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Part I Tropone-acetylene cycloadducts: the chemistry of bicyclo-[3.2.2] nonatrienones: Part II The reactions of nitrosobenzene with cyclic polyolefins

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    PART II. THE REACTIONS OF NITROSOBENZENE WITH
    CYCLIC POLYOLEFINS.

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Part I. Tropone-acetylene cycloadducts: The chemistry of

bicyclo-[3.2.2]-nonatrienones

Part II. The reactions of nitrosobenzene with cyclic polyolefins

by

Philip David Carpenter

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Head of Major Department

Dean of Graduate College

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Ames, Iowa
1971

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PART I: TROPONE--ACETYLENE CYCLOADDUCTS: THE
CHEMISTRY OF BICYCLO-[3.2.2]-NONATRIENONES

INTRODUCTION

Tropone

Tropone was first formulated and prepared because of the suggestion
based upon Hückel's rule (1) that the molecule might be represented as a
hybrid between a covalent form (I) and an aromatic dipolar form (II) (2). The
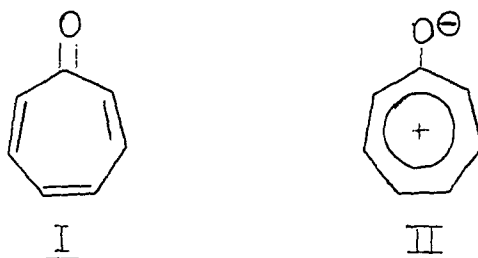
evidence which supports this concept is its high dipole moment of 4.3 D (3)
and the 1582 cm^{-1} carbonyl band found in its infrared spectrum (3,4). That
II does not contribute to the overall molecular structure to a very large
degree is shown by the relatively small dipole moment of 4.3 D as compared
to 3.04 D for cycloheptanone (5). The chemical properties of tropone are
more easily explained without recourse to any aromatic character (6). One
would not expect an "aromatic reaction" such as electrophilic substitution
to occur with tropone since II has the characteristics of a tropylium ion.
Since tropylium ions are themselves electrophilic reagents, they are quite
resistant to electrophilic attack (2).

The most notable contribution of II to the chemical properties of
tropone is the reduced reactivity of the carbonyl group toward normal
carbonyl reagents. This is exemplified by the fact that tropone will form
a semicarbazone and arylhydrazones only under forcing conditions (7). The

reaction of tropone with Grignard and lithium reagents and lithium

aluminum hydride proceed to give 1,8 conjugate addition products (8).
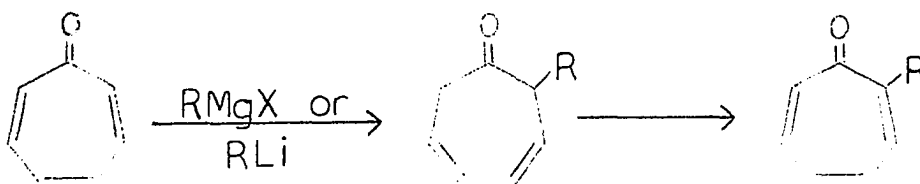
Hydrazine and hydroxylamine also react with tropone via conjugative

additive mechanisms to form 2-amino-tropone (6).
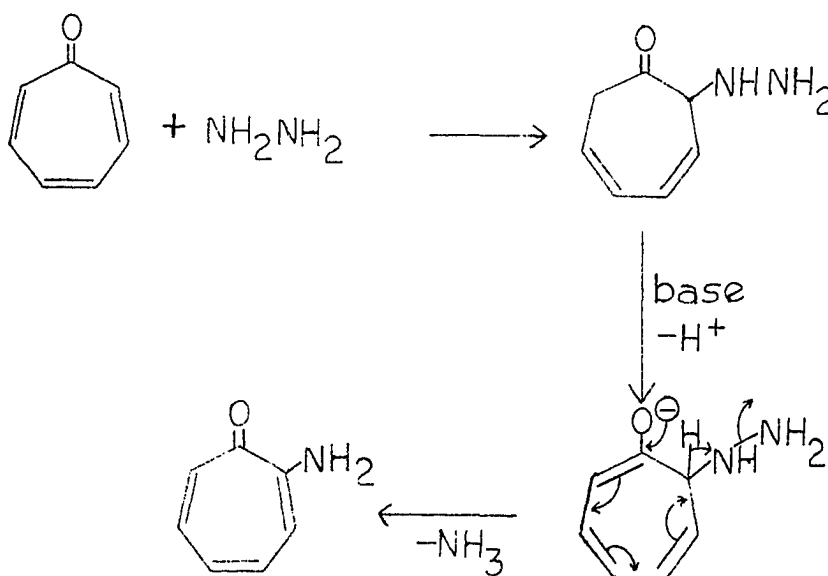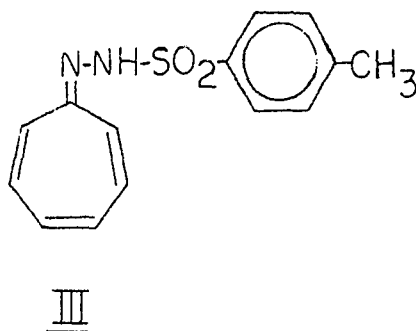

Tropylidene

When this research was started in 1966, cycloheptatrienylidene

(commonly called tropylidene) was an unknown species. The synthesis of

this molecule was of considerable interest because of the question of the

ground state multiplicity of the carbene. From a consideration of the

orbitals involved and the Hückel 4n + 2 rule (1), it was felt that this

system might well possess a singlet ground state whereas most carbenes

possess triplet ground states (9).

The logical starting point for the synthesis of tropylidene would

seem to be tropone. Base-induced decomposition of the tosyl hydrazone of

tropone (III) according to the method of Cristol and Harrington (10) was

III

felt to be one of the best potential routes to tropylidene or 7-diazo-

cycloheptatriene, the immediate precursor of tropylidene. Since the

carbonyl character of tropone is reduced, it was felt that a method of

synthesis of III other than the direct reaction of tropone and tosyl-

hydrazine must be developed. An extension of the method of Hübel (11)

was felt to be the most promising. Before this obviously involved

sequence was undertaken, however, it was learned that III could be formed

directly from tropone and tosylhydrazine hydrochloride (12).
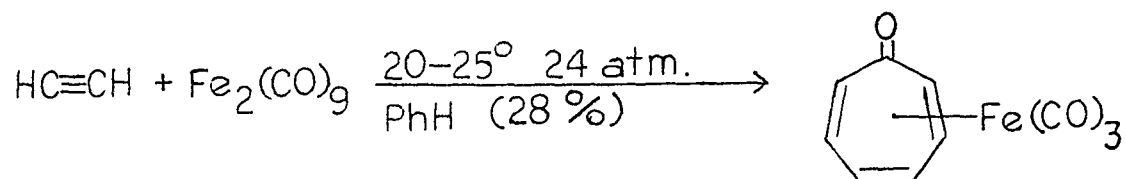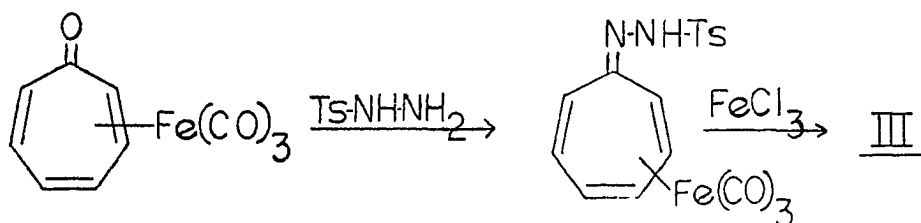
It was hoped that III could be decomposed with base in the presence

of an olefin like Z-2-butene to lend insight into the multiplicity of the

carbene species. If tropylidene possessed a singlet ground state,

stereospecific addition would be expected whereas if it had a triplet

ground state, a mixture of isomers would be expected (13). Treatment
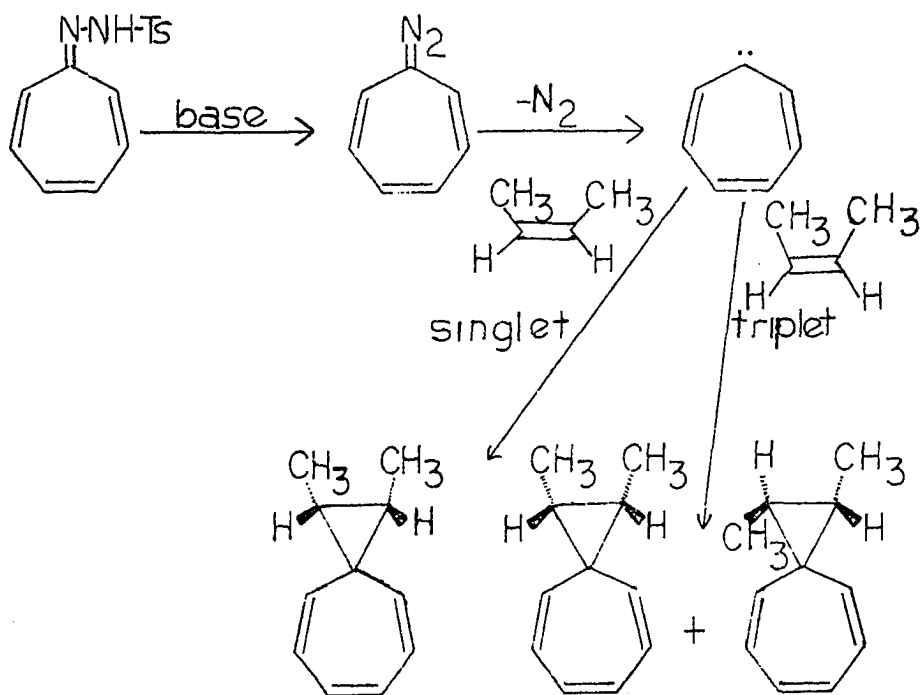
of <u>III</u> with NaOCH$_3$ and heat only resulted in the formation of the sodium

salt of <u>III</u>, however, isolated as a chocolate brown powder. This salt

was then pyrolyzed without solvents according to the procedure of Kaufman

(14) at ca. 10^{-5}mm pressure. At 115°C, a reddish-brown vapor was distilled

leaving a theoretical yield of sodium-<u>p</u>-toluene sulfinate, the other

product expected in the production of 7-diazo-cycloheptatriene from the

sodium salt of <u>III</u>. The reddish-brown distillate, collected in a liquid-

nitrogen cooled trap, was heated at reflux in a solution of methyl
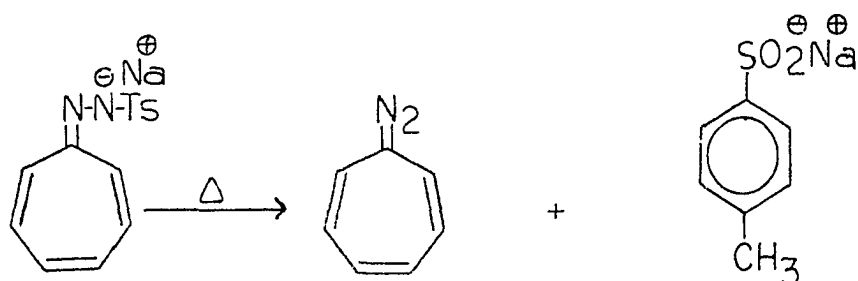
acrylate for two hours. Mass spectral analysis of the major product

isolated by thick layer chromatography indicated that it was most likely

the dimer of tropylidene, heptafulvene.
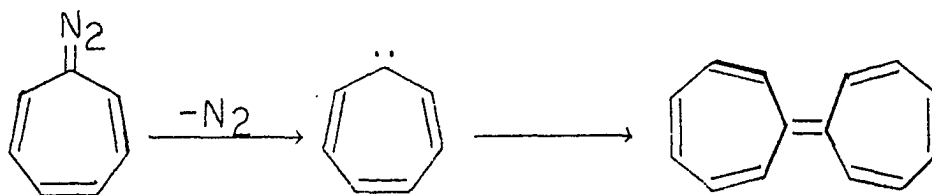
Further attempts to study tropylidene were abandoned at this point
because of the appearance of the report by Jones and Ennis (15). Their
research paralleled ours, both completed and planned. They found that
irradiation of the sodium salt of III in cyclohexene produced a 50%
recovery of heptafulvene but no addition product. Irradiation in the
presence of the electrophilic olefin, dimethyl fumarate, however, resulted
in a 47% yield of the stereospecific trans addition product plus a 10%
yield of the dimer. Even though the stereospecific addition was
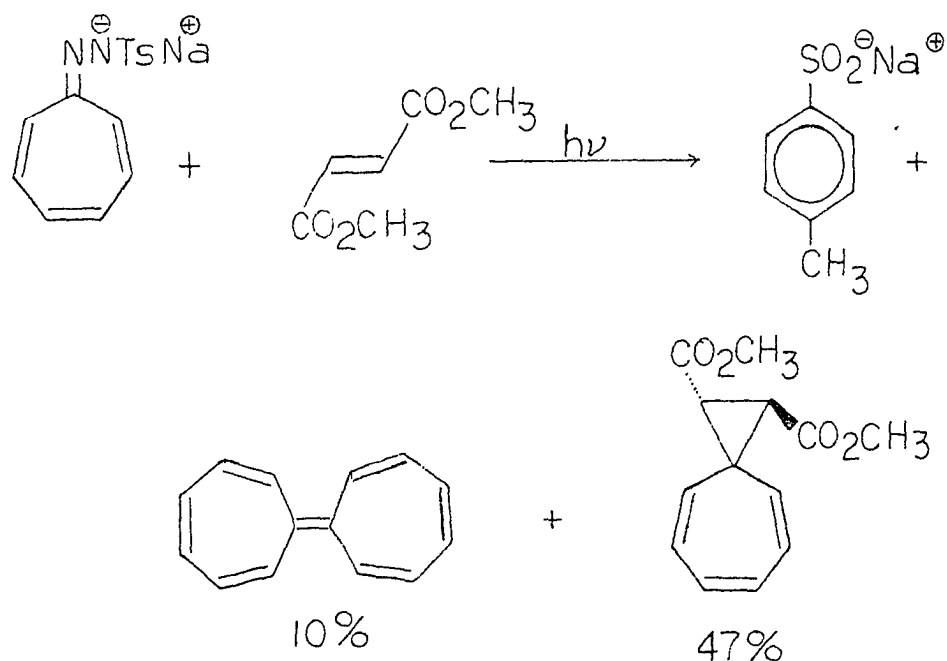
indicative of a singlet carbene, Jones made no commitment as to the nature
of the intermediate in the reaction. He did state that the products were
those anticipated of a carbene of low electrophilicity and relatively
high nucleophilicity, though.

The same results were reported by a Japanese group soon after the
appearance of Jones' paper (16). They reported that the pyrolysis of the

sodium salt of III at high vacuum in the presence of dimethyl fumarate or dimethyl maleate lead to the same trans addition compound isolated by Jones and Ennis. Thus the addition to dimethyl maleate must occur by a stepwise addition, the mechanism accepted for triplet carbene additions (13).

The question of the multiplicity of tropylidene at that point was therefore still open. It was obvious from the evidence cited that addition to olefins could not be used as a criterion of ground state multiplicity in this case. This was also demonstrated earlier by Moritani's research group in Japan. They found that even though both dibenzo-(a,d)-cycloheptatrienylidene and tribenzo-(a,c,e)-cycloheptatrienylidene add to olefins in a stereospecific manner (17), they both have triplet ground states as determined by esr spectroscopy (18).

Soon after the appearance of the two reports of the chemistry of tropylidene, Gleiter and Hoffmann published the results of their extended Hückel calculations on tropylidene (19). Their findings show that tropylidene should have a triplet ground state lying only 11-20 kcals lower in energy than the singlet. It was pointed out that tropylidene lies in the region where firm predictions were not being made. These predictions were found to be valid by Moritani, however (20). He isolated 7-diazo-cycloheptatriene by pyrolysis of the lithium or sodium salt of III at very high vacuum conditions. Irradiation of this diazo compound, found to be surprisingly stable, in the presence of electrophilic olefins led to stereospecific addition. Dilution studies as well as esr spectroscopy confirmed the ground state of tropylidene to be triplet.

Troponoid Cycloadditions

As a continuation of our interest in tropone chemistry, our attention turned to the thermal cycloaddition reactions of tropone. The Woodward-Hoffmann orbital symmetry rules put forth in 1965 (21) predict that tropone is "allowed" to undergo the following thermal cycloadditions: $\pi^4s + \pi^2s$, $\pi^6s + \pi^4s$, $\pi^2s + \pi^8s$, $\pi^6s + \pi^8s$, $\pi^2s(a) + \pi^2a(s)$, $\pi^6s(a) + \pi^2a(s)$, $\pi^4s(a) + \pi^4a(s)$, $\pi^4s(a) + \pi^8a(s)$, and $\pi^6s(a) + \pi^6a(s)$.

Prior to the formulation of the Woodward-Hoffmann rules, only Diels-Alder type ($\pi^4s + \pi^2s$ cycloadditions) reactions of tropone had been reported.

$$(22)$$

$$(23)$$

10

 (24)

 (25)

X= Cl, Br
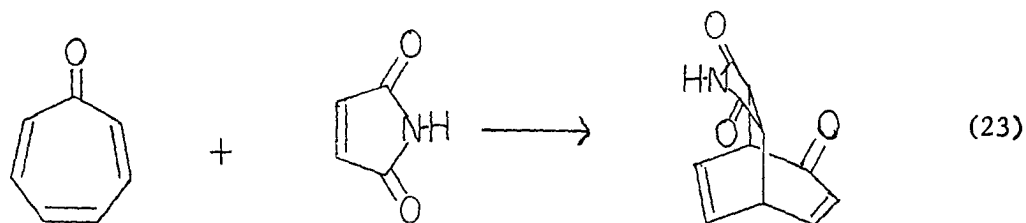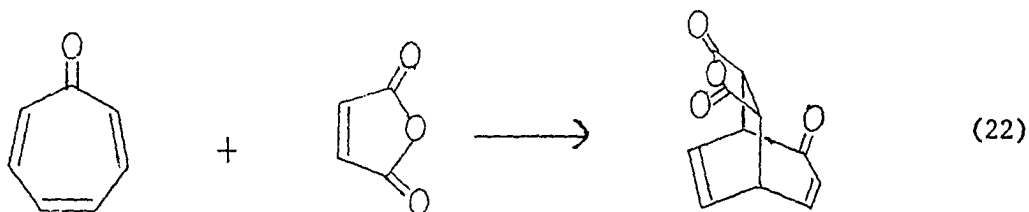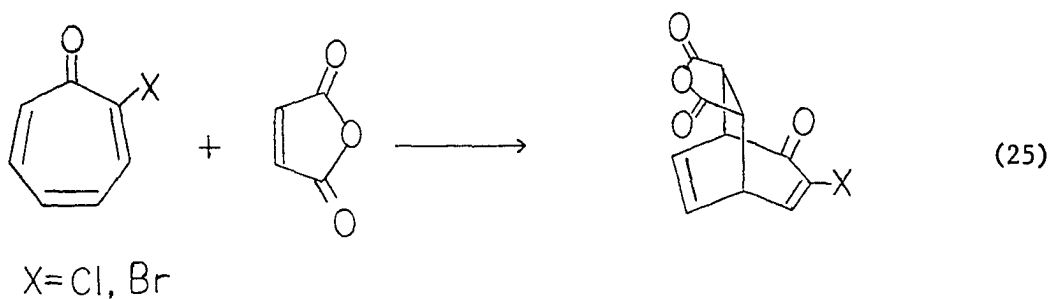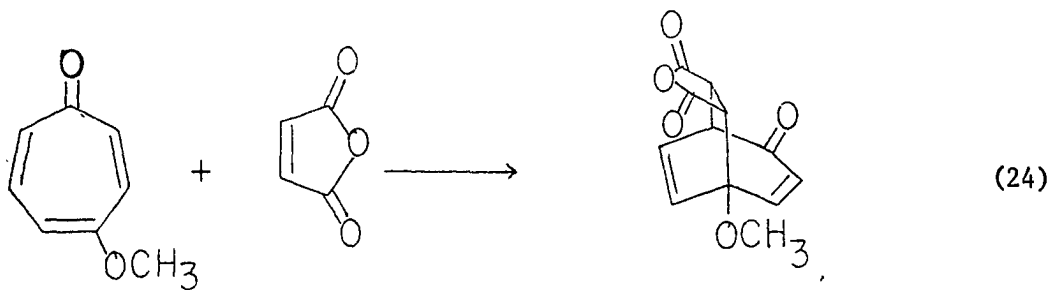
Following the theoretical predictions of Woodward and Hoffmann, a number of examples substantiating their predictions were reported.

 (26, 27)

 (28)

 (29)
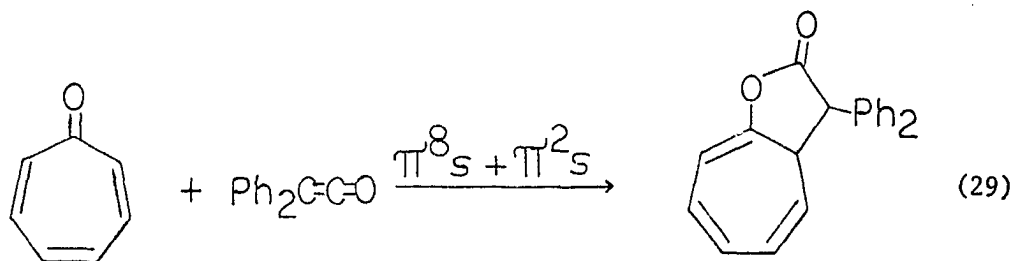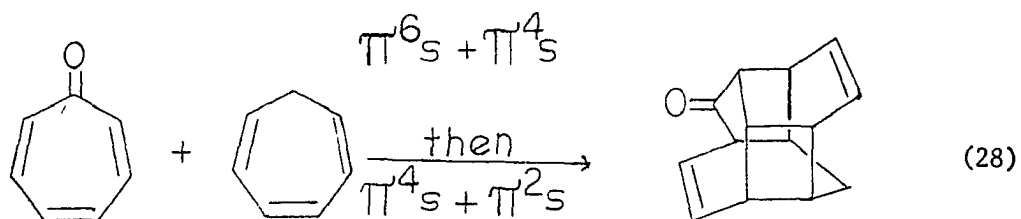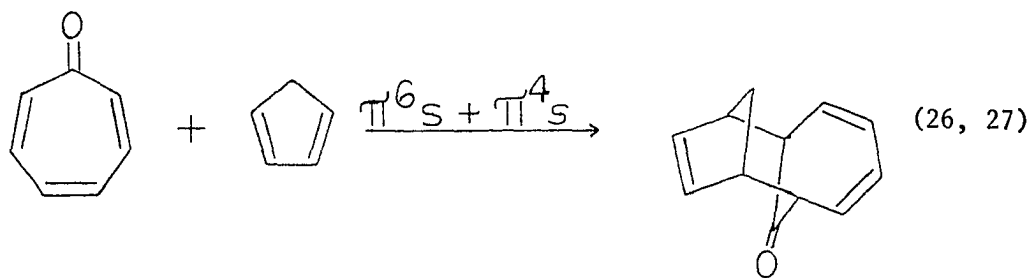
RESULTS AND DISCUSSION

6,7-Dicarbomethoxy-Bicyclo-[3.2.2]-Nona-3,6,8-Trien-2-One

Historical

Because of the relative paucity of cycloaddition reactions of tropone

at the time this research was started and a basic disagreement with a

literature report by Dauben and Pratt (30), a study of the reaction of

tropone and dimethyl acetylenedicarboxylate (DMADC) was undertaken. Dauben

and Pratt contend that tropone and DMADC do not react to form the expected

$\pi^4s + \pi^2s$ adduct but react via a cyclopropanone intermediate like a

cycloheptatriene (31). This report was difficult to accept   .
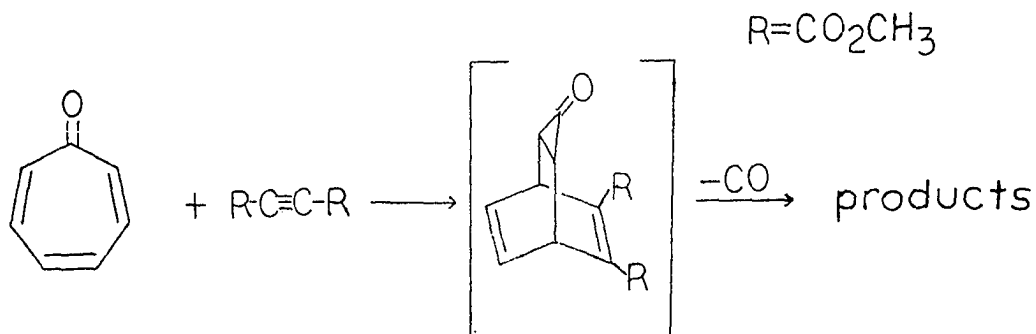
for a number of reasons: a) in no other cycloaddition reaction of tropone

was a cyclopropanone or cyclopropane derivative even remotely considered,

b) tropone has a different electronic nature than cycloheptatriene and

would not be expected to react similarly, and c) the cyclopropanone

intermediate would be expected to have a high internal energy content and

given a choice of reaction pathways, another would undoubtedly be followed.

At the time this research was started, the bicyclo-[3.2.2]-nonatrienone

system was unknown. The first report of the bicyclo-[3.2.2]-nonatriene

ring system, itself, had only been appeared the previous year (32). It

was felt that the reaction of tropone and an acetylene should react in the

usual $\pi^4 s + \pi^2 s$ fashion thus producing the desired bicyclo-[3.2.2]-

nonatrienone in one step. This system was desired in order to test the

possibilities of extensive charge delocalization in a bicyclic system and

generation of a bicyclotropylium ion, the vinylog of the extensively

studied norbornadiene system. This interesting theoretical system was

first alluded to in the literature by Goldstein in 1965 (32). It was

also of interest to see whether if such a system, once generated, would

have as much stability as the tropylium ion itself and, if not, what the

differences would be. DMADC was the acetylene of choice because it has

proven to be a very good dienophile in Diels-Alder reactions, is much

easier to obtain and handle than most acetylenes and, of course, it was

the acetylene used in Dauben's report.

Soon after this research was started, two reports appeared in the

literature on the preparation of bicyclo-[3.2.2]-nonatrienones, only one

of which involves a cycloaddition reaction of tropone, however. Goldstein

(33)
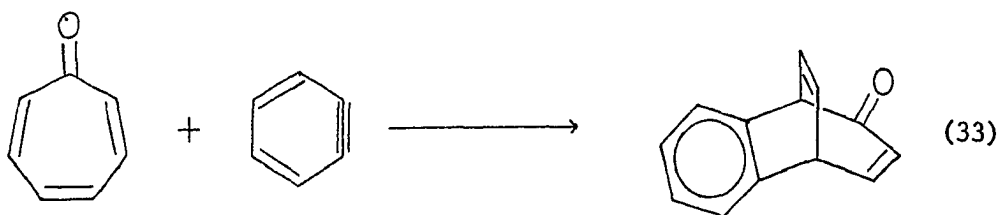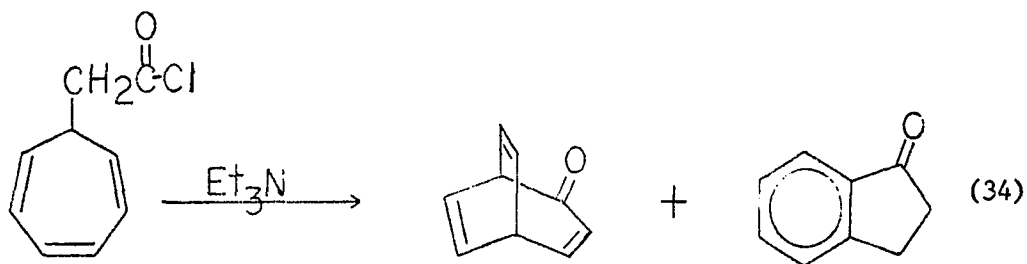
and Odell (34) further found that treatment of the corresponding bicyclo-
[3.2.2]-nonatrienol with $AlCl_3$ led to a facile rearrangement to barbaralol.
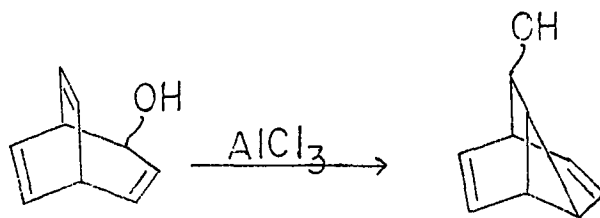
Since barbaryl tosylate undergoes solvolysis rather sluggishly, it was
felt that there was no delocalized intermediate leading to barbaralol.
This was not felt to be expected if a stabilized (charge delocalized)
bicyclotropylium was a real intermediate. This result was actually
thought of as being experimental proof for theoretical predictions.
Goldstein reported that the bicyclo-[3.2.2]-nonatrienyl carbonium ion is
predicted by theoretical considerations to be destabilized and anti-
bicycloaromatic (35). This prediction turns out to be questionable,
however, and will be covered in detail later.

Results

A xylene solution of an 8 : 1 molar ratio of DMADC and tropone, respectively, was heated at 145°C under a nitrogen stream for 24 hours. The product, a thick dark oil, separated into 3 component parts upon careful alumina chromatography. Only the first of these proved to be non-polymeric, however, and upon standing, a white crystalline compound, mp 126-132°C (recrystallized from ether/hexane, mp 131-132°C), was isolated from this fraction in 16% yield based on tropone. The mass spectrum of this compound showed a parent ion at m/e 310 and major daughter ions at m/e 251, 192, 133, and 74 thus indicating the presence of four carbomethoxy groups. The nmr spectrum showed absorptions at 3.90 and 8.00 ppm integrating 6:1 respectively. The infrared spectrum confirmed the presence of the carbomethoxy groups and shows that the compound may be aromatic by the absorptions found in the 1450-1600 cm^{-1} region (36). This spectral data suggests that the reaction product may be a tetracarbomethoxybenzene. The simple nmr spectrum and significantly higher melting point of the reaction product eliminate the 1,2,3,5 isomer from consideration. The 1,2,4,5 isomer was eliminated by the fact that a mixed melting point of the reaction product and authentic material prepared from the readily available 1,2,4,5-benzene tetracarboxylic acid was depressed. The spectral properties for this isomer were strikingly similar to those of the reaction product, difference appearing only in the fingerprint region of the infrared spectra. That the reaction product was actually the remaining 1,2,3,4 isomer was shown by a comparison of spectral and melting point

data with authentic material prepared from 1,2,3,4-tetramethyl benzene by
the method of Zacharewicz and Uzarewicz (37).

The formation of 1,2,3,4-tetracarbomethoxy benzene was felt to arise
in one of two ways: A polymerization of DMADC in some manner or by
decomposition of a 2:1 adduct of DMADC and tropone. The first possibility
was eliminated by heating DMADC under the same conditions and noting no
change in spectral properties or formation of 1,2,3,4-tetracarbomethoxy
benzene. More will be said about the second possibility later.

Quite different results were obtained when an equal molar ratio of
tropone and DMADC was heated in toluene at 110°C under a nitrogen stream
for 24 hours. Most of both starting materials was recovered, no .
tetracarbomethoxy benzene was isolated, and a small amount of a material
shown by mass spectroscopy to be a 1:1 adduct of tropone and DMADC was
separated after careful silica gel and alumina column chromatography.
A large scale reaction heated at 100°C in nitromethane under a nitrogen
flow for a week produced a 43% yield (based on tropone) of the same 1:1
adduct along with a 28% recovery of DMADC. No evidence for other reaction
products was obtained. That this 1:1 adduct was in fact the expected
π^4s + π^2s cycloaddition product (IV) was shown by spectral evidence.
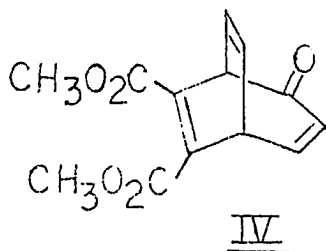
6,7-dicarbomethoxy-bicyclo-[3.2.2]-nona-3,6,8-trien-2-one

The mass spectrum showed the presence of two carbomethoxy groups and a ketone function. The infrared spectrum exhibited absorptions at 1756

m/e 248 $\xrightarrow{\text{-CO} \quad m^*}$ m/e 220

m/e 248 $\xrightarrow[m^*]{\text{-CO}_2\text{CH}_3}$ m/e 189

m/e 220 $\xrightarrow[m^*]{-\text{OCH}_3}$ m/e 189

m/e 189 $\xrightarrow[-\text{OCH}_3]{m^*}$ m/e 158

m/e 189 $\xrightarrow[-\text{CO}_2\text{CH}_3]{m^*}$ m/e 130

m/e 158 $\xrightarrow[-\text{CO}]{m^*}$ m/e 130

m/e 130 $\xrightarrow[-\text{CO}]{m^* -\text{CO}_2\text{CH}_3}$ m/e 102
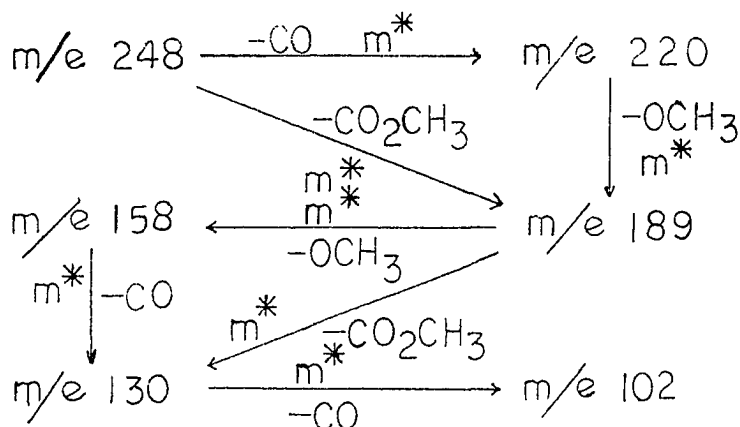
(shoulder), 1739, 1720, 1678, 1650, and 1600 cm^{-1} thus indicating the presence of three distinct olefinic groups as well as the ester and keto moieties (36) and the ultra violet spectrum showed one absorption at 218 mμ (ϵ=1.17 x 10^4) indicative of α-β unsaturated ketones or esters (36). The nmr spectrum was quite complex but compared very favorably with known tropone $\pi^4 s + \pi^2 s$ cycloaddition reaction products in the literature (34, 38). The results of decoupling experiments using a Varian HA-100 nmr spectrometer are shown below:
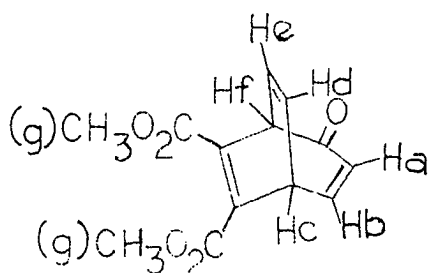
Ha = 5.17 ppm - doublet of doublet of doublets

Hb = 7.07 ppm - doublet of doublet of doublets

Hc = 4.15 ppm - doublet of doublet of doublet of doublets

Hd = 6.79 ppm - doublet of doublet of doublets

He = 6.51 ppm - doublet of doublet of doublets

Hf = 4.43 ppm - doublet of doublet of doublets

Hg = 3.75 ppm - singlet

Jab = 11.0 cps

Jde = 8.60 cps

Jef = 6.25 cps

Jcd = 6.25 cps

Jac = 0.90 cps

Jbc = 8.40 cps

Jaf = 1.00 cps

Jce = 1.50 cps

Jaf = 1.50 cps
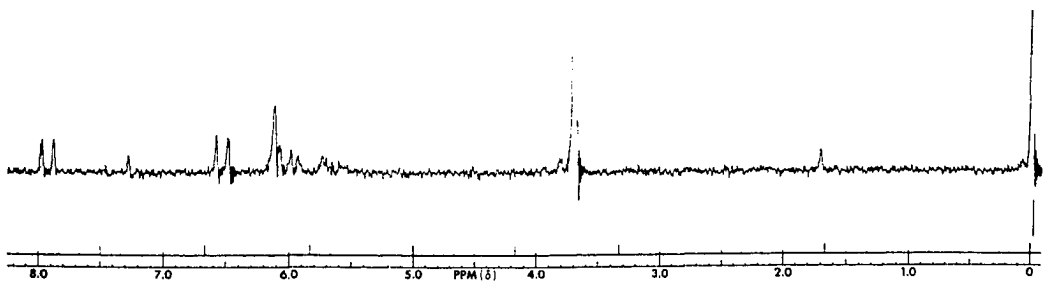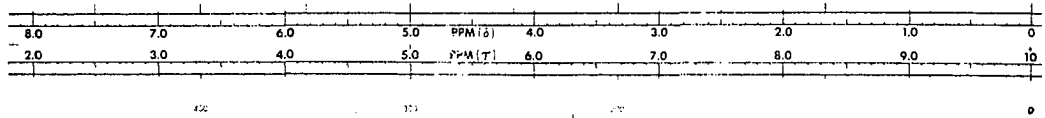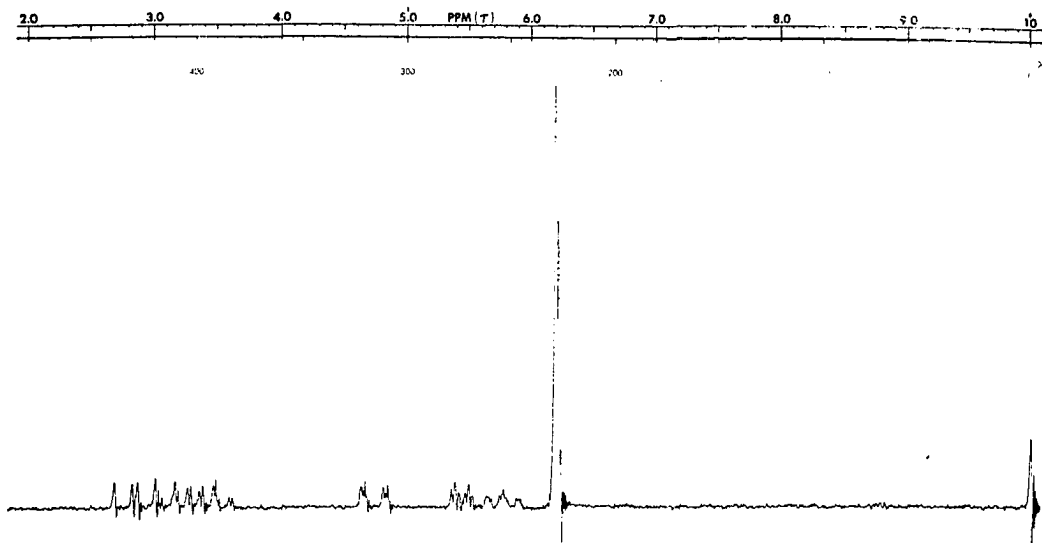
Figure 1. Nuclear magnetic resonance spectra

    a) 6,7-dicarbomethoxy-bicyclo-[3.2.2]-
        nona-3,6,8-trien-2-one

    b) 1,5-dicarbomethoxy-bicyclo-[4.3.0]-
   nona-3,6,8-trien-2-one

A xylene solution of equal molar amounts IV and DMADC was heated at reflux under a nitrogen stream for 24 hours. Chromatographing the dark reaction mixture produced a 15% yield of a white crystalline material, mp 130-132°C (recrystallized from ether/hexane, mp 132-133°C), which had identical spectral properties exhibited by the 1,2,3,4-tetracarbomethoxy benzene isolated from the first reaction carried out at 145°C. It was therefore concluded that IV is actually formed at 145° but reacts further with DMADC and then undergoes a thermal cleavage of some sort to form the tetracarbomethoxy benzene. That IV was actually present in the original reaction mixture was shown by reexamination of the nmr spectrum of the mother liquors from which 1,2,3,4-tetracarbomethoxy benzene was isolated. The complete spectrum of IV could be picked out of this spectrum. Uninterpretable peaks still remained in this spectrum which turned out to be important and will be covered later as well as the mechanistic interpretations of these results.

The adduct, IV, proved to be very difficult to purify. Even after repeated and varied chromatographing, a colorless or crystalline substance could not be produced. During an attempted distillation, it was found that a material isomeric to IV (by mass spectroscopy) was isolated along with IV. Only about half of the material was able to be distilled; the residue in the distillation flask turned dark and hard upon extensive heating past 150°. Reexamination of the nmr spectrum of the mother liquors from the 145°C reaction and that from the reaction between IV and DMADC revealed the same absorptions as those found in the spectrum of the isomeric material. Thus it was felt that a thermal rearrangement

of <u>IV</u> was occurring at temperatures of 145°C and above. To check this possibility, controlled pyrolyses experiments were carried out.

A vapor-phase pyrolysis at 375°C and 0.3 mm Hg through a glass bead filled column produced two materials: a white crystalline solid, mp 77-78°C in approximately 80% yield and a yellow oil in about 20% yield. Exact yields could not be calculated because of the inability to completely separate the oil from the solid. The nmr spectrum of this solid (7.92 (d, J=6 cps, 1H), 6.52 (d, J=6 cps, 1H), 6.70-5.50 (m, 4H), and 3.80 ppm (s, 6H)) was identical to the isomeric material discussed previously. The pair of downfield doublets was very similar to those found in 4,4-dimethyl-2-penten-1-one at 5.88 (J=6 cps, 1H) and 7.50 δ (J=6 cps, 1H). The remainder of the peaks were assigned to olefinic and carbomethoxy protons. The mass spectrum was strikingly similar to that of <u>IV</u>, the same pattern being noted with slight intensity differences and the appearance of one metastable (m/e 195). The infrared spectrum indicates the presence of at least two different types of carbonyl groups, one of which is conjugated, and the presence of a conjugated diene system by the absorptions at 1734, 1720, 1654, 1600, and 1590 cm^{-1} (36). The u.v. spectrum confirms the presence of an α,β-unsaturated ketone chromophore located in a 5-membered ring (216 mμ, ε = 1.19 x 10^4) as well as the presence of a conjugated diene system in a six-membered ring (256 mμ, ε = 2.40 x 10^3) (36). Consideration of this data indicates that the structure of the major pyrolysis product is a dicarbomethoxy-dihydroindenone. This
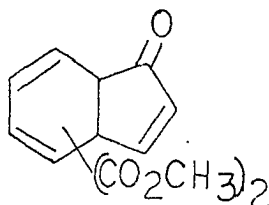
postulate was placed upon much firmer grounds by a comparison of the

nmr   spectrum of the pyrolysis product with those of several known

dihydroindenones (39).   The absence of protons upfield from the

carbomethoxy protons, the appearance of doublets for the A,B pattern

of the α,β unsaturated ketone group, and the presence of 4 olefinic pro-

tons demand that the carbomethoxy groups be at the bridgehead.   The

cis-ring fusion, as shown (V), was assigned because of the u.v. spectrum
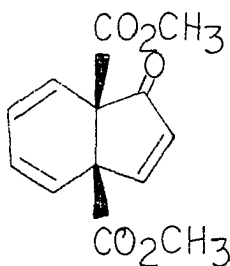
V

1,5-dicarbomethoxy-bicyclo-[4.3.0]-nona-3,6,8-trien-2-one

(36) and the ability of V to form an adduct with maleic anhydride, mp

280-281°C (mass spectroscopy shows a parent ion at m/e 356).   It is

known that trans-fused dihydroindenones do not form an adduct with

maleic anhydride (40).

The other 20% of the pyrolysis products was never able to be crystal-
lized or made colorless. Extensive and careful column chromatographing

eventually separated the oil into three major component parts. Since

each similar nmr spectrum indicated aromatic protons and each mass

spectrum showed the presence of a parent ion of m/e 248 and the presence

of two carbomethoxy groups, it was felt that the yellow oil consisted of

isomeric indanones like VI. This is not surprising since it is known
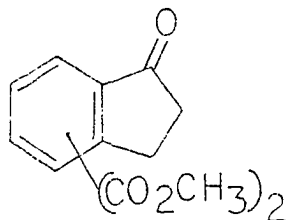
VI

that dihydroindenones with protons at the bridgehead usually rearrange

to indanones like VI during workup (34, 41, 42).

Pyrolysis of IV in solution at 155-160°C for 24 hours yielded the

same mixture of products as described in the vapor-phase pyrolysis.

The problem of obtaining an analytical sample of IV still remained,

however. This problem was eventually overcome by the discovery that V

crystallizing from the sample of IV which had been distilled caused the

crystallization of IV. Unfortunately, fractional crystallization could

not be utilized to separate IV and V, but small amounts of this solid

mixture were successfully used to seed a relatively pure sample of IV to

yield white needles, mp 51-52°C, after one additional recrystallization

from ether/hexane. An elemental analysis of this material was satis-

factory for the proposed composition.

The mechanism of thermal interconversions in this system seems

to most easily rationalized by scheme I, $R=CO_2CH_3$. The initial

Scheme I
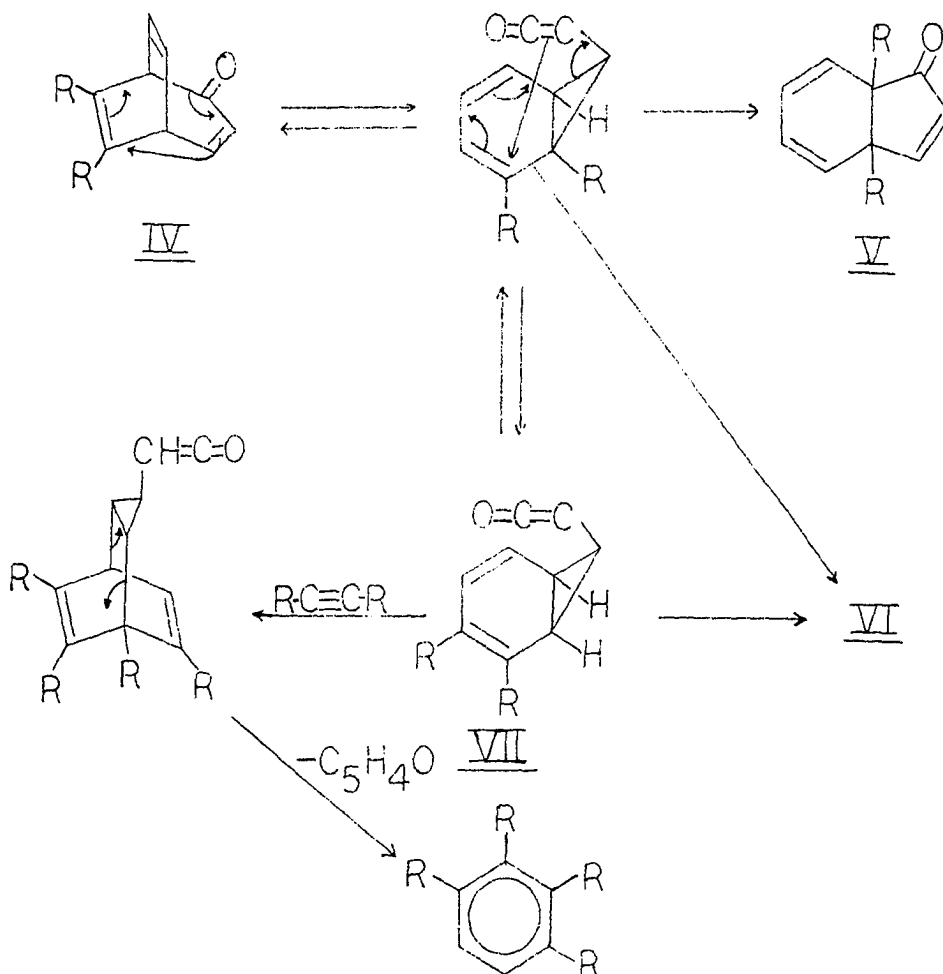
Cope rearrangement or [3,3]-sigmatropic shift is not unlike those

reported in the literature for similar systems (43). These papers

are concerned with the photochemical generation and trapping of the

ketene intermediates from very similar bicyclo-[3.2.2]-nonatrienone start-
ing materials. Chapman's technique (43a) for detecting these ketene
intermediates involves using infrared spectroscopy at liquid nitrogen
temperatures. This same technique was applied to IV and showed strong
evidence for the ketene intermediate, as expected. Allowing the photo-
product to warm to room temperature resulted in the formation of a
substance whose spectral properties were identical with V (44). That the
same ketene intermediate was occurring during the thermolysis of IV was
also shown by low temperature infrared spectroscopy carried out on the
product trapped from a pyrolyis of IV (44). Again, allowing this ketene
to warm to room temperature produced V. The formation of V from the
ketene intermediate is precedented by Goldstein and Odell's report that
a nearly equal amount of indanone is produced along wit bicyclo-[3.2.2]-
nona-3,6,8-trien-2-one from a known ketene precursor ( ). Trapping
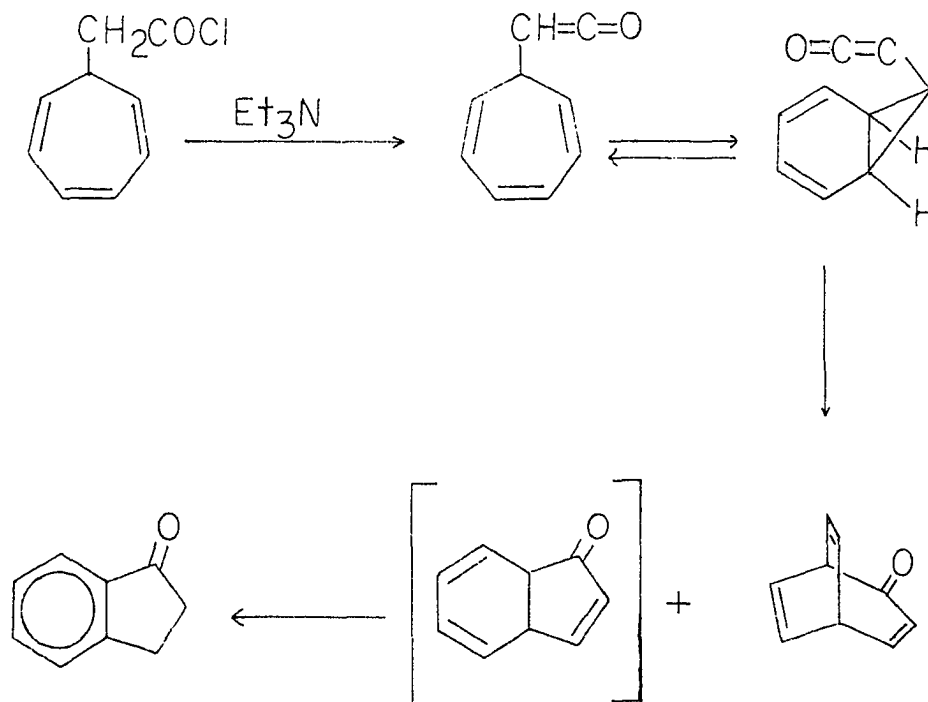
of rearranged ketene <u>VII</u> by DMADC with subsequent thermal decomposition

to produce 1,2,3,4-tetracarbomethoxy benzene is very similar to the

observation of Korte, Buechel, and Wiese that 1,2-dicarbomethoxy

benzene is produced upon pyrolysis of the reaction product of DMADC and

methylcycloheptatrienyl-acetate (45) and the production of benzene

$$R=CO_2CH_3$$
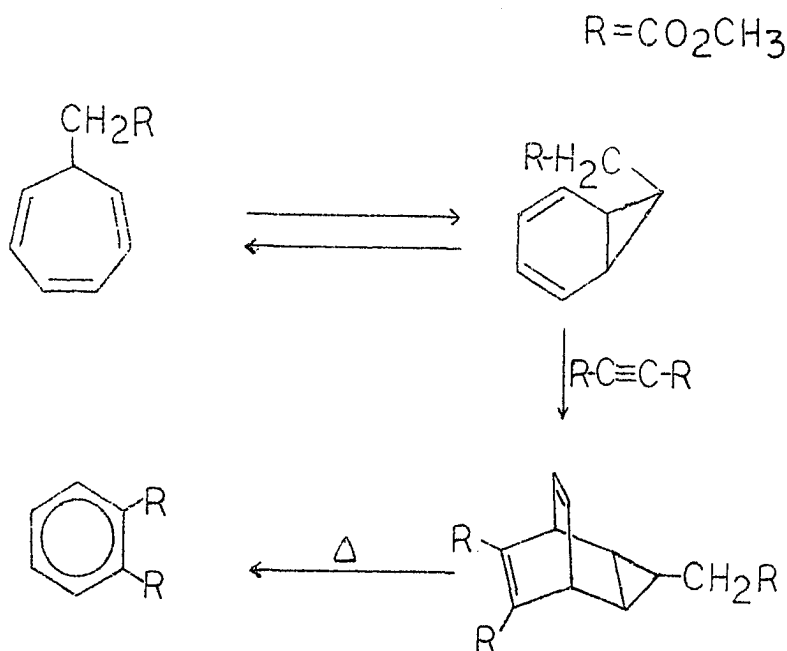
from the pyrolysis of tricyclo-$[3.2.2.0^{2,4}]$-nona-triene reported by

Katz and Cerefice (46).
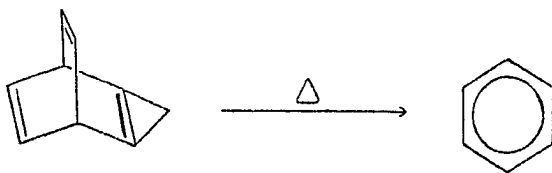
The similarity in yields of 1,2,3,4-tetracarbomethoxy benzene and
isomeric products indicates that these yields might be used as a crude
measure of the tendency for rearrangement of the ketene first formed
during the pyrolysis. With no dienophile present, any rearranged ketene
such as VII would not be trapped and could undergo an internal cycliza-
tion to yield dihydroindenones of different structure than V. Such
products would not have the carbomethoxy groups at the bridgehead and
would isomerize to the corresponding indanones as expected at such high
temperatures (34, 41, 42).

The specificity shown in the pyrolysis of IV seems quite surprising
when it is noted that the initial Cope rearrangement could involve the
unsubstituted ethylene bridge as well as the substituted one, and the
ketenes formed from this rearrangement could cyclize in more than one way.
Each of these possibilities increases the pathways leading to dihydroin-
denones with proton-bearing bridgeheads and thus to indanones. The high
yield of V recovered from this pyrolysis seems to be most easily explained
by the electron-withdrawing properties of the carbomethoxy group. It is
known that electron-withdrawing groups on an olefin increase the tendency
for that group to undergo the Cope rearrangement (47). This should cause
an involvement of the disubstituted ethylene bridge much more than the
unsubstituted one in the initial ketene formation. This same inductive
effect should also cause a more facile attack of the ketene olefin on the
carbomethoxy-bearing olefinic carbon than on the proton-bearing one in
the first-formed norcaradienyl ketene intermediate. This would then
result in a specificity for forming the dihydroindenone, V. These

specificities appear to be borne out by the high yield of $\underline{V}$ isolated from

the pyrolysis. The fact that the yields of isomeric products are slightly

higher than the 1,2,3,4-tetracarbomethoxy benzene indicates that the

specificity is not of the order of 100% since isomers must be arising

from the routes described above as well as rearranged ketenes. But the

similarity of the yields also indicates that the carbomethoxy substituents

control the reaction pathways to a very high degree.

Originally it was felt that the mechanism of 1,2,3,4-tetracarbomethoxy

benzene formation was similar to that shown by Zimmerman and Grunewald

in the formation of naphthalene compounds from thermal reactions of DMADC

and Barrelene (48). All attempts to isolate such an intermediate failed,

$$R = CO_2CH_3$$
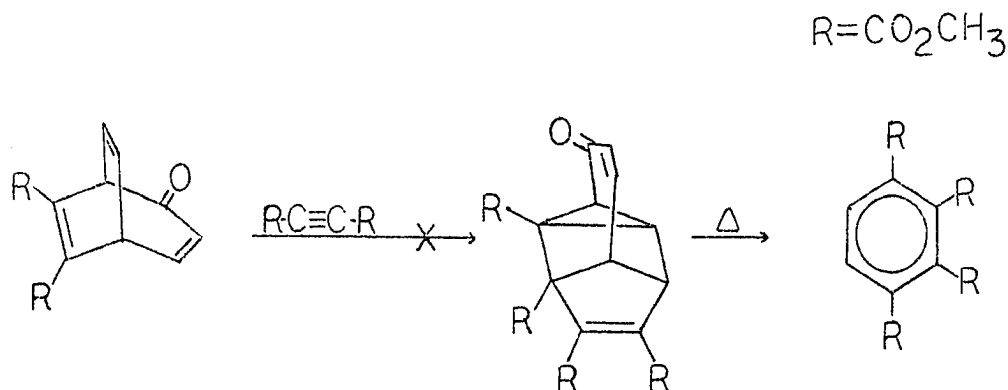
however, even when using the powerful dienophile 4-phenyl-1,2,4-triazoline-

3,5-dione. Thus the mechanism as presently written appears to be the

best explanation for the experimental results.

The problem of attempting to form an extensively charge delocalized

species solvolyticly was then undertaken. It was felt that protonation

of the ketone function of IV should be a good method for introducing a

carbonium ion into the system. Isolation, separation and structural

identification of the products of nucleophilic attack on the resulting

ion(s) was to be the method of determining the extent of delocalization.

Recovering products formed from each or many of the possible ions would

be interpreted as having formed an intermediate exhibiting extensive

charge delocalization. Solutions of IV, H_2SO_4, and the progressively

less nucleophilic solvents CH_3OH, CH_3CO_2H, CF_3CH_2OH, and CF_3CO_2H were

stirred until spectral data indicated that IV was completely gone. In

each case, ca. 100% yield of the corresponding Michael addition product

was isolated. As a reflection of the nucleophilicity of the solvent,
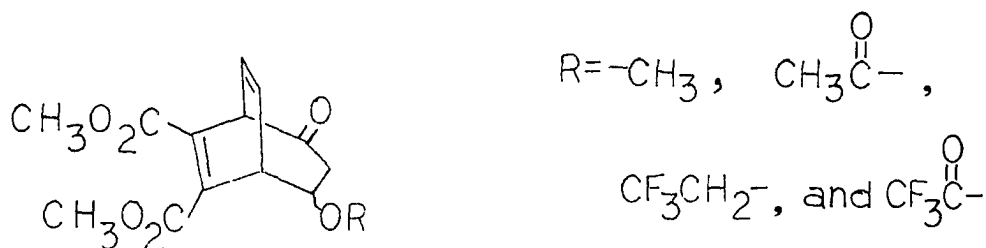
the time necessary for the disappearance of IV increased from CH_3OH ----->

CH_3CO_2H -----> CF_3CH_2OH -----> CF_3CO_2H. These results indicate that not

only was the charge not delocalized throughout the ring system but had

never resided on the carbonyl carbon. It has been subsequently shown

that the energy difference between the bicyclo-[3.2.2]-nonatrienyl cation

and the barbaryl cation is 6-8 kcal/mole and if the first is ever formed,

it rapidly rearranges to the thermodynamically more stable barbaryl form (49).

Thus Goldstein's prediction and observation that the bicyclo-[3.2.2]-nonatrienyl cation is destabilized and antibicycloaromatic seems to be better explained by the lower energy content of the barbaryl cation. The fact that no barbaryl products were isolated from the sovolysis of IV lends chemical verification to Olah's finding that protonation of ketones leads to species in which the charge is localized on the oxygen to a much greater extent than on the carbonyl carbon (50).

Subsequent Troponoid Cycloadditions

A wealth of examples of cycloaddition reactions of tropone have appeared in the literature since the time that this research was started. These will be listed below in equation form according to the type of reaction.

$\pi^4 s + \pi^2 s$

(51)

(38)

R=H, OCH₃, OH

(52)

(51)

(33)   (53)

$$\pi^6{}_s + \pi^4{}_s \quad (54)$$

$$\pi^6{}_s + \pi^4{}_s \quad (55)$$

(56)

(56)

$$(56)$$

$$(56)$$

$$(57)$$

$$\underline{\pi^6{}_s + \pi^4{}_s}$$

$$(26, 27, 55) \quad + \pi^4{}_s + \pi^2{}_s \quad (55)$$

$$\pi^4{}_s + \pi^2{}_s \quad (54)$$

$$(58, 59) \quad \pi^8{}_s + \pi^2{}_s \quad (59)$$
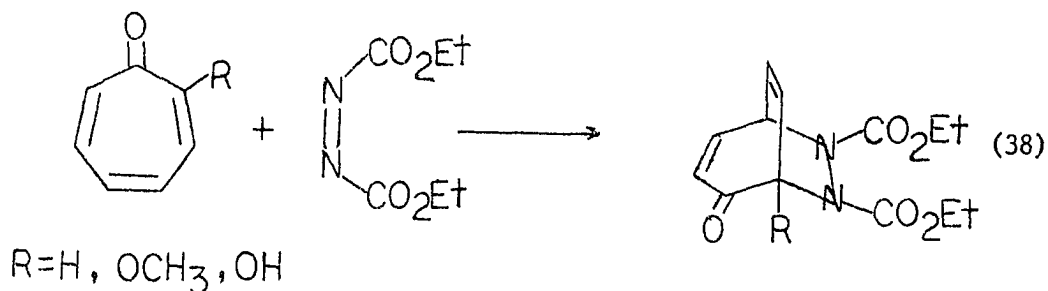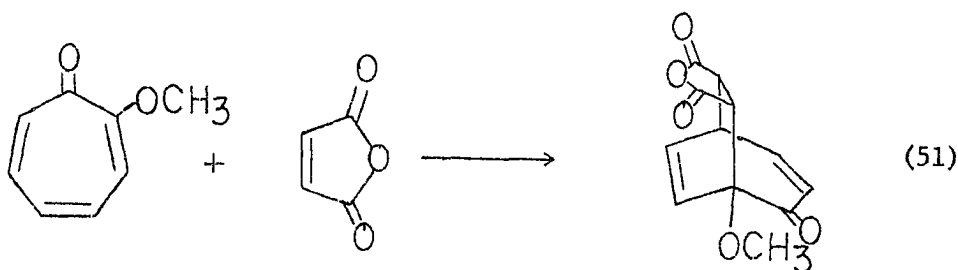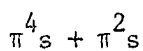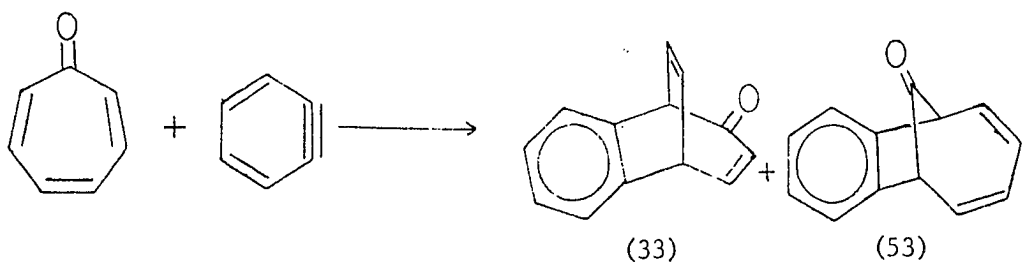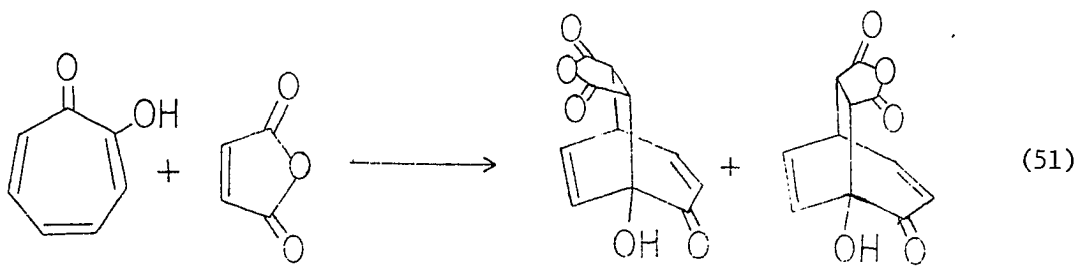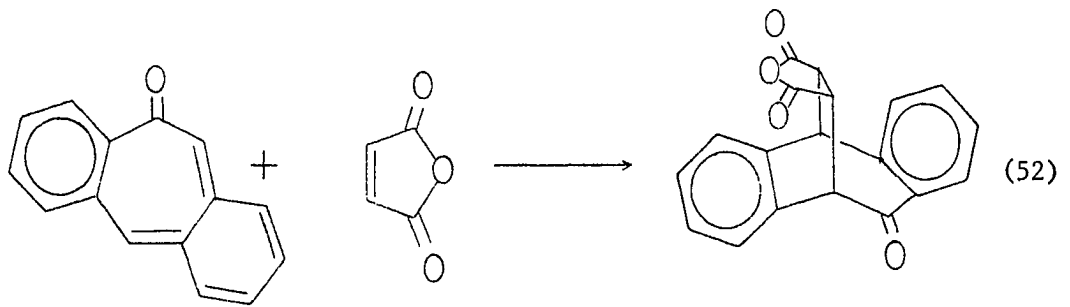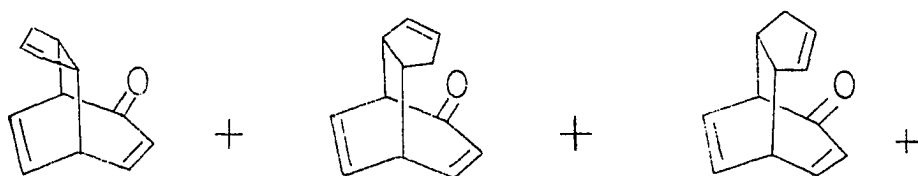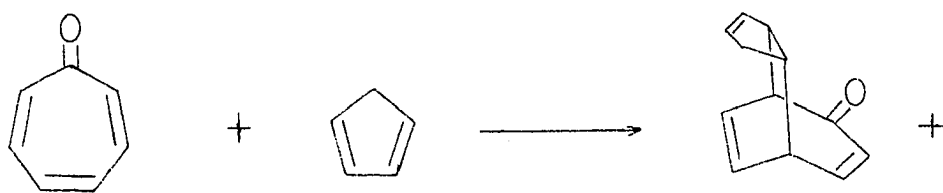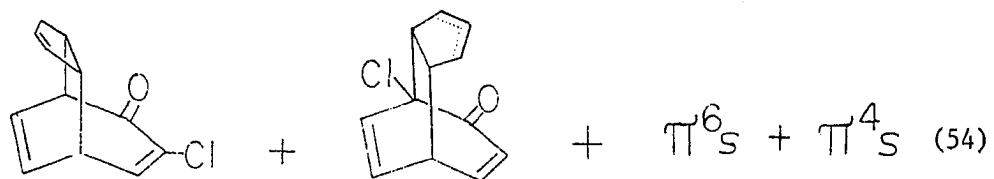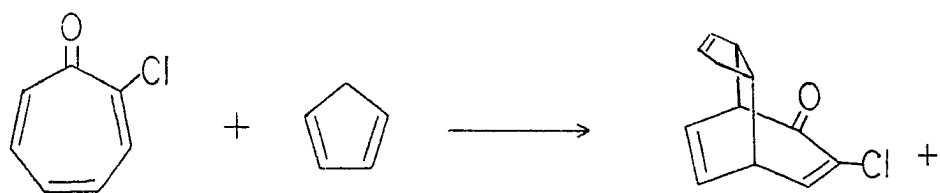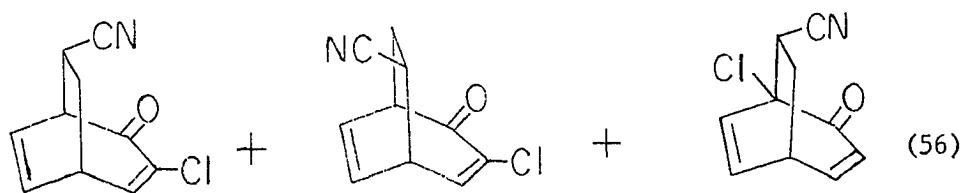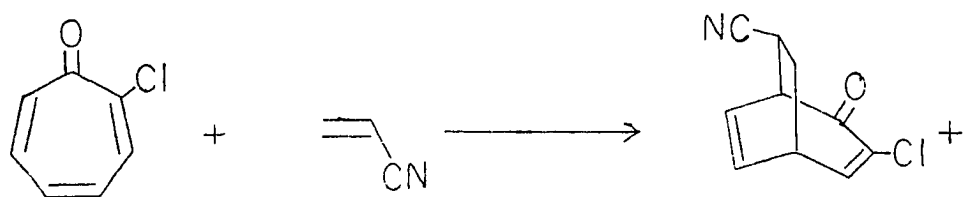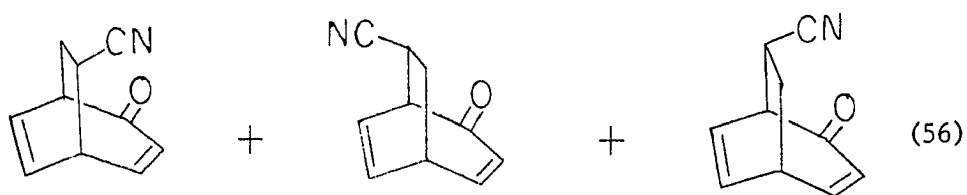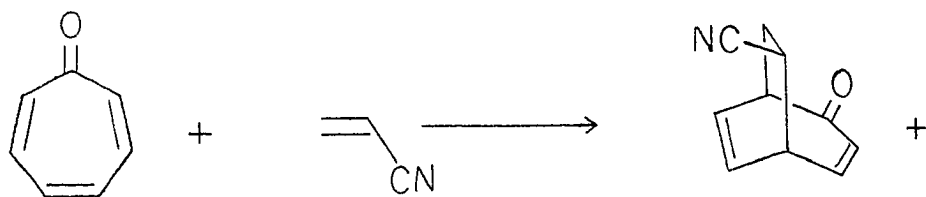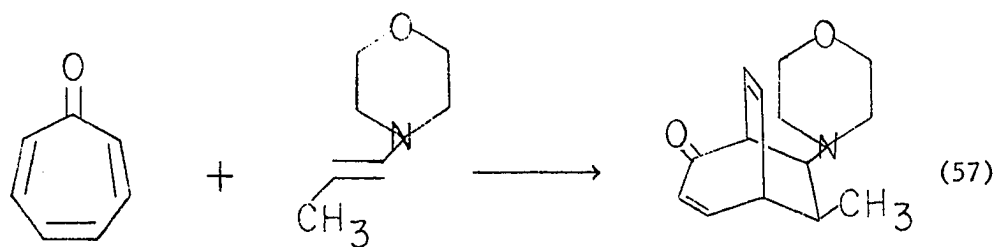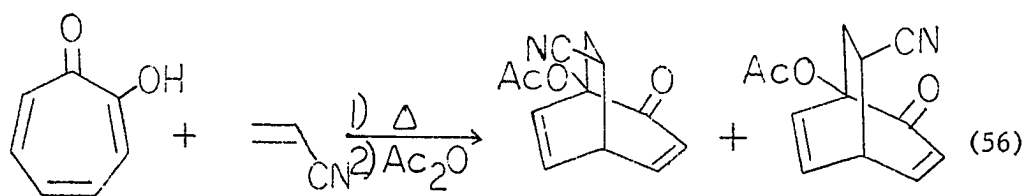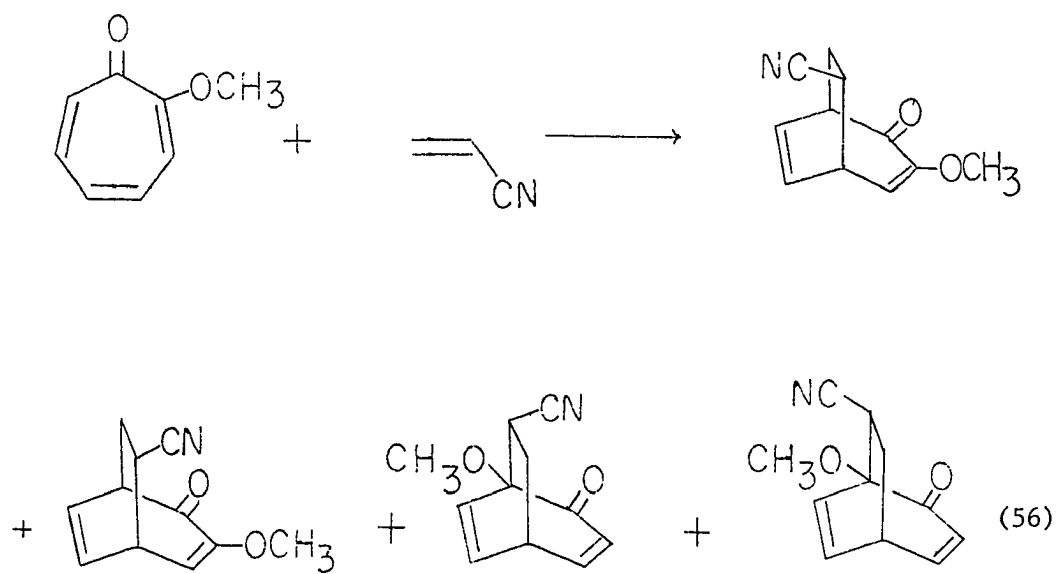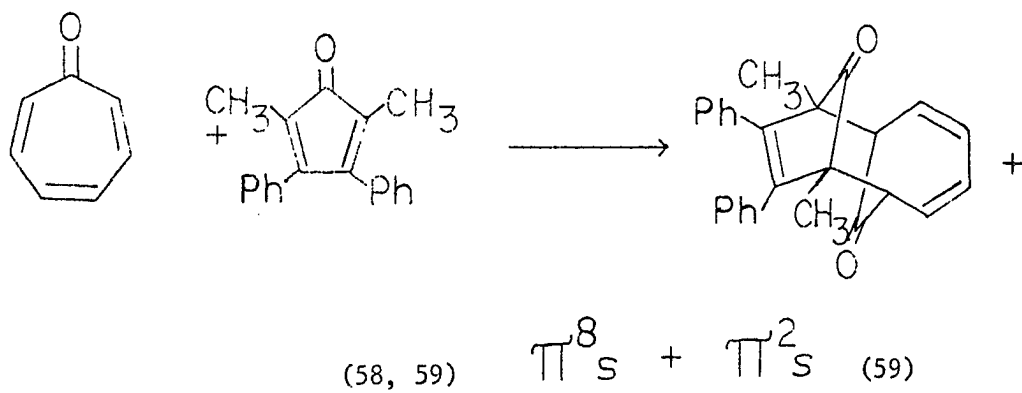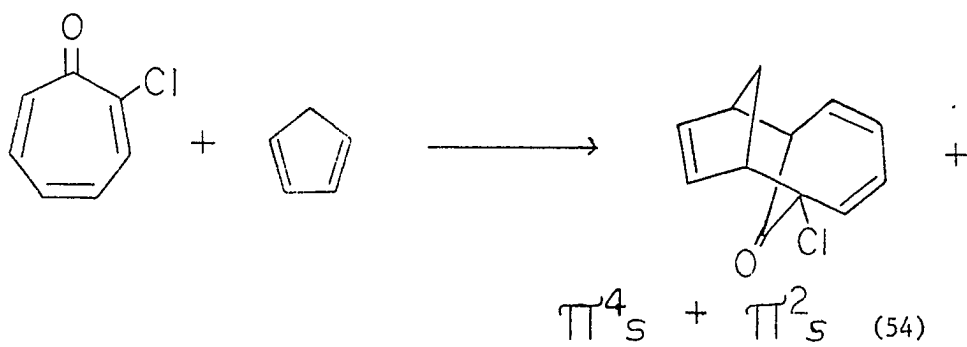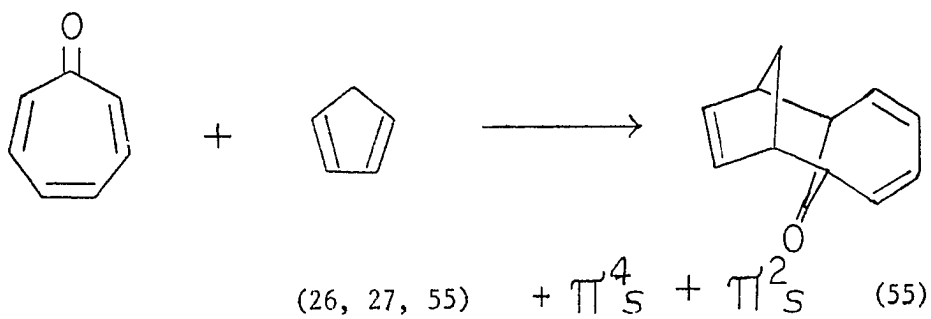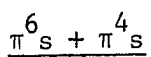
$\pi^6 s + \pi^4 s$ followed by internal $\pi^4 s + \pi^2 s$

(28, 60)

(60, 61)

(62)

$\pi^8 s + \pi^2 s$

(29, 63, 64)

(65)

(59)
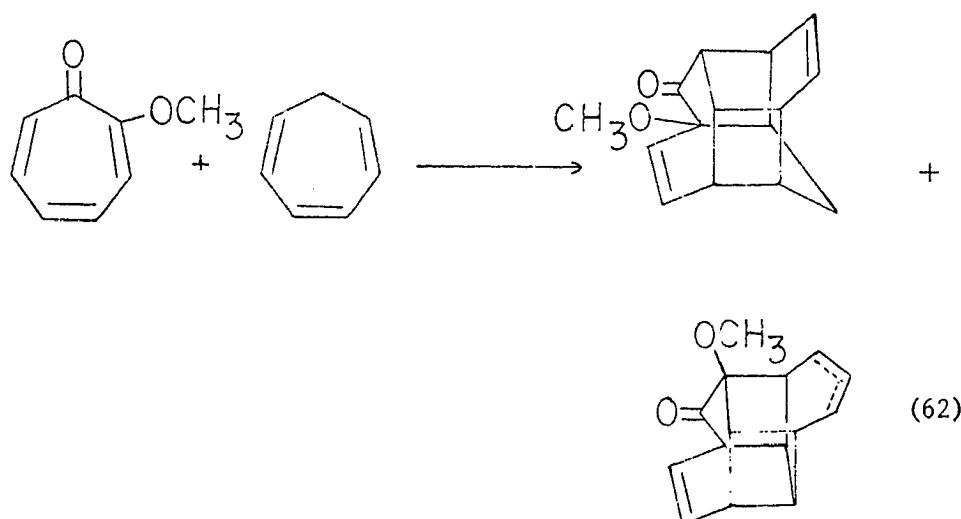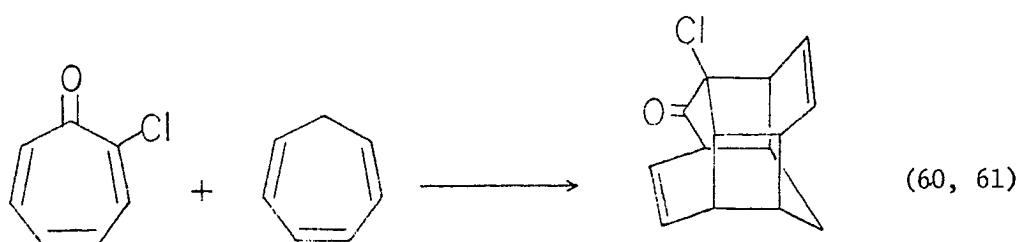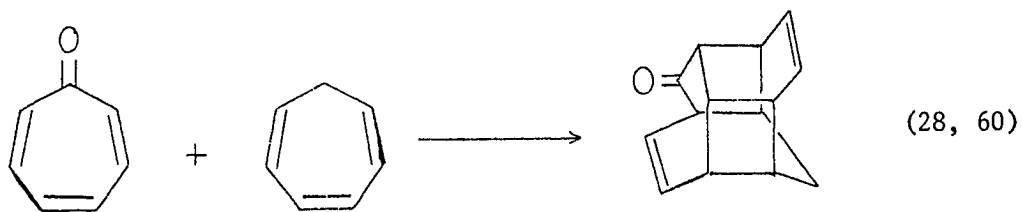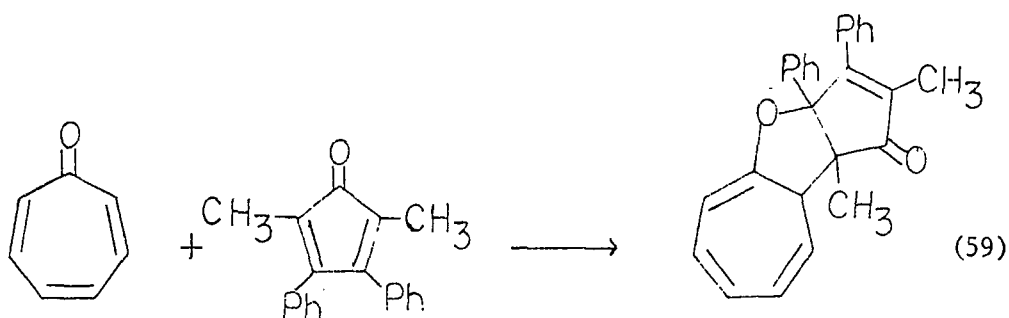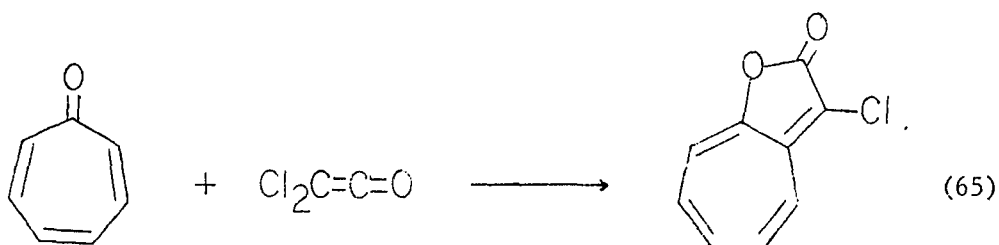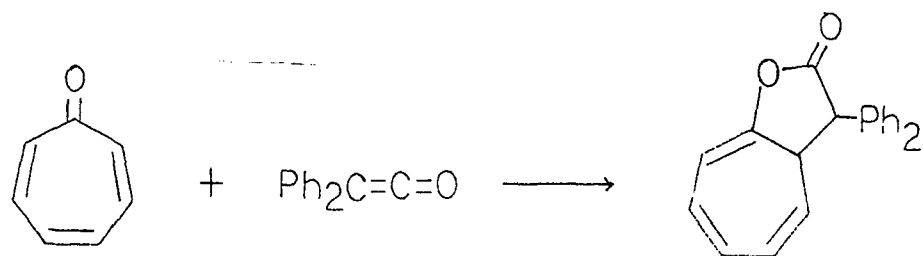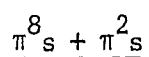
It should be pointed out that the authors originally felt that the initial reaction between tropone and the ketenes was a $\pi^2 s + \pi^2 s$ cycloaddition followed by a rearrangement to the isolated products. It

was subsequently shown, however, that at least in the diphenyl ketene
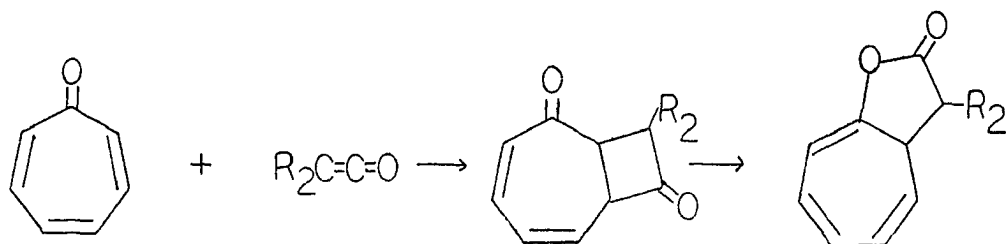
addition, a concerted $\pi^8s + \pi^2s$ cycloaddition had actually taken place.

$\pi^8s + \pi^6s$ and all thermal cis-trans cycloadditions

No reports in the literature.

Miscellaneous Thermal Reactions of Troponoid Systems

A number of thermal reactions of tropones has appeared in the liter-
ature which do not follow Woodward-Hoffmann rules or which can not be
classified as cycloadditions (66), but will be included here for complete-
ness and because of the interesting nature of the resulting products.

$$\text{tropone} + Ph_2C=C=O \xrightarrow{-CO_2} \text{product} \qquad (29)$$

(69)   NC CN   ←   CH$_2$(CN)$_2$ +

(68)   OCH$_3$ Cl Cl Cl Cl   +   OCH$_3$ Cl Cl Cl Cl   ←   CH$_3$OH   Cl Cl Cl Cl   +

(67)   O   Cl Cl Cl Cl   +   Cl Cl Cl Cl   ←   Cl Cl Cl Cl   +

$$\text{(structure)} \quad + \quad NC-CH_2-CO_2Et \quad \longrightarrow \quad \text{(structure)} \qquad (69)$$

$$\text{(structure)} \quad + \quad \text{(structure)} \quad \longrightarrow \quad \text{(structure)} \qquad (57)$$

$$R_1 = R_2 = (CH_2)_4, \ (CH_2)_3$$
$$R_3 = H$$

$$\text{(structure)} \quad + \quad \begin{array}{c} CH_3SO_2Cl \\ \text{or} \\ CH_3SO_2CH_3SO_2Cl \end{array} \quad \xrightarrow{Et_3N} \quad \text{(structure)} \qquad (70)$$

(64)

(70)
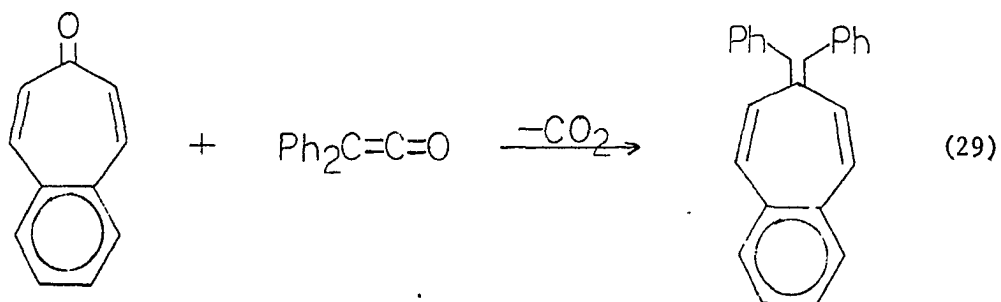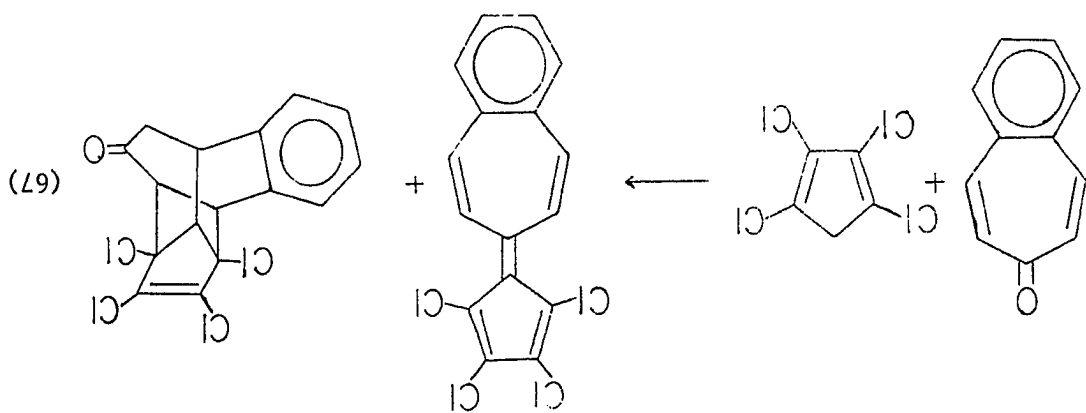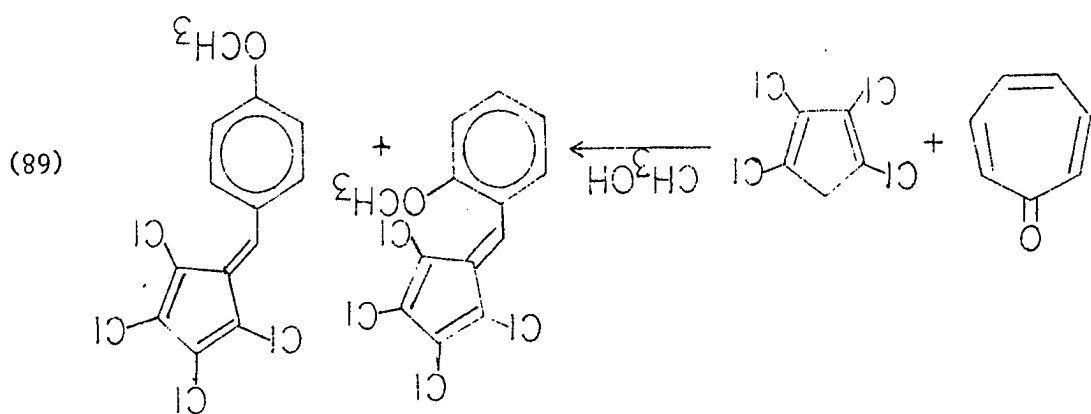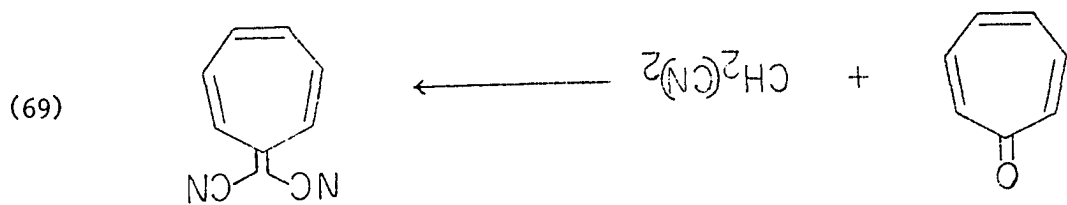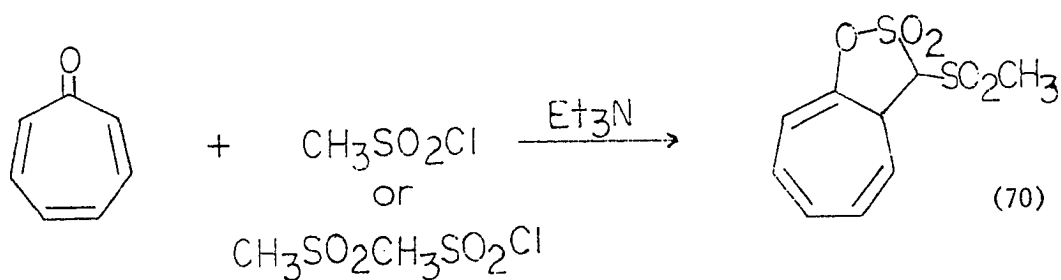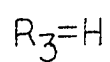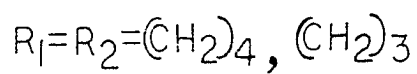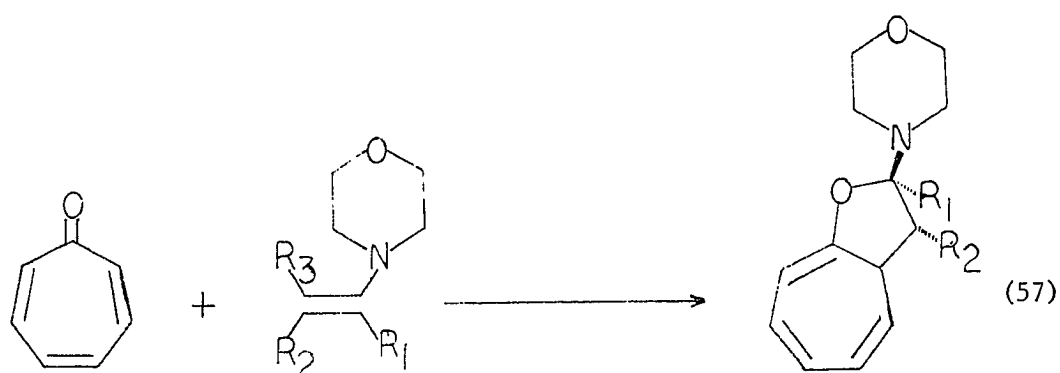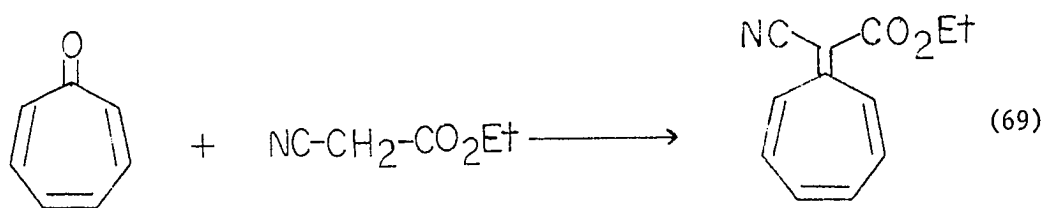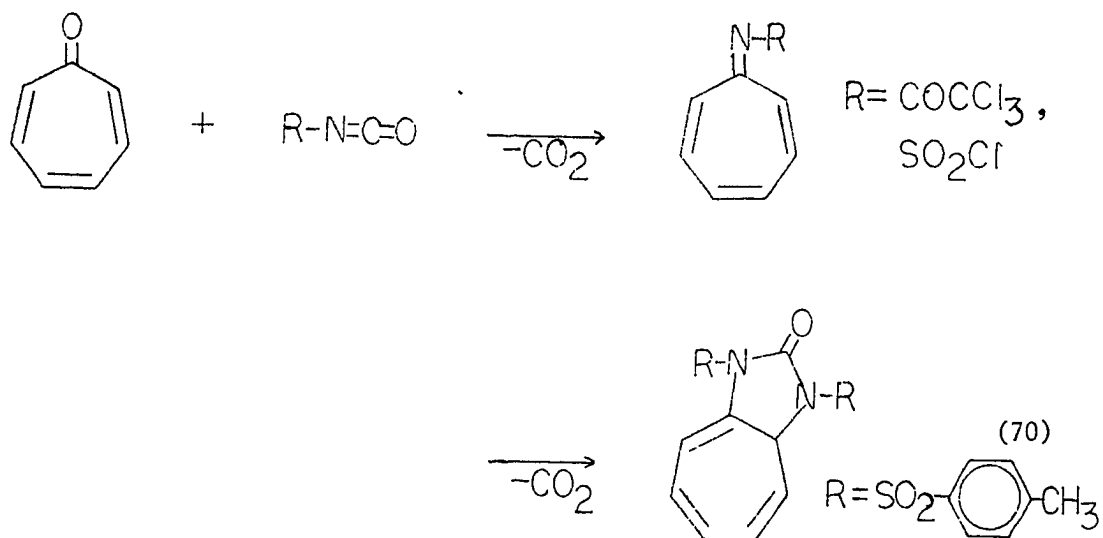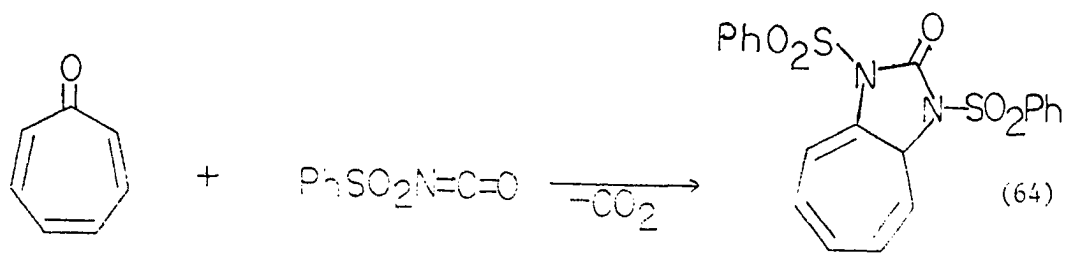
Photochemical Cycloaddition Reactions of Troponoid Systems

In addition to the numerous examples of thermal cycloadditions of tropone, there has been a number of reports of photochemical reactions since the formulation of the Woodward-Hoffmann symmetry rules. These

rules predict that the "allowed" additions are of the order $\pi^2s + \pi^2s$, $\pi^6s + \pi^2s$, $\pi^4s + \pi^4s$, $\pi^4s + \pi^8s$, $\pi^6s + \pi^6s$, $\pi^4s(a) + \pi^2a(s)$, $\pi^6s(a) + \pi^4a(s)$, $\pi^8s(a) + \pi^2a(s)$, and $\pi^6s(a) + \pi^8a(s)$. A list of representative examples of the photochemical reactions of tropone are shown below in equation form according to reaction order:

$\underline{\pi^2s + \pi^2s}$

(71)

(72, 73)

$\underline{\pi^6 s + \pi^2 s}$

(74, 75)

$\underline{\pi^6 s + \pi^6 s}$

(76)

(41)

$\underline{\pi^4s + \pi^2a}$

(76, 77, 78)

(41)
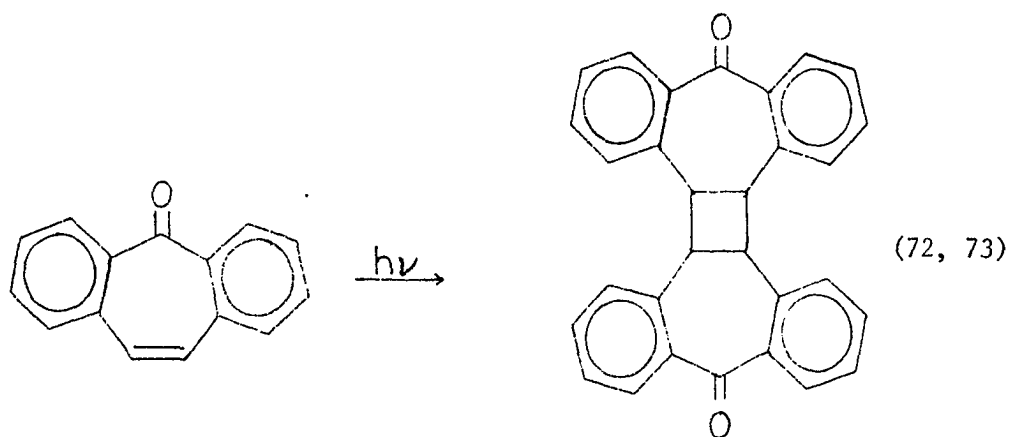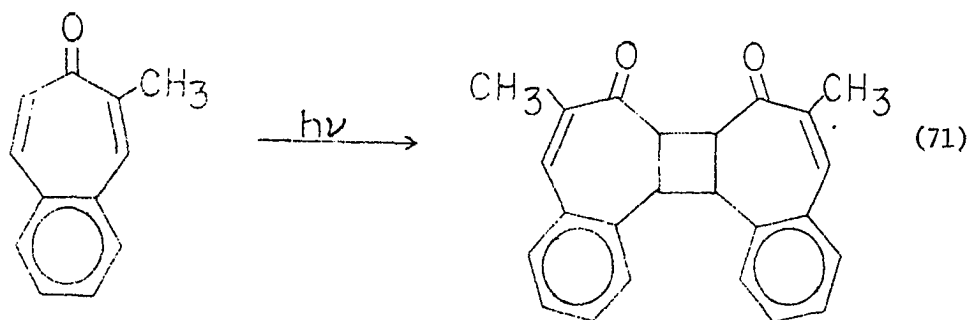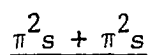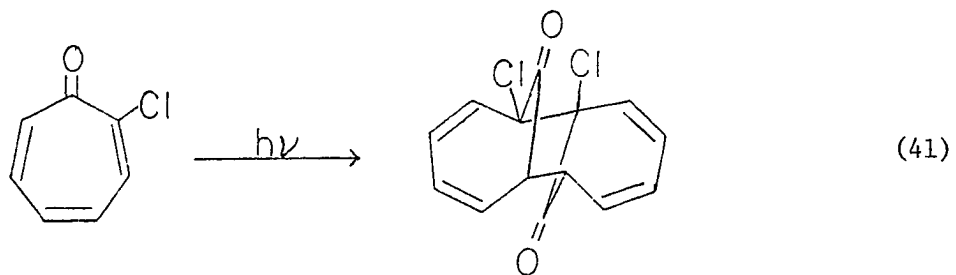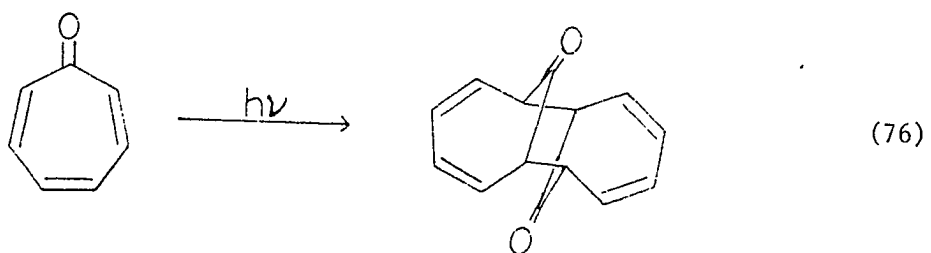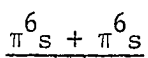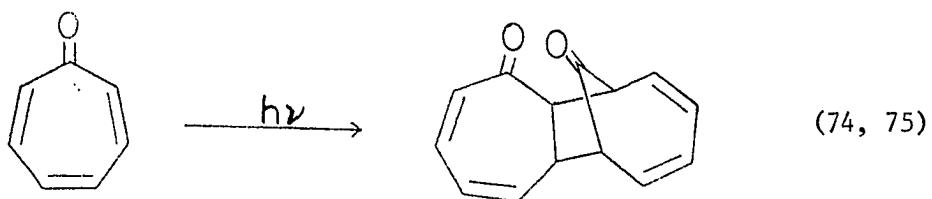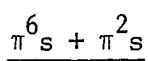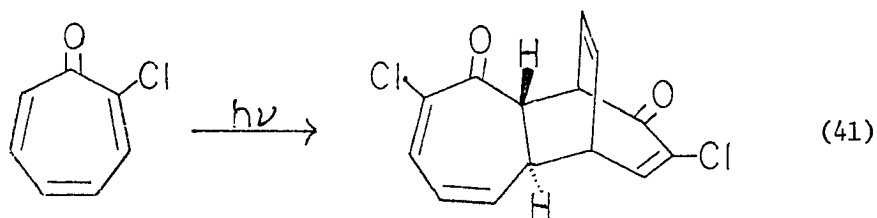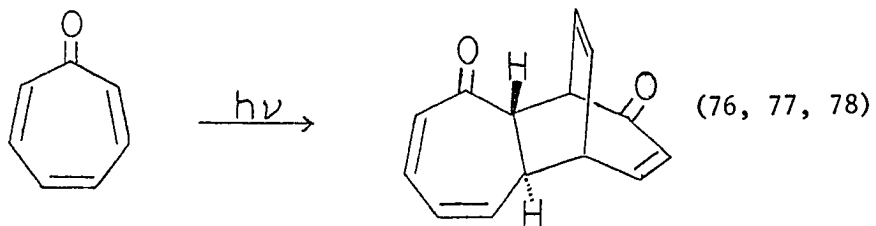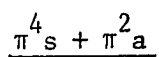
A number of photodimerizations of troponoid systems have been also reported to occur via two-step mechanisms. These are listed below.

R=Ph, Cl

(79)

(74, 75, 77)

(80)
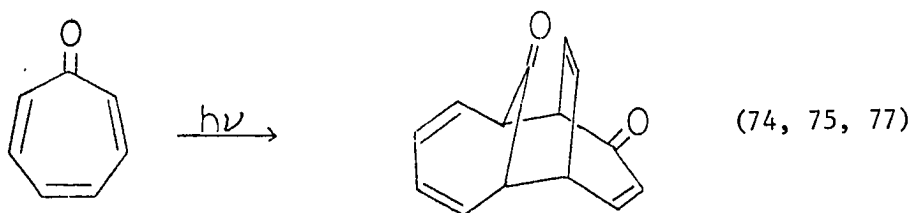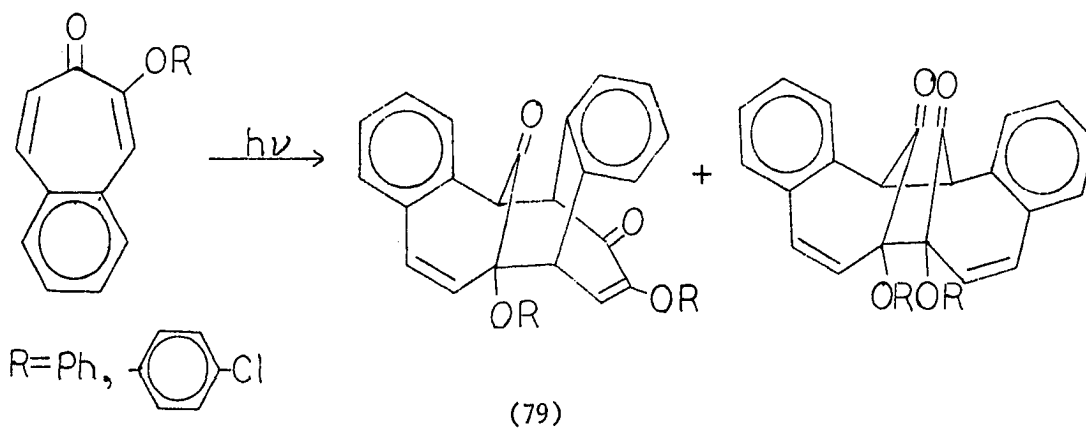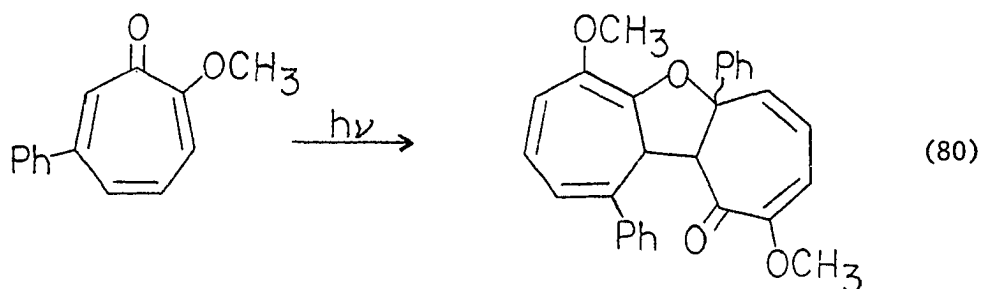
For a more complete discussion of the theory, mechanisms and for additional examples, the reader is referred to a number of reviews which have been published on the photochemistry of troponoid systems (81).

It is interesting to note that there has been no report of a· violation of the Woodward-Hoffmann rules in either the thermal or photochemical cycloaddition reactions of troponoid compounds.

46

SUMMARY

It has been reported that tropone does not react with dimethyl-
acetylene dicarboxylate (DMADC) in the usual manner to give the expected
adduct (Scheme II) but reacts to form a rearranged compound which has

Scheme II
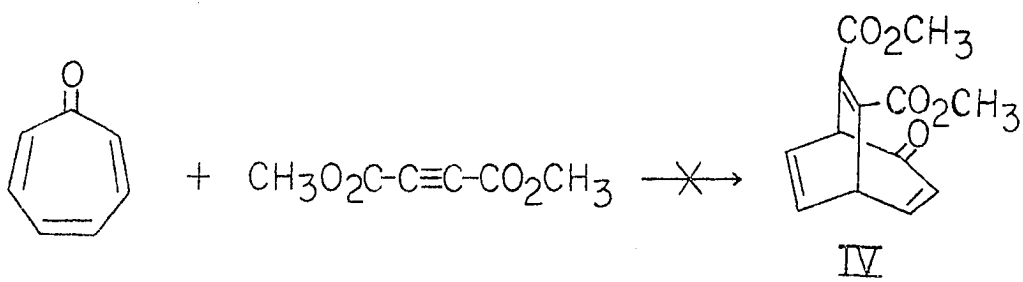
lost the elements of CO. This reaction has been restudied with the
following results: at 150°C, a mixture of starting materials, the adduct
shown above (IV), the isomeric material, 1,5-dicarbomethoxy-bicyclo-
[4.3.0]-nona-3,6,8-trien-2-one (V), and 1,2,3,4-tetracarbomethoxy
benzene were isolated. This is contrasted to reaction at 100°C from which
only the adduct (IV) was isolated in 47% yield. Heating purified IV
with DMADC at 150°C resulted in the production of V and tetracarbomethoxy
benzene. Heating IV above 150°C either in the gas phase or as a solution
resulted in a complete disappearance of IV and > 80% yield of V. A
mechanism of these transformations, supported by both experimentation
and literature precedence, is shown on the following page (with R = -CO$_2$
CH$_3$):
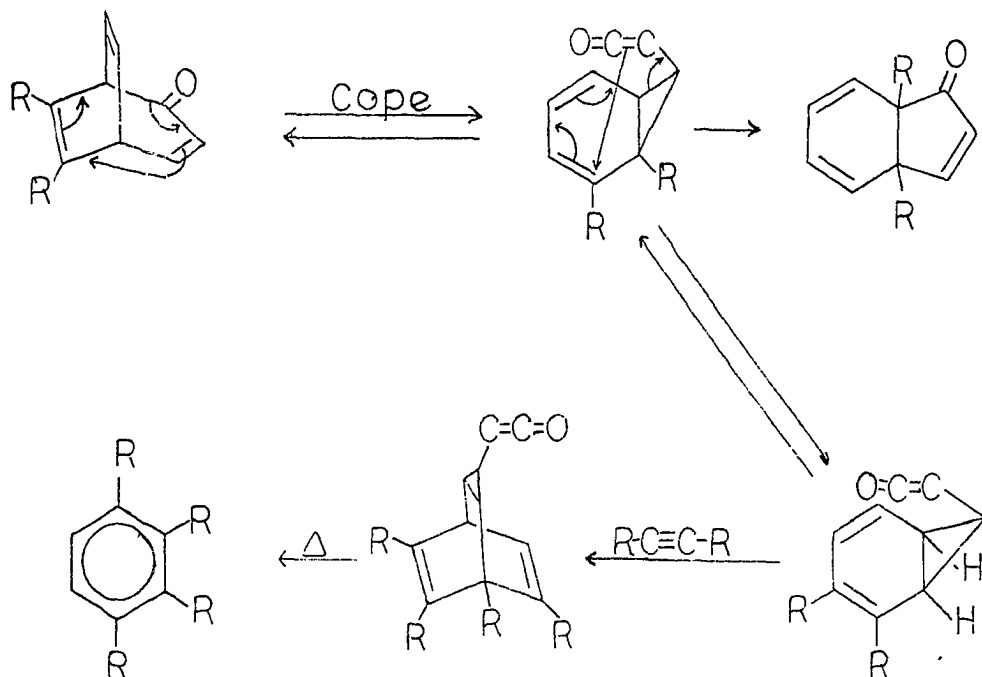
In the hopes of preparing a stabilized bicyclo-tropylium ion, IV was
solvolyzed in various acidic media of differing nucleophilicity. As pre-
dicted by Goldstein, however, no bicyclo-[3.2.2] ion was formed and only
the Michael addition product was isolated in each case (scheme III,
R = -CO$_2$CH$_3$ and S = OCH$_3$, O$_2$CCH$_3$, OCH$_2$CF$_3$, and O$_2$C-CF$_3$).

Scheme III
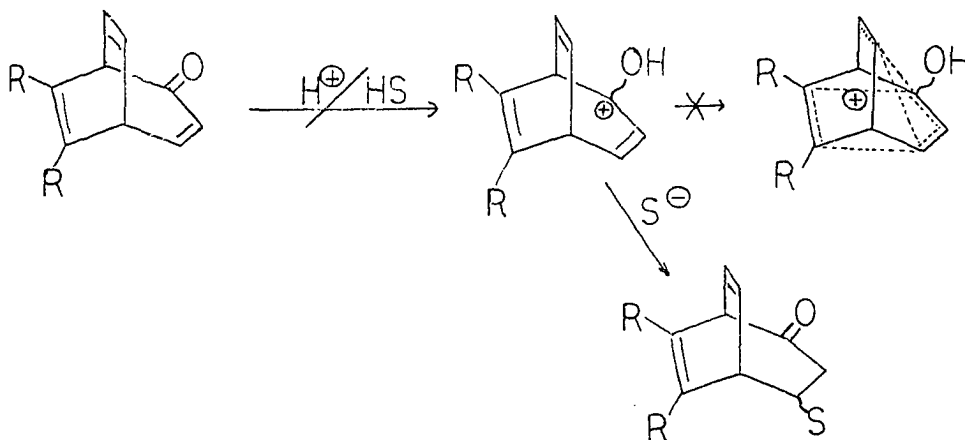
EXPERIMENTAL

General

nmr spectra were recorded on Varian A60 (modified), HA-100, and Perkin-Elmer R-20B spectrometers. Infrared spectra were recorded on a Perkin-Elmer 21 and Beckman IR12 spectrometers. Ultra violet spectra were recorded on a Cary 14 and mass spectra were obtained using an Atlas MAT model CH4 single focusing mass spectrometer.

All recorded melting points are corrected and were taken on a Kofler Hot Stage-Bausch and Lomb melting point apparatus.

Analytical analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Chemalytics, Inc., Tempe, Arizona.

Methods

Reaction of tropone with DMADC at 145°

A solution of 1.0 g tropone (94 mmoles), 9.0 g DMADC (8 molar excess) and 10 ml. xylene was heated at reflux at 145° under a N_2 stream for 24 hours. The solvent was removed on the rotovac and the dark residue passed through an alumina chromatographic column. Three bands were collected, the first with 50:50 $CCl_4/CHCl_3$ and the last two with ether and methanol. Upon standing, 450 mg. (16%) of a solid, mp 126-131°, recrystallized once from ether-hexane, mp 131-132°, crystallized from the solution. The remainder of first band would yield no more crystalline solid.

Preparation of 1,2,4,5-tetracarbomethoxybenzene

A solution of 10.0 g of 1,2,4,5-benzene tetracarboxylic acid was

heated at reflux in 200 ml. methanol and 3 ml. conc. sulfuric acid for

2 hours. Cooling the solution to $-5°C$ yielded 10.4 g (85%) of a white

solid, mp 139-144°, recrystallized from methanol, mp 144-145°.

The nmr spectrum was identical to that reported for the product

of the reaction between tropone and DMADC, the infrared spectrum only

slightly different, but a mixed melting point showed a depression,

mp 75-102°.

Preparation of 1,2,3,4-tetracarbomethoxybenzene

1,2,3,4-benzene tetracarboxylic acid was prepared by the method of

Zacharewicz and Uzarewicz (37) by oxidation of 1,2,3,4-tetramethylbenzene

with potassium permanganate. The acid could not be esterified with

methanol/acid so it was treated with diazomethane as an ether suspension.

The ester, in solution, was separated from the insoluable material by

filtration. Upon cooling, crystallization afforded the desired product,

mp 131-132°. The spectral properties were identical with those of the

white solid isolated in the attempted cycloaddition reaction and mixed

melting point showed no depression, mp 130-132°.

Large scale reaction of tropone and DMADC at 100°C

The reaction was carried out as before using 13.4 g DMADC and 10.0 g

of tropone in 75 ml. nitromethane at 100° for 7 days. The solvent was

removed at reduced pressure, the residue taken up in ether and washed repeatedly with water until TLC indicated that no tropone remained. The ether layer was dried, concentrated, and chromatographed on a silica gel column. One wide band weighing 13.4 g was collected with 50% $CCl_4/CHCl_3$. Calculations based upon nmr integrals indicated that 9.6 g (43%) of this was IV (a light yellow oil) and the remaining 3.8 g (28%) was DMADC. This remaining starting material was removed by low temperature, high vacuum vapor distillation.

Crystallization from an ether solution with recrystallization from ether-hexane gave a white solid, mp 51-52°. Elemental analysis: Calculated: C: 62.90; H: 4.84; found: C: 62.89; H: 4.91.

Reaction of DMADC with IV

A solution of 2.0 g IV and 2.0 g DMADC (1.3 excess) in 25 ml. xylene was heated at 145-150° under a N_2 flow for 24 hours. The black residue was chromatographed on silica gel using varying proportions of $CCl_4/CHCl_3$ as eluents. From the first band crystallized 0.45 g (15%) of a white solid, mp 130-132°C, recrystallized from ether-hexane, mp 132-133°C. Spectral properties were identical to the known 1,2,3,4-tetracarbomethoxybenzene described above. An nmr spectrum of the material stripped from the column with an ether wash showed no evidence for any other isomeric products.

Pyrolysis of IV at 375° and 0.3 mm Hg
_____

A 0.5 g (2.15 mmole) sample of IV was placed in a pyrolysis apparatus
shown schematically below:
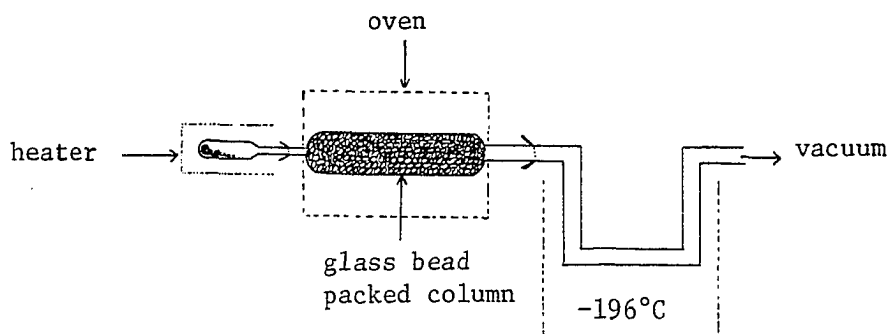
The sample was sublimed over an 18 hour period. The products were col-
lected in the trap in two different spots: 0.1 g of a yellow oil in the
outlet of the pyrolysis column and inlet of the trap and 0.4 g of white
needles, mp 74-77°, further into the trap. Most of the separation of
these components was physical with the remainder carried out by recrystal-
lizing from ether-hexane. Recrystallization afforded a solid, mp 77-78°C
(elemental analysis: Calc'd: C: 62.90, H: 4.84; found: C: 62.82,
H: 4.84). The yellow oil exhibits the following spectral properties:
$\delta_{TMS}^{CCl_4}$: 2.66, 3.15, 3.75, 3.87, and 7.5-8.00 ppm; $\upsilon_{max}^{CHCl_3}$: 2925, 1734,
1720, 1633, and 1600 cm^{-1}.

Pyrolysis of IV in xylene at 150°
_____

A sample of 0.5 g IV was heated in 4 ml. xylene at 145-150° for 24
hours to produce a yellow solution. Upon cooling, 0.4 g (80%) white

needles was collected, mp 76-77.   nmr   data on this and the mother

liquors were identical to that of the white solid and that of the yellow

oil, respectively, formed during the vapor phase thermolysis.

Reaction of $\underline{V}$ with maleic anhydride

A benzene solution of 44 mg. of $\underline{V}$ and 18 mg. maleic anhydride was

heated at reflux for 23 hours. The benzene was stripped from the reac-

tion mixture on the rotovac and to the resultant mixture of solid and

oil was added 1/2 ml. $DCCl_3$. The solid was not soluable so the sample

was filtered. The solution nmr was almost identical with that of the

starting material. A melting point taken on the solid filtered from the

solution was 280-281°C. The mass spectrum showed $M^{+} = 346$.

Solvolysis of $\underline{IV}$ in methanol

A solution of 0.50 g $\underline{IV}$ in 10 ml. anhydrous CH_3OH containing 10 drops

conc. H_2SO_4 was stirred 40 hours. The solvent was removed on the rotovac

and residue poured into 100 ml. water. Extracting the aqueous solution

three times with 50 ml. portions of $CHCl_3$ followed by drying and concen-

tration on the rotovac yielded .54 g (95%) of a pale yellow oil:

$\delta_{TMS}^{CCl_4}$: 2.77 (d, J=7 cps, 2H), 3.33 (d, J=2cps, 3H), 3.47-4.24 (m, 3H)

3.79 (s, 6H), and 6.03-6.61 (m, 2H); $\upsilon_{max}^{CHCl_3}$: 3040, 1745, 1670, and 1635

cm^{-1}; mass spec: M^{+}=m/e 280; and elemental analysis satisfactory for

the proposed composition.

Solvolysis of IV in acetic acid

A solution of 0.53 g IV in 10 ml. acetic acid containing 15 drops conc. H_2SO_4 was stirred 42 hours. The reaction mixture was poured into 150 ml. H_2O and concentrated Na_2CO_3 added until bubbling ceased. This aqueous solution was extracted three times with 50 ml. portions of $CHCl_3$. The combined extracts were washed with 2 25 ml. portions of saturated Na_2CO_3, once with water, dried over $MgSO_4$ and concentrated on the rotovac to yield 0.50 (96%) g of a pale yellow oil: $\delta^{CCl_4}_{TMS}$ 1.98 (d, J=1.5 cps, 3H), 2.77 (d, J=7 cps, 2H), 3.62-4.26 (m, 3H), 3.78 (s, 6H), and 5.97-6.67 (m, 2H); and mass spec: $M^{+} \cdot = m/e$ 308.

Solvolysis of IV in 3,3,3-triflouroethanol

A solution of 0.50 g IV in 5 ml. CF_3CH_2OH containing 6 drops of conc. H_2SO_4 was stirred for 46 hours. The majority of the solvent was removed on the rotovac and the residue poured into 100 ml. water. Extracting three times with 50 ml. portions of $CHCl_3$, drying over $MgSO_4$ and concentrating yielded .58 g (100%) of a pale yellow oil: $\delta^{CCl_4}_{TMS}$: 2.78 (d, J=7 cps, 2H), 3.44-4.28 (m, 5H), 3.77 (s, 6H), and 5.95-6.58 (m, 2H): $\nu^{CHCl_3}_{max}$ 3040, 1750, 1670, and 1630 cm^{-1}; and mass spec: $M^{+} \cdot =$ m/e 348.

Solvolysis of IV in trifluoracetic acid

To a nmr tube containing 50 mg. IV was added 1/2 ml. of pure CF_3CO_2H and the reaction followed on the nmr. The reaction was deemed

complete after standing for two weeks: $\delta_{TMS}^{CF_3CO_2H}$: 3.20 (d (J=7 cps) of

d (J=2 cps), 2H, 3.83-4.65 (m, 3H), 4.03 (s, 6H), 6.38-6.88 (m, 2H).

The sample was worked up as in the solvolysis of IV in acetic acid for

a mass spec sample: $M^{+\cdot}$=m/e 362.

PART II. THE REACTIONS OF NITROSOBENZENE WITH CYCLIC POLYOLEFINS

INTRODUCTION

The reactions of nitrosobenzenes with simple olefins have been
extensively studied. With mono-olefins, two reaction paths are followed
depending upon the type of olefin: alkenes containing allylic protons on
sp^3 centers generally undergo an "ene" reaction with the accompanying
production of azoxybenzenes (82, 83). For example, 2,3-dimethyl-2-butene
is reported to undergo a reaction with nitrosobenzene according to the
following mechanism (83). The esr spectrum of the radical intermediate
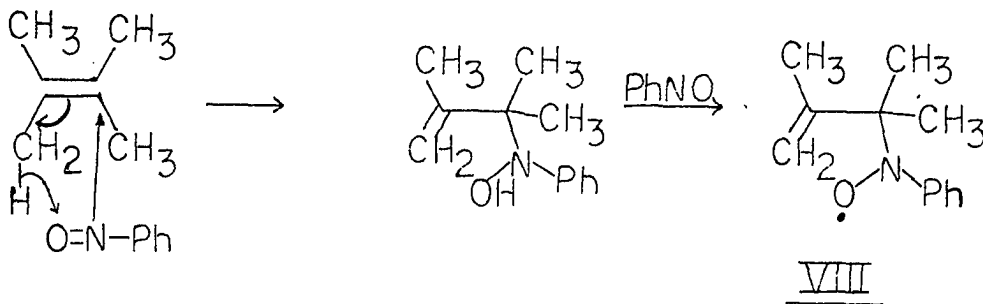
(VIII) was recorded and used as primary evidence for this mechanism.
Coupling of the phenyl hydroxylamine resulting from the oxidation of the
intermediate hydroxylamine adduct with unreacted nitrosobenzene followed
by loss of water easily accounts for the high yields of azoxybenzenes
isolated from these reactions.

Certain olefins containing no allylic protons undergo 2+2 cyclo-
additions with nitrosobenzenes to form oxazetidines (84). Thus,
nitrosobenzene and 1,1-diphenyl-ethylene react to form 2,3,3-triphenyl-
1,2-oxazetidine.

$$CH_2 {=} CPh_2 \quad + \quad Ph{-}NO \longrightarrow$$
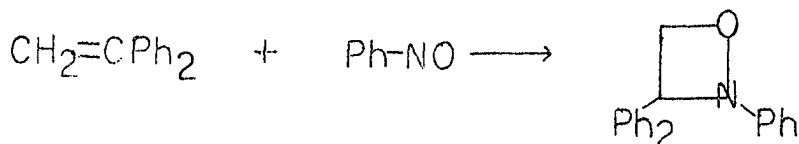
The most studied reaction of nitrosobenzene with olefins, however, is its reaction with dienes. Studies made using suitably substituted arylnitroso compounds with 1,3-cyclohexadiene or 2,3-dimethyl-1,3-butadiene yielded a Hammett rho constant of +2.51-2.57 (85). The energy and entropies of activation for these types of reactions are 11.4-11.6 kcal/mole and -31--36 e.u., respectively. Therefore, since these values fall within the ranges previously determined for known Diels-Alder additions, and since the kinetics of nitrosobenzene reactions with dienes is second order, these cycloadditions have been classified as further examples of the Diels-Alder reaction (85).

The direction of addition is very susceptible to the electronic properties of the substituents on the diene (85). Thus it has been found that an electron-withdrawing substituent on the diene will be found α to the oxygen in the resulting cycloadduct. Bulky substituents also exhibit the same type of directing effect. Thus the product of nitroso-benzene and 1-phenyl-1,3-butadiene is exclusively IX (85). Groups with
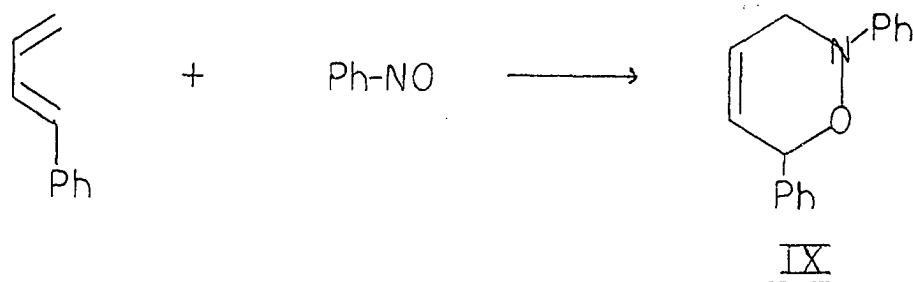
weak inductive characteristics and small bulk cannot exert powerful

orientation influences and mixtures are usually obtained. Thus,
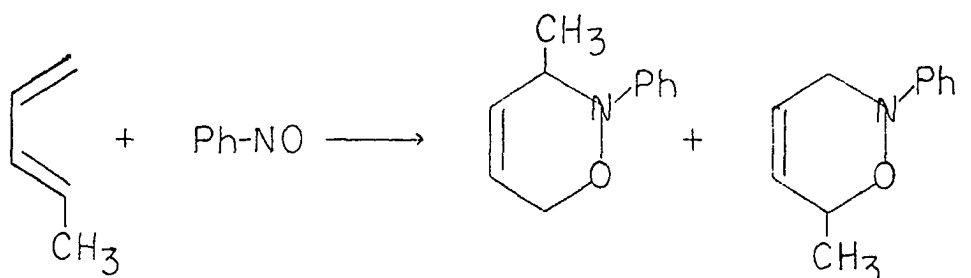
In contrast to the amount of work carried out in the areas described

above, the reaction of nitrosobenzene with trienes has only received

scant attention and with much less conclusive results. The most logical

triene held in an all cis conformation is cycloheptatriene. The usual

cycloaddition products of the reactions of dienophiles and cycloheptatriene

are the result of trapping the norcaradiene valence tautomer (31). Thus
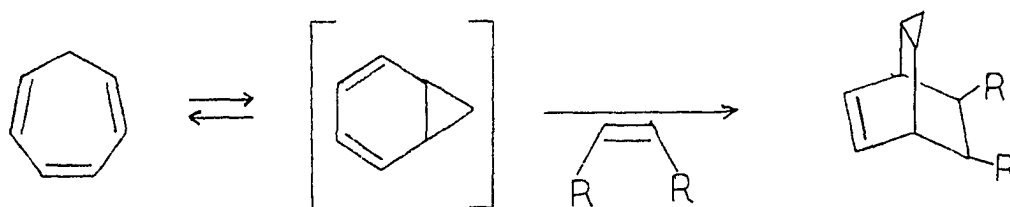
the published results of the reaction of nitrosobenzene with cyclo-

heptatriene, available at the outset of our investigations, seemed very

strange. Kresze and Schulz first reported the results of this reaction

in 1961 (86). From a consideration of spectral data, they concluded that

a cyclopropyl-containing molecule such as that shown above was not

recovered in their reaction. Instead, they reported that the structure of

the resultant cycloadduct was X or XI. These results were presumably
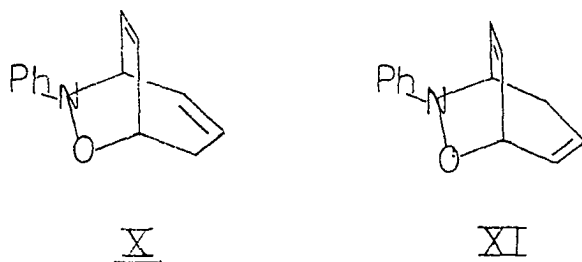
substantiated two years later by Griffen and co-workers (87) as part of a

study of the production of small ring bicyclic compounds from nitroso-

benzene cycloadducts. Thus, they reported the following simple prepara-

tion of bicyclo-[3.2.0]-heptane.
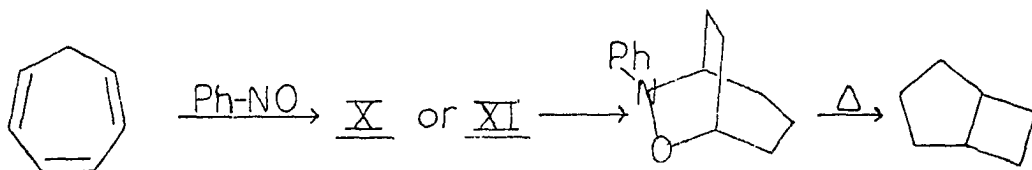
Three years later, while failing to acknowledge the aforementioned

previously reported work in this area, Hutton and Waters reported the

results of their study of this reaction (88). The spectral properties

60

reported by these workers were identical to those reported by Kresze and

Schulz. Their interpretation of these results differed, however, and

led to XII as their choice for the structural assignment for the cyclo-

adduct. Later, well after our research efforts had substantiated the

XII

correctness of this structural assignment (by x-ray crystallography),

Burns and Waters reported chemical proof for this structural assignment

(89). They found that the spectral and physical properties of an adduct

formed by the reaction of p-chloro-nitrosobenzene and cycloheptadiene

followed by hydrogenation were distinctly different from those of a

sample of the product formed by the reaction of p-chloro-nitrosobenzene

and cycloheptatriene followed by hydrogenation.

Because of the obvious literature conflict caused by the appearance

of Hutton and Water's paper, the fact that none of the structures, X, XI, or

XII correspond to the usual cycloaddition products of cycloheptatriene,

and a general lack of knowledge concerning the general reactivity and

mechanism of nitrosobenzene-triene reactions, a study of the reactions

between nitrosobenzene and selected cyclic trienes was undertaken.

RESULTS AND DISCUSSION

Cycloheptatrienes

A 1:1 molar ratio of nitrosobenzene and cycloheptatriene was stirred in anhydrous ether over a three day period. During this time, the reaction mixture gradually changed color from the green of the monomeric nitrosobenzene to a very dark red. The solvent was removed and the dark residual oil chromatographed on a column of silica gel to separate the components. The first band isolated contained a small amount of unreacted starting materials and azoxybenzene, a side product also reported by Hutton and Waters (88). The next band was concentrated to give a 35% yield of a reddish oil which was treated with activated charcoal to give white plates, mp 106-107°C (lit. (86, 88) 106°C). The nmr spectrum (Fig. 2) as well as the other physical and spectral properties were identical to those previously reported. As can be seen, the resonances of the four olefinic protons of the cycloadduct appear at 5.95δ. Hutton and Waters felt that this was best explained by the more symmetrical product XII. Since there was no proof for this assignment when our research was started, we hoped that reacting nitrosobenzene with various substituted cycloheptatrienes would lead to cycloadducts that would be more useful in making positive structural assignments. It was felt that if the reaction product was analagous to X or XI, a substituent in the 7-position should alter the required fortuitous equivalence of the different olefinic protons whereas if it was like XII, little difference would be expected in the appearance of the olefinic proton resonances. It

was also felt that reacting nitrosobenzene with substituted cyclohepta-
trienes might lead to mixtures of isomeric products. Such a finding
could supply additional evidence toward the mechanistic interpretation
of these reactions. One would expect mixtures of products if the mech-
anism was a nonconcerted stepwise addition with tropylium ions or
cycloheptatrienyl radicals as possible intermediates. These studies were
carried out using 7-methyl and 7-phenyl-cycloheptatriene as well as
cycloheptatriene, itself.

As previously noted, identical physical and spectral properties were
exhibited by the reaction product of nitrosobenzene and cycloheptatriene
as reported in the literature ($\lambda_{max}^{C_6H_{12}}$: 2.44 (ε=7130), 268 (ε=3290,
shoulder), and 280 mμ (ε=1870); $\delta_{TMS}^{CCl_4}$: 2.14-2.40 (m, 2H), 4.00-4.30
(m, 1H), 4.53-4.89 (m, 1H), 5.93 (broad s, 4H), and 6.68-7.46
(m, 5H); and mass spec.: M^{+}=199). The reaction product of 7-phenyl-
cycloheptatriene and nitrosobenzene recovered in 26% yield had a mp of
150-151°C (white needles from Skelly B) and exhibited the following
spectral properties: $\lambda_{max}^{C_6H_{12}}$: 244 (ε=22,990), 270 (shoulder, ε=8760),
and 285 mμ (shoulder, ε=5210) and $\delta_{TMS}^{CDCl_3}$: 3.97 (m, 1H), 4.63 (m, 1H),
5.25 (m, 1H), 5.80-6.34 (m, 4H), and 7.18 (broad s, 10H). The product
of 7-methyl-cycloheptatriene and nitrosobenzene was recovered in 25%
yield, had a mp of 93-94°C (white needles from Skelly B) and exhibited
the following spectral properties: $\lambda_{max}^{C_6H_{12}}$: 244 (ε=10,430), 268
(shoulder, (ε=4710) and 285 mμ (shoulder, ε=2079); and $\delta_{TMS}^{CCl_4}$: 0.98

(d, J=8 cps, 3H), 2.59 (m, 1H), 3.93 (m, 1H), 4.58 (m, 1H), 5.91 (broad

s, 4H), and 6.67-7.33 (m, 5H). It should be pointed out that these were

the only adducts found in these reactions. Spectral evidence indicated

that there was no build up and/or disappearance of any other adduct-like

compounds and that the products isolated were those being formed through-

out the course of the reaction.

It was noted that in the nmr spectra of both of the substituted

adducts the olefinic proton absorptions were broadened, moreso in the

case of the phenyl substituted product. This could be taken as a priori

evidence for the bicyclo-[3.2.2] skeleton, but such a conclusion was

rendered doubtful since the uv spectra of the adducts indicated that a

conjugated diene moiety was likely to be present. This discrepancy was

resolved by the use of nmr decoupling experiments carried out on a

Varian HA100 spectrometer. If one examines the two structures, it is

seen that in the compound possessing the bicyclo-[3.2.2] skeleton, the
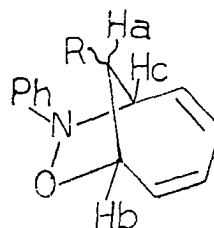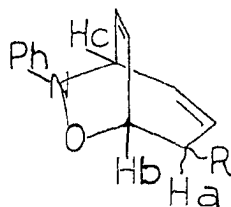
methyne proton Ha (R=CH$_3$ or Ph) should be coupled with only Hb and very

little if at all with Hc whereas in the bicyclo-[4.2.1] structure, Ha

should be equally coupled with Hb and Hc. Each of the three adducts

was decoupled and gave the same results. The numerical results obtained

Fig. 2. Nuclear magnetic resonance spectra

   a. 8-phenyl-7,8-oxaza-bicyclo-[4.2.1]-nona-
       2,4-diene

   b. 8-phenyl-9-methyl-7,8-oxaza-bicyclo-[4.2.1]-
       nona-2,4-diene

   c. 8,9-diphenyl-7,8-oxaza-bicyclo-[4.2.1]-
       nona-2,4-diene
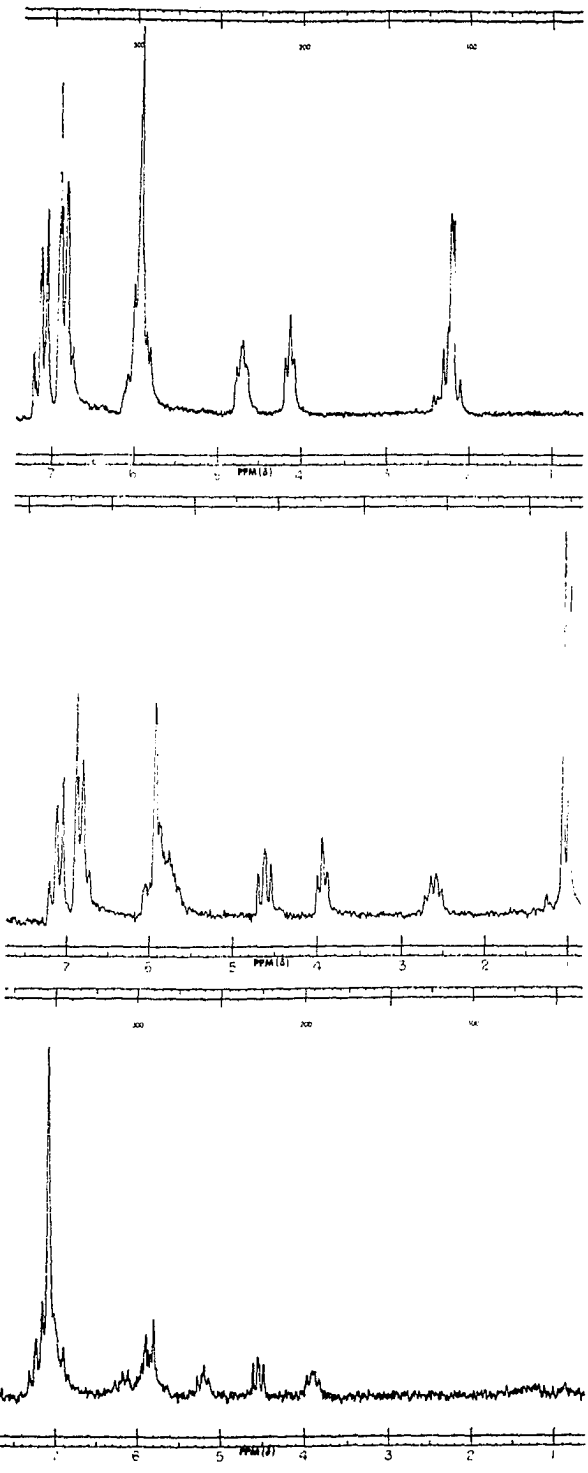
from the methyl-substituted compound will be cited to exemplify the

general overall results. Irradiation of the methyne multiplet at 2.59 δ

caused a collapse of the overlapping doublet of doublets at 3.93 and

4.58 δ to doublets as well as a collapse of the doublet at 0.98 δ to a

singlet. Irradiation of either of the bridgehead protons at 3.93 or

4.58 δ caused a collapse in the pattern of the methyne multiplet at

2.59 δ. These results are only consistent with the bicyclo-[4.2.1]

structure, of course. This structural assignment was confirmed by an

x-ray analysis of the reaction product of p-bromo-nitrosobenzene and

7-methyl-cycloheptatriene (we grateful acknowledge Dr. J. Clardy and

Che Man Lee of Iowa State University for performing this analysis). The

structure of this cycloadduct was found to be:
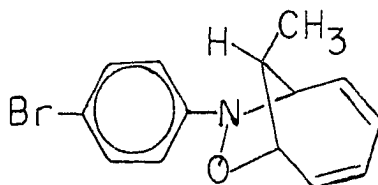
Since the spectral properties (ir, nmr, and uv) were practically identi-

cal with the non-brominated adduct, it was felt that the structural

correlation could be safely made to the other adducts. Beside corroborat-

ing the basic skeletal structural assignment of the molecule, the x-ray

analysis proved that the stereochemistry of the adduct was anti. This

is easily rationalized since one would expect the addition to occur from

the least hindered side of the cycloheptatriene. (More will be said

later regarding mechanism and stereochemistry of addition later in this

discussion section.) Thus the structure of the three addition products

are XIII, XIV and XV:

XIII   XIV   XV
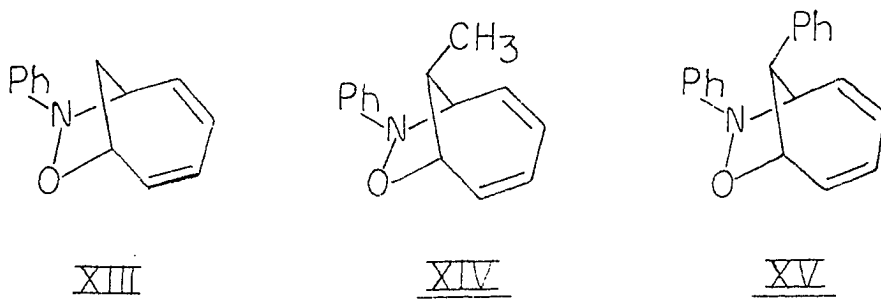
The results of Griffen, et al. (87) now become questionable in the

light of the positive proof for the bicyclo-[4.2.1] skeleton of the

adducts. If the pyrolysis carried out in his structure proof was straight

forward, norcarane should have been the isolated product instead of the

reported bicyclo-[3.2.0]-heptane. Their reaction sequence was therefore
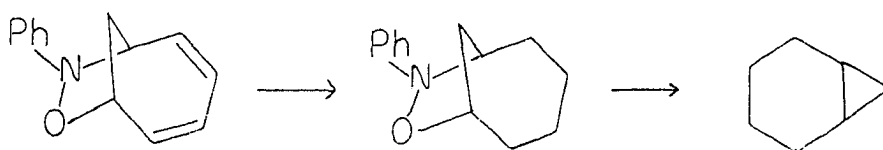
repeated. No norcarane was detected in the mixture of products isolated

from a vapor-phase pyrolysis (520°C, < 0.001 mm Hg) of the hydrogenated

form of XIII. A comparison of nmr spectra and vpc retention times of

authentic bicyclo-[3.2.0]-heptane with those of the reaction mixture

indicates that the major reaction product might be bicyclo-[3.2.0]-heptane

as reported. One is therefore forced to conclude that this pyrolysis is

not a simple diradical coupling process but involves a hydrogen rearrange-

ment to yield the observed product. It is not surprising, therefore, that

the incorrect structural assignment for the adduct was made from this data.

It should be pointed out that our work represents a more substantial

structure proof for the 1,6 addition products than that of Burns and Waters

(89), even excluding our x-ray analysis. Their chemical proof rested upon

the reaction of 1,3-cycloheptadiene with a nitrosobenzene. It has been re-

ported by others that nitrosobenzene does not react with 1,3-cyclohepta-

diene (85).

On the other hand, the credibility of Hamer's reports (85) can be

questioned. He has reported that an uncharacterized solid adduct can be

isolated from the reaction of nitrosobenzene and cyclooctatetraene and that

nitrosobenzene reacts with cyclooctadiene only very sparingly. These re-

actions were repeated under a variety of conditions in our laboratories and

extremely contrary results were obtained. No trace of an adduct was found

in reactions of nitrosobenzene with cyclooctatetraene carried out for long

periods of time and/or at elevated temperatures. The reaction also failed

using para-bromo-nitrosobenzene, a more reactive dienophile than nitroso-

benzene. On the other hand, a facile reaction of nitrosobenzene and

cyclooctadiene was noted. Whereas a 5% isolated yield was reported after

a reaction time of one month, a 45% yield of adduct was isolated in our

laboratory after stirring for just a few days at room temperature. Such

large inconsistencies as these have caused confusion and general incredi-

bility in the field of nitrosobenzene cycloadditions.

69

The mechanism of adduct formation is of considerable interest since, outwardly, the adduct appears to be a 6+2 and would therefore represent a possible violation of the Woodward-Hoffmann rules. If one holds these rules to be inviolable, then the formation of the 6+2 adduct must be stepwise or involve rearrangement of a primary reaction product. Both mechanisms have been postulated to explain the formation of previously isolated 6+2 adducts. Murphy and McCarthy (90) claim a two-step mechanism explains the 1,6 addition of nitrosobenzene and E-ethyl-azodicarboxylate to 1-carboethoxy-azepine. A rearrangment of a primary

$Q = CO_2CH_3$; $R = Ph$, $X = O$; $R = Q$, $X = NQ$
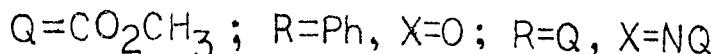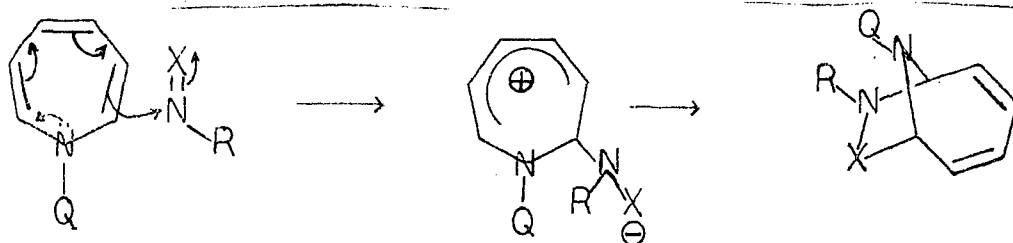
reaction product was postulated (91) to explain the 6+2 addition product isolated from the reaction of chloro-sulfonyl-isocynate with cyclo-heptatriene. The expected route of a cyclo-addition of a cycloheptatriene

$R = SO_2Cl$
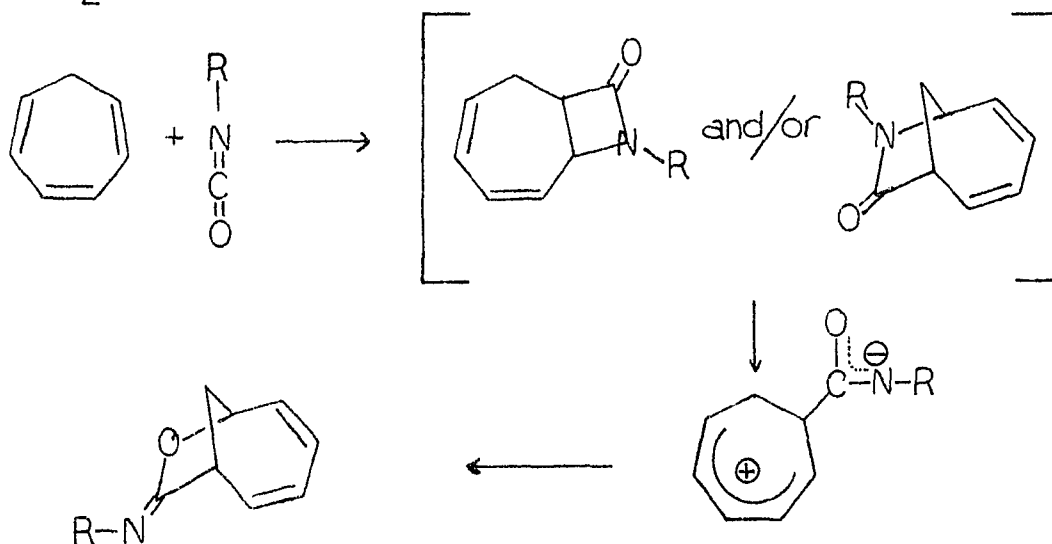
with nitrosobenzene would be via the norcaradiene valence tautomer to

form a bicyclo-[3.2.2.0^{5,7}]-nonene (31).   If such a primary product is
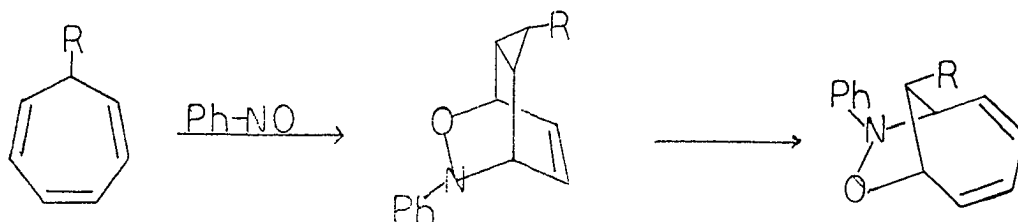
formed in these reactions, it must quickly rearrange to the observed

1,6 addition product since no trace of a cyclopropyl-containing product

has ever been noted.   Another possibility along these lines, although

there is no literature precedence for it, is the 1,4 addition of nitroso-

benzene to cycloheptatriene in Diels-Alder fashion to form a product

which then rearranges to the observed product.
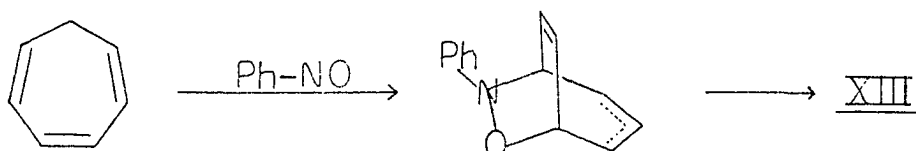
In consideration of a stepwise addition mechanism, two alternatives

seem possible: an electrophilic dipolar addition similar to that pro-

posed by Murphy and McCarthy (90) or a diradical coupling process.   The

latter process would seem to be much more likely since it is known that

nitrosobenzene exists in the diradical (triplet) form in solution (92).
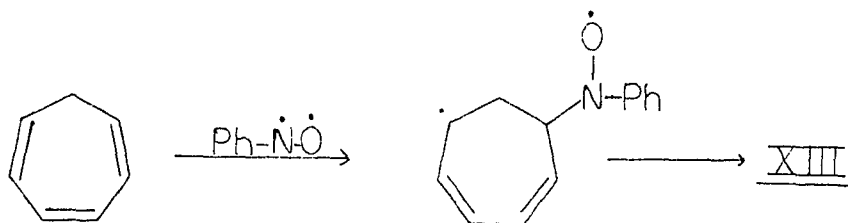
One additional possibility exists for the formation of the 1,6 addition product, however. These additions could be the first recorded examples of thermally-allowed concerted $\pi^6s + \pi^2a$ or $\pi^6a + \pi^2s$ cycloadditions. Since the stereochemical restrictions usually associated with cis-trans cycloadditions are relaxed in the freely-rotating diradical nitroso compound, the possibilities are much better than in the usual case.

Cyclooctatrienes

The isolation of an intermediate or of two different products derived from a common intermediate would certainly eliminate a number of mechanistic possibilities. In the hope of achieving this, a study of the reaction of nitrosobenzene with 1,3,5-cyclooctatriene was undertaken. Cyclooctatriene was chosen for two reasons: it was hoped that the larger size would slow the reaction sufficiently so that multiple products would be formed via a possible stepwise addition pathway. More important, however, is the fact that 1,3,5-cyclooctatriene can be isolated in pure form and kept from isomerizing to its bicyclic tautomer. If a comparable 1,6 addition product could be isolated from 1,3,5-cyclooctatriene, it would show that the adduct isolated in the cycloheptatriene additions
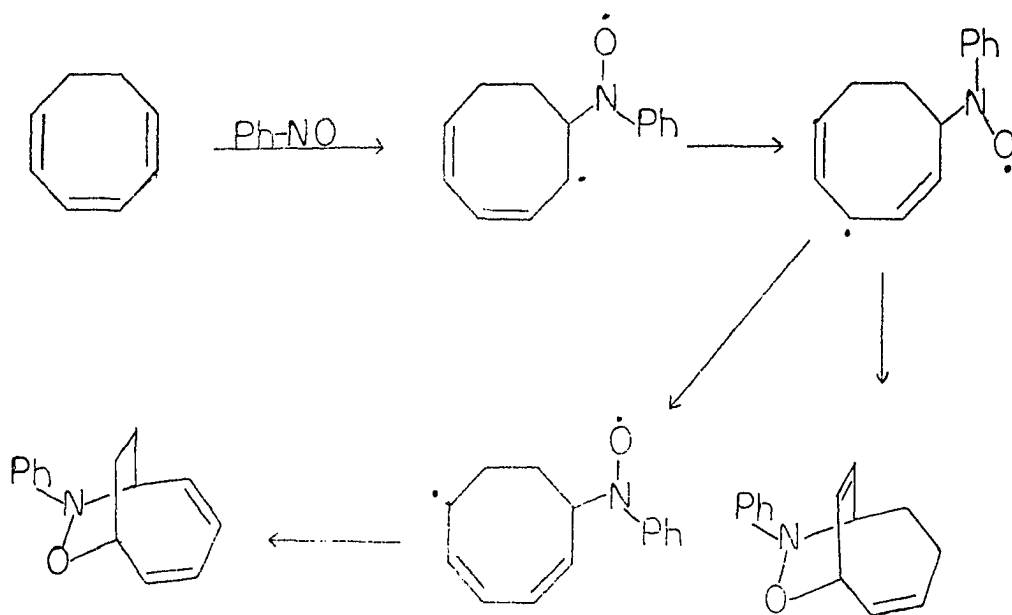
was not being formed from the bicyclic valence tautomer but from the

triene tautomer. It was also hoped that additional information could be

obtained from this molecule to help differentiate between the remaining

mechanistic possibilities.

The residue of the reaction between nitrosobenzene and a 75:25 mix-

ture of 1,3,5:1,3,6-cyclooctatriene, the usual thick dark product, was

chromatographed carefully on a column of silica gel to yield four bands.

The first two proved to be a mixture of azoxybenzene and an adduct in

varying proportions. Calculations based upon nmr integrals showed that

a 48% yield of the adduct was present in the two fractions. The

second band, a pale yellow oil, yielded white crystals, mp 32-33°C, upon

cooling in a solution of 80:20 EtOH:H_2O which exhibited the following

spectral properties: $\delta_{TMS}^{CCl_4}$: 1.40-2.70 (m, 4H), 4.14 (m, 1H), 4.56

(m, 1H), 5.19-6.12 (m, 4H), and 6.50-7.64 (m, 5H); ν_{max}^{neat} : 3040, 2970,

2910, 1608 and 1507 cm^{-1}; $\lambda_{max}^{C_6H_{12}}$:   252 mμ (ε=13,410) and 287 mμ

(ε=2215); and mass spec. showed M^{+}·=213. A comparison of this data with

that from the adduct of nitrosobenzene and cycloheptatriene indicates

that the best structural assignment is that of a comparable conjugated

diene adduct, XVI .
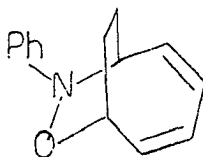
XVI

The third band was found to be a mixture of two materials, one of

which was also found in the fourth band. Rechromatographing these frac-

tions on a 50:50 silica gel:alumina column resulted in the isolation

of a solid material, mp 93-94°C, and an oil. The spectral properties

indicate that the crystalline material is the $\pi^4 s + \pi^2 s$ cycloaddition

product of nitrosobenzene and bicyclo-[4.2.0]-octa-2,4-diene, the

valence tautomer of 1,3,5-cyclooctatriene which had not been completely

removed from the starting material. The remaining oil was suspected to

be the nitrosobenzene cycloadduct of the 1,3,6-cyclooctatriene impurity

contained in the starting material. This was confirmed by synthesizing

pure 1,3,6-cyclooctatriene and reacting it with nitrosobenzene.

Chromatographing the dark reaction mixture produced a 49% yield of a

Fig. 3. Nuclear magnetic resonance spectra

    a.   8-phenyl-7,8-oxaza-bicyclo-[4.2.2]-deca-
        2,4-diene

    b.   8-phenyl-7,8-oxaza-bicyclo-[4.2.2]-deca-
        3,9-diene
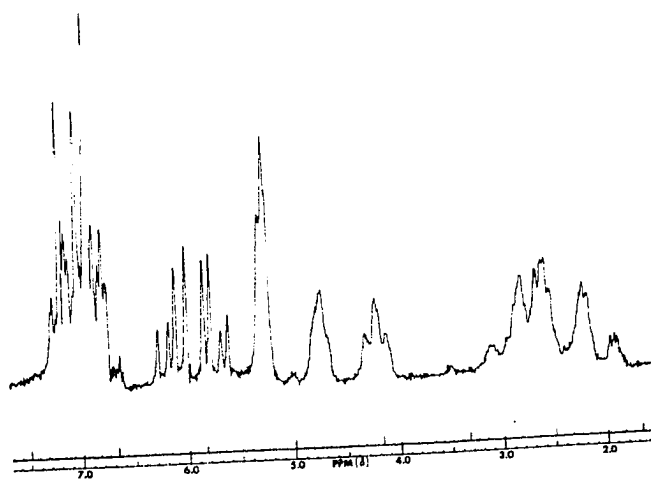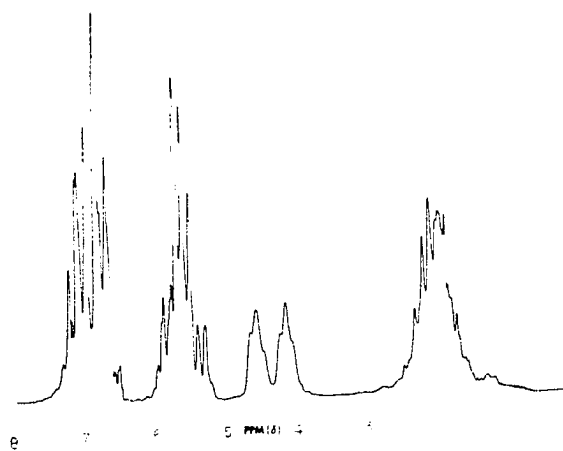
pale yellow oil which produced white crystals, mp 52-54°C, upon cooling

in a 80:20 solution of EtOH:H_2O.   This material exhibited the follow-

ing spectral properties: $\delta^{CCl_4}_{TMS}$: 1.74-3.18 (m, 4H), 4.00-4.33 (m, 1H),

4.56-4.87 (m, 1H), 5.24 (very broad S, 2H), 5.69 (d(J=10 cps), of d

(J=4 cps), 1H), 6.10 (d(J=10 cps) of d (J=6 cps), 1H), and 6.70-7.40

(m, 5H); ν^{neat}_{max} : 3070, 3015, 2970, 2905, 1600 and 1495 cm^{-1};

$\lambda^{C_6H_{12}}_{max}$: 253 mμ (ε=9050) and 284 mμ (ε=1740); and mass spec shows

$M^{+}_{\cdot}$=213.   The same olefinic proton patterns at 5.69 and 6.10 δ were

noted in the reaction product of 1,3-cyclooctadiene and nitrosobenzene

(mp 83-84°C, lit. (93): mp 83.5-84.5).   The only possible structural

assignment, therefore is XVII, the expected product.
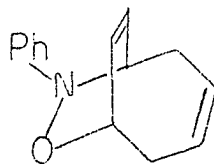
XVII

That XVI and XVII had the same basic structural skeletal system

was shown by hydrogenating each to yield tetrahydroderivatives exhibit-

ing identical nmr spectra.

The results of these experiments failed to define a unique mech-

anism but did reduce the number of possibilities. It was felt at this

time that the remaining possibilities were: a stepwise radical addition,

a concerted cis-trans cycloaddition, or a rearrangement of a primary

reaction product. The easiest and most conclusive way to differentiate

these possibilities was to isolate intermediate reaction products and

see if these could be isomerized to a formal 1,6 addition product. Look-

ing at this possibility in equation form (Scheme IV), it was felt that

Scheme IV
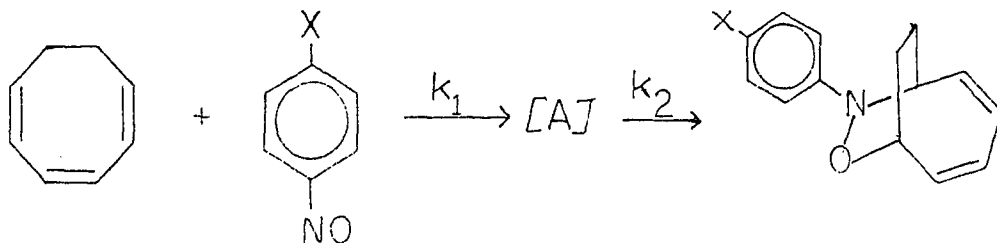
if k_1 could be increased relative to k_2, there might be a possibility of

isolating A, whatever it might be. It is known that with X= electron

withdrawing groups the rate of reaction increases markedly between

nitrosobenzene and dienes (94). Since X=—NO_2 has the greatest rate

enhancing properties, a study of the addition of p-nitro-nitrosobenzene

with 1,3,5-cyclooctatriene was undertaken.

Stirring an excess of p-nitro-nitrosobenzene with the mixture of

1,3,5-cyclooctatriene, 1,3,6-cyclooctatriene and bicyclo-[4.2.0]-octa-

2,4-diene (an undetermined amount of each) for 32 hours produced a deep

yellow oil upon removal of the solvent. The addition of Skelly B to this

oil resulted in the formation of a yellow solid, mp 192-193°C after one

recrystallization from EtOH. This was identified as 4,4'-dinitro-

azoxybenzene, an expected side product. The residual material was care-

fully chromatographed twice on a column of silica gel to yield four

different products: a small additional amount of the azoxybenzene, the

π^4s + π^2s adducts derived from the 1,3,6-cyclooctatriene and bicyclo-[4.2.0]-octa-2,4-diene impurities, and a bright yellow oil which yielded bright yellow needles, mp 105-108°C, upon cooling in 80:20 EtOH:H$_2$O. The nmr spectrum ($\delta_{CDCl_3}^{TMS}$: 1.33-2.50 (m, 4H), 4.56 (m, 1H), 4.84 (t, 1H), 5.40-7.0 (many-lined m, 4H), 6.65 (d, J=10 cps, 2H), and 7.90 (d, J=10 cps, 2H)) had the same characteristic pattern as found in the spectrum of XVII for the ethylene bridge of a bicyclo-[4.2.2]-adduct as well as additional fine structure in the olefinic region. That this product was the π^4s + π^2s adduct XVIII was shown by nmr decoupling experiments
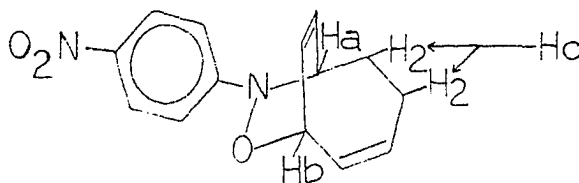
XVIII

carried out on a Varian HA-100 nuclear magnetic resonance spectrometer. Irradiation of the multiplet at 4.56 δ (Ha) caused a noticeable collapse of the pattern at 1.33-2.50 δ (Hc) but only a slight change in the olefinic region. Irradiation of the upfield resonances (Hc) caused a collapse of the multiplet at 4.56 δ (Ha) but no change in the triplet at 4.84 (Hb). Irradiation of this triplet had no effect on the upfield region but caused a considerable collapse in the olefinic resonances. Since the chemical shift of the bridgehead protons found in the various adducts isolated from the cyclooctatriene series all were very similar, it was felt that the same conclusion could be drawn about the shift of

the bridgehead protons found in XVIII. It can be safely concluded that

the upfield bridgehead protons in the "symmetrical" adducts are those α

to the nitrogen and those downfield are α to the oxygen. Since the

downfield proton is coupled directly to the olefinic region and shows a

much cleaner pattern, it was decided that the olefin in the 4-membered

bridge is on the same side as oxygen, as shown in XVIII. This is the

expected product, if one considers 1,3,5-cyclooctatriene as a vinyl-

substituted diene. Since a vinyl group is electron-withdrawing, it would

be expected that the vinyl group would be located α to the oxygen-bearing

carbon in the product.

Heating a sample of XVIII to 65° for 20 hours resulted in complete

rearrangement to a material, mp 132-134°C, the spectral properties of

which indicate that it is the 1,6 addition product XIX. The nmr spectrum
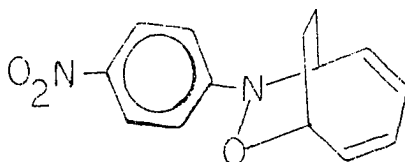
XIX

$(\delta_{CDCl_3}^{TMS}$: 1.87-2.50 (m, 4H), 4.48 (m, 1H), 4.84 (m, 1H), 5.81 (m, 4H),

6.55 (d, J=10 cps, 2H), and 8.03 (d, J=10 cps, 2H)) is very similar to

that of XVI.

A strong inclination exists to argue by analogy that the other

systems studied are reacting in the same manner. It must be acknowledged,

however, that one or more other mechanisms might be operating in these

Fig. 4. Nuclear magnetic resonance spectra

  a. 8-p-nitro-phenyl-7,8-oxaza-bicyclo-[4.2.2-
      deca-2,9-diene

  b. 8-p-nitro-phenyl-7,8-oxaza-bicyclo-[4.2.2]-
      deca-2,4-diene
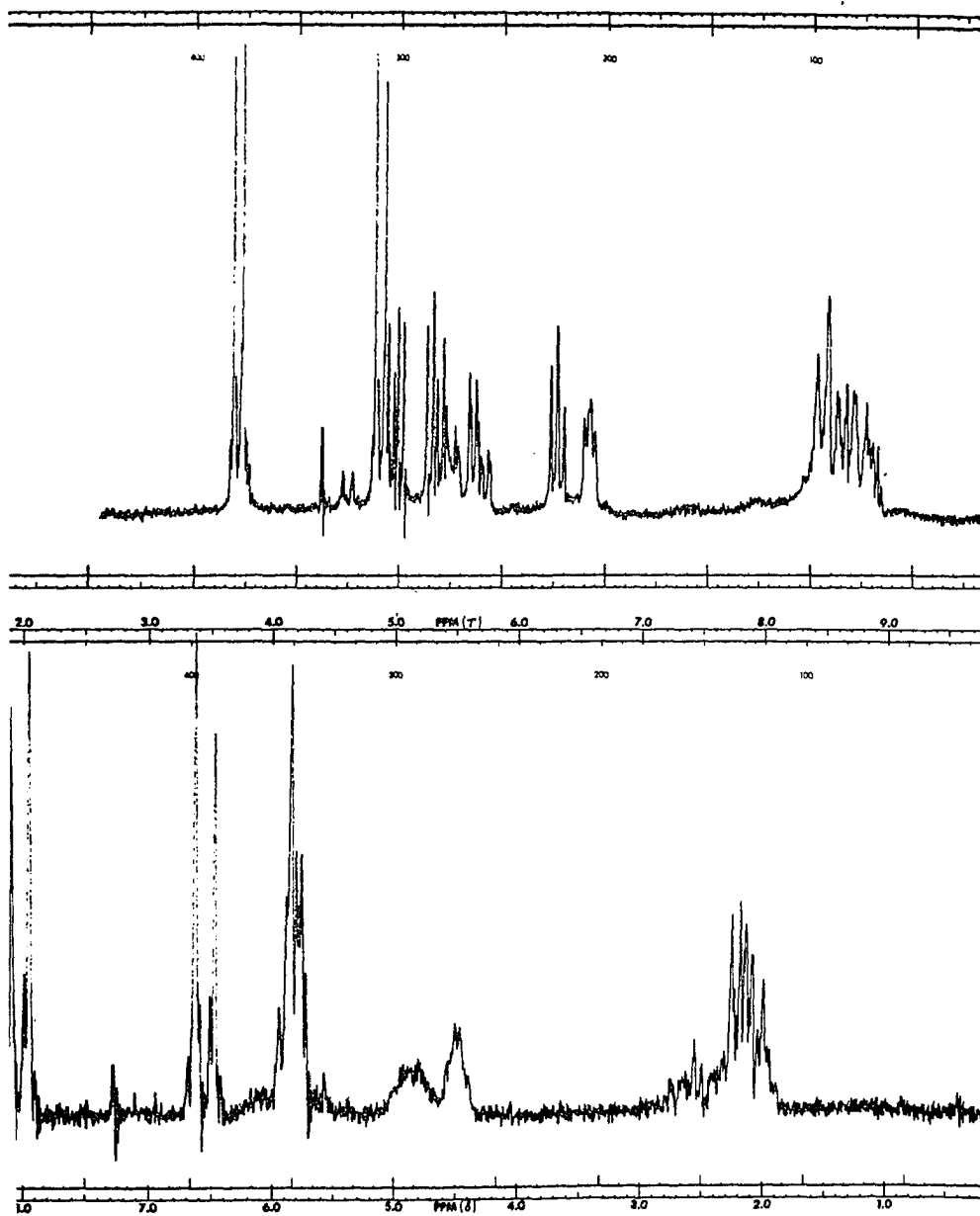
cases. Without isolating comparable products to XVIII, 100% certainty

can not be expressed as to the mechanism of formation of the 1,6 addition

product in these cases.

The mechanism of rearrangement of the $\pi^4 s + \pi^2 s$ adduct to the 1,6

addition product can be looked upon in two fashions. There could be

C-O bond fission followed by reclosure of the rearranged allylic car-

bonium ion as in the Scheme V or a thermally-allowed 1,3 sigmatropic

Scheme V
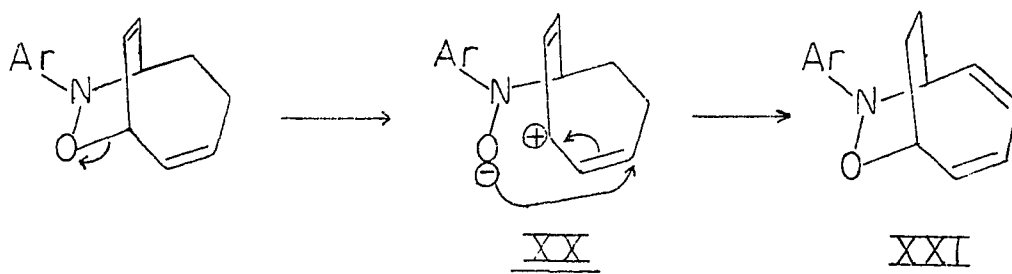
shift. This type of shift is possible because the required stereochemical

inversion of the migrating center has no meaning in this case. The later

possibility is favored. The carbonium ion formed in the initial C-O bond

fission is di-allylic and could rearrange in two ways, both of which

would produce conjugated dienes. The concerted reaction found in the
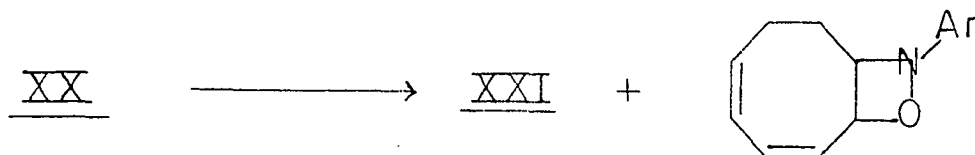
1,3 sigmatropic shift also favors the production of only one product, as found. A study of models shows that the centers involved in the shift have orbitals lying in close proximity to each other, whereas the centers for the other possible 1,3 sigmatropic shift are widely separated. The driving force for this rearrangement would appear to be the production of a more thermodynamically stable conjugated diene. It should also be pointed out that the stereochemistry noted in the cycloheptatriene additions is quite consistent with an approach from the least hindered side of the triene to form an initial $\pi^4 s + \pi^2 s$ adduct. Rearrangement to the 1,6 addition product does not involve this center and following the mechanisms through leads one to the observed results.

To the best of our knowledge, this is the first recorded example of the reaction of either a cycloheptatriene or 1,3,5-cyclooctatriene with a dienophile through the triene-tautomer in Diels-Alder fashion. In no other report of the chemistry of these molecules has a diene portion of the triene ever reacted with dienophiles.

Hutton and Waters implied that the azoxybenzene formed in the reaction of nitrosobenzene and cycloheptatriene was the result of a proton abstraction by azoxybenzene from cycloheptatriene followed by coupling to another molecule of nitrosobenzene (88). It was not clear whether these authors meant to imply that the cycloaddition product was a result of the attack of nitrosobenzene on the cycloheptatrienyl radical. This possibility was discounted when we found that azoxybenzene was also formed in the reaction with 3,7,7-trimethyl-cycloheptatriene, 1,3,5-cyclooctatriene and 1,3,6-cyclooctatriene. A control reaction also showed that

azoxybenzene was formed when an ether solution of nitrosobenzene was stirred for three days at room temperature under a nitrogen flow. It is also known that azoxybenzene is easily formed from nitrosobenzene under varied solvent conditions (95).

SUMMARY

It has been reported that the structure of the reaction product of

nitrosobenzene and cycloheptatriene is both X and XI (R=H) from an

analysis of the same spectral data. This literature conflict was resolved
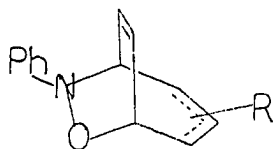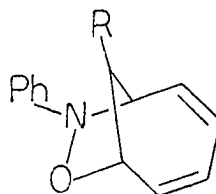
X   XI

by repeating these reactions using 7-methyl and 7-phenyl-cycloheptatriene

as well as cycloheptatriene itself. Spectral data coupled with nuclear

magnetic resonance decoupling experiments indicated that the crude struc-

tural assignment of these products should be that of XI (R=H, CH$_3$, Ph).

An x-ray crystallographic analysis of the product of p-bromo-nitroso-

benzene and 7-methyl-cycloheptatriene confirms this assignment as well as

pinpointing the stereochemistry on the one-carbon bridge. The final

structural assignment for these products, therefore, is XII (R=H, CH$_3$, Ph).
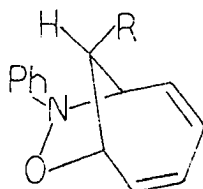
XII

The mechanism of formation of this 1,6 addition product is of considerable interest since it represents a possible violation of the Woodward-Hoffmann symmetry rules. The formation is a two-step process, however, thus eliminating it from the sphere of Woodward-Hoffmann rules. This conclusion was drawn from a study of nitrosobenzene with 1,3,5-cyclooctatriene. This molecule was chosen because of the ability to isolate the triene tautomer in pure form and to keep it from tautomerizing to the bicyclic form, something not possible with the cycloheptatrienes used. It was found that the reaction of 1,3,5-cyclooctatriene with $\underline{p}$-nitro-nitrosobenzene produced a thermally-allowed $\pi^4 s + \pi^2 s$ cycloaddition product which then rearranged to the 1,6 addition product with heat.
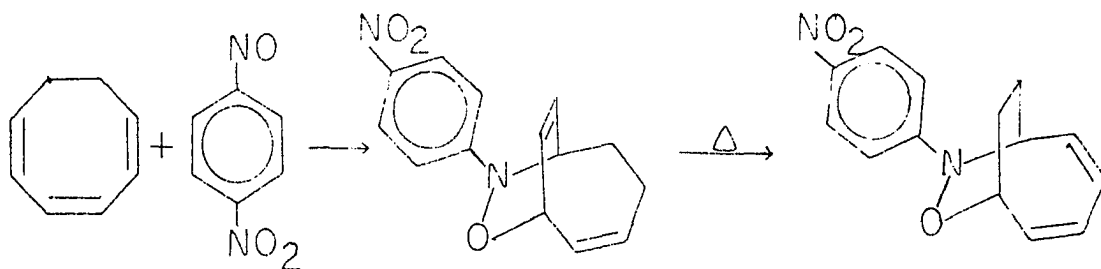
The inability to isolate the corresponding $\pi^4 s + \pi^2 s$ cycloadduct in the other reactions of trienes with nitrosobenzenes make it impossible to state with 100% certainty that a corresponding mechanism is being followed in these cases although we favor this explanation.

EXPERIMENTAL

General

The nitrosobenzene used in these reactions was prepared by the

procedure found in Organic Syntheses (96) and had a mp of 68°C. Instru-

mentation and analytical analyses were the same as mentioned previously.

Methods

The reaction of nitrosobenzene with cycloheptatriene

A solution of 2.5 g of cycloheptatriene (practical containing toluene)

and 2.25 g nitrosobenzene was stirred for 3 days in 25 ml. dry Et_2O at

room temperature. The solvent was removed on the rotovac and the residue

column chromatographed on silica gel using CCl_4 as an eluent. The first

band isolated was a mixture of azoxybenzene and unreacted starting

materials. The next band was concentrated to yield 1.74 g (35% yield) of

a reddish-colored oil. Treatment of this oil was activated charcoal in

$CHCl_3$ followed by filtration, concentration, and cooling in a 80:20

Et_2O:Skelly B solvent afforded white plates, mp 101-105°C, recrystallized

once from hexane, mp 106-107°C.

The reaction of nitrosobenzene with 7-phenyl-cycloheptatriene

A solution of 1.50 g 7-phenyl-cycloheptatriene (obtained from Medford

Robins of Professor Trahanovsky's group) and 1.90 g (1:2 molar ratio)

nitrosobenzene in 20 ml. t-butanol was heated at 70°C for 5 hours after

being purged with N_2. The solvent was removed on the rotovac and the

residual dark oil column chromatographed on silica gel using CCl_4 as an eluent. The first band isolated was a mixture of azoxybenzene and unreacted starting materials. The second band, a light reddish-colored oil yielded 650 mg. (26% yield) of a solid, mp 148-150°C, recrystallized once from Skelly B, mp 150-151°C, upon cooling in a 90:10 Et_2O: Skelly B mixture. <u>Anal.</u>: calculated: C: 82.90, H: 6.18; found: C: 82.68, H: 6.44.

Preparation of 7-methyl-cycloheptatriene

Tropylium fluoroborate (14.7 g), prepared by the method of H. J. Dauben, Jr., et al. (97), was suspended in a dried Et_2O solvent cooled to 0°C and reacted with 55 ml. of a cold 5.18% solution of CH_3Li in Et_2O. An exothermic reaction was noted with the formation of a gelatinous precipitate while stirring for 1/2 hour. The solid was filtered and the Et_2O removed on the rotovac to yield 4.27 g (49% yield) of a pale yellow liquid. This liquid exhibited the following nmr spectrum consistent with the proposed structure: δ_{TMS}^{neat} : 1.23 (d, J=6 cps, 3H), 1.36-1.97 (m, 1H), 4.85-5.21 (4-line m, 2H), 5.87-6.39 (m, 2H), and 6.46-6.73 (m, 2H).

It was found by repetition of this reaction that maximum yields were obtained by distillation of the crude reaction mixture without filtration of the solid produced during the reaction. A low temperature, atmospheric pressure distillation was used to remove the solvent and a vacuum bulb-to bulb distillation to obtain the pure colorless product. The receiver in this distillation was cooled with an ice-methanol mixture

and the vacuum source was a water aspirator.

The reaction of nitrosobenzene and 7-methyl-cycloheptatriene

A solution of 4.27 g of 7-methyl-cycloheptatriene and 4.30 g of nitrosobenzene in 20 ml. of dried Et_2O was stirred for 42 hours at room temperature. A nmr spectrum of the crude reaction product showed a considerable amount of starting materials remaining so another 1.0 g of nitrosobenzene was added and the mixture stirred for another 24 hours. Little or no change was noted in the nmr spectrum of this mixture so it was worked up in the usual manner. The solvent was stripped off on the rotovac and the residual dark oil column chromatographed on silica gel using CCl_4 as an eluent. The first band contained unreacted starting materials and azoxybenzene. A wide band was then collected, concentrated, treated with charcoal, and cooled in a 80:20 Et_2O:Skelly B solvent to yield 1.0 g (12% yield) of white needles, mp 93-94°C. Anal.: Calculated: C: 78.87, H: 7.04; found: C: 78.83, H: 7.06.

The preparation of p-bromo-nitrosobenzene

A solution of 50 g of p-bromo-nitrobenzene, 6 g NH_4OH, 70 ml. H_2O, and 250 ml. 95% EtOH was heated to reflux in a 500 ml., 2-necked flask fitted with a mechanical stirrer and reflux condenser. To this solution was added 75 g of zinc dust over a 5-10 min. period. The resultant mixture was stirred for 15-30 minutes and poured hot into a solution of 95 g of $FeCl_3$ in one liter of water at 0°C. Stirring this solution, kept close to 0°C by the addition of ice, produced 16.8 g (36% yield) of a

light yellow solid, mp 94-96°C after one recrystallization from a cold 80:20 EtOH:H$_2$0 solution (lit. (98) mp 95°C).

The reaction of p-bromo-nitrosobenzene with 7-methyl-cycloheptatriene

A solution of 1.5 g 7-methyl-cycloheptatriene and 3.5 g of p-bromo-nitrosobenzene in 55 ml. dry Et$_2$0 was stirred for 168 hours at room temperature. The solvent was stripped off on the rotovac and the residue column chromatographed on silica gel using CCl$_4$ as an eluent. As usual, the first fraction was a mixture of azoxybenzene and unreacted starting materials. The next fraction was concentrated, treated with charcoal twice in CHCl$_3$ and crystallized from hexane to yield 425 mg. (12% yield) of small white needles, mp 130-131°C. This product exhibited the following nmr spectrum consistent with the proposed structure: $\delta_{TMS}^{CCl_4}$: 1.04 (d, J=7 cps, 3H), 2.38-3.00 (m, 1H), 3.78-4.09 (m, 1H), 4.41-4.78 (m, 1H), 5.48-6.30 (m (broad "grassy" S), 4H), 6.75 (d, J=9 cps, 2H), and 7.26 (d, J=9 cps, 2H).

Hydrogenation of bicyclo-[4.2.1]-8-phenyl-7,8-oxaza-nona-2,4-diene

A hexane solution of 0.529 g of the compound named above was hydrogenated over Pd/C until hydrogen uptake was very slow. Calculations showed that very close to the theoretical amount was taken up. The solution was filtered, washed twice with 0.5 $\underline{M}$ HCl to remove any free amine resulting from hydrogenolysis of the N-O bond, once with water, dried, and concentrated to give nearly 100% yield of a colorless oil exhibiting the following nmr spectrum consistent with a fully-saturated

analog of the starting material: $\delta_{TMS}^{CCl_4}$: 0.73-2.40 (m, 8H), 3.67-4.17

(m, 1H), 4.60-5.06 (m, 1H), and 6.78-7.25 (m, 5H). An infrared spectrum

showed no alcohol or amine absorptions.

Pyrolysis of bicyclo-[4.2.1]-8-phenyl-7,8-oxaza-nonane

A 0.25 sample of the above compound was pyrolyzed through a glass

bead filled column at 500-520°C and < 0.001 mm. Hg over a 10 hour period.

The product, collected in a liquid nitrogen cooled trap, was a greenish

colored oil. This product exhibited the following nmr absorptions:

$\delta_{TMS}^{CCl_4}$: 0.70-3.00 and phenyl absorptions in the 7 ppm region consistent

with the expected nitrosobenzene derivatives from the pyrolysis. ·

Preparation of bicyclo-[3.2.0]-heptane

A sample of bicyclo-[3.2.0]-hept-6-ene was gratefully received

from the Professor O. L. Chapman group. This was then hydrogenated in

benzene Pd/C. Calculations showed that just over half the theoretical

amount of hydrogen was taken up. A nmr spectrum showed no olefinic

protons in the hydrogenated product, however. It was found that the

starting material contained a considerable amount of Et_2O. The

hydrogenated product exhibited the following nmr spectrum: $\delta_{TMS}^{C_6H_6}$:

0.95-3.0 ppm.

Preparation of 1,3,5-cyclooctatriene

The above named compound was prepared by the method of Jones (99)

which is the basic reduction of cyclooctatetraene with zinc. Any

bicyclo-[4.2.0]-octa-2,4-diene present was removed by the reaction with excess maleic anhydride. The product was isolated by vacuum distillation and was shown by nmr integrals to be a 75:25 mixture of 1,3,5- and 1,3,6-cyclooctatriene, respectively. The mixture exhibited the following

nmr spectrum: δ_{TMS}^{neat} : 2.37 (broad S), 2.55–2.86 (m) (together 4H), and 5.12–6.24 (6H).

Preparation of 1,3,6-cyclooctatriene

The above named compound was also prepared by the method of Jones (99). The product was isolated as previously. The $AgNO_3$ complex was prepared by heating a solution of 25 ml. 95% EtOH, 2 g of the product mixture, and excess powdered $AgNO_3$ to reflux for 30 minutes. The solution was filtered while hot, cooled to 0°C, and filtered to yield white crystals, mp > 200°C. Treatment of a small portion of these crystals with an aqueous solution of concentrated NH_4OH and extraction with pentane yielded a mixture richer in the 1,3,6 isomer (as judged by nmr). Recrystallization of the remainder of the complex from hot EtOH and similar treatment afforded a 85:15 mixture of 1,3,6-:1,3,5-cyclooctatriene. The nmr spectrum was the same as reported in the 1,3,5-cyclooctatriene preparation only with differing intensities.

The reaction of 1,3,5-cyclooctatriene with nitrosobenzene

A solution of 2.0 g of a 75:25 mixture of 1,3,5- and 1,3,6-cyclo-octatriene, respectively, and excess nitrosobenzene in 450 ml. $CHCl_3$ was

stirred at room temperature for 20 days. The solvent was removed and the residue column chromatographed on alumina using CCl_4 as an eluent. The resulting fractions each had varying compositions of azoxybenzene and products so all fractions were combined and rechromatographed on a 50:50 mixture of alumina:silica gel using 75% CCl_4 and Skelly B as an eluent. Fraction one contained an adduct whose spectra were consistent with a $\pi^6 s + \pi^2 s$ addition product but mostly azoxybenzene. Fraction two contained the same products but mostly adduct. Fraction three contained a mixture of two different adducts and fraction four (the balance of the material remaining on the column removed with Et_2O) contained one of the adducts found in fraction three plus some impurities. Calculations based upon nmr integrals showed that bicyclo-[4.2.2]-3-phenyl-2,3-oxaza-deca-5,7-diene was prepared in 48% yield and bicyclo-[4.2.2]-3-phenyl-2,3-oxaza-deca-6,9-diene in 53% yield.

Fraction two was taken up in a solution of 80:20 EtOH:H_2O and cooled to 0°C to produce crystals, mp 32-33°C after one recrystallization from hexane. _Anal._: calculated: C: 78.84, H: 7.09; found: C: 78.00, and H: 7.09.

This reaction was repeated with the following changes: it was carried out under a N_2 flow, Et_2O was used as the solvent, and it was only stirred for 3 days. The same results were obtained only more starting materials were recovered.

Repeating the reaction once more on a larger scale (> 10 g of the triene mixture) resulted in a larger amount of each of the products observed earlier. More important, however, was the possibility of the

isolation of a side product, tricyclo-[4.2.2.0^{5,8}]-3-phenyl-2,3-oxaza-

9-decene, mp 93-94°C (white needles from EtOH). The nmr of this material

is: $\delta^{CCl_4}_{TMS}$: 1.27-2.34 (m, 4H), 2.73-3.18 (m, 2H), 4.17-4.68 (m, 2H),

5.95-6.70 (m, 2H), and 6.70-7.30 (m, 5H). The spectrum of this material

was also seen in the previous reactions.

The reaction of nitrosobenzene with 1,3-cyclooctadiene

A solution of 1.1 g each of nitrosobenzene and 1,3-cyclooctadiene

was stirred in anhydrous ether for 3 days. The solvent was removed and

the residual dark oil passed through a silica gel column using CCl_4 as

an eluent. The first band was azoxybenzene and the second a yellow oil

(1.0 g, 45%). This oil was taken up in 80:20 EtOH:H_2O and cooled to

-5°C to yield white needles, mp 83-84°C (lit. (93): 83.5-84.5). The nmr

spectrum of this material is: $\delta^{CCl_4}_{TMS}$: 1.25-2.50 (m, 8H), 4.0-4.37 (m, 1H),

4.6-4.89 (m, 1H), 5.69 (d (J=10 cps) of d (J=4 cps), 1H), 6.10 (d (J=10

cps) of d (J=6 cps), 1H), and 6.70-7.4 (m, 5H).

The preparation of p-nitro-nitrosobenzene

Para-nitro-nitrosobenzene was prepared by Caro's acid (100) oxida-

tion of p-nitroaniline according to the revised method of Hamer, et al.

(85). The 92% yield reported by Borel and Devel (101) for the oxidation

of 3-nitro-4-aminotoluene to the nitroso compound or the 28% yield reported

for this compound (85) was not duplicated. From 32 g of amine was isolated

2.1 g (7%) of nitroso compound, mp 116-118°C (lit. (85): 118°C).

The reaction of p-nitro-nitrosobenzene with 1,3,5-cyclooctatriene

An anhydrous ether solution of approximately 1 g of 1,3,5-cyclo-
octatriene (this is only an estimated amount since the sample was contami-
nated with unknown but small amounts of 1,3,6-cyclooctatriene and bicyclo-
[4.2.0]-octa-2,4-diene impurities) and excess p-nitro-nitrosobenzene was
stirred for 32 hours. The solvent was removed and Skelly B added to the
resultant dirty yellow oil. A dirty yellow solid, recrystallized from
Et_2O, mp 191-193°C (4,4'-dinitro-azoxybenzene, lit. (102):mp 193°C) was
filtered and the mother liquors passed through a 50:50 alumina:silica
gel chromatographic column using CCl_4 as an eluent. Each fraction was
a mixture so the fractions showing the presence of no azoxybenzene were
rechromatographed on a silica gel column. Again almost each fraction was
a mixture (of the adducts of each of the olefins in the mixture) but one
pure sample of the major product was isolated. The nmr spectrum of this
product, which crystallized into bright yellow needles, mp 98-105°C after
cooling in an $EtOH-H_2O$ mixture (recrystallized from Skelly B-Et_2O,
mp 105-108°C) was described in the results and discussion section.
Additional spectral properties are: $\nu_{max}^{CHCl_3}$: 3100, 1608 (w), 1520,
1328, 1256, 1120, and 800 cm^{-1}; and the mass spectrum shows M$^{\ddot{+}}$=258.

Isomerization of bicyclo-[4.2.2]-7-p-nitrophenyl-7,8-oxaza-deca-2,9-diene
to bicyclo-[4.2.2]-7-p-nitrophenyl-7,8-oxaza-deca-2,4-diene

A sample of the $\pi^4 s + \pi^2 s$ adduct XVIII was heated to 65° in both 95%
EtOH and $CHCl_3$ for 20 and 8 hours, respectively. Removal of the solvents

and the addition of an EtOH-H$_2$O mixture with cooling resulted in the production of bright yellow needles, mp 126-132°C (recrystallized from Skelly B-Et$_2$O, mp 132-134°C). The nmr spectrum of this material was discussed in results and discussion section; additional spectral data on this compound are listed as follows: $\nu_{max}^{CHCl_3}$: 3100, 1605 (m), 1519, 1328, 1255, 1122, and 800 cm^{-1}; and the mass spectrum shows M$^{\ddot{+}}$=258.

The hydrogenation of bicyclo-[4.2.2]-7-phenyl-7,8-oxaza-deca-2,4-diene and bicyclo-[4.2.2]-7-phenyl-7,8-oxaza-deca-2,9-diene

A 0.281 g sample of the first and a 0.317 g sample of the second compound mentioned above was hydrogenated in pentane over a Pd/C catalyst until hydrogen uptake was very slow. Only the first took up the theoretical amount of hydrogen. An examination of the nmr spectrum of each of the hydrogenated materials indicated the following: the first of the above had no olefinic protons remaining while the other did. The absorptions found for the totally hydrogenated compound were also found in the incompletely hydrogenated material, however: $\delta_{TMS}^{CCl_4}$: 0.75-3.10 (m, 12H), 3.82-4.72 (m, 2H) and 6.5-7.43 (m, 5H).

The reaction of nitrosobenzene with itself

A solution of nitrosobenzene in dry Et$_2$O was stirred for 3 days at room temperature under a N$_2$ flow. The solvent was removed and a nmr spectrum taken of the residue. The definite presence of azoxybenzene was noted by observance of the characteristic multiplet at 8.1-8.3 ppm.

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