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THESIS ABSTRACT

THE OHIO STATE UNIVERSITY
GRADUATE SCHOOL

NAME: McKelvey, Timothy Aaron QUARTER/YEAR: Spring/1987

DEPARTMENT: Chemistry DEGREE: M.S.

ADVISER'S NAME: Czarnik, Anthony W.

TITLE OF THESIS: RATE ACCELERATION OF THE RETRO DIELS-ALDER REACTION OF ANTHRACENE CYCLOADDUCTS BY POLYSILOXY SUBSTITUENTS

The effects of diene substitution on the rate of the retro Diels-Alder reaction are not well understood. Siloxy substituents have, however, been shown to increase the rate of cycloreversion. In an effort to find cycloaddition/cycloreversion systems that are relatively fast in both directions, polysiloxy anthracenes were synthesized. The Diels-Alder reactivity (both forward and retro) of polysiloxyanthracenes with acrylonitrile was investigated and compared to that of nonsilylated anthracenes. The siloxy substituents slow the forward reaction moderately and accelerate the retro reaction significantly. The unexpected slowing of the forward reaction has been rationalized as being due to ring strain preventing complete conjugation of oxygen lone pairs. Theses, Anthracenes,

(mjm)

AW Czarnik

Adviser's Signature

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RATE ACCELERATION OF THE RETRO DIELS-ALDER REACTION OF ANTHRACENE CYCLOADDUCTS BY POLYSILOXY SUBSTITUENTS

A THESIS

Presented in Partial Fulfillment of the Requirements for
the degree Master of Science in the
Graduate School of the Ohio State University

by

Timothy Aaron McKelvey, B.S.

* * * * *

The Ohio State University
1987

Master's Examination Committee:
Dr. Anthony Czarnik
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Approved by

AW Czarnik

Adviser
Department of Chemistry

DEDICATION

In loving memory of Brian McKelvey and David Finn

ACKNOWLEDGMENTS

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INTRODUCTION

Introduction

This research project is explicitly tied to the Diels-Alder (DA) catalysis cycle for carbonyl transformations.[1] As such, an understanding of the need for, and the basic principles of such a cycle are essential to understanding the nature of this project. Therefore, a fairly extensive desription of this catalytic scheme follows a description of the need to improve the process of carbonyl transformations. Since the DA catalysis cycle utilizes Diels-Alder cycloaddition/cycloreversion systems, a brief overview of the Diels-Alder and retro-Diels-Alder reactions is also provided. Lastly, this part will introduce the author's attempt to fill some vital technology voids.

Background

Acrylamide is a major industrial chemical due to the increasing use of its polymers in surfactant production, waste water treatment, and oil recovery.[2] Carboxamides are generally prepared via hydration of the corresponding nitriles.[2] However, the strongly acidic or basic conditions required also promote hydrolysis of the product carboxamide to the carboxylic acid as well as hydrolysis of other functional groups present.[1,2] Even under forcing conditions, nitrile hydrations are slow, as are other carbonyl transformations such as alcoholysis of carboxamides to carboxylic esters. An effective catalytic cycle for carbonyl conversions would increase the usefulness of nitriles and carboxamides as synthetic precursors as well as eliminate the problems which occur where such precursors are already used. In 1984, Czarnik introduced a novel catalytic cycle which formally catalyzes the conversion of acrylamide to ethyl acrylate.[1]

DA catalysis cycle for α,β unsaturated carbonyl transformations:

The title catalysis cycle is depicted schematically in Figure 1.[1] The cycle is characterized by Diels-Alder cycloaddition of 9-(2-pyridyl)anthracene (1) and acrylamide to yield ortho adduct (2) and meta adduct (3). Compound 2 undergoes ethanolysis to 4 in the presence of metal ions and refluxing ethanol, whereas 3 does not. Cycloreversion of 4 yields 1 and ethyl acrylate.[1] An extension of this work performed by Nanjappan is depicted in Figure 2.[3] In this case, the ortho adduct (5) of 1 and acrylonitrile is hydrated to a carboxamide adduct (7). Meta adduct (6) remains intact.[3] This phenomenon can be adequately explained in terms of the ability of ortho adducts to chelate metals due to the proximity of the pyridyl nitrogen and nitrile nitrogen (or carbonyl oxygen as the case may be). Ligation thereby polarizes the carbonyl group and facilitates nucleophilic attack.[4]

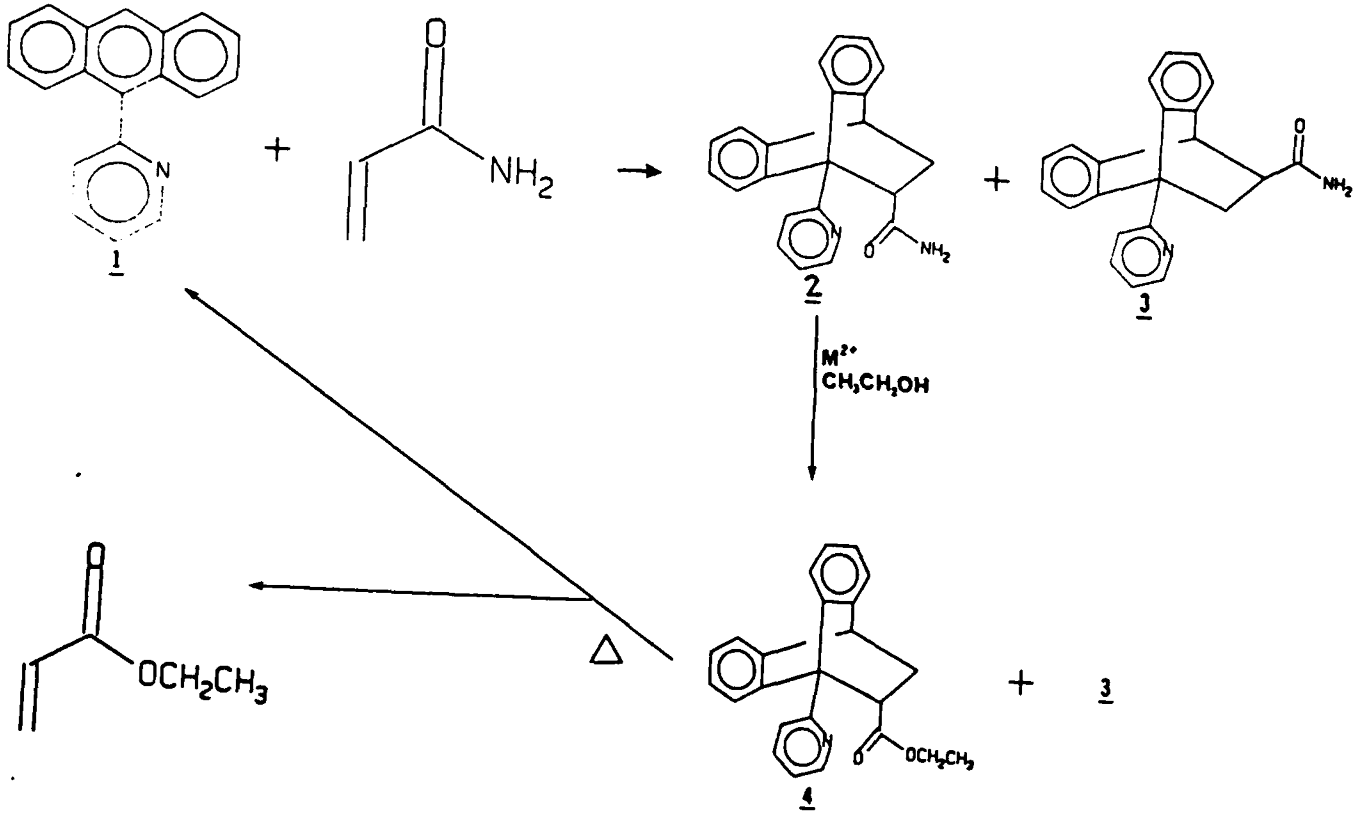

FIGURE 1 : Diels-Alder catalytic cycle for carbonyl transformations.

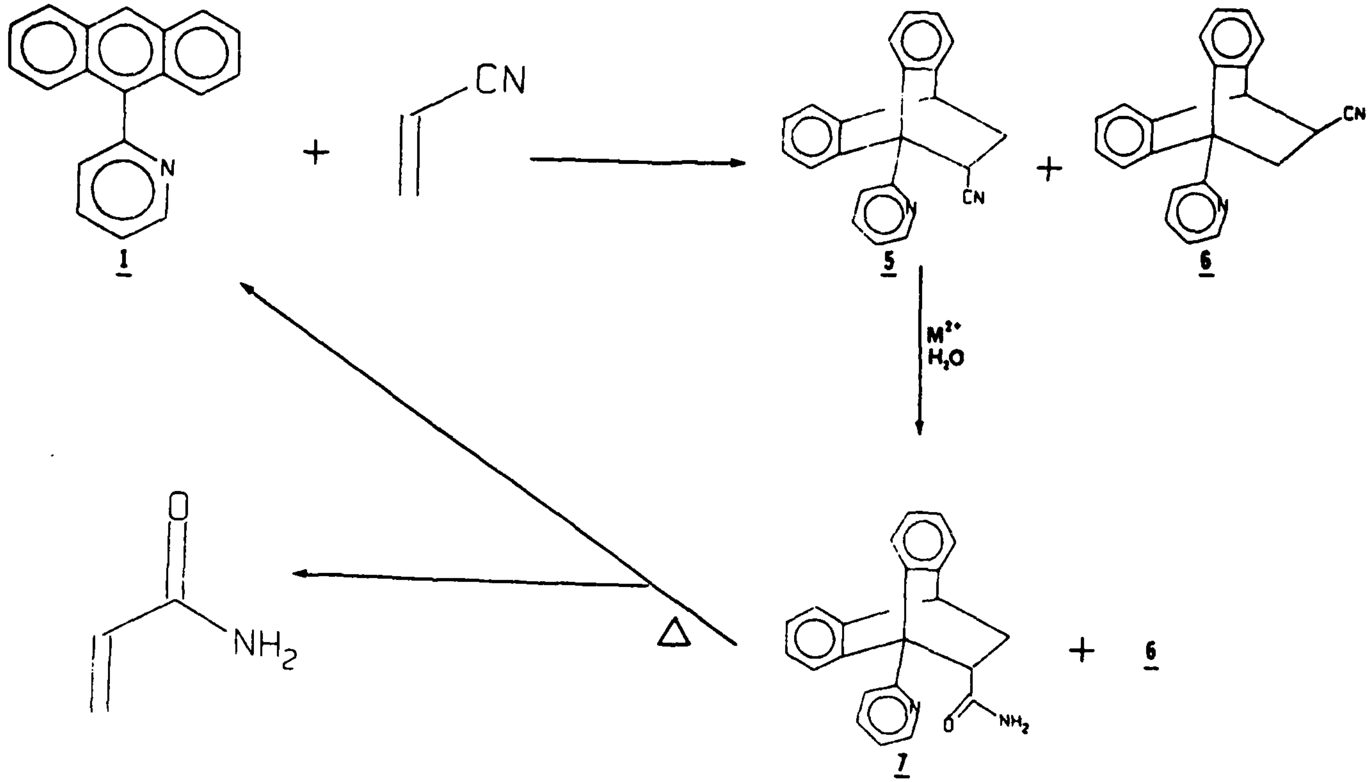

FIGURE 2 : Nanjappan modification of the Diels-Alder catalytic cycle.

A current drawback of the DA catalysis cycle is the high temperature required for cyloreversion of adducts following the carbonyl transformation. To be practical, the cycloaddition, carbonyl transformation and cycloreversion must all occur at reasonable rates and temperatures. Data related to cycloreversion temperatures and subtstituent effects are lacking.[5,6]

Apparently, steric interactions play a minor role in the retro-Diels-Alder reaction. Steric bulk dramatically decreases the rates of cycloaddition while only slightly accelerating the cycloreversion.[6,7] This has been rationalized in terms of the late transition state for cycloaddition, and conversely the early transition state for cycloreversion.[6]

Diels-Alder cycloaddition/cycloreversion reactions:

The Diels-Alder (DA) reaction is a $\pi^4s + \pi^2s$ electrocyclic reaction. That is, a component with 4π electrons (diene) and a 2π component (dienophile) condense suprafacially to form a cyclohexene moeity as shown in Figure 3. The factors facilitating the Diels-Alder reaction can, in general, be attributed to electron withdrawing substituents on the dienophile and electron donating substituents on dienes.

Anthracenes participate as dienes in the Diels-Alder reaction as shown in Figure 4. Anthracene cycloadditions occur almost exclusively across the 9,10 positions. At elevated temperatures, the adducts cyclorevert in a retro-Diels-Alder reaction to yield the starting anthracene and dienophile.

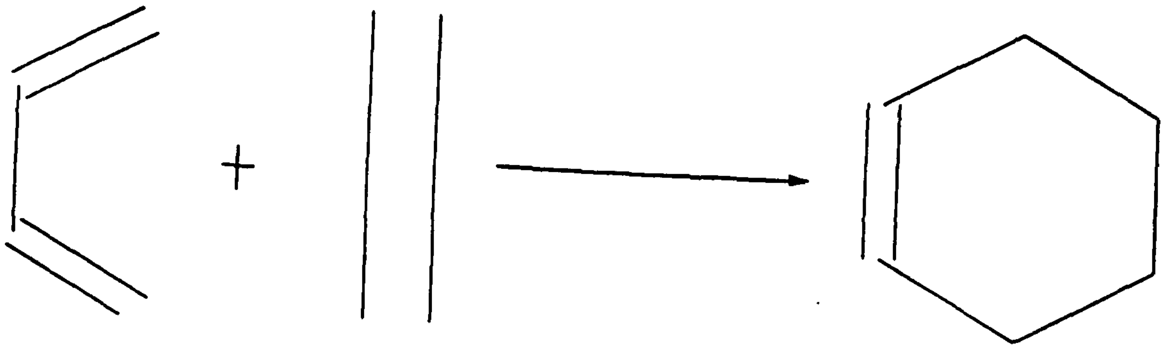

FIGURE 3 : Diels-Alder reaction scheme (general).

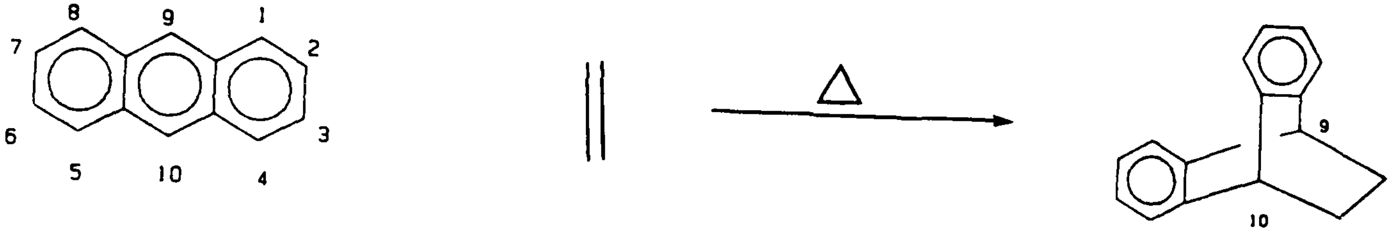

FIGURE 4 : Diels-Alder reaction scheme (anthracene).

The retro-Diels-Alder reaction, a $\pi^2s + \sigma^2s + \sigma^2s$ electrocyclic process, is depicted in Figure 5. Until recently, a systematic study of substituent effects on retro-Diels-Alder (rDA) reaction rates had never been reported.[6] Although Nanjappan noted these cycloreversions were accelerated by electron withdrawing and conjugating substituents, even if highly electron donating,[6] the study only encompassed investigation of substituents on the dienophile component. This research group is currently investigating a wide variety of 9,10-disubstituted anthracenes, and the impact of those substituents on the rate of rDA reactions. Until such information is available further advances will have to be based on what literature precedents are available and chemical intuition.

Literature citings of anionic accelerated rDA reactions appeared in the 1960's and 1970's.[8] In 1980, cycloreversions were accelerated not only by an alkoxy anion, but also by the trimethylsiloxy substituent.[9] Chung's work confirms this phenomenon for adducts of bis-9,10-(trimethylsiloxy)anthracene.[10]

Summary

In order for the DA catalysis cycle to have practical utility, the Diels-Alder reaction must be reversible at reasonable temperatures. More simply, a cycloaddition/cycloreversion equilibrium must be established. For this to occur, the rDA reaction must at least be on the same time scale as the DA reaction at a given temperature. Compound 8 , bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene, (Figure 6) was proposed as a theoretically

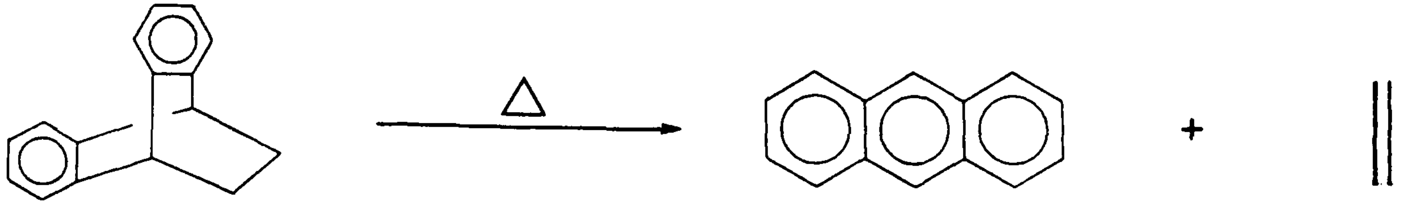

FIGURE 5 : Retro Diels-Alder reaction scheme.

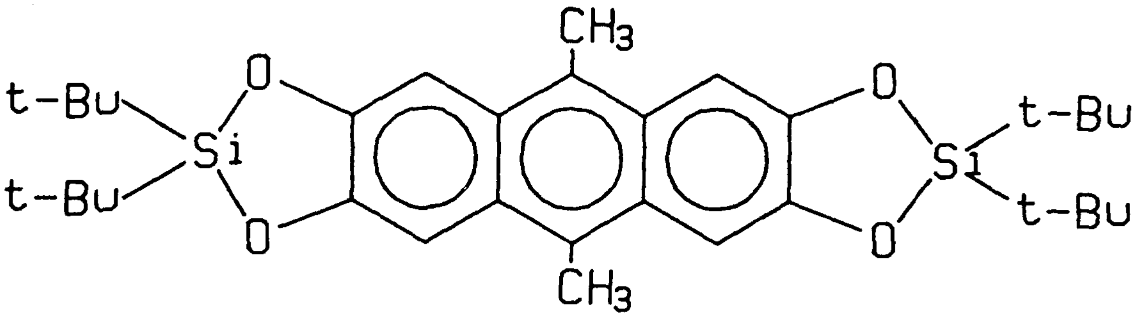

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FIGURE 6 : Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (8).

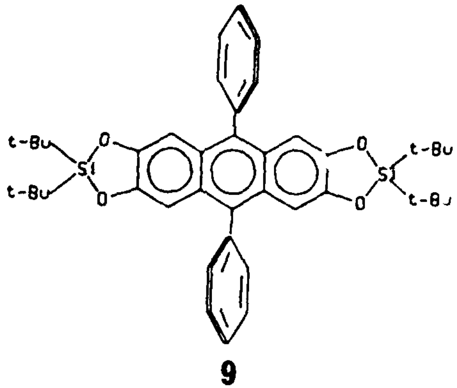
interesting molecule which should be synthesized and investigated for DA/rDA reactivity.[11] Cycloaddition was expected to be facile due to the strongly electron donating siloxy substituents and the lack of steric bulk at the reactive site. The heavily siloxy substituted adducts of 8 presented a high potential for facile cycloreversion. The objective of this research project was to synthesize and investigate the Diels-Alder reactivity (both forward and reverse) of polysiloxyanthracenes and the cycloadducts thereof.

CHAPTER I

SYNTHESIS OF POLYSILOXYANTHRACENES AND RELATED COMPOUNDS

Introduction

Three novel compounds, bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (8), bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene (9, Figure 7), and the Diels-Alder adduct (10) of 8 and acrylonitrile were synthesized. Compounds 8 and 10 were synthesized for their potential to provide vital Diels-Alder/retro Diels-Alder reactivity data for the DA catalysis cycle discussed previously. The bis-(dimethylsiladioxy) (11A, Figure 8) and bis- (diphenylsiladioxy) (11B) derivatives of 9,10-dimethylanthracene were also target molecules. The inability to isolate 11B indicated it and 11A may be too reactive to isolate easily. Thus, effort was directed solely at synthesizing the di-t-butylsilylene derivative. Limited successes in the synthesis of 8 lead to the proposal of 9 as a potentially useful singlet oxygen sponge, as shown in Figure 9.



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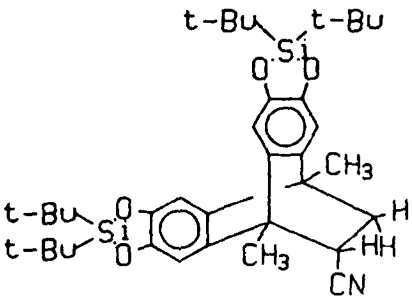

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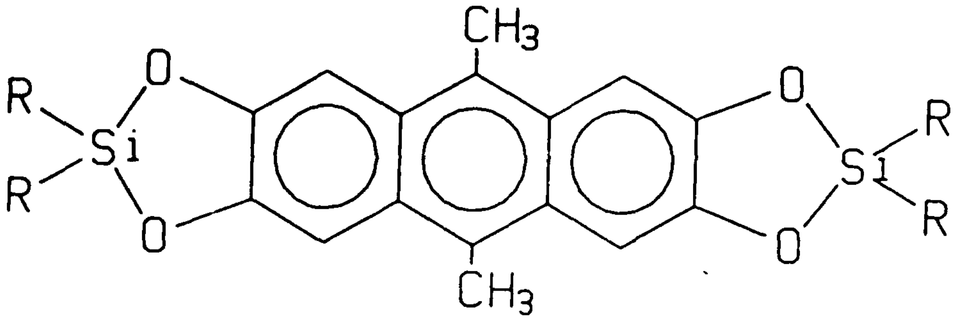
FIGURE 7 : Bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene (9) and bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (10).



11 A. R = Me
B. R = Ph

FIGURE 8 : Bis-(dimethylsiladioxy)[b,i]-9,10-dimethylanthracene (11A) and bis-(diphenylsiladioxy)[b,i]-9,10-dimethylanthracene (11B).

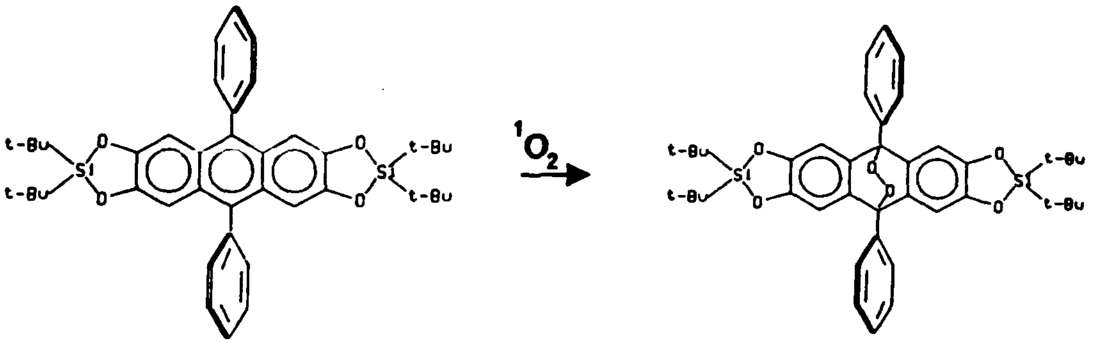


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FIGURE 9 : Diels-Alder reaction of Bis-(di-t-butylsiladioxy)-[b,i]- 9,10-diphenylanthracene with singlet oxygen.

Materials and Methods

Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl anthracene (8):

The overall synthesis of 8 is depicted schematically in Figure 10. A combination of procedures from Boldt[12] and Lindsey[13] yielded 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene (13) by condensing veratrole (12) and acetaldehyde in the presence of sulfuric acid . Cleavage of the four methoxy functions with boron tribromide[12] worked famously. Thus, the prime starting material, 9,10-dimethyl-2,3,6,7-tetrahydroxyanthracene (14), was very readily accessible.

The silylation of 14 to form 8 with di-t-butyldichlorosilane is an extremely clean and high yielding reaction, however, finding appropriate reaction conditions was not as straightforward as expected.

Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (10):

Compound 8 is useful for studying the kinetics of the Diels-Alder reaction. However, an understanding of the retro Diels-Alder reactivity of adducts of 8 was also required if useful data for the DA catalysis cycle was to be obtained. Thus, the

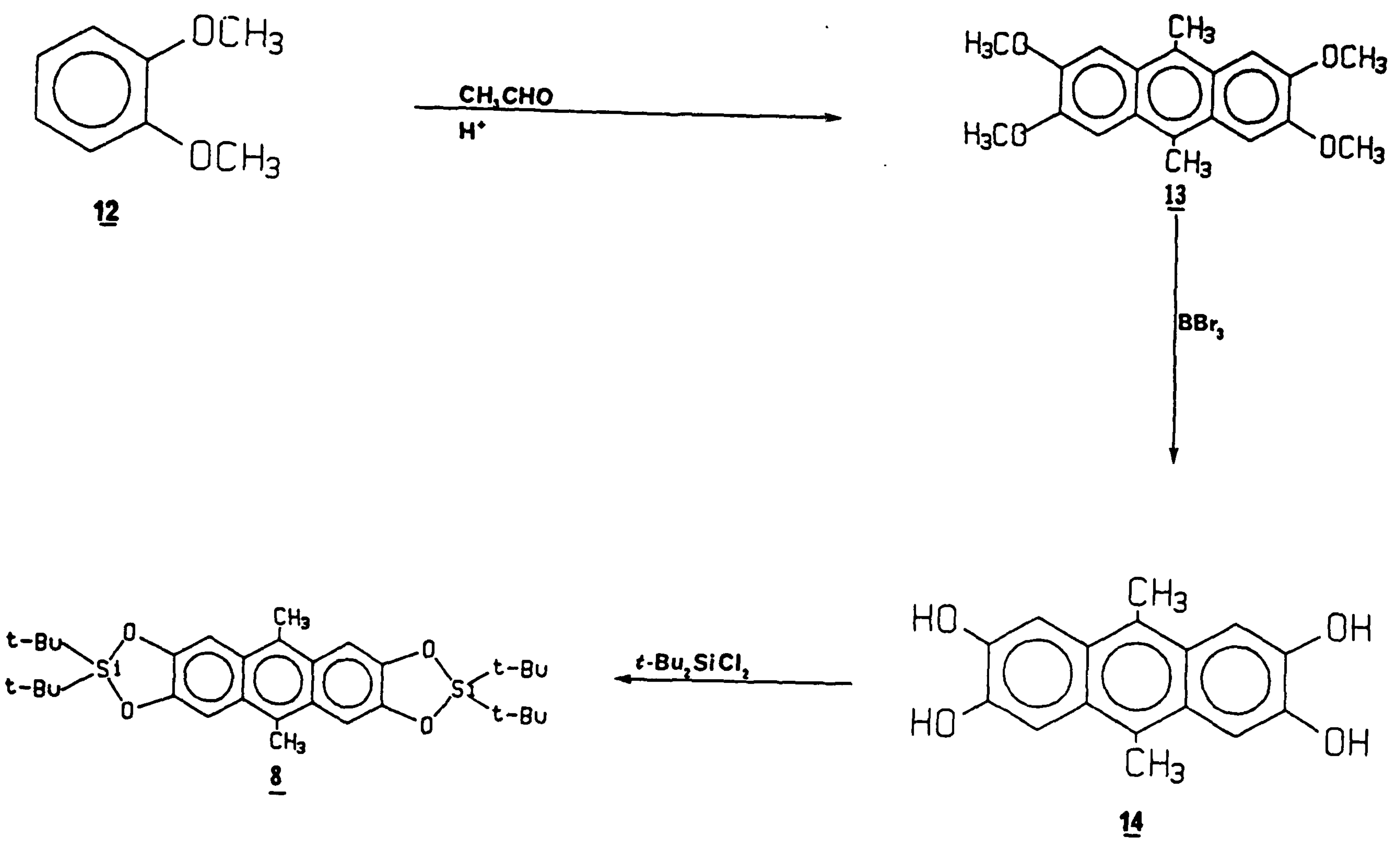

FIGURE 10 : Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene.

title cycloadduct was synthesized. No problems were encountered. The reaction shown in Figure 11 was carried out in refluxing acrylonitrile. Butylated hydroxytoluene (BHT, 16) was added as a radical inhibitor to avoid arylonitrile polymerization.

Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene (9):

As mentioned earlier, compound 9 was proposed as a potential singlet oxygen sponge, or reversible singlet oxygen trap. The endoperoxide adduct (15) may prove to be a convenient, controllable chemical source of singlet oxygen.[14] Endoperoxide adducts of other 9,10-diphenylanthracenes have proven synthetically useful for this purpose,[15] that is, they thermally decompose to parent anthracene and singlet oxygen, which can be trapped by singlet oxygen acceptors.[15] The mechanism of decomposition of 1,4 anthracene endoperoxides is fairly well established as concerted, whereas debate lingers over the mechanism for decomposition of 9,10 endoperoxides.[15] It appears as though these compounds decompose via the singlet diradical intermediate ^1D shown in Figure 12.[15] At this point the diradical can decompose to parent anthracene and singlet oxygen or intersystem cross to triplet diradical ^3D which decomposes to parent anthracene and triplet oxygen. Electron donating groups appear to facilitate the loss of singlet vs. triplet oxygen.[15] Thus, compound 9 is, potentially, a very useful tool.

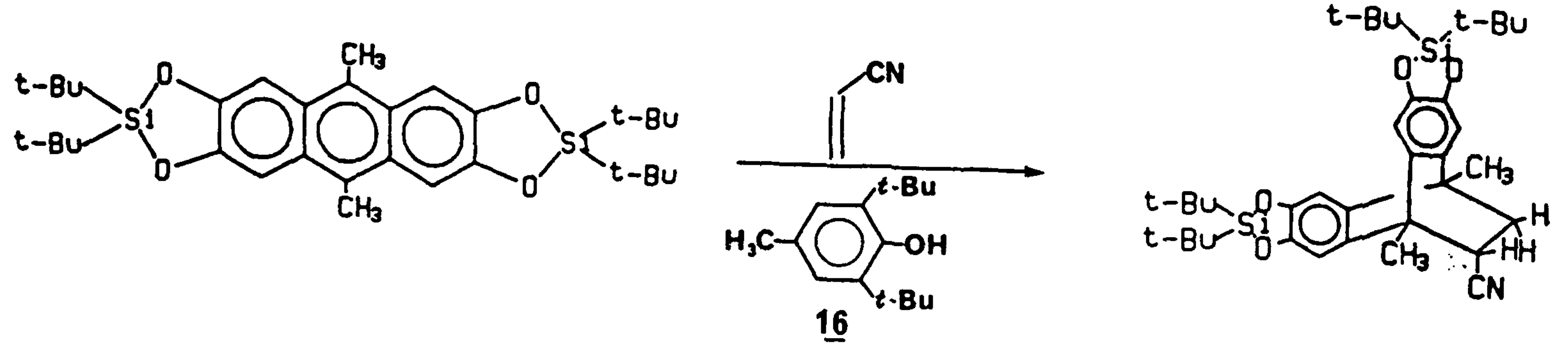

FIGURE 11 : Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene.

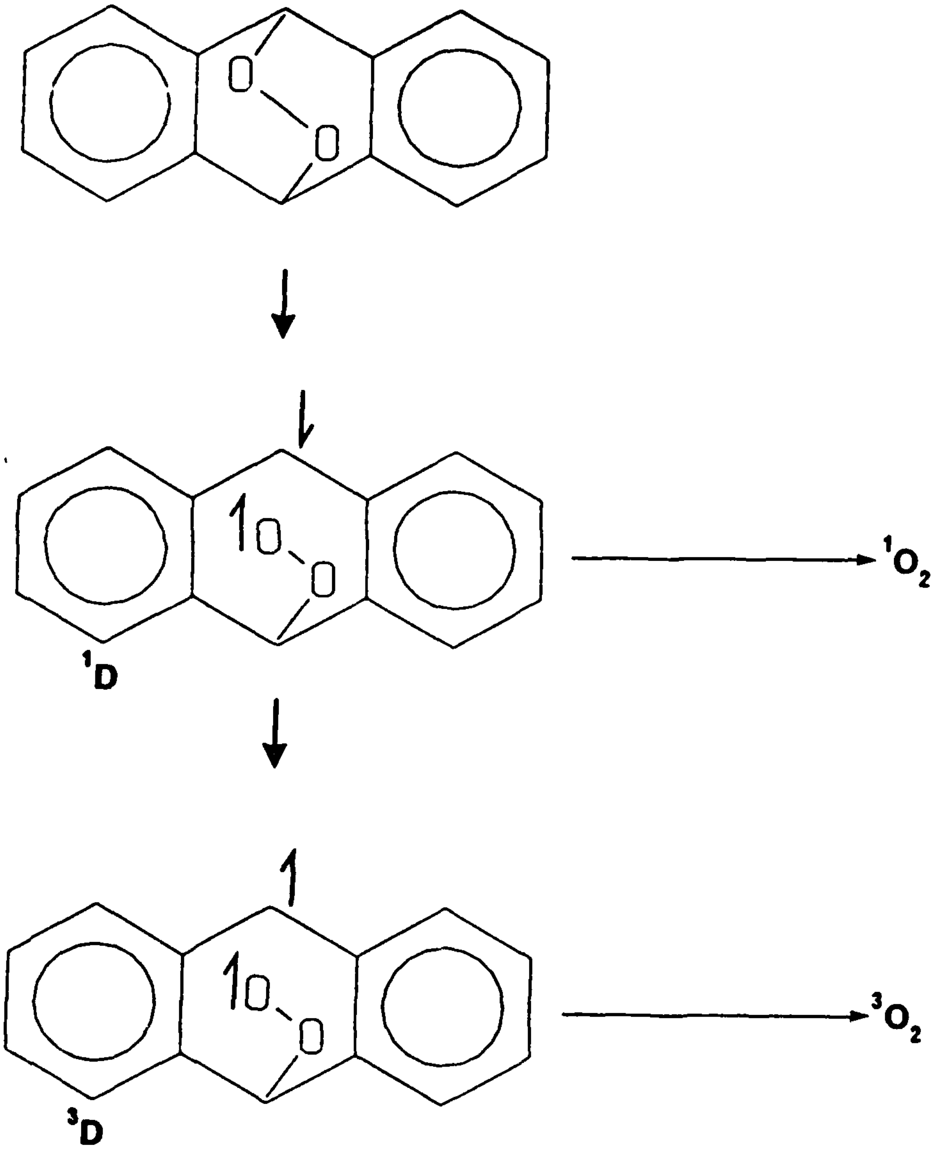

FIGURE 12 : Proposed mechanism for loss of molecular oxygen from anthracene endoperoxides.

The synthesis of bis-(di-t-butyldioxasilyl)[b,i]-9,10-diphenylanthracene was very straightforward. The reaction scheme in Figure 13 mimicks the synthesis of the related 9,10-dimethyl derivative. The first step is higher yielding for the 9,10-dimethyl derivative, but the last two are virtually the same. Investigations into the reactivity of this compound with singlet oxygen are left to future researchers.

Results and Discussion

Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (8):

Several unsuccessful attempts to isolate 11B from the reaction of 14 with diphenyldichlorosilane coupled with Corey's citing[16] of the instability of five membered silylene rings indicated attention should be focused primarily on the more stable di-t-butylsilylene derivative.

The temporary nonavailability of di-t-butyldichlorosilane[17] from the manufacturer apeared to be only a momentary setback since a novel silylating agent, di-t-butylsilyl ditriflate,[18] was introduced in 1984.[16] The silylation was run with limited success using this new reagent. Enough product was produced to characterize by ^{1}H NMR (Plate I) and mass spectrometry (Plate II), but not enough to isolate in a synthetically useful sense.

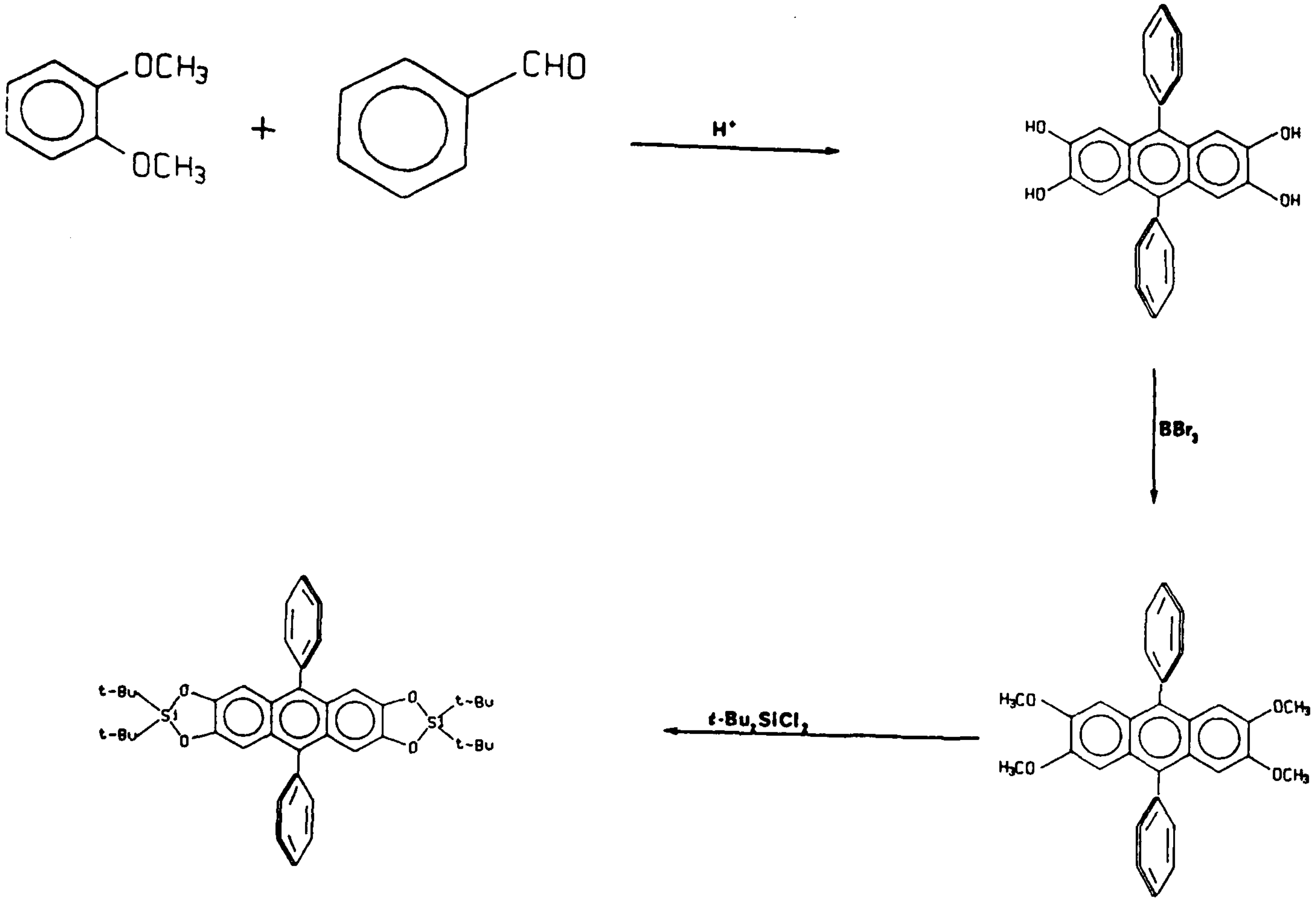

FIGURE 13 : Synthesis of bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene.

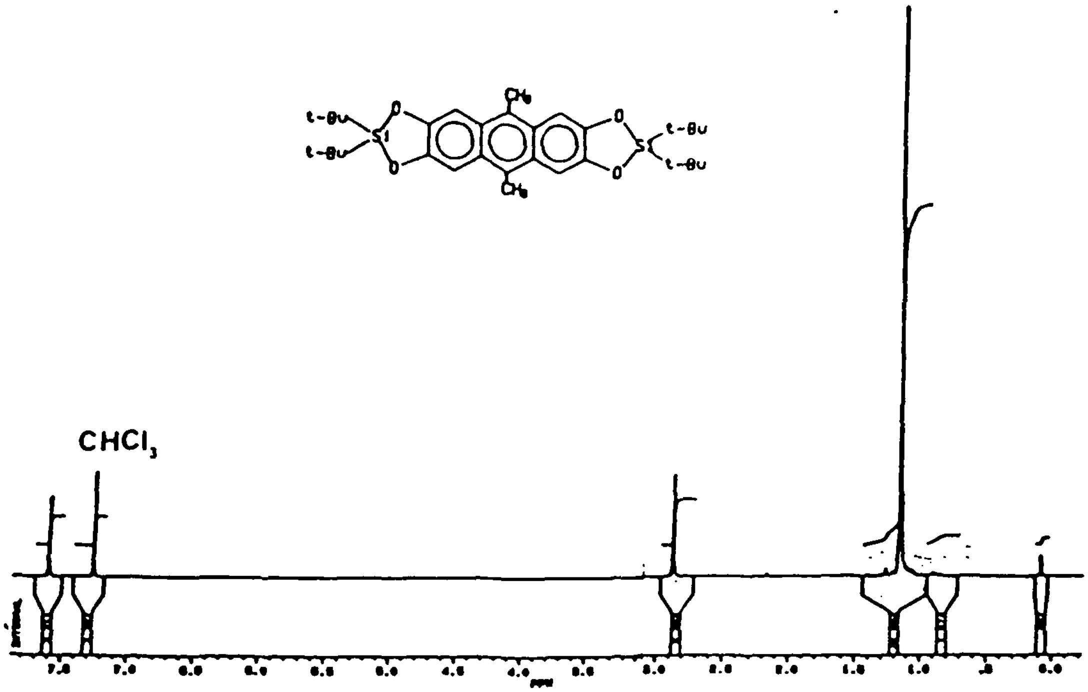

PLATE I : ^{1}H NMR spectrum of compound 8.

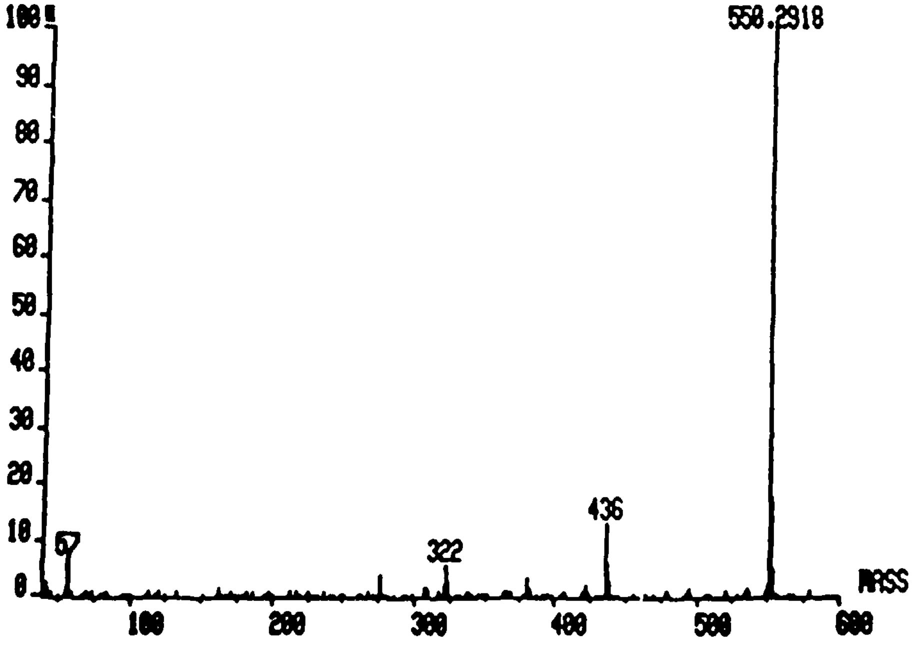

PLATE II : Mass Spectrum of compound 8.

Five theories were proposed for the inability to isolate the product from a seemingly straightforward reaction: 1) improperly purified starting material/reagents; 2) hydrolytic instability of product to traces of water in solvents/ atmosphere; 3) thermal oxidation; 4) photooxidation/ photodimerization; and 5) that the starting material had some unexpected lack of reactivity toward silylation. The first two theories were readily discounted as the sole sources of incomplete reaction. Extreme care was taken in purification and drying of starting material, solvents and bases. The possibility of photochemical processes was a primary concern. A 10^{-4} M solution of 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene in freshly degassed chloroform completely decomposes upon exposure to indirect sunlight in less than 45 minutes. ^{1}H NMR of the reaction products indicates simple dimerization is not the only product. Thus, it is possible that degassing was not totally effective. Reaction of anthracenes with singlet oxygen to form endoperoxides (Figure 14) is well documented.[14,19,20,21] At first glance, the concentration of singlet oxygen in solution could not be expected to account for any major decomposition; the fact that anthracenes are photosensitizers could account for an excessively high concentration of singlet oxygen in solution if degassing was not effective. This possibility prompted an expansion of the scope of this project, to include the synthesis of 9, which was discussed earlier. The potential for oxidation, photooxidation and photodimerization was minimized by degassing solvents and protecting the reaction vessel from light.

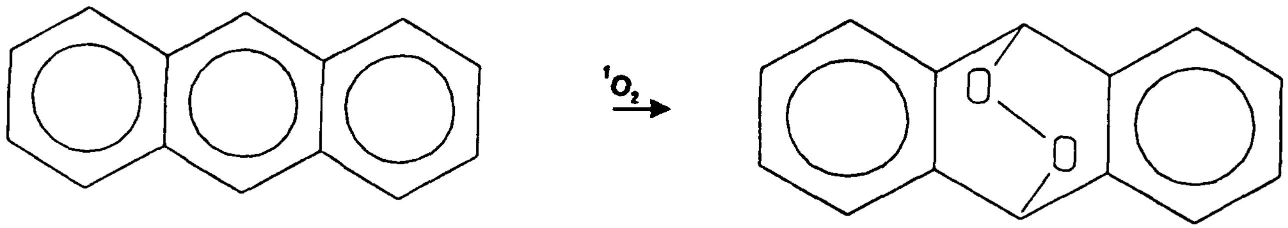

FIGURE 14 : Formation of anthracene endoperoxides.

When these precautions were taken and a significant yield of 8 was still not achieved, a fundamental change to the reaction was made. The reaction depicted in Figure 15 was attempted, but to no avail.

About this time, di-t-butyldichlorosilane became available. The first attempt with this reagent in refluxing acetonitrile[22] yielded 8 as the only detectable product in 78% yield after recrystallization. Various repititions show the reaction to be marvelously consistent with the only yield limitation being the individual's persistence to recover trace amounts from the mother liquor following crystallization. The reaction with di-t-butylsilylditriflate was repeated under identical conditions and a 0% yield of 8 was obtained.

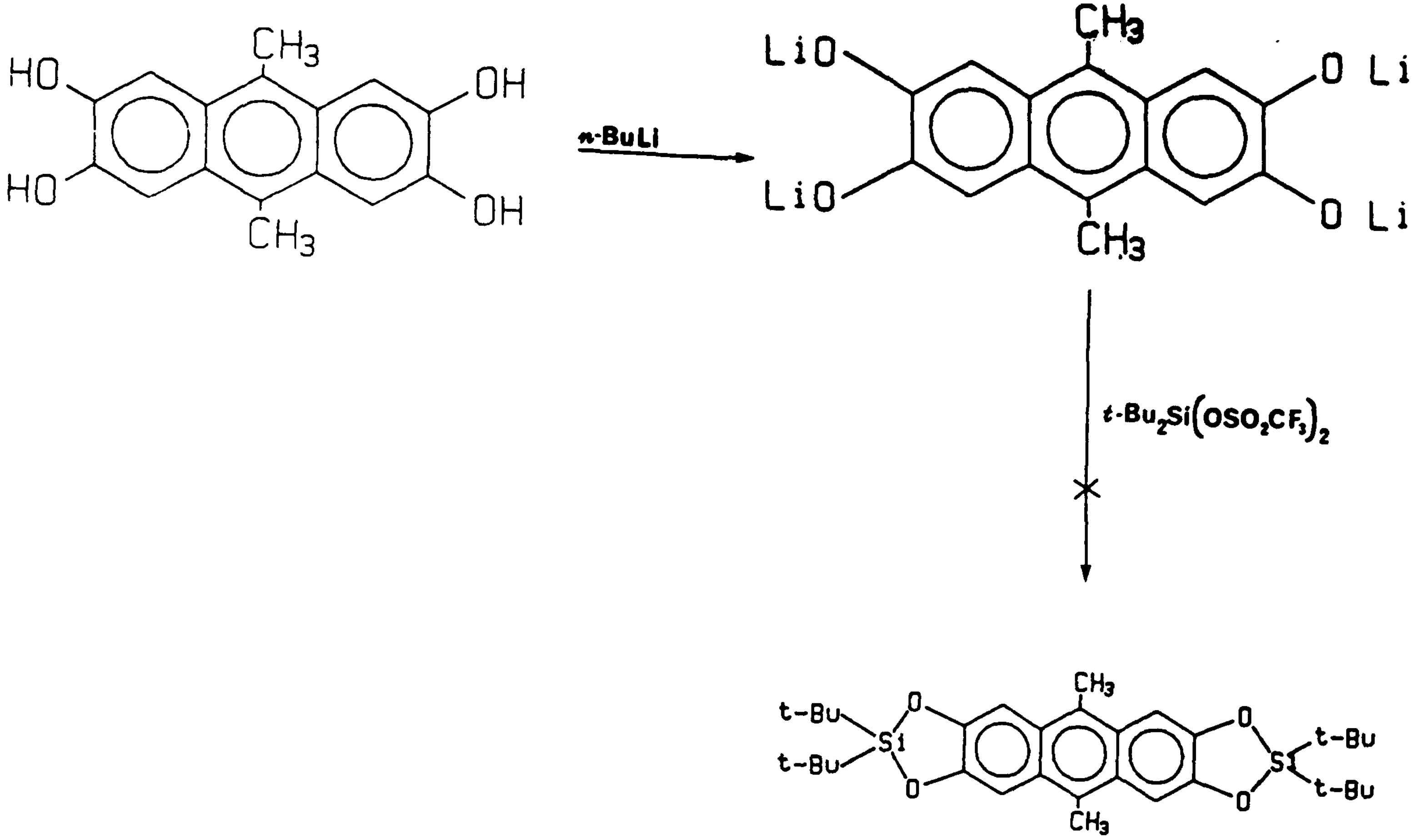

FIGURE 15 : Unsuccessful synthesis of *bis*-(di-t-butylsiladioxy)-[b,i]9,10-dimethylanthracene.

EXPERIMENTAL

General:

All reagents and solvents used were bought from Aldrich Chemical Company or the Ohio State University stores unless otherwise noted. Melting points were determined on an Electrothermal Melting Point Apparatus and are uncorrected. UV spectra were taken on a Hewlett-Packard 8451A Diode Array Spectrophotometer. Mass spectra were obtained from the Ohio State University Chemical Instrument Center by use of a VG-70-250s (or Kratos MS-30) mass spectrometer. High field NMRs (^{1}H and ^{13}C) were accomplished on a Bruker 250 MHz machine. Triethylamine was distilled from potassium hydroxide. Dichloromethane and acetonitrile solvents wer dried over calcium chloride and calcium hydride respectively, then distilled from phosphorous pentoxide.

9,10-Dimethyl-2,3,6,7-tetramethoxyanthracene (13):

Reagents and reaction conditions are a combination of those cited by Boldt[12] and Lindsey.[13] To an ice cooled solution of veratrole (32 mL, 250 mmol) in acetic acid (125 mL) was slowly added an ice cooled solution of acetaldehyde (21 mL, 375 mmol) in methanol (20 mL). The resulting solution was stirred for 1 h. Concentrated H_2SO_4 (95%, 125 mL) was added dropwise over 90 min. The reaction was stirred at 0°C for 20 h, then poured over ice water[23] (1400 mL) to give a yellow/pink mixture. A beige solid was collected and crystallized from chloroform and dried to yield 9.13 g (22.4%) of 13, mp> 340°C as pale yellow flakes: ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 4, Ar-H), 4.10 (s, 12, OCH_3), 2.95 (s, 6, Ar-CH_3); MS m/e 326 (M^+, base peak), 327 (M^++1), 311 (M^+-CH_3), 283 (M^+-C_3H_7), 268 (M^+-C_3H_7-CH_3); HRMS m/e 326.1523 ($C_{20}H_{22}O_4$ requires 326.1518).

9,10-Dimethyl-2,3,6,7-tetrahydroxyanthracene (14):

This compound was prepared by the procedure of Boldt.[12] 9,10-Dimethyl-2,3,6,7-tetramethoxyanthracene (8.0 g, 24.5 mmol) was suspended in freshly dried and distilled dichloromethane (350 mL). Boron tribromide (6.5 mL, 69 mmol) was quickly injected. After 90 min, and several color changes, the reaction mixture reached a greenish yellow color. The crude product was collected as a bright yellow solid and washed with water (2 x 100 mL). The crude product was crystallized from acetic acid and dried in a vaccuum oven for 24 h at 80°C to yield (5.56 g, 84%)[24] of 14, which decomposes without melting 235-250°C, as greenish brown needles: ^{1}H NMR (DMSO-d^6) δ 9.45 very broad (Ar-OH), 7.40 (s, 4, Ar-H), 2.71 (s, 6, Ar-CH_3); MS, m/e 270 (M^+, base peak), 271 (M^++1), 255 (M^+-CH_3), 253 (M^+-OH), 242 (M^+-C_2H_4), 241 (M^+-C_2H_5), 227 (M^+-C_3H_7); HRMS m/e 270.0886 ($C_{16}H_{14}O_4$ requires 270.0892).

Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (<u>8</u>):

9,10-Dimethyl-2,3,6,7-tetrahydroxyanthracene (400.0 mg, 1.48 mmol) was dissolved in freshly dried and distilled acetonitrile (50 mL) in a 100 mL, 3 neck round bottom flask under nitrogen atmosphere. The solution was mixed at room temperature for 15 min. Freshly dried and distilled triethylamine (0.8 mL, 5.74 mmol) was injected and a yellow precipitate immediately formed; the contents were stirred an additional 5 min. Di-t-butyldichlorosilane (0.7 mL, 3.31 mmol) was added dropwise over 5 min and the temperature was increased to gentle reflux for 16 h. The reaction mixture was evaporated under reduced pressure to a dark solid, taken up in chloroform (300 mL), and proportioned between chloroform and sodium bicarbonate/water solution (twice). The chloroform layer was then washed with sodium chloride/water, dried over potassium carbonate, and evaporated under reduced pressure to give a pale yellow-green solid, which was crystallized from chloroform to yield 810 mg (99%) of <u>8</u>, mp > 340°C as off-white granules: ^{1}H NMR ($CDCl_3$) δ 7.61 (s, 4, Ar-$\underline{H}$), 2.90 (s, 6, Ar-$C\underline{H}_3$), 1.15 (s, 36, $C(C\underline{H}_3)_3$); ^{13}C NMR ($CDCl_3$) δ 148.79 ($\underline{C}$-OR), 126.64 (unlabled quaternary Carbon), 124.75 (C-$\underline{C}$-CH_3), 104.55 ($\underline{C}$-H), 26.17 [C-$(\underline{C}H_3)_3$], 21.56 [$\underline{C}$-$(CH_3)_3$], 14.90 (Ar-$\underline{C}H_3$); MS, m/e 550 (M^+, base peak), 551 (M^++1), 552 (M^++2), 436 (M^+- 2 t-Bu), 322 (M^+-4 t-Bu), 57 (t-Bu^+); HRMS m/e 550.2942 ($C_{32}H_{46}O_4Si_2$ requires 550.2935).

9,10-Diphenyl-2,3,6,7-tetramethoxyanthracene (15):

To an ice cooled solution of veratrole (32 mL, 250 mmol) in acetic acid (125 mL) was slowly added an ice cooled solution of benzaldehyde (25 mL, 246 mmol) in methanol (21 mL). The resulting solution was stirred in an ice bath for 10 min. Concentrated H_2SO_4 (95%, 125 mL) was added dropwise over 30 min. The reaction vessel was kept at 0°C for 20 h, then the contents were poured over ice water (1000 mL). The bright yellow-green residue was collected, washed with water (2 x 100 mL), and dissolved in chloroform. The bright yellow-green solution turned red while evaporating under reduced pressure. The solution was evaporated to a red residue. Methanol selectively solublized impurities. A bright yellow solid was collected from the methanol mixture and was dried to yield 6.93 g (12.5%) of 15, purified by crystalization from chloroform with a few drops of ethanol: ^1H NMR ($CDCl_3$) δ 7.55 (m, 10, Ph-$\underline{H}$), 6.82 (s, 4, Ar-$\underline{H}$), 3.72 (s, 12, $OC\underline{H}_3$); MS, m/e 450 (M^+), 451 (M^++1), 436 (M^++1-CH_3), 420 (M^++1-OCH_3), 228 (base peak); HRMS m/e 450.1829 ($C_{30}H_{26}O_4$ requires 450.1829).

9,10-Diphenyl-2,3,6,7-tetrahydroxyanthracene (16):

9,10-Diphenyl-2,3,6,7-tetramethoxyanthracene (1.69 g, 3.74 mmol) was suspended in freshly dried and distilled dichloromethane (200 mL). To this mixture was added boron tribromide (1.5 mL, mmol). The mixture immediately turned dark purple and eventually turned pale green. A pale green solid was collected and washed with water (2 x 100 mL). The green paste was crystallized from ethanol to give 16 (yield undetermined)[25] mp 284-286°C as pale yellow transparent rhomboids that turn opaque brown upon drying: ^{1}H NMR (DMSO-d^6) δ 9.4-9.2 very broad (Ar-O$\underline{H}$), 7.50 (m, 10, Ph-$\underline{H}$), 6.65 (s, 4, Ar-$\underline{H}$), 3.4 (q, $CH_3C\underline{H}_2OH$), 3.35 ($CH_3CH_2O\underline{H}$), 1.05 (t, $C\underline{H}_3CH_2OH$). Anal. ($C_{26}H_{18}O_4 \cdot$ 2EtOH) Calc. C= 74.06, H= 6.21, O= 19.73; Found C= 73.76, H= 6.17[26]. MS, m/e 394 (M^+, base peak), 395 (M^++1), 377 (M^+-OH), 366 (M^+-C_2H_4); HRMS m/e 394.1230 ($C_{26}H_{18}O_4$ requires 394.1205).

Bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene (9):

9,10-Diphenyl-2,3,6,7-tetrahydroxyanthracene (16.0 mg, .041 mmol) was dissolved in freshly dried and distilled acetonitrile (5 mL). As triethylamine (.025 mL, 0.16 mmol) was added, the red solution immediately turned dark. Di-t-butyldichlorosilane (.017 mL, .08 mmol) was injected. The reaction temperature was increased to gentle reflux for 20 h. The orange reaction mixture was evaporated to dryness under reduced pressure, taken up in chloroform (100 mL) and extracted twice with sodium bicarbonate/water solution (100 mL). The chloroform layer was then washed with sodium chloride/water solution (100 mL) and dried over potassium carbonate. The chloroform layer was then evaporated under reduced pressure to a yellow solid which was crystallized from carbon tetrachloride, yield and melting point undetermined: ^{1}H NMR

($CDCl_3$) δ 7.50 (m, 10, Ph-H), 6.94 (s, 4, Ar-H), 1.07 (s, 36, $C(CH_3)_3$); MS, m/e 674 (M^+, base peak), 675 (M^++1), 560 (M^+-2 t-Bu), 446 (M^+-4 t-Bu), 57 (t-Bu^+); HRMS m/e 674.3253 ($C_{42}H_{50}O_4Si_2$ requires 674.3248).

9,10-Dimethyl-11-cyanoethanoanthracene (27):

9,10-Dimethylanthracene (181.5 mg, 87.9 mmol) was placed in a glass pressure tube with acrylonitrile (10 mL) and 2,6-di-t-butyl-4-methylphenol (2 crystals) to inhibit acrylonitrile polymerization. The pressure tube was sealed, wrapped in aluminum foil and warmed in an oil bath at 50°C for 21 h. The resulting solution was evaporated to dryness, crystallized from ethanol and dried to yield 206.3 mg (98.6%) of 27, mp 143-146°C as colorless crystals: ^1H NMR ($CDCl_3$) δ 7.3 (m, 8, Ar-H), 2.75 (dd, 1, NC-C-H), 2.17 (s, 3, NC-C-C-CH_3), 2.11 (dd, 1, NC-C-CH cis to CN), 1.98 (s, 3, NC-C-C-C-CH_3), 1.46 (dd, 1, NC-C-CH trans to CN), 1.52 (s, H_2O).

9,10-Dimethyl-2,3,6,7-tetramethoxy-11-cyanoethanoanthracene (26):

9,10-Dimethyl-2,3,6,7-tetramethoxyanthracene (30.45 mg, .093 mmol) was added to a glass pressure tube along with acrylonitrile (10 mL) and 2,6-di-t-butyl-4-methylphenol (2 crystals). The pressure tube was sealed, wrapped in aluminum foil and placed in an oil bath at 84°C for 21 h. The resulting solution was evaporated to dryness under reduced pressure and crystallized from isopropanol to yield 29.4 mg (83%) of 26, mp 162-165°C as off white granules: ^1H NMR ($CDCl_3$) δ 6.88 (overlapping singlets, 4, Ar-$\underline{H}$), 3.88 (overlapping singlets, 12, $OC\underline{H}_3$), 2.72 (dd, 1, NC-C$\underline{H}$), 2.14 (s, 3, NC-C-C-C$\underline{H}_3$), 2.07 (dd, 1, NC-C-C$\underline{H}$ cis to CN), 1.96 (s, 3, NC-C-C-C-C$\underline{H}_3$), 1.86 (dd, 1, NC-C$\underline{H}$ trans to CN); MS, m/e 379 (M^+), 380 (M^++1), 326 (M^+-acrylonitrile), 311 (M^+-acrylonitrile-CH_3), 283 (M^+- acrylonitrile - C_3H_7), 69 (base peak); HRMS m/e 379.1774 ($C_{23}H_{25}NO_4$ requires 379.1783).

Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (<u>10</u>):

Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (231 mg, .42 mmol) was added to a pressure tube with acrylonitrile (10 mL) and 2,6-di-t-butyl-4-methylphenol (2 crystals). The pressure tube was sealed and wrapped in aluminum foil and placed in an oil bath at 85°C for 44 h. The resulting orange solution was evaporated under reduced pressure to an orange oil. The oil was taken up in a minimal amount of hot carbon tetrachloride. Upon cooling, impurities precipitated out. The orange mixture was eluted through a Celite plug with carbon tetrachloride and the filtrate was evaporated to yield 213 mg (84.1%) of <u>10</u> which partially melts and resolidifies from 106-116°C as a pale orange solid: ^1H NMR

($CDCl_3$) δ 7.0-6.8 (overlapping singlets, 4, Ar-$\underline{H}$), 2.65 (dd, 1, NC-C$\underline{H}$), 2.05 (s, 3, Ar-C$\underline{H}_3$ overlapping dd, 1, NC-C-C$\underline{H}$ cis to CN), 1.80 (s, 3, Ar-C$\underline{H}_3$ overlapping dd, 1, NC-C-C$\underline{H}$ trans to CN), 1.15-1.0 overlapping singlets, 36, C(C$\underline{H}_3$)$_3$), MS, m/e 603 (M^+), 604 (M^++1), 550 (M^+- acrylonitrile, base peak), 436 (M^+- acrylonitrile - 2 t-Bu), 322 (M^+- acrylonitrile - 4 t-Bu), 57 (t-Bu^+); HRMS m/e 603.3200 ($C_{35}H_{49}NO_4Si_2$ requires 603.3201).

CHAPTER II

DIELS-ALDER REACTIVITY OF POLYSILOXYANTHRACENES AND RELATED COMPOUNDS

Introduction

In order to test for acceleration/deceleration of the Diels-Alder reaction by polysiloxy substituents, reaction rates for the Diels-Alder reactions of 8, 13, and 17 (9,10-dimethylanthracene, Figure 16) were determined.

Materials and Methods

Diels-Alder reactions of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (8):

Kinetic runs for the Diels-Alder reaction of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene were conducted at room temperature. 9,10-Dimethyl-2,3,6,7-tetramethoxyanthracene and 9,10-dimethylanthracene were used as comparison compounds. The dienophiles used were: acrylonitrile (18, Figure 17), maleimide (19), N-methylmaleimide (20), and N-phenylmaleimide (21).

Since the parent anthracenes absorb radiation in the near ultraviolet (uv) region and the cycloadducts do not, reaction

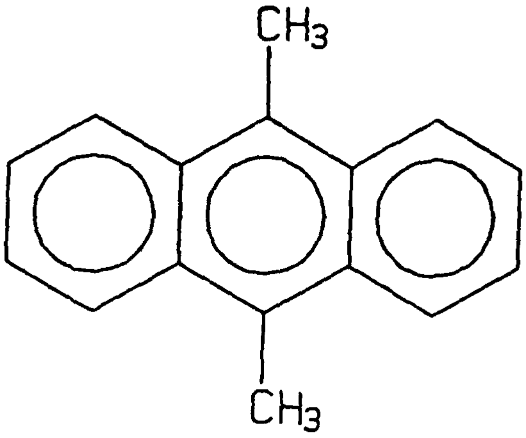

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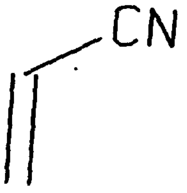
FIGURE 16 : 9,10-dimethylanthracene (17).



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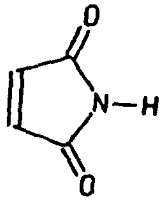

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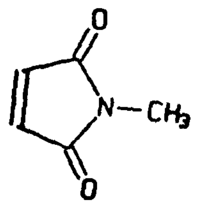

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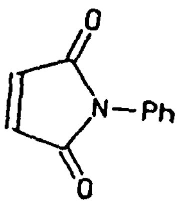

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FIGURE 17 : Dienophiles used in Diels-Alder kinetic studies.

kinetics were easily monitored spectrophotometrically. In accordance with Beer's law, uv absorption is directly proportional to the concentration of absorbing material. Thus, a logrithmic plot of absoption [ln (D_t)] versus time (t) is linear with slope equal to the negative of the rate constant k_{obs}. All reactions were run under psuedo-first order conditions, therefore the rate equation is: $r = k_{obs}$ [diene] = k_2 [diene] [dienophile], where k_2 is the true second order rate constant. Since the concentration of dienophile is much greater than the concentration of diene, the dienophile concentration remains virtually unchanged throughout the reaction. Thus, $k_2 = k_{obs}$ / [dienophile]. A typical Diels-Alder kinetic plot is shown in Plate III.

Results and Discussion

Diels-Alder reactivity of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene:

All three anthracene derivatives are quite reactive toward cycloaddition. Second order rate constants for the reaction of each anthracene with acrylonitrile are given in Table 1. Surprisingly, electron donating groups in the 2,3,6,7 positions lessen the reactivity of 9,10-dimethyanthracene toward cycloaddition. An even more unexpected result is that the highly electron donating siloxy substituent does not slow the reaction as much as the lesser donating methoxy function.

Kinetic data for the reaction of the anthracenes with the

PLATE III : Typical kinetic plot of a Diels-Alder reaction.

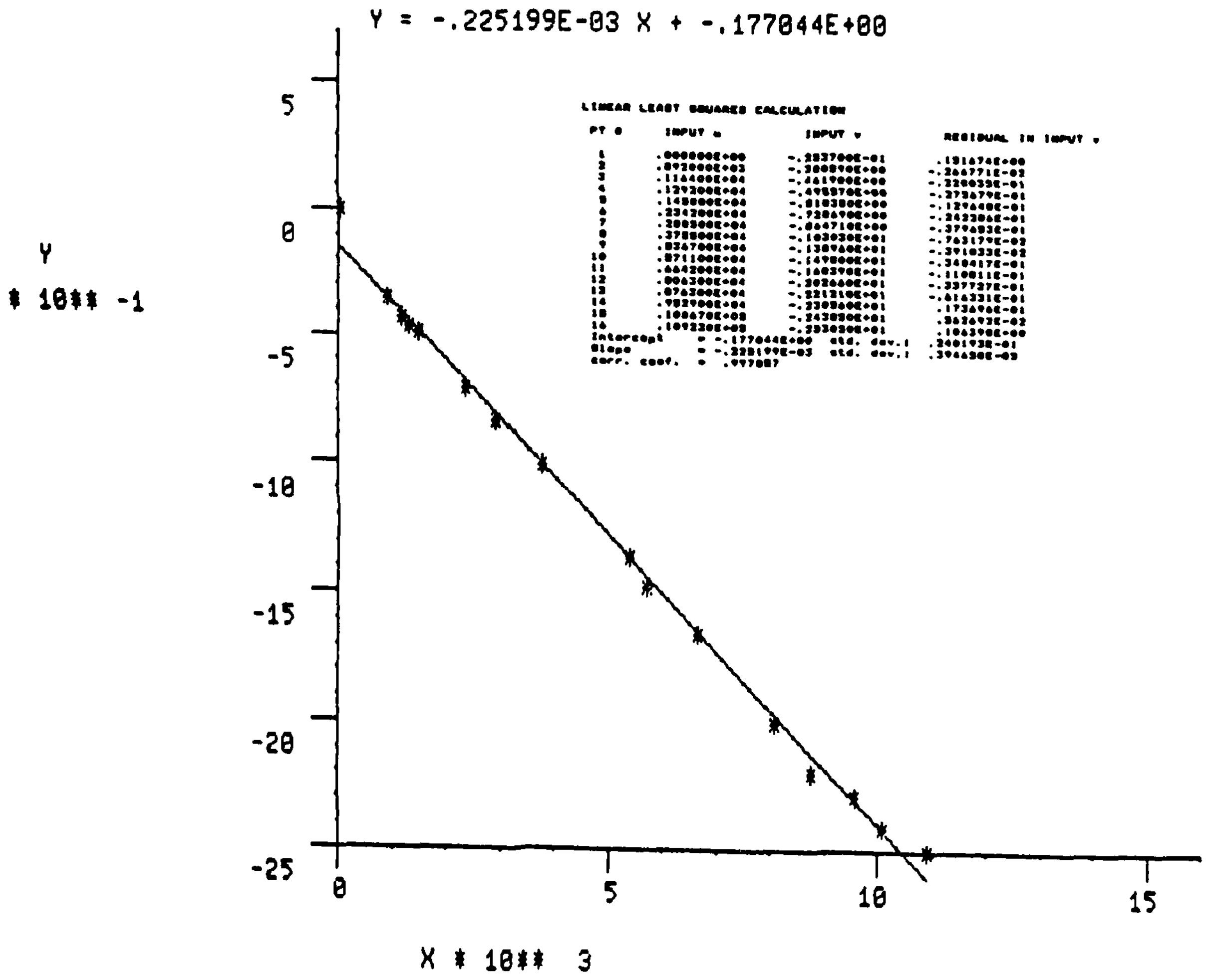

TABLE 1

Second order rate constants for the Diels-Alder reaction of compounds 8, 13, and 17 with acrylonitrile at 25°C.

compd	% of reaction used to calc. rate constants	# of data points	correlation coefficient	k_2, $M^{-1}s^{-1}$ 10^7
17	1-90	9	.999	16.67
8	1-90	16	.998	3.98
13	1-44	10	.999	1.06

TABLE 2

Second order rate constants for the Diels-Alder reaction of compounds 8, 13, and 17 with maleimide at 25°C.

compd	% of reaction used to calc. rate constants	# of data points	correlation coefficient	k_2, $M^{-1}s^{-1}$ 10^3
17	1-70	6	.999	24.83
8	1-93	13	.999	3.07
13	1-60	8	.996	1.69

TABLE 3

Second order rate constants for the Diels-Alder reaction of compounds 8, 13, and 17 with N-methylmaleimide at 25°C.

compd	% of reaction used to calc. rate constants	# of data points	correlation coefficient	k_2, $M^{-1}s^{-1}$ 10^3
17	1-95	7	.993	85.17
8	1-90	10	.999	9.27
13	1-90	5	.990	5.98
17*	1-75	6	.999	124
8*	1-50	5	.998	11.6

* Reaction conducted in heptane solvent (not chloroform).

TABLE 4

Second order rate constants for the Diels-Alder reaction of compounds 8, 13, and 17 with N-phenylmaleimide at 25°C.

compd	% of reaction used to calc. rate constants	# of data points	correlation coefficient	$k_2, M^{-1}s^{-1}$ 10^3
17	1-97	12	.996	63.33
8	1-90	13	.999	2.57
13	1-90	7	.999	3.74

TABLE 5

Relative Diels-Alder reactivities of compounds 8, 13, and 17 vs various dienophiles.

Dienophile	Compound		
	8	13	17
acrylonitrile	1.00	0.27	4.19
maleimide	1.00	0.55	8.09
N-methylmaleimide	1.00	0.65	9.18
N-phenylmaleimide	1.00	1.46	24.64

maleimide series are given in Tables 2-4. Again, it was confirmed that 9,10-dimethylanthracenes with electron releasing groups in the 2,3,6,7 positions react slower than 9,10-dimethylanthracene itself, and the siloxy substituent slows the reaction less than the methoxy function. However, it was not surprising to find a decrease in the relative reactivy of the siloxy compound as the bulkiness of the dienophile increased. The relative reactivity of the tetramethoxy compound vs 9,10-dimethylanthracene remained virtually constant throughout the series of dienophiles. Relative reactivities were determined for each series of reactions by dividing $k_2(x)$ by $k_2(8)$, where $k_2(x)$ is the second order rate constant of reaction for compound x (8,13 or 17) and $k_2(8)$ is the rate constant for compound 8. These data are displayed in Table 5, and clearly indicate a steric factor in the Diels-Alder reaction for the bis-(di-t-butylsiladioxy) substituted compound. That is, the t-butyl groups interfere with the approch of the dienophile, thereby slowing the reaction. As the dienophile subtituents grow in bulk, the relative reactivity of compound 8 decreases. However, the steric factor (of the methoxy groups) cannot be responsible for the lesser reactivity of 13 compared to 17 since the relative reactivity of 13 compared to 16 remains constant.

Two rationalizations were developed to account for the reactivity order, the first of which is more plausible in the author's estimation:

1. Steric interactions between the methoxy methyls and each other as well as the 1,4,5,8 protons do not allow the methoxy oxygen to attain a conformation (at room temperature)

in which it can conjugate with the anthracene ring. Thus, the methoxy groups are net electron withdrawers due to the inductive effect of oxygen. The proposed steric interactions are shown in Figure 18.

In the siladioxy compound, the ring strain associated with a five membered ring allows the siloxy oxygen lone pairs to conjugate, but only partially. Thus, the siloxy functions provide a net electron withdrawing effect, but to a lesser extent than methoxy.

2. There are two possible mechanisms of reaction, concerted and dipolar. 9,10-Dimethylanthracene reacts via one mechanism, the related siloxy compound reacts via the other, and the methoxy compound may be reacting via either. A dipolar mechanism suggests a polar transition state which can be stablized by polar solvents. This theory implies there should be a significant change in the reactivity of 8 vs 17 when shifting from a polar solvent to nonpolar. As Table 3 indicates, there is no significant change,thus, the practicality of this theory is questionable.

Diels-Alder reactivity of bis-(di-t-butylsiladioxy)-9,10-diphenylanthracene (9):

Bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene was tested for its Diels-Alder reactivity. As expected, it showed no signs of reacting with N-methylmaleimide after eight days at room temperature.

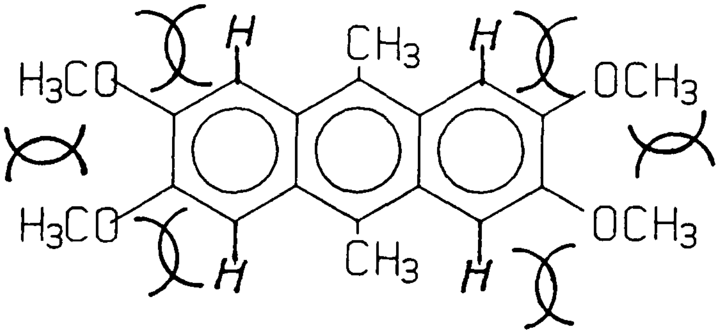

FIGURE 18 : Potential steric interactions in 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene.

Experimental

General:

All dilutions were made using volumetric gassware. All reactions were run at room temperature (24.5°C). All plots were made using LSTSQ least squares program.

Diels-Alder reactions of 8, 13, and 17 with acrylonitrile:

Each anthracene derivative was dissolved in deoxygenated chloroform. The concentration of each solution was adjusted such that a uv absorbance of approximately 1.7 was obtained for the most prominent peak. Each anthracene solution (10.0 mL) was diluted with acrylonitrile (10.0 mL) in a foil wrapped, glass stoppered flask. Each solution was then well mixed, and an initial uv absorption measurement was taken. UV measurements were taken periodically (vs 1:1 chloroform/arylonitrile reference) until the absorbance dropped to 0. The observed rate constant k_{obs} was determined by taking the negative of the slope of the plot

ln (D_t) vs t where D_t is the absorption at time t. The second order rate constant, k_2, was calculated from the equation $k_2 = k_{obs}/$ [acrylonitrile], where [acrylonitrile] is the initial concentration of acrylonitrile.

Diels-Alder reaction of 8, 13, and 17 with maleimide:

A stock solution (1.008×10^{-4} M in chloroform) of each anthracene derivative was prepared, as well as a stock solution of maleimide (5.02×10^{-3} M in chloroform). To each anthracene solution (10.0 mL) was added maleimide solution (10.0 mL) in a foil wrapped, glass stoppered flask. Reaction solutions were well mixed and initial uv spectra immediately taken. UV spectra were periodically taken (vs 2.51×10^{-3} M maleimide in chloroform reference) until the most prominent peak decreased to 0. The observed and second order rate constants were determined in the same manner as the acrylonitrile experiment above.

Diels-Alder reaction of 8, 13, and 17 with N-methylmaleimide:

A stock solution (1.008×10^{-4} M in chloroform) of each anthracene derivative was prepared, as well as a stock solution of N-methylmaleimide (5.02×10^{-3} M in chloroform). To each anthracene solution (10.0 mL) was added N-methylmaleimide solution (10.0 mL) in a foil wrapped, glass stoppered flask. Reaction solutions were well mixed and initial uv spectra immediately taken. UV spectra were periodically taken (vs 2.51×10^{-3} M N-methylmaleimide in chloroform reference) until the most prominent peak decreased to 0. The observed and second order rate constants were determined in the same manner as the acrylonitrile experiment above.

Diels-Alder reaction of 8, 13, and 17 with N-phenylmaleimide:

A stock solution (1.008×10^{-4} M in chloroform) of each anthracene derivative was prepared, as well as a stock solution of N-phenylmaleimide (5.02×10^{-3} M in chloroform). To each anthracene solution (10.0 mL) was added N-phenylmaleimide solution (10.0 mL) in a foil wrapped, glass stoppered flask. Reaction solutions were well mixed and initial uv spectra immediately taken. UV spectra were periodically taken (vs 2.51×10^{-3} M N-phenylmaleimide in chloroform reference) until the most prominent peak decreased to 0. The observed and second order rate constants were determined in the same manner as the acrylonitrile experiment above.

Diels-Alder reaction of 8 with N-methylmaleimide (heptane solvent):

A stock solution (1.26×10^{-4} M in n-heptane) of 8 was prepared, as well as a stock solution of N-methylmaleimide (7.88×10^{-4} M in n-heptane). To the anthracene solution (3.0 mL) was added N-methylmaleimide solution (20.0 mL) in a foil wrapped, glass stoppered flask. The reaction solution was well mixed and an initial uv spectrum immediately taken. UV spectra were periodically taken (vs 20:3 N-methylmaleimide: n-heptane reference) until the most prominent peak decreased to 0. The observed and second order rate constants were determined in the same manner as the acrylonitrile experiment above.

Diels-Alder reaction of 17 with N-methylmaleimide (heptane solvent):

A stock solution (1.72×10^{-4} M in n-heptane) of 17 was prepared, as well as a stock solution of N-methylmaleimide (7.88×10^{-4} M in n-heptane). To the anthracene solution (3.0 mL) was added N-methylmaleimide solution (20.0 mL) in a foil wrapped, glass stoppered flask. The reaction solution was well mixed and an initial uv spectrum immediately taken. UV spectra were periodically taken (vs 20:3 N-methylmaleimide: n-heptane reference) until the most prominent peak decreased to 0. The observed and second order rate constants were determined in the same manner as the acrylonitrile experiment above.

CHAPTER III

RETRO DIELS-ALDER REACTIVITY OF POLYSILOXYANTHRACENE CYCLOADDUCTS AND RELATED COMPOUNDS

Introduction

Reaction rates for the decomposition of the Diels-Alder adducts of 8, 13, and 17 with acrylonitrile were determined. The effect of electron donating groups in the 2,3,6,7 positions is acceleration of the retro Diels-Alder reaction.

Materials and Methods

Retro Diels-Alder reactivity of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (10):

The cycloadducts of 8 (10), 13 (26, Figure 19), and 16 (27, Figure 20) with acrylonitrile were decomposed in phenyl ether at 200°C, and the formation of the parent anthracene was monitored spectrophotometrically. The unimolecular rate constant k_1 was determined from the plot of ln $(D_\infty - D_t)$, where D_∞ is the absorption at $t=\infty$ and D_t is the absorption at time t, versus time. k_1 is the negative of the slope of the resulting line. A typical plot is shown in Plate IV.

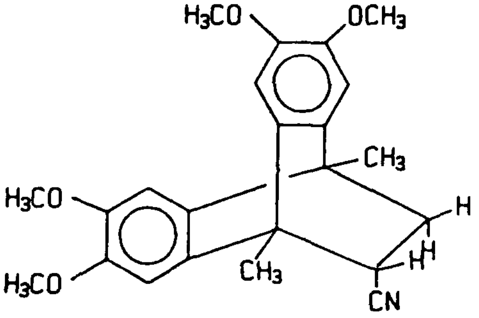

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FIGURE 19 : 9,10-dimethyl-2,3,6,7-tetramethoxy-11-cyanoethanoanthracene (26).

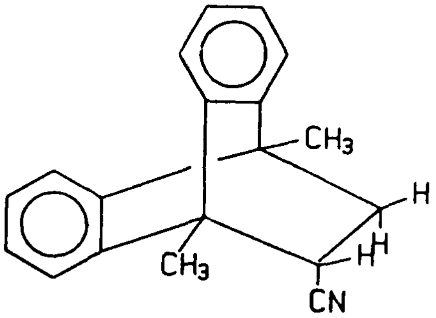

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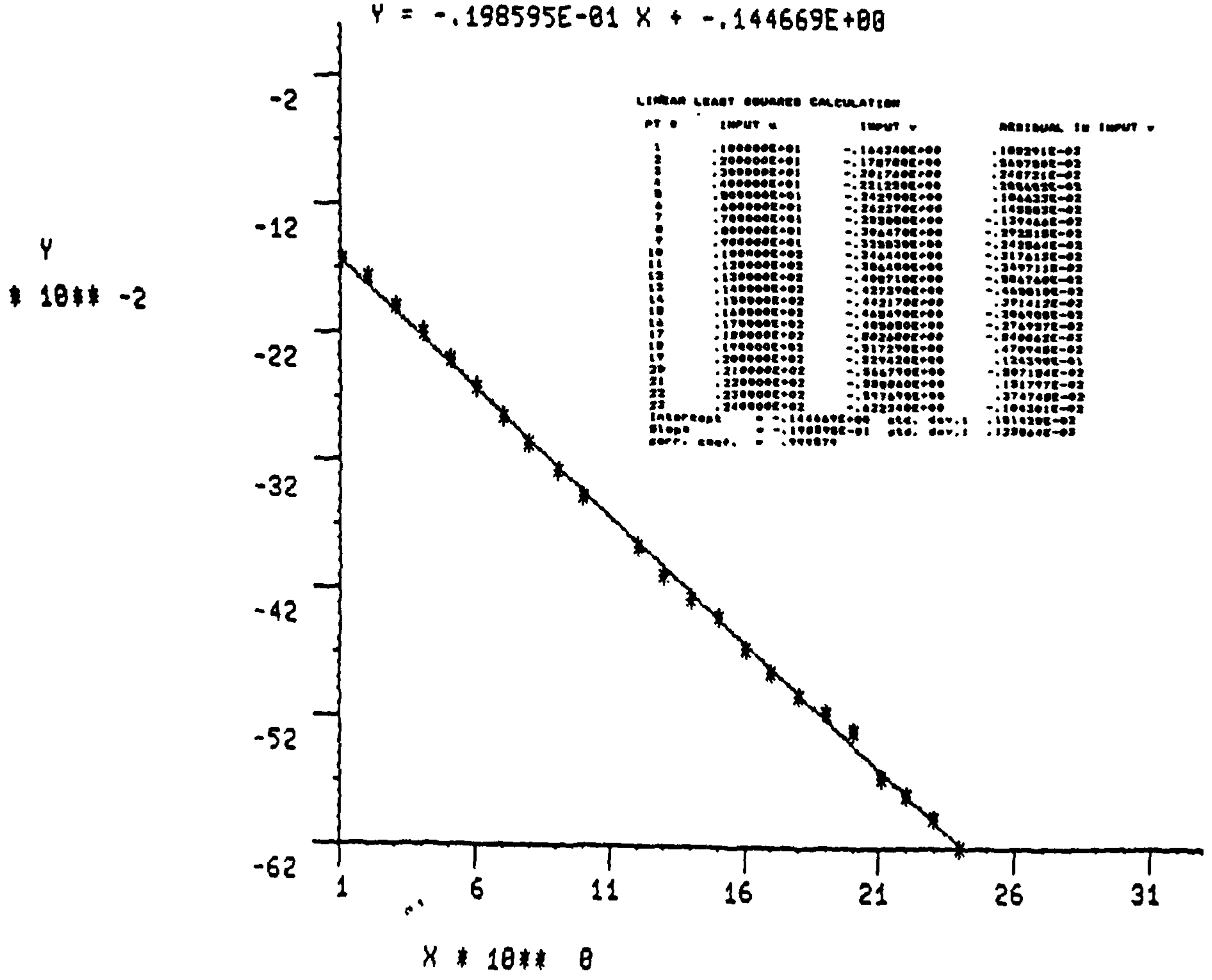
FIGURE 20 : 9,10-dimethyl-11-cyanoethanoanthracene (27).

PLATE IV : Typical kinetic plot of a retro Diels-Alder reaction.



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   3     .300000E+01     -.201760E+00      .240721E-02
   4     .400000E+01     -.221220E+00      .286645E-02
   5     .500000E+01     -.242900E+00      .104435E-02
   6     .600000E+01     -.262370E+00      .145803E-02
   7     .700000E+01     -.285080E+00     -.139446E-02
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   9     .900000E+01     -.325830E+00     -.242864E-02
  10     .100000E+02     -.346440E+00     -.317615E-02
  11     .120000E+02     -.386480E+00     -.349711E-02
  12     .130000E+02     -.408710E+00     -.586760E-02
  13     .140000E+02     -.427390E+00     -.468810E-02
  14     .150000E+02     -.442170E+00      .371412E-03
  15     .160000E+02     -.465490E+00     -.306905E-02
  16     .170000E+02     -.485080E+00     -.276937E-02
  17     .180000E+02     -.502680E+00     -.540062E-03
  18     .190000E+02     -.517290E+00      .470945E-02
  19     .200000E+02     -.529420E+00      .124390E-01
  20     .210000E+02     -.566790E+00     -.507184E-02
  21     .220000E+02     -.580840E+00      .151797E-02
  22     .230000E+02     -.597690E+00      .374748E-02
  23     .240000E+02     -.622240E+00     -.104301E-02
 Intercept      = -.144669E+00   std. dev.:   .181620E-02
 Slope          = -.198595E-01   std. dev.:   .128066E-03
 corr. coef.    =   .999879
```

Due to concurrent decomposition of the newly formed anthracene under the reaction conditions, D_∞ values were calculated. A control experiment, in which the parent anthracene was subjected to the reaction conditions, indicated no significant error would be introduced if the reaction were followed for the first half life. In practice, only the first 20-40% of each reaction was used to calculate k_1.[27] Values for the rate constants and reaction half lives ($t_{1/2}$) are depicted in Table 6. Reaction half lives were determined by $t_{1/2} = \ln 2 / k_1$. A significant rate acceleration due to substituents in the 2,3,6,7 positions was noted.

Results and Discussion

Retro Diels-Alder reactivity of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (10):

The kinetic data in Table 6 show a very significant rate acceleration of the rDA reaction due to alkoxy and siloxy substituents in the 2,3,6,7 positions. Compound 10 undergoes the cycloreversion 19 times as fast as the adduct of 9,10-dimethylanthracene; the adduct of 13 cycloreverts at 14 times the rate. The order of reactivity is exactly as expected based upon electron donating capabilities.

TABLE 6

First order rate constants of Retro-Diels-Alder Reactions of Cycloadducts 10, 26, and 27 in diphenyl ether at 200°C.

comp	% of reaction used to calculate rate constants	# of data points	correlation coefficient	k_1, sec^{-1} 10^4
27	1-23	12	.994	0.24
10	1-37	16	.999	4.52
26	1-39	23	.999	3.32

Experimental

General:

All retro Diels-Alder reactions were run at 200°C. Reaction temperatures were maintained at 200 ± .5°C by Therm-O-Watch LG-1000 SS temperature controller. All reactions were run in 100 mL 3 neck round bottom flasks fitted with capped distilling column, thermometer and glass stopper. Transfers and dilutions were accomplished using volumetric glassware.

Retro Diels-Alder reaction of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (10):

Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene (13.60 mg, 2.25 x 10^{-2} mmol) was dissolved in 4.0 mL diphenyl ether. An aliquot (1.0 mL) of this solution was added to diphenyl ether (74.0 mL) which had previously been equilibrated to 200 °C. The uv absorption at 378 nm, due to the formation of 8, was followed spectrophotometrically for 16 min (36% reaction). Based upon the absorption of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene in phenyl ether, the absorption at $t = \infty$ (D_∞) was calculated to be 0.9711. For each measured absorption (D_t), the value ln (D_∞-D_t) was determined and plotted vs time t (min). k_1, the unimolecular decomposition constant was determined as the negative of the slope of the resulting straight line. The reaction half life, $t_{1/2}$ was determined from $t_{1/2} = .693/ k_1$.

Retro Diels-Alder reaction of 9,10-Dimethyl-2,3,6,7-tetramethoxy-11-cyanoethanoanthracene (26):

9,10-Dimethyl-2,3,6,7-tetramethoxy-11-cyanoethanoanthracene (10.00 mg, 2.63×10^{-2} mmol) was dissolved in 4.0 mL diphenyl ether. An aliquot (1.0 mL) of this solution was added to diphenyl ether (74.0 mL) which had previously been equilibrated to 200 °C. The uv absorption at 378 nm, due to the formation of 13, was followed spectrophotometrically for 24 min (39% reaction). Based upon the absorption of 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene in phenyl ether, the absorption at $t = \infty$ (D_∞) was calculated to be 0.8836. For each measured absorption (D_t), the value $\ln (D_\infty - D_t)$ was determined and plotted vs time t (min). k_1, the unimolecular decomposition constant was determined as the negative of the slope of the resulting straight line. The reaction half life, $t_{1/2}$ was determined from $t_{1/2} = .693/ k_1$.

Retro Diels-Alder reaction of 9,10-Dimethyl-11-cyanoethanoanthracene (27):

9,10-Dimethyl-11-cyanoethanoanthracene (8.02 mg, 3.09×10^{-2} mmol) was dissolved in 5.0 mL diphenyl ether. An aliquot (1.0 mL) of this solution was added to diphenyl ether (74.0 mL) which had previously been equilibrated to 200 °C. The uv absorption at 378 nm, due to the formation of 17, was followed spectrophotometrically for 175 min (23% reaction). Based upon the absorption of 9,10-dimethylanthracene in phenyl ether, the absorption at $t = \infty$ (D_∞) was calculated to be 0.8474. For each measured absorption (D_t), the value $\ln (D_\infty - D_t)$ was determined and plotted vs time t (min). k_1, the unimolecular decomposition constant was determined as the negative of the slope of the resulting straight line. The reaction half life, $t_{1/2}$ was determined from $t_{1/2} = .693/ k_1$.

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Introduction

The effect on the Diels-Alder reactivity of electron donating groups in the 2,3,6,7 positions of 9,10-dimethylanthracene has been investigated. The results were surprising initially, but can be rationalized. Such a rationalization is provided below. A series of experiments is required to conclude the rationalization is valid. The recommendations section provides several alternatives which can provide evidence for/against this rationalization. If the rationalization appears to be valid, the recommended experiments will also provide valuable information for the DA catalysis cycle.

The effect on the retro Diels-Alder reactivity of electron donating groups in the 2,3,6,7 positions of 9,10-dimethyl-11-cyanoethanoanthracene was investigated. The resulting acceleration due to methoxy and siloxy substitution was expected. The reactivity order is not necessarily inconsistent with results of the forward Diels-Alder reaction. Again, several experiments could be conducted to determine the nature of siloxy and alkoxy substituents in the 2,3,6,7 positions, and there effect on DA/rDA reactivity.

The conclusions and recommendations are numbered sequentially with respect to the particular chapter of this thesis from which they were drawn.

Conclusions

I-1. Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene was synthesized.

I-2. Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethyl-11-cyanoethanoanthracene was synthesized.

I-3. Bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene was synthesized.

II-1. The relative reactivity order for the Diels-Alder reaction of 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene vs 9,10-dimethylanthracene is not consistent with the methoxy groups acting as electron donating substituents.

II-2. The extreme decrease in reactivity due to methoxy substitution can be rationalized as being due to intramolecular steric interactions which preclude the methoxy lone pairs from conjugating with the anthracene ring. Thus, oxygen's inductive effect makes the methoxy group electron withdrawing.

II-3. The relative reactivity order for the Diels-Alder reaction of bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene vs 9,10-dimethylanthracene is not consistent with the siladioxy substituents acting as electron donating functions.

II-4. The moderate decrease in the reactivity of compound 8 vs 9,10-dimethylanthracene can be rationalized as being due to siloxy oxygen lone pairs only partially conjugating with the anthracene ring. The ring strain associated with a planar five membered ring may not allow the oxygens to fully donate electrons by resonance. Thus, inductive and resonance effects compete, making the siloxy compound intermediate in its reactivity.

II-5. It does not appear the difference in reactivities is due to a difference in mechanism of reaction.

II-6. Bis-(di-t-butylsiladioxy)[b,i]-9,10-diphenylanthracene may not be as useful as expected since the same arguments made above may apply.

III-1. The relative reactivities of compounds 10 26, and 27 in the retro Diels-Alder reaction are consistent with methoxy and siladioxy subtituents acting as electron donating functions.

III-2. Conclusion III-1 is not necessarily incompatible with conclusion II-1.

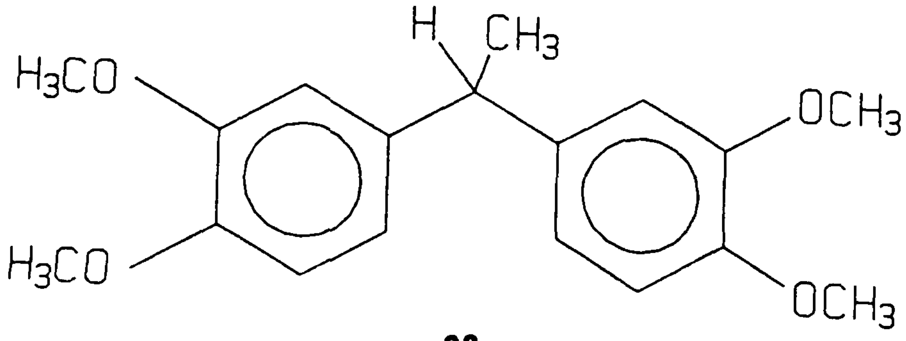
III-3. The apparent dichotomy between conclusions III-1 and II-1 can be rationalized as follows: At elevated temperatures (i.e. 200°C) a significantly higher proportion of higher energy conformations may exist. Thus, both the methoxy and siladioxy groups may conjugate and thereby give rise to significant rate accelerations of the retro Diels-Alder reaction.

Recommendations

I-1. For silylations similar to the synthesis of 8, use di-t-butyldichlorosilane preferentially over the corresponding ditriflate.

I-2. Investigate the use of 3,3',4,4'-tetramethoxydiphenylethane (28, Figure 21) as a starting material over veratrole if large scale syntheses of compound 13 or its derivatives are desired.

II-1. Perform temperature dependency studies of the relative reactivity of 9,10-dimethyl-2,3,6,7-tetramethoxyanthracene. If the rationalizations presented above



28

FIGURE 21 : 3,3',4,4'-tetramethoxydiphenylethane (28).

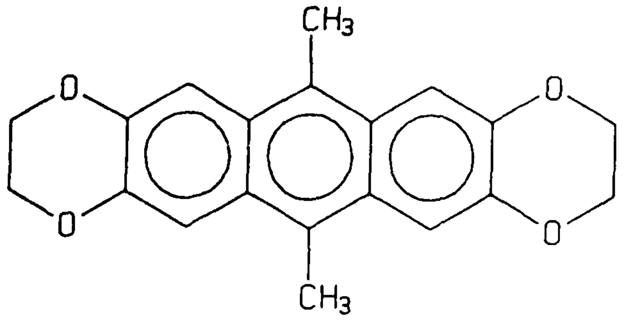
hold, the relative rectivity should increase with an increase in temperature.

II-2. Synthesize compound 29 (Figure 22) and investigate its Diels-Alder reactivity with respect to 9,10-dimethylanthracene. This compound should not have the steric or ring strain problems discussed earlier. A relative reactivity greater than that of compound 17 would support the rationalization of steric interactions. A relative reactivity greater than that of compound 10 would support the ring strain rationalization.

II-3. If recommendations II-1 and II-2 are carried out and show promise in approaching or exceeding the Diels-Alder reactivity of 9,10-dimethylanthracene, synthesize and investigate the reactivity of compound 30, Figure 23.

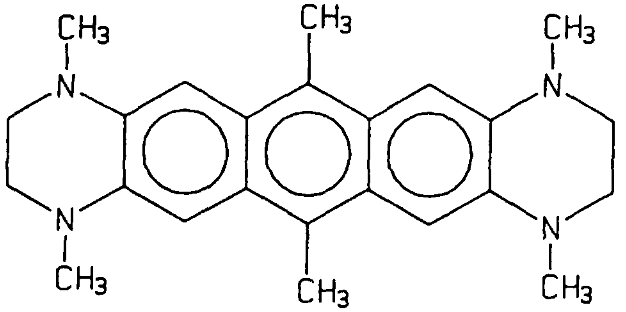
II-4. If recommendations II-1 and II-2 show no promise in approaching the reactivity of 9,10-dimethylanthracene, conduct DA kinetic studies (compound 8 vs 17) in a highly polar solvent such as dimethylformamide. Perhaps a change in mechanism will be indicated.

II-5. If none of the above recommendations prove fruitful, synthesize and investigate the D.A. reactivity of



29

FIGURE 22 : Bis-(1,4-dioxacyclohexa)[b,i]-9,10-dimethylanthracene (29).



30

FIGURE 23 : Bis-(N,N-dimethyl-1,4-diazacyclohexa)[b,i]-9,10-dimethylanthracene (30).

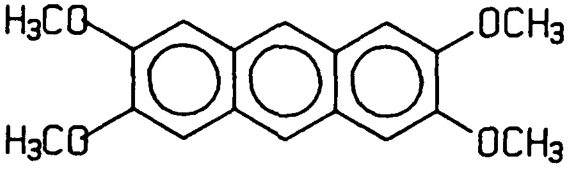
compounds 31 (Figure 24) and 32 (figure 25) vs anthracene. Any "unusual" effects due to 9,10-dimethyl substitution would be eliminated.

II-6. If recommendations II-1 through II-3 show promise, undertake a similar approach for the 9,10-diphenyl derivative when investigating its ability to undergo reversible $^1O_2$ addition.

II-7. Compare the ^{13}C NMR chemical shifts of the 9,10 carbons in compound 8 vs 17. Since the chemical shift is directly related to electron density,[28] the electron donating vs withdrawing characteristics of the siladioxy groups should be seen.

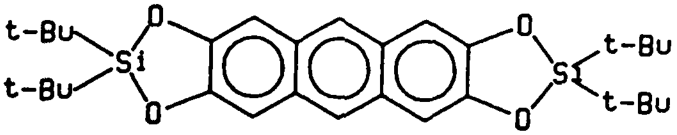
III-1. Convert 9,10-dimethyl-2,3,6,7-tetramethoxy-11-cyano-ethanoanthracene to compound 33 (Figure 26).

III-2. Investigate the rDA reactivity of 33. Reactivity on the order of, or significantly greater than that of the siladioxy compound will support previous rationalizations.



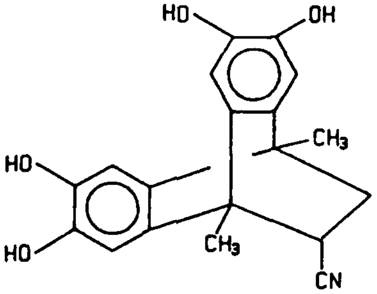
31

FIGURE 24 : 2,3,6,7-tetramethoxyanthracene (31).



32

FIGURE 25 : Bis-(di-t-butylsiladioxy)[b,i]-anthracene (32).



33

FIGURE 26 : 2,3,6,7-tetrahydroxy-9,10-dimethyl-11-cyanoethanoanthracene (33).

III-3. If recommendations II-3 and III-2 show promise:

a. continue with recommendation II-4.

b. Synthesize DA adducts of compounds 29 and 30.

c. Investigate the rDA reactivities of the cycloadducts of 29 and 30.

APPENDIX A

NOMENCLATURE

Substituted anthracenes are named based upon the numbering system shown in Figure 27. Thus, structure 34 in Figure 28 would be named 1,4-dichloro-5,8-dimethylanthracene. Anthracenes with fused rings are named based upon the lettering system shown in Figure 29. Benz[a]-anthracene would thus be the name for compound 35 in Figure 30.

Organosilicon compounds have no accepted IUPAC nomenclature system[29]. A simple informal nomenclature system is in common use and is quite practical[29]. Ambiguities are minimized by naming substituted organic fragments, then alkoxy fragments, then halogen fragments followed by "silane" for tetravalent silicon atoms[29]. "silyl" and "siloxy", for R_3Si- and R_3SiO- respectively, are used instead of "silane" when the silicon function is a substituent of a more significant moiety. Thus, compound 8 (Figure 31) is named: bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene

bis-	2 groups
(di-t-butylsiladioxy)	"oxy ending"
[b,i]	fused across b and i sides
9,10-dimethylanthracene	more significant moiety

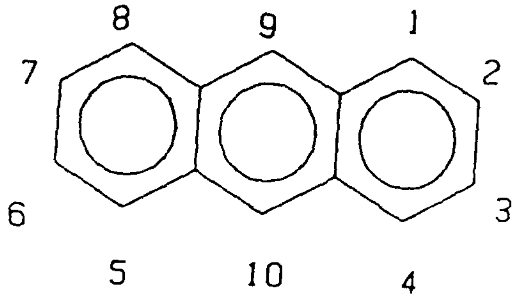
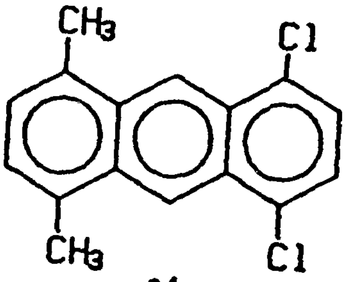


FIGURE 27 : Numerically labelled anthracene



34

FIGURE 28 : 1,4-dichloro-5,8-dimethylanthracene (34).

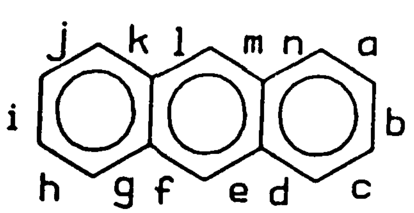
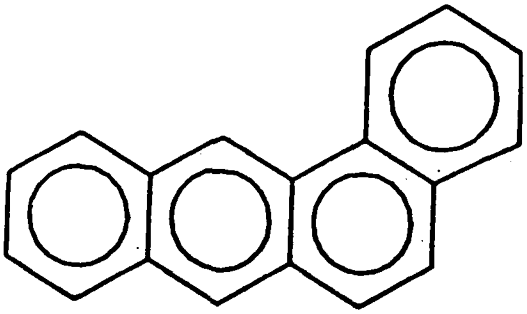
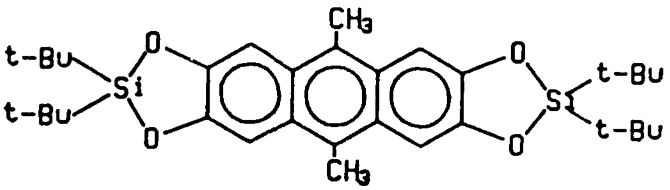


FIGURE 29 : Alphabetically labelled anthracene.



35

FIGURE 30 : Benz[a]-anthracene (35).



8

FIGURE 31 : Bis-(di-t-butylsiladioxy)[b,i]-9,10-dimethylanthracene (8).

APPENDIX B

DATA RELATIVE TO CHAPTER I

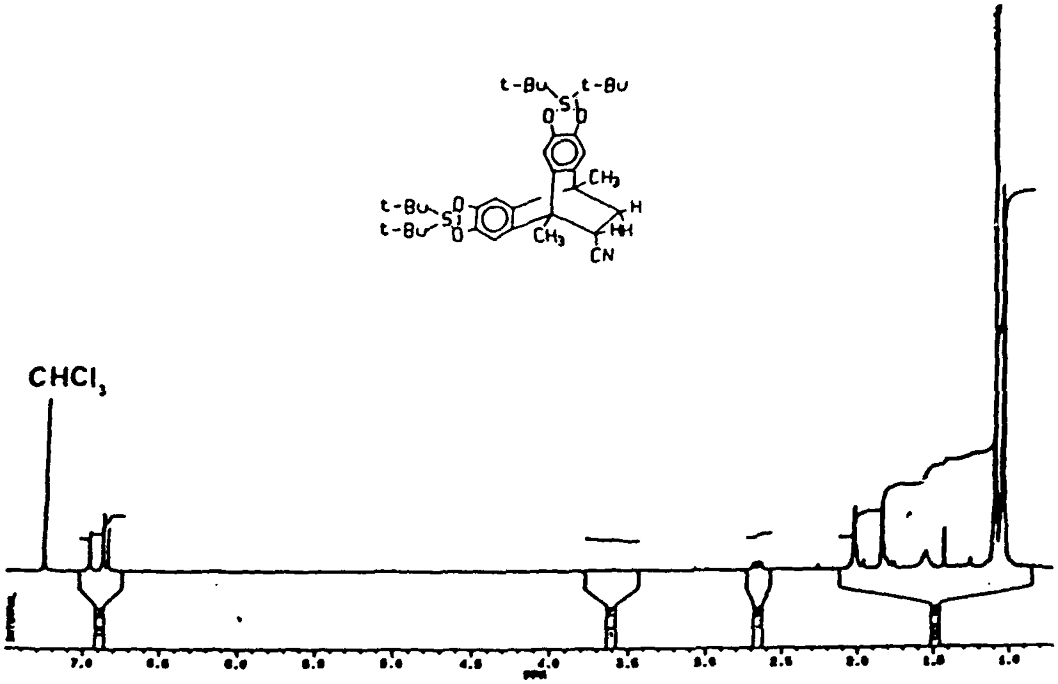


PLATE V : ^1H NMR spectrum of compound 10.

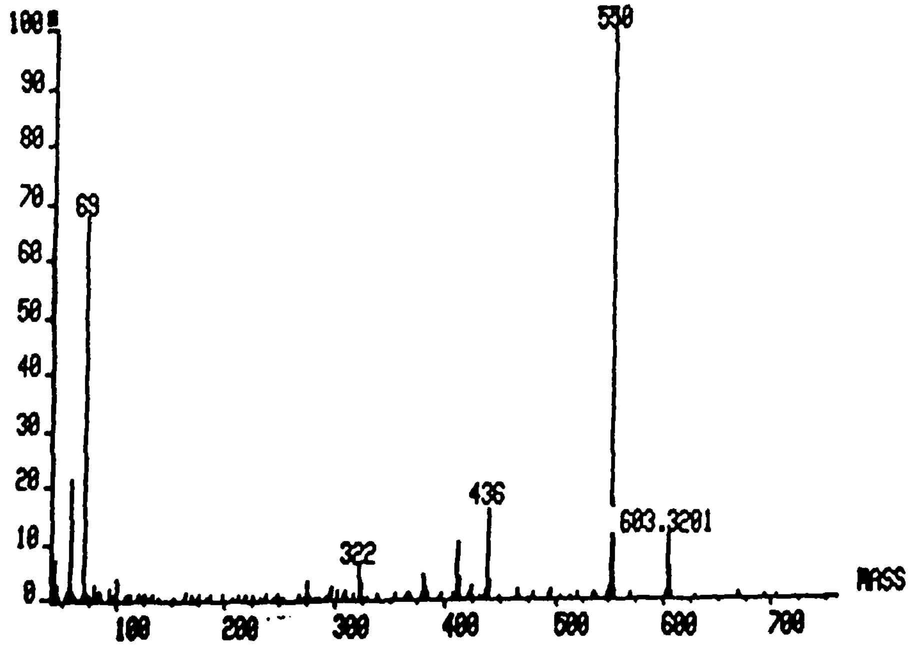


PLATE VI : Mass Spectrum of compound 10.

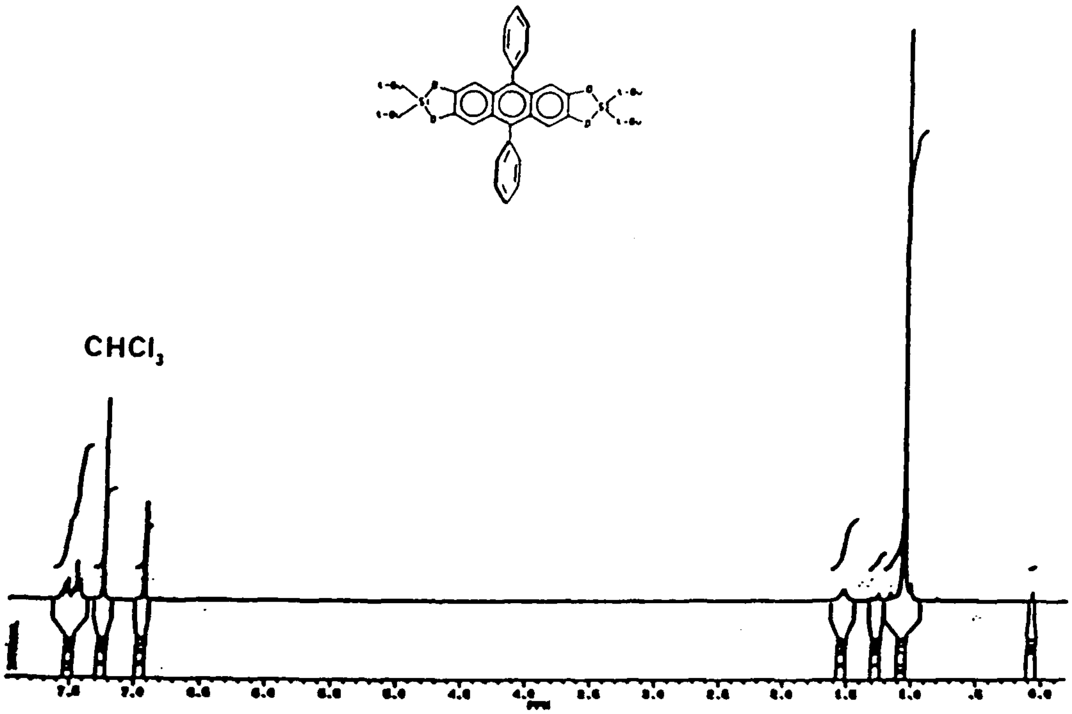


PLATE VII : ^{1}H NMR spectrum of compound 9.

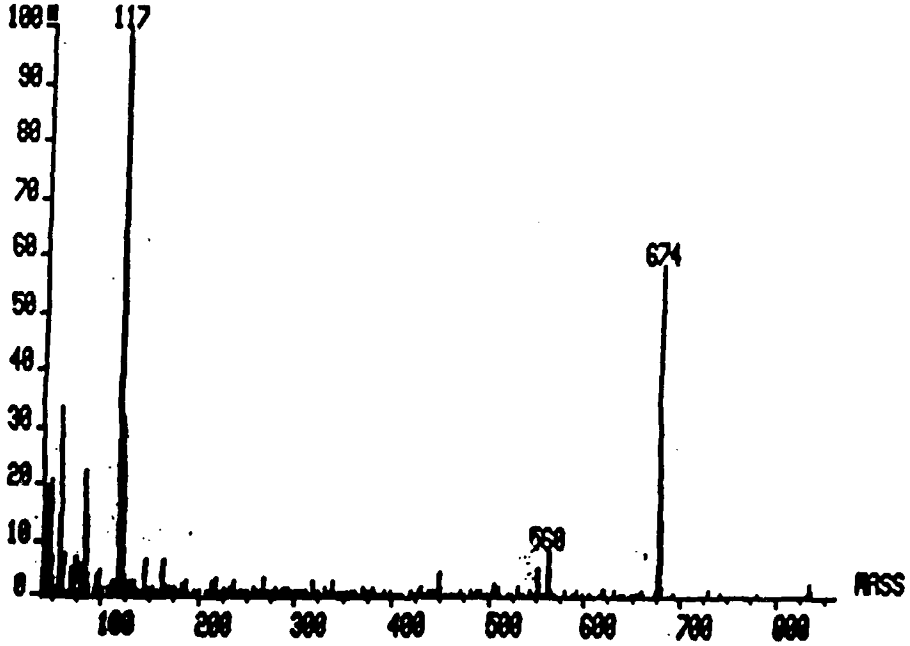


PLATE VIII : Mass Spectrum of compound 9.

PLATE IX : CPK space filling model of compound 8.

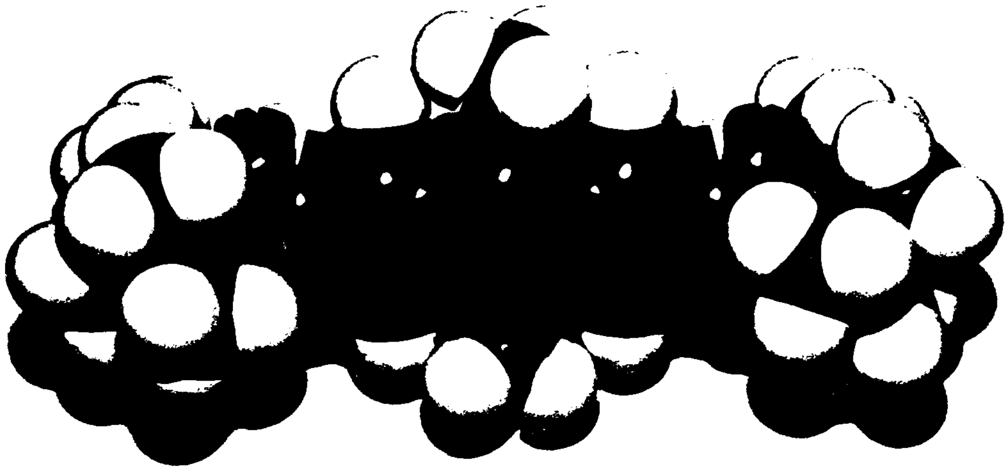
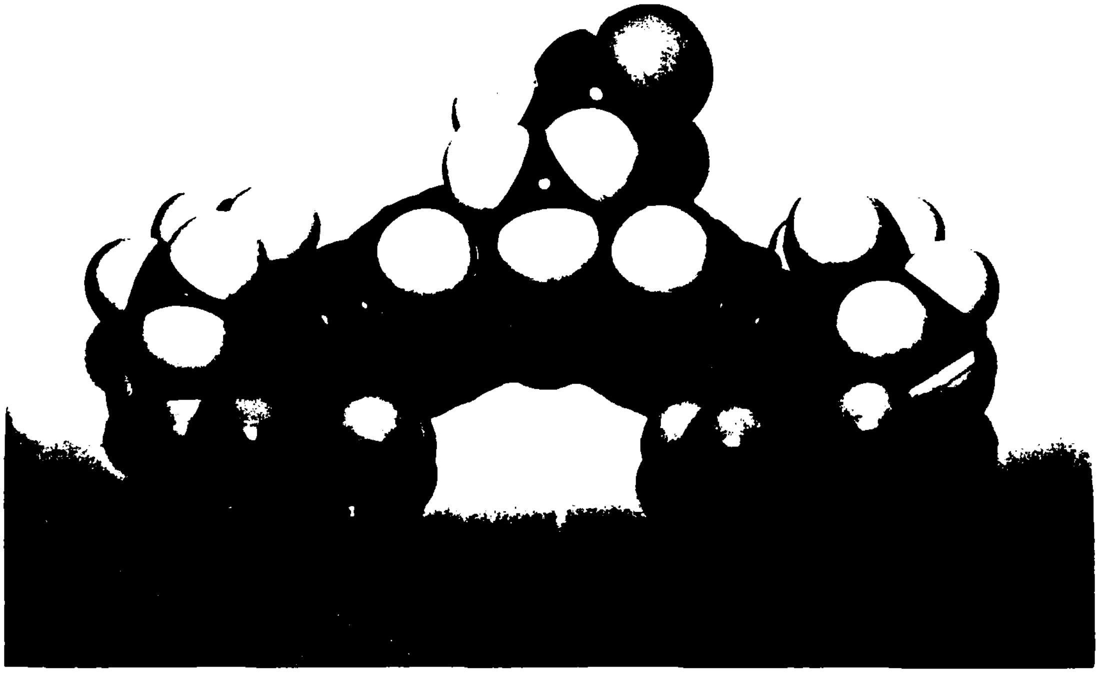


PLATE X : CPK space filling model of compound 10.



APPENDIX C

DATA RELATIVE TO CHAPTER II

TABLE 7 : LSTSQ data for the Diels-Alder reaction of compound 8 with acrylonitrile.

```
LINEAR LEAST SQUARES CALCULATION

PT #        INPUT u              INPUT v              RESIDUAL IN INPUT v

  1       .000000E+00         -.253700E-01          .151474E+00
  2       .892000E+03         -.380590E+00         -.266771E-02
  3       .116400E+04         -.461980E+00         -.228035E-01
  4       .129200E+04         -.495570E+00         -.275679E-01
  5       .145800E+04         -.518350E+00         -.129648E-01
  6       .234200E+04         -.728690E+00         -.242286E-01
  7       .288500E+04         -.864710E+00         -.379453E-01
  8       .375500E+04         -.103030E+01         -.763179E-02
  9       .536700E+04         -.138960E+01         -.391033E-02
 10       .571100E+04         -.149800E+01         -.348417E-01
 11       .664200E+04         -.168390E+01         -.110811E-01
 12       .806300E+04         -.202660E+01         -.337727E-01
 13       .876300E+04         -.221210E+01         -.616331E-01
 14       .952900E+04         -.230560E+01          .173696E-01
 15       .100670E+05         -.243850E+01          .562692E-02
 16       .109230E+05         -.253050E+01          .106398E+00
 Intercept      = -.177044E+00  std. dev.:  .240193E-01
 Slope          = -.225199E-03  std. dev.:  .394658E-05
 corr. coef.    =  .997857
```

TABLE 8 : LSTSQ data for the Diels-Alder reaction of compound 13 with acrylonitrile.

```
LINEAR LEAST SQUARES CALCULATION

PT #        INPUT u              INPUT v              RESIDUAL IN INPUT v

  1       .000000E+00          .134370E+00         -.167774E-02
  2       .870000E+03         -.692980E+00         -.725895E-02
  3       .114100E+04         -.963980E+00         -.222827E-01
  4       .126800E+04         -.108143E+01         -.197733E-01
  5       .143400E+04         -.122159E+01         -.313608E-02
  6       .231800E+04         -.204365E+01          .979658E-02
  7       .286100E+04         -.252829E+01          .380537E-01
  8       .373100E+04         -.332371E+01          .644024E-01
  9       .534300E+04         -.496887E+01         -.581239E-01
 Intercept      =  .136048E+00  std. dev.:  .212372E-01
 Slope          = -.944562E-03  std. dev.:  .810780E-05
 corr. coef.    =  .999742
```

TABLE 9 : LSTSQ data for the Diels-Alder reaction of compound 17 with acrylonitrile.

```
LINEAR LEAST SQUARES CALCULATION

PT #        INPUT u              INPUT v              RESIDUAL IN INPUT v

  1       .000000E+00         -.771580E+00         -.979876E-02
  2       .976000E+03         -.815480E+00          .469131E-02
  3       .116500E+04         -.831240E+00          .218400E-03
  4       .149600E+04         -.852970E+00         -.168923E-02
  5       .243000E+04         -.906700E+00          .458151E-03
  6       .267200E+04         -.915440E+00          .619602E-02
  7       .292200E+04         -.940240E+00         -.364751E-02
  8       .385200E+04         -.990830E+00          .138097E-02
  9       .676200E+04         -.115421E+01          .121139E-01
 10       .973000E+04         -.135381E+01         -.992285E-02
 Intercept      = -.761781E+00  std. dev.:  .347294E-02
 Slope          = -.598259E-04  std. dev.:  .815493E-06
 corr. coef.    =  .999288
```

TABLE 10 : LSTSQ data for the Diels-Alder reaction of compound 8 with maleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u           INPUT v          RESIDUAL IN INPUT v

  1      .000000E+00     -.456570E+00       .168472E-01
  2      .300000E+02     -.494400E+00      -.715122E-02
  3      .620000E+02     -.516790E+00      -.147875E-01
  4      .119000E+03     -.535950E+00      -.766749E-02
  5      .202000E+03     -.568660E+00      -.211009E-02
  6      .294000E+03     -.594540E+00       .144268E-01
  7      .125700E+04     -.104920E+01       .376093E-02
  8      .141100E+04     -.112464E+01      -.676897E-03
  9      .152400E+04     -.117731E+01      -.124790E-02
 10      .304900E+04     -.186710E+01       .120681E-01
 11      .419800E+04     -.242028E+01      -.113619E-01
 12      .440700E+04     -.252114E+01      -.158618E-01
 13      .560700E+04     -.304478E+01       .137619E-01
 Intercept      = -.473417E+00  std. dev.:  .445186E-02
 Slope          = -.461053E-03  std. dev.:  .175324E-05
 corr. coef.    =  .999920
```

TABLE 11 : LSTSQ data for the Diels-Alder reaction of compound 13 with maleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u           INPUT v          RESIDUAL IN INPUT v

  1      .000000E+00     -.809010E+00       .203841E-01
  2      .320000E+02     -.963130E+00      -.141843E-01
  3      .650000E+02     -.108460E+01      -.123667E-01
  4      .121000E+03     -.128370E+01      -.225135E-02
  5      .203000E+03     -.157750E+01       .102997E-01
  6      .298000E+03     -.194460E+01      -.188150E-02
 Intercept      = -.829394E+00  std. dev.:  .930875E-02
 Slope          = -.373399E-02  std. dev.:  .588928E-04
 corr. coef.    =  .999503
```

TABLE 12 : LSTSQ data for the Diels-Alder reaction of compound 17 with maleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u           INPUT v          RESIDUAL IN INPUT v

  1      .100000E+01     -.742570E+00       .228920E-01
  2      .989000E+03     -.102093E+01      -.324604E-02
  3      .118200E+04     -.105160E+01       .153540E-01
  4      .151200E+04     -.116726E+01      -.160618E-01
  5      .244600E+04     -.140136E+01      -.117252E-01
  6      .268900E+04     -.144659E+01      -.149209E-01
  7      .293700E+04     -.155482E+01      -.398401E-01
  8      .410400E+04     -.176535E+01       .475480E-01
 Intercept      = -.765207E+00  std. dev.:  .199326E-01
 Slope          = -.255285E-03  std. dev.:  .856338E-05
 corr. coef.    =  .994641
```

TABLE 13 : LSTSQ data for the Diels-Alder reaction of compound 8 with N-methylmaleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u            INPUT v            RESIDUAL IN INPUT v

  1      .000000E+00      -.474090E+00        .262313E-01
  2      .260000E+02      -.520580E+00        .160250E-01
  3      .980000E+02      -.611770E+00        .253130E-01
  4      .142000E+03      -.700560E+00       -.207374E-02
  5      .194000E+03      -.789470E+00       -.184163E-01
  6      .248000E+03      -.872170E+00       -.257578E-01
  7      .359000E+03      -.103531E+01       -.339942E-01
  8      .134800E+04      -.237694E+01        .455295E-02
  9      .158100E+04      -.270578E+01        .870960E-03
 10      .166200E+04      -.281244E+01        .724872E-02
 Intercept     = -.500321E+00  std. dev.:  .920634E-02
 Slope         = -.139553E-02  std. dev.:  .107477E-04
 corr. coef.   =  .999763

LINEAR LEAST SQUARES CALCULATION
```

TABLE 14 : LSTSQ data for the Diels-Alder reaction of compound 13 with N-methylmaleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u            INPUT v            RESIDUAL IN INPUT v

  1      .000000E+00      -.819000E+00        .265375E+00
  2      .280000E+02      -.124832E+01        .146519E+00
  3      .101000E+03      -.222986E+01       -.255958E-01
  4      .145000E+03      -.296385E+01       -.271713E+00
  5      .164000E+03      -.302857E+01       -.125761E+00
  6      .197000E+03      -.356634E+01       -.297626E+00
  7      .251000E+03      -.391560E+01       -.482136E-01
  8      .362000E+03      -.474122E+01        .357016E+00
 Intercept     = -.108437E+01  std. dev.:  .158372E+00
 Slope         = -.110880E-01  std. dev.:  .829296E-03
 corr. coef.   =  .983629
```

TABLE 15 : LSTSQ data for the Diels-Alder reaction of compound 17 with N-methymaleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u            INPUT v            RESIDUAL IN INPUT v

  1      .100000E+01      -.754080E+00        .202277E-01
  2      .992000E+03      -.161400E+01        .533464E-01
  3      .118200E+04      -.179330E+01        .452448E-01
  4      .151200E+04      -.233320E+01       -.197256E+00
  5      .244600E+04      -.289920E+01        .784171E-01
 Intercept     = -.773407E+00  std. dev.:  .106928E+00
 Slope         = -.901149E-03  std. dev.:  .732649E-04
 corr. coef.   =  .990230
```

TABLE 16 : LSTSQ data for the Diels-Alder reaction of compound 8 with N-phenylmaleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u          INPUT v          RESIDUAL IN INPUT v

  1      .000000E+00     -.941570E+00       .303127E-01
  2      .230000E+02     -.951080E+00       .296703E-01
  3      .530000E+02     -.979000E+00       .133169E-01
  4      .103000E+03     -.996410E+00       .151844E-01
  5      .187000E+03     -.104985E+01      -.586930E-02
  6      .270000E+03     -.109890E+01      -.229186E-01
  7      .374000E+03     -.113432E+01      -.174701E-01
  8      .444000E+03     -.116589E+01      -.228227E-01
  9      .440600E+04     -.269579E+01      -.251694E-01
 10      .453500E+04     -.276748E+01      -.471233E-01
 11      .478700E+04     -.285262E+01      -.351045E-01
 12      .573100E+04     -.312865E+01       .528257E-01
 13      .599800E+04     -.324925E+01       .351679E-01
 Intercept     = -.971883E+00  std. dev.:  .118962E-01
 Slope         = -.385551E-03  std. dev.:  .373083E-05
 corr. coef.   =  .999485
```

TABLE 17 : LSTSQ data for the Diels-Alder reaction of compound 13 with N-phenylmaleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u          INPUT v          RESIDUAL IN INPUT v

  1      .000000E+00     -.851650E+00      -.921221E-01
  2      .250000E+02     -.107520E+01      -.769827E-01
  3      .550000E+02     -.131470E+01      -.300555E-01
  4      .790000E+02     -.151750E+01      -.371367E-02
  5      .940000E+02     -.166640E+01      -.940004E-02
  6      .105000E+03     -.174120E+01       .208233E-01
  7      .157000E+03     -.219730E+01       .611972E-01
  8      .189000E+03     -.249710E+01       .669196E-01
  9      .235000E+03     -.291260E+01       .906080E-01
 10      .272000E+03     -.325640E+01       .100068E+00
 11      .378000E+03     -.420080E+01       .167711E+00
 12      .446000E+03     -.531280E+01      -.295054E+00
 Intercept     = -.759528E+00  std. dev.:  .583850E-01
 Slope         = -.954758E-02  std. dev.:  .269998E-03
 corr. coef.   =  .996025
```

TABLE 18 : LSTSQ data for the Diels-Alder reaction of compound 17 with N-phenylmaleimide.

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u          INPUT v          RESIDUAL IN INPUT v

  1      .100000E+01     -.798040E+00       .110619E-02
  2      .994000E+03     -.133915E+01       .199794E-01
  3      .118400E+04     -.148386E+01      -.175838E-01
  4      .151400E+04     -.165752E+01      -.514668E-02
  5      .244800E+04     -.218681E+01      -.772542E-02
  6      .269000E+04     -.23  .05E+01      -.494192E-03
  7      .293900E+04     -.244611E+01       .986455E-02
 Intercept     = -.798582E+00  std. dev.:  .100132E-01
 Slope         = -.563931E-03  std. dev.:  .514164E-05
 corr. coef.   =  .999792
```

TABLE 19 : LSTSQ data for the Diels-Alder reaction of compound 8 with N-methylmaleimide (heptane solvent).

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u           INPUT v          RESIDUAL IN INPUT v

  1      .000000E+00      -.154780E+01       .542017E-02
  2      .690000E+02      -.156810E+01       .181186E-01
  3      .196000E+03      -.166130E+01      -.143452E-01
  4      .262000E+03      -.169190E+01      -.133815E-01
  5      .121000E+04      -.212770E+01       .418796E-02
 Intercept     = -.155322E+01  std. dev.:  .906152E-02
 Slope         = -.478238E-03  std. dev.:  .161406E-04
 corr. coef.   =  .998296
```

TABLE 20 : LSTSQ data for the Diels-Alder reaction of compound 17 with N-methylmaleimide (heptane solvent).

```
LINEAR LEAST SQUARES CALCULATION

 PT #      INPUT u           INPUT v          RESIDUAL IN INPUT v

  1      .000000E+00      -.145480E+01      -.171711E-02
  2      .730000E+02      -.182090E+01       .469636E-02
  3      .200000E+03      -.247350E+01       .167746E-03
  4      .240000E+03      -.267630E+01       .148472E-02
  5      .266000E+03      -.284630E+01      -.358393E-01
  6      .282000E+03      -.286090E+01       .312075E-01
 Intercept     = -.145308E+01  std. dev.:  .191743E-01
 Slope         = -.510292E-02  std. dev.:  .933373E-04
 corr. coef.   =  .999332
```

PLATE XI : CPK space filling model of compound 13 (view #1).

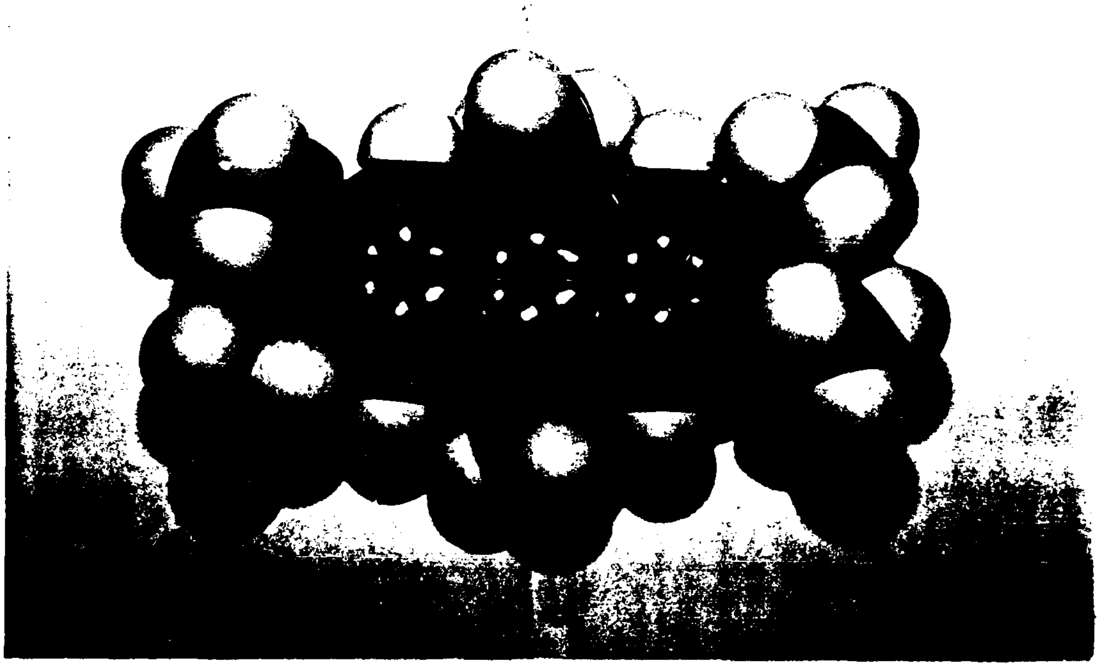


PLATE XII : CPK space filling model of compound 13 (view #2).

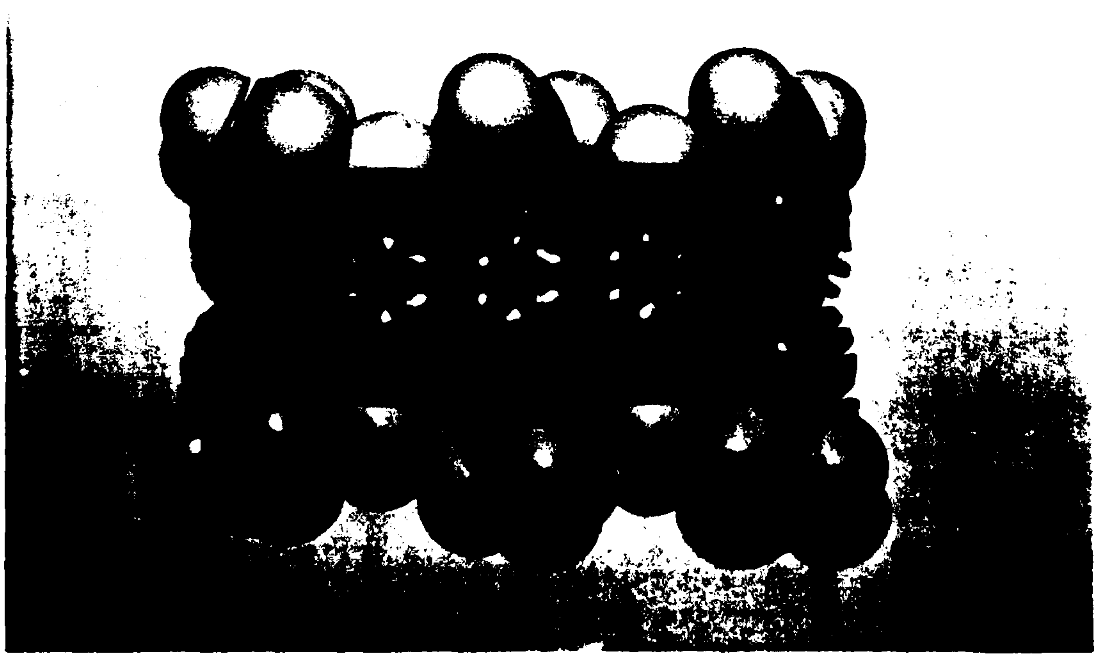


PLATE XIII : CPK space filling model of compound 13 (view # 3).

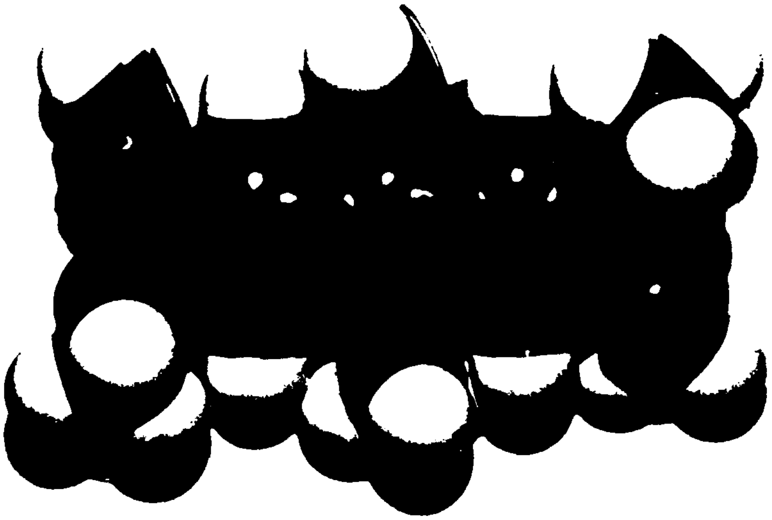
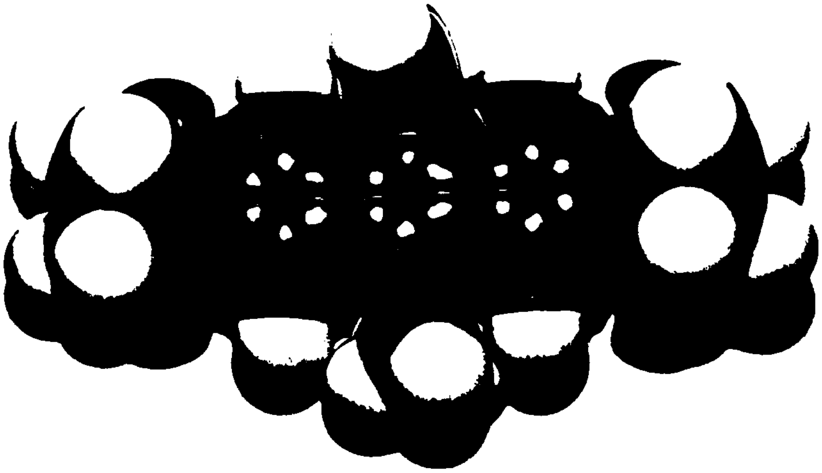


PLATE XIV : CPK space filling model of compound 29.



APPENDIX D

DATA RELATIVE TO CHAPTER III

TABLE 21 : LSTSQ data for the retro Diels-Alder reaction of compound 10 in diphenylether at 200°C.

```
LINEAR LEAST SQUARES CALCULATION

PT #      INPUT u            INPUT v           RESIDUAL IN INPUT v

 1       .100000E+01      -.842500E-01       .916272E-02
 2       .200000E+01      -.122780E+00      -.228731E-02
 3       .300000E+01      -.145420E+00       .215266E-02
 4       .400000E+01      -.176810E+00      -.215737E-02
 5       .500000E+01      -.202960E+00      -.122740E-02
 6       .600000E+01      -.232930E+00      -.411743E-02
 7       .700000E+01      -.254010E+00       .188254E-02
 8       .800000E+01      -.280730E+00       .224251E-02
 9       .900000E+01      -.313690E+00      -.363751E-02
10       .100000E+02      -.339710E+00      -.257754E-02
11       .110000E+02      -.367220E+00      -.300757E-02
12       .120000E+02      -.395460E+00      -.416760E-02
13       .130000E+02      -.423000E+00      -.462763E-02
14       .140000E+02      -.447670E+00      -.221766E-02
15       .150000E+02      -.469300E+00       .323231E-02
16       .160000E+02      -.488260E+00       .113523E-01
Intercept      = -.663328E-01   std. dev.:  .257459E-02
Slope          = -.270800E-01   std. dev.:  .264258E-03
corr. coef.    =  .999324
```

TABLE 22 : LSTSQ data for the retro Diels-Alder reaction of compound 26 in diphenylether at 200°C.

```
LINEAR LEAST SQUARES CALCULATION

PT #      INPUT u            INPUT v           RESIDUAL IN INPUT v

 1       .100000E+01      -.164340E+00       .188291E-03
 2       .200000E+01      -.178780E+00       .560780E-02
 3       .300000E+01      -.201760E+00       .248731E-02
 4       .400000E+01      -.221250E+00       .285682E-02
 5       .500000E+01      -.242900E+00       .106633E-02
 6       .600000E+01      -.262370E+00       .145583E-02
 7       .700000E+01      -.285080E+00      -.139466E-02
 8       .800000E+01      -.306470E+00      -.292515E-02
 9       .900000E+01      -.325830E+00      -.242564E-02
10       .100000E+02      -.346440E+00      -.317613E-02
11       .120000E+02      -.386480E+00      -.349711E-02
12       .130000E+02      -.408710E+00      -.586760E-02
13       .140000E+02      -.427390E+00      -.468810E-02
14       .150000E+02      -.442170E+00       .391412E-03
15       .160000E+02      -.465490E+00      -.306908E-02
16       .170000E+02      -.485030E+00      -.276957E-02
17       .180000E+02      -.502680E+00      -.540062E-03
18       .190000E+02      -.517290E+00       .470945E-02
19       .200000E+02      -.529420E+00       .124390E-01
20       .210000E+02      -.566790E+00      -.507154E-02
21       .220000E+02      -.580060E+00       .151797E-02
22       .230000E+02      -.597690E+00       .374748E-02
23       .240000E+02      -.622340E+00      -.104301E-02
Intercept      = -.144669E+00   std. dev.:  .181428E-02
Slope          = -.198595E-01   std. dev.:  .125864E-03
corr. coef.    =  .999579
```

TABLE 23 : LSTSQ data for the retro Diels-Alder reaction of compound 27 in diphenylether at 200°C.

```
LINEAR LEAST SQUARES CALCULATION

PT #      INPUT u            INPUT v           RESIDUAL IN INPUT v

 1       .100000E+02      -.201350E+00       .143056E-02
 2       .200000E+02      -.215260E+00       .212783E-02
 3       .300000E+02      -.231720E+00       .275095E-03
 4       .400000E+02      -.258950E+00      -.123476E-01
 5       .500000E+02      -.262330E+00      -.112037E-02
 6       .600000E+02      -.262850E+00       .129669E-01
 7       .700000E+02      -.285690E+00       .473417E-02
 8       .900000E+02      -.321540E+00      -.190130E-02
 9       .100000E+03      -.341730E+00      -.748403E-02
10       .110000E+03      -.350550E+00      -.169676E-02
11       .120000E+03      -.366430E+00      -.296949E-02
12       .140000E+03      -.386690E+00       .598504E-02
Intercept      = -.188173E+00   std. dev.:  .392261E-02
Slope          = -.144073E-02   std. dev.:  .485910E-04
corr. coef.    =  .994513
```

In his review of this thesis, Dr. Platz voiced concern over the accuracy of the k_1 values obtained. His primary concern was that k_1 values will be extremely sensitive to an accurate D_∞ value. He recommended two courses of action: 1. To obtain an estimate of the accuracy of k_1 values, systematically vary D_∞ and recalculate k_1 for each; and 2. Obtain the best fit of k_1 and k_2 to the curve described by:

$$B = A_0\ k_1\ (e^{-k_1 t} - e^{-k_2 t})/\ k_2 - k_1$$

for the presumed $A \longrightarrow B \longrightarrow C$ system.

Unfortunately, the curve fitting suggestion could not be accomplished. As the parent anthracene decomposes, it gives rise to a compound which is uv absorbing in the same region as the parent anthracene. Therefore, the time variable values for B could not be obtained over the required range.

However, for each cycloadduct (10, 26, and 27), the calculated D_∞ value was varied by +10, +25, -10, and -25%. For each new D_∞ value, k_1 was recalculated. The results are displayed in Table 24. Please note that even if the error associated with D_∞ is 25%, 10 cycloreverts ten times faster than 27 in the worst case.

Over the range -25% to +25%, the error associated with k_1 is approximately equal to the error associated with D_∞. A realistic error estimate for D_∞ is ± 10% with a maximum error estimate of ± 20%. Thus, I conclude that the error associated with the rDA k_1 values is ± 20% and the rate acceleration by polysiloxy substituents is a real phenomenon.

TABLE 24: Dependence of k_1 for the retro Diels-Alder reaction of 10, 26 and 27 on the calculated D_∞ value.

Compound	k_1 (min^{-1}) X 10^2				
D_∞	$1.25D_i$	$1.10D_i$	D_i	$.90D_i$	$.75D_i$
10	2.04	2.39	2.71	3.12	4.03
26	1.48	1.76	1.99	2.29	2.97
27	.11	.13	.15	.16	.20

D_i is the original D_∞ value.

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23. This step is crucial to the ease of workup and yield. If too little or too much ice is used, a purple tar forms. Workup then requires an extra step, continuos extraction with chloroform, and yield drops to 8% or less. After the ice water has equilibrated to 0°C, the crushed ice should account for approximately 1/3 of the volume.

24. Crystallization from acetic acid (Boldt's procedure) indeed works, however for my purposes, I found ethanol to be a better crystallizing solvent.

25. Difficulties were encountered trying to crystallize from acetic acid, thus, after several attempts, ethanol was used. A true yield could not be determined, but qualitatively, it was much higher than 50%.

26. NMR and Microanalysis indicate this compound probably exists as 9,10-diphenyl-2,3,6,7-tetrahydroxyanthracene ·2 EtOH in the solid form after crystallization from ethanol.

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