IVc indicates a parent ion at  $m/e$  126, corresponding to cyclononane.

Surprisingly, IVc did not react with n-butyllithium in THF; however, it was metalated in TMEDA to give a tan solid which could be dissolved in THF for spectral measurements. This anion gives a particularly interesting nmr spectrum (Figs. 3, 4). Neither the chemical shifts nor the coupling constants correspond with those predicted for a cyclic monoanion. That this anion has not opened to give IVa is certain by comparison with the spectrum of IVa as described earlier (Fig. 1). Models indicate that the cyclonatrienyl anion cannot be planar; thus, poor overlap might explain some of the anomaly. Quenching with water followed by hydrogenation gives a product with a mass spectral parent ion at  $m/e$  126, corresponding to cyclononane and indicating that neither ring opening nor addition of butyllithium to the hydrocarbon has occurred. The spectrum of the anion in Fig. 4 was obtained approximately 75 minutes after that in Fig. 3, indicating that the anion has undergone further change, but the quenched, hydrogenated product from the longer reaction time gave the same mass spectral results. It is probable that the homoaromatic dianion (IVc) was formed, though well-defined spectral parameters obtained in this case differ somewhat from those obtained by earlier

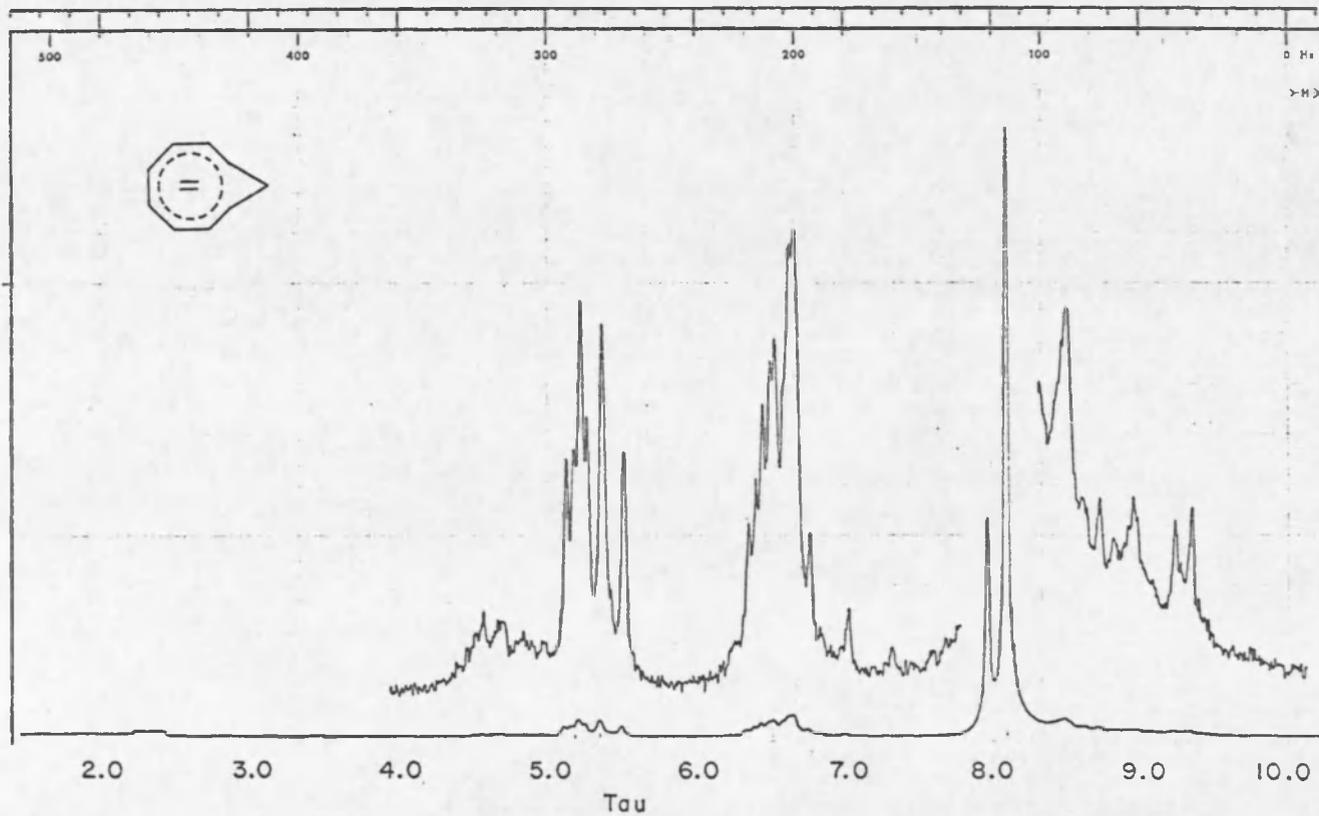


Fig. 3. Initial Homocyclooctatetraene Dianion--T-60

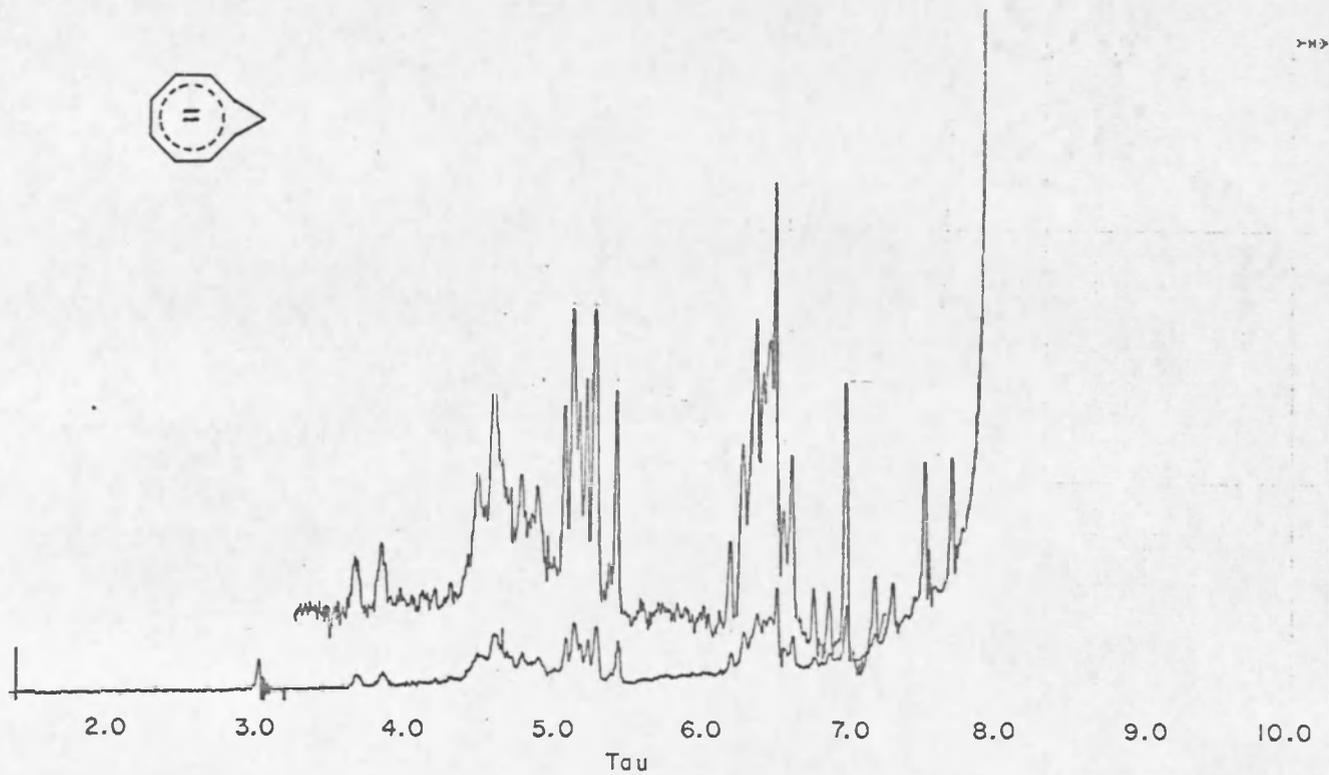
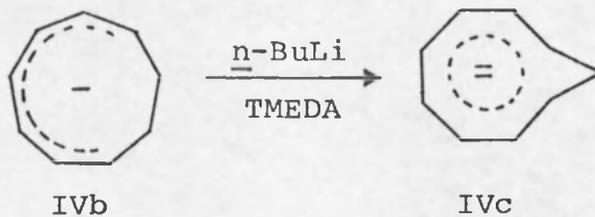


Fig. 4. Later Homocyclooctatetraene Dianion--T-60

workers who prepared this anion by another route [8]. Subsequent  $D_2O$  quenching and CMR spectral results have rendered it very likely that this substance is indeed the dianion.<sup>1</sup>



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1. Portions of the work reported in this thesis have been reported in [9] and [10].

## REFERENCES

1. West, P., J. I. Purmont, and S. V. McKinley, J. Amer. Chem. Soc., 90, 797 (1968).
2. Bates, R. B., D. W. Gosselink, and J. A. Kaczynski, Tetrahedron Letters, 205 (1967).
3. Bates, R. B., and D. A. McCombs, Tetrahedron Letters, 977 (1969).
4. Bates, R. B., W. H. Deines, D. A. McCombs, and D. E. Potter, J. Amer. Chem. Soc., 91, 4608 (1969).
5. Bates, R. B., S. Brenner, W. H. Deines, D. A. McCombs, and D. E. Potter, J. Amer. Chem. Soc., 92, 6345 (1970).
6. Hauser, C. F., T. W. Brooks, M. L. Miles, M. A. Raymond, and G. B. Butler, J. Org. Chem., 28, 372 (1963).
7. Okamura, W. H., T. I. Ito, and P. M. Kellett, J. Chem. Soc., 1317 (1971).
8. Ogliaruso, M., R. Rieke, and S. Winstein, J. Amer. Chem. Soc., 88, 4731 (1966).
9. Bates, R. B., S. Brenner, and B. I. Mayall, J. Amer. Chem. Soc., 94, 4765 (1972).
10. Barfield, M., R. B. Bates, W. A. Beavers, I. R. Blacksberg, S. Brenner, B. I. Mayall, and C. S. McCulloch, J. Amer. Chem. Soc., 97, 900 (1975).

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113