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THE UNIVERSITY OF ALBERTA

THE CYCLIC 10-ELECTRON SYSTEM

by

Ⓒ Ko Hojo

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
AND RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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EDMONTON, ALBERTA

Fall, 1971

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance a thesis entitled

THE CYCLIC 10-ELECTRON SYSTEM

submitted by Ko Hojo in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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To my mother and Kiyomi

ABSTRACT

The preparation of two pure, crystalline [10]-annulenes has now been achieved. The geometry of these compounds has been established as (*cis*)^5- and *trans*,(*cis*)^4-cyclodeca-1,3,5,7,9-pentaene.

Both ^1H and ^{13}C nmr spectra of (*cis*)^5-[10]-annulene (II) are found to be temperature-invariant over a range of -20° to -160°. It is concluded that II is not a planar molecule, and unique conformational changes are suggested to explain the equivalence of all the nuclei on the ring. On the other hand, the ^{13}C and ^1H spectra of *trans*,(*cis*)^4-[10]annulene (III) exhibit marked temperature dependence. This dependence is interpreted in terms of a stepwise migration of the "trans" double bond around the ring. It is now established that both [10]-annulenes are non-aromatic.

Reaction of cyclononatetraenide anion (IV) with methylene chloride and *n*-butyllithium produces isobullvalene (XV), *trans*,(*cis*)^4-[10]annulene (III), and *cis*-9,10-dihydronaphthalene (VII). Low temperature techniques are perfected so that isolation in pure form of thermally unstable species such as III and XV is now possible.

Low temperature photolyses of the C_9H_{10} compounds, cis- and trans-bicyclo[6.1.0]nonatriene (XXII and XXIII), and cis-bicyclo[4.3.0]nonatriene (XIX), in all cases reach a photo-stationary state with a similar product distribution. Thermally unstable $(cis)^4$-cyclononatetraene (XXV) and trans,$(cis)^3$-cyclononatetraene (XXI) are isolated and well-characterized, and their roles in the photochemistry of C_9H_{10} hydrocarbons have been clarified.

The synthesis of N-carbethoxyazonin (XXXIV) has been accomplished by photolysis of its valence isomers, 9-azabicyclo[6.1.0]nona-2,4,6-triene (XXXII) and 4-azabicyclo[5.2.0]nona-2,5,8-triene (XXXIII). Physical and chemical properties of this nine-membered 10π-electron system are discussed.

ACKNOWLEDGMENTS

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The author is indebted to Mr. R. Swindelhurst and his staff, particularly to Mr. G. Bigam, for measurements of nmr spectra, and to Dr. Hogg and his staff for mass spectra measurements.

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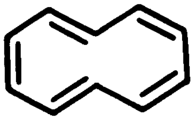
CHAPTER 1

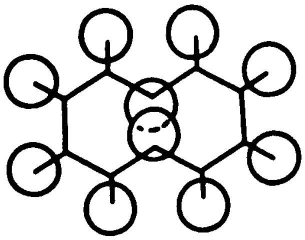
INTRODUCTION

Several decades ago, Hückel formulated his famous $(4n + 2)\pi$ rule[1] which states that "Those monocyclic coplanar systems of trigonally hybridized atoms which contain $(4n + 2)\pi$ electrons will possess relative electronic stability". Further recent refinements[2] of this rule permit the prediction that $(4n + 2)\pi$-electron ring systems impart positive π-electron contribution to the resonance energy (aromatic) while $(4n)\pi$-electron systems impart negative contribution (anti-aromatic). When n is greater than or equal to six both $(4n + 2)$ and $(4n)\pi$-electron systems are predicted to converge toward non-aromaticity.

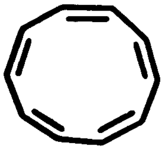
The validity of this prediction is evident from a bulk of experimental results documented in the last two decades.[3] The monocyclic systems examined so far include three to thirty-membered ring systems including ionic and neutral species. It is reasonable to assume that [10]annulenes, as simple vinylogs of benzene, would possess aromatic character, provided that such compounds were planar. However, in spite of a number of synthetic attempts over many years, none were successful in providing parent [10]annulenes. On the basis of molecular models, Mislow pointed out that [10]annulene (I) with cis, trans, cis, trans, cis-geometry should contain appreciable repulsion between the two internal hydrogens, as indicated below, causing distortion from coplanarity in the molecule.[4] Accordingly, this compound is not likely to be aromatic.



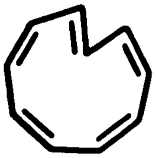
I



[10]Annulene may also exist in other geometrical forms, such as (cis)^5-[10]annulene (II) and trans,(cis)^4-[10]annulene (III).



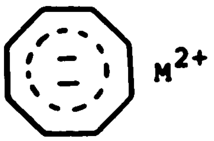
II

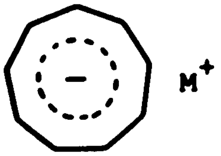


III

Compound II forms a carbon-carbon bond angle of 144° in a planar regular decagon structure, and the deviation from the normal strainless sp^2 hybridized bond angle is 24°. This deviation would cause internal strain and consequently would raise the ground state energy level of the molecule; yet any resonance energy associated with a planar system of alternating double bonds would lower these energy levels. The properties of the molecule then would depend on the degree to which each of these factors is operating. To date, not even crude estimates of the resulting ground state energy levels have been made.

Recently, successful syntheses of stable anionic 10π-systems, cyclooctatetraenyl dianion[5] and cyclononatetraenyl anion (IV)[6] were reported. In these planar aromatic anions, the bond angles of each compound are 135° and 140°, respectively, and are not greatly different from that (144°) of the hypothetical planar [10]annulene II.

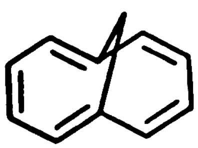




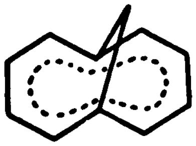
IV

The observed thermal stability of the ionic species is, at least, attributed to the electron charge evenly distributed over a planar ring. Any processes leading to bicyclo compounds imply the departure from coplanarity and should eventually cause a localization of the electron charge. One would expect high energy barriers for these processes. In contrast, cyclization reactions of neutral [10]annulenes obviously would not involve the repulsion of the formal charge and release the ring strain existing in the planar structure. From these arguments it is rather clear that [10]annulene II would be a (thermally) reactive species. However, it is still possible that II might exhibit some aromatic character in the ground state. No discussion concerning III has been recorded in the literature until very recently.

In recent years, there were numerous synthetic attempts directed at the parent and substituted [10]annulenes.[7] Several bridged or benz-fused [10]annulenes have been reported.[8] Among them was a successful synthesis of 1,6-methano[10]annulene (V) reported by Vogel and coworkers.[8] In this molecule, the interfering 1,6-hydrogens of I are in effect replaced by a methylene group to form a nearly planar [10]-annulene periphery.

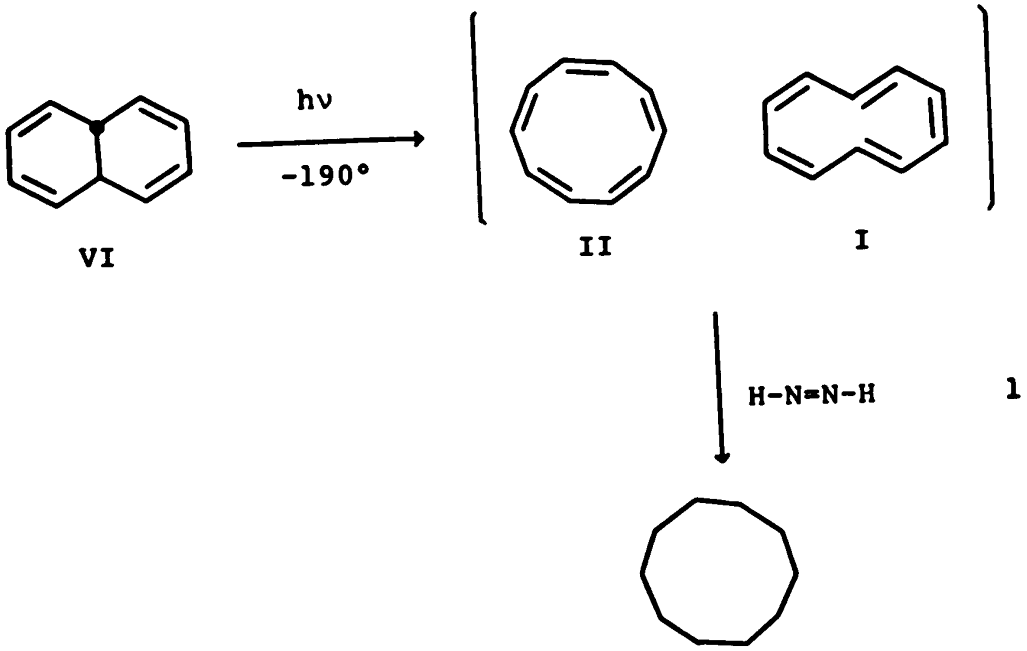


V



This compound exhibits a proton nmr spectrum indicative of the presence of a diamagnetic ring current, and a uv spectrum very similar to that of naphthalene. It also undergoes electrophilic substitution reactions. These properties are characteristic of aromatic compounds.

When the possibility of the existence of the parent [10]annulene was still open to question, van Tamelen and Burkoth reported the first trapping experiment of parent [10]annulene.[9] Irradiation of <u>trans</u>-9,10-dihydronaphthalene (VI) at -190° and subsequent reduction with diimide at -80° purportedly gave cyclodecane (reaction 1).



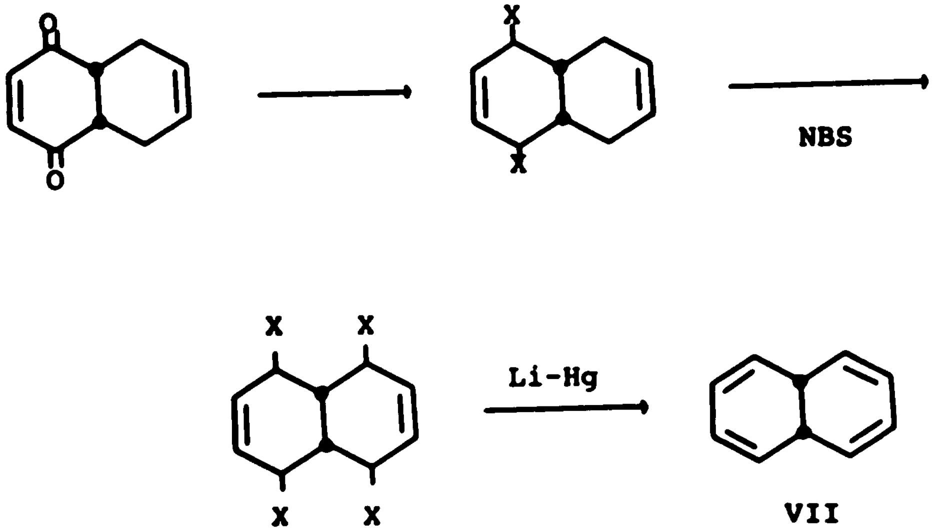
Except for the claim of having trapped I and/or II, no properties of these compounds were recorded.

A number of valence bond isomers of [10]-annulenes have been reported, and they are generally denoted as $(CH)_{10}$ compounds. Elucidation of the chemistry of some of these compounds is directly responsible for the successful synthesis of [10]-annulenes. The chemistry of these $(CH)_{10}$ isomers is briefly summarized in this section.

A. Compounds of central importance to [10]annulene problem

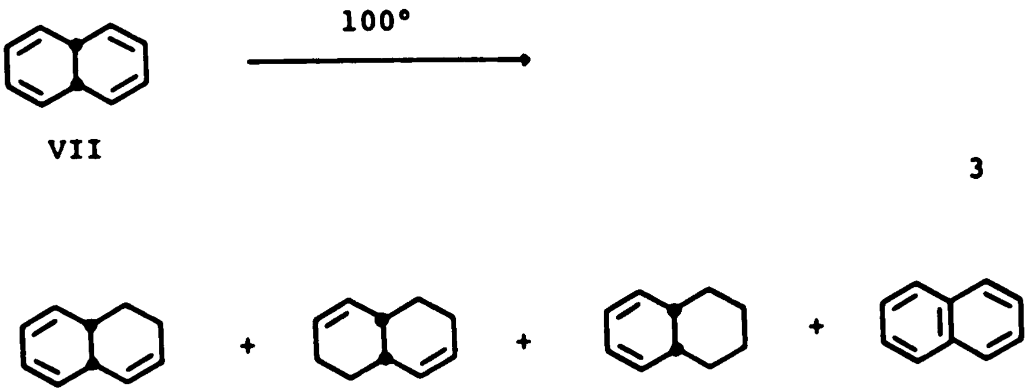
i) *cis*-9,10-Dihydronaphthalene (VII)

In 1963, van Tamelen and Pappas reported a rational synthesis of VII, the first valence bond isomer closely related to [10]annulene.[10] A butadiene-*p*-benzoquinone adduct was converted to a diol (X = OH) and then to a dibromide (X = Br).



2

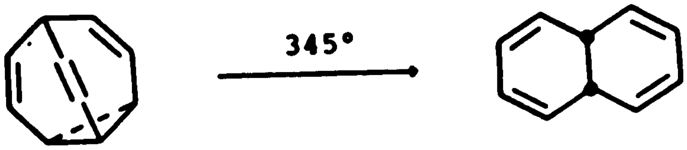
Treatment of the dibromide with NBS, followed by reductive elimination of bromine (Li-Hg) afforded the desired material (reaction 2). Both spectral [nmr: A_2B_2 multiplet (8 H) centered at τ 4.39 and a broad singlet (2 H) at τ 6.75; uv: λ_{max} = 247 nm, ε = 6000] and chemical evidence (hydrogenation to <u>cis</u>-decalin) was in agreement with structure VII. An attempt by Doering and Rothenthal to observe a temperature dependent nmr spectrum of VII proved futile because another intermolecular reaction occurred at about 100° (reaction 3).[11]



3

ii) Tricyclo[3.3.2.$0^{4,6}$]deca-2,7,9-triene (Bullvalene) (VIII)

In 1963 Schröder and coworkers reported the first preparation of bullvalene (VIII) by the uv irradiation of a cyclooctatetraene dimer (mp 76°).[12] Chemical and spectral data conclusively established the structure. As predicted by Doering and Roth,[13] compound VIII underwent a rapid reversible valence bond isomerization via degenerate Cope rearrangement. Such a process made all the protons equivalent as shown by its temperature dependent nmr spectra (singlet τ 5.78, at 100°). By careful pyrolysis (flow system), compound VIII was isomerized to VII (reaction 4).[14]



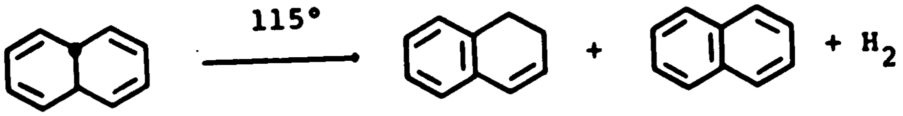
VIII VII

4.

The possible intermediacy of tetracyclo[4.4.0.0^{2,10}0^{5,7}]-deca-3,8-diene (IX) (see p. 15) in this process was suggested by Schröder for the first time.[15] The reverse reaction (VII → VIII) by a photochemical transformation was also reported.[16] A detailed kinetic investigation of the thermal reaction of VIII was reported later.[17]

iii) *trans*-9,10-Dihydronaphthalene (VI)

In 1967, van Tamelen and Burkoth reported a synthesis of VI following a scheme analogous to the one employed for the preparation of VII.[9] Although the observed nmr spectrum [singlet at τ 4.2 (8 H) and singlet at τ 7.2 (2 H)] agreed with structure VI, the reported uv spectrum differed from that reported from our laboratory (*vide infra*). In the same year, we reported[18] that thermal isomerization of bicyclo[6.2.0]-deca-2,4,6,9-tetraene (X, see p. 11) led to compound VI, which was isolated in a pure form. Both chemical (hydrogenation to *trans*-decalin) and spectral (nmr: same as above) evidence was in agreement with the previous structural assignment.[9] The uv spectrum of VI displayed λ_{max} at 276 nm (ϵ = 3850).[19] Compound VI underwent complex intra- and inter-molecular hydrogen transfer reactions to produce naphthalene, 1,2-dihydronaphthalene and hydrogen (reaction 5). The explanation for these processes was offered elswhere.[19]

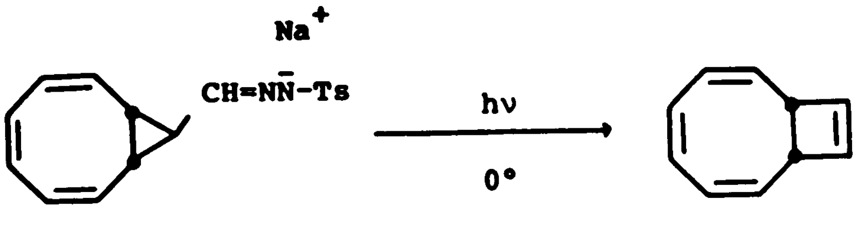


VI

5

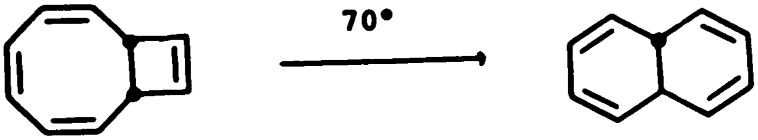
iv) Bicyclo[6.2.0]deca-2,4,6,9-tetraene (X)

In 1967, we reported the synthesis of bicyclo[6.2.0]deca-2,4,6,9-tetraene (X).[18] Uv irradiation of the sodium salt of bicyclo[6.1.0]nona-2,4,6-triene-9-carboxaldehyde tosylhydrazone (XI)[20] at 0° gave X as a major product (reaction 6). A low temperature work-up, including chromatographic purification at 0°, provided pure material. Both spectral (nmr, mass spectrum, and uv) and chemical (hydrogenation to bicyclo[6.2.0]decane) data were fully compatible with the structure X.



XI X 6

Compound X was thermally labile and isomerized quantitatively to compound VI at 70° with a half-life of 67 min (reaction 7).

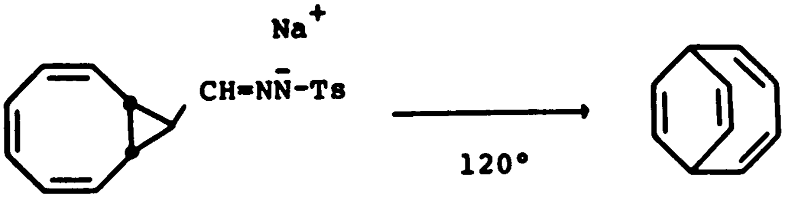


X VI 7

In the same year, Schröder and Martini reported the preparation of a derivative of X.[21]

v) Bicyclo[4.2.2]deca-2,4,7,9-tetraene (XII)

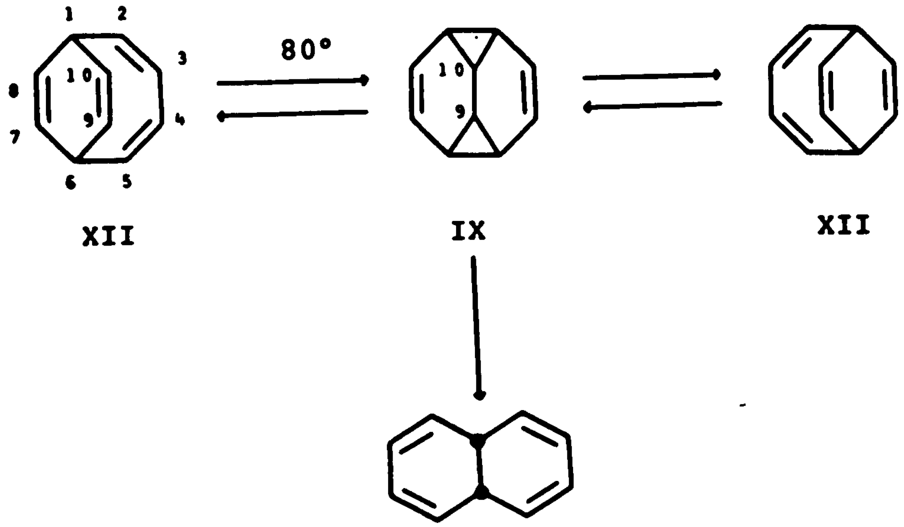
In early 1967 Jones and Scott reported a preparation of XII.[20] The thermal decomposition of the dry sodium salt of tosylhydrazone XI provided XII as a major product (40%) which was separated by preparative glpc (reaction 8).



XI XII

8

Both spectral and chemical data were consistent with structure XII. A unique degenerate intramolecular Diels-Alder reaction of XII through the intermediate IX (reaction 9) was subsequently reported by three groups.[22] The experiment performed in our laboratory[17] showed that deuterium atoms originally incorporated at H-7,8 positions of XII scrambled completely to H-3,4,7,8,9, 10 positions after heating at 80° for 1 hr. More direct evidence for this process was also included in our communication.



XII IX XII

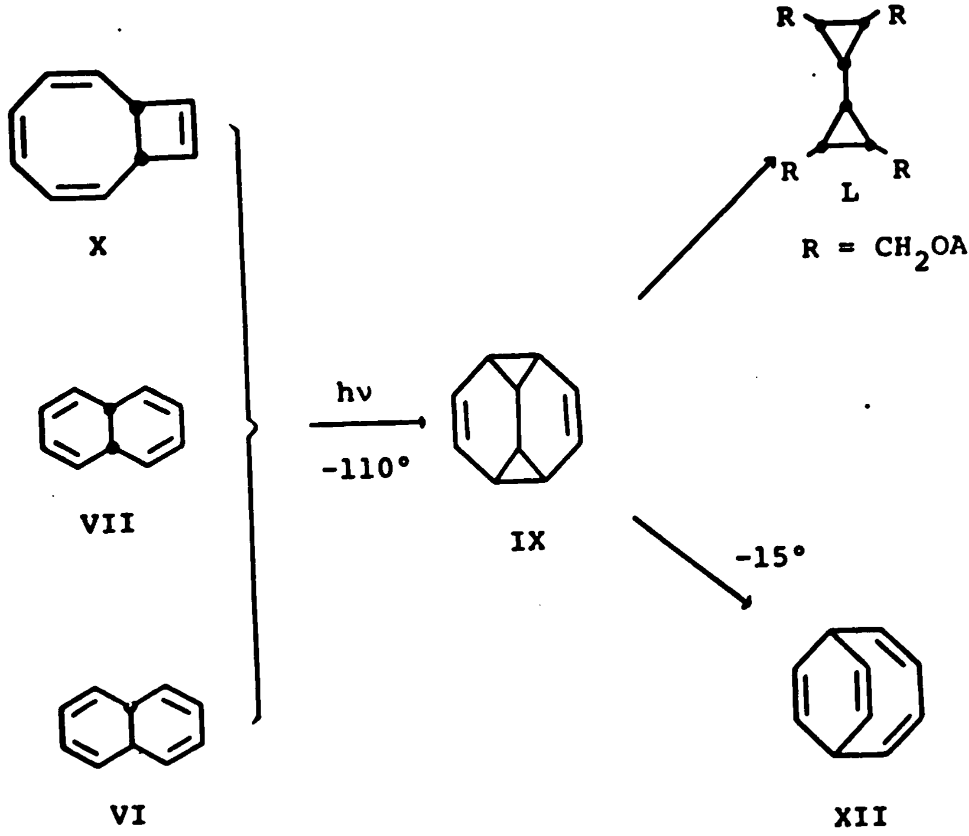
9

VII

Compound XII exhibited temperature dependent nmr spectra. The signals due to the olefinic protons coalesced at 180° (40 MHz). Approximate mean life times were estimated to be about 0.5 sec at 140° and 0.025 sec around 175°. Compound XII thermally isomerized to VII.[20] A detailed mechanistic investigation of this process suggested the scheme depicted above.[22] The facile photochemical conversion of XII to bullvalene (VIII) was also described by Jones and Scott, who proposed the involvement of IX in this transformation.[20] The facile metal-catalyzed rearrangement of VIII to XII reported by Schröder and coworkers improved the preparative method of XII,[23] and therefore of VII.

vi) Tetracyclo$[4.4.0^{2,10}.0^{5,7}]$deca-3,8-diene (IX)

In 1968, we reported the first isolation and characterization of IX.[24] Irradiation of VI, VII, and X at -110°, produced a 65% yield of a new species IX (reaction 10). The nmr spectrum of this material exhibited a broad singlet at τ 4.2 (4 H), a complex multiplet at τ 8.5 (2 H), and a broad singlet at τ 8.8 (4 H), which was compatible with the structure IX. The unambiguous structure determination was achieved chemically by ozonolysis at low temperature, followed by reduction with sodium borohydride and acetylation to provide a tetraacetate identical with all cis-tetraacetate L prepared in an unambiguous manner (reaction 10).



10

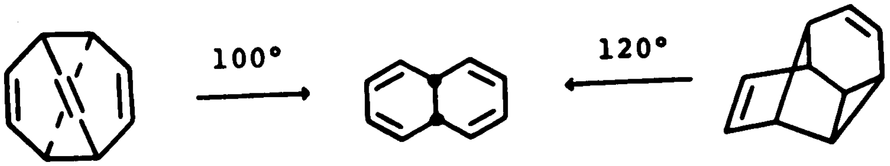
Compound IX (a white solid at low temperature) quantitatively isomerized to XII by a reverse Diels-Alder reaction (half-life 1.7 hr at -14.9°).

The successful isolation of a derivative of IX was also reported in 1968 by an Israeli group.[25] Compound IX was also produced by the low temperature photolysis of various $(CH)_{10}$ compounds (particularly VIII and XII).[26]

B. Other $(CH)_{10}$ hydrocarbons

i) Tricyclo[5.3.0.0^{4,8}]deca-2,5,9-triene (XIII) and Tetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene (XIV)

Both compounds XIII and XIV have been obtained in photochemical reactions of various $(CH)_{10}$ compounds.[27] The structure of XIII was established beyond doubt in our laboratory by chemical and spectral means.[27c]

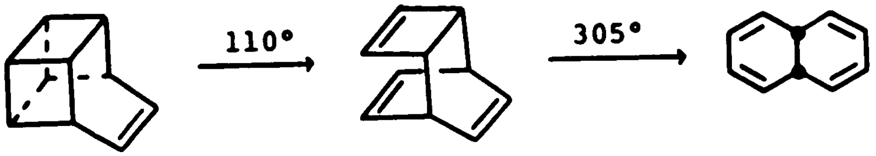


11

The structural assignment to XIV was outlined by Jones based on nmr spectroscopy.[27b] Both compounds isomerized readily to VII (reaction 11). The thermal rearrangement of tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene (isobullvalene) (XV) to XIII will be described later (see p. 68).

ii) Pentacyclo[4.2.2.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene (XVI), Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (XVII) and Tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene (XVIII)

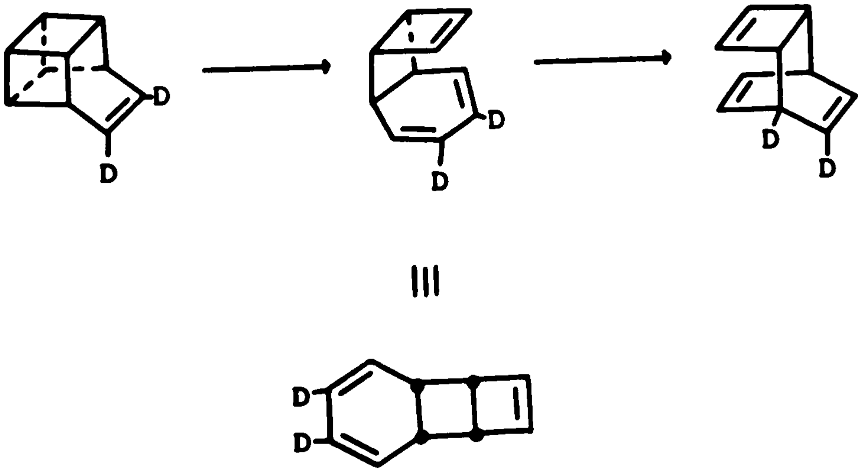
In 1966, pentacyclic hydrocarbon XVI (basketene) was independently synthesized both by Masamune and coworkers and by Dauben and coworkers.[28a,b] XVI underwent a clean unimolecular rearrangement at 110° ($\tau_{1/2}$ = 34 min) to "Nenitzescu's hydrocarbon" (XVII),[29] which in turn, isomerized to VII at 305° (reaction 12).[16]



XVI XVII VII

12

The reaction (XVI → XVII) was studied by deuterium labelling experiments.[30] The reaction did not involve a simple bond cleavage to give XVII, but instead proceeded in two steps involving a new intermediate (XVIII).



XVIII

13

This proposal was supported by the recent successful chemical synthesis of XVIII by Vedejs.[31] XVIII indeed isomerized to XVII at 70° ($\tau_{1/2}$ = 28 min).

Many of the thermal and photochemical interconversions among $(CH)_{10}$ isomers have been illustrated in the foregoing paragraphs. In general, photochemical reactions provide complex photo-products even at temperatures low enough to quench thermolysis of any thermo-labile species that may be involved. In contrast, most thermal reactions of $(CH)_{10}$ compounds are clean unimolecular reactions. A survey of the thermal interconversion of $(CH)_{10}$ compounds is summarized in Fig. 1.

In this thesis, the synthesis and physical and chemical properties of two [10]annulenes (II and III) is presented. Studies extending to the nine-membered conjugated monocyclic systems are also included.

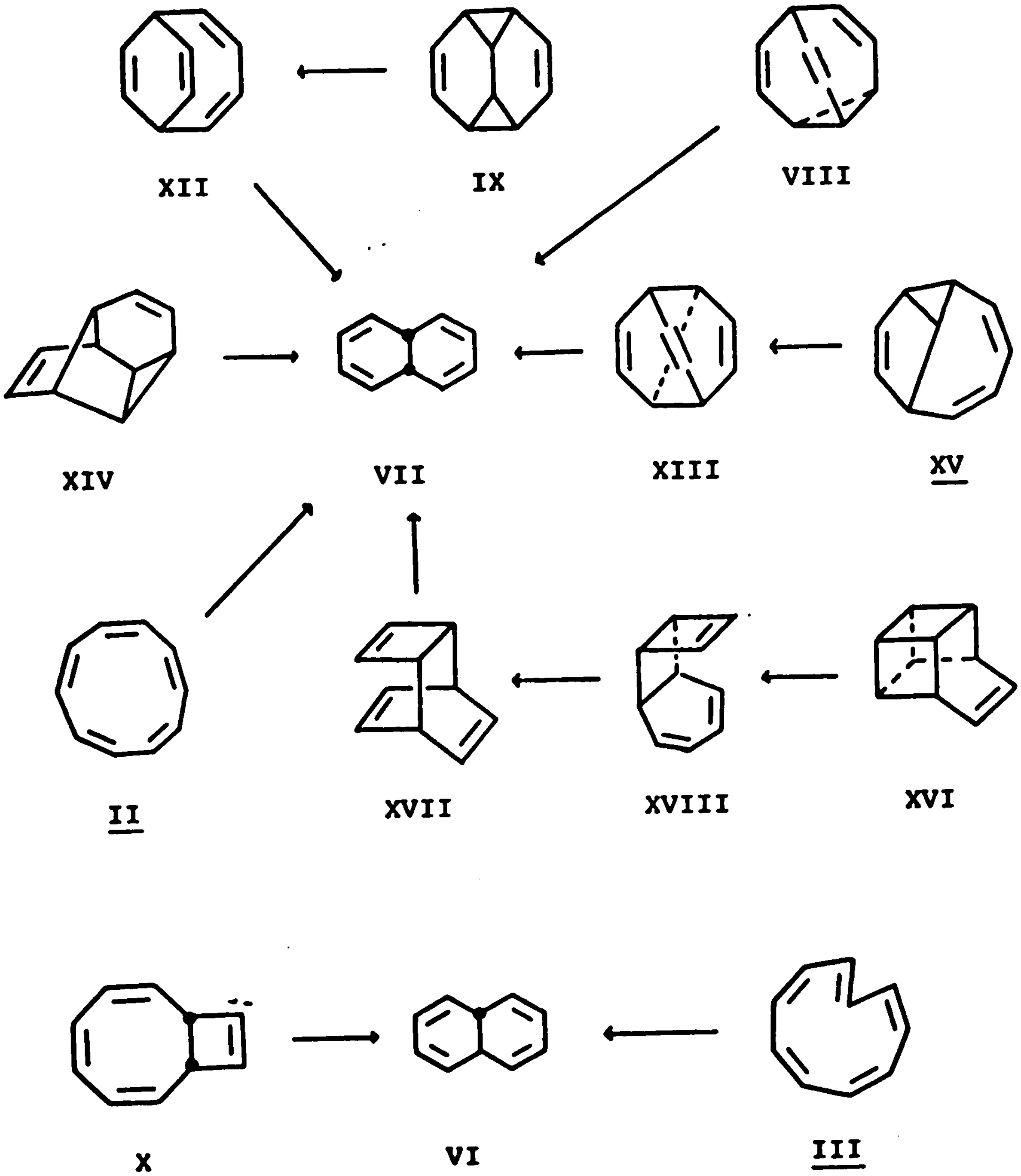


Figure 1: Thermal isomerization of $(CH)_{10}$ compounds. The compounds with underlined numbers are those which are described in this thesis.

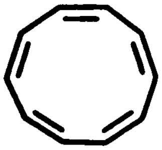
CHAPTER 2

RESULTS AND DISCUSSION

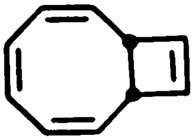
[10]Annulenes

i) Synthesis of [10]annulenes (II and III)

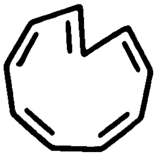
Our entry into the area of [10]annulene chemistry was initiated by the synthesis of one of the most promising valence isomers of [10]annulene. Bicyclo-[6.2.0]deca-2,4,6,9-tetraene (X) which possesses a cyclobutene unit, would be expected to undergo ring-opening readily by either thermal or photochemical means. Woodward-Hoffmann selection rules[32] permit evaluation of possible reaction processes pertinent to this system.



II



X

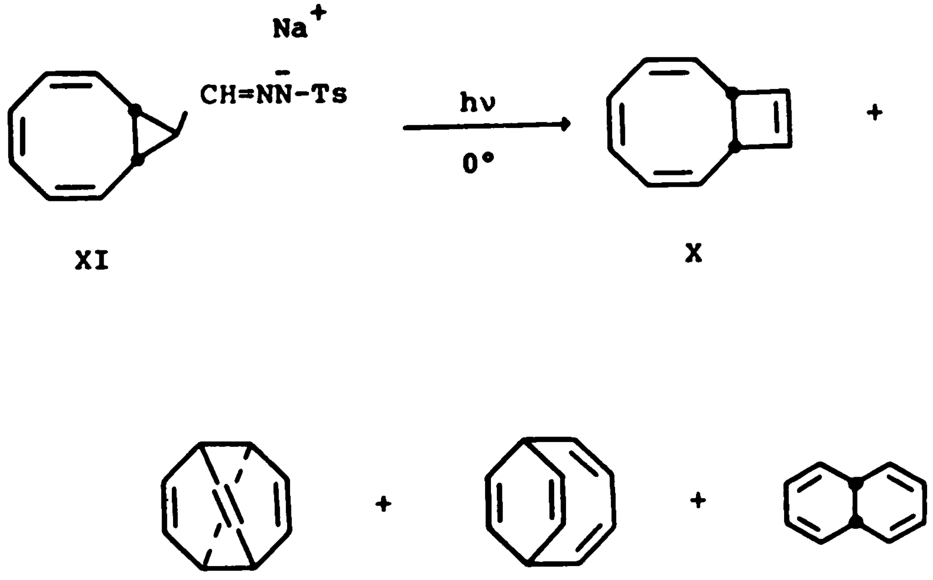


III

For instance, the molecular orbitals of X can be correlated with those of planar (cis)^5-[10]annulene (II) (σ-symmetry) in their excited states. Thus disrotatory ring-opening of X to II is predicted to be a photolytic process. On the other hand, compound X may undergo thermally-induced conrotatory ring-opening to provide trans,(cis)^4-[10]annulene (III).

The initial work performed mainly by R. Seidner in our laboratory[19] is essential to the present work and is described in some detail.

The photolytic decomposition of the sodium salt of bicyclo[6.1.0]nona-2,4,6-triene-trans-9-carboxaldehyde tosylhydrazone (XI) was carried out at 0° (reaction 14). Isolation and purification of the desired material was achieved by fractional distillation and alumina chromatography.



XI X

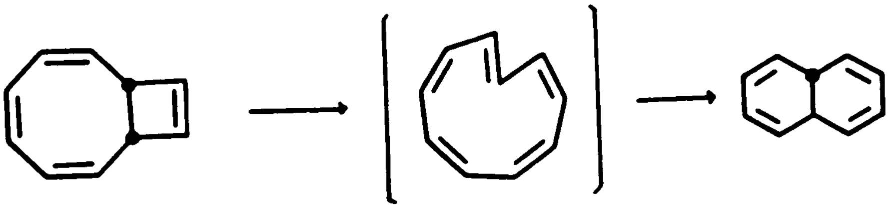
14

XIII XII VII

An nmr spectrum of one of two then unknown $(CH)_{10}$ compounds X formed in this reaction showed a sharp singlet at τ 3.98 (2 H) characteristic of the olefinic signal of symmetrically substituted cyclobutenes, a broad singlet at τ 6.32 ascribed to two allylic protons, and other olefinic signals (6 H) at τ 4.1-4.3. The other spectral data (mass spectrum and uv) were compatible with the structure X. This assignment was confirmed by hydrogenation to the perhydro-compound identical in every respect with authentic bicyclo[6.2.0]decane, independently synthesized by two different routes.

An nmr spectrum of the other new $(CH)_{10}$ compound was compatible with structure XIII and a definite structural proof was provided by chemical means.[27c]

Compound X was found to isomerize to VI at 70° ($\tau_{1/2}$ = 67 min). A tentative rationalization for this reaction was offered as follows (reaction 15):



15

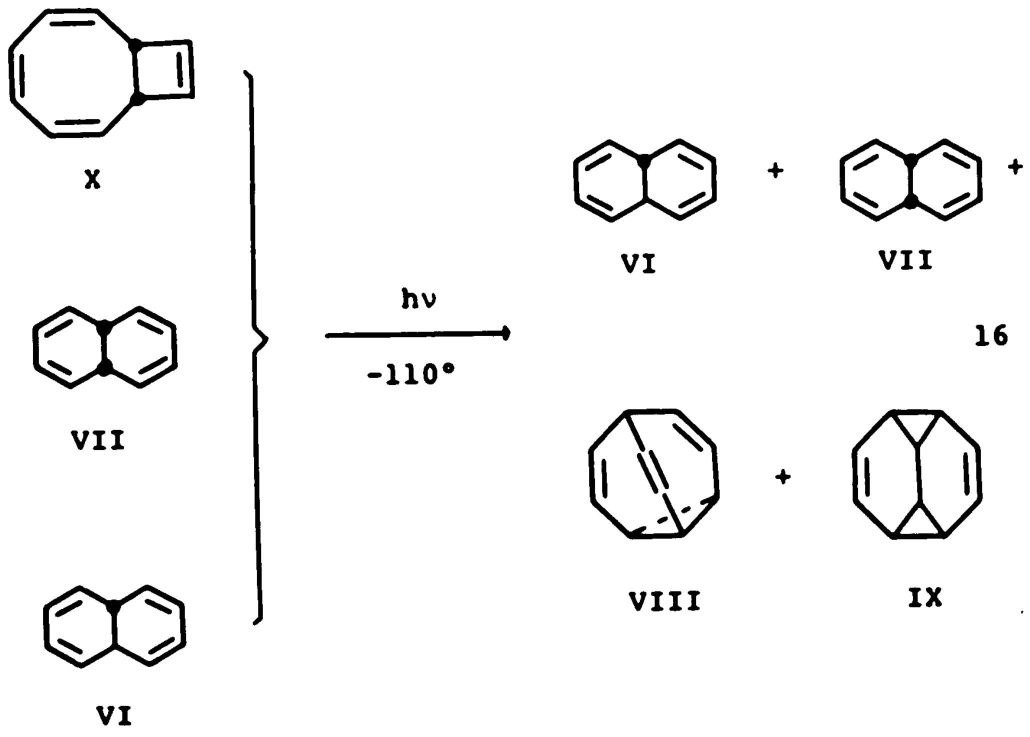
X III VI

The conrotatory ring-opening of the cyclobutene unit produced *trans*,(*cis*)^4-[10]annulene (III) as an intermediate, which in turn cyclized in a disrotatory manner to give VI.

Subsequently, extensive photochemical reactions of X were performed in order to detect [10]annulenes. The photolysis procedure was refined at this stage in order to handle and detect thermally unstable compounds. The photo-apparatus was a quartz nmr tube placed in an accurately temperature-controlled quartz jacket.

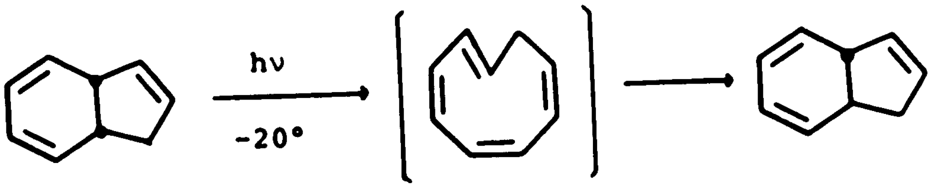
A spiral type low-pressure lamp and a cylindrical mirror surrounding this apparatus proved adequate for the delicate photolytical experiment. The detailed description of this apparatus has been illustrated previously.[19]

Irradiation of X, VII, or VI at -110° (conducted by R. Seidner) produced a similar equilibrium mixture of VI, VII, VIII, and IX in each case (reaction 16). A thermo-labile species IX was obtained as a major component (60-65%).



The presence of VI (15-20%) and VII (5-10%) in the equilibrium mixture, and the formation of IX from VI, X, and VII were noteworthy. The involvement of [10]annulenes as photochemically or thermally unstable species in this system was very likely and would rationalize these observations. However, careful monitoring of the photolysis of X, VII, and VI from the begining to the stationary state did not provide any evidence for any compounds other than those mentioned above.

In connection with the results described above, work on C_9H_{10} hydrocarbons reported by Vogel and co-workers in 1965[33] attracted our particular attention. They described a low temperature (-20°) photolysis of cis-bicyclo[4.3.0]nonatriene (XIX) that produced trans-bicyclo[4.3.0]nonatriene (XX) as a major product (reaction 17).



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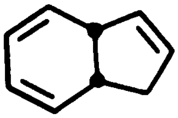
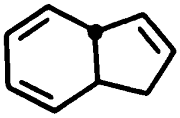
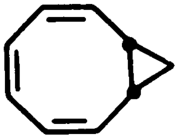
Their attempt to isolate the anticipated precursor of XX, trans,(cis)^3-cyclononatetraene (XXI), was unsuccessful. In order to elucidate the photochemical behavior of C_9H_{10} compounds and to compare the results with those of $(CH)_{10}$ compounds, experiments with a series of C_9H_{10} compounds (XIX, XX, XXII, and XXIII) were performed.[34] The details of these experiments will be discussed later (p. 72).



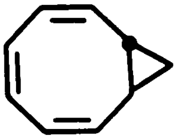
XIX



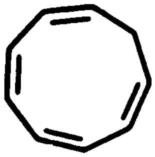
XX



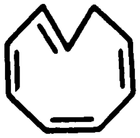
XXII



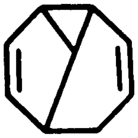
XXIII



XXV



XXI



XXIV

The major feature of this work is summarized below: (i) Irradiation (2537 A) of XIX, XXII, and XXIII at -60° produced a photo-stationary state in which a mixture of similar composition (XIX, XX, XXII, XXIII, and XXIV) was observed by glpc analysis in all three cases, whereas irradiation of XX produced XXIV exclusively. (ii) Hydrogenation of the cold reaction mixture produced cyclononane (20-28%). (iii) Isolation and structural assignment of two cyclononane precursors, (*cis*)^4-cyclononatetraene (XXV) and *trans*,(*cis*)^3-cyclononatetraene (XXI), was achieved. These results suggested the involvement of interconversions of cyclononatetraenes (XXI $\rightleftarrows$ XXV) in these photolyses and later experiments demonstrated that these processes indeed were playing an important role (see p. 94 for detailed discussions).

The low temperature hydrogenation procedure utilizing rhodium-catalysis developed in our laboratory allowed the detection of unstable species such as XXI and XXV. This hydrogenation proceeded at a reasonable rate at low temperature; for instance, cyclodecene can be hydrogenated at -80° (half-life of *ca.* 55 min).[19]

From the observations noted in the photochemical behavior of C_9H_{10} compounds and from the close similarity of these reactions to those of $(CH)_{10}$ compounds, it seemed certain that monocyclic $(CH)_{10}$ compounds, [10]annulenes, would very probably be formed during the irradiation of X, VII, and VI. Reexamination[35] of these reactions (reaction 16) at various temperatures (-60°, -110°, and -190°) revealed that the reaction progress was strongly dependent on the temperature and that new thermo-labile species were formed by irradiation at -60°, where no thermolyses of these species were taking place.[19] Of the three starting materials employed, only VII produced a noticeable amount (5-10%) of the new species. Removal of IX by crystallization, and subsequent hydrogenation of the mother liquors enriched in the new species produced cyclodecane.[19] The most reasonable precursors of cyclodecane were obviously [10]annulenes.

At this point our efforts were directed at the isolation of the pure [10]annulenes. In this way, and this way only, could the properties of these compounds be fully studied.

Special devices were designed for this purpose. All required operations had to be conducted at about -80° in order to separate compounds whose energy barrier for thermolysis was approximated to be 15 kcal/mole. A special column chromatography apparatus designed for this purpose is shown in Fig. 2. The column support was immersed in a vacuum sealed glass vessel which contained a dry ice–acetone mixture. At the bottom, the column was connected to glass jointed capillaries of different sizes and lengths in order that the rate of the elution could be controlled. The receiver was usually a 50- or 100-ml round bottom flask which was also cooled by a dry ice–acetone mixture. Into the space surrounding the capillary and inside the flask, a cold nitrogen flow from a copper heat-exchange coil immersed in liquid nitrogen was introduced during the whole operation.

The choice of quantity and activity of aluminum oxide (neutral) used in the chromatography was important to maximize separation of the desired material and minimize the loss due to permanent adsorption on alumina. Purified n-pentane containing a small amount (0.5-5%) of methylene chloride was employed as the moving phase.

Successful isolation and purification was also strongly dependent upon the purity of the starting

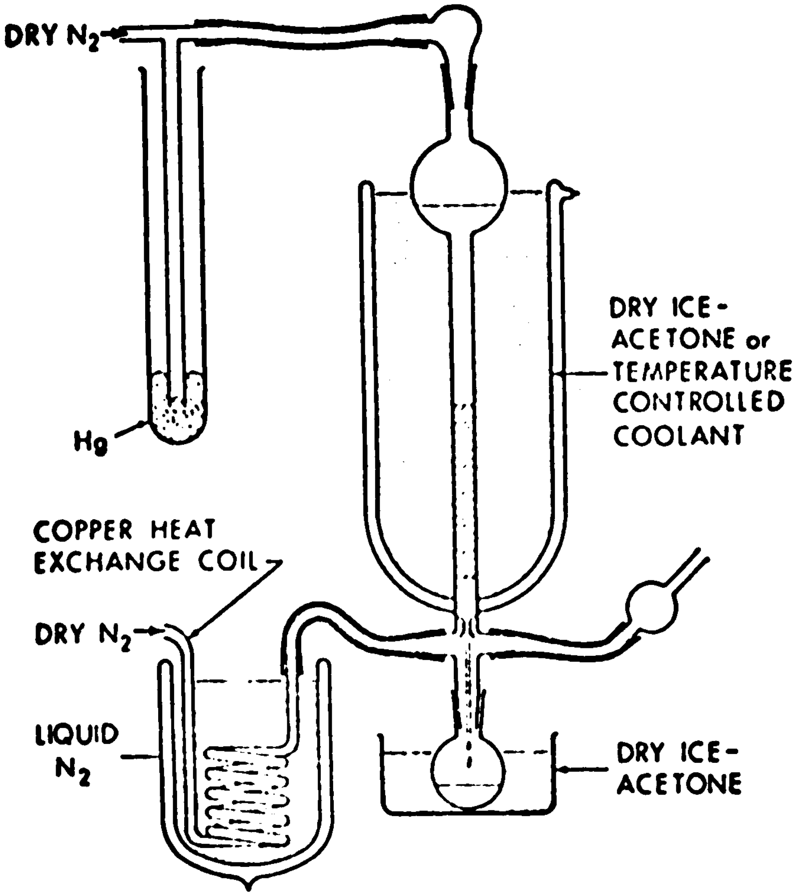


Figure 2: Low temperature chromatography apparatus

material. VII was prepared by careful pyrolysis (flow system, 410°) of XII. This method was found to be superior to the pyrolysis of VIII as a source of VII, since large amounts of thermal products of VII accompanied the latter pyrolysis (500°). Compound XII was readily available from the reaction of VIII with mercuric bromide reported recently by Shröder and coworkers.[23]

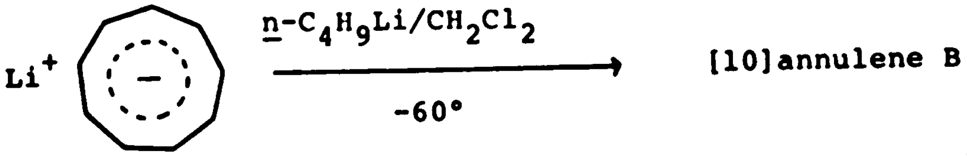
Storage of VII in a dilute solution was also necessary to prevent intermolecular reactions (reaction 3). The yield of the desired material was also found to be dependent on the concentration of starting material in solution.

After examination of various photolytic conditions, irradiation (2537 A) of a concentrated (2 M) solution of VII in tetrahydrofuran was performed on a preparative scale at -60°. The photo-assembly for this purpose has previously been described.[19] A quartz tube containing the sample was irradiated in a Dewar-type quartz cell. The inside cell was filled by purified <u>n</u>-pentane and the temperature was maintained by a copper heat-exchange coil in which temperature controlled coolant (methanol, -70°) was circulated. Irradiation by a low-pressure spiral type lamp was continued for

5 hr. The solution was then cooled to -80° overnight, and the crystalline precipitate (consisting of VIII and IX) was removed by drawing off the mother liquor with a pre-cooled pipette. The mother liquor, now enriched in desired materials, contained ca. 10% and 20% of [10]annulenes (A and B) together with approximately 55% of VII and a small amount of VI and IX (nmr and glpc analysis). This mixture was then subjected to the low temperature alumina chromatography on aluminum oxide (Woelm, neutral, 1.5 wt % of water). Each fraction was examined by glpc trace (90°) and nmr spectroscopy (-60°). The separation of [10]annulene B from other photo-products was readily achieved by three consecutive chromatographic separations. The fraction containing a mixture of only [10]annulene A (20%) and VII (80%) was also readily obtained at an earlier stage.

The final separation of compound A from VII was rather tedious and inefficient because of poor separation under these chromatographic conditions. Various methods were tried in vain to improve this process including the use of silver nitrate both mixed with the alumina, or dissolved in solution. By repeating the chromatography and by circulating the fractions containing substantial amounts of A, the concentration of A in the mixture was gradually increased, and finally an amount of A large enough for spectroscopic measurements (uv and nmr) was obtained. The nmr spectra of these annulenes are reproduced in Fig. 3 and Fig. 4.

In addition to this photochemical synthesis of [10]annulenes, another preparative route to B was achieved by a chemical reaction. Treatment of cyclononatetraenide in ether with methylene chloride and n-butyllithium at -60° afforded a ca. 15% yield of B (reaction 18):[26,36]



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IV

Separation and purification of the desired material B from the reaction mixture was achieved by low temperature alumina chromatography in a manner similar to that described above. The details of this part will be discussed later.

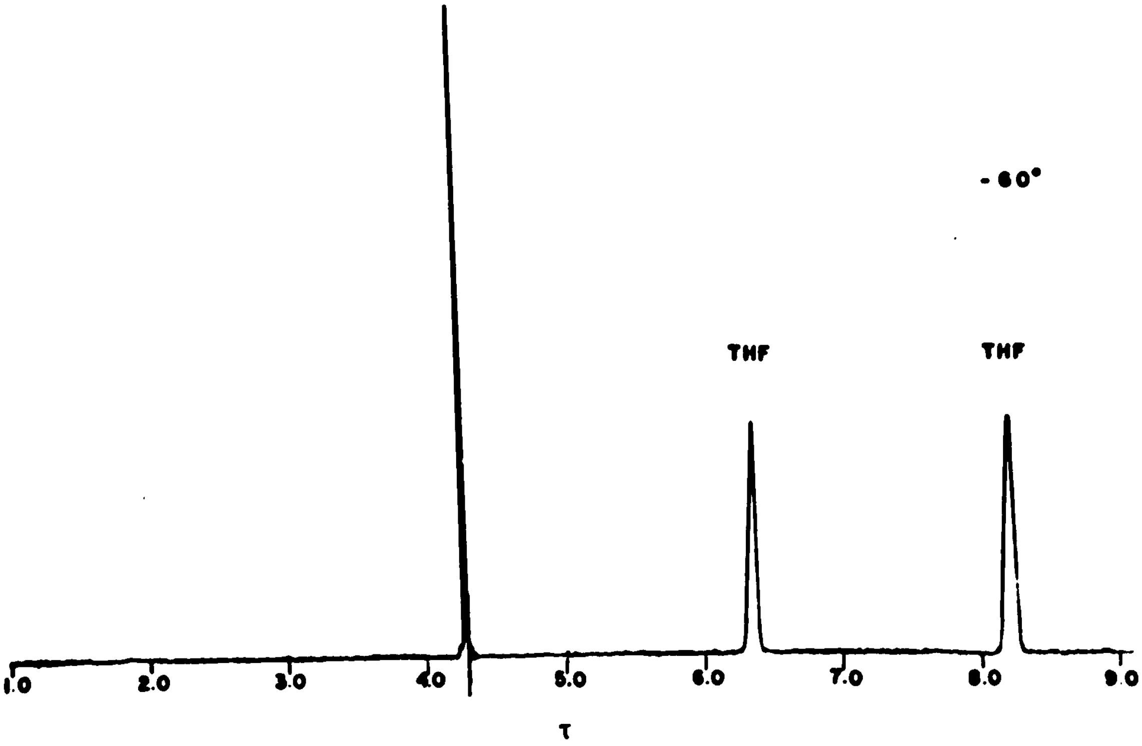


Figure 3: Nmr spectrum of A (II) measured at -60° in d_8-THF (100 MHz)

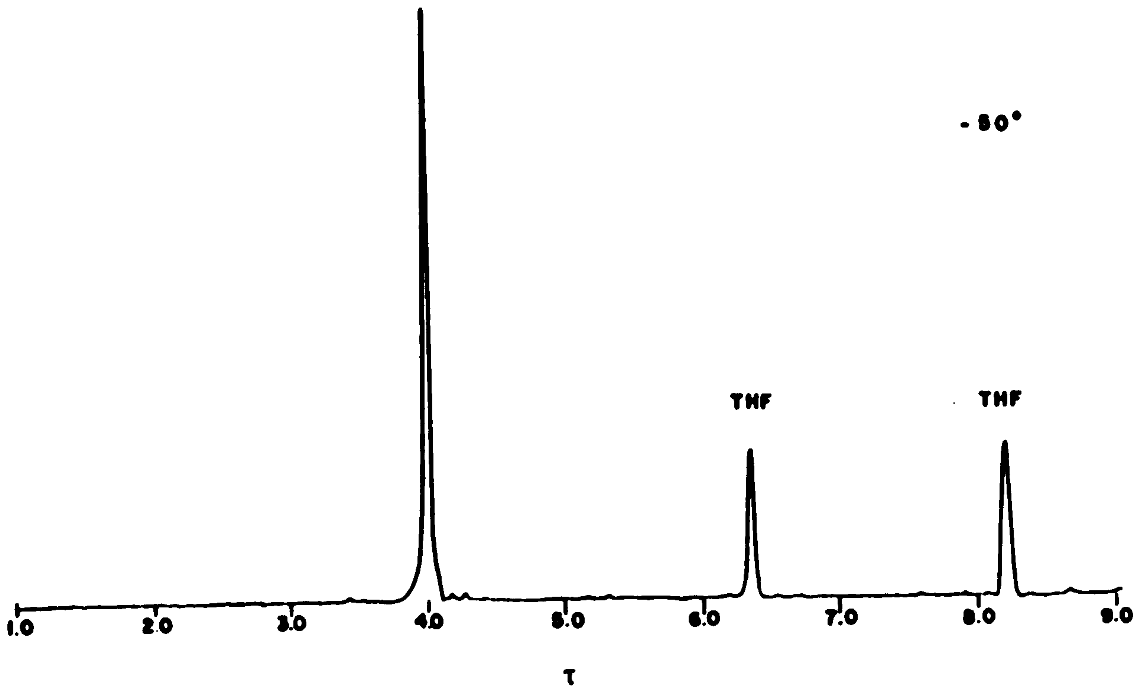
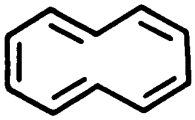


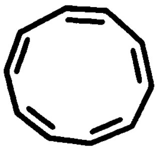
Figure 4: Nmr spectrum of B (III) measured at -50° in d_8-THF (100 MHz)

ii) Physical properties and geometry of [10]annulenes

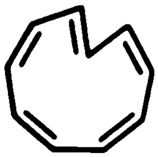
In the previous section, the synthesis of two [10]annulenes, A and B, was described. In this section, physical properties and the structural assignment of these annulenes will be discussed. Of eight possible combinations of cis and/or trans double bonds for [10]annulenes, only three (I, II, and III) are structurally possible.



I



II



III

That [10]annulenes A and B have the (cis)^5- and trans, (cis)^4-structurea, respectively, has now been confirmed by spectral and chemical data.

(1) Assignment of the $(cis)^5$-[10]annulene structure to A

Upon thermolysis compound A quantitatively isomerized to cis-9,10-dihydronaphthalene (VII) as shown by the uv (*vide infra*) and nmr spectroscopy. The kinetics of this process will be presented later. Application of Woodward-Hoffmann selection rules[32] to the present system eliminates structure III for A.

As was shown previously (Fig. 3), a proton nmr spectrum of A exhibited a sharp singlet at τ 4.20 in d_8-THF. The signal did not show any appreciable changes between -20° and -160° in d_8-THF–$(CD_3)_2O$ (1:1). The half-height line width of the signal remained constant ($W_{1/2}$ = 0.6 Hz) within this temperature range.

A proton decoupled ^{13}C nmr spectrum of A measured at -90° in d_8-THF (Fig. 5A) showed a sharp singlet at 2950 Hz (130.4 ppm, 22.34 MHz) from TMS [cf. cyclooctatetraene (132.0 ppm)] and again the signal was found to be temperature-invariant over a range of -40° to -160° in d_8-THF–$(CD_3)_2O$ (1:1). Even proton coupled ($J_{^{13}C-H}$ = 158 Hz) spectra were virtually temperature independent over a range -40° to -100° (Fig. 5B).

The equivalence of all nuclei (H or C) strongly suggests structure II for compound A, and further

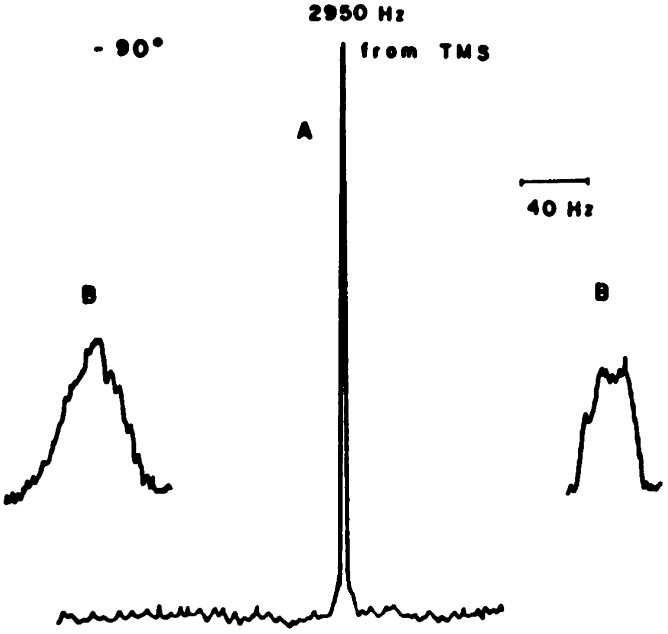


Figure 5: ^{13}C nmr spectrum (22.34 MHz) of A (II) in d_8-THF measured at -90°. 5A indicates a proton decoupled spectrum and 5B a proton coupled spectrum, respectively.

demands either planarity of the molecule or a low energy barrier (presumably less than 5 kcal/mole) for a process averaging the magnetic environments of the nuclei. The former possibility is excluded mainly from the spectral data; that is, the proton chemical shift value and the uv spectrum of this compound. Planar [10]annulenes are predicted to show aromatic properties according to Hückel's rule. Currently the most common criterion for aromaticity is the presence of an induced diamagnetic ring current indicated by the chemical shift values of proton nmr spectroscopy. Any ring current would shift vinylic protons downfield to the "aromatic region".[38] Experimentally, as shown in Fig. 3, the nmr spectrum of A displays a resonance at τ 4.20, typical of olefinic protons, indicating the absence of a noticeable ring current.

The uv spectrum of this compound measured at -55° is shown in Fig. 6. The extinction coefficient of A was evaluated by thermal conversion of the spectral sample to <u>cis</u>-9,10-dihydronaphthalene (VII) (λ_{max} 245 nm, ε = 8100).[39] The uv spectrum of A exhibited absorption maxima at 235 nm (shoulder,

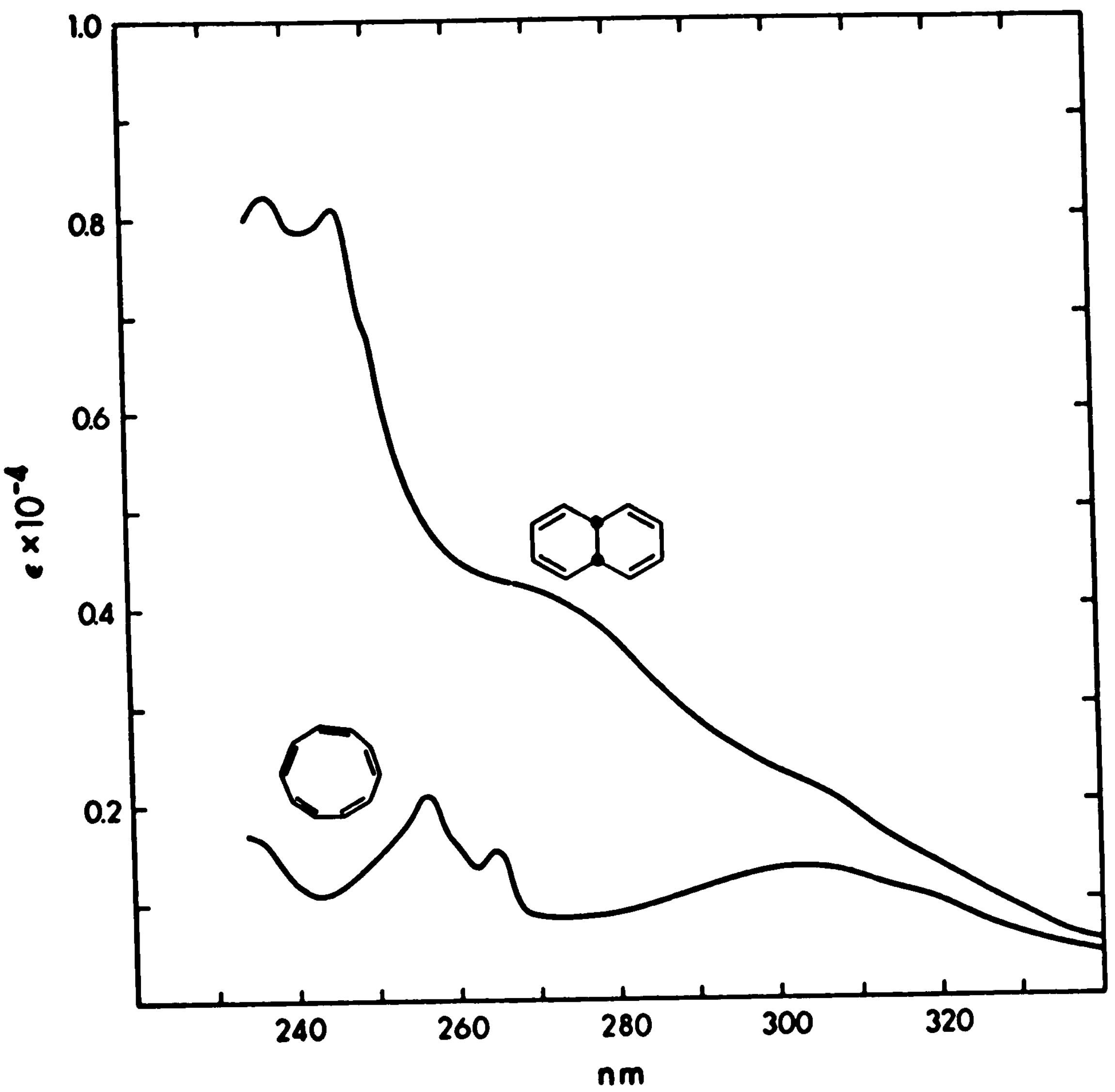


Figure 6: Uv spectrum of A (II) measured at -55° in methanol.

ε 1490), 256 (2040), 265 (1340), and 305 (1400).

The general spectral features of A are significantly different from those of 1,6-methano[10]annulene (V)[8a] and of cyclononatetraenide anion (IV),[6] and closely resemble those of (cis)[4]-cyclononatetraene (XXV), a typical cyclic polyene (see Fig. 14, p. 85). The weak intensities of absorptions suggest a lack of effective conjugation of double bonds in the molecule. From these spectral data, the planar structure for [10]annulene A is highly unlikely.

Inspection of a non-planar model of (cis)[5]-[10]annulene (II) (Fig. 7) constructed with slight distortion of normal bond angles reveals that the molecule exists in a conformation with a symmetry element (σ), and that the conformational change from IIA to IIB is achieved (through a low energy barrier) by pseudo-rotating two single bonds, in the manner indicated below. A sequence of similar processes (IIA to IIE) achieves the complete equivalence of all nuclei. This operation is reminiscent of the interconversion of twist-boat cylohexane conformers[40] and is quite different from that of cyclooctatetraene, which proceeds through a coplanar conformation.[41]

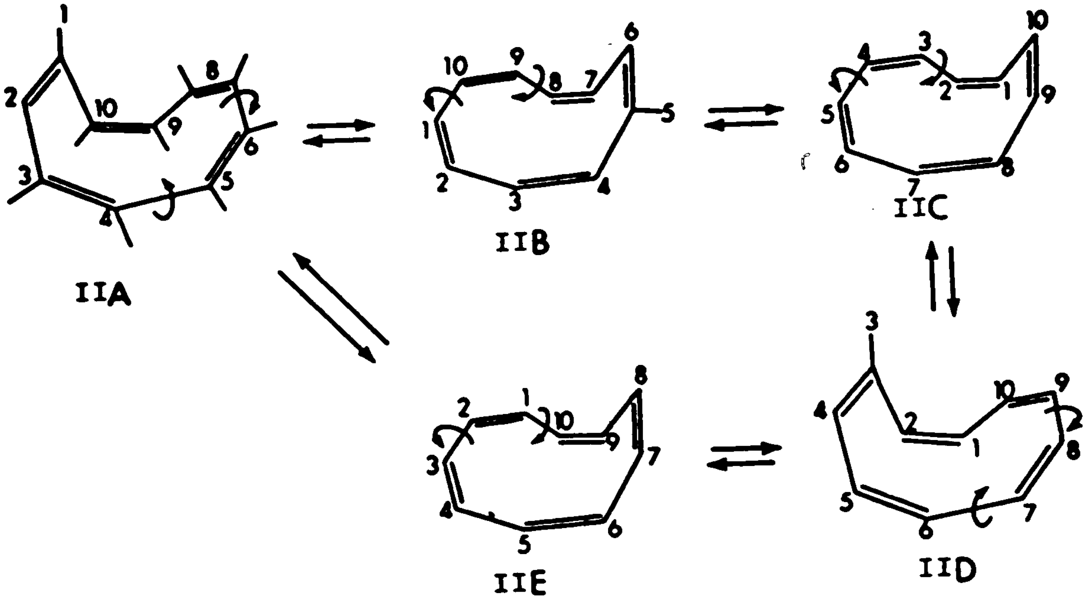


Figure 7: Conformational changes of II

Other possibilities such as ring inversion or shifting of single and double bonds are conceivable as processes by which the magnetic environment of the nuclei is averaged.* Both mechanisms demand a transition state close to planar geometry; accordingly these changes require energy barriers larger than that for conformational changes described above.

The possibility of bond shifts is best examined by looking for changes in coupling constants between ^{13}C and the two protons attached to adjacent carbon atoms. The proton coupled ^{13}C spectrum (Fig. 5B) shows no appreciable change of signals in the temperature range -40° to -100°. Two interpretations are feasible: (i) Bond shift processes are operating much faster than the nmr time scale even at -100°, or (ii) the processes

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* For instance, in cyclooctatetraene derivatives,[41] both processes are known to be operating with the activation energy, $\Delta G^{\ddagger}$ (for bond shift at -2°) = 17.1 kcal/mole and $\Delta G^{\ddagger}$ (for the ring inversion at -2°) = 14.8 kcal/mole, respectively.

are not taking place at all throughout the entire temperature range examined. The choice between the two is not possible at present. No experimental evidence has been secured regarding the possibility of ring inversion. The last two processes, bond shift and ring inversion, are not demanded at the present time to explain the total equivalence observed in the nmr spectra.

In summary, the observed chemical and physical properties of [10]annulene A are fully compatible with its structural assignment to non-planar $(\underline{cis})^5$-[10]annulene (II).

(2) Assignment of trans,$(\underline{cis})^4$-[10]annulene structure to B

Compound B isomerized quantitatively to trans-9,10-dihydronaphthalene (VI) upon thermolysis, which was shown by nmr and uv spectroscopy.

The uv spectrum of B measured at -55° in methanol is shown in Fig. 8. The extinction coefficient of B was estimated by thermal conversion of the spectral sample to VI. The reported ε value for VI

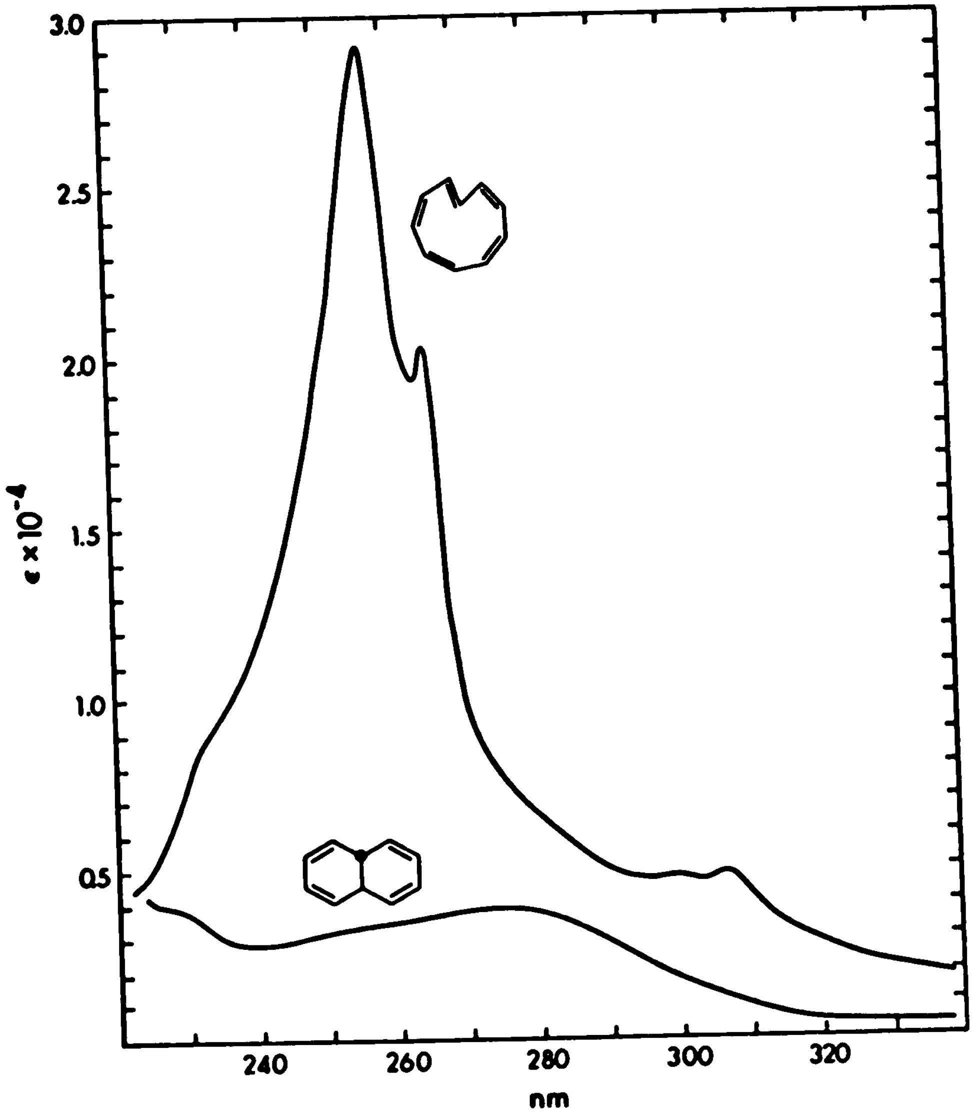

Figure 8: Uv spectrum of B (III) measured at -55° in methanol

(λ_{max} 276 nm, ε = 3850)[19] was employed. Compound B showed uv maxima at 257 nm ($\varepsilon = 2.9 \times 10^4$) and 265 ($2.0 \times 10^4$). The spectral features are dissimilar to those of methano[10]annulene (V) and rather close to those of trans,(cis)^3-cyclononatetraene (XXI) (see Fig. 16).

Application of selection rules[32] to the observed thermolysis of B to VI eliminates structure II for B. Of the remaining two structures, I is excluded based on two grounds: (i) as was noted previously (reaction 18) the reaction of lithium cyclononatetraenide (IV) with methylene cloride and n-butyllithium produced [10]annulene B. The formation of B from a nine-membered ring system with all cis-geometry suggests the structure with at least three consecutive cis-double bonds, i.e., compound III. (ii) the proton nmr spectrum of B displays a marked temperature dependence (fig. 9). A sharp singlet at τ 4.14 at -40° tends to broaden upon cooling. Below -80°, two major lines appear with gradual separation upon further cooling. Below -100°, separation of the two lines centered at τ 3.95 and 4.18 remains constant, thus indicating that dynamic processes are frozen at this temperature.

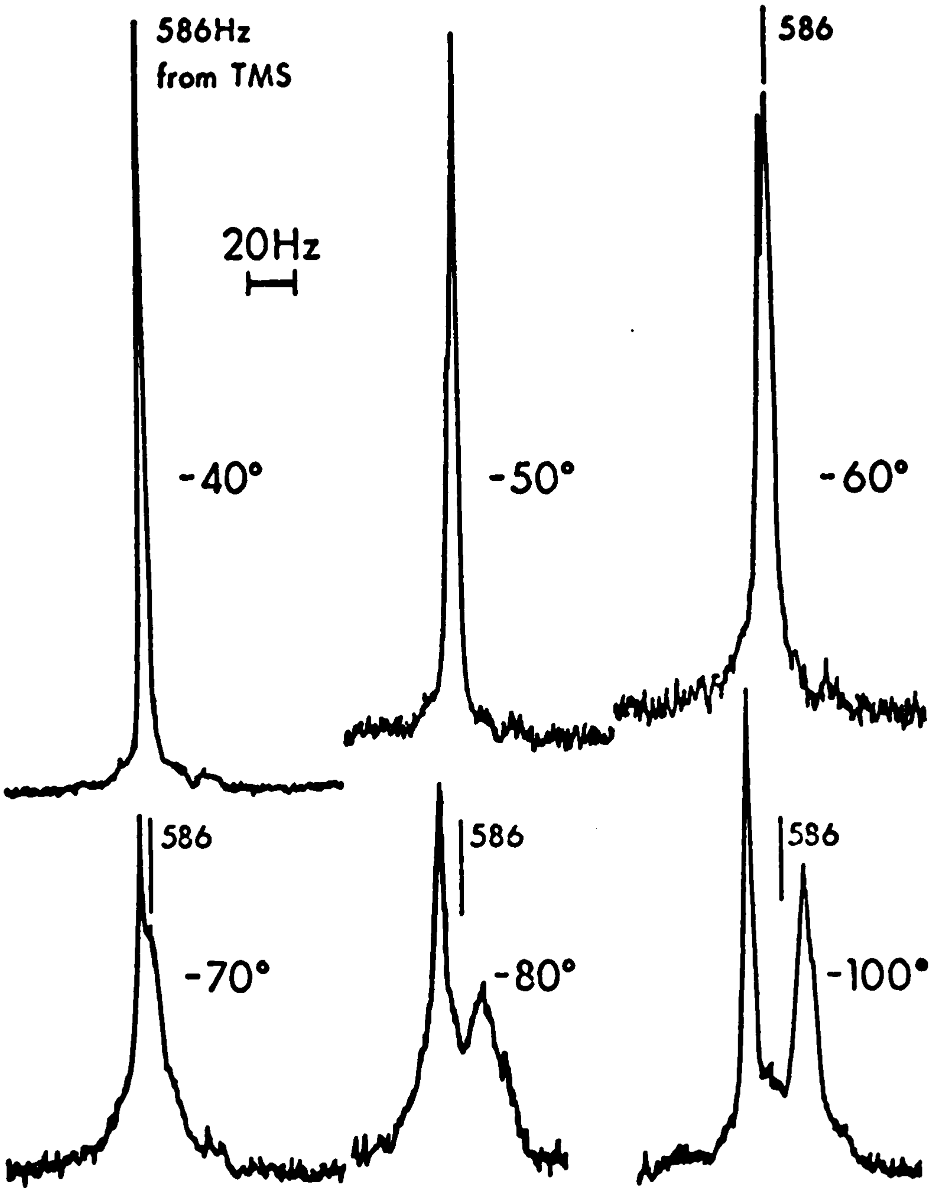

Figure 9: Temperature dependent ^{1}H nmr spectra of B (III) in 3-methylpentane-d_{14} (100 MHz)

Proton-decoupled ^{13}C spectra of B in d_8-THF show five different carbon signals of equal intensity at 2905, 2975, 2979, 2993, and 2998 Hz from TMS (22.63 MHz) at -100° (Fig. 10). The signals rapidly change upon warming and finally merge to a sharp singlet at 2970 Hz, 131.0 ppm (weighed averaged position) at -40°.* This indicates that all the nuclei achieve equivalence at this temperature. Therefore, there must exist a process which permits the migration of a "trans" double bond (or bonds) around the ring to achieve a cycle of the automerization.

Inspection of Dreiding models of III indicates that there exists a stable and puckered conformer (IIIA), which can be converted into a less stable and near-coplanar conformer (IIIA' or IIIA") through rotation a or b (Fig. 11). Bond migration (process c) is possible in these conformers retaining cis, trans, cis, cis, cis-geometry to IIIB" and IIIJ', which in turn are converted to IIIB and IIIJ by operation b and a respectively.

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* At this temperature, B (III) slowly isomerized to VI (see reaction 20).

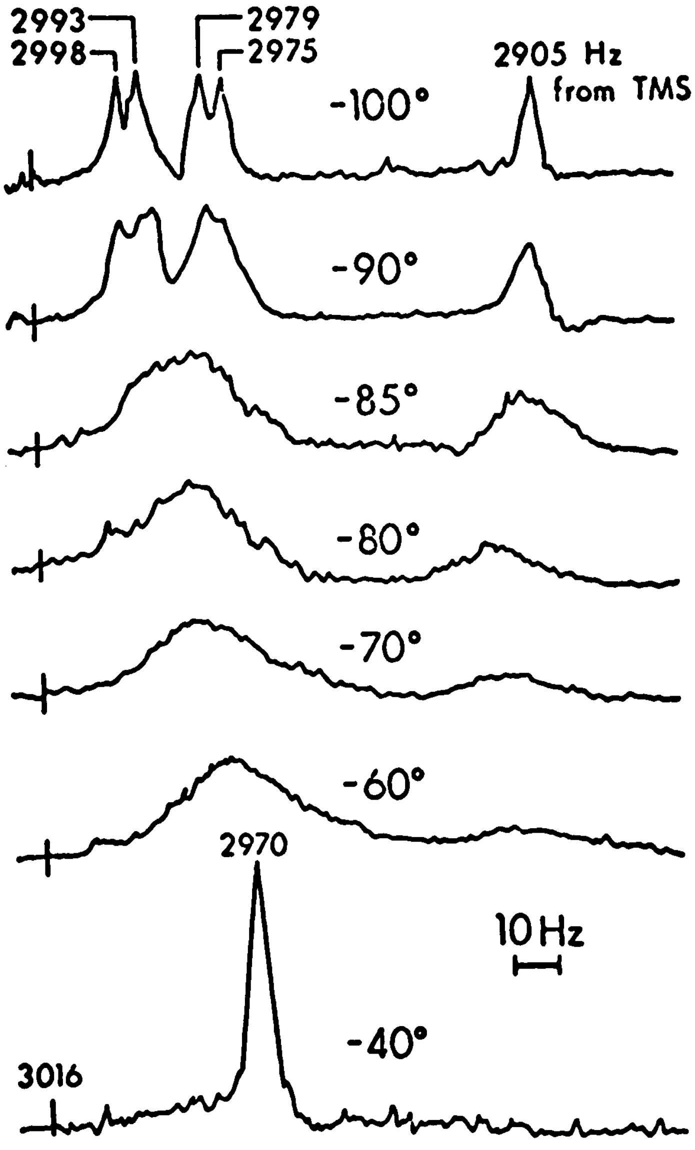


Figure 10: Temperature dependent ^{13}C nmr spectra of B (III) in d_8-THF (22.63 MHz)

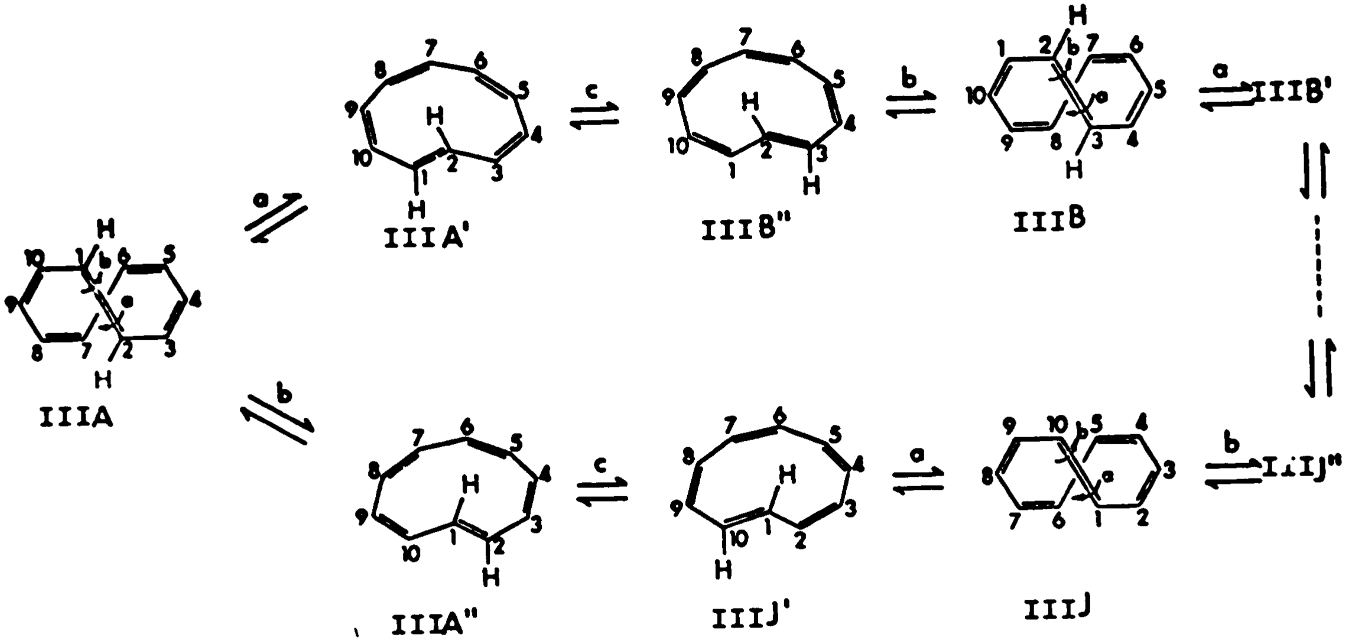
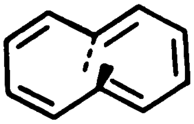


Figure 11: Bond migration of III

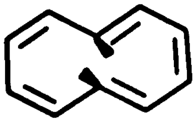
Thus the original 1,2-trans,(cis)^4-[10]annulene is now converted into 1,10-trans,(cis)^4- or 2,3-trans,(cis)^4-[10]annulene. Repeating the same operations through conformers similar to IIIA' or IIIA" (which are presumably close to a transition state of this automerization), one trans-double bond can rotate along the ring, all the nuclei (H or C) of the system ultimately achieving equivalence.

Comparison of ^{13}C spectra with those simulated on a computer (performed by Prof. D. L. Rabenstein) on the basis of the above mechanism supports the interpretation that only one process (transfer of one double bond to the next position) is responsible for the variation with temperature of the conformation of III. The activation enthalpy for this process is roughly estimated to be 10 kcal/mole.

On the other hand, inspection of molecular models of compound I reveals that in typical conformers Ia and Ib with trans and cis internal hydrogens, the van der Waals interactions between H-1 and H-6, and between the p-orbitals of C-1 and C-6 are expected to be enormously large, and thus these conformers may possibly exist only at a position close to the transition state on the reaction coordinate.

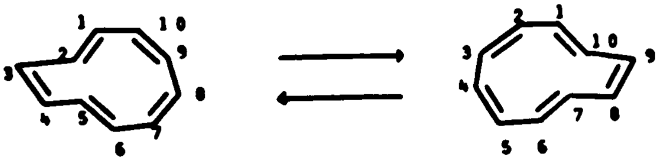


Ia

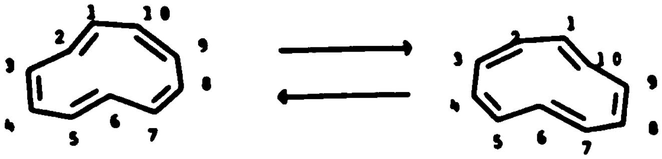


Ib

Only two kinds of slightly more stable conformers Ic and Id are feasible for this molecule. In these conformers, the reversible double bond shift at position 1,2 to 1,10 and at the same time 5,6 to 6,7 retaining trans, cis, trans, cis, cis-geometry is possible ($Ic \rightleftarrows Ic'$, $Id \rightleftarrows Id'$).



Ic   Ic'



Id   Id'

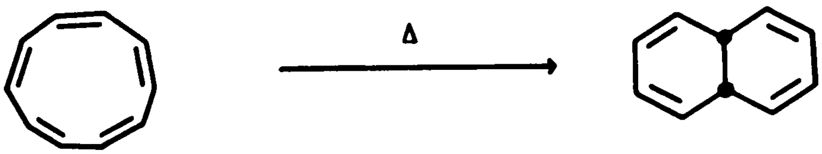
However, further migration of double bonds--for instance 1,10 to 10,9 and at the same time 6,7 to 5,6 and so on--retaining the configuration to achieve eventually total equivalence, is highly unlikely. Under these seemingly forced conditions, isomerization to bicyclic compounds would dominate the process. The structural assignment of B to compound III is thus assured.

It is interesting to speculate that a bond migration in annulenes, in general, takes place in a nearly planar transition state, all the while retaining the original geometry.

iii) Thermal reactions of [10]annulenes

As described previously, both [10]annulenes (II and III) are stable at low temperature (below -50°), and any geometrical isomerization of III to II does not take place between the temperatures -45° to -20°, where cyclization of III to VI begins. This behavior is quite similar to that observed with thermo-labile cyclic polyenes such as *trans*,(*cis*)^3-cyclononatetraene (XXI) (see reaction 37) and *trans*,(*cis*)^3-oxonin.[42] The energy barrier required for geometrical isomerization in these systems is apparently higher than that required for cyclization.

Compound II isomerized quantitatively to VII as was indicated by nmr and uv spectroscopy. The kinetic study of this thermal process was performed in an isothermal bath and analysed by nmr spectroscopy (at -50°, in d_6-acetone) at two different temperatures. Both the increase of VII (τ 4.35-4.65) and the decrease of II (τ 4.24) were measured simultaneously. The following kinetic parameters were obtained for this process (reaction 19):



19

II VII

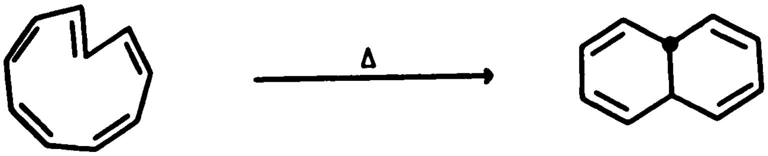
$$k_{-14.25 \pm 0.1} = (1.28 \pm 0.06) \times 10^{-5}\ \mathrm{sec}^{-1}$$

$$k_{6.2 \pm 0.1} = (2.43 \pm 0.02) \times 10^{-4}\ \mathrm{sec}^{-1}$$

$$\Delta H^{\ddagger} = 20.2 \pm 0.7\ \mathrm{kcal/mole}$$

$$\Delta S^{\ddagger} = -2.6 \pm 2.5\ \mathrm{eu}$$

Compound III was extremely thermally unstable and quantitatively isomerized to VI (reaction 20). Kinetic studies of III were again conducted in an isothermal bath. The production of VI (τ 7.2) was measured relative to the internal standard (CH_2Br_2, τ 4.7) at -60° (d_6-acetone, 100 MHz nmr spectroscopy). Treatment of the data provided the following kinetic parameters:



20

III VI

$$k_{-25.5 \pm 0.1} = (5.15 \pm 0.25) \times 10^{-4}\ \mathrm{sec}^{-1}$$

$$k_{-44.5 \pm 0.1} = (2.52 \pm 0.14) \times 10^{-5}\ \mathrm{sec}^{-1}$$

$$\Delta H^{\ddagger} = 17.4 \pm 0.6\ \mathrm{kcal/mole}$$

$$\Delta S^{\ddagger} = -3.0 \pm 2.5$$

These results indicate that III is far more unstable than the similar cyclic polyenes, trans,(cis)^3-cyclononatetraene (XXI), and aromatic trans-cyclononatetraenide (XXVI).* These results also show the lack of the resonance stabilization normally associated with an aromatic structure. Because of the observed instability of II and III, further chemical reactions were not attempted. However, it seems certain that these compounds could be expected to behave as monocyclic polyenes.

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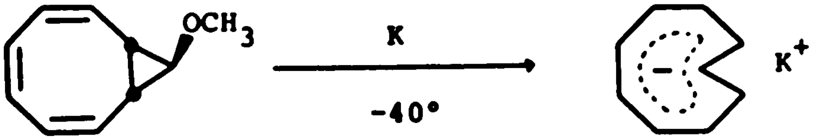
* Preparation of XXVI was reported recently by Boche and coworkers. Reaction of 9-methoxybicyclo[6.1.0]-nonatriene with potassium metal at -40° yielded XXVI (reaction 21).[43]

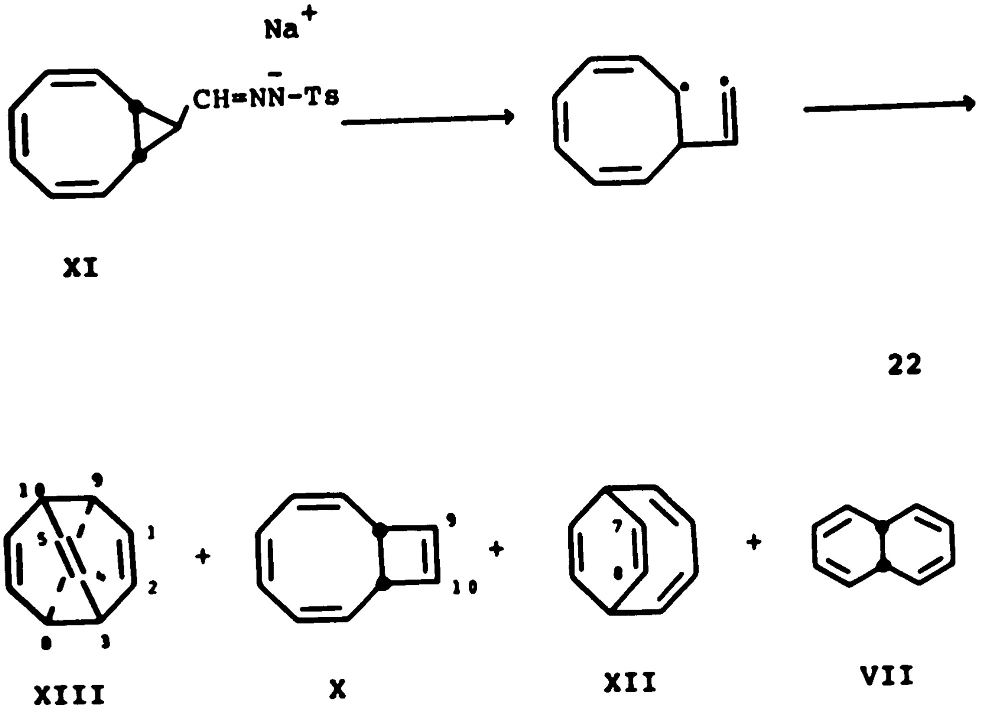


21

XXVI

Tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene

At an early stage of our work on the synthesis of [10]annulene, we were investigating the photolytic decomposition of sodium salt of tosylhydrazone XI. This reaction produced X, XII, VII, XIII, and cyclooctatetraene (see reaction 14). The explanation for the formation of these products from XI was offered as follows (reaction 22):[19,27c]



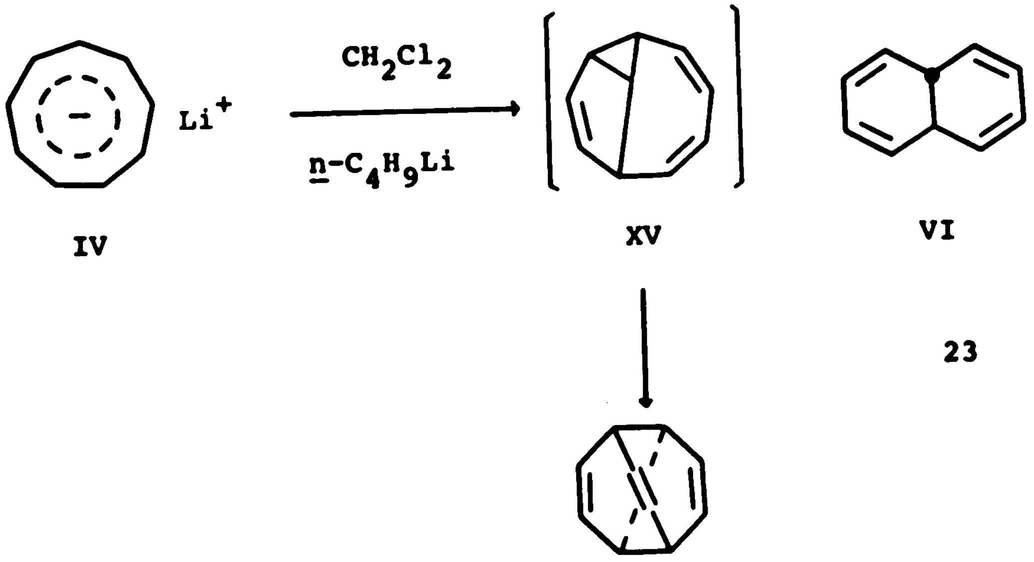
22

A cyclopropyl carbene generated photochemically underwent bond cleavage to a diradical species which led directly to the formation of cyclooctatetraene, X, and XII. Evidence to support this mechanism was provided by experiments utilizing specifically labelled XI.[17] Thus photolysis of 9,10-dideuteriotosylhydrazone (XI') yielded 9,10-deuterio-(X), and 7,8-deuterio-(XII).

As to the formation of XIII, the situation was not straightforward. In this molecule, deuterium atoms were incorporated in the olefinic (τ 3.32, H-2,6), allylic (τ 6.85, H-8,9), and diallylic (τ 7.53, H-3,10) positions, suggesting that XIII was formed after a complex bond reorganization. It was possible that compound XIII was not produced directly but rather formed by thermolysis of the initially generated unstable species. Indeed some indications of this possibility were observed during the investigation of the photochemical behavior of XII and bullvalene (VIII).[26]

In order to elucidate this point, the photochemical decomposition of XI and subsequent separation of the products were carefully performed at -30°. An nmr spectrum (measured at -50°) of the crude reaction mixture demonstrated the existence of a thermo-labile species which isomerized to XIII upon warming to 55° for 5 min.

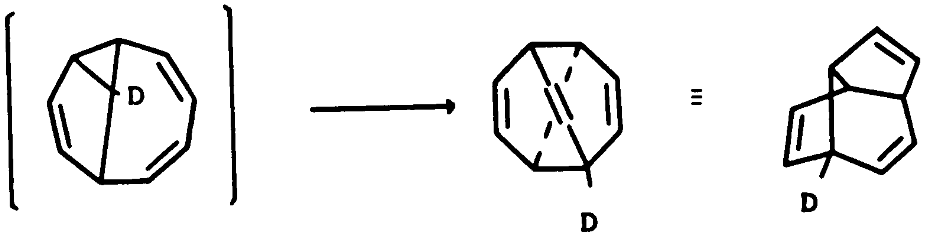
While we were involved in this problem, Katz and Cheung reported an entirely different reaction which produced XIII as a major product.[36a] In their experiment reaction of cyclononatetraenide with methylene chloride and n-butyllithium at low temperature, and subsequent work-up at room temperature provided compound XIII along with a small amount of VI (reaction 23):



23

XIII

They explained the formation of XIII by assuming that IV first provided a new intermediate, tricyclo-[5.3.0.0^{2,10}]deca-3,5,8-triene (XV) which in turn thermally rearranged to XIII. This interpretation was consistent with the fact that the same reaction utilizing CD_2Cl_2 gave hydrocarbon XIII' deuterated at position 1 (reaction 24):



XV'

XIII'

24

This result relates closely to our problem concerning the origin of XIII. In addition, formation of VI in this reaction would imply the possible existence of another thermo-labile species. Katz's experiments are comprised of four steps: (i) addition of methylene chloride to the cyclononatetraenide solution at -60°, (ii) addition of n-butyllithium at

-30° to -40°, (iii) reaction at room temperature overnight, and (iv) extraction and distillation.

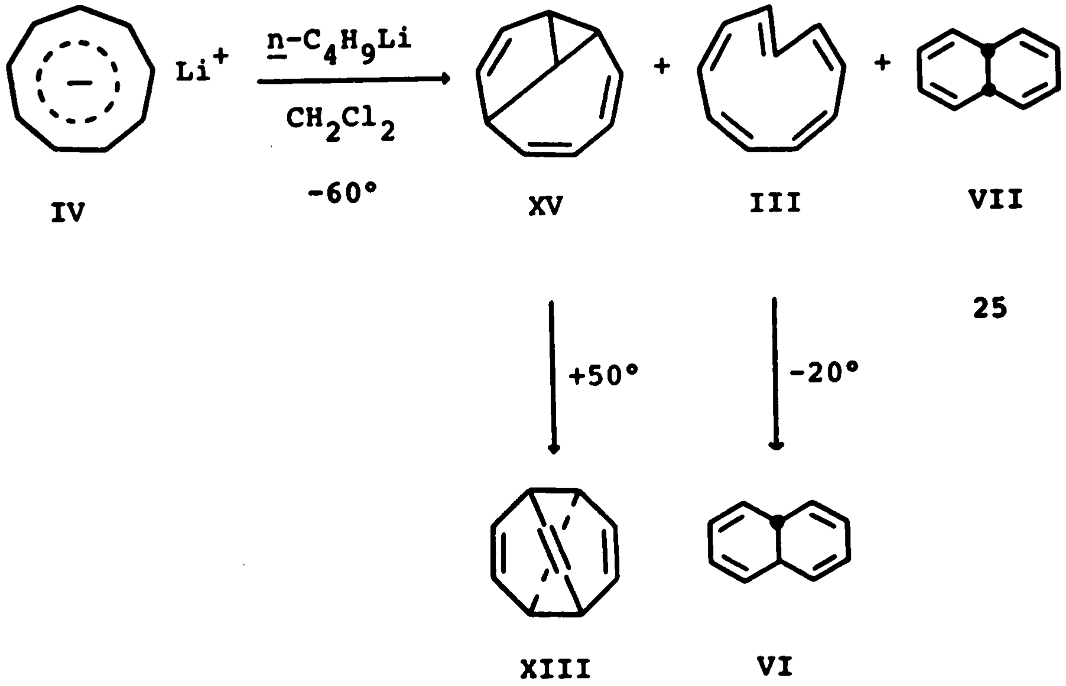
In a preliminary experiment, this reaction was repeated with special care to perform the reaction at as low temperature as possible. The glpc analysis, accompanied after step (i) and (ii), demonstrated that methylene chloride did not react with IV at -20° in 3 hr, but did react immediately upon addition of _n_-butyllithium in _n_-hexane. The reaction proceeded rapidly even at -60° and completed at the end of addition. The glpc analysis indicated the presence of XIII (65%), _trans_-9,10-dihydronaphthalene (VI, 15%), and _cis_-9,10-dihydronaphthalene (VII, 18%) in the reaction mixture. Each peak was identified by co-injection with authentic samples. It should be noted that the glpc analysis only indicates a relative ratio of various thermolysis products when the reaction mixture contains thermolabile species which isomerize inside the column (90°) or injection ports (120°).

The cold reaction mixture was decantated into a pre-cooled (-80°) flask and concentrated _in vacuo_. Extraction of the residue with cold _n_-pentane and concentration _in vacuo_ yielded a yellow liquid. All the operations were performed at -50° to -60°.

An nmr spectrum of this liquid (measured at -55°) in $CDCl_3$ demonstrated the existence of the new compound with complex signals in olefinic and aliphatic regions, in addition to the characteristic peak of VII (τ 6.3). In contrast to the glpc analysis of the same reaction mixture, none of the peaks due to XIII and VI were observed in the spectrum at this temperature.

When the sample was gradually warmed to -20° in the nmr probe, a peak attributable to VI (τ 7.2), appeared with a concomitant signal change at τ 4.0. Upon further warming to 30°, the characteristic signals of XIII emerged at the expense of the peaks due to a labile species, and the process was completed in 10 min at 55°. The nmr spectrum of the warmed sample consisted of XIII, VI, and VII with an approximate ratio of 65:15:18, in good agreement with the glpc analysis.

The precursor of VI was confirmed to be *trans*,(*cis*)^4-[10]annulene (III). Hydrogenation of the same cold reaction mixture gave cyclodecane (15%), *cis*-decalin (18%), and hydrogenation products of the new species (45%). By means of low temperature column chromatography [10]annulene III was isolated from this reaction mixture in a pure form; it displayed the same temperature dependent proton nmr spectra as those shown in Fig. 9.



The separation and purification of the precursor (XV) of XIII was achieved by repeated fractional distillations utilizing a cold finger at -13° <u>in vacuo</u>. The nmr spectrum of the new compound XV measured at -50° in $CDCl_3$ (Fig. 12) exhibited a complex multiplet at τ 3.8-4.5 (5 H), a doublet at τ 4.9 (1 H), a broad triplet at τ 6.3 (1 H), and a fine multiplet at τ 8.0-8.6 (3 H).

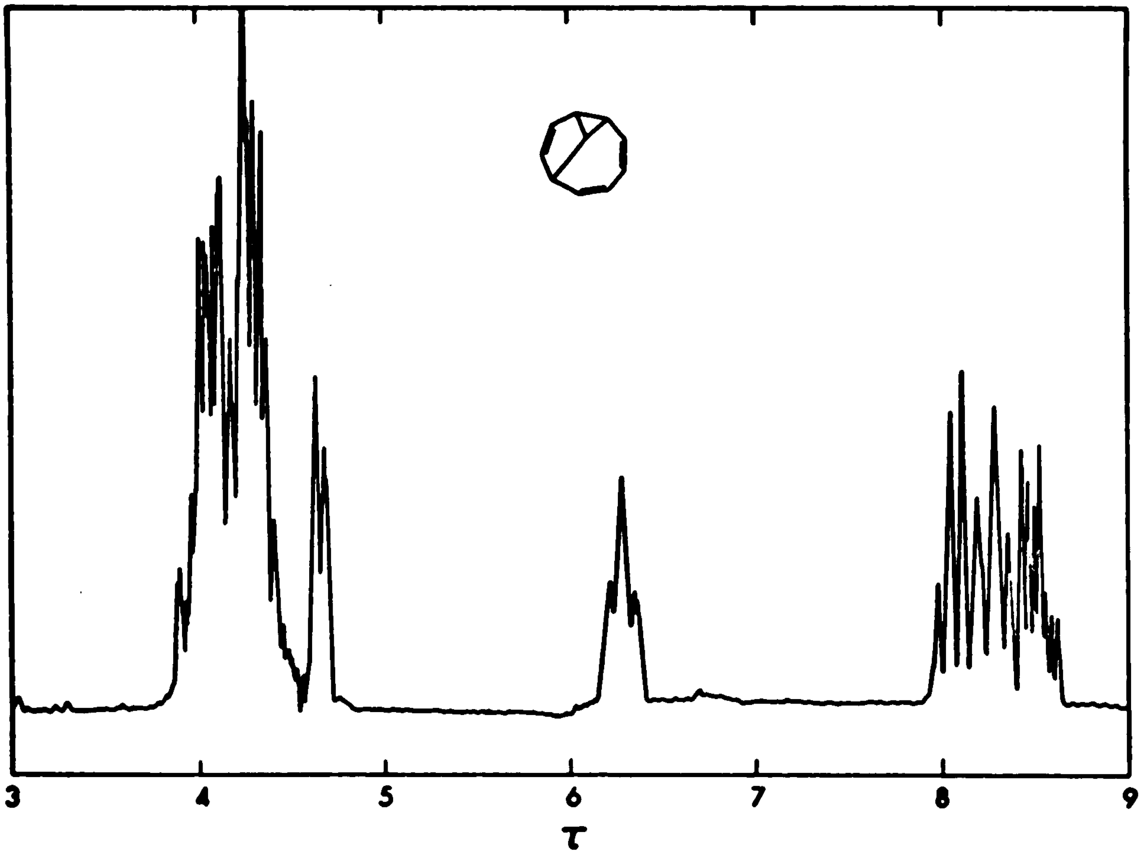
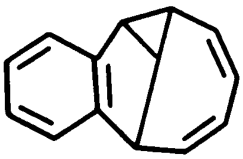
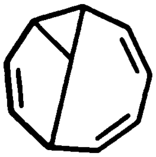


Figure 12: Nmr spectrum of XV measured at -50° in $CDCl_3$ (100 MHz)

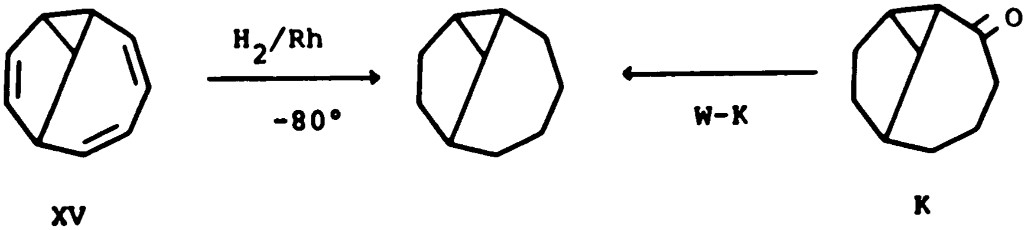
Decoupling experiments on this system did not simplify the complex multiplets at low and high fields.
The spectrum showed a pattern quite similar to that of 8,9-benztricyclo[5.3.0.$0^{2,10}$]deca-3,5,8-triene reported recently by Vedejs.[44]





XV

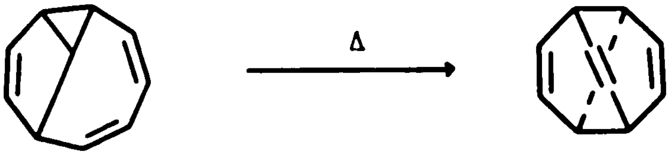
Hydrogenation of XV over rhodium carried out at -80° afforded three compounds. The major component (80%) of the hydrogenated products was found to be tricyclic ($\underline{m}/\underline{e}$ 136) and proved identical with authentic tricyclo[5.3.0.$0^{2,10}$]decane (nmr and mass spectroscopy, and glpc trace) prepared by the Wolf-Kishner reduction of the corresponding ketone K (reaction 26).[45]



26

Thus, the structure of the new compound was established as tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene (XV).

Compound XV isomerized quantitatively to XIII by the divinyl cyclopropane rearrangement as was shown by nmr spectroscopy. The kinetics of this reaction were examined. Samples in $CDCl_3$ were heated in an isothermal bath at two different temperatures and the increase of XIII (τ 3.3) relative to the internal standard ($CHCl_3$) was measured by nmr spectroscopy at -20°. The following kinetic parameters (first order) were calculated for this process (reaction 27):



27

XV XIII

$$k_{11.1} = (7.15 \pm 0.33) \times 10^{-5}\ \text{sec}^{-1}$$

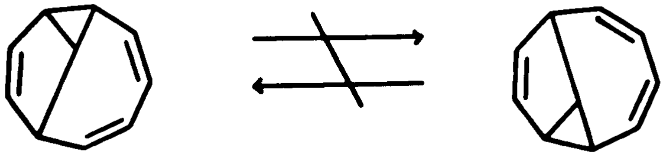
$$k_{30.8} = (6.90 \pm 0.15) \times 10^{-4}\ \text{sec}^{-1}$$

$$\Delta H^{\ddagger} = 19.2 \pm 0.8\ \text{kcal/mole}$$

$$\Delta S^{\ddagger} = -10.0 \pm 2.8$$

The activation energy observed for this process was smaller than that ($\Delta H^{*} = 22.3$ kcal/mole, $\Delta S^{*} = -1.8$ eu) for the rearrangement of a known model compound, <u>endo</u>-6-vinylbicyclo[3.1.0]hexa-2-ene.[46] Since no experimental errors were reported, it is rather difficult to assess these parameters in comparison with those observed for compound XV.

The possibility of a degenerate rearrangement of XV (reaction 28) was eliminated by nmr studies which showed no appreciable change of the signals over the temperature range -60° to +20°.

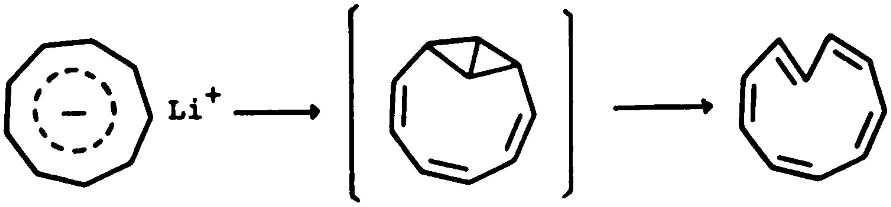


XV

28

Formation of III in reaction 25 is worthy of comment. Since formation of (<u>cis</u>)^5-[10]annulene (II) (which was stable at this reaction temperature) was not detected, III might possibly arise from a discrete intermediate which thermally isomerized uniquely to III. Compound XXVII is an attractive candidate for such an intermediate (reaction 29). The transformation from

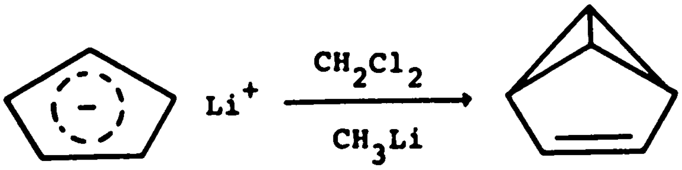
XXVII to III is a well established symmetry allowed ${}_{\sigma}2_s + {}_{\sigma}2_a$ process. A facile bond reorganization of the bicyclo[1.1.0] unit of XXVII which is conjugated with double bonds would be expected to take place even at low temperatures.



IV XXVII III

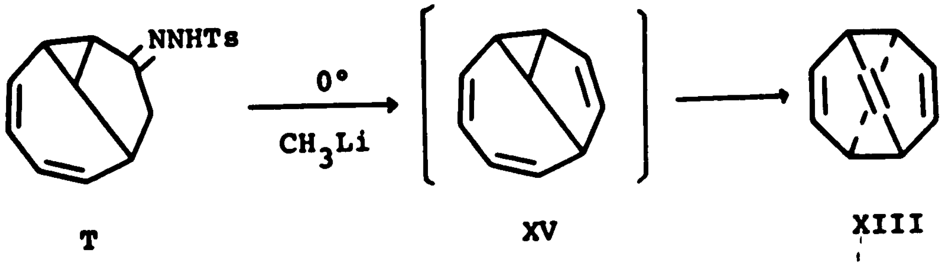
29

A recent report by Katz and coworkers which described the successful synthesis of benzvalene in the analogous reaction (reaction 30) supports this rationalization.[48]



30

Upon completion of this part of the work, an attempted synthesis of XV was reported by Vedejs.[49] Treatment of tosylhydrazone T with methyllithium at 0° produced XIII instead of XV (reaction 31). Although their attempt to isolate XV was unsuccessful, the intermediacy of XV in this reaction seemed certain.

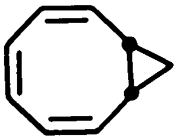


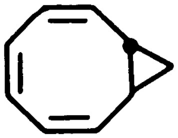
31

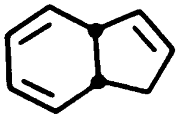
Cyclononatetraenes

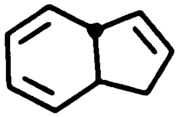
i) Photolysis of C_9H_{10} compounds

In order to understand the photochemical behavior of bicyclic $(CH)_{10}$ compounds involved in generation of [10]annulene (see reaction 16), photochemical reactions of some bicyclic C_9H_{10} compounds were initiated. Our primary concern in this study was the detection and isolation of cyclononatetraenes which were expected to take part in the photochemical transformations of several C_9H_{10} compounds.[33] The following four compounds were employed as starting materials:


XXII


XXIII


XIX

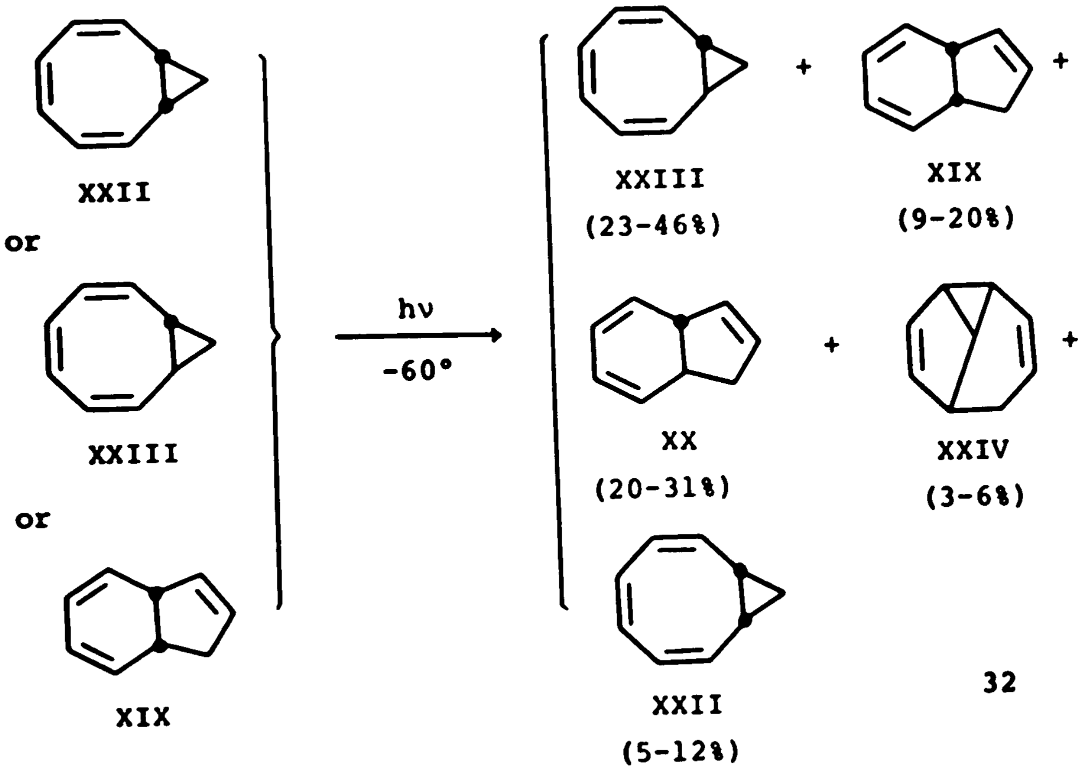

XX

The formal application of the selection rules to these systems allows one to correlate compounds XXII and XX with (cis)^4-cyclononatetraene (XXV), and compounds XXIII and XIX with trans,(cis)^3-cyclononatetraene (XXI) in their excited states.

Hydrocarbon XXII was readily available from the reaction of cyclooctatetraenyl dianion with methylene chloride.[6] Thermolysis of XXII at 90° provided XIX.[50] Compounds XX and XXIII were prepared by low temperature photolysis (2537 A) of XXII. XX was isolated by preparative glpc.[33] The isolation of XXIII was achieved by distillation using a cold finger or by crystallization. Column chromatography on alumina was also useful for this purpose.

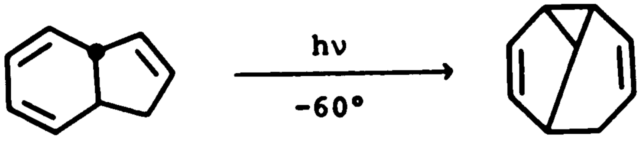
Although some reactions of XXIII had been reported in the literature,[51] no evidence for its structure had been provided. It was found that this compound was thermally stable to 190° in a dilute solution, but that it underwent a rapid polymerization when the sample was stored neat even at low temperature. Thus, it was necessary to store this material in a highly dilute solution. The nmr spectrum of XXIII showed multiplets at τ 3.95-4.32 (6 H), 8.2-8.7 (2 H), and 9.05-9.3 (2 H). The proposed structure was confirmed by hydrogenation of XXIII to the corresponding perhydrocompound which was found to be identical with authentic *trans*-bicyclo[6.1.0]nonane (nmr and ir spectra).[52]

Photolysis of C_9H_{10} compounds was performed on the photo-apparatus described previously[19] (see p. 33) and the reaction progress was monitored by glpc trace. When a ca. 0.8 M solution (THF) of XXII, XXIII, or XIX was irradiated (2537 A) at -60°, the reaction reached a photo-stationary state in 1-2.5 hr. Prolonged irradiation did not change the composition of photo-products appreciably. All three starting materials produced an equilibrium mixture of quite similar product distribution. The glpc analysis (column temperature 90°) indicated the formation of the following compounds (reaction 32). Each compound was separately isolated and identified.



32

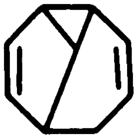
On the other hand, irradiation of XX produced exclusively tricyclic compound XXIV (reaction 33).



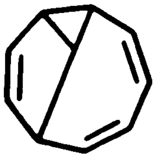
XX XXIV

33

The new compound XXIV was tentatively assigned as tricyclo[4.3.0.0^{2,9}]nona-3,7-diene based on the facts: (i) the nmr spectrum of this compound exhibited multiplets at τ 4.02-4.78 (4 H), 6.78-7.12 (1 H), and 7.42-9.00 (5 H), and spectral features closely resembled those of XV.



XXIV



XV

(ii) upon hydrogenation, this compound yielded a mixture of three hydrocarbons of which a major component was tricyclic (*m/e* 122). The others were bicyclic (*m/e* 124).

In contrast to the low temperature photolysis, irradiation of XXII, XXIII, and XIX at room temperature was found to be strikingly different, producing XXIV as the major compound. This result strongly suggested that some thermally unstable species were involved in reaction 32. In particular, the different photochemical behavior of XX in reaction 32 and 33 was important since a major amount of XX was always noticed in the photolysis of XXII, XXIII, and XIX (glpc analysis), while only a trace amount of XXIV was found in the reaction mixture.

At this stage, it was necessary to establish the real composition of the cold photolysate. The nmr spectrum measured at low temperature was not definitive because of complex overlapping of signals of the various photo-products. The low temperature hydrogenation procedure developed concurrently in our laboratory, was therefore applied to this system. This procedure proved especially useful for determining the accurate composition of complex reaction mixtures containing thermo-labile materials. The existence of cyclononatetraene can be detected as cyclononane by this method.

Hydrogenation of the photolysate carried out at -80°, indeed produced cyclononane (19-28%, see Table 1), which was isolated by preparative glpc and identified unambiguously by comparison with an authentic material (nmr, ir, mass spectrum, and glpc). It was essential to ascertain that each compound in the reaction mixture afforded the corresponding perhydro-compound by hydrogenation under the same conditions. In fact, each compound gave the corresponding perhydro-compound under the exactly same hydrogenation conditions*: XXII' (96%), XXIII' (96%), XIX' (93%), XX' (94%), and XXIV' (94%). The precursors to cyclononane were demonstrated beyond doubt to be cyclononatetraenes.

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* <u>cis</u>-Decalin was used as an internal standard and the yield was determined by glpc analysis. Each perhydro-compound (XXII', XXIII', XIX', and XX') was identified by comparison with the authentic material.[53]

Table 1

Analysis of cold photolysate of XXII, XXIII, and XIX

Starting material	Method of analysis	Product distribution XXII	XXIII	XIX	XX	XXIV	C + D
XXII[a]	(i)	9	36	9	31	3	
	(ii)	9	36	6	2	2	28
	(iii)	9	35	10	27	6	
XXIII[b]	(i)	5	43	10	24	6	
	(ii)	5	39	4	2	8	21
	(iii)	5	37	10	24	7	
XIX[c]	(i)	12	23	20	20	5	
	(ii)	11	22	11	4	2	19
	(iii)	9	18	17	19	8	

Length of photolysis at -60° (min): a 150; b 40; c 330.

cis-Decalin was used as an internal standard throughout this work.

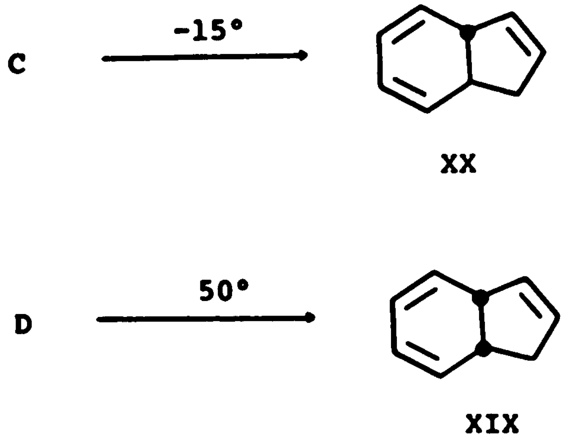
(i) Glpc trace of cold photolysate.

(ii) Glpc trace of hydrogenation mixture of cold photolysate.

(iii) Glpc trace of hydrogenation mixture after the photolysate being heated at 50° for 1 hr.

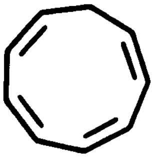
The products obtained in method (ii) and (iii) represent the corresponding perhydro-compounds [XXII', XXIII', XIX', XX' and C'+ D'(cyclononane)].

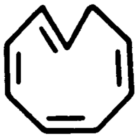
Furthermore, careful thermolysis of the cold photolysate at different temperatures, followed by hydrogenation at -80°, made it possible to detect two kinds of cyclononane precursors in this photolysate. One of these precursors C isomerized at -15° to XX ($\tau_{1/2} \simeq 90$ min) and the other D to XIX at 50° in 1 hr (reaction 34).

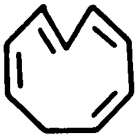


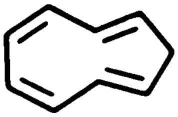
34

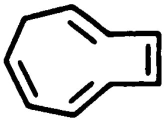
Five geometrical isomers are feasible for cyclononatetraenes:


XXV


XXI


XXVIII


XXIX


XXX

The tentative assignment of (cis)^4-cyclononatetraene (XXV) to compound D is based on the following facts: (i) protonation of all cis-cyclononatetraenide (IV) is known to produce XIX after work-up, possibly by thermolysis of intermediate (cis)^4-cyclononatetraene (XXV).[6] (ii) the similar system, 1,3,5-(cis)^3-cyclononatriene, is known to provide quantitatively cis-bicyclo[4.3.0]nona-2,4-diene by thermolysis.[48] (iii) compound D provided XIX by thermolysis at 50° in 1 hr. Application of the selection rules[32] excludes the possibility of XXI, XXVIII, and XXIX for this process.

The tentative assignment of trans,(cis)^3-cyclononatetraene (XXI or XXVIII) to compound C is again based on: (i) the similar system, trans, cis, cis-cyclonona-1,3,5-triene, is known to rearrange thermally to trans-bicyclo[4.3.0]nona-2,4-diene.[33] (ii) compound C thermally isomerized to XX. Application of selection rules to this system eliminates the possibility of XXV, XXIX, and XXX for this process. The choice between two trans,(cis)^3-cyclononatetraenes (XXI and XXVIII) is not made at this stage.

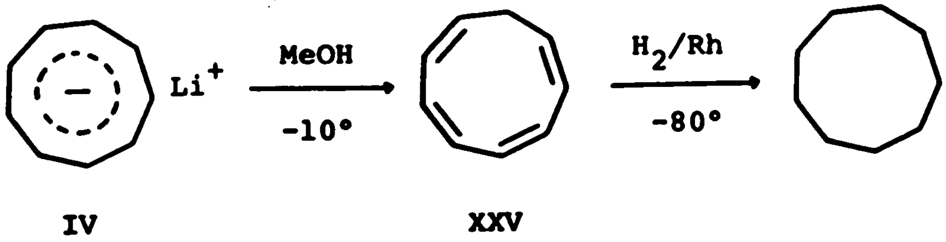
ii) Isolation of cyclononatetraenes

Once the approximate life times of trans,(cis)^3-cyclononatetraene (C) and (cis)^4-cyclononatetraene (D) were estimated, it was clear that C and D could be isolated without thermal rearrangement, provided that isolation procedures were carried out below -50° and below 0°,respectively.

At this point the isolation procedure of these species was carefully examined. Considering the fact that compound D (XXV) was relatively thermally stable, the earlier reports concerning protonation of cyclononatetraenide anion (IV) were examined as a promising source of this species.[6] The experiment was performed with special care to prevent any thermal reactions of the protonated compound. To lower the reaction temperature, methanol was chosen as a proton source.

In a preliminary experiment, addition of methanol to IV in tetrahydrofuran was performed at -80° (reaction 35) and the process followed by low temperature nmr spectroscopy. It was found that protonation took place at -10° in 2 hr with formation of a new species XXV which isomerized to XIX at 50° in 1 hr, in agreement with the previous observation of thermal behavior of D (see reaction 34).

With this information the protonation of IV was readily achieved on a preparative scale, and the new material produced was purified by distillation onto a cold finger at -10° to yield a pale yellow liquid (≈ 95% pure, observed as XIX by glpc).

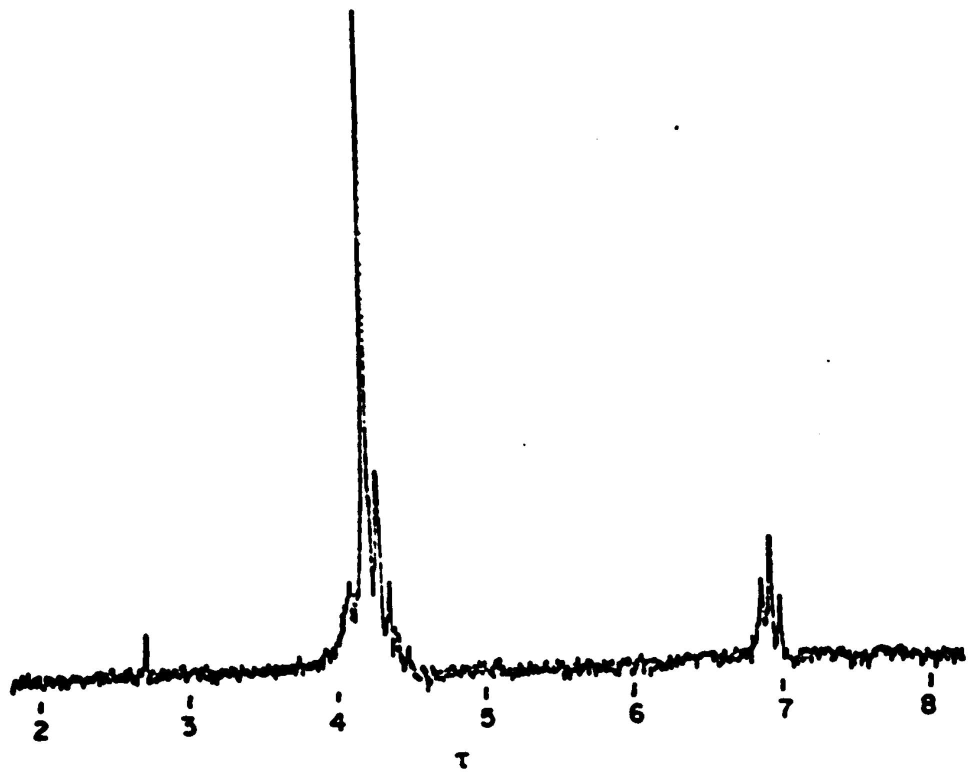


35

Hydrogenation of this material at -80° provided the corresponding perhydro-compound (99%) which was identical with an authentic cyclononane (glpc, mass spectrum, nmr, and ir). Thus the protonation product was concluded to be (<u>cis</u>)^4-cyclononatetraene (XXV).

The nmr spectrum of XXV exhibited 8 olefinic protons centered at τ 4.2 and 2 diallylic protons at τ 6.9 (triplet, $\underline{J}$ = 6 Hz), indicating the monocyclic (symmetrical) structure (Fig. 13).

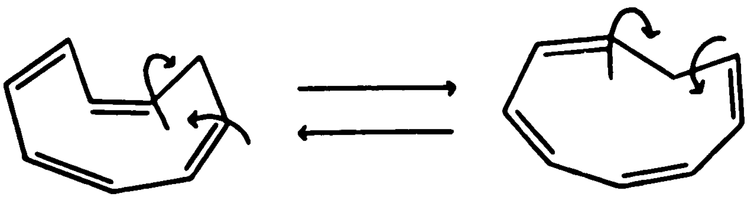
Figure 13: Nmr spectrum of XXV at 0° in $CDCl_3$ (100 MHz)



The uv spectrum of XXV measured at -50° (Fig. 14) displayed absorption maxima at 250 nm, 258, 268, 274, and 284. The concentration of XXV was estimated by thermal conversion of XXV to XIX. A uv maximum of XIX (262 nm, $\varepsilon = 3400$) was employed for the calculation.[55]

Inspection of Dreiding models indicates that the molecule very likely exists in a conformation in which the π-orbitals of double bonds are almost perpendicular to each other. Thus, only weak conjugation would be expected in this system as reflected in the uv spectrum.

Conformational changes of this molecule are noteworthy. Compound XXV very likely exists in a conformer A, which is readily convertible to conformer B (identical with A) by pseudo-rotating the two single bonds as indicated below:



A B

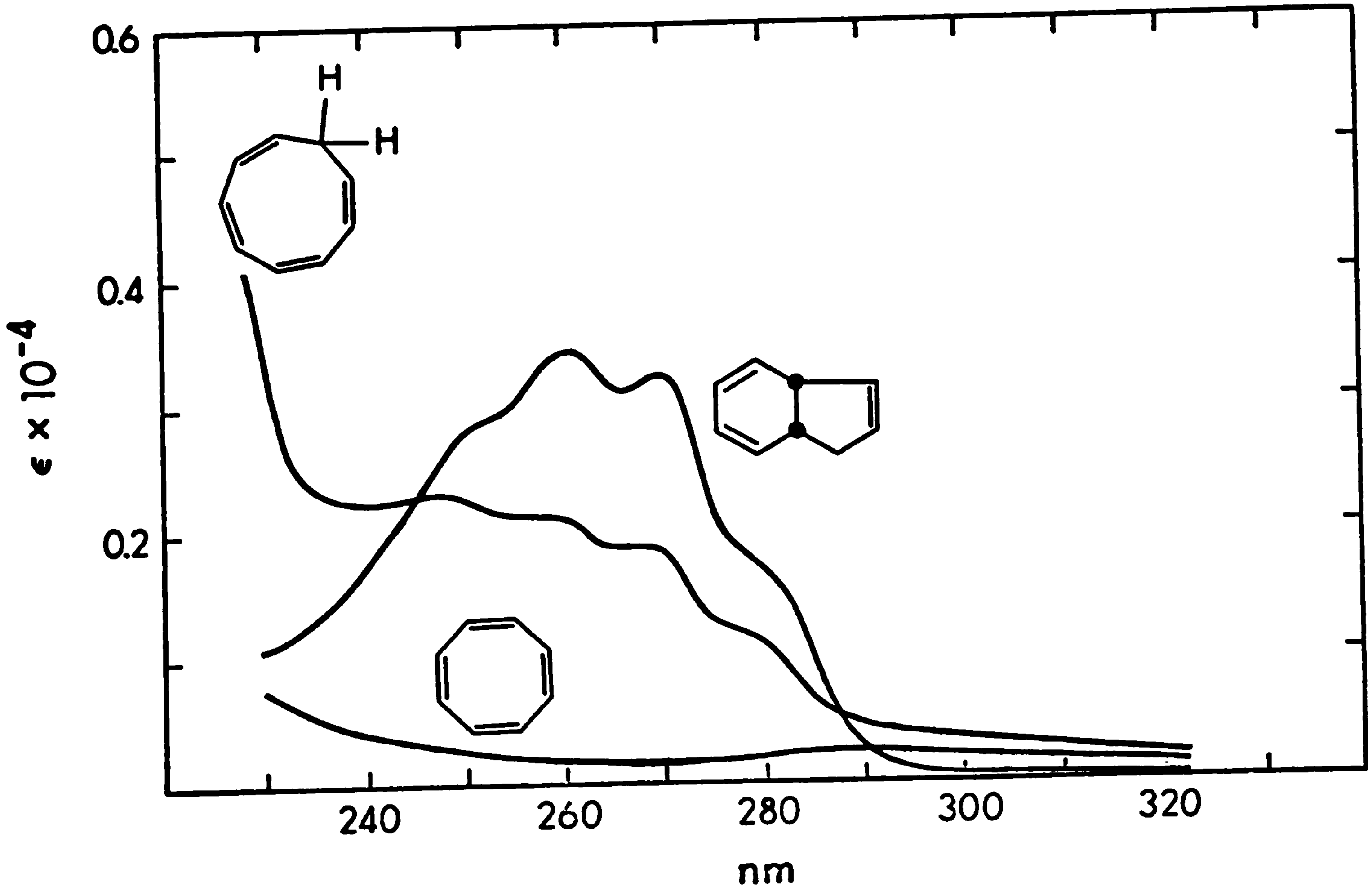
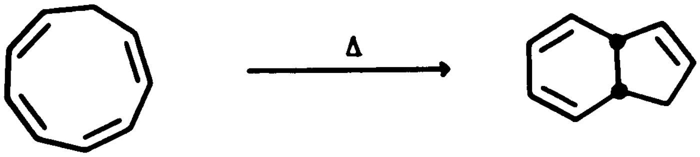


Figure 14: Uv spectrum of XXV measured at -50° in methanol

The energy barriers for this process are expected to be quite low and the rapid conformational changes, compared with the nmr time scale, result in the achievement of molecular symmetry ($\underline{C}_2$) as observed by nmr spectroscopy. This process was not frozen over the temperature range 0° to -120° (nmr measurement performed by R. Seidner).

Thermolysis of XXV proceeded with first order kinetics to provide XIX as shown by the nmr and uv spectroscopy (reaction 36). This process followed by the uv spectroscopy provided the following kinetic parameters (by R. Seidner).



36

XXV XIX

$k_{15.0} = (5.38 \pm 0.11) \times 10^{-5}\ \text{sec}^{-1}$

$k_{35.1} = (6.55 \pm 0.13) \times 10^{-4}\ \text{sec}^{-1}$

$\Delta H^{\ddagger} = 21.4 \pm 0.04$ kcal/mole

$\Delta S^{\ddagger} = -3.9 \pm 1.2$ eu

The successful isolation of XXV was simultaneously reported by other groups.[56]

The isolation of trans,(cis)^3-cyclononatetraene (C) from the photolysis mixture was achieved in the following manner: compounds XXII and XXIII readily crystallized from suitable solvent systems (e.g., 3-methylpentane) at low temperature, thus those compounds were readily removed from the crude photolysate. However, compound C was not separable from XIX and XX. Therefore we chose the (photochemical) conditions which suppressed the formation of XIX and XX in order to enrich the amount of C in the filtrate. Irradiation of XXIII was performed at -60° in n-pentane for 9 min. The mother liquor enriched in C (70%) was separated from the crystalline compounds.

Later, with the development of low temperature chromatography techniques, it was possible to isolate C from the cold photolysate of XXII in high purity (≃ 95%).

The nmr spectrum (-50°) of pure compound C* (Fig. 15)

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* Two trans,(cis)^3-cyclononatetraenes, XXI and XXVIII are possible for compound C. The structure assignment was not possible by spectral data (nmr and uv spectroscopy). For further discussion, see p. 99.

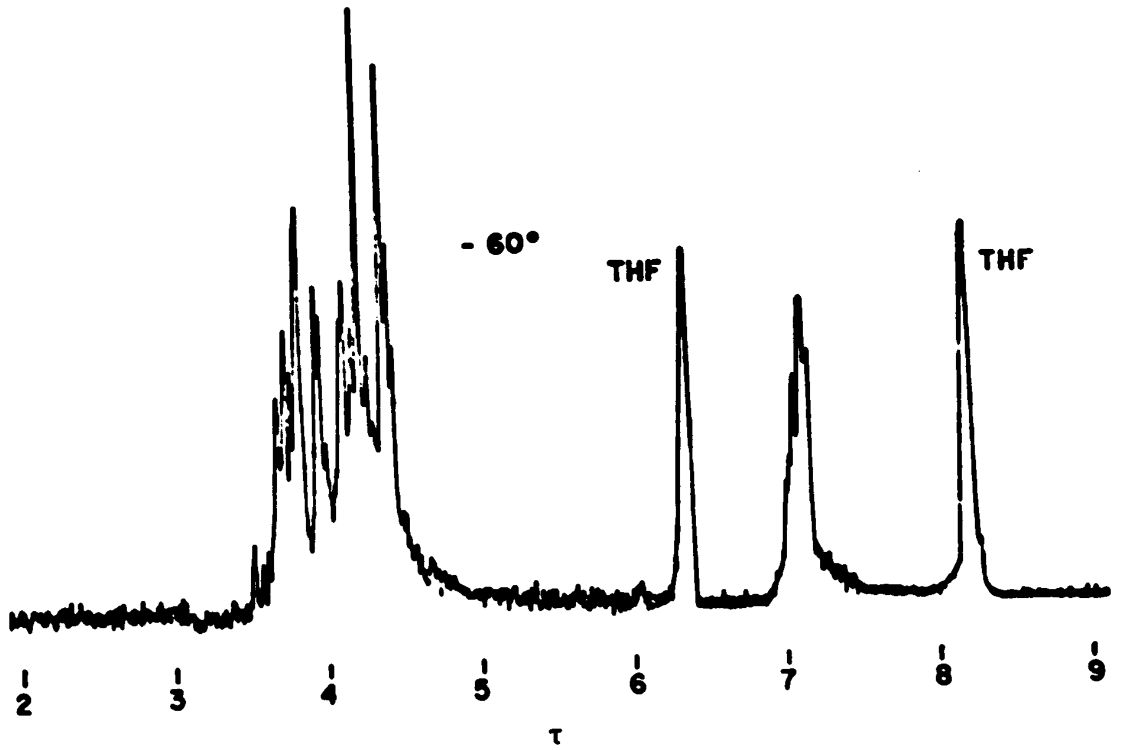
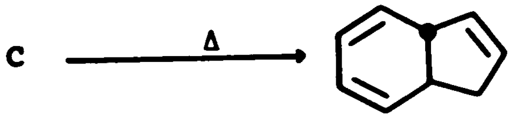


Figure 15: Nmr spectrum of trans,$(cis)^3$-cyclononatetraene (C) measured at -60° in d_8-THF (100 MHz)

exhibited eight olefinic protons at τ 3.5-4.7 and two diallylic protons at τ 7.0-7.2. The spectrum did not show any appreciable change between -30° to -105°.

The uv spectrum measured at -50° (Fig. 16) showed absorption maxima at 230 nm ($\epsilon = 1.25 \times 10^4$) and 318 ($2.2 \times 10^3$). The concentration of C was calculated after thermal conversion of C to XX ($\lambda_{max} = 260$, $\epsilon = 3700$).[33]

Compound C isomerized quantitatively to XX (reaction 37) according to nmr and uv analysis.



XX

37

It is conceivable that the protonation of <u>trans</u>-cyclononatetraenide (XXVI) would yield <u>trans</u>,(<u>cis</u>)^3-cyclononatetraene C (XXI and/or XXVIII). Protonation of XXVI at different positions could produce three geometrical isomers of cyclononatetraenes, XXV, XXI, and XXVIII.

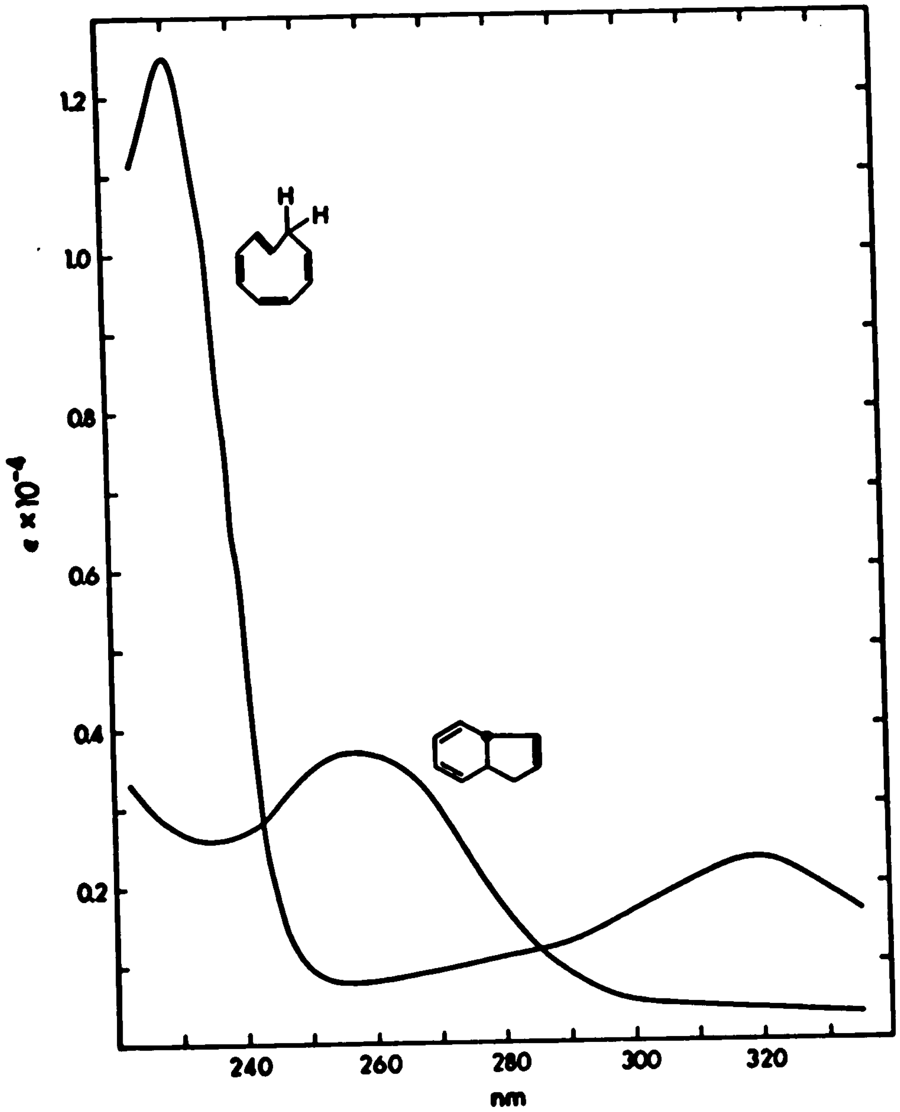
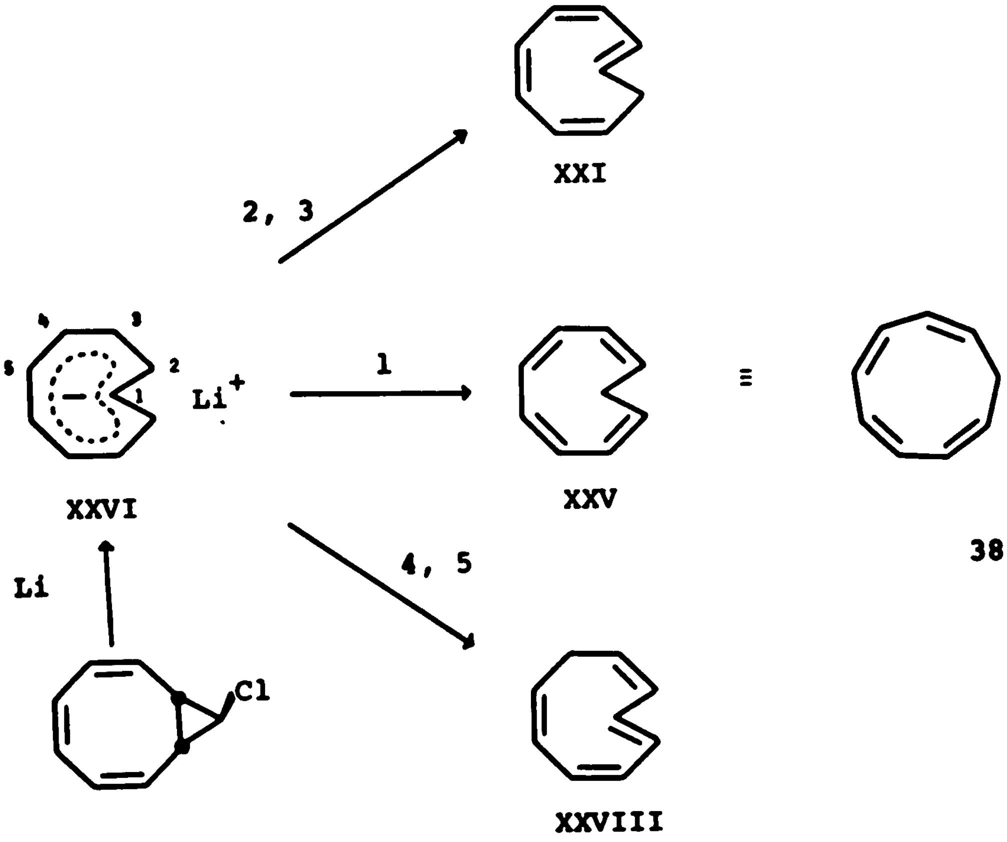
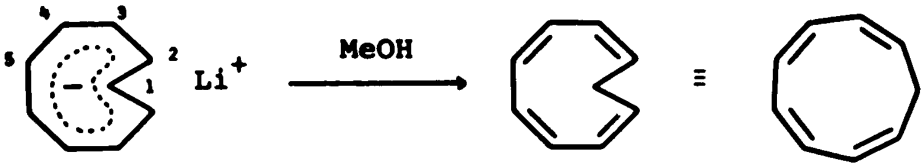


Figure 16: Uv spectrum of trans,(cis)^3-cyclononatetraene (C) measured at -50° in methanol



The synthesis of XXVI was reported recently by Boche and coworkers (see reaction 21).[43] In our experiment the same anion was prepared by reaction of _anti_-9-chloro-_cis_-bicyclo[6.1.0]nonatriene with lithium metal in THF at low temperature. The nmr analysis (-60°) of the products showed 65% of XXVI [τ 2.7 (dd, 2 H), 3.0-3.6 (m, 6 H), and 13.5 (t, 1 H)] and 35% of cis-anion IV [τ 2.87 (s)] in the reaction mixture. The thermal conversion of XXVI to IV occurred above 20° and the process was completed at 40° in 10 min. Thus, it was apparent that cis-anion IV was formed directly in the reaction, and not as the result of thermal isomerization of XXVI.

The protonation experiment was performed in an nmr tube by addition of a small amount (less than the amount of the anions present) of cold methanol at -80°. The nmr analysis (measured at -60°) indicated that all the methanol added was consumed immediately and most of the peaks due to trans-anion XXVI disappeared with formation of (cis)^4-cyclononatetraene (XXV) (reaction 39).



XXVI XXV

39

However, the sharp signal due to cis-anion IV remained unchanged. Accurate integration demonstrated that the amount of trans-anion XXVI consumed corresponded to the amount of tetraene XXV formed. Upon addition of excess methanol at low temperature all trans-anion XXVI which remained in solution in the previous experiment was immediately converted to tetraene XXV, while again cis-anion IV remained unchanged. The ratio of tetraene XXV formed to the remaining cis-anion was found to be 65:35.

As the solution was gradually warmed up in the nmr probe, the protonation of IV proceeded at -10° with an approximate half-life of 25 min. The final product observed in the spectrum was solely XXV (reaction 39). This was confirmed by glpc analysis, demonstrating that the only species formed was XXV (≈ 95%, observed as XIX).

From these experiments, it is evident that the protonation of XXVI takes place exclusively at position-1 to provide XXV. Furthermore, trans-anion XXVI, as shown by the rate of protonation, is more reactive (basic) than cis-anion IV. This could result either from the relatively high π-electron density at position-

1 of XXVI or from possible deviation of this position from the coplanarity. However, any definitive explanation of this specific protonation must await further studies.

iii) Photolysis of cyclononatetraene

From the investigation of the photolysis of some C_9H_{10} compounds described previously, (cis)^4-cyclononatetraene XXV is assumed to participate in a photo-stationary equilibrium with other valence isomers. Based on this assumption, the photolysis of XXV under the same conditions is predicted to produce a distribution of products quite similar to that obtained from the photolysis of XXII, XXIII, and XIX. Irradiation (2537 A) of compound XXV was performed at -60° and the photolysate was analysed in the same manner as described previously: (i) the cold photolysate was subjected to glpc analysis, (ii) a portion of the cold reaction mixture was hydrogenated at -80°, and (iii) another portion was heated at 50° for 30 min, then hydrogenated. The results are summarized in Table 2.

Table 2

Glpc analysis of cold photolysate of XXV

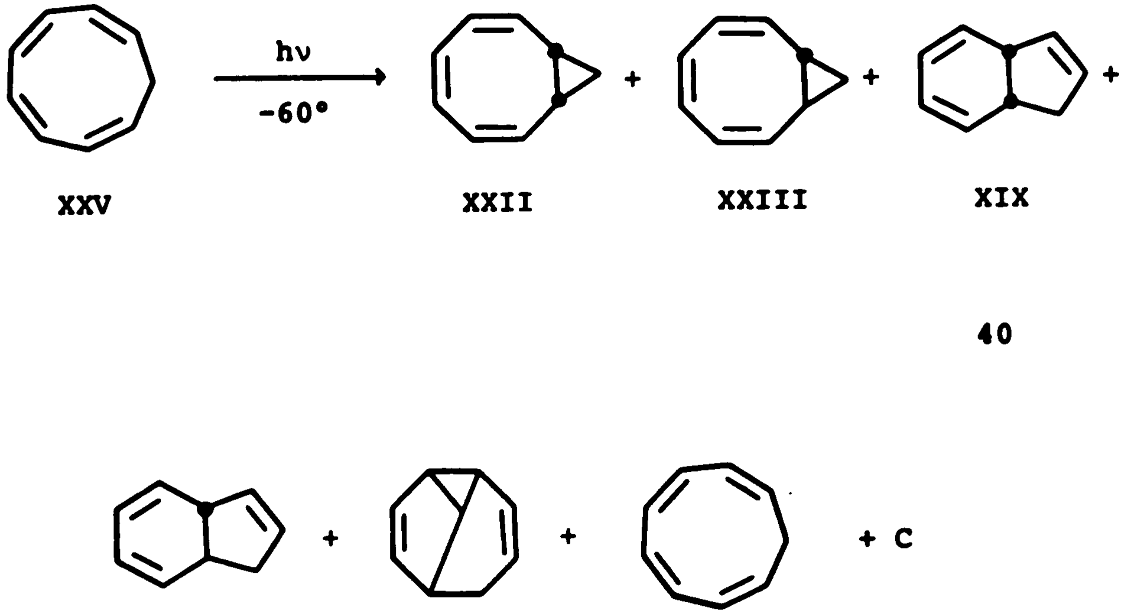
Method of analysis	Product distribution					
	XXII	XXIII	XIX	XX	XXIV	C + D
(i)	6	18	12	12	7	
(ii)	5	14	7	2	4	20
(iii)	5	16	13	13	4	

Irradiation length 165 min.

cis-Decalin was used as an internal standard.

The products obtained in method (ii) and (iii) represent the corresponding perhydro-compounds (XXII', XXIII', XIX', XX', XXIV', C' + D').

The analysis of these data indicates the following products in the cold reaction mixture (reaction 40):



XXV XXII XXIII XIX

40

XX XXIV XXV

It is apparent that irradiation of XXV yields a reaction mixture similar to that obtained by photolysis of XXII, XXIII, and XIX (see Table 1).

The observation that the photolysis of XXII, XXIII, XIX, and XXV provides a similar product distribution except for the starting material strongly suggests that all these compounds and two cyclononatetraenes constitute a photochemical equilibrium and that slow leakage occurs upon prolonged irradiation to produce XXIV from XX as well as other polymeric materials. It is also demonstrated that the geometrical isomerization of double bonds in cyclononatetraenes is occurring and that the rate of ring-closure of the tetraenes into bicyclo compounds is comparable to that of ring-opening process of the latter compounds.

A scheme for these photochemical processes is presented in Fig. 17. Assuming that Woodward-Hoffmann rules are applicable to the present photochemical reactions, compound XXII and XX can be correlated with (cis)^4-cyclononatetraene (XXV), and compound XXIII and XIX with trans,(cis)^3-cyclononatetraene (XXI) in their excited states. Process c is the photo-induced isomerization of the double bond in monocyclic systems.

Two possibilities exist for the structure of trans,(cis)^3-cyclononatetraenes (XXI or XXVIII) as described previously (see p. 80). Process e is an

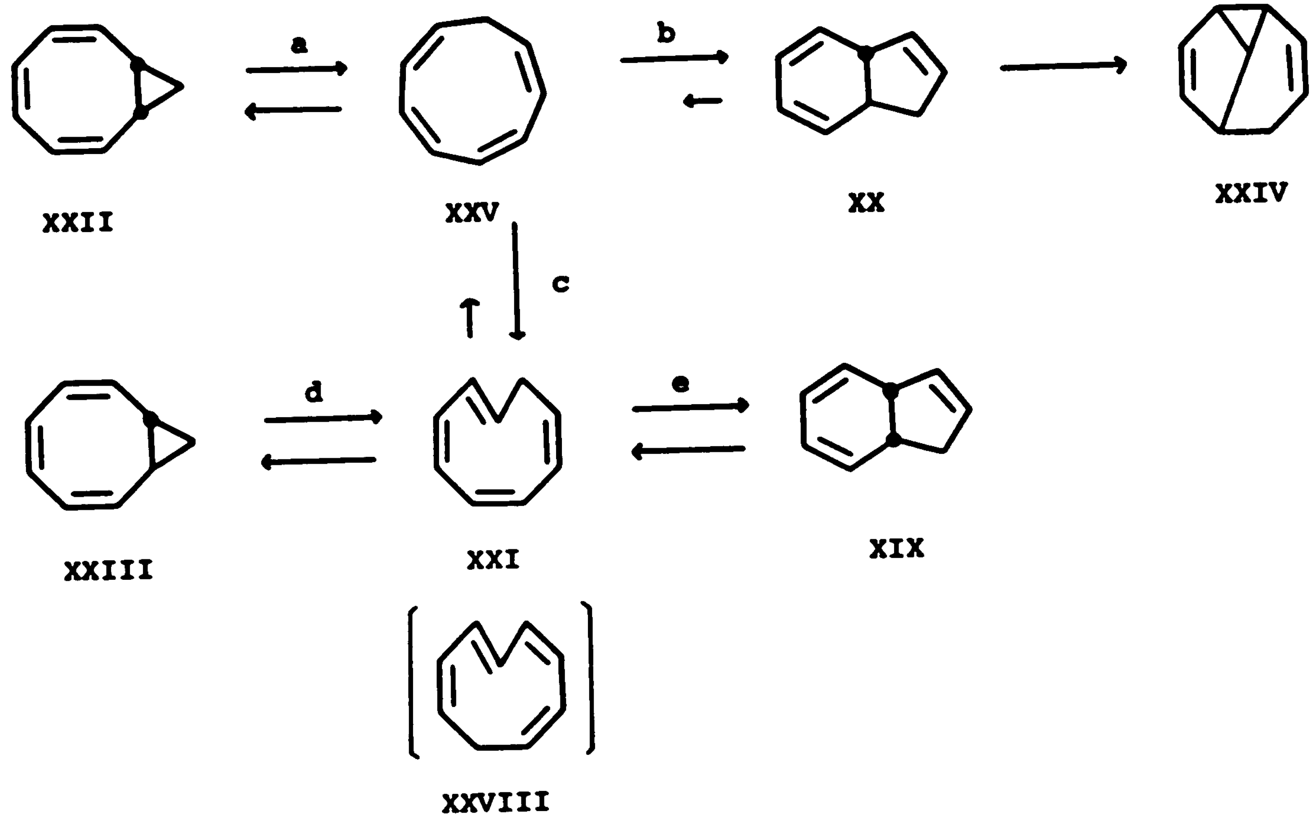


Figure 17: Photochemical transformations of C_9H_{10} compounds

allowed process for both XXI and XXVIII, and process c is also possible for both compounds. However, in order to link compound XXIII to XIX, the involvement of XXI would be favored. In this connection, the structure of trans,(cis)^3-cyclononatetraene C is assigned as XXI.

Irradiation of XXV through a Pyrex (> 3000 A) or a Corex (> 2800 A) filter gave an equilibrium mixture consisting of starting material XXV (25-35%) and XXII (65-75%) which supported process a (vide supra). Irradiation of XXV through a Vycor filter or without any filter yielded first XXII and then XIX (analysed by nmr spectroscopy and glpc trace). Upon irradiation by a high-pressure mercury lamp without filter, both trans- and cis-bicyclo[6.1.0]nonatriene (XXII and XXIII) produced cis-bicyclo[4.3.0]nonatriene as the major product (65%).

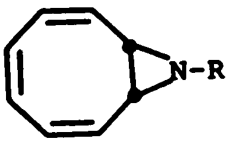
These results may reasonably be interpreted by the same scheme shown in Fig. 17. Obviously the relative ratio of products will be governed by the relative quantum yield of each process, which of course highly depends on wavelength of the light employed in the photolysis.

N-Carbethoxyazonin

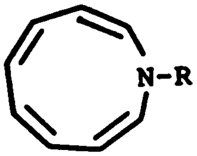
i) Synthesis of N-carbethoxyazonin

Concurrent to the successful synthesis of parent [10]annulenes, investigations have been extended to nine-membered monocyclic 10π-electron systems containing a hetero atom. Such systems are important as next higher homologs of the five-membered 6π-electron systems. Preparation and some reactions of several valence bond isomers of these monocyclic systems in recent years indicate the importance and interest in these species.[57] Recently Garrat and coworkers reported the first chemical synthesis of dibenz-oxonin and -thionin.[58]

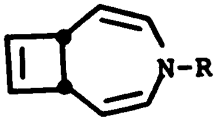
For our synthetic approach to N-carbethoxyazonin (XXXIV), 9-azabicyclo[6.1.0]nona-2,4,6-triene (XXXII), and 4-azabicyclo[5.2.0]nona-2,5,8-triene (XXXIII) were chosen as starting materials. Compound XXXII was readily available by reaction of carbethoxynitrene with cyclooctatetraene, and thermolysis of XXXII yielded XXXIII.[57a]



XXXII



XXXIV



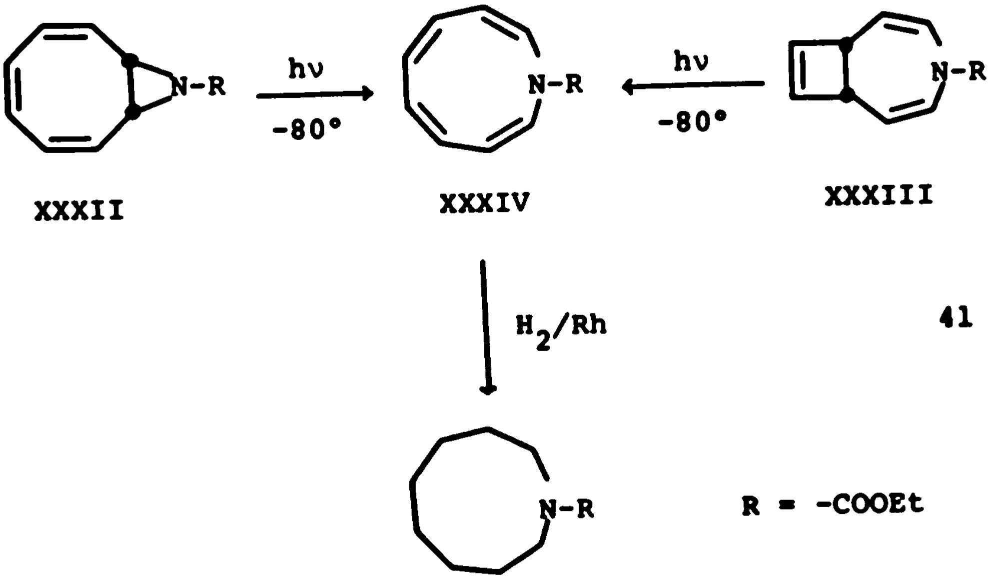
XXXIII

R = -COOEt

Application of selection rules to the present systems shows that both XXXII and XXXIII are correlated photochemically with azonin with (*cis*)^{4}-geometry (XXXIV) by disrotatory ring-opening of 8π- or 4π-electron systems. From the investigations described previously, photochemical reactions of these species are anticipated to proceed analogously to those of bicyclo[6.2.0]deca-2,4,6,9-tetraene (X) which produces [10]annulenes II and III,[19] and to those of bicyclo[6.1.0]nonatriene (XXII) which produces cyclononatetraenes XXV and XXI.

The synthesis of azonin from these compounds was attempted under various photolytic conditions.

Finally, the generation of XXXIV was achieved by brief irradiation (2537 A) of a dilute solution of XXXII (or XXXIII) at -80° (reaction 41). Typically, a 5 mM solution of XXXII in n-pentane (or in ether) was irradiated in a conventional preparative photo-apparatus by a spiral type low-pressure mercury lamp at -80° for 15 min (or 25 min in case of XXXIII). After removal of the solvent, the photolysate was subjected to silicic acid column chromategraphy (eluted with $CHCl_3$) at 0°, and each fraction was analysed by nmr spectroscopy at -20°.



XXXII XXXIV XXXIII

41

R = -COOEt

The nmr spectrum (Fig. 18) of the new compound XXXIV isolated in a pure form (yield 8.2%) showed AB doublets at τ 3.68 (2, $\underline{J}_{AB}$ = 10.5 Hz, H_α) and 4.82 (2, $\underline{J}_{AB}$ = 10.5 Hz, H_β), and a broad singlet at τ 4.22 (4, H_γ and H_δ), as well as ethyl signals. The mass spectrum gave the molecular ion peak $\underline{m}/\underline{e}$ 191.0944 (calcd for $C_{11}H_{13}NO_2$ 191.0946). That all the protons appeared in the olefinic region indicated a monocyclic structure. Furthermore, existence of one set of protons with a characteristic AB pattern (attributed to α- and β-protons) implied the (symmetrical) structure with four cis-double bonds. These spectral data were in agreement with the structure of N-substituted $(\underline{cis})^4$-azonin (XXXIV).

An unambiguous structural determination of this compound was provided by catalytic hydrogenation (Rh) at low temperature to the saturated material which was found to be identical with independently prepared authentic N-carbethoxyazacyclononane (nmr, ir, mass spectrum, and glpc with different columns) (reaction 41).

The composition of the cold photolysate was examined. From the experiments performed with photochemical reactions of several C_9H_{10} compounds, the presence of geometrical isomer of XXXIV was expected. In order to clarify this point, the cold photolysate (maintained at

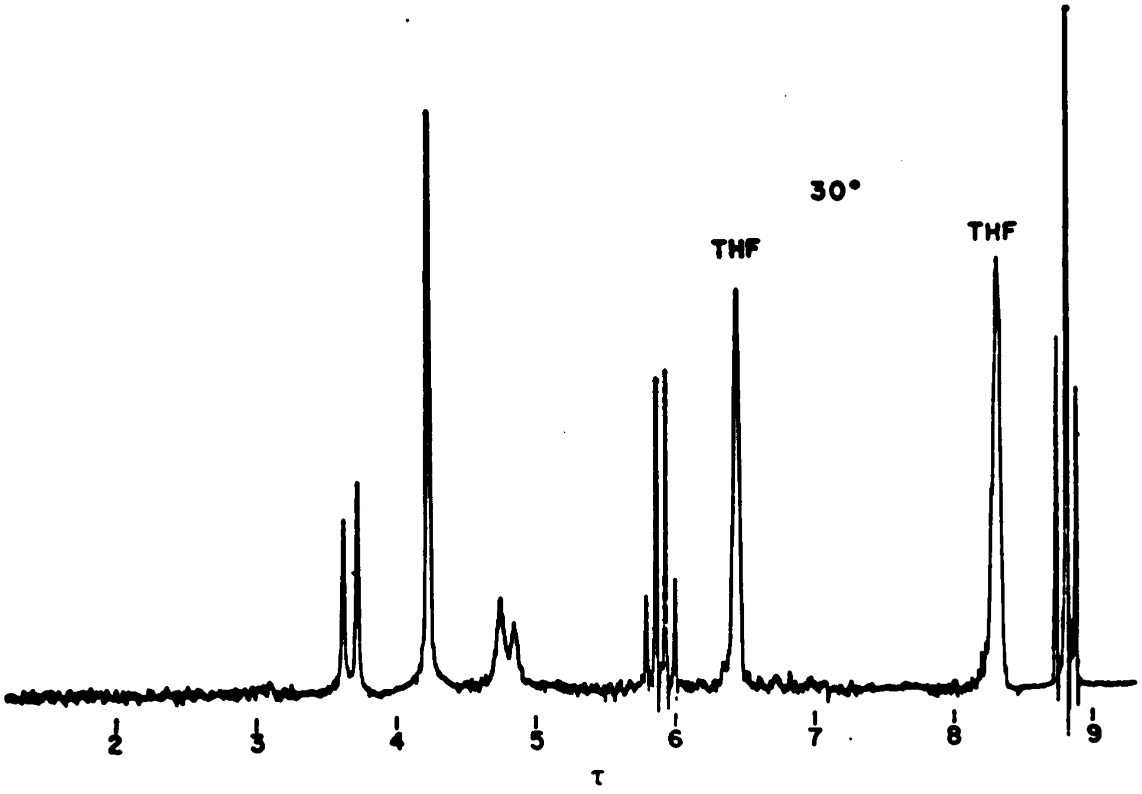
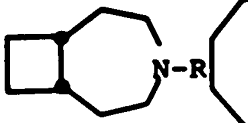
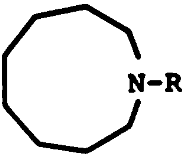
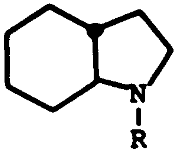
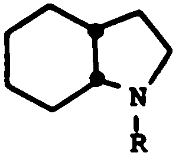
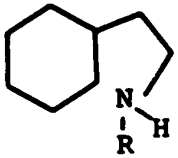
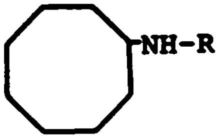


Figure 18: Nmr spectrum of XXXIV measured at 30° in d_8-THF (100 MHz)

-80°) was analysed in the following manner: the cold photolysate was divided into three portions. (i) the first portion was hydrogenated at -80°, (ii) the another solution was allowed to warm at -15° for 1 hr and then hydrogenated at -80°, and (iii) the rest was heated at 50° for 2 hr and then hydrogenated at -80°. Percentage yields of hydrogenated products [calculated relative to the internal standard (S) (*vide infra*)] are tabulated below. The products were determined by comparison with authentic materials (XXXII', XXXIII', XXXIV', XXXV', XXXVI', and XXXII") prepared in an unambiguous manner (R = -COOEt).[59]

Table 3: Analysis of cold photolysate of XXXII

Method	 XXXIII'*	 XXXIV'	 XXXV'	 XXXVI'		 XXXII"**	XXXII'"**	Others
(i)	5.6	22.5	1.1	8.4	9.3	21.4	28.3	3.4
(ii)	6.8	21.2	3.3	9.6	9.6	20.6	24.5	4.3
(iii)***	11.6	1.5	5.2	32.6	10.0	3.8	30.2	5.1

N-Carbethoxypiperidine (S) was used as the standard.

*, **, *** See next page.

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* Since starting material XXXII had been contaminated with XXXIII (~ 5%), the possible photochemical formation of XXXIII was not certain.

** Upon hydrogenation, XXXII yielded XXXII" and two other unidentified materials XXXII'" (*m*/*e* 197 and 199). Only trace (~ 1%) of N-carbethoxy-9-azabicyclo-[6.1.0]nonane (XXXII') was noted. Hydrogenation of XXXIII, XXXIV, and XXXVI provided the corresponding perhydro-compounds. Hydrogenation of pure XXXV was not attempted.

*** At this temperature (+50°), complete thermal isomerization of XXXIV to XXXVI took place with slow transformation of XXXII to XXXIII (see p. 124 and 125).

Examining the results, formation of XXXV* and XXXVI by photolysis is evident. Furthermore, a slight increase of XXXV upon warming to -15° and +50° suggests the presence of thermal precursor of XXXV (possibly trans,(cis)^3-azonin) in the cold photolysate. Further studies of this species were not attempted.

The successful isolation of XXXIV was also reported by another group simultaneously.[60]

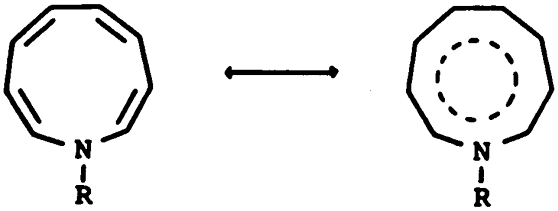
ii) Physical properties of N-carbethoxy-(cis)^4-azonin (XXXIV)

Since the assignment of the all-cis geometry to the azonin XXXIV is secure from the data described in the previous section, physical properties of this molecule are worth considering. The nmr spectrum (Fig. 18) of XXXIV shows one set of AB signals, indicating the presence of a symmetry element in this molecule. There are two ways of considering this symmetry in the molecule observed by nmr spectroscopy.

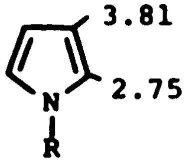
---

* Compound XXXV was isolated from the reaction mixture by repeated chromatography and characterized by nmr spectroscopy.

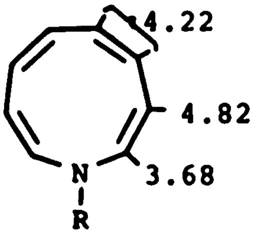
One possibility is that the compound in question possesses a planar structure. In this case, effective conjugation of the non-bonding electrons of the nitrogen atom with the adjacent double bonds is feasible.



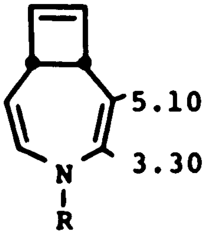
The resulting 10π-electron system should exhibit aromatic character according to Hückel's rule.[1] This possibility can be best examined by proton nmr spectroscopy. For convenience, chemical shifts (τ values) of the molecules which possess a structural feature similar to XXXIV are shown below:



XXXVII



XXXIV



R= -COOEt

XXXIII

Comparison of chemical shifts of the ring protons of XXXIV with those of XXXIII (non-aromatic) and N-carbethoxypyrrole (XXXVII, aromatic) indicates that N-carbethoxyazonin exhibits no significant diamagnetic ring current.

The uv spectrum (Fig. 19) of XXXIV (measured at 5°) shows absorption maxima at 215 nm ($\log\varepsilon$ = 3.95) and 265 (3.53). Spectral features closely resemble those of $(\underline{cis})^4$-cyclononatetraene (XXV) (Fig. 14).

These spectral data strongly suggest a non-planar conformation and therefore non-aromaticity for XXXIV. Inspection of Dreiding models using a trigonal planar nitrogen atom[*] reveals that the molecule exists in two identical non-planar conformations.

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[*] Crystalline structures of amides and carbamates have shown that these molecules possess planar trigonal nitrogen atoms and the C-N bond (of the amide N) and four atoms attached to these C and N atoms are coplanar or nearly so (within 0.01 A).[62] In solution, these conformations are assumed to be at potential minima of rotation along the C-N axis.

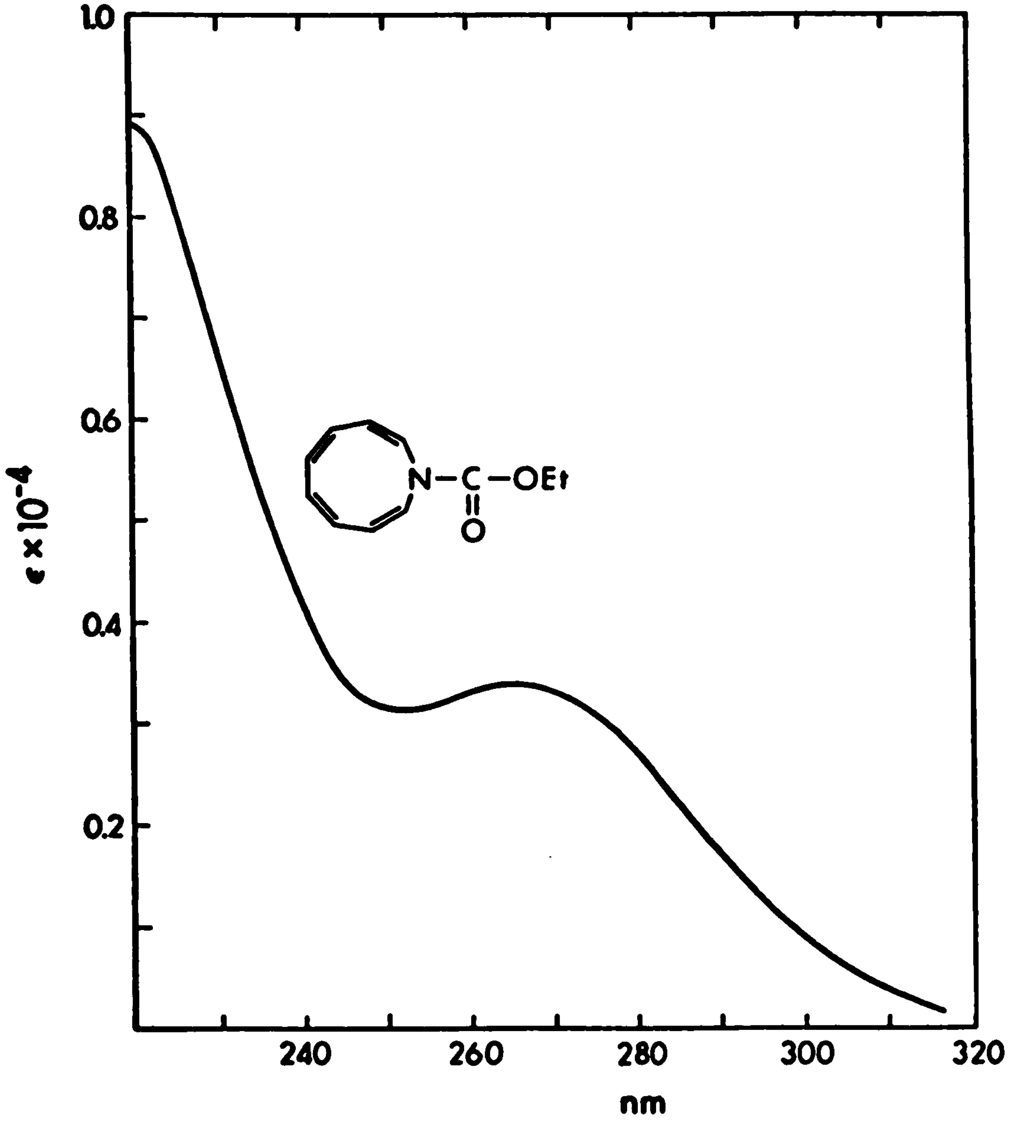
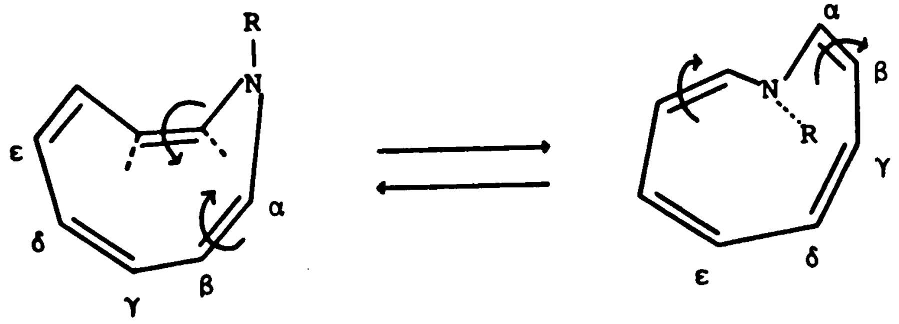


Figure 19: Uv spectrum of XXXIV measured at +5° in methanol

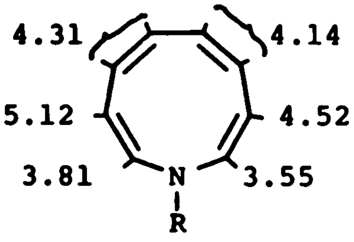
The conformational change from one to the other is readily achieved by pseudo-rotating the two bonds indicated below:



This process is similar to that noted previously for the conformational change of $(\underline{cis})^4$-cyclononatetraene (see p. 84), thus the change is expected to proceed rapidly compared with the nmr time scale, producing apparent molecular symmetry ($\underline{C}_2$).

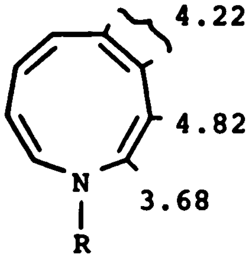
The nmr spectrum of XXXIV in d_8-THF showed a marked temperature dependence (Fig. 20). At low temperatures (-20° to -100°), two doublets centered at τ 3.55 (H_α) and 3.81 ($H_{\alpha'}$), two broad singlets at τ 4.14 (H_γ and H_δ) and 4.31 ($H_{\gamma'}$ and $H_{\delta'}$), and two doublets centered at τ 4.52 (H_β) and 5.12 ($H_{\beta'}$) were apparent, indicating that the molecule lost the symmetry at low temperatures and that every proton in the ring now occupied unique magnetic environments.

Figure 20: Temperature dependent nmr spectra of XXXIV in d_8-THF (100 MHz)



-20°

R = -COOEt



30°

Upon warming, two doublets (H_α and $H_{\alpha'}$) centered (-20°) at τ 3.55 and 3.81 coalesced at 0° and time-averaged at 30° (τ 3.68). Similar behavior was observed for two doublets (H_β and $H_{\beta'}$), and for two broad singlets (H_γ, H_δ, $H_{\gamma'}$, and $H_{\delta'}$).

There are three possible explanations for these phenomena: (i) conformational changes of the ring, (ii) inversion of nitrogen, and (iii) restricted rotation of the carbamate group around the C-N bond.

Possibility (i) is discarded based on two grounds: (a) as already pointed out (vide supra), conformational changes of the azonin are similar to those of (cis)^4-cyclononatetraene and (cis)^4-oxonin. And yet, these systems do not show any temperature dependent nmr spectra between -10° and -110°.[63] (b) the process required for conformational changes of the ring would not be highly dependent of changes in solvents. However, a strong dependence of the coalescence temperature (Tc) is observed in the present case (vide infra).

The distinction between possibilities (ii) and (iii) is discussed in some detail.[64] In general,[65] the inversion at the nitrogen atom with sp^3 hybridization proceeds from one pyramidal form to the other through the sp^2 hybridized transition state. The energy barriers for this process are usually quite low, and only the inversion of nitrogen incorporated in a small ring can be detected by nmr spectroscopy. Conjugation of the nitrogen atom with a double bond or carbonyl group is known to lower the energy barriers. In compound XXXIV, the nitrogen atom is incorporated in a nine-membered ring system conjugated with a carbethoxy group and two double bonds. Under these circumstances a fairly planar geometry about the nitrogen atom in the ground state,* and accordingly, a very low energy barrier would be expected for inversion of nitrogen. The observed experimental value (≃ 13 kcal/mole) is assumed to be too high for this process.

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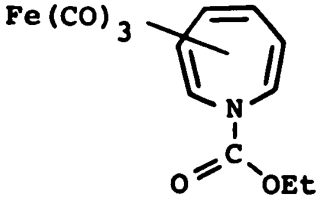
* See the proceeding footnote on p. 110.

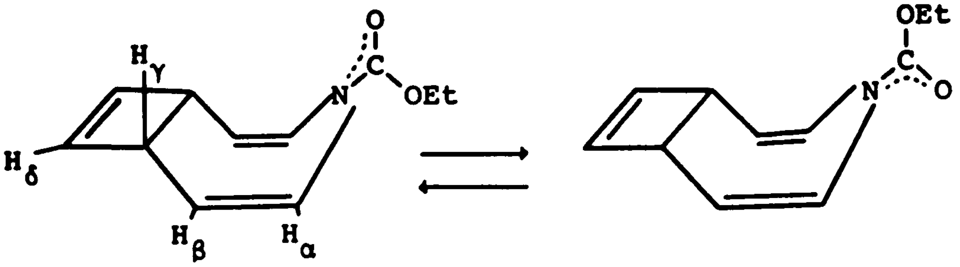
On the other hand, the restricted rotation of the N,N-dimethylcarbamate is known to have an activation energy of 16.5 kcal/mole. The replacement of the methyl groups on the nitrogen atom by double bonds lowers the energy for this process.[66] The observed value for compound XXXIV suggests that mechanism (iii) is a reasonable one.

However, recently Anastassiou and coworkers utilizing the same findings which were already published by us proposed that the temperature variable nmr spectra of XXXIV are due to a suppressed nitrogen inversion.[67] The following three reasons were presented by them in favor of this mechanism: (a) the effect of solvent polarity on the temperature of coalescence (Tc). It was claimed based on the experiments by Roberts and Griffith[68] that the increase of the solvent polarity facilitated nitrogen inversion and lowered the Tc, whereas the increase of the polarity of the solvent restricted the rotation and raised the Tc. In the present case Tc of XXXIV in chloroform (ϵ 4.8) was observed to be -10° and in acetonitrile (ϵ 38.8) -28°. (b) the observed separation of the two low-field doublets (H_α and $H_{\alpha'}$) at low temperature was less than that between the two doublet resonances at high-field

(H_β and $H_{\beta'}$). They stated that if the restricted rotation were occurring, then the more closely located α-protons would be most heavily affected. (c) they argued that if rotation of the carbamate were to be restricted, the ethyl signals would be expected to undergo detectable broadning at low temperatures. They cited the case of restricted rotation of N-carbethoxyazepine iron tricarbonyl which led to the actual splitting within the ethyl resonances.[69]



Let us criticize the interpretation presented by Anastassiou and show that our original analysis of these phenomena is indeed correct. Concerning their first criterion "the effect of the solvent polarity on Tc", we must point out that this effect has been investigated by Roberts and Griffith with only pyramidal nitrogen compounds, N-benzyl-O,N-dimethylhydroxylamine and its related compounds and that it is not appropriate to compare XXXIV with these decisively different systems. An appropriate molecule which possesses a structure similar to XXXIV, for example compound XXXIII should be chosen for comparison instead. If any temperature dependence in the nmr is observed in this system, it must be ascribed to a restricted rotation of the carbamate group.*



XXXIII

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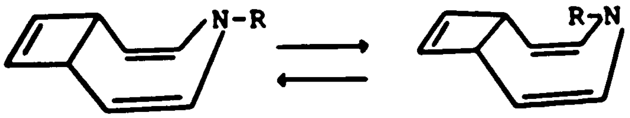
[*] If slow inversion of pyramidal nitrogen occurs between P and Q, it could cause a temperature dependence of the nmr spectra. In this case, P and Q are highly unlikely to be equally populated.



P Q

The protons of XXXIII assigned to the α-positions at room temperature (τ 3.30, *J* = 10.5 Hz) and β-positions (τ 5.10, *J* = 10.5 Hz) were found to coalesce completely at -25° (CS_2–THF-d_8) and another set of resonances corresponding to α- and β-protons appeared below -50° (Fig. 21). These two sets of protons with equal intensity appeared as two overlapping doublets, centered at τ 3.25, 3.35 (dd, *J* = 10.5 Hz), and at τ 5.05, 5.15 (dd, *J* = 10.5 Hz), respectively. $\Delta G^{\ddagger}$ was found to be ~13 kcal/mole at -25°. The ethyl signal began to broaden below -100°. In this case both α- and β-protons were shifted an equal amount (10 Hz from the original positions). As described above there is no doubt in this case that the origin of this temperature dependence is attributable to the restricted rotation of the carbamate group.

N-Carbethoxypyrrole (XXXVII) and N-acetylpyrrole (XXXVIII), which are planar molecules, were also found to show temperature dependent nmr spectra.[70] The Tc of XXXVII was -41° in $CDCl_3$ ($W_{1/2}$ = 17 Hz). In this case, only the α-protons were affected by the rotation being frozen at low temperature. In this molecule, the nitrogen atom is known to possess sp^2 hybridization, and obviously a restricted rotation

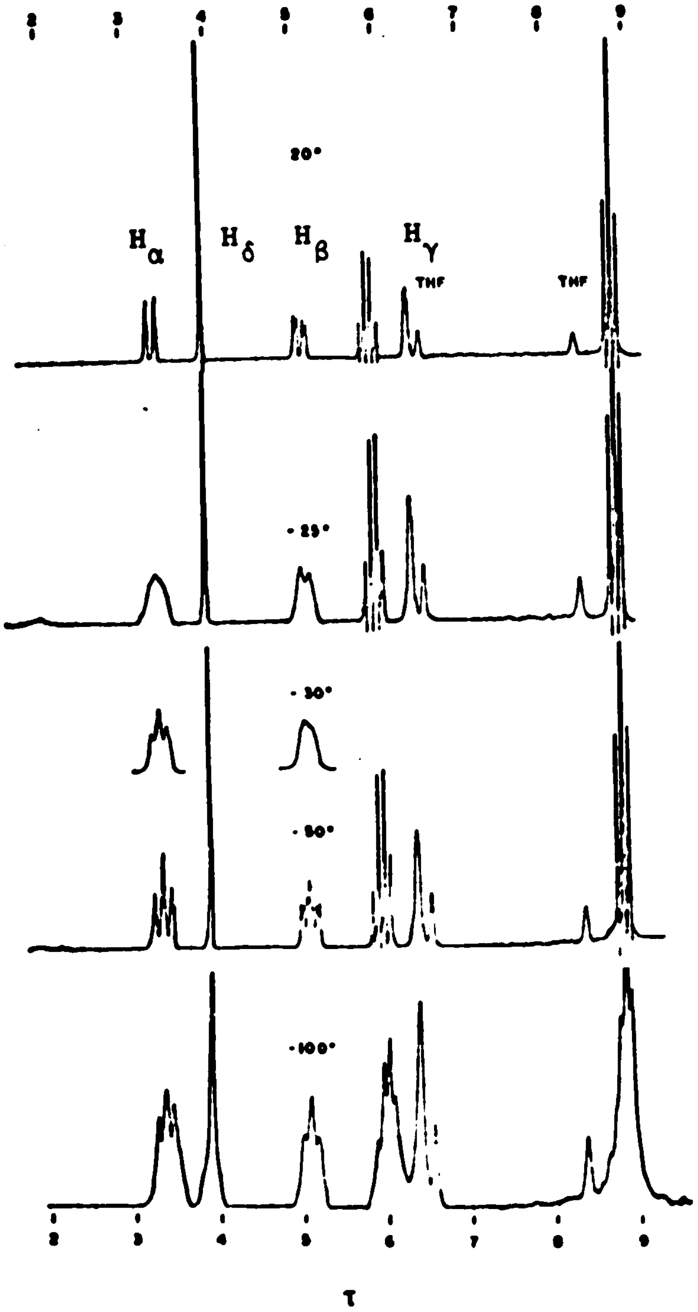


Figure 21: Temperature dependent nmr spectra of XXXIII in CS_2-THF-d_8 (100 MHz)

is the only origin for this observation.

The effect of the solvent polarity on Tc of XXXIV is compared with those of XXXIII, XXXVII, and XXXVIII. The results are summarized below:

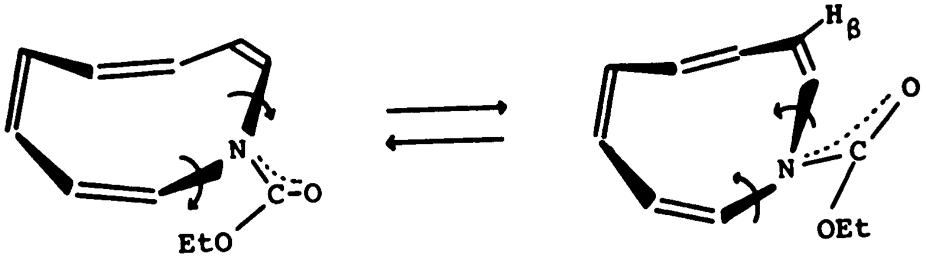
Table 4

Dependence of coalescence temperatures on solvents

Compound	Tc		Δ Tc
	CD_3CN (ε 38.8)	$CDCl_3$ (ε 4.8)	
XXXIV	-28°	-10°	18°
XXXIII	-41	-22	18
XXXVII	solvent frozen below -45°	-41	
XXXVIII	-33	-18	15

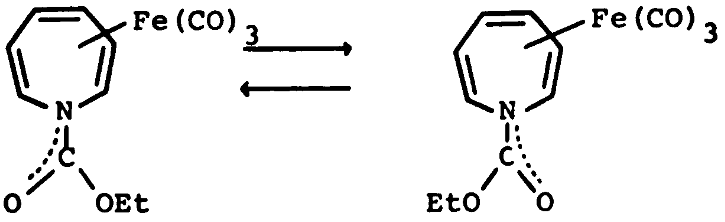
Clearly, the same trend of solvent effect on Tc is observable both for XXXIV and those systems which definitely involve a restricted rotation. It is apparent that the statement (a) is not applicable to compound XXXIV.

Consider the statement (b); the larger shift of the β-protons compared with the α-protons appears quite unusual, particularly when one compares this case with that of pyrrole, where only the α-protons are affected. However, this illusion can be solved by inspection of Dreiding models of XXXIV, using a trigonal planar nitrogen atom, which demonstrates that the carbonyl group approaches the β-proton of the ring as much as the α-proton in one of the two likely ring conformations.



In compound XXXIII, both α- and β-protons are affected to the same amount. In the pyrrole case, the nitrogen atom is incorporated in the planar molecule, and therefore β-protons do not possibly experience appreciable changes of magnetic environment by the rotation being frozen.

The third point can be easily disproved since the ethyl group in azepine iron tricarbonyl in the two rotatomers experiences a different environment. At low temperatures, the iron tricarbonyl moiety is known to be fixed on one side of the ring.[69] Accordingly, it is expected to observe the ethyl splitting at the temperature where the rotation is frozen.



However, in case of XXXIV, the ethyl group experiences a chemically equivalent environment in either rotatomer. Under these circumstances, it is expected that this type of splitting cannot be observed.

In summary, we must conclude these temperature dependent nmr spectra of XXXIV originate from the hindered rotation around the C-N bond which obviously carries a partial double bond character.

iii) Thermolysis of XXXII, XXXIII, and XXXIV

Compound XXXIV was found to be thermally unstable and underwent clean unimolecular rearrangement at 50° in 1 hr, as shown by nmr and uv spectroscopy. The nmr spectrum of the thermal product exhibited one proton at τ 3.35 (dd, H-2), four protons at τ 4.05-4.42 (m, centered at τ 4.14 and 4.34, H-4,5,6,7), and one proton at τ 5.12 (dd, H-3), AB protons centered at τ 5.01 (J_{AB} = 14 Hz, H-8) and 6.08 (J_{AB} = 14 Hz, H-9), and ethyl signals centered at τ 5.86 (2 H) and 8.77 (3 H).

The uv spectrum in methanol showed λ_{max} 227 (log ε = 4.204), 261 (3.477), and 291 (2.932).

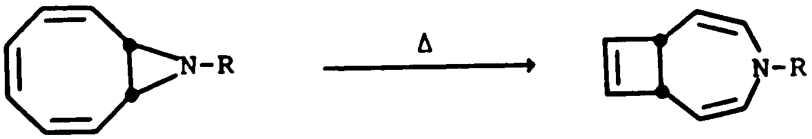
The structural assignment of the thermal product as N-carbethoxy-8,9-dihydroindole was compatible with spectral data. The stereochemistry at the ring juncture was determined by low temperature hydrogenation to the perhydro-compound which proved to be identical in every respect with authentic N-carbethoxy-*cis*-perhydroindole

XXXIV XXXVI XXXVI'

R = -COOEt

(nmr, mass spectrum, ir, and glpc) (reaction 42). Thus, the thermal product is concluded to be N-carbethoxy-cis-8,9-dihydroindole. The rate of thermolysis measured by uv spectroscopy indicated a half-life for this process to be 45 min at 40°.

In connection with this thermal process, the thermal rearrangement of XXXII and XXXIII was investigated. The mechanistic importance of these reactions will be discussed later. A kinetic study of the thermolysis of XXXII to XXXIII was performed in an isothermal bath and analysed by nmr spectroscopy at low temperatures. The following kinetic parameters were calculated for this process (reaction 43):



XXXII R = -COOEt XXXIII 43

$$k_{47.1} = (5.16 \pm 0.21) \times 10^{-5}\ \text{sec}^{-1}$$

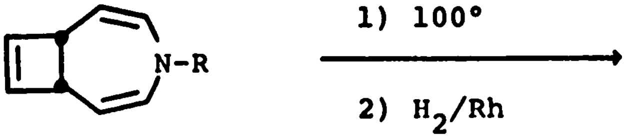
$$k_{67.4} = (5.17 \pm 0.11) \times 10^{-4}\ \text{sec}^{-1}$$

$$\Delta H^{\ddagger} = 23.9 \pm 0.9\ \text{kcal/mole}$$

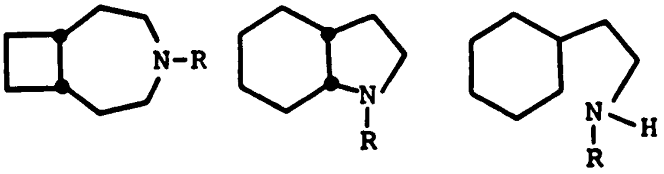
$$\Delta S^{\ddagger} = -3.5 \pm 2.6\ \text{eu}$$

The observed stereospecific rearrangement (low activation energy) suggests a concerted process for this reaction. The general Cope rearrangement (divinyl aziridine rearrangement) seems the most reasonable explanation for this process.[71]

Further thermolysis of XXXIII was studied at higher temperatures. When XXXIII was heated above 120° or a longer period below that temperature, XXXIII yielded a complex reaction mixture. A dilute solution of XXXIII was heated under nitrogen at 100° and the reaction mixture was analysed by nmr spectroscopy. The nmr analysis showed only the presence of N-carbethoxy-cis-dihydroindole (XXXVI). The same reaction mixture was then hydrogenated over rhodium and analysed by mass spectroscopy coupled with glpc. In these analyses, even trace amounts of N-carbethoxy-trans-dihydroindole were not detected. The results are shown below (reaction 44).



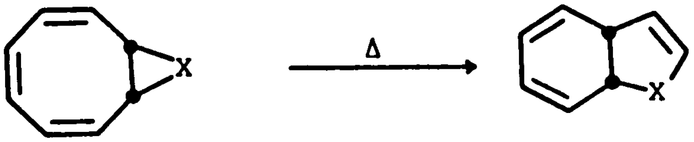
XXXIII



44

(at 100°)	XXXIII'	XXXVI'		Others
1 hr	55.5%	31.5%	5.5%	7.5%
3	3	77	3.3	16.7

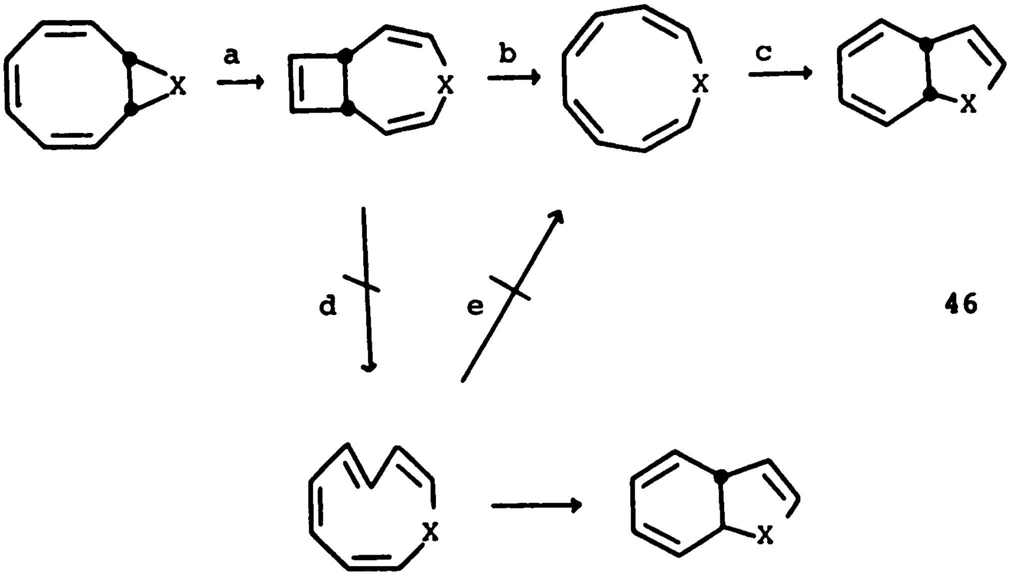
Thus, it was proven that XXXII rearranged to XXXVI via XXXIII. This process is quite general as exemplified by the isomerization of cis-bicyclo[6.1.0]-nonatriene (XXII) to cis-bicyclo[4.3.0]nonatriene (XIX)[50] and cyclooctatetraene epoxide to cis-benzdihydrofuran (reaction 45).[57c]



45

X = CH_2, O, N-R

It can be readily conceived that a similar mechanism is operating in all these cases. Several mechanisms have been suggested recently for the rearrangement of XXII.[72] However, except for the present case an intermediate such as XXXIII has not yet been prepared. The reaction probably proceeds in the following manner (reaction 46):

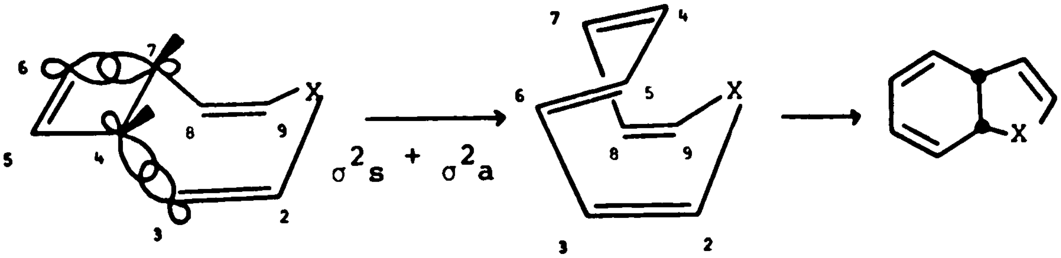


46

X = CH_2, O, N-R

Process a is a Cope rearrangement observed in XXXII. Process c is also operative in all three cases (X = CH_2, O, and N-R) described above. The path d is a conrotatory ring-opening of a cyclobutene unit. In general, the geometrical isomerization of trans- to cis-double bonds (process e) of monocyclic systems has not been experienced under thermal conditions with all

9- and 10-membered ring systems such as cyclononatetraenes (see p. 89), oxonin,[42] and [10]annulenes (see p. 57), but instead, stereospecific cyclization takes place. The fact that the observed thermal products are solely cis-isomers suggests the absence of trans,(cis)^3-tetraenes in these reactions, and therefore process d is disfavored. Considering process b there exist several symmetry allowed- or disallowed-pathways (including other intermediates). For example, symmetry allowed bond reorganization ($_{\sigma}2_s + _{\sigma}2_a$) between two σ bonds ($C_3$-$C_4$ and C_6-C_7) is predicted to produce XXXIV.



A diradical cleavage of the σ bond between C-4 and C-7 may also produce directly XXXIV without complex bond reorganization. The distinction between these two mechanisms or from others, requires a more definite (for instance a labelling experiment) proof before it is established.

CHAPTER 3

EXPERIMENTAL

Physical data

All melting points and boiling points are uncorrected.

Ir spectra were obtained on a Perkin-Elmer Model 21 infrared spectrometer.

Proton nmr spectra were determined using Varian Associates A-60 and HR-100 spectrometers. ^{13}C spectra were recorded on a Bruker HFX-10 spectrometer, 10 mm nmr tubes being used. Signals were locked on the deuterium signals of the solvent. For both proton and ^{13}C spectra chemical shifts were measured from an internal tetramethylsilane reference.

Mass spectra were obtained on A.E.I. MS-9 and MS-12 mass spectrometers.

Uv spectra were measured either with a Cary Model 14 or a Perkin-Elmer 402 spectrometer.

Glpc analyses were performed on three systems. All analyses were carried out with glpc-3 unless otherwise stated.

Glpc-1: F&M Model 700 gaschromatograph (preparative) containing a 10 ft. x 1/4 in.

column packed with 10% silicon rubber (S.E.30) on Chromasorb p (30-60 mesh).

Glpc-2: Aerograph Model A-700 (preparative) containing a 10 ft. x 3/8 in. column packed with 10% silicon rubber (UC W98) on Chromasorb WAW (80-100 mesh).

Glpc-3: F&M Model 5750 (analytic) containing a 6 ft. x 3/16 in. column packed with 10% silicon rubber (UC W98) or with polypropylene glycol adipate (Reoplex 400).

Apparatus

Photolyses were performed using three systems:

Type-1: a conventional preparative photo-apparatus (200 ml capacity) employing either a Hanovia medium-pressure lamp type L (450 Watts) or a cylindrical low-pressure spiral lamp. Three types of filters (Engelhard Pyrex, Corex, and Vycor) were used.

Type-2: a quartz jacket fitted on a Varian variable temperature assembly (accessory for V-4502 EPR). The sample for photolysis was contained in a quartz nmr tube which was then placed in the jacket.

Type-3: a quartz Dewar bottle filled with solvent (e.g. n-pentane). The temperature was controlled by a copper heat-exchange coil placed inside the Dewar flask. As the photolysis vessel, a quartz glass tube (9 mm) was used.

A low-pressure spiral mercury lamp (2537 A) and a reflection mirror were used with type-2 and -3 photo-apparatus. The detailed description of these photo-apparatus was reported previously.[19]

Low temperature column chromatography was performed with three types of columns.

Type-1: a column immersed in a cylindrical glass vessel in which ice water was placed.

Type-2: a column enclosed in a glass jacket through which a temperature-controlled coolant (0° to -30°) was circulated.

Type-3: a column (shown on p. 32) immersed in a Dewar vessel into which dry ice – acetone was placed. Aluminum oxide (Woelm neutral, deactivated with 1.5 wt % of water), and purified n-pentane containing 0 to 5% of methylene chloride were used.

Three types of "cold finger" apparatus were employed in distillation at low temperatures:

- Type-1: a simple cylindrical flask fitted with cold finger tray.
- Type-2: a cylindrical flask with a straight-path cooling jacket between the bottom and the tray.
- Type-3: a cylindrical flask with a spiral-path cooling jacket between the bottom and the tray.

A temperature-controlled coolant was circulated through the jacket with type-2 and -3 apparatus.

Low temperature uv measurement

The uv spectra of thermo-labile species were measured at -55 ± 5° with a Perkin-Elmer 404. The door of the sample chamber was removed and a flat quartz-window Dewar (Worden Quartz Products Inc., No. 4503, 7, total path length 4 cm) filled with reagent grade methanol was aligned in front of the sample-beam slit. The solution inside the Dewar was cooled by a copper heat-exchange coil through which nitrogen, pre-cooled by another copper heat-exchange coil immersed in liquid nitrogen, was passed.

The temperature of the solution was monitored. Into the cooled methanol, a quartz cell (path length 1 cm) with a long glass tube inlet (Emission tubes, cat. No. 4504, 2, Worden Quartz Products Inc.,) and containing a solution of the sample in cold methanol (ca. 5 ml) was immersed. Moisture was expelled from the top of the methanol solution as well as from the windows of the Dewar flask by a rapid stream of nitrogen. The windows of the cell were aligned perpendicular to the uv light. All spectra were run in a darkened room. A 4 cm standard uv cell (as opposed to the special low temperature cell described above) containing methanol at room temperature was used as a reference. The dilution of the sample solution was performed by first removing half of the solution with a long capillary connected to a vacuum line. Cold methanol then was added until the cell was two thirds filled. Mixing was achieved by bubbling nitrogen through the solution. This process was repeated until the desired spectrum was obtained.

After the uv absorbance (A) of the sample had been measured, the cell was removed from the Dewar flask and allowed to warm to room temperature for 10-15 min during which the sample was converted completely to the single thermal product. The warmed sample was cooled to the same temperature (-55°) and the absorbance of the thermal product (A_1) was recorded. Finally the uv of the methanol base line was recorded at -55°. To correct the base line and to avoid errors, the same sample employed above was rerun at room temperature in standard uv cells (path length 1 cm), and the absorbance of thermal product at room temperature (A_2) was recorded. From the known extinction coefficient ε_2 of the thermal product at its uv maximum, the concentration of the thermal product (c_2) at room temperature was obtained. Calculation of the ε value of thermo-labile species was performed based on the assumption that the extinction coefficient does not change appreciably with temperature. Calculations were made in 2 nm intervals utilizing A_2, A_1, and A values corresponding to each wave length, from equation:

$$\varepsilon = (A/c_2)(A_2/A_1)$$

General low temperature hydrogenation procedure with rhodium[19]

Methanol (20 ml) was placed in a three-necked flask, and nitrogen was introduced into the solution through a sintered glass tube. To the solution was added rhodium trichloride trihydrate (125 mg, 0.5 mmole) and charcoal (500 mg). After the rhodium salt had completely dissolved (*ca*. 5 min), $NaBH_4$ (40 mg, *ca*. 1 mmole) in 1 ml methanol was introduced dropwise. The nitrogen stream was replaced by hydrogen which was introduced at a rate of *ca*. 6 ml/min and the temperature of the solution was lowered to -80°. The sample in cold methanol was added by a pre-cooled pipette. The reaction was continued overnight at -80° and the reaction progress was monitored by glpc analysis. After completion of the hydrogenation, the sample was filtered and the methanol removed *in vacuo*. The residual solution was extracted with *n*-pentane, and the solvent was evaporated.

Synthesis of (cis)^5- and trans,(cis)^4-[10]annulene (II and III)

A 10% etheral solution of XII prepared by the treatment of VIII with mercuric bromide[23] was pyrolyzed to VII in a flow system[73] at 410°, the product being condensed in a flask at -80°. The solution was concentrated at -50° in vacuo and distilled onto a cold finger at -10°. The distillate was transferred to a pre-cooled (0°) flask and weighed quickly. Immediately the product was diluted with enough cold purified tetrahydrofuran to form a 2 M solution which was then stored at -80°. A 2 M solution of VII (4.8 g) in THF (16 ml) (85% purity, 8% of VIII, 7% of naphthalene and others) was partitioned into five quartz tubes (0.9 x 30 cm). The photolysis was carried out with the type-3 photoapparatus. The Dewar flask was filled with purified n-pentane which was then cooled and maintained at -60° by circulating a cold (-70°) methanol solution from a refrigeration apparatus (L.T.9, Neblab. Instruments Inc.) through the heat-exchange coil. A sample was equilibrated at -60°. A slow flow of nitrogen was bubbled through the sample solution by means of a capillary tube. Bubbling was maintained during the whole process. Irradiation (using a spiral low-pressure mercury lamp) was continued for 5 hr at -60°. No precipitation occurred during the irradiation period although a thin film was deposited on the inner wall of the tube. The reaction mixture, analysed by glpc and by nmr (-60°), consisted of IX (49%), VII (25.8%), II (4.2%), VI (2%), III (8%), and VIII and naphthalene (11%). Major compounds (IX and VIII) crystallized when left to stand at -80° overnight. The mother liquor was decanted quickly, the crystals were washed with two 2 ml portions of cold (-80°) THF, and the combined solution was kept in dry ice powder in a Dewar flask. At this stage three batches of photolysates were combined. The solvent was evaporated at -68° to -60° *in vacuo*. The resulting viscous syrup was triturated with four 5 ml portions of cold *n*-pentane using a pre-cooled pipette. The solvent was removed completely *in vacuo* and 5 ml of pre-cooled *n*-pentane was added. The solution now enriched in II and III was subjected to low temperature alumina chromatography (type-3).

For the first run (3 batches), 100 g of aluminum oxide (Woelm neutral, 1.5 wt % water) was employed, and the mixture was eluted with purified n-pentane containing 0-5% methylene chloride. A pre-cooled pipette was used to charge the column with the mixture. Each fraction was analysed by glpc and the solvent was removed at -65° to -55° *in vacuo* from the desired fractions to be analysed by nmr (-60°). Typically, fractions 1 and 2 {(50 ml) n-pentane, (100 ml) 2% CH_2Cl_2 – n-pentane} contained no $(CH)_{10}$ compounds, fractions 3 to 5 {(90 ml) 4% CH_2Cl_2 – n-pentane} VI, VII, II, and III, fractions 6 and 7 {(60 ml) 5% CH_2Cl_2 – n-pentane} mainly IX, and fraction 8 {(100 ml) 10% CH_2Cl_2 – n-pentane} mainly VIII. In the second chromatography (type-3), fractions 3 to 5 described above were combined with those from another run (3 batches), and chromatographed over 50 g of alumina and eluted with 0 to 2% CH_2Cl_2 – n-pentane. Fraction 1 {(50 ml) n-pentane, (50 ml) 1% CH_2Cl_2 – n-pentane} contained no $(CH)_{10}$ compounds, fractions 2 and 3 {(50 ml) 1% CH_2Cl_2 – n-pentane} III as the major component with a small amount of VI and VII, fraction 4 {(30 ml)

2% CH_2Cl_2 – n-pentane} VII (88%) and II (12%), fractions 5 and 6 {(60 ml) 2% CH_2Cl_2 – n-pentane} VII (83-77%) and II (17-23%), and fractions 7 to 9 {(130 ml) 2% CH_2Cl_2 – n-pentane} VII (84-72%) and II (26-28%). Fractions 2 and 3 enriched in III were further purified by repeated chromatographic separations (twice) on aluminum oxide (15 and 10 g, 0.5% CH_2Cl_2 – n-pentane) which afforded ca. 300 mg of III (65% III and free from VI and VII): nmr (-50°, d_8-THF) singlet at τ 4.0. This sample was used for kinetic measurements (p. 145). Physical data of pure III are described on p. 153.

Fraction 4 from the chromatography using 50 g of alumina (see above) was discarded, fractions 7 to 9 were saved, and fractions 5 and 6 were rechromatographed over 30 g of aluminum oxide being eluted with n-pentane containing 1-2% of CH_2Cl_2. The best fractions (26% of II and 74% of VII) in this chromatography were combined with fractions 7 to 9 in the previous chromatography. In a similar manner, rechromatographing the better fractions gradually increased the content of II. After repeated chromatographic separations, II was obtained finally as spectrophotometrically (nmr) pure crystalls (below -60°)*: nmr (d_8-THF, -50°) τ 4.20 (s); uv max (MeOH, -50°, measured according to the general method described on p. 134) 235 nm (sh, ε = 1490), 256 (2040), 265 (1340), and 305 (1400).

^{13}C nmr measurement of [10]annulenes (II and III)

Each sample was dissolved in cold (-80°) d_8-THF (1.5 ml) containing TMS (150 μl) and placed in 10 mm nmr tube kept at -80°.

i) (*cis*)^5-[10]annulene (II)

The ^{13}C spectrum of a 150 mg sample (23-31% of II and 77-69% of VII) in d_8-THF and in d_8-THF – $(CD_3)_2O$ (1:1) were measured over a temperature range from -40° to -160°. Since compound VII, in a separate experiment under the same conditions, exhibited three peaks with a 2:2:1 ratio at 2890 Hz (127.2 ppm), 2810 (124.0), and 755 (33.2) from TMS, the signals due to II were readily identified. The proton decoupled nmr spectrum of II exhibited a single peak at 2950 Hz (130.4 ppm) from TMS which was temperature independent over a range

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* This sample was, at least, 95% pure.

from -40° to -150°. The proton coupled spectrum ($J_{^{13}C-H}$ = 158) of II was also temperature independent over a range from -40° to -100°.

ii) trans,(cis)^4-[10]annulene (III)

The proton decoupled spectra of ca. 30 mg (estimated by glpc) of III* were run over a temperature range -40° to -100°. The spectra, measured with 5000 to 500 Hz sweep width, showed five peaks of equal intensity at 2905, 2975, 2979, 2993, and 2998 Hz at -100°, and a single peak at 2970 Hz (130.0 ppm) at -40° from TMS. The spectra are illustrated on p. 51. The compound VI, isolated from the cold reaction mixture obtained by photolysis of VII and purified by alumina chromatography at -80° in a separate experiment, exhibited three peaks at 2998 Hz (132.2 ppm), 2856 (125.6), and 865 (38.1) from TMS with a relative intensity of 2:2:1. The sample of III used above was therefore not contaminated with VI.

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* For the purity of this sample, see p. 153.

Kinetic runs of (*cis*)^5-[10]annulene (II)

A cold (-80°) solution of *ca*. 200 mg (estimated by glpc) of a mixture of 20.7% II and 79.3% VII, prepared by photolysis of VII, was dissolved in deuterioacetone (3 ml) containing TMS (150 μl) and distributed into six nmr tubes kept at -80°. The thermolysis of II was performed in an isothermal bath (Precision Lol Temptrol, Precision Scientific) of ethylene glycol maintained at -14.5 ± 0.2° and +6.2 ± 0.2°. Two samples were run at each temperature and the reaction was quenched by cooling to -80°. The analysis was achieved by nmr (100 MHz, sweep width 100 Hz) at -60°. Both the decrease of II (τ 4.24) and the increase of VII (τ 4.35-4.65) were measured (averaged over three integrations for each spectrum). Ten points were collected over the duration of the thermolysis at each temperature. The results are demonstrated on p. 56.

Kinetic runs of *trans*,(*cis*)^4-[10]annulene (III)

A cold (-80°) solution of 100 mg (estimated by glpc) of III (65% pure, no thermal products) in deuterioacetone (3 ml) containing methylene bromide (10 μl) and TMS (150 μl) was distributed into six nmr tubes immersed in dry ice – acetone Dewar using pre-cooled pipettes. The kinetics were run in an isothermal bath (L.T. 9 Neblab. Instruments Inc.) of methanol. Two samples were run at each temperature and the reaction was quenched in dry ice – acetone bath (-80°). The process was followed by 100 MHz nmr at -60°. The increase of VI (τ 7.2) was measured three times against methylene bromide signal (τ 4.7) (500 Hz sweep width). The temperature of the bath remained constant to within ± 0.1° during the whole process. Ten points were collected during the thermolysis at each temperature. The results are shown on p. 57 .

Synthesis of tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene (XV)

To a vigorously stirred suspension of small pieces of lithium metal (1.3 g, 220 mmole) in dry ether (80 ml) maintained at -80° was added under nitrogen 9-chlorobicyclo[6.1.0]nona-2,4,6-triene {6.64 g, 44 mmole, a mixture of syn- and anti-isomers (1:5.3)} prepared from the reaction of cyclooctatetraene dianion with chloroform.[6] The reaction temperature was gradually raised to room temperature over a period of 2.5 hr and stirring was continued for another 0.5 hr at room temperature. The solution was transferred by nitrogen pressure to a dry three-necked flask kept under nitrogen, through a dry glass tube packed with a small amount of cotton in order to filter the solution from lithium chloride and excess lithium metal. To this solution, stirred under nitrogen and maintained at -40°, was added dry methylene chloride (8.6 g, 100 mmole). Stirring was continued for 10 min and then 100 mmole of n-butyllithium in 60 ml of n-hexane was added dropwise over a 45 minute period at this temperature. After the solution had been stirred for another 30 min, the excess butyllithium was decomposed at -40° by addition of cold (-78°) methanol (1 ml). The reaction mixture was cooled to -80° and filtered quickly through a pre-cooled (-25°) Buchner funnel into a pre-cooled flask (-80°). The solvent was evaporated completely at -50° *in vacuo*. The residual liquid was triturated with cold *n*-pentane (*ca*. 3 ml) and transferred to a pre-cooled cylindrical flask. The solvent was removed at -50° *in vacuo*, and all volatile fractions were distilled onto a cold finger (type-1) at -20° to -10°/0.001 mm. Glpc analysis of this distillate (500 mg) demonstrated the following compounds: XV (50-75%, observed as XIII), VII (7-18%), VI (5-15%), and unidentified compounds (5-15%) (relative yields of the products varied with individual runs within the range indicated above).

Isolation of pure material was achieved by fractional distillation (twice) onto a cold finger (type-3).

(pressure 0.001 mm)

Fraction	Distillate	Jacket Temp	Bottom Temp
1 and 2	*ca*. 650 mg equal amounts of VI, VII, and XV	-23° to -18° (2 hr)	-20° to -15°
3	*ca*. 600 mg XV (70%)	-18° to -13° (2 hr)	-15° to -10°
4	*ca*. 120 mg XV (75%), VII, and naphthalene	-13° to -8° (1 hr)	-5° to 0°
5	*ca*. 30 mg naphthalene, and unidentified materials	-8° to -3° (1 hr)	0° to 5°

Fraction 3 was redistilled in a similar manner. The best fraction (*ca*. 60 mg, 90% purity, distilled between -18° to -10°/0.001 mm (jacket temp)) was taken up in pre-cooled deuteriochloroform: nmr τ 3.9-4.55 (complex multiplet, 5 H), 4.65 (broad doublet, 1 H), 6.30 (broad triplet, 1 H), and 7.95-8.60 (complex multiplet, 3 H). The spectrum is illustrated on p. 66 .

Hydrogenation of tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene (XV) at -80°

The procedure was the same as described on p. 137. Compound XV (50 mg) in cold ether (1 ml) was hydrogenated over rhodium catalyst in methanol at -80°. The reaction mixture was filtered and the solvent removed at 0°/100 mm. The residue was extracted with three 10 ml portions of *n*-pentane and dried over sodium sulfate. The solvent was removed at -10° to 0°/100 mm, and the residue distilled onto a cold finger (type-1). Glpc (Reoplex column, 90°) and mass spectral analysis demonstrated the following products (retention times are indicated): compound A 11.0 min (10%, *m/e* 138 bicyclic), B 17.3 min (9%, *m/e* 138, bicyclic), and C 21.1 min (79%, *m/e* 136, tricyclic). Compound C collected by preparative glpc-1 was shown to be identical {nmr, mass spectrum, and glpc (Reoplex and UC W98)} with an authentic material prepared by a

Wolf-Kishner reduction of the corresponding ketone.[45]

Kinetic runs of tricyclo[5.3.0.0^{2,10}]deca-3,5,8-triene (XV)

A cold (-40°) solution of XV (145 mg) in deuteriochloroform (3.25 ml) containing TMS (150 µl) was partitioned into ten nmr tubes. The solutions were degassed and the tubes sealed. The thermolyses were carried out in an isothermal bath at 30.8 ± 0.1° and 11.1 ± 0.1°, with five samples used at each temperature. The formation of XIII (τ 3.3) was measured against the internal standard (chloroform at τ 2.73) by 100 MHz nmr run at -20°. All the samples were kept in a dry ice – acetone bath before and after each run, and were placed one minute in an ice water bath before being immersed in the kinetic bath. The results are illustrated on p. 68 .

Detection of trans,(cis)^4-[10]annulene (III) in the reaction mixture

A solution of lithium cyclononatetraenide (14 mmole) in ether (50 ml) was stirred mechanically under a nitrogen atomosphere and then cooled to -60°.

Dry methylene chloride (2.9 g, 29 mmole) was added, and stirring was continued for 10 min, followed by dropwise addition of butyllithium (29 mmole) in _n_-hexane (20 ml) over a period of 1 hr at -55 ± 5°. The reaction mixture was cooled to -80° and cold methanol (1 ml) and ether (50 ml) were added, and the reaction mixture was stored undisturbed overnight at -80°. The cold solution was decanted quickly into a pre-cooled (-80°) flask, and the solvent was evaporated at -60° to -50° _in vacuo_.

In order to filter out solids, the viscous residue was transferred with two 7 ml portions of cold ether to an alumina column (type-3) (aluminum oxide, neutral Grade II, 10 g) maintained at -80°, and eluted with cold ether. All the $(CH)_{10}$ compounds were eluted in the first 120 ml portion of ether. This solution was reduced to 2 ml at -65° to -55° under reduced pressure. Glpc analysis of this residue demonstrated that XV (observed as XIII, 64.5%), III(observed as VI, 13.5%), VII (13.5%), and other unidentified materials (8.1%) were present in the reaction mixture. Approximately one-third of this solution was transferred by pre-cooled pipette to a pre-cooled flask, and the solvent removed *in vacuo* at -60°. The residue was diluted with pre-cooled deuteriochloroform and transferred into an nmr tube maintained at -80°, and examined by nmr.

The rest of the solution was hydrogenated according to the general method described on p. 137. The hydrogenated reaction mixture was worked up as described previously (p. 149). The mixture, analysed by glpc and mass spectrometry, was composed of the following materials, each identified by comparison with an authentic sample. Retention times (Reoplex column, 80°) are indicated: cyclononane (7.2 min, *m/e* 126, 1.6%), *trans*-decalin (7.9 min, *m/e* 138, 2.3%), unknown (9.3 min, *m/e* 140, 17.8%), compound A (10.6 min, *m/e* 138, 10.6%), *cis*-decalin (11.6 min, *m/e* 138, 17.8%), cyclodecane (13.4 min, *m/e* 140, 15.2%), compound B (15.1 min, *m/e* 138, 3.4%), and compound C (19.5 min, *m/e* 136, 28%). Compound A, B, and C proved identical with those obtained by hydrogenation of XV (see p. 149).

Isolation of trans,(cis)^4-[10]annulene (III) from the reaction mixture

The reaction was carried out in essentially the same manner as described in the previous section except that the reaction was scaled up two fold. Three batches of the reaction mixture were combined. After filtration through an alumina column at -80°, the mixture was subjected to alumina chromatography (type-3) (aluminum oxide Woelm neutral containing 1.5 wt % of water, 100 g) and was eluted with *n*-pentane. Each fraction was analysed by glpc. In the first chromatography, compound III with other minor unidentified materials was separated from VII and XV. Repeated chromatographic separations (total 5 times) finally afforded spectrophotometrically pure crystalls (below -60°)* of III (*ca*. 35 mg): nmr (d_8-THF, -50°) τ 4.0 (s); uv max (MeOH, -55°) 257 nm ($\varepsilon = 2.9 \times 10^4$), 265 ($2.0 \times 10^4$), and uv min 263 ($1.9 \times 10^4$). Temperature dependent nmr spectra are shown on p. 49. ^{13}C nmr spectrum is reproduced on p. 51.

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* This sample was, at least, 95% pure.

Materials used for photolysis of C_9H_{10} compounds

Compound XXII was prepared according to Katz' method.[6a] Compound XIX was obtained by thermolysis of XXII at 90°[50] or more conveniently by thermal isomerization of XXV at 50°. Compounds XX and XXIII were prepared by low temperature photolysis (2537 A) of XXII.[33] XX was isolated by preparative chromatography (glpc-2) from the reaction mixture. Compound XXIII was isolated from the same photolysis mixture by fractional distillation onto a cold finger (type-2) after the mixture had been heated in diphenyl ether at 120° for 1 hr. (By fractional distillation, XXIII could be readily separated from all compounds except XXII. Thermal conversion of XXII to XIX at 120° at which temperature XXIII was stable, was necessary to achieve complete separation.) Hydrogenation of XXIII yielded a single product with nmr and ir identical with those of authentic trans-bicyclo[6.1.0]nonane. Compound XXIV was prepared by photolysis (2537 A) of XXII at room temperature, and purified by preparative glpc-2: nmr (CCl_4) τ 4.02-4.78 (m, 4 H), 6.78-7.12 (1 H), 7.42-7.60 (0.4 H), 7.65-8.12 (2.1 H), 8.12-8.41 (1.3 H), and 8.48-9.00 (1.2 H). Hydrogenation of XXIV at low temperature yielded three compounds. The major compound was found to be tricyclic (*m/e* 122), while the other two proved to be bicyclic (*m/e* 124).

The retention times of C_9H_{10} compounds relative to *cis*-decalin on glpc-3 (UC W98, 95°) are tabulated below:

C_9H_{10} compound	XX	XIX	XXIV	XXII	XXIII	*cis*-decalin
	0.32	0.36	0.49	0.54	0.62	1.0

Isolation of (*cis*)^4-cyclononatetraene (XXV)

To a stirred solution of lithium cyclononatetraenide (IV) (13 mmole) in tetrahydrofuran (10 ml) at -80° under nitrogen was added cold methanol (1 ml). Stirring was continued for another 10 min at this temperature and the reaction temperature was gradually raised to 0° over a period of 30 min, and held at this temperature for another 15 min. Subsequently the solution was cooled to -30°, and transferred to a pre-cooled cold finger apparatus (type-1). The solvent was removed *in vacuo* at -50°. All volatile substances (mainly XXV and residual THF) were collected in the cold finger at 0° *in vacuo*. Fractional distillation of the volatile substances using a cold finger type-3 (jacket temp -20° to -12°/0.04 mm, bottom temp -7° to 0°, 20 min) provided *ca*. 1.0 g (98% purity) of XXV: nmr ($CDCl_3$, -50°) τ 3.9-4.6 (m, centered at τ 4.2, 8 H) and 6.9 (t, *J* = 6 Hz, 2 H); uv max (MeOH, -50°) 250 nm (ε = 2300), 258 (2360), 268 (1920), 274 (1280), and 284 (760).

The low temperature rhodium-catalyzed hydrogenation of XXV provided a 98% yield of cyclononane (*cis*-decalin was used as internal standard) which was shown to be identical (nmr, mass spectrum, ir, and glpc) with a prepared authentic sample.

Isolation of *trans*,(*cis*)^3-cyclononatetraene (XXI)

i) Crystallization method

A solution of compound XXIII (125 mg) in 200 ml *n*-pentane was irradiated for 9 min at -80° with a low-pressure mercury lamp in a conventional preparative photoapparatus (type-1). The outside of the cell was cooled with a dry ice – acetone bath, and the jacket between the solution and the lamp was cooled by a stream of cold nitrogen. Stirring of the reaction mixture was accomplished by magnetic stirring and by a slow stream of nitrogen introduced at the bottom of the apparatus. The solvent was removed at -60° *in vacuo* and the residue was dissolved in cold 3-methylpentane (3 ml), and transferred to a pre-cooled pear-shaped flask (20 ml). The solvent was removed *in vacuo* at -55° to -60° and the residue dissolved in cold d_{14}-3-methylpentane (0.3 ml), and cooled at -80° for 2 hr. The major compound (XXIII) crystallized out. The mother liquor now enriched in the desired material XXI (70% of XXI and 30% of XXIII) was withdrawn with a pre-cooled pipette.

ii) Chromatography method

Typically, a solution of XXII (1 g) in purified *n*-pentane (160 ml) was irradiated by a low-pressure mercury lamp at -80° for 4 hr in a way similar to that described above. The glpc trace of the reaction mixture indicated compounds XX (27%, corresponds to XXI), XIX (7%), XXIV (3%), XXII (22%), and XXIII (40%). The reaction mixture was transferred to a pre-cooled (-78°) flask and the solvent was removed at -68° to -60° *in vacuo*. The residual yellow syrup was triturated with two 2 ml portions of pre-cooled *n*-pentane. The *n*-pentane extracts enriched in XXI (*ca*. 45%) were subjected to the low temperature alumina chromatography type-3 (aluminum oxide 100 g, Woelm neutral, Grade II, *n*-pentane). Each fraction was analysed by glpc. Typically, in the first run, fractions 1 and 2 (total 150 ml) contained only solvent, fraction 3 (50 ml) mainly XXIII (80%), fraction 4 (25 ml) a mixture of XXII and XXIII, fractions 5 to 10 (total 65 ml) mainly XXI (70%), and fraction 11 (40 ml) mainly XXV. Fractions 5 to 10 were combined and rechromatographed on aluminum oxide (Woelm neutral, Grade II, 100 g, *n*-pentane). Fractions 1 to 3 (total 200 ml) contained only solvent, fractions 4 and 5 (total 50 ml) pure XXIII, fractions 6 and 7 (total 35 ml) a mixture of XXII and XXIII, fractions 8 and 9 (total 25 ml) pure XXI (95%), and fractions 10 to 12 (total 90 ml) 85-90% of XXI and 15-10% of XXV. Fractions 8 and 9 were combined, solvent was removed at -50° *in vacuo* and taken up in cold d_8-THF (0.4 ml): nmr (d_8-THF, -50°) τ 3.5-4.7 (m, 8 H), and 7.0-7.2 (broad triplet, 2 H). The spectrum did not show any appreciable change between -30° and -105°. Uv max (MeOH, -50°) 230 nm ($\varepsilon = 1.25 \times 10^4$), and 318 ($2.2 \times 10^3$). The concentration of XXI was calculated by converting the same sample to XX by warming to room temperature for 20 min. The procedure was essentially the same as that described on p. 134. As an extinction coefficient of XX, λ_{max} 260 nm ($\varepsilon = 3700$)[33] was employed. Both nmr and uv spectra of XXI are shown on p. 88 and 90.

The preparation of mono *trans*-cyclononatetraenide (XXVI)

Small pieces of lithium (180 mg) were dispersed in dry tetrahydrofuran (5 ml) under nitrogen. The solution was cooled to -78° in dry ice – acetone bath and stirred magnetically. Anti-9-chloro-*cis*-bicyclo-[6.1.0]nonatriene (560 mg) was added and stirring was continued at this temperature for 30 min, and then at -70° to -65° for 2.5 hr. After most of the starting material had been consumed (analysis by glpc), the solution was filtered under positive nitrogen pressure through a glass tube equipped with a coarse sintered glass disc into a second flask maintained under a nitrogen atomosphere and at -78°. The filtered solution was transferred by a pre-cooled pipette to nmr tubes with all operations performed under a nitrogen atomosphere. The nmr of the product indicated 65-75% of trans-cyclononatetraenide (XXVI) and 35-25% of cis-cyclononatetraenide (IV). (The relative yields of the both compounds varied with individual runs within the range defined above.) Protonation was accomplished by addition of cold methanol at -80° and the products were analysed by nmr and glpc trace. Hexamethyldisilane (5 μl, τ 9.5) was used as an internal standard. The results are described on p. 92 .

Low temperature photolysis of C_9H_{10} compounds

i) Photolysis by low-pressure lamp

The photolyses of XXII, XXIII, XIX, XX, and XXV were performed under the same conditions. A type-3 photo-apparatus described on p. 133, and a low-pressure spiral mercury lamp (2537 A) were used. A ca. 0.8 M solution of sample in THF (3 ml) containing cis-decalin (internal standard) was irradiated in a quartz glass tube (9 mm) at -60°, and the reaction progress was monitored by glpc. Typically, a solution of XXV (95 mg) in cold tetrahydrofuran (3 ml) was irradiated at -60°. After the reaction reached equilibrium (140 min), the solution was cooled to -80° and analysed by glpc. Subsequently, approximately half of the cold reaction mixture (ca. 1.5 ml) was hydrogenated at -80° by the usual method described on p. 137. The analysis of the reaction mixture was achieved by glpc using two different columns (Reoplex and UC W98 at 60°). All saturated compounds were identified by comparison with authentic samples. The remainder of the cold reaction mixture was heated at 50° for 1 hr, and then hydrogenated under exactly the same conditions as above, and analysed in the same way. The results are demonstrated on p. 78 and 95.

ii) Photolysis by high-pressure lamp

Irradiation of XXII, XXIII, and XXV was performed under the same conditions using a super high-pressure mercury lamp (200 Watts) with a type-2 photoapparatus. Three types of filters, Pyrex (> 3000 A), Corex (> 2800 A), and Vycor (> 2500 A) were employed. Typically, the irradiation of XXV (30 mg) in d_8-THF (0.3 ml) containing TMS was effected in a quartz nmr tube using a Pyrex or Vycor filter. The products were analysed by nmr (-60°) and glpc. These results are described on p. 99 .

Synthesis of N-carbethoxyazonin (XXXIV)

A solution of XXXII (200 mg) in ether or *n*-pentane (200 ml) was equilibrated at -80° in a conventional preparative photoapparatus (type-1). The outside of the vessel was cooled with a dry ice – acetone mixture and a rapid flow of nitrogen was passed through the cooling jacket between the lamp and the solution. Stirring was accomplished by a magnetic stirring bar and by a low flow rate of nitrogen bubbling into the solution. The irradiation was achieved by a spiral low-pressure mercury lamp (1.8 meter, 120 mA) for 10-15 min at -80°. The yellow solution was transferred to a pre-cooled flask. Seven batches of photolysate were combined at this stage, and the solvent was removed by a rotatory evaporator at 0°. The residue was triturated with four 24 ml portions of cold (0°) n-pentane. {The residual solids consisted of polymeric materials (nmr).} The removal of the solvent at 0° provided 1.10 g of liquid which was subjected to silicic acid (100 g) column chromatography. Two types of chromatographic columns (type-1 and -2, see p. 133) were used. The mixture was eluted with pre-cooled chloroform and each fraction was analysed by nmr at -40°. The reaction mixture was separated effectively by repeated chromatography (twice). Typically, fraction 1 (100 ml) contained only solvent, fractions 2 and 3 (30 ml) a mixture (134 mg) of [16]annulene and its photoprecursor ($C_{16}H_{16}$) which was an impurity in the starting material XXXII, fractions 4 to 7 (40 ml) XXXIV as the major product (466 mg), and fractions 8 to 12 (80 ml) XXXII (220 mg). Fractions 4 to 7 were combined and rechromatographed under the same conditions. Fractions 1 to 5 contained only solvent, fractions 6 to 8 (30 ml) pure XXXIII (34 mg), fraction 9 (10 ml) a mixture (31 mg) of XXXIII (60%) and XXXIV (40%), fraction 10 (10 ml) a mixture (24 mg) of XXXIII (60%), and XXXIV (40%), fractions 11 and 12 (20 ml) pure XXXIV (76 mg), fractions 13 and 14 (20 ml) a mixture (70 mg) of XXXIV (55%) and XXXV (45%), and fractions 15 to 17 pure XXXII (173 mg). The pure material XXXIV in fractions 11 and 12 showed: nmr (d_8-THF, 30°) τ 3.68 (d, $\underline{J}_{AB}$ = 10.5 Hz, 2 H), 4.22 (broad singlet, 4 H), 4.82 (d, $\underline{J}_{AB}$ = 10.5 Hz, 2 H), and ethyl signals; mass spectrum (direct injection) $\underline{m}/\underline{e}$ 191.0944 (parent peak), calcd for $C_{11}H_{13}NO_2$ 191.0946; ir ($CHCl_3$, measured at 0° in Variable temperature chamber, Barnes Infrared Analytical Accessories) 3.36 m, 5.84 s, 6.15 sh, 6.75 w, 6.80 w, 7.11 s, 7.23 s, 7.28 sh, 7.46 m, 7.63 s, 7.96 m, 8.55 m, 8.93 m, 9.73 m, and 10.60 w μ; uv max (MeOH, 5°, Cary Model 14 M) 265 nm (log ϵ = 3.53) and min 253 (3.50). The nmr and uv spectra are reproduced on p. 104 and p. 111, respectively.

The hydrogenation of XXXIV (11 mg) was carried out at -80° over rhodium catalyst under exactly the same conditions as described on p. 137. The solvent was removed *in vacuo* and the residue was triturated with two 10 ml portions of *n*-pentane. Distillation of the crude product (8 mg) *in vacuo* provided pure (glpc) material (6 mg) which proved to be identical (nmr, ir, mass spectrum, and glpc on two different columns) with authentic N-carbethoxyazacyclononane prepared by a conventional method.

Rechromatography of fractions 13 and 14 (*vide supra*) provided a new material XXXV. Nmr ($CDCl_3$) of this compound exhibited a typical AB-type signal at τ 6.25 (J_{AB} = 24 Hz, 1 H) and 6.78 (J_{AB} = 24 Hz, 1 H) and multiplets centered at τ 3.05, 3.30, 3.65, 4.0, and 4.75.

Analysis of the cold photolysate of XXXII by low temperature hydrogenation

A solution of XXXII (171 mg, 0.9 mmole) and N-carbethoxypiperidine (80 mg, internal standard) in ether (200 ml) was irradiated at -80° for 10 min in a conventional photo-apparatus (type-1) under the same conditions described on p. 162. The ether solution was concentrated to *ca*. 6 ml *in vacuo* at -55°, and then distributed into three pre-cooled flasks.
The first portion was maintained at -80°, the second portion was allowed to warm to -15° and maintained at that temperature for 1 hr, and the third portion was heated at 50° for 2 hr. These three portions were hydrogenated at -80° under the same conditions by the general method described on p. 137. After filtration, the solvent was removed *in vacuo* and the residue extracted with three 8 ml portions of benzene. The work-up procedure was identical for each part.
Removal of solvent from the three extracts yielded 42 mg, 47 mg, and 48 mg of reaction mixture respectively.
These reaction mixtures were analysed by comparison with authentic samples {glpc-3 (Reoplex column, temp 170°) and mass spectrum (MS-12)}.

Temperature dependent nmr spectra of XXXIV, XXXIII, XXXVII, and XXXVIII

A solution of XXXIV (20 mg) in deuterated solvent (deuteriotetrahydrofuran or deuteriochloroform) (0.35 ml) containing TMS (35 μl) was degassed and sealed in an nmr tube. The sample was equilibrated for at least 10 min at each temperature and the spectra (100 MHz) were run over the temperature range +20° to -90°. The operating temperature was calibrated. Similarly, the spectra of XXXIII, XXXVII, and XXXVIII were run in deuteriochloroform (40 mg in 0.33 ml), in deuterioacetonitrile (40 mg in 0.33 ml), and in a 1:1 mixture of deuteriotetrahydrofuran and carbon disulfide (0.4 ml) (30 mg). Coalescence temperatures were determined for each compound and are summarized on p. 121. The temperature dependent spectra of XXXIV and XXXIII are reproduced on p. 113 and p. 120, respectively.

Thermolysis of some C_8H_8N-R compounds

i) Thermolysis of XXXIV

A solution of XXXIV (20 mg) in d_8-THF (0.35 ml) containing TMS was degassed and vacuum sealed at 0° in an nmr tube. The thermolysis of XXXIV began at +40° as evidenced by the decreased intensity of its nmr signals after 10 min reaction. Approximately half of the original peaks had disappeared following heating at 52° for 10 min, and the reaction was complete at this temperature in 1 hr, producing XXXIV: nmr τ 3.35 (dd, 1 H), 4.05-4.42 (m, 4 H), 5.12 (dd, 1 H), 5.01 (J_{AB} = 14 Hz, 1 H), and 6.08 (J_{AB} = 14 Hz, 1 H); uv max (MeOH) 227 nm (ε = 16000), 261 (3000), and 291 (855).

The low temperature hydrogenation of XXXIV (20 mg) was effected under the usual reaction conditions (rhodium/charcoal, MeOH, see p. 137). The similar work-up described on p.165 yielded the single product (8 mg) which was proved to be identical (nmr, mass spectrum, and glpc on different columns at 180°) with authentic N-carbethoxy-cis-perhydroindole.

ii) Thermolysis of N-carbethoxy-9-azabicyclo[6.1.0]-nona-2,4,6-triene (XXXII)

The kinetic runs of XXXII were carried out in a silicon oil bath constructed from a large Dewar flask placed in a wooden box with a door. Heat supplied to the bath was controlled by a proportioning controller. The bath temperature never varied more than ± 0.2° from the set temperature. A 0.156 mole solution of XXXII (165 mg) (purified by low temperature (-20°) chromatography type-2, with silicic acid – chloroform) containing acetonitrile (12 μl) and TMS (250 μl) in deuteriochloroform (5.5 ml) was partitioned into ten nmr tubes. The tubes were degassed and sealed. The reactions were run at two different temperatures (47.1° and 67.4°). Five samples were used for each run, and quenched at -80°. Before initiation of heating, samples were kept at room temperature for 2 min to avoid errors due to too large a temperature increase. The processes were followed by nmr (100 MHz) maintained at -20°. The decrease of the XXXII singlet (τ 6.9) was measured against acetonitrile (τ 8.0). Ten points were taken for each temperature and these fitted nicely on a straight line corresponding to the first order kinetic equation. The kinetic parameters obtained for this reaction are summarized on p. 125.

iii) Thermolysis of N-carbethoxy-4-azabicyclo[5.2.0]-nona-2,5,8-triene (XXXIII)

A dilute solution of XXXIII (24 mg) in toluene (100 ml) was heated under nitrogen at 100° for 1, 2, and 3 hr. The solvent was removed *in vacuo* at room temperature. The residue first was analysed with nmr and then was hydrogenated over rhodium (see p. 137) at 0° for 0.5 hr followed by warming to room temperature for 3 hr. The reaction mixture was worked up in the same way as described on p. 165 and analysed by glpc (Reoplex column, 170°) and mass spectrum (AEI MS-12).
The results are described on p. 127.

REFERENCES

1. E. Hückel, Z. Phyzik, 70, 204 (1931).
2. For instance see: (a) M. J. S. Dewar in "Aromaticity", p 177, special publication No. 21 of the chemical society, London (1967), (b) M. J. S. Dewar and G. J. Gleicher, J. amer. Chem. Soc., 87, 685 (1965). For recent review see: (c) H. P. Figeys in "Topics in Carbocyclic Chemistry", Vol I, p 269, Logos Press Limited (1969).
3. For instance see: (a) G. M. Badger, "Aromatic Character and Aromaticity" Cambrige University Press, Cambrige, England (1969), (b) Reference 2a. (c) A. Streitwieser, "Molecular Orbital Theory" p 256, John Wiley & Sons Inc., New York (1961).
4. K. Mislow, J. Chem. Phys., 20, 1489 (1952).
5. T. J. Katz, J. Amer. Chem. Soc., 82, 3784 (1960).
6. (a) T. J. Katz and P. J. Garratt, ibid., 85, 2852 (1963); 86, 5194 (1964), (b) E. A. LaLacette and R. E. Benson, ibid., 85, 2853 (1963); 87, 1941 (1965).
7. See references cited in review articles by T. L. Burkoth and E. E. van Tamelen in "Nonbenzenoid Aromatics", p 63, J. P. Snyder, Ed., Academic Press, New York (1969).

8. (a) E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, *3*, 228 (1964), (b) V. Boekelheide and R. J. Windgassen, Jr., *J. Amer. Chem. Soc.*, *83*, 462 (1961). (c) K. Grohmann and F. Sondheimer, *ibid.*, *89*, 7119 (1967).

9. E. E. van Tamelen and T. L. Burkoth, *ibid.*, *89*, 451 (1967), see also E. E. van Tamelen and R. H. Greeley, *Chem. Commun.*, 601 (1971).

10. E. E. van Tamelen and B. Pappas, *J. Amer. Chem. Soc.*, *85*, 3296 (1963).

11. W. von E. Doering and J. W. Rosenthal, *ibid.*, *89*, 4534 (1967).

12. (a) G. Schröder, *Ber.*, *97*, 3140 (1964), (b) G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, *6*, 414 (1967).

13. W. von E. Doering and W. R. Roth, *Tetrahedron*, *19*, 715 (1963).

14. W. von E. Doering and J. W. Rothenthal, *J. Amer. Chem. Soc.*, *88*, 2078 (1966).

15. (a) reference 12, (b) G. Schröder, "Cyclooctatetraene" Verlag Chemie, Gmbh, Weinheim (1965).

16. W. von E. Doering and J. W. Rothenthal, *Tetrahedron Letters*, 349 (1967).

17. R. T. Seidner, N. Nakatsuka and S. Masamune, *Can. J. Chem.*, *48*, 187 (1970).

18. S. Masamune, C. G. Chin, K. Hojo and R. T. Seidner, J. Amer. Chem. Soc., 89, 4804 (1967).

19. R. T. Seidner, ph D. thesis, University of Alberta, Alberta, Canada (1969).

20. M. Jones, Jr., and L. T. Scott, J. Amer. Chem. Soc., 89, 150 (1967).

21. G. Schröder and Th. Martini, Angew, Chem., Int. Ed. Engl., 6, 806 (1967).

22. (a) M. Jones, Jr., and B. Fairless, Tetrahedron Letters, 4881 (1968), (b) W. Crimme, H. J. Riebel and E. Vogel, Angew. Chem., Int. Ed. Engl., 7, 823 (1968), (c) reference 17.

23. H. P. Loffer and G. Schröder, ibid., 7, 736 (1968).

24. S. Masamune R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka and G. Bigam, J. Amer. Chem. Soc., 90, 5286 (1968).

25. E. Babad, D. Ginsburg and M. B. Rubin, Tetrahedron Letters, 2361 (1968).

26. K. Hojo, R. T. Seidner and S. Masamune, J. Amer. Chem. Soc., 92, 6641 (1970).

27. (a) reference 18, (b) M. Jones, Jr., J. Amer. Chem. Soc., 89, 4236 (1967), (c) S. Masamune, H. Zenda, M. Wiesel, N. Nakatsuka and G. Bigam, ibid., 90, 2727 (1968), (d) reference 26.

28. (a) S. Masamune, H. Cuts and M. Hogben, Tetrahedron Letters, 1017 (1966), (b) W. G. Dauben and D. L. Whalen, ibid., 3743 (1966).

29. E. N. Cain, R. Vukov and S. Masamune, Chem. Commun., 98 (1969).

30. H. H. Westberg, E. N. Cain and S. Masamune, J. Amer. Chem. Soc., 91, 7512 (1969).

31. E. Vedejs, Chem. Commun., 536 (1971).

32. (a) R. B. Woodward and R. Hoffmann, J. Amer. Chem. Soc., 87, 395, 2046, 2511 (1965), (b) R. Hoffmann and R. B. Woodward, Accounts Chem. Res., 1, 17 (1968), (c) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry" Academic Press, New York (1970).

33. E. Vogel, W. Grimme and E. Dinne, Tetrahedron Letters, 391 (1965).

34. S. Masamune, P. Baker and K. Hojo, Chem. Commun., 1203 (1969).

35. S. Masamune and R. T. Seidner, ibid., 542 (1969).

36. (a) T. J. Katz and J. J. Cheung, J. Amer. Chem. Soc., 91, 7772 (1969), (b) T. J. Katz, J. J. Cheung and N. Acton, ibid., 92, 6643 (1970).

37. S. Masamune, K. Hojo, Kiyomi Hojo, G. Bigam and D. L. Rabenstein, J. Amer. Chem. Soc., 93, 4966 (1971).

38. L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. BenEfraim, Y. Gaoni, R. Wolovsky and A. A. Bothner-By, ibid., 84, 4307 (1962).

39. Uv spectrum of pure VII was measured by Dr. R. T. Seidner in our laboratory. The observed ε value was different from that reported previously.[10]

40. For example see: E. L. Eliel, "Stereochemistry of Carbon Compounds" McGraw--Hill Book Company Inc., (1962).

41. (a) F. A. L. Anet, J. Amer. Chem. Soc., 84, 672 (1962), (b) F. A. L. Anet, A. J. R. Bourn and Y. S. Lin, ibid., 86, 3577 (1964), (c) J. F. M. Oth cited in reference 2b,p 302.

42. S. Masamune, S. Takada and R. T. Seidner, J. Amer. Chem. Soc., 91, 7769 (1969).

43. G. Boche, D. Martens and W. Danzer, Angew. Chem., Int. Ed. Engl., 8, 984 (1969).

44. E. Vedejs, Tetrahedron Letters, 2633 (1968).

45. W. von E. Doering, E. T. Fossel and R. L. Kaye, Tetrahedron, 21, 25 (1965).

46. J. M. Brown, Chem. Commun, 227 (1965).

47. (a) reference 32c and literatures, cited therein (b) G. L. Closs and P. E. Pfeffer, J. Amer. Chem. Soc., 90, 2452 (1968).

48. T. J. Katz, E. J. Wang and N. Acton, ibid., 93, 3782 (1971).

49. E. Vedejs, R. A. Shepherd and R. P. Steiner, ibid., 92, 2158 (1970).

50. E. Vogel, Angew. Chem., 73, 548 (1961).

51. (a) E. Vogel and W. Grimme, cited in reference 31, (b) R. Rieke, M. Ogliaruss, R. McClung and S. Winstein, J. Amer. Chem. Soc., 84, 4729 (1966).

52. A. C. Cope and J. K. Hecht, ibid., 85, 1780 (1963). The author is thankful to Professor E. J. Corey and Dr. J. I. Shulman for providing him with spectra of XXIII'.

53. (a) E. LeGoff, J. Org. Chem., 29, 2048 (1964), (b) N. L. Allinger and J. L. Coke, J. Amer. Chem. Soc., 82, 2553 (1960), (c) See also reference 52.

54. D. S. Glass, J. W. H. Watthey and S. Winstein unpublished results cited in reference 33. See also J. W. H. Watthey and S. Winstein, J. Amer. Chem. Soc., 85, 3715 (1963).

55. Uv spectra of XIX was measured in methanol. See also reference 6a.

56. (a) reference 37, (b) G. Boche, H. Bohme and D. Martens, Angew. Chem., Int. Ed. Engl., 8, 594 (1969), (c) P. Radlick and G. Alford, J. Amer. Chem. Soc., 91, 6529 (1969), (d) A. G. Anastassiou, V. Orfanosand and J. H. Gebrian, Tetrahedron Letters, 4491 (1969).

57. (a) S. Masamune and N. T. Castellucci, Angew. Chem., Int. Ed. Engl., 3, 582 (1964), (b) A. C. Cope, R. T. Moore and W. R. Moore, J. Amer. Chem. Soc., 80, 5505 (1958), (c) G. Buchi and E. M. Burgess, ibid., 84, 3104 (1962), (d) T. J. Katz, C. R. Nicholson and C. A. Reilly, ibid., 88, 3832 (1966), (e) A. G. Anastassiou, ibid., 90, 1527 (1968), (f) J. M. Holovka, P. D. Gardner, C. B. Stow, M. L. Hill and T. V. van Auken, ibid., 90, 5041 (1968).

58. A. P. Bendra, J. A. Elix, P. J. Garrat and R. H. Mitchel, ibid., 90, 7372 (1968).

59. F. E. King, D. M. Bovey, K. G. King and R. L. Whitehead, J. Chem. Soc., 250 (1953), (b) H. Booth and F. E. King, ibid., 2688 (1958).

60. (a) S. Masamune, K. Hojo and S. Takada, Chem. Commun., 1204 (1969), (b) A. G. Anastassiou and J. H. Gebrian, J. Amer. Chem. Soc., 91, 4011 (1969).

61. (a) G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *ibid*., *82*, 5846 (1960), (b) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, *41*, 966 (1963), (c) references 5 and 6.

62. For instance see: I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett and R. J. Haluska, *J. Amer. Chem. Soc*., *90*, 5023 (1968). J. L. Katz and B. Post, *Acta. Cryst*., *13*, 624 (1960).

63. S. Masamune and R. T. Seidner, unpublished results cited in reference 64.

64. K. Hojo and S. Masamune, *J. Amer. Chem. Soc*., *92*, 6690 (1970).

65. For a recent review, see: H. Kessler, *Angew. Chem*., *Int. Ed. Engl*., *9*, 219 (1970).

66. (a) J. C. Woodbrey and M. T. Rogers, *J. Amer. Chem. Soc*., *84*, 13 (1962), (b) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem*., *66*, 540 (1962).

67. A. G. Anastassiou, R. P. Celluna and J. H. Gebrian, *Chem. Commun*., 365 (1970).

68. D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc*., *87*, 4089 (1965).

69. H. Günther and R. Wenzel, *Tetrahedron Letters*, 4155 (1967).

70. T. Matuo and H. Shosenji, Chem. Commun., 501 (1969).

71. For example see S. J. Rhoads in "Molecular Rearrangement" Mayo, Ed., Part 1, p 655, Interscience Publishers (1963).

72. (a) S. W. Staley and T. J. Henry, J. Amer. Chem. Soc., **91**, 1239 (1969), (b) P. Radlick and W. Fenical, ibid., **91**, 1560 (1969), (c) P. Radlick and G. Alford, ibid., **91**, 6529 (1969), (d) J. C. Barborak, T. M. Su, P. von R. Schleyer, G. Boche and G. Schneider, ibid., **93**, 279 (1971), (e) A. G. Anastassiou and R. C. Griffith, ibid., **93**, 3083 (1971), (f) J. E. Baldwin and A. H. Andrist, ibid., **93**, 4055 (1971).

73. W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin and M. Saunders, Tetrahedron, **23**, 3943 (1967).