I. Photochemistry of Bicyclic Azoxy Compounds
II. Investigations on the Tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]-decane System

By

WILLIAM DAVID LOEHLE

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
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To Lucy

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

I. PHOTOCHEMISTRY OF BICYCLIC AZOXY COMPOUNDS
II. INVESTIGATIONS ON THE TETRACYCLO[5.3.0.$0^{2,6}$.$0^{5,8}$]-DECANE SYSTEM

By

William David Loehle

December, 1971

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Department of Chemistry

The Diels-Alder adduct of 3,5-dimethyl-4,4-diethylisopyrazole-1-oxide and 4-methyl-1,2,4-triazoline-3,5-dione was prepared. Heating the adduct in refluxing chloroform or neat to its melting point caused loss of nitrogen and water and formation of 6,8-dimethylene-7,7-diethyl-3-methyl-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione. In contrast, the adduct upon photolysis loses only nitrogen to give 6-methylene-7,7-diethyl-3,8-dimethyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione. The 4-phenyl-1,2,4-triazoline-3,5-dione adduct reacted similarly. The simplest mechanism for the photolysis reaction involves abstraction of a methyl hydrogen via a five-membered transition state by the azoxy oxygen and formation of an intermediate hydroxyazo compound which loses nitrogen to give the alcoholic product.

However, photolysis of azoxy-t-butane, which has nine

hydrogens available for such a five-membered transition state, fails to yield any of the olefinic or alcoholic products expected. To see if more precise geometric placement of the methyl and azoxy oxygen was required, two model compounds--1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene-2-oxide and 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo[2.2.1]-oct-2-ene-2-oxide--were synthesized. These have almost identical placement of the two necessary groups as the original azoxy compounds. However, upon photolysis, no alcoholic products were obtained, only tars.

The failure of these closely related model systems to react indicated that they were still significantly different from the original azoxy compounds. The most likely point of difference involves the two other nitrogens across the ring from the azoxy group. Involvement of these nitrogens in the reaction requires some sort of cross ring interaction. Such interactions through space of nonconjugated groups have been reported for other systems, and are usually identified by anomalies in their uv spectra. Uv data are presented to support such cross ring interaction in this system. Proof of the participation of the extra nitrogens in the photolysis reaction is not available, but is strongly suggested by the uv data and the failure of the model systems to react.

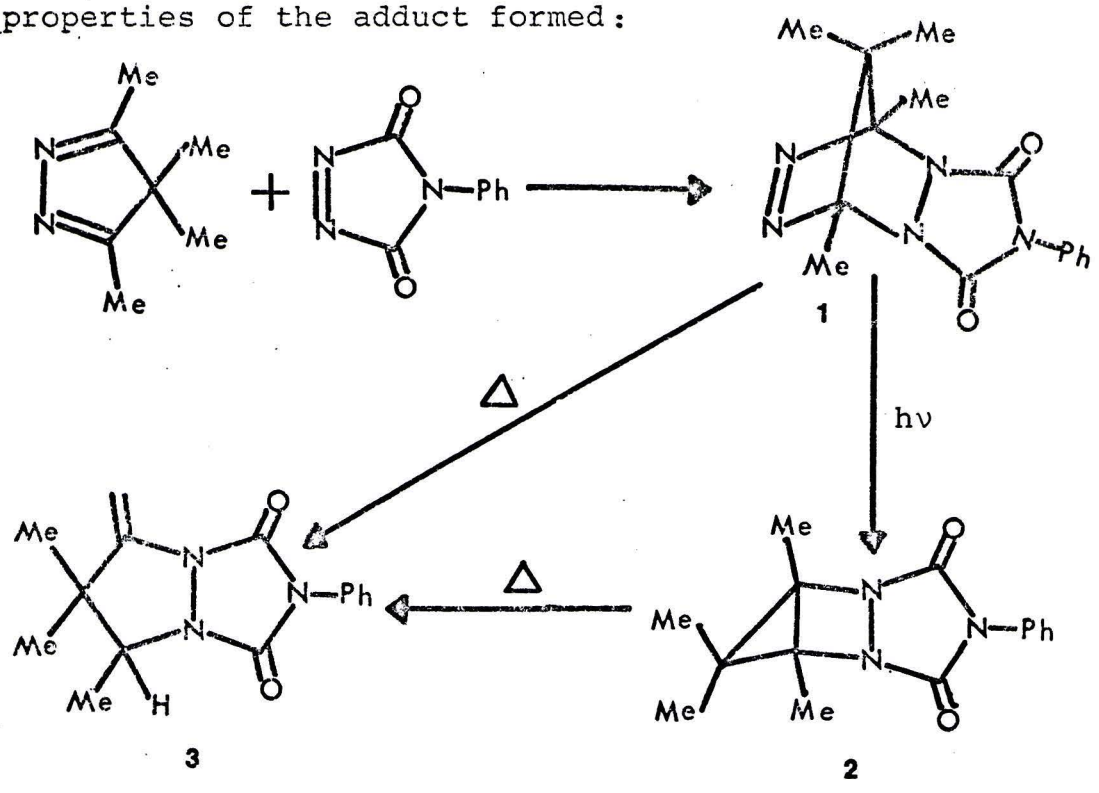
Although many tetracyclodecanes have been synthesized in recent years, the tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]decane system was unknown. We were interested in this system,

and in particular in the tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-3,9-diene, because of the facile Cope rearrangements that it should undergo. Three approaches to this system were tried. The first involved the 1,4-dehydrobromination of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane. Use of various strong bases resulted in no elimination products. The second approach involved the 1,4 debromination of 3-bromo-pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane. Again no elimination products were obtained. The final and successful approach involved zinc and acetic acid reduction of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]deca-7,10-dione to yield a derivative of the desired system--tetracyclo[5.3.0.$0^{2,6}$.-$0^{5,8}$]deca-4,9-dione. This was reduced to the diol with LAH but all attempts at double dehydration to give the desired diene were unsuccessful. Thus, there was success in preparing the new ring system, but none in preparing the diene derivative that was sought.

I. PHOTOCHEMISTRY OF BICYCLIC AZOXY COMPOUNDS

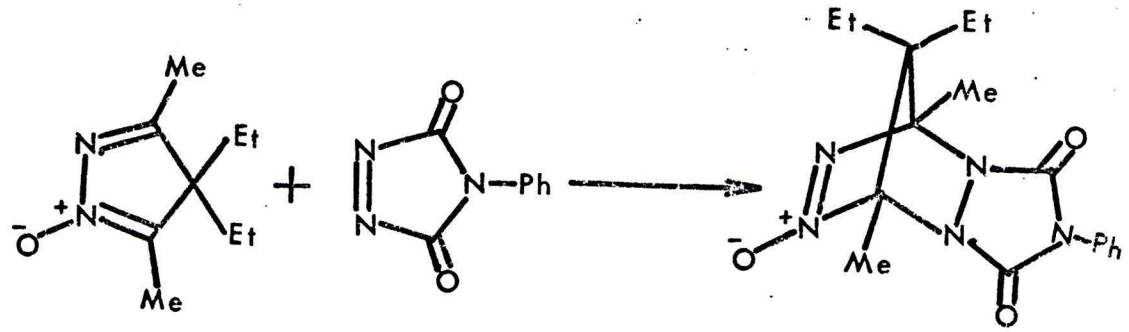
Introduction

Diels-Alder reactions utilizing azines as dienes have appeared only rarely in the literature. Early attempts gave only 2:1 adducts.[1a,b] Recently, however, tetrazines have found utility as dienes.[2a,b] Finally, azines themselves have been found to react with certain strong dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione.[3] Evnin and Arnold also investigated the thermal and photochemical properties of the adduct formed:



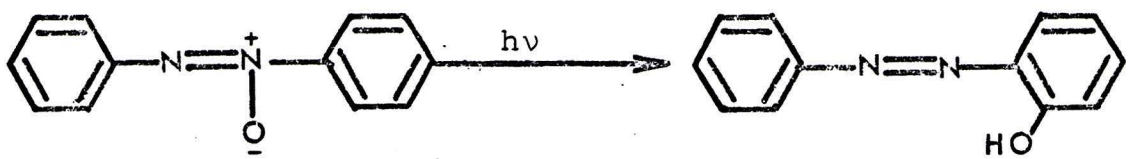
Azines have since been reported to react with pyrazoline-diones,[4] cyclopropene[5], and cyclobutadiene.[6]

Despite the increase in the use of azines as dienes, azine oxides have received little attention. The first successful use of azine oxides in Diels-Alder reactions was made recently by Williams.[7] This involved the use of a cyclic azine oxide (4) and the powerful dienophile phenyltriazolinedione:

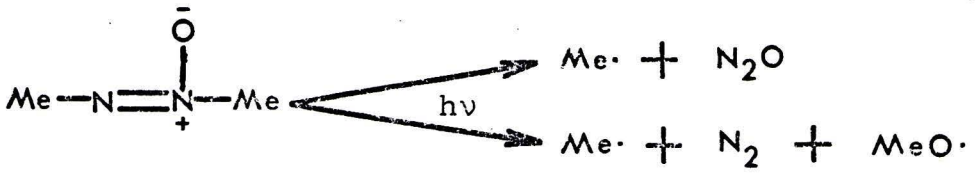


4 5

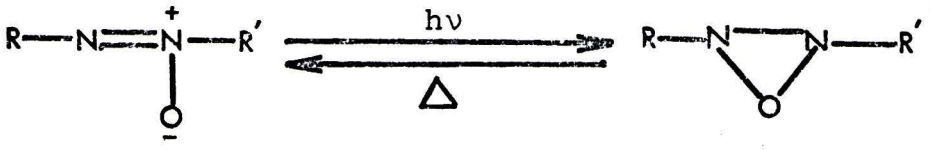
We were interested in the photochemical reactions that these adducts might undergo. The literature reports very little about the photochemical behavior of azoxy compounds. Most reports concern aromatic substituted azoxy compounds which have been known since 1903 to undergo a photochemical rearrangement:[8]



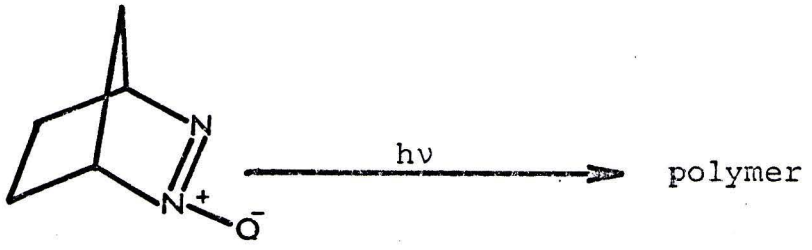
The work on aliphatic azoxy compounds is limited to two areas. The first involves azoxy methane which yields nitrogen, nitrous oxide, methane and ethane, via two postulated initial reactions.[9]



The other involves the reversible formation of oxadiaziridines:[10]



Even this reaction, however, was not observed for the only bicyclic azoxy compound for which data are available:

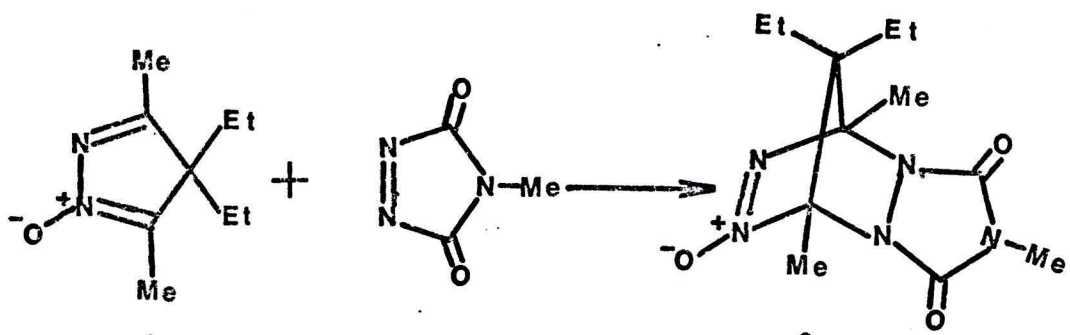


Thus, from the little information that is available, it appears that the photolysis of aliphatic azoxy compounds is not very productive, except in the way that azo compounds are reactive; i.e., cleavage of the carbon nitrogen bonds.

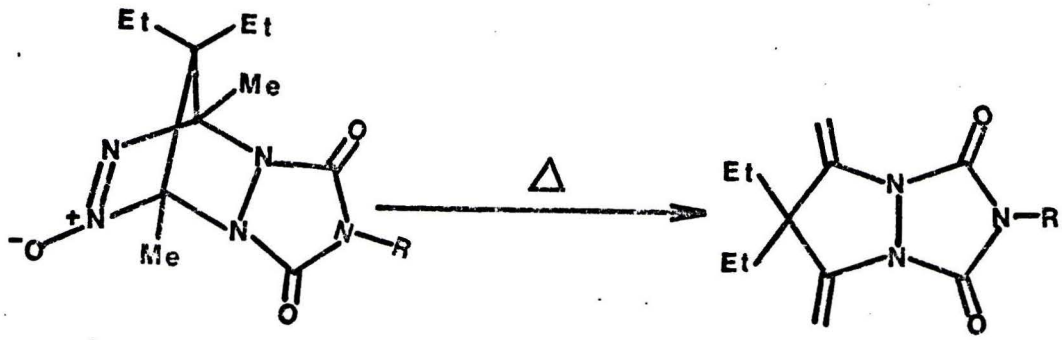
We were interested in seeing whether the unusual azoxy compounds we had obtained via the Diels-Alder reaction of azine oxides were more productive photochemically due to the presence of the other heteroatoms in the molecules.

Preparation and Reactions of Polycyclic Azoxy Compounds Containing Two Cross Ring Nitrogens

Following the work of Williams,[7] we prepared the Diels-Alder adduct of the cyclic azine oxide 4 and 4-methyltriazolinedione. Thus, addition of methyltriazolinedione in methyl chloride to the azine oxide in the same solvent at 0° produced a 95% yield of a white solid (6), mp 103-104°(dec.). Structure was confirmed by elemental analysis, and the mass spectrum with a parent peak at m/e 281. Other data were similar to those of the adduct of Evnin and Arnold. (See table of nmr data.)



Preliminary work by Williams[7] had shown that adduct 5 decomposed thermally with loss of nitrogen and water to give a diene (7).



5, R=Ph

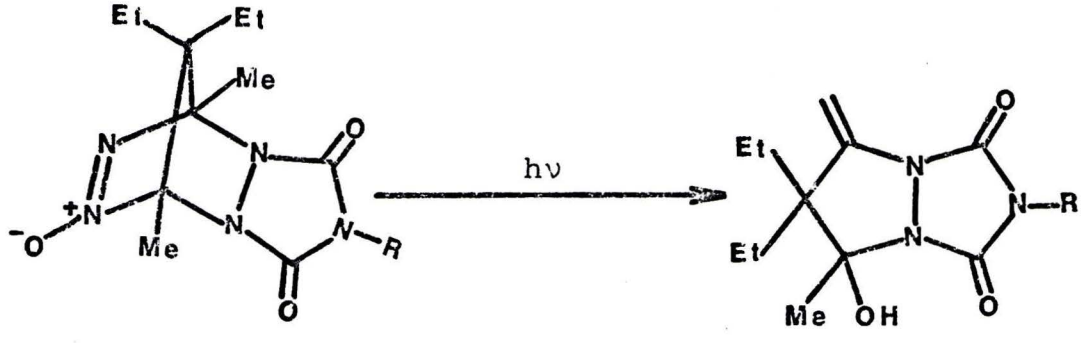
6, R=Me

7, R=Ph

8, R=Me

We obtained similar results with 6, either in refluxing chloroform or upon heating to the melting point in a neat state.

However, it was the photochemical reactions that were of primary interest to us. Thus, photolysis of the adducts 5 and 6 using a 450 watt medium pressure lamp and a Pyrex filter with benzene as a solvent proceeded smoothly to yield solid products in yields of 65% and 85%, respectively:



5, R=Ph

6, R=Me

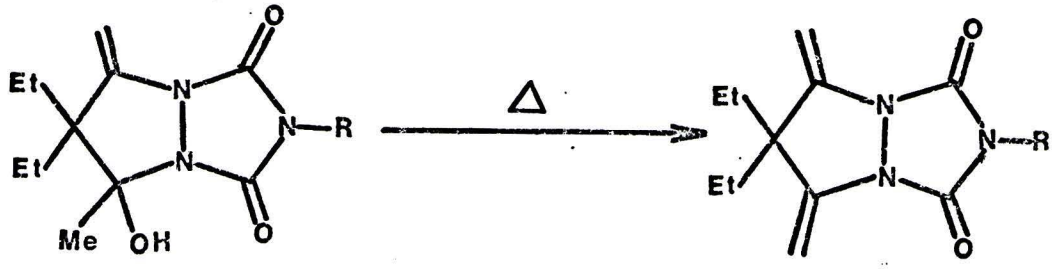
9, R=Ph

10, R=Me

The elemental analysis and mass spectral data were con-

sistent with the proposed structures (9,10) involving loss of nitrogen from the parent molecule. An ir absorption at 3400 cm^{-1} and nmr spectra similar to the respective dienes 7 and 8, as well as the olefin 3 produced from the adduct of Evnin and Arnold, completed the structural identifications. (See table of nmr data, especially the absorptions for the vinyl protons in each case.)

Heating the alcohols neat to 150° and 180°, respectively, yielded the dienes 9 and 10:



7, R=Ph

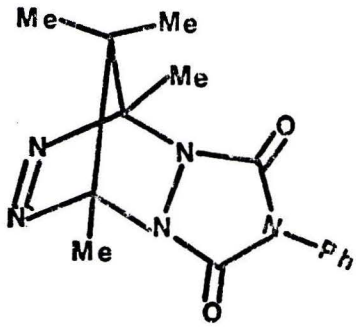
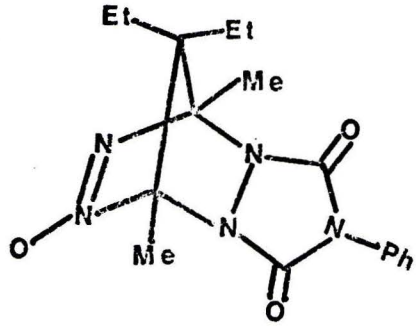
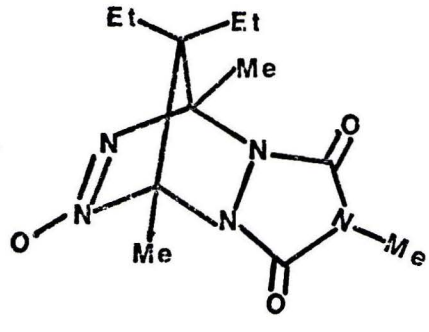
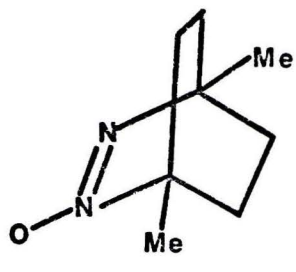
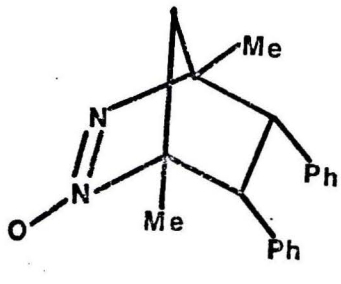
8, R=Me

9, R=Ph

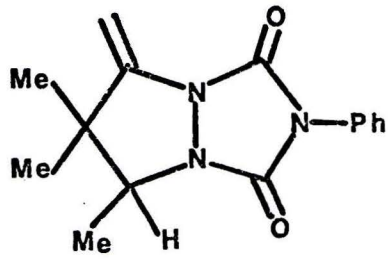
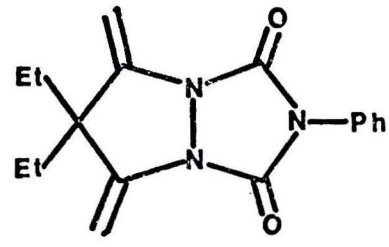
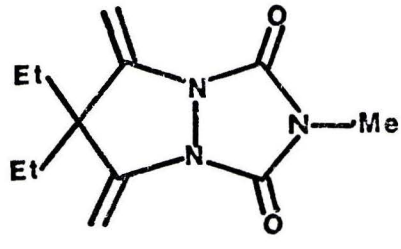
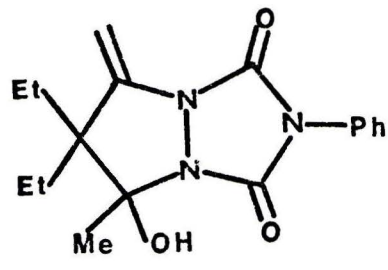
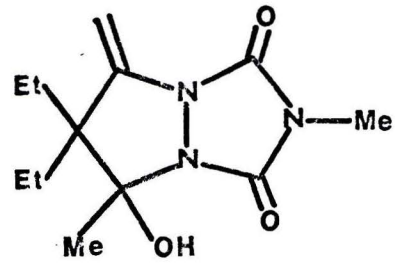
10, R=Me

However, refluxing either alcohol in chloroform or in chloroform containing a catalytic amount of acid resulted in no reaction and recovery of all starting material. This failure to react under the conditions that led to formation of the dienes 7 and 8 from the original azoxy compounds 5 and 6 would seem to rule out these alcohols as intermediates in the thermal diene production.

Table I. Nmr Data

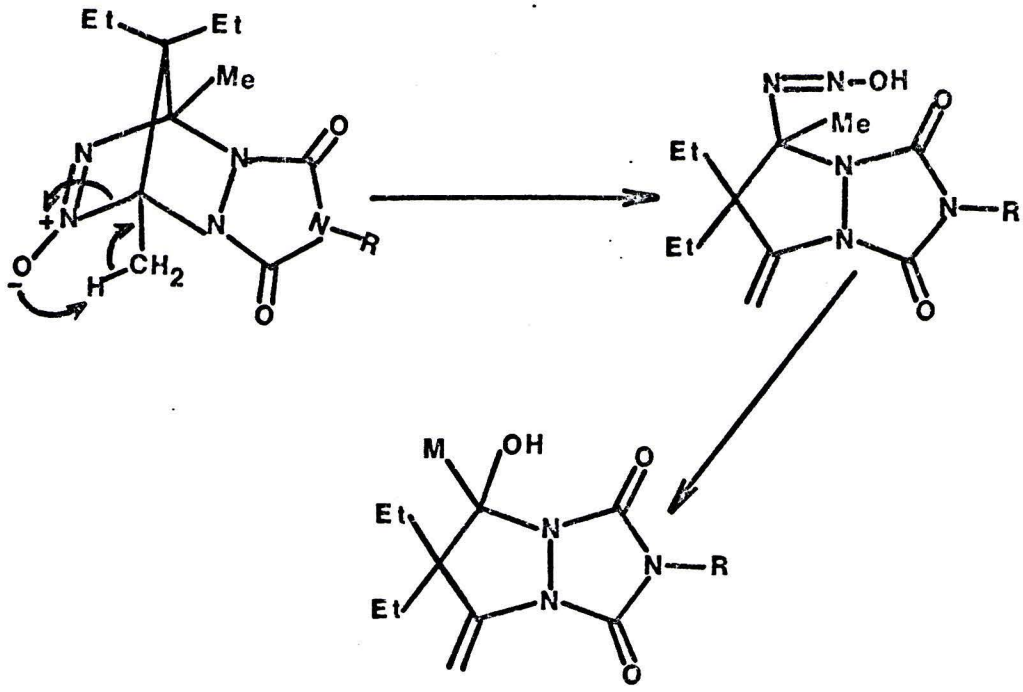
Compound	Number	τ	Mult.	Area
	1	2.60 7.82 8.93 9.47	s s s s	5 6 3 3
	5	2.72 8.00 8.03 8.20-9.25	m s s m	5 3 3 10
	6	7.05 7.98 8.02 8.00-9.25	s s s m	3 3 3 10
	13	8.28 8.55 8.60	m s s	8 3 3
	25	2.97 5.97 6.01 7.79 7.82 8.25 8.50	m s s s s s s	10 1 1 1 1 3 3

I continued

Compound	Number	τ	Mult.	Area
	3	2.20	m	5
		4.66	d	1
		5.50	d	1
		6.25	q	1
		8.61	d	3
		8.76	s	3
		8.82	s	3
	7	2.47	m	5
		4.42	d	2
		5.42	d	2
		8.19	bq	4
		9.03	bt	6
	8	4.55	d	2
		5.55	d	2
		6.88	s	3
		8.25	bq	4
		9.13	bt	6
	9	2.54	bs	5
		4.41	d	1
		5.55	d	1
		5.73	bs	1
		8.20	s	3
		8.28	m	4
		9.09	m	6
	10	4.55	d	1
		4.95	bs	1
		5.60	d	1
		7.00	s	3
		8.14	s	3
		8.00-8.60	m	4
		8.70-9.20	m	6

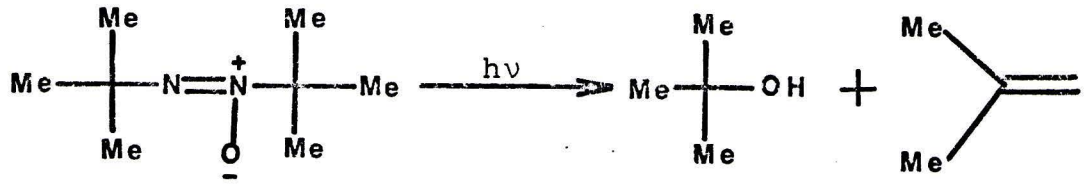
Preparation and Reactions of Azoxy Compounds Without Extra Nitrogens

With the results of these photolyses in hand, we turned to exploring the scope of this new found reaction. A quick glance at the products and reactants suggested a mechanism involving abstraction of a proton by the oxygen and subsequent loss of nitrogen from the intermediate hydroxyazo compound with recombination of the hydroxyl group and the ring system:



The main requirement for this mechanism would seem to be the availability of hydrogen to form a five-membered transition state with the azoxy oxygen. One readily available compound that met this requirement was 11,

azoxy-t-butane.[11] Application of the proposed mechanism would lead to isobutene and t-butanol:

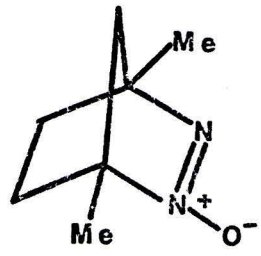


11

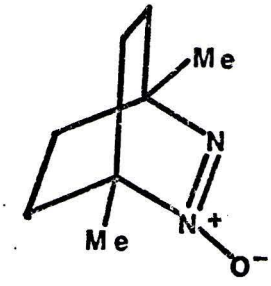
Photolysis of azoxy-t-butane with a 450 watt lamp via quartz led to the disappearance of all starting material in three hours as determined by tlc analysis. The solution had turned a deep brown and a polymeric solid covered the walls of the reaction vessel. Nitrogen gas was bubbled through the solution during the reaction, venting through a dry ice cooled trap. Analysis of the trap contents by nmr spectroscopy and mass spectrometry showed only solvent and no isobutene.

The failure of this compound, which has a maximum number of hydrogens in the right position to form the five-membered transition state, indicates that more is involved in the actual rearrangement than we had first believed. One obvious extension would be to assume that the rigid geometry present in the original tricyclic system is also necessary, along with an available hydrogen, for the reaction to take place. To test this, we decided to synthesize some bicyclic azoxy compounds with methyl groups in the same rigid position that they occupy in the original compounds.

Two different systems were decided upon--the bicyclo-[2.2.1] system (12) and the bicyclo[2.2.2] system (13):

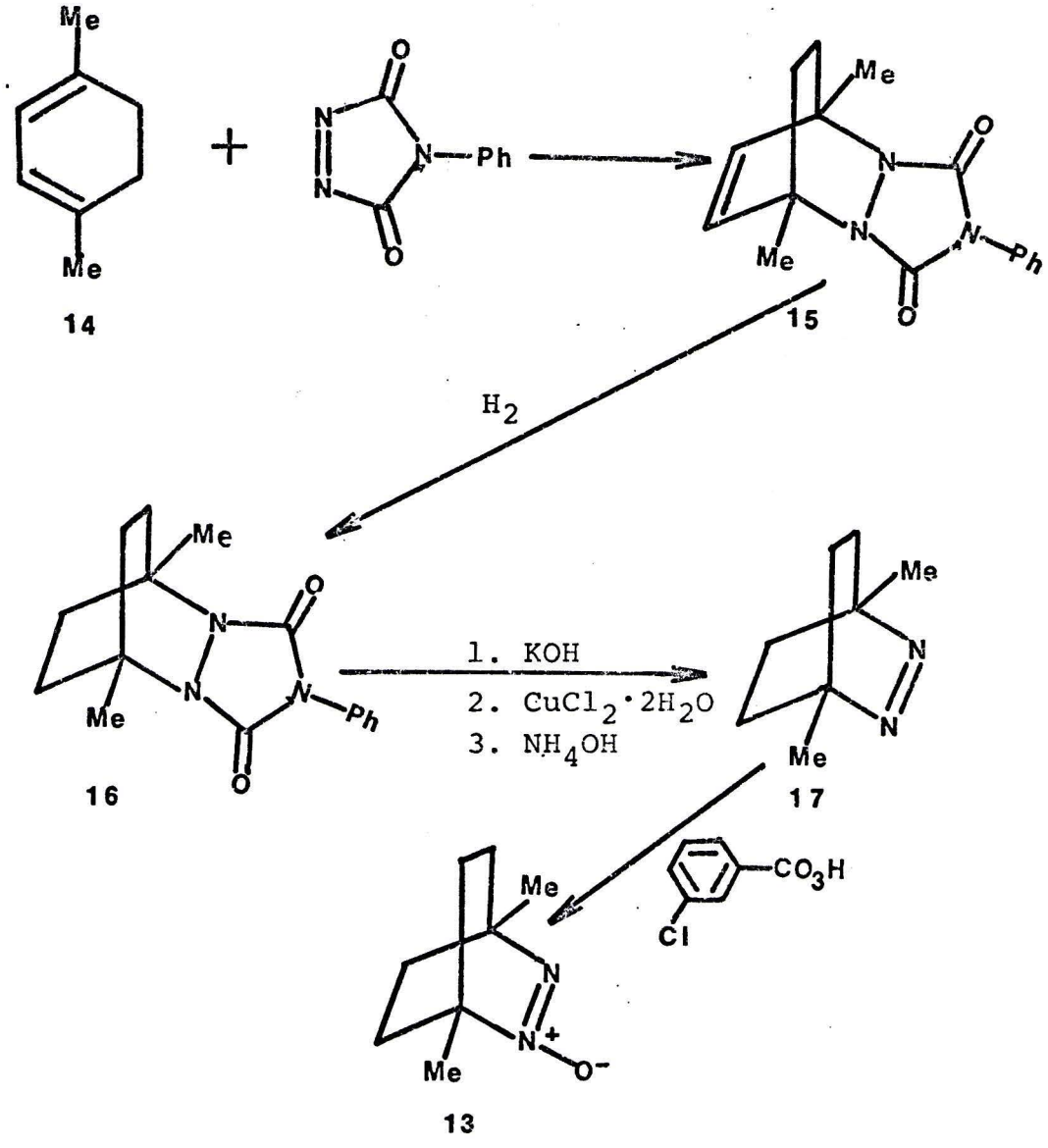


12



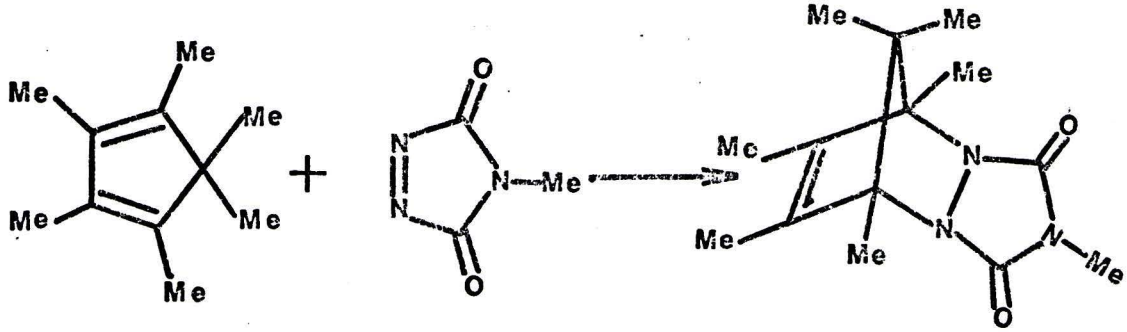
13

The [2.2.2] system proved to be the easiest to make. Entry into the system was obtained via the hydrolysis of the triazolinedione adduct of the 1,4-dimethyl-1,3-cyclohexadiene (14),[12] and oxidation of the resulting azo compound to the desired azoxy compound. Reaction of the diene with the phenyltriazolinedione yielded the 1:1 adduct (15) in 50% yield. Hydrogenation over Pd/C yielded 16 in 90% yield. Its nmr spectrum showed no vinyl peaks. Hydrolysis was accomplished using potassium hydroxide in ethylene glycol at 170° under nitrogen. Work-up with cupric chloride dihydrate yielded a red copper complex in 63% yield, which upon decomposition with ammonium hydroxide yielded azo compound 17 in 95% yield. Oxidation with m-chloroperbenzoic acid yielded azoxy compound 13 in 80% yield. All spectral and analytical data were consistent with the azoxy structure. For example, the nmr spectrum revealed two singlets at τ8.55 and 8.60:



The synthesis of the bicyclo[2.2.1] system proved more difficult. Preparation of the 1,4-dimethyl-1,3-cyclopentadiene analogous to the previous case was not possible due to the ease of rearrangement in the cyclopentadiene series. Instead, to stop any rearrangements, we decided to make the hexamethylcyclopentadiene 18.[13] This reacted readily with the methyltriazolinedione to give 1:1 adduct 19 in 98% yield. However, all attempts to hydrogenate the double bond failed. Introduction of

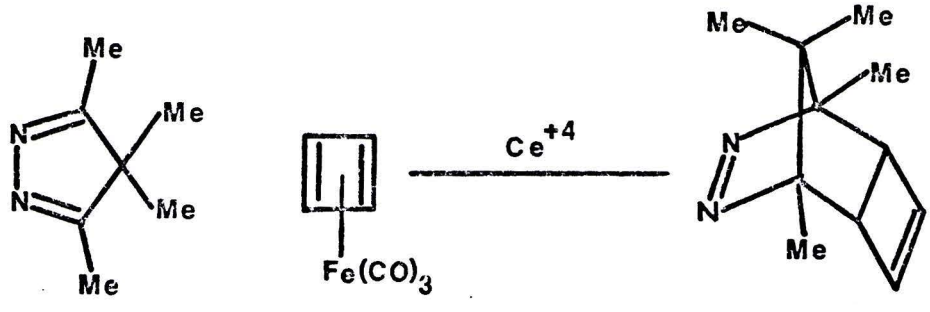
the azo linkage without reduction of this double bond would lead to retro Diels-Alder reaction with production of hexamethylcyclopentadiene and nitrogen. Thus, this route to a [2.2.1] system was abandoned:



18 19

The failure to hydrogenate is evidently due to the presence of the methyl group hanging over the azo group coupled with the urazole ring system under the azo group. This hindrance to approach of the double bond to the catalyst causes the reaction to fail.

With the failure of this approach, another direction was tried, based on a recent report by Paquette that cyclobutadiene reacts with azines to yield Diels-Alder adducts:[14]

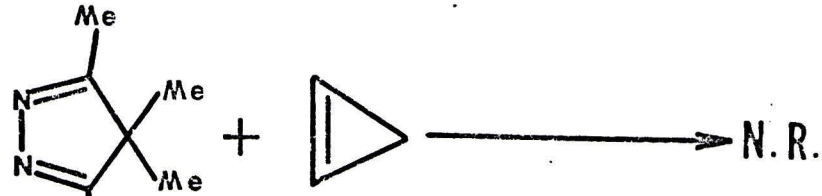


20

Oxidation of the appropriate adduct should give the desired azoxy compound. However, when we tried the reaction

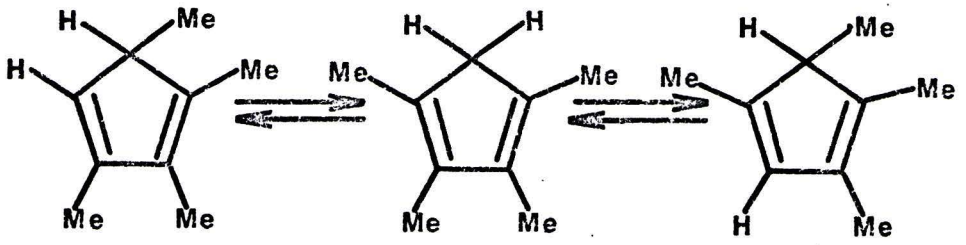
with 3,4,4,5-tetramethylisopyrazole (20),[15] the adduct was formed in very poor yield, about 15%, and was difficult to separate from impurities. Hydrogenation of the cyclobutene moiety and oxidation with m-chloroperbenzoic acid gave a solid with mass and nmr spectra consistent with successful oxidation, but which could not be purified enough to get a satisfactory elemental analysis. Since precious cyclobutadiene was being wasted, we abandoned this route also.

Another attempt involved the reaction of cyclopropene with azines.[5] However, the tetramethyl azine 20 gave only starting material:



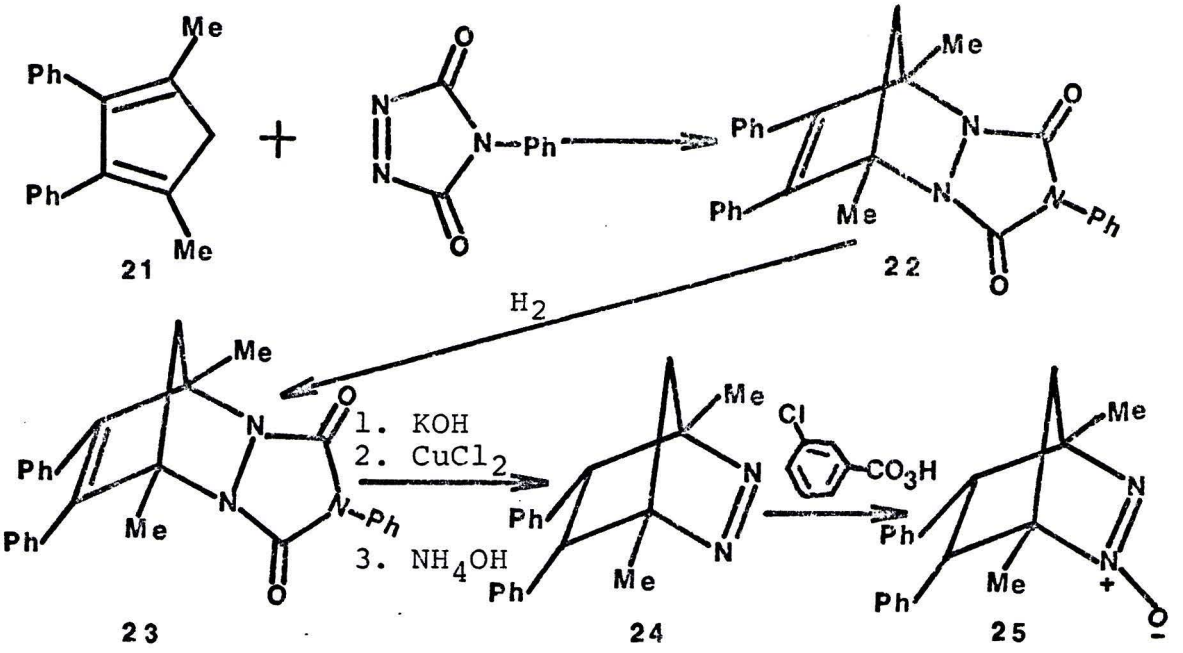
20

Since each alternative approach had also failed, we returned to our original approach, but modified it so as to avoid the problems that had been encountered with the hexamethylcyclopentadiene. Since the main problem seemed to be in the methyl groups on the bridging carbon, the obvious solution seemed to be to eliminate them and use the 1,2,3,4-tetramethyl-1,3-cyclopentadiene instead. However, this diene cannot be synthesized in pure form due to the facile rearrangement that can occur to give an equilibrium mixture of the three possible tetramethyl isomers.[16]



Separation of one isomer by glpc is possible, but it quickly isomerizes to the equilibrium mixture from which it was isolated.

However, if two of the methyl groups are replaced by phenyl groups, the preferred isomer is the 1,4-dimethyl-2,3-diphenyl-1,3-cyclopentadiene 21, the one we needed.[17] Reaction of this diene with phenyltriazolinedione yielded the 1:1 adduct 22 in 82% yield. One interesting point is the fact that the white adduct becomes a red solution upon melting due to a retro Diels-Alder reaction occurring to give back the red triazolinedione:

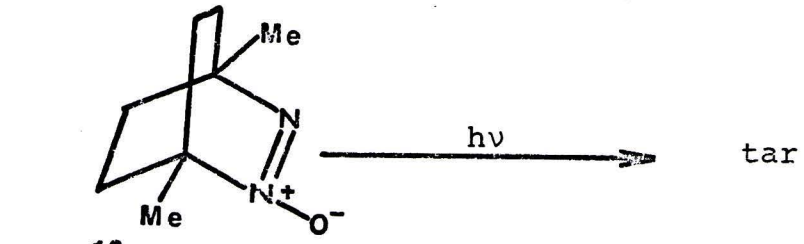


Without the interfering methyl group over the double bond, the hydrogenation prodeeded, but not without difficulty. Reaction with hydrogen using a Pd/C or Pt/C catalyst and a pressure of 50 psi resulted in a more extensive reaction than simple reduction of the double bond as shown by the disappearance of the methyl singlet in the nmr spectrum. However, reaction with a Pt/C catalyst and 15 psi of hydrogen gave the desired product 23 in 95% yield. The fact that this solid does not turn red upon melting indicates that the double bond has gone. The nmr spectrum also revealed a peak at τ6.29 with the area of two hydrogens.

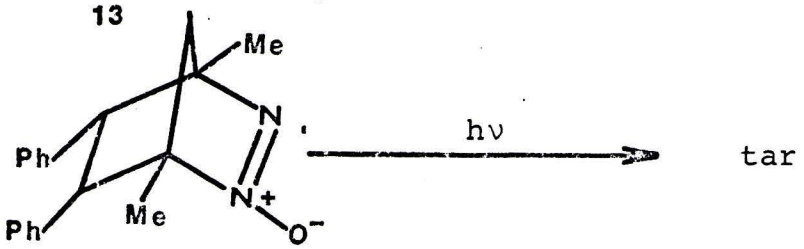
The hydrolysis of 23 proceeded smoothly under the conditions worked out earlier. Thus, heating at 170° in ethylene glycol with potassium hydroxide and a cupric chloride work-up led to a rusty red solid in 82% yield. Treatment with a concentrated ammonium hydroxide solution produced the azo compound 24 in 74% yield. The uv spectrum contained a typical azo absorption at 353.5 mμ (ε250) and a shoulder at 341 mμ.

Oxidation of the azo compound in methylene chloride with m-chloroperbenzoic acid yielded the desired azoxy compound 35 in 95% yield. Spectroscopic and analytical data were consistent with the structure; i.e., the ir spectrum contained a strong absorption at 1515 cm^{-1}; the uv spectrum contained a peak at 231.5 mμ (ε4,804) as a shoulder on end absorption; and the nmr spectrum of the methyl groups had two singlets at τ7.79 and 7.82, consistent with the introduction of one oxygen atom.

Now that we had succeeded in synthesizing the two desired model systems with azoxy groups and methyl groups in the precise locations that they occurred in the original azoxy compounds, photolyses of the azoxy compounds 13 and 25 were run in methylene chloride using a 450 watt medium pressure lamp via quartz:



13



25

In both cases the solution turned deep brown. Tlc monitoring of the reactions indicated complete disappearance of the starting material in four hours. Evaporation of the solutions gave dark oils. Chromatography on silica gel with methylene chloride and ether gave two fractions of dark oils. Both fractions in each case, however, had no definite peaks, only broad mounds of absorptions in their nmr spectra, possibly indicative of polymeric material. No indication was found that any of the alcohols that would have been expected if the proposed mechanism had been operative were present.

In addition, the azoxy compounds 13 and 25 showed a much greater thermal stability than had the original

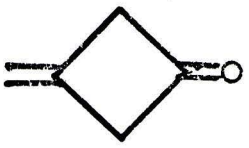
azoxy compounds. Thus, heating the azoxy compounds to 220° gave no nitrogen evolution and no volatile products. This also indicates that these azoxy compounds have properties different from the original ones.

Discussion

The failure of these azoxy compounds to react according to the proposed mechanism means that they are still basically different from the original azoxy compounds. There are several possible explanations for this difference in the two groups of azoxy compounds. The most reasonable one involves the two extra nitrogens across the ring in the original azoxy compounds. The third nitrogen and the two carbonyl groups in the urazole moiety are also possible considerations. The influence of any of these groups on the azoxy linkage would involve an interaction through space between nonconjugated groups.

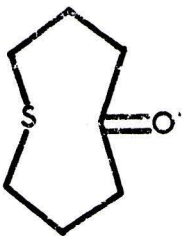
Such interactions have been known for some time, and are frequently identified by anomalies in the uv spectra of the compounds involved. In a recent review on this phenomenon,[18] two distinct types of interaction were recognized.

The first, called transannular conjugation, occurs when the groups are nonconjugated in the classical sense, but are suitably oriented so that there can be orbital overlap in the usual pi fashion; i.e., parallel orbitals. In these cases the uv spectra are similar to those of normally conjugated compounds; that is, a strong 210-260 mμ band for carbonyls:



λ 214 mμ

ε 1500

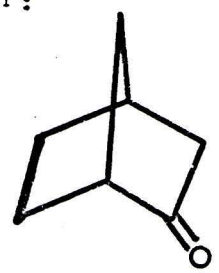


λ 238 mμ

ε 2538

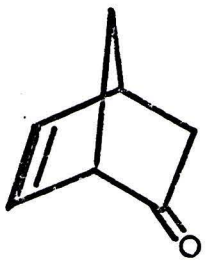
This is called a photodesmotic band (Greek for "link caused by light") because the transition is believed to involve a weak bond in the excited state.

The second type is called homoconjugative and involves orbital overlap in a crosswise manner, that is, partially sigma in character. For carbonyl groups the result is an increased $n \rightarrow \pi^*$ band and a shift to longer wavelength:



λ 295 mμ

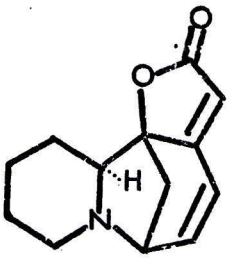
ε 27



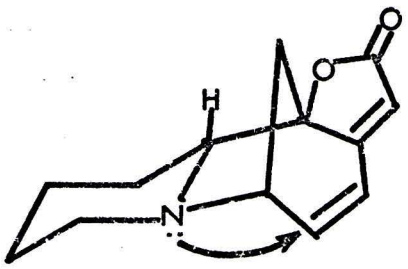
λ 300 mμ

ε 292

Most of the reported homoconjugative interactions involve carbonyl and olefin groups. Recently, however, several reports of interaction between the lone pair on nitrogen and olefins have been made. The first of these involved two isomeric alkaloids--phyllochysine (26) and securinine (27):[19]



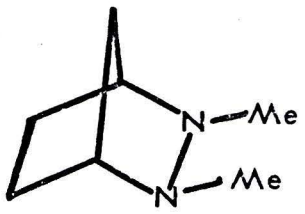
26



27

In ethanol a long wavelength absorption appears at 305 and 325 mμ, respectively. This band is absent in an acidic chloroform solution. This is interpreted as meaning that an interaction occurs between the lone pair on nitrogen and the dienone system which is absent when the lone pair is tied up by the acidic solution.

The second report concerns the 2,3-diazabicyclo-[2.2.1]hep-5-ene system.[20] For the N,N dimethyl compound 28 a peak appears in the uv spectrum which exhibits a blue shift upon going to a less polar solvent, indicative of an $n \rightarrow \pi^*$ interaction. Since the only available n electrons are on the nitrogens and the only pi system across the ring, this is interpreted as evidence for a cross ring homoconjugative interaction between these nitrogens and the double bond:

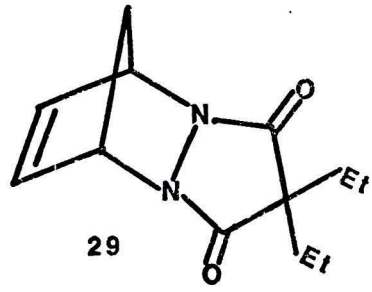


28

Uv data for compound 28

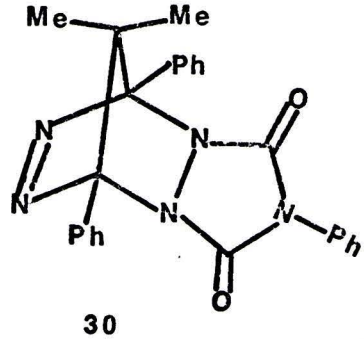
EtOH	Dioxane	Cyclohexane
λ 242 mμ	λ 263 mμ	λ 266 mμ
ε 580	ε 600	ε 680

The bicyclic adduct of pyrazoline and cyclopentadiene, 29, has also been reported to have uv spectra indicative of a similar cross ring interaction:[21]



29

Interaction between the lone pair on nitrogen and the cross ring nitrogen double bond also exists, as evidenced by the long wavelength uv spectra reported for the tetraazabicyclo[2.2.1]heptene (30) system:[3]

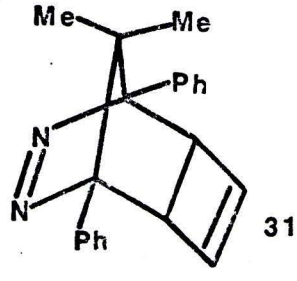


30

λ 400 mμ

ε 562

The corresponding diazabicyclo[2.2.1]heptene (31) has a much different spectrum despite having the same type of azo chromophore:[14]

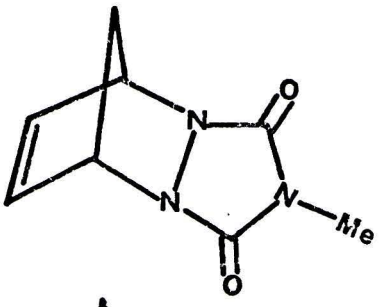
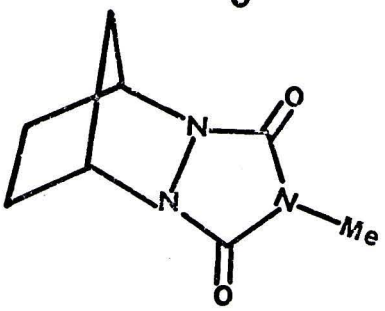
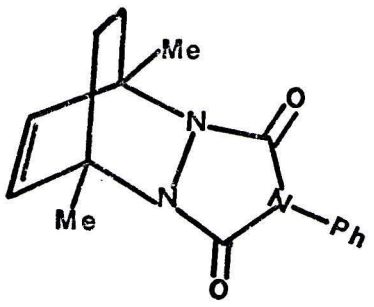
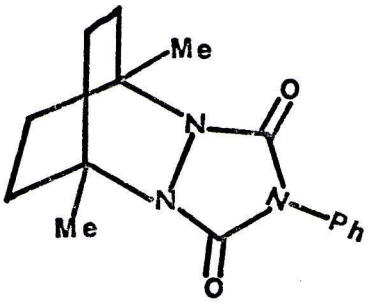
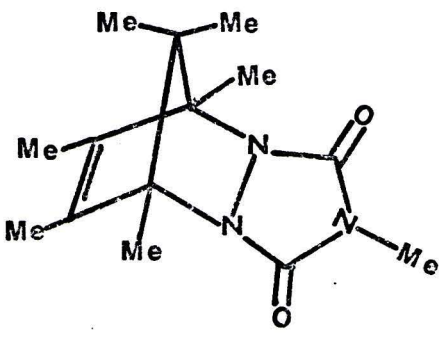


31

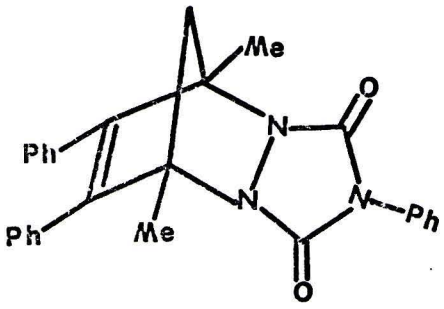
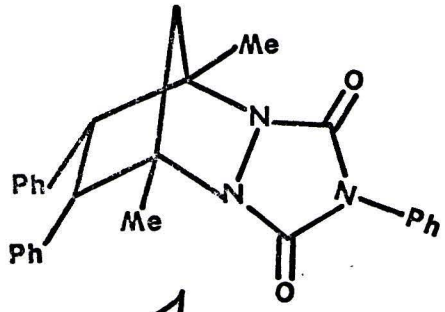
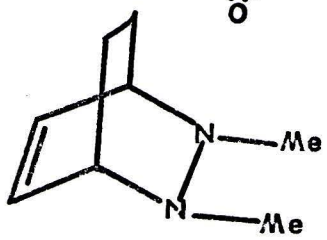
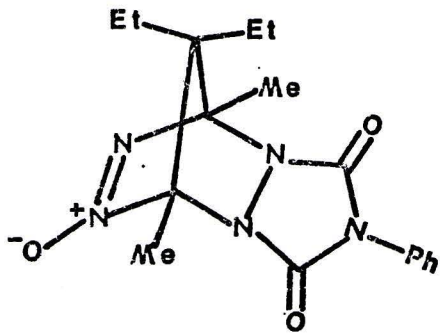
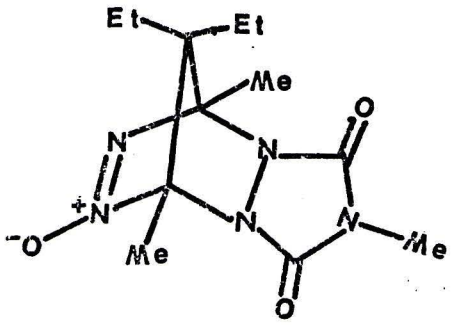
λ 343 mμ	λ 353 mμ
ε 64	ε 64

The shift to longer wavelength and the large increase in intensity of the absorption in going from 31 to 30 strongly suggests a homoconjugative type of interaction between the lone pairs on nitrogen and the azo pi system.

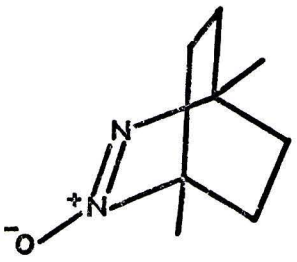
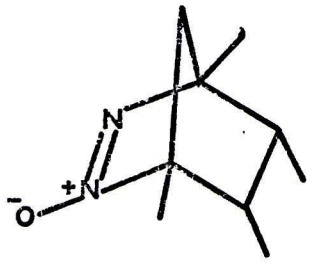
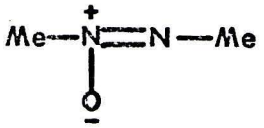
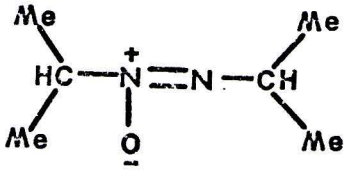
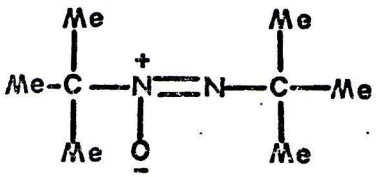
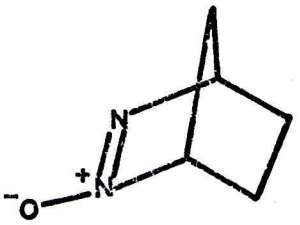
Table II. Uv Data

Compound	Number	Solvent	λ	ε
	32	Ethanol	217 248	2,070 Shoulder
	33	Ethanol	227	3,826
	15	Ethanol	219 244	11,040 Shoulder
	16	Ethanol	217	12,900
	19	Ethanol	221 273	11,310 Shoulder

II continued

Compound	Number	Solvent	λ	ε
	22	Ethanol	222	28,410
			260	11,170
			273	Shoulder
	23	Ethanol	216	22,820
	34	Ethanol	243	361
		Cyclohexane	263	400
	5	Ethanol	212	15,600
			314	926
		Cyclohexane	221	15,200
			317	720
	6	Ethanol	231	7,220
			268	Shoulder
			314	830

II continued

Compound	Number	Solvent	λ	ε
	13	Ethanol	230 287	6,420 70
	25	Ethanol	231.5	Shoulder
	35	Ethanol	217 274	7,250 44
	36	Ethanol	220.5 278	6,920 53
	11	Ethanol	220 282	5,025 26
	37	Ethanol	228	6,000

From the data presented in the table it is possible to demonstrate that interaction between the lone pair on nitrogen and the cross ring olefinic pi system also occurs when the nitrogens are in a urazole ring. Thus, the data for 32, 15, and 19 show a shoulder at higher wavelength in addition to the basic urazole low wavelength absorptions. This extra absorption is at much too long a wavelength to be accounted for by the olefin itself as neither norbornene nor bicyclo[2.2.2]octene have absorptions this high. Also, for the two compounds 32 and 15 which can be reduced to 33 and 16, this extra absorption disappears. This all indicates that a cross ring interaction is responsible for this absorption.

Although all of the literature references for cross ring interaction between nitrogens and double bonds involve bicyclo[2.2.1] systems, the data for 34 show that it exists in bicyclo[2.2.2] systems as well. In fact, the data for 34 are almost exactly the same as the data for 21, the analogous bicyclo[2.2.1] system.

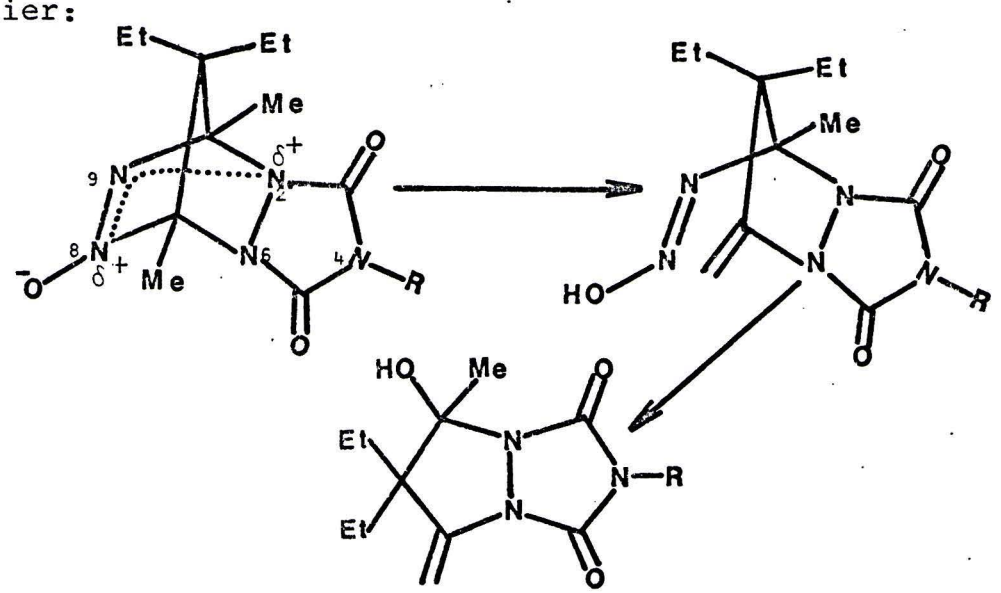
Now that we have shown that this cross ring interaction phenomenon occurs in bicyclo[2.2.2] and [2.2.1] systems, between urazole nitrogens and double bonds, and between nitrogens and azo pi systems, we turn to the question of urazole nitrogens and azo pi systems. The data for some typical azoxy absorptions are given in the table, numbers 35,36,11, and 37. All of these have a major peak at 217-228 mμ, which is the $\pi \rightarrow \pi^*$ peak. In

addition, most of these compounds show a second and much weaker peak at 272-282 mμ, assigned to the n → π* peak. The two model compounds that we synthesized, 13 and 25, show this same pattern of dual absorptions except that the second one is hard to see due to its small intensity and the long tail of the larger peak as it moves to higher wavenumbers in the rigid system. Thus, only 13 has a shoulder for the second absorption.

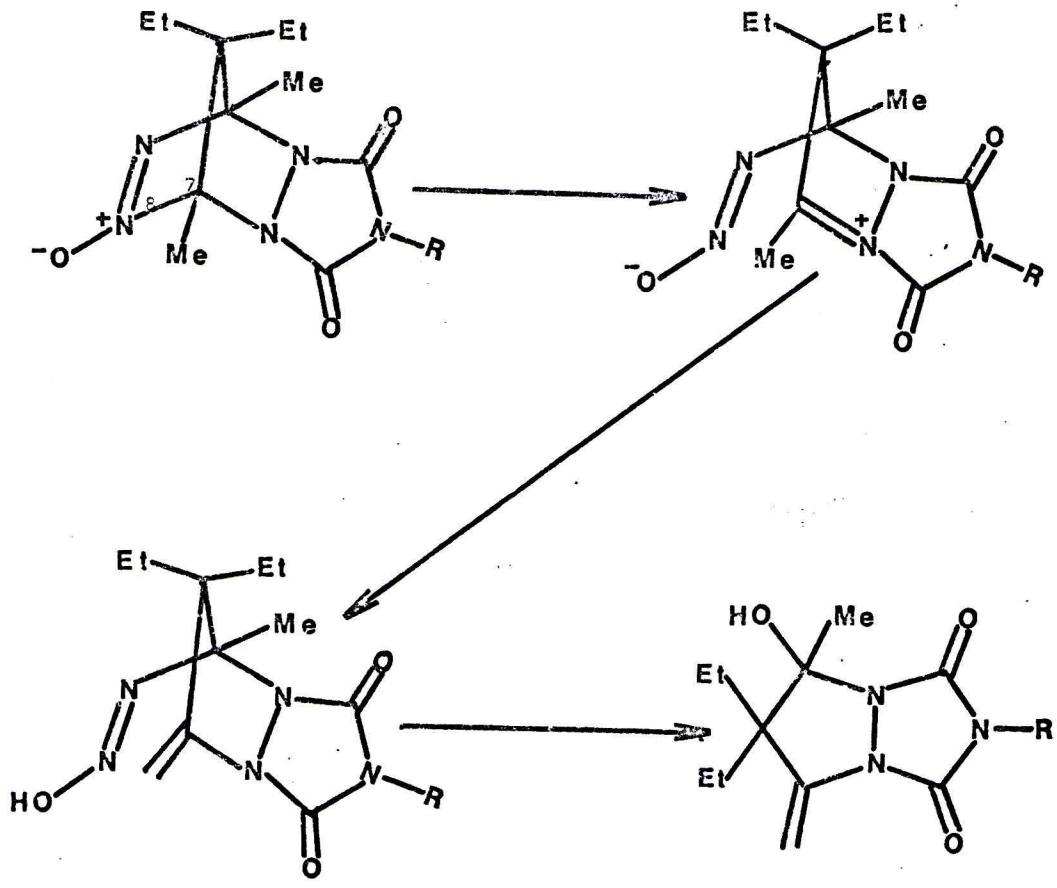
However, the picture changes completely for the two Diels-Alder adducts that we synthesized (5 and 6). Each one shows typical low wavelength urazole absorption and a second weaker absorption at very long wavelength. We believe that these absorptions near 314 mμ are n → π* azoxy absorptions. As such, they are shifted some 30 or 40 mμ further than normal and also are some 20 times more intense than normal. This shift to longer wavelength and increase in intensity points quite convincingly to a cross ring interaction between the two cross ring urazole nitrogens and the azoxy pi system. The shift and increase in intensity very closely parallel those found for the interaction of the urazole nitrogens with the cross ring azo pi system in compounds 30 and 31 as shown earlier.

We believe that this interaction is borne out by the photolytic reactions of the tetraaza compounds which have a much different type of reactivity than their diaza counterparts. Thus, we feel that the formation of the alcohol and diene products is a direct result of the

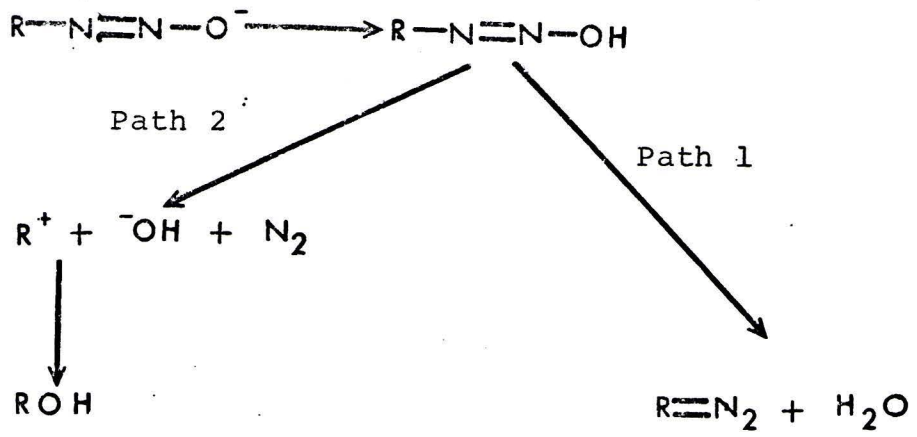
participation of the lone pair on nitrogen across the ring with the azoxy linkage. The fact that it does occur seems sure, but the exact nature of the interaction is much more in doubt. In accordance with the mechanism that we drew originally, there could be partial bonding or electron donation from nitrogen 2 to nitrogen 9 across the ring with a Norrish Type II process occurring as we showed earlier:



However, there is another very real possibility which involves no need to invoke cross ring interactions, but rather a Norrish Type I scission of the 7-8 bond with the positive charge spread to the neighboring nitrogen, followed by a hydrogen abstraction and then decomposition of this hydroxyazo compound to the product alcohol.[22] This would explain the need for the extra nitrogens in the system without using the cross ring interaction:



Either mechanism leads eventually to a hydroxyazo compound. These are well known intermediates in the synthesis of diaza compounds. For example, treatment of a nitrosourea with strong base affords a diazotate which picks up a proton to become a hydroxyazo compound. At this point it can either lose a water molecule and become a diazo compound, Path 1, or dissociate into a carbonium ion, a hydroxyl anion, and a nitrogen molecule in a solvent cage with subsequent recombination of the charges species to form an alcohol, Path 2. Thus, alcohol formation is often an undesired by-product of diazo formation:[23]

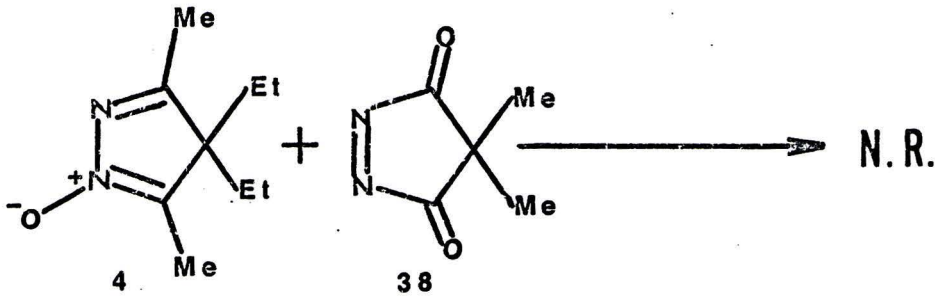


Since, in our case, water loss is impossible due to the lack of available protons, the decomposition to alcohol is the only path open to the hydroxyazo compound. This may explain the excellent yields that these reactions gave.

In conclusion, we can say that novel thermal and photochemical reactions have been found for the new Diels-Alder adducts that were synthesized. Model compound reactions point to the necessity of having the extra nitrogens present in the system for these unique reactions to take place. The spectral data seem to indicate that cross ring interactions do occur in these and other related systems. The exact extent that these interactions play in determining the path of these unique reactions is not clearly understood, but several possibilities have been put forth. The evidence indicates that the interactions are very much involved in these reactions.

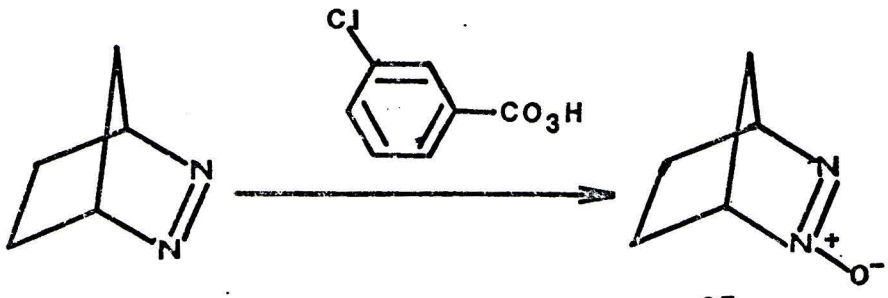
Related Synthetic Efforts

We attempted to prepare other azoxy compounds of the types 5 and 6, in order to check on the universality of the reactions found. To this end we added a solution of 4,4-dimethylpyrazoline-3,5-dione (38) in methylene chloride to a solution of 4 in methylene chloride. The deep blue color of the pyrazolinedione slowly disappeared, but analysis of the nmr spectrum of the residue indicated only starting azine oxide and no adduct. Other than the triazolinediones, 38 had been the dienophile most reactive with azines. That it was indeed less reactive is seen by the fact that the triazolinedione reacted rapidly and quantitatively with azines while the pyrazolinedione reacted slowly and in lower yield:[4]



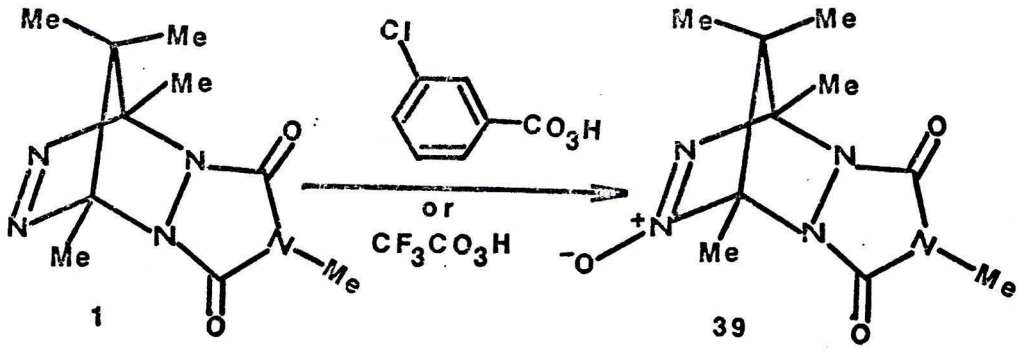
In an attempt to circumvent the use of these less reactive and hard to come by azine oxides, we turned our attention to the use of cyclic azines. These were usually easy to obtain from the appropriate dione and hydrazine; however, they cannot be oxidized to azine oxides unless

they have aromatic substituents on the carbons at the ends of the diene system.[7] Since we needed methyl groups in these positions to test our reaction, this route to azine oxides was useless. However, it was possible to react these azines with dienophiles to form bicyclic azo compounds. Azo compounds of this type have been oxidized to azoxy compounds:[24]



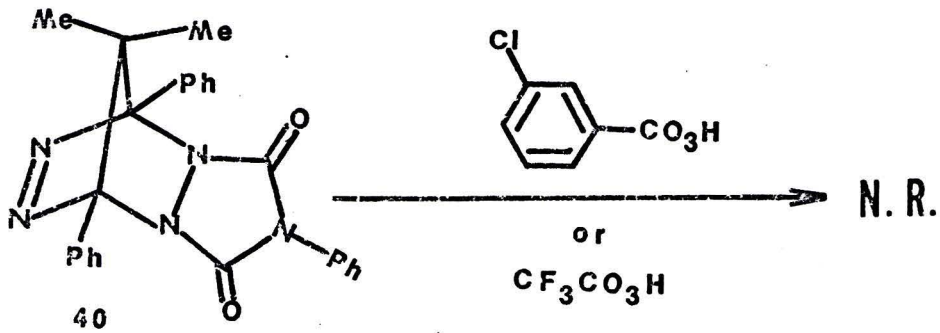
37

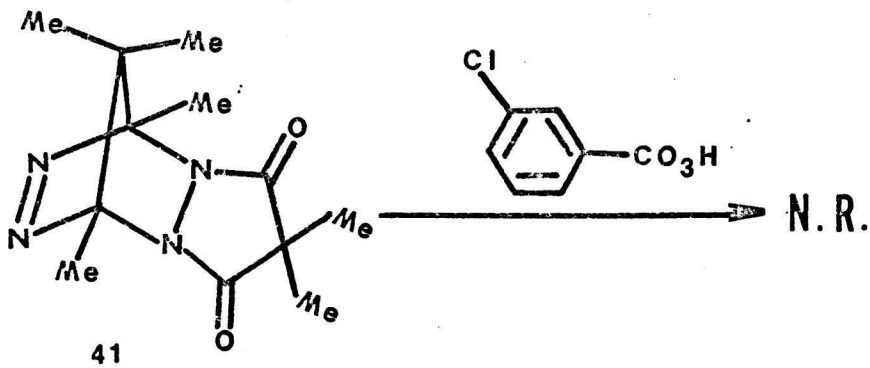
Thus, all we had to do was oxidize the adduct,1, of Evnin and Arnold to get another compound on which to test our reaction. Treatment of this adduct in methylene chloride/ether (1/3) at 0° with a sodium carbonate buffer and trifluoroperacetic acid resulted in a 50% conversion to oxide as measured by nmr spectroscopy. The oxide shows up quite clearly in the nmr spectrum; the singlet for the bridgehead methyl groups moves upfield from τ 7.82 and splits into two singlets at τ8.04 and 8.07. This type of behavior was found to be characteristic of all oxidations of azo compounds that we performed. The splitting into two singlets is indicative of the dissymmetry introduced into the molecule by the oxide nitrogen.



Rerunning the reaction on this 50% converted material raised the conversion to 60%. Another repetition gave 65% conversion. Heating caused the destruction of all oxide and recovery of only starting material. Attempts to separate the mixture by column chromatography failed. Attempts to accomplish the oxidation using m-chloroperbenzoic acid proceeded in a similar manner, but more slowly. Analysis of the nmr spectrum indicated a maximum conversion of 56% after five days at room temperature.

Our lack of success in this case was mirrored in other attempts to oxidize such azo compounds to azoxy compounds. In the other cases, however, not even a partial conversion was achieved:





41

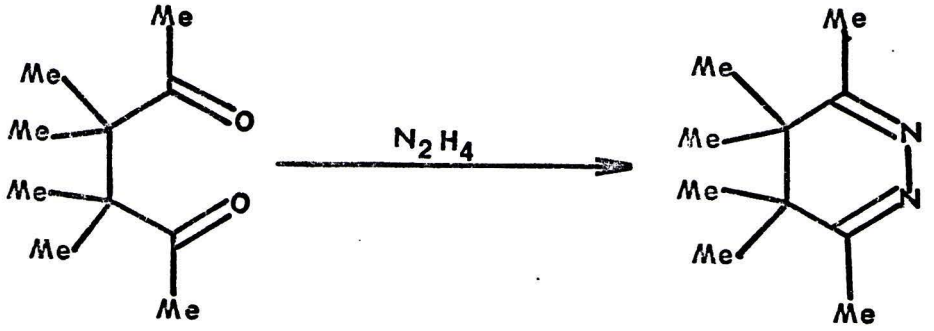
The lack of success in these systems is most mysterious. The failure may be due to some influence by the extra nitrogens in the system, or it may be due to some influence by the extra nitrogens in the system. Or, it may be primarily steric in nature and caused by the methyl group hanging over the azo linkage and the urazole ring hanging below it. The exact cause remains unknown.

Although these other bicyclo[2.2.1]azoxy compounds would have been interesting, we did have two good examples of this system. We wanted to know if the same reaction would occur in a bicyclo[2.2.2]azoxy system. Thus, we spent considerable time attempting to synthesize such a system.

Our efforts were channeled in two separate directions. The first involved reaction of the appropriate azine oxide with triazolinedione, or reaction of the azine with triazolinedione and then oxidation of the adduct to the desired azoxy compound.

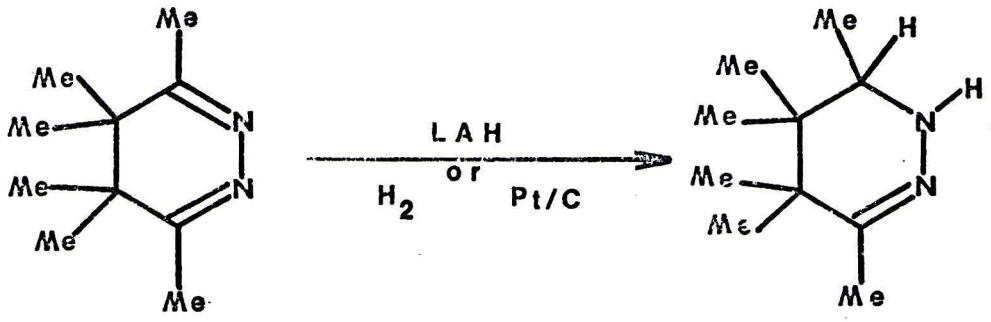
The azine oxide was unavailable by the route we had used previously to make azine oxides because the necessary

dioxime could not be synthesized.[25] We were able to make the azine 43 by the reaction of the dione 42 with hydrazine:



42 43

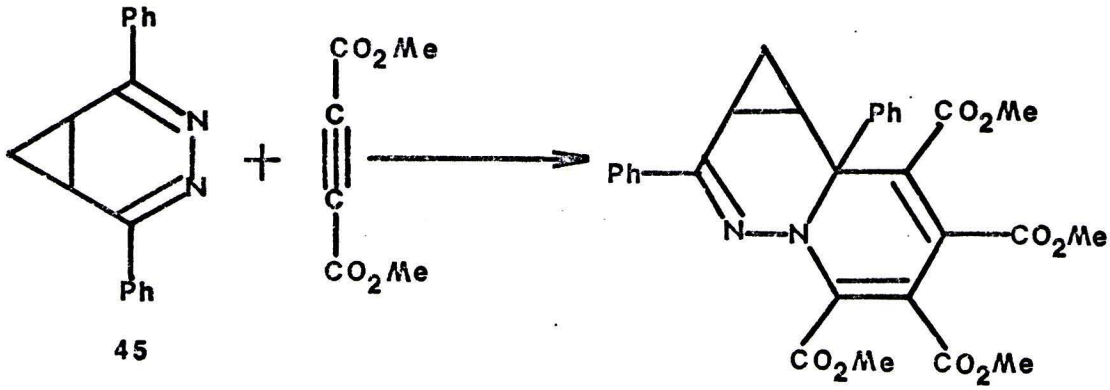
Chemical proof of the azine structure follows from its reaction with lithium aluminum hydride in ether or Pt/C catalyzed hydrogenation to the reduced product 44:



43 44

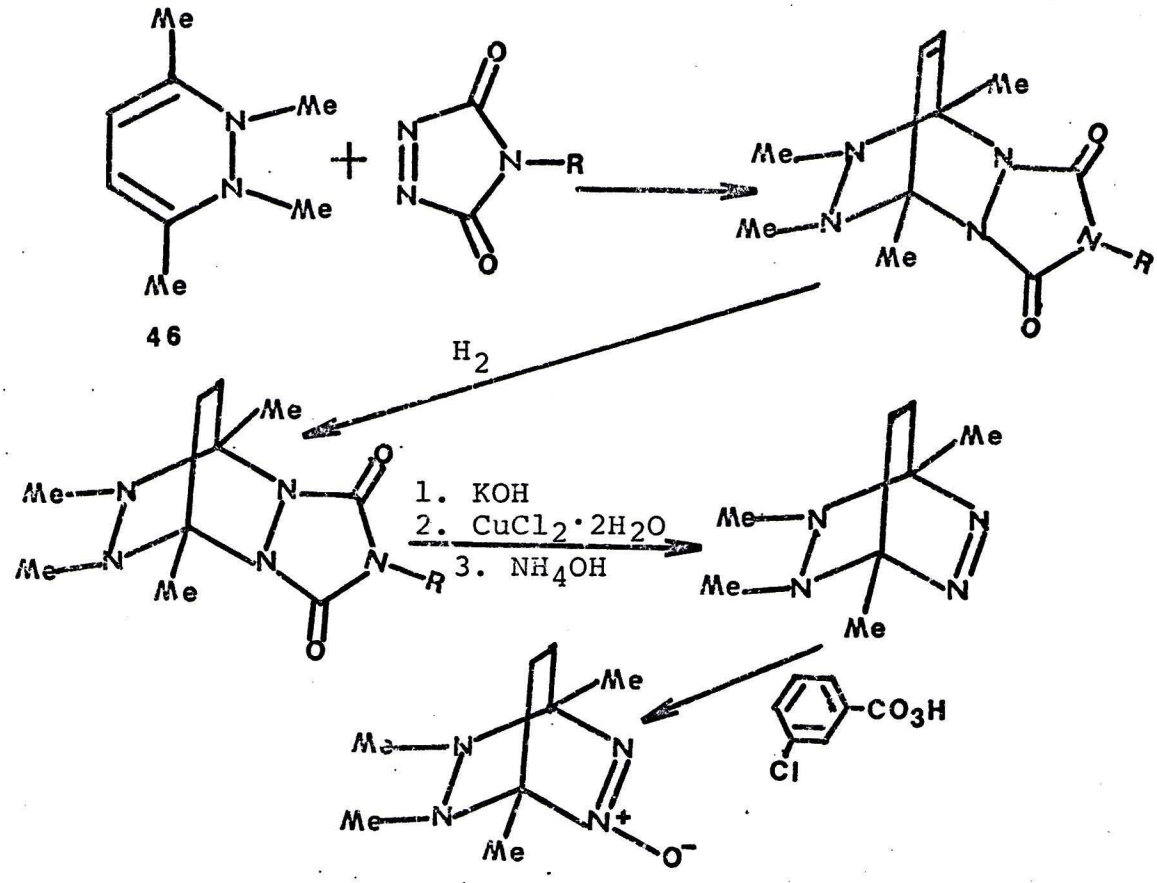
Attempts to oxidize 43 led to immediate gas evolution and destruction of the starting material. We attempted to use 43 in a Diels-Alder reaction with triazolinedione but obtained only a gum and no product. Analysis of the nmr spectrum was not encouraging as to adduct formation, and tlc showed many products. Repetition at -78° with gradual warming until reaction occurred (as evidenced by loss of red color) led to the same results. This failure to react in the desired manner may be explained by the results

obtained on another six-membered ring azine, 45,[26] which also failed to undergo a Diels-Alder reaction:



45

With entrance to the desired system blocked from this direction, we tried our other route. This involved use of 1,2-dihydropyridazines instead of azines in Diels-Alder reactions, followed by hydrolysis to azo compounds and oxidation to the desired azoxy compound:



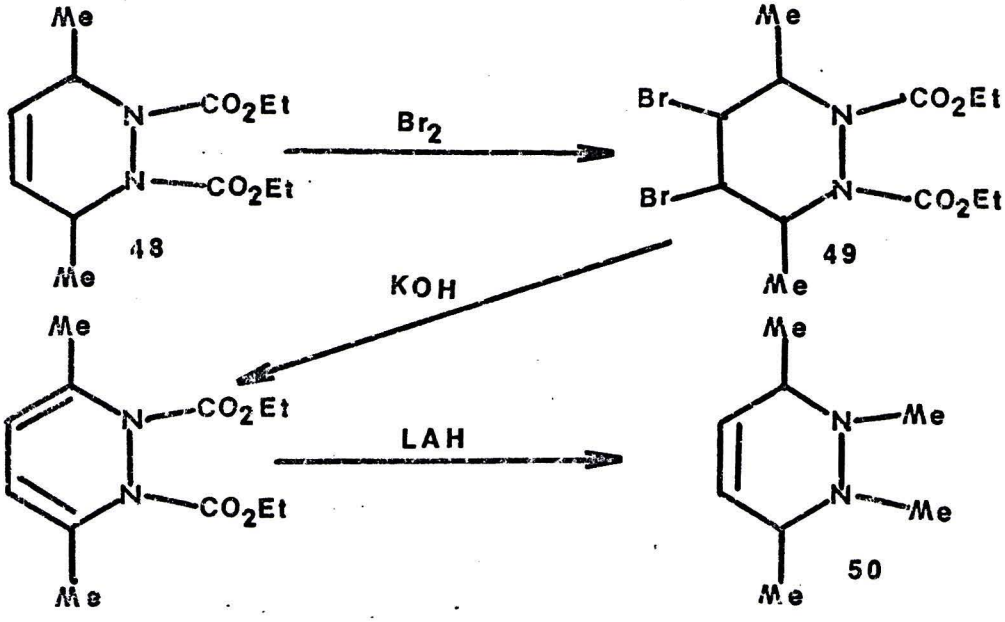
46

The success of this method depended initially on the preparation of the required dihydropyridazine (46). An unsubstituted precursor, 47, to this compound had been reported.[27] All that was needed was the conversion of the two carboethoxy groups into methyl groups:

47

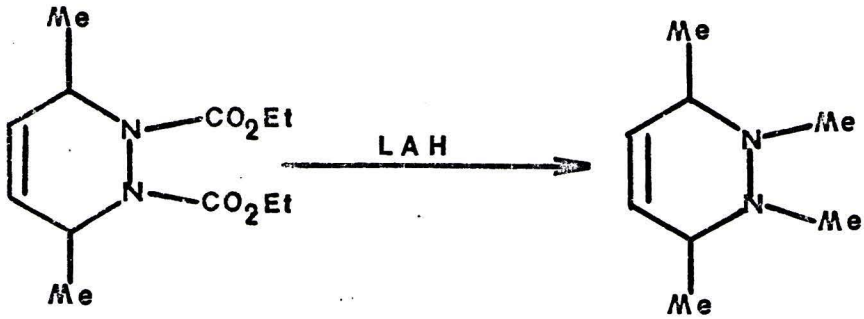
Reductions of this type were well known[28] and little difficulty was expected.

Using the adduct of diethylazodicarboxylate and 2,4-hexadiene (48), we obtained the bromination product, 49, easily. However, the dehydrobromination step yielded a mixture. Analysis of the nmr spectrum indicated partial success, and the reduction was run on the mixture. The only identified product was not the diene, but rather 50:

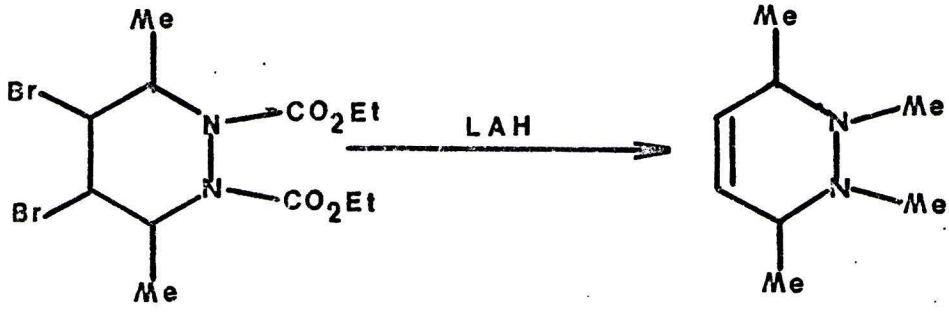


48 49 50

We also obtained 50 from the reduction of 48 with lithium aluminum hydride. It was expected here, but unusual in the previous case. We also obtained 50 from the reduction of the dibromide 49:



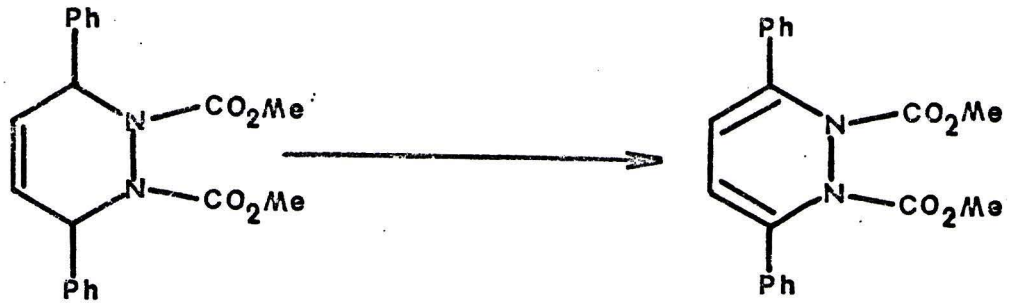
48 50



49 50

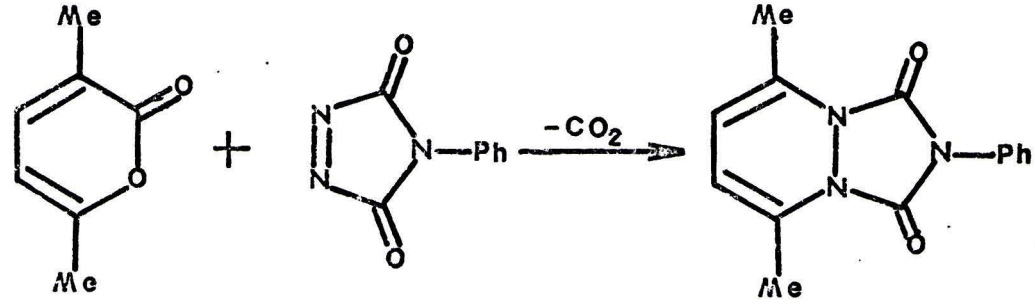
Since 50 seemed to be the result of any reduction, we attempted using it in a bromination-dehydrobromination scheme, but this failed when addition of bromine caused immediate formation of tar and no products soluble in organic solvents were found.

Another attempt to obtain the diene system involved selenium dioxide oxidation of the olefin to a diene as had been done in a similar case:[29]



However, no diene was found when methyl instead of phenyl substituents were involved.

In one last attempt to introduce the diene system, we looked at adducts that could lose carbon dioxide to give back the diene system:



51

However, reaction of 3,6-dimethyl-α-pyrone (51) with triazolinedione led to no adduct. Distillation of the residue yielded only starting α-pyrone. Thus, all of our attempts to produce a bicyclo[2.2.2]azoxy compound to test the extension of our new reaction failed.

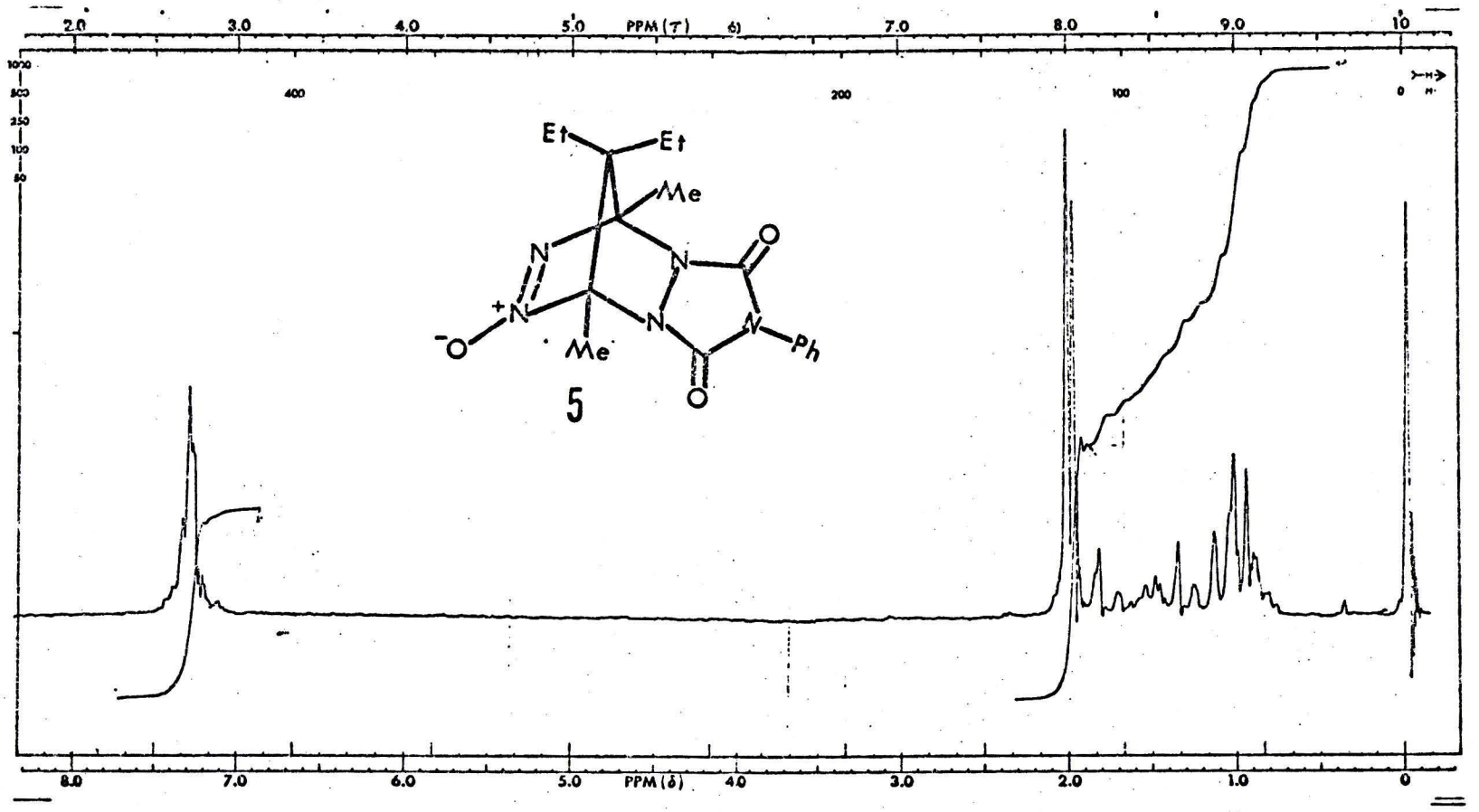
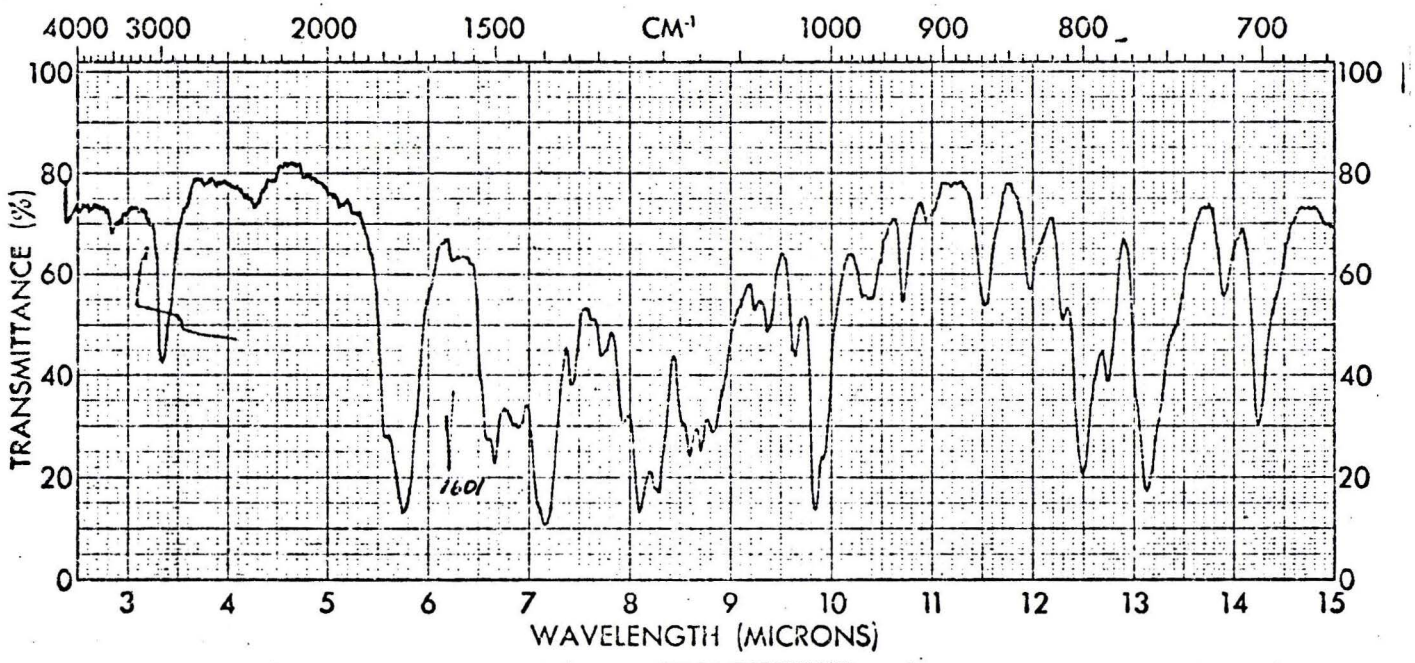
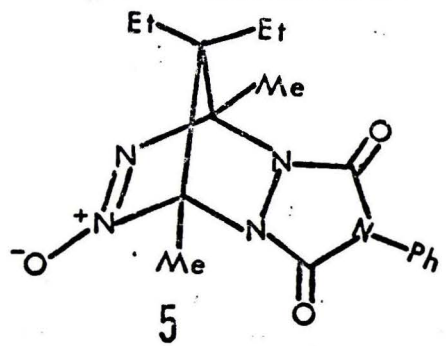


Figure 1. Nmr spectrum of 4-phenyl-1,7-dimethyl-10,10-diethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-8-oxide.





5

Figure 2. Ir spectrum of 4-phenyl-1,7-dimethyl-10,10-diethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-8-oxide.

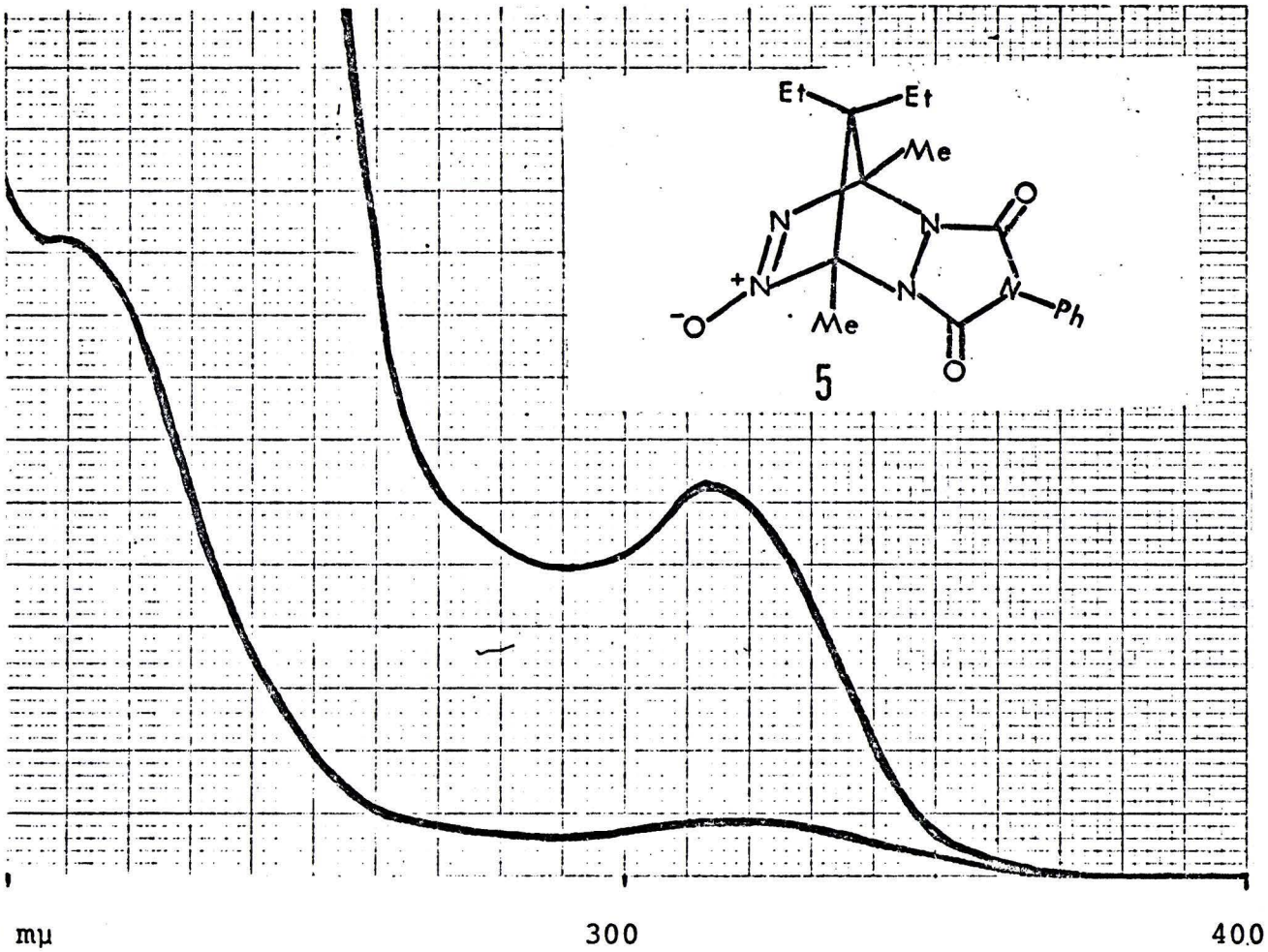


Figure 3. UV spectrum of 4-phenyl-1,7-dimethyl-10,10-diethyl-3,5-diketo-2,4,-6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-8-oxide.

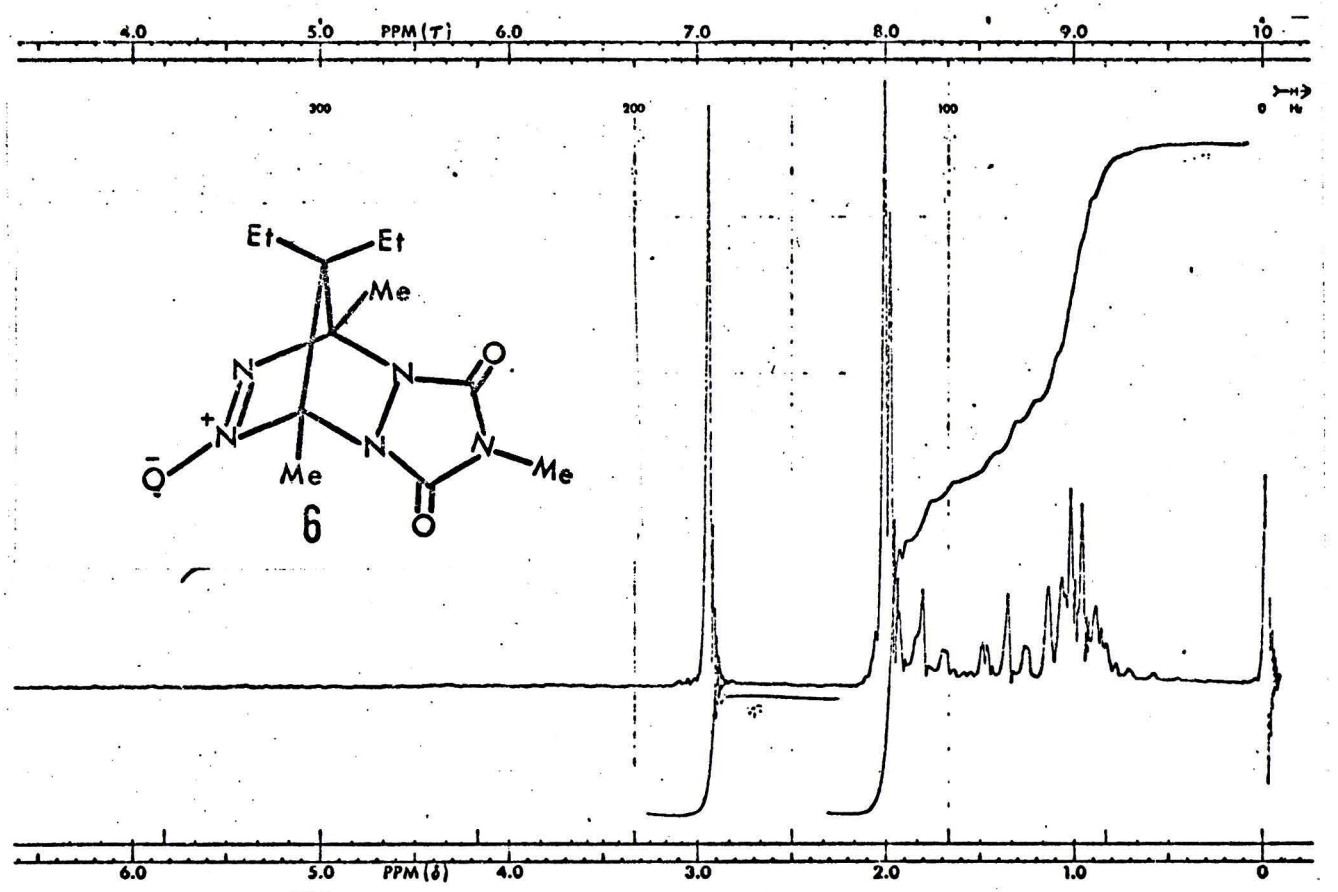
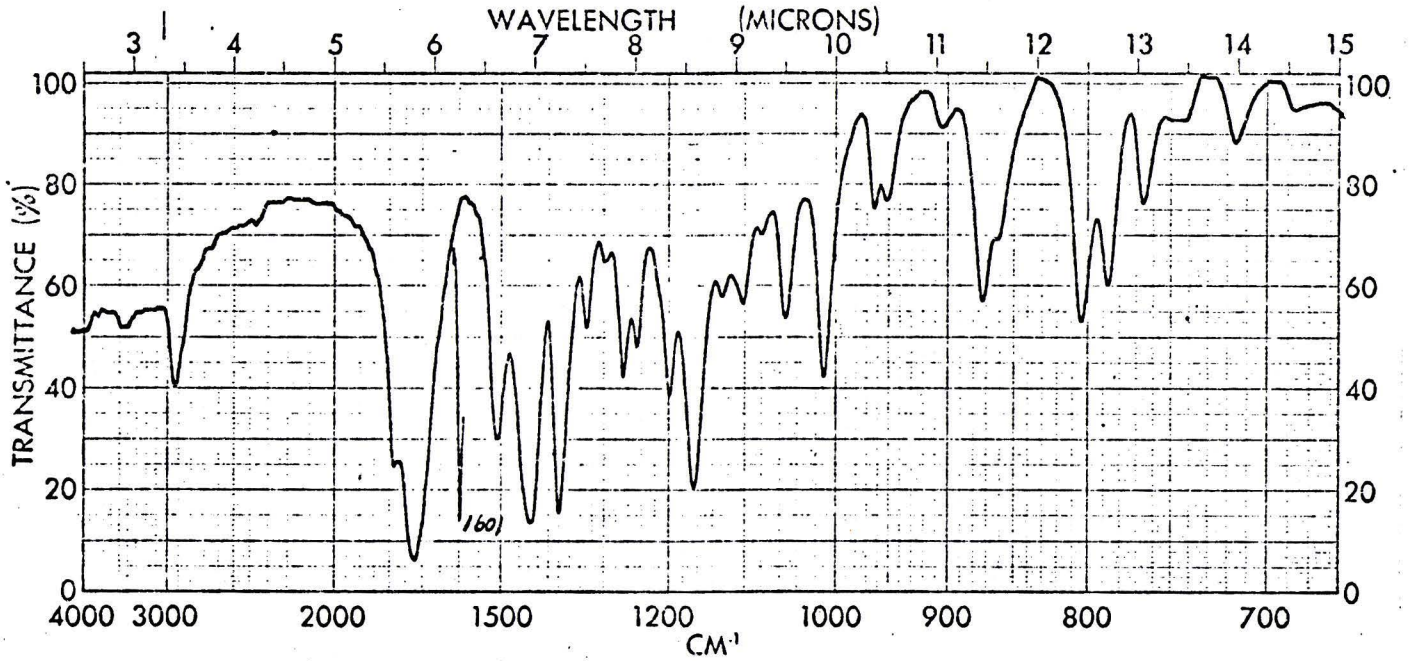
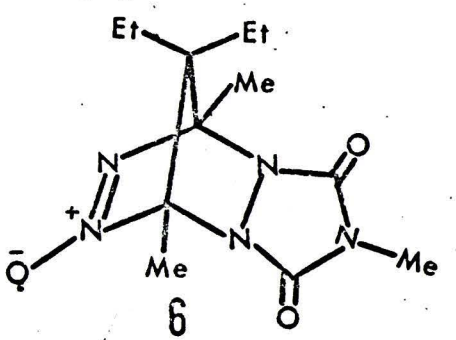


Figure 4. Nmr spectrum of 1,4,7-trimethyl-10,10-diethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-8-oxide.





6

Figure 5. Ir spectrum of 1,4,7-trimethyl-10,10-diethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-8-oxide.

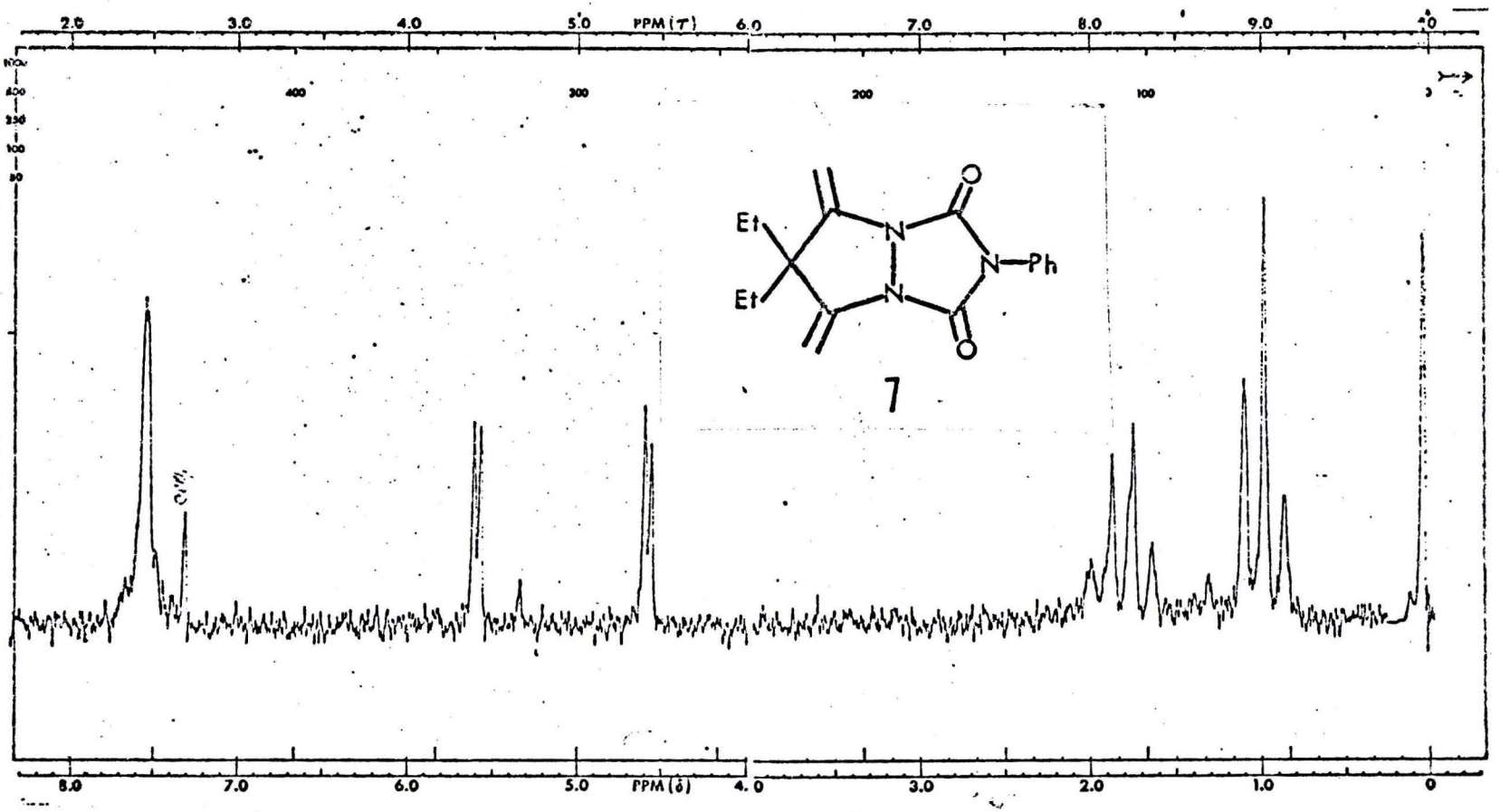
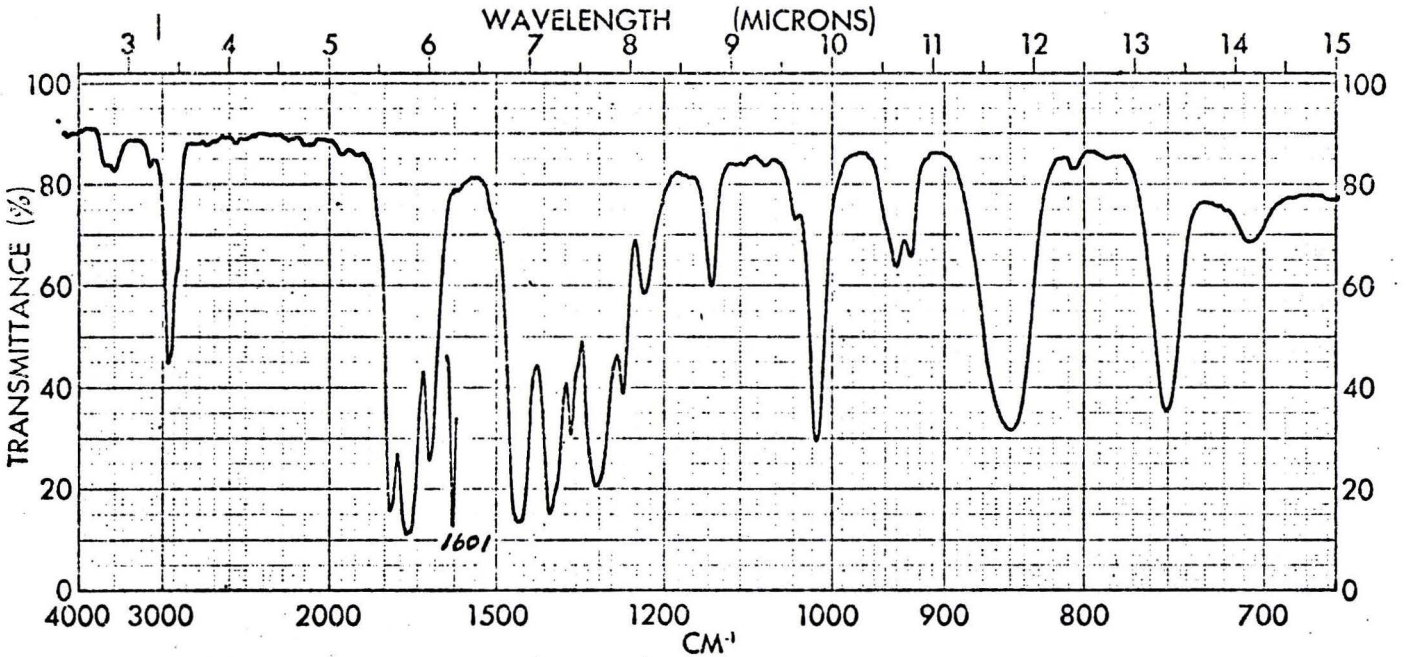


Figure 6. Nmr spectrum of 6,8-dimethylene-7,7-diethyl-3-phenyl-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.



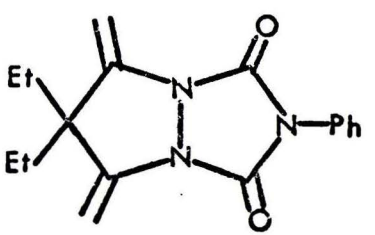


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Figure 7. Ir spectrum of 6,8-dimethylene-7,7-diethyl-3-phenyl-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.

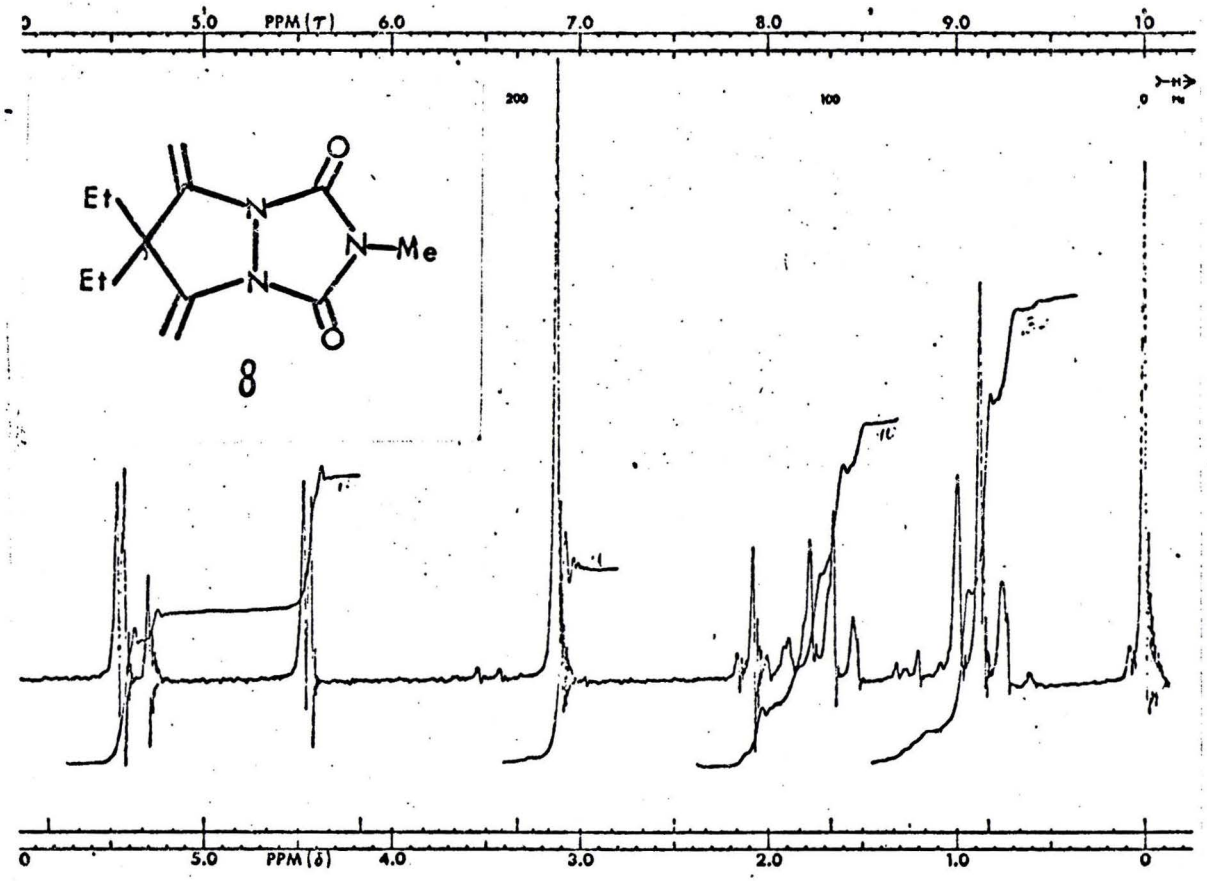
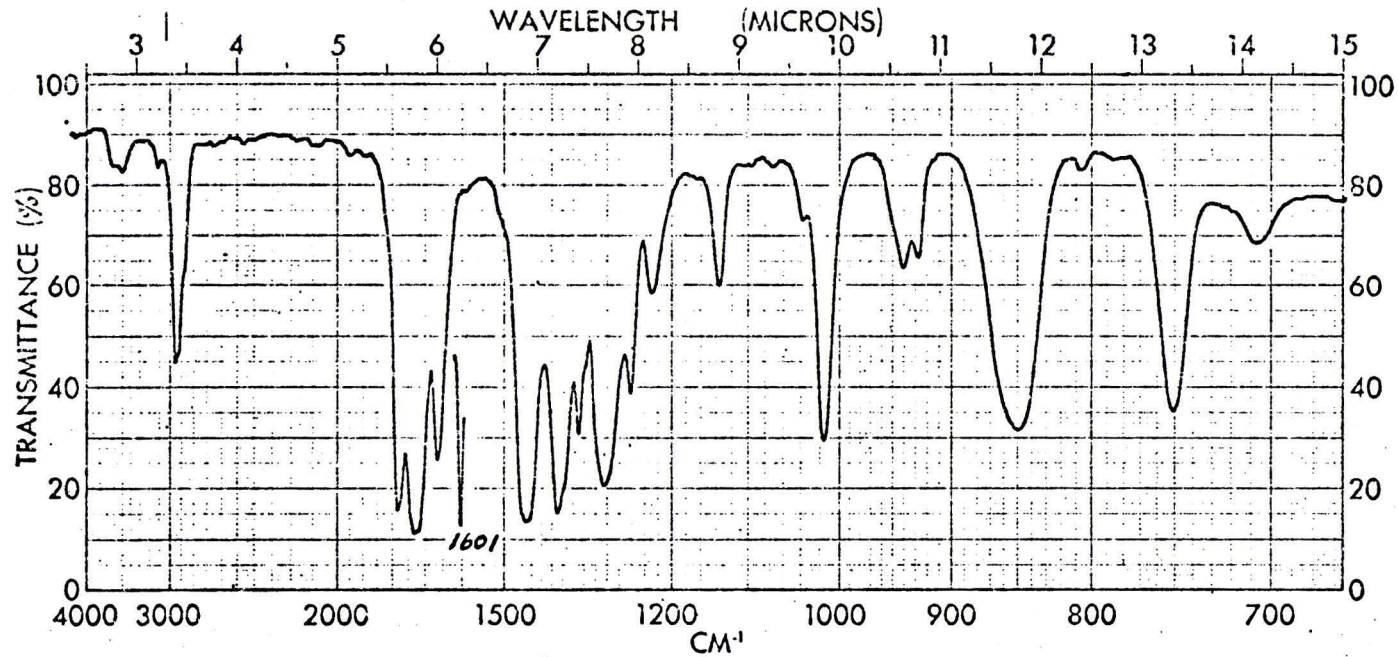


Figure 8. Nmr spectrum of 6,8-dimethylene-7,7-diethyl-3-methyl-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.



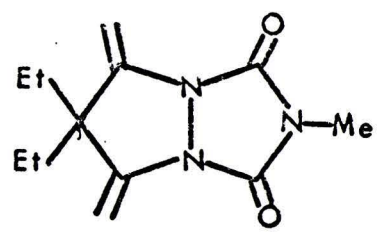


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Figure 9. Ir spectrum of 6,8-dimethylene-7,7-diethyl-3-methyl-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.

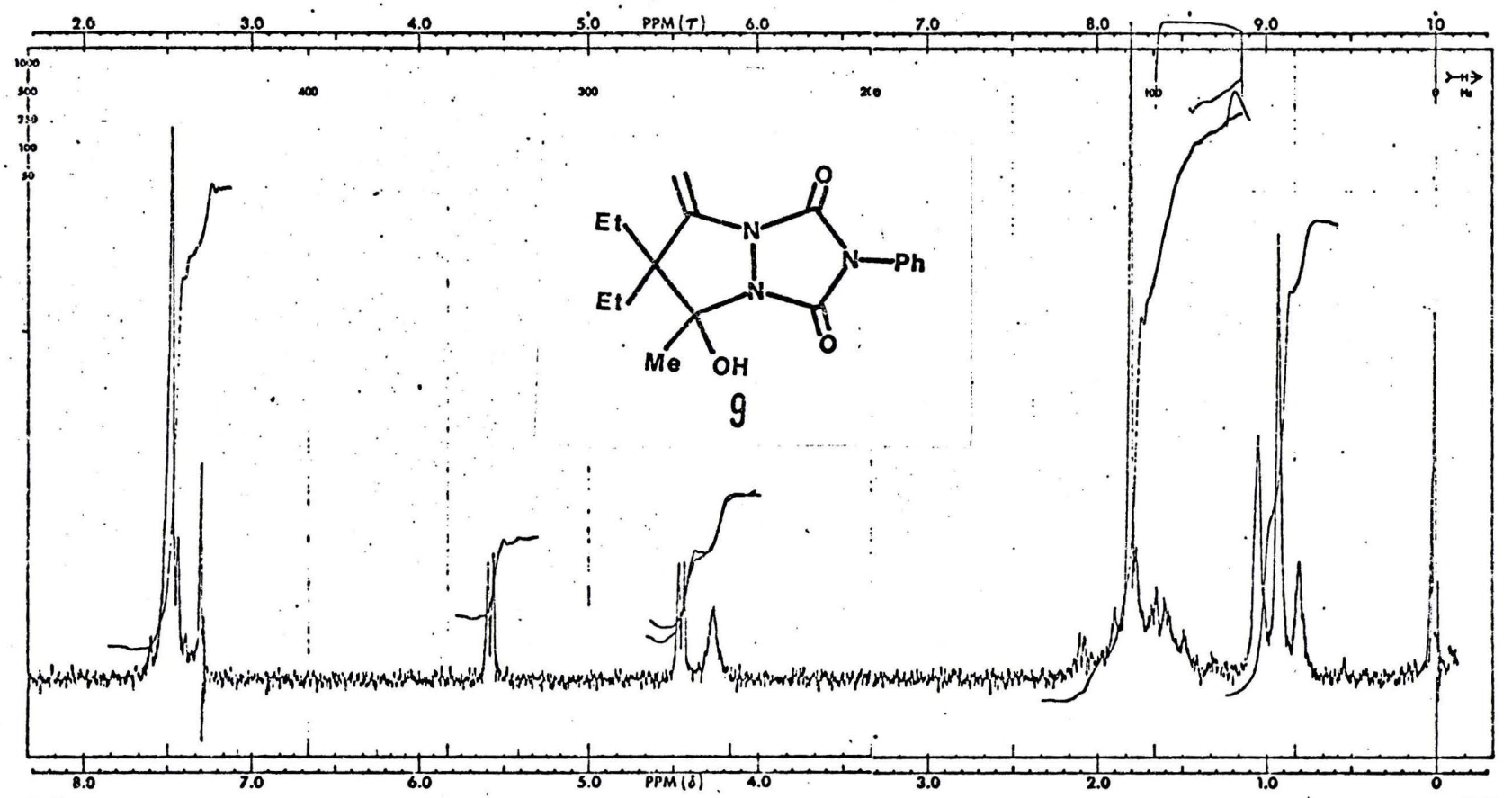
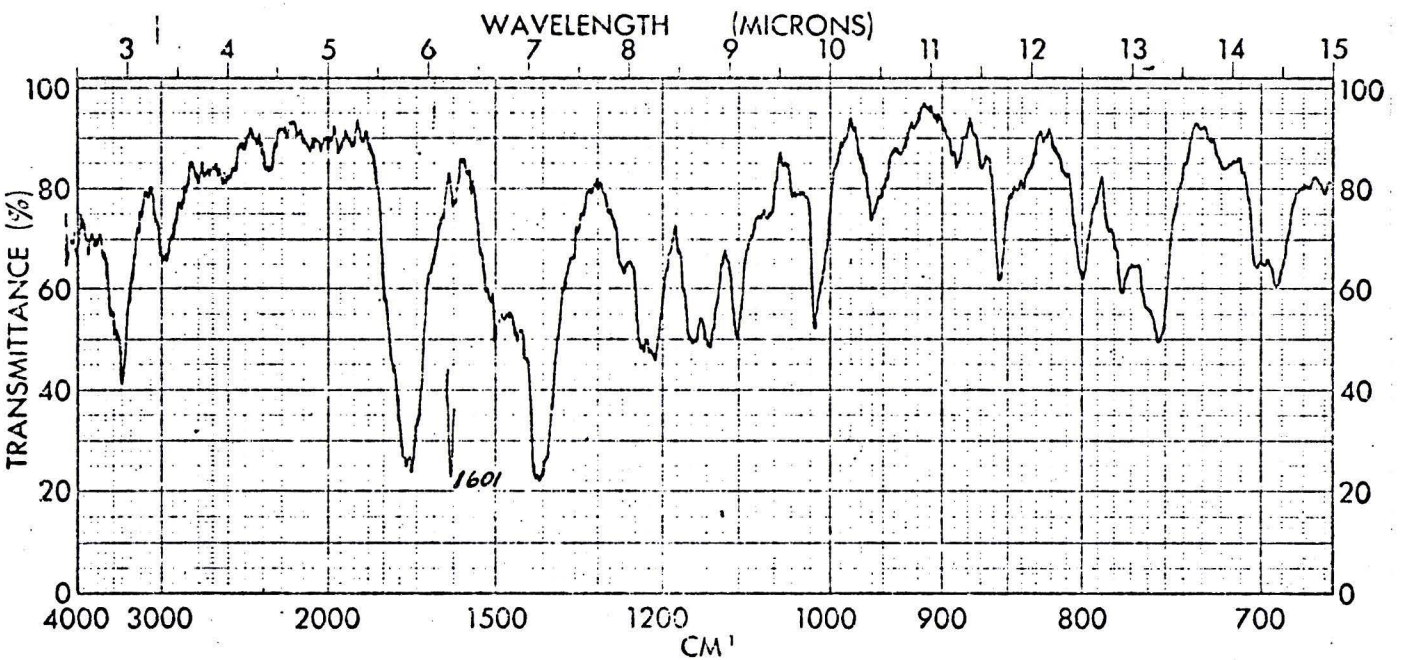


Figure 10. Nmr spectrum of 3-phenyl-6-methylene-7,7-diethyl-8-methyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.



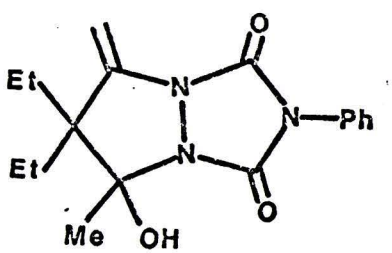


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Figure 11. Ir spectrum of 3-phenyl-6-methylene-7,7-diethyl-8-methyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.

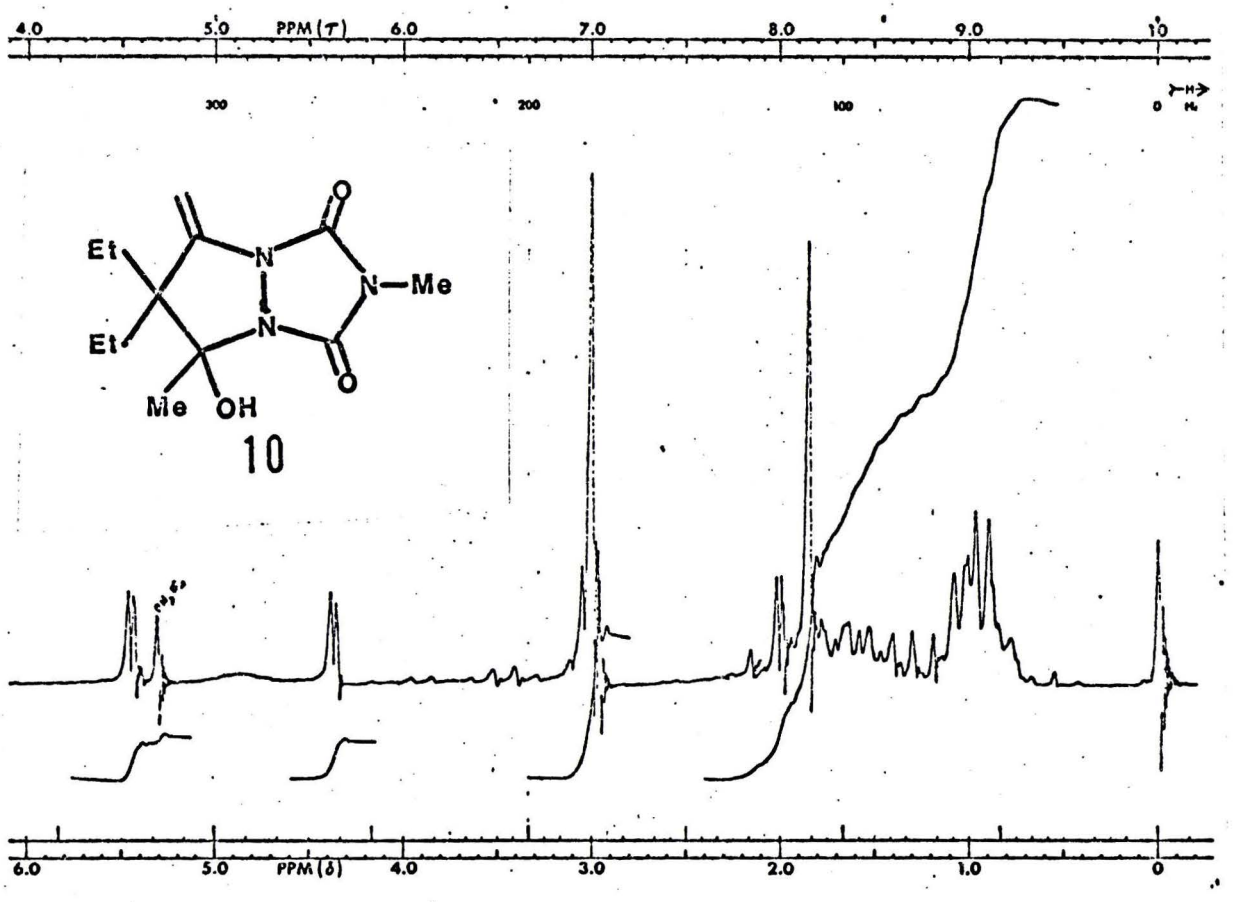
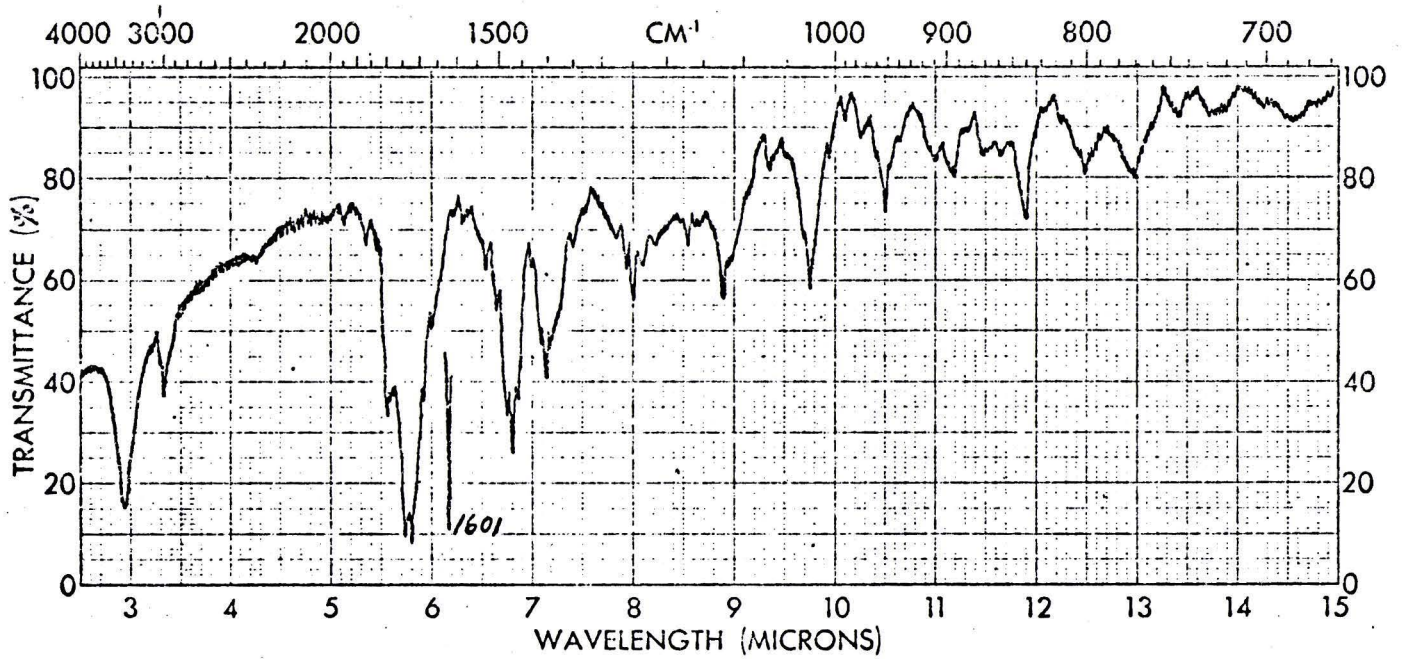


Figure 12. Nmr spectrum of 6-methylene-7,7-diethyl-3,8-dimethyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.



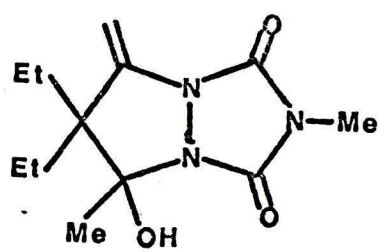


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Figure 13. Ir spectrum of 6-methylene-7,7-diethyl-3,8-dimethyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione.

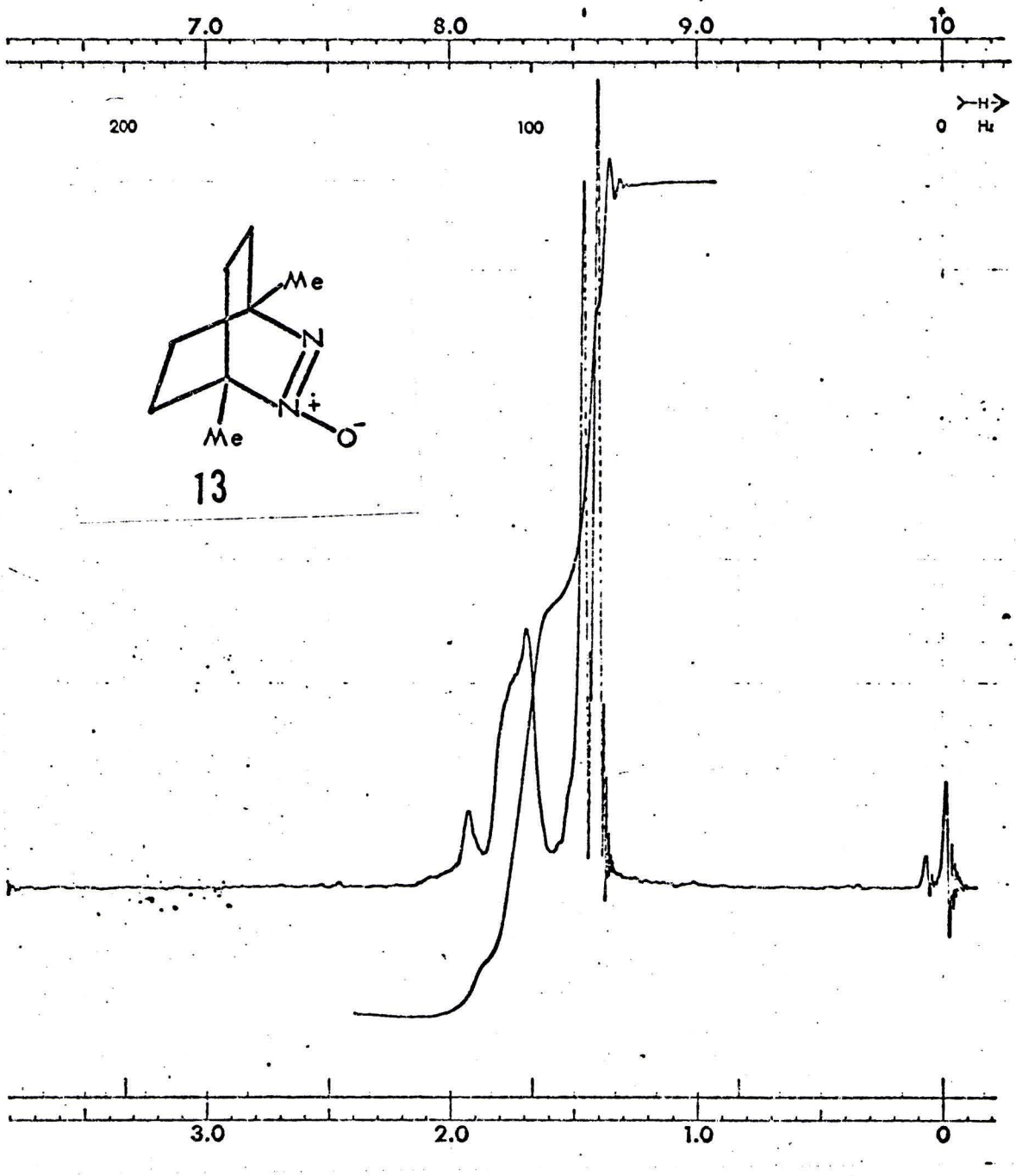
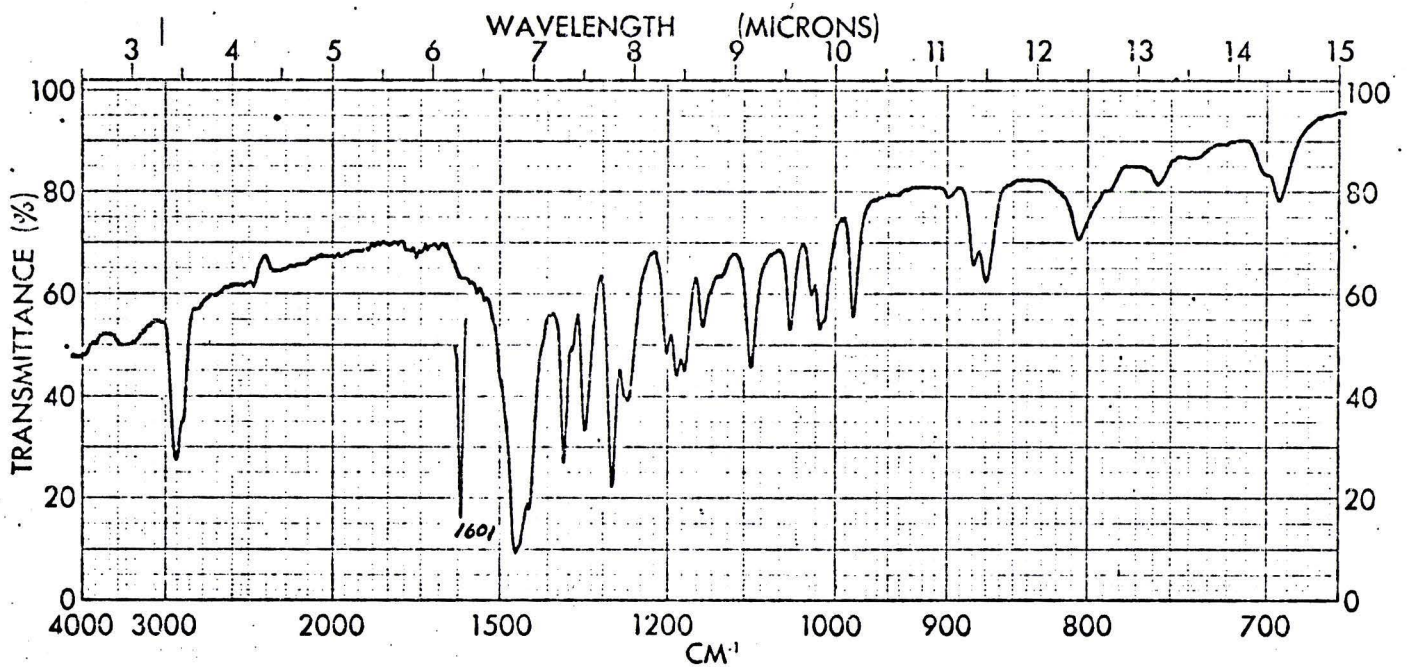


Figure 14. Nmr spectrum of 1,4-dimethyl-2,3-diazabicyclo-[2.2.2]oct-2-ene-2-oxide.



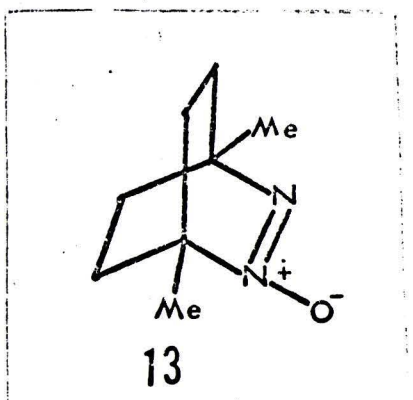


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Figure 15. Ir spectrum of 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene-2-oxide.

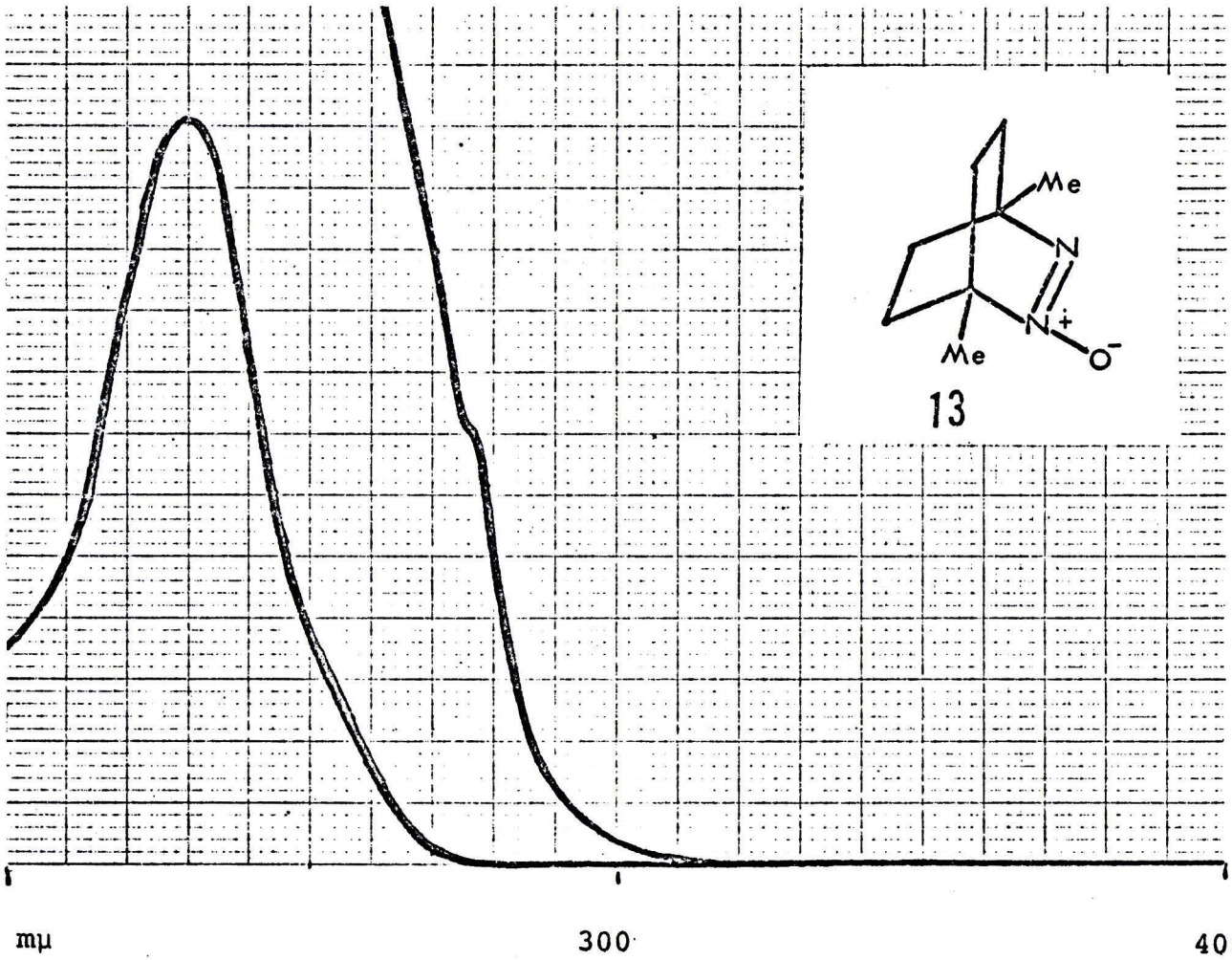


Figure 16. UV spectrum of 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene-2-oxide.

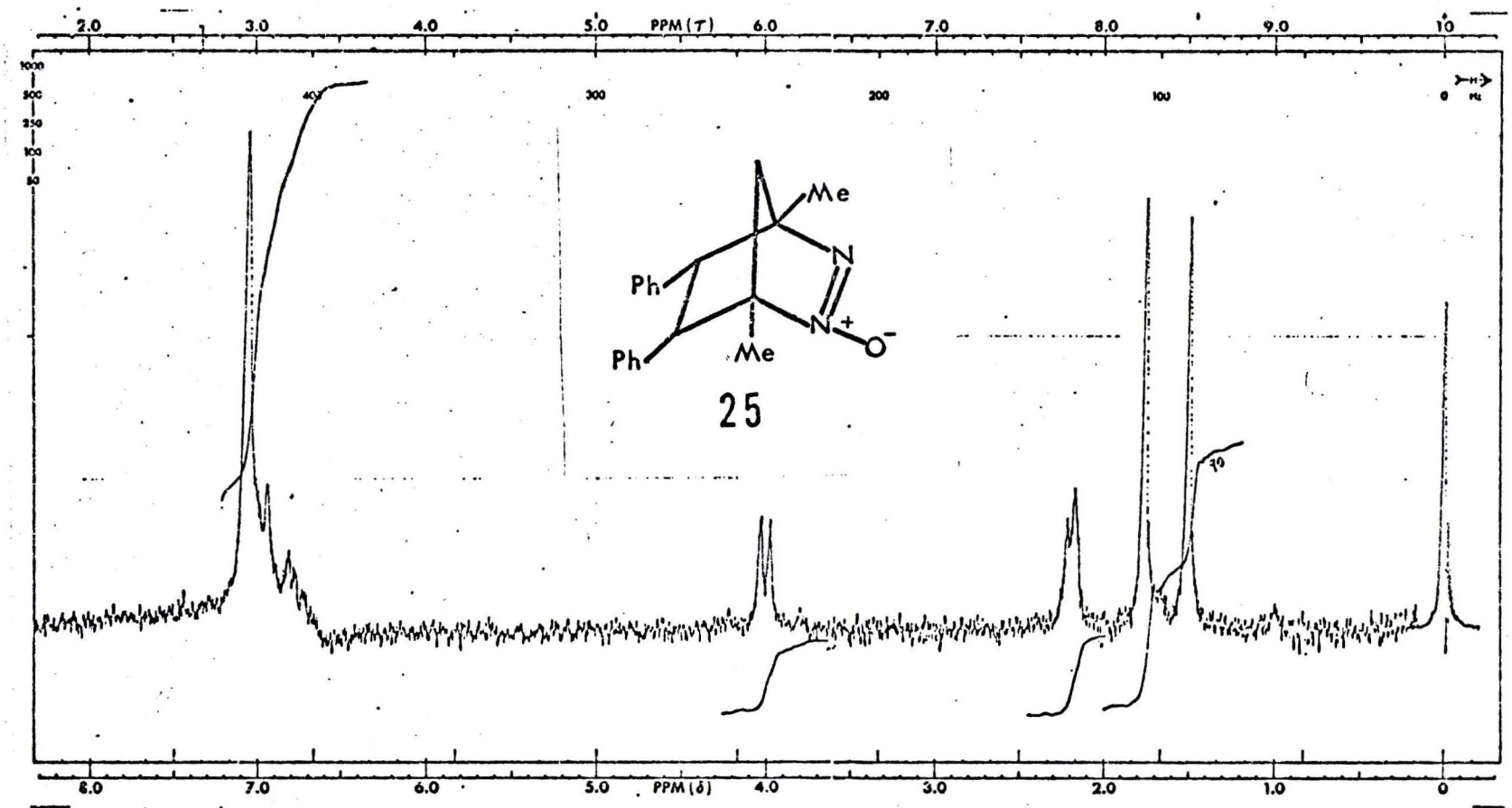
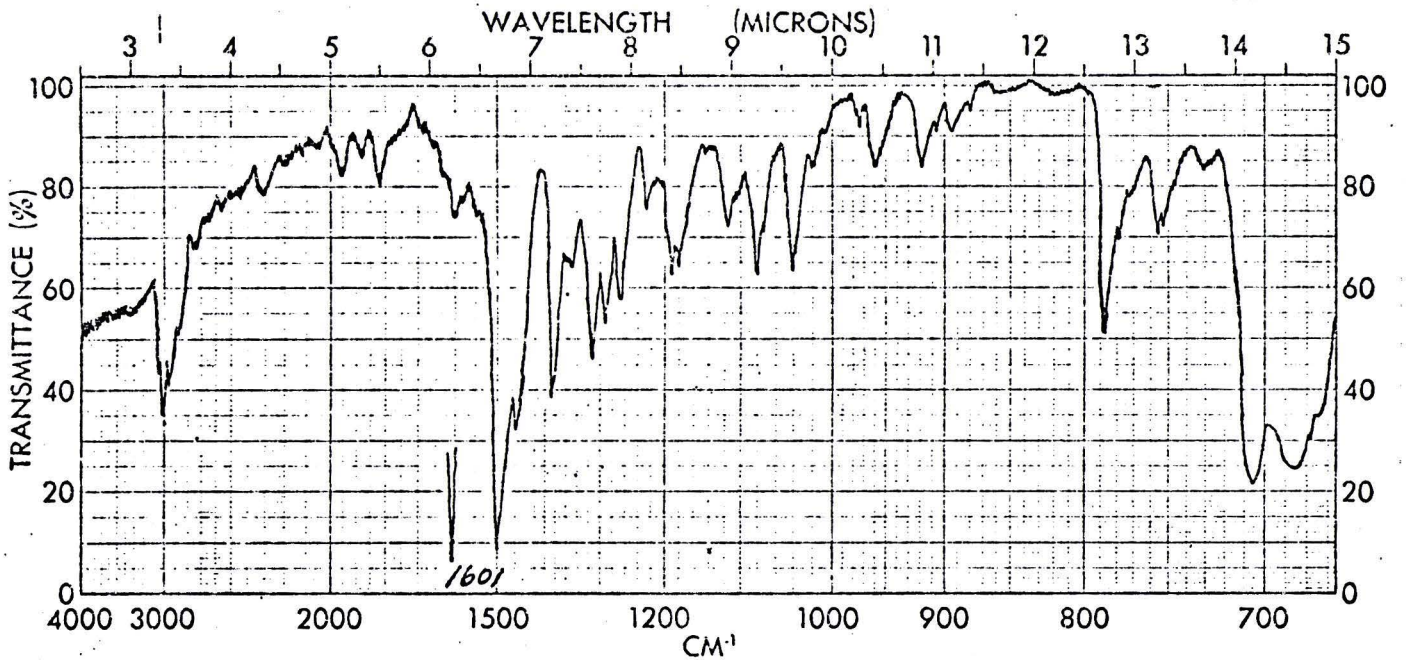
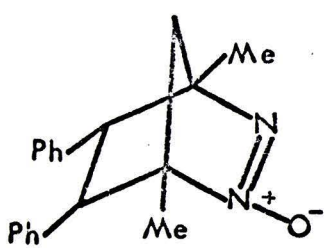


Figure 17. Nmr spectrum of 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]oct-2-ene-2-oxide.





25

Figure 18. Ir spectrum of 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]oct-2-ene-2-oxide.

Experimental

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Model 137 spectrophotometer or on a Beckman IR 10 spectrophotometer. Ultraviolet spectra were recorded on a Cary Model 15 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained from a Varian Model A-60-A spectrometer, utilizing TMS as an internal standard. Mass spectral data were obtained from an Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee; and Atlantic Microlab, Inc., Atlanta, Georgia.

The glpc analyses were carried out on a Varian Aerograph Model A-90-P3 gas chromatograph equipped with the column listed in the text.

All reagents which are not referenced were available commercially.

Preparation of 1,4,7-trimethyl-10,10-diethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene-8-oxide (6). A solution of 0.84 g (5 mmole) of 4 in 50 ml of methylene chloride was placed in a 100 ml flask equipped

with magnetic stirrer, addition funnel and external ice bath. After cooling to 0°, a solution of 0.57 g (5 mmole) of 4-methyl-1,2,4-triazoline-3,5-dione[30] in 25 ml of methylene chloride was added dropwise and then stirred for two hours at 0° and one hour at room temperature. The pink color gradually lightened to yellow. The solution was evaporated to an oil, chromatographed on silica gel with methylene chloride/ether (5/1) to yield 1.3 g (95%) of a clear oil that solidified on standing: mp (from ethanol) 103-104° (dec); ir (KBr), 2930, 1790, 1720, 1510, 1435, 1380, 1270, 1245, 1200, 1165, 1055, 1010, 960, 950, 870, 805, 785; nmr ($CDCl_3$), τ7.05 (s, 3H), 7.98 (s, 3H), 8.02 (s, 3H), 8.00-9.25 (m, 10H); ms (70 eV) m/e (rel intensity), 281 (3.2), 235 (10.9), 208 (100), 207 (19.2), 151 (40.0), 149 (13.7), 133 (4.0), 122 (5.1), 94 (5.7), 93 (6.3), 91 (5.7), 79 (6.3), 77 (6.5), 69 (5.9), 67 (9.9), 65 (5.1), 55 (26.9), 53 (9.3), 43 (11.7), 42 (18.0), 41 (26.1), 39 (14.3); uv (ethanol) λ_{max} 314 mμ (ε830), 268 mμ (ε4,060), 231 mμ (ε7,220).

Anal. Calcd for $C_{12}H_{19}N_5O$: C, 51.25; H, 6.76; N, 24.91. Found: C, 51.31; H, 6.91; N, 24.88.

Preparation of 6,8-dimethylene-7,7-diethyl-3-methyl-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione (8). A 0.50 g (1.8 mmole) sample of 6 was placed in a 5 ml flask connected to a gas measuring buret. This was heated until melting began and 36 ml of gas evolved (40 ml theoretical). Gas chromatography on a 5' SE 30 column at 185° gave 160 mg (40%)

of a colorless oil: ir (film), 2950, 2850, 1780, 1730, 1660, 1450, 1390, 1350, 1300, 1260, 1230, 1135, 1020, 940, 925, 850, 750; nmr ($CDCl_3$), τ 4.55 (d, J=2 Hz, 2H), 5.55 (d, J=2 Hz, 2H), 6.88 (s, 3H), 8.25 (bq, J=7 Hz, 4H), 9.13 (bt, J=7 Hz, 6H); ms (70 eV) m/e (rel intensity), 235 (51.9), 208 (12.9), 207 (100), 150 (5.9), 149 (7.3), 122 (23.4), 121 (9.4), 114 (12.5), 107 (11.7), 99 (13.9), 94 (22.5), 93 (26.7), 91 (22.5), 85 (11.2), 79 (23.9), 77 (21.1), 65 (11.1), 55 (9.0), 53 (14.8), 43 (33.7), 41 (25.3), 39 (21.1).

Anal. Calcd for $C_{12}H_{17}N_3O_2$: C, 61.28; H, 7.23; N, 17.87. Found: C, 61.35; H, 7.31; N, 17.37.

Preparation of 3-phenyl-6-methylene-7,7-diethyl-8-methyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione (9). A solution of 0.5 g (1.4 mmole) of 1,7-dimethyl-4-phenyl-10,10-diethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.-$0^{2,6}$]dec-8-ene-8-oxide (5) in 250 ml of dry benzene under nitrogen stirring was photolyzed with a 450 watt Hanovia medium pressure lamp through a Pyrex filter for two hours with water cooling. Evaporation of the solvent gave a yellow-brown solid. Chromatography on silica gel, first with methylene chloride and then with ether, gave 0.28 g (65%) of a tan solid. Recrystallization from ethyl acetate/pentane (1/3) yielded a buff solid: mp 149.5-150.5°; ir (KBr), 3400, 3000, 1730, 1720, 1500, 1410, 1230, 1210, 1160, 1140, 1100, 1015, 750; nmr ($CDCl_3$), τ 2.54 (bs, 5H), 4.41 (d, J=2 Hz, 1H), 5.55 (d, J=2 Hz, 1H), 5.73 (bs, 1H), 8.20

5.73 (bs, 1H), 8.20 (s, 3H), 8.28 (m, 4H), 9.09 (m, 6H); ms (70 eV) m/e (rel intensity), 315 (73.5), 297 (23.8), 286 (24.5), 273 (13.6), 272 (18.4), 270 (20.4), 264 (23.8), 217 (9.1), 215 (33.4), 204 (9.5), 181 (12.9), 178 (24.5), 177 (28.6), 154 (17.7), 153 (14.5), 139 (29.1),1138 (24.5), 119 (20.2), 112 (16.6), 93 (63.3), 91 (20.4), 81 (15.2), 77 (14.3), 55 (23.8), 43 (100), 41 (29.3), 39 (14.8).

Anal. Calcd for $C_{17}H_{21}N_3O_3$: C, 64.76; H, 6.67; N, 13.33. Found: C, 64.69; H, 6.76; N, 13.45.

Preparation of 6-methylene-7,7-diethyl-3,8-dimethyl-8-hydroxy-1,3,5-triazobicyclo[3.3.0]octa-2,4-dione (10). A solution of 0.50 g (1.8 mmoles) of 6 in 100 ml of dry benzene was placed in a photolysis well with nitrogen purge. This was photolyzed with a 450 watt medium pressure Hanovia lamp through a Pyrex filter for two hours. The mixture was evaporated to an oil and chromatographed on silica gel with methylene chloride. Then the ether eluent was collected and evaporated to 360 mg (85%) of a colorless oil which slowly crystallized: ir (KBr), 3400, 2950, 1770, 1720, 1450, 1380, 1120, 1025, 945, 835, 765; nmr ($CDCl_3$), τ4.55 (d, J=2 Hz, 1H), 4.95 (bs, 1H), 5.60 (d, J=2 Hz, 1H), 7.00 (s, 3H), 8.14 (s,3H), 8.00-8.60 (m, 4H), 8.70-9.20 (m, 6H); ms (70 eV) m/e (rel intensity), 253 (76.8), 238 (10.1), 237 (10.0), 236 (9.7), 235 (22.2), 225 (15.8), 224 (45.9), 211 (51.2), 210 (19.3), 208 (37.7), 207 (40.1), 196 (40.1), 195 (18.4), 194 (23.2), 168 (15.8), 164 (10.3), 155 (21.7), 154 (13.2), 153 (75.4), 142 (100),

(s, 3H), 8.28 (m, 4H), 9.09 (m, 6H); ms (70 eV) m/e (rel intensity), 315 (73.5), 297 (23.8), 286 (24.5), 273 (13.6), 272 (18.4), 270 (20.4), 264 (23.8), 217 (9.1), 215 (33.4), 204 (9.5), 181 (12.9), 178 (24.5), 177 (28.6), 154 (17.7), 153 (14.5), 139 (29.1), 1138 (24.5), 119 (20.2), 112 (16.6), 93 (63.3), 91 (20.4), 81 (15.2), 77 (14.3), 55 (23.8), 43 (100), 41 (29.3), 39 (14.8).

Anal. Calcd for $C_{17}H_{21}N_3O_3$: C, 64.76; H, 6.67; N, 13.33. Found: C, 64.69; H, 6.76; N, 13.45.

Preparation of 6-methylene-7,7-diethyl-3,8-dimethyl-8-hydroxy-1,3,5-triazobicyclo[3.3.0]octa-2,4-dione (10). A solution of 0.50 g (1.8 mmoles) of 6 in 100 ml of dry benzene was placed in a photolysis well with nitrogen purge. This was photolyzed with a 450 watt medium pressure Hanovia lamp through a Pyrex filter for two hours. The mixture was evaporated to an oil and chromatographed on silica gel with methylene chloride. Then the ether eluent was collected and evaporated to 360 mg (85%) of a colorless oil which slowly crystallized: ir (KBr), 3400, 2950, 1770, 1720, 1450, 1380, 1120, 1025, 945, 835, 765; nmr ($CDCl_3$), τ 4.55 (d, J=2 Hz, 1H), 4.95 (bs, 1H), 5.60 (d, J=2 Hz, 1H), 7.00 (s, 3H), 8.14 (s, 3H), 8.00-8.60 (m, 4H), 8.70-9.20 (m, 6H); ms (70 eV) m/e (rel intensity), 253 (76.8), 238 (10.1), 237 (10.0), 236 (9.7), 235 (22.2), 225 (15.8), 224 (45.9), 211 (51.2), 210 (19.3), 208 (37.7), 207 (40.1), 196 (40.1), 195 (18.4), 194 (23.2), 168 (15.8), 164 (10.3, 155 (21.7), 154 (13.2), 153 (75.4), 142 (100), 139 (50.3), 138 (44.4), 116 (55.6), 115

(54.6), 110 (32.4), 96 (29.5), 81 (30.4), 55 (36.2), 43 (79.7), 41 (30.4).

Anal. Calcd for $C_{12}H_{19}N_3O_3$: C, 56.92; H, 7.51; N, 16.60. Found: C, 56.66; H, 7.73; N, 16.68.

Pyrolysis of 3-phenyl-6-methylene-7,7-diethyl-8-methyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione (9). A solution of 70 mg (0.22 mmole) of 9 in 25 ml of chloroform was placed in a 50 ml flask equipped with stirrer and condenser. This was heated to reflux for two hours. No reaction was indicated by tlc and nmr spectroscopy. The mixture was evaporated to a solid. This solid was heated neat for 1/2 hour at 150°. Analysis of the nmr showed all 9 gone and 7 present. Chromatography on silica gel with methylene chloride yielded 55 mg (85%) of solid, mp 125°, identical with diene formed from thermolysis of the tricyclic azoxy compound 5 as shown by nmr spectroscopy.

Pyrolysis of 6-methylene-7,7-diethyl-3,8-dimethyl-8-hydroxy-1,3,5-triazabicyclo[3.3.0]octa-2,4-dione (10). A solution of 25 mg (0.1 mmole) of 10 in 25 ml of chloroform was placed in a 50 ml flask equipped with stirrer and condenser. This was heated to reflux for two hours. Analysis of the nmr spectrum indicated no reaction. Addition of 2 drops of hydrochloric acid to the solution also resulted in unchanged 10. The mixture was evaporated to a solid. This was heated neat at 110° but produced no reaction as seen by tlc and nmr spectroscopy. Heating at 180° gradually converted 10 to 8 (20 mg, 85% yield) as shown by nmr spectroscopy.

Photolysis of azoxy-t-butane (11). A solution of 0.7 g (4.4 mmole) of 11[11] in 250 ml of dry benzene was photolyzed for three hours with a 450 watt medium pressure Hanovia lamp through quartz. Tlc showed all starting material had been consumed by this time. The solution was a deep brown at the end of the time period, and a dark polymeric solid was present. The solution was purged with nitrogen during the reaction and the gasses passed through a dry ice cooled coil trap. The contents of the trap were transferred on the vacuum line to a carbon tetrachloride filled nmr tube. Analysis of the nmr spectrum showed benzene peaks but no vinyl peaks for the expected isobutylene. Ms analysis of the manifold contents likewise showed no peaks for isobutylene.

Preparation of 1,7-dimethyl-4-phenyl-2,4,6-triazatricyclo-[5.2.2.$0^{2,6}$]undec-8-ene-3,5-dione (15). A 9 g sample of the mixture obtained from the pyrolysis of 2,5-dimethyl-2,5-diacetoxy-3-hexene[12] (nmr spectroscopy showed approximately 50% was the desired 14) and 200 ml of methylene chloride were placed in a 500 ml flask equipped with a stirrer and addition funnel. A solution of 14 g (0.124 mole) of methyltriazolinedione[30] in 100 ml of methylene chloride was added dropwise. The pink color disappeared immediately, leaving a yellow solution. This was evaporated to a yellow solid. Recrystallization from ethanol and water yielded 12 g (48%) of light yellow solid; mp 152°; ir (KBr), 2900, 1750, 1700, 1400, 1300, 1260, 1240, 1140, 1120, 1060, 1010,

860, 780, 755, 740, 690; nmr ($CDCl_3$), τ2.62 (bs, 5H), 3.76 (s, 2H), 8.09 (s, 6H), 7.69-8.79 (m, 4H); ms (70 eV) m/e (rel intensity), 283 (46.8), 255 (6.4), 242 (10.0), 241 (49.2), 178 (44.2), 177 (85.2), 119 (23.0), 108 (93.3), 107 (100), 106 (34.2), 94 (69.1), 93 (80.6), 91 (62.2), 79 (20.4), 77 (33.4), 75 (18.4), 74 (15.4), 53 (12.8), 51 (13.4), 41 (21.5); uv (ethanol) λ_{max} 244 mμ (ε5,220), 219 mμ (ε11,040).

Anal. Calcd for $C_{16}H_{17}N_3O_2$: C, 67.83; H, 6.05; N, 14.83. Found: C, 67.62; H, 6.16; N, 14.97.

Preparation of 1,7-dimethyl-4-phenyl-2,4,6-triazatricyclo-[5.2.2.$0^{2,6}$]undecane-3,5-dione (16). A solution of 10 g (0.035 mole) of 15 in 250 ml of ethyl acetate was placed in a 500 ml thick-walled bottle and 0.5 g of 5% palladium on charcoal added. The bottle was placed on a Parr hydrogenator, filled with hydrogen (50 psi), and shaken at room temperature overnight. The catalyst was filtered off and the filtrate evaporated to a white solid. Recrystallization from ethanol produced 9 g (90%) of a white solid: mp 156-157°; ir (KBr), 2900, 1750, 1700, 1500, 1440, 1400, 1280, 1260, 1120, 1100, 750, 740, 690; nmr ($CDCl_3$), τ2.64 (m, 5H), 8.14 (m, 8H), 8.28 (s, 6H); ms (70 eV) m/e (rel intensity), 285 (83.8), 255 (6.4), 178 (13.6), 149 (5.9), 119 (23.1), 110 (10.9), 109 (100), 108 (33.4), 96 (7.7), 93 (11.6), 91 (10.4), 81 (7.9), 67 (15.4), 55 (14.8), 41 (14.8); uv (ethanol) λ_{max} 217 mμ (ε12,900).

Preparation of 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (17). A solution of 3.0 g (0.0105 mole) of 16 and 6 g (0.107 mole) of potassium hydroxide in 25 ml of ethylene glycol was placed in a 50 ml flask equipped with condenser, stirrer, and nitrogen inlet. This was heated under nitrogen for 2 1/2 hours at 170°, cooled, diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to an oil. This was dissolved in a minimum amount of water and acidified with dilute hydrochloric acid. A solution of 8 g (0.052 mole) of cupric chloride dihydrate in 100 ml of water was added. The blue solution turned green and, upon sitting overnight, a solid precipitated. The solid was filtered and washed with ether, producing 1.80 g (63%) of a dark red solid, the copper complex. This was added to 50 ml of concentrated ammonium hydroxide, stirred for 1/2 hour, extracted with ether, dried over sodium sulfate, and evaporated to 0.90 g (95%) of an off-white solid. Sublimation at room temperature and 0.25 mm produced a white solid, mp 71-72° (lit. 70.5-71.5°[31]); ir (KBr), 2900, 2840, 1430, 1360, 1320, 1250, 1200, 1160, 1090, 1020, 810; nmr (CH_2Cl_2), 8.31 (s, 6H), 8.34-9.16 (m, 8H).

Preparation of 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene-2-oxide (13). A solution of 0.7 g (5 mmole) of 17 in 25 ml of methylene chloride was placed in a 50 ml flask and 0.9 g (5.2 mmole) of m-chloroperbenzoic acid added. This was stirred for one hour at room temperature, washed

with a sodium carbonate solution and water, dried over sodium sulfate, and evaporated to a solid. This was sublimed at 80°/1 mm, producing 0.5 g (65%) of white solid: mp 104-106°; ir (KBr), 2900, 2850, 1500, 1460, 1440, 1370, 1330, 1285, 1260, 1200, 1190, 1185, 1090, 1050, 1015, 980, 870, 850; nmr (CH_2Cl_2), τ8.28 (m, 8H), 8.55 (s, 3H), 8.60 (s, 3H); ms (70 eV) m/e (rel intensity), 154 (32.2), 139 (4.3), 137 (5.7), 124 (15.4), 109 (57.1), 108 (63.7), 107 (10.9), 96 (31.1), 95 (61.5), 93 (12.0), 91 (8.1), 82 (12.0), 81 (30.4), 69 (13.9), 68 (85.6), 67 (15.7), 56 (16.8), 55 (100), 54 (12.8), 53 (23.1), 43 (14.6), 42 (36.6), 41 (52.7), 39 (43.9); uv (ethanol) λ_{max} 230 mμ (ε6,420), 287 mμ (ε70).

Anal. Calcd for $C_8H_{14}N_2O$: C, 62.34; H, 9.09; N, 18.18. Found: C, 62.06; H, 9.02; N, 18.18.

Preparation of 1,4,7,8,9,10,10-heptamethyl-3,5-diketo-2,4,6-triazatricyclo[5.2.1.$0^{2,6}$]dec-8-ene (19). A solution of 6.0 g (0.04 mole) of hexamethylcyclopentadiene (18)[13] in 100 ml of methylene chloride was placed in a 300 ml flask equipped with a magnetic stirrer and addition funnel. A solution of 4.5 g (0.04 mole) of methyltriazolinedione[30] in 100 ml of methylene chloride was added dropwise and the red color disappeared immediately. The mixture was stirred at room temperature for one hour and evaporated to light yellow solid. Recrystallization from ethanol/water produced 10.2 g (98%) of lustrous white plates, mp 93-95°; ir (KBr), 3000, 1770, 1700, 1460, 1400,

1200, 1100, 1060, 1020, 860, 800, 765; nmr (CH_2Cl_2), τ7.20 (s, 3H), 8.35 (s, 6H), 8.45 (s, 6H), 9.03 (s, 3H), 9.35 (s, 3H); ms (70 eV) m/e (rel intensity), 263 (5.6), 248 (2.4), 194 (5.6), 151 (16.7), 150 (100), 149 (23.3), 148 (3.1), 137 (6.9), 136 (15.0), 135 (97.5), 133 (10.3), 121 (7.5), 120 (17.4), 119 (32.5), 115 (6.5), 107 (16.4), 105 (18.1), 93 (12.1), 91 (18.2), 77 (11.1), 57 (17.5), 56 (11.1), 41 (17.4), 39 (11.7); uv (ethanol) λ_{max} 273 mμ (ε1,170), 221 mμ (ε11,310).

Anal. Calcd for $C_{14}H_{21}N_3O_2$: C, 63.87; H, 7.98; N, 15.97. Found: C, 63.88; H, 8.07; N, 16.07.

Attempted hydrogenation of 1,4,7,8,9,10,10-heptamethyl-3,5-diketo-2,4,6-triazatricyclo[5,2,1,$0^{2,6}$]dec-8-ene (19). A solution of 1.75 g (6.7 mmole) of 19 in 75 ml of ethanol was placed in a Parr hydrogenator bottle and 100 mg of 10% Pd/C added. The mixture was shaken under hydrogen (60 psi) for two hours, filtered, and evaporated to starting material.

Repetition using 100 mg of PtO_2 for 16 hours gave no reaction.

Repetition using 100 mg of Pd/C and 25 mg of PdO_2 with one drop of hydrochloric acid gave a purple solution, but analysis of the nmr spectrum of the solution showed no reaction.

Repetition using Pd/C and 3 drops of 60% perchloric acid gave no reaction.

Reaction of cyclopropene with 3,4,4,5-tetramethylisopyrazole (20). A solution of 2.5 g (0.02 mole) of 20[15] in 150 ml of methylene chloride was placed in a 300 ml flask equipped with stirrer, gas inlet tube and calcium chloride exit tube. A stream of cyclopropene and nitrogen generated by the method of Closs and Krantz[32] from 38 g (0.5 mole) of allyl chloride was bubbled in for eight hours. The solution was very dark, but analysis of the nmr spectrum of the solution showed only starting material and no adduct.

Preparation of 1,7-dimethyl-4,8,9-triphenyl-3,5-diketo-2,4,6-triazatricyclo [5.2.1.$0^{2,6}$]dec-8-ene (22). A solution of 1.5 g (6.1 mmole) of 21[17] in 100 ml of methylene chloride was placed in a 250 ml flask equipped with a stirrer and addition funnel. A solution of 1.08 g (6.1 mmole) of phenyltriazolinedione[30] in 100 ml of methylene chloride was added dropwise and the red color disappeared immediately. The mixture was evaporated to a light yellow solid. Recrystallization from benzene produced 2.1 g (82%) of white cubelike crystals: mp 199° (dec); ir (KBr), 1775, 1725, 1520, 1460, 1415, 1325, 1270, 1150, 1120, 1025, 800, 780, 745, 700; nmr ($CDCl_3$), τ2.60 (s, 5H), 2.85 (s, 10H), 7.72 (s, 1H), 7.82 (s, 1H), 8.04 (s, 6H); ms (70 eV) m/e (rel intensity), 418 (1.5), 246 (100), 245 (6.7), 231 (14.8), 229 (5.9), 217 (5.5), 216 (9.3), 215 (13.5), 202 (6.6), 177 (5.6), 155 (10.9), 153 (8.1), 129 (5.9), 119 (11.4), 115 (12.1), 108 (10.1), 101 (8.4), 91 (18.2), 77 (10.3), 51 (6.2); uv (ethanol)

λ_{max} 222 mμ (ε28,410, 260 mμ (ε11,170), 273 mμ (ε10,510).

Anal. Calcd for $C_{27}H_{23}N_3O_2$: C, 76.96; H, 5.46; N, 9.98. Found: C, 76.73; H, 5.56; N, 10.08.

Preparation of 1,7-dimethyl-4,8,9-triphenyl-3,5-diketo-2,4,6-triazatricyclo[5.2.1.$0^{2,6}$]decane (23). A solution of 2.1 g (5 mmole) of 22 in 450 ml of ether/ethyl acetate (1/1) was placed in a Parr hydrogenator bottle and 0.2 g of 5% Pt/C added. The mixture was shaken under hydrogen (15 psi) overnight, filtered, and evaporated to 2.0 g of white solid. Recrystallization from benzene produced a 95% yield of a white solid: mp 242-243°; ir (KBr), 3050, 3000, 1780, 1720, 1620, 1520, 1470, 1425, 1335, 1200, 1150, 1125, 1080, 1030, 920, 875, 815, 770, 710, 700; nmr ($CDCl_3$), τ2.54 (m, 5H), 2.94 (s, 10H), 6.29 (s, 2H), 7.76 (s, 1H), 7.88 (s, 1H), 8.16 (s, 6H); ms (70 eV) m/e (rel intensity), 423 (0.74), 247 (2.7), 246 (4.2), 242 (14.1), 180 (31.0), 179 (18.6), 178 (13.8), 165 (18.1), 131 (21.8), 130 (11.7), 129 (43.0), 128 (25.0), 127 (10.5), 123 (100), 119 (98.5), 115 (31.5), 105 (23.0), 97 (21.5), 96 (30.0), 91 (69.9), 83 (17.0), 82 (11.5), 77 (25.0), 67 (11.2), 65 (10.8), 64 (11.2), 55 (23.5), 42 (14.8), 41 (14.3), 39 (10.3); uv (ethanol) λ_{max} 216 mμ (ε22,820).

Attempted hydrogenation with Pt/C or Pd/C at a pressure of 60 psi resulted in the destruction of the original structure as shown in the nmr spectrum by disappearance of the singlet for the methyl groups at τ8.04.

Preparation of 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]hept-2-ene (24). A solution of 1.27 g (3.1 mmole) of 23 and 2 g (36 mmole) of potassium hydroxide in 15 ml of ethylene glycol was placed in a 25 ml flask equipped with a stirrer, condenser and nitrogen inlet. This was heated to 170° under nitrogen for two hours, cooled and poured into water, extracted with ether, and evaporated to an oil. Water was added and the mixture acidified with 5% HCl. To this was added 25 ml of water containing 3 g (17.5 mmole) of cupric chloride dihydrate. The blue solution turned green immediately and a red-brown solid precipitated. This was left overnight and dried in vacuo, producing 1.0 g (82%) of a rusty brown solid. To this was added 25 ml of concentrated ammonium hydroxide and the mixture stirred for 1/2 hour. The solution turned deep blue with a white precipitate. The mixture was added to water and extracted with ether, dried over sodium sulfate, and evaporated to a white solid. This was chromatographed on silica gel with benzene, and then the methylene chloride eluent was collected and evaporated to 0.5 g of white solid. Recrystallization from methanol/water gave a white powder: mp 105-106°; ir (KBr), 3050, 2950, 2900, 1620, 1510, 1470, 1400, 1320, 1180, 1090, 1045, 925, 855, 785, 755, 705; nmr (CCl_4), τ3.15 (s, 10H), 6.32 (s, 2H), 8.09 (s, 1H), 8.18 (s, 6H), 8.50 (s, 1H); ms (70 eV) m/e (rel intensity), 248 (22.5), 239 (5.8), 234 (15.4), 233 (43.5), 219 (22.1), 205 (11.8), 204 (11.8), 180 (22.1), 179 (23.3),

178 (17.5), 172 (25.0), 171 (100), 170 (17.9), 165 (13.2), 158 (13.9), 157 (75.0), 156 (21.3), 155 (21.7), 143 (43.3), 142 (26.3), 129 (35.8), 128 (24.6), 115 (40.0), 104 (24.2), 91 (72.5); uv (ethanol) λ_{max} 353 mμ (ε250), 341 mμ (ε163 shoulder).

Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.61; H, 7.25. Found: C, 82.74; H, 7.50.

Preparation of 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]hept-2-ene-2-oxide (25). A solution of 1.0 g (3.6 mmole) of 24 in 150 ml of methylene chloride was placed in a 250 ml flask equipped with a stirrer and 0.70 g (4 mmole) of m-chloroperbenzoic acid was added. The mixture was stirred at room temperature for 12 hours, washed with sodium carbonate solution, dried over sodium sulfate, and evaporated to a solid. This was chromatographed on silica gel with methylene chloride, skipping the first yellow band and collecting the rest of the eluent. This was evaporated to 1.0 g (95%) of a white solid. Recrystallization from benzene gave very fine needles: mp 201-202°; ir (KBr), 3030, 3000, 2900, 1515, 1490, 1470, 1400, 1325, 1300, 1270, 1190, 1045, 965, 920, 790, 705, 690; nmr ($CDCl_3$), 2.97 (m, 10H), 5.97 (s, 1H), 6.01 (s, 1H), 7.79 (s, 1H), 7.82 (s, 1H), 8.25 (s, 3H), 8.50 (s, 3H); ms (70 eV) m/e (rel intensity), 292 (0.35), 248 (1.0) 233 (6.5), 181 (22.8), 180 (100), 179 (22.2), 178 (10.6), 165 (9.0), 152 (1.8), 128 (3.5), 115 (5.6), 91 (10.9), 79 (4.2), 78 (55.6), 77 (12.3), 52 (9.3), 51 (10.8),

50 (7.6), 39 (7.1); uv (ethanol) λ_{max} 231.5 mμ (ε4,804 shoulder on end absorption).

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.08; H, 6.85; N, 9.59. Found: C, 78.05; H, 6.88; N, 9.44.

Photolysis of 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene-2-oxide (13). A solution of 0.25 g (1.6 mmole) of 13 in 150 ml of methylene chloride was placed in a photochemical apparatus under nitrogen purge. This was photolyzed with a 450 watt medium pressure lamp via quartz for four hours. Tlc showed that the starting material was all consumed. The mixture was evaporated to an oil and chromatographed on silica gel with ether and methylene chloride. Both fractions gave nmr spectra with no sharp peaks, only broad absorptions.

Photolysis of 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]hept-2-ene-2-oxide (25). A solution of 0.58 g (1.7 mmole) of 25 in 150 ml of methylene chloride was placed in a photochemical apparatus under nitrogen and photolyzed with a 450 watt medium pressure lamp via quartz for four hours. Tlc analysis showed that all starting material was consumed. Chrmoatography on silica gel with methylene chloride and ether gave dark oils whose nmr spectra showed only broad absorptions in the alkyl and aromatic regions, possibly indicative of polymeric material.

Thermolysis of 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene-2-oxide (13). A 0.2 g (1.3 mmole) sample of 13 was

placed in a 5 ml flask connected to a gas measuring buret. This was heated to melting (106°) but there was no gas evolution. On heating to 230°, blackening occurred, but nothing distilled out of the reaction vessel. Analysis of the nmr spectrum showed starting material still present.

Thermolysis of 1,4-dimethyl-5,6-diphenyl-2,3-diazabicyclo-[2.2.1]hept-2-ene-2-oxide (25). A 0.29 g (1 mmole) sample of 25 was placed in a 5 ml flask connected to a gas measuring buret. This was heated to 230°, but there was no gas evolution or apparent change. Analysis of the nmr spectrum showed only starting material present.

Preparation of 2,3-dimethyl-2,3-diazabicyclo[2.2.2]oct-5-ene (34). A suspension of 1.0 g (0.026 mole) of lithium aluminum hydride in 200 ml of ether was placed in a 300 ml flask equipped with a stirrer and addition funnel. A solution of 5 g (0.02 mole) of 2,3-dicarboethoxy-2,3-diazabicyclo[2.2.2]oct-5-ene[33] in 15 ml of ether was added dropwise. The mixture was stirred at room temperature for two hours, diluted with a minimum amount of water, and filtered. The solid was washed with ether and the ether dried over sodium sulfate and evaporated to an oil. Distillation at 40°/4 mm produced 0.4 g (15%) of a clear, colorless oil. Gas chromatography on an 8' GESF column at 130° gave only one product: ir (film), 3000, 2900, 1440, 1380, 1180, 1120, 1085, 980, 900, 860, 825, 725; nmr (CCl_4), τ3.66 (m, 2H), 6.83 (m, 2H), 7.77 (s, 6H),

7.98 (m, 2H), 8.88 (m, 2H); ms (70 eV) m/e (rel intensity), 138 (30.3), 96 (3.8), 95 (44.2), 81 (5.0), 80 (32.7), 79 (29.1), 77 (8.7), 68 (7.4), 67 (5.4), 60 (59.4), 59 (45.4), 58 (8.1), 55 (6.3), 53 (4.9), 51 (5.5), 45 (22.0), 43 (100), 42 (21.6), 41 (11.4), 39 (13.1); uv (ethanol) λ_{max} 243 mμ (ε356), (cyclohexane) λ_{max} 263 mμ (ε400).

Anal. Calcd for $C_8H_{14}N_2$: C, 69.57; H, 10.14. Found: C, 69.74; H, 10.30.

Reaction of 3,5-dimethyl-4,4-diethylisopyrazole-1-oxide (4) with 4,4-dimethylpyrazoline-3,5-dione (38). A solution of 0.80 g (6.2 mmole) of 4,4-dimethyl-1,2-dihydropyrazoline-3,5-dione[34] in 100 ml of methylene chloride was placed in a 250 ml flask equipped with a stirrer, gas inlet tube, and external ice bath. A 10 g sample of sodium sulfate was added. After cooling to 0°, N_2O_4 gas was bubbled in for 10 minutes, resulting in a deep blue solution. The resulting solution was filtered and concentrated to half volume. The concentrate was added to a solution of 1.0 g (6 mmole) of 4 in 100 ml of methylene chloride at 0°. The deep blue color disappeared very slowly to yield a yellow solution. The solution was evaporated to an oil. Analysis of the nmr spectrum indicated only 4 present and no adduct.

Attempted oxidation of 1,4,7,10,10-pentamethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]deca-8-ene (1). A solution of 1.2 g (5 mmole) of 1[3] in 50 ml of ether/

methylene chloride (3/1) was placed in a 100 ml flask equipped with a magnetic stirrer, addition funnel and external ice bath. A 1.75 g (16.5 mmole) sample of sodium carbonate was added. After cooling to 0°, a solution made by adding 2.1 g (10 mmole) of trifluoroacetic anhydride to 0.37 g (10 mmole) of 90% hydrogen peroxide in 15 ml of ether at 0° was added dropwise over one hour. After stirring at 0° for four hours, water was added, the layers separated, and the organic layer washed with a sodium carbonate solution and water. The resulting solution was dried over sodium sulfate and evaporated to a solid. Analysis of the nmr spectrum of this solid showed approximately a 50% conversion to the oxide as demonstrated by the appearance of new peaks at τ7.00 (s, 3H), 8.04 (s, 3H), 8.07 (s, 3H), 8.74 (s, 3H), and 9.11 (s, 3H), as well as a typical azoxy absorption at 1520 cm^{-1} in the ir spectrum. Repetition of the experiment with stirring times changed to 1/2 hour at 0°, 1/2 hour at room temperature, and three hours at reflux led to a solid which nmr data identified as pure starting material.

Treatment of the 50% oxidized mixture with a second treatment of oxidizing solution of the same strength with stirring for 10 hours led, after the usual work-up, to a 60% conversion as measured by nmr spectroscopy. One more treatment raised the conversion to 65%. Chromatography on silica gel was tried with methylene chloride/acetone (1/1), but no pure oxide was obtained, only mixtures.

Attempted oxidation of 1,4,7,10,10-pentamethyl-3,5-diketo-2,4,6,8,9-pentaazatricyclo[5.2.1.$0^{2,6}$]deca-8-ene (1). A solution of 2.37 g (10 mmole) of 1 in 50 ml of chloroform was placed in a 100 ml flask equipped with magnetic stirrer and 2.8 g (14 mmole) of m-chloroperbenzoic acid added. The mixture was stirred at room temperature with analysis by nmr spectroscopy to determine conversion to the oxide. Conversions were 8% in two hours, 33% in 24 hours, 50% in 72 hours, and 56% in 120 hours. Addition of excess peracid did not increase the conversion percentage. Refluxing gave no conversion. As in the previous case, no pure oxide could be isolated.

Attempted oxidation of 1,4,4,7,10,10-hexamethyl-3,5-diketo-2,6,8,9-tetraazatricyclo[5.2.1.$0^{2,6}$]non-8-ene (41)[4]. A solution of 250 mg (1 mmole) of 41 in 50 ml of methylene chloride was placed in a 100 ml flask equipped with magnetic stirrer and 260 mg (1.5 mmole) of m-chloroperbenzoic acid added. The reaction mixture was stirred at room temperature for three days. The reaction was followed by nmr spectroscopy, but at the end of three days no reaction had occurred and only 41 was present, with no oxide observable.

Attempted oxidations of 1,4,7-triphenyl-10,10-dimethyl-3,5-diketo-2,4,6,8,9-pentaaza[5.2.1.$0^{2,6}$]non-8-ene (40). A solution of 4.7 g (11 mmole) of 40[3] in 100 ml of methylene chloride was placed in a 250 ml flask equipped

with a stirrer and 2.1 g (12 mmole) of m-chloroperbenzoic acid added. The mixture was stirred at room temperature for 24 hours. Analysis of the nmr spectrum indicated no change in 40 at this time.

A solution of 2.1 g (5 mmole) of 40 in 100 ml of ether/methylene chloride (1/1) was placed in a 250 ml flask equipped with a magnetic stirrer, addition funnel and external cooling bath, and 3.5 g (42 mmole) of sodium carbonate added. After cooling to 0°, a solution made by adding 2.1 g (10 mmole) of trifluoroacetic anhydride to 0.37 g (10 mmole) of 90% hydrogenpperoxide in 10 ml of ether at 0° was added dropwise over one hour. After stirring for three hours, water was added and the solution extracted with ether. The ether extracts were washed with a sodium carbonate solution, dried over sodium sulfate, and evaporated to a solid. Analysis of the residue by nmr spectroscopy indicated pure 40 and no oxide.

Preparation of 3,4,4,5,5,6-hexamethyl-4,5-dihydropyridazine (43). A solution of 8.0 g (48 mmole) of 42^{35} and 5.0 g (156 mmole) of anhydrous hydrazine in 50 ml of benzene was placed in a 100 ml flask equipped with a magnetic stirrer and condenser. The mixture was heated to reflux overnight. The water layer that developed was removed and the solution dried over sodium sulfate. Evaporation led to an oil which was distilled at 85-87°/0.7 mm to give 6 g (78%) of a clear, colorless liquid. Cooling in dry ice caused crystallization to a white solid: mp (from hexane)

43-44°; ir (film), 3000, 2920, 1600, 1580, 1480, 1440, 1400, 1380, 1290, 1130, 920, 760; nmr (benzene), τ8.09, (s, 6H), 9.33 (s, 12H); ms (70 eV) m/e (rel intensity), 166 (44.0), 151 (17.6), 110 (19.6), 100 (11.4), 86 (29.3), 85 (18.6), 84 (52.8), 83 (11.7), 78 (79.2), 77 (15.5), 69 (95.4), 67 (13.4), 57 (17.8), 55 (24.4), 53 (14.7), 52 (17.6), 51 (18.7), 50 (13.5), 43 (64.5), 42 (42.1), 41 (100), 39 (42.5); uv (ethanol) λ_{max} 246 mμ (ε2,177), 227 mμ (ε2,730).

Anal. Calcd for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91. Found: C, 72.10; H, 10.97.

Preparation of 3,4,4,5,5,6-hexamethyl-2,3,4,5-tetrahydropyridazine (44). A solution of 1.66 g (10 mmole) of 43 in 50 ml of acetic acid was placed in a 500 ml Parr hydrogenator pressure bottle and 0.20 g of 5% Pt/C added. After shaking under 40 psi of hydrogen for two hours, the solution was neutralized with a sodium hydroxide solution and extracted with ether. The ether extracts were dried over sodium sulfate and evaporated to a colorless liquid. This was chromatographed on silica gel with ether to yield 1.42 g (85%) of a colorless oil. Hydrogen chloride gas was bubbled into an ether solution of this oil to produce a white precipitate, mp 184°. Oil data: ir (film), 3300, 2950, 1465, 1440, 1400, 1380, 1365, 1320, 1155, 1140, 1120, 1100, 1030, 990, 760; nmr (CCl_4), τ4.90 (bs, 1H), 6.80 (q, J=6 Hz, 1H), 8.29 (s, 3H), 9.00 (s, 3H), 9.04 (s, 3H), 9.10 (d, J=6Hz, 3H), 9.25 (s, 3H), 9.30 (s,

3H); ms (70 eV) m/e (rel intensity), 168 (26.4), 153 (9.9), 149 (12.8), 111 (15.5), 97 (8.2), 96 (8.7), 84 (66.8), 83 (16.5), 76 (8.0), 69 (72.6), 57 (12.8), 55 (14.8), 44 (100), 43 (16.0), 42 (49.4), 41 (58.6), 39 (16.5).

Anal. Calcd for $C_{10}H_{21}N_2Cl$: C, 58.66; H, 10.34; N, 13.68. Found: C, 58.48; H, 10.43; N, 13.41.

A suspension of 0.50 g (13 mmole) of lithium aluminum hydride in 50 ml of ether was placed in a 100 ml flask with a magnetic stirrer and addition funnel. A solution of 1.0 g (6 mmole) of 43 in 10 ml of ether was added dropwise and stirred for one hour at room temperature. The mixture was poured onto ice and hydrochloric acid, neutralized with a sodium hydroxide solution, and extracted with ether. The extracts were dried over sodium sulfate and evaporated to 0.90 g (89%) of a colorless oil identical to 44 by nmr spectroscopy and ir spectroscopy.

Attempted oxidation of 3,4,4,5,5,6-hexamethyl-4,5-dihydropyridazine (43). A solution of 1.0 g (6 mmole) of 43 in 25 ml of methylene chloride was placed in a 50 ml flask equipped with a stirrer. This was cooled to 0° and 1.05 g (6.1 mmole) of m-chloroperbenzoic acid was added. Gas evolution began immediately. The mixture was stirred for one hour, diluted with water and extracted with ether, washed with a sodium carbonate solution and water, dried over sodium sulfate, and evaporated to an orange oil. Analysis of the nmr spectrum showed no oxide present.

Reaction of 3,3,4,4-tetramethyl-2,5-hexanedione (42) with hydroxylamine hydrochloride. A solution of 1.7 g (10 mmole) of 42[35] and 3.0g (4.2 mmole) of hydroxylamine hydrochloride in 50 ml of pyridine was placed in a 100 ml flask equipped with a stirrer and condenser. This was refluxed for eight hours and added to ice water, but no solid formed. The mixture was extracted with ether, dried over sodium sulfate and evaporated to an oil. Analysis of the nmr spectrum showed no dioxime.

Reaction of 3,4,4,5,5,6-hexamethyl-4,5-dihydropyridazine (43) with phenyltriazolinedione. A solution of 2.0 g (12 mmole) of 43 in 50 ml of methylene chloride was placed in a 250 ml flask equipped with a stirrer and addition funnel. A solution of 2.1 g (12 mmole) of phenyltriazolinedione[30] in 100 ml of methylene chloride was added dropwise at room temperature. The red color disappeared immediately but was replaced by a deep green-black color. Evaporation produced a dark gum. Analysis of the nmr spectrum showed a myriad of peaks and tlc showed several components.

Repetition of the experiment but with the addition done at -78° gave no fading of the red color. Warming to -30° led to loss of the red color, but the green color appeared immediately. Work-up produced the same results as above.

Preparation of 1,2-dicarboethoxy-3,6-dimethyl-4,5-dibromohexahydropyridazine (49). A solution of 10.2 g (0.04 mmoles)

of 1,2-dicarboethoxy-3,6-dimethyl-1,2,3,6-tetrahydropyridazine (48)[36] in 100 ml of carbon tetrachloride was placed in a 250 ml flask equipped with a stirrer and addition funnel. A 6.4 g (0.04 mmole) sample of bromine was added dropwise. The solution was stirred for one hour and then evaporated to a yellow oil. Distillation at 140°/0.001 mm yielded 11 g (66%) of a clear colorless oil: ir (film), 2950, 1720, 1465, 1410, 1380, 1310, 1290, 1190, 1130, 1045, 755; nmr (CCl_4), τ5.13-6.14 (m, 8H), 8.05-8.97 (m, 12H); ms (70 eV) m/e (rel intensity), 418 (8.7), 416 (17.3), 414 (8.7), 337 (8.9), 335 (8.9), 265 (18.5), 263 (18.5), 256 (26.7), 183 (28.7), 169 (35.9), 139 (35.4), 131 (30.8), 123 (22.6), 111 (100), 109 (21.4), 95 (28.7), 85 (24.6), 82 (31.8), 81 (47.2), 67 (36.4), 55 (62.1), 41 (67.2).

Attempted preparation of 1,2,3,6-tetramethyl-1,2-dihydropyridazine (46). A solution of 8.0 g (19.2 mmole) of 49 and 3 g (19.2 mmole) of potassium hydroxide in 40 ml of ethanol was placed in a 100 ml flask equipped with stirrer and condenser. The mixture was heated to 100° for three hours, cooled, and the solid which formed was filtered off. The filtrate was concentrated to a dark oil and distilled at 108-110°/0.001 mm. Analysis of the nmr spectrum showed the presence of vinyl peaks at τ4.27 and a singlet at τ8.20, indicating possible success, along with extra peaks. The mixture was used with no further purification.

A suspension of 1.5 g of LAH in 50 ml of ether was placed in a 100 ml flask equipped with a stirrer and addition funnel. A 3 g sample of the above mixture in 10 ml of ether was added dropwise and stirred two hours longer at room temperature. To this was added 1.5 ml of water. The mixture was filtered and the solid washed with ether. The combined ether solutions were dried over sodium sulfate and evaporated to an oil. Analysis of the nmr spectrum showed the only vinyl peak (τ4.57) to be from the 1,2,3,6-tetramethyl-1,2-diaza-1,2,3,6-tetrahydropyridazine (50).

Preparation of 1,2,3,6-tetramethyl-1,2,3,6-tetrahydropyridazine (50). A suspension of 5 g (0.13 mole) of lithium aluminum hydride in 300 ml of ether was placed in a 500 ml flask equipped with a stirrer, addition funnel and external ice bath. A solution of 27 g (0.105 mole) of 48^{36} in 25 ml of ether was added dropwise. (Cooling was necessary to moderate the force of the reaction.) The mixture was stirred for three hours and then 5 ml of water, 10 ml of 15% sodium hydroxide, and 15 ml of water were added. The mixture was filtered and the solid washed with ether. The ether solution was dried over sodium sulfate and evaporated to an oil. Distillation at 63°/20 mm yielded 4.0 g (25%) of colorless liquid: ir (film), 3000, 2900, 2800, 1455, 1370, 1330, 1230, 1130, 1100, 1090, 1040, 815, 750; nmr (neat), τ4.57 (m, 2H), 7.16 (q, J=6 Hz, 2H), 7.73 (s, 6H), 8.93 (d, J=6 Hz, 6H);

ms (70 eV) m/e (rel intensity), 140 (73.9), 126 (8.9), 125 (13.8), 111 (19.3), 109 (9.9), 95 (11.6), 84 (7.5), 82 (38.4), 81 (9.7), 70 (8.3), 68 (7.7), 67 (42.0), 59 (34.8), 58 (15.7), 56 (30.4), 55 (15.9), 53 (7.7), 43 (100), 42 (24.6), 41 (15.7), 39 (10.4); uv (ethanol) λ_{max} 332 mμ (ε210).

Anal. Calcd for $C_8H_{16}N_2$: C, 68.57; H, 11.43. Found: C, 68.32; H, 11.51.

Reduction of 1,2-dicarboethoxy-3,6-dimethyl-4,5-dibromo-1,2-diazahexahydropyridazine (49). A suspension of 2 g (52.6 mmole) of LAH in 100 ml of ether was placed in a 250 ml flask equipped with a stirrer and addition funnel. A solution of 10 g of 49 in 10 ml of ether was added dropwise and the mixture was stirred one hour at room temperature. To this was added 2 ml of water, 3 ml of 15% NaOH, and 6 ml of water. The solid was filtered off, washed with ether, dried over sodium sulfate, and evaporated to an oil. Analysis of the nmr spectrum showed 1,2,3,6-tetramethyl-1,2,3,6-tetrahydropyridazine (50) present.

Attempted bromination of 1,2,3,6-tetramethyl-1,2,3,6-tetrahydropyridazine (50). A solution of 4.0 g (2.8 mmole) of 50 in 40 ml of carbon tetrachloride was placed in a 100 ml flask and a solution of 4.5 g (2.8 mmole) of bromine in 15 ml of carbon tetrachloride was added dropwise. On the bottom of the flask a thick, black tar

formed; this tar was insoluble in carbon tetrachloride and ether.

Attempted oxidation of 1,2-dimethoxy-3,6-dimethyl-1,2,3,6-tetrahydropyridazine. A solution of 4.56 g (20 mmole) of 1,2-dimethoxy-3,6-dimethyl-1,2,3,6-tetrahydropyridazine[37] and 2.2 g (20 mmole) of selenium dioxide in 50 ml of acetic acid was placed in a 100 ml flask equipped with a stirrer and condenser. The mixture was refluxed for four hours and then cooled. A black solid was filtered. The filtrate was evaporated and distilled, yielding 1 g of liquid at 102°/0.4 mm, identical with starting material.

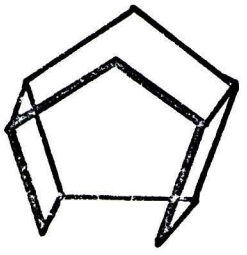
Attempted reaction of 3,6-dimethyl-α-pyrone (51) with phenyltriazolinedione. A solution of 1.0 g (8.1 mmole) of 51[38] in 40 ml of methylene chloride was placed in a 100 ml flask equipped with a stirrer and addition funnel. A solution of 1.4 (8.1 mmole) of phenyltriazolinedione[28] in 25 ml of methylene chloride was added dropwise. The red color disappeared slowly. The mixture was evaporated to an oil. Analysis of the nmr spectrum showed starting material still present. Distillation at 74-76°/1 mm yielded 0.5 g of starting material, 51.

II. INVESTIGATIONS ON THE TETRACYCLO[5.3.0.$0^{2,6}$.$0^{5,8}$]DECANE SYSTEM

Results and Discussion

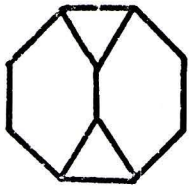
Polycyclic compounds have been the subject of intensive research in recent years. Many new ring systems have been synthesized and investigated. Among these have been several of the tetracyclodecane geometry:

tetracyclo[6.2.0.$0^{3,6}$.$0^{4,10}$]decane (52)[39]



52

tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]decane (53)[40]

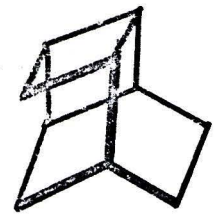


53

tetracyclo[4.4.0.$0^{2,5}$.$0^{7,10}$]decane (54)[41]

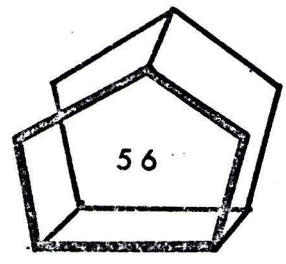
54

tetracyclo[4.2.2.$0^{2,5}$.$0^{4,10}$]decane (55)[42]



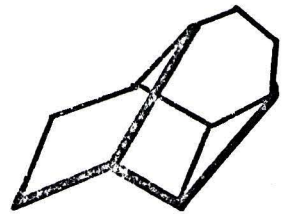
55

tetracyclo[4.4.0.0^{3,9}.$0^{4,8}$]decane (56)[43]



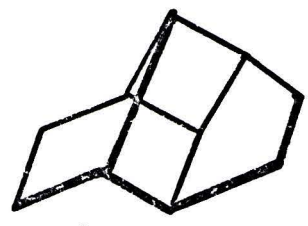
56

tetracyclo[4.4.0.0^{2,8}.$0^{5,7}$]decane (57)[44]



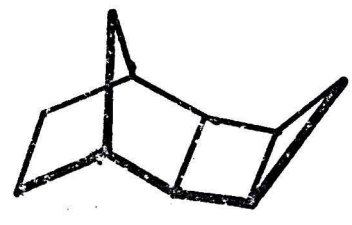
57

tetracyclo[5.2.1.$0^{2,6}$.$0^{3,10}$]decane (58)[45]



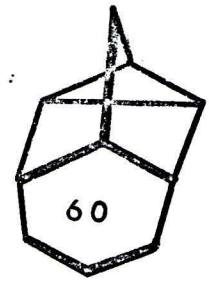
58

tetracyclo[5.2.1.$0^{2,6}$.$0^{3,5}$]decane (59)[46]



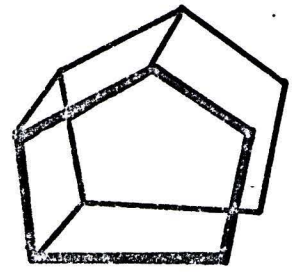
59

tetracyclo[5.3.0.$0^{2,10}$.$0^{3,8}$]decane (60)[47]



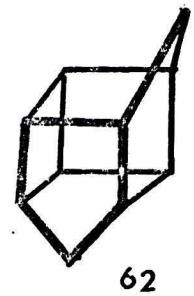
60

However, the tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]decane system (61) was unknown:



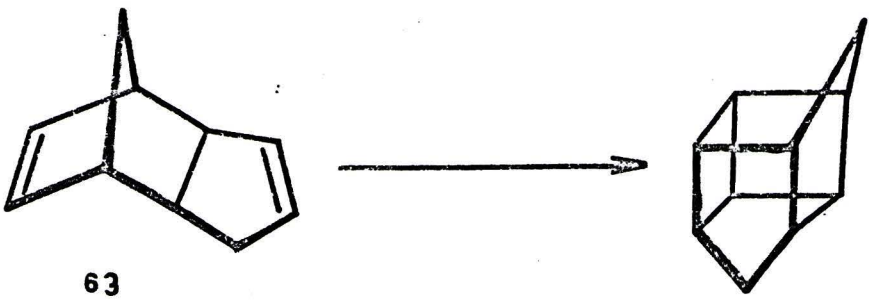
61

We were interested in this system, particularly in the tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-3,9-diene (64). We approached the system synthetically in two different ways. The first started from the well known pentacyclo[5.3.0.-$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane system (62):



62

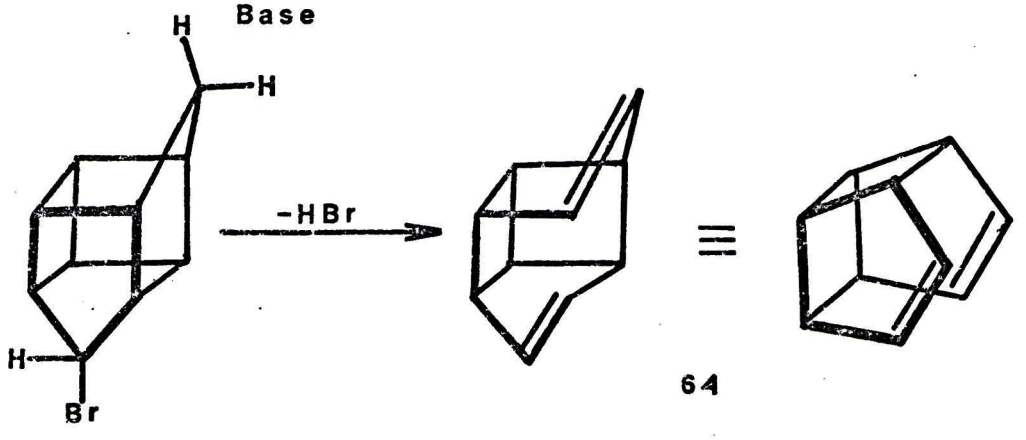
All derivatives of this system have been prepared by the photolysis of the appropriate 3a,4,7,7a-tetrahydro-4,7-methanoindene, 63:[48a,b]



63

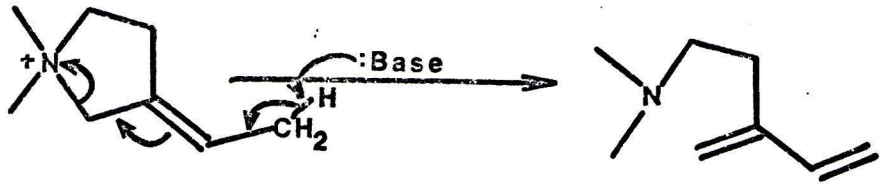
These derivatives have been used primarily as intermediates in the preparation of other interesting polycyclic compounds such as cubane[49] and homo-cubane.[50] Solvolyses of the tosylate derivatives of 62 have been conducted and bridged carbonium ions proposed as intermediates.[51a,b]

We hoped to use system 62 as a precursor to the desired tetracyclic system, 61. To accomplish this transformation we were depending on a 1,4 elimination of hydrogen bromide with concurrent formation of two double bonds and ring opening of one of the cyclopentanes:



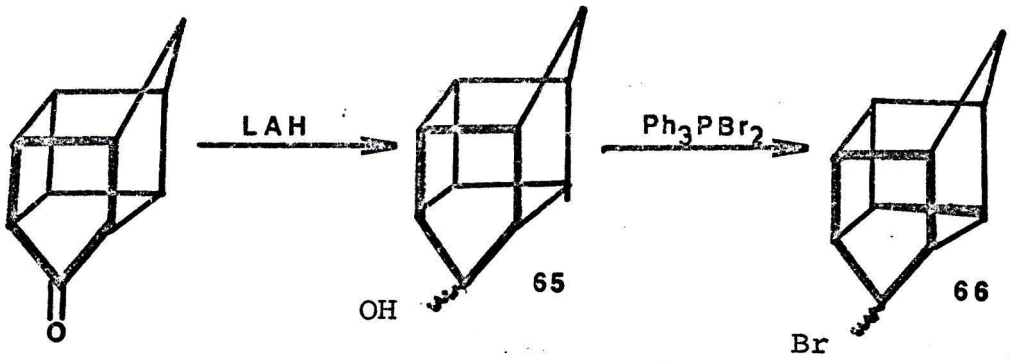
64

1,4 eliminations are well documented occurrences in the literature. They frequently involve ring opening and multiple olefin formation also.[52]



In our case it was hoped that the ring strain present in the pentacyclic system would be relieved to some degree in going to the tetracyclic system and thus provide a driving force for the reaction.

The starting point for our attempts in this direction was the known pentacyclic alcohol 65.[53] Since this was formed by lithium aluminum hydride reduction of the corresponding ketone, a mixture of isomers was obtained. The reported ratio is 80% exo and 20% endo. Treatment of this mixture with triphenylphosphine dibromide in dimethylformamide at reflux led smoothly to a light yellow oil (66). The presence of the bromide was demonstrated by appearance in the mass spectrum of peaks at m/e 212 (0.2) and 210 (0.2). According to the present view of the mechanism of this reaction,[54] inversion about the carbon with the alcohol moiety should occur in the introduction of the bromide. This means that in our case the major product should be the endo bromide from the exo alcohol. This is important because the desired elimination should occur through this isomer. Nmr analysis of 66 showed a 62:38 mixture:

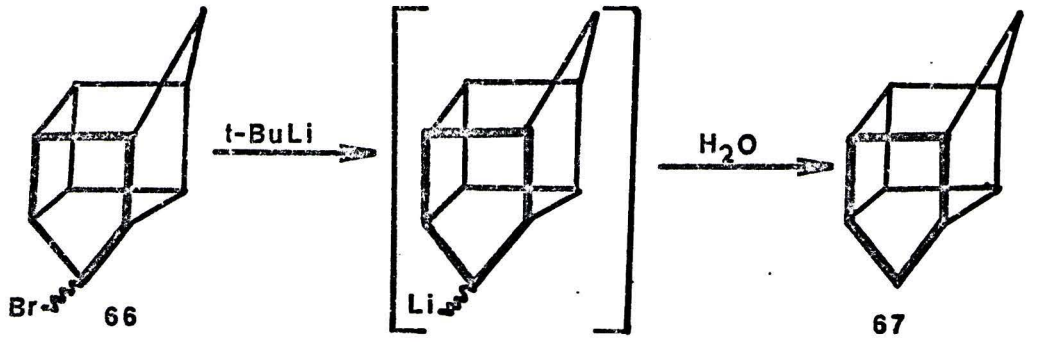


Despite the synthesis of the right isomer, however, our efforts to induce the desired 1,4 elimination were in vain. Treatment of 66 with potassium t-butoxide in t-butanol yielded only starting material. Also, potassium t-butoxide in dimethyl sulfoxide gave back only starting material. Finally, potassium t-butoxide in hexamethylphosphoramide gave starting material also.

Treatment of 66 with the sodium salt of 2-n-butylhexanol in refluxing 2-n-butylhexanol gave only starting material. Similarly, treatment with lithium chloride in dimethylformamide at 100° also gave no reaction. Lastly, starting material was the only product of treatment of 66 with sodium amide in refluxing benzene.

Our string of failures abated somewhat in the reaction of 66 with t-butyllithium in hexane. At 0° no reaction occurred, but refluxing for 30 hours under nitrogen resulted in the disappearance of all bromide. Glpc separation of the main component after work-up yielded a white solid. Mass spectral analysis showed loss of the bromine and appearance of a new parent peak at m/e 132. Comparison of the nmr spectrum with that of 1,3-bishomocubane (67)[55]

confirmed that this was indeed the product. This probably was formed via a lithium exchange reaction followed by protonation in the water work-up:



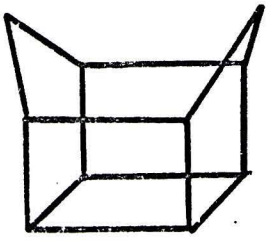
66 67

Our final attempt at forcing the dehydrobromination to occur utilized n-butyllithium in refluxing hexane. After 24 hours 66 was all consumed and glpc separation of the major component yielded a thick yellow oil. Analysis and mass spectral data indicated loss of the bromide and appearance of a new parent peak at m/e 188 corresponding to the gain of C_4H_9. Nmr analysis confirmed the presence of the alkyl chain from a nucleophilic displacement of the bromide by the butyl group,68:

66 68

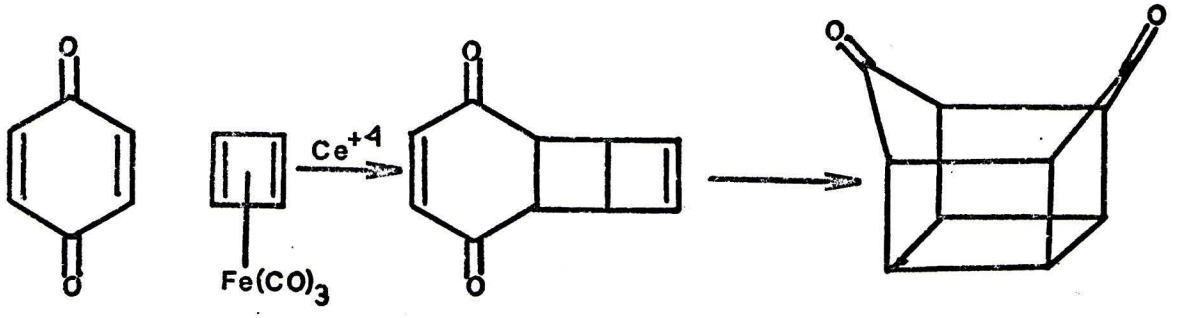
This system then seemed determined not to yield the desired product. Evidently the proton that must be abstracted to start the process is not sufficiently acidic and other competing reactions take place preferentially.

Since this was the case, we reluctantly turned our attention to the other possible route to the desired system. This involved the pentacyclo[4.4.0.$0^{2,5}$.$0^{4,8}$.$0^{3,9}$]-decane, 69:



69

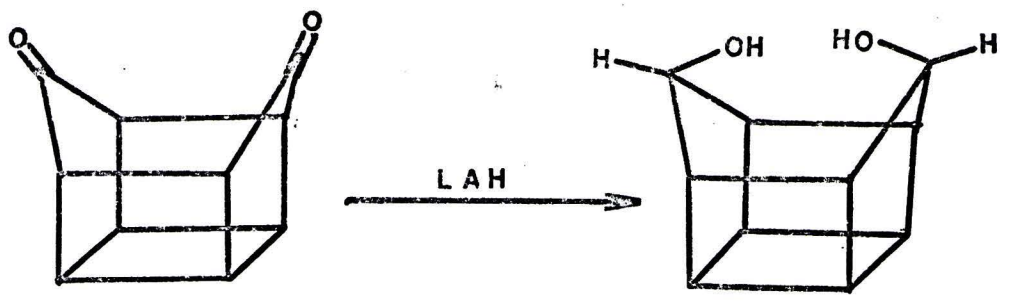
The simplest and most traveled route to this system is via the photolysis of the appropriate adduct of quinone and cyclobutadiene, as pioneered by Pettit et al.:[56]



70

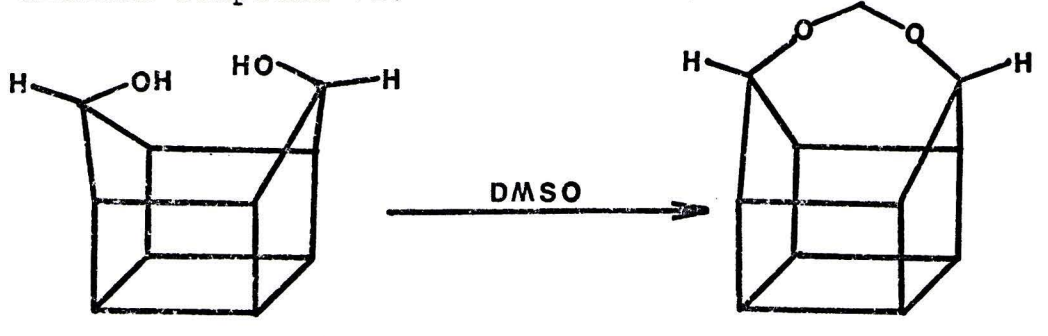
Main uses of this system to date have also been in the preparation of various substituted cubanes.[56] Again, though, no routes to the desired tetracyclic system, 61, were known.

Our starting point in this system was the known 7,10-diketone, 70. This was converted by lithium aluminum hydride in refluxing tetrahydrofuran into a white solid, 71, in 85% yield. Analysis and mass spectral data showed the gain for four protons and the ir spectrum showed peaks at 3300 cm^{-1}:



70 71

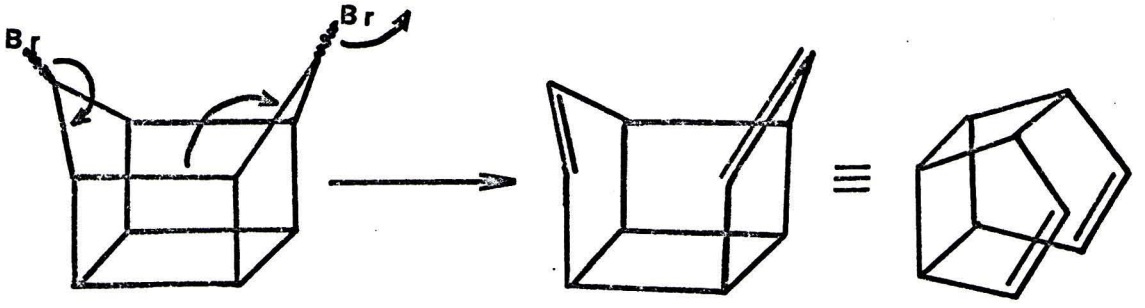
Use of models indicated that the probable configuration of the diols would be with both hydroxy groups pointing into the center of the cage. This was confirmed by the reaction of the diol with dimethyl sulfoxide at 160°. If one hydroxy group were in and one out, the result would have been a dehydration with ether formation.[57] Both groups out would have led to nothing happening. Instead, glpc collection of the major product after work-up was a white solid. Analysis and mass spectral data indicated the gain of 12 mass units. The ir spectrum showed no hydroxy absorptions, and the nmr spectrum showed a new singlet at τ5.20. These data are best explained by the dioxane compound 72:



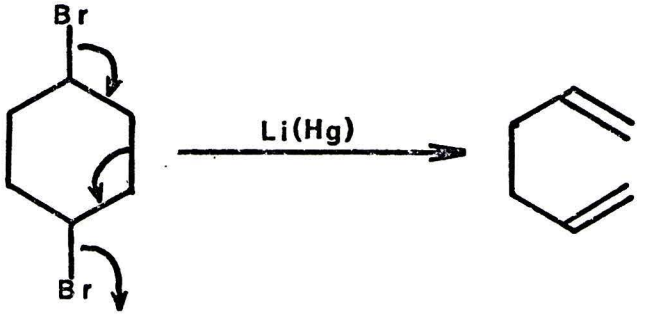
71 72

The use of this system as a route to the desired system 61 involved another 1,4 elimination with concurrent ring opening and formation of two double bonds. The main

difference was that this one involved loss of a bromine molecule. There was good analogy for this reaction in the report on the debromination of 1,4-dibromocyclohexane:[58]



64

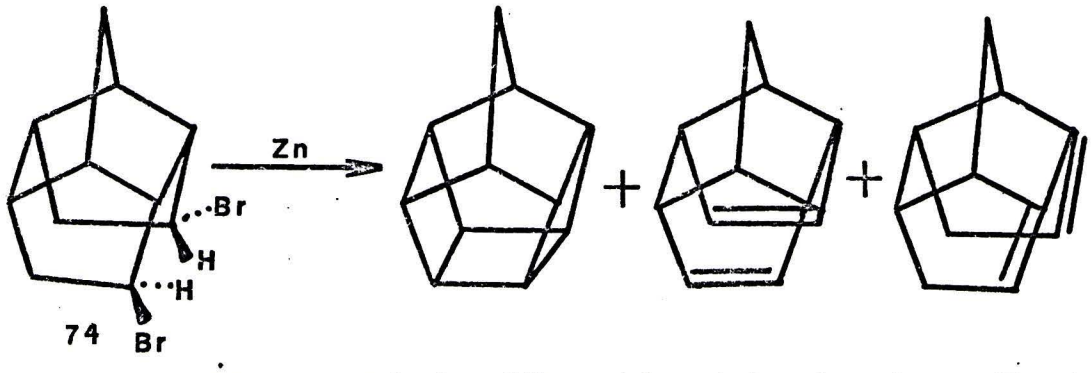


The initial problem was converting the diol into the dihalide. Treatment of the diol with thionyl chloride in pyridine yielded no reaction. Also, treatment with triphenylphosphine dibromide gave no product. Nor did reaction with gaseous hydrogen bromide in methylene chloride yield any bromide. Also, reaction with trifluorochloroethyldiethylamine[59] and lithium bromide in methylene chloride gave no reaction. Lastly, treatment of the diol with phosphorus tribromide in pyridine gave nothing.

However, neat phosphorus tribromide at 130° for 20 hours did cause a reaction to occur. Work-up and chromatography gave 73, a white solid, in 25% yield. Analysis and mass spectral peaks at m/e 292(.2), 290(.4),

and 288(.2) indicated acquisition of two bromines. The nmr spectrum gave two broad singlets at τ6.73 and 5.33 in ratio of 8:2.

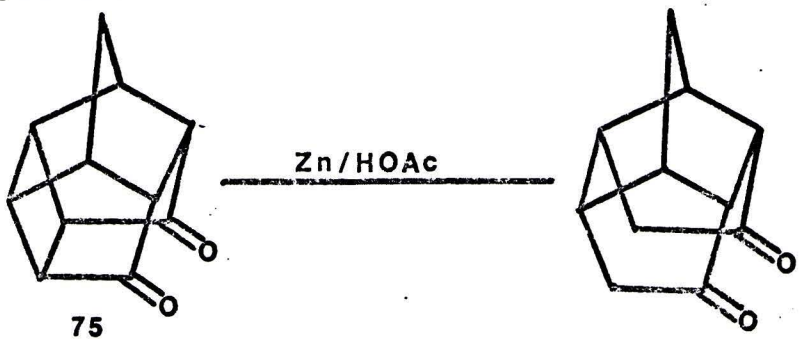
With the necessary dihalide in hand we turned to the problem of debromination. The obvious choice was the usual one--zinc and hot ethanol--because it had been very effective in a similar reaction in a closely related cage system (74):[60]



However, treatment of the dibromide with zinc in refluxing ethanol for two hours gave only starting material and no hydrocarbon products.

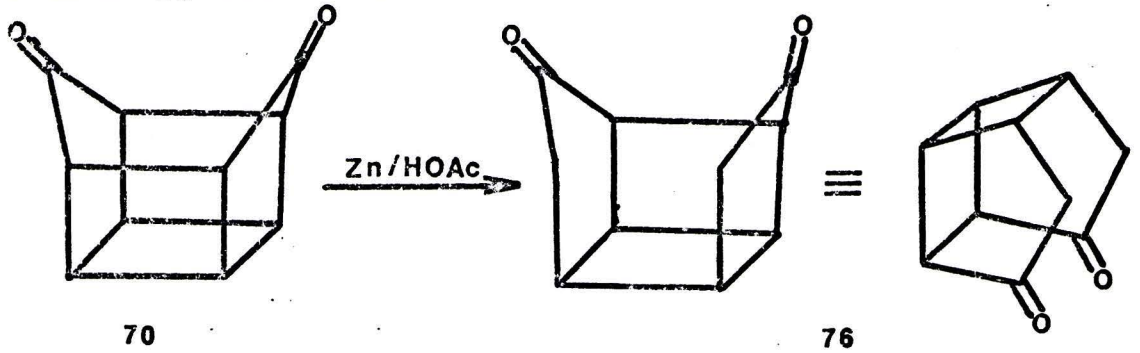
We then turned to the procedure reported for the dibromocyclohexane using lithium amalgam. Treatment of the dibromide with 0.4% lithium amalgam in ether for five days, work-up with water, and injection of the residue on the glpc gave two peaks with the right retention time for C_{10} hydrocarbons. Collection of the peaks and analysis of the mass spectra and nmr spectrum indicated possible success, although in low yield. Attempts to reproduce these results in ether or tetrahydrofuran were not successful.

This route seemed another dead end until a report appeared in the literature which showed the way to the desired system 61:[61]



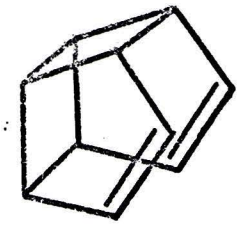
75

Treating the diketone 70 with zinc and acetic acid under the reported conditions yielded after work-up an 80% yield of a white solid, 76. Elemental analysis and mass spectral data indicated the gain of two protons. The ir spectrum still contained the carbonyl group absorptions, and the nmr spectrum contained two broad absorptions at τ6.56 and 7.55 in ratio of 6:4. The reaction appeared to succeed for our dione also:



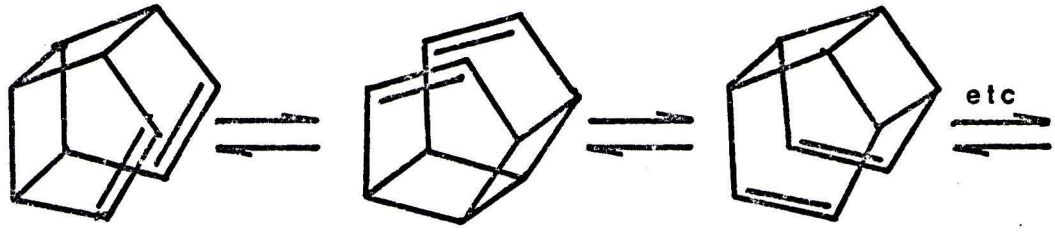
70 76

Thus, we had arrived at the first of our goals, the synthesis of the tetracyclic system 61. Once we knew that we had an entry into the system, we turned to our second goal, the introduction of two double bonds into the system at the 3 and 9 positions.



64

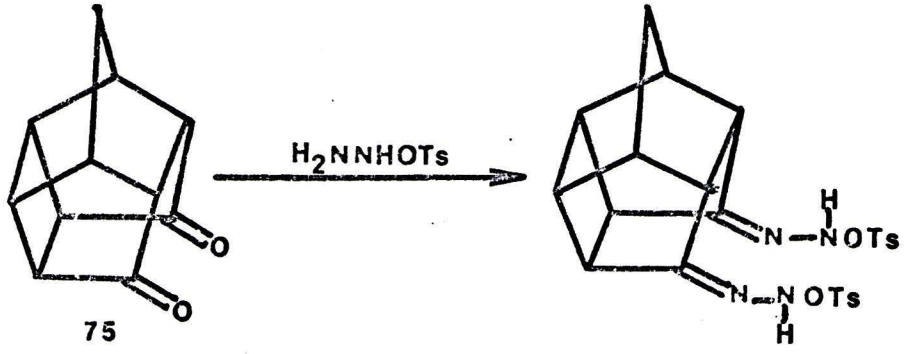
We believed that this would be an interesting compound because the geometry of its double bonds was such that the potential for undergoing facile Cope rearrangements was quite large. This would lead to a series of degenerate rearrangements that would eventually make all of the carbons in the molecule equivalent by nmr spectroscopy if the rate of rearrangement were fast enough:



The analogy to the bullvalene system[62] is obvious, with bullvalene's cyclopropane unit replaced by a cyclobutane. This rearrangement and other thermal and photochemical reactions of the diene seemed quite interesting as it is a $C_{10}H_{10}$ hydrocarbon, many of which have been synthesized recently.

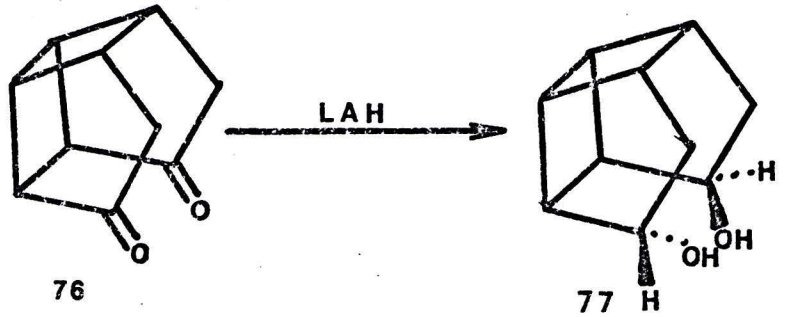
Our initial attempt at entry into this system involved preparation of the ditosylhydrazone and then reaction of it with base to yield the diene. However,

problems arose in making the necessary ditosylhydrazone. The cage compound, 75, yielded a solid upon treatment with tosylhydrazine in ethanol with 1% HCl added. Treatment of 76 under the same conditions led to gradual darkening of the solution, but no solid ever precipitated:



75

Our next attempt at entry into this system involved reduction of the dione to the diol with lithium aluminum hydride in ether. This proceeded smoothly to give a white solid, 77, in 80% yield. Elemental analysis and mass spectral data indicated the gain of four hydrogens. The ir spectrum contained hydroxyl absorptions at 3250 cm^{-1}. The presence of the new hydrogens was demonstrated in the nmr spectrum by the splitting of the methylene hydrogens into a broad doublet, and new peaks at τ5.05 and 5.63, with an area of two hydrogens each:



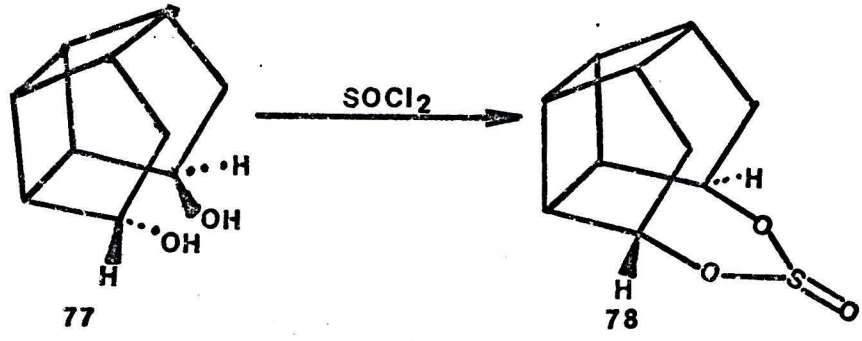
76 77

Attempts were then made to doubly dehydrate this diol

to the desired diene. Among the methods tried was sublimation of the diol into a tube filled with activated alumina at 500° and 0.01 mm. No hydrocarbons were found in the dry ice traps placed between the pump and the alumina. Reaction with phosphorus oxychloride and pyridine at room temperature resulted in no hydrocarbons as determined by tlc.[63] Reaction with zinc chloride at 230° neat and 200 mm vacuum gave no hydrocarbons in the intervening traps as determined by glpc. Reaction of the diol with phenyl isocyanate in ether at room temperature yielded a solid which had phenyl and amide peaks in the nmr spectrum. Pyrolysis of this solid at 220° under full vacuum again gave no hydrocarbons in the intervening traps. Reaction with tosyl chloride and sulfur dioxide in dimethylformamide[64] at room temperature gave only starting material. Reaction of the diol with a solution formed by the action of five parts ethanol with two parts phosphorus pentoxide[65] at 90° again gave no hydrocarbon products. Treatment of the diol with sodium hydride in tetrahydrofuran/ether, addition of carbon disulfide, and addition of methyl iodide resulted in a yellow solid. Analysis of the nmr spectrum showed the normal cage peaks plus a singlet at τ7.42, indicative of xanthate formation. Pyrolysis of this solid at 250°/85 mm and analysis of the nmr spectrum of the intervening trap contents showed no peaks in the olefinic region. Finally, reaction of the diol with (carboxysulfamoyl)triethylammonium hydroxide,

inner salt, methyl ester,[66] in acetonitrile and heating to reflux yielded no hydrocarbon products by tlc or glpc.

After these many failures we decided to try and make the dihalide instead, in the hope that the double dehydrobromination would be easier to accomplish. To this end we reacted the diol with triphenylphosphine dibromide in dimethylformamide, but obtained no bromide product. Reactions with phosphorus tribromide under the conditions that worked for the last diol yielded an oil that analyzed for the dibromide by mass spectrum, but its nmr spectrum contained too many peaks to be pure dibromide. We concluded that it must have been a mixture of several isomers. Reaction of the diol with thionyl chloride in refluxing chloroform proceeded smoothly with consumption of the diol. Work-up by chromatography on silica gel yielded a white solid, mp 135-136°. However, the mass spectrum indicated no chlorine present, but rather a new parent peak at m/e 212. The ir spectrum contained no hydroxyl absorptions. This points to the formation of the cyclic sulfite, 78:

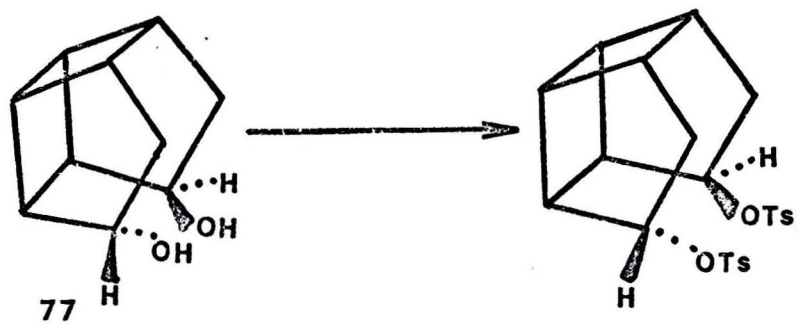


77 78

Similar results were reported for the analogous cage compound 75. One positive result of the reaction is that

it establishes that the configuration of the hydroxy groups is with both groups pointing into the center of the cage.

With this route blocked also, we tried the formation of the ditosylates since they can act as leaving groups much as the dibromide could. Thus, reaction of the diol with tosyl chloride in a minimal amount of pyridine at 0° yielded an oil that solidified to a solid, mp 91-92°, in 91% yield. Analysis of the nmr spectrum showed cage peaks plus the normal phenyl pattern at τ2.06, 2.21, 2.67 and 2.79 for tosylates and the methyl peak at τ 7.62:



Reaction of the ditosylate with potassium t-butoxide in dimethylsulfoxide at room temperature under vacuum gave no hydrocarbons in the traps by glpc and no peaks in the olefinic region of the nmr spectrum. Analysis of the pot residue showed starting material. Heating of the mixture to 50° resulted in blackening of the solution due to heat decomposition. Reaction of the ditosylate with lithium amide in liquid ammonia resulted in starting material also.

In concluding this section we find that there was some success in making the new tetracyclic system, 61, but that there was little success in synthesizing the desired

diene, 64. This was particularly puzzling in light of the success enjoyed by others in the analogous system, 74, with only one more carbon. It was hard to see the difference that this one fewer carbon would make, especially since our entry into the new system was via a reaction that had also worked in the larger system.

The correctness of our approach was demonstrated in the announcement by Pettit[67] that he had synthesized the desired diene 64 using the debromination of the dibromide 73. He was successful using slightly different reagents than we had employed. From the nmr data reported by Pettit we were able to see small amounts of the desired diene in some of our nmr spectra from the lithium amalgam reaction. We noted then that these spectra seemed promising but were unable to isolate any of the diene or obtain reproducible results.

The diene as synthesized by Pettit has all the interesting properties we had expected it to have in the way of facile rearrangement, and confirms our reasons for attempting the synthesis.

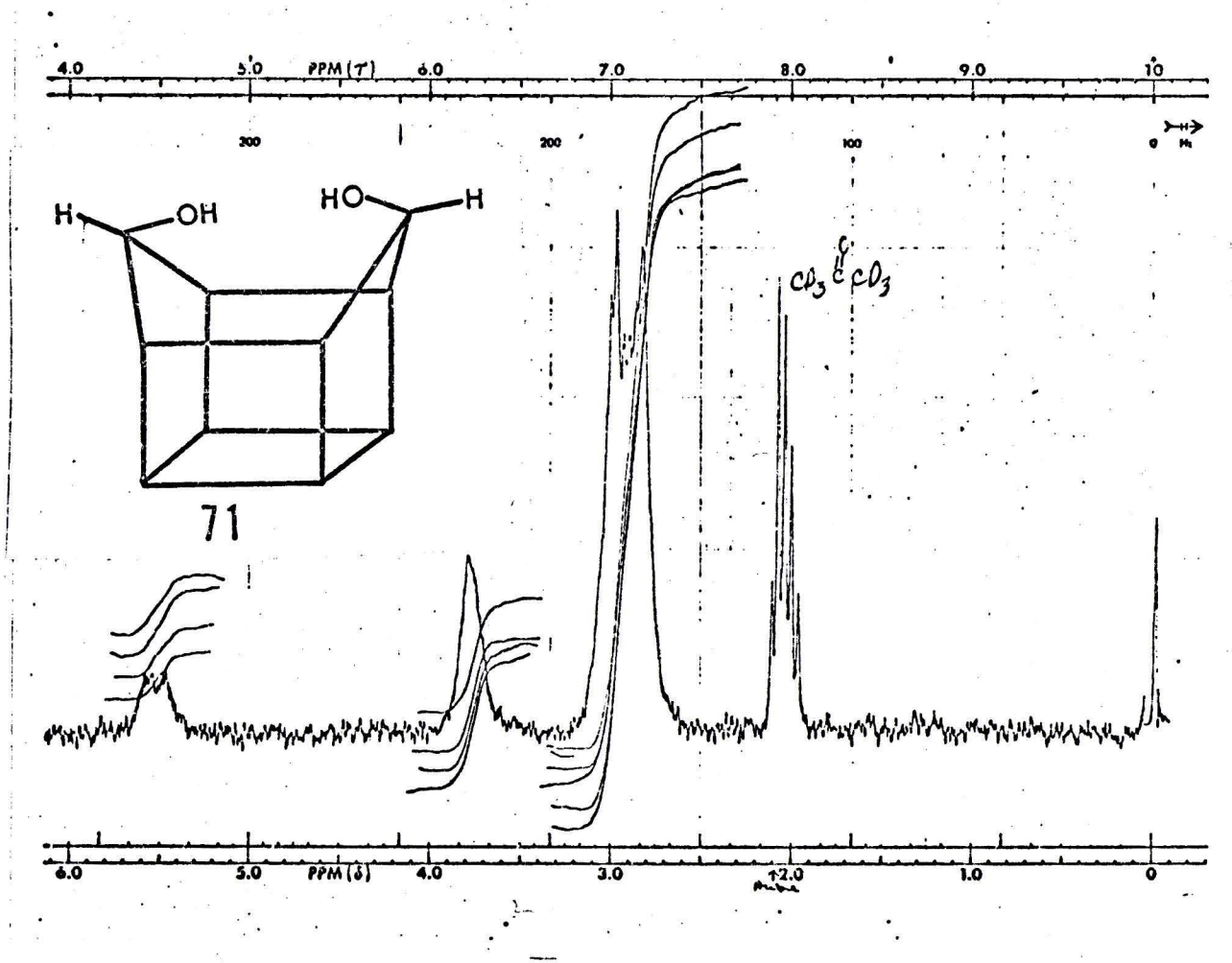
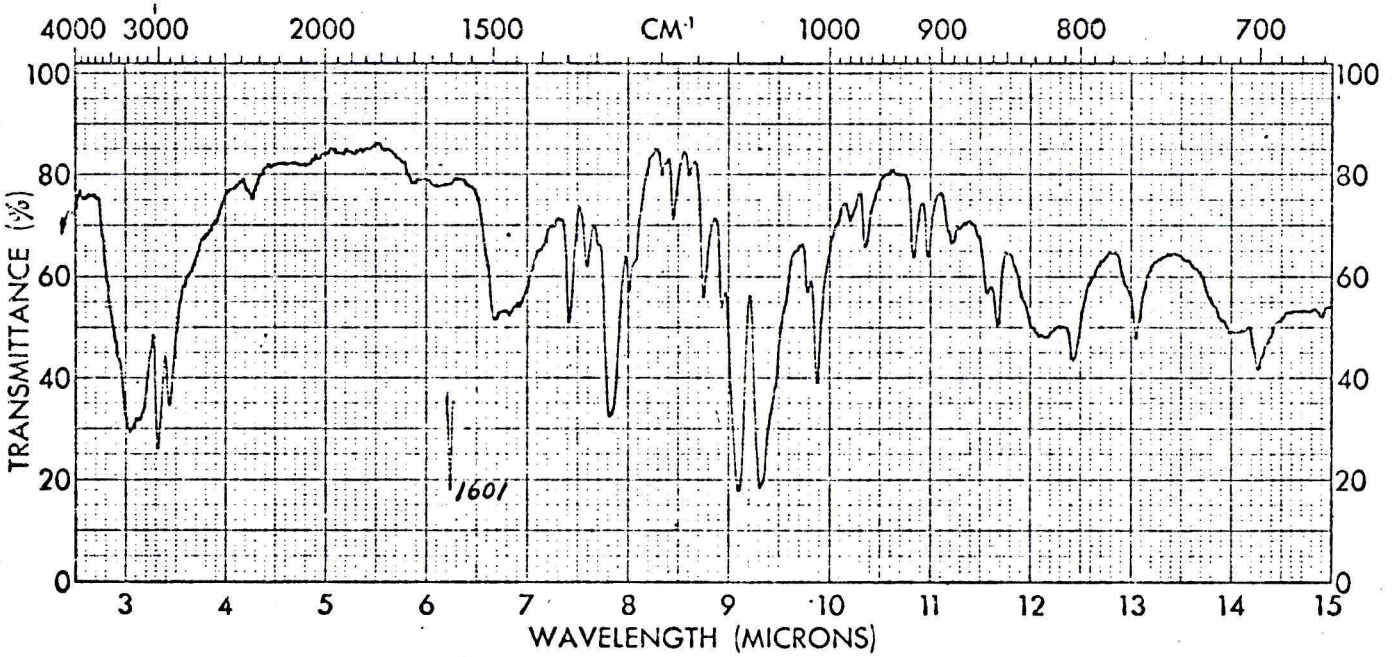
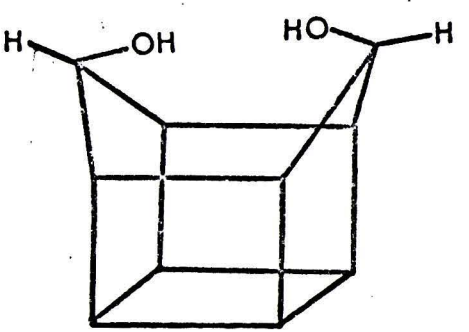


Figure 19. Nmr spectrum of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]deca-7,10-diol.





71

Figure 20. Ir spectrum of pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-7,10-diol.

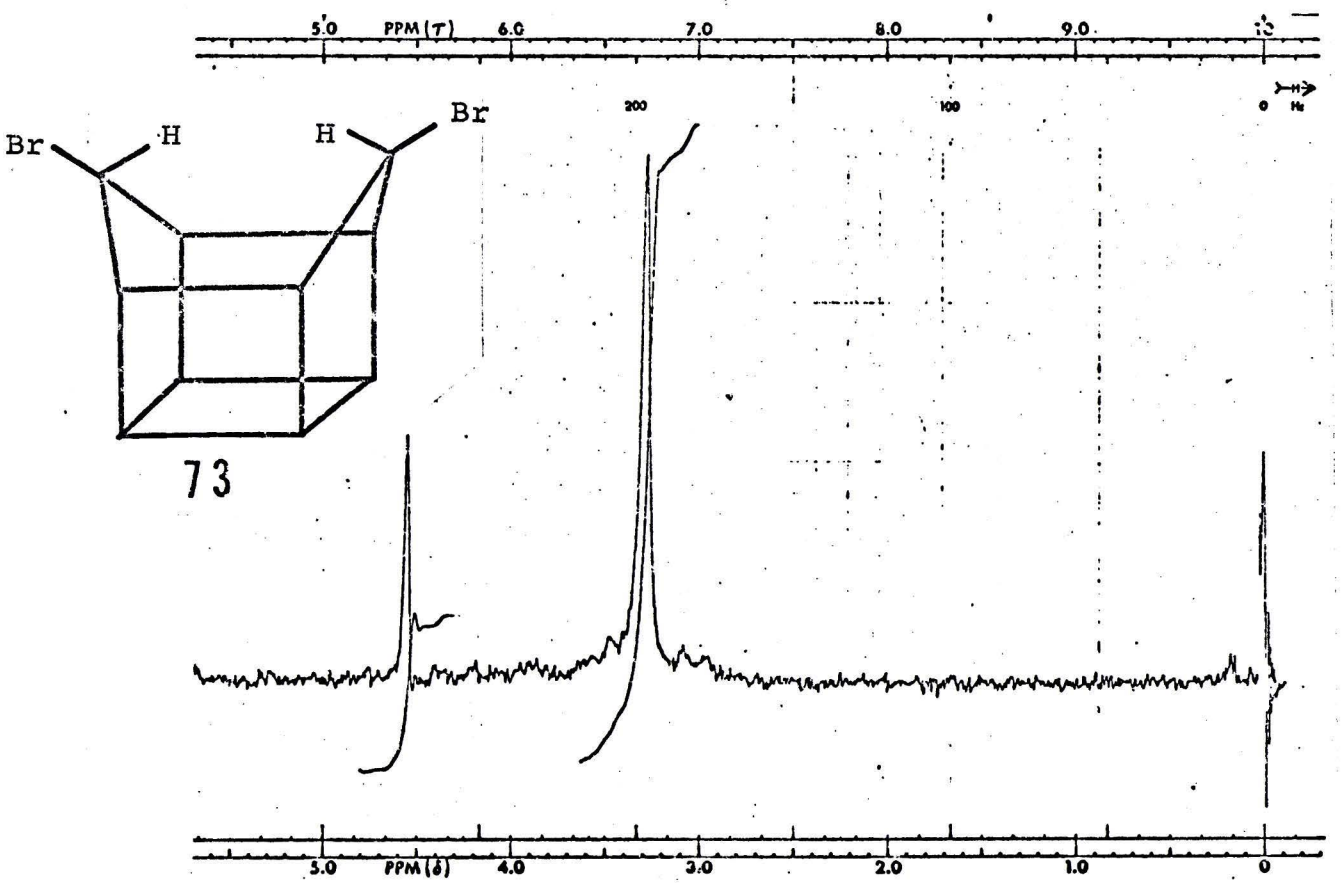
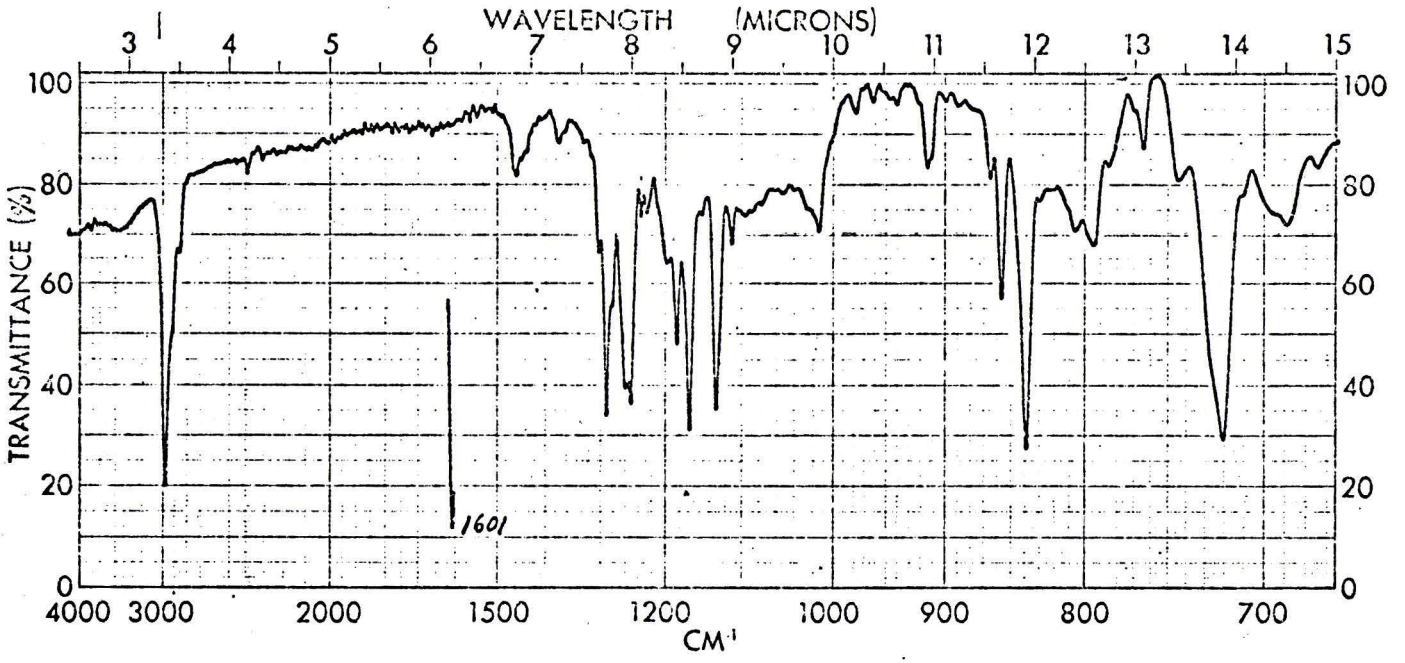
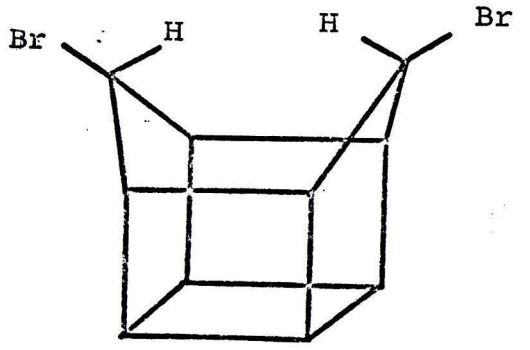


Figure 21. Nmr spectrum of 7,10-dibromopentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane.





73

Figure 22. Ir spectrum of 7,10-dibromopentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane.

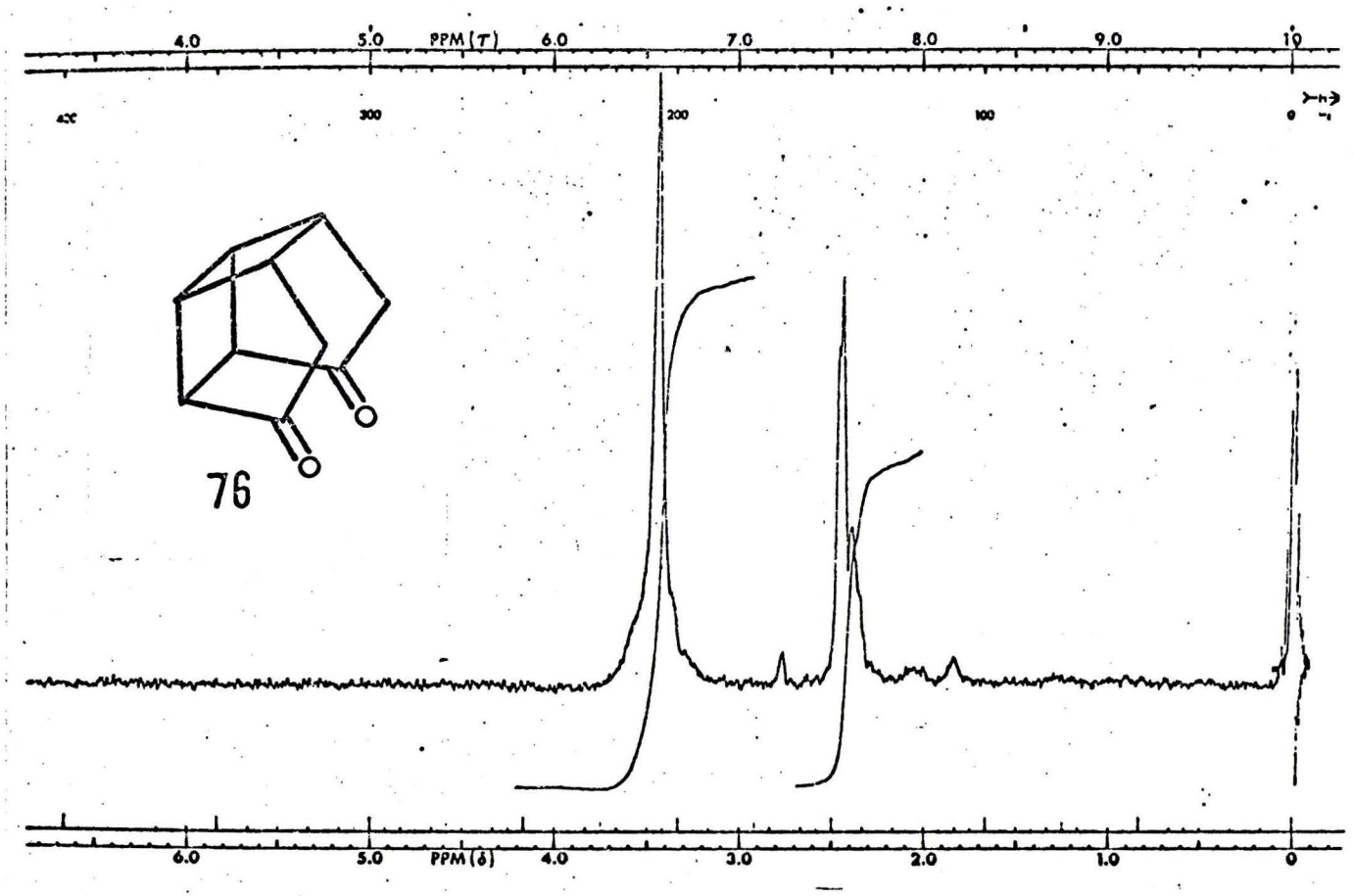
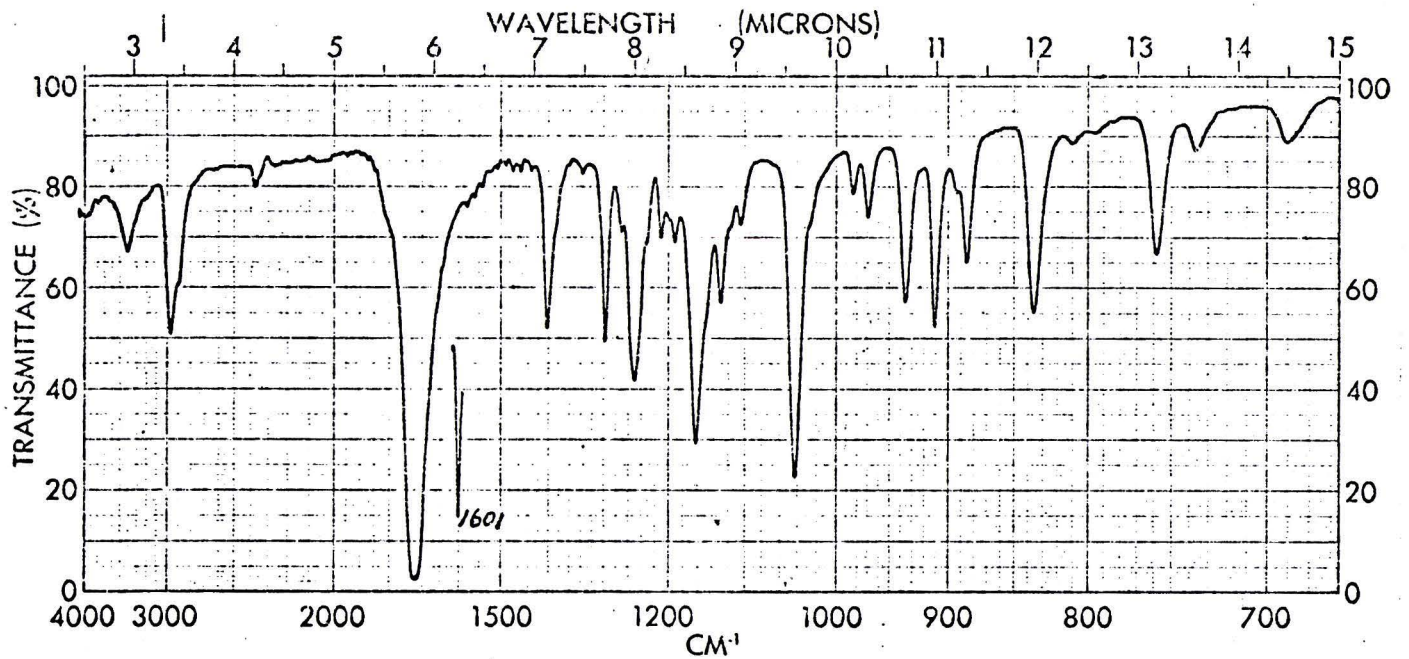
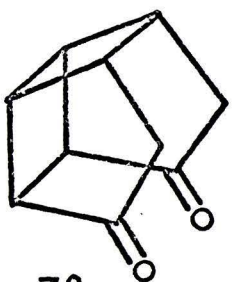


Figure 23. Nmr spectrum of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-dione.





76

Figure 24. Ir spectrum of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-dione.

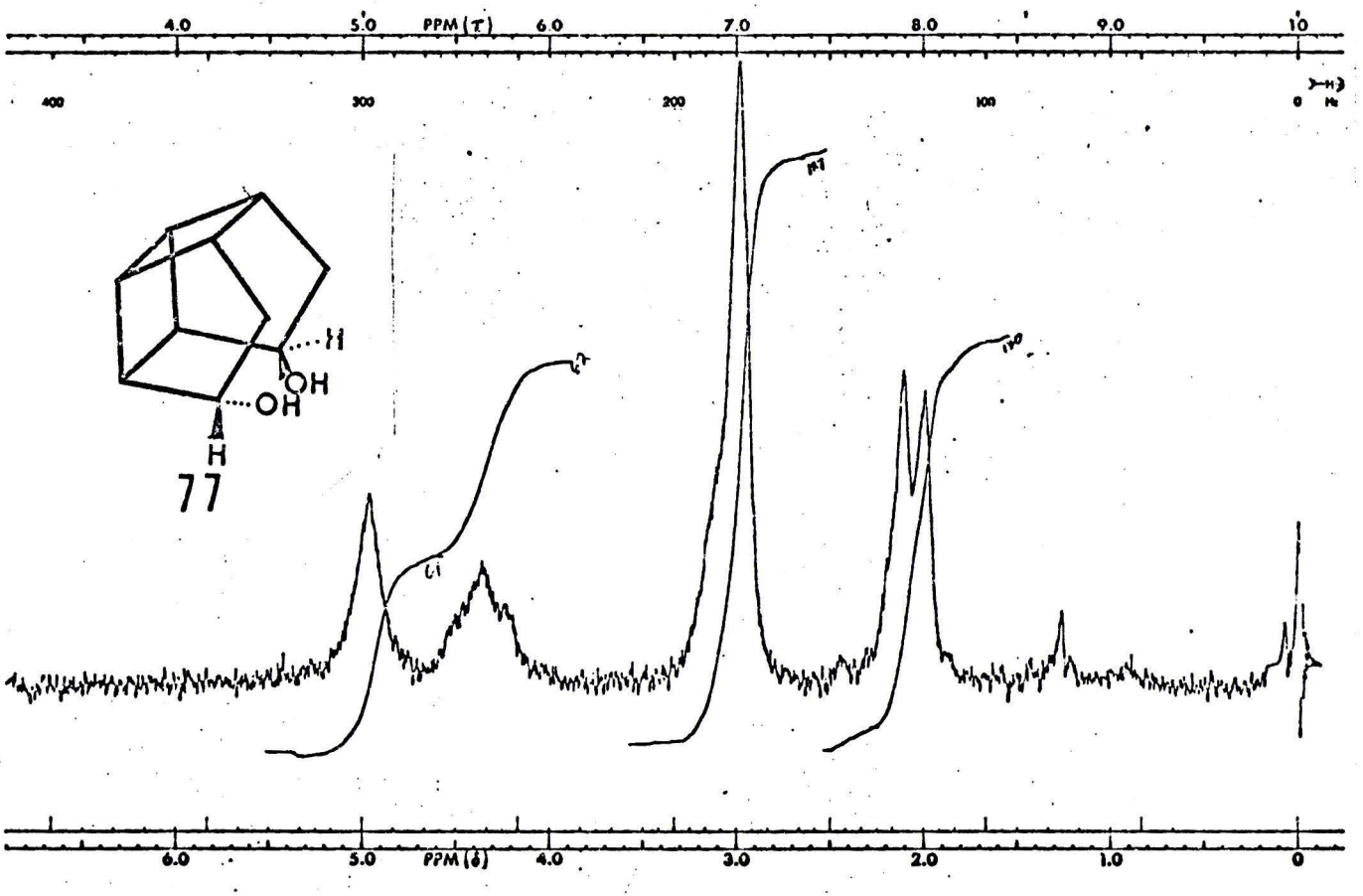
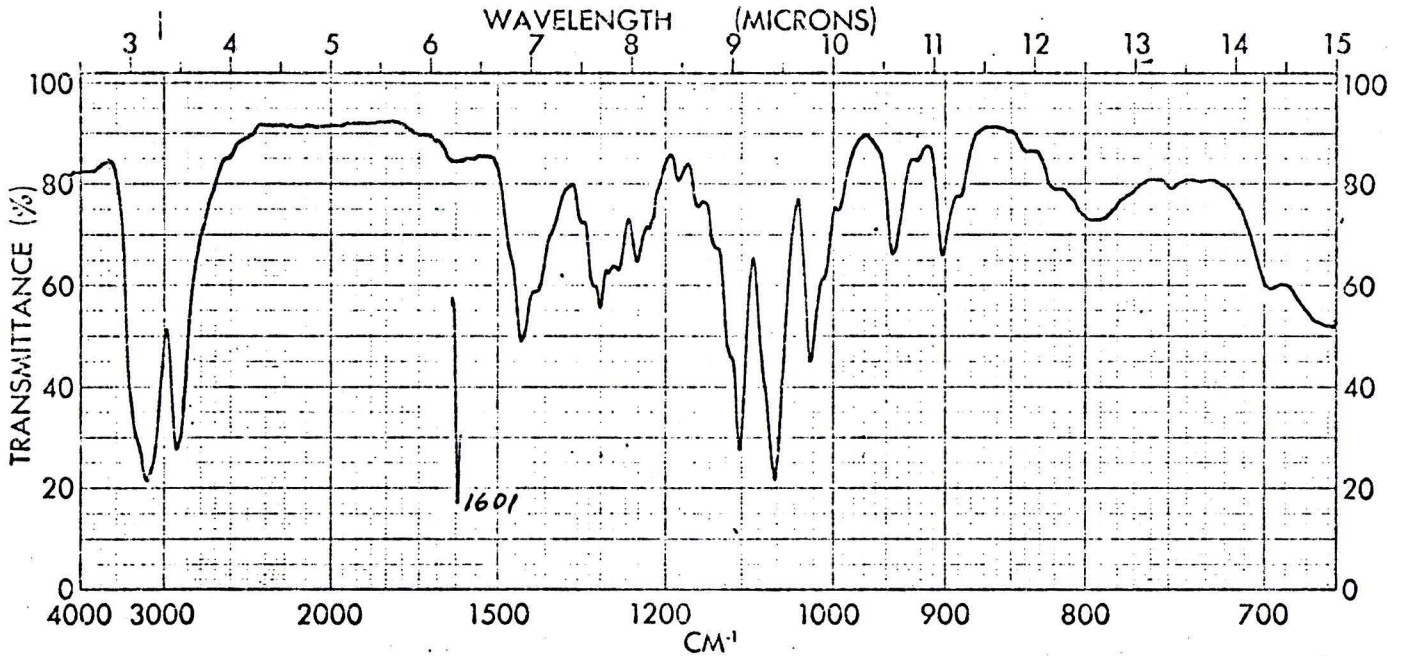


Figure 25. Nmr spectrum of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol.



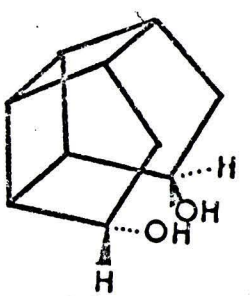


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Figure 26. Ir spectrum of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol.

Experimental

Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on either a Perkin-Elmer Model 137 spectrophotometer or on a Beckman IR 10 spectrophotometer. Ultraviolet spectra were recorded on a Cary Model 15 spectrometer. Nuclear magnetic resonance (nmr) spectra were obtained from a Varian Model A-60-A spectrometer, utilizing TMS as an internal standard. Mass spectral data were obtained from an Hitachi Perkin-Elmer RMU-6E mass spectrometer.

Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee; and Atlantic Microlab, Inc., Atlanta, Georgia.

The glpc analyses were carried out on a Varian Aerograph Model A-90-P3 gas chromatograph equipped with the column listed in the text.

All reagents which are not referenced were available commercially.

Preparation of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]-decane (66). A solution of 2.2 g (0.015 mole) of 3-hydroxypentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane[53] and 3.9 g (0.015 mole) of triphenylphosphine in 50 ml of dimethylformamide was placed in a 100 ml three-neck flask equipped

with a stirrer, addition funnel and condenser. The solution was cooled to 0°, and 2.4 g (0.015 mole) of bromine added dropwise. This was heated to reflux for 15 hours, cooled, poured into 300 ml of water, and extracted with ether. The ether was dried over sodium sulfate and evaporated to a brown solid. Chromatography on silica gel with pentane/methylene chloride (1/1) produced an oil. Distillation at 60°/ 0.04 mm gave 2.0 g (63%) of a light yellow oil: ir (film), 3000, 1300, 1280, 1265, 1200, 950, 780, 725; nmr (CCl_4), τ5.75 (s, 1H), 7.12 (m, 4H), 7.33 (m, 4H), 8.44 (m, 2H); ms (70 eV) m/e (rel intensity), 212 (0.2), 210 (0.2), 146 (5.0), 144 (5.0), 131 (37.2), 129 (9.4), 116 (12.7), 115 (13.8), 91 (26.2), 77 (11.8), 66 (100), 65 (24.2), 63 (9.9), 53 (8.3), 51 (17.6), 50 (9.1), 39 (29.7).

Anal. Calcd for $C_{10}H_{11}Br$: C, 56.87; H, 5.21. Found: C, 56.73; H, 5.29.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with potassium t-butoxide in t-butanol. A solution of 0.6 g (2.8 mmole) of 66 and 0.67 g (6 mmole) of potassium t-butoxide in 25 ml of t-butanol was placed in a 50 ml flask equipped with magnetic stirrer. This was stirred and heated to 50° for 24 hours. Analysis of the reaction by tlc showed no change in the starting material. Water was added and the solution extracted with ether, dried over sodium sulfate, and evaporated in vacuo yielding 0.6 g of liquid identical with starting material by nmr spectroscopy.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with potassium t-butoxide in dimethylsulfoxide. A solution of 0.7 g (3.3 mmole) of 66 and 0.67 g (6 mmole) of potassium t-butoxide in 30 ml of DMSO was placed in a 50 ml flask equipped with magnetic stirrer. This was stirred and heated to 55° for 24 hours. Monitoring the reaction by tlc showed no change in starting material. The mixture was heated to 100° for 24 hours more, diluted with water, extracted with ether, washed with water, dried over sodium sulfate, and evaporated to an oil identical with starting material as shown by nmr spectroscopy.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with potassium t-butoxide in hexamethylphosphoramide. A solution of 2.1 g (0.01 mole) of 66 and 3.4 g (0.03 mole) of potassium t-butoxide in 15 ml of hexamethylphosphoramide (freshly distilled from 13X molecular sieves at 115-117°/ 10 mm) was sealed in a glass tube under vacuum after degassing and heated to 100° for two hours. The solution turned deep brown-green. It was cooled, diluted with water, extracted with ether, washed with water, dried over sodium sulfate, and evaporated to brown oil. Analysis of the reaction by tlc showed starting material and no faster moving spots with pentane.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with 2-butylcyclohexanoxide, sodium. A 10 g (0.064 mole) sample of 2-butylcyclohexanol was placed in

a 50 ml flask equipped with a magnetic stirrer and condenser. A 0.5 g (0.022 mole) sample of sodium was added and the mixture was heated to reflux (210°). The sodium slowly dissolved to give a clear, light yellow solution. This was cooled and 3.5 g (0.017 mole) of 66 was added. The mixture was heated to 180° for four hours, cooled and diluted with water, dried over sodium sulfate, and evaporated to a liquid. The nmr spectrum showed only starting material.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with lithium chloride in dimethylformamide. A solution of 0.84 g (4 mmole) of 66 and 0.50 g (0.011 mole) of anhydrous lithium chloride in 20 ml of DMF was placed in a 50 ml flask equipped with a stirrer, condenser and nitrogen inlet. The mixture was heated to 100° for five hours, cooled, diluted with water, extracted with ether, washed with water, dried over sodium sulfate, and evaporated to an oil. The nmr spectrum showed this to be only starting material.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with sodium amide in benzene. A solution of 1.0 g (4.7 mmole) of 66 in 50 ml of benzene was placed in a 100 ml flask equipped with a stirrer, condenser and nitrogen inlet, and 0.2 g (5 mmole) of sodium amide added. This was refluxed for five hours, cooled, diluted with water, extracted with ether, washed with water, dried over sodium

sulfate, and evaporated to an oil. The nmr spectrum showed only starting material present.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with t-butyllithium. A solution of 1.0 g (4.7 mmole) of 66 in 50 ml of ether was placed in a 100 ml flask equipped with a stirrer and nitrogen inlet. A 4 ml sample of 1.6M t-butyllithium in hexane was injected and the mixture was stirred at 0° for five hours, diluted with water, extracted with ether, washed with water, dried over sodium sulfate, and evaporated to an oil. The nmr spectrum showed only starting material present.

Reaction of 3-bromopentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]decane (66) with t-butyllithium at reflux. A solution of 1.0 g (4.7 mmole) of 66 and 5 ml of 1.6M t-butyllithium in 50 ml of pentane was placed in a 100 ml flask equipped with a stirrer, condenser and nitrogen inlet. This was heated to reflux for 30 hours under nitrogen, cooled, diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to an oil. Collection of the only peak in the right region of the glpc on an 8' GESF column at 160° yielded a white solid. The ms and nmr spectrum indicated that this was 1,3-bishomocubane (67) by comparison to spectra of known material: mp 134-135°.[55]

Preparation of 3-butylpentacyclo[5.2.1.$0^{2,6}$.$0^{4,9}$.$0^{5,8}$]-decane (68). A solution of 1.0 g (4.7 mmole) of 66 in

50 ml of hexane was placed in a 100 ml three-neck flask equipped with a condenser, nitrogen inlet and septum cap. An 8 ml (12.8 mmole) sample of 1.6M n-butyllithium was added via syringe and the solution refluxed 24 hours. Water was added and the mixture extracted with ether, dried over sodium sulfate, and evaporated. The residue was anlayzed by glpc using a 12' silicon oil column at 200°. Only one peak was found in the proper area and it was collected as a thick yellow oil: ir (film), 3000, 2900, 1480, 1380, 1300, 950; nmr (CCl_4), τ7.33 (bs, 8H), 8.49-9.32 (m, 12H); ms (70 eV) m/e (rel intensity), 188 (1.3), 173 (0.3), 159 (0.6), 145 (1.3), 131 (12.0), 122 (33.0), 117 (7.1), 115 (5.2), 93 (6.9), 91 (14.6), 81 (9.0), 80 (100), 79 (31.0), 78 (5.4), 77 (8.9), 67 (6.5), 66 (20.0), 65 (7.0), 41 (5.8), 39 (6.2).

Anal. Calcd for $C_{14}H_{20}$: C, 89.38; H, 10.62. Found: C, 89.30; H, 10.55.

Preparation of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-7,10-diol (71). A 350 mg (2 mmole) sample of pentacyclo-[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-7,10-dione monohydrate (70)[56] was placed in a Soxhlet extraction thimble, and extracted into a 0.20 g (5.2 mmole) suspension of lithium aluminum hydride in 100 ml of THF, refluxed overnight, cooled, and aqueous sodium potassium tartrate added. It was then extracted with ether, dried over sodium sulfate, and evaporated. Chromatography on silica gel with ether and then acetone gave, after evaporation, 270 mg (85%) of white

crystals: mp 275° (dec); ir (KBr), 3300, 3000, 2900, 1275, 1100, 1080, 1015; nmr (D_6 acetone), τ7.08 (m, 8H), 6.22 (m, 2H), 4.47 (m, 2H); ms (70 eV) m/e (rel intensity), 164 (2.8), 146 (6.1), 145 (18.8), 133 (13.2), 131 (12.7), 128 (7.7), 126 (6.6), 118 (49.7), 117 (100), 116 (25.4), 115 (35.9), 103 (8.8), 91 (34.8), 82 (38.1), 81 (29.3), 79 (17.1), 78 (12.7), 77 (17.7), 55 (12.1), 53 (12.7), 41 (8.8), 39 (17.7).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.17; H, 7.32. Found: C, 73.04; H, 7.32.

Preparation of 9,11-oxohexacyclo[6.3.2.$0^{2,7}$.$0^{3,6}$.$0^{5,12}$.-$0^{4,13}$]tridecane (72). A solution of 473 mg (2.9 mmole) of 71 in 30 ml of DMSO was placed in a 50 ml flask equipped with a condenser and magnetic stirrer and the mixture heated to 160° for 15 hours, cooled and poured into 100 ml of water, extracted with pentane, dried over sodium sulfate and evaporated. This gave 322 mg (59%) of a white solid. Purification on a glpc 6' Carbowax 20M column at 220° produced a white solid: mp 161°; ir (KBr), 3000, 2900, 1465, 1350, 1290, 1255, 1190, 1155, 1140, 1110, 1090, 1065, 995, 965, 955, 715, 700; nmr (CCl_4), τ5.20 (s, 2H), 5.90 (m, 2H), 6.87 (s, 4H), 6.89 (s, 4H); ms (70 eV) m/e (rel intensity), 176 (0.19), 146 (8.0), 145 (9.4), 129 (12.0), 118 (42.1), 117 (100), 116 (28.6), 115 (63.2), 91 (45.5), 82 (24.7), 81 (63.2), 78 (12.2), 77 (11.0), 66 (35.9), 65 (32.6), 63 (11.8), 53 (22.9), 51 (17.0), 39 (33.7).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.82. Found: C, 75.30; H, 6.78.

Reaction of pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-7,10-diol (71) with thionyl chloride with pyridine. A solution of 100 mg (0.61 mmole) of 71 in 25 ml of pyridine was placed in a 50 ml flask equipped with a magnetic stirrer and addition funnel. This was cooled to 0° and 400 mg (3.4 mmole) of thionyl chloride in 5 ml of pyridine was added. The mixture was warmed to room temperature, stirred overnight, refluxed for three hours, cooled and ice water added. The mixture was extracted with ether, dried over sodium sulfate, and evaporated to a solid. The ir spectrum showed only starting material.

Reaction of pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-7,10-diol (71) with 1,1,2-trifluoro-2-chloroethyldiethylamine.[59] A solution of 112 mg (0.7 mmole) of 71 in 30 ml of methylene chloride was placed in a 50 ml flask equipped with a magnetic stirrer and 260 mg (2.1 mmole) of lithium bromide added. This was cooled to 0° and 320 mg (1.6 mmole) of 1,1,2-trifluoro-2-chloroethyldiethylamine was added in two portions. The mixture was stirred for four hours and the solvent evaporated. Full vacuum was placed on the residue but no cage compounds came over as evidenced by nmr spectroscopy. The residue was extracted with ether and evaporated to a solid. The ms showed no bromine incorporation.

Reaction of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-7,10-diol (71) with triphenylphosphine dibromide. A solution of 70 mg (0.43 mmole) of 71 in 25 ml of dry DMF was placed in a 50 ml flask equipped with a magnetic stirrer, condenser and nitrogen inlet. To this was added 4.5 ml of a solution prepared by adding 0.80 g (5 mmole) of bromine to 1.52 g (5 mmole) of triphenylphosphine in 50 ml of dry DMF. The mixture was heated to 90°, stirred overnight, diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to an oil. The ms of the oil revealed no bromine present.

Reaction of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-7,10-diol (71) with phosphorus tribromide, in pyridine. A solution of 140 mg (0.45 mmole) of phosphorus tribromide in 10 ml of benzene was placed in a 50 ml flask equipped with a stirrer. A 5 ml sample of pyridine was added and the mixture was cooled to -5°. A solution of 112 mg (0.68 mmole) of 71 in 5 ml of pyridine was added slowly and the mixture then warmed to room temperature, stirred overnight, diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to 90 mg of solid. The ms showed no bromine incorporation and the ir spectrum showed only starting material.

Reaction of pentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-7,10-diol (71) with phosphorus tribromide neat. A solution of 180 mg (1.1 mmole) of 71 in 3 ml of phosphorus tribromide

was placed in a 5 ml flask equipped with a stirrer. This was stirred at room temperature for 48 hours, diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to a solid. Chromatography on silica gel with ether gave no product. Elution with acetone gave back starting material.

Preparation of 7,10-dibromopentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-decane (73). A 365 mg (2.2 mmole) sample of 71 was placed in a 10 ml one-neck flask and 6 ml of phosphorus tribromide was added. The mixture was heated at 130° for 20 hours, cooled, and diluted cautiously with water. It was then extracted with ether, dried over sodium sulfate and evaporated. Chromatography on silica gel with pentane/methylene chloride (4/1) gave, after evaporation, 155 mg (25%) of a white solid: mp 112-113°; ir (KBr), 3000, 1295, 1260, 1165, 1130, 860, 840, 720, 650; nmr (CCl_4), τ5.33 (bs, 2H), 6.73 (bs, 8H); ms (70 eV) m/e (rel intensity), 292 (0.2), 290 (0.3), 288 (0.2), 211 (23.4), 209 (23.6), 146 (63.9), 144 (64.5), 131 (12.6), 130 (100), 129 (93.3), 128 (24.7), 127 (13.0), 86 (14.6), 77 (12.1), 66 (12.1), 65 (45.4), 64 (40.0), 63 (13.6), 52 (51.8), 51 (29.4), 50 (10.2), 49 (20.2), 43 (24.3), 39 (29.4).

Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48. Found: C, 41.55; H, 3.70.

Reaction of 7,10-dibromopentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-decane (73) with zinc and ethanol. A suspension of 95 mg

(0.33 mmole) of 73 and 2 g (31 mmole) of zinc in 50 ml of ethanol was placed in a 100 ml flask equipped with a stirrer and condenser. This was refluxed for two hours, cooled and filtered, and the filtrate washed with ether and dried over sodium sulfate. The solvents were evaporated. Injection of the residue on an 8' GESF glpc column at 130° showed only solvent. The residue was chromatographed on silica gel with pentane/methylene chloride (4/1), yielding 60 mg of starting material.

Reaction of 7,10-dibromopentacyclo[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-decane (73) with lithium amalgam. A suspension of 60 mg (0.21 mmole) of 73 and 4 g of 0.4% lithium amalgam in 5 ml of ether was placed in a 50 ml flask equipped with stirrer. This was stirred at room temperature for five days, filtered and evaporated to a solid. Gas chromatography on an 8' GESF column at 120° showed two peaks with correct retention times. These were collected and the ms and nmr spectrum were consistent with the desired product, but in very small amounts. Subsequent reactions failed to reproduce these results.

Preparation of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-dione (76). A suspension of 0.40 g (2.3 mmole) of pentacyclo-[4.4.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane-7,10-dione monohydrate (71) and 1 g of zinc dust in 20 ml of acetic acid was placed in a 50 ml flask equipped with a stirrer. This was stirred for 24 hours, added to ice water, and extracted

with methylene chloride. It was then washed with dilute NaOH solution and water, and dried over sodium sulfate. Evaporation produced 0.30 g (80%) of a white solid. Sublimation at 120°/1 mm yielded a white solid: mp 202-203°; ir (KBr), 2960, 2900, 1720, 1400, 1300, 1250, 1160, 1040, 940, 910, 895, 835; nmr ($CDCl_3$), τ 6.56 (m, 6H), 7.55 (bs, 4H); ms (70 eV) m/e (rel intensity), 162 (79.1), 149 (30.5), 106 (50.0), 105 (23.0), 92 (34.7), 91 (100), 82 (23.0), 81 (62.5), 80 (12.5), 79 (22.2), 78 (77.0), 77 (15.3), 53 (67.3), 52 (47.9), 51 (35.4), 50 (18.0), 41 (16.0), 39 (38.2).

Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.07; H, 6.17. Found: C, 74.16; H, 6.25.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-dione (76) with tosylhydrazine. A suspension of 162 mg (1 mmole) of 76 and 410 mg (2.2 mmole) of tosylhydrazine in 25 ml of ethanol containing 1% HCl was placed in a 50 ml flask equipped with a condenser. All solid dissolved and on refluxing the mixture turned dark slowly, but no new solid formed. The mixture was diluted with water, extracted with ether, and dried over sodium sulfate. Evaporation produced an oil. Analysis of the nmr spectrum showed no tosylhydrazone present.

Preparation of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77). A suspension of 0.20 g (5.2 mmole) of LAH in 50 ml of ether was placed in a 100 ml three-neck flask equipped

with a stirrer and addition funnel. To this was added a solution of 0.15 g (0.93 mmole) of 76 in 10 ml of methylene chloride, dropwise. It was stirred at room temperature for two hours, poured onto ice and HCl, extracted with ether, dried over sodium sulfate, and evaporated to 0.13 g (80%) of a white solid. Sublimation at 140°/1 mm yielded a white solid: mp 250-251°; ir (KBr), 3250, 2900, 2850, 2150, 1450, 1420, 1300, 1240, 1110, 1100, 1060, 1020, 945, 900; nmr ($CDCl_3$), τ5.05 (bs, 2H), 5.63 (m, 2H), 7.01 (bs, 6H), 7.95 (bd, J=7 Hz, 4H); ms (70 eV) m/e (rel intensity), 166 (4.0), 148 (6.3), 131 (8.2), 119 (16.8), 105 (10.3), 92 (8.6), 83 (44.0), 82 (25.2), 79 (14.0), 78 (9.4), 77 (11.5), 67 (14.3), 66 (100), 55 (14.9), 53 (7.8), 41 (10.5), 39 (13.6).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.29; H, 8.43. Found: C, 72.43; H, 8.50.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (76) with alumina. A 112 mg (0.7 mmole) sample of 77 was placed in a tube wrapped with heater tape and connected to a tube furnace heated to 500° and connected further to a dry ice cooled trap and 0.01 mm vacuum source. By heating the sublimation tube to 120°, 77 was sublimed into the tube furnace which was filled with coarse, activated dry alumina. Heating was continued slowly for eight hours until no diol condensed when the heater tape was removed. The trap was then washed with pentane. Glpc analysis on an 8' GESF column at 150° showed only solvent peaks.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with phosphorus oxychloride. A solution of 50 mg (0.3 mmole) of 77 in 10 ml of pyridine and 20 ml of pentane was placed in a 50 ml flask equipped with a stirrer. A 1/2 ml sample of phosphorus oxychloride was added and the mixture stirred at room temperature for 24 hours. Water was added and the pentane layer separated. The water was extracted with pentane, the pentane solutions combined, dried over sodium sulfate, and evaporated to an oil. The nmr spectrum showed no olefinic peaks and tlc with pentane gave no spots.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with zinc chloride. A mixture of 50 mg (0.3 mmole) of 77 and 2 g (14.7 mmole) of zinc chloride was placed in a 10 ml flask. This was heated to 230°/200 mm with a dry ice trap between the pump and the flask. After two hours the solid turned black. The nmr spectrum of a CCl_4 solution of the trap contents showed no olefinic protons at all. Glpc analysis on an 8' G.E. fluro silicone fluid column at 150° gave no peaks with the desired retention time.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with phenyl isocyanate and pyrolysis of resultant solid. A solution of 55 mg (0.33) mmole) of 77 in 25 ml of ether was placed in a 50 ml flask equipped with a stirrer. An 80 mg (0.67 mmole) sample of phenyl isocyanate was added and the mixture was stirred overnight. Evaporation

produced 130 mg of solid. The nmr spectrum indicated urethane formation.

For pyrolysis, the residue was placed in a 5 ml flask, connected to a full vacuum via a coil trap, and heated to 220° for one hour. The CCl_4 wash of the coil trap yielded no cage or olefinic peaks in the nmr spectrum.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with tosyl chloride and sulfur dioxide in dimethylformamide.[62] A solution of 50 mg (0.3 mmole) of 77 and 190 mg (1.1 mmole) of tosyl chloride in 10 ml of DMF was placed in a 25 ml flask equipped with a stirrer. This was cooled to 0° and 80 mg (1 mmole) of pyridine added. It was then warmed to 10°, 1 ml of DMF containing 5% sulfur dioxide added, and the mixture stirred at room temperature for four hours. It was diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to a solid. The nmr spectrum showed only starting material.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with phosphorus esters.[68] A 0.50 mg (0.3 mmole) sample of 77 was added to a solution made from 5.7 g of P_4O_{10} and 4.6 g of ethanol in a 25 ml flask. The mixture was heated to 90° for six hours with a nitrogen purge exiting into a coil trap with a 100 mm vacuum. Analysis of the nmr spectrum of a CCl_4 wash of the trap yielded no cage or olefinic peaks.

Attempted xanthate elimination of tetracyclo[5.3.0.$0^{2,6}$.-

$0^{5,8}$]deca-4,9-diol (77). A 0.30 g (7.6 mmole) sample of sodium hydride as a 61% dispersion was placed in a 100 ml three-neck flask equipped with stirrer, condenser and nitrogen inlet. The mineral oil was washed off with three washes of pentane. A solution of 320 mg (1.9 mmole) of 77 in 50 ml of ether/tetrahydrofuran (1/1) was added. The mixture was refluxed for two hours. A 380 mg (5 mmole) sample of carbon disulfide was added and the mixture refluxed two hours. A 710 mg (5 mmole) sample of methyl iodide was added and the mixture refluxed two hours more. This was cooled and diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to a yellow solid. The nmr spectrum indicated cage peaks and a methyl singlet (τ7.42). A 300 mg sample of this residue was placed in a 25 ml flask fitted with condenser, vacuum connection at 85 mm and a coil trap in a dry ice bath. The residue was heated to 250° for one hour under vacuum. The trap was washed with $CDCl_3$, but the nmr spectrum of the washings showed no peaks in the olefinic region.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with (carboxysulfamyl)triethylammonium, hydroxide, inner salt, methyl ester.[66] A solution of 0.474 g (2 mmole) of the above salt in 25 ml of acetonitrile was placed in a 100 ml flask equipped with a stirrer, condenser and addition funnel. A solution of 166 mg (1 mmole) of 77 in 50 ml of acetonitrile was added and the mixture heated to reflux for two hours. It was then cooled, diluted with

water, extracted with ether, dried over sodium sulfate, and the solvent removed by distillation. Analysis by glpc and tlc showed no hydrocarbon products.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with triphenylphosphinedibromide. A solution of 0.42 g (1.6 mmole) of triphenylphosphine and 0.25 g (1.6 mmole) of bromine in 25 ml of DMF was placed in a 50 ml flask equipped with a stirrer and condenser. A 50 mg (0.3 mmole) sample of 77 was added and the mixture heated to reflux for four hours, cooled and diluted with water. It was then extracted with ether, dried over sodium sulfate, and evaporated to a yellow solid. The nmr spectrum showed mainly starting material.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol (77) with phosphorus tribromide. A solution of 100 mg (16 mmole) of 77 in 5 ml of phosphorus tribromide was placed in a 10 ml flask equipped with a stirrer and condenser. This was heated to 120° for five hours and water was added cautiously. The water was extracted with ether, dried over sodium sulfate, and evaporated to an oil. Chromatography on silica gel with pentane/methylene chloride (4/1) gave 50 mg of oil. The ms showed a trio of peaks at 290, 292 and 294, but the nmr spectrum showed a myriad of peaks.

Preparation of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-diol, cyclic sulfite (78). A solution of 100 mg (0.6 mmole) of

77 and 143 mg (1.2 mmole) of thionyl chloride in 50 ml of chloroform was placed in a 100 ml flask equipped with a stirrer and condenser. This was heated to reflux for 12 hours. Tlc showed no starting material remained, but a faster spot was present. The solution was evaporated and chromatographed with benzene. Then the methylene chloride eluent was collected. This was evaporated to 75 mg (60%) of a solid. Sublimation at 120°/0.2 mm gave a white solid: mp 135-136°; ir (KBr), 3000, 1275, 1220, 1125, 1065, 1020, 955, 920, 905, 795, 780, 700; nmr ($CDCl_3$), τ5.17 (m, 2H), 6.46 (m, 2H), 6.88 (bs, 4H), 7.69 (bd, J=6 Hz, 4H); ms (70 eV) m/e (rel intensity), 212 (27.3), 149 (14.0), 148 (3.8), 147 (6.6), 131 (9.1), 130 (14.7), 119 (29.9), 117 (14.3), 105 (19.0), 104 (15.2), 92 (15.2), 91 (50.6), 83 (26.4), 82 (16.5), 79 (27.3), 77 (19.5), 67 (19.0), 66 (100), 65 (18.6), 55 (11.0), 53 (12.6), 51 (11.1), 41 (25.1), 39 (24.7).

Anal. Calcd for $C_{10}H_{12}SO_3$: C, 56.60; H, 5.66; S, 15.09. Found: C, 56.89; H, 5.77; S, 14.81.

Preparation of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-ditosylate (79). A solution of 166 mg (1 mmole) of 77 in 316 mg (4 mmole) of pyridine was placed in a 5 ml flask. This was cooled to 0°, 380 mg (2 mmole) of p-toluenesulfonyl chloride added in small portions, and the mixture stirred for 1/2 hour. The initial clear solution became a thick paste. It was diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to 430 mg (91%) of

an oil that solidified on standing. Recrystallization from hexane produced a tan solid: mp 91-92°; nmr ($CDCl_3$), τ2.02 (s, 2H), 2.14 (s, 2H), 2.61 (s, 2H), 2.73 (s, 2H), 5.13 (m, 2H), 7.13 (bs, 6H), 7.57 (s, 6H), 8.0 (d, J=8 Hz, 4H).

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-ditosylate (79) with potassium t-butoxide in dimethylsulfoxide. A mixture of 1.25 g (2.6 mmole) of 79 and 1.34 g (12 mmole) of potassium t-butoxide was placed in a 25 ml flask equipped with a magnetic stirrer, addition funnel, and distillation head connected via a dry ice cooled trap to a vacuum pump. A 15 ml portion of DMSO was added all at once and the mixture stirred at room temperature. Analysis of the nmr spectrum of a pentane wash of the trap showed no absorptions in the olefinic region. Water was added to the flask and the mixture was extracted with ether, dried over sodium sulfate, and evaporated to an oil. The nmr spectrum showed starting material still present. Repetition of the experiment, but with heating of the reaction flask to 50° for two hours, produced nothing in the trap again and no starting material remained in the flask. Heat seems to decompose the tosylate.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-ditosylate (79) with lithium amide in liquid ammonia. A 50 ml portion of liquid ammonia was condensed in a 100 ml flask equipped with a stirrer, dry ice condenser, gas inlet tube and external ice bath. A catalytic amount of

hydrated ferric nitrate and 15 mg (21 mmole) of lithium was placed in the flask and 1.4 g (3 mmole) of 79 in methylene chloride was added. This was stirred overnight while being allowed to come to room temperature, diluted with water, extracted with ether, dried over sodium sulfate, and evaporated to an oil. The nmr spectrum showed only unreacted starting material.

Reaction of tetracyclo[5.3.0.$0^{2,6}$.$0^{5,8}$]deca-4,9-ditosylate (79) with lithium bromide in acetone. A mixture of 0.47 g (1 mmole) of 79 and 0.7 g (8 mmole) of lithium bromide in 25 ml of acetone was placed in a 50 ml flask equipped with a stirrer. This was stirred at room temperature for 24 hours, evaporated and chromatographed on silica gel with methylene chloride/ether (1/1). The nmr spectrum of the residue left after evaporation showed no cage peaks at all.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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