THE CHEMISTRY OF CYCLOALKENE FUSED NAPHTHALENES AND ANTHRACENES

A Dissertation

Presented to

The Faculty of the Department of Chemistry

College of Natural Sciences and Mathematics

University of Houston

In Partial Fullfillment

of the Requirements for the Degree

Doctor of Philosophy

by

Wesley E. Cravey

May 1978

To Melanie, without whom
nothing is worth having

ACKNOWLEDGEMENT

I am deeply thankfull for the leadership and friendship of my research advisor, Dr. R. P. Thummel. His help and advice made graduate school a little easier.

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I would like to thank my parents for helping me make it this far and Melanie's parents, especially Mrs. Jemison, for her tirless typing.

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ABSTRACT

A general two step synthesis of fused ring naphthalenes is described. This synthetic route includes the Diels-Alder addition of benzyne to a 1,2-dimethylenecycloalkane or a 1-vinylcycloalkene, followed by aromatization utilizing 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). This Diels-Alder approach is used to propare both isomers of the four-, five-, and six-membered fused ring naphthalenes. The Diels-Alder approach is also adopted to give the first syntheses of anthro[a]cyclobutene and anthro[b]cyclobutene, which represent the smallest fused ring anthracenes known to date.

The chemistry of 1,4-dihydronaphtho[b]cyclobutene(52) has been explored. It is found that the cyclobutene carbon-carbon double bond of 52 is reactive toward cycloaddition as well as oxidation. The four-membered ring of 52 is found to undergo ring opening to give 1,2,3,4-tetrahydro-2,3-dimethylenenaphthalene (94), which also undergoes cycloaddition reactions.

The apparent oxidation rate difference observed between 1,4-dihydronaphtho[b]cyclobutene and 1,4-dihydronaphtho[a]-cyclobutene with DDQ let to an indepth kinetic study. For this kinetic study, a series of 1,4-dihydrobenzenes and naphthalenes has been prepared. The rate of oxidation of these dihydroaromatic compounds has been measured by following the disappearance of the uv absorption of DDQ at 3900 Å, under pseudo-first-order conditions. The pseudo-first-order rate constants are calcuclated, as well as the second-order

rate constants, and relative rate constants. From the relative rate constants of the 1,4-dihydrobenzene series, it is observed that a definite relationship exists between the number of electron donating groups attached to the 1,4-dihydroaromatic nucleus and the relative rate of oxidation. This relationship is interpreted as evidence for a carbonium ion intermediate.

Using the new evidence for a carbonium ion intermediate, the existing proposed mechanisms for DDQ oxidation are re-examined, and a new mechanism proposed. The evidence for a carbonium ion intermediate, as well as other rate data, led us to propose a two step mechanism. This mechanism involves: 1) abstraction of a hydride from the 1,4-dihydroaromatic nucleus by DDQ followed by formation of a tight ion pair, and 2) loss of a proton resulting in formation of the aromatic compound.

This mechanism is substantiated by the rate data obtained from the oxidation of the 1,4-dihydronaphthalene series.

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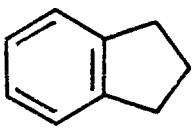
INTRODUCTION

INTRODUCTION

In 1930 Mills and Nixon[1] proposed that the five-membered ring of indan (1) might distort the geometry of the aromatic nucleus enough to stabilize one Kekulé resonance form



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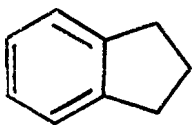
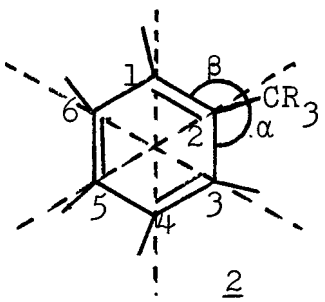


1b

relative to the other. For geometric reasons Mills and Nixon proposed that the carbon-carbon bond of indan common to both rings would have more single bond character. They



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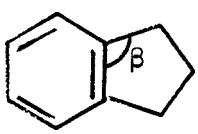
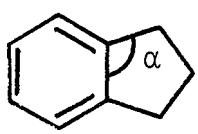


1a

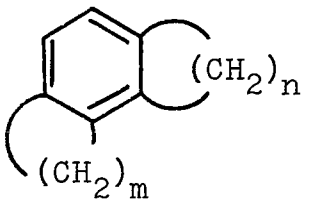


1b

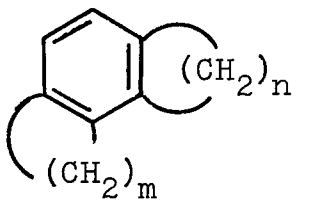
argued that the angle α is smaller than β for the unstrained, substituted Kekulé resonance form of benzene (2) shown above, therefore structure 1b required less angular distortion than structure 1a. The angle α was defined as the angle between the two carbon-carbon single bonds extending from the carbon-carbon double bond, [CR_3-C2-C3]. The angle β was defined as the angle between the carbon-carbon double bond and the external carbon-carbon single bond, [CR_3-C2-C1].

Thummel and Nutakul[2] found that the position of two small rings on a benzene nucleus affected the physical

properties of the system. They suggested that a possible explanation might be the stability of one Kekulé resonance form relative to the other. Assuming that a carbon-carbon double bond is more stable exo- to a small ring rather than



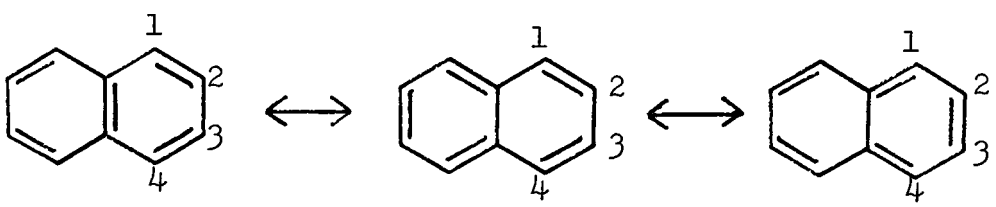
3a



3b

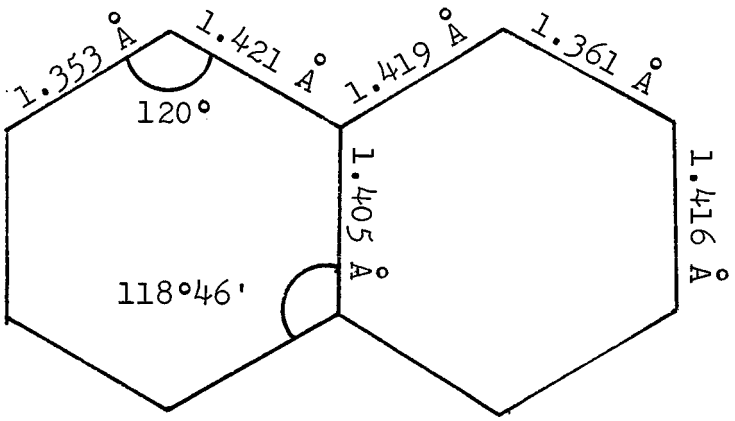
endo-, then structure 3b should be less stable than 3a.

Naphthalene (4) has three Kekulé resonance contributers. Considering about equal contribution from all three forms, there is more carbon-carbon double bond character between carbons one and two than between carbons two and three. The

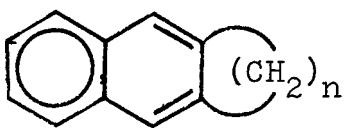


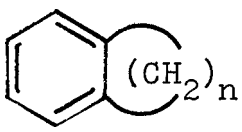
4a 4b 4c

X-ray structure[3] of naphthalene reinforces these observations by indicating a shorter carbon-carbon bond length between carbons one and two than between two and three. Therefore one might expect bond alternation induced by the introduction of a small fused-ring to be accomplished more easily for naphthalene than for benzene. Another factor favoring bond

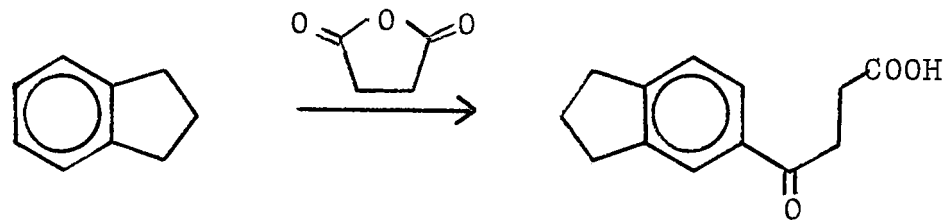


alternation is the resonance energy of naphthalene. When the resonance of benzene is disrupted, 37 Kcal/mole of energy is lost, but only 25 Kcal/mole is lost when the aromaticity of one ring of naphthalene is destroyed.





Both isomers of the three, four and five membered fused-ring naphthalenes have been prepared. In 1939 Sen-Gupta[4] prepared naphtho(b)cyclopentene (8) from indan (1) in four steps.



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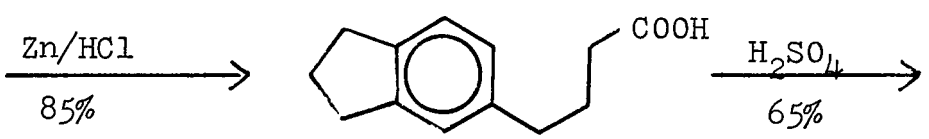

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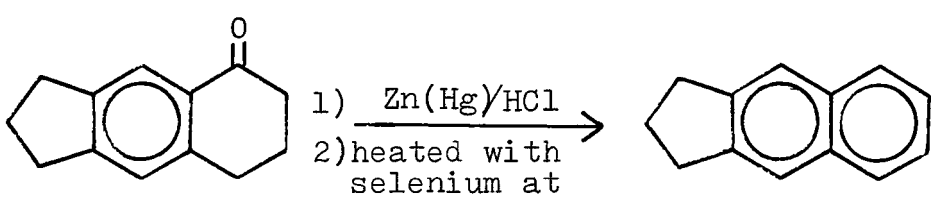

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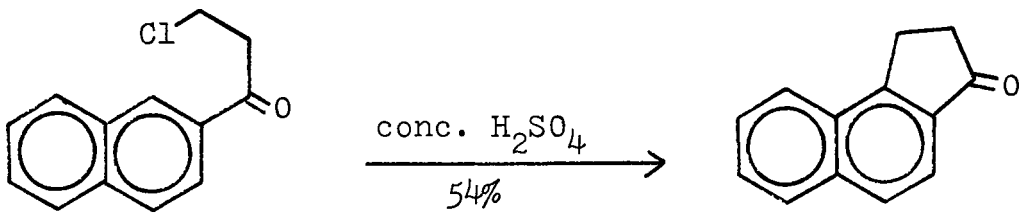
Dannenberg and Rahman[5] prepared naphtho(a)cyclopentene (11) from 1-[β-naphthoyl]-2-chloro-ethane (9).



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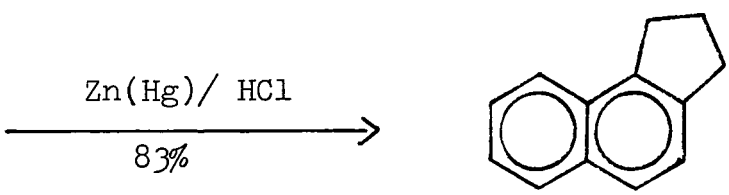

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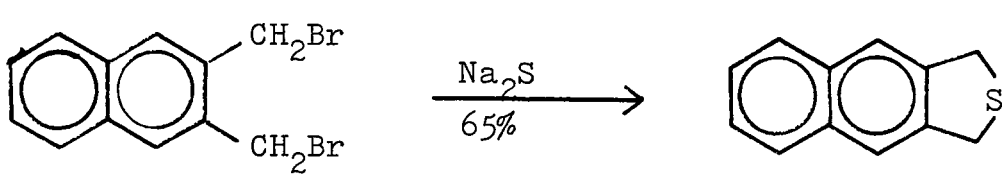
In 1959 Cava and Deana[6] reported the pyrolytic decomposition of 1,3-dihydronaphtho[2,3-C]thiophene-2,2-dioxide (14) to provide the first synthesis of naphtho(b)cyclobutene (15).



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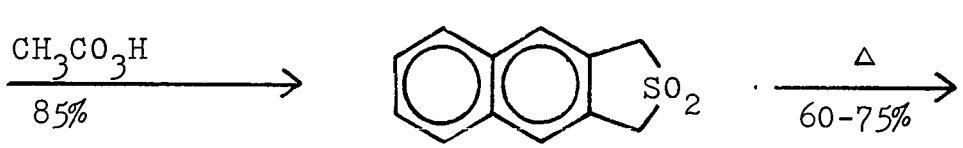

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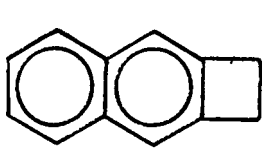

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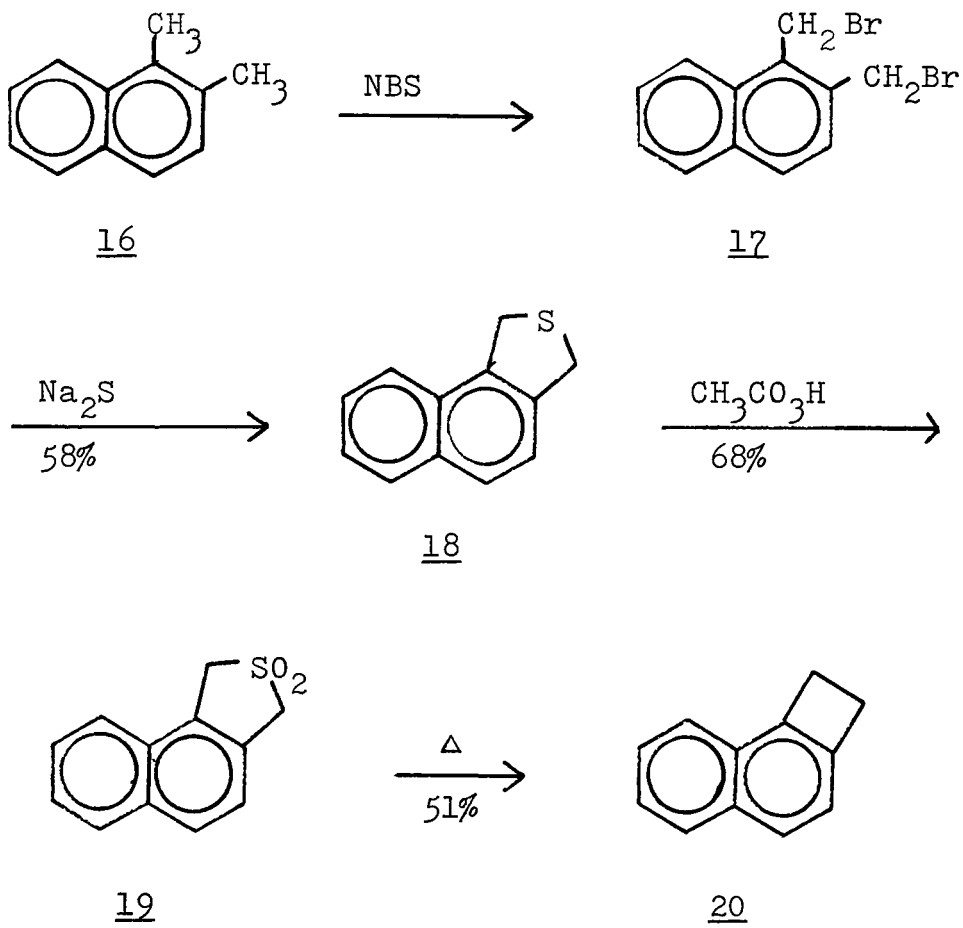
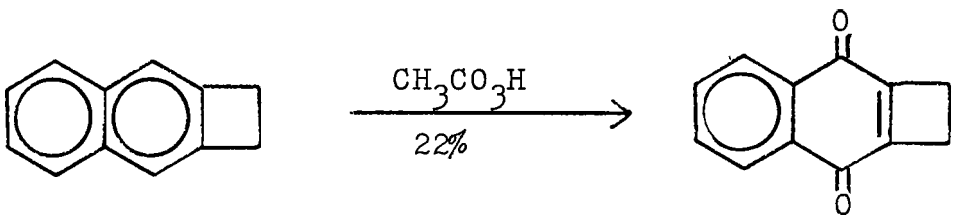
Compound 14 was prepared in two steps from 2,3-bis(bromomethyl)naphthalene (12). Cava and Shirley[7] prepared naphtho(a)-cyclobutene (20) by an analogous route. Benzylic bromination of 1,2-dimethylnaphthalene (16) gave 1,2-bis(bromomethyl)-naphthalene (17). Treatment of 17 with sodium sulfide followed by treatment with peracetic acid, and finally pyrolysis gave 20.

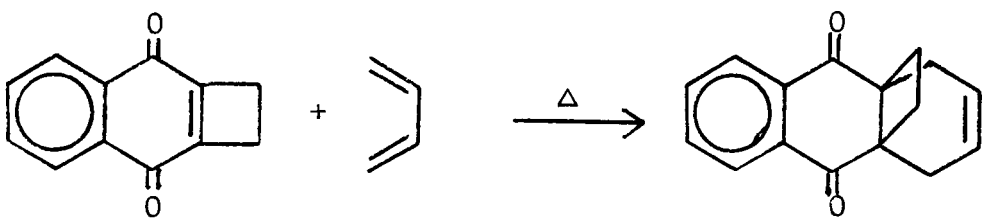


Oxidation of 15, with peracetic acid gave 1,2-dihydrocyclobuta[b]naphthalene-3,8-dione (21).[8] The quinone nucleus of 21 underwent Diels-Alder reaction with 1,3-butadiene to



15 21

provide 22. The analogous reaction of 1,3-butadiene with 2,3-dimethyl-1,4-naphthoquinone (23) was unsuccessful. The enhanced reactivity of 21 is attributed to a relief of the cyclobutene ring strain when cycloaddition occurs. When 21 was heated to 200°C, ring opening occurred to provide diene



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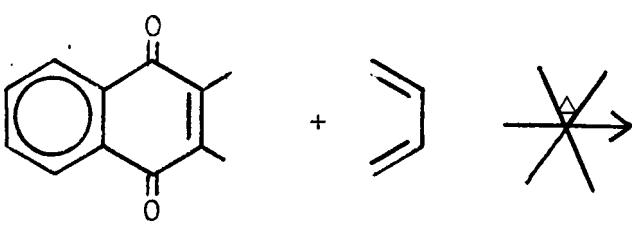

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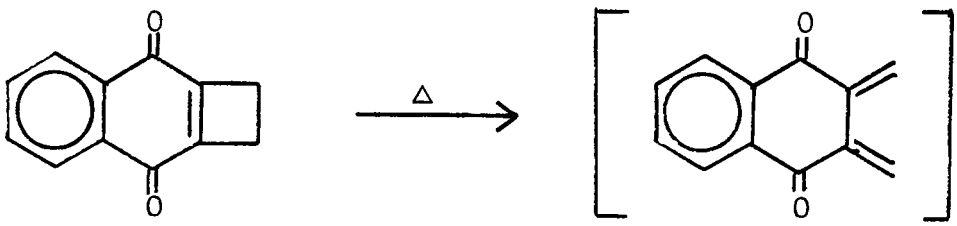
24 which then underwent Diels-Alder addition to unreacted 21, to give dimer 25. The intermediate diene 24 was also



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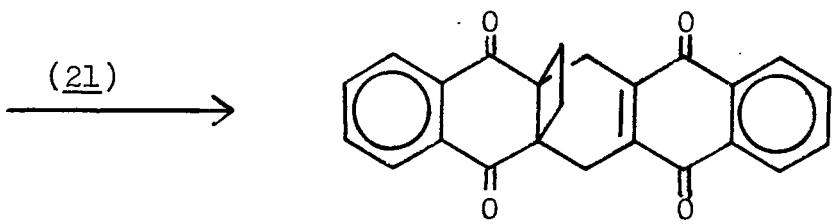

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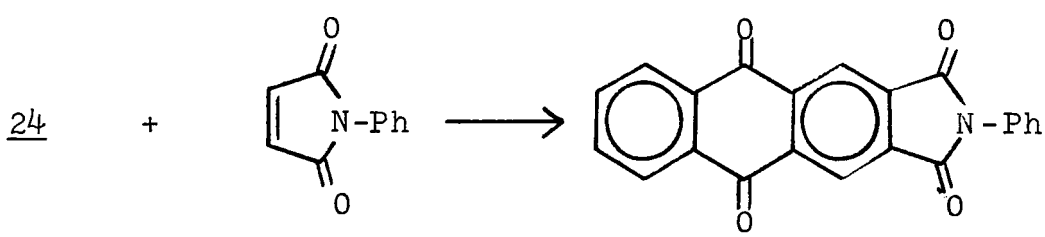
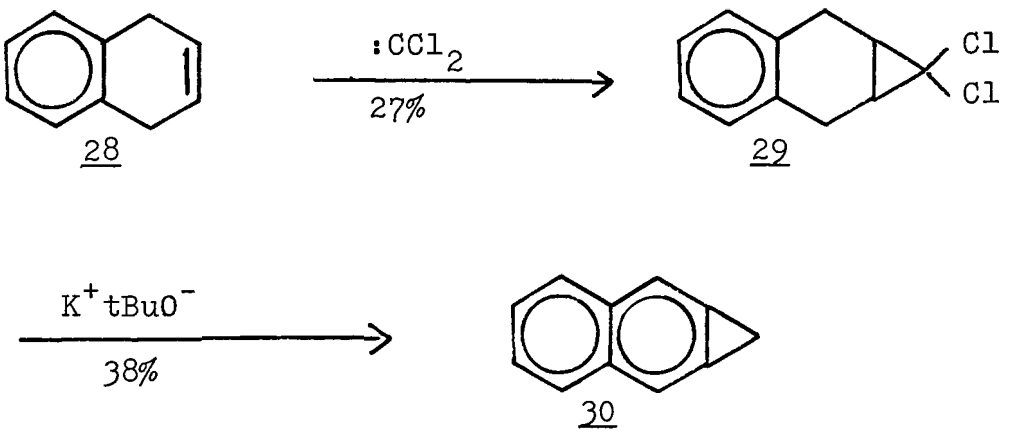
trapped with N-phenylmaleimide (26) to give the corresponding aromatized Diels-Alder adduct (27).

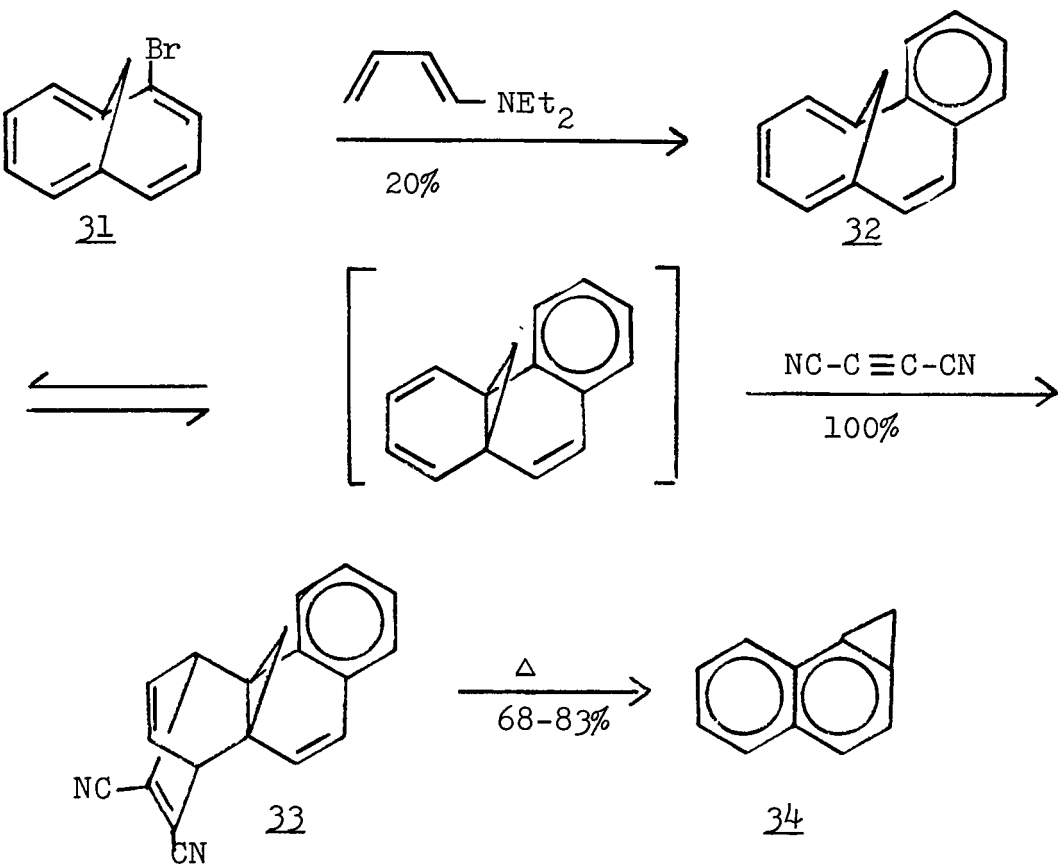


26 27

Naphtho(b)cyclopropene (30) has been prepared by Billups and Chow.[9] Dichlorocarbene addition to 1,4-dihydronaphthalene (28) gave 29. Treatment of 29 with an eight-fold excess of potassium tert-butoxide effects a double dehydrochlorination accompanied by double-bond migration to give 30.

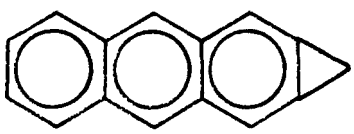


Naphtho(a)cyclopropene (34) was prepared by Vogel and co-workers.[10] Heating a mixture of 2-bromo-1,6-methano[10]-annulene (31) and N,N-diethyl-1,3-butadienylamine with potassium tert-butoxide in toluene gave 2,3-benzo-1,6-methano[10]-annulene (33). Diels-Alder addition of 32 to dicyanoacetylene



gave 33, which underwent a retro-Diels-Alder reaction to give naphtho(a)cyclopropene (34).

Garratt and Davalian[11] attempted the preparation of anthro(b)cyclopropene (35) but were unsuccessful. Garratt has suggested that the apparent instability of this molecule might indicate a higher degree of bond fixation than in the corresponding naphtho(b)cyclopropene.



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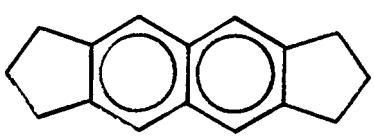
Several naphtho(b,e)dicycloalkenes have been reported. Sen-Gupta and Bhattacharjee[12] have prepared naphtho(b,e)dicyclopentene (36). Garratt and Davalian[11] have prepared cyclopropa(e)-cyclobuta(b)naphthalene (37). Vogel and Ippen[13]



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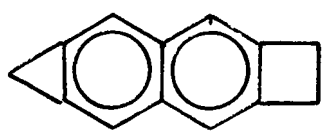

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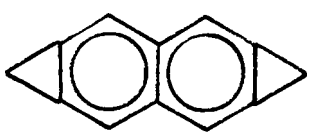

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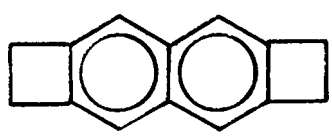
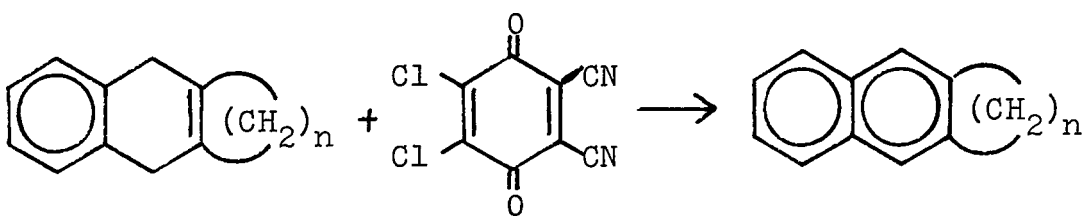


39

have prepared naphtho(b,e)dicyclopropene (38) and recently Thummel and Nutakul[14] have prepared naphtho(b,e)dicyclobutene (39).

Our synthetic approach to fused ring naphthalenes, as well as to anthrocyclobutenes, involves the formation of a 1,4-dihydroaromatic species which is then oxidized by 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (40) (DDQ). The observed rate differences for the oxidation of various fused-ring 1,4-dihydronaphthalenes led us to investigate the mechanism of the oxidation of 1,4-dihydroaromatics by DDQ and other quinones.



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Braude[15] and coworkers have carried out an extensive study of dehydrogenations employing various quinones. In a kinetic study[15b] of the dehydrogenation of 1,4-dihydronaphthalene using 1,4-benzoquinone,2-methyl-1,4-benzoquinone,chloro-1,4-benzoquinone and tetrachlorobenzoquinone, Braude concluded the following:

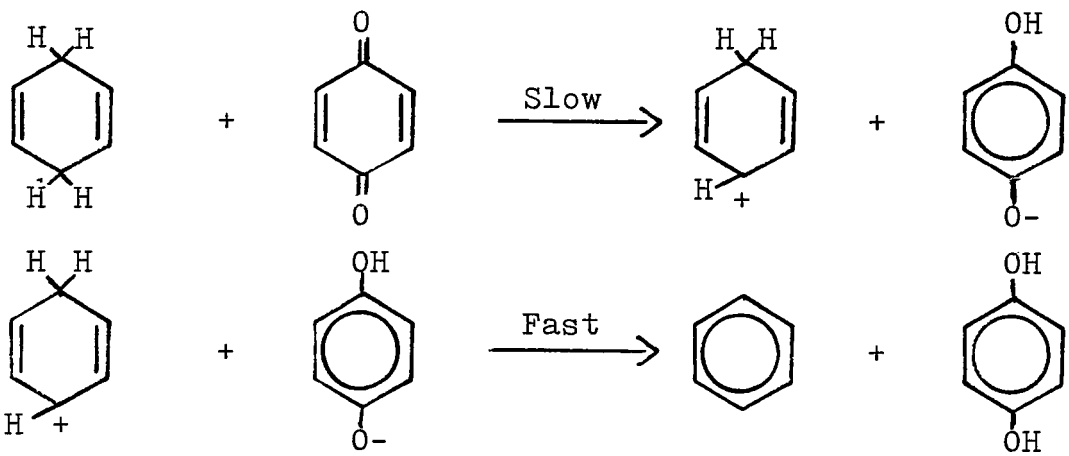
1) The reactions are essentially bimolecular,
2) The reactions are faster in a polar solvent than a nonpolar solvent, but are not light sensitive,

3) The reactivity of a quinone is enhanced by electron withdrawing groups,

4) With less reactive quinones, marked product catalysis is observed.

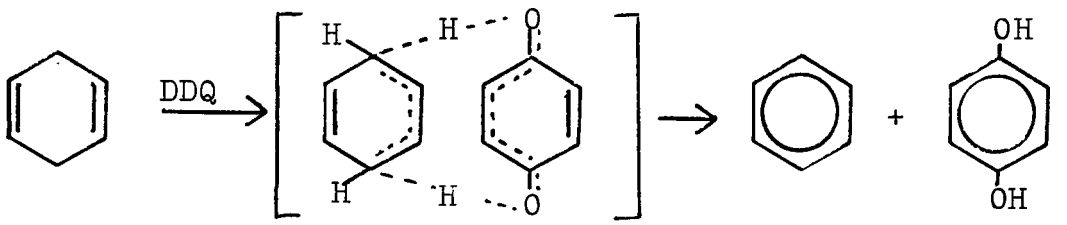
He explained the above observations by a two step, heterolytic mechanism involving a rate determining hydride transfer followed by a rapid proton transfer.

TWO STEP MECHANISM

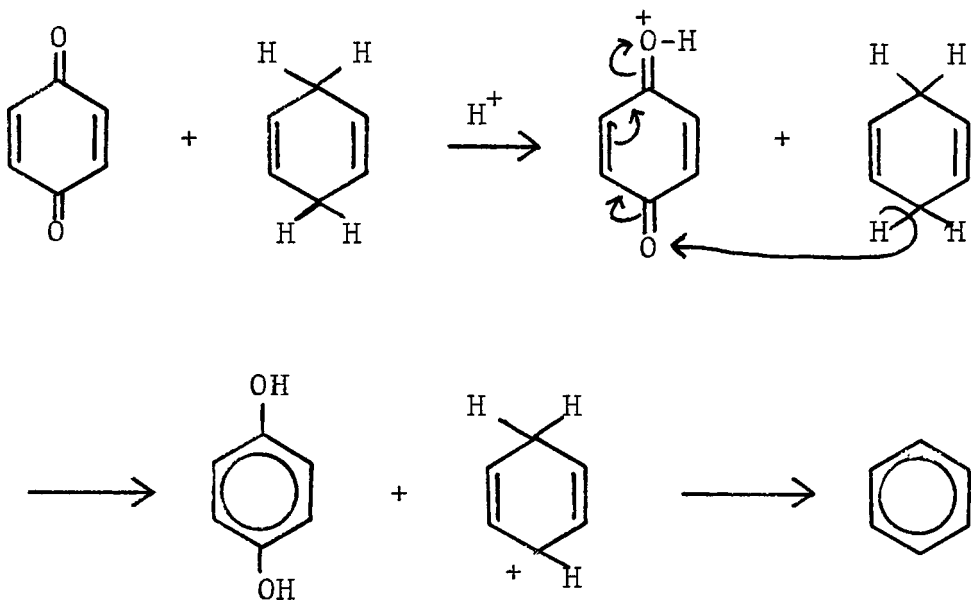


Braude ruled out a one step, simultaneous transfer of two hydrogens. He claimed that in the one step mechanism the quinone must be difunctional with one oxygen displaying

ONE STEP MECHANISM



electrophilic reactivity and the other displaying nucleophilic reactivity. Braude argued that if the transfer were synchronized exactly and the quinone is difunctional then the reactivity of the quinone should not be influenced by electron-withdrawing or electron-donating groups on the quinone. Another important factor to consider, was the spatial orientation which is required for a synchronous, one-step mechanism. Braude used 1,2- and 1,4-dihydronaphthalenes and could find no evidence for the importance of spatial orientation. Further evidence for a two step mechanism was its ability to explain the catalytic effect of acidic conditions. If the quinone is protonated, the resultant conjugate acid will be a far more powerful reagent than the neutral quinone. The positive character of the protonated carbonyl would increase the electrophilic reactivity of the other carbonyl, or β carbon.



Addition of a hydride ion would thus yield a neutral hydroquinone directly.

Braude[15c] also studied the rates of oxidation of 1,4-dihydrobenzene, 1,4-dihydronaphthalene and 9,10-dihydroanthracene with benzoquinone, chloranil and thymoquinone. The rate of aromatization of the dihydroaromatic compounds was also measured in several solvents. The results indicated that the ease of dehydrogenation decreases in the sequence 1,4-dihydrobenzene $>$ 1,4-dihydronaphthalene $>$ 9,10-dihydroanthracene. The relative rate ratios were 100:50:10, respectively, for all three quinones studied. He attributes this rate difference to the resonance energy gained (ΔE_R) by aromatization. The approximate values of ΔE_R are 36 Kcal/mol for 1,4-dihydrobenzene, 30 Kcal/mol for 1,4-dihydronaphthalene and 25 Kcal/mol for 9,10-dihydroanthracene. These values were obtained by subtracting the resonance energy of the dihydro compound from the resonance energy of the aromatic compound[a] (i.e.: 1,4-dihydronaphthalene has a resonance energy of 37 Kcal/mole, and naphthalene has a resonance energy of 67 Kcal/mole, $\therefore$ 67-37 = 30 Kcal).

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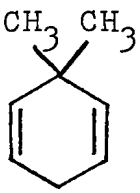
[a]The values for resonance energies are those given by Braude. More acceptable values are: naphthalene = 61 Kcal/mole and 1,4-dihydronaphthalene = 37 Kcal/mole.

Roček and Müller[16] studied quinone oxidations to determine if the process involves a one electron transfer (hydrogen atom) or a two electron transfer(hydride). The rates of oxidation of various 1,4-dienes were determined by uv spectrophotometric measurement of the disappearance of the DDQ absorption at 3900 Å. Roček observed a primary isotope effect in the oxidation of perdeuterio-tropilidene as compared with tropilidene (K_H/K_D = 4.0). A higher isotope effect was noted for 1,2,3-triphenyl-3-deuteriocyclopropene (K_H/K_D = 6.9). He interpreted these results as definite evidence for the carbon-hydrogen bond being broken in ghe rate determining step. The oxidation of 1,4-pentadiene occurs 10^4 times slower than that of tropilidene. He interpreted this rate difference as evidence of hydride abstraction. Hydride abstraction from tropilidene would yield an aromatic species whereas hydride abstraction from 1,4-pentadiene would yield only a pentadienyl cation. The higher reactivity of tropilidene is therefore due to formation of an aromatic species. Like tropilidene, triphenylcyclopropene is oxidized about 10^4 times faster than 1,4-pentadiene. The abstraction of a hydrogen atom would yield an unstable triphenylcyclopropenium radical with the odd electron in an antibonding orbital. Hydride abstraction, however, would yield the aromatic 1,2,3-triphenylcyclopropenium cation.

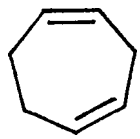
Roček further observed that 1,4-cyclohexadiene is oxidized 2,000 times faster than 1,4-pentadiene, which he attributed

to considerable aromatic stabilization in the transition state. He concluded that in the case of 1,4-cyclohexadiene the two carbon-hydrogen bonds muxt be broken simultaneously in the rate determining step.

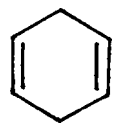
Roček and Stoos[17] further investigated rate differences in the oxidation of 1,4-pentadiene and 1,4-cyclohexadiene. To explore a potential concerted mechanism, Roček prepared 3,3-dimethyl-1,4-cyclohexadiene (41) and 1,4-cycloheptadiene (42), two compounds which cannot aromatize in a single step but yet are reasonable models for 1,4-cyclohexadiene (43). The



41

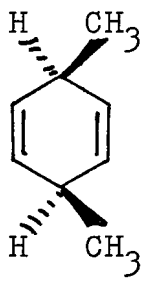


42

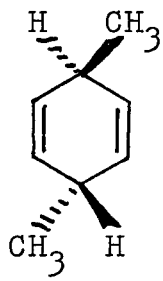


43

oxidation rates of 41 and 42 were comparable with that of 1,4-pentadiene, but 1/2000 times as fast as that of 43. He also propared cis-3,6-dimethyl-1,4-cyclohexadiene (44) and trans-3,6-dimethyl-1,4-cyclohexadiene (45) to heop determine the stereochemistry of the elimination. Table I lists the



44



45

TABLE I

Rates[b] of Oxidations with DDQ
in Glacial Acetic Acid

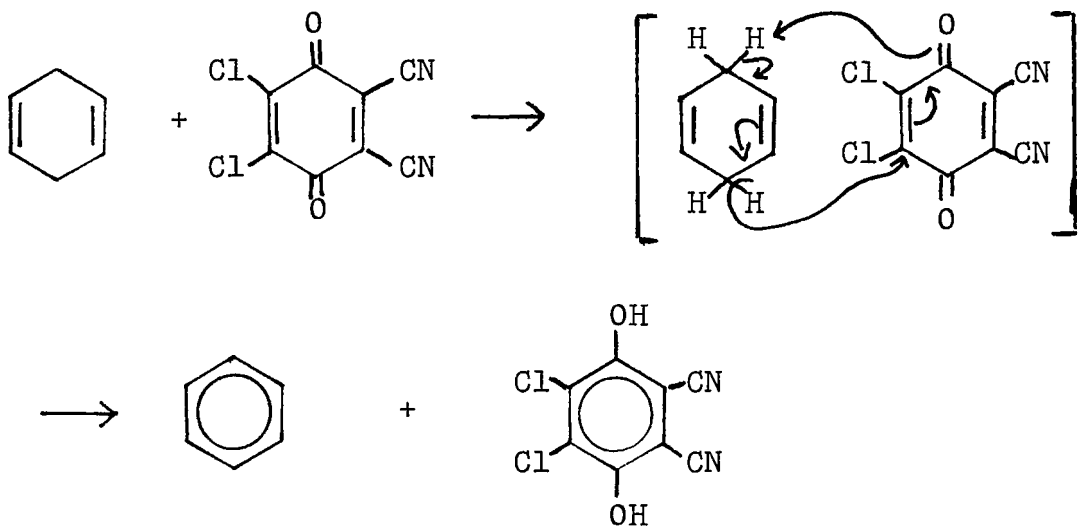
Substrate	Krel
Cyclohexene	.04
1,4-Pentadiene	1.00
3-Methyl-1,4-cyclohexadiene	5.00
3,3-Dimethyl-1,4-cyclohexadiene	5.00
1,4-Cycloheptadiene	37.0
trans-3,6-Dimethyl-1,4-cyclohexadiene	150
1,4-Cyclohexadiene	2240
cis-3,6-Dimethyl-1,4-cyclohexadiene	3200
1,2,3-Triphenylcyclopropene	2430
Tropilidene	8340

[b]All rates were pseudo-first order.

relative rates of oxidation of the compounds Roček studied. The rate of oxidation for the trans isomer 45 is only five to thirty times that of those compounds not capable of aromatizing in one step, whereas the cis-isomer 44 has an oxidation rate comparable with those compounds capable of aromatizing in one step (ie tropilidene). Based on the observed oxidation rates, he proposed a concerted transfer of the two cis-hydrogens of a 1,4-dihydroaromatic nucleus to DDQ. However, Roček agrees with Braude and rejects the one step mechanism Braude argued against. The concerted transfer of two hydrogens to the carbonyl oxygens of DDQ would involve eight π-electrons and is thus forbidden by orbital synnetry, (6π-electrons of the quinone and 2π-electrons of the diene, $[{}_{\pi}6_{s} + {}_{\pi}2_{s}] = 8$, 4n+2 = thermally allowed). Ročck also states that quinones react essentially as unsaturated ketones and that a hydride should add either to the carbonyl carbon or to a ring carbon, but not to oxygen.

Ročck therefore proposed a concerted mechanism, with

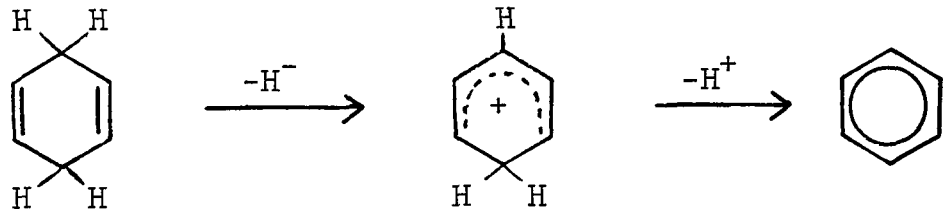
CONCERTED MECHANISM



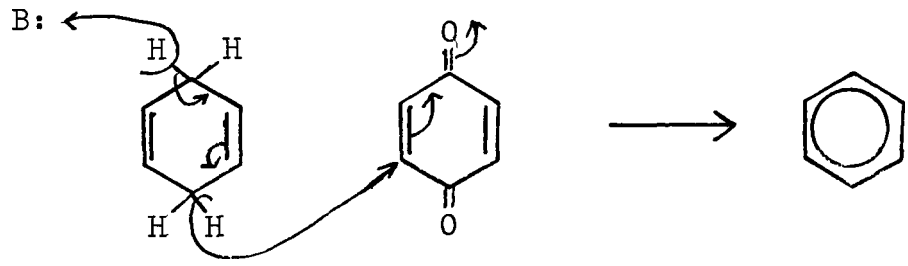
two cis-hydrogens being transferred to DDQ simultaneously with the hydride attacking in a 1,4-fashion. The concerted mechanism involves only six π-electrons and is therefore allowed by the rules of orbital symmetry. He concedes that the concerted mechanism applies only when there are two cisoid hydrogens and another mechanism must function for the oxidation of compounds of different conformations.

Müller[18] has examined two proposed mechanisms for the DDQ oxidation of 1,4-dihydroaromatic compounds, as well as a third mechanism which he has proposed. He has attempted to correlate the existing facts with his own experimental data. Müller states that the higher reactivity of 44 suggests a cyclic mechanism but could be explained by an alternative interpretation. The cis-isomer (44) is not as sterically hindered as the trans-isomer (45). There should be interaction between the methyl group and hydrogen since both are axial in 45 but no such interaction should occur in 44. Müller also attributes the fact that 44 aromatizes faster than 1,4-cyclohexadiene to its ability to form a tertiary carbonium ion, rather than a secondary one. Müller rejects mechanism A by the same arguments given by Roček. He also attacks mechanism C, stating that all the arguments favoring a concerted mechanism also favor a 1,4-elimination, mechanism B. Despite small dependence on changes in basicity, Müller notes that a solvent change might influence the oxidation potential of the quinone.[19] Thus an expected rate enhancement caused by a more basic

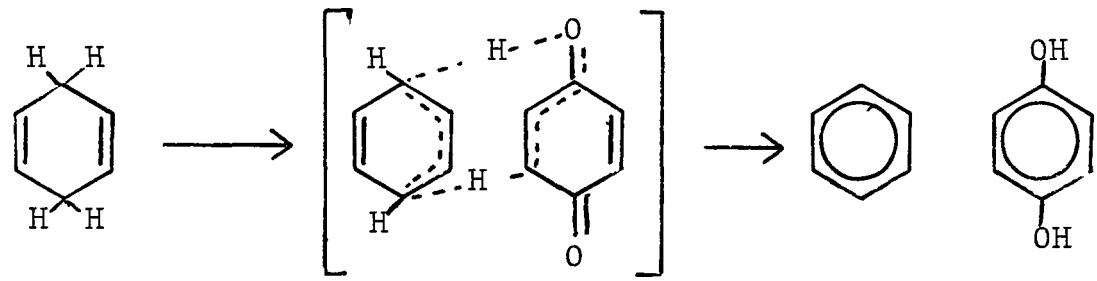
MECHANISM A (IONIC)



MECHANISM B (1,4-ELIMINATION)

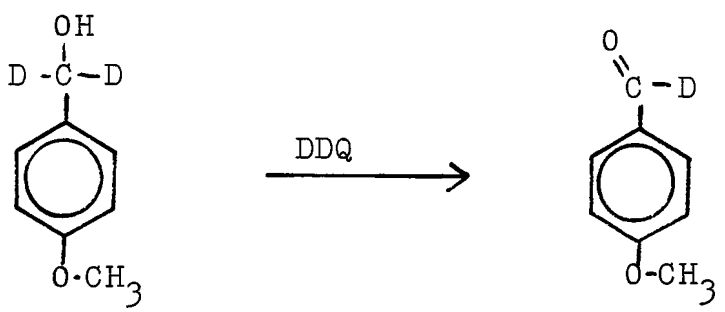


MECHANISM C (CONCERTED)



solvent may be counter-balanced by a lower oxidation potential of the quinone.[a]

Müller has provided perhaps the most convincing evidence in favor of the removal of two hydrogens in the rate determining step. Perdeuterio-1,4-cyclohexadiene was prepared and the kinetic isotope effect for DDQ oxidation was measured. After corrections for contaminants a value of K_H/K_D = 10 was established. This isotope effect appears to be too high for a single primary and secondary isotope effect, but rather suggests the breaking of two carbon-hydrogen bonds in the rate determining step. However this argument is somewhat weakened by a kinetic isotope effect of K_H/K_D = 10 for the DDQ oxidation of anisyl alcohol (46) which involves the breaking of only one carbon-deuterium bond.



46 47

[a]The rate of oxidation increases as the oxidation potential of the quinone increases

Müller carried out a parallel study using as an oxidant, triphenylmethylfluoroborate, which is known to react through a hydride transfer,[20] but unlike DDQ cannot involve a cyclic mechanism.[c] Under pseudo-first order conditions, he found that the relative rates of oxidation for various 1,4-dihydroaromatic compounds were comparable to those obtained with DDQ. In particular the cis isomer 44 aromatized faster than the trans 45. The hydride mechanism A had been ruled out, and triphenylmethylfluoroborate gave the same observation as did DDQ and yet could not react in a cyclic mechanism. Therefore Müller suggests that there is no need to invoke a cyclic mechanism for DDQ but rather favors mechanism B, a 1,4-elimination with the proton being lost to solvent or to a conjugate base.

The following section will discuss a new synthetic approach to ring-fused naphthalenes and anthrocyclobutenes as well as present additional kinetic data on the oxidation of 1,4-dihydroaromatic compounds which may help explain the mechanism of DDQ oxidations.

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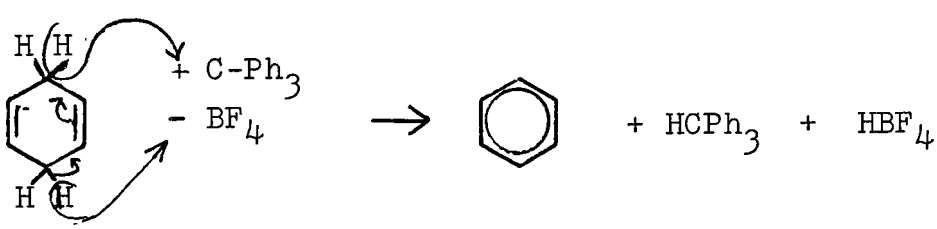
[c] A cyclic mechanism could be envisioned involving tight ion pairs.



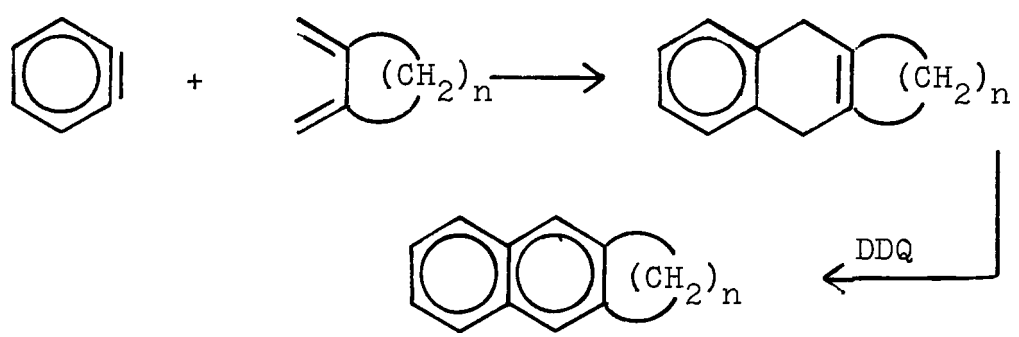
THE CHEMISTRY OF
1,4-DIHYDROAROMATIC COMPOUNDS

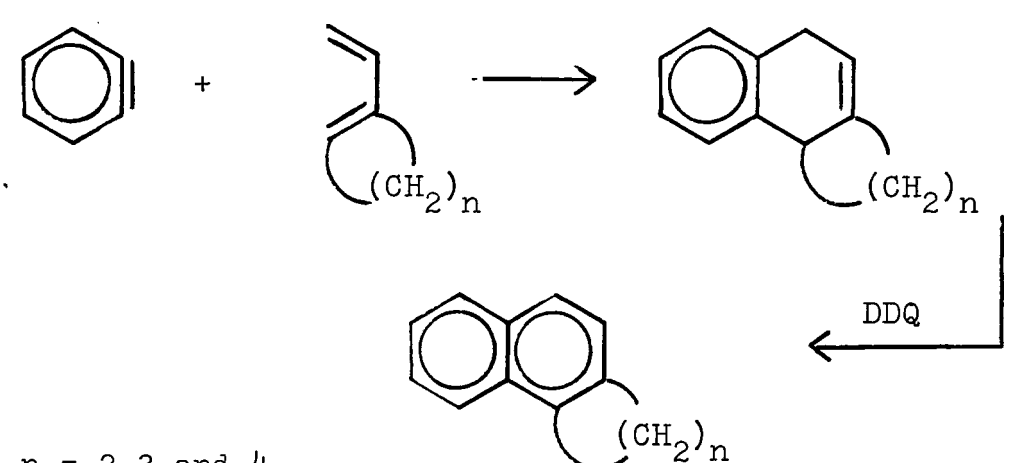
The Chemistry of 1,4-Dihydroaromatic Compounds

Part A:

The Synthesis and Reactions of 1,4-Dihydroaromatic Compounds

A Diels-Alder approach was used to prepare dihydronaphthocycloalkenes and dihydroanthrocycloalkenes. In previous preparations of naphthocyclobutenes[6,7] the strained cyclobutene ring was formed in the final step. By the Diels-Alder approach to naphthocyclobutenes, the strain is incorporated into the species undergoing cycloaddition. Addition of a 1,2-dimethylenecycloalkane or a 1-vinylcycloalkene to benzyne gave a 1,4-dihydronaphthocycloalkene, which, when

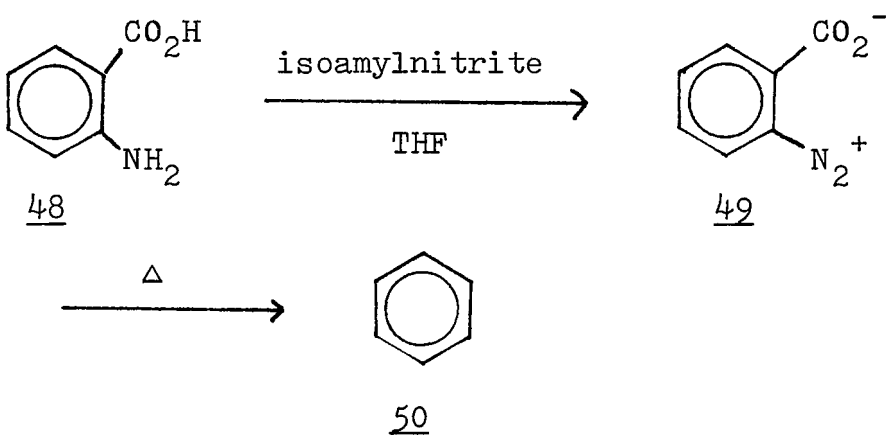




n = 2,3 and 4

oxidized by DDQ, gave the corresponding fused ring naphthalenes.

The compounds listed in Table II, except for 70 and 71 were all propared by the same synthetic procedure. A solution of anthranilic acid (48) and isoamyl nitrite in tetrahydrofuran was stirred for several hours yielding a tan precipitate, benzenediazonium-2-carboxylate[21] (49) which was collected but not allowed to dry. The dry compound 49 will detonate when exposed to heat or friction. Benzyne (50) was prepared by



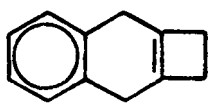
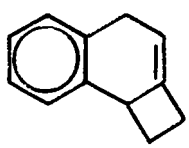
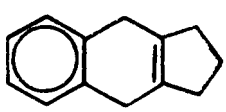
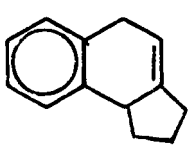
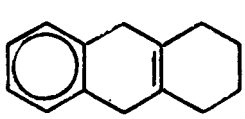
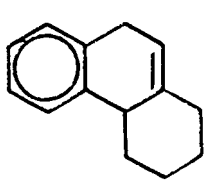
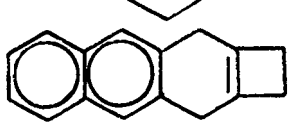
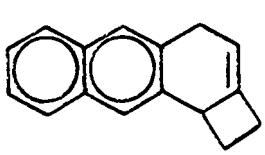
48 49 50

thermal decomposition of 49 in refluxing dichloromethane, resulting in loss of the tan color, turning black, and gas evolution.

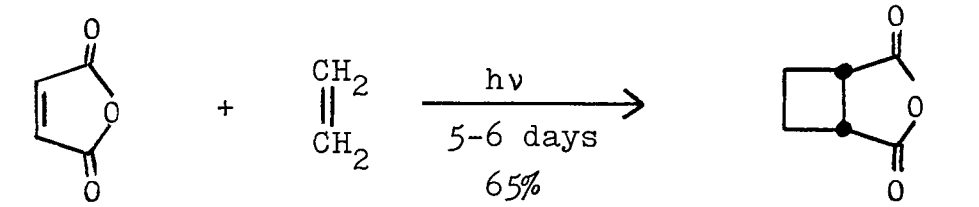
The diene, 1,2-dimethylene cyclobutane[24] (51), was prepared by a six-step synthesis starting from maleic anhydride (53). Irradiation, with a 450 Watt Hanovia uv light, for five to six days, of an ethylene-saturated dichloromethane solution of (53), gave cis-1,2-cyclobutanedicarboxylic acid anhydride (54)[22] which when treated with phosphorous pentachloride[23] afforded trans-1,2-cyclobutanedicarboxylic

TABLE II

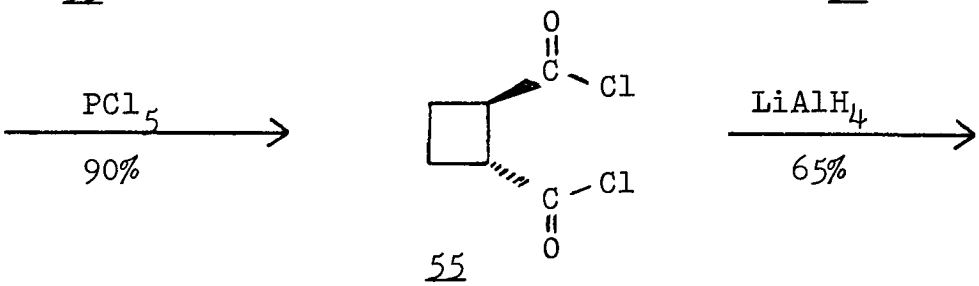
1,4-Dihydro Fused-Ring Naphthalenes and Anthracenes

Compounds		mp	Cyclo-addition Yields
	52	69-70°C	25%
	60	oil[a]	50%[b]
	74	67-68°C	55%
	75	oil[a]	--
	76	66-65°C	25%
	77	oil[a]	22%
	70	135-136°C	9%
	71	98-101°C	5.4%

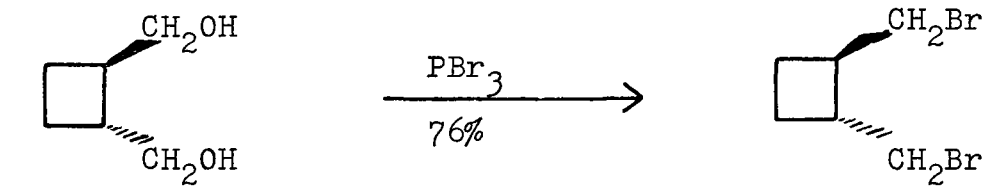
[a]product purified by vpc
[b]yield prior to purification by vpc



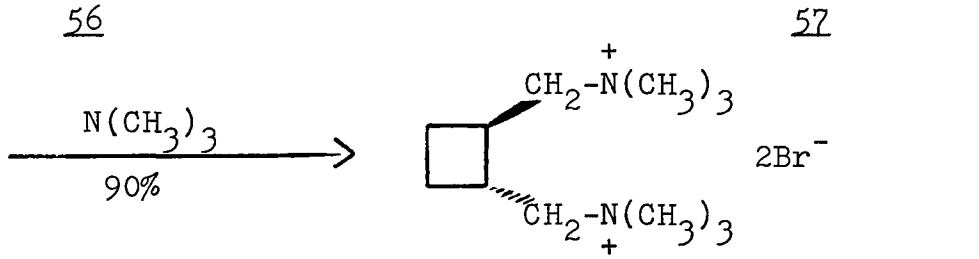
53 54



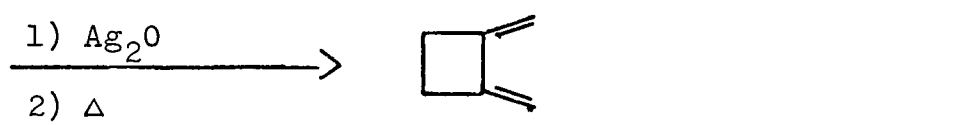
55



56 57



58

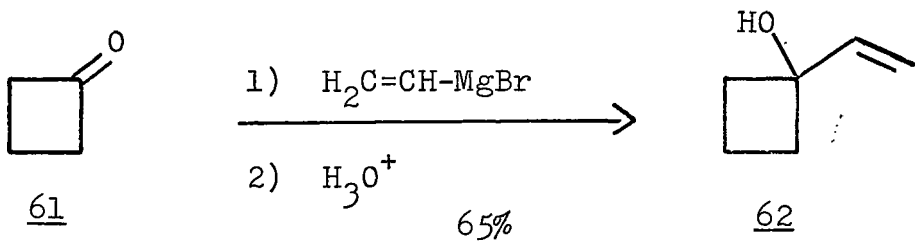


51

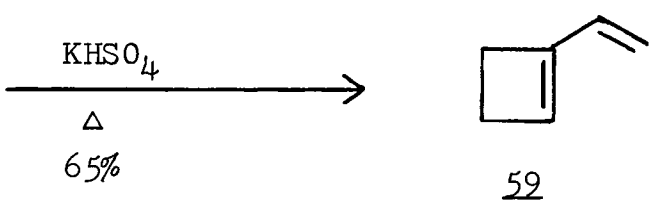
acid chloride (55). Reduction of 55 with lithium aluminum hydride gave trans-1,2-bis(hydroxymethyl)-cyclobutane[24] (56). The acid chloride 55 must be added slowly to the ethereal solution and at -78°C to avoid an exothermic reaction. Bromination of 56 with phosphorus tribromide afforded trans-1,2-bis(bromomethylene)cyclobutane[24] (57), which when heated with a two fold excess of trimethylamine gave trans-1,2-bis(trimethylaminomethyl)cyclobutane dibromide[24] (58). Treatment of 58 with silver oxide and water, followed by pyrolysis of the resulting hydroxide salt, gave the diene 51, trimethyl amine and water. The diene 51 was separated from the water and used without further purification in the Diels-Alder addition.

The sterochemistry of compound 55 was studied. The dimethyl ester of the acid chloride 55 was prepared. The dimethyl ester was also prepared from cis-54 by treatment with methanol and para-toluene sulfonic acid. Vpc analysis of these two diesters indicated them to be different isomers. When the dimethyl ester prepared from 54 was treated with sodium methoxide, it was completely epimerized to the isomer obtained from 55. Fonken and Shiengthong[25] found that the cis-dimethyl ester was converted to the trans-isomer by treatment with sodium methoxide. Therefore, the ester obtained from 54 was the cis-isomer and the ester obtained from 55 was the trans-isomer. Thus, the acid chloride 55 was the trans-isomer.

The 1-vinylcyclobutene 59 was prepared in two steps from cyclobutanone (61). Treatment of cyclobutanone with vinyl magnesium bromide, followed by hydrolysis afforded 1-vinyl cyclobutanol[26] (62). Dehydration of the allylic



61 65% 62

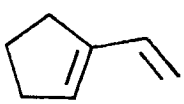


65% 59

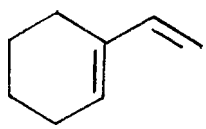
alcohol (62) was accomplished by treatment with potassium bisulfate[27] to give 59.

The aromatization of 52 and 60 using DDQ in carbon tetrachloride, was monitored by NMR. It was observed that 52 aromatized in approximately ten minutes at room temperature whereas the reaction mixture of 60 and DDQ had to be warmed to 40°C for approximately four hours. This apparent rate difference led us to carry out a more careful kinetic study of these two compounds as well as their higher homologs. The preparation of these homologs is outlined below.

The two dienes, needed for the Diels-Alder synthesis of the 1,4-dihydronaphthocyclopentenes and the 1,4-dihydrocyclohenenes, 1-vinylcyclopentene[26] (63) and 1-vinylcyclohenene[28,a] (64), were prepared from cyclopentanone and cyclohenanone, respectively, by a route analogous to that of 1-vinylcyclobutene.

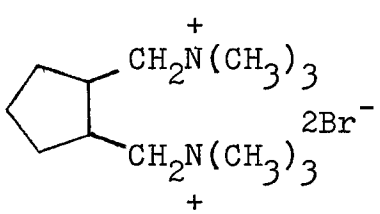


63



64

A Hoffmann elimination of 1,2-bis(trimethylamino-methyl)-cyclopentane dibromide[24,b] (65) afforded 1,2-dimethylenecyclopentane (66). Pyrolysis of hexahydrophthalyl diacetate[b] (67)

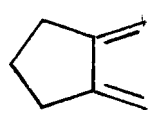


65

1) Ag_2O/H_2O

2) Δ

75%



66

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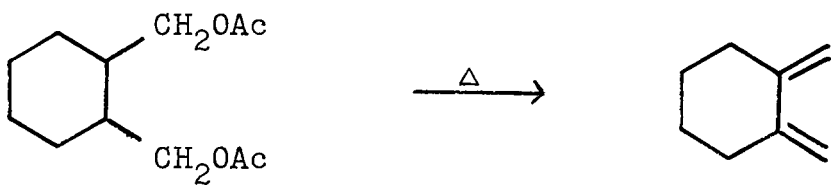
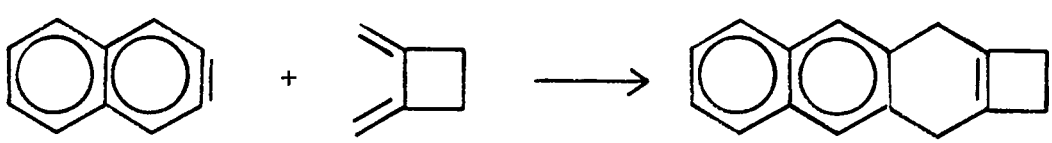
[a] prepared by Dr. R. P. Thummel
[b] prepared in part by W. Nutakul

gave 1,2-dimethylene cyclohexane [29,a] (68).

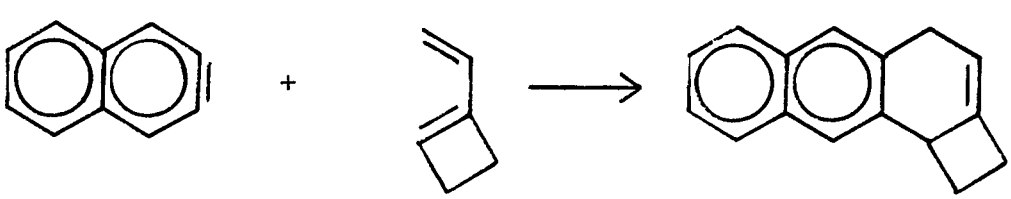


67 68

The 1,4-dihydroanthrocyclobutenes were also prepared by the Diels-Alder approach. Addition of 2,3-dehydronaphthalene (69) to 1,2-dimethylenecyclobutane (51) gave 1,4-dihydroanthro-(b)cyclobutene (70). Addition of 69 to 1-vinylcyclobutene (59) gave 1,4-dihydroanthro(a)cyclobutene (71). The 2,3-dehydro-naphthalene (69) was generated by the thermal decomposition



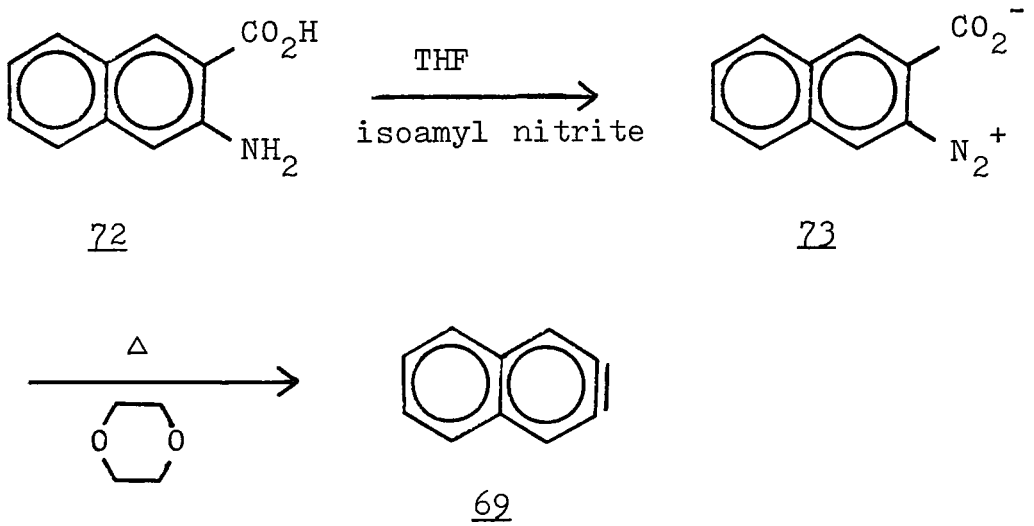
69 51 70



69 59 71

[a] prepared by Dr. R. P. Thummel

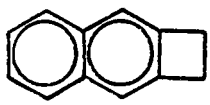
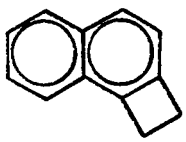
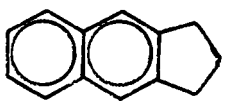
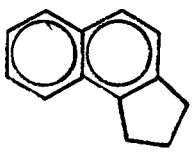
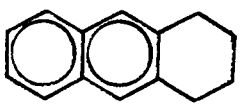
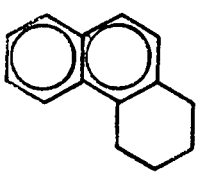
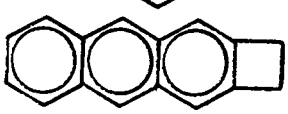
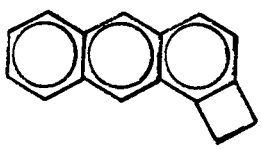
of naphthalene-3-diazonium-2-carboxylate (73), which was prepared by the treatment of 3-amino-2-naphthoic acid[30] (72) with isoamyl nitrite.



The fused-ring polynuclear aromatic compounds of Table III were all prepared by DDQ oxidation of the corresponding 1,4-dihydro-compounds in either benzene or chloroform. The rate of oxidation of each 1,4-dihydro-aromatic compound listed in Table II was measured (see discussion of results). We therefore decided to prepare additional 1,4-dihydroaromatic compounds for a more in depth kinetic study. The annelated 1,4-dihydrobenzenes were chosen to study the effects that substituents on the dihydroaromatic nucleus would have on the rate of oxidation. Table IV lists the 1,4-dihydroaromatic compounds prepared. As noted in Table IV all the compounds were either prepared by a Birch reduction or by a Diels-Alder route.

TABLE III

Fused-Ring Naphthalenes and Anthracenes

Compound		mp/bp	Reference
	(15)	85-86°C	6
	(20)	oil[a]	7
	(8)	95°C	4
	(11)	oil[a]	5
	(101)	101-102°C	42
	(102)	56-58°C	43
	(78)	245-247°C	--
	(79)	103-105°C	--

[a]purified by preparative vpc

TABLE IV

1,4-Dihydroaromatic Compounds

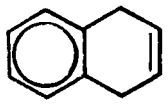
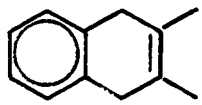
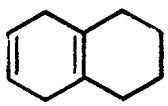
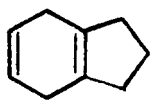
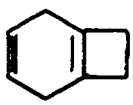
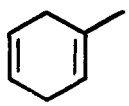
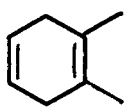
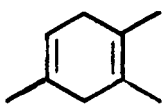
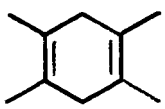
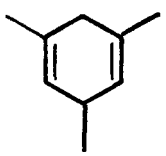
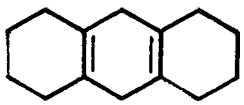
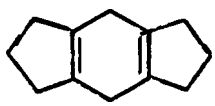
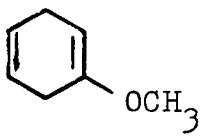
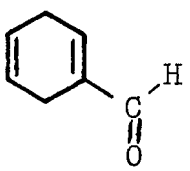
Compound		Method of proparation
	80	Birch reduction of naphthalene[31]
	81	Diels-Alder addition of benzyne and 2,3-dimethyl-1,3-butadiene
	82	Birch reduction of tetralin[32]
	83	Birch reduction of indan[33]
	84	Diels-Alder addition followed by two steps, literature preparation[34]
	85	Birch reduction of toluene[35]
	86	Birch reduction of o-xylene[36]
	88	Birch reduction of 1,3,4-trimethylbenzene
	89	Birch reduction of durene
	87	Birch reduction of 1,3,5-trimethylbenzene

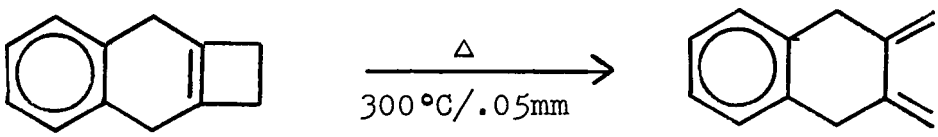
TABLE IV con't

Compound		Method of preparation
	90	Birch reduction of 1,2,3,4,6,7,8,9-octahydroanthracene
	91	Birch reduction of benzo[1,2:4,5]dicyclopentene
	92	Birch reduction of anisol[37]
	93	Diels-Alder addition of 1,3-butadiene and propargalaldehyde [38]

Part B:

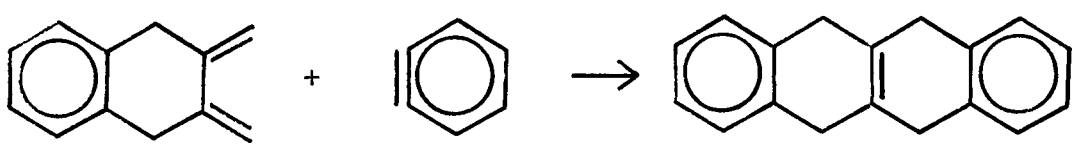
Chemistry of 1,4-Dihydronaphtho(b)cyclobutene

The strained cyclobutene ring of 1,4-dihydronaphtho(b)-cyclobutene (52) proved to be reactive toward ring opening, cycloaddition and oxidation. When (52) was passed through a one foot spiral glass tube heated to 300°C and evacuated to .05 mm, 2,3-dimethylene-1,2,3,4-tetrahydronaphthalene (94) was obtained. Treatment of 94 with one equivalent of benzyne



52 94

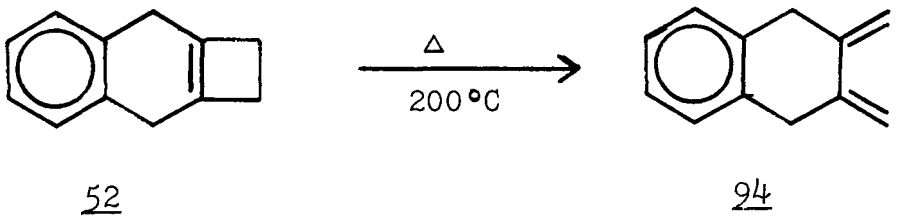
gave 5,6,11,12-tetrahydronaphthacene (95). Treatment of 95 with DDQ gave naphthacene (96). When 52 was sealed in a glass



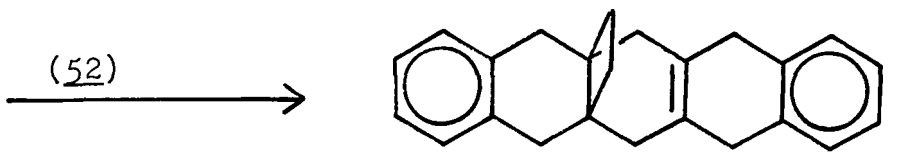
94 50 95

96

tube and heated to 220°C for eight hours, the dimer 97 was formed. This dimer could conceivably result from the formation of 94 followed by a Diels-Alder addition of 94 with unreacted 52. Compound 52 was also sealed in a glass tube

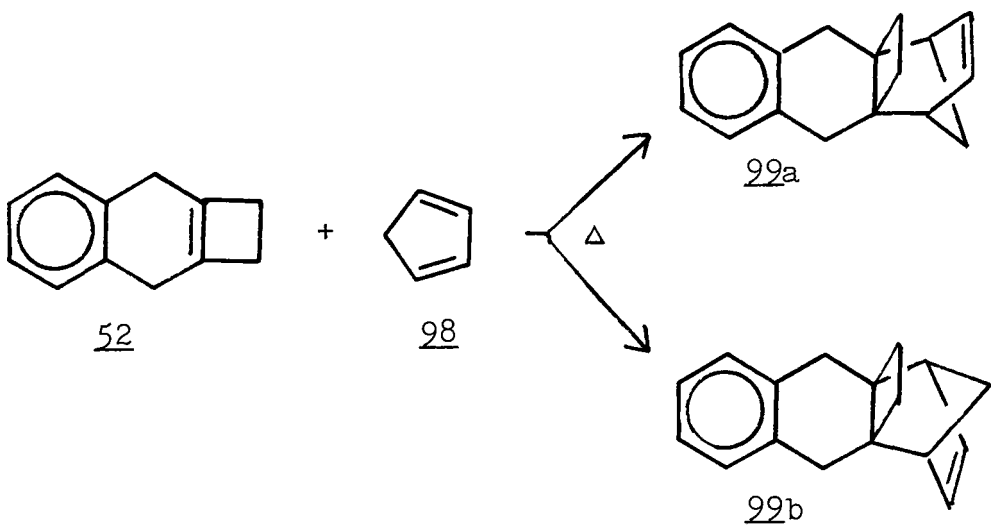


52 94



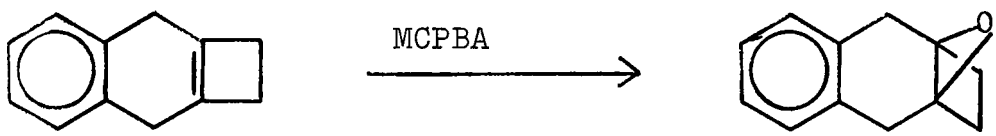
97

with ~4 equivalents of cyclopentadiene (98) and heated to 160°C for 20 hours to give the Diels-Alder adduct 99.

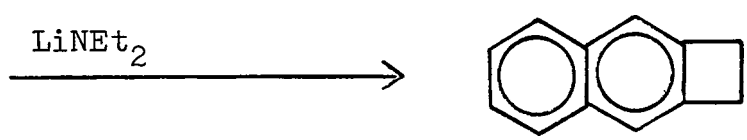


52 98 99a 99b

The stereochemistry of this adduct could not be determined from the spectral data obtained. Treatment of 52 with meta-chloroperbenzoic acid in dichloromethane gave 1,4-dihydronaphtho(b)cyclobutene oxide (100). When 100 was treated with lithium diethyl amide[39] followed by aqueous workup the aromatized compound 15 was obtained. Attempted oxidation of

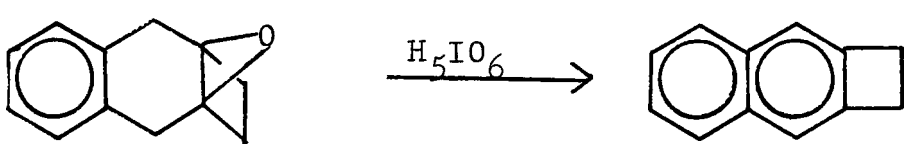


52 100



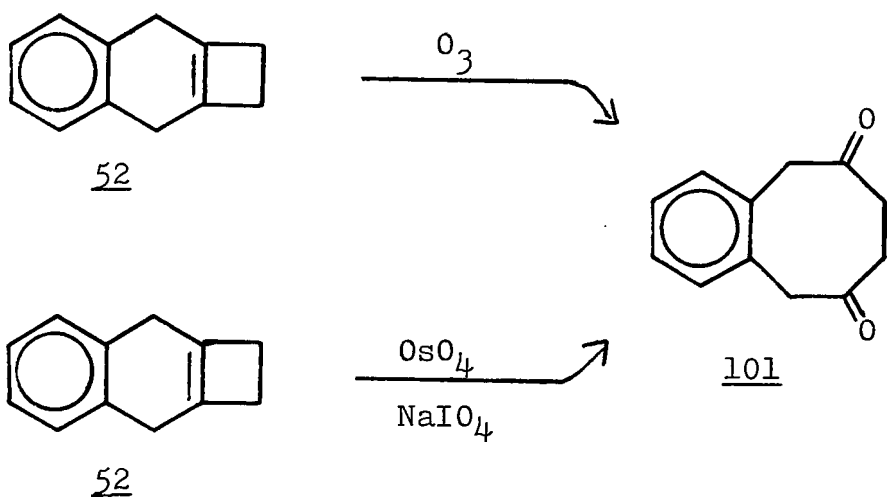
15

100 with periodic acid[40] failed to give the corresponding diol, but rather gave the aromatic compound 15. Compound 53 was



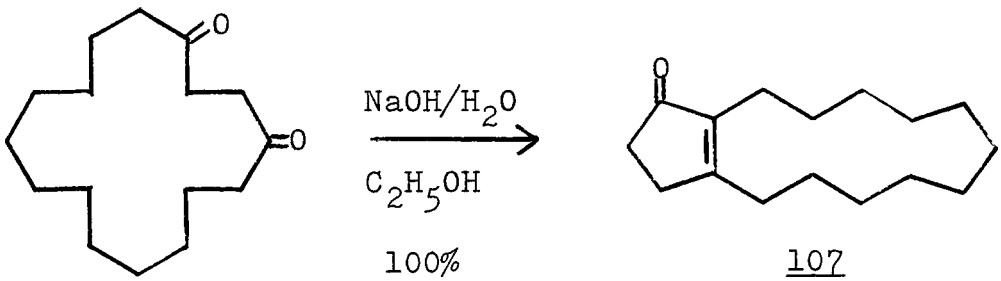
100 15

also subjected to ozonolysis in dichloromethane and the diketone was believed to be formed although the white gummy solid obtained resisted all attempts at purification. However treatment of 52 with a catalytic amount of osmium tetraoxide and two equivalents of sodium meta-periodate[41] gave the diketone (101) as a crystalline material, mp 75.5°C.



Although purification of the product of ozonolysis of 52 was not possible, comparison of the NMR of that mixture with the product of the osmiumtetraoxide catalyzed oxidation, indicated the diketone to be the major component. Attempted Aldol condensations of 101, even under very mild conditions (saturated sodium bicarbonate solution at 5°C for one min) afforded a mixture of compounds as evidenced by TLC. However, an analogous aldol condensation was carried out by

Corey and Helquist [53] as shown below.



106 107

DISCUSSION OF RESULTS

DISCUSSION OF RESULTS

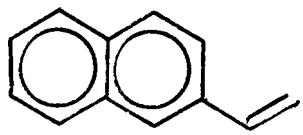
Part A:

Fused-Ring Naphthalenes and Anthracenes

The synthetic approach to fused-ring polynuclear aromatic compounds described in the preceeding section has several advantages and disadvantages. To prepare four and five-membered fused-ring naphthalenes by existing literature procedures, different multistep syntheses are required.[4,5,6,7] The Diels-Alder approach can prepare each of the four-, five-, and six-membered fused-ring naphthalenes by one general route. The previously reported overall yields of fused-ring naphthalenes are, in general, higher than those obtained by the Diels-Alder approach. The lower yields, however, are offset somewhat by the ease with which the latter approach can be carried out. Our synthetic approach has an added advantage in the synthesis of naphtho[a]cyclobutene. The four-membered ring is incorporated into the diene undergoing cycloaddition. Thus for the addition of 1-vinylcyclobutene with benzyne there is relief of steric strain by migration of the double bond out of the four membered ring.

The Diels-Alder addition of 1-vinylcyclobutene to benzyne provided 1,4-dihydronaphtho[a]cyclobutene (60) as well as a side product. Vpc analysis of the Diels-Alder reaction mixture indicated two products, each showing approximately equal area peaks. The longer retention time peak was isolated and identified as 60. The shorter retention time peak was isolated but could not be fully characterized.

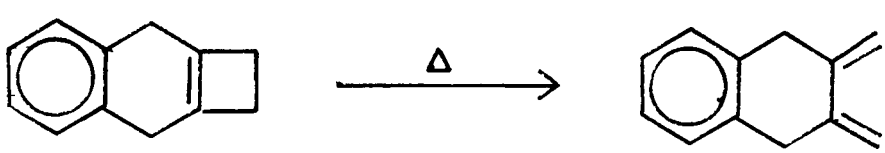
Its NMR spectra indicated five aromatic protons and seven vinylic protons. Comparison of its IR with an authentic sample ruled out the possibility of 2-vinylnaphthalene (102).



102

It is believed that the side product is an isomer of phenylhexatriene. However, there are eleven isomers of phenylhexatriene and no further efforts at characterization were attempted.

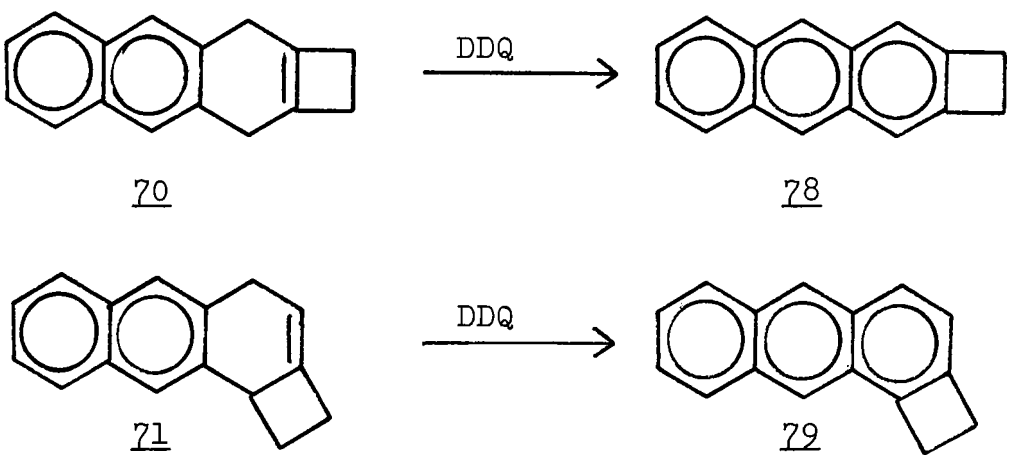
The cyclobutene carbon-carbon double bond of 52 is very reactive toward oxidation and cycloaddition. The cyclobutene ring of 52 is also labile toward ring-opening, producing a reactive diene (94). The diene 94 was found to undergo Diels-Alder addition with benzyne. Analogous results were observed by Cava[8] with compound 21 (see introduction).



52 94

The Diels-Alder approach to fused-ring naphthalenes was also adapted to provide the first synthesis of anthrocyclobutenes. The anthrocyclobutenes represent the smallest fused-ring anthracenes yet known. Both

1,4-dihydroanthro[b]cyclobutene (70) and 1,4-dihydroanthro-[a]cyclobutene (71) were prepared by a Diels-Alder addition. Aromatization of 71 proceeded much more slowly than did the aromatization of 70. As noted in the kinetic section (part B this chapter) this slow oxidation is analogous to the aromatization of 1,4-dihydronaphthocyclobutenes. The slow aromatization of 71 might be explained by angle strain arguments. In the aromatization of 71, considerable angle strain is incorporated in the four-membered fused-ring, whereas in the aromatization of 70 there is relief of strain in the four-membered fused-ring. Aromatization of 70 changes a carbon-carbon double bond in the four-membered ring to a longer aromatic bond. Aromatization of 71 changes a carbon-carbon single bond in the four-membered ring to a shorter aromatic bond.



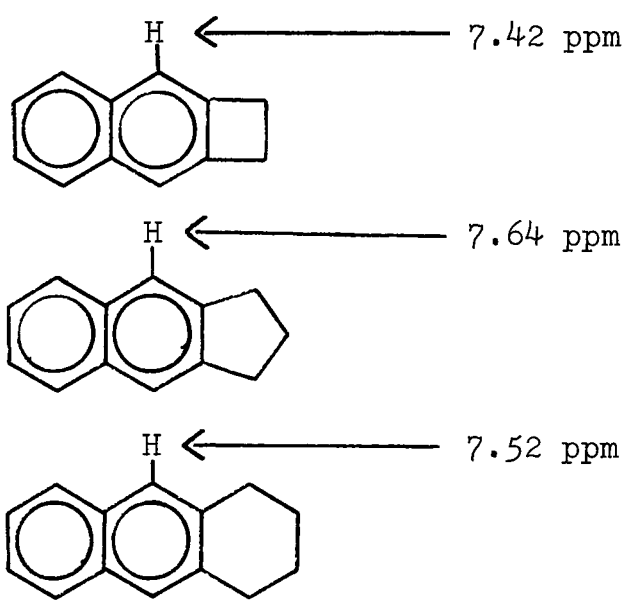
70 78

71 79

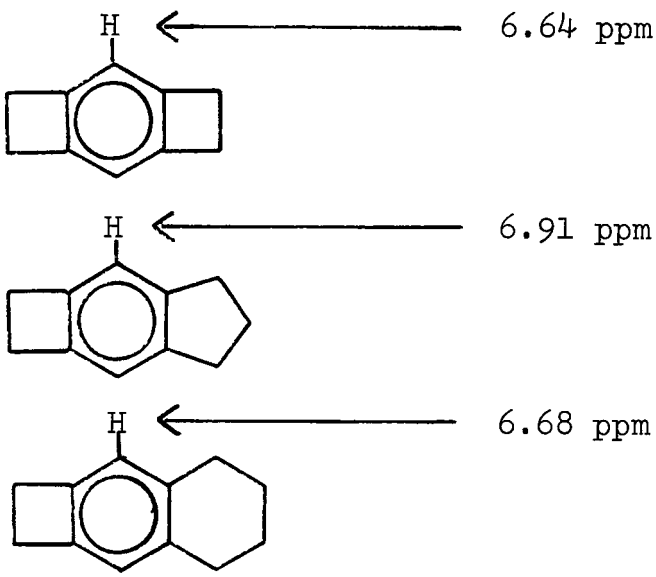
As stated in the introduction, bond alternation induced by small ring fusion might occur more readily for naphthalene than for benzene. To observe the effects of small ring

fusion, the isomeric naphthocyclobutenes were examined by NMR and photoelectron spectroscopy (PES).

Finnegan[44] and Streitwieser[45] have reported that, for a fused-ring aromatic compound, the acidity of the proton attached to a carbon α to a fused-ring increases as the size of the fused-ring decreases. Streitwieser argued that the atomic orbitals of the bridgehead carbon used in bonding to the small ring are higher in p-character, therefore leaving an orbital higher in s-character bonded to the ortho carbon. This rehybridization of the bridgehead carbon causes an inductive polarization of the ortho carbon-hydrogen bond. Rehybridization arguments would predict a downfield NMR chemical shift due to decreased shielding, for the protons α to the fused-ring of naphtho[b]cyclobutene, as compared to the protons α to the fused-ring of naphtho[b]cyclopentene or 1,2,3,4-tetrahydroanthracene. The chemical shifts observed are listed below:



The expected downfield shift is not observed for naphtho[b]-cyclobutene. However, Thummel and Nutakul[2,25] have observed similar chemical shifts for mono-annelated and <u>para</u>-<u>bis</u>-annelated benzenes. Thummel attributes this unusual upfield



shift of the aryl protons α to a fused four-membered fused-ring to a possible local anisotropy effect and/or angle distortion resulting in the proton being pushed from the geometric center of the benzene nucleus.

A sample of naphtho[a]cyclobutene and naphtho[b]cyclobutene was given to professor Ken Houk, at LSU, Baton Rouge, for a photoelectron spectroscopy study.[46] Measurements of the first four ionization potentials for the isomeric naphthocyclobutenes were compared with CNDO/S calculated molecular orbitals. Figure 1 is a correlation diagram showing the correspondence between the first four ionization potentials(IP's) of naphthalene and the naphthocyclobutenes. The changes in the first four IP's of naphthalene upon

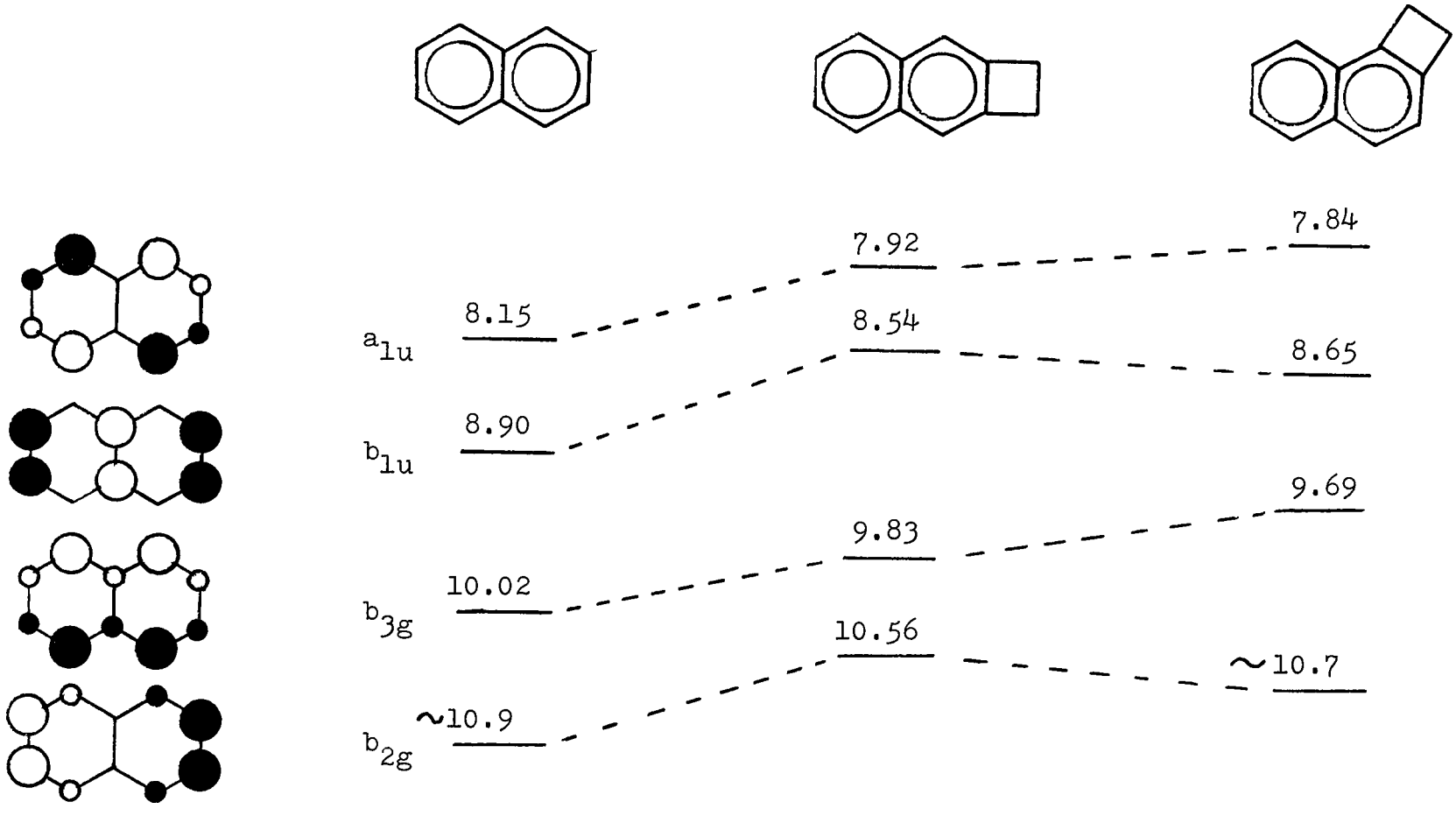


FIGURE 1

Correlation Diagram of the First Four Ionization Potentials of Naphthalene and the Naphthocyclobutenes

cyclobutene fusion can be understood in terms of the shapes of the naphthalene π MO's shown schematically at the left of Figure 1. For example, the first IP is influenced more by [a]-fusion than by [b]-fusion, since the coefficients at the site of substitution are larger for [a]-fusion. The second IP is influenced more by [b]-fusion than by [a]-fusion, and the third more by [a]-fusion than [b]-fusion, and the fourth more by [b]-fusion than by [a]-fusion. Houk found that distortion of an aromatic nucleus by strained-ring fusion has a significant influence on the IP's.

Part B:

DDQ Oxidations of 1,4-Dihydropolynuclear aromatic Compounds

As stated in the previous section, the rate of oxidation of 1,4-dihydronaphtho[b]cyclobutene (52) with DDQ in carbon tetrachloride as observed by NMR appeared to be greater than that of 1,4-dihydronaphtho[a]cyclobutene (60). This observation led us to conduct a more in depth study of the mechanism of DDQ oxidations. A series of 1,4-dihydroaromatic compounds was prepared and the rates of oxidation of these substances were determined. This kinetic data was then used along with existing literature rate data to examine the mechanism of DDQ oxidations.

The DDQ oxidation of 1,4-dihydroaromatic compounds has been claimed by Braude[15] to be essentially a bimolecular reaction. Thus the rate of oxidation is a function of both DDQ and the 1,4-dihydroaromatic compound. Under pseudo-

$$A + B \longrightarrow \text{Products}$$

$$\text{Rate} = k\,[A]\,[B]$$

$$\frac{-d[A]}{dt} = k\,[A]\,[B]$$

first order kinetic conditions one reactant is present in a large excess, therefore the observed rate is dependent on the concentration of the reactant not present in excess.

$$A + B \longrightarrow \text{Products}$$

$[A_o]$ $[B_o]$

$$\text{Rate} = k[B_o - X]\ [A_o - X]$$

since $[B_o - X] = [B_o]$, then

$$k_{observed} = k\ [B_o]$$

$$\therefore \text{Rate} = k_{observed}[A_o - X]$$

$$\frac{-d[A]}{dt} = k_{observed}[A]$$

where: $[A_o]$, $[B_o]$ = initial concentrations
and X = the loss of concentration as the reaction proceedes

However, the first order rate constant observed is also a function of the concentration of the species in large excess. The second-order rate constant can be obtained by dividing the observed rate constant by the initial concentration of the reactant present in large excess.

$$k_{obserbed} = k[B_o]$$

$$\therefore k = \frac{k_{observed}}{[B_o]}$$

k = the second-order rate constant

The 1,4-dihydroaromatic compounds which were prepared, as well as their rates of oxidations, are listed in Table V. The rates were measured under pseudo-first-order conditions, with the 1,4-dihydroaromatic compounds present in a greater than ten-fold excess. The pseudo-first-order rate constant (k_1) was determined by following the disappearance of the DDQ absorption at 3900Å. The values listed in Table V are the second-order-rate constants ($k_2=k_1/[\text{substrate}]$), and the relative rate constants (k_{rel}), relative to 1,4-dihydronaphthalene.

From Table V one notices a relationship between the substituents on the 1,4-dihydrobenzene nucleus and the relative rate of oxidation. Figure 2 shows the natural log of the relative rate of oxidation plotted against the number of methyl substituents attached to the 1,4-dihydrobenzene. If a carbonium ion intermediate is invoked, in the rate-determining step, such a species should be stabilized by electron-donating alkyl groups. The rate-enhancing effect of the methyl substituents on the 1,4-dihydroaromatic compound supports the involvement of such an intermediate. Further support for such an intermediate is evidenced by 2,5-dihydrobenzaldehyde (92). The electron-withdrawing group of (92) should destabilize a carbonium ion intermediate thus decreasing the rate of oxidation. This slow oxidation rate is observed, with 2,5-dihydrobenzaldehyde oxidizing $\sim$55 times slower than 1,4-cyclohexadiene. The effect of fused ring substituents on the rate of oxidation of

TABLE V

Rates of Oxidation of 1,4-Dihydrobenzenes in Glacial Acetic Acid at 25°C

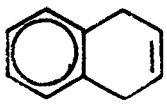
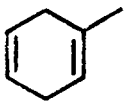
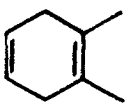
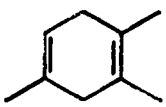
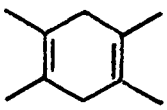
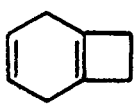
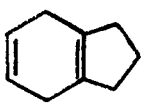
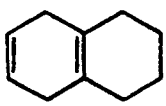
Substrate		Molarity ($X10^{-2}$)	$10^2 k_2 (M^{-1} sec^{-1})$	k_{rel}
	80	3.04	15.0	1
	102	7.8	5.12	.34 (±.05)
	85	5.53	150	10 (±.5)
	86	3.01	1500	100 (±5)
	88	2.82	18,900	~1200
	89	2.36	too fast to measure	>1200
	84	1.40	78.3	5.2 (±.05)
	83	2.44	447	30 (±1.5)
	82	2.63	305	20 (±1.5)

TABLE V con't

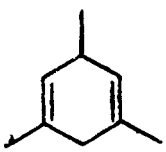
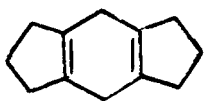
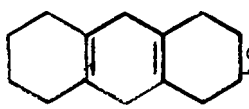
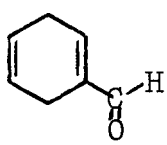
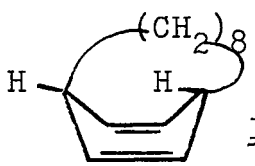
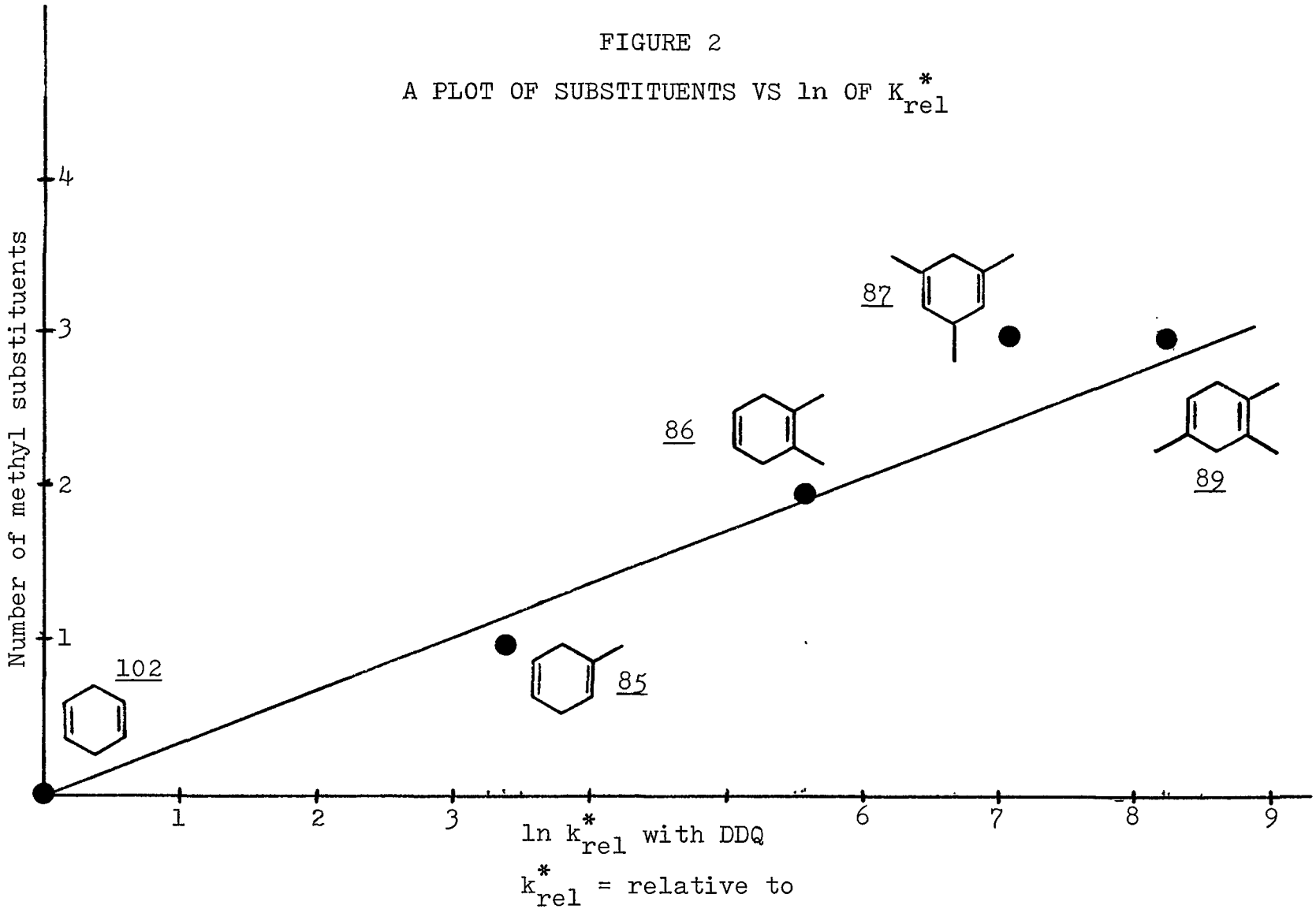
Substrate	Molarity ($X10^{-2}$)	$10^2 k_2 (M^{-1} sec)$	k_{rel}
 87	3.10	6,140	409 (±1.0)
 91	3.13	10,000	670
 90	1.87	9,000	600
 92	3.83	.09	.006 (±.001)
 104	17.99	.294	.019 (±.001)

FIGURE 2

A PLOT OF SUBSTITUENTS VS ln OF K^{*}_{rel}



k^{*}_{rel} = relative to

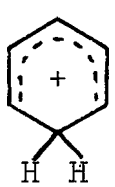
1,4-dihydroaromatic compounds also suggest the possibility of a carbonium ion intermediate. Each of the mono-annelated compounds have two methylene carbons attached to the 1,4-dihydroaromatic nucleus. However, the electron donating effect of a five-or six-membered, fused ring is greater than that of a four membered, fused ring. This effect is observed in the relative rates, with 84 oxidizing slower than either 82 or 83. The electron donating effects of the five-and six-membered, fused rings are probably very similar, yet 83 oxidizes faster than 82. This small rate difference between 83 and 85 may be due to steric effects. The five-membered, fused ring of 82 is almost planar whereas the six-membered, fused ring of 83 can exist in several non-planar conformations which might hinder DDQ approach to the 1,4-dihydrobenzene nucleus. The data in Table V therefore strongly suggest a carbonium ion intermediate.

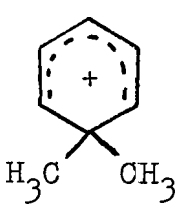
The three mechanisms discussed in the introduction were reexamined in light of this new evidence for a carbonium ion intermediate. These mechanisms are: (A) Braude's hydride transfer mechanism, (C) Rocěk's cyclic-concerted mechanism, and (B) Müller's 1,4-elimination mechanism.

Braude[15] proposed a hydride abstraction in the rate-determining step resulting in the formation of an intermediate carbonium ion. This mechanism is reinforced by our evidence for a carbonium ion intermediate. Invoking Braude's mechanism the relative rates of the compounds in

Table V are what would be expected. Braude's carbonium ion mechanism is further substantiated by the observation that the DDQ oxidation of tropilidene occurs much faster than that of 3,3-dimethyl-1,4-cyclohexadiene.

Braude's mechanism, however, cannot explain certain other observations. If formation of the carbonium ion alone was the rate determinig factor in DDQ oxidations, then why does 1,4-cyclohexadiene oxidize 2,000 times faster than either 1,4-pentadiene or 3,3-dimethyl-1,4-cyclohexadiene (41)? Both 1,4-pentadiene and 41 can form pentadienyl cation of approximately the same stability as that of the

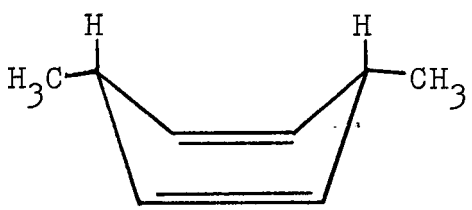




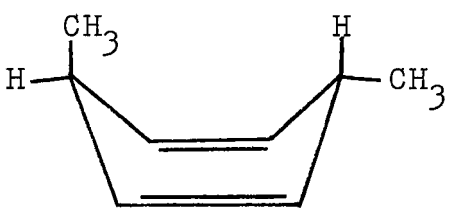
1,4-cyclohexadienyl cation. By the above argument, as well as those presented by Roček (see Introduction), the simple hydride transfer mechanism was rejected for 1,4-cyclohexadienes.

Roček's[17] cyclic concerted mechanism has two factors in its favor. The rate difference between cis and trans-3,6-dimethyl-1,4-cyclohexadiene can well be accounted for by a concerted cis elimination of two hydrogens in the 1 ,4-position. This concerted cis elimination would also account for the kinetic isotope effect of K_H/K_D = 10 observed for

the DDQ oxidation of perdeuterio-1,4-cyclohexadiene. In an attempt to refute Roček's mechanism, Müller[18] argued that the rate difference between the oxidation of 44 and 45 might be due to steric effects rather than the proper geometry for cis-elimination. Müller considered both 44 and 45 to have boat conformations as shown below. He suggested that



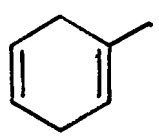
44



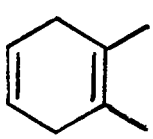
45

the cis isomer 44 should be more reactive than the trans isomer 45. Based on steric arguments he claims that 45 is of higher energy than 44 due to the methyl-hydrogen interior flag pole interaction. It should be pointed out that these arguments are based on ground state energetics and may not hold for transition state intermediates. However, more recent NMR evidence[47] indicates that 1,4-cyclohexadiene is a planar molecule. It has also been shown that cis-3,6-dimethyl-1,4-cyclohexadiene exist as a boat conformer whereas trans-3,6-dimethyl-1,4-cyclohexadiene is planar. Therefore, the basis for Müller's reasoning appears to be false and his argument can be ruled out. There does, however, appear to be a definite preference for cis-elimination.

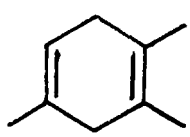
Roček's concerted cyclic mechanism cannot explain the rate differences observed for the alkylated 1,4-dihydrobenzenes listed in Table V. A completely concerted mechanism forms no intermediate. Thus electron withdrawing or electron donating groups on a 1,4-dihydroaromatic compound should have no effect on a symmetrical transition state. The position of the methyl groups in 85, 86, 88, and 89 should not hinder either side of the 1,4-cyclohexadiene more than the other for hydride abstraction. A possible explanation for these rates of oxidation using a concerted cyclic



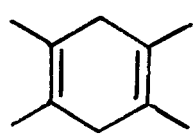
85



86



88

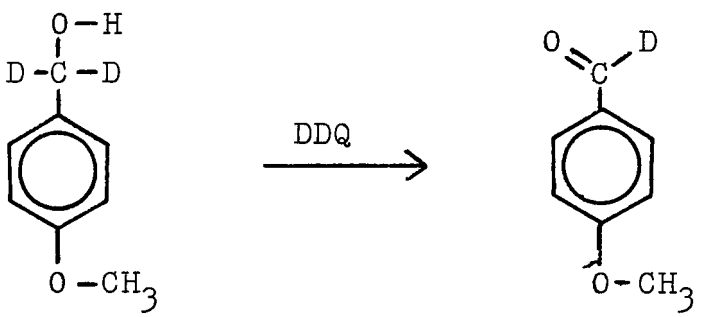


89

mechanism might be stability of the resulting product. However, if product development control was an important factor, then 1,4-cyclohexadiene (102) should aromatize faster than 1,4-dihydronaphthalene (80). The resonance energy gained for the aromatization of 1,4-cyclohexadiene is 36 Kcal/mole compared to 25 Kcal/mole for 1,4-dihydronaphthalene. Yet 102 oxidizes slower than 80, therefore, there is little liklihood of product development control's accounting for rate differences of a factor of ten or more.

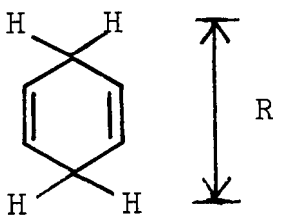
The kinetic isotope effect of K_H/K_D= 10 observed for

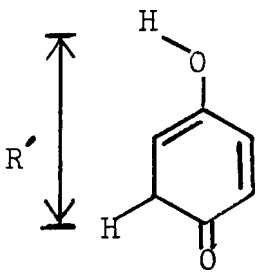
the DDQ oxidation of perdeuterio-1,4-cyclohexadiene may not be conclusive evidence for a concerted mechanism. A similar isotope effect of K_H/K_D= 10 was observed for the DDQ oxidation of anisyl alcohol (46). This observation somewhat weakens the evidence for a concerted cis-elimination based on the isotope effect. For there to be a concerted cis-elimination,



46 47

some preferred spatial orientation should be observed. The distance between cis-hydrogens at the 1,4-positions of a 1,4-dihydroaromatic compound will be defined as R, and the distance between the points of attachment of two hydrogens to a quinone nucleus (assuming 1,4-addition to occur) as shown below, will be defined as R'. When R≈R' conditions would be favorable for a simultaneous abstraction of two cis-1,4-hydrogens from a 1,4-dihydroaromatic compound by the quinone in a 1,4-fashion. When R differs significantly from R' then synchronous abstraction of two cis-hydrogens is less favorable. Therefore the preferred spatial orientation will be considered as the case where R ≈ R'.





The distance[a] from hydrogen to hydrogen at the 1,4-position for a boat conformer of 1,4-cyclohexadiene is 3.35 Å and 4.4 Å for the planar conformer. The distance R' (as previously defined) is 4.6 Å. Therefore if one assumes ground state conformations to have some effect on activation energies, then a planar conformation for a 1,4-dihydroaromatic compound should be favored for a concerted cis-elimination by DDQ. The oxidation rates of compounds 87 and 88 indicate that the planar conformer is favored; however, the oxidation rates of 44 and 102 indicate that the boat conformer is favored for a concerted cis-elimination. These relative rate observations were interpreted as evidence for a lack of spatial orientation. Braude[15] also noted a lack of a preferred spatial orientation in using 1,2- and 1,4-dihydroaromatic compounds with both 1,2-and 1,4-quinones.

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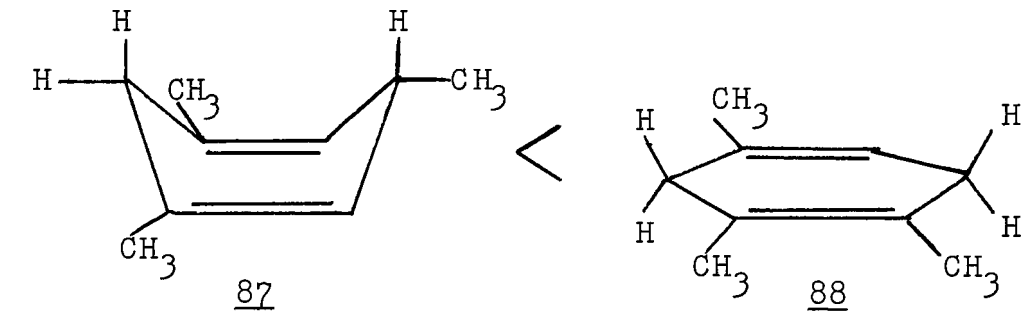
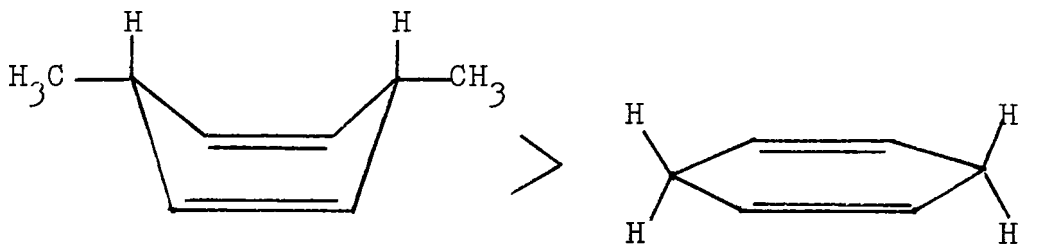
[a]Dreiding models were used to estimate distances.

Relative Oxidation Rates



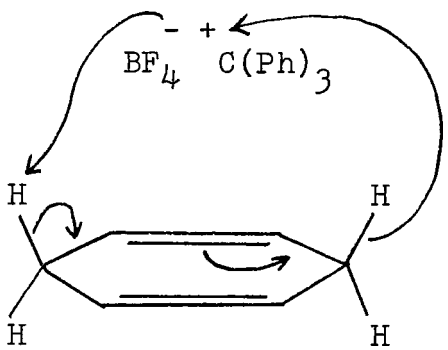
87 88



44 102

Evidence against Rocek's concerted mechanism is also provided by the oxidation rates obtained with triphenylmethyl fluoroborate. Müller[18] conducted a rate study of a series of 1,4-dihydroaromatic compounds using both DDQ and triphenylmethylfluoroborate. It was observed that comparable relative rates were obtained for both oxidants (for example 44 oxidized faster than 45 for both oxidants). Müller argues that triphenylmethyl fluoroborate cannot undergo a cyclic concerted

mechanism, but rather must invoke either solvent or conjugate base to remove the proton. However, Rocek's mechanism might still be invoked if one considers the triphenylmethyl fluoroborate mechanism as shown below:



Müller proposed a 1,4-elimination, invoking DDQ to abstract a hydride and the solvent or a conjugate base to abstract a proton. By use of a third molecule to remove the proton, Müller has avoided any preferred spacial orientation arguments. Müller's mechanism is very similar to Rocek's mechanism, in that it is a concerted elimination with the formation of no intermediates.

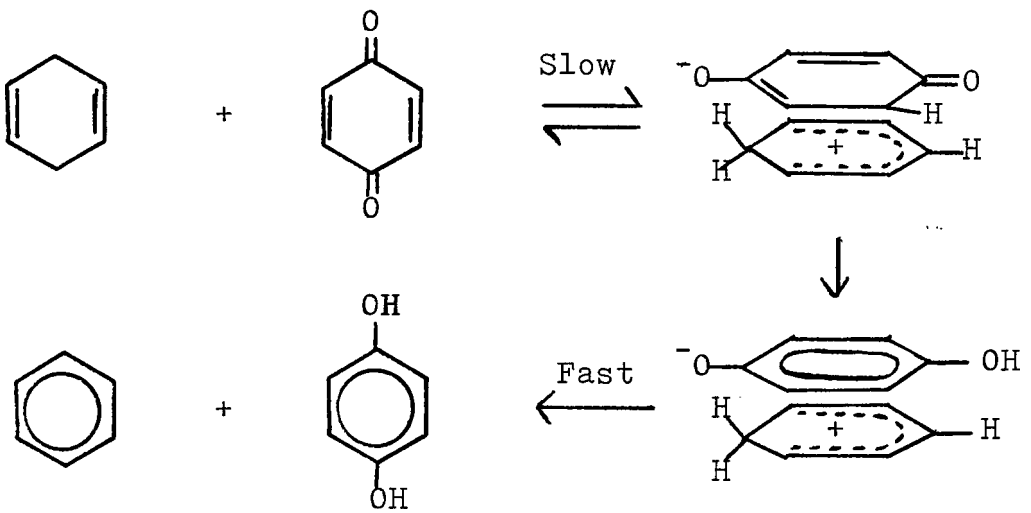
Müller's mechanism cannot explain the rate difference observed in Table V. The same arguments presented against Rocek's concerted mechanism also hold against Müller's concerted mechanism except for spatial orientation requirements. Müller's mechanism cannot explain why cis-elimination should be favored over trans-elimination. It would appear that if two different molecules were removing a hydride and a proton

simultaneously from the 1,4-positions of a 1,4-dihydroaromatic compound, that trans-1,4-hydrogens would be favored over the cis-1,4-hydrogens. The trans-1,4-hydrogens of a 1,4-dihydroaromatic compound should afford the least steric hindrance for a ter molecular transition state.

The evidence for a carbonium ion intermediate together with the arguments for and against the three existing mechanisms, suggest a possible fourth mechanism for DDQ oxidations of 1,4-dihydroaromatic compounds. There is convincing evidence for the following:

1) carbonium ion intermediate
2) cis-elimination preferred
3) essentially a bimolecular reaction
4) product development control has little effect
5) not a free radical reaction (see introduction)

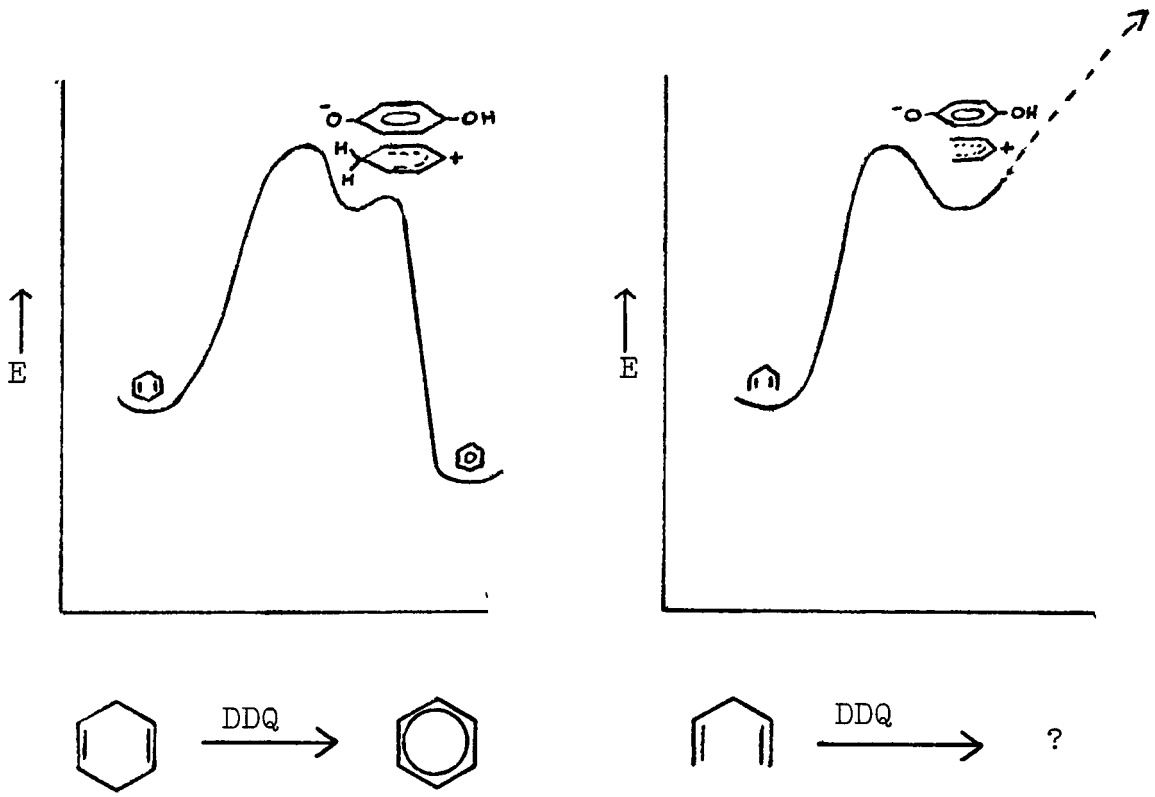
The above observations might be explained by the following mechanism. A hydride is abstracted from a 1,4-dihydroaromatic compound by DDQ followed by formation of a tight ion pair which establishes an equilibrium with reactants. Removal of a proton then drives the reaction to the aromatic compound and reduced DDQ. If the 1,4-dihydroaromatic compound has a pair of cis-hydrogens then proton abstraction by the hydroquinone anion should be very rapid, thus the equilibrium will be driven to the right. If there



is no pair of cis-hydrogens, then the abstraction of the proton must be accomplished by another species, such as solvent or conjugate base. If removal of the proton becomes difficult then the second step approaches or becomes the slow step thus, the equilibrium of the first step is slowly disturbed, resulting in a slow oxidation rate. This mechanism would explain why cis-3,6-dimethyl-1,4-cyclohexadiene (44) oxidizes faster than the trans-isomer (45). Since this mechanism is a two step process with the formation of an intermediate carbonium ion, the rate data from Table V can be explained. This mechanism can also explain why 1,4-pentadiene oxidizes much slower than 1,4-cyclohexadiene. Energy diagrams representing reaction of each diene with DDQ are presented in Figure 3. Both 1,4-pentadiene and 1,4-cyclohexadiene may form tight ion pairs of approximately the same stability but

FIGURE 3

Energy Diagram of the Reaction of
1,4-Cyclohexadiene and 1,4-Pentadiene with DDQ



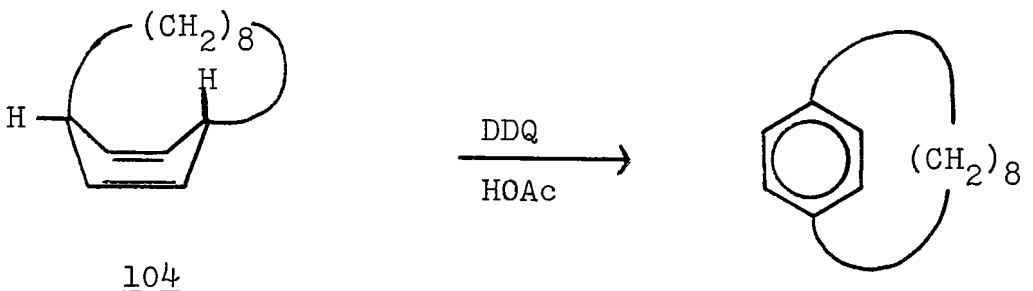
decomposition of the ion pair must differ. The ion pair formed between DDQ and 1,4-cyclohexadiene should quickly undergo a proton transfer to give benzene. The ion pair formed between DDQ and 1,4-pentadiene, on the other hand, would exist in equilibrium with 1,4-pentadiene and DDQ until some other reactant intervened (i.e.: solvolysis of the pentadienyl cation). This slow decomposition of the tight-ion pair would result in the second step becoming the rate determining step.

To determine what happens to a compound which cannot be aromatized by DDQ, allylbenzene was stirred with DDQ in refluxing acetic acid for two days. Analysis by NMR indicated only unreacted allylbenzene, however a small quantity (< 20%) of an insoluble white solid (mp >300°C, charred at 210°C) was obtained.

103

The oxidation of 104 is an example of a slow oxidation rate due to the inaccessibility of one of the 1,4-hydrogens on the 1,4-cyclohexadiene nucleus. Compound 104 is capable of

aromatization and has an allylic hydrogen readily accessible for hydride abstraction. However, once the hydride is abstracted by a DDQ molecule, loss of the allylic proton is very slow. Compound 104 oxidizes approximately 25 times slower than 1,4-cyclohexadiene. Analysis of the product of the DDQ oxidation indicates that the expected [18]-paracyclophane (105) was obtained.



104 105

Table VI lists the rates of oxidations for 1,4-dihydronaphthalenes and dihydroanthracenes. This rate data will be discussed in terms of the proposed tight-ion pair two step mechanism. The Gibbs free energy of the aromatic and dihydroaromatic compounds were calculated to estimate any possible product development control. The distances between cis-benzylic hydrogens were also estimated to determine if there is preferred spatial orientation.

It is observed that the rate of oxidation for the dihydronaphthalene series (Table VI) increases in the order of 1,4-dihydronaphthalene < 1,4-dihydronaphthocyclobutene < 1,4-dihydronaphthocyclohexene < 1,4-dihydronaphthocyclopentene, with the exception of 1,4-dihydronaphtho[a]cyclobutene (60), (this exception will be discussed later). This observed rate order is in agreement with the relative rates observed in the dihydrobenzene series. It is also observed that the symmetrical isomer of the four- and six-membered fused-ring naphthalenes oxidizes two to four times faster than the corresponding unsymmetrical isomer. This difference could be explained by a preference for syn-elimination. For the symmetrical isomers there are two pairs of cis-benzylic hydrogens as opposed to only one pair for the unsymmetrical isomer. However, for the 1,4-dihydronaphthocyclopentenes, the unsymmetrical isomer oxidizes 0.5 times as fast as the symmetrical isomer. This small rate difference might be due to product development control or differences in the ground

TABLE VI

Rates of Oxidation of 1,4-Dihydropolynuclear Aromatics with DDQ in Glacial Acetic Acid

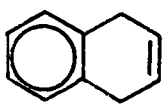
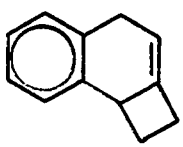
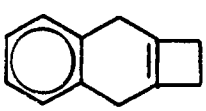
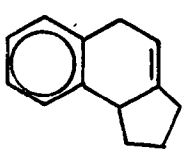
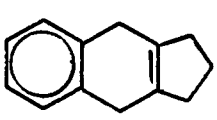
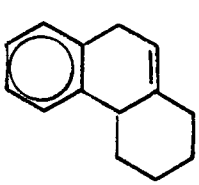
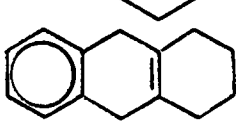
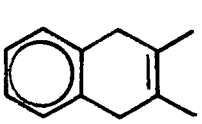
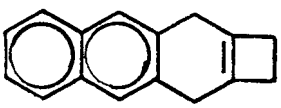
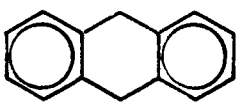
Substrate		Molarity ($X10^{-2}$)	$10^2 k_2 (M^{-1} sec^{-1})$	k_{rel}
	80	3.04	15.0	1
	60	2.54	12.6	.84 (±.05)
	52	2.17	49.4	3.3 (±.05)
	75	2.08	320	21.3(±.5)
	74	1.88	219	14.6(±.5)
	77	2.50	64.5	4.3 (±.05)
	76	2.23	159	10.6(±.5)
	81	1.85	272	18.1(±.5)

TABLE VI con't

Substrate	Molarity ($X10^{-2}$)	$10^2 k_2 (M^{-1} sec^{-1})$	K_{rel}
 70	1.07	117	7.8 (±.5)
	2.99	5.2	.34 (±.1)

state of the reactants which are reflected in the activation energy.

To determine if the stability of the product has any effect on the rate of the oxidation, the Gibbs free energy of the fused-ring naphthalene series was calculated. Using Benson's [48] group equivalents, the $\Delta H°$, $\Delta S°$ and $\Delta G°$ values the dihydro- and the aromatic compounds were calculated. The Gibbs free energy gained by the aromatization was then calculated, ($\Delta G = \Delta G°_{aromatic} - \Delta G°_{dihydro-}$). It should be noted that these values were calculated by additive group values and are only estimated values. Figure 4 shows a graphic representation of the energy gained by aromatization. Obvious trends are noticed, each symmetrical isomer gains approximately 1.64 Kcal/mole. This gain in ground state difference cannot account for the rate difference between four-five-and six-membered fused ring naphthalenes. This gain of 1.64 Kcal/mole is what would be expected of a homologous series, using Benson's additive group equivalents. However, as calculated, 1,4-dihydronaphtho[a]cyclobutene is 0.53 Kcal/mole lower in energy than naphtho[a]cyclobutene. This energy difference appears reasonable since aromatization of 1,4-dihydronaphtho[a]-cyclobutene results in the incorporation of ring strain in the four-membered fused ring. Figure 5 shows a possible potential energy diagram for the aromatization of the 1,4-dihydronaphthocyclobutenes. The activation energy for the formation of the tight ion pair for the symmetrical isomer should be less than that for the

TABLE VII

Thermodynamic Properties Calculated

Using Benson Group Equivalence

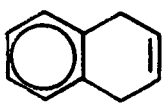
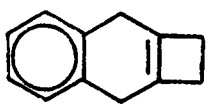
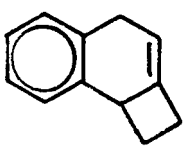
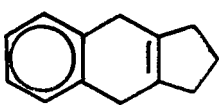
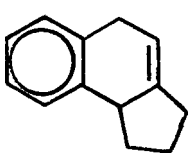
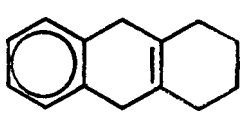
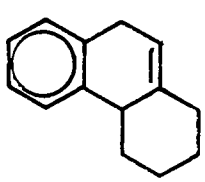
Compound	ΔH_F°(Kcal/mol)	ΔS°(cal/mol)	ΔG°(Kcal/mol)
	33.89	64.1	14.79
	57.67	71.35	36.41
	55.25	71.87	33.83
	28.82	77.57	5.70
	30.40	78.01	7.15
	1.37	82.69	-5.27
	19.15	78.93	-4.37

TABLE VII con't

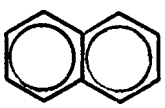
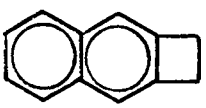
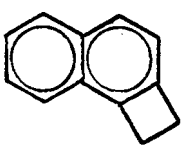
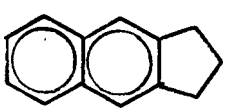
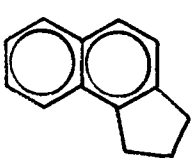
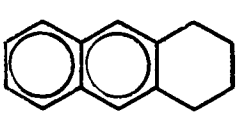
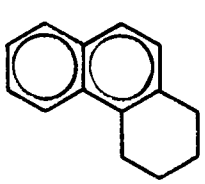
Compound	ΔH_F°(Kcal/mol)	ΔS°(cal/mol)	ΔG°(Kcal/mol)
	36.12	80.50	12.13
	61.39	89.32	34.77
	61.39	90.69	34.36
	32.54	95.54	4.07
	32.54	98.63	3.15
	23.09	100.66	-6.91
	23.09	102.03	-7.31

FIGURE 4

Calculated Ground State Energies

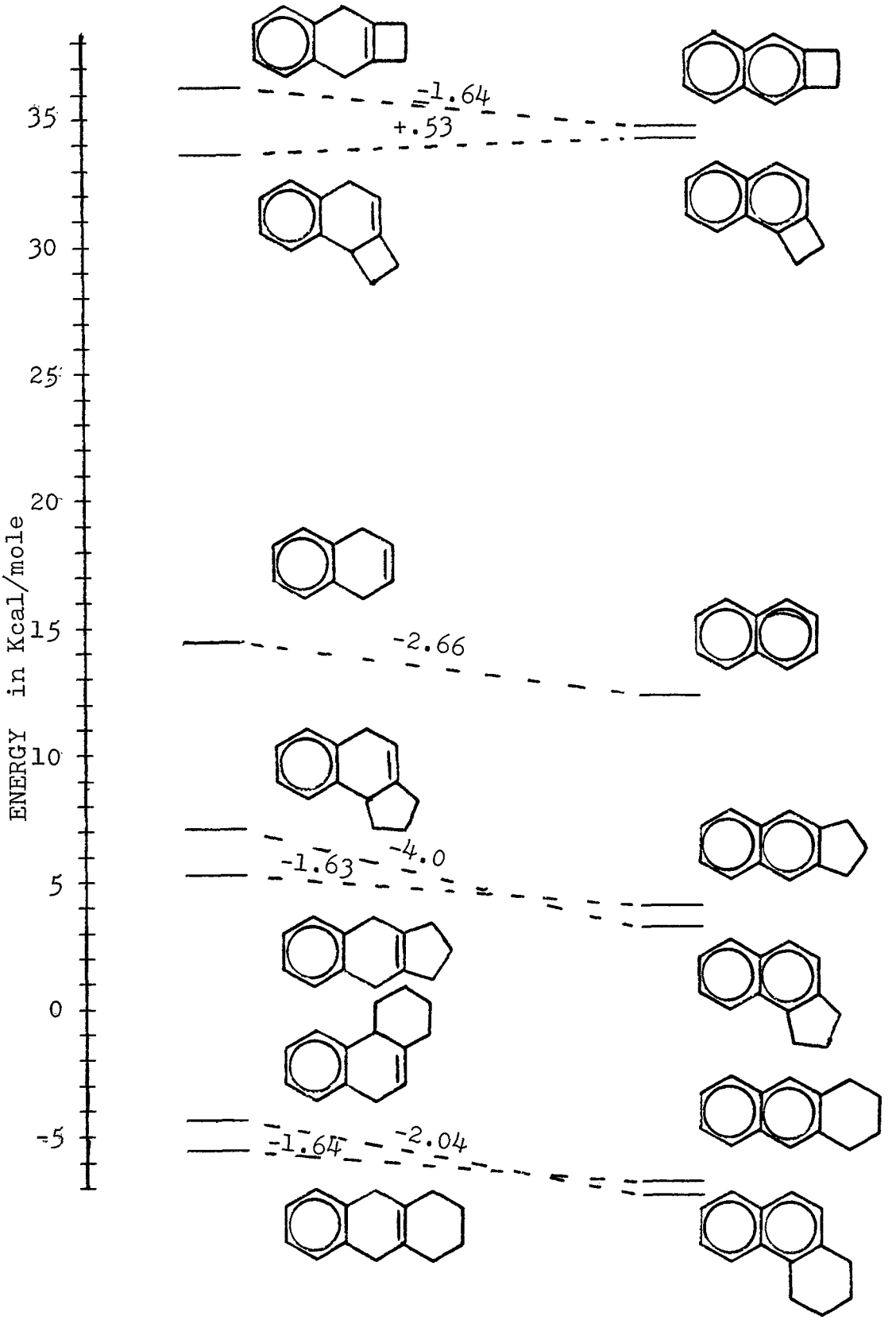
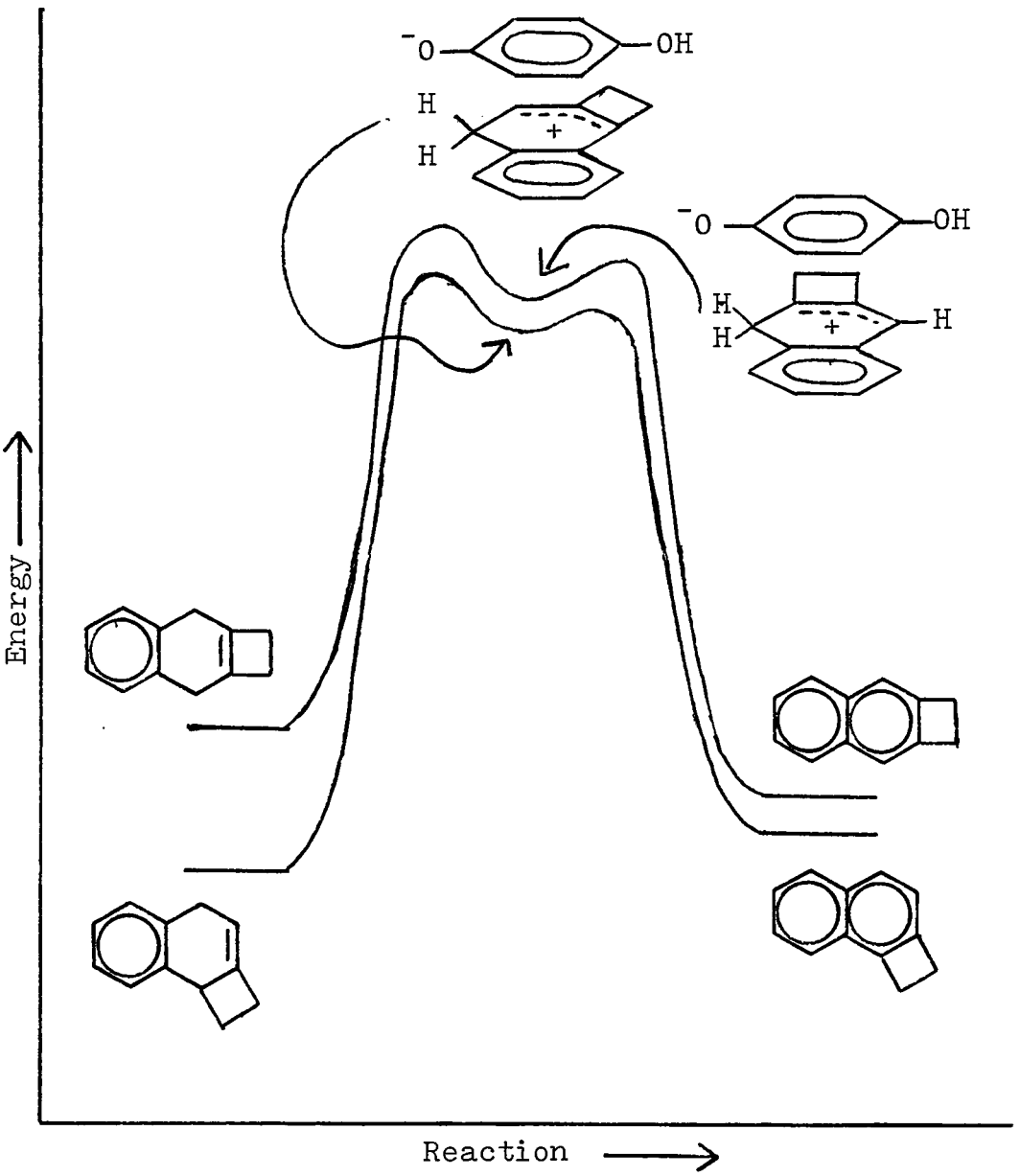
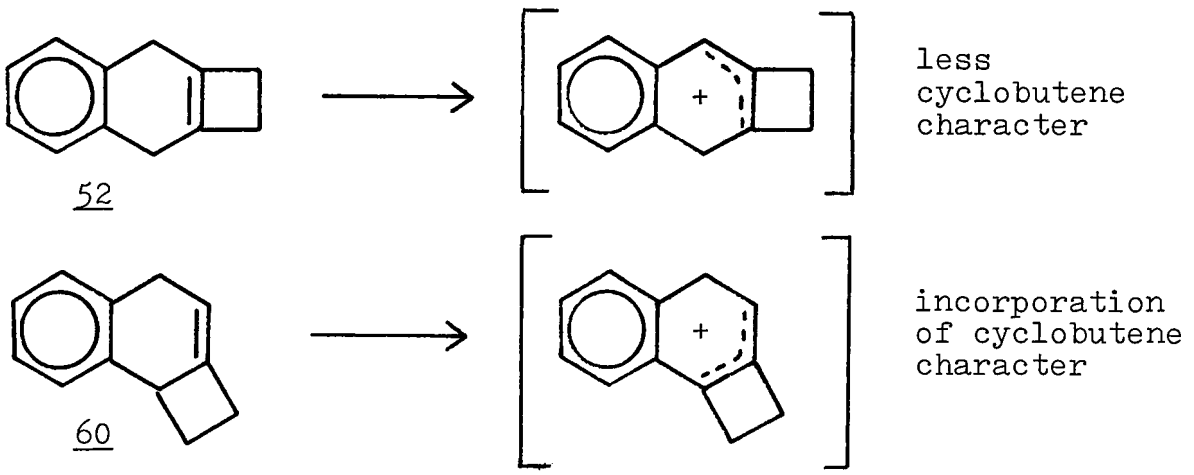


FIGURE 5

Energy Diagram for Oxidation of 1,4-Dihydronaphthocyclobutenes



unsymmetrical isomer. For the symmetrical isomer, formation of the carbonium ion results in less carbon-carbon double bond character for the four-membered ring. For the unsymmetrical



isomer, formation of the carbonium ion can result in formation of cyclobutene character.

The Benson group equivalent calculations may help explain why the unsymmetrical isomer of 1,4-dihydronaphthocyclopentene oxidizes faster than the symmetrical isomer. It is observed from Figure 4 that the ground state energy of 1,4-dihydronaphtho[b]cyclopentene is lower than that of 1,4-dihydronaphtho[a]cyclopentene. The opposite is noted for the aromatic species, with naphtho[a]cyclopentene having the lowest energy. Using the calculated ground state energies and assuming approximately equal transition state energies, Figure 6 is a possible energy diagram for the oxidation of the 1,4-dihydronaphthocyclopentenes. The observed rate difference between the two isomers might be due to differences

in activation energy is shown in Figure 6.

The question of whether there is a preferred spatial orientation, was investigated by estimating the distances between cis-1,4-benzylic hydrogens for the 1,4-dihydronaphthalene series. Using Dreiding models, the distances between the cis-benzylic hydrogens of the 1,4-dihydronaphthalenes were measured. The symmetrical isomers presented a problem, in that two conformations exist, the boat or planar conformers. The planar conformer was used for measurements of the symmetrical isomers, since evidence presented by Rabideau [47] suggests the planar conformer is preferred in the ground state. Table VIII lists these measurements. As seen from Table VIII, there appears to be no correlation between the ground state conformations and the relative rates of oxidations.

FIGURE 6

Energy Diagram for the Oxidation
of 1,4-Dihydronaphthocyclopentenes

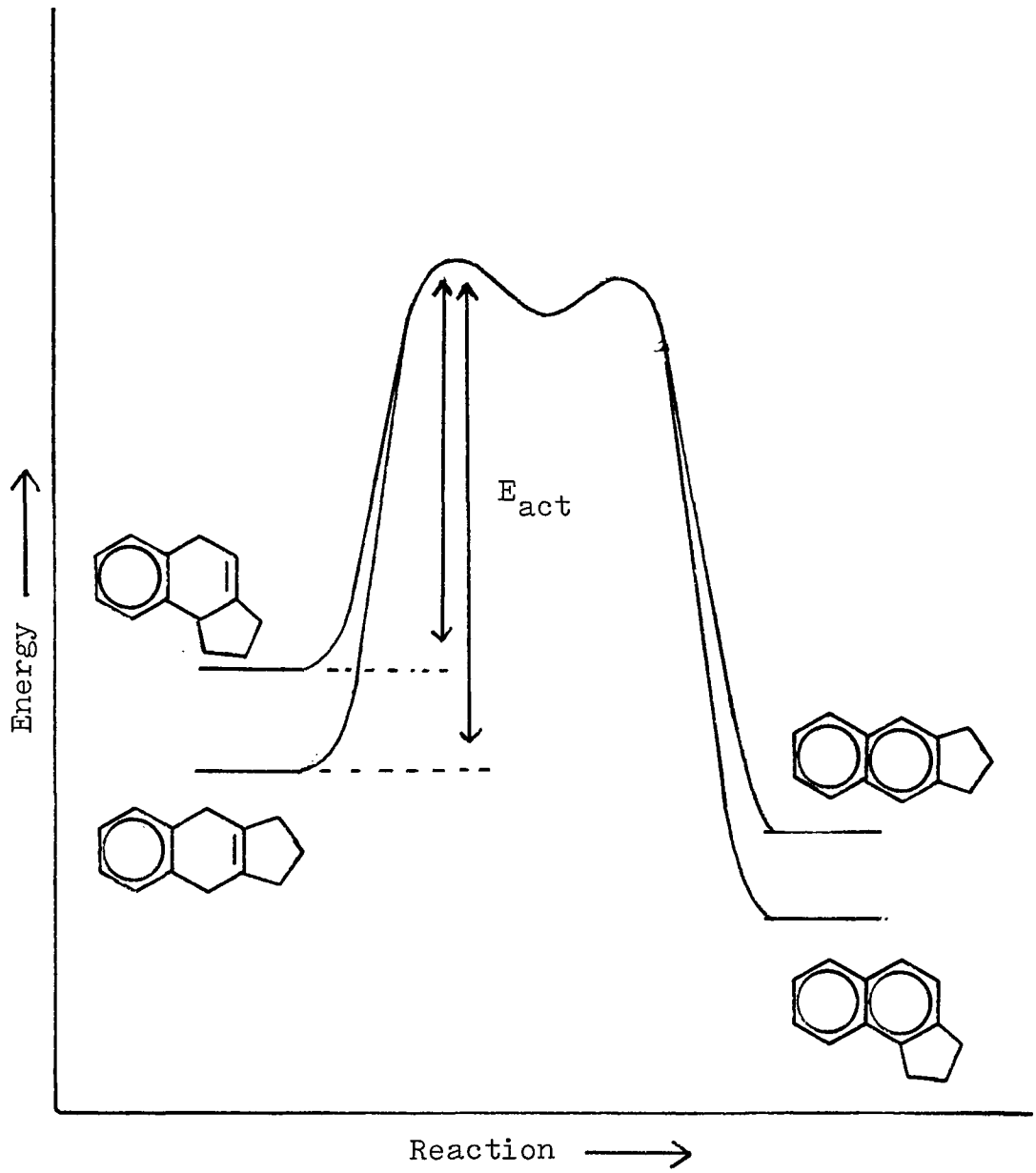
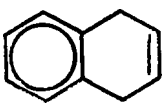
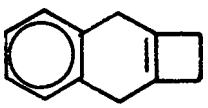
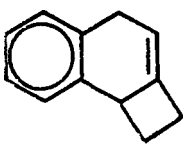
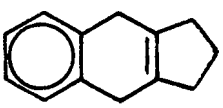
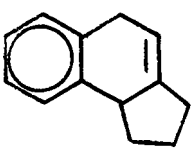
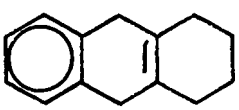
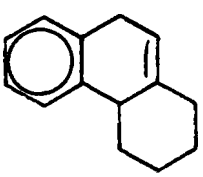


TABLE VIII

Estimated Distances Between cis-1,4-Hydrogens of 1,4-Dihydronaphthalenes

Compound	Distance (R)	Difference (R' - R)
	4.2 Å	.4 Å
	4.4 Å	.2 Å
	3.3 Å	1.3 Å
	4.2 Å	.4 Å
	3.0 Å	1.6 Å
	4.2 Å	.4 Å
	4.5 3.2 Å 3.25	.1 1.4 Å 1.35

R = the distance between cis-hydrogens at the 1,4-position of a 1,4-dihydroaromatic compound

R' = the distance between the points of attachment of two hydrogens to a quinone nucleus (assuming 1,4-addition)

EXPERIMENTAL

EXPERIMENTAL

All melting points are uncorrected. IR spectra were obtained on either a Perkin-Elmer 137 spectrophotometer or a Beckman 4250 spectrophotometer. NMR spectra were obtained on either a Varian Associates T-60 NMR spectrometer or a Varian Associates EM-390 NMR spectrometer. UV absorptions were obtained on a Gilford 240 spectrophotometer. VPC analyses were performed on either a Varian Associates 920 gas chromatograph equipped with a thermal conductivity detector, or a Varian Associates 940 gas chromatograph equipped with a flame ionization detector, or a Varian Associates 2400 gas chromatograph equipped with a flame ionization detector. The columns used for analysis or purification are as follows:

Column A - 10 ft x 1/8 in 10% Carbowax
20 M on chromsorb w 60/80 mesh

Column B - 8 ft x $\frac{1}{4}$ in 10% Carbowax
20 M on chromsorb w 60/80 mesh

Column C - 5 ft x 1/8 in 1.5% OV-101
on chromsorb G 100/120 mesh

Column D - 9 ft x 1/8 in 1% OV-17
on chromsorb G 60/80 mesh

Each compound in the experimental section has a WC number, this number refers to the number given to that compound in the research notebooks. All mass spectra were obtained by

direct sample introduction into a Hewlett Packard 5933A GC-Mass Spectrometer system, unless specified otherwise. High-Resolution mass spectral analyses were performed by Dr.R. Grigsby at the Department of Bio-chemistry and Bio-phisic, Texas A & M University, on a CEC21-110B double focusing magnetic secter spectrometer at 70 ev. Exact masses were determined by peak matchaing.

The silica gel used for column chromatography was neutral, 600-800 mesh. The solvent petroleum ether refers to petroleum ether, bp. 30-60°C, which was purified by simple distillation.

cis-1,2-Cyclobutanedicarboxylic Acid Anhydride (54) (WC-287) Following the procedure of Bloomfield and Owsley,[22] 120 g (1.22 mol) of maleic anhydride in three liters of ethyl acetate and 6 g of acetophenone, were placed in a three liter round bottomed flask equipped with a reflux condenser, gas dispersion tube, and a pyrex immersion well fitted with a 450 watt Hanovia uv lamp. Ethylene gas was bubbled through the ice-cooled mixture for five minutes prior to irradiation to purge the solution. With continued cooling and a continuous stream of ethylene, the reaction mixture was irradiated for four to five days. The reaction was followed by VPC (Column D, 150°C). After irradiation the ethyl acetate was removed by distillation until approximately 200 ml of residue remained. The hot solution was filtered to remove any insoluble polymers, and the remaining ethyl acetate removed by further distillation. The residue was fractionally distilled (120-130°C/6 mm) to give 93 g (61%) of cis-1,2-cyclobutanedicarboxylic acid anhydride, mp 77-78°C, (lit.[49] mp 76.5-77°C); ir (KBr) 3020 (s), 2980 (s), 1865 (b), 1790 (b), 1260 (s), 1235 (m), 1110 (s), 925 (b), and 615 (s) cm^{-1}.

trans-1,2-Cyclobutanedicarboxylic Acid Chloride (55) (WC-316) In a 500-ml round bottomed flask equipped with a reflux condenser, was weighed 137.9 g (0.66 mol) of phosphorus pentachloride[23] and 75.6 g (0.60 mol) of cis-1,2-cyclobutanedicarboxylic acid anhydride. The two solids were melted

together at 135°C. The resulting liquid was heated (135°C) and stirred for eight hours. The reaction mixture was allowed to cool at room temperature and the $POCl_3$ was distilled at room temperature under vacuum (~2 mm) and collected in an acetone-dry ice cooled flask. The remaining black tarry residue was distilled at 45°C/.1 mm to give 97.1 g (90%) of a colorless oil, (lit.[50] bp 49.5-50.5°C/0.65 mm) IR (thin film) 2900 (m), 1790 (s), 1050 (b), 880 (m) and 740 (m) cm^{-1}.

trans-1,2-Bis(hydroxymethyl)cyclobutane[24] (56) (WC-317)
In a two liter three necked flask, fitted with a reflux condenser, addition funnel and an overhead stirrer, was placed 41 g (1.08 mol) of lithium aluminum hydride in one liter of anhydrous diethyl ether. The flask was cooled in an acetone-Dry ice bath and 97 g (.54 mol) of 1,2-cyclobutanedicarboxylic acid chloride in 100 ml of anhydrous diethyl ether was slowly added over a period of one to two hours. After addition, the reaction mixture was refluxed overnight. The reaction mixture was then allowed to cool and with rapid stirring 41 ml of water was slowly added. With continued rapid stirring 41 ml of 15% sodium hydroxide was slowly added followed by 123 ml of water. The mixture was stirred until the gray colored residue had turned white (six to ten hours). Suction filtration gave a colorless etheral solution which was dried over magnesium sulfate

and the ether removed on a rotary evaporator to give 43.61 g (75%) of the diol. The trans-1,2-bis(hydroxymethyl)cyclobutane was used without further purification; NMR (CCl_4) δ 4.6 (m, 2H, O<u>H</u>), 3.45 (m, 4H, C<u>H</u>$_2$OH) and 1.9 ppm (m, 6H, C<u>H</u>$_2$); IR (thin film) 3325 (b), 2950 (m), 1480 (b), and 1020 (m) cm^{-1}.

trans-1,2-Bis(bromomethylene)cyclobutane[24] (57) (WC-319) Over a period of one hour 103 g (0.38 mol) of phosphorus tribromide was added dropwise to an ice cooled solution of 43 g (.371 mol) of 1,2-bis(hydroxymethyl)cyclobutane. After addition the ice bath was removed and the reaction mixture allowed to come to room temperature, during which time large quantities of hydrogen bromide gas was evolved. The mixture was warmed to 85°C and stirred overnight. Distillation, 48-55°C/.16 mm (lit.[24] bp 71°C/1.8 mm) gave 68.8 g (76%) of trans-1,2(bromomethylene)cyclobutane. NMR (CCl_4) δ 3.4 (m, 4H, C<u>H</u>$_2$-Br) and 1.9 ppm (m, 6H, C<u>H</u>$_2$); IR (thin film) 2990 (s), 1460 (s), 1280 (s), 1240 (s), and 1100 (b) cm^{-1}.

trans-1,2-Bis(dimethylaminomethyl)-cyclobutane Dimethobromide[24] (58) (WC-286) Into two large thick walled test tubes was divided 43.0 g (0.17 mol) of trans-1,2-bis(bromomethylene)-cyclobutene and 35 ml of methanol. The tubes were placed in an acetone-Dry ice bath and 35 ml of trimethylamine

condensed in each. The tubes were sealed and heated to 85°C overnight. The solid obtained was removed and triturated with ethyl acetate to provide a white solid, mp 245-250°C (lit.[24] mp 200°C)[a] in 90% yield; NMR (D_2O) δ 3.5 (m, 4H, $C\underline{H}_2$-N), 3.2 (s, 18H, $C\underline{H}_3$) and 2.3 ppm (m, 6H, $C\underline{H}_2$).

1,2-Dimethylenecyclobutane[24] (51) (WC-295) To a stirred solution of 16.85 g (47 mmol) of trans-1,2-bis(dimethylaminomethyl)cyclobutane dimethobromide and 30 ml of water, in a 100-ml round bottomed flask, was added 23.88 g (.103 mol) of silver oxide. The solution was stirred for one hour and filtered. The filter cake was washed with 5-10 ml of water and the filtrates combined. The filtrate was distilled through a short path still head using a micro burner. As the distillate was collected, the water was removed using a pipette. The distillation, 150°C/760 mm was continued until the pot residue was dry. Removal of the remaining water gave 3.10 g (90%) of dimethylene cyclobutane. The diene was used with no further purification. NMR (CCl_4) δ 5.08 (m, 2H, C=C-H), 4.62 (m, 2H, C=C-H) and 2.48 ppm (m, 4H, C=C-$C\underline{H}_2$).

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[a]Compound 58 is extremely hydroscopic and Blomquist states that no attempt was made to obtain a pure sample. This might account for the difference in melting points.

1,Vinyl Cyclobutanol[25] (62) (WC-285) A carefully dried 3-necked, 500-ml, round bottomed flask, equipped with a mechanical stirrer, dry-ice condenser and addition funnel, was charged with 7.29 g (0.3 mol) of magnesium, and the magnesium was covered with dry tetrahydrofuran. To the rapidly stirred mixture was added a solution of 37.5 g (0.35 mol) of vinylbromide and 75 ml of tetrahydrofuran in 3 ml portions until the Grignard reaction was initiated. The remaining vinylbromide solution was added at a rate to maintain a gentle reflux. The mixture was stirred until all the magnesium had dissolved, cooled to 35°C, and 14.0 g (0.2 mol) of cyclobutanone[a] in 30 ml of tetrahydrofuran added slowly. After addition the reaction was refluxed for 90 min, cooled to 35°C, and hydrolyzed with 40 ml of saturated ammonium chloride solution. The resulting precipitate was removed by filtration, washed with diethyl ether, and the organic extracts evaporated on a steam bath, through a 60 cm Vigreaux column. The oil obtained was distilled to give 12.14 g (65%) of 1-vinylcyclobutanol, bp 66-69°C/45 mm, (lit.[25] bp 49-50°C/15 mm). NMR (CCl_4) δ 6.3-4.9 (ABX pattern, 3H, $C\underline{H}_2$= $C\underline{H}$-), 4.0 (broad s, 1H, $O\underline{H}$) and 2.2-1.4 ppm (m, 6H, -$C\underline{H}_2$-); IR (thin film) 3360, 2290, 1246, 1150 and 920 cm^{-1}.

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[a]prepared by J. Pegram

1-Vinylcyclobutene (59) (WC-370) Following a procedure for the dehydration of 1-vinylcyclopentanol[26] 1.7 g (15.4 mmol) of 1-vinylcyclobutanol and .1 g of potassium bisulfate were heated to reflux (~120°C) for one hour, in a 25-ml roundbottomed flask equipped with a reflux condenser. The reflux condenser was replaced with a short path still head and a mixture of water and 1-vinylcyclobutene distilled. Removal of the water, using a disposable pipette, gave 0.5 g (65%) of 1-vinylcyclobutene; NMR (CCl_4) δ 6.5-4.9 (ABX pattern, 3H, $C\underline{H}_2$=C$\underline{H}$-) 5.8 (m, 1H, C=C-$\underline{H}$) and 2.5 ppm (m, 4H, $C\underline{H}_2$); IR (thin film) 3045, 2920, 1574, 984, 903, 846 and 767 cm^{-1}.

1-Vinylcyclopentanol (WC-364) Following the procedure for the preparation of 1-vinylcyclobutanol, a Grignard reagent was prepared using 14.58 g (0.6 mol) of magnesium, 75 g (0.7 mol) of vinyl bromide and 150 ml of dry tetrahydrofuran. To the cooled Grignard reagent was added 50.0 g (0.53 mol) of cyclopentanone in 50 ml of dry tetrahydrofuran. After workup, distillation gave 41.9 g (70%) of 1-vinylcyclopentanol, 48°C/11 mm (lit.[25] bp 45°C/6.5 mm); ir (thin film) 3400 (b), 2970 (m), 1090 (m) and 920 (s) cm^{-1}.

1-Vinylcyclopentene (63) (WC-365) The procedure described by Seyferth[25] was followed using 8 g (0.071 mol) of 1-vinylcyclopentanol and 1 g of potassium bisulfate. Distillation

gave 4.41 g (65%) of 1-vinylcyclopentene, bp 160°C/760 mm (lit.[25] bp 109-112°C/760 mm); NMR (CCl_4) δ 6.5-4.9 (ABX pattern, 3H, $C\underline{H}_2=C\underline{H}$), 5.6 (m, 1H, $C=C\underline{H}_2$), 2.4 (m, 4H, $C=C-C\underline{H}_2$) and 1.9 ppm (m, 2H, $C\underline{H}_2$).

1,2-Dimethylenecyclopentane (66) (WC-352) A Hoffmann elimination of 1,2-bis(dimethylaminomethyl)cyclopentane dimethobromide[24] was carried out analogous to that in the preparation of 1,2-dimethylenecyclopentane (75% yield), which was used without further purification. NMR (CCl_4) δ 5.3 (t, 2H, $C=C-\underline{H}$), 4.8 (t, 2H, $C=C-\underline{H}$), 2.4 (m, 4H, $C=C-C\underline{H}_2$) and 1.7 ppm (m, 2H, $C\underline{H}_2$).

1,4-Dihydronaphtho[b]cyclobutene (52) (WC-296) Treatment of 9.5 g (.07 mol) of anthranilic acid with 14 g (.12 mol) of isoamyl nitrite in 50 ml of dry tetrahydrofuran provided benzenediazonium-2-carboxylate as a tan precipitate.[21] This material was collected by filtration and combined with 100 ml of dichloromethane to which was added 2.2 g (.028 mol) of 1,2-dimethylenecyclobutane. The mixture was refluxed for two hours until gas evolution had ceased. It was then cooled, washed three times with saturated sodium bicarbonate solution and dried over magnesium sulfate. Filtration and evaporation of the solvent gave a yellow oil which was chromatographed on 35 g of silica gel, eluting with petroleum ether, to provide 1.10 g (25%) of 1,4-dihydronaphtho[b]cyclobutene, mp 69-70°C; NMR ($CDCl_3$) δ 7.15 (s, 4H, Ar-$\underline{H}$), 3.3

(s, 4H, Ar-C$\underline{H}_2$) and 2.6 ppm (s, 4H, cyclobutyl protons); IR (KBr) 3070, 2945, 2910, 2885, 2830, 1495, 1430, 1286, 1175, and 737 cm^{-1}.

1,4-Dihydronaphtho[a]cyclobutene (60) (WC-293) Following the above procedure, 25 mmol of benzenediazonium-2-carboxylate was reacted with 1.0 g (12 mmol) of 1-vinylcyclobutene. Chromatography of the crude product on 10 g of silica gel, eluting with petroleum ether, provided 0.98 g (50%) of a colorless oil. Analysis of this material by VPC (Column A) showed two equal area peaks. Both of these peaks were isolated by preparative VPC. The first peak showed NMR (CCl_4) δ 7.25 (broad s, 5H, Ar-$\underline{H}$), 6.55 (m, 3H) and 5.6-5.0 ppm (overlapping m, 4H) and IR (thin film): 3100, 1498, 1452, 916, and 700 cm^{-1}. The IR did not correspond to 2-vinylnaphthalene and thus the material was considered to be an isomer of phenylhexatriene. Isolation of the second peak provided 1,4-dihydronaphtho[a]cyclobutene as a colorless oil: NMR (CCl_4) δ 6.98 (s, 4H, Ar-$\underline{H}$), 5.5 (broad s, 1H, =C-$\underline{H}$), 3.8 (broad m, 1H), 3.2 (m, 2H), 2.8-2.3 (m, 3H), and 2.0 ppm (m, 1H); IR (thin film) 3025, 2985, 2870, 1486, 1457, 1433, 1215, 1005, and 816 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 156 (92, parent), 141 (92), 128 (100) and 115 (36).

Naphtho[b]cyclobutene (15) (WC-297) To a stirred solution of 0.29 g (1.28 mmol) of 2,3-dichloro-5,6-dicyanobenzoquinone DDQ in 25 ml of dry benzene was added 0.10 g (.64 mmol) of 52. The reaction mixture was stirred at room temperature for one hour until the peak corresponding to 52 had disappeared by VPC. The mixture was filtered and the benzene evaporated to give a black residue which was chromatographed on 10 g of silica gel, eluting with petroleum ether to provide .08 g (81%) of 4, mp 85-86°C; lit.[7] mp 86.5°C: NMR ($CDCl_3$) δ 7.5 (m, 6H, Ar-H) and 3.28 ppm (s, 4H, Ar-CH_2); IR (KBr) 3060, 2920, 870, and 740 cm^{-1}.

Naphtho[a]cyclobutene (20) (WC-294) To a stirred solution of 1.43 g (6.3 mmol) of DDQ in 50 ml of dry benzene was added 0.49 g of 50% pure 60 (3.14 mmol). The reaction mixture was refluxed for 30 min., filtered, and the benzene evaporated. The black residue was dissolved in petroleum ether, filtered, and the solvent evaporated to give 0.17 g of a yellow oil. This oil was first distilled (.01 mm) and then chromatographed on 35 g of silica gel, eluting with petroleum ether, to afford .048 g of 20 as a colorless oil: NMR ($CDCl_3$) δ 7.45 (m, 6H, Ar-H) and 3.25 ppm (m, 4H, Ar-CH_2); IR (thin film) 3060, 2930, 1595, 1365, 810, 775 and 732 cm^{-1}.

1,4-Dihydronaphtho[b]cyclopentene (74) (WC-352) The procedure used for the preparation of 1,4-dihydronaphtho[b]-cyclobutene was followed using 1 g (0.011 mol) of

1,2-dimethylenecyclopentane[24] and the benzenediazonium-2-carboxylate obtained from 5.3 g (0.04 mol) of anthranilic acid. Recrystallization from methanol gave 1.02 g (55%) of 1,4-dihydronaphtho[b]cyclopentene, mp 67-68°C; NMR (CCl_4) δ 7.05 (s, 4H, Ar-H), 3.35 (s, 4H, Ar-CH_2) and 2.4 ppm (m, 2H, CH_2); IR (KBr) 2900 (s), 1500 (m), 1455 (m) and 740 (s) cm^{-1}.

1,4-Dihydronaphtho[a]cyclopentene (75) and Naphtho[a]cyclopentene (102) (WC-366) Following the procedure for the preparation of 1,4-dihydronaphtho[b]cyclobutene, 5 g (8.6 mmol) of 1-vinylcyclopentene was treated with benzyne. Benzyne was obtained by treatment of 21 g (0.16 mol) of anthranilic acid with 20 g (0.17 mol) of isoamyl nitrite, followed by pyrolysis. The crude reaction mixture was filtered through 30 g of silica gel, followed by 30 ml of dichloromethane. The solvent was removed on a rotary-evaporator and the tarry residue distilled (70°C/0.1 mm), on a Kugelrohr apparatus to give ~2ml of a yellow oil containing some solid material, (believed to be benzoic acid). The oil was dissolved in dichloromethane, washed with sodium bicarbonate, and dried over magnesium sulfate. Analysis by vpc (Column A, 150°C) indicated two compounds each of which were isolated by preparative VPC (Column B, 150°C). The short retention time peak (~4 min) proved to be 1,4-dihydronaphtho[a]cyclopentene; NMR (CCl_4) δ 7.02 (m, 4H,

Ar-H), 5.65 (m, 1H, C=C-H), 3.2 (m, 3H, Ar-CH_2), 2.4 (m, 4H, CH_2), and 1.9 ppm (m, 2H, CH_2); IR (thin film) 2960 (s), 1500 (m), 1460 (m), and 760 (s) cm^{-1}.

The longer retention time peak (~ 10 min) proved to be naphtho[a]cyclopentene; NMR (CCl_4) δ 7.45 (m, 6H, Ar-H). 3.2 (q, 4H, Ar-CH_2) and 2.25 ppm (m, 2H, CH_2); IR (thin film) 3060 (s), 2950 (s), 2840 (s), 1700 (m), 1520 (m), 810 (s), and 770 (s) cm^{-1}.

1,2,3,4,5,10-Hexahydroanthracene (76) (WC-357) To a stirred slurry of 50 ml of dichloromethane and the benzenediazonium-2-carboxylate obtained from 9.5 g (0.07 mol) of anthranilic acid and 14 g (0.12 mol) of isoamyl nitrite, was added 2.5 g (0.023 mol) of 1,2-dimethylenecyclohexane.[28a] The procedure for 1,4-dihydronaphtho[b]cyclobutene was followed yielding a crude oil which after column chromatography on 30 g of silica gel, eluted with petroleum ether, gave a white solid. Recrystallization from methanol gave 1.1g of a white solid, mp 65-66°C, (25%) which proved to be 1,2,3,4,5,10-hexahydroanthracene; NMR ($CDCl_3$) 7.1 (s, 4H, Ar-H), 3.23 (s, 4H, Ar-CH_2), 2.0 (m, 4H, C=C-H) and 1.7 ppm (m, 4H, CH_2); IR (KBr) 2930 (s), 2860 (s), 1500 (m), 1460 (m), and 740 (s) cm^{-1}.

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[a]prepared by R. P. Thummel

1,2,3,4,4a,9-Hexahydrophenanthrene (77) (WC-353) Following the procedure described for 1,4-dihydronaphtho[b]cyclobutene, 5.4 g (0.05 mol) of 1,-vinylcyclohexene[27a] and the benzenediazonium-2-carboxylate obtained from 9.5 g (0.07 mol) of anthranilic acid, were reacted. Purification by column chromatography 60 g silica gel, eluted with petroleum ether, gave 2 g (22%) of a liquid which proved to be 1,2,3,4, 4a, 9-hexahydrophenanthrene; NMR (CCl_4) δ 7.2 (m, 4H, Ar-H), 5.5 (m, 1H, C=C-H), 3.3 (m, 3H, Ar-CH_2) and 1.8 ppm (m, 8H, CH_2); IR (thin film) 2930 (s), 1450 (m), 790 (m) and 735 (m) cm^{-1}.

Naphtho[b]cyclopentene (8) (WC-352-a) Following the procedure used for naptho[b]cyclobutene, 0.1 g (0.58 mol) of 1,4-dihydronaphtho[b]cyclopentene was treated with 0.2 g of DDQ. The crude product was recrystallized from methanol to give 0.09 g (90%) of a white solid, mp 95°C, (lit.[4] 94°C) identified as naphtho[b]cyclopentene by its spectral data; NMR ($CDCl_3$) δ 7.64 (m, 6H, Ar-H), 3.0 (t, 4H, Ar-CH_2) and 2.2 ppm (t, 2H, CH_2); IR (KBr) 2940 (s), 950 (s), 880 (s), and 745 (s) cm^{-1}.

1,2,3,4-Tetrahydroanthracene (101) (WC-358) Treatment of 0.1 g (0.5 mmol) of 1,2,3,4,5,10-hexahydroanthracene with

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[a]prepared by R. P. Thummel

0.2 g of DDQ, as described in the procedure for naphtho[b]-cyclobutene, gave a solid which after column chromatography on 10 g of silica gel, eluted with petroleum ether, afforded 0.08 g (80%) of 1,2,3,4-tetrahydroanthracene, mp 101-102°C (lit.[30] 98-100°C); NMR ($CDCl_3$) δ 7.5 (m, 6H, Ar-H), 2.95 (m, 4H, Ar-CH) and 1.9 ppm (m, 4H, CH_2); IR (KBr) 2925 (s), 1500 (m), 860 (s), and 740 (s) cm^{-1}.

1,4-Dihydroanthro[b]cyclobutene (70) (WC-331) In a 100 ml round bottomed flask were placed 0.5 g (2.7 mmol) of 3-amino-2-naphthoic acid,[29] 0.5 ml of concentrated HCl, 20 ml of tetrahydrofuran, and 0.63 g (5.4 mmol) of isoamyl nitrite. The mixture was stirred for one hour and the resulting orange precipitate was collected by filtration and washed with dioxane (distilled from sodium). The wet precipitate was transferred to a 100-ml roundbottomed flask to which was added 30 ml of dioxane, 0.2 ml of propylene oxide, and approximately 0.5 g (6.3 mmol) of 1,2-dimethylenecyclobutane. This mixture was rapidly heated to 100°C in an oil bath and stirred until no further gas evolution was observed. The red solution was cooled and filtered through 30 g of silica gel, washing with 200 ml of dichloromethane. The oil obtained by evaporation of solvent was taken up in petroleum ether and removed from a tarry precipitate. The petroleuum ether was evaporated and the resulting yellow oil was chromatographed on 30 g of silica gel, eluting with petroleum ether. A

white solid (50 mg, 9% yield) was obtained which appeared to be 85% pure by NMR. This material was subjected to preparative TLC (SilicAR TLC-7GF) to provide 40 mg of 70, mp 135-136°C: Nmr ($CDCl_3$) δ 7.8-7.2 (m, 4H), 7.60 (d, 2H, J=2.5 Hz), 3.50 (broad s, 4H, cyclobutenyl H) and 2.67 ppm (broad s, 4H, Ar-CH); IR (KBr) 3050, 2935, 2908, 2865, 2830, 868, and 746 cm^{-1}.

Anthro[b]cyclobutene (78) (WC-337) In a 5 mm NMR tube was placed 40 mg of 70 and 0.5 ml of carbon tetrachloride. To this solution was added 0.10 g of DDQ and the tube was heated in a water bath at 40°C. The reaction was followed by NMR. After 16 hours the peaks corresponding to 70 had completely disappeared while those corresponding to 78 had grown in. The solution was filtered through silica gel and the solvent removed to provide a white solid, mp 245-247°C: NMR ($CDCl_3$) δ 8.35 (s, 2H, $H_{9,10}$), 7.95 (m, 2H, $H_{5,8}$), 7.56 (s, 2H, $H_{1,4}$), 7.33 (m, 2H, $H_{6,7}$) and 3.38 ppm (s, 4H, Ar-CH_2); IR (KBr) 3060, 2965, 2935, 1415, 1290, 955, 902, and 740 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 204 (100, parent) 203 (42), 202 (41), 101 (46), 89 (18), and 88 (18). High Resol. MS: MW= 204.0932 (Calculated $C_{16}H_{12}$ = 204.0939)

1,4-Dihydroanthro[a]cyclobutene (71) (WC-335) Followed the same procedure as 70 utilizing 0.5 g (2.7 mmol) of 3-amino-2-naphthoic acid[29] and 0.5 g (6.3 mmol) of 1,vinyl-cyclobutene. After workup there was obtained 30 mg (5.4%)

of solid material, mp 98-101°C which was identified as 71 by its spectral properties: NMR ($CDCl_3$) δ 7.9-7.2 (m, 6H, Ar-H), 5.67 (broad s, 1H, =CH), 4.05 (broad s, 1H, Ar-CH), 3.40 (braod s, 2H, Ar-CH_2), and 3.0-2.0 ppm (overlapping m, 4H, cyclobutyl H); IR (KBr) 2955, 1659, 1562, 1510, 880, and 755 cm^{-1}.

Anthro[a]cyclobutene (79) (WC-389) A solution of 30 mg of 71 and 0.10 g DDQ in 0.5 ml of $CDCl_3$ was placed in a 5 mm NMR tube. The tube was warmed to 45°C in a water bath and the reaction followed by NMR. After three days the upfield peaks corresponding to 71 had disappeared. The solution was filtered through silica gel; the solvent evaporated; and the residue purified by preparative TLC (silicAR TLC-7GF) eluting with petroleum ether to provide 20 mg of 79, mp 103-105°C: NMR ($CDCl_3$) δ 8.42 and 8.25 (singlets, 2H, H_9 and H_{10}), 8.1-7.7 (m, 3H, H_4, H_5, H_8), 7.6-7.2 (m, 3H, H_3, H_6, H_7) and 3.35 ppm (m, 4H, cyclobutyl H); IR (KBr): 2950, 2920, 1260, 1095, 900 and 795 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 204 (100, parent), 203 (48), 202 (46), 101 (47), 100 (20), and 88 (20), High Resolution Mass Spectrum , MW= 204.0930 (Calculated for $C_{16}H_{12}$ = 204.0939)

2,3-Dimethylene-1,2,3,4-tetrahydronaphthalene (94) (WC-275) A pyrolysis apparatus was constructed from a 12 inch long, 1 inch diameter spiral of 0.25 inch (o.d.) pyrex tubing. At the bottom end of this tube was attached a 15 ml round bottomed flask equipped with a side arm for the introduction of nitrogen. At the top of the tube was a trap cooled in a Dry ice-acetone bath and connected to the vacuum line. The spiral tube was heated to 300-310°C in a vertical tube furnace and evacuated to 0.05 mm. A 1.50 g (9.6 mmol) sample of 1,4-dihydronaphtho[b]cyclobutene (52) placed in the 15 ml flask was rapidly forced into the hot zone by heating with a micro burner. After all the sample had evaporated from the pot, a slow bleed of nitrogen was continued until no further material collected in the cold trap. The pyrolyzed material (1.03 g) was collected and subjected to a second pyrolysis under the same conditions to ultimately yield 1.00 g (67%) of a white solid which NMR analysis showed to consist of a mixture of 30% of unreacted 52 and 70% of diene 94. Pure 94, mp 64°C, was isolated by preparative vpc: NMR (CCl_4), δ 7.04 (s, 4H, Ar$\underline{H}$), 5.3 (broad s, 2H, =C$\underline{H}_2$), and 3.50 ppm (s, 4H, Ar-C$\underline{H}_2$); IR (thin film) 3013, 2920, 2870, 2820, 1501, 1460, 1425, 888, and 743 cm^{-1}.

5,6,11,12-Tetrahydronaphthacene (95) (WC-278) A 0.10 g (.64 mmol) sample of 52 was subjected to a double pyrolysis as described above. The crude pyrosylate was taken up in 20 ml of dichloromethane to which was added 1.28 mmol of benzenediazonium-2-carboxylate generated as described above. The mixture was refluxed for two hours, cooled, and the dichloromethane removed under vacuum. The residue was chromatographed on 60 g of silica gel, eluting with petroleum ether, to yield .04 g (27%) of 95 as a white solid, mp 160-165°C: NMR ($CDCl_3$) δ 7.1 (s, 8H, ArH), and 3.45 ppm (s, 8H, ar-CH); IR (KBr) 2980, 2910, 1540, 1305, 1075, and 785 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 232 (60, parent), 229 (30), 217 (31), and 104 (100). Treatment of a small sample of 95 with DDQ in refluxing benzene resulted in the formation of a material which had an R_f identical to that of naphthacene(96).

Sealed Tube Pyrolysis of 52 (WC-298) In a small, heavy wall tube was placed 0.10 g (.64 mmol) of 1,4-dihydronaphtho-[b]cyclobutene 52. The tube was sealed and heated to 200°C for 8 hours. After cooling, the resulting yellow oil was chromatographed on 35 g of silica gel, eluting with petroleum ether, to afford 0.40 g (40%) of adduct 99, mp 133-134°C: NMR (CCl_4) δ 7.0 (8H, ArH) and 3.2, 2.7, 2.05, 1.9 ppm (overlapping m, 16H); IR (KBr) 3060, 3020, 2930, 1500, 1490, 1440, and 750 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 312 (54, parent), 284 (4), 156 (100), 141 (74)

128 (36), and 114 (34).

1,4-Dihydronaphtho[b]cyclobutene Oxide (100) (WC-329) A solution of 0.20 g (1.28 mmol) of 1,4-dihydronaphtho[b]cyclobutene in 15 ml of dichloromethane under nitrogen was cooled in an ice bath. A solution of 0.30 g (1.47 mmol) of meta-chloroperbenzoic acid in 10 ml of dichloromethane was then slowly added. The reaction mixture was stirred for one hour and then allowed to warm to room temperature and stirred an additional 23 hours. The organic phase was then washed with 10% sodium thiosulfate, 5% sodium bicarbonate, water, and saturated sodium chloride solution. Drying over magnesium sulfate and evaporation of the solvent provided 0.18 g (80%) of epoxide 100, mp 94-95°C: NMR ($CDCl_3$) δ 7.08 (s, 4H, ArH), 3.27 (s, 4H, $ArCH_2$) and 2.10 ppm (s, 4H, cyclobutyl H); IR (KBr) 2950, 2850, 1440, 1155, and 765 cm^{-1}; mass spectrum (70 eV) m/e (rel intensity) 172 (58, parent), 144 (23), 130 (50), 129 (100), 128 (66), 116 (74), and 115 (79).

Reaction of 100 with Lithium Diethylamide (WC-338) To a stirred, ice-cold mixture of 0.04 g (.58 mmol) of diethylamine in 3 ml of anhydrous ether was added 0.3 ml of 2.4 M n-butyllithium in hexane. The solution was stirred for 10 min and 0.05 g (.29 mmol) of epoxide 100 was added. The reaction mixture was stirred at 4°C for 20 min and for an

additional two hours at room temperature. It was then poured into 30 ml H_2O and extracted with ether. The ether extracts were dried over magnesium sulfate, filtered, and evaporated to provide a material which showed an NMR spectrum consistent with that of naphtho(b)cyclobutene.

Diels-Alder Adduct of Cyclopentadiene with 1,4-Dihydro-Naphtho[b]cyclobutene (99) (WC-300) Approximately 3 ml of cyclopentadiene was distilled directly into a small thick walled tube containing 0.08 g (.51 mmol) of 1,4-dihydronaphtho[b]cyclobutene. The tube was cooled in an acetone-Dry ice bath, sealed and heated to 160°C for 20 hours in an oil bath. The tube was opened and the yellowish white solid removed with dichloromethane. The dichloromethane was evaporated on a rotary evaporator and the crude solid dissolved in petroleum ether and filtered to remove insoluble compounds. The petroleum ether was evaporated and the resulting solid was chromatographed on 37 g of silica gel, eluting with petroleum ether to give 0.08 g (70%) of a white solid, mp 140-145°C; NMR ($CDCl_3$) δ 7.1 (s, 4H, Ar-H), 5.55 (m, 2H, C=C-H), 3.32 (s, 4H, $ArCH_2$) and 2.2-1.2 ppm (m, 8H, CH_2).

Ozonlysis of 1,4-Dihydronaphtho[b]cyclobutene (WC-330) A dichloromethane solution (30 ml) of 1.0 g (0.64 mmol) of 1,4-dihydronaphtho[b]cyclobutene was placed in a 100 ml gas dispersion bottle. The solution was cooled to -78°C in an

acetone-Dry ice bath and a stream of ozone[a] and oxygen was bubbled through the reaction until a blue color persisted. Oxygen was bubbled through the reaction mixture until the blue color disappeared. The reaction mixture was washed with 20 ml of water, 20 ml of 10% sodium hydroxide, 20 ml of water, 20 ml of 10% sodium thiosulfate and dried over sodium sulfate. The dichloromethane was removed on a rotary evaporator leaving 1.0 g (88%) of a gummy white solid, mp 114-115°C, which resisted all attempts to purification; NMR (CCl_4) δ 7.15 (broad s, 4H, Ar-H). 3.6 (s, 4H, Ar-CH_2), and 2.45 ppm (s, 4H, O=C-CH_2). The solid was too gummy to take an IR.

[a]Ozones generated on a Welsbach T-23 Ozonator, settings: 8 lbs of O_2, 90 volts, and a flow rate of .03 to .04.

Benzocycloocta-4,7-dione (101) (WC-408) In a 25 ml round bottomed flask was placed 0.05 g (0.32 mmol) of 1,4-dihydronaphtho[b]cyclobutene, 5 ml of water and 5 ml of diethyl ether. To the stirred reaction mixture was added 20 mg of osmiumtetroxide (2 ml of 1% aqueous solution), upon which the reaction turned black. The reaction mixture was maintained at 23°C-24°C and 0.17 g (0.79 mmol) of sodium metaperiodiate was added. After the addition, the reaction mixture was stirred for 90 min, during which time, the black color was slowly replaced by a light yellow color. The reaction mixture was extracted twice with 30 ml portions of diethyl ether. The ether extracts were dried over magnesium sulfate and the ether removed on a rotary evaporator. A dark brown oil was obtained which was chromatographed on 10 g of silica gel, eluted with ethanol, to give 48 mg (80%) of benzocycloocta-4,7-dione, mp 75.5°C; NMR (CCl_4) δ 7.2 (s, 4H, Ar-H), 3.65 (s, 4H, Ar-CH_2) and 2.5 ppm (s, 4H, CH_2-C=O); IR (thin film) 2980 (s), 1720 (b), 1450 (s), 1330 (s), 1280 (m), 1200 (s), 1125 (m) and 760 (m) cm^{-1}.

4,7-Dihydroindan (83) (WC-362) As described by Giovannini and Wegmuller,[33] 200 ml of liquid ammonia (distilled) was collected in a 500 ml three neck flask, equipped with an acetone-Dry ice condenser, addition funnel and overhead stirrer. Small pieces of sodium metal (15 g, .65 mole) were carefully added to the stirred ammonia, followed by addition of 30 g

(0.25 mol) of indan in 30 ml of methanol. The reaction mixture was stirred at -78°C for two hours then allowed to warm to room temperature and the ammonia evaporated. The residue was washed into a separatory funnel with 250 ml of ice water and extracted three times with 100 ml portions of diethyl ether. The ether extracts were dried over magnesium sulfate, evaporated on a rotary evaporator and distilled, 61°C/11 mm, to give 20 g (67%) (lit.[33] bp 59°C/11 mm) of 4,7-dihydroindan. Further purification by preparative VPC (10% cbwx 20 m, $\frac{1}{4}$" x 8", 120°C) gave 4,7-dihydroindan (> 99% pure); NMR (CCl_4) δ 5.62 (m, 2H, C=C-H). 2.55 (m, 4H, C=C-CH_2)and 2.2 ppm (m, 6H, CH_2); IR (thin film) 3030 (s), 2900 (b), 1655 (s), 1450 (b), 1040 (s), 920 (s) cm^{-1}.

1,2,3,4,5,8-Hexahydronaphthalene[32] (82) (WC-368) Following the procedure for 1,4-dihydroindan, 30 g (.23 mol) of tetralin in 25 g of methanol was reduced with 15 g (.65 mol) of sodium in 250 ml of liquid ammonia. After workup there was obtained 29 g of liquid which appeared to be 70 to 75% hexahydronaphthalene and 25-30% unreacted starting material, by VPC (Column A). Preparative VPC gave 1,2,3,4,5,8-hexahydronaphthalene (> 99% pure); NMR (CCl_4) δ 5.6 (broad s, 2H, C=C-H), 2.43 (broad s, 4H, C=C-CH_2), and 1.75 ppm (m, 8H, CH_2); IR (thin film) 2940 (b), 1500 (s), 1450 (b) cm^{-1}.

1-Methyl-1,4-cyclohexadiene (85) (WC-400) Following the procedure of Krapcho and Bothner,[35] 23 g (0.25 mol) of toluene, in 25 ml of anhydrous methanol, was reduced with 250 ml of liquid ammonia and 15 g (0.65 mol) of sodium. The crude oil obtained was flashed distilled, 50-110°C/760 mm, to give 20 ml of an oil which when analyzed by VPC (Column A) appeared to contain both the reduced and the aromatic compounds (70%/30% respectively). Preparative VPC gave 1-methyl-1,4-cyclohexadiene (99% pure); NMR (CCl_4) δ 5.63 (broad s, 2H, C=C-H), 5.4 (m, 1H, C=C-H), 2.6 (m, 4H, C=C-CH_2) and 1.68 ppm (s, 3H, CH_3).

1,3,5-Trimethyl-1,4-cyclohexadiene[35] (87) (WC-398) The procedure described for 4,7-dyhydroindan was followed using 30 g (0.25 mol) of 1,3,5-trimethylbenzene in 25 ml of methanol and 15 g (0.65 mol) of sodium in 250 ml of liquid ammonia. Evaporation of the ether after workup gave 29 g of an oil which appeared to be 25% reduced compound and 75% aromatic, by VPC. Distillation 0-150°C/760 mm gave 5 ml of an oil enriched in the reduced component. Preparative VPC (Column B, 90°C) afforded 1,3,5-trimethyl-1,4-cyclohexadiene (> 98%); NMR (CCl_4) δ 5.25 (m, 2H, C=C-H), 2.42 (m, 3H, C=C-CH), 1.68 (s, 6H, C=C-CH_3) and 1.0 ppm (d, 3H, CH-CH_3) ; IR (thin film) 2880-2810 (b), 1455 (b), 1390 (m), 930 (s), anal 825 (s) cm^{-1}.

1,2,4,5-Tetramethyl-1,4-cyclohexadiene (88) (WC-406) To a stirred solution of 100 ml of monoethylamine (distilled through sodium hydroxide) and 100 ml of ethylene diamine[41] (freshly distilled) was added 10 g (.074 mol) of durene. The mixture was stirred until all the durene had dissolved, and 2.57 g (.373 mol) of lithium was added. Once all the lithium had dissolved (two hours) the deep blue solution was cooled in an ice bath and slowly hydrolyzed with a mixture of 100 ml of water and 100 ml of diethyl ether. The organic layer was separated, washed with 15% HCl until the washes were acidic, and dried over magnesium sulfate. Evaporation of the solvent gave 9.5 g of an oil which appeared to be 67-70% 1,4-dihydrodurene by VPC (Column B, 110°C). Upon sitting, long white needles grew out of the oil. The crystals were collected and recrystallized from ethanol to afford 1,4-dihydrodurene (99% pure by vpc); NMR (CCl_4) δ 2.45 (s, 4H, C=C-CH_2) and 1.6 ppm (s, 12H, CH_3); IR (KBr) 2920-2800 (s), 1440 (m), 1385 (m) and 1168 (s) cm^{-1}.

3,6-Dihydrobenzo[1,2:4,5]dicyclopentene (91) (WC-367) Following the procedure described for 4,7-dihydroindan, 2 g (12.6 mmol) of benzo[1,2:4,5]dicyclopentene[a,2] in 20 ml of anhydrous methanol and 20 ml of anhydrous diethyl ether (used for solubility) was reacted with 2 g of sodium in 100 ml of liquid

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[a]prepared by W. Nutakul

ammonia. After workup a white solid was obtained, which when recrystallized from ethanol afforded 1.6 g (80%) of 3,6-dihydrobenzo[1,2:4,5]dicyclopentene (> 99% pure); NMR (CCl_4) δ 2.5 (s, 4H, C=C-C$\underline{H}_2$) and 2.4 to 1.8 ppm (m, 12H, C$\underline{H}_2$); IR (KBr) 2900 (b), 1480 (s), 1420 (s), 1340 (s), 1300 (s), 1195 (s), and 910 (m) cm^{-1}.

1,2,3,4,5,6,7,8,9,10-Decahydroanthracene (90) (WC-383) The procedure of 4,7-dihydroindan was followed utilizing 2.34 g (12.6 mmol) of 1,2,3,4,6,7,8-octahydroanthracene[a] in 20 ml of anhydrous diethyl ether (used for solubility) and 2 g of sodium in 100 ml of liquid ammonia. After workup a white solid was obtained which after recrystallization from ethanol gave 1,2,3,4,5,6,7,8,9,10-decahydroanthracene, mp 73°C (lit.[51] 67°C) which was further purified by preparative VPC (Column B, 150°C); NMR ($CDCl_2$) δ 2.4 (s, 4H, C=C-C$\underline{H}_2$) and 2.0-1.5 ppm (m, 16H, C$\underline{H}_2$); IR (KBr) 2950-2800 (b), 1510 (s), 1450 (m), 1300 (s), 1275 (s) and 1140 (s) cm^{-1}.

1,4-Dihydronaphthalene[31] (80) (WC-318) A 2-liter, three necked flask, equipped with a large reflux condenser, addition funnel and an overhead mechanical stirrer, was charged with 64 g (.5 mol) of naphthalene and 46 g (2 mol) of sodium. The two solids were stirred together at 140-145°C until an emulsion

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[a]prepared by W. Nutakul

of dispersed sodium and liquid naphthalene was obtained. The reaction was allowed to cool to 60°C and 150 ml of dry benzene was added. The reaction mixture was heated to 90-100°C in an oil bath and 600 ml of absolute ethanol was slowly added. More benzene was added when stirring became difficult. The reaction mixture was allowed to cool to room temperature and poured over 225 g of hydrochloric acid and 1.5 liters of crushed ice. The benzene layer was removed and the aqueous layer extracted twice with 100 ml portions of benzene. The combined benzene extracts were dried over sodium sulfate and the solvent was removed on a rotary evaporator. Distillation of the resulting oil gave 53.77 g (60-65°C/4mm) of 1,4-dihydronaphthalene (85% pure). Further purification by spinning band distillation (81°C/10 mm) gave 1,4-dihydronaphthalene (> 99% pure); NMR (CCl_4) δ 6.9 (s, 4H, Ar-H), 5.75 (m, 2H, C=C-H), and 3.25 ppm (broad s, 4H, Ar-CH_2); IR (thin film) 3030 (s), 2890-2820 (b), 1500 (s), 1460 (s) and 1430 (s) cm^{-1}.

1,4-Dihydro-2,3-dimethylnaphthalene (81) (WC-382) Following the procedure described for 1,4-dihydronaphtho[b]cyclobutene, 12.3 g (.15 mol) of 2,3-dimethyl-1,3-butadiene was reacted with the benzyne prepared from 20 g (.146 mol) of anthranilic acid and 20 g (.17 mol) of isoamyl nitrite. After addition the crude reaction mixture was filtered through 30 g of silica gel and the solvent removed on a rotary evaporator. The resulting crude oil was distilled (70°C/.3 mm) on a Kugelrohr

distillation apparatus to give 4.4 g of an oil which gave two peaks by VPC (Column B, 120°C). Preparative VPC of the shorter retention time peak gave 1,4-dihydro-2,3-dimethylnaphthalene (> 98%);NMR ($CDCl_3$) δ 7.0 (s, 4H, Ar-H), 3.25 (s, 4H, Ar-CH_2) and 1.75 ppm (s, 6H, CH_2); IR (thin film) 2940 (b), 1700 (b), 1430 (m), 875 (s) and 740 (s) cm^{-1}.

Bicyclo[4,2,0]octa-1(6),3-diene[34] (84) (WC-391) Following the procedure described by Thummel,[34] leadtetraacetate oxidation of 2 g (10.1 mmol) of bicyclo[4,2,0]octa-3-ene-1,6-dicarboxylic acid gave 0.2g (20%) of bicyclo[4,2,0]octa-1(6),-3-diene; NMR (CCl_4) δ 5.65 (broad s, 2H, C=C-H) and 2.5 ppm (broad s, 8H, C=C-CH_2).

1,2-Dimethyl-1,4-cyclohexadiene[36] (86) (WC-385) A Birch reduction of o-xylene, analogous to that for indan, utilizing 30 g (0.27 mol) of o-xylene in 25 g of methanol and 15 g of sodium in 250 ml of liquid ammonia. Workup gave an etheral solution which was evaporated through a 42 cm Vigreaux condenser to give approximately 50 ml of an oil. Atmospheric distillation of the oil gave ~20 ml of an oil. Preparative vpc (Column B, 70°C) of the residue afforded 1,2-dimethyl-1,4-cyclohexadiene (99% pure); NMR (CCl_4) δ 5.6 (t, 2H, C=C-H), 2.55 (m, 4H, C=C-CH_2) and 1.6 ppm (s, 6H, CH_3); IR (thin film) 2910 (b), 1460 (b), 1380 (m), 1260 (s), and 1010 (b) cm^{-1}.

1,2,4-Trimethyl-1,4-cyclohexadiene (88) (WC-408) In an analogous procedure to that for 4,7-dihydroindan, 30 g (.25 mol) of 1,2,4-trimethylbenzene, in 25 ml of methanol was reduced with 15 g (.65 mol) of sodium in 250 ml of liquid ammonia. Evaporation of the etheral solution, obtained from workup, gave approximately 30 ml of an oil. Distillation, 50-110°C/760 mm, gave 5 ml of oil, enriched in 1,2,4-trimethyl-1,4-cyclohexadiene. Preparative VPC (Column B, 110°C) gave 1,2,4-trimethyl-1,4-cyclohexadiene (99% pure); NMR (CCl_4) δ 5.3 (m, 1H, C=C-H), 2.5 (m, 4H, C=C-CH_2) and 1.6 ppm (s, 9H, CH_3); IR (thin film) 2980-2820 (b), 1500 (m), and 910 (s) cm^{-1}.

2,5-Dihydroanisole (92) (WC-409) Eastman's procedure,[37] for the Birch reduction of anisole, was followed, giving a product mixture of 2,5-dihydroanisole and 2,3-dihydroanisole. Two Kugelrohr distillations (50°C/.3 mm) gave 2,5-dihydroanisole (> 95% pure) (lit.[37] bp 148°C); NMR (CCl_4) δ 5.65 (m, 2H, C=C-H), 4.55 (m, 1H, C=C-H), 3.45 (s, 3H, O-CH_3) and 2.7 ppm (m, 4H, C=C-CH_2); IR (thin film) 3010-2820 (b), 1695 (s), 1390 (m), 1220(s), and 1170 (s) cm^{-1}.

2,5-Dihydrobenzaldehyde[38] (93) (WC-410) In a small thick-walled tube was placed 1.0 g (18 mmol) of propargaldehyde and the tube was cooled in an acetone-dry ice bath. An excess (~4 ml) of 1,3-butadiene was condensed into the tube and it

was sealed. The tube was heated to 120°C for eight hours in an oil bath, cooled, opened and the resulting thick oil removed with chloroform. The chloroform was removed on a rotary-evaporator and a Kugelrohr distillation, 70°C/.3 mm, gave 1.7 g (80%) of 2,5-dihydrobenzaldehyde. The product was purified further by a second distillation, (99% pure); NMR (CCl_4) δ 9.4 (s,1H, O=C-H), 5.7 (m, 3H, C=C-H) and 2.9 ppm (m, 4H, C=C-CH_2); IR (thin film) 3020 (m), 2840 (m), 1690 (b), 1640 (s), 1190 (b), and 960 (m) cm^{-1}.

General Kinetic Procedure: A Gilford 240 spectrophotometer was equilibrated and calibrated (as described in the operator's manual) at 390 mm for a glacial acetic acid sample, using the visible source through a blue filter. The cell compartment of the spectrometer was kept at 25°C by a flow of constant temperature water from a Haake circulation bath. A stock solution ($\sim 1.6 \times 10^{-3}$ M) of DDQ was prepared from 10 ml of glacial acetic acid and $\sim$20 mg of DDQ. Into a 1 cm x 1 cm x 3 cm uv cuvette was weighed the substrate to be oxidized (for pseudo-first-order kinetic conditions, the substrate must be in at least a ten-fold excess of the concentration of DDQ). Using a pipette, 2.0 ml of glacial acetic acid was added to the cuvette, the substrate and acid mixed well. The open cuvette was placed in the spectrometer and allowed to equilibrate at 25°C. The cover plate of the spectrometer was fitted with a septum, through which was inserted a syringe needle. The cover plate was aligned on the spectrometer such that the needle was in the open cuvette. While reading the absorbance at 390 nm on a strip chart recorder with a known chart speed, 0.4 ml of the DDQ stock solution was syringed through the needle into the cuvette. An immediate deflection was noted upon addition of the DDQ. The decay of the DDQ absorption and time, were recorded and followed until no further decrease in absorption was observed. This final absorption was taken as A_∞. The absorptions (A_t) at time t were read from the chart paper and the log of ($At-A_\infty$) was plotted against time.

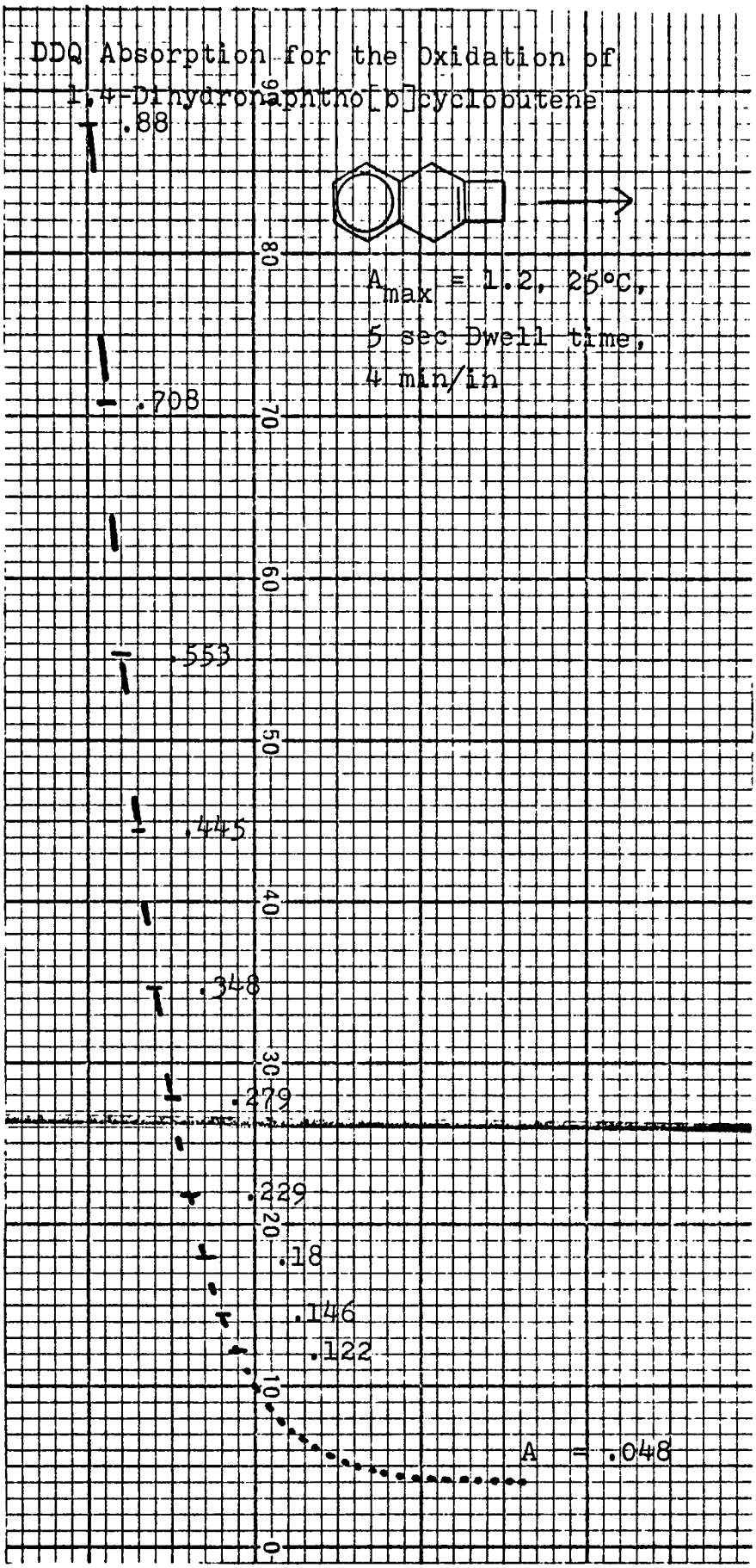
The slope of the line was graphically determined and used to find the pseudo-first-order rate constant (K_1= -slope x 2.303). The second-order-rate constant was then calculated using K_1 and the molar concentration of the substrate ($K_2 = K_1/[substrate]$).

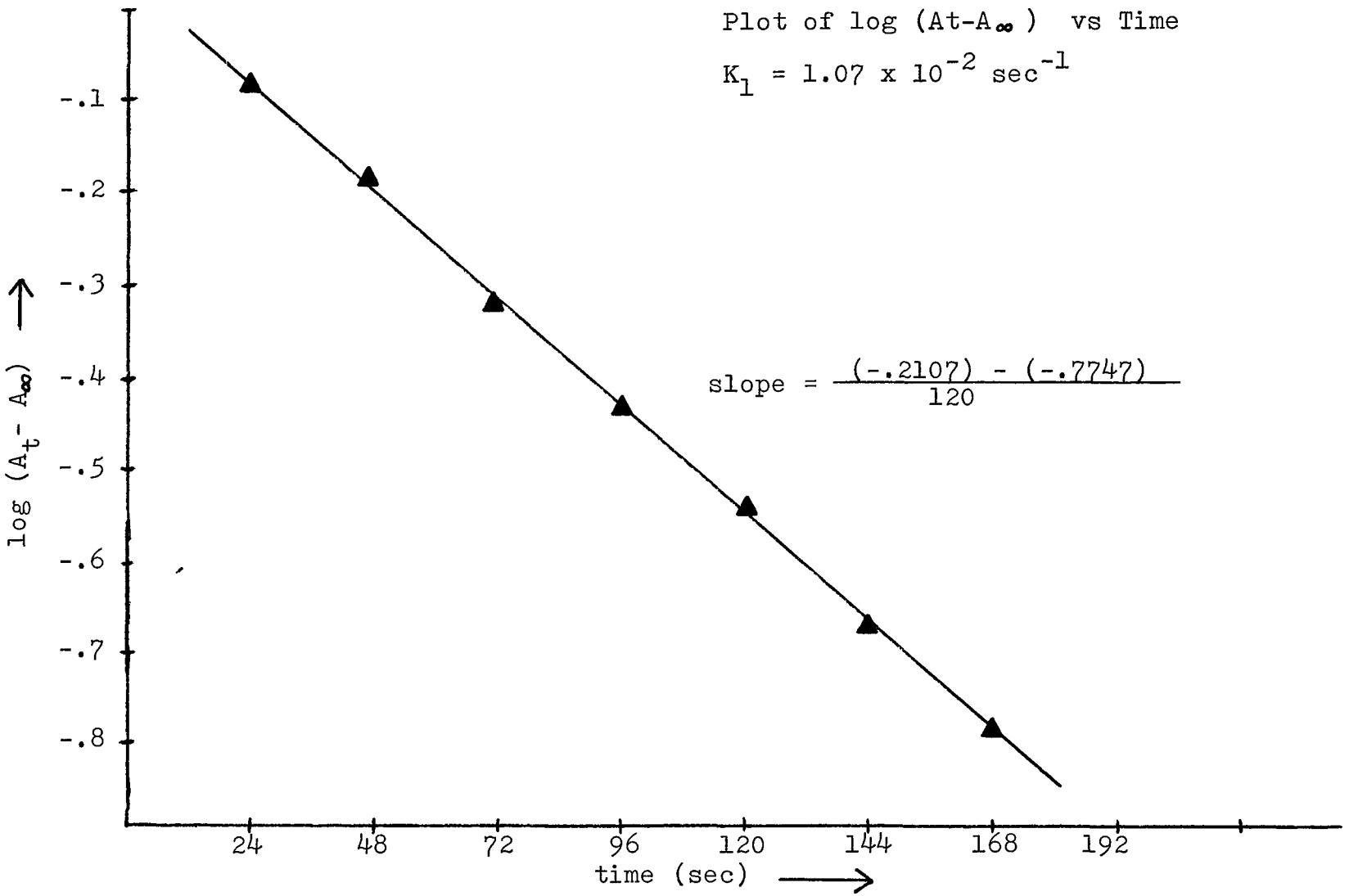
For substrates which oxidize slowly (longer than four to five minutes), the above procedure was modified as follows. The stock solution was added directly to the cuvette containing the substrate. The cuvette was capped, shaken, and placed in the spectrometer. The cover plate (without the aforementioned septum and syringe needle) was placed on the spectrometer, and absorption readings were taken. The dwell time was set for 0.5 sec and placed on automatic. This automatically removes the sample from the beam of light when a reading is not being taken. The sample is then returned to the light beam for 0.5 sec for an absorbance reading. For slow samples this procedure is used to prevent a DDQ absorption decrease caused by the light source (for samples that oxidize in less than five minutes, this prevention is not necessary). The above procedure is then followed to determine the rates.

A Typical Kinetic Run: For the aromatization of 1,4-dihydronaphtho[b]cyclobutene to naphtho[b]cyclobutene, .00811 g of 1,4-dihydronaphtho[b]cyclobutene was weighed into the uv cuvette and 2.0 ml of glacial acetic acid was added using a pipette. The solid was dissolved and the uv cuvette, without a lid, was placed in the spectrometer. The cover plate for the spectrometer, fitted with a septum and syringe needle, was aligned such that the needle was in the cuvette. The absorption at 390 m was read with the strip chart recorder running at 4 min/inch. Using a 1 ml syringe 0.4 ml of DDQ stock solution was directly injected into the uv cuvette. The absorbance was noted to rise immediately to ~1.05 and then slowly decay. The following readings were taken:

Time (sec)	At-A	
0	1.008	
24	.8016	
48	.6156	
72	.486	
96	.3696	
120	.2868	
144	.2269	
168	.168	
192	.1272	
216	.0984	
280	.048	taken as A_∞

The log of $A_t - A_\infty$ was plotted against time and the negative slope of that straight line multiplied by 2.303 gave K_1 = 1.07×10^{-2} sec^{-1}. The actual concentration of 1,4-dihydronaphtho[b]cyclobutene and DDQ were calculated to be 2.166×10^{-2} M and 1.64×10^{-3} M respectively. Dividing K_1 by the concentration of 1,4-dihydronaptho[b]cyclobutene gave K_2 = 4.94×10^{-1} M^{-1} sec^{-1}.


DDQ Absorption for the Oxidation of
1,4-Dihydronaphtho[b]cyclobutene
.88
.708
.553
.445
.348
.279
.229
.18
.146
.122
A = .048
A_{max} = 1.2, 25°C,
5 sec Dwell time,
4 min/in
90
80
70
60
50
40
30
20
10
0


Plot of log (At-A∞) vs Time
K1 = 1.07 x 10-2 sec-1
slope = (-.2107) - (-.7747) / 120
log (At- A∞)
-.1
-.2
-.3
-.4
-.5
-.6
-.7
-.8
24
48
72
96
120
144
168
192
time (sec)

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