



8-1984

Naphthalene-2,3-Dialdehyde: A Synthone to 7,9-Polymethylene-8H- Cyclohepta[B]Naphthalene-8-One and a Study of Their Aromaticity

Edward O. Crapps
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/dissertations>

 Part of the [Organic Chemistry Commons](#)

Recommended Citation

Crapps, Edward O., "Naphthalene-2,3-Dialdehyde: A Synthone to 7,9-Polymethylene-8H-Cyclohepta[B]Naphthalene-8-One and a Study of Their Aromaticity" (1984). *Dissertations*. 2380.
<https://scholarworks.wmich.edu/dissertations/2380>

This Dissertation-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Dissertations by an authorized administrator of ScholarWorks at WMU. For more information, please contact maira.bundza@wmich.edu.



NAPHTHALENE-2,3-DIALDEHYDE: A SYNTHON TO 7,9-POLYMETHYLENE-
8H-CYCLOHEPTA[b]NAPHTHALENE-8-ONE AND A STUDY OF
THEIR AROMATICITY

by

Edward C. Crapps

A Thesis
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Chemistry

Western Michigan University
Kalamazoo, Michigan
August 1984

NAPHTHALENE-2,3-DIALDEHYDE: A SYNTHON TO 7,9-POLYMETHYLENE-
8H-CYCLOHEPTA[b]NAPHTHALENE-8-ONE AND A STUDY OF
THEIR AROMATICITY

Edward C. Crapps, Ph.D.

Western Michigan University, 1984

This report describes the synthesis of naphthalene-2,3-dialdehyde, and an analytical method for determining its purity by thin layer chromatography. Subsequently, the dialdehyde was condensed with various cyclic ketones to generate a series of polymethylene bridged naphthotropones. It was found that planarity and aromaticity increase with the size of the methylene bridge, although, the bridge must contain six or more methylene groups for the latter to be true. The claim for aromaticity is supported by NMR and IR data, which indicates the positive charge for a perchlorate cation salt is delocalized over the naphthalene and tropone ring system. Furthermore, from the available data, the order of aromaticity for the following tropone derivatives is: tropone > naphthotropone > benzotropone > pyrazolotropone > furotropone.

INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.
2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.
3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.
4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.
5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.

**University
Microfilms
International**
300 N. Zeeb Road
Ann Arbor, MI 48106

8425233

Crapps, Edward C.

NAPHTHALENE-2,3-DIALDEHYDE: A SYNTHON TO 7,9-POLYMETHYLENE -
8H-CYCLOHEPTA(B) NAPHTHALENE-8-ONE AND A STUDY OF THEIR
AROMATICITY

Western Michigan University

PH.D. 1984

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Copyright 1984

by

Crapps, Edward C.

All Rights Reserved

Copyright by
Edward C. Crapps
1984

DEDICATION

My mother has waited a long time for this deserving dedication for partial fulfillment of her dream.

We have gone through a lot of good and bad times together, and it has been very seldom in my life that I have been able to say, "mama everything is okay." It's always been trials and tribulations from place to place in my career, mainly because I am too honest and too fair, to let my mother tell it. But, that's the way I was raised. And I feel that it is only fair and honest to dedicate all my efforts that it took to acquire this degree to you Mama, Lillie Crapps, the sweetest lady I know.

ACKNOWLEDGEMENTS

It has been an honor to work for Professor Robert E. Harmon, a fine chemist, humanitarian, and friend. Any value and significance of this research is due to his outstanding chemical insight. His comprehensive knowledge of chemistry combined with patience and friendship made this endeavor possible.

The author would like to express his gratitude to Western Michigan University faculty and staff and to his colleagues in the Department of Chemistry for their help and suggestions.

He is especially grateful to his mother and family for their patience, understanding, encouragement, and support during this endeavor.

Edward C. Crapps

TABLE OF CONTENTS

	ACKNOWLEDGEMENTS	ii
	LIST OF TABLES	v
Chapter		
I.	INTRODUCTION	1
II.	STATEMENT OF THE PROBLEM	4
III.	REVIEW OF LITERATURE	5
	Aromaticity	5
	Tropones and Benzotropones	8
IV.	RESULTS AND DISCUSSIONS	13
	Preparation of Naphthalene-2,3-dialdehyde	13
	Spectral Data for the Dialdehyde vs. the Tetrabromide	18
	Analytical Method for Determining Purity of Dialde-	
	hyde	21
	Calculation	22
	Synthesis of 7,9-Polymethylene-8H-cyclohepta[b]naph-	
	thalene-8-ones	24
	Naphthotropylium Ions	29
V.	EXPERIMENTAL	32
	Instrumentation	32
	General	32
	Materials	32
	Preparations	33

Naphthalene-2,3-dialdehyde	33
2,2,3,3-Tetrabromodimethylnaphthalene	33
7,9-Pentamethylene-8H-cyclohepta [b] naphthalene- 8-one	34
7,9-Hexamethylene-8H-cyclohepta [b] naphthalene-8- one	35
7,9-Nonamethylene-8H-cyclohepta [b] naphthalene- 8-one	36
7,9-Decamethylene-8H-cyclohepta [b] naphthalene- 8-one	36
2,7-Dimethyl-4,5-Naphtho [b] tropone	37
1-Ethoxy-1,3-dihydronaphtho [2,3-c] furan	38
7,9-Pentamethylenecyclohepta [b] naphthalene-8-ol	38
7,9-Hexamethylenecyclohepta [b] naphthalene-8-ol.	39
2,7-Pentamethylenecyclohepta [4,5-b] naphthotro- pylium perchlorate	40
2,7-Hexamethylenecyclohepta [4,5-b] naphthotro- pylium perchlorate	40
VI. CONCLUSION	41
REFERENCES	42

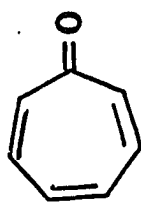
LIST OF TABLES

1.	Physical Data of Naphthotropones	25
2.	Physical Data of Benzotropones	26
3.	Physical Data of Benzotropone Versus Naphthotropone . . .	27
4.	Physical Data of Naphthotropones Versus Benzotropones . .	28

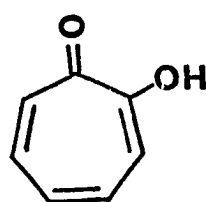
CHAPTER I

INTRODUCTION

The tropones 1 and tropolones 2 make up a very important and interesting class of nonbenzenoid aromatic compounds and many of their derivatives were first encountered in several quite different kinds of natural products (1).

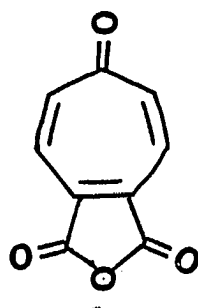


1

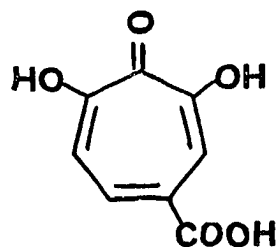


2

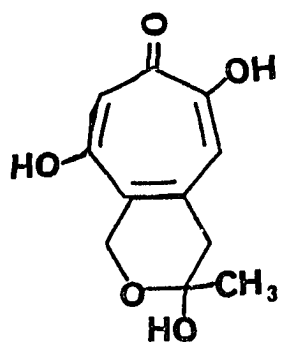
For example, it has been recognized that the tropolone system of the Penicillium Stipitatum, namely, stipitatic 3 (2) acid, puberulic acid 4 (3), and sepedonin 5 (4) are secondary vegetable metabolites.



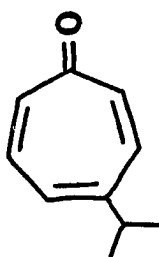
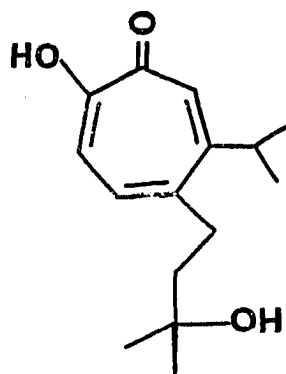
3



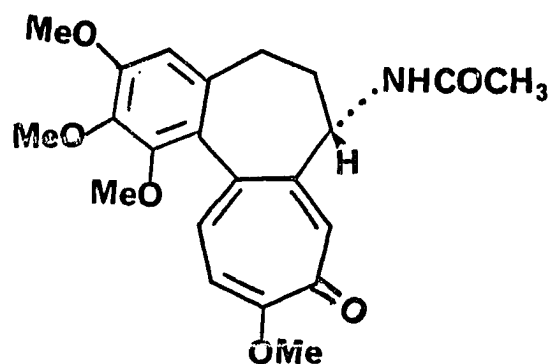
4

5

On the other hand, β -thujaplicin 6 was isolated from the oil of the Formosan cedar and nookatinol 7 is found in the heartwood of various Cupressales (5).

67

The alkaloidal tropolones have been given much medical, chemical, and botanical attention, which marks the long history of the active ingredient of Colchicum autumnale L. (Liliaceae). Its most common active component, colchicine 8, has been used for years in the treatment of gout. Although colchicine was reported to arrest mitosis in 1889, little research was done in this area until 1940, because



8

scientists did not realize the genetic potentialities and possible therapeutic value of the agent in combating cancer. The biological aspects of colchicine 8 and related compounds have been reviewed (6), as well as the chemistry of colchicine (7,8,9).

CHAPTER II

STATEMENT OF THE PROBLEM

This project was undertaken with two objectives in mind:

1. To synthesize naphthalene-2,3-dialdehyde from readily available starting materials, using analytical methods to describe its purity.
2. To synthesize a series of 7,9-polymethylene-8H-cyclohepta-[b]naphthalene-8-ones and several 7,9-polymethylene-8H-cyclohepta[b]-naphthalenium ions, and to describe their abilities to sustain a ring current, depending on the size of the polymethylene bridge, as an indicator of their aromaticity.

CHAPTER III
REVIEW OF LITERATURE

Aromaticity

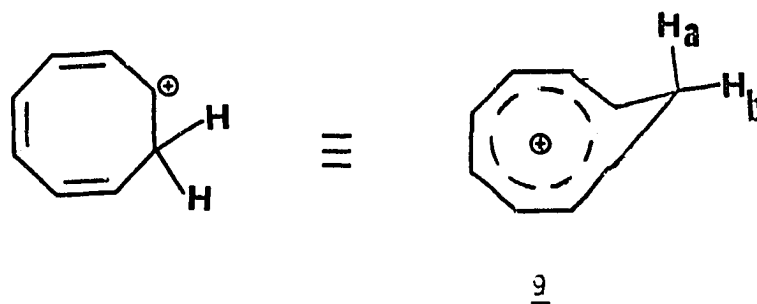
Originally, aromaticity has been associated with the properties of benzene, in terms of its chemical reactivity (10). For example, aromatic hydrocarbons were considered to be unsaturated systems which generally underwent substitution as opposed to addition reactions. Later, thermodynamic stability played an ever increasing role in defining aromaticity. That is to say, benzene has a lower enthalpy than cyclohexatriene (model system); the latter has been attributed to the molecular framework of benzene. Also, benzene is able to sustain a ring current due to its ability to delocalize the electron density over the carbons of the entire molecular ring.

Today, aromaticity is usually expressed in terms of molecular orbital terminology (M.O.T.). That is, structures which have a particular stable series of occupied π -molecular orbitals are called aromatic. This M.O. description of structure and aromaticity results in the Hückel rule. It is derived from simple Hückel molecular orbital (HMO) theory, and states that planar monocyclic completely conjugated hydrocarbons will be aromatic when the ring contains $4n + 2$ π -electrons, such systems have all electrons paired in bonding M.O.'s. This provides the theoretical basis of the Hückel rule.

All attempts to describe just how stable a given aromatic molecule

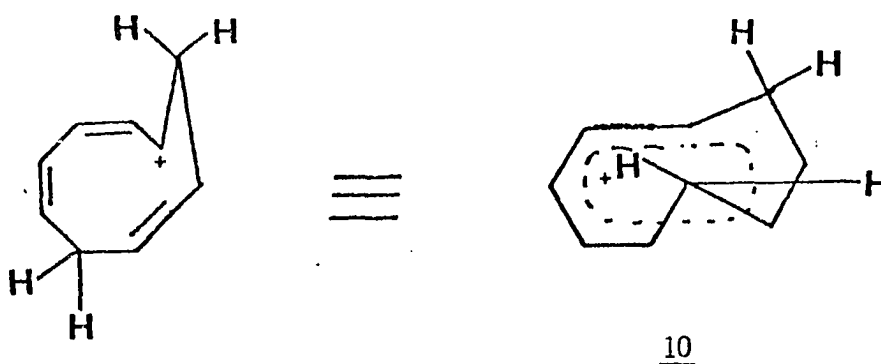
is in terms of simple HMO calculations are based on the delocalization energy. This value for the π -electrons of benzene is $6\alpha + 8\beta$, while the value for the hypothetical localized model cyclohexatriene is $6\alpha + 6\beta$, the sum of three isolated C=C bonds (11,12). The difference of 2β is called the delocalization energy or resonance energy (R.E.). This quantity is often useful for comparing related systems. It is not a real, measurable physical quantity; it is a comparison between a real molecule and a nonexistent one. The resonance energy for benzene lies between 20-40 Kcal/mole.

It is reasonable to say that aromaticity is best defined in terms of its stability derived from the delocalization of bonding electrons. An aromatic molecule is characterized by its appreciable stabilization relative to a noncyclic polyene. An antiaromatic system is one that is destabilized relative to a polyene model (13), and the term nonaromatic can be applied to molecules for which the calculated energy and the energy of the polyene model are comparable. On the other hand, homoaromaticity is a term used to describe systems in which a stabilized cyclic conjugated system is formed by bypassing one saturated carbon atom (14). An example is the cyclooctatrienyl cation 9.



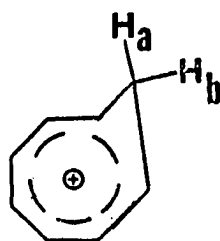
If two saturated carbon atoms were present, the term bishomo-aromatic would apply (15). Stabilization in such systems depends not only on the presence of a favorable electronic system, but also on the ability of the molecule to adopt a geometry favorable for overlap of the π -system.

Ions such as 9 and 10 have been isolated (16) and exhibit aromatic



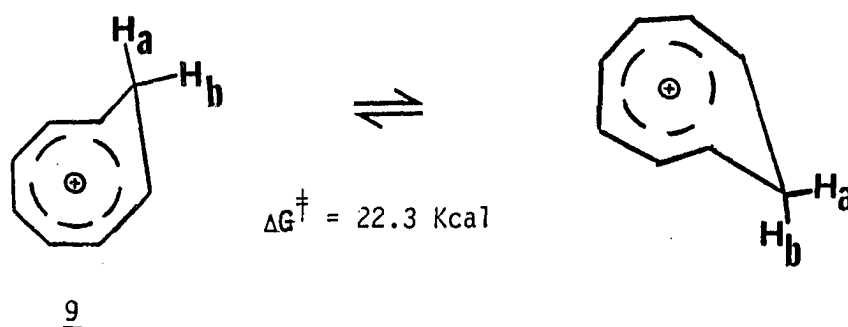
characteristics. Compound 9 illustrates how NMR spectroscopy has been an instrumental tool, capable of assessing aromaticity. Aromatic compounds are characterized by their ability to exhibit a diamagnetic ring current, which is responsible for a large magnetic anisotropy effect in aromatic compounds. The H_a proton lies above the plane of the ring, in the cone of the shielded region of the diamagnetic ring current, and its signal appears at a relatively high field compared to that of H_b . The occurrence of these chemical shift phenomena can be taken as evidence for aromaticity. It is not an absolute criterion, however, since model compounds must be used to estimate the chemical shift expected in the absence of a ring current, and a poor choice of a model can give misleading results (17). Thus, protons a and b

exhibit sharply different NMR chemical shifts (16). Proton a appears at $\Delta-0.68$ while H_b appears at $\Delta 5.2$. This indicates the existence of an aromatic ring current.



9

The π -system also contributes to imposing a high barrier to conformational flip of the saturated carbon ($\Delta G^\ddagger = 22.3$ Kcal), because

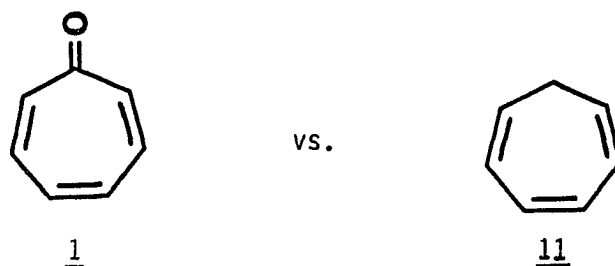


9

the molecule would have to temporarily lose planarity required for aromaticity in the region of the π -system carbons for such a conformational change.

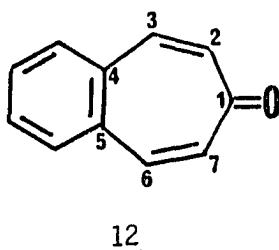
Tropones and Benzotropones

Based on NMR studies, one can conclude that tropone 1 is planar and has double bond alternation (18). The IR spectrum gives further support. That is, the carbonyl absorbs at 1594 cm^{-1} , which is typical



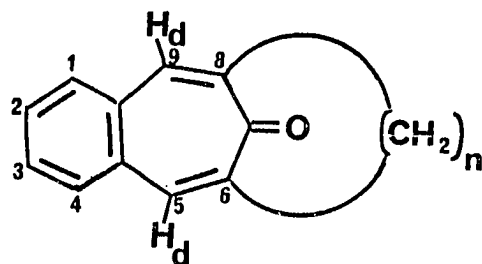
for such conjugated systems (19). Furthermore, the resonance stabilization energy of tropone is 14 Kcal/mole while that of cycloheptatriene 11 is only 8 Kcal/mole (20). This means that tropone is more stable than cycloheptatriene 11 and that the former can sustain a ring current.

X-ray crystallographic analysis of 4,5-benzotropone 12 shows the

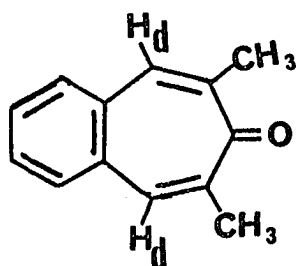


fused ring to be almost planar. Namely, the carbonyl oxygen is displaced out of the plane (of the ring system) by 0.2\AA , while the carbon is displaced by 0.1\AA (21). The IR carbonyl absorption occurs at 1590 cm^{-1} , which is expected for a conjugated ketone 12 able to sustain a ring current.

Kloster-Jensen wanted to confirm the degree of planarity of the tropone ring by forcing the tropone ring out of planarity. This was done by placing a polymethylene bridge across C-6 to C-8, generating a series of 6,8-polymethylenebenzotropones 13 by varying the value of "n". It was found that the tropone ring is planar only if $n \geq 7$ (22).

13

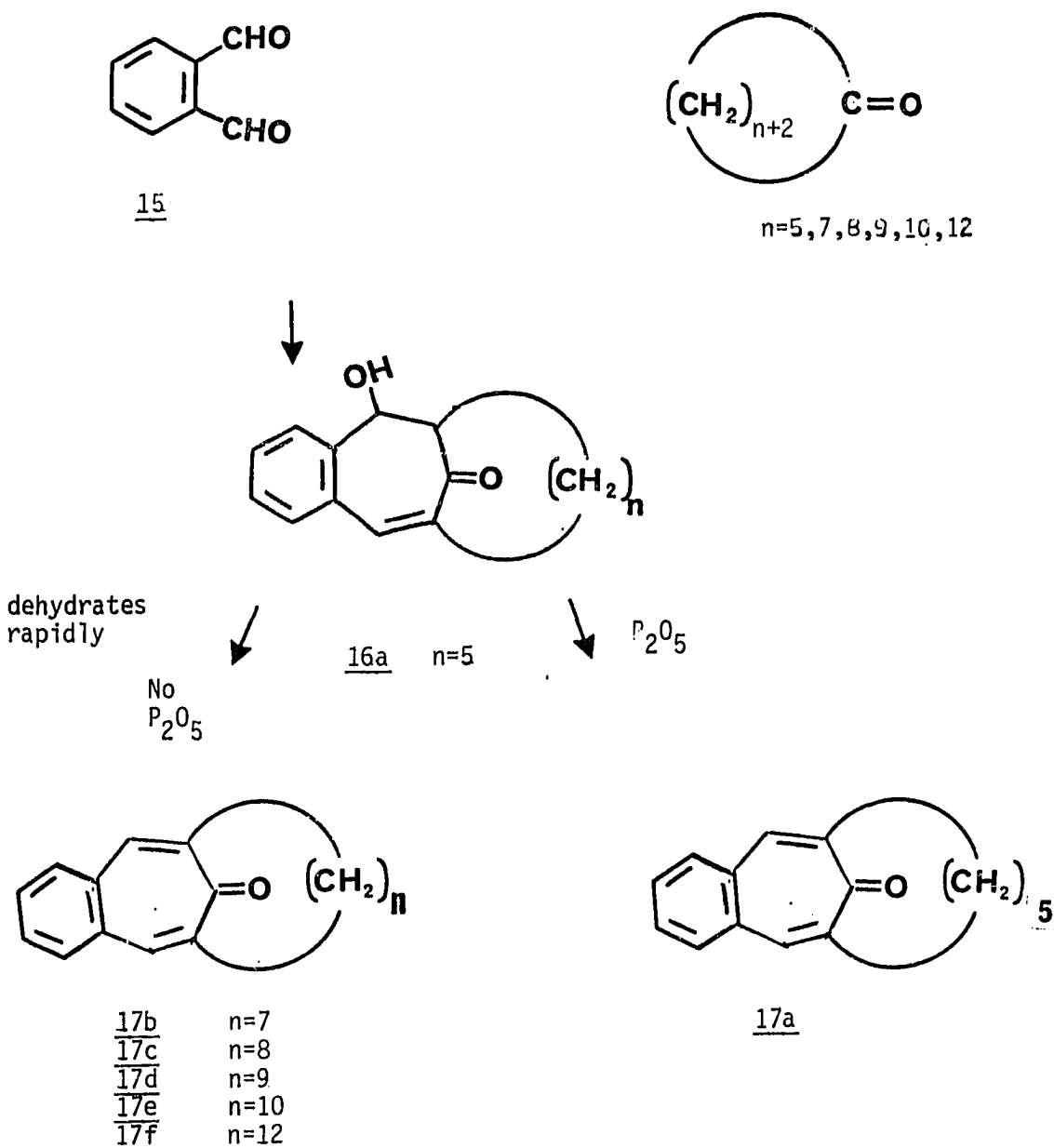
Similar results (23,24) were obtained by Harmon and Suder, and were substantiated by proton NMR. In 2,7-dimethyl-4,5-benzotropone 14,

14

protons H_d resonate at $\Delta 7.7$ which is consistent for a planar conjugated system. In contrast to 14, protons H_d in 13 resonate at $\Delta 6.78$ when $n \leq 7$, indicating that, the tropone ring lacks planarity and cannot as well sustain a ring current. However, when $n=9$, the H_d protons in 13 resonate at $\Delta 7.81$. This downfield shift of the H_d protons in the tropone ring is attributed to an increase in planarity of the tropone ring system. Planarity increases with increasing "n" ($n \geq 7$). Dehydration of the 3-hydroxy precursor is rapid in those cases where $n \geq 7$. The driving force is the energy gained by attainment of a planar conjugated system. On the other hand, when $n \leq 7$, the intermediate adduct had to be treated with P_2O_5 to accomplish the same results.

See Scheme 1.

Scheme 1



These polymethylenebenzotropone 17a-f are prepared by condensing phthalaldehyde 15 with various cyclic ketones to give aldol-type

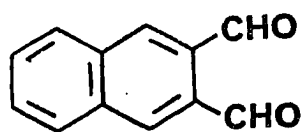
condensation products, which dehydrate (if $n \geq 7$) to form 6,8-poly-methylenebenzotropones 17a-f in 20-84% yields (23,24).

CHAPTER IV

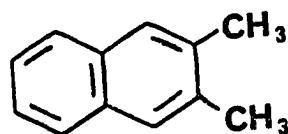
RESULTS AND DISCUSSION

Preparation of Naphthalene-2,3-dialdehyde

Naphthalene-2,3-dialdehyde 18 has been synthesized by several workers (25-29) with varying degrees of difficulty, in fair to poor yields, which do not lend themselves to macrogram scale-up. In the present paper, we report the synthesis of the dialdehyde 18 from readily available 2,3-dimethylnaphthalene, with the potential for macrogram scale-up, which can function as a synthon for the production of various 7,9-polymethylene-8H-cycloalkyl[b]naphthalene-8-ones in yields ranging from 45-71%.

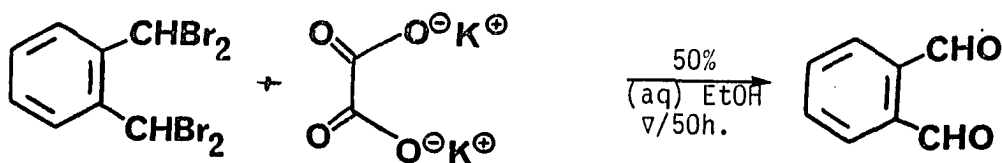


18



19

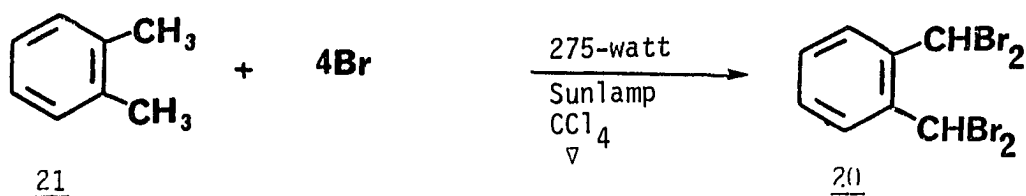
It is known from the literature (30) that phthalaldehyde 15 may be purchased from Aldrich or prepared from $\alpha,\alpha,\alpha',\alpha'$ -tetrabromo-o-xylene 20 by treating it with potassium oxalate in 50% (aqueous) ethanol at reflux for 50 hours. The product 15 was steam distilled.



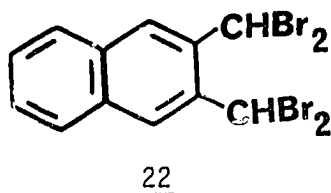
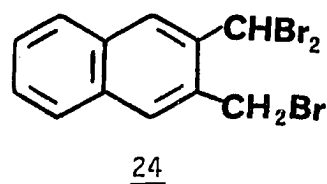
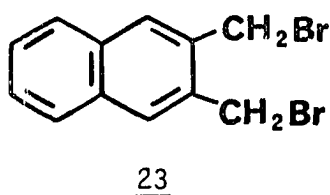
20

15

It is also known that 20 is synthesized from 1,2-dimethylbenzene 21 and bromine in the presence of a 275-watt sun lamp. In an analogous manner, 2,2,3,3-tetrabromodimethylnaphthalene 22 was prepared in 82% yield.



The progress of the reaction was followed by thin layer chromatography (TLC). If monitored, one can isolate the dibromide 23, or the tribromide 24, if the reaction is stopped at either point. Subsequently, 22 was refluxed in the presence of 50% (aqueous) EtOH and potassium oxalate; it was not necessary to steam distill 18 as was the case with phthalaldehyde 15.



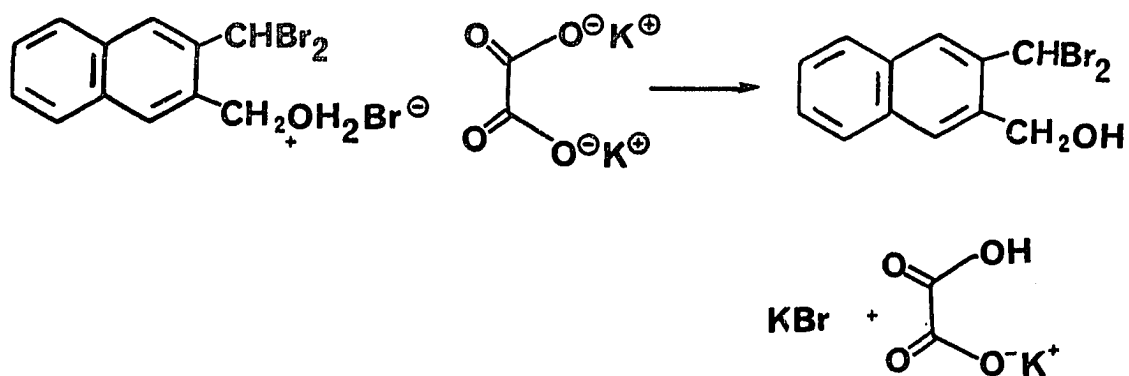
The pure dialdehyde 18 was isolated in 28% yield, plus a mixture of 22 and 18 in a ratio of 90:10 respectively. The latter was

Scheme 2

1. H_2O displaces Br^- in $\text{S}_{\text{N}}2$ fashion.



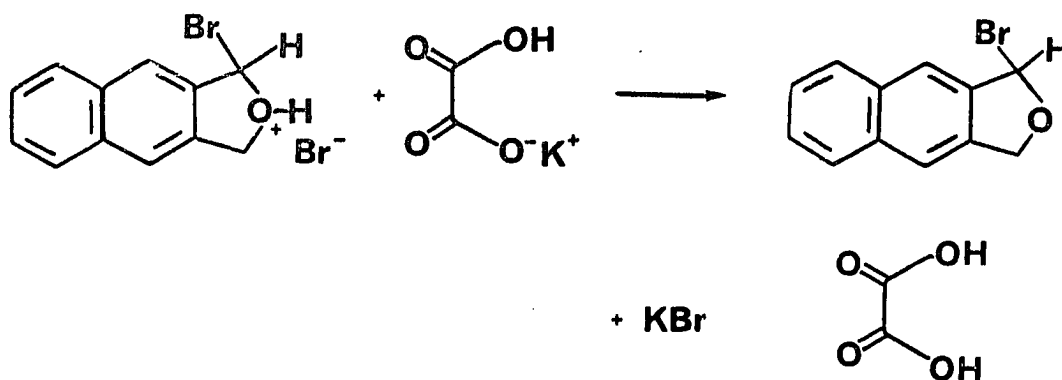
2. Potassium oxalate abstracts a proton.



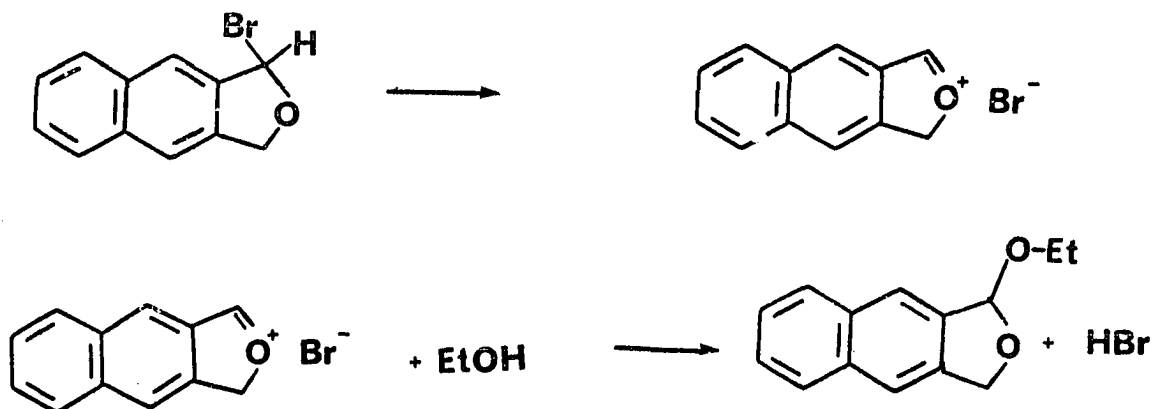
3. Internal nucleophilic displacement of Br^- by $-\text{OH}$ function.



4. Potassium oxalate abstracts a proton.

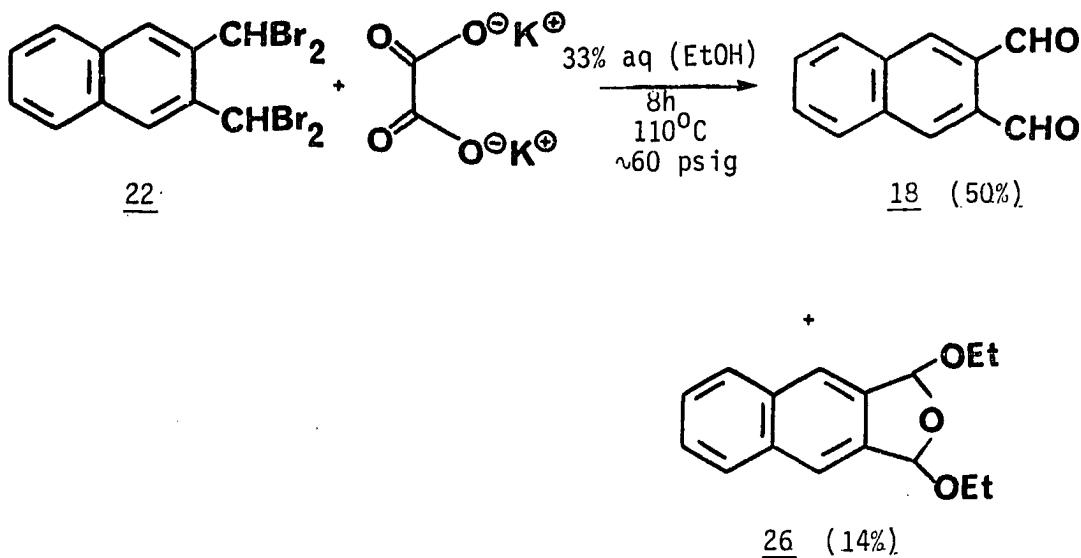


5. Internal displacement of Br^- by oxygen, followed by attack of EtOH (hemiacetal would be unstable).



6. HBr reacts with potassium oxalate

With these encouraging results, we proceeded to use an analogous high pressure procedure to the dialdehyde 18, with decreased reaction time. Note: Prolonged heating causes the dialdehyde to discolor. Two products were expected: 26 and 18.

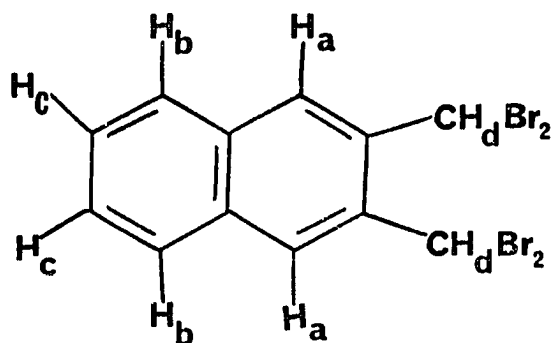


Indeed the expected products were obtained in the yields indicated, although 18 was contaminated with trace amounts of the tetrabromide 22. There was also ~11% of an unidentified oil, which appears to be a mixture of 18 and 26 by NMR. 26 was vacuum distilled away from the latter oil at 130°C and 0.5 mmHg.

It is not practical nor necessary to remove impurities (the tetrabromide 22) in the dialdehyde 18. The latter oxidizes readily on silica gel or in solution in the absence of an inert atmosphere in attempting further purification. The former 22 does not react with the cyclic ketones under the reaction conditions used, although 18 does react with them to give the desired 7,9-polymethylene-8H-cyclo-alkyl[b]naphthalene-8-ones 27a-d. Consequently, it is only necessary to know the amount of impurity 22 present. This was accomplished with analytical TLC, to be discussed later.

Spectral Data for the Dialdehyde vs. the Tetrabromide

The NMR spectrum for the tetrabromide 22 shows four distinctly different types of protons.

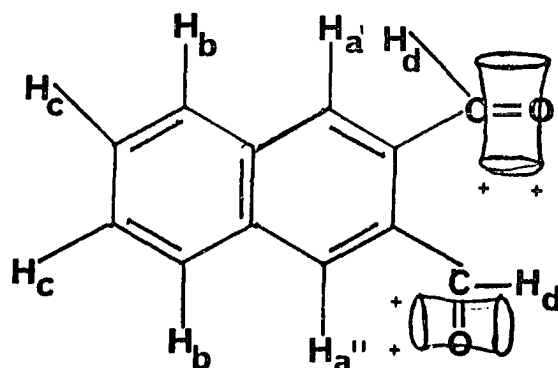


NMR(CDCl₃): Δ8.1 (s,2Hd), Δ7.6-7.8 (m,2Hc), Δ7.3-7.55 (m,2Hb), Δ7.2

(S, 2H_a), IR (KBr) 3500-3140 cm⁻¹ (w)

Unlike the tetrabromide, H_a protons are not equivalent in the dialdehyde due to anisotropic effects of the adjacent aldehydic groups.

That is:



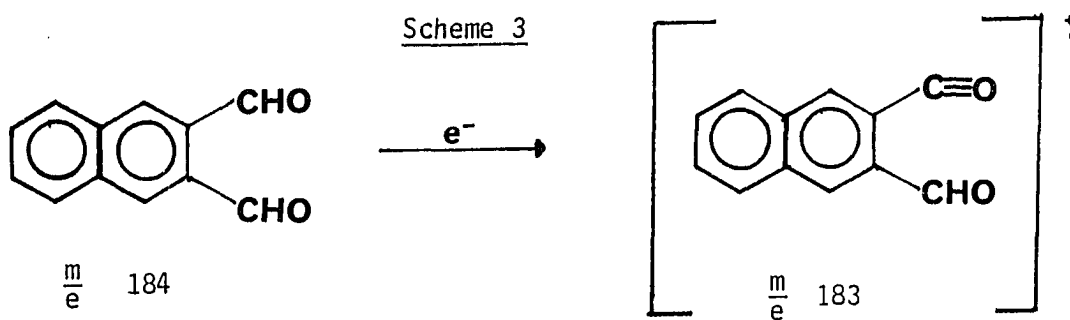
NMR(CDCl₃): Δ8.35(S, 2H_d), Δ7.95(m, 2H_c, 1H_{a'}), Δ7.65(m, 2H_b, 1H_{a''})

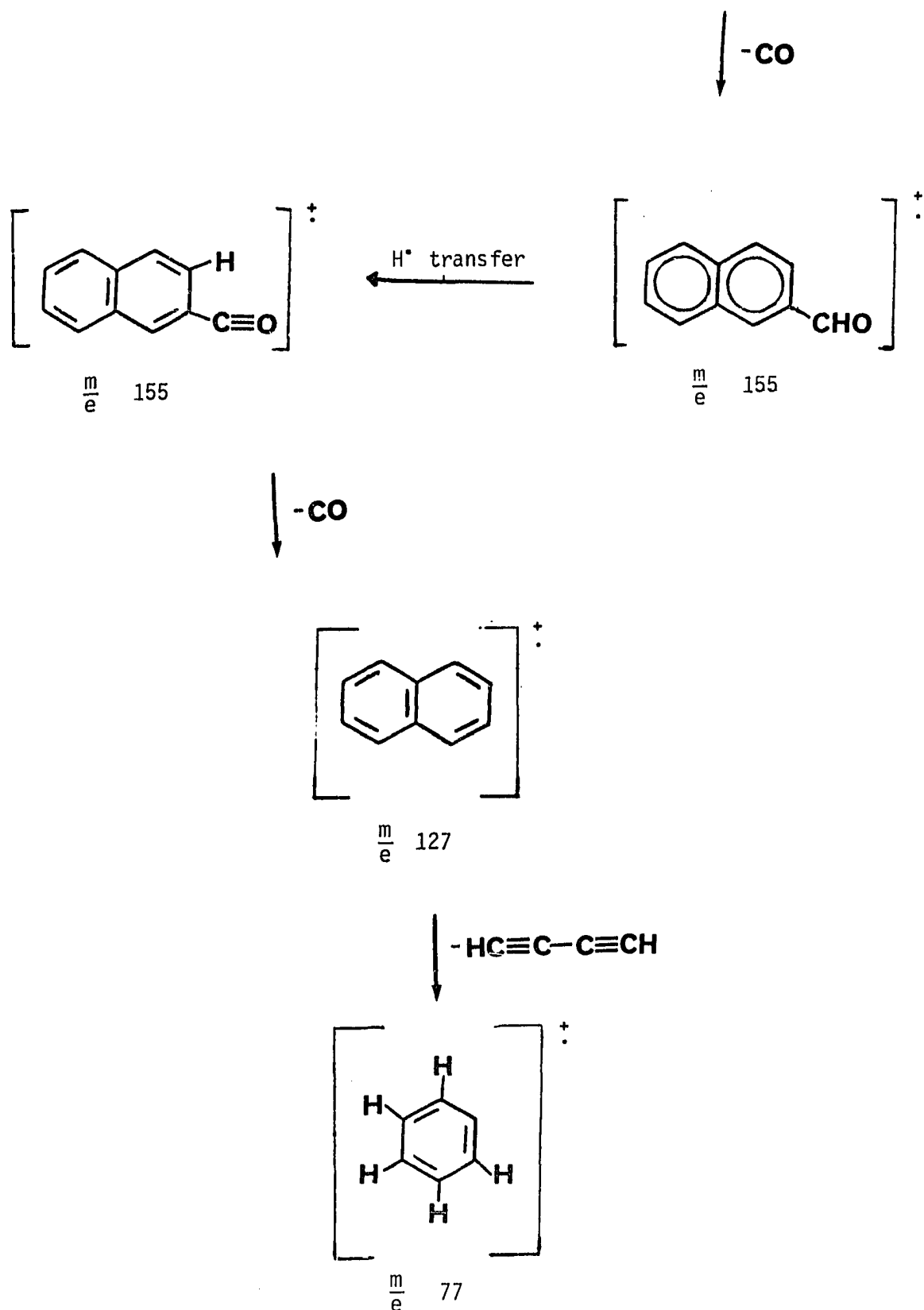
IR(KBr): 3500-3300 cm⁻¹, c=O (1715-1570) cm⁻¹, centered at 1685 cm⁻¹

H_{a''} is shielded to a greater degree than H_{a'}, because it is located in a region of high electron density.

The IR absorption at 3500-3300 cm⁻¹ is characteristic for the naphthalene ring system.

The proposed structure 18 is further supported by mass spectroscopy data (M⁺ @ $\frac{m}{e}$ 184). For the fragmentation pattern, see Scheme 3.

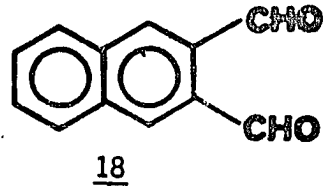
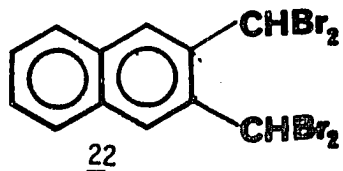




Analytical Method for Determining Purity of Dialdehyde

The concentration of tetrabromide 22 in the dialdehyde 18 reaction mixture was determined by Analytical Thin Layer Chromatography. The Anatech plates once developed were scanned on a spectrodensitometer equipped with a dual wavelength system. The maximum absorption of the above compounds occurred at 300 m μ . All peaks were read at this wavelength.

Standard concentration curves were made for both the tetrabromide and the dialdehyde at the concentrations shown below.

<u>Compound</u>	<u>Concentration ($\mu\text{g}/\text{spot}$)</u>
 <u>18</u>	2.5, 2.0, 1.5, 1.0, 0.5
 <u>22</u>	1.25, 1.0, 0.75, 0.50, 0.25

The tetrabromide 22 will be used to illustrate the procedure; the same procedure was used for the dialdehyde 18. That is, the standards and the unknown samples were spotted in duplicate, and were run on the same plate to minimize experimental error. The tetrabromide migrates with an $R_f = 0.54$ while that of the dialdehyde is 0.22. Therefore,

any unknown compound which migrates with an R_f value of 0.54 was assumed to be the tetrabromide 22. The solvent system was 20% EtOAc/79.5% hexane/0.5% isopropanol. Other solvent systems (CH_2Cl_2 ; 10% EtOAc/1% isopropanol/89% hexane) were tried so as to correlate the unknown compound with the known standard 22 or 18. Since the unknown R_f value was 0.54, it was concluded that unknown must be the tetrabromide, which was the same in more than one solvent system. This claim was supported by NMR, IR, and mass spectra data.

The computer plotted area versus concentration for the standard tetrabromide and dialdehyde which generated the following statistical parameters: slope 0.1356, intercept 0.1038, variance 0.3710 and correlation coefficient 0.9952.

Ideally the correlation coefficient should be 1.000, but it is 0.9952, which means that all points fall on a straight line whose intercept is zero. The latter means that our data is good and so is the method.

From these standard curves, the computer determined the amount of tetrabromide in the unknown sample by using the linear regression line model. Since the unknowns were run in duplicates, two concentrations were recorded (1.0977 $\mu\text{g}/\text{spot}$ and 1.1190 $\mu\text{g}/\text{spot}$). The average concentration (1.11 $\mu\text{g}/\text{spot}$) was used.

Calculation

$$1 \text{ spot} = 25\lambda$$

$$1,000\lambda = 1 \text{ mL}$$

The Original Tetrabromide Concentration

2,606 $\mu\text{g/mL}$ 0.8 mL of this solution was diluted to 10 mL of solution, resulting in a concentration of 208.48 $\mu\text{g/mL}$. 6 mL of this solution was diluted to 25 mL of solution, resulting in a concentration of 50.03 $\mu\text{g/mL}$.

Therefore, to calculate the % yield of tetrabromide in unknown is as follows:

$$\frac{1.11 \mu\text{g}}{\text{spot}} \times \frac{1 \text{ spot}}{25\lambda} \times \frac{1,000\lambda}{\text{mL}} = \frac{44.4\mu\text{g}}{\text{mL}} \text{ tetrabromide in unknown}$$

$$\frac{44.4 \mu\text{g}}{\text{mL}} \times 25 \text{ mL} = X\mu\text{g/mL} \quad (6 \text{ mL})$$

$$X\mu\text{g/mL} = 185$$

$$\frac{185 \mu\text{g}}{\text{mL}} \times 10 \text{ mL} = \frac{Y\mu\text{g}}{\text{mL}} \quad (0.8 \text{ mL})$$

$$Y\mu\text{g/mL} = 2,312.5 \mu\text{g/mL}$$

% Tetrabromide 21 in Unknown

$$\% \text{ tetrabromide } \underline{21} \text{ in unknown} = \frac{2,312.50 \mu\text{g/mL}}{2,606 \mu\text{g/mL}} \times 10^2$$

$$\% \text{ tetrabromide} = 88.74 \%$$

$$\% \text{ dialdehyde} = 8.8 \%$$

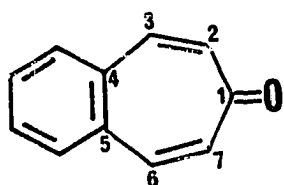
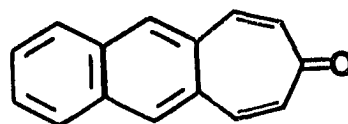
$$\% \text{ unknown residue } (R_f=0.96) = 1.5 \%$$

The above method enables us to determine the composition of any

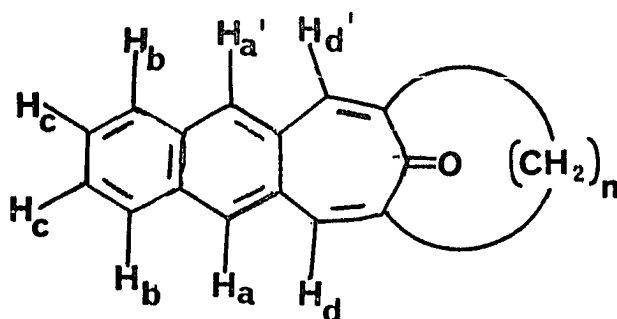
unknown mixture of tetrabromide and dialdehyde. Therefore, we can proceed to synthesis of 7,9-polymethylene-8H-cycloalkyl[b]naphthalene-8-ones 27a-d.

Synthesis of 7,9-Polymethylene-8H-cyclohepta[b]naphthalene-8-ones

For the sake of brevity these 7,9-polymethylene-8H-cyclohepta[b]naphthalene-8-ones 27a-d will be called 4,5-naphthotropones similar to 4,5-benzotropone 12, which are named after the parent compound tropone 1.

1227

These naphthotropones 27a-d were prepared by condensing naphthalene-2,3-dialdehyde 18 with various cyclic ketones to give aldol-type condensation products in 45-70% yield, similar to benzotropone preparation (31).



27a n=5
27b n=6

27c n=9
27d n=10

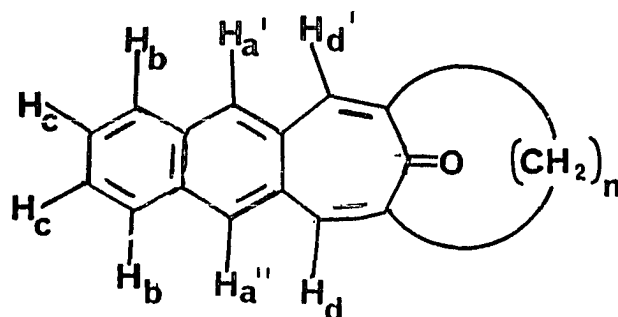
All that remains is to compare naphthotropone's ability to sustain a ring current relative to the benzotropone derivatives (31), as the size of the polymethylene bridge is varied across C-2 and C-7 if named as a tropone. It has already been shown that for 4,5-benzotropones if $n \geq 7$, the tropone ring is nearly planar and can sustain a ring current; if $n \leq 7$, it cannot. This becomes evident when one looks at the NMR spectra.

If the H_d protons resonate at $\Delta 7.2$ or lower field, the tropone ring system must sustain a ring current. See Tables 1, 2, and 3.

Table 1
Physical Data of Naphthotropones

Compound	n	NMR (CDCl ₃) Δ						% Yield
		H_d	H_c	H_b	$H_{a''}$	$H_{d'}$	$H_{a'}$	
27a	5	7.9	7.7	7.37	7.37	5.35	6.62	62
27b*	6	7.81	7.75	7.41	7.02	-----	-----	48
27c*	9	7.88	7.78	7.45	7.29	-----	-----	77
27d*	10	7.95	7.80	7.40	7.40	-----	-----	49

* $H_d = H_{d'}$ when $n \geq 6$

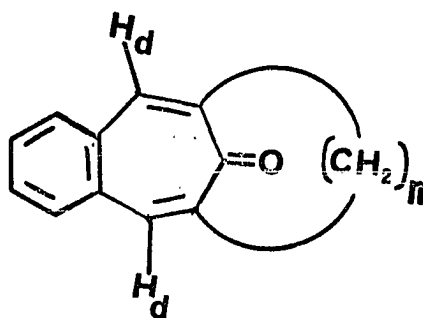


27 n=0

Table 2
Physical Data of Benzotropones (23,24)

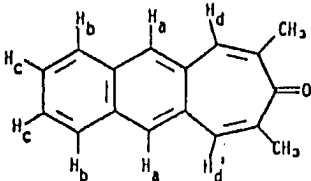
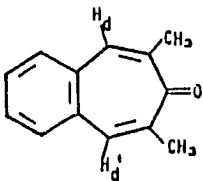
Compound	n	NMR (CDCl ₃) Δ	
		H _d	Aromatic
17	0	7.60	7.58
17a	5	6.78	7.05-7.60
17*	6	-----	-----
17d	9	7.31	7.48
17e	10	7.27	7.44

*Was not prepared



17 n=0

Table 3
Physical Data of Benzotropone Versus Naphthotropone

							
<u>29</u>						<u>14</u>	
n	*NMR (CDCl ₃) Δ					n	*NMR (CDCl ₃)
	H _d	H _c	H _b	H _a	% Yield		H _d
0	8.0	7.8	7.5	7.5	58.5	0	7.7

$$*H_d = H_d'$$

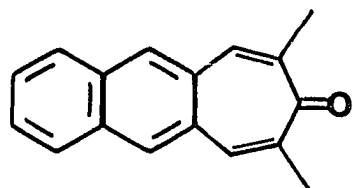
In all cases, when $n \geq 6$ in naphthotropones, H_d resonates at a field below $\Delta 7.2$, whereas, the same is true for benzotropones only if $n \geq 7$. On the other hand, in naphthotropones, when $n \leq 6$ 27a, the H_d protons are unequivalent, one resonates at a higher field than the other, and thus the tropone ring has been forced out of planarity, the more stable situation. Similar results were obtained in benzotropone series for $n \leq 7$. The above NMR spectra data seem to imply that the additional benzene ring in naphthotropone enhances the system's ability to sustain a ring current over benzotropone. In all cases, the H_d proton in naphthotropone resonates at a lower field than the H_d in benzotropone, which is further supported by the H_d resonance in 29 and 14. Consequently, one could conclude that naphthotropones sustain a

ring current better than benzotropones because the former is more planar, therefore, naphthotropone is more aromatic than benzotropone. Similar ideas have been alluded to by other workers (21,32), namely, tropone is more aromatic than benzotropone which is more aromatic than furotropone.

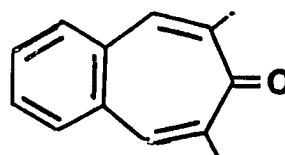
It has also been demonstrated with IR spectroscopy that the carbonyl absorption occurs at 1590 cm^{-1} for conjugated ketones, which can sustain a ring current like benzotropones 17b-f with $n \geq 7$. The IR data found in Table 4 illustrates that the above is true for naphthotropones 27b-d as well.

Table 4
Physical Data of Naphthotropones Versus Benzotropones

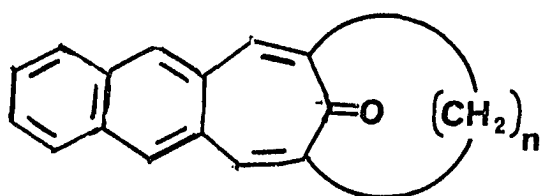
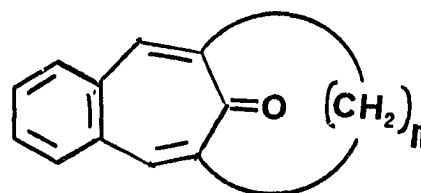
Compound	n	IR(KBr) c=O (cm^{-1})	Compound	n	IR(Nujol) c=O (cm^{-1})
29	0	1587	14	0	1596
27a	5	1665	17	0	1596
27b	6	1645	17a	5	1697
27c	9	1605	17c	9	1610
27d	10	1580	17d	10	1610



29

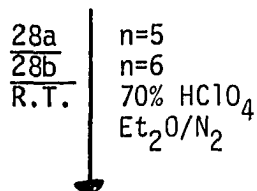
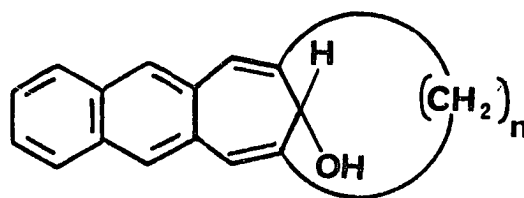
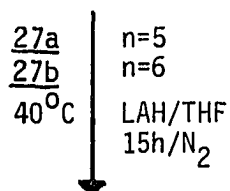
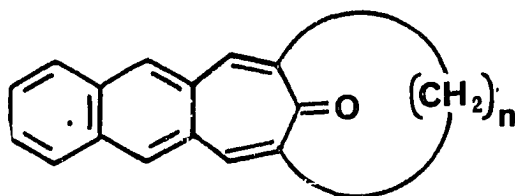


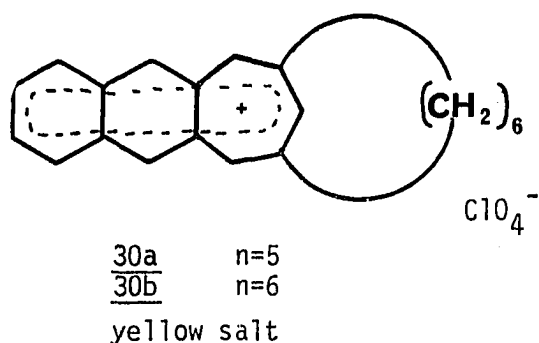
14

27a-d17a-d

Naphthotroponium Ions

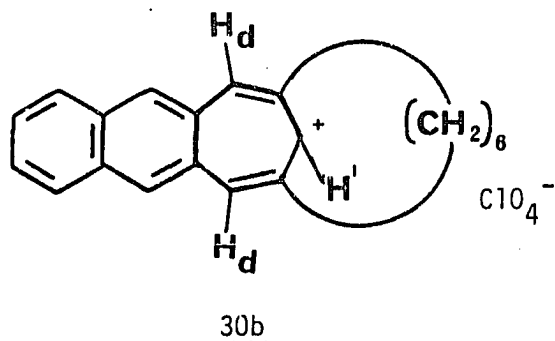
Naphthotropones 27a and 27b are converted to the alcohol by reduction of the carbonyl function with lithium aluminum hydride (LAH) in tetrahydrofuran (THF) in 61% and 87% yields, respectively.





Perchlorate 30 was isolated while 30b was not. This is not surprising since 6,8-polymethylene-4,5-benzotropylium perchlorates have been isolated only if $n=10$ or 12 (31). The inability to isolate these perchlorates with lower values of n have been attributed to slight deviations in planarity of the tropone ring (31). In essence, the positive charge cannot be sufficiently stabilized if the ring system is not absolutely planar, resulting in an inhibition of formation of a stable perchlorate salt. Although 30b has an n value less than 7, the positive charge is sufficiently stabilized to enable its isolation. This supports the claim that naphthotropones are more aromatic than benzotropones.

Further NMR evidence was collected on the perchlorate 30b. The



H_d protons, in 30b, give an NMR signal at $\delta 8.3$ while H' absorbs at

Δ7.2. All the unsaturated ring protons in 30b absorb in the aromatic region of the NMR spectrum.

CHAPTER V

EXPERIMENTAL

Instrumentation

General

Melting points (uncorrected) were determined on a Thomas-Hoover Unimelt instrument, and are expressed in degrees Celsius. Compounds were identified by IR, NMR, and MS. IR spectra were run as KBr pellets on a Perkin-Elmer 1320 Infrared Spectrophotometer. Proton NMR spectra were recorded in CDCl_3 solution with TMS as internal standard using a Varian EM 390 Spectrometer. Mass spectra were obtained at 70 eV on a Finnigan MAT CH7. The plates for analytical TLC were spotted with a multispotter (Analytical Instrumental Specialty Company, TLC, multiscanner). These plates were read on a Shimadzu Dual Wavelength GLC Scanner Model CS-910, equipped with CR 1A^o Chromatopac Data Processor which is connected to a Harris Computer. Micro-analyses were carried out at Midwest Microlab, Ltd., Indianapolis, IN. TLC on silica gel plates (Merck, 60, F₂₅₄, precoated, 0.2 mm) was usually used to follow the reactions and to control the purity of the products.

Materials

Aldrich supplied the cycloalkylketones and the 2,3-dimethylnaphthalene. No purification was necessary. All solvents were reagent

grade.

Preparations

Naphthalene-2,3-dialdehyde

A suspension containing 11.75 g (2.78×10^{-2} mole) of 2,2,3,3-tetrabromodimethylnaphthalene, 10.0 g (5.43×10^{-2} mole) of potassium oxalate in 150 mL of 33% aqueous ethanol was placed into an autoclave at 60 psig and 110°C for 8 hours. The autoclave was allowed to cool to room temperature before venting. The product was removed with acetone. The resulting mixture was filtered, the filtrate was concentrated in vacuo to leave an oil which solidified. The latter was filtered and washed with cold heptane, and was recrystallized from acetone/heptane. The dialdehyde was isolated 2.74 g (50%), shown to be the same as authentic sample by TLC. NMR (CDCl_3): $\Delta 8.35(\text{s}, 2\text{H})$, $\Delta 7.95(\text{m}, 3\text{H})$, $\Delta 7.65(\text{m}, 3\text{H})$. IR(KBr): $3500\text{--}3300$ (w) cm^{-1} . Mass Spectrum: M^+ (observed) 184 calculated for $\text{C}_{12}\text{H}_8\text{O}_2$: 184.0522. Other ions at $\frac{m}{e}$ 183, 156, 155, 154, 128, 127, 126, 77, and 51.

2,2,3,3-Tetrabromodimethylnaphthalene

In a 1-L three-necked flask equipped with an oil-lubricated Trubore stirrer, a dropping funnel, a thermometer extending nearly to the bottom of the flask, and a reflux condenser attached to a gas absorption trap were placed 2,3-dimethylnaphthalene (25.0 g, 16.0×10^{-2} mole) and 300 mL carbontetrachloride. A General Electric R.S. Reflector Type 275-watt sun lamp was placed approximately 1 cm from the flask so as to

admit the maximum amount of light. The stirrer was started, and reaction solution was heated with the aid of the sun lamp at or near reflux temperature.

A total of 114.9 g (72.0×10^{-2} moles) of bromine was added in portions from the dropping funnel to the reaction flask at such a rate that the bromine color is removed as fast as it is added. Otherwise, the reaction mixture will become too vigorous and some of the bromine will be lost with the evolved hydrogen bromide. After all the bromine had been added (10-14 hours), the reaction was allowed to stir overnight in the presence of the sun lamp. The reaction solution was allowed to cool to room temperature (R.T.); a tan product was filtered and washed with excess cold heptane.

The crude product was analytically pure, but if not, it may be recrystallized from heptane, or flash chromatographed on silica gel with methylene chloride. The total yield of 2,2,3,3-tetrabromodimethylnaphthalene, m.p. 158-158.5⁰, was 61.9 g (82%). NMR (CDCl₃): δ 8.1(S, 2H), δ 7.6-7.8(m, 2H), δ 7.3-7.55(m, 2H), δ 7.2(S, 2H). IR(KBr): 3500-3300 (aromatic ring) cm⁻¹.

Anal. Calculated for C₁₂H₈Br₄: C, 30.54; H, 1.71; Br, 67.75

Found: C, 30.18, H, 1.78, Br, 68.02

7,9-Pentamethylene-8H-cyclohepta[b]naphthalene-8-one

A solution containing 0.46 g (2.34×10^{-3} moles) of naphthalene-2,3-dialdehyde, 0.32 g (2.54×10^{-3} moles) of cyclooctanone, and 75 mL of absolute ethanol, and 15 mL of saturated sodium hydroxide in methanol

was heated at reflux for 1/2 hour. The reaction was shown to be complete by TLC (silica gel; solvent: CH_2Cl_2). The solvent was then removed in vacuo and 100 mL of water was added to the residue. This mixture was extracted with ether, dried (MgSO_4), filtered, and evaporated in vacuo. The crude product was chromatographed on silica gel and eluted with methylene chloride, to yield 0.4 g (61%) of pure compound (m.p. 203° sharp). NMR(CDCl_3): $\Delta 7.9(\text{s}, 1\text{H})$, $\Delta 7.7(\text{m}, 2\text{H})$, $\Delta 7.37(\text{m}, 3\text{H})$, $\Delta 6.62(\text{s}, 1\text{H})$, $\Delta 5.35(\text{d}, 1\text{H})$, $\Delta 2.77(\text{b}, 2\text{H})$, $\Delta 2.34(\text{b}, 3\text{H})$, $\Delta 2.05-1.55(\text{b}(\text{s}), 5\text{H})$. IR(KBr): $1665(\text{c}=\text{o}) \text{ cm}^{-1}$.

7,9-Hexamethylene-8H-cyclohepta[b]naphthalene-8-one

A solution containing 0.93 g (4.74×10^{-3} moles) of naphthalene-2,3-dialdehyde, 0.72 g (5.13×10^{-3} moles) of cyclononane, and 150 mL of absolute ethanol, and 20 mL of saturated sodium hydroxide in methanol was heated under reflux and nitrogen for 1/2 hour. The reaction was shown to be complete by TLC (silica gel; solvent: 1.5% EtOAc/ CH_2Cl_2). The solvent was then removed in vacuo and 100 mL of water was added to the residue. This mixture was extracted with ether, dried (MgSO_4), filtered, and evaporated in vacuo. The crude product was chromatographed on silica gel and eluted with methylene chloride, to yield 0.41 g (48%) pure compound (m.p. 168° sharp). NMR(CDCl_3): $\Delta 7.81(\text{s}, 2\text{H})$, $\Delta 7.75(\text{m}, 2\text{H})$, $\Delta 7.41(\text{m}, 2\text{H})$, $\Delta 7.02(\text{s}, 2\text{H})$, $\Delta 3.23(\text{b}, 2\text{H})$, $\Delta 2.51(\text{b}, 2\text{H})$, $\Delta 1.13-2.02(\text{b}(\text{s}), 8\text{H})$. IR(KBr): $1645(\text{c}=\text{o}) \text{ cm}^{-1}$.

Anal. calculated for $\text{C}_{21}\text{H}_{20}\text{O}$: C, 87.46; H, 6.99

Found: C, 87.27; H, 7.00

7,9-Nonamethylene-8H-cyclohepta [b] naphthalene-8-one

A solution containing 0.40 g (2.03×10^{-3} moles) of naphthalene-2,3-dialdehyde, 0.35 g (1.92×10^{-3} moles) of cycloundecanone, and 75 mL of absolute ethanol, and 15 mL of saturated sodium hydroxide in methanol was heated under reflux and nitrogen for 2 hours. The reaction was shown to be complete by TLC (silica gel; solvent: 1.5% EtOAc/ CH_2Cl_2). The solvent was then removed in vacuo and 100 mL of water was added to the residue. This mixture was extracted with ether, dried (MgSO_4), filtered, and evaporated in vacuo.

The crude product was chromatographed on silica gel and eluted with methylene chloride, to yield 0.49 g (77%) pure compound (m.p. $151.5\text{--}152.5^\circ$). NMR(CDCl_3): $\Delta 7.88(\text{s}, 2\text{Hd})$, $\Delta 7.78(\text{m}, 2\text{Hc})$, $\Delta 7.45(\text{m}, 2\text{Hb})$, $\Delta 7.29(\text{s}, 2\text{Ha})$, $\Delta 3.6(\text{m}, 2\text{H})$, $\Delta 2.3\text{--}1.1(\text{m}, 16\text{H})$. IR(KBr): $3600\text{--}3300\text{ cm}^{-1}$, $2900\text{--}2990\text{ cm}^{-1}$, 2860 cm^{-1} , and $1605(\text{c}=\text{o})\text{ cm}^{-1}$. Mass spectrum: M^+ (observed) 330, calculated for $\text{C}_{24}\text{H}_{26}\text{O}$, 330.1977. Other ions at $\frac{\text{m}}{\text{e}}$ 331, 302, 254, 247, 246, 245, 231, 208, and 205.

7,9-Decamethylene-8H-cyclohepta [b] naphthalene-8-one

A solution containing 0.27 g (1.37×10^{-3} moles) of naphthalene-2,3-dialdehyde, 0.33 g (1.68×10^{-3} mole) of cyclododecanone, 75 mL of absolute ethanol, and 15 mL of saturated sodium hydroxide in methanol was heated under reflux and nitrogen for 1 hour. The reaction was shown to be complete by TLC (silica gel; solvent: 2% EtOAc/ CH_2Cl_2). The solvent was then removed in vacuo and 100 mL of water was added to the residue. This mixture was extracted with ether, dried (MgSO_4),

filtered, and evaporated in vacuo.

The crude product was chromatographed on silica gel and eluted with methylene chloride, to yield 0.23 g (49%) pure compound (m.p. 153-154⁰). NMR(CDCl₃): Δ 7.95(s,2H), Δ 7.80(m,2H), Δ 7.40(m,4H), Δ 3.05-2.60(b(s),3H), Δ 1.80-1.50(m,5H), Δ 1.2 (u(s),12H). IR(KBr): 3600-3300 cm⁻¹, 2900-2990 cm⁻¹, 1580 (c=o) cm⁻¹, 1430-1460 cm⁻¹. Mass spectrum: M⁺ (observed) is 344. Calculated for C₂₅H₂₈O is 344.2133. Other ions $\frac{m}{e}$ 345, 316, 215, 208, 207, 205, 202, 191.

2,7-Dimethyl-4,5-Naphtho[b] tropone

A solution containing 0.21 g (1.06×10^{-3} moles) of naphthalene-2,3-dialdehyde, 0.95×10^{-3} g (1.10×10^{-3} moles) of 3-pentanone, and 75 mL of absolute ethanol, and 15 mL of saturated sodium hydroxide in methanol was heated under reflux and nitrogen for 2 hours. The reaction was shown to be complete by TLC (silica gel; solvent 1% EtOAc/CH₂Cl₂). The solvent was then removed in vacuo and 100 mL of water was added to the residue. This mixture was extracted with ether, dried (MgSO₄), filtered, and evaporated in vacuo. The crude product was chromatographed on silica gel and eluted with 2-L of methylene chloride, then 5% EtOAc/CH₂Cl₂, to yield 1.45×10^{-1} g (58%) pure compound (m.p. 190-192⁰). NMR(CDCl₃): Δ 8.0(s,2H), Δ 7.8(m,2H), Δ 7.5(m,4H), Δ 2.3(s,6H). IR(KBr): 3550-3300 cm⁻¹ and 1587 (c=o) cm⁻¹.

Anal. calculated for C₁₇H₁₄O: C, 87.15; H, 6.02

Found: C, 86.97; H, 6.07

1-Ethoxy-1,3-dihydronaphtho[2,3-c]furan

A suspension containing 26.48 g (6.73×10^{-2} moles) of 2,2,3-tribromodimethylnaphthalene, 21.98 g (1.19×10^{-1} moles) of potassium oxalate in 150 mL of 33% aqueous ethanol was placed into an autoclave at 60 psig and 110° for 17 hours. The autoclave was allowed to cool to room temperature before venting. The product was removed with acetone. The resulting mixture was filtered, the filtrate was concentrated in vacuo to an oil which solidified. The crude product was recrystallized from CH_2Cl_2 -heptane to yield 9.74 g (68%) pure compound (m.p. $129-130^{\circ}$). NMR(CDCl_3): $\Delta 7.78(\text{m}, 4\text{H})$, $\Delta 7.38(\text{m}, 2\text{H})$, $\Delta 6.3(\text{s}, 1\text{H})$, $\Delta 5.22(\text{q}, 2\text{H})$, $\Delta 3.80(\text{m}, 2\text{H})$, $\Delta 1.30(\text{t}, 3\text{H})$. IR(KBr): $3500-3300 \text{ cm}^{-1}$, and 2970 cm^{-1} .

Anal. calculated for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48, H, 6.59

Found: C, 78.25; H, 6.61

Mass spectrum: M^+ (observed) is 214. Calculated for $\text{C}_{14}\text{H}_{14}\text{O}_2$: is 214.099. Other ions at $\frac{m}{e}$ 185, 170, 169, 142, 141, 139, 129, 115, and 85.

7,9-Pentamethylenecyclohepta[b]naphthalene-8-ol

A suspension containing 0.12 g (4.45×10^{-4} moles) of 7,9-pentamethylene-8H-cyclohepta[b]naphthalene-8-one 27a, 0.15 g (3.95×10^{-3} moles) of lithium aluminum hydride, and 10 mL of dry tetrahydrofuran (THF) was stirred for 17 hours at 40° , under nitrogen. The reaction was shown to be complete by TLC (silica gel; solvent: 4% MeOH/25% EtOAc/71% CH_2Cl_2). The reaction mixture was cooled in an ice bath, and

cold water was added slowly, with stirring. The reaction mixture was filtered and THF removed in vacuo. The resulting aqueous layer was extracted with methylene chloride, dried (MgSO_4), filtered, and concentrated in vacuo to give a white solid. The alcohol was recrystallized (from CH_2Cl_2 /heptane) to give 7.5×10^{-2} g (61%) (m.p. 116-117^o).
 NMR(CHCl_3): $\Delta 7.93(\text{s}, 1\text{H})$, $\Delta 7.72(\text{m}, 2\text{H})$, $\Delta 7.39(\text{m}, 3\text{H})$, $\Delta 6.40(\text{s}, 1\text{H})$, $\Delta 4.8$ (d, 1H), $\Delta 4.2(\text{d}, 1\text{H})$, $\Delta 2.80-1.10(\text{m}, 12\text{H})$. IR(KBr): 3600-3100 $\text{cm}^{-1}(\text{s})$, 2875 cm^{-1} and 1110 cm^{-1} .

7,9-Hexamethylenecyclohepta [b]naphthalene-8-one

A suspension containing 0.32 g (1.77×10^{-3} moles), 7,9-hexamethylene-8H-cyclohepta [b]naphthalene-8-one 27b, 0.21 g (5.53×10^{-3} moles) of lithium aluminum hydride, and 10 mL of dry tetrahydrofuran (THF) was stirred for 17 hours at 40^o, under nitrogen. The reaction was shown to be complete by TLC (silica gel; solvent: CH_2Cl_2). The reaction mixture was cooled in an ice bath, and cold water was added slowly, with stirring. The reaction mixture was filtered and THF removed in vacuo. The resulting aqueous layer was extracted with methylene chloride, dried (MgSO_4), filtered and concentrated in vacuo to give a white solid, 0.45 g (93%), recrystallization was not necessary, but acetone can be used to recrystallize alcohol. NMR(CDCl_3): $\Delta 7.7(\text{unres}(\text{s}) \text{ over a m}, 4\text{H})$, $\Delta 7.3(\text{m}, 2\text{H})$, $\Delta 6.4(\text{s}, 2\text{H})$, $\Delta 4.1(\text{s}, 1\text{H})$, $\Delta 2.8(\text{b}, 2\text{H})$, $\Delta 2.3(\text{b}, 3\text{H})$, $\Delta 1.9-1.2(\text{b}, 6\text{H})$. IR(KBr): 3600-3200 (s) (-OH) cm^{-1} , 3030 cm^{-1} , 2970 cm^{-1} , and 1100 cm^{-1} .

2,7-Pentamethylenecyclohepta [4,5-b] naphthotropylium perchlorate

A solution containing 7.5×10^{-2} g (2.71×10^{-4} moles) of 7,9-pentamethylenecyclohepta [b] naphthalene-8-ol 28a was dissolved in 25 mL anhydrous ether at 5°C , 1 mL of 70% HClO_4 was added slowly. The reaction solution turned yellow, TLC (silica gel; solvent: CH_2Cl_2) showed the reaction was complete. The ether layer was isolated and dried (MgSO_4), filtered, and concentrated in vacuo to a dark oil, which was flash chromatographed on silica gel with methylene chloride. No product was isolated.

2,7-Hexamethylenecyclohepta [4,5-b] naphthotropylium perchlorate

A solution containing 0.45 g (1.55×10^{-3} moles) of 7,9-hexamethylenecyclohepta [b] naphthalene-8-ol was dissolved in 25 mL of anhydrous ether at 5°C , 1 mL of 70% HClO_4 was added slowly. The reaction solution turned yellow, TLC (silica gel, solvent: CH_2Cl_2), showed the reaction was complete. The ether layer was isolated and dried over MgSO_4 , filtered, and concentrated in vacuo to an oil, which was flash chromatographed on silica gel with methylene chloride. A gold solid was isolated. NMR(CDCl_3): $\Delta 8.3(\text{s}, 2\text{H})$, $\Delta 7.9(\text{q}, 2\text{H})$, $\Delta 7.4(\text{d}, 2\text{H})$, $\Delta 7.3(\text{q}, 2\text{H})$, $\Delta 7.2(\text{s}, 1\text{H})$, $\Delta 3.0(\text{q}, 3\text{H})$, $\Delta 2.0-1.2(\text{m}, 9\text{H})$. IR(KBr): $3350-3600 \text{ cm}^{-1}$, 2920 cm^{-1} , 1450 cm^{-1} , 920 cm^{-1} , and 740 cm^{-1} . Mass spectrum: M^+ (observed) is 273. Calculated for the cation $\text{C}_{21}\text{H}_{21}$ is 273.1638. Other ions at $\frac{m}{e}$ 275, 274, 270, 245, 232, 216, 215, 213, 207, 205, and 203.

CHAPTER VI

CONCLUSION

This report gives a reasonable synthesis of naphthalene-2,3-dialdehyde 18 from readily available starting materials at an affordable price in two steps, with the potential for macrogram production. Furthermore, an analytical method was devised for analyzing the purity of the dialdehyde 18.

The above enabled a series of 7,9-polymethylene-8H-cycloalkyl [b]naphthalene-8-ones 27b-d to be prepared, which made it possible to study the effect of the polymethylene bridge on the aromaticity and the planarity of the naphthotropylium ions. The former 27b-d were prepared by the condensation of various cyclic ketones and the dialdehyde 18, which enabled confirmation that the tropone ring system is planar if $n \geq 6$, thus implying that naphthotropones are more aromatic than benzotropones since the latter is planar only if $n \geq 7$. Reduction of the naphthotropones with lithium aluminum hydride gave the corresponding alcohols, which were converted to the naphthotropylium perchlorates, and are isolatable only if $n \geq 6$. This salt forms only if the tropone ring is planar as was supported with proton NMR data, which indicates the positive charge is delocalized over the naphthalene and tropone ring system 30b if $n \geq 6$. In short, from the available data, the order of aromaticity for the following tropone derivatives is: tropone > naphthotropone > benzotropone > pyrazolotropone (33) > furotropone.

REFERENCES

1. Yamato, M., Ishikawa, T., Hashigaki, K. & Ishikawa, S. Anti-tumor activity of isochromanytropolones. Chem Pharm. Bull., 1983, 31, 2952-2954.
2. Scott, A.I., Guilford, H. & Lee, E. Biosynthesis of the fungal tropolones. Stipitaic and stipitatic acids. J. Am. Chem. Soc., 1971, 93, 3534-3536.
3. Richards, J.H. & Ferretti, L.D. Tropolone biogenesis. Biochem Biophys Research Commun., 1960, 2, 107-110.
4. McInnes, A.G., Smith, D.G. & Vining, L.C. Use of carbon-12 in biosynthetic studies. Incorporation of isotopically labelled acetate and formate into the fungal tropolone, sepedonin. Chem. Commun., 1968, 1669-1670.
5. Battersby, A.R., Herbert, R.B. & McDonald, E. Alkaloid biosynthesis. Part XVIII. Biosynthesis from the 1-phenethylisoquinoline system. J. Chem., Soc., Perkin Trans., 1972, 1, 1741-1745.
6. Eigsti, O.J. & Dustin, P. Jr. Colchicine in agriculture, medicine biology, and chemistry. Ames, Iowa: Iowa State College Press, 1955.
7. Cook, J.W. & London, J.D. Colchicine. Alkaloids, 1952, 2, 261-329.
8. Wildman, W.C. Colchicine. Alkaloids, 1960, 6, 247-288.
9. Wildman, W.C. Colchicine. Alkaloids, 1970, 8, 199-212.
10. Snyder, J.P. Nonbenzenoid aromatics. (Vol. I). New York: Academic Press, 1969.
11. Streitwieser, A. Jr. Molecular orbital theory for organic chemists. New York: John Wiley and Sons, 1961.
12. Coulson, C.A. & Streitwieser, A. Jr. Dictionary of pi-electron calculations. San Francisco: W.H. Freeman Company, 1965.
13. Breslow, R. Antiaromaticity. Acc. Chem. Res., 1973, 6, 393-398.
14. Winstein, S. Nonclassical ions and homoaromaticity. Q. Rev. Chem. Soc., 1969, 23, 141-176.

15. Warner, P. & Winstein, S. Protonated cis-bicyclo(6.1.0)nona-2,4,6-triene, a monocyclic 1,3-bishomotropylium ion. J. Am. Chem. Soc., 1971, 93, 1284-1285.
16. Keller, C.E. & Pettit, R. The protonation of cyclooctatetraene. J. Am. Chem. Soc., 1966, 88, 604-606.
17. Jones, A.J. Criteria for aromatic character. Rev. Pure. Appl. Chem., 1968, 18, 253-280.
18. Veracini, C.A. & Pietra, F. Molecular structure of tropone from its ¹H nuclear magnetic resonance spectrum in a nematic solvent. J. Chem. Soc. Chem. Commun., 1972, 1262-1263.
19. Krebs, A. & Schrader, B. Spektroskopische untersuchungen an cyclopropenone. Justus Liebigs Ann. Chem., 1967, 709, 46-58.
20. Jackson, W., Hung, T. & Hopkins, H. Delocalization energies of troponoids from bomb calorimetric and vapor pressure measurements. J. Chem. Thermodyn., 1971, 3, 347-353.
21. Hata, T., Shimanouchi, H. & Sasada, Y. An X-ray determination of the structure of 4,5-Benzotropone. Tetrahedron Lett., 1969, 753.
22. Kloster-Jensen, E., Tarkoy, N., Eschenmoser, A. & Heilbronner, E. Untersuchungen in der benzotropylium-reiche. III. 2,7-poly-methylene-4,5-benzotropone Helv. Chim. Acta, 1956, 39, 786-805.
23. Harmon, R.E., Suder, R.E. & Gupta, S.K. Preparation of 2,7-poly-methylene-4,5-benzotropylium perchlorates. Canad. J. Chem., 1970, 48, 195-196.
24. Harmon, R.E., Suder, R.E. & Gupta, S.K. Preparation of 2,8-(poly-methylene)benzohomotropylium cations. J. Chem. Soc., Chem. Commun., 1972, 472-473.
25. Mallouli, A. & Lepage, Y. Convenient synthesis of naphthalene-anthracene-, and naphthacene-2,3-dicarboxaldehydes. Synthesis, 1980, 689.
26. Cook, J.W., Hunter, L. & Schoental, R. Naphthalene-2,3-dialdehyde. J. Chem. Soc. Suppl. I, 1949, 228.
27. Weygard, F., Kinkel, K.G. & Tiedjen, D. Die darstellung aromatischer o-dialdehyde aus o-dialkoholen uber die cyclischen selenigsauereester. Chem Ber., 1950, 83, 394-413.
28. Firouzbad, H. & Mostafavipoor, Z. Barium manganate: A versatile oxidant in organic synthesis. Bull. Chem. Soc. Jpn., 1983, 56, 914-917.

29. Hsu, A.C. & Cava, M.P. 1,1,2,2-Tetrabromonaphtho(b)cyclobutene: A new source of naphtho(b)cyclobutene-1,2-dions and substituted naphtho(b)cyclobutasienes. J. Org. Chem., 1979, 44, 3790-3793.
30. Bill, J.C. & Tarell, D.S. o-phthalaldehyde, Org. Syn. Coll., Vol. 4, 1963, 807-810.
31. Suder, R.E. Preparation and properties of benzotropones and benzohomotropones. Unpublished doctoral dissertation, Western Michigan University, 1979.
32. Cook, M.J. & Forbes, E.J. (4,5-c)Furotropone: A new heterocyclic system. Tetrahedron, 1968, 24, 4501-4508.
33. Greco, C.V. & Pesce, H. [4,5-c(d)] Pyrazolotropone: A new aromatic ring system. J. Org. Chem., 1972, 37, 676-677.