This is to certify that the

thesis entitled

Synthesis of Dipyrazolopentalene Derivatives

presented by

John Howard Camp

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemistry

Eugene LeGoff
Major professor

Date 6 March 1986

SYNTHESIS OF DIPYRAZOLOPENTALENE DERIVATIVES

by

John Howard Camp

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ABSTRACT

SYNTHESIS OF DIPYRAZOLOPENTALENE DERIVATIVES

by

John Howard Camp

The preparation of dipyrazolopentalene derivatives was investigated. Synthesis and treatment of bis(dimethylaminomethylene)-bicyclo[3.3.0]octane diones with hydrazine in ethanol gave partially saturated derivatives. These compounds resisted attempts to introduce unsaturation into the pentalene ring system. A substituted bis(dimethylaminomethylene)bicyclo[3.3.0]octane dione was sought where the added substituent would lead to the easy formation of carbon-carbon double bonds within the pentalene ring system. Both phenylseleno groups and phenylsulfenyl groups were tested with the latter proving to be superior. Treatment of 4,8-bis(dimethylamino-methylene)-2,6-bis(phenylthio)bicyclo[3.3.0]octane-3,7-dione with hydrazine lead to the formation of the dipyrazolo derivative. Oxidation with sodium periodate gave the phenylsulfinyl derivative and thermal elimination of phenylsulfenic acid lead to the formation of 1,5-dihydro-1,2,5,6-tetraazadicyclopenta[a,e]pentalene.

To my parents

whose love, support, and faith in me

has helped make this thesis possible.

ACKNOWLEDGEMENTS

I would like to thank Dr. LeGoff for all of his help, guidance, support, and infinite patience with me.

I would also like to thank those special people whose friendship and support have not only helped keep me in school but have also helped keep me sane, especially Steve H., Linda K., CaryE B., Bob H. and Carol H., Mark R., John L., Bill H., Bob R. and last but not least Steve D.

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INTRODUCTION

Armit and Robinson[1] in 1922 first considered that pentalene 1 might be an "aromatic" compound but later withdrew their suggestion[2] since a sextet of electrons could not be developed in each ring. Early HMO calculations of Brown[3] predicted pentalene would have a considerable delocalization energy. Subsequent valence bond treatment and more extensive molecular orbital calculations suggested that the structure with localized bonds would be more stable. The PMO method predicts that pentalene is an antiaromatic system, the transannular bond not contributing to the stabilization of this compound which can be considered as a slightly perturbed form of cyclooctatetraene (Figure 1).

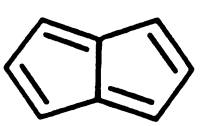

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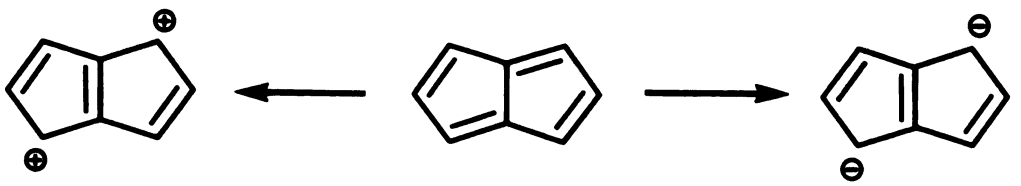
Figure 1: Pentalene.

Although pentalene appears to be an antiaromatic compound it can, in principle, acquire aromaticity by oxidation to the corresponding dication or by formation of the dianion (Scheme 1). Formation of the dication has

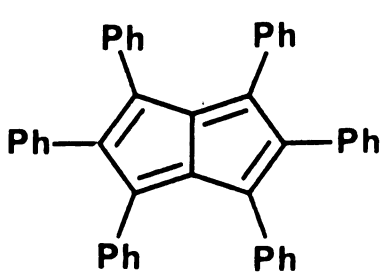
so far been unsuccessful. The dianion has been prepared by treating a dihydroderivative of 1 with butyl lithium (BuLi)[4].



1

Scheme 1

The only pentalenes that have been isolated as stable compounds are either substituted by large groups which sterically protect the molecule such as 2[5] and 3[6], substituted by push-pull substituents such as 4[7], or benzoannelated such as 3 and 5[8] (Figure 2).



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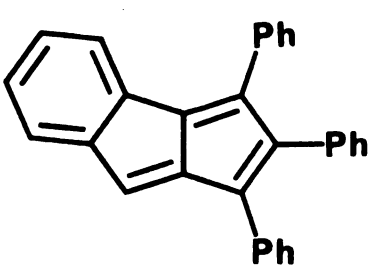

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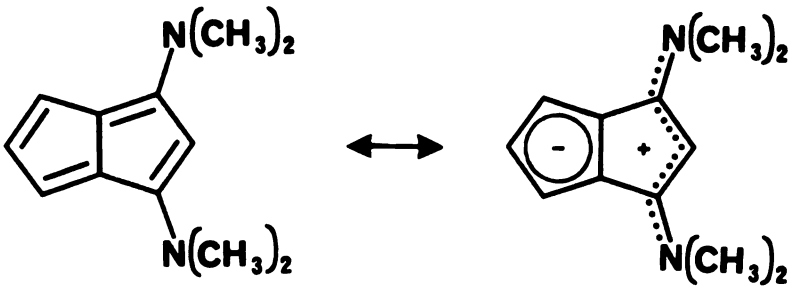

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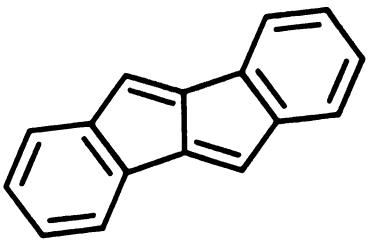


5

Figure 2: Stable pentalene derivatives which have been synthesized.

The most extensively studied derivative has been 5. Indeno[2,1-a]indene (also known by its trivial name dibenzopentalene) has been known for almost one century[8a]. It is a bronze colored solid which polymerizes easily in acidic solutions. Its general chemistry is that of a conjugated diene, the central double bonds readily adding four hydrogen atoms or four bromine atoms. Its long wave absorption in the U.V. shows a significant difference from that of linear dienes with the same number of π-electrons and indicates some degree of resonance interaction in the excited state of the molecule[8b](Table 1).

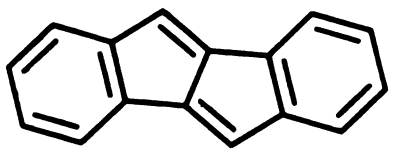
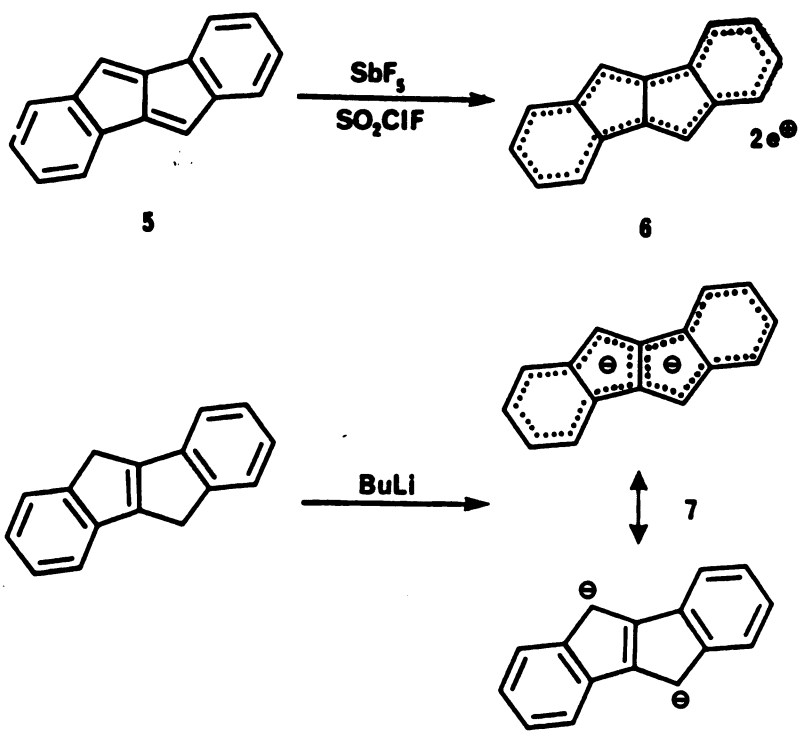
Compound	U.V. Absorption (nm)
PhCH=CH—CH=CHPh	299 (ϵ = 30000)
	273 (ϵ = 61000) 281 (ϵ = 69000) 415 (ϵ = 415)

Table 1

Delocalization of the π-system to form charged aromatic species has been accomplished by treatment of 5 with antimony pentafluoride and sulfonyl chloride fluoride to provide dication 6[9] and by treatment of a dihydroderivative of 5 with butyl lithium to provide dianion 7[10] (Scheme 2).



While carbocyclic derivatives of pentalene have been studied to a great extent very little work has been done on their isoelectronic heterocyclic analogs. A number of pentalene derivatives have been prepared where one or two heteroatoms have been incorporated into the pentalene unit[11] (Figure 3). No examples exist however where the pentalene unit is stabilized by heteroaromatic rings.

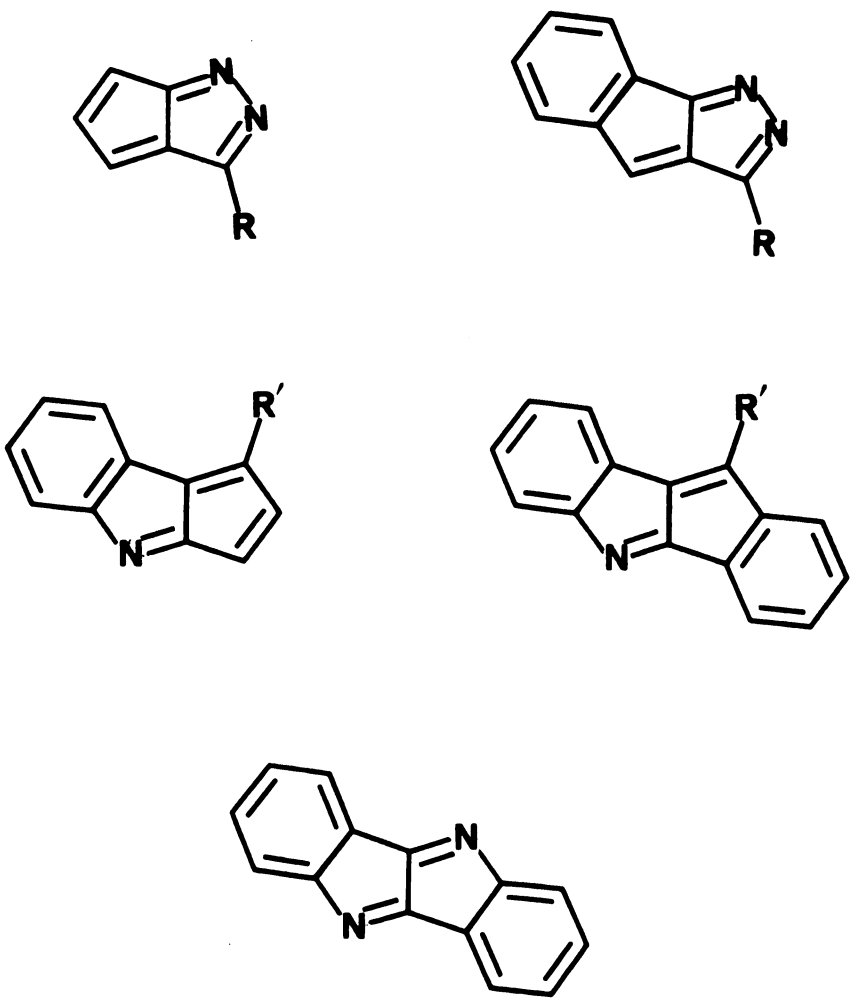


Figure 3: Heteroatom derivatives of pentalene.

Such heteroannelated systems would be isoelectronic to the benzoannelated systems. Heterocyclic systems which could be used would include such 5-membered ringed systems as pyrroles, furans, thiophens, imidazoles, pyrazoles, and isoxazoles all of which are isoelectronic with benzene.

Examples of heteroannelated analogs of dibenzopentalene are the isomeric dipyrazolopentalenes 8 and 9 (Figure 4).

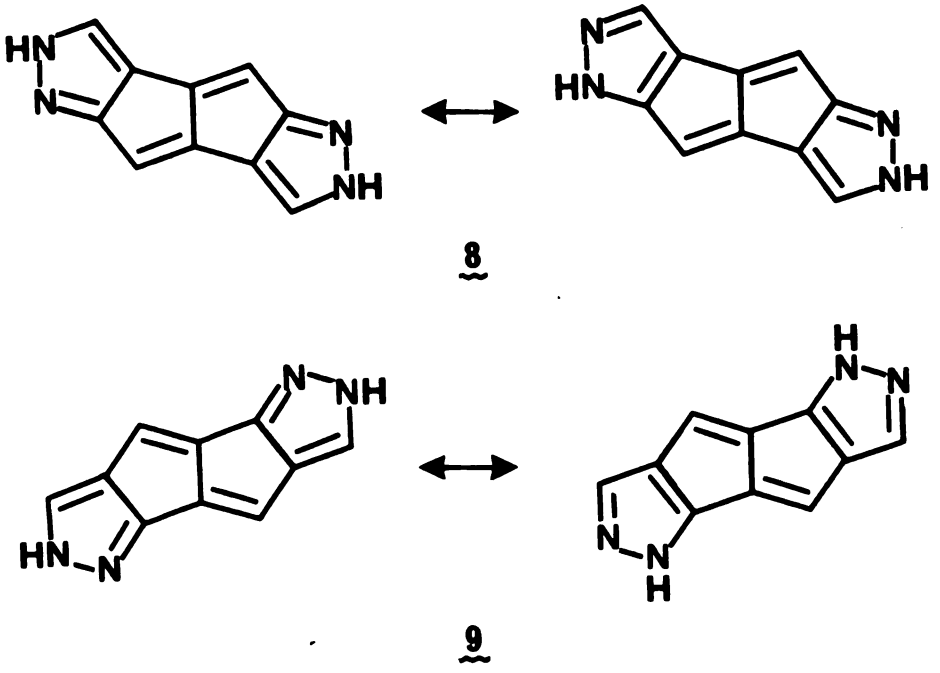


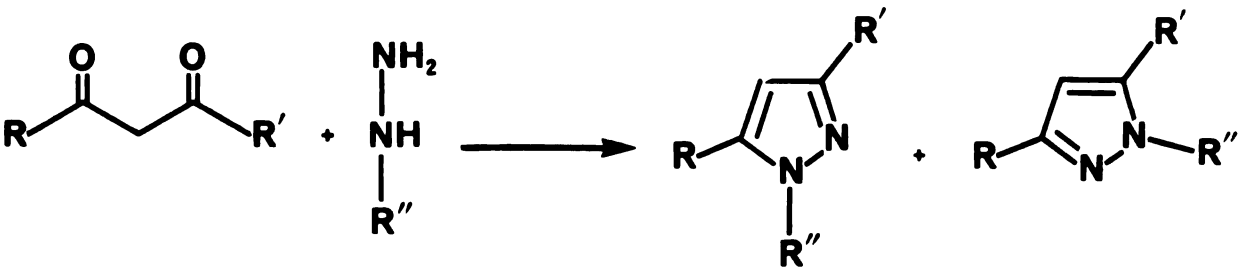
Figure 4: The isomeric dipyrazolopentalenes and their tautomers.

The pyrazole system should serve to stabilize the inner pentalene unit in the much the same way as the benzene system does for dibenzopentalene. Consequently the central double bonds would be expected to behave as a conjugated diene. The fully aromatic derivatives of 8 and 9 are neutral unlike their analog - the dibenzopentalene dianion 7.

The synthesis of 8 and 9 could be envisioned as involving construction of the pyrazole rings onto a more saturated derivative of pentalene with further functionalization to give the desired product. The synthesis of pyrazoles has been well studied. The two main ring-synthetic pathways to pyrazoles involves either (i) formation of the 1,5- and 2,3-bonds or (ii) formation of the 1,5- and 3,4-bonds (Figure 5).

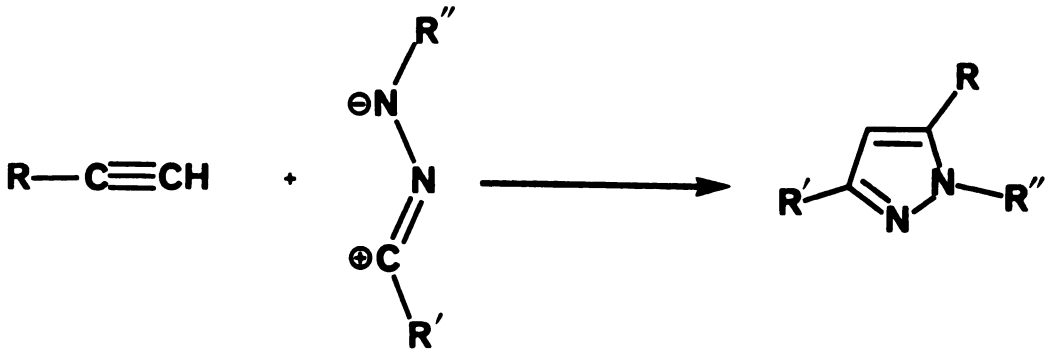
Figure 5: The main ring synthetic pathways to pyrazoles.

The standard method (type i) of synthesis of pyrazoles consists in the condensation of a 1,3-dicarbonyl compound with hydrazine or its derivatives (Scheme 3). A review has been published on this subject[12].



Scheme 3

Type (ii) syntheses of pyrazoles comprise the 1,3-dipolar addition of a diazoalkane to an acetylene which is activated by an electron withdrawing substituent[13] (Scheme 4).



Scheme 4

N-Unsubstituted pyrazoles exist as a mixture of tautomers (Figure 6). For the sake of convenience only one tautomer is usually represented but it should be understood that it exists in equilibrium with its other tautomer.

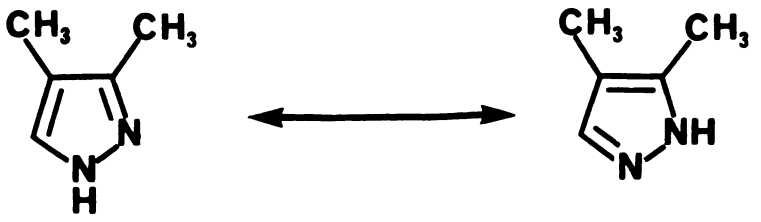


Figure 6: Tautomeric forms of an N-unsubstituted pyrazole.

When these molecules are unsubstituted on the the pyrrole nitrogen they generally exist as crystalline compounds with relatively high melting and boiling points. This is due to the ability of the the molecule to form intermolecular hydrogen bonds. Such compounds are usually soluble in polar solvents. Pyrazole forms strainless dimers and trimers (Figure 7).

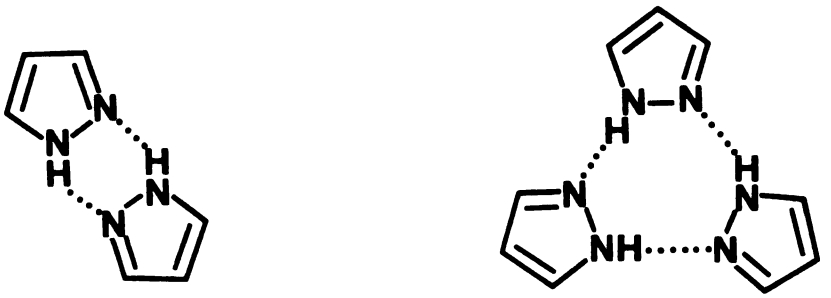


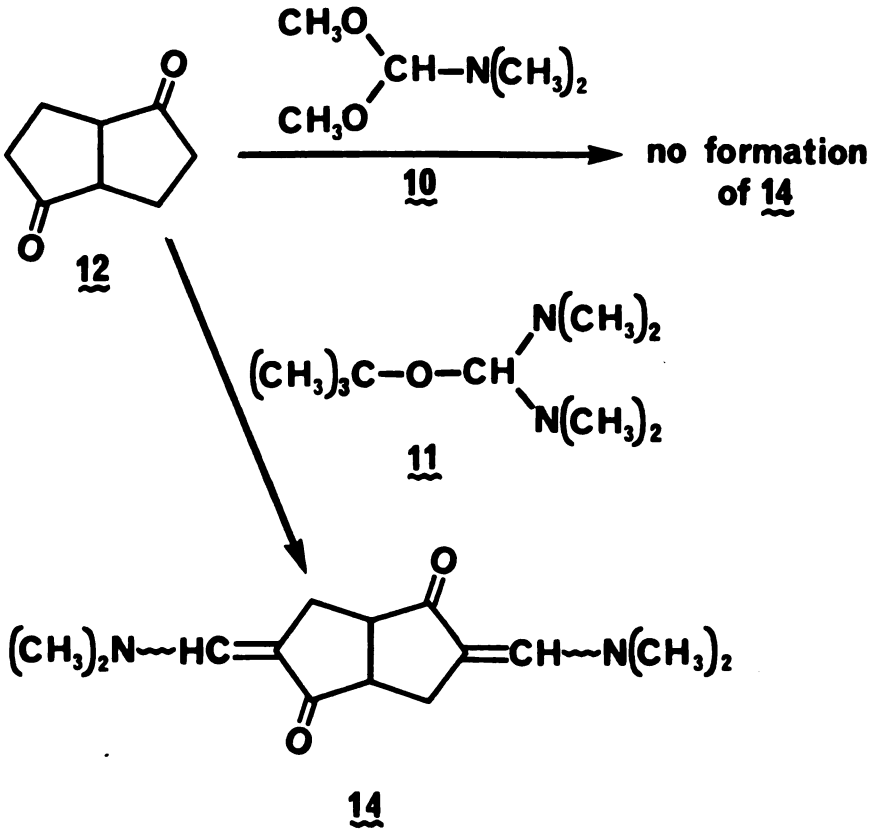
Figure 7: Examples of intermolecular hydrogen bonding of N-unsubstituted pyrazoles.

In this thesis we will investigate various synthetic approaches

towards the preparation of compounds 8 and 9. The type (i) method will be employed in the construction of the pyrazole unit.

RESULTS AND DISCUSSIONS

It is well known that 1,3-ketoaldehydes and their enamine derivatives yield pyrazoles upon treatment with hydrazine. These enamine derivatives can be prepared by a variety of methods. The classical approach required a two step formylation and enamine formation sequence. This proved limited as a general method because of low overall yields and the need for isolation of the intermediate α,β-ketoaldehydes. Derivatives of dimethyl formamide are known to react with a variety of activated methylene compounds to form the corresponding enamine derivatives directly. The dialkyl derivatives of dimethyl formamide (for example 1,1-dimethoxytrimethylamine 10) react with systems containing only strongly acidic methylene groups. An alternative class of dimethyl formamide reagents are the alkoxy bis-(dimethylamino)methanes. *Tert*-butoxybis(dimethylamino)methane 11[14,15] for example reacts with a much wider variety of active methylene compounds. This point is demonstrated in the following sequence (Scheme 5).



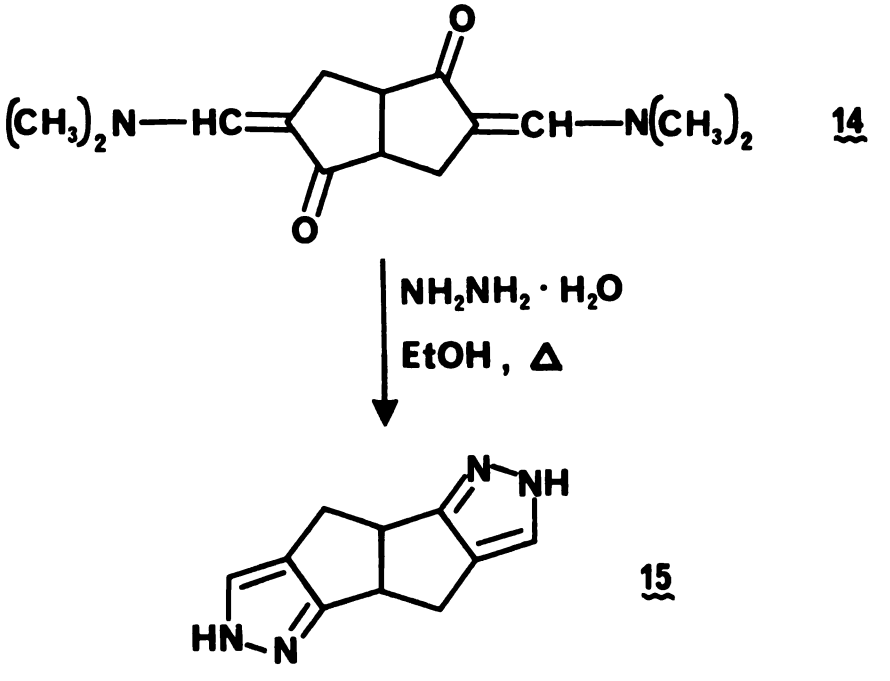
Scheme 5

The methylene units of bicyclo[3.3.0]octane-2,6-dione 12 are activated by the carbonyl unit and react with 11 to give a quantitative yield of 14. They are not strongly acidic though and consequently do not react with 10 to give 14.

Trost[16] based his assignments of the stereochemistry of the enamines on the proton NMR absorption of the N-methyl groups. He assigned the E-configuration to enamines when their N-methyl signals appeared at δ 3.00+0.05. Signals which appeared approximately 15Hz

downfield were assigned the Z-configuration. Wasserman[17] also used this data in his stereochemical assignments of enamines. When N-methyl proton signals fell on the edge or just beyond Trost's limits of δ3.00+0.05 he decided not to make a stereochemical assignment. The N-methyl protons of 14 fall just beyond Trost's limit (δ3.08) and consequently no stereochemistry is assigned. Fortunately there is no problem in not knowing the stereochemistry since it does not affect the outcome of the next reaction and also because it is lost in the next step.

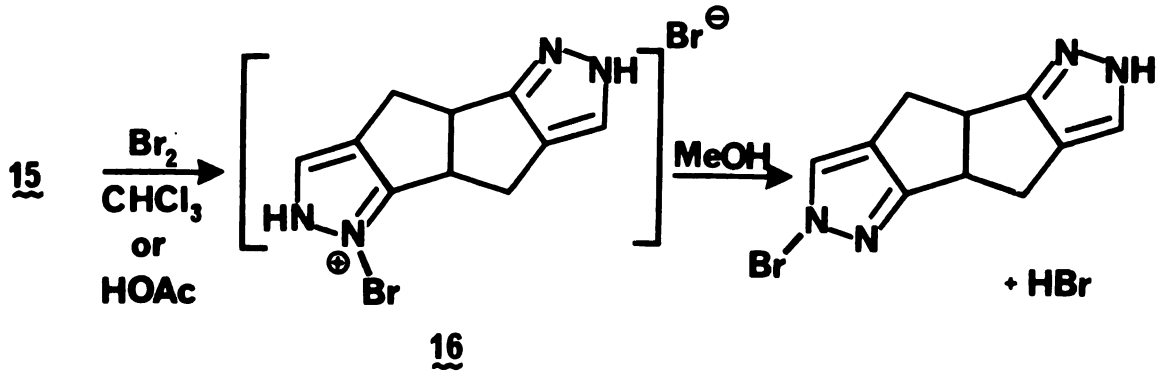
Refluxing equimolar amounts of 14 and hydrazine hydrate in ethanol resulted in the formation of *bis*-pyrazole 15 which precipitated as a white solid in high yield (Scheme 6)



Scheme 6

Bis-pyrazole 15 is insoluble in almost all organic solvents except for the very polar trifluoroacetic acid. It slowly darkened at temperatures above 200^{0}C but did not melt at temperatures exceeding 360^{0}C. These results are consistant with what would be expected with intermolecular hydrogen bonding.

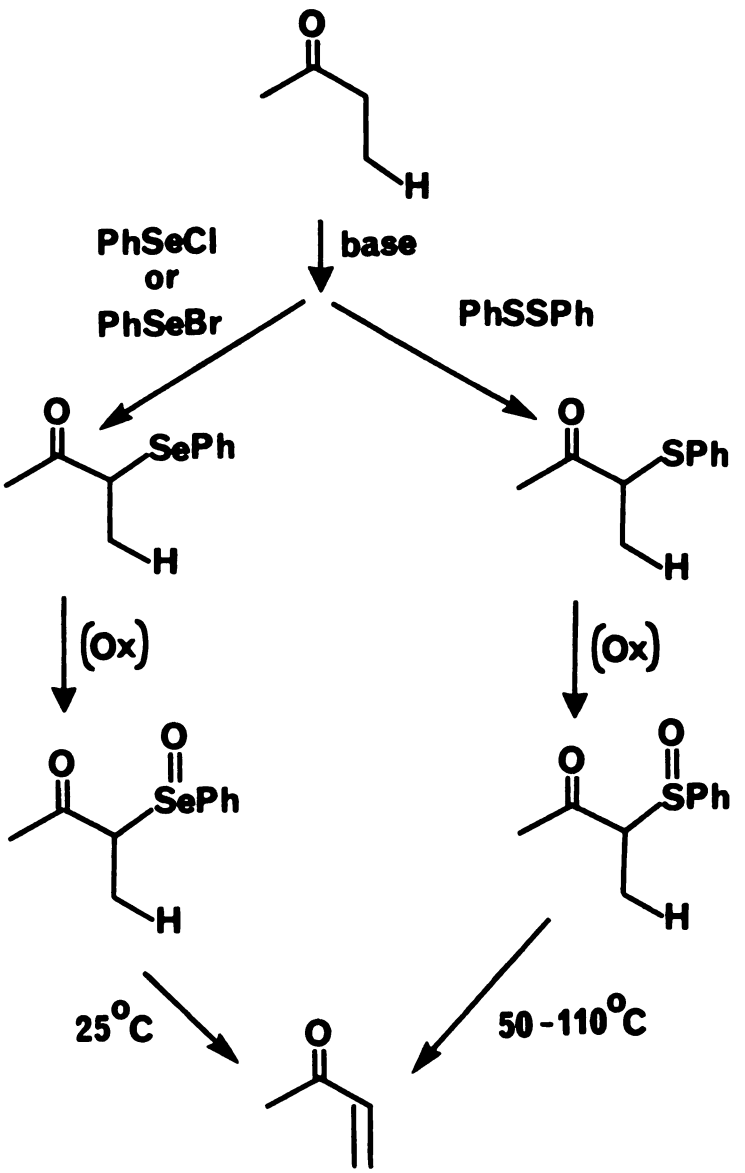
Our next step was to functionalize the 4 and 8 positions with a substituent which could be easily removed to form a carbon-carbon double bond. The most logical choice seemed to be halogenation of these positions. Dehydrohalogenation would then lead to 9. Upon investigation we found that very little work appears to have been done concerning halogenation of alkyl substituents of pyrazoles. In our hands we found thionyl chloride, sulfuryl chloride, N-chlorosuccinimide, and N-bromosuccinimide to be ineffective halogenating agents. Excess bromine in either acetic acid or chloroform did react with 15 to give an orange solid but proton NMR showed the 4 and 8 positions to be unaffected. Mass spectral analysis confirmed however that bromine was incorporated. When treated with methanol the product dissolved to give a very acidic solution. This result is consistant with what would be expected for the formation of the pyrazole salt 16 (Figure 8). This is a known type of bromination of pyrazoles[18].



16

Figure 8: Possible structure of the salt formed upon reaction of excess bromine with 15 and its reaction product upon treatment with methanol.

It became apparent that the functionalization of the 4 and 8 positions of 15 were not going to be as straightfoward as first imagined. An alternative route proposed was to functionalize these positions first and then construct the pyrazole rings. Our strategy involved synthesizing starting materials which incorporated functionality suitable for conversion to a carbon-carbon double bond later on in the sequence. It has been demonstrated that phenylthio[19] and phenylseleno[20] groups can satisfy this requirement. Both are easily incorporated into α-hydrogen -containing ketones and subsequent oxidation followed by elimination gives a double bond (Scheme 7).



Scheme 7

The 4 and 8 positions of bicyclo[3.3.0]octane-2,6-dione 12 cannot be easily functionalized without going through many steps. Its isomer however, bicyclo[3.3.0]octane-3,7-dione 17, can be readily functionalized in one step. The methylene unit α to the carbonyl can be treated with a phenylselenating or phenylsulfenylating agent and the α'-methylene unit

can later be converted to an enamine (Figure 9)

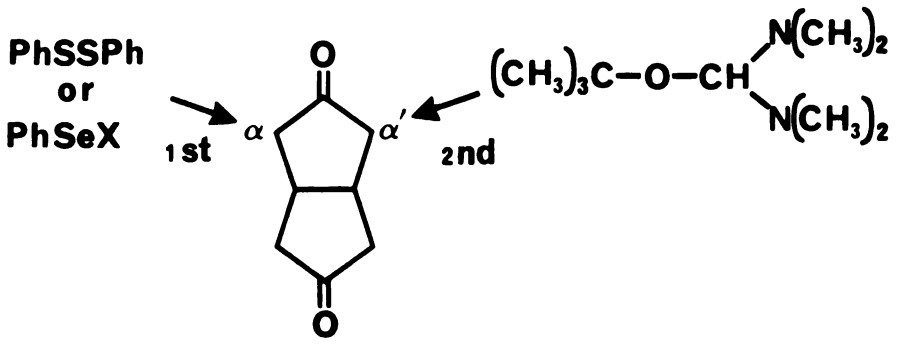
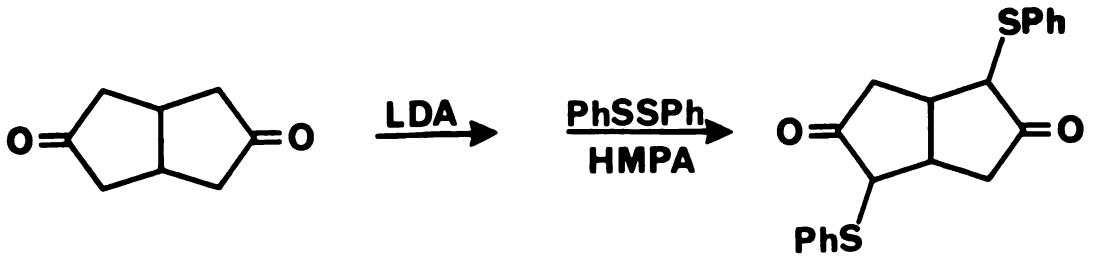


Figure 9: Proposed method of functionalization of compound 17.

Dione 17 was treated with both phenylselenyl chloride and phenylselenyl bromide to give an unstable product. Proton NMR and IR suggested that at least one phenylseleno group was incorporated but the product decomposed rapidly during workup and purification. Because of this no further work was carried out on this system. The phenylthio derivative of 17 proved to be much more stable and so our efforts were concentrated in this area.

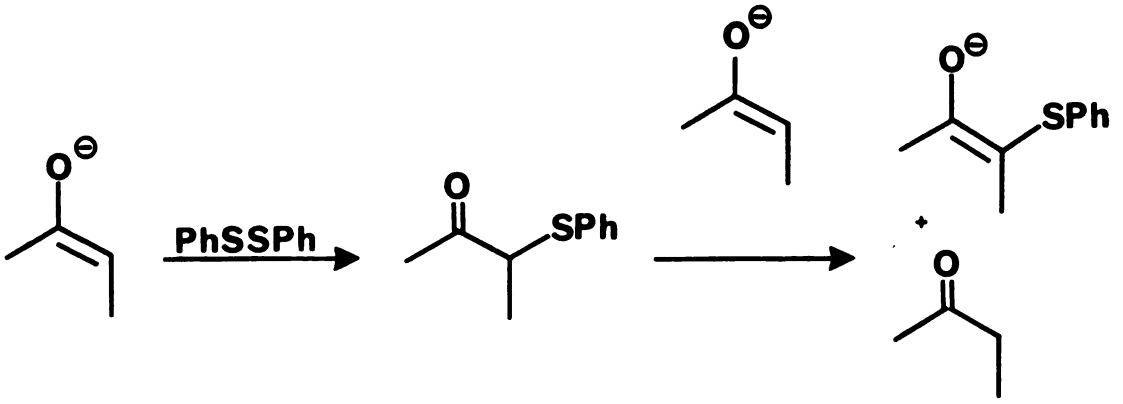
Treatment of 17 with lithium diisopropylamide (LDA) followed by diphenyl disulfide and hexamethylphosphoramide (HMPA) gave a 59% yield of compound 18 (Scheme 8) The only preparation of 18 prior to this was by Bertz[21]. He isolated but did not characterize a *bis*-sulfide in 18% yield as a byproduct of the *mono*-sulfenylation of 17.



17 18

Scheme 8

Trost found that the kinetic acidity of the initially sulfenylated product sometimes necessitated the use of excess base[19] (Scheme 9).



Scheme 9

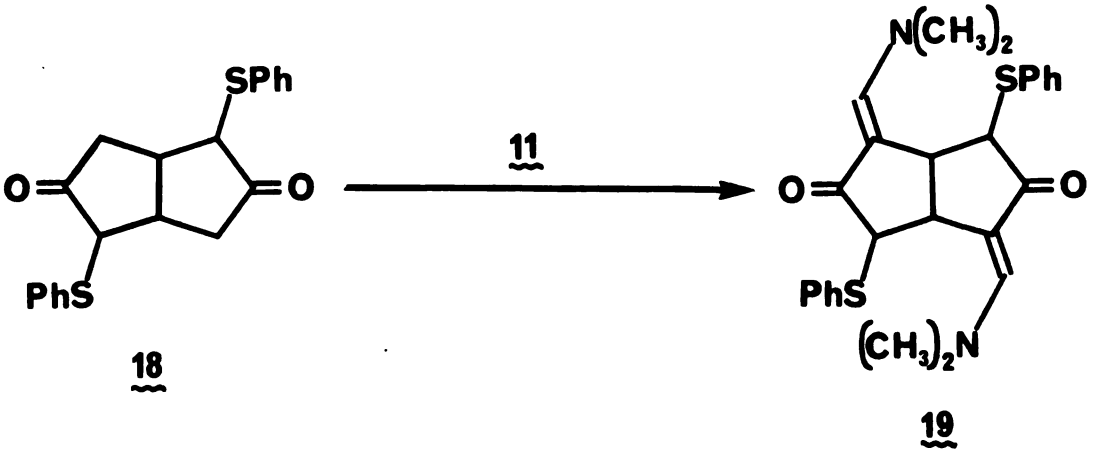
Also, in some cases, Trost found that in the presence of HMPA there was sufficient competition between the enolate and the amide base for diphenyl disulfide so that an excess of the disulfide was preferred. In order to avoid any of these possible problems we typically used 2.5

equivalents of base and disulfide for each position being funtionalized.

We found that the presence of HMPA enhanced the yield (from 30% without HMPA to 50-100% with HMPA). If HMPA was added during enolate formation yields were typically in the 50% range. In this case the product was contaminated with an alkyl group-containing impurity (possibly the reaction product of the disulfide and the amide base). If instead HMPA was added along with diphenyl disulfide the formation of the impurity was apparently avoided and yields of crude product ranged from 66-100%. Careful chromatography of the crude product mixture (silica gel, benzene) yielded three stereoisomers. The major isomer (R_f=0.38) comprised 70% of the product mixture while the other two isomers (R_f=0.11 and 0.5) combinded comprised 10-15% with the difference being other undesired side products. The unseparated product mixture could be used in subsequent steps since all three stereoisomers would ultimately give the same end product (*bis*-pyrazole 8). The major stereoisomer was routinely carried through subsequent steps by itself however since the intermediate products generated required little effort to purify and characterize.

Treatment of *bis*-sulfide 18 with a fourfold excess of the aminal

ester 11 lead to the formation of *bis*-enamine 19 in 70-88% yield (Scheme 10). The amount of 11 used could be cut to 1.1 equivalents for each site being functionalized if the reaction was run in a suitable solvent such as THF or methanol. Both methods gave nearly identical yields.

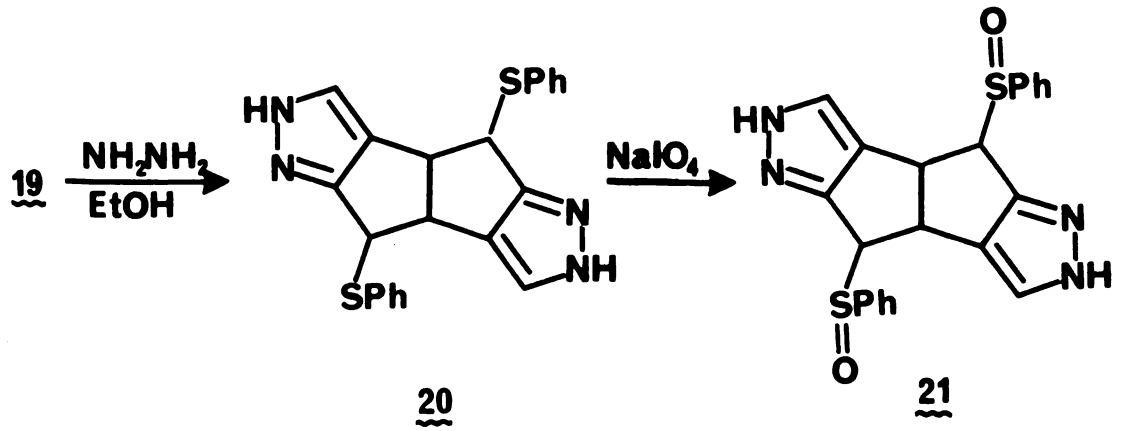


18 19

Scheme 10

The N-methyl proton signals for 19 appear at δ3.00. Because this is well within the limits Trost set for enamines with the E-configuration we have tentatively assigned that configuration to 19. This structural assignment is surprising since it was felt that the steric interaction between the dimethylamino group and the phenylthio group would be great enough to cause the enamine to assume the Z-configuration.

Bis-enamine 19 was treated with hydrazine hydrate in refluxing ethanol to give *bis*-pyrazole 20 as a white solid (Scheme 11).



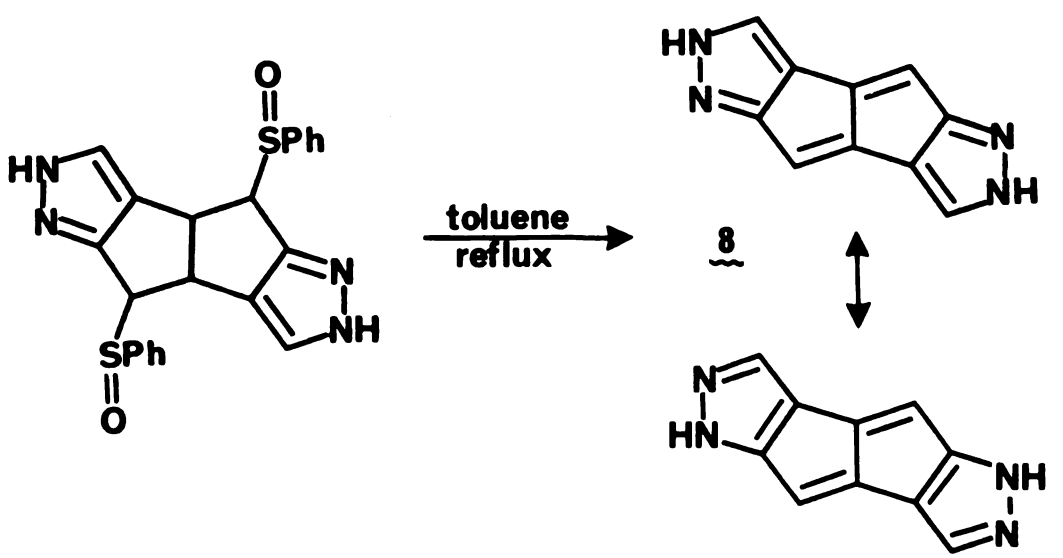
Scheme 11

When nearly pure 19 was used the yields were typically around 70%. Yields dropped substantially to 26-29% when unpurified 19 was used. We found that bulky substituents on the *bis*-pyrazole have a significant affect on melting point and solubility. Its parent compound (prepared from 17 using the method employed in the synthesis of 15) melted at temperatures above 360^{0}C while 20 melted at 140-142^{0}C. Also, while its parent compound was soluble in only very polar solvents (ex. trifluoroacetic acid) *bis*-pyrazole 20 was readily soluble in a range of solvents. The bulky phenylthio substituent apparently decreases the ability for the pyrazole unit to effectively hydrogen bond with other pyrazole units.

The dehydrosulfenylation sequence involves first oxidation followed by thermolysis. The oxidation of sulfides to sulfoxides is a facile

transformation which can be accomplished with any of the following reagents: hydrogen peroxide, ozone, dinitrogen tetroxide, sodium periodate, *tert*-butylhypochlorite, m-chloroperbenzoic acid and other peracids. Sodium periodate was chosen as the oxidizing agent of choice because of its reported high yields, mild reaction conditions and ease of workup. An aqueous solution of the oxidizing agent was added slowly to a cold methanolic solution of the *bis*-sulfide in order to minimize the danger of overoxidation to the sulfone. The presence of sulfones or unoxidized sulfides in the product would decrease the yield in the next step since these groups do not thermally eliminate to form carbon-carbon double bonds.

The thermal cis-elimination of pure sulfoxide 20 (toluene, 111°C) occurred smoothly over 15 hours to give a 70% yield of 8 (Scheme 12).



Scheme 12

1,5-Dihydro-1,2,5,6-tetraazadicyclopenta[a,e]pentalene 8 is a slightly brownish orange powder not melting below 300°C. This coupled with the fact that compound 8 is only soluble in polar solvents (such as ethanol) leads to the conclusion that a high degree of intermolecular hydrogen bonding is occurring. This would be expected for this molecule. The N-H proton signal appears as a broad peak at δ7.0-7.8 while the pyrazolic C-H and pentalenic C-H proton signals appear as sharp singlets at δ7.26 and δ6.15 respectively. A set of seven signals are observed in the C^{13} NMR: δ129.2, 129.0, 128.5, 123.0, 116.5, 116.0, 115.5. One or two signals can be observed for the C-3 and C-5 carbons on the pyrazole ring when C^{13} NMR spectra are run in polar aprotic solvents (in this case dimethyl sulfoxide d_6). These extra signals are due to tautomerisation. The tautomeric forms of 8 would give rise to seven signals in the C^{13}NMR which is what is observed.

The purity of the starting sulfoxide was very important since the use of impure sulfoxide gave erratic and misleading results. An impurity which turned orange when heated in solution gave the illusion that the reaction rate had accelerated (from 15 hours to 2 hours). Not surprisingly very little or no product was detected on workup. It was thought that either the product formed was in some way polymerizing or

that the eliminated phenylsulfenic acid was reacting with the product or starting material. The use of several sulfenic acid traps (calcium carbonate and trimethyl phosphite) failed to remedy this situation. Also, when product was detected in the proton NMR it was lost during isolation from the NMR solvent and purification. All of these problems were solved by careful purification of the sulfoxide.

Work remains to be done to find out what types of chemical reactions compound 8 will undergo. Of special interest will be determining if the central double bonds of 8 will act like a conjugated diene as predicted and the conversion of 8 to its fully aromatic derivative 22 (Figure 10).

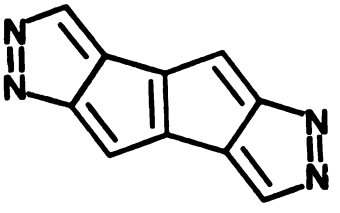


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Figure 10: 1,2,5,6-tetraazadicyclopenta[a,e]pentalene.

Work also remains to successfully prepare compound 9 and its fully aromatic derivative. Hopefully some of the products synthesized in this thesis (especially compound 18) will find further synthetic utility in the future.

EXPERIMENTAL

General Methods

Melting points were measured in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Varian T-60 at 60 MHz or a Brucker WM-250 at 250MHz. Carbon 13 NMR spectra (proton decoupled) were obtained on a Brucker WM-250 at 62.9 MHz. Chemical shifts are reported in parts per million downfield from tetramethylsilane internal standard. Infrared (IR) spectra were measured on a Perkin Elmer 599 grating spectrometer. Mass spectra (MS) were obtained on a Finnigan 4000 instrument with an ionizing voltage of 70 eV. Unless otherwise noted, solvents were reagent grade and were used as received. THF was dried by distillation from potassium-benzophenone. n-Butyl lithium was obtained from Aldrich as a 10.5 M solution in hexanes and was titrated according to the method of Watson and Eastham[22]. Diphenyl disulfide was recrystallized from methanol. HMPA was distilled and stored over molecular sieves. All reactions were carried out under an atmosphere of

nitrogen. Elemental analyses were performed at Galbraith Laboratories, Inc.

1,3-Dimethylacetonedicarboxylate

(This procedure is based on a Japanese patent)[23]. To 350 g of 97% sulfuric acid (3.6 moles) was added 70 g of citric acid monohydrate (0.33 moles) and mechanically stirred for 3 hours at 23-27^{0}C. It was then warmed to 43-47^{0}C for two hours to complete decarboxylation. The reaction mixture was cooled to 35-40^{0}C with the help of an ice bath. While in the ice bath 280 g of 80% methanol (7.0 moles) was slowly added over 30 minutes so as to maintain the reaction temperature at 35-40^{0}C. After addition a volume of chloroform equal to the volume of the reaction solution was added and stirred for one hour at 35-45^{0}C. The two layers were separated. The acid layer was extracted with chloroform (1 x 200 ml). The combined chloroform layers were extracted with dilute aqueous sodium carbonate solution (1 x 100 ml), dilute sulfuric acid (1 x 100 ml) and saturated aqueous sodium chloride solution (1 x 100 ml). The solution was dried over anhydrous sodium sulfate and the solvent evaporated to give a light yellow oil. The oil was

distilled at 100^{0}C (0.5 mm) to give 40 g of a colorless oil (77%). This preparation represents a quick and efficient synthesis for when large amounts of this compound are needed on short notice. This compound was used in the preparation of bicyclo[3.3.0]octane-3,7-dione[24] 17.

3,7-Bis(dimethylaminomethylene)bicyclo[3.3.0]octane-2,6-dione 14

Dione 12 (1.0 g, 7.2 mmol) (prepared according to the method of Hagedorn and Farnum)[25] was added all at once to 5.0g of bis(dimethylamino)-t-butoxymethane, 11, (28.8 mmol) with stirring. After 45 minutes a precipitate formed. The reaction was diluted with hexanes, filtered, and the precipitate washed with a small volume of hexanes to give a light yellow powder. Recrystallization from ethanol gave 1.79 g of light tan crystals (100%). Mp = 230-232^{0}C (dec.); IR (chloroform): 3014, 1655, 1556 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz): 7.26 (s, 2h), 3.08 (s, 12H), 2.9-3.1 (br s, 4H), 2.86 (s, 2H); MS m/e (relative intensity): 248 ($M^{\oplus}$,59.4%), 84 (100).

2,4,4a,6,8,8a-Hexahydro-1,2,5,6-tetraazadicyclopenta[a,e]pentalene 15

To 1.5 g of *bis*-enamine 14 (6.0 mmol) in absolute ethanol (50 ml) was added 0.6 g of hydrazine hydrate (12 mmol) and the solution refluxed overnight. The resulting precipitate was filtered and washed with ethanol to give a white solid. Recrystallization from methanol gave 1.07 g of small white crystals (95%). Mp = >360°C (slowly darkens above 200°C); ^{1}H NMR (trifluoroacetic acid, 250 MHz): 7.82 (s, 2H), 4.85 (s, 2H), 3.30 (dd, J=3.9,18 Hz); MS m/e (relative intensity): 186 ($M^{\oplus}$, 100%), 158 (29.7%).

2,6-Bis(phenylthio)bicyclo[3.3.0]octane-3,7-dione 18

Diisopropyl amine (17.17 g, 170 mmol) in 150 ml of dry THF was cooled to -78°C and n-butyl lithium (19 ml of a 9.125 M solution, 170 mmol) was added slowly *via* syringe. Dione 17 (4.8 g, 34 mmol) in 25 ml of THF was slowly added dropwise to the solution of base and the reaction was stirred at -78°C for one hour. The cooling bath was removed and the reaction stirred an additional 15 minutes. Diphenyl disulfide (37g, 170 mmol) in HMPA (30.7 g, 170 mmol) and 25 ml of THF

was added rapidly and the reaction stirred for two hours at room temperature. The reaction was quenched by pouring into a separatory funnel containing 250 ml of ether and 250 ml of 10% HCl. The organic layer was extracted with an additional portion of 250 ml of 10% HCl followed by washing with saturated sodium bicarbonate solution (1 x 40 ml) and saturated sodium chloride solution (1 x 200 ml). Drying over anhydrous sodium sulfate and removal of the solvent left an orange oil. The crude product was absorbed onto 20 g of silica gel and applied to the top of a column containing 250 g of silica gel packed with hexanes. When diphenyl disulfide was no longer detected in the eluate (TLC, silica gel, hexanes, R_f=1.0) the solvent was changed to ether whereupon a mixture of stereoisomers eluted (10.35 g). These isomers could be separated by column chromatogrphy on silica gel packed with benzene. The major stereoisomer (R_f=0.38) was collected as a bright yellow oil (7.35 g, 59.7%). An analytical sample was obtained by recrystallization from methanol as orange-pink flakes. Mp = 135-137^{0}C; IR (neat): 3055, 1735,1582 cm^{-1}; ^{1}H NMR ($CDCL_3$, 60MHz): 7.33 (m, 10H), 3.34 (d, J=5Hz, 2H), 2.83 (br s, 2H), 2.38 (dd, J=8,14 Hz, 4H).

Anal. Calcd for $C_{20}H_{18}O_2S_2$: C, 67.76; H, 5.12

Found: C, 67.33; H, 5.08

The other two stereoisomers isolated (TLC, silica gel, benzene, R_f=0.11 and 0.50) (1.55 g, 15%) gave very similar ^{1}H NMR data to that of 18.

4,8-Bis(dimethylaminomethylene)-2,6-bis(phenylthio)bicyclo[3.3.0]-octane-3,7-dione 19

Bis-sulfide 18 (7.35 g, 20.7 mmol) in 20 ml of dry THF was added to aminal ester 11 (1.5 g, 86.2 mmol) in 100 ml of dry THF. The reaction was stirred at room temperature until all the starting *bis*-sulfide was consumed (as monitored by TLC, silica gel, ether, R_f=0.38). This typically took three to four hours. The solution was poured into 500 ml of ether and swirled to precipitate a black oil. The resulting yellow solution was poured into 1000 ml of hexanes. Upon standing for one hour the product deposited itself on the sides of the container as an orange solid (7.5 g, 77%). This compound was used in the next step without further purification. An analytical sample was obtained by recrystallization from ethanol. Mp = 188-190^{0}C; IR (chloroform): 3015,

2923, 1669, 1570 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz): 7.50 (m, 4H), 7.26 (m, 8H), 3.30 (s, 2H), 3.28 (s, 2H), 3.00 (s, 12H).

4,8-Bis(phenylthio)-2,4,4a,6,8,8a-hexahydro-1,2,5,6-tetraazadicyclopenta[a,e]pentalene 20

Hydrazine hydrate (1.0 g, 20.0 mmol) was added to 2.0 g of *bis*-enamine 19 (4.3 mmol) in 100 ml of absolute ethanol and the solution refluxed for 36 hours. The solvent was evaporated under reduced pressure and the residue absorbed onto 10 g of silica gel. This was applied on top of a column containing 100 g of silica gel packed with ether:THF (60:40). The title compound eluted first and the solvent was removed to give a yellow solid. Washing the solid with small portions of ether removed the yellow coloration leaving 1.2 g of a white crystalline solid (70%). Mp = 140-142°C; IR (chloroform): 3345, 3055, 1582 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz): 7.53 (m, 4H), 7.26 (m, 6H), 6.53 (d, J=2 Hz, 2H), 6.33 (s, 2H), 3.16 (s, 2H), 2.1 (d, J=10 Hz, 2H); MS m/e (relative intensity): 402 ($M^{\oplus}$, 2.4%), 184 (23.7%), 110 (100%).

4,8-Bis(phenylsulfinyl)-2,4,4a,6,8,8a-hexahydro-1,2,5,6-tetreaza-dicyclopenta[a,e]pentalene 21

To an ice cold solution of 1.2 g of *bis*-pyrazole 20 (2.9 mmol) in 100 ml of methanol was added dropwise with rapid stirring 1.23 g of sodium periodate (5.8 mmol) dissolved in a minimum of water. The solution was allowed to warm to room temperature and stirred for 12 hours. The solution was filtered and the precipitate washed with 20 ml of methanol. The filtrate was concentrated, ethanol (20 ml) added and the solution evaporated to dryness. The residue was chromatographed on a column of silica gel packed with ether:acetone (50:50). The component with R_f=0.6 was collected and the solvent removed to yield 0.17g of a light yellow powder (13%). Mp = 170°C (dec.)(softens at 158°C); IR (chloroform): 3440, 3010, 1595, 1032 cm^{-1}, ^1H NMR (acetone d_6, 60 MHz): 6,4-7.8 (m, 12H), 4.4 (s, 2H), 3.0 (s, 2H).

1,5-Dihydro-1,2,5,6-tetraazadicyclopenta[a,e]pentalene 8

Bis-sulfoxide 21 (0.17 g, 0.39 mmol) was heated in 50 ml of

refluxing toluene for 15 hours. During this time the originally yellow solution slowly turned brownish-orange and solid deposited on the sides of the flask. The solution was evaporated to dryness and the residue was chromatographed on two 20 x 20 cm TLC plates (ether, R_f=0.22) to give 0.05 g of a light orange powder (70 %). Mp = >300^{0}C; IR (nujol): 3179, 1620, 1535, 1021, 813, 710 cm^{-1}, ^{1}H NMR (dimethyl sulfoxide d_6, 60 MHz): 7.26 (s, 2H), 7.0-7.8 (br, 2H), 6.15 (s, 2H); ^{13}C NMR (dimethylsulfoxide d_6, 62.9 MHz): 129.2, 129.0, 128.5, 123.0 116.5 116.0 115.5; MS m/e (relative intensity): 182 ($M^{\oplus}$, 100%), 154 (M-N_2, 12.6%); U.V. $_{max}$ (ethanol): 375 nm (ϵ = 750).

APPENDIX

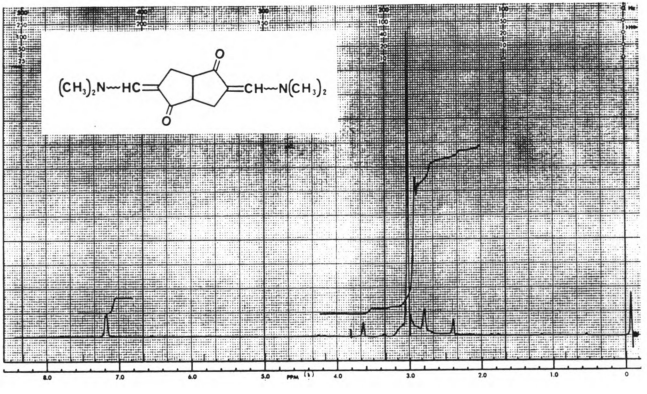

Figure A1: 60 MHz ^{1}H NMR spectrum of 3,7-bis(dimethylaminomethylene) bicyclo[3.3.0]octane-2,6-dione (14).

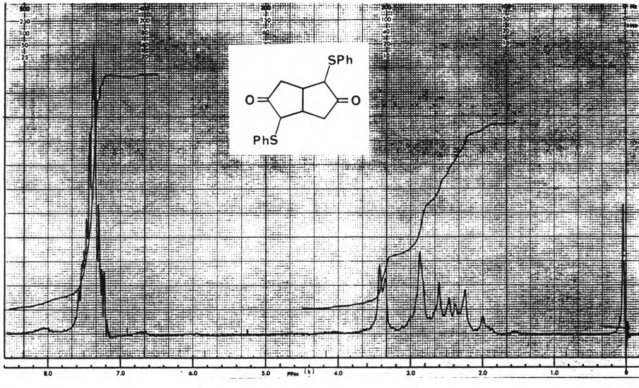

Figure A2: 60 MHz ^{1}H NMR spectrum of 2,6-bis(phenylthio)bicyclo[3.3.0]-octane-3,7-dione (18).

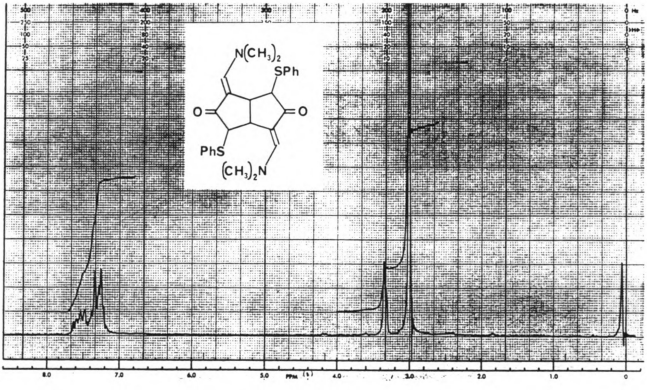

Figure A3: 60 MHz ^{1}H NMR spectrum of 4,8-bis(dimethylaminomethylene) 2,6-bis(phenylthio)bicyclo[3.3.0]octane-3,7-dione (19).

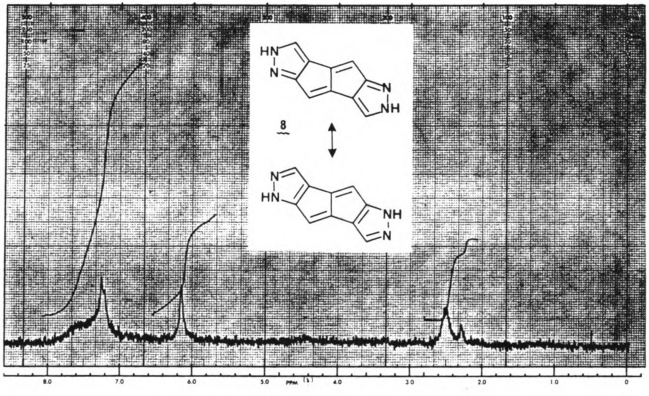

Figure A4: 60 MHz ^{1}H NMR spectrum of 1,5-dihydro-1,2,5,6-tetraaza-dicyclopenta[a,e]pentalene (8).

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