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presented by

Michio Sasaoka

has been accepted towards fulfillment
of the requirements for

Ph.D degree in Organic Chemistry

Harold Hart
Major professor

Date Sep. 7, 1978

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PART I

SYNTHESIS AND REACTIONS OF SUBSTITUTED NAPHTHALENE 2,3-EPOXY-1,4-ENDOPEROXIDES

PART II

SYNTHESIS AND PROPERTIES OF BENZO[1,2-c:3,4-c':5,6-c"]TRITHIOPHENE, A TRISTHIAHEXARADIALENE

By

Michio Sasaoka

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1978

31071

ABSTRACT

PART I

SYNTHESIS AND REACTIONS OF SUBSTITUTED NAPHTHALENE 2,3-EPOXY-1,4-ENDOPEROXIDES

PART II

SYNTHESIS AND PROPERTIES OF BENZO[1,2-c:3,4-c':5,6-c"]TRITHIOPHENE, A TRISTHIAHEXARADIALENE

By

Michio Sasaoka

In Part I of this thesis the 1,4-endoperoxides of 1,2,3,4-tetramethyl- and octamethylnaphthalene were studied. 1,2,3,4-Tetramethyl and octamethylnaphthalene **21** and **22** react with singlet oxygen to give their 1,4-endoperoxides, **23** and **24** respectively. Oxidation of the carbon-carbon double bond in **23** and **24** with *m*-chloroperbenzoic acid gave the stable, crystalline 1,2,3,4-tetramethyl-2,3-epoxy-1,4-epidioxy-1,2,3,4-tetrahydronaphthalene **25** and 1,2,3,4,5,6,7,8-octamethyl-2,3-epoxy-1,4-epidioxy-1,2,3,4-tetrahydronaphthalene **26**. Epoxidation occurred predominantly *syn* to the peroxide bridge.

The *syn*-epoxyperoxides underwent acid-catalyzed solvolytic rearrangement to the stable peroxyacetals, 4-methoxy-1,4,5,8-tetramethyl-6,7-benzo-2,3-dioxabicyclo[3.2.1]oct-6-en-8-ol **31a** and 4-methoxy-1,4,5,8-tetramethyl-6,7-(3',4',5',6'-tetramethylbenzo)-2,3-dioxabicyclo[3.2.1]oct-6-en-8-ol **44** respectively, but the *anti*-epoxyendoperoxide **25a** was recovered under similar conditions. The rearrangement involves a 1,2-aryl migration. Catalytic hydrogenolysis of **31** gave cis-1-acetyl-1,2,3-trimethylindan-2,3-diol **35**, which was obtained independently from the acid-catalyzed methanolysis of the *syn*-epoxide of 1,2,3,4-tetramethylnaphthalene-1,4-endoxide **39**. Deuterium labeling studies support the proposed mechanism for these rearrangements.

Thermolysis of the epoxyendoperoxide **25s** occurs with O-O bond cleavage, as established by trapping the intermediate diradical with good hydrogen donors (diglyme, benzhydrol) to give 1,2,3,4-tetramethyl-2,3-epoxy-1,2,3,4-tetrahydronaphthalene-1,4-diol **27s**, synthesized independently by hydrogenolysis of **25s**. In the absence of trapping agent, thermolysis of **25s** occurs with loss of a methyl group to give 2,3,4-trimethyl-2,3-epoxy-4-hydroxy-1,2,3,4-tetrahydronaphthalenone **53**. Thermolysis and photolysis of **26** gave hexamethylbenzo[b]furan.

Reactions of **23** with bromine or trifluoroacetic acid were also studied.

In Part II of this thesis, synthesis of benzo[1,2-c:3,4-c':5,6-c"]trithiophene **86**, the first example of a heteroaromatic molecule in which the carbon-carbon "double bonds" of the central six-membered ring are all exocyclic, was described.

Oxidation of 1,3,4,6,7,9-hexahydrobenzo[1,2-c:3,4-c':5,6-c"]-trithiophene **114**, prepared from hexakis(bromomethyl)benzene and sodium sulfide (80-90% yield), with DDQ or *o*-chloranil gave **86**. Unlike benzo[c]thiophene, **86** is unreactive toward dienophiles. It forms crystalline 1:1 charge transfer complexes with TCNE, DDQ, TCNQ and chloranil. Protonation of **86** in FSO_3H (-20°C) gives a stable dication.

86 undergoes electrophilic bromination (Br_2, CCl_4, room temperature). Metallation of **86** followed by reaction with DMF or CO_2 gave the monoaldehyde and monocarboxylic acid of **86**, respectively.

The overall aromaticity of systems such as **86** was further illustrated by synthesis of benzo[1,2-c:3,4-c']dithiophene **91** via the DDQ oxidation of 1,3,4,6-tetrahydrobenzo[1,2-c:3,4-c']dithiophene.

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Professor Harold Hart for his enthusiasm, encouragement and guidance throughout the course of this study.

Appreciation is extended to Michigan State University, National Science Foundation, and National Institutes of Health for financial support in the form of teaching and research assistantships.

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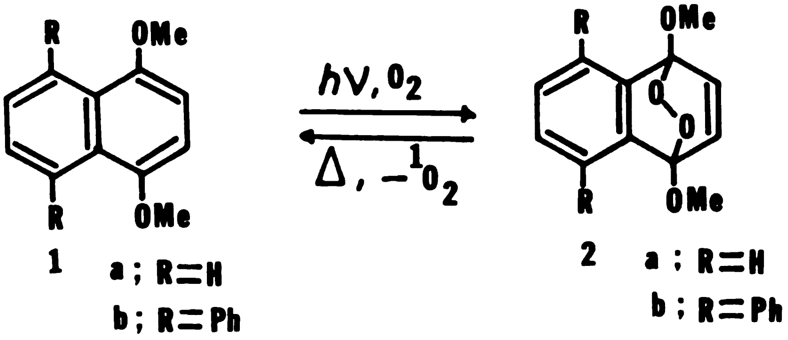
PART I

SYNTHESIS AND REACTIONS OF SUBSTITUTED NAPHTHALENE 2,3-EPOXY-1,4-ENDOPEROXIDES

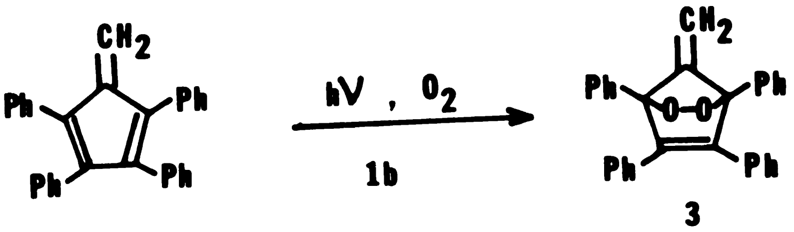
INTRODUCTION

Endoperoxides of polycyclic aromatic compounds have been the subject of many investigations owing to their synthetic usefulness[1] and their biological importance.[2] Anthracenes and higher polyarenes are well known to give endoperoxides with singlet oxygen,[3] but only a few naphthalene endoperoxides have been similarly prepared.

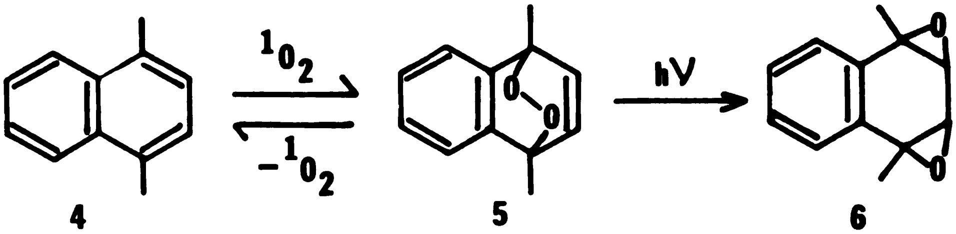
The irradiation of 1,4-dimethoxynaphthalene 1a with a photosensitizer gave its 1,4-endoperoxide 2a.[4] Direct photooxidation of 1,4-dimethoxy-5,8-diphenylnaphthalene 1b at -50°C resulted in the formation of endoperoxide 2b.[5] This peroxide decomposed at room temperature and much faster at 70°C into 1b and singlet oxygen. The decomposition was instantaneous at 110°C and was accompanied by a blue glimmer. In the latter case naphthalene 1b acted as a photosensitizer of the photooxidation. Photosensitization by 1b was demonstrated by its acceleration



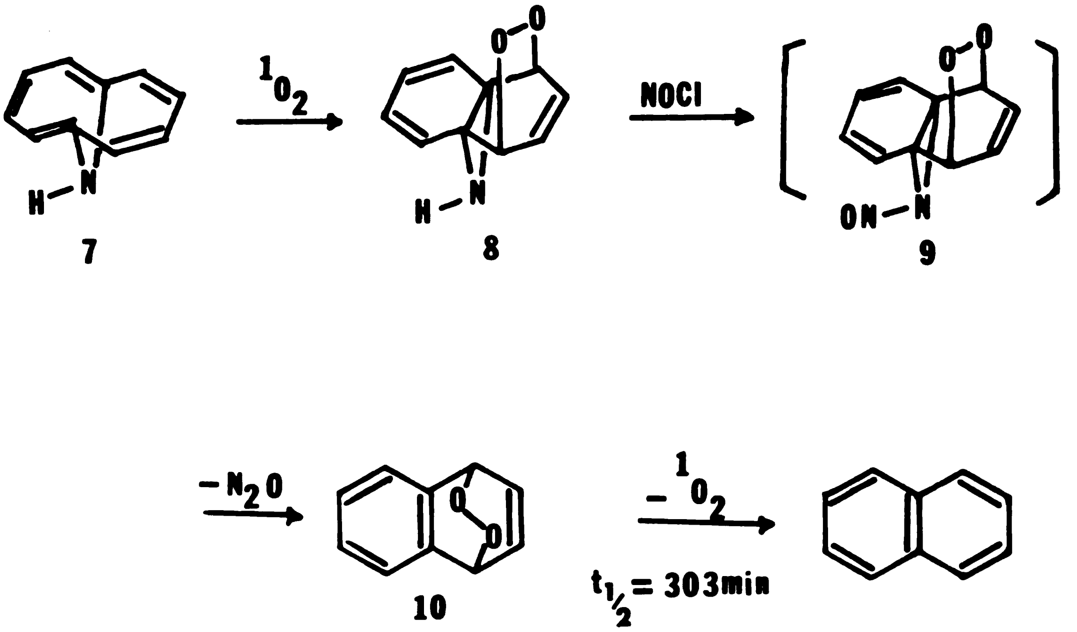
of the photooxidation of tetraphenylfulvene to the endoperoxide **3**.



The Rose Bengal sensitized photooxidation of 1,4-dimethylnaphthalene **4** afforded an unstable peroxide **5** which dissociated at room temperature to **4** and singlet oxygen.[6] Irradiation of **5** in ether at -50°C precipitated an isomeric bis-epoxide **6**.

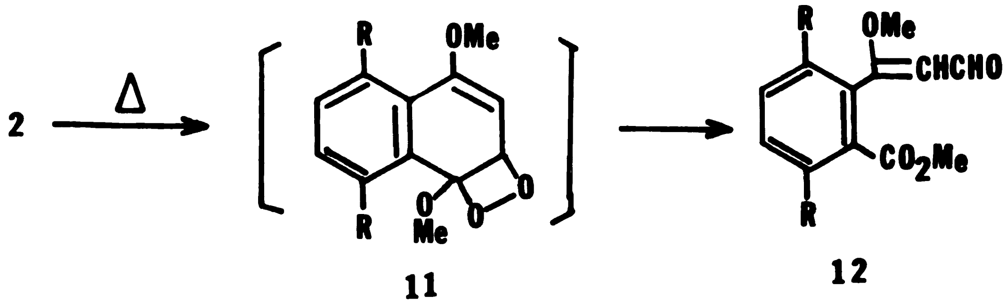


Electron-donating groups on the 1- and 4-positions are necessary for the reaction of naphthalenes with singlet oxygen. Naphthalene itself does not react with singlet oxygen. However, the endoperoxide of naphthalene was prepared by a different method.[7] The reaction of 1,6-imino[10]annulene **7** with singlet oxygen afforded the 1,4-endoperoxide **8** which was treated with nitrosyl chloride to give the endoperoxide of naphthalene **10** by eliminating N_2O from the resulting

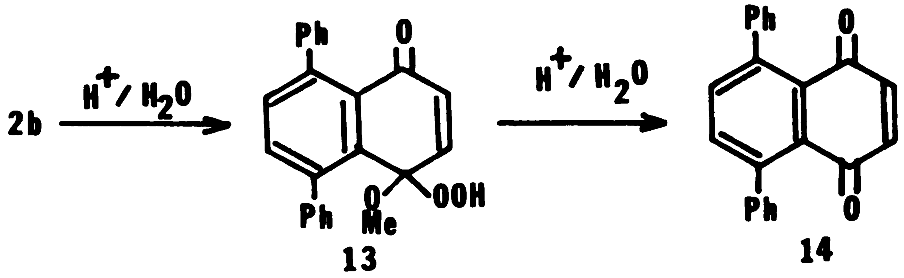


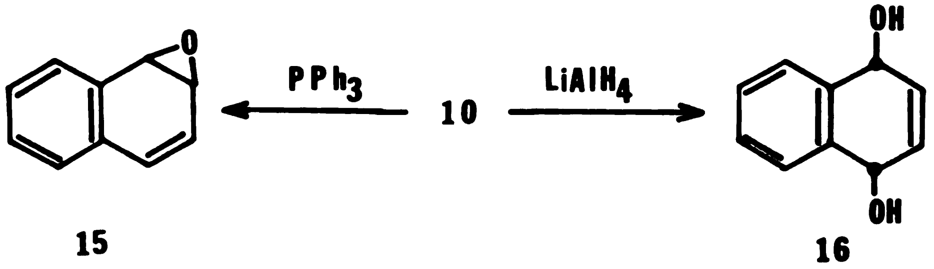
N-nitrosoazidine 9. The peroxide 10 underwent thermal cleavage to naphthalene and oxygen with a half-life of 303 min at 20°C. No evidence for the formation of the isomeric 1,2:3,4-diepoxide was obtained.

Only a few reactions of these naphthalene endoperoxides are



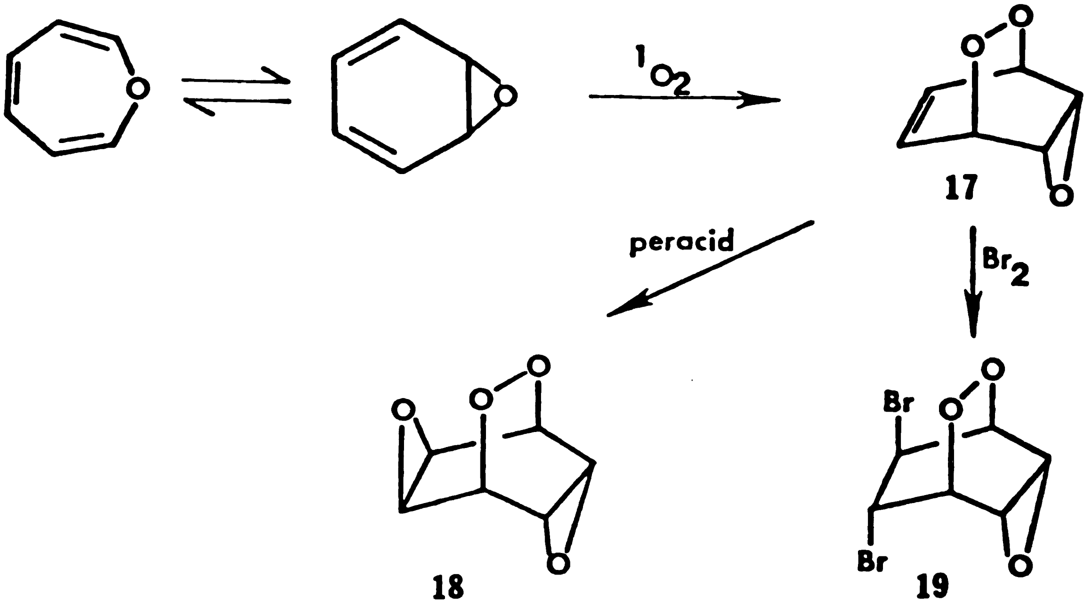
known. When **2** was heated, a small amount of an unsaturated aldehyde **12** was obtained, as well as **1** and oxygen probably via the intermediate dioxetane **11**.[8] Acid hydrolysis of **2b** gave 5,8-diphenyl-1,4-naphthoquinone **14**.[5] The intermediate hydroperoxide **13** was isolated.

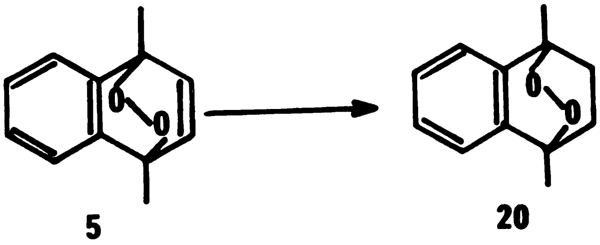




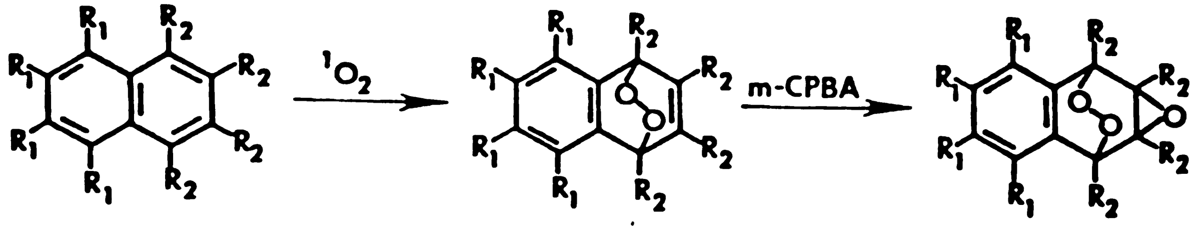
Reaction of **10** with triphenylphosphine gave the partially deoxygenated product **15**.[7] Reduction of **10** with $LiAlH_4$ gave the unsaturated cis diol **16**.

Naphthalene endoperoxides have an isolated 2,3-double bond which could be used for further functionalization of the molecule, and it was the purpose of this work to explore that possibility. Indeed, a similar double bond in oxepin endoperoxide 17 was found to undergo epoxidation and bromine addition.[9] More recently, the reduction of such strained double bonds by diimide without reducing the peroxide bond has been described.[10] For example, 5 was reduced to the cyclic peroxide 20.





We were able to epoxidize the 1,4-endoperoxides of 1,2,3,4-tetramethylnaphthalene[11] and octamethylnaphthalene[12] to give extremely stable epoxyperoxides 25 and 26. These peroxides were handled without difficulty and melted without explosion, whereas peroxides 18 and 19 were reported to explode when heated. The explosion of crude 17 was also reported.[9]



21; R_1=H,R_2=CH_3
22; R_1=R_2=CH_3

23; R_1= H,R_2=CH_3
24; R_1=R_2=CH_3

25; R_1=H,R_2=CH_3
26; R_1=R_2=CH_3

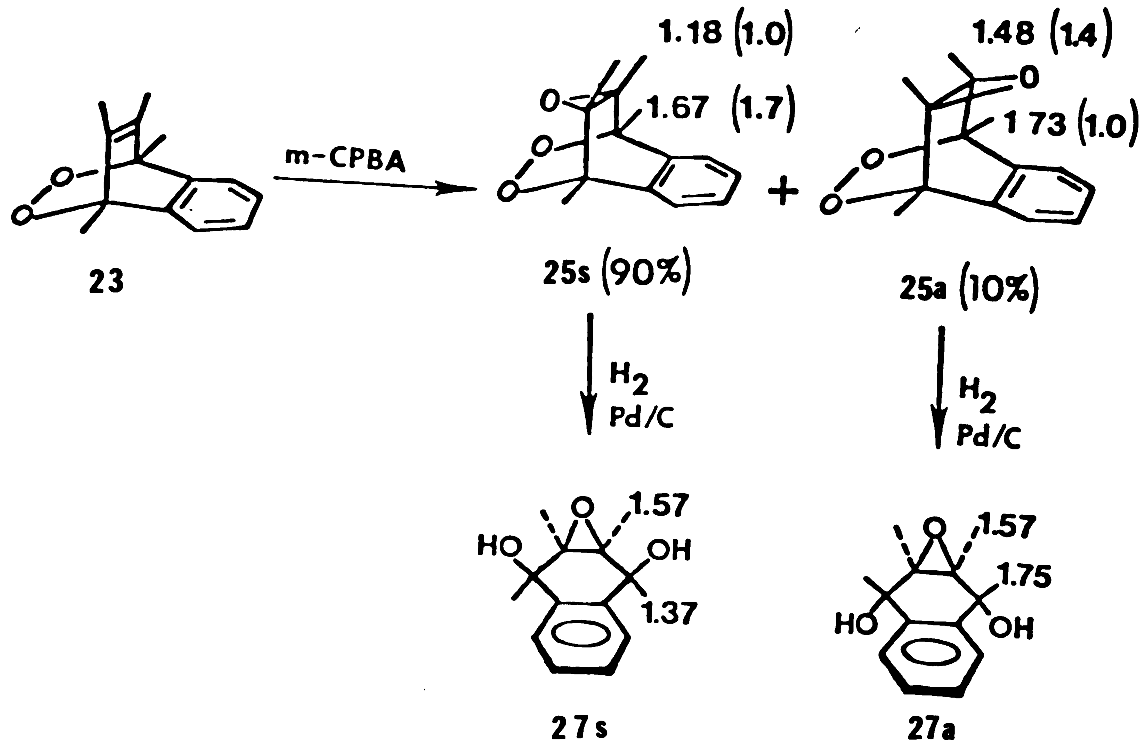
It is the purpose of this part of the thesis to describe the synthesis and chemistry of these compounds.

Results and Discussion

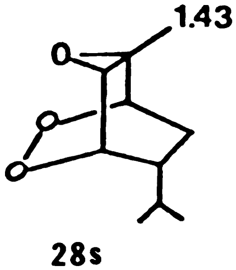
1. The epoxyendoperoxide of 1,2,3,4-Tetramethylnaphthalene

Oxidation of endoperoxide **23**[11] with *m*-chloroperbenzoic acid (*m*-CPBA) gave two isomeric epoxyendoperoxides in a 9:1 ratio.[13] These isomers were separated after recrystallization from ether. The major isomer formed colorless rods and the minor isomer formed colorless cloudy plates which could be separated mechanically (tweezers). Catalytic hydrogenolysis of each isomer gave an epoxydiol. The NMR spectra of the epoxyendoperoxides and diols were consistent with the symmetry of their structures.[14] The peak assignments for the various methyl groups in **25** and **27** were made through deuterium labeling (*vide infra*).

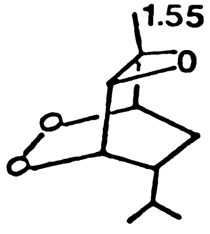
The major isomer was assigned the *syn* configuration and the minor isomer the *anti* configuration on the basis of the chemical shifts of the methyl groups on the epoxide rings, and on dipole moments.[15] The upfield chemical shift of the epoxide methyls in the *syn* isomer (δ1.18) compared with those of the ascaridole epoxides **28**[13] can be attributed to the shielding effect of the aromatic ring. A similar upfield shift was observed in the dibenzobarrelene epoxide **29**.[16] The downfield shift of the benzylic methyls in **27a** (δ1.75; *syn* to the epoxide oxygen) relative to those in **27s** (δ1.37; *anti* to the



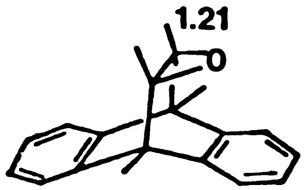
epoxide oxygen) add support to the assignment. Finally, the dipole moments of the major ($\mu=4.2\pm0.1$ D) and minor ($\mu=1.7\pm0.1$ D) isomers confirm the assignment.



28s



28a



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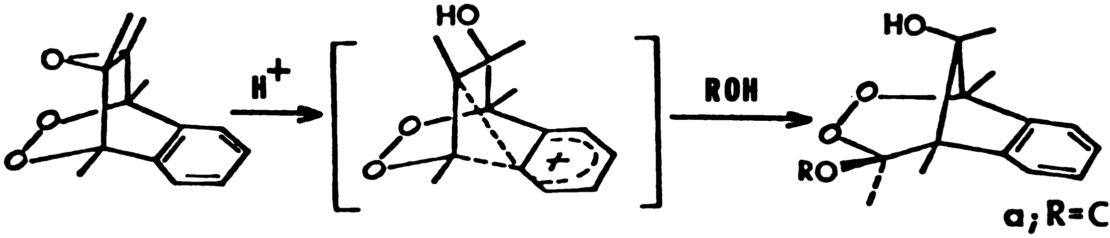
2. Acid-catalyzed Solvolysis of **25s**

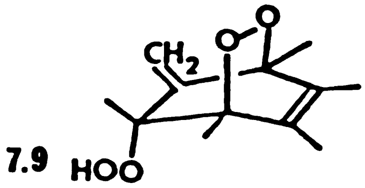
When **25s** was treated with trifluoroacetic acid (TFA) in methylene chloride (0°C, 20 min) in the presence of methanol or ethanol a single product, assigned structure **31**, was obtained in quantitative yield. Although the mass spectrum of **31** did not show an M^+ peak (the highest m/e peak corresponded to M^+-H_2O), elemental analysis and a positive test with HI in acetone suggested that the peroxide group was still present.



25s **30** **31**

a; $R=CH_3$
b; $R=C_2H_5$

The ^1H NMR spectrum of **31a** showed singlets for three of the C-methyl groups (δ1.10, 1.38, 1.45), but the fourth C-methyl group was a doublet at δ0.75 (J=1.4 Hz). This methyl group was coupled (verified by decoupling) with the hydroxyl proton which (at 180 MHz) appeared as a quartet at δ5.78 (J=1.4 Hz). This result is consistent with protonation and ring opening at the epoxide oxygen and not the peroxide oxygen, for if the latter had occurred one would expect to find a $\mathrm{HOO\overset{|}{\underset{|}{C}}CH_3}$ moiety, with the hydroperoxy proton at lower field than δ5.78, and not coupled to the geminal methyl group. The chemical shift of the hydroperoxy proton of **32**, for example, is δ7.9 and coupling with the geminal methyl protons was not observed.[17] The



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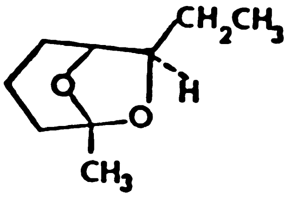
lower than usual chemical shift of the hydroxyl proton in 31a and its coupling with the geminal methyl protons can be explained by its strong hydrogen bonding with an oxygen of either the peroxide or methoxy group (ν_{O-H} 3450 cm^{-1}). The ^{1}H NMR spectrum of 31b was similar to that of 31a (except for ethoxy signals in place of the methoxy singlet at δ3.40).

The ^{13}C NMR spectra of 31a and 31b were also consistent with the assigned structures. The ^{13}C peak assignments for 31a, shown on the structure, are based on deuterium labeling and comparison with 31b. The unique quaternary carbon signal at δ109.2 ppm supports the peroxyacetal structure. The chemical shift of the acetal carbon of 33, for example, is 107.6 ppm from TMS.[18]



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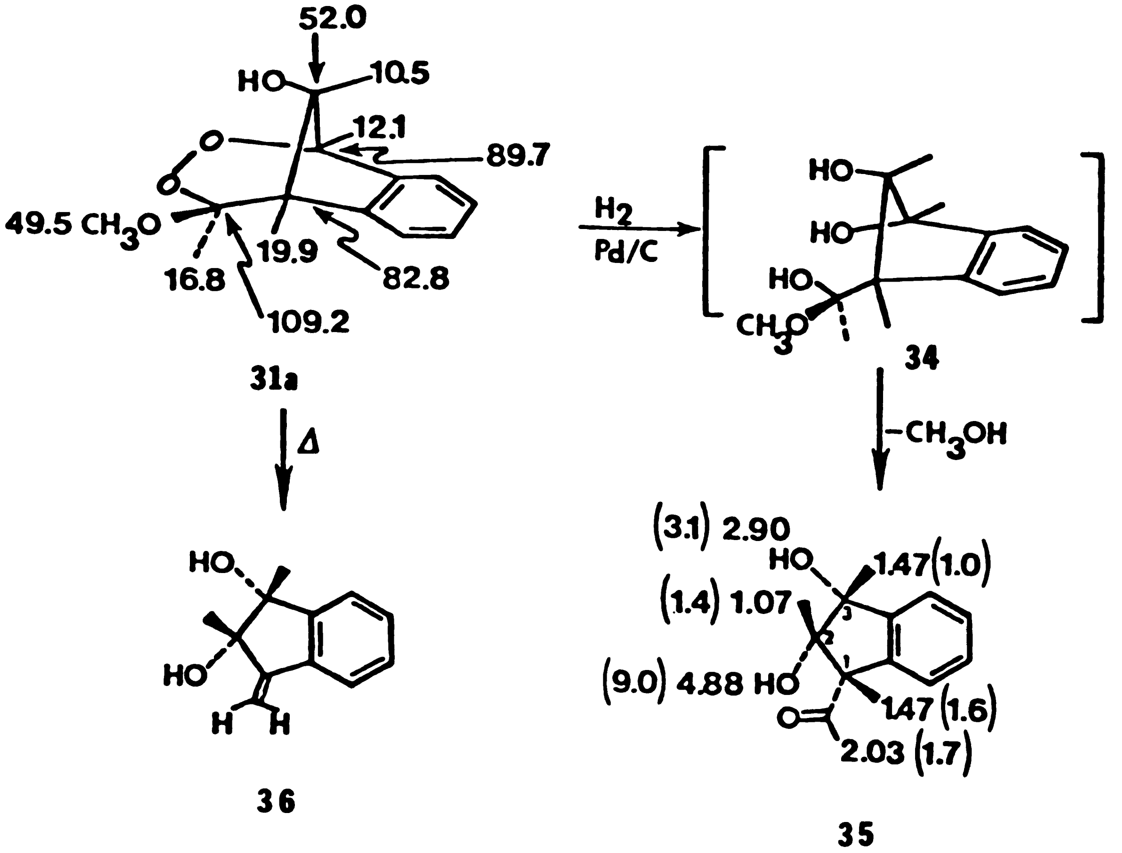
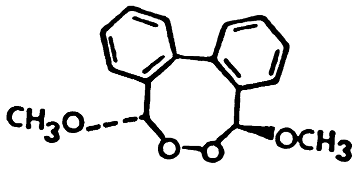
To prove the structure, 31a was subjected to catalytic hydrogenolysis. Reaction with hydrogen (Pd/C) in ethanol was complete in 30 min at room temperature, and gave the acetylindandiol 35 as the sole product (the presumed intermediate hemiacetal 34 was not isolated).



The alcohol and carbonyl functionality in 35 were clear from the infrared spectrum (ν_{O-H} 3440, $\nu_{C=O}$ 1700 cm^{-1}), and the ^{1}H NMR spectrum showed the acetyl methyl (δ2.03) and hydroxyl protons (δ2.90 and 4.88) as well as singlets at δ1.07(3H) and 1.47(6H) for the remaining methyl groups. Europium shift slopes are shown on the structure. The ^{13}C NMR spectrum of 35 showed the presence of four different methyl groups. The structure of 35 was confirmed by independent synthesis (vide infra).

Thermolysis of 31a (refluxing xylene) gave an unsaturated diol assigned structure 36 in 22% yield. The infrared spectrum of 36 showed bands for the hydroxyl and terminal methylene groups. The ^1H NMR spectrum showed two methyl singlets (δ1.35, 1.42), two methylene protons (δ5.27, 5.52) and a broad singlet for the two hydroxyl protons (δ2.53).

The formation of peroxyacetal 31 from 25s can be rationalized by protonation of the epoxide oxygen and ring-opening with aryl participation to give 30. Stereospecific reaction of 30 with the nucleophile results in 31.[19] Consistent with this mechanism, the *anti* epoxyendoperoxide 25a was recovered unchanged on treatment with TFA under conditions identical to those which caused rapid conversion of 25s to 31.[20,21] It is perhaps surprising that the peroxyacetal 31 survived the acidic conditions of its preparation. Indeed, treatment of 31a with TFA in ethanol did not bring about alkoxy group exchange nor any other reaction. There is some precedent for the acid stability of 31. The benzylic peroxyacetal 37 is also a stable cyclic peroxide, produced by the acid-catalyzed methanolysis of phenanthrene ozonide.[22]



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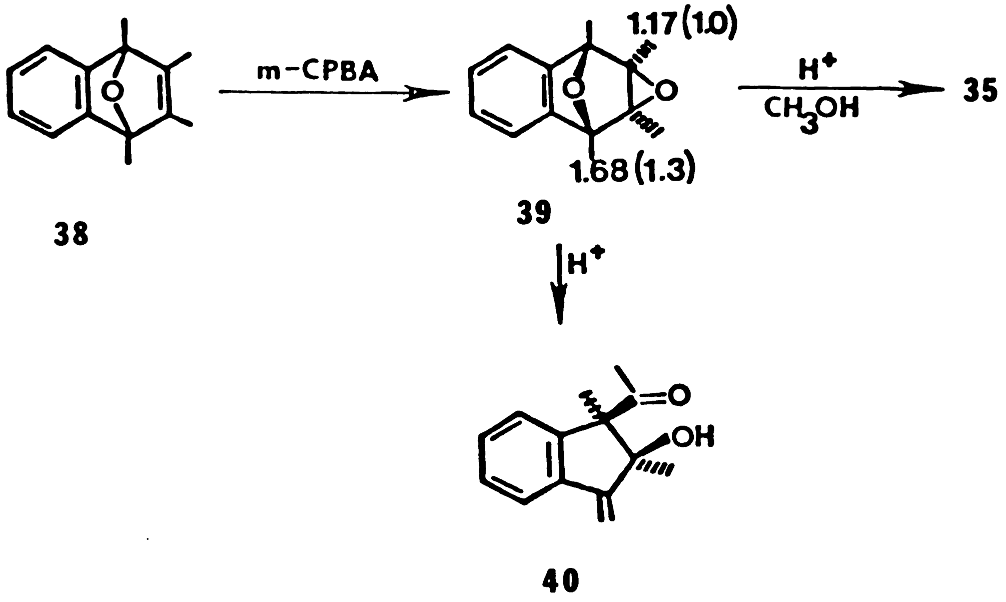
3. 1,2,3,4-Tetramethylnaphthalene-1,4-endoxide Epoxide

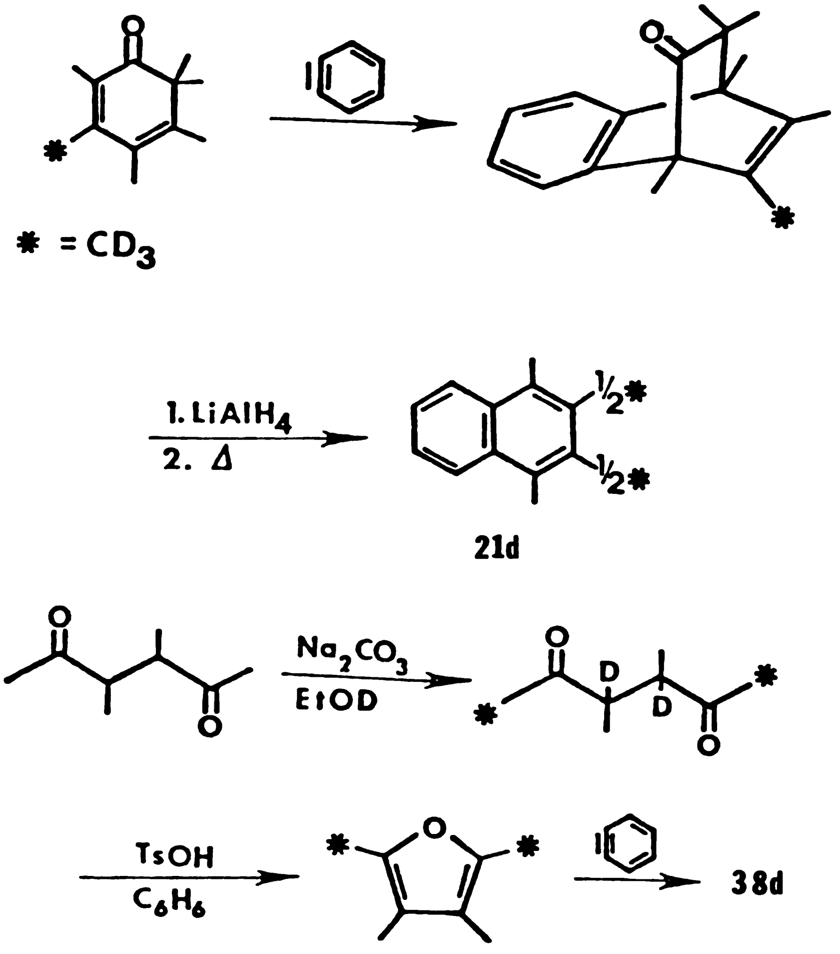
For comparison with 25s, the naphthalene-1,4-endoxide epoxide 39 was prepared and solvolyzed in acid. Epoxidation of naphthalene-1,4-endoxide 38[23] with *m*-CPBA gave the epoxyendoxide 39 as a single isomer. The *syn* stereochemistry is assigned on the basis of the chemical shifts and europium shift slopes of the methyl signals, which are nearly identical with those of 25s, and quite different from those of 25a.

When 39 was treated with TFA and methanol under the same conditions as for 25s, it was converted in analogous fashion to 35. If the methanol was omitted, the product was instead the unsaturated keto-alcohol 40, whose structure was assigned from spectral data and



mechanistic considerations. The formation of 35 or 40 from 39 can be rationalized by protonation at the epoxide oxygen, ring-opening with aryl participation to give the bridged ion 41 which, in the absence of nucleophile loses a proton to give 40, or in the presence of methanol is captured to give the acetal 42. Unlike the peroxyacetal 31, which is stable and easily isolated from the acidic medium, 42 is much more strained and solvolyzes to 35 under the reaction conditions (Scheme II, p. 16).

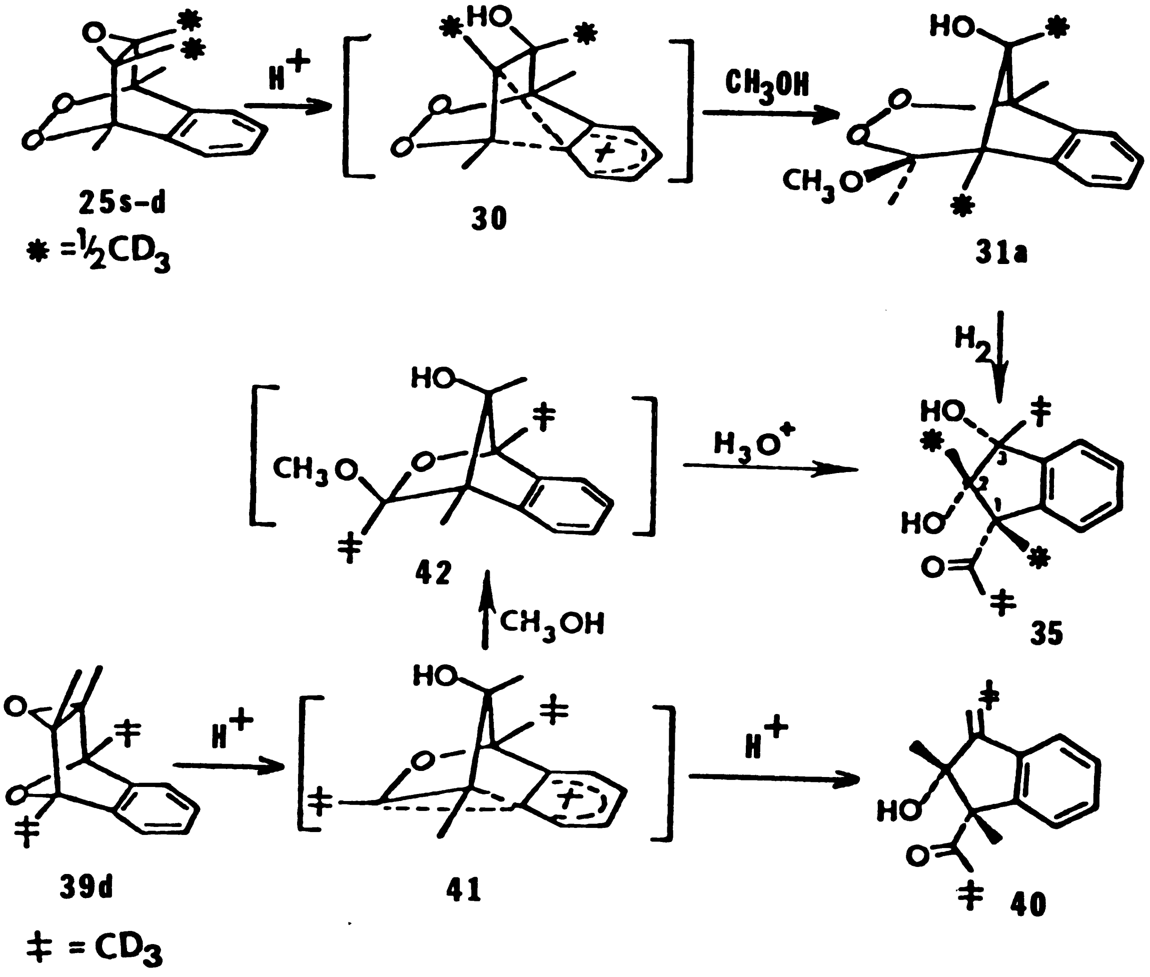
Scheme I



4. Deuterium Labeling Studies

Deuterium labeling was used to verify structural and NMR assignments and to be sure that our mechanistic scheme for the acid-catalyzed solvolytic rearrangements of 25s and 39 was correct. The preparation of the labeled compounds is outlined in Scheme I (for details, see the Experimental Section). The expected and observed labeling consequences are outlined in Scheme II.

Scheme II



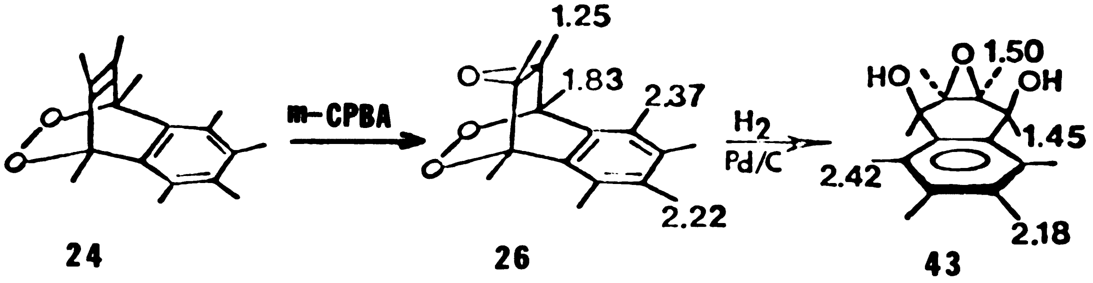
Labeled tetramethylnaphthalene **21d** was converted, via singlet oxygen and m-CPBA to **25s-d** which, according to Scheme II should give **35** labeled at the C_1 and C_2 methyls. In fact, the peaks at δ1.07 and 1.47 were diminished in intensity. Since the peak at δ1.47 represented two methyl groups with accidental degeneracy, shift reagent was used, and established that it was the peak with the higher slope that was diminished in intensity. These results are consistent with the label being at C_1 (δ1.47, slope 1.6) and C_2 (δ1.07).

Tetramethylfuran labeled at the C_2 and C_5 methyls was converted to **39d** which, with TFA and methanol, gave **35** with label in the C_3 methyl (δ1.47, slope 1.0) and acetyl methyl (δ2.03). Thus the label results are entirely consistent with the mechanisms put forth in Scheme II.

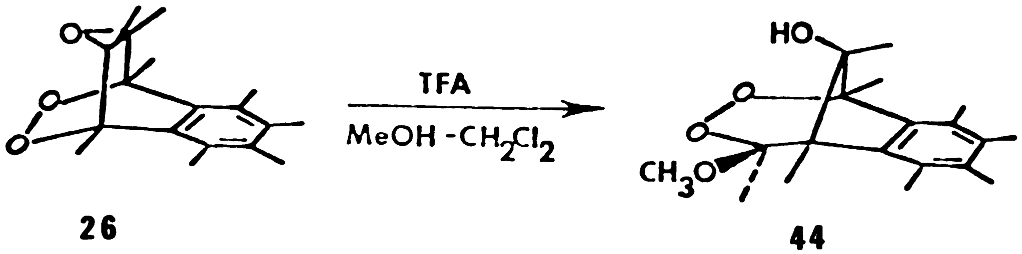
The ^1H NMR assignments in **35** were made as follows. The peak at δ2.03 is clearly the acetyl methyl. The methyl at C_1 has an environment almost identical with that of the C_3 methyl of **40** (δ1.47 and 1.48 respectively). The C_3 methyl is similar to that of the C_3 methyl in **36** (δ1.47 and 1.42). The central methyl in all these compounds comes at somewhat higher field than the benzylic methyls (δ1.07 in **35**, 1.35 in **36** and 1.28 in **40**; it appears at highest field in **35**, where it is not adjacent to an exocyclic methylene double bond).

5. Octamethylnaphthalene Epoxyendoperoxide

Octamethylnaphthalene-1,4-endoperoxide[12] was oxidized with m-CPBA to give the epoxyendoperoxide **26**. Only a single isomer, assigned the syn geometry, was isolated. The chemical shifts of the epoxide methyl groups in 26 (compare with 25s) and of the benzylic methyls in 43 (compare with 27s) favor this assignment. Consistent with this



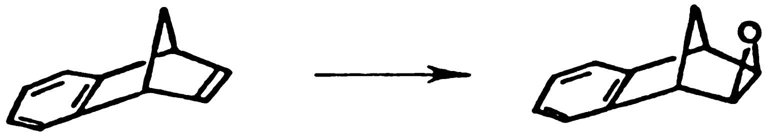
stereochemistry, 26 underwent quantitative, rapid solvolytic rearrangement to the peroxyacetal 44 on treatment with TFA in methanol/methylene chloride. The product liberated iodine instantaneously from



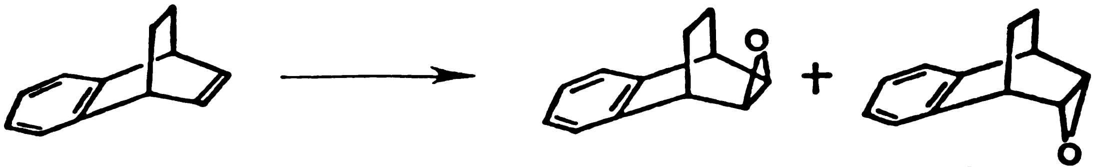
HI in acetone, showed a parent peak at m/e 320 in its mass spectrum, and had a ^{1}H NMR spectrum comparable to that of 31a except for the aromatic methyl substituents.

It is worth noting that in each epoxidation described here (i.e., 23, 24 and 38) the predominant or exclusive product was the syn isomer (corresponding to exo if the oxygen bridge is replaced by a carbon bridge). This result may be rationalized as an effect of the oxygen bridge. It is known that the direction of epoxidation can be controlled by coordination of the oxidizing agent with an oxygen atom already present in the substrate.[24] In the present case, coordination with the peroxide bridge in 23 or 24, or the endoxide bridge in 38 could account for the observed *syn* orientation.

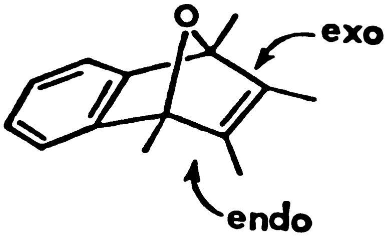
Alternatively, a steric factor may be involved, particularly with 38. It is well known that most reagents attack bicyclic [2.2.1] systems from the *exo* face, thus avoiding the crowdedness of the *endo* face.[25] For example, epoxidation of benzonorbornadiene 45 gave only the *exo*-oxide 46.[26] The [2.2.2] alkene dihydrobenzobarrelene 47, on the other hand, gave equal amounts of 48 and 49.[27] However, the steric crowdedness of the *endo* face of 23 and 24 may be more significant than usual for [2.2.2] bicyclic systems because of the peroxide bridge. The O-O bond, which is shorter than a C-C single bond, tends to expand the O-C-C bond angle and contract the C_2-C_1-C_{8a} bond angle. Consequently either the steric factor or coordination with the oxygen bridge (or both) may rationalize the *syn* epoxidation of 23, 24 and 38.



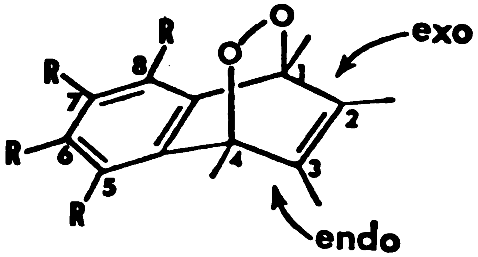
45 **46**



47 **48** **49**



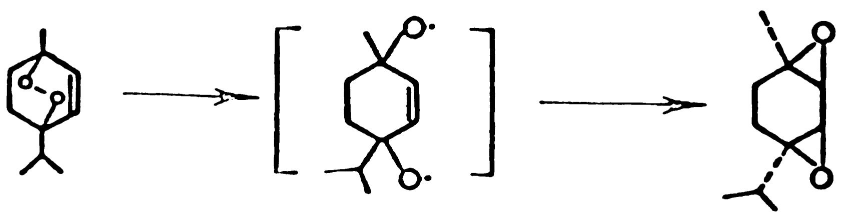
38



23(or 24)

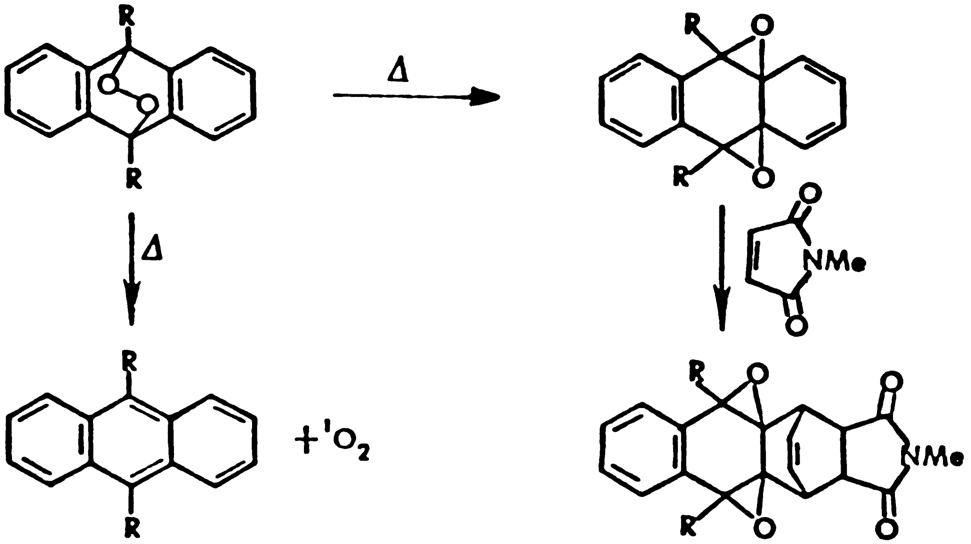
6. Thermolysis of Epoxyendoperoxides

The thermal rearrangement of ascaridol 50 to the diepoxide 51 has been known for many years;[28] the mechanism involves rate-determining homolytic O-O bond cleavage followed by rapid addition of the oxygens to the double bond.[29] For anthracene endoperoxides, two types of thermal reactions are known. O-O bond cleavage may give a diepoxide, which can be trapped with a dienophile,[30] or C-O bond cleavage may occur, with the extrusion of singlet oxygen and reformation of the anthracene.[31] Naphthalene endoperoxides, on the other hand, only



50 **51**

extrude oxygen, the rearrangement to diepoxides so far being unknown.[32]



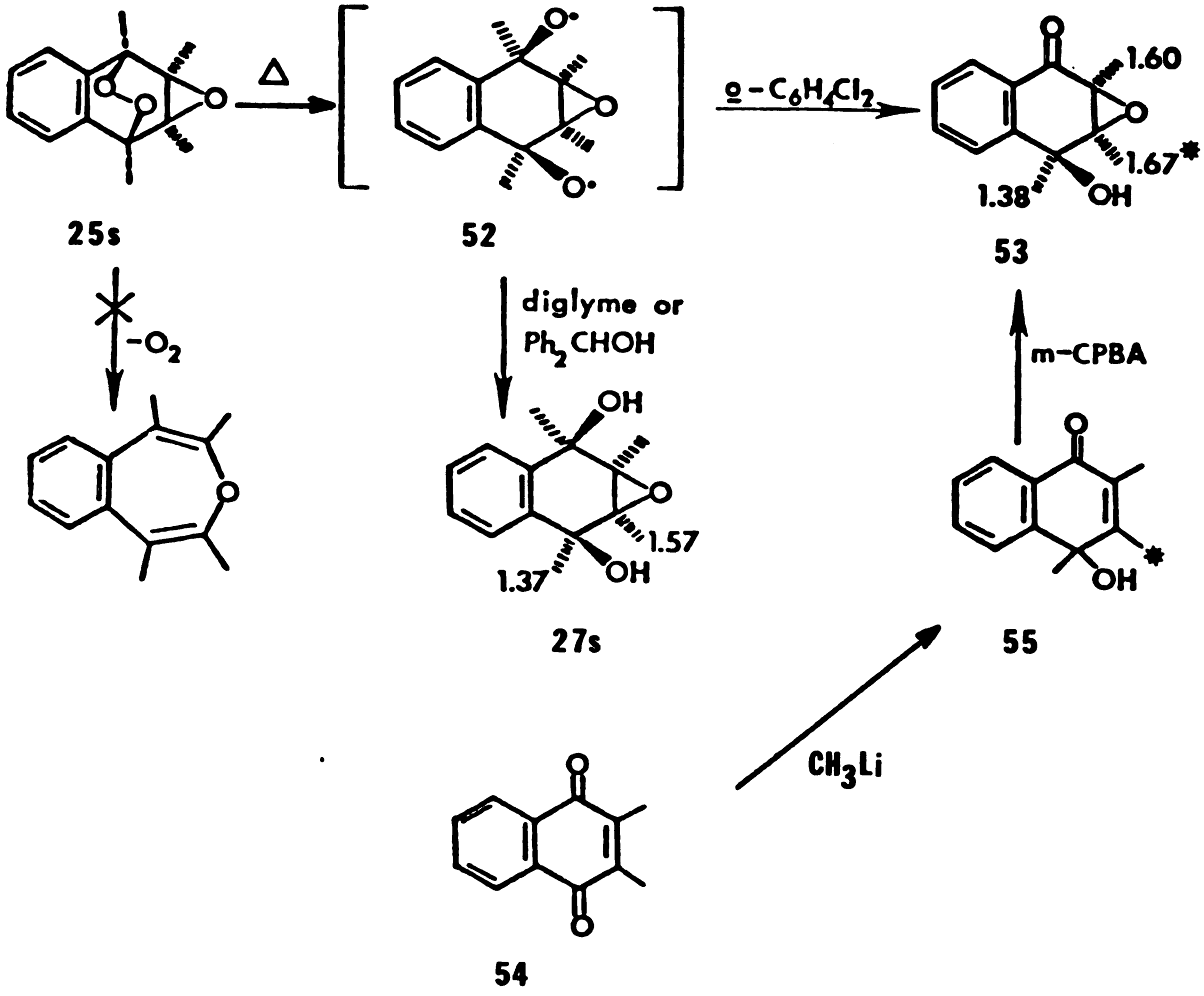
It was of interest to investigate the thermolysis of naphthalene epoxyendoperoxides such as 25 or 26, for oxygen extrusion could provide a useful benzoxepin synthesis. In fact, however, decomposition of 25s in refluxing o-dichlorobenzene gave instead of an oxepin a ketone assigned structure 53.[33] The compound showed infrared peaks for the hydroxyl, conjugated carbonyl and epoxide functions, and had an ^{1}H NMR spectrum with three methyl singlets and a broad singlet for the hydroxyl proton. The structure and the stereochemical relationship between the epoxide ring and the hydroxyl group (cis) was confirmed by independent synthesis.

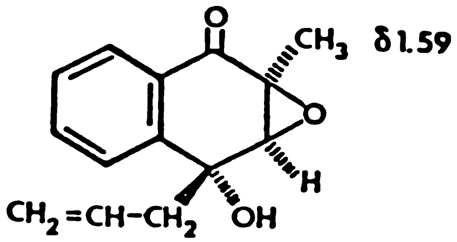
2,3-Dimethyl-1,4-naphthoquinone (54) and methyllithium afforded the ketoalcohol 55 which was oxidized with m-CPBA to give a product identical with 53 obtained from 25s. The epoxidation of 55 should be controlled by and occur cis to the hydroxyl function.[24]

NMR comparisons further support the stereochemical assignment.

Treatment of 55 with CH_3ONa/CH_3OD exchanged protons on the β-enone methyl group, and epoxidation gave labeled 53 lacking the methyl signal at δ1.67; furthermore, exchange of the OH proton of 53 in D_2O sharpened the singlet at δ1.38. Consequently the methyl signals in 53 are confidently assigned as shown on the structure. The chemical shift of the C_4 methyl (δ1.38) compares favorably with the benzylic methyls of 27s (δ1.37) and not with those of 27a (δ1.75), consistent with all cis stereochemistry. Also, the C_2 methyl shift in 53 (δ1.60) is similar to that recently reported for 56.[34]

Although the precise mechanism for the formation of 53 is not clear, the diradical 52 seemed to be one plausible intermediate. Indeed, when the thermolysis was carried out in the presence of a

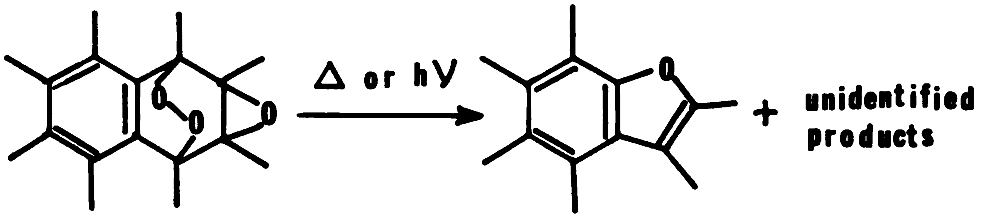




56

good hydrogen donor (diglyme solvent) the diol 27s was obtained in quantitative yield. Also, if the thermolysis was carried out in o-dichlorobenzene to which benzhydrol was added, the products were 27s and benzophenone. Thus 25s seems to decompose thermally by O-O, not C-O bond cleavage. Trapping of 52 is one of the few examples of diradical trapping by external chemical means.[35]

Thermolysis of 26 was not as clean as 25. Analysis of the reaction mixture by g.l.c. showed at least seven thermolysis products, and only one of them could be separated and isolated pure. It was identified as hexamethylbenzofuran 57 (15%). The ^{1}H NMR (180 MHz) spectrum of 57 showed six singlets, at δ2.24, 2.27, 2.30, 2.33, 2.39

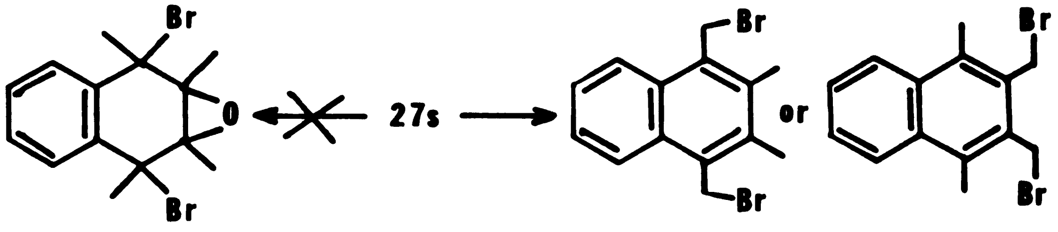


26 **57**

and 2.52. The mass spectrum showed an M^+ peak at m/e 202. The uv spectrum was very similar to that of benzo[b]furan. Photolysis of 26 also gave 57 with other unidentified products. The precise mechanism for the formation of 57 is not clear.

7. Reaction of 27 with HBr

Reaction of 27s with HBr was attempted because the dibromide 58 could serve as a good precursor to tetramethylbenzoxepin. However, when 27s was treated with dry HBr in ether, a naphthalene derivative considered to be either 59 or 59a was obtained. The ^{1}H NMR spectrum



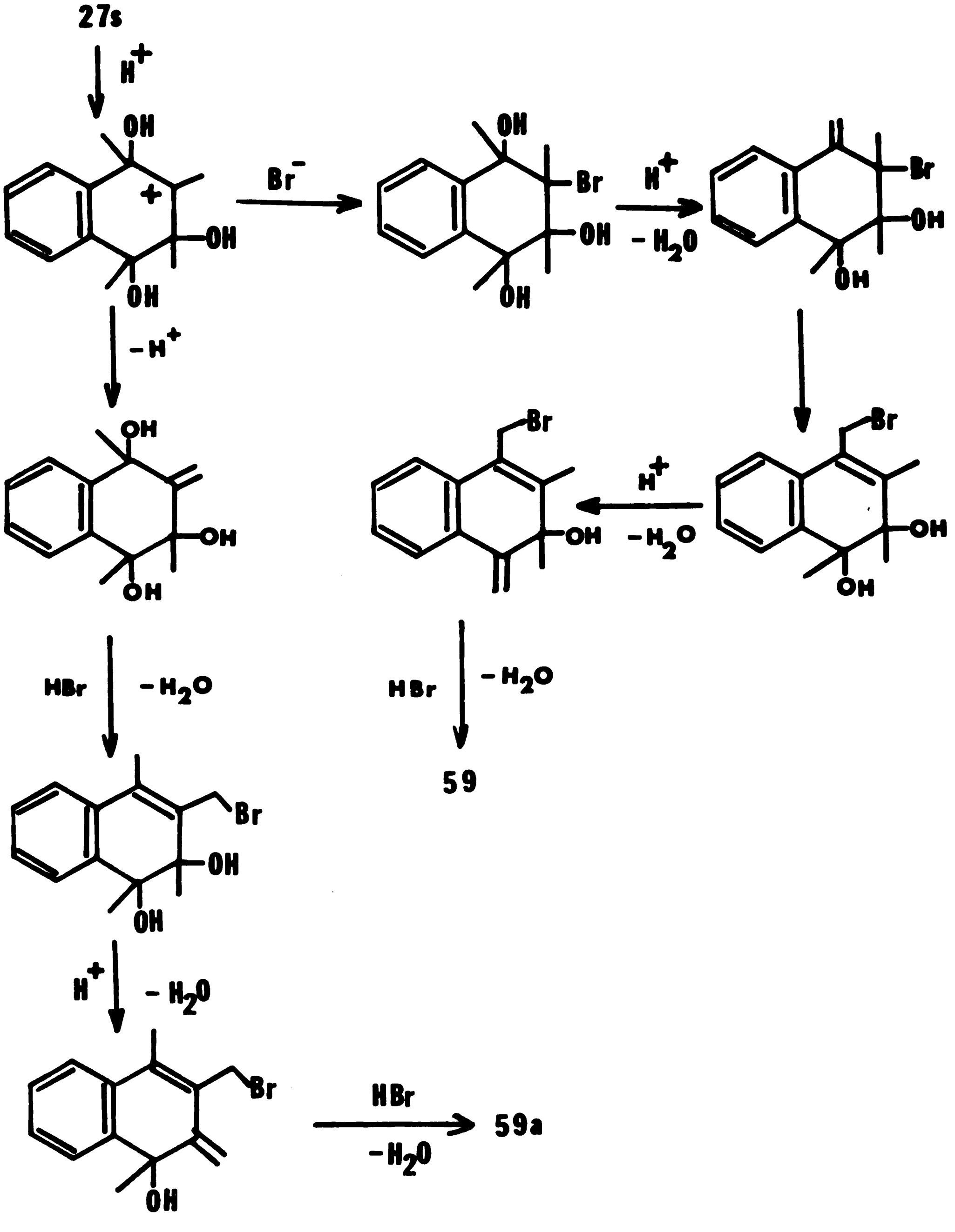
58 59 59a

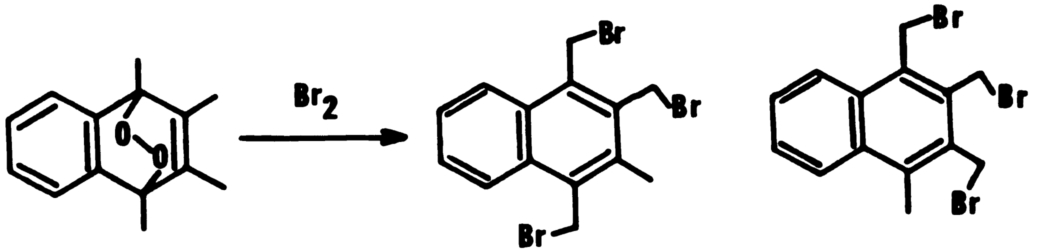
had peaks at δ2.45(s,6H) and 4.92(s,4H) besides the multiplet in the aromatic proton region. The mass spectrum showed M^+ peaks at m/e 344, 342 and 340. One possible mechanism for the formation of 59 or 59a is shown in Scheme III.

8. Reaction of 23 with Bromine

When 23 was treated with bromine in carbon tetrachloride, the tribromide 60 was obtained in 11% yield. The ^{1}H NMR spectrum of 60 showed four singlets at δ2.68(3H), 4.72(2H), 4.88(2H), and 4.97(2H) and multiplets for four aromatic protons. The mass spectrum proved

Scheme III

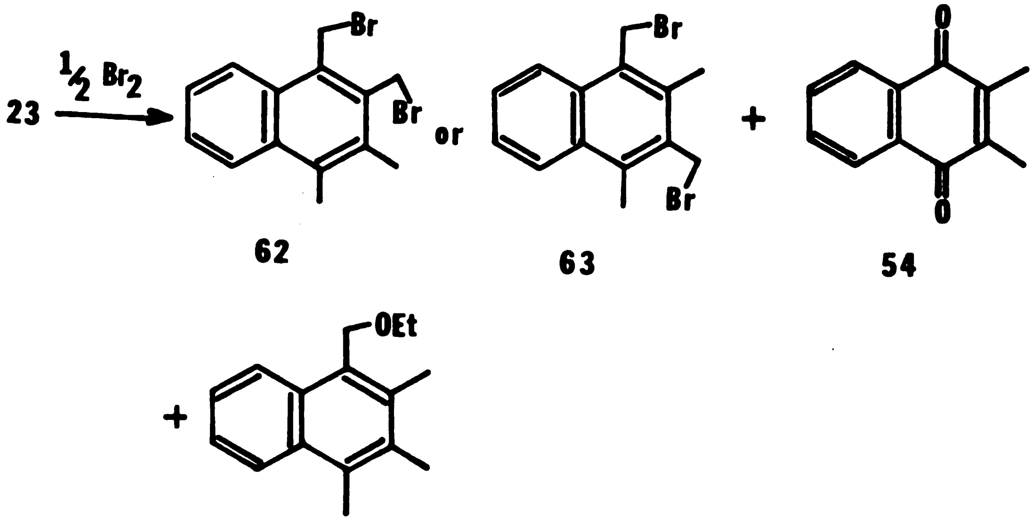




23 **60** **61**

that the product had three bromine atoms. The structure 61 can also account for these spectral data. However the melting point of 61 (193-194°C) which was reported in the literature[36] was different from observed melting point of the product (211-213°C).

In order to trap some intermediate in the formation of 60, 23 was treated with a half equivalent mole of bromine. From this reaction at least five products were observed and three of them were separated by chromatography on silica gel with chloroform as an eluent. They were identified as dibromide 62 or 63, naphthoquinone 54,[37] and



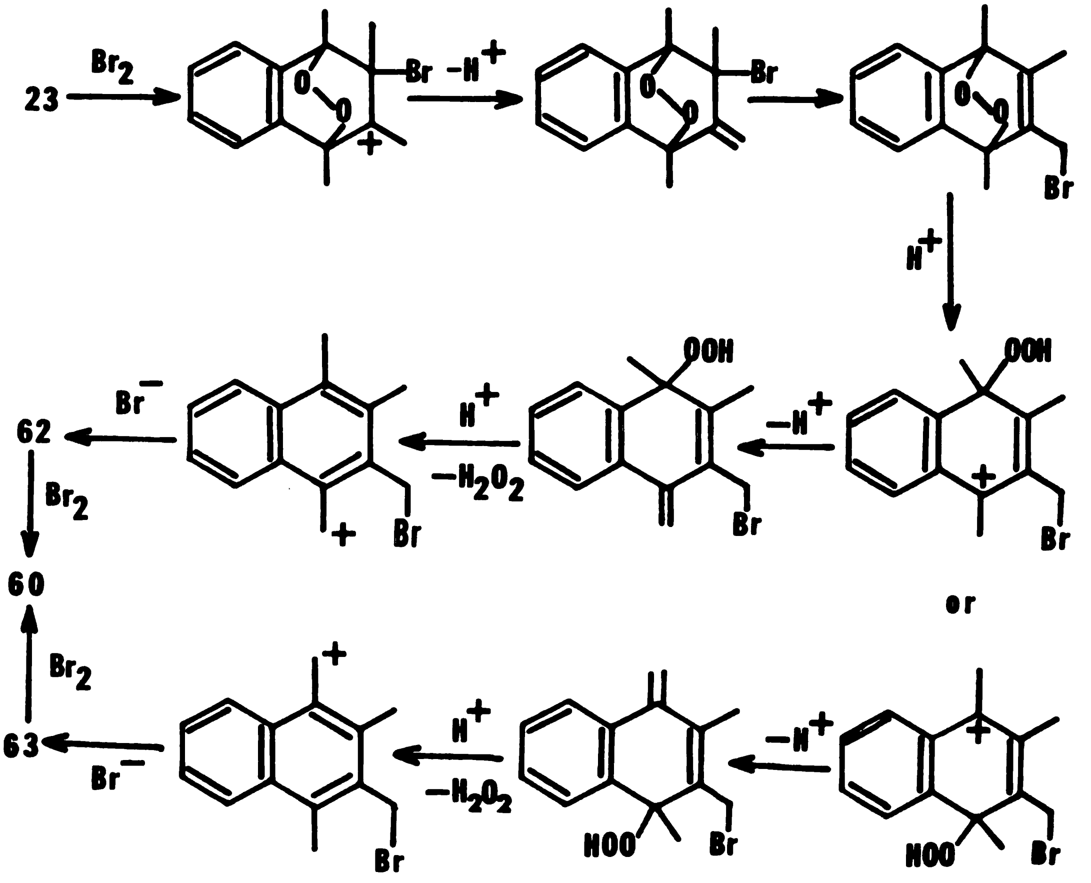
62 **63** **54**

64

another naphthalene derivative 64. It is obvious that the ethoxyl group of 64 came from ethanol which was present in the chloroform used as an eluent.

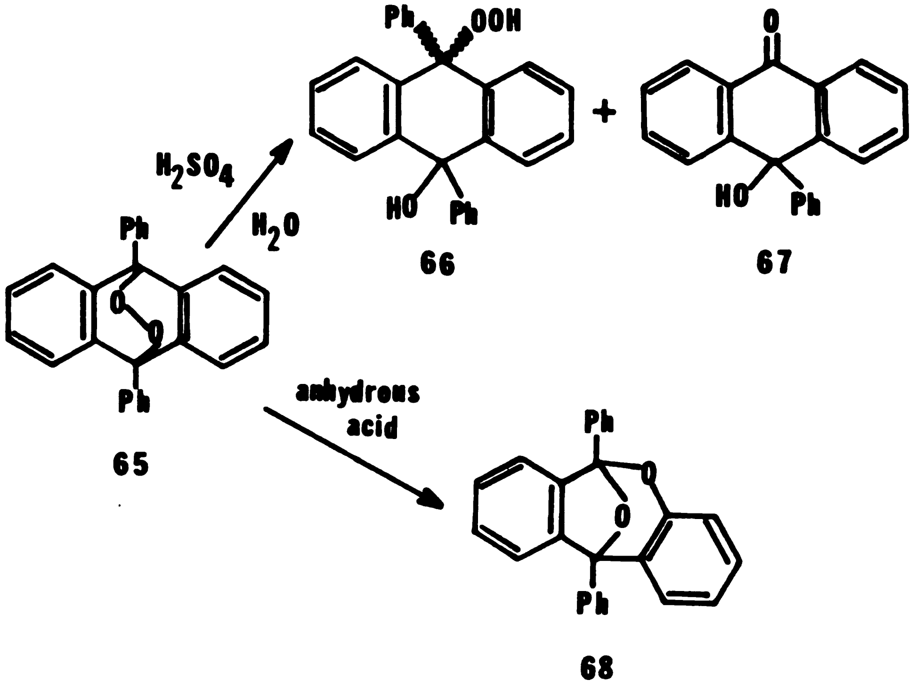
The ^{1}H NMR spectrum of the dibromide showed four singlets at δ2.57 (3H), 2.67(3H), 4.67(2H), and 4.92(2H) and multiplets for the four aromatic protons. The mass spectrum showed the presence of two bromine atoms. A unique choice between the two alternative structures was not made, but its intermediacy in the formation of 60 was proved by treating the dibromide with bromine to give 60 in a good yield. A possible mechanism for the formation of 60 and 62 or 63 from 23 is summarized in Scheme IV. Other products 64 and 54 were probably formed by the reaction of 23 with protons which were produced during the reaction (see section 9).

Scheme IV

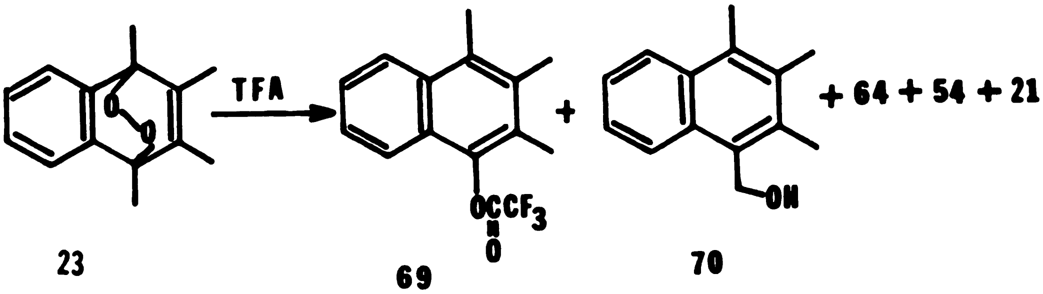


9. Reaction of 23 with TFA

A few reactions of alkyl substituted anthracene endoperoxides with acids are reported. For example, when 9,10-diphenylanthracene endoperoxide 65 was treated with aqueous sulfuric acid two products 66 and 67 were isolated. Reaction with an anhydrous acid, however, afforded 68.[38]



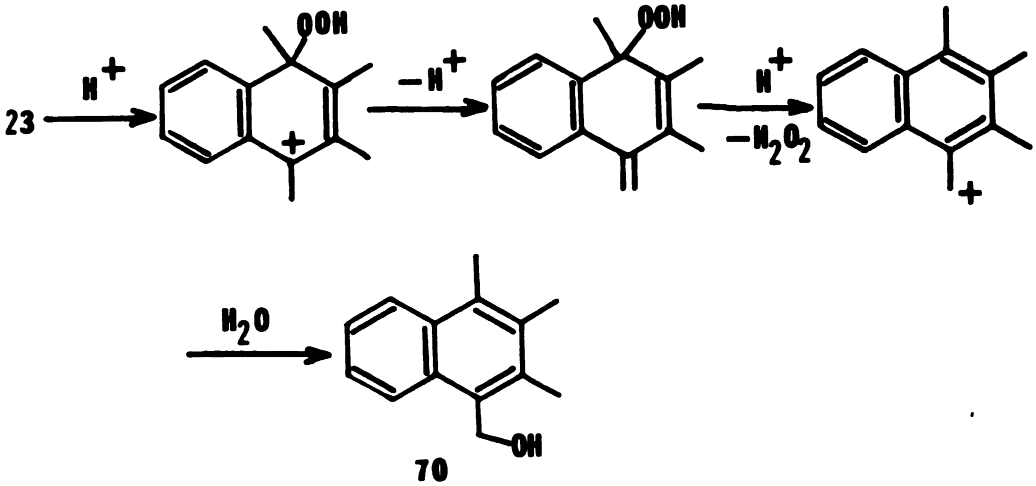
However, no reactions of alkyl substituted naphthalene endoperoxides with acids are known. Therefore 23 was treated with TFA. The reaction products were separated by silica gel chromatography with chloroform as an eluent. The five products isolated were 69, 70, 64, 54 and tetramethylnaphthalene 21 in 9.5, 4.5, 11, 1 and 1% yield respectively. Structural assignments of these products were made



on the basis of their spectral data. Hydroxymethylnaphthalene 70 is a known compound.[39] The ^1H NMR spectrum of 69 showed three singlets at δ2.05(3H), 2.38(3H), 2.58(3H) and multiplets for four aromatic protons. The mass spectrum showed an M^+ peak at m/e 282. The trifluoroacetate functionality was clear from the infrared spectrum ($\nu_{C=O}$ 1780, ν_{C-O} 1230, 1170, 1130 cm^{-1}). The ^1H NMR spectrum of 64 showed ethoxyl [δ1.23(t,3H), 3.62(q,2H)] and allylic methyl protons (δ2.38, 2.47, 2.58) as well as a singlet at δ4.88(2H) and multiplets for four aromatic protons. The infrared spectrum showed the ether functionality (ν_{C-O} 1090 cm^{-1}). The mass spectrum showed an M^+ peak at m/e 228. These results suggest that 64 and 54 were produced in the reaction of 23 with bromine by the protonation of 23.

The mechanisms for the formation of 69, 54 and 21 are not clear. A possible mechamism for the formation of 70 is shown in Scheme V.

Scheme V



EXPERIMENTAL

1. General Procedures

^1H NMR spectra were measured at 60 MHz on a Varian T-60 or at 180 MHz on a Bruker WH-180 spectrometer against tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined on a Varian CFT-20 spectrometer. UV spectra were determined on Unicam SP-800 spectrometer. IR spectra were determined on a Perkin-Elmer Model 167 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 spectrometer. High resolution mass spectra were obtained with a Varian CH5 spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Eagle Harbor, Michigan. Melting points are uncorrected.

2. Epoxidation of 1,2,3,4-Tetramethyl-1,4-epidioxy-1,4-dihydronaphthalene (23)

A methylene chloride solution (50 mL) of 85% m-chloroperbenzoic acid (m-CPBA, 4.4 g) was added dropwise at 0°C to a solution of 23[11] (3.97 g, 18.4 mmol) in 20 mL of CH_2Cl_2. The mixture was stirred at 0°C for 18 h during which time m-chlorobenzoic acid precipitated from solution. The solid was removed by suction filtration and the filtrate was washed with aqueous sodium sulfite. It was then washed with aqueous Na_2CO_3, water and dried ($MgSO_4$). The solvent was removed under vacuum at room temperature to give colorless solids which showed NMR peaks due to the syn (25s, 90%) and anti (25a, 10%) isomers of 1,2,3,4-tetramethyl-2,3-epoxy-1,4-epidioxy-1,2,3,4-tetrahydronaphthalene. The solids were recrystallized from ether in a crystallizing dish covered by Parafilm. Colorless cloudy plates (25s, 3.42 g, 80%) and colorless rods (25a, 0.28 g, 7%) obtained after slow evaporation of the ether were separated mechanically.

For 25s: mp 154-156°C. IR (nujol) 1125(m), 1100(s), 1070(m), 865 cm^{-1}(s); ^1H NMR($CDCl_3$) δ1.18(s,6H), 1.67(s,6H), 7.23(s,4H); ^{13}C NMR($CDCl_3$) 11.7, 14.2, 66.3, 79.7, 122.0, 128.3, 140.0 ppm from TMS; for europium shift data, see structure; mass spectrum, m/e (rel. intensity) 232(1), 216(1), 200(6), 173(100).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.48; H, 6.94.

For 25a: mp 174-177°C. IR (nujol) 1120(s), 1075(m), 1065(s), 1050(m), 870(m), 845 cm^{-1}(m); ^1H NMR ($CDCl_3$) δ1.48(s,6H), 1.73(s,6H), 7.0-7.4(m,4H); ^{13}C NMR ($CDCl_3$) 11.1, 15.4, 56.5, 82.7, 120.8, 128.3, 136.0 ppm from TMS; for europium shift data, see structure; mass spectrum, m/e (rel. intensity) 232(0.5), 216(2), 200(22), 173(100).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.34; H, 6.91.

3. Epoxidation of 1,2,3,4,5,6,7,8-Octamethyl-1,4-epidioxy-1,4-dihydronaphthalene (24)

A methylene chloride solution (15 mL) of 85% m-CPBA (897 mg) was added dropwise at 0°C to a solution of 24 in 10 mL of CH_2Cl_2. The mixture was stirred at 0°C for 24 h. Work-up in the manner described for the preparation of 25 gave a colorless solid which was nearly pure. Recrystallization from ether-$CHCl_3$ gave pure 1,2,3,4,5,6,7,8-octamethyl-2,3-epoxy-1,4-epidioxy-1,2,3,4-tetrahydronaphthalene 26, mp 200-201°C. IR (nujol) 1120(s), 1100(s), 1080 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.25(s,6H), 1.83(s,6H), 2.22(s,6H), 2.37(s,6H); uv (cyclohexane) λ_{max} 275 nm (ε=420), 225(6840); mass spectrum, m/e (rel. intensity) 288(6), 256(4), 202(100).

Anal. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39. Found: C, 74.89; H, 8.32.

4. Catalytic Hydrogenolysis of 25 and 26

Medium pressure catalytic hydrogenolysis (20-30 psi of H_2) of 25s, 25a and 26 in ethanol with palladium on charcoal (10%, Matheson, Coleman and Bell) at room temperature gave the corresponding diols 27s, 27a and 43 with 65%, 62% and 82% yields respectively.

For 27s: mp 162-163.5°C. IR (nujol) 3450(s), 3400(s), 3320(s), 1100(s), 1090 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.37(s,6H), 1.57(s,6H), 2.27 (bs,2H), 7.0-7.3(m,2H), 7.3-7.6(m,2H); mass spectrum, m/e (rel. intensity) 234(4), 200(8), 173(100).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.73;

H, 7.76.

For 27a: mp 161-162.5°C. IR (nujol) 3200(s), 1100(s), 1065 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ1.57(s,6H), 1.75(s,6H), 2.60(s,2H), 7.1-7.6(m,4H).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H,7.74. Found: C, 71.68; H, 7.75.

For 43: mp 198-200°C. IR (nujol) 3590(s), 3450(s), 1325(s), 1085(s), 1065 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.45(s,6H), 1.50(s,6H), 2.18 (s,8H,CH_3 and OH), 2.42(s,6H); mass spectrum, m/e(rel. intensity) 290(10), 273(3), 257(6), 230(24), 229(100).

Anal. Calcd for $C_{18}H_{26}O_3$: C, 74.44, H, 9.03. Found: C, 74.08; H, 8.80.

5. 4-Methoxy-1,4,5,8-tetramethyl-6,7-benzo-2,3-dioxabicyclo[3.2.1]-oct-6-en-8-ol (31a)

To a solution of 25s (900 mg) in a mixed solvent of CH_2Cl_2 (15 mL) and MeOH (3 mL), 6 mL of trifluoroacetic acid (TFA) was added dropwise over 5 min at 0°C with stirring. After additional stirring for 15 min at 0°C, the reaction mixture was poured into aqueous Na_2CO_3 slowly with vigorous stirring. The organic layer was separated, washed and dried ($MgSO_4$). Evaporation of the solvent under vacuum left a colorless solid which showed NMR peaks due only to 31a. No further purification than rinsing with petroleum ether was necessary, mp 98-100°C. IR (nujol) 3450(s), 1035 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ0.75 (d,3H,J=1.4 Hz,C_8 methyl), 1.10(s,3H,C_4 methyl), 1.38(s,3H,C_5 methyl), 1.45(s,3H,C_1 methyl), 3.40(s,3H, methoxyl), 5.78(bs,1H, hydroxyl), 6.7-7.3(m,4H,arom). With a Bruker WH-180 spectrometer, the broad singlet at δ5.78 was resolved to a quartet with J=1.4 Hz. Irradiation of the doublet at δ0.75 changed this quartet to a singlet; ^{13}C NMR ($CDCl_3$) 10.5, 12.1, 16.8, 19.9, 49.5, 52.0, 82.8, 89.7, 109.2, 122.2, 123.0, 127.9, 128.7, 141.1, 146.8 ppm from TMS; uv (MeOH) λ_{max} 272 nm (ε=400), 265(420), 258(340), 252(200); mass spectrum, m/e (rel. intensity) 246(1.5,M^+-H_2O), 133(100).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.27; H, 7.40.

6. 4-Ethoxy-1,4,5,8-tetramethyl-6,7-benzo-2,3-dioxabicyclo[3.2.1]-oct-6-en-8-ol (31b)

To a solution of 25s (250 mg) in a mixed solvent of CH_2Cl_2 (10 mL) and EtOH (2 mL), 3 mL of TFA was added dropwise over 5 min at 0°C with stirring. Stirring was continued for 15 min at 0°C. Workup in the manner described for 31a gave a colorless oil which was nearly pure 31b (300 mg). The colorless oil was chromatographed on silica gel with $CHCl_3$ as an eluent to give pure 31b. IR (neat) 3460 (s), 1045 cm^{-1}(s); ^{1}H NMR ($CDCl_3$) δ0.75(d,3H,J=1.4 Hz), 1.10(s,3H), 1.28 and 1.38(t and s respectively,6H), 1.45(s,6H), 3.2-4.1(m,2H), 6.07(bs,1H), 6.9-7.4(m,4H); ^{13}C NMR ($CDCl_3$) 10.5(q), 12.1(q),15.3 (q), 17.4(q), 19.9(q), 52.0(s), 58.0(t), 82.9(s), 89.7(s), 109.0(s), 122.2(d), 123.0(d), 127.9(d), 128.7(d), 141.3(s), 146.9(s) ppm from TMS; mass spectrum, m/e (rel. intensity) 260(0.5,M^+-H_2O), 190(13), 172(75), 84(100). Addition of a small quantity of 31a or 31b to a solution of hydroiodic acid in acetone liberated iodine.

7. 1-Acetyl-1,2,3-trimethylindan-2,3-diol (35)

Medium pressure catalytic hydrogenolysis (24 psi of H_2) of 31a (200 mg) in ethanol with palladium on charcoal (10%, Matheson Coleman and Bell) at room temperature for 30 min gave 35 (110 mg, 62%), mp 105-107°C (petroleum ether). IR (nujol) 3440(s), 3290(s), 1700 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ1.07(s,3H), 1.47(s,6H), 2.03(s,3H), 2.90(s,1H), 4.88(s,1H), 7.0-7.4(m,4H); for europium shift data, see the structure; ^{13}C NMR ($CDCl_3$) 18.8, 20.3, 20.9, 29.4, 61.0, 80.4, 86.4, 123.7, 124.4, 128.2, 129.0, 144.2, 144.9 ppm from TMS; mass spectrum, m/e (rel. intensity) 216(2,M^+-H_2O), 200(6), 191(3), 181(2), 174(51), 173(100).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.80; H, 7.71.

8. 1-Methylene-2,3-dimethylindan-2,3-diol (36)

Peroxyacetal 31a (400 mg) was heated in *o*-xylene at reflux for 10 h. Evaporation of the solvent under vacuum left a light brown residue which was purified by g.l.c. (10% SE30, 165°C) to give a colorless solid. The solid was recrystallized from petroleum ether to give pure 36 (65 mg, 22%), mp 96-97°C. IR (nujol) 3430(s) 3320 (s), 1790(m), 1660(m), 900 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.35(s,3H), 1.42 (s,3H), 2.53(bs,2H), 5.27(s,1H), 5.52(s,1H), 7.0-7.6(m,4H); mass spectrum, m/e (rel. intensity) 190(21), 175(54), 172(59), 156(36), 129(100).

Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.88;

H, 7.44.

9. 1,2,3,4-Tetramethyl-1,4-endoxy-1,4-dihydronaphthalene (38)

A mixture of 3,4-dimethyl-2,5-hexanedione[23] (12.4 g), p-toluenesulfonic acid (catalytic amount) and benzene (80 mL) was heated under reflux for 6 h during which time the water produced was removed azeotropically. The volatile solvent was removed under vacuum, and the brown oily residue was distilled under reduced pressure as described in the literature[23] to give pure 2,3,4,5-tetramethylfuran (9.5 g, 77%).

A mixture of tetramethylfuran (3.0 g), benzenediazonium-2-carboxylate hydrochloride (5.3 g), propylene oxide (36 mL) and 1,2-dichloroethane (100 mL) was heated gradually until gas evolution commenced. The mixture was then heated under reflux for 2 h. The volatile solvents were removed under vacuum, and the residue was dissolved in ether and washed with dilute aqueous NaOH, water, and dried ($MgSO_4$). The brown oil which remained after removal of the ether was chromatographed on silica gel with $CHCl_3$ as an eluent to give pure 38 [23](2.8 g, 57%).

10. 1,2,3,4-Tetramethyl-1,4:2,3-diepoxy-1,2,3,4-tetrahydronaphthalene (39)

A solution of 85% m-CPBA (487 mg) in 13 mL of CH_2Cl_2 was added dropwise to a solution of 38 (400 mg) in 2 mL of CH_2Cl_2 with stirring at 0°C. Stirring was continued for 5 h during which time m-chlorobenzoic acid precipitated from solution. The solid was removed by suction filtration and the filtrate was washed with aqueous Na_2SO_3, Na_2CO_3, water and dried ($MgSO_4$). The solvent was removed under vacuum at room temperature to give a colorless oily solid (420 mg) which showed NMR peaks due only to 39. It was used for further reactions without purification. IR (nujol) 1160(s), 1130(s), 1085(s), 1070 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ1.17(s,6H,$C_{2,3}$ methyls), 1.68(s,6H,$C_{1,4}$ methyls), 7.03(s,4H); ^{13}C NMR ($CDCl_3$) 9.1, 11.8, 68.5, 84.8, 119.7, 126.6, 149.5 ppm from TMS. For europium shift data, see structure.

11. Reaction of 39 with TFA in CH_2Cl_2-MeOH

TFA (1.4 mL) was added dropwise to a solution of 39 (200 mg) in a mixed solvent of methylene chloride (30 mL) and methanol (1.4 mL) with stirring at 0°C. The mixture was stirred at 0°C for an additional 1.5 h. After work-up as in the preparation of 31, the solvent was removed under vacuum to give a yellow oil which was chromatographed on silica gel with $CHCl_3$ as an eluent to give pure 35 (80 mg, 37%).

12. 1-Methylene-3-acetyl-2,3-dimethylindan-2-ol (40)

TFA (1.4 mL) was added dropwise to a solution of 39 (200 mg) in 30 mL of methylene chloride with stirring at 0°C. After additional stirring for 1.5 h and work-up as for 31, the solvent was evaporated under vacuum to give a yellow oil whose NMR spectrum showed peaks due to 40 and some small impurities peaks. The yellow oil was chromatographed on silica gel with $CHCl_3$ as eluent to give pure 40 as colorless needles (30%), mp 87-90°C. IR (nujol) 3400(s), 1790(m), 1700(s), 1650(m), 900 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.28(s,3H), 1.48(s,3H), 1.82(s,3H), 3.25(s,1H), 5.22(s,1H), 5.45(s,1H), 7.0-7.6(m,4H); mass spectrum, m/e (rel. intensity) 216(5), 200(3), 198(4), 184(4),183 (4), 173(90), 156(100).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.68; H, 7.35.

When **39** (420 mg) was allowed to stand in a flask for 10 days, it decomposed to a brown oil. Chromatography of this oil on silica gel with $CHCl_3$ as an eluent gave **40** (178 mg, 42%).

13. Deuterium Labeling Experiments

A. 1,4-Dimethyl-2,3-dimethyl-d_3-naphthalene **21d** was prepared as follows. A mixture of 2,4,5,6,6-pentamethyl-3-methyl-d_3-cyclohexa-2,4-dienone[40] (6.01 g), benzenediazonium-2-carboxylate hydrochloride (6.5 g), propylene oxide (10 mL) and 1,2-dichloroethane (85 mL) was heated gradually, until gas evolution commenced. After the solution became clear, the reaction mixture was heated under reflux for 1 h. The volatile solvents were removed under vacuum. The oily residue was dissolved in ether and washed with dilute aqueous NaOH, water, and dried ($MgSO_4$). The light brown residue which remained after the solvent evaporated was recrystallized from methanol to give 1,3,4,7,7-pentamethyl-2-methyl-d_3-5,6-benzobicyclo[2.2.2]octa-2,5-dien-8-one (5.23 g). This ketone (2.5 g) was reduced with lithum aluminum hydride in ether at room temperature in the usual manner to give the corresponding alcohol (2,3 g). This alcohol, without purification, was heated in o-xylene under reflux for 51 h. Evaporation of the solvent to dryness gave a colorless solid which was recrystallized from petroleum ether to give pure **21d** which showed two methyl singlets at δ2.37 and 2.57 with relative intensities of 0.6:1.0.

Starting with **21d** and using the same methods as described above, **25d**, **27d**, **31a-d** and **35d** were prepared. For **25s-d**, the ^{1}H NMR peak at δ1.18 was reduced in area. For **25a-d**, the singlet at δ1.48 was reduced in area. For both **27s-d** and **27a-d**, the singlet at δ1.57 was reduced in area. For **31a-d**, the doublet at δ0.75 and the singlet at δ1.38 were reduced in their intensities. The ^{13}C NMR peaks at 10.5, 19.9, 52.0 and 82.8 ppm showed diminished intensities. For **35d**, the singlets at δ1.07 and 1.47 had reduced intensities.

B. **39d** was prepared as follows. A mixture of 3,4-dimethylhexan-2,5-dione(14.1 g), sodium carbonate (4.5 g), ethanol-d (31 mL), and D_2O (60 mL) was stirred at room temperature for 18 h. The mixture was poured into 250 mL of methylene chloride and washed with aqueous NaCl. Any residual base was removed with solid CO_2. After drying ($MgSO_4$), the solvent was evaporated under vacuum to give the deuterated diketone as an oil (12.35 g). The diketone was converted to deuterated tetramethylfuran by catalysis with p-toluenesulfonic acid as described for the nondeuterated compound, since the reported $ZnCl_2$ method[23] resulted in deuterium loss. The 2,5-dideuteromethyl-3,4-dimethylfuran was converted to **38d** and **39d** by the same method used for the unlabeled material. The ^{1}H NMR spectrum of **39d** showed that the peak at δ1.68 ($C_{1,4}$ methyls) was reduced in area by about 50%.

Starting with **39d**, **35d** was prepared as with the unlabeled material.

The ^{1}H NMR spectrum of 35d showed reduced intensity of the signals at δ1.47 and 2.03. Of the methyls which are accidentally degenerate at δ1.47 , the one which moves least with europium shift reagent was decreased in intensity.

14. 4-Methoxy-1,4,5,8-tetramethyl-6,7-(3',4',5',6'-tetramethylbenzo)-2,3-dioxabicyclo[3.2.1]oct-6-en-8-ol (44)

The reaction of 26 (150 mg) with TFA (2 mL) in the same manner as described for the preparation of 31 afforded 44 quantitatively as a colorless oil. The product liberated iodine from HI in acetone, showed a parent peak in its mass spectrum, and had a ^{1}H NMR spectrum comparable to that of 31a except for the aromatic methyl substituents. The elemental analysis was not obtained. IR (neat) 3470(s), 1120 cm^{-1}(s); ^{1}H NMR (CDCl$_3$) δ0.77(d,3H,J=1.4 Hz), 1.12(s,3H), 1.57(s,6H), 2.17(s,6H), 2.27(s,3H), 2.31(s,3H), 3.35(s,3H), 5.53(bs,1H); mass spectrum, m/e (rel. intensity) 320(<1), 203(100).

15. 2,3,4-Trimethyl-2,3-epoxy-4-hydroxy-1,2,3,4-tetrahydronaphthalenone (53)

Compound 25s (100 mg) was heated in *o*-dichlorobenzene (20 mL) under reflux for 2 h. The solvent was removed under vacuum to give a brown oily residue whose NMR spectrum showed peaks due to the starting material and to 53. Separation and purification by chromatography on silica gel with CHCl$_3$ as the eluent gave two fractions. The first fraction was starting material (27 mg). From the second fraction, **53** was obtained (18 mg), mp 113-114°C. IR (nujol) 3565(s), 3460(s), 1680(s), 1100(s), 1080 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.38(s,3H), 1.60(s,3H), 1.67(s,3H), 2.47(bs,1H), 7.0-7.8(m,4H); mass spectrum, m/e (rel. intensity) 218(1), 175(100).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.42; H, 6.44.

16. Trapping of Diradical **52**

A. **25s** (355 mg) in 8 mL of diglyme was heated at reflux under nitrogen for 2 h. The ^1H NMR spectrum of the diglyme solution after heating showed peaks due only to **27s**. Evaporation of the solvents left an oily brown residue to which 3 mL of petroleum ether was added. On standing overnight in a refrigerator, colorless crystals deposited which were recrystallized from petroleum ether to give pure **27s** (220 mg, 61%).

B. A mixture of **25s** (100 mg) and benzhydrol (80 mg) was heated in 10 mL of o-dichlorobenzene at reflux for 7 h. The brown oil which was obtained after the removal of the solvent under vacuum was chromatographed on silica gel with $CHCl_3$ as the eluent. The first fraction gave a small amount of starting material. From the second fraction, benzophenone (17 mg) was obtained, identified by its IR spectrum. From the third fraction, **27s** (30 mg) was obtained.

17. 2,3,4-Trimethyl-4-hydroxy-1,4-dihydronaphthalenone (55)

To a solution of 2,3-dimethyl-1,4-naphthoquinone[37] (558 mg) in dry ether (100 mL) was added dropwise at -78°C under nitrogen 2.0 mL of commercial 1.77 M methyllithium (ether). The mixture was stirred for 15 min, then warmed to room temperature. After additional stirring for 1 h, water (20 mL) was added with vigorous stirring. The separated aqueous layer was extracted with ether, and the combined ether layers were washed with dilute hydrochloric acid, saturated sodium chloride solution, and dried ($MgSO_4$). Removal of the ether under vacuum gave a pale yellow solid which was rinsed with petroleum ether to give colorless 55 (400 mg, 67%), mp 163-164°C. IR (nujol) 3420(s), 1635 cm^{-1}(s); ^{1}H NMR ($CDCl_3$) δ1.55(s,3H,C_4 methyl), 1.87(s,1H,OH), 1.92(bs,3H,C_2 methyl), 2.13 (bs,3H,C_3 methyl), 7.2-8.0(m,4H,arom); mass spectrum, m/e (rel. intensity) 202(32), 187(100).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.79; H, 6.36.

Treatment of 55 with excess sodium methoxide in methanol-d for 1 h at room temperature[40] gave labeled 55 lacking the signal at δ2.13.

18. Epoxidation of 55

To a solution of 55 (202 mg) in methylene chloride (10 mL) was added 300 mg of 85% *m*-CPBA in 10 mL of the same solvent. The mixture was stirred for 7 h at room temperature, washed with aqueous sodium sulfite (2x), aqueous sodium carbonate (4x), saturated sodium chloride (2x) and dried ($MgSO_4$). Removal of the solvent under vacuum gave a colorless residue which, after rinsing with petroleum ether (30-60°C) gave 180 mg (83%) of pure 53 (IR, NMR, mp and mmp identical with the thermolysis product of 25s). Starting with labeled 55 (vide supra) the resulting labeled 53 lacked the signal at δ1.67 in its NMR spectrum.

19. Hexamethylbenzo[b]furan (57); Thermolysis of 26

Epoxyendoperoxide 26 (288 mg, 1 mmol) in a sealed tube was heated at 210°C for 2.5 h. After heating, the oily material in the tube was chromatographed on silica gel with $CHCl_3$ as an eluent. The first fraction was a mixture of 57 and octamethylnaphthalene 22. The second fraction was nearly pure 57. After g.l.c. (20% SE30, 200°C), pure 57 was obtained as a colorless solid (30 mg, 15%). IR ($CHCl_3$) 1630 (m), 1100 cm^{-1}(s); ^1H NMR ($CDCl_3$, at 180 MHz) δ2.24(s,3H), 2.27(s,3H), 2.30(s,3H), 2.33(s,3H), 2.39(s,3H), 2.52(s,3H); uv(ethanol) λ_{max} 292 nm(ε=1400), 288(1320), 280(1670), 256(14320), 224(13130); mass spectrum, m/e (rel. intensity) 202(94), 187(100), 177(16); high resolution mass spectrum, calculated for $C_{14}H_{18}O$ m/e 202.13568, observed m/e 202.13576.

Thermolysis of 26 in refluxing benzene for 340 h gave similar results.

20. Photolysis of 26

A solution of 26 (360 mg) in 650 mL of CH_3CN was irradiated for 4 h (450 W Hanovia, Corex, room temperature). Benzofuran **57** was the only product which was isolated and identified after separation and purification by g.l.c. (20% SE30, 200°C), (6 mg, 2.4%).

21. Reaction of **27** with HBr

Dry hydrogen bromide gas was passed through a solution of **27** (40 mg) in 5 mL of dry ether at 0°C until the solution was saturated. The solution was stirred for 30 min at 0°C, then poured into aqueous Na_2CO_3 solution slowly with stirring. After the ether layer was washed with water and dried the solvent was evaporated under reduced pressure to give colorless solids. Recrystallization of the solids from ether gave colorless needless of **59** (or **59a**) in about 30% yield, mp 229-230°C. IR (nujol) 1210 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ2.45(s,6H), 4.92(s,4H), 7.3-7.6(m,2H), 7.7-8.1(m,2H); mass spectrum, m/e (rel. intensity) 344(2.5), 342(5), 340(2.5), 263(25), 261(25), 182(100). The elemental analysis was not obtained.

22. Reaction of **23** with Br_2

A. To a solution of **23** (200 mg) in 20 mL of CCl_4, Br_2 in CCl_4 was added dropwise at 0°C until the color of Br_2 was not decolorized. The solution was washed with aqueous $Na_2S_2O_3$ solution, water, and dried ($MgSO_4$). Evaporation of solvent left a brown residue to which a small amount of $CHCl_3$ was added. Colorless solids precipitated and the solids were separated and rinsed with ether to give **60** (42 mg, 11%), mp 211-213°C. IR (nujol) 1210(s), 1190(m), 765(s), 760 cm^{-1}(s); ^{1}H NMR ($CDCl_3$) δ2.68(s,3H), 4.72(s,2H), 4.88(s,2H), 4.97(s,2H), 7.3-7.6(m,2H), 7.8-8.1(m,2H); mass spectrum, m/e (rel. intensity) 424(2), 422(5), 420(5), 418(2), 343(18), 341(35), 339 (19), 262(21), 260(20), 181(100), 165(71).

B. To a solution of **23** (751 mg) in 20 mL of CCl_4, 3.28 mL of bromine solution (0.53 M) in carbon tetrachloride was added dropwise at 0°C with stirring. After stirring for 30 min the solvent was evaporated under vacuum to leave a pale yellow oily residue. The residue was chromatographed on silica gel with chloroform as the eluent. The first fraction gave a colorless solid which was recrystallized from ether to give 82 mg of **62** (or **63**). The second fraction gave an unidentified product (15 mg). From the third and the fourth fractions, small amounts of **54** and **64** respectively were obtained.

For **62** (or **63**): mp 161-165°C. IR (nujol) 1210(s), 1190(m), 760 cm^{-1}(s); ^{1}H NMR ($CDCl_3$) δ2.57(s,3H), 2.67(s,3H), 4.67(s,2H), 4.92(s,2H), 7.1-7.7(m,2H), 7.7-8.3(m,2H); mass spectrum, m/e (rel. intensity) 344(6), 342(12), 340(6), 263(67), 261(68), 182(100).

For **64**, see p. 47.

23. Reaction of **62** (or **63**) with Br_2

To a solution of **62** (or **63**) (17 mg) in 1 mL of carbon tetrachloride, 0.5 mL of Br_2 solution (0.098 M) in CCl_4 was added. The mixture was stirred for 6 h at room temperature and the solvent was removed under vacuum to give a colorless solid. The solid was rinsed with ether twice to give pure **60** (15 mg).

24. Reaction of **23** with TFA

TFA (3 mL) was added dropwise to a solution of **23** (1.0 g) in 20 mL of carbon tetrachloride at 0°C and the mixture was stirred for 1.5 h at the same temperature. The mixture was poured into aqueous sodium carbonate solution with vigorous stirring. The organic layer was washed with water (3x) and dried (Na_2SO_4). The residue obtained by evaporation of the solvent under vacuum was chromatographed on silica gel with chloroform as the eluent. The first fraction gave 1-trifluoroacetyl-2,3,4-trimethylnaphthalene (**69**) which was purified by g.l.c. (20% SE30, 5 feet x 0.25 inch, 227°C), (125 mg, 9.5%). The second fraction gave 1-ethoxymethyl-2,3,4-trimethylnaphthalene (**64**) which was similarly purified by g.l.c. (116 mg, 11%). The third fraction gave a mixture of **54** and **21** which was separated to 3 mg of **54** and 3 mg of **21** by g.l.c. as above. The fourth fraction gave 1-hydroxymethyl-2,3,4-trimethylnaphthalene (**70**) which was recrystallized from cyclohexane to give colorless needles of **70** (42 mg, 4.5%).

For **69**: IR ($CHCl_3$) 1780(s), 1230(s), 1170(s), 1130 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ2.05(s,3H), 2.38(s,3H), 2.58(s,3H), 7.2-7.7(m,3H), 7.8-8.1(m,1H); uv (ethanol) λ_{max} 297 nm (sh,ε=300), 288(400), 275 (400), 234(1400); mass spectrum, m/e (rel. intensity) 282(73), 185 (100).

For **64**: IR ($CHCl_3$) 1090 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ1.23(t,3H), 2.38(s,3H), 2.47(s,3H), 2.58(s,3H), 3.62(q,2H), 4.88(s,2H), 7.1-7.5(m,2H), 7.7-8.2(m,2H); mass spectrum, m/e (rel. intensity) 228 (37), 213(11), 184(55) 183(84), 182(100), 169(59).

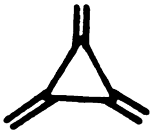
For **70**: mp 176-177°C (lit.[39] 177-177.5°C). IR (nujol) 3240(s), 1000cm^{-1}(s); ^{1}H NMR ($CDCl_3$) δ1.50(s,1H), 2.37(s,3H), 2.47(s,3H), 2.58(s,3H), 5.07(s,2H), 7.1-7.5(m,2H), 7.7-8.2(m,2H); mass spectrum, m/e (rel. intensity) 200(100), 183(45), 182(60), 171(70), 157(60).

PART II

SYNTHESIS AND PROPERTIES OF BENZO[1,2-c:3,4-c':5,6-c"]TRITHIOPHENE, A TRISTHIAHEXARADIALENE

INTRODUCTION

Radialenes are a class of compounds possessing n ring atoms and n double bonds, all of which are exocyclic.[41] They have been the subject of extensive investigation with both theoretical[42] and synthetic interest. Their feature of main interest is the extent of conjugation available into the ring. In the series 71 - 74, [3][43]- and [4][44] radialene (71 and 72) have been known for some years. [5]Radialene 73 is still unknown. Only hexaalkyl derivatives of [6]radialene 74 were known[45] until the parent hexaradialene was reported just recently.[46]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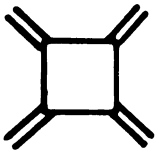
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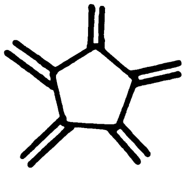
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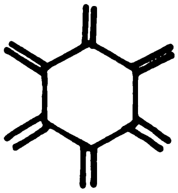
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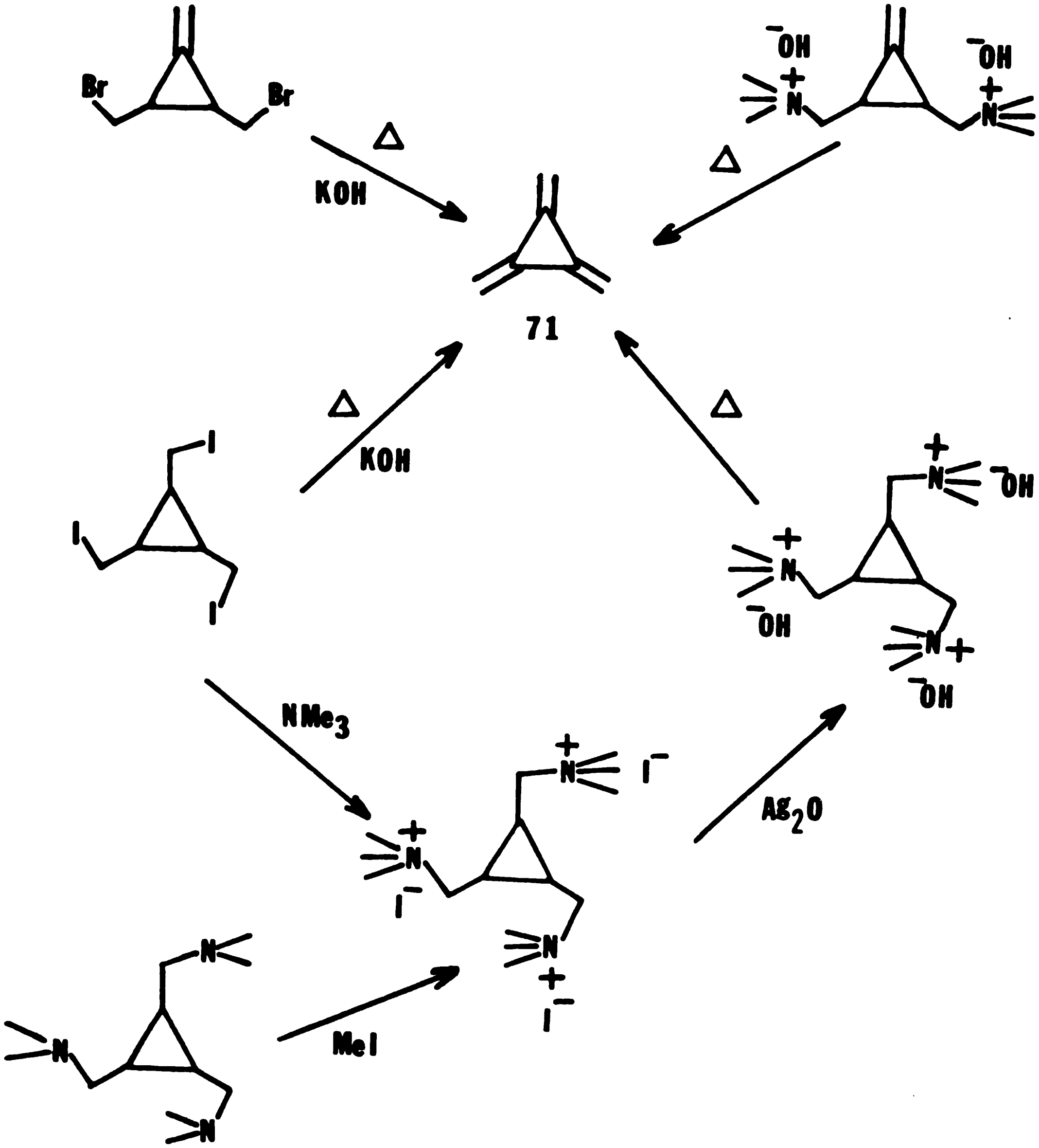
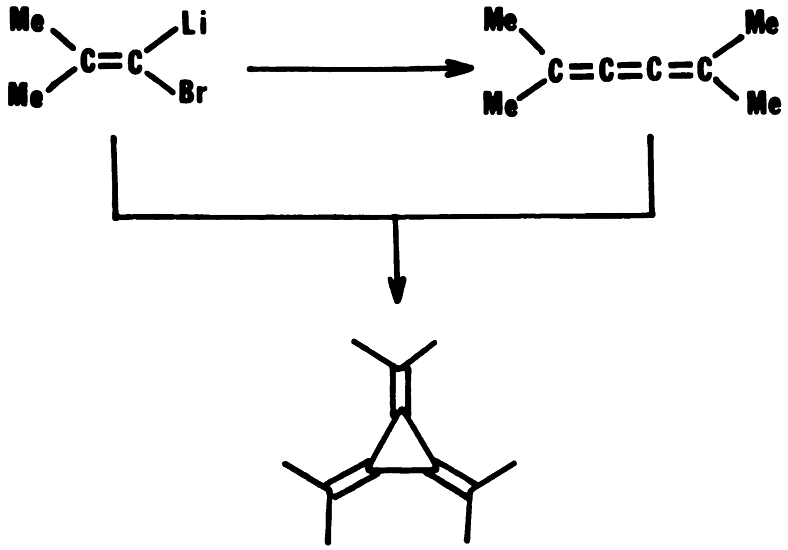
The first synthesized member of the series was [3]radialene, an isomer of benzene. The initial success of Blomquist in 1959 was followed by Griffin's synthesis, which improved the yield and made further characterization of the compound possible.[43] Radialene 71 showed marked sensitivity to oxygen which is in agreement with theoretical predictions of high free valency anticipated at the terminal carbons of the exocyclic double bonds.[42] The synthesis of **71** is summarized in Scheme I.

Scheme I



The hexamethyl derivative of 71 was prepared by in situ addition of a vinyl carbene to an allene.[47] Although the parent hydrocarbon 71 was air sensitive and polymerized rapidly, hexamethyl [3]radialene 75 turned out to be a surprisingly stable crystalline compound.



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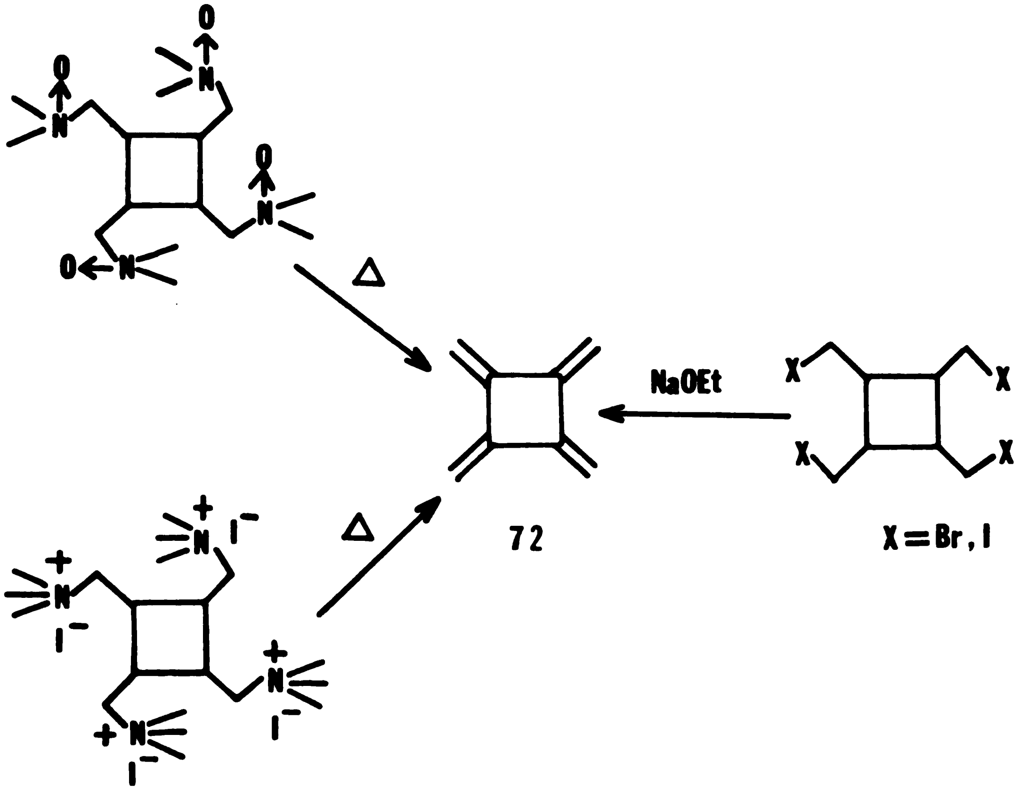
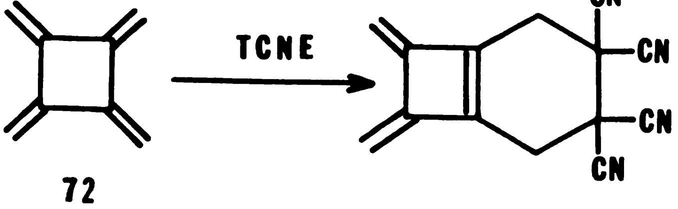
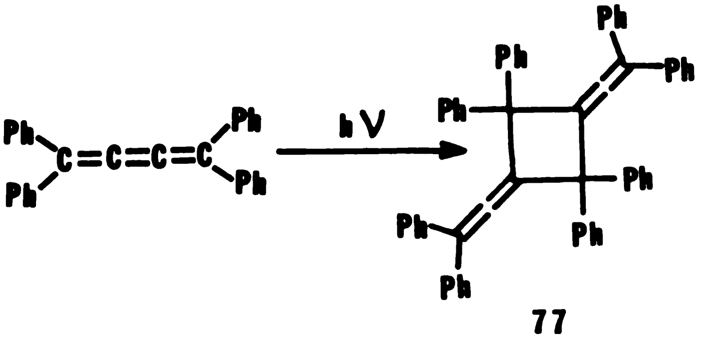
[4]Radialene which, like cyclobutadiene, possesses four sp^2-hybridized carbon atoms in the ring, was prepared by similar methods.[44] Hydrocarbon 72 was found to be remarkably stable to dilute mineral acids and strong bases. However, like [3]radialene, it was air sensitive. The radialene gave a mono Diels-Alder adduct with tetracyanoethylene (TCNE), but a second cycloaddition did not occur even with a large excess of TCNE.


Δ
Δ
NaOEt
72
X = Br, I


TCNE
72
CN
CN
CN
CN

An octaphenyl derivative of 72 was reported as a stable crystalline photodimer of tetraphenylbutatriene at almost same time as the parent radialene was reported.[48] However it was found later that the structure of the photodimer is actually 77, not 76.[49]



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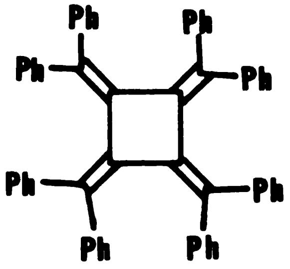

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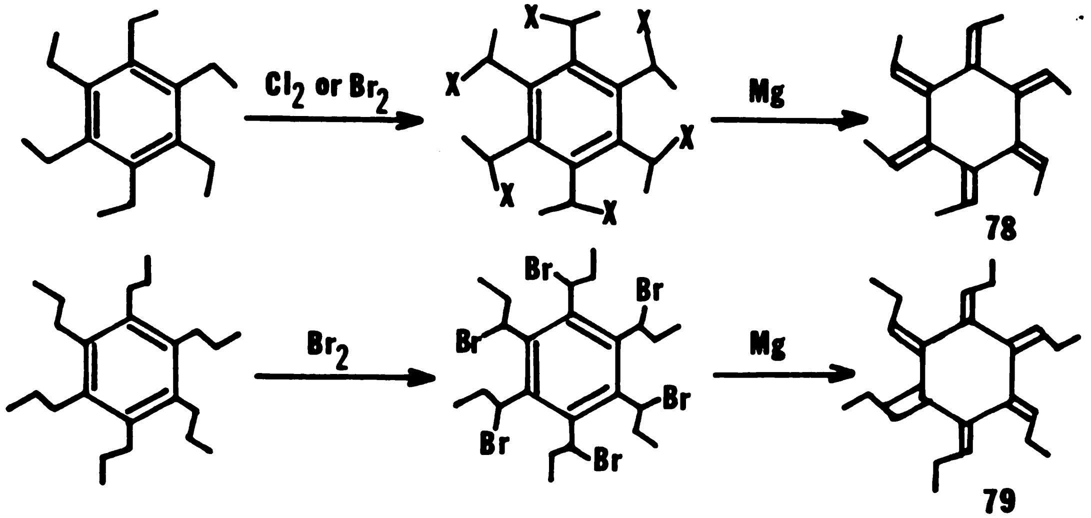
In 1960 the first [6]radialene was reported by Hopff,[45] as its hexamethyl and hexaethyl derivatives. These hexaalkyl hexaradialenes, prepared as shown below, were stable crystalline compounds.



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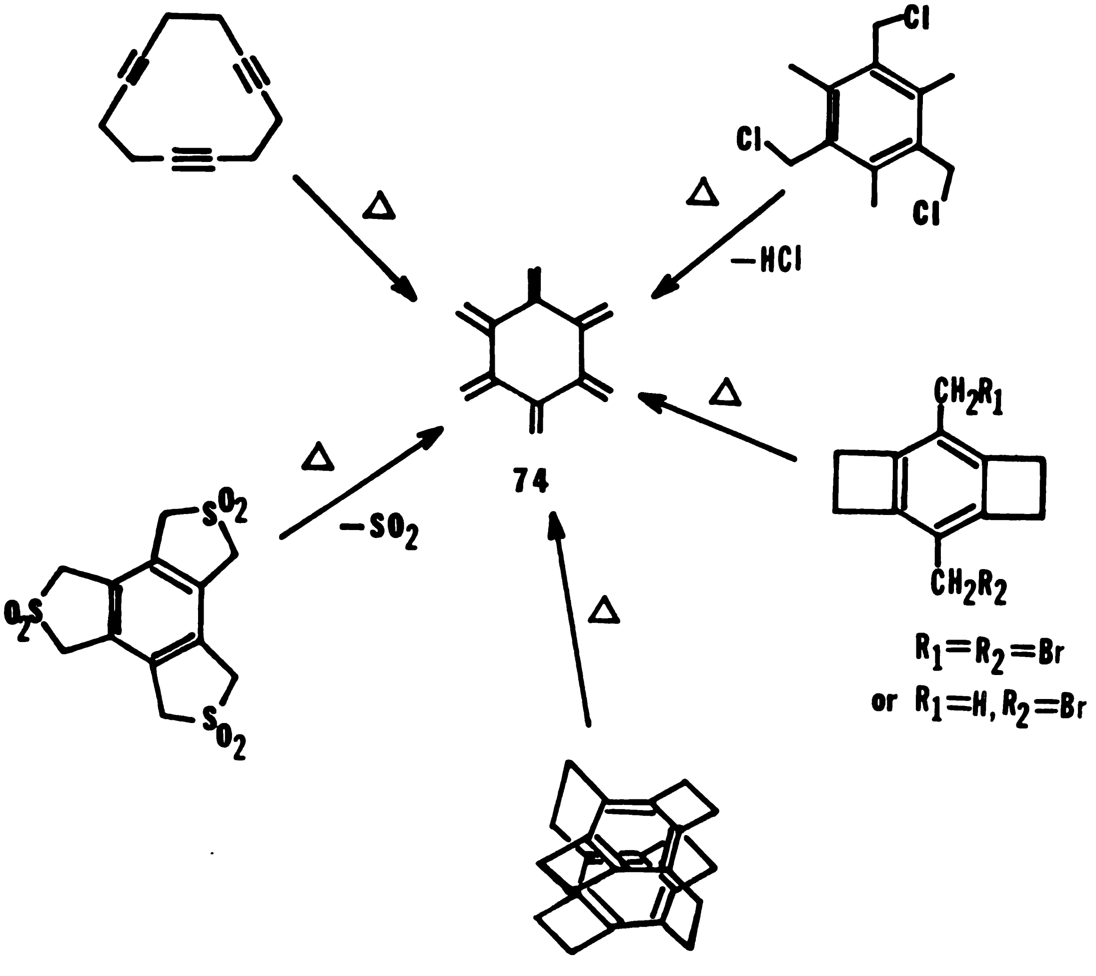
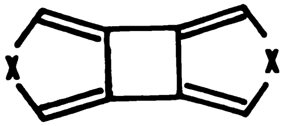
The parent hexaradialene 74 was synthesized by three different groups just recently.[46] Hexaradialene was found to be an air sensitive colorless solid, reasonably stable in solution if kept below -40°C. The various syntheses of 74 are summarized in Scheme II.

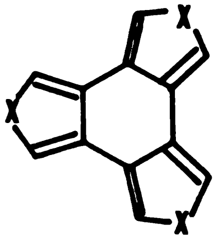
Scheme II



In the case of the [4]- and [6]radialenes, one can replace two hydrogen atoms by one heteroatom and form radialene derivatives in which every exocyclic double bond is in a heteroaromatic ring (80, 81). The tetraphenyl derivative of 80 (X=S) was reported as a stable



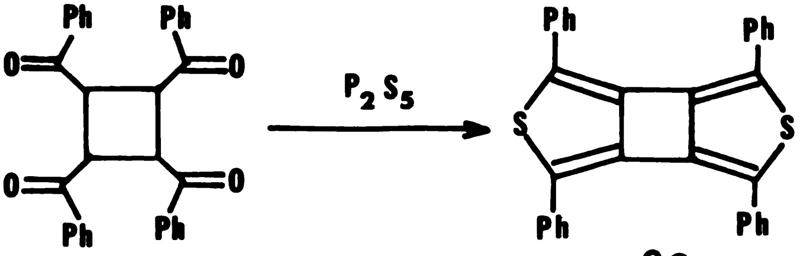
80



81

X=O, S, NR etc.

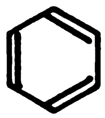
crystalline compound by Garratt.[50] Since the parent compound is still unknown, it is not known whether the stability of 82 is due



82

to its heteroaromatic rings or its phenyl substituents.

Hexaradialene can be viewed as a benzene which is converted in a formal sense from having six overlapping p orbitals associated with endocyclic "double bonds" to having those orbitals associated with exocyclic carbon-carbon "double bonds". In the same sense 81 is an exocyclic benzene and 84 and 85 are partially exocyclic



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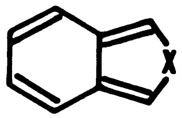

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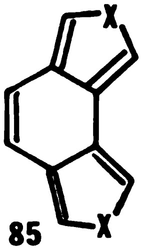

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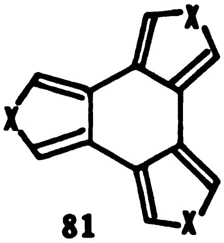
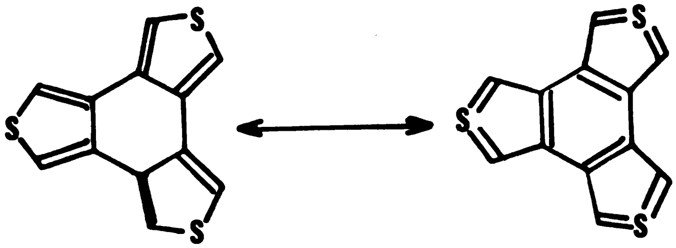


81

X=O,S,NR etc.

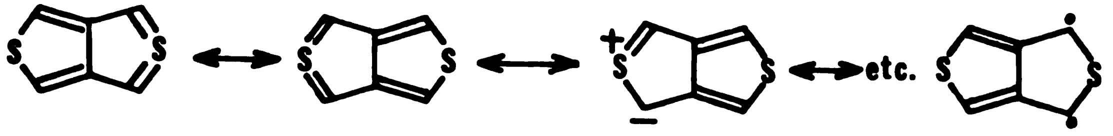
benzenes,[51] if we exclude nonclassical forms which use d orbitals of X or dipolar forms of these compounds. For example it is possible that structures of the type 86a may contribute to the overall structure of 86 (81, X=S), because in the structure 86a the endocyclic



86 **86a**

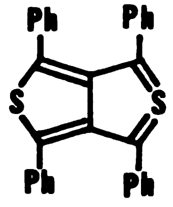
aromaticity of the six-membered ring is restored. Actually a few examples of such nonclassical condensed thiophenes are known.[52]

Thieno[3,4-c]thiophene 87 has a nonclassical structure in which both sulfur atoms have partial tetracovalent character. Without sulfur d-orbital participation the molecule must either have the character of a thiocarbonyl ylid 87a or a diradical 87b.



87 **87a** **87b**

Tetraphenylthieno[3,4-c]thiophene **88** was the first example of an isolable nonclassical condensed thiophene.[53] It was found to be



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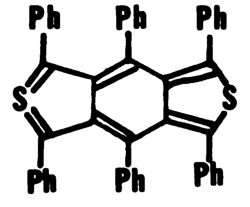

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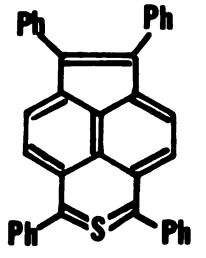
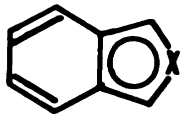


90

nonpolar and its benzene solution gave no ESR signal.[54] The structure was confirmed by an X-ray analysis.[55] Other similar examples, such as **89**[56] and **90**[57] have been reported.

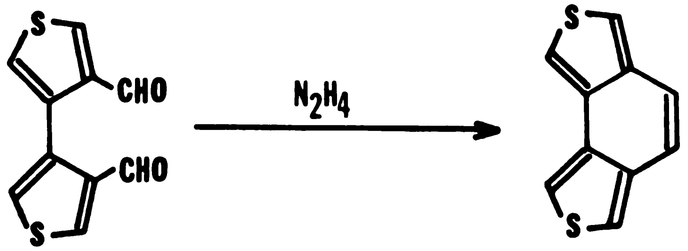
Orthoquinoidal heterocycles of the type **84** show extreme chemical reactivity, particularly in cycloaddition reactions which restore the endocyclic aromaticity of the six-membered ring.[58] The most recent view of their electronic structure suggests an aromatic heterocyclic ring with a relatively noninteracting butadiene moiety **84a**.[59]



84a

It seemed likely that, if the number of exocyclic double bonds were increased (as in 85 or 81), the additional heteroaromatic rings would diminish reactivity and restore overall aromaticity to the structure.

Two examples of compounds of the type 85 have been reported. Benzo[1,2-c:3,4-c']dithiophene 91 (85, X=S) was obtained from 4,4'-diformyl-3,3'-bithienyl by reaction with hydrazine.[60] 7H-Pyrrolo-[3,4-e]isoindole 93 (85, X=NH) was prepared from 92 by 1,2-elimination of methanesulfinic acid followed by spontaneous tautomerization of the product.[61] This synthesis was reported after the present work was well in progress. Both compounds were remarkably stable compared to their homologues of the type 84. Compounds of the type 81 were unknown until the present work. A synthesis of 94 has recently been proposed but not yet realized.[62] It is the purpose of this part of the thesis to describe the synthesis and properties of benzo[1,2-c:3,4-c':5,6-c"]trithiophene 86, the first example of such a molecule.



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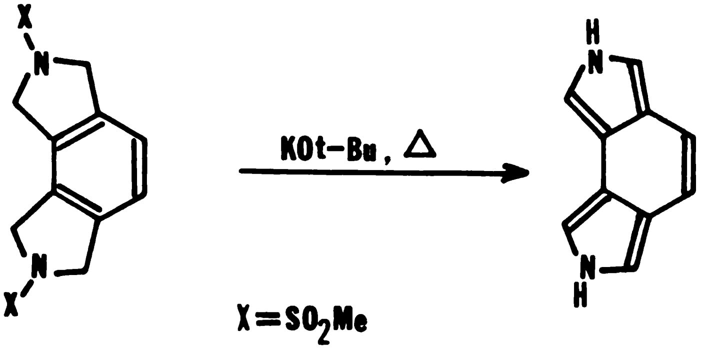

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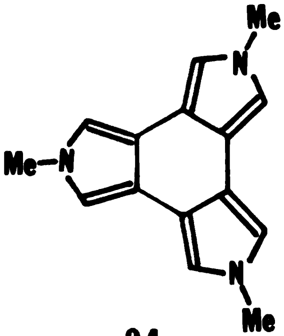
93



94

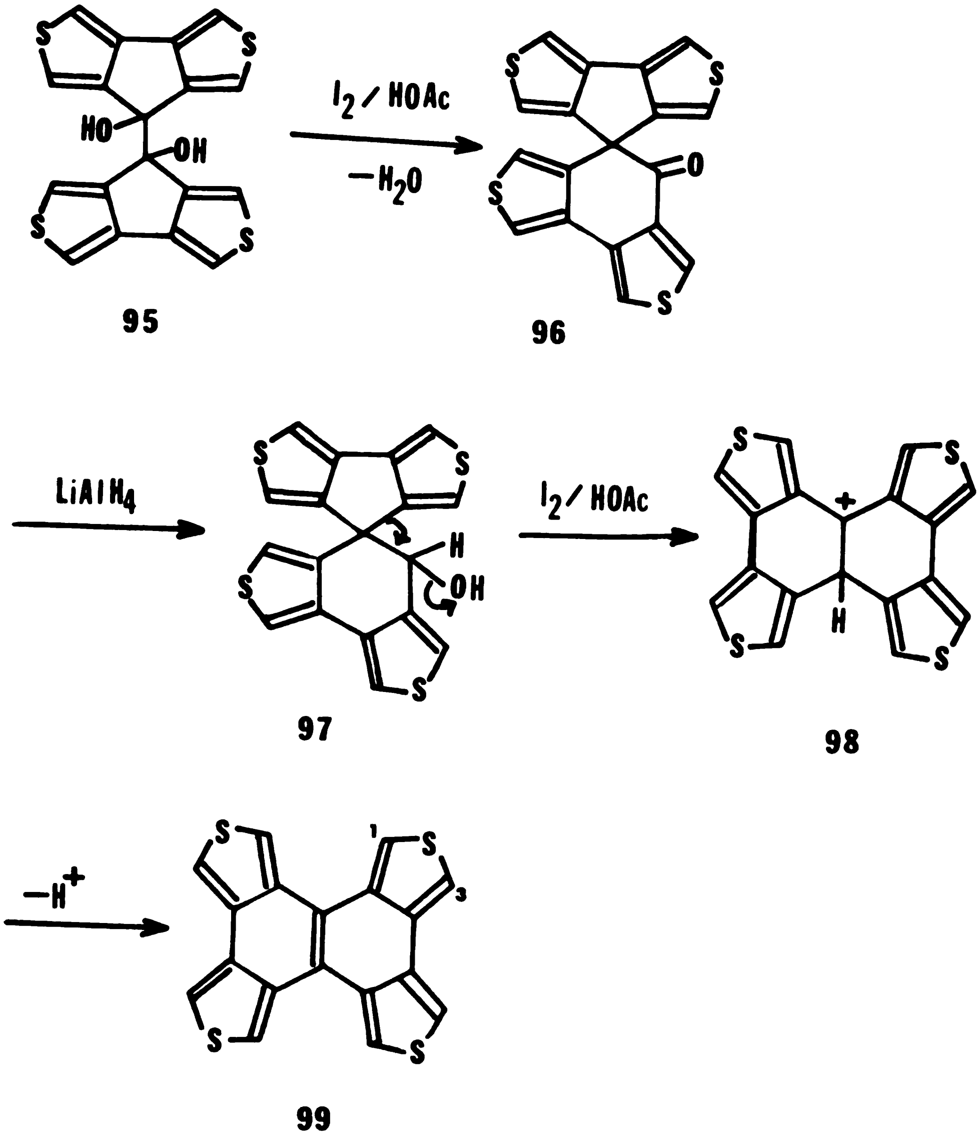
RESULTS AND DISCUSSION

1. Synthesis of Benzo[1,2-c:3,4-c':5,6-c"]trithiophene, a Tristhiahexaradialene (**86**)

Tristhiahexaradialene **86** is a thiophene analogue of triphenylene. The syntheses of thiophene analogues of polycyclic arenes reported in the literature fall into two categories. One involves initial formation of a thiophene derivative followed by cyclization to a polycyclic system. The synthesis of benzodithiophene **91** is an example of this type.

The synthesis of naphthotetrathiophene **99**, a thiophene analogue of dibenzo[g,p]chrysene also falls into this category.[63] The diol **95**, when heated in boiling acetic acid with a catalytic amount of iodine, underwent pinacol rearrangement to give ketone **96**, which was reduced to the alcohol **97**. With **97** a similar rearrangement was repeated to give **99**. The starting diol **95** was prepared by a pinacol reduction of cyclopentadithiophenone **100** which is a thiophene analogue of fluorenone. The synthesis of **100**,[64] which is summarized in Scheme III, also belongs to the same category. Thiophene analogues of fluorenes were prepared similarly.[65]

However, the application of this straightforward coupling method to the synthesis of benzotrithiophene **86**, as shown in Scheme IV, may not be fruitful, because treatment of **101** with n-butyllithium,



95

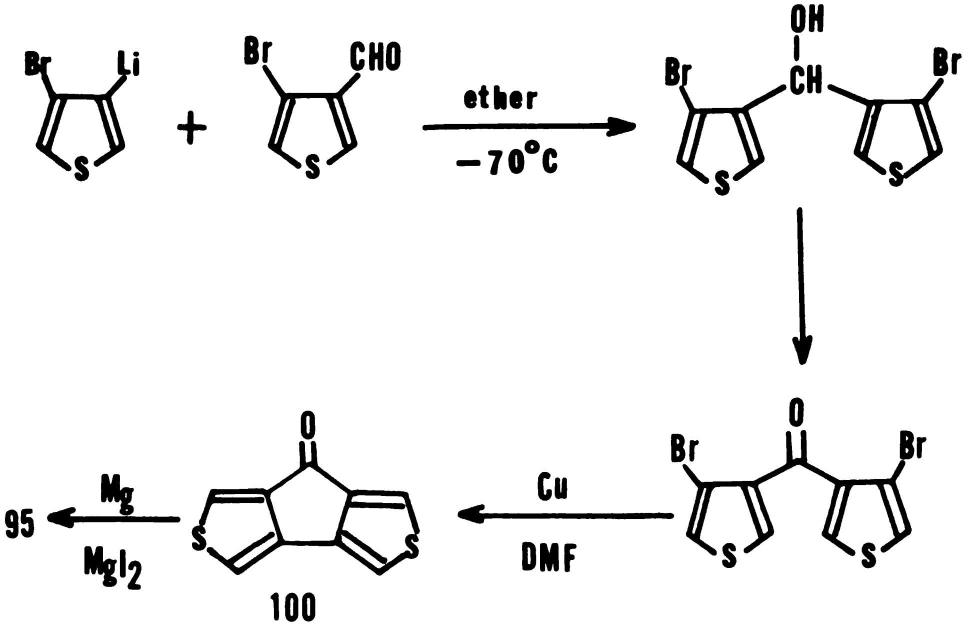
96

97

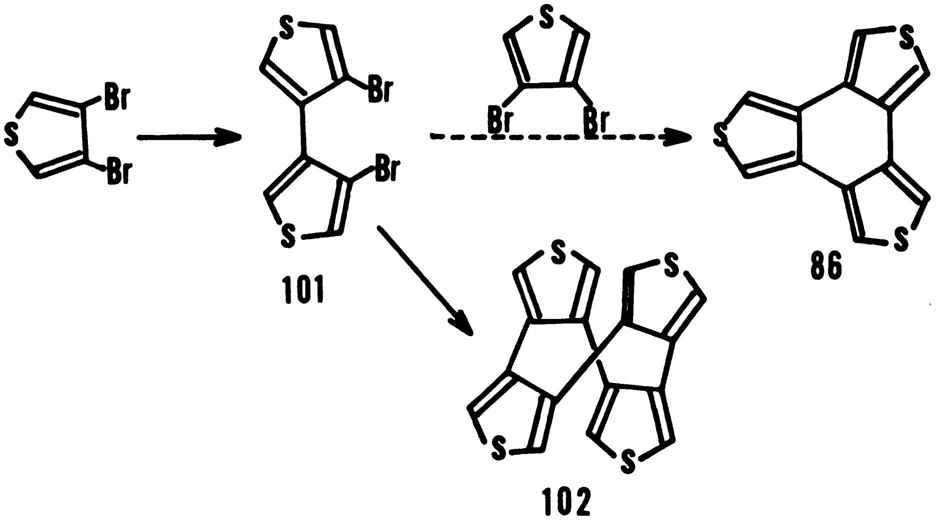
98

99

Scheme III

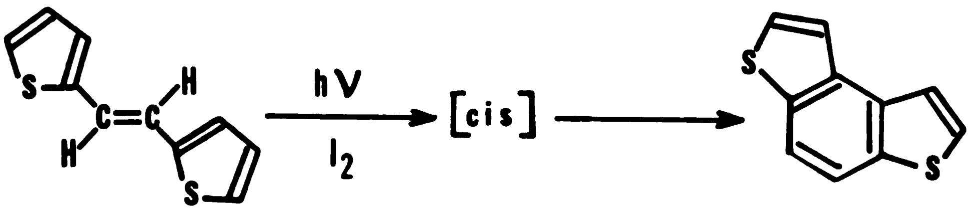


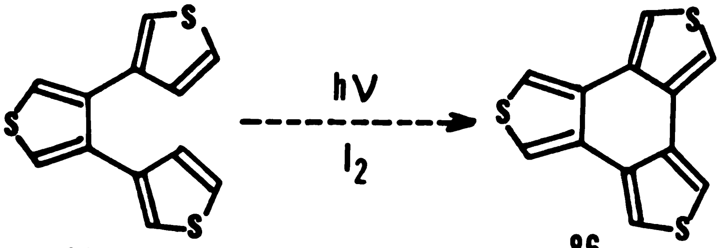
Scheme IV



then with $CuCl_2$, afforded the thiophene tetramer 102.[66] Therefore some complexities can be expected in the reaction of 101 with 3,4-dibromothiophene under similar conditions.

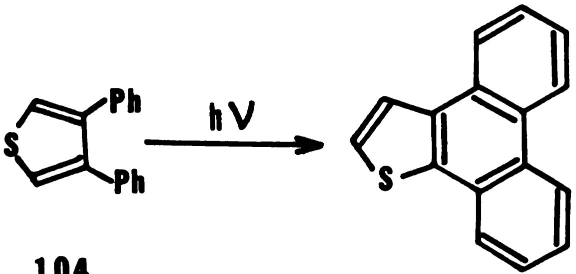
It is well known that cis-stilbene in the presence of an oxidizing agent undergoes a photochemically induced cyclization to yield phenanthrene.[67] This photochemical cyclization reaction was used to prepare the thiophene analogue of phenanthrene.[68] A similar photochemical reaction can be envisioned to prepare 86 from 103, but the result of irradiation of 104, in which 105 was obtained instead of 106,[69] suggests that an analogous isomerization would occur.





103

86



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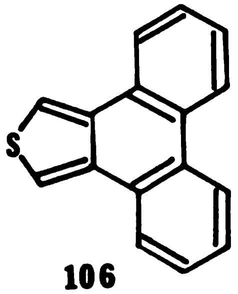
105



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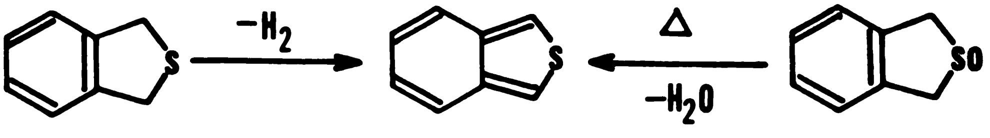
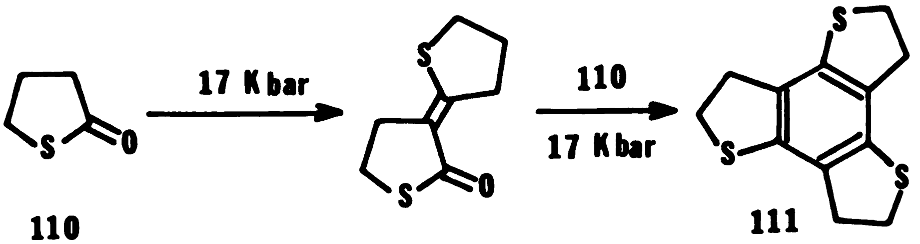
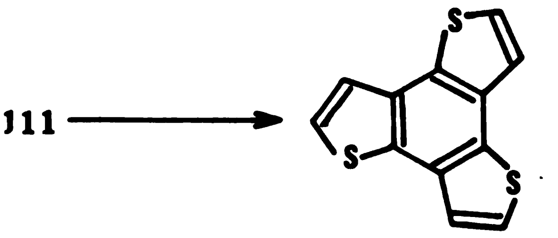
The other strategy for making thiophene analogues of polycyclic arenes involves the formation of thiophene rings in the final step. Benzo[c]thiophene 108 was originally prepared from sulfide 107 by catalytic dehydrogenation at high temperature.[70] Later, Cava reported



107 **108** **109**

that the dehydration of sulfoxide 109 yielded 108 in a better yield.[71] Since benzotrithiophene 86 was expected to be more aromatic than benzo[c]thiophene 108, dehydrogenation or dehydration of a proper precursor seemed to be a reasonable route to 86. Actually an isomeric benzotrithiophene 112 was prepared from the reaction of tris-sulfide

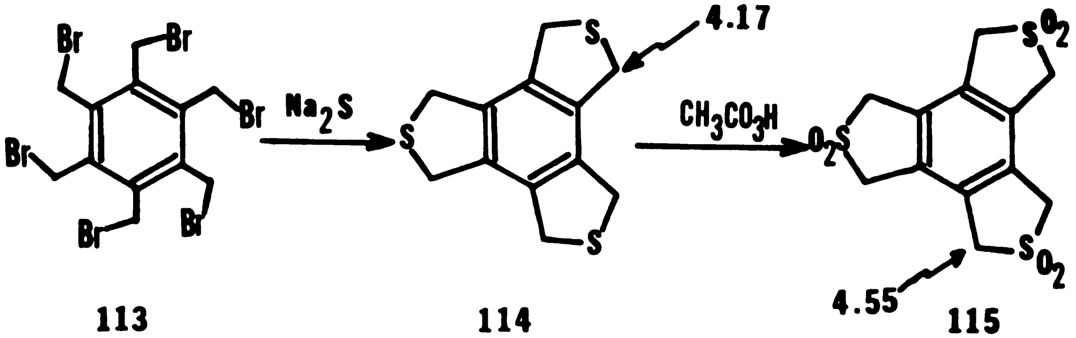




112

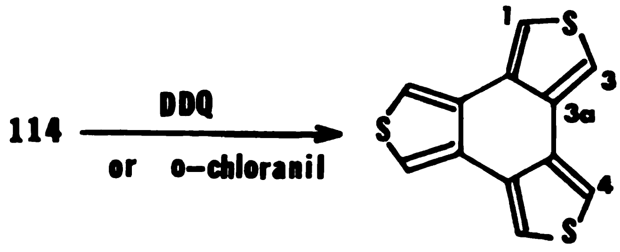
111 with chloranil.[72] The tris-sulfide **111** was obtained from the condensation of three molecules of thiolactone **110** under very high pressure.

Treatment of hexakis(bromomethyl)benzene **113**[73] with $Na_2S \cdot 9H_2O$ in a mixture of ethanol, THF and water at reflux gave (80-90%) the tris-sulfide **114** as a pale yellow solid which, owing to its low solubility, was not purified. The NMR spectrum of **114** in DMSO-d_6 showed only a singlet at δ4.17. Oxidation of **114** with peracetic acid at room temperature for 14 h gave the corresponding tris-sulfone **115** whose NMR spectrum in DMSO-d_6 showed a singlet at δ4.55. The mass spectrum of the sulfone showed a molecular ion peak at m/e 348 and fragment peaks at m/e 284 (M^+-SO_2), 220 (M^+-2SO_2), 156 (M^+-3SO_2) and 64 (SO_2^+). The mass spectrum suggests that **115** may serve, under appropriate conditions, as a precursor of hexaradialene **74**. This prediction was recently verified by Boekelheide and his coworkers.[46]



113 **114** **115**

Dehydrogenation of tris-sulfide **114** with either DDQ or o-chloranil in refluxing chlorobenzene afforded benzotrithiophene **86** as colorless needles. The NMR spectrum of **86** showed a singlet at δ7.52 in $CDCl_3$, somewhat downfield from that of the C-2 proton in thiophene



86

(δ7.19).[74] This downfield shift is possibly due to deshielding by the adjacent thiophene rings. A similar downfield shift of thiophene ring protons was observed for naphthotetrathiophene 99 (δ8.77, type H-1; δ8.42, type H-3).[63] The ^{13}C NMR spectrum of 86 consisted of two peaks, at δ117.4 and 132.4 corresponding to C-1-and C-3a-type carbons respectively. These shifts may be compared with those of thiophene (C-2,124.9;C-3,126.7)[75] and triphenylene (C-1,123.7;C-2, 127.6;C-4a,130.2).[76] A large proton chemical shift difference (0.9 ppm) between 86 and 99, and the upfield shift of C-1-type carbons of 86 compared to those of thiophene will be discussed later.

2. Physical and Chemical Properties of 86

Benzotrithiophene 86 is a stable crystalline compound. Its mass spectrum showed a molecular ion peak at m/e 245.96416 (calculated for $C_{12}H_6S_3$ 245.96318) as a base peak. The IR spectrum showed an absorption at 3100 cm^{-1} (heteroaromatic C-H). The ultraviolet spectrum of 86 is similar to that of triphenylene (Figure 1).[77] The longest wavelength absorption (320 nm) occurs at appreciably

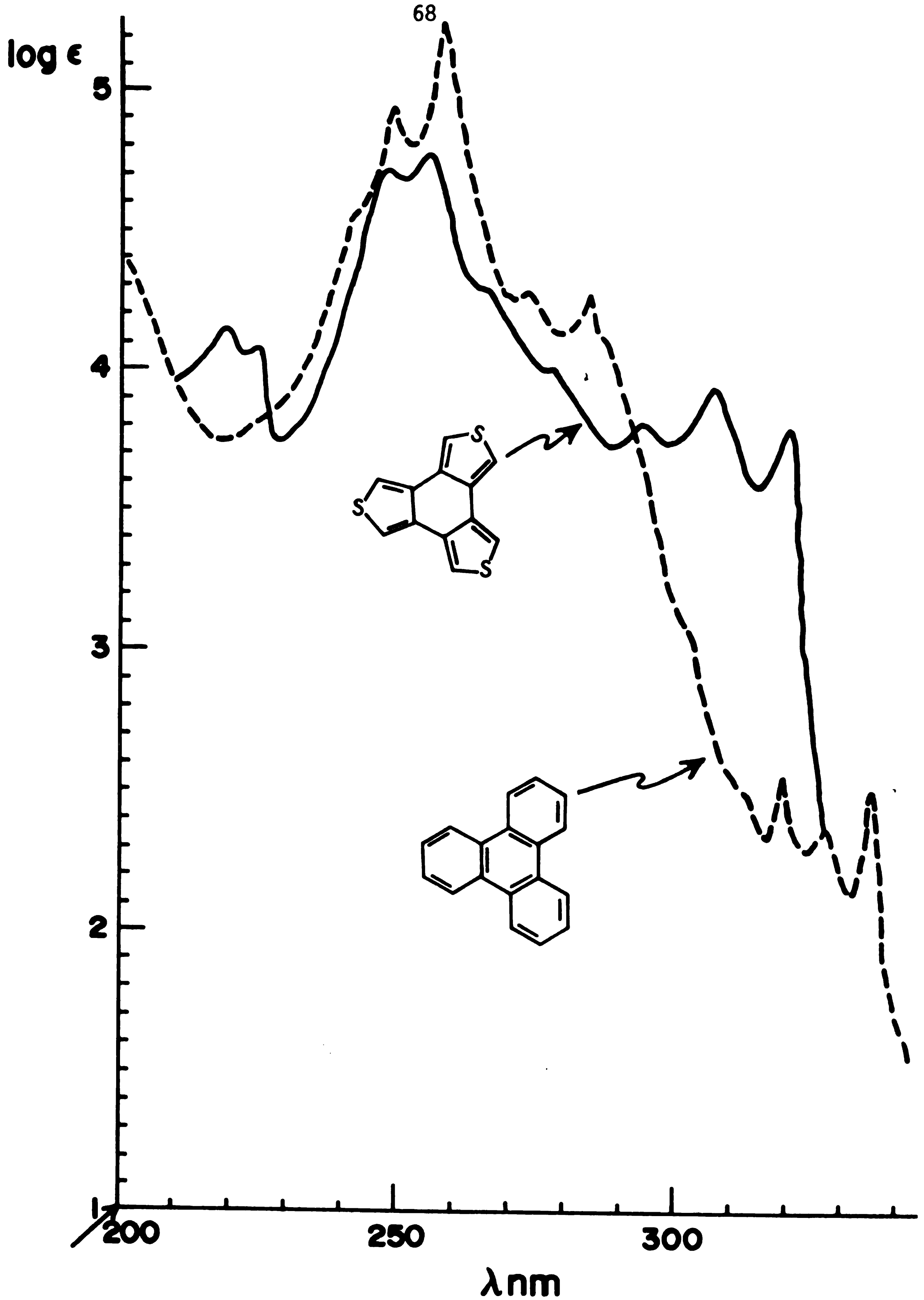
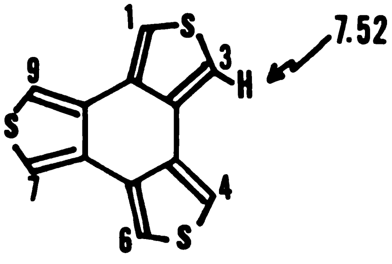


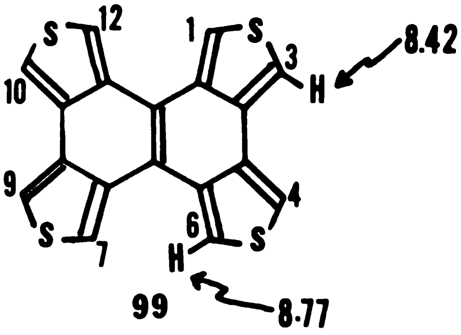
Figure 1. uv spectra of 86 (—) and triphenylene (---).

lower energy than that of the tris-benzo[b]isomer **112** (286 nm).[72] A similar but even larger difference is observed for benzo[c]thiophene (343 nm)[70] and benzo[b]thiophene (298 nm).[78]

The ^1H NMR spectrum of **86** was compared with that of **99** (<u>vide supra</u>). The large downfield shift of the C-3 proton in **99** from **86** is possibly due to the steric effect of neighboring thiophene rings. The buttressing effect between C-1 and C-12 protons would cause the compression of C-3 and C-4 protons which would shift these protons downfield.

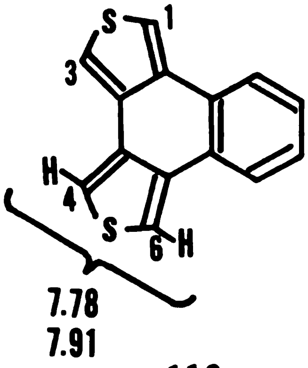


86



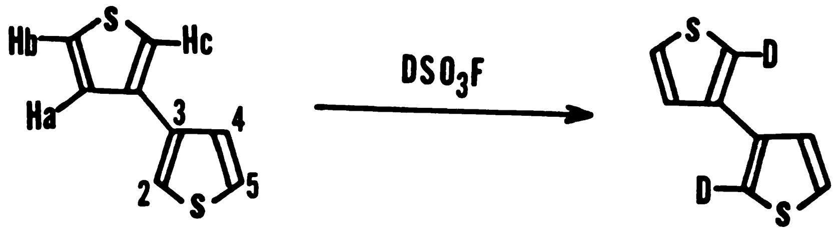
99

In order to examine the degree of this steric effect, the chemical shifts of **99** were compared with those of **116**. The difference between the C-3 protons in **99** and **116** (0.51-0.64 ppm) can be attributed to the buttressing effect of the C-1 and C-12 protons in **99**.



116

The ^{13}C NMR spectrum of 86 showed an upfield shift of the C-1-type carbons (*vide supra*). The shift can be explained by the β-effect of C-9a-type carbons. For the comparison, 3,3'-bithiophene 117 and its dideuterated derivative 117d were prepared and their ^{13}C NMR spectra were measured. The position of deuteration of 117 with deuterated fluorosulfonic acid was confirmed by studying the ^{1}H NMR spectra of 117 and 117d. The ^{1}H NMR spectrum of 117 (DMSO-d_6) at 180 MHz showed three sets of doublets of doublets centered at δ7.52 (J_{ab}=4.9 Hz, J_{ac}=1.3 Hz), 7.59 (J_{ab}=4.9 Hz, J_{bc}=2.9 Hz) and 7.77 (J_{ac}=1.3 Hz, J_{bc}=2.9 Hz) due to H_a, H_b and H_c respectively. The assignment of protons was made based on a comparison of the coupling constants with those of thiophene ($J_{2,3}$=4.7 Hz, $J_{2,5}$=2.9 Hz, $J_{2,4}$=1.0 Hz).[79] The NMR spectrum of 117d showed that the peaks centered at δ7.77 were reduced in area, thus proving that deuterium exchange occurred exclusively at the C-2 position.[80]



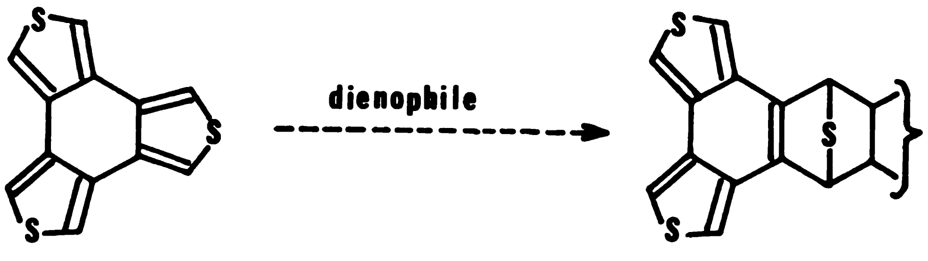
117

117d

Comparison of the ^{13}C NMR spectrum of 117 and 117d made it possible to assign the high field peak at δ119.7 to C-2-type carbons, because it was the only peak which was reduced in intensity in 117d compared to 117. The remaining peaks were at δ126.0, 126.3 and 137.2. This proved that the connection of two thiophene rings at the C-3 positions shifts the C-2-type carbons upfield probably because of the β-effect of the C-3 carbon in the other thiophene ring.

Thus the downfield shift of protons and the upfield shift of C-1-type carbons of 86 compared to those of thiophene were caused by the connection of thiophene rings. However no evidence that these shifts were caused by conjugation around the central six membered ring was obtained.

In contrast to 84, benzotrithiophene 86 did not readily add dienophiles (*i.e.*, dimethyl acetylenedicarboxylate, benzyne, singlet oxygen). This is probably because the aromaticity of the product from 84 is greater than that of the product from 86. Cycloaddition of 86 with a dienophile gives a benzodithiophene derivative 118 while 84 with a dienophile gives a benzene derivative. However, the unreactivity of 86 toward dienophiles may also indicate that the overall aromaticity is enhanced as the number of exocyclic double bonds is increased from 84 to 86.



86

118

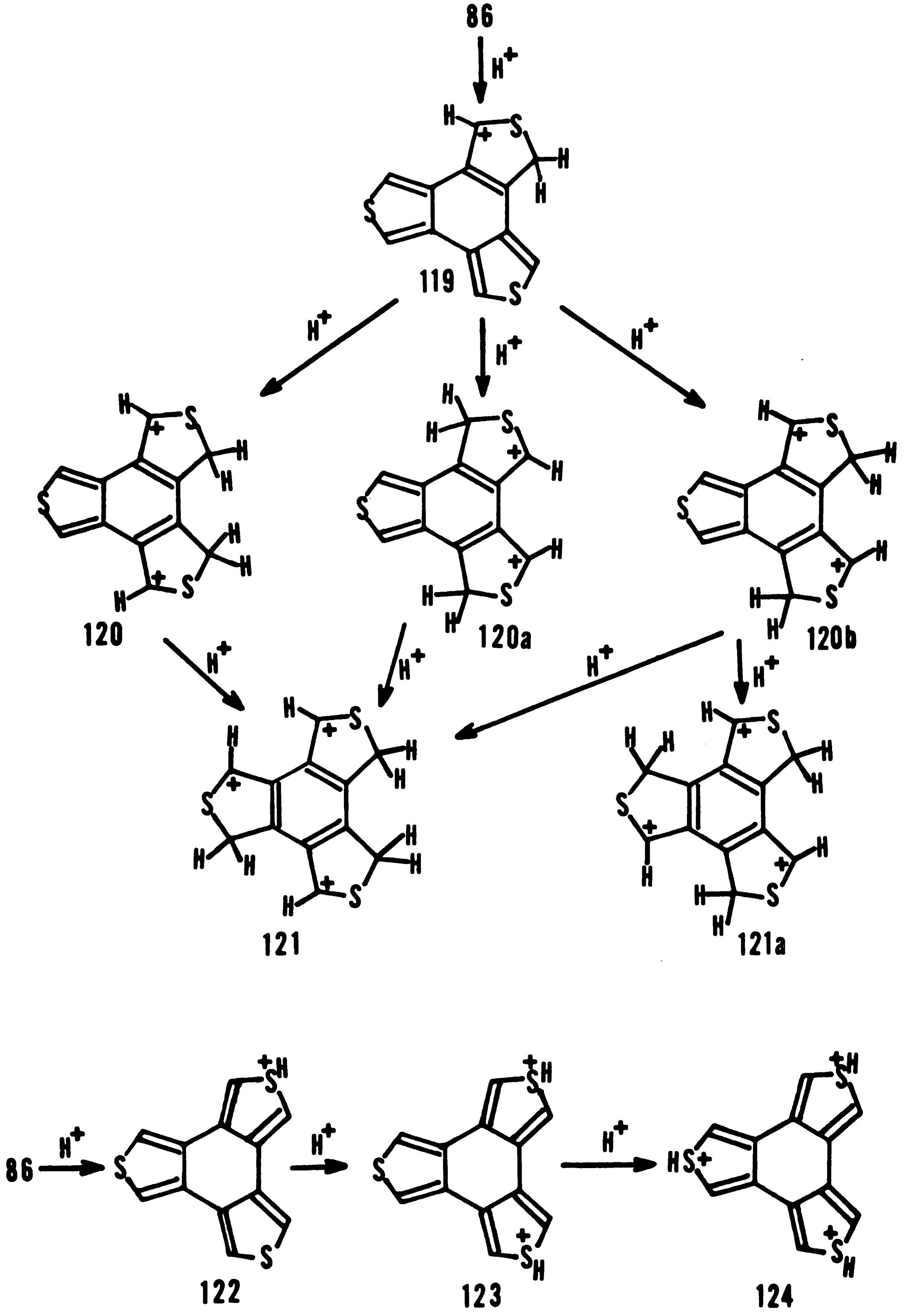
Compound 86 does form intensely colored, air- and moisture-stable crystalline 1:1 charge-transfer (CT) complexes with TCNE, DDQ, TCNQ (all dark blue, CT band near 610 nm), and chloranil (dark red, CT band at 527 nm). The CT bands occurred at about 50 nm longer wavelength than for those of triphenylene.[81] Oxidation of 86 with $SbCl_5$ in methylene chloride gave a rather stable blue radical cation.[82]

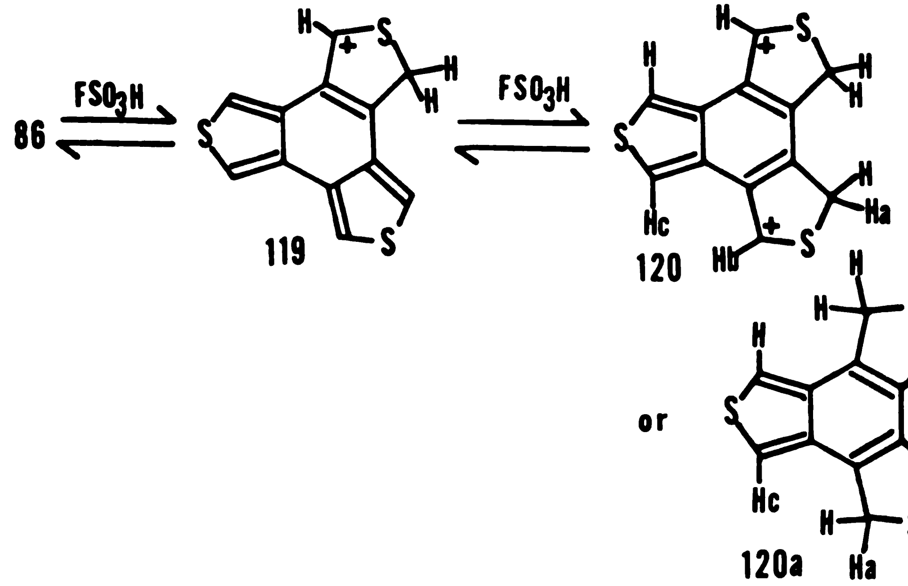
3. Protonation of 86

It is known that electrophilic substitution of thiophene occurs preferentially at the 2-position.[83] The NMR observation of protonated thiophenes showed that protonation occurred exclusively at the 2-position.[84] In benzotrithiophene, two types of protonation are possible: (a) at the sulfur atom; (b) at the C-1-type carbon. For each type of protonation, mono-, di-, and trications are possible. Every cation that can be formed from 86 by protonation at either carbon or sulfur but not both is summarized in Scheme V.

In FSO_3H-SO_2ClF at -20°C to -78°C compound 86 gave a single species. The ^1H NMR spectrum (-20°C) had peaks at δ5.90(d,4H,J=1.5 Hz), 9.34 (s,2H) and 11.45(t,2H,J=1.5 Hz). The doublet at δ5.90 became a sharp singlet by irradiation of the triplet at δ11.45. For a possible structure of this species, all structures but 120 and 120a were ruled out on symmetry grounds. The doublet, singlet, and triplet were assigned to H_a, H_c, and H_b respectively (p. 74). The chemical shifts of H_a and H_b agree well with those obtained on protonation of thiophene with HF-BF_3 at C-2 (δ5.40(H_2) and 11.27(H_5)).

Scheme V





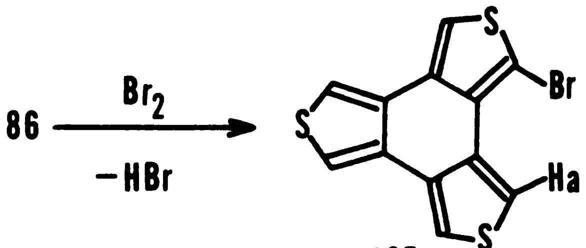
With FSO_3D, exchange was rapid at H_a (δ5.90 peak nearly absent in 5 min, δ11.45 peak a singlet; quench gave **86-d$_2$**) but extensive at all positions after 8 h (quench gave mainly **86-d$_5$** and **86-d$_6$**). Although the monoprotonated species **119** could not be detected, rapid exchange of two protons and slow exchange of the remaining protons can best rationalized by assuming a rapid equilibrium between **120** or **120a** and **119** but slow deprotonation of **119** in the strongly acidic medium.

A unique choice between the diprotonated species was not possible. Neither the "meta" dication **120b** nor the trication **121** was observed. It seems plausible to assume that monocation **119** can only be protonated to give the "para" dication **120**, in which the largest charge separation can be attained, and that **120** is not further protonated to give trication **121** because two positive charges would be located "ortho" each other. However the "ortho" dication **120a** cannot be ruled out completely. One might argue that 119 is protonated to give 120a instead of 120 to avoid steric repulsion between the two adjacent sets of methylene protons, and the same reason could explain the absence of 121.

4. Bromination of 86

Treatment of 86 with one equivalent of Br_2 in CCl_4 at room temperature gave a monobromo derivative contaminated with a small amount of a dibromide. The ^1H NMR spectrum of the monobromide 125 showed a doublet at δ8.37 due to H_a, and a multiplet at δ7.47 due to the remaining protons.

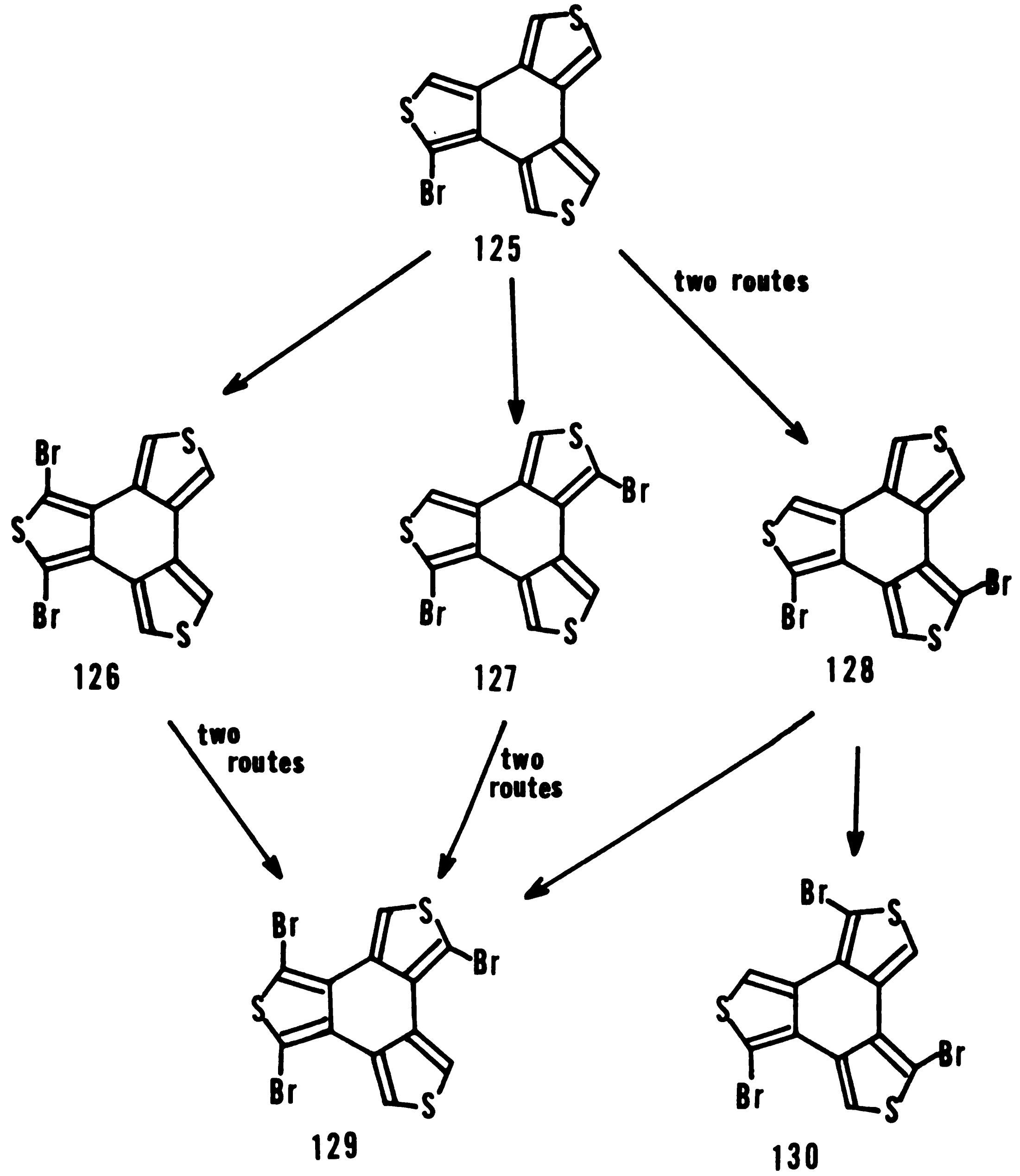
Similarly di- and tribromo derivatives were obtained, depending on the Br_2/86 mole ratio. Isomer separation was difficult, but NMR analysis showed that three dibromo and two tribromo compounds were formed, these being the isomers possible without having two sterically interfering bromines in the same "wedge" of the structure. These possibilities are summarized in Scheme VI.



125

The isomer ratios were statistical. For example, treatment

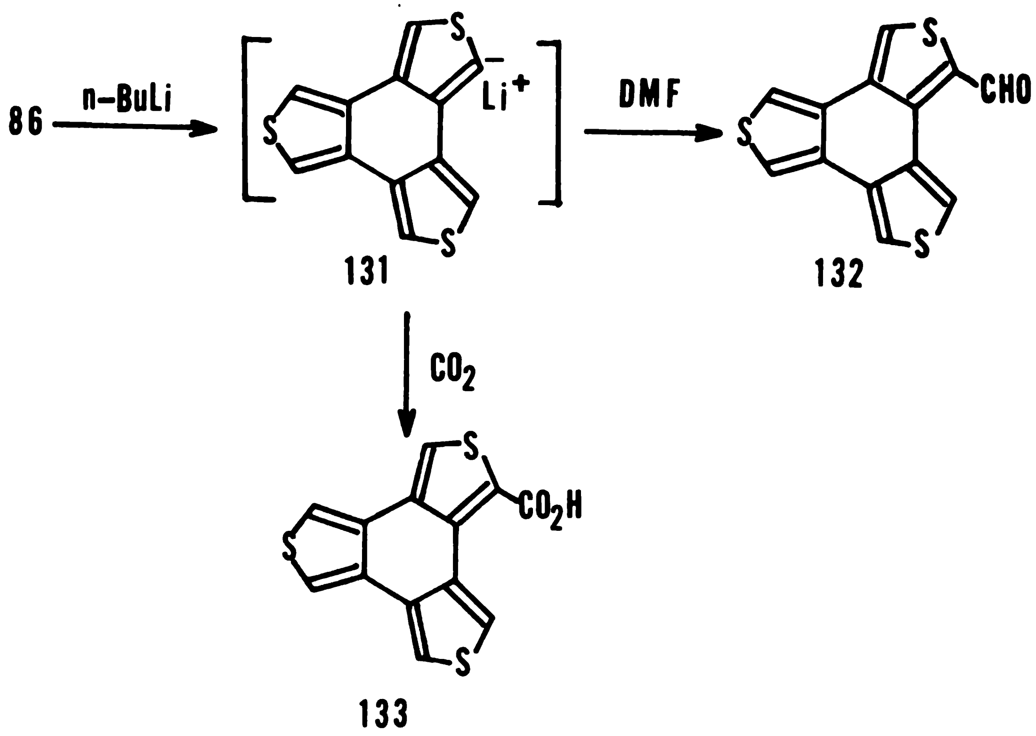
Scheme VI



of 86 with three equivalents of Br_2 afforded a mixture of tribromo derivatives. The ^1H NMR spectrum of the mixture at 60 MHz showed two singlets with equal areas, but at 180 MHz there were two singlets at $\delta 8.57$ and 8.58, and two sets of doublets at $\delta 8.62$ and 8.65, with equal areas for each signal. The only way to explain the splitting pattern and the integration of the spectrum is that both doublets and one of the singlets are due to 129 and the other singlet is due to the isomer 130 with a three to one ratio of 129 to 130. This three to one ratio agree well with the statistical ratio for the formation of 129 and 130, as shown in Scheme VI.

5. Metalation of 86 with Butyllithium

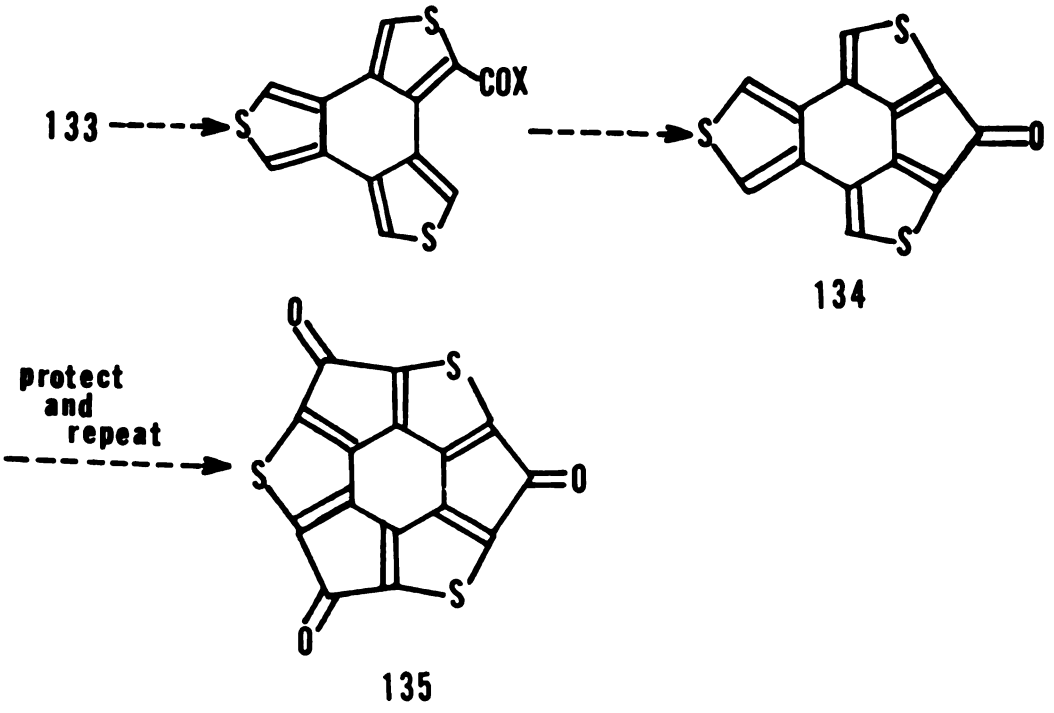
Metalation of 86 was also possible. For example, treatment with excess butyllithium in ether at -25°C followed by addition of



dimethylformamide gave the yellow aldehyde 132. The product was proved to be the monoaldehyde by its ^{1}H NMR and mass spectra. The NMR spectrum consisted of two singlets at δ7.97 (1H,C-3 proton) and 10.13(1H, aldehyde), one doublet at δ8.72(1H,J=2.5 Hz,C-9 proton), and a multiplet at δ7.58(3H,C-4,-6,-7 protons). The IR spectrum showed a conjugated carbonyl absorption at 1645 cm^{-1}.

It was of interest to investigate the metalation of 86, because the carboxylic acid 133 which can be obtained from 131 with CO_2 could serve as a useful starting material to prepare the interesting compound 135 in which the remaining "wedges" in 86 are closed.

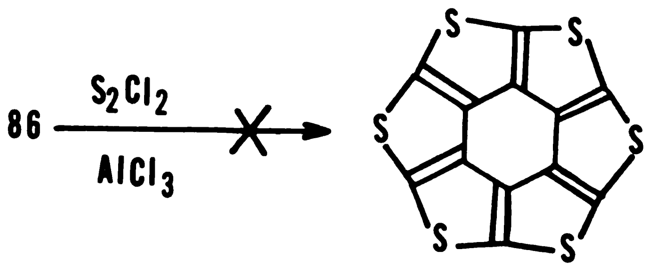
Scheme VII



Treatment of 86 with butyllithium followed by passing CO_2 gas though the reaction mixture afforded the monocarboxylic acid 133. Because of the low solubility of 133, its NMR spectrum could not be measured. However the mass spectrum showed a molecular ion peak at m/e 290 and the IR spectrum showed chracteristic absorptions for a carboxylic acid (3600-2400 and 1670 cm^{-1}).

The preparation of the acid chloride of 133 was not successful. The reaction of 133 with thionyl chloride afforded a yellow, unidentified product. The NMR spectrum could not be measured owing to low solubility. The IR spectrum showed a carbonyl absorption (1720 cm^{-1}) and a heteroaromatic C-H absorption (3100 cm^{-1}). The absorption of the carboxylic acid group disappeared completely. The mass spectrum (m/e 386) and the IR spectrum (1720 cm^{-1}) were not suitable for either the acid chloride or the conjugated cyclic ketone 134.

The reaction of 86 with sulfur monochloride and aluminum chloride to give the similar compound 136 was also unsuccessful.



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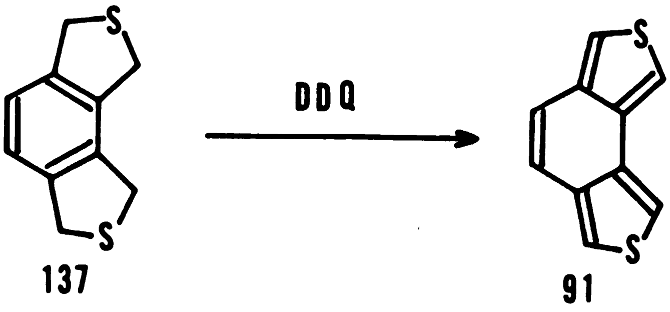
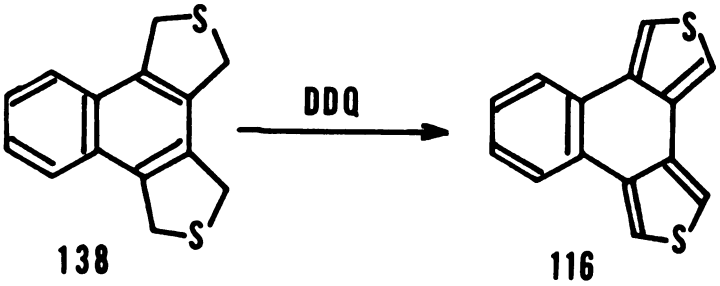
6. Application of the Mild Dehydrogenation Method to the Synthesis of 91

The same mild dehydrogenation used to synthesize 86 was successful for the preparation of benzodithiophene 91. Treatment of 137 with DDQ afforded 91 in 35% yield. The precursor 137 was prepared in two steps (46%) from prehnitene by an improved modification of the literature procedures.[85] The overall yield (three steps) of the previous synthesis of 91 was 4.2% from 3,4-dibromothiophene, which itself must be synthesized from thiophene (two steps, 42%).[60]



137 91

This simple mild dehydrogenation was also successful for the synthesis of naphthodithiophene 116 from 138.[86]



138 116

In conclusion, benzo[1,2-c:3,4-c':5,6-c"]trithiophene, a tristhiahexaradialene, is a new type of heteroaromatic compound. It is clear that, although exocyclic benzenes of type 84 are highly reactive toward cycloaddition, those of type 85 and 81 are much more like aromatic compounds in their reactivity.

EXPERIMENTAL

1. General Procedures (see Part I of Thesis).

2. 1,3,4,6,7,9-Hexahydrobenzo[1,2-c:3,4-c':5,6-c"]trithiophene (114)

A solution of 15 g of $Na_2S \cdot 9H_2O$ in 40 mL of water was diluted with 800 mL of ethanol and 400 mL of THF. Then hexakis(bromomethyl) benzene 113 (6.4 g) was added to the solution and the mixture was heated at reflux for 19 h with vigorous stirring. The mixture was cooled to room temperature and the resulting light yellow precipitate was separated by suction filtration. The solids were washed well with water, then with ethanol, and dried under vacuum. The crude 114 (2.4 g) thus obtained was subjected to further reaction without purification. However the purification of 114 was possible by sublimation under reduced pressure, mp 250-256°C dec. IR (nujol) 1195(m), 875(m), 725 cm^{-1}(s); ^1H NMR (DMSO-d_6) δ4.17(s); high resolution mass spectrum, calculated for $C_{12}H_{12}S_3$m/e 252.01013, observed m/e 252.01065.

3. 1,3,4,6,7,9-Hexahydrobenzo[1,2-c:3,4-c':5,6-c"]trithiophene 2,2,5,5,8,8-hexaoxide (115)

A mixture of 114 (2.0 g) and 50 mL of peracetic acid was stirred for 14 h at room temperature. The colorless precipitate was separated by centrifugation. The solid was repeatedly washed with water and separated (centrifuge) until the peracetic acid was removed, then dried under vacuum to give crude 115 (1.5 g), mp > 320°C. IR (nujol) 1315(s), 1145(s), 1125(s), 1105 cm^{-1}(s); ^1H NMR (DMSO-d_6) δ4.55(s); mass spectrum, m/e (rel. intensity) 348(M^+, trivial), 284(M^+-SO_2,25), 220(M^+-$2SO_2$,42), 156(M^+-$3SO_2$,85), 64(SO_2^+,100); high resolution mass spectrum, calculated for $C_{12}H_{12}S_3O_6$ m/e 347.97961, observed m/e 347.98022.

4. Benzo[1,2-c:3,4-c':5,6-c"]trithiophene (86)

To a solution of o-chloranil (1.6 g) in 250 mL of chlorobenzene, 0.5 g of 114 was added and the mixture was heated at reflux for 4 h with vigorous stirring. After the solution was cooled to room temperature, the brown precipitate was removed and the solvent was evaporated from the filtrate under vacuum. The brown residue was dissolved in benzene and chromatographed on basic alumina with benzene as an eluent. Colorless needles of 86 (225 mg, 46%) were obtained from the first fraction, mp 236-238°C. IR (nujol) 3100(m), 870(m), 855(s), 850(s), 780 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ7.52(s); ^{13}C NMR ($CDCl_3$) 117.4, 132.4 ppm from TMS; uv (EtOH) λ_{max} 320 nm (ε=6210), 306(8730), 294(6420), 277(sh,10050), 265(sh,19680), 256(59250), 248(50840); mass spectrum m/e (rel. intensity) 246(100), 201(13), 170(12), 123(13); high resolution mass spectrum, calculated for $C_{12}H_6S_3$ m/e 245.96318, observed m/e 245.96416. DDQ (1.35 g) could be used in place of o-chloranil to give 86 in a similar yield.

5. 3,3'-Bithiophene (118)

To a solution of 3-bromothiophene (5.0 g) in 50 mL dry ether, 17 mL of 2.2 M n-BuLi in hexane was added at -78°C under nitrogen atmosphere. The mixture was stirred for 15 min. At the same temperature dry $CuCl_2$ (5.2 g) was added to the solution, and the mixture was stirred for an additional 2 h. After the mixture was warmed to room temperature, it was stirred over night. Then the mixture was cooled to 0°C and 50 mL of 4N HCl was added with vigorous stirring. The ether layer was separated and washed with 4N HCl and water. After it was dried over $MgSO_4$ the solvent was removed to give light brown solids. The solids were purified on a short alumina column with $CHCl_3$ as the eluent to give 118 (1.6 g), mp 128-130°C (lit.[87] 132°C). ^{1}H NMR (DMSO-d_6) δ7.52(dd,2H,J_{ab}=4.9 Hz, J_{ac}=1.3 Hz), 7.59(dd,2H,J_{ab}=4.9 Hz,J_{bc}=2.9 Hz), 7.77(dd,2H,J_{ac}= 1.3 Hz,J_{bc}=2.9 Hz); ^{13}C NMR ($CDCl_3$) 119.7, 126.0, 126.3, 137.2 ppm from TMS,

6. Deuteration of 118

In a 50-mL round-bottomed flask was placed 400 mg of 118, and about 20 mL of SO_2ClF was condensed in the flask at -78°C under a N_2 atmosphere. Then approximately 1 mL of DSO_3F was added and the mixture was stirred vigorously to give an orange solution of carbonium ion. The stirring was continued for 5 h at -78°C under a N_2 atmosphere. The solution was poured into aqueous Na_2CO_3 with vigorous stirring. The mixture was extracted with ether and the ether layer was washed with water and dried ($MgSO_4$). Evaporation of the ether gave **118-d$_2$** as a colorless solid (328 mg). IR (nujol) 2310 cm^{-1}(m, heteroaromatic C-D).

7. C.T. complex of **86**

To a solution of **86** (100 mg) in 20 mL of benzene, 52 mg of TCNE in 10 mL of benzene was added with stirring. Evaporation of the solvent left a dark blue solid. The solid was recrystallized from $CHCl_3$ to give dark blue rods (120 mg), mp 183-190°C (dec.). When the solid was heated to about 160°C it changed color from blue to white and started melting at 183°C with the color changing to blue again. The C.T. complex of **86** with TCNE thus obtained showed IR and mass spectra corresponding to a mixture of **86** and TCNE. ^1H NMR ($CDCl_3$) δ7.53(s); C.T. band ($CHCl_3$) λ_{max} 608 nm (ε=90).

Similarly C.T. complexes of **86** with DDQ, TCNQ and chloranil were prepared. The complex with DDQ melted at 255-260°C with decomposition. When it was heated to about 200°C, the color was changed from blue-black to brown. The complex with TCNQ melted at 239-240°C. It showed a C.T. band at 612 nm (ε=190). The complex with chloranil melted at 195-200°C with decomposition. When it was heated to about 115°C, the color was changed from red to brown. The complex showed a C.T. band at 527 nm (60).

8. Protonation of 86

About 30 mg of 86 and a small amount of tetramethylammonium tetrafluoroborate were placed in a 10 mm NMR tube into which about 2.5 mL SO_2ClF was condensed at -78°C. To the mixture, 1 mL of FSO_3H was added and the contents were mixed using a "super mixer" (Matheson Scientific, cat. No. 601-0005) to give a dark red solution. The ^1H NMR spectrum of the carbonium ion thus prepared was obtained at 180 MHz using $(CH_3)_4NBF_4$ (δ3.13) as an internal standard. For a description of the spectrum, see text.

9. Deuteration of 86

Deuterated 86 was obtained by the same method which was used for deuteration of 118. The degree of deuteration was checked by mass spectrometry. When the carbonium ion solution was quenched 5 min after addition of acid, 86-d_2 was obtained. Benzotrithiophene recovered after 8 h was mainly penta- and hexadeuterated. IR (nujol) 2300 cm^{-1}(m, heteroaromatic C-D).

10. Bromination of 86

To a solution of 86 (50 mg) in 8 mL of CCl_4 three equivalents of Br_2 in CCl_4 were added dropwise at room temperature with stirring. The mixture was stirred for 30 min and the solvent was removed under vacuum to give colorless solids (82 mg). The solids were recrystallized from $CHCl_3$ to give a mixture of tribromide 129 and 130 in a

3 to 1 ratio. IR (nujol) 3110 cm^{-1}(w, heteroaromatic C-H); ^1H NMR ($CDCl_3$) δ8.57(s,1H), 8.58(s,1H), 8.62(d,J=2.9 Hz,1H), 8.65(d,J=2.9 Hz, 1H); mass spectrum, m/e (rel. intensity) 486(43), 484(100), 482(94), 480(32), 405(18), 403(27), 401(13), 324(21), 322(18), 243(12); high resolution mass spectrum, calculated for $C_{12}H_3Br_3S_3$ m/e 479.69467, observed m/e 479.69275.

Similarly monobromide and a mixture of dibromides were obtained by changing the amount of Br_2. However the contamination by other bromides could not be avoided. The separation of isomers was not achieved.

For 125: mp 110°C (dec.); IR (nujol) 3100(m), 870(m), 855(m), 780(s), 735 cm^{-1}(m); ^1H NMR ($CDCl_3$) δ7.47(m,4H), 8.37(d,J=3.0 Hz); high resolution mass spectrum, calculated for $C_{12}H_5BrS_3$ m/e 323.87369, observed m/e 323.87302.

For dibromides : ^1H NMR ($CDCl_3$) δ7.45(m,2H), 8.40(m,2H); high resolution mass spectrum, calculated for $C_{12}H_4Br_2S_3$ m/e 401.78421, observed m/e 401.78348.

11. 1-Benzo[1,2-c:3,4-c':5,6-c"]trithiophenecarboxaldehyde (132)

To a solution of 86 (100 mg) in 50 mL of dry ether, about 6.6 mmol of n-BuLi in hexane (3 mL) was added at -25°C under a N_2 atmosphere with stirring. The mixture was stirred for 1 h at the same temperature, then DMF (1.0 mL) was added. Stirring was continued for an additional 2 h at -25°C, after which the mixture was warmed to room temperature. About 10 mL of water was added with vigorous stirring. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layers were washed with dilute hydrochloric acid and water, then dried ($MgSO_4$). Evaporation of the ether gave a yellow solid which was purified by preparative thin layer chromatography (silica gel) with $CHCl_3$ as a developing solvent to give pure 132 (69 mg), mp 170-173°C. IR (nujol) 3100(m), 2720(s), 1645 cm^{-1}(s); ^1H NMR ($CDCl_3$) δ7.58(m,3H), 7.97(s,1H), 8.72 (d,J=2.5 Hz,1H), 10.13(s,1H); mass spectrum, m/e (rel. intensity) 274(51), 246(100), 201(35).

12. 1-Benzo[1,2-c:3,4-c':5,6-c"]trithiophenecarboxylic acid (133)

To a solution of 86 (100 mg) in 50 mL dry ether, about 3.3 mmol of n-BuLi in hexane (1.5 mL) was added at -25°C under a N_2 atmosphere with stirring. The mixture was stirred for 1 h at the same temperature. Then dry CO_2 gas was passed through the solution for 5 min. The solution was warmed to room temperature, 10 mL of water was added and the mixture was stirred vigorously for 2 h. The aqueous layer was separated and acidified with concentrated hydrochloric acid to give a yellow precipitate. The precipitate was collected by suction filtration, washed with water and dried under vacuum to give crude 133 (113 mg), mp 230-235°C (dec.). IR (nujol) 3600-2400(s), 1670 cm^{-1} (s); mass spectrum, m/e (rel. intensity) 290(3), 246(100), 201(6).

13. Reaction of 133 with thionyl chloride

The crude acid 133 (100 mg) was heated in 3 mL of $SOCl_2$ at reflux for 6 h with vigorous stirring. Distillation of the excess thionyl chloride under reduced pressure left a yellow solid (82 mg). The difficult solubility properties of the solid prevented the measurement of its NMR spectrum. Its IR spectrum in nujol showed the absence of the carboxylic group. IR (nujol) 3100(m, heteroaromatic C-H), 1720 cm^{-1}(s); mass spectrum, m/e (rel. intensity) 386(21), 384(18), 352(24), 350(45), 342(18), 340(18), 316(100), 308(23), 306 (44), 272(95), 244(44).

14. 1,3,4,6-Tetrahydrobenzo[1,2-c:3,4-c']dithiophene (137)

1,2,3,4-Tetrakis(bromomethyl)benzene was prepared from prehnitene by the literature method.[88] This tetrabromide (13.0 g) was added to a mixture of $Na_2S \cdot 9H_2O$ (20.8 g), EtOH (350 mL), and water (30 mL). The mixture was heated under reflux for 16 h with vigorous stirring, then cooled to room temperature. About 400 mL of water was added and the mixture was cooled in an ice bath. The light brown precipitate which formed was collected by suction filtration, washed with water several times and with EtOH twice and dried under vacuum to give 137 (4.5 g), mp 110-115°C (lit.[85] mp 115-117°C). ^{1}H NMR ($CDCl_3$) δ4.12(bs,4H), 4.20(bs,4H), 7.00(s,2H).

15. Benzo[1,2-c:3,4-c']dithiophene (91)

Treatment of 137 (0.5 g) with DDQ (1.3 g) as described in the preparation of 86 afforded 91 (0.17 g, 35%), mp 111-112°C (lit.[60] mp 112-113°C).

16. Reaction of 86 with sulfur monochloride

To a solution of 86 (246 mg) in 20 mL of carbon disulfide, 440 mg of $AlCl_3$ and 405 mg of S_2Cl_2 were added at 0°C. The mixture was stirred for 3 h at 0°C and for 17 h at room temperature. Then it was poured onto cracked ice. The reddish brown precipitate formed was collected by suction filtration and washed with water then with methanol and dried under vacuum (357 mg), mp > 350°C. The solid was not soluble in either water or organic solvents, and could not be identified. The carbon disulfide layer was separated from aqueous layer and evaporation of the solvent gave sulfur (65 mg).

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15. We are indebted to Dr. Rodney Willer for suggesting and arranging for the dipole moment measurments, and to Professor E.L. Eliel for obtaining the results.

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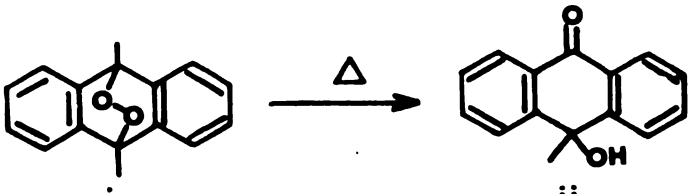

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