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# Cyclooctatrieneium Dicationium Ion

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CYCLOOCTATRIENEIUM  
DICARBONIUM ION

by

Carl George Seefried Jr. UC 1966  
"/

Senior Thesis Submitted  
in Partial Fulfillment  
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY  
UNION COLLEGE  
MAY 1966



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This Thesis  
Submitted by

Carl George Sefried Jr

to the

Department of Chemistry of Union College  
in partial fulfillment of the requirements of the degree of  
Bachelor of Science with a Major in Chemistry  
is approved by

Kevork V. Nakhbedian



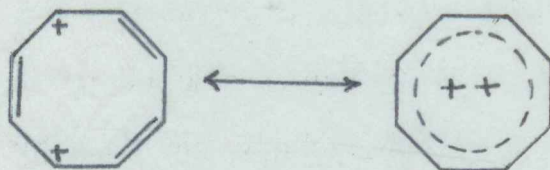
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INTRODUCTION

The peculiar group of chemical molecules termed "aromatic" have had particular significance in all fields of chemistry because of the unusual reactions they undergo. These reactions occur because of the additional stabilization energy that these molecules possess. This stability arises from the arrangement of delocalized  $\pi$  - electrons in the molecules.

This investigation is concerned with the anticipated "aromatic" properties that the cyclooctatrieneium dicarbonium ion should possess.



(8 structures)

A theoretical study of the ion's supposed "aromaticity" and its comparison to other aromatic compounds is developed. Proposed syntheses and past studies are explored to ascertain the most favourable one for production of this dicarbonium ion. The experimental problems encountered in the first step in an attempt of its synthesis are interpreted and conclusions drawn. Finally, suggestions for further work leading to the actual synthesis are advanced.



THEORETICAL

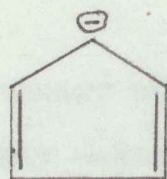
In physical-organic chemistry, the term "aromatic" is used rather loosely for the designation of a certain group of characteristic, but not very precisely defined, physical and chemical properties, and also for the description of the particular (always cyclic) compounds which exhibit these properties. Of the various criteria for aromaticity which have been suggested, two seem the most useful. The first is resonance energy; this quantity tells us how much more stable a compound is than a second hypothetical compound having the same set of bonds as the first in the cyclic conjugated system. A second feature pointing to aromaticity in a compound is its tendency to undergo substitution reactions with a number of reagents that ordinarily simply add across the double bond in olefins. In the addition reactions these cyclic conjugated systems are destroyed, whereas in substitution reactions they are preserved. As with other effects related to conjugation, aromaticity requires that the atoms comprising the conjugated system lie in or near a common plane.

Thus, benzene is said to be aromatic because it combines a high degree of apparent unsaturation with both a high thermochemical stability and a relatively small tendency to enter into addition reactions. Other substances which have similar properties, and which are likewise said to be aromatic, include a large number of more complex hydrocarbons,

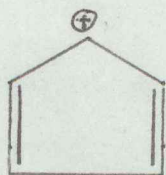
such as diphenyl methane, biphenyl and naphthalene, with two (or more) isolated, conjugated or condensed benzene rings. Still other aromatic substances contain heterocyclic rings, in which the hetero atoms are most commonly nitrogen, sulfur, or oxygen. In many instances, as with pyridine, pyrimidine and quinoline, the heterocyclic rings are six-membered and quite analogous to the carbocyclic hydrocarbons. In many other instances, as in pyrrole, thiophene and furan, the rings are five-membered and hence superficially different from the foregoing. As we shall see, a few compounds with seven-membered rings seem also to have a recognizable aromatic character.

The significance of an aromatic sextet of electrons has long been recognized in organic chemistry; most aromatic hydrocarbon and heterocyclic compounds can be divided into rings which include six unsaturation ( $\pi$ -) electrons per ring. A question of long-standing puzzlement was "why six electrons?" Part of the answer lies in the geometry of the six-membered ring. The internal angle of a plane hexagon,  $120^\circ$ , is exactly the bond angle of a trigonal carbon. Strainless six-membered ring systems can be built from such carbons. However, angle strain is not the whole answer. The cyclopentadienyl anion, I, with six electrons is relatively stable, whereas the corresponding cation, II, with four electrons, is not. Cycloheptatrienyl anion, III, with eight electrons is relatively unstable, whereas the cation, IV, with six electrons is comparatively stable.

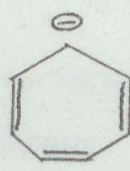




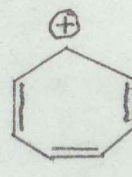
I



II



III



IV

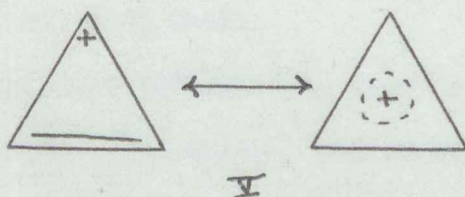
These examples and others were recognized decades ago by E. Huckel, who found a satisfying explanation in simple Molecular Orbital Theory, hereafter referred to as MO Theory. This theory leads to a rule, usually referred to as the  $4n+2$  rule, which may be stated as follows: those monocyclic coplanar systems of trigonally hybridized atoms which contain  $4n+2$   $\pi$  electrons will possess relative electronic stability. This rule is inherent in the form of the molecular orbitals (MOs) which can be written for such systems. The results of these equations may be expressed graphically in the following manner: to obtain the MO energy levels for a cyclic system of  $k$  atoms, inscribe a  $k$ -fold regular polygon within a circle of radius  $2\beta$  such that one apex is at the lowest point. The value  $\beta$  is the resonance integral for adjacent atoms. The distance of each apex from the horizontal mid-line then represents an energy level in units of  $\beta$ . Each set of energy levels may then be thought of as a shell. The lowest-lying MO is always single and can harbor two electrons. The remaining low-lying orbitals occur in pairs, each MO of which can accommodate two electrons. Hence, each low-lying shell above the first requires four electrons to become filled; that is,  $4n+2$  electrons yield filled shell configurations. This feature also comes out of free electron



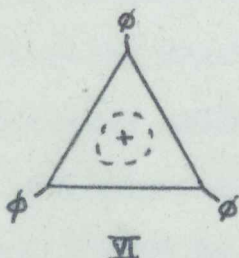
MO theory which ascribes a particular significance to the doubly degenerate levels. In this theory each successive level corresponds to an increase in orbital angular momentum. The lowest level has zero angular momentum. For succeeding levels a degeneracy arises, for the angular momentum can be ascribed a clockwise or counterclockwise direction around the ring. Hence, the levels occur as degenerate pairs. In MO theory the degeneracy arises from the equivalence of orthogonal descriptions of the nodal planes.

This procedure is obviously analogous to the more familiar one in which a complex atom is considered to be built up by the successive addition of electrons to the initially bare nucleus. Just as the especially stable and unreactive atoms of the rare gases are obtained when each electronic shell that is occupied at all is completely full, so also the most stable and least reactive molecules may be expected to result when there are no partially occupied groups of orbitals with the same energy, or, in other words, when the total number of  $\pi$  - electrons is  $4n + 2$ .

The cyclopropenyl cation, V, with two electrons, obeys the  $4n + 2$  rule ( $n = 0$ ) and should be stable. The cyclopropenyl radical and anion both have electrons in antibonding MO's; they also have unfilled shells and should be relatively unstable in theory. The parent cation has not been isolated;

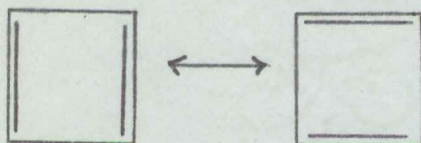


on the other hand, the triphenyl derivative, VI, has been synthesized and is found to be relatively stable. (1) MO calculations of VI have been reported. (2) The cation has



the same filled-shell characteristic of the parent cyclopropenyl cation and a total delocalization energy (DE) of  $9.19 \beta$ , which exceeds the sum of the DE's of three benzene rings by  $3.19 \beta$ .

The cyclobutadiene ring system has fundamental significance as the first cyclic polyene for which Kekule structures can be written, VII. Square cyclobutadiene has four electrons and does not fit the  $4n+2$  rule. A pair of non-bonding molecular orbitals (NBMO's) is each singly occupied; the model has no resonance stabilization and this strained ring system should theoretically be an exceedingly unstable substance. The cyclobutadiene ring structure has eluded a number of ingenious attempts at synthesis; recent work shows that it is capable of existence at least transiently. These clever experiments provide definite evidence of but little





resonance energy in this system.

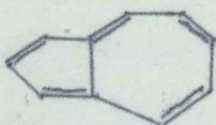
The cyclopentadienyl cation has four electrons and an unfilled bonding shell. We expect the cation to be electronically unstable and, in agreement, the parent cation has never been observed in solution. Cyclopentadienyl anion has a full complement of six  $\pi$ - electrons with the bonding shells filled. The relatively high stability of this system is reflected in the great acidity of cyclopentadiene. This hydrocarbon is predicted by MO considerations to have a  $pK_a$  of 17, a value consistent with qualitative observations.

In benzene the two bonding shells that compromise three MO's are completely filled by six electrons. The aromatic character of benzene may be associated with  $\pi$ - electronic stability in a strainless six-membered ring. Any additional electrons added to benzene must be stored in highly antibonding MO's. Benzene, therefore, has a rather low electron affinity.

The cycloheptatrienyl or tropylium  $\pi$ - system has three bonding MO's in two shells. These shells are completely filled by six electrons; hence, the tropylium cation should be relatively stable. The most conclusive evidence supporting the belief that a seven-membered ring with six  $\pi$ - electrons can have significant aromatic character has been obtained by Doering and Knox. (3) These authors have found that cycloheptatrienyl bromide,  $C_7H_7Br$ , is not a typical nonpolar substance, but is instead a salt, which is largely, if not entirely, dissociated into the cycloheptatrienyl cation,  $C_7H_7^+$ ,

and the bromide ion,  $\text{Br}^-$ . Since the former ion doubtless has the shape of a regular plane heptagon, it can be described as a hybrid of seven completely equivalent structures in each of which there are just six aromatic electrons. The eighth electron of the tropylium anion must also be placed in a NBMO and this leaves an incomplete shell. In consequence, cycloheptatriene is not markedly acidic.

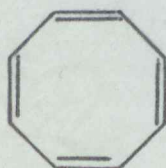
Azulene, VIII, as an example of a ten  $\pi$  - electron



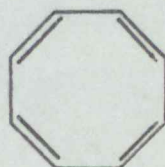
VIII

aromatic system, may be regarded as a combination of a tropylium cation and a cyclopentadiene anion sharing a common edge. Such a view is consistent with the rather high dipole moment of azulene and with its tendency to undergo electrophilic substitution on the more negative five-membered ring.

Cyclooctatetraene, with eight  $\pi$  - electrons, does not fit the  $4n+2$  rule; the last two electrons occupy an unfilled shell. The hydrocarbon synthesized by Willstatter, Cope and Reppe behaves as a highly unsaturated polyene and certainly has no aromatic character. (4) With cyclooctatetraene, the two structures, IX and X, are equivalent if the molecule



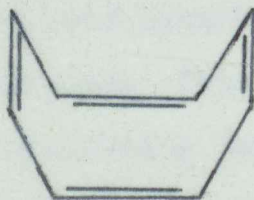
IX



X



has the symmetry of a regular plane octagon and if, therefore, each C-C-C bond angle is equal to  $135^\circ$ . Since, however, the normal value for this angle is more nearly  $120^\circ$ , the molecule would then be highly strained and perhaps unstable. There is reason to suppose that the most stable configuration would be one in which the ring is puckered into the "tub" form. Under such circumstances, structures IX and X are not at all equivalent, since one of them is strain free, whereas the other is highly strained because of a dihedral angle greater than  $0^\circ$  at its double bonds. Consequently, the substance would have essentially the former, much more stable structure, with only a small contribution from the latter, less stable one; thus, the resonance energy should be small.



This interpretation is in complete agreement with the available experimental evidence. From crystal-structure and electron-diffraction studies by Bastiansen, Hedberg and Hedberg (5) and from spectroscopic studies by Lawrenson and Rushworth (6), the ring has been shown to be definitely puckered in the "tub" form. The internuclear distances have been found by Springall, White and Cass (7) to be more nearly those expected for an individual one of the structures

IX or X than for a hybrid of the two.

Since the structural basis of an aromatic system - a regular polygonal conformation - is lacking in cyclooctatetraene, the extensive  $\pi$  - electron delocalization energy (DE) expected of the regular octagonal molecule must fail to compensate for the exceptionally large compressional strain associated with the angular distortion of the framework. Calculations for cyclooctatetraene indicate that a simple extension of Huckel type MO Theory may be used in this case to estimate the relative stability of geometric configurations of a molecule with a non-planar  $\pi$  - electron system. It is necessary to modify only the resonance integral,  $\beta$ , to take into account the relative twist of neighboring p orbitals. The effect on  $\beta$  of varying bond lengths is somewhat larger here than in planar ring systems. This has been taken into account by means of an approximation due to Mulliken. The effect of bond length is smaller than that due to twist, so that the qualitative results do not depend critically on the approximation.

$$E(\text{tub}) = 8\alpha + 9.8\beta$$

The energy of four isolated double bonds would be  $9.5\beta$ , so the calculations of Ahlers and Hornig (8) predict a stabilization energy of  $.3\beta$  or about 5 kcal/mole. Their experimental resonance energy is 4 kcal/mole and this agrees with that found by Springall, White and Cass. (9)

The electrolytic reduction of cyclooctatetraene has been shown by Katz, Reinmuth and Smith (10) by oscillogpolarography



to proceed by reversible addition of two electrons to the hydrocarbon, followed by an irreversible pseudo-first order reaction of the dianion with the solvent. The hydrocarbon is reduced at the dropping mercury electrode at a relatively low half-wave potential, -1.5 volts versus saturated calomel electrode. Two electrons are involved in the reduction, and the half-wave potential is independent of pH, which means that no hydrogen ions take part in the reduction step.

The high degree of stabilization due to  $\pi$ -electron delocalization characteristic of carbocyclic aromatic systems and not found in cyclooctatetraene, is to be found in the dianion. The results confirm the conclusions derived by means of proton NMR and ESR techniques. They report that the energy required to compress cyclooctatetraene to the "aromatic" conformer is about 22 kcal/mole. It is concluded that the molecular orbitals involved are non-bonding and consistent with a regular octagonal geometry for the dianion. These results leave no doubt that cyclooctatetraene is non-planar because of  $\pi$ -electronic instability and not because of steric strain.





$$H_{r,s} = \int \psi_r^H \psi_s d\tau = \int \psi_s^H \psi_r d\tau = \text{resonance integral}$$

$$S_{r,s} = \int \psi_r \psi_s d\tau = \int \psi_s \psi_r d\tau = \text{overlap integral}$$

$$H_{r,r} = \int \psi_r^H \psi_r d\tau = \text{coulombic integral} - E_0 = \text{a constant}$$

If the respective  $\psi_r$ 's are normalized, then  $S_{r,r} = 1$ .

If we assume no overlap between adjacent orbitals, then  $S_{r,s} = 0$ .

Let all resonance integrals for adjacent atoms =  $\beta$ .

If we assume that all resonance integrals for adjacent atoms are zero, then the secular equations become:

$$c_1(H_{11} - ES_{11}) + c_2(H_{12}) + c_8(H_{18}) = 0$$

$$c_2(H_{22} - ES_{22}) + c_1(H_{21}) + c_3(H_{23}) = 0$$

$$c_3(H_{33} - ES_{33}) + c_2(H_{32}) + c_4(H_{34}) = 0$$

$$c_4(H_{44} - ES_{44}) + c_3(H_{43}) + c_5(H_{45}) = 0$$

$$c_5(H_{55} - ES_{55}) + c_4(H_{54}) + c_6(H_{56}) = 0$$

$$c_6(H_{66} - ES_{66}) + c_5(H_{65}) + c_7(H_{67}) = 0$$

$$c_7(H_{77} - ES_{77}) + c_6(H_{76}) + c_8(H_{78}) = 0$$

$$c_8(H_{88} - ES_{88}) + c_7(H_{87}) + c_1(H_{81}) = 0$$

Let  $E_0 = 0$ ,  $E = x$  and  $\beta = 1$ . Then, rewriting we get:

$$-c_1x + c_2 + c_8 = 0$$

$$-c_2x + c_1 + c_3 = 0$$

$$-c_3x + c_2 + c_4 = 0$$

$$-c_4x + c_3 + c_5 = 0$$

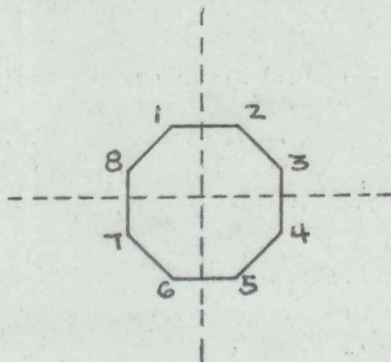
$$-c_5x + c_4 + c_6 = 0$$

$$-c_6x + c_5 + c_7 = 0$$

$$-c_7x + c_6 + c_8 = 0$$

$$-c_8x + c_7 + c_1 = 0$$

Considering the symmetry of the ion, we obtain:



$A_g$	$A_g$	$B_g$	$B_g$
$c_1 = c_2$	$c_1 = -c_2$	$c_3 = c_4$	$c_3 = -c_4$
$c_3 = c_8$	$c_8 = -c_3$	$c_2 = c_5$	$c_2 = -c_5$
$c_4 = c_7$	$c_7 = -c_4$	$c_1 = c_6$	$c_1 = -c_6$
$c_5 = c_6$	$c_6 = -c_5$	$c_8 = c_7$	$c_8 = -c_7$

A.) For the combination  $A_g B_g$ :

$$c_1 = c_2 = c_5 = c_6$$

$$c_3 = c_8 = c_4 = c_7$$

The secular equations become:

$$-c_1 x + c_1 + c_3 = 0$$

$$-c_3 x + c_1 + c_3 = 0$$

Solving for  $x$ :

$$x = 0, 2$$

B.) For the combination  $A_g B_g$ :

$$c_1 = c_2 = -c_6 = -c_5$$

$$c_3 = c_8 = -c_4 = -c_7$$



The Secular equations become:

$$-c_1x + c_1 + c_3 = 0$$

$$c_3x - c_1 + c_3 = 0$$

Solving for x:

$$x = \pm 1.414$$

C.) For the combination  $A_a B_a$ :

$$c_1 = -c_2 = c_5 = -c_6$$

$$c_3 = -c_8 = -c_4 = c_7$$

The secular equations become:

$$c_1x + c_1 + c_3 = 0$$

$$c_3x + c_1 + c_3 = 0$$

Solving for x:

$$x = -2, 0$$

D.) For the combination  $A_a B_s$ :

$$c_1 = -c_2 = c_6 = -c_5$$

$$c_3 = -c_8 = c_4 = -c_7$$

The secular equations become:

$$c_1x + c_1 + c_3 = 0$$

$$-c_3x - c_1 + c_3 = 0$$

Solving for x:

$$x = \pm 1.414$$

Therefore, the roots for the secular equations are:

$$x = -2, 0, \pm 1.414, 2, 0, \pm 1.414$$

$$E(DE \pi) = 2(2\beta) + 2(1.414)\beta + 2(1.414)\beta$$

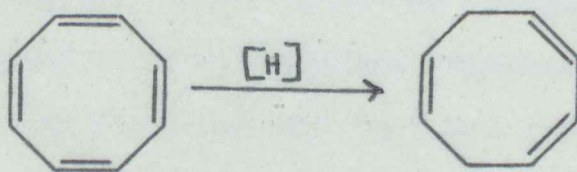
$$E(DE \pi) = 9.66\beta$$

$$\text{Delocalization Energy} = 9.66\beta - 6\beta = 3.66\beta$$

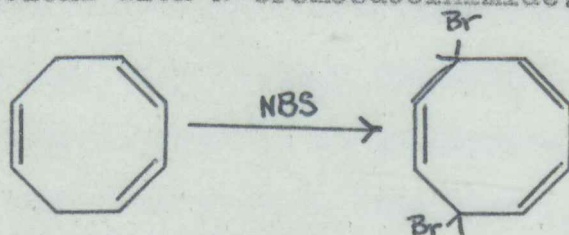
SYNTHETIC PROPOSAL

The original proposal we had to obtain the cyclooctatrieneium dicarbonium ion included the following steps:

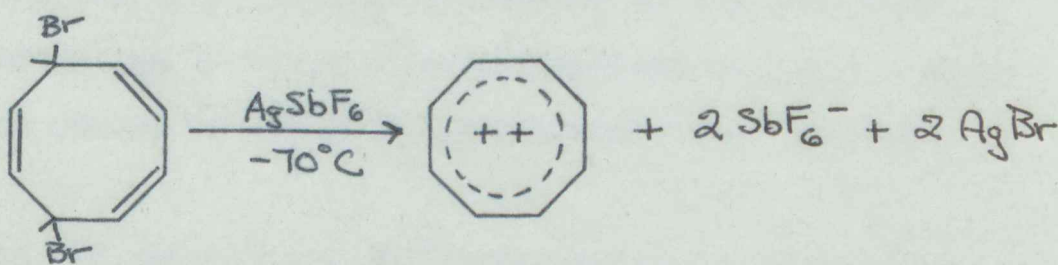
(1) The reduction of cyclooctatetraene to 1,3,6 - cyclooctatriene.



(2) Di-bromination of 1,3,6 - cyclooctatriene at the 5- and 8- positions with N-bromosuccinimide.



(3) Removal of the bromide ions to form the dicarbonium ion.



Reppe, Schlichting, Klager and Toepel have reported (12) that lithium adds to cyclooctatetraene in ether to give a dilithium derivative, which on reaction with methanol yields 1,3,6 - cyclooctatriene. They reported that sodium also adds to cyclooctatetraene under similar conditions. A less



complex mixture of products was obtained by Cope and Hochstein (13) by the addition of two equivalents of sodium to cyclooctatetraene in liquid ammonia.

Elofson (14) has shown that cyclooctatetraene can be determined quantitatively by polarographic analysis. The electrolytic reduction of cyclooctatetraene at the dropping mercury electrode was investigated by Craig, Elofson and Ressa. (15) The UV spectra of the mixture produced showed 75% 1,3,6 - cyclooctatriene and 25% 1,3,5 - cyclooctatriene. Isomerization of 1,3,6 - cyclooctatriene to 1,3,5 - cyclooctatriene during slow distillation was encountered and it appears probable that 1,3,6 - cyclooctatriene was the product formed upon electrolytic reduction and that 1,3,5 - cyclooctatriene was formed by isomerization.

Later it was shown by Roth (16) that 1,3,6 - cyclooctatriene, 1,3,5 - cyclooctatriene and bicyclo [4,2,0] octa - 2,4 - diene are in a dynamic equilibrium at 225° and that the isomerization of 1,3,6 - cyclooctatriene to 1,3,5 - cyclooctatriene occurs by way of a 1,5 intramolecular hydrogen shift.

Sanne and Schlichting (17) have reported a method for reducing cyclooctatetraene in aqueous solution using a slight excess of activated zinc in the presence of 0.2 equivalents of alkali. Purification of their product yielded 84% 1,3,6 - cyclooctatriene (bp<sub>58</sub> 64-65°C; n<sub>D</sub> 1.5056) and 8% 1,3,5 -

cyclooctatriene (bp<sub>58</sub> 71°C; n<sub>D</sub> 1.5236). This was the reaction attempted in the present work for the reduction of cyclooctatetraene. They have also noted that 1,3,5 - cyclooctatriene reacts with oxygen to form a polymeric product of the form (C<sub>8</sub>H<sub>10</sub>O<sub>2</sub>)<sub>n</sub>.

The IR and UV spectra of 1,3,5 - and 1,3,6 - cyclooctatriene have been reported by Sanne and Schlichting (ibid).

The American Petroleum Institute (18) have produced the IR and UV spectra for cyclooctatetraene. The principal absorption bands of the IR and Raman spectra for these compounds have been listed by Lippincott, Lord and McDonald.

(19) The UV molar absorption coefficients for 1,3,5 - and 1,3,6 - cyclooctatriene at  $\epsilon_{265}$  are 3600 and 200 respectively. The value for the 1,3,5 - cyclooctatriene indicates a conjugation of three carbon-carbon double bonds. The IR spectra for cyclooctatetraene shows a strong absorption line at 1639 cm<sup>-1</sup> which is the typical stretch frequency for non-conjugated aliphatic carbon-carbon double bonds.

Sanne and Schlichting (20) report the reaction of 1,3,6 - cyclooctatriene with N-bromosuccinimide to produce mono- and di- bromocyclooctatriene. Sanne (21) reports the same reaction with melting points: 8 - bromo derivative, bp<sub>12</sub> = 88-90°C and 5,8 - dibromo derivative, bp<sub>12</sub> = 130-5°C.



EXPERIMENTAL

The first step in the proposed synthesis was the reduction of cyclooctatetraene to 1,3,6 - cyclooctatriene; the method employed by Sanne and Schlichting was followed to obtain the reduction.

The amounts of reacting compounds used by Sanne and Schlichting had to be scaled down because of the limited amount of cyclooctatetraene available. Into a 500 ml three-neck flask were added 20 gr. cyclooctatetraene, 51 ml of methanol, 7 ml of water and 15 gr. of zinc dust. A water condenser was placed in the middle neck and a thermometer extending into the mixture was placed in one side neck. A teflon-enclosed magnetic stirrer was placed in the mixture and the third neck stoppered. The apparatus was then placed upon a Magnotherm hot plate.

The mixture was warmed with stirring until the temperature reached 70°C. During the course of two hours, 1.2 ml of 40% NaOH was introduced through the stoppered neck with stirring and the temperature was not allowed to go above 80°C. After further stirring for a half hour, the mixture was allowed to cool to room temperature. The reaction mixture was added to 256 ml of water.

At this time it was noted that the remaining zinc had adsorbed the dark yellow organic product. Cyclooctatetraene itself is a dark yellow liquid,  $bp_{760} = 142-3^{\circ}C$  and  $n_D = 1.5394$ .

Successive washings with petroleum ether (30-60°C) appeared to have removed most of the product from the zinc. A total of 115 ml of petroleum ether was added to the organic layer during the washings. The petroleum ether was removed from the organic layer by means of a rotary evaporator. The petroleum ether vapours were collected in a Dewar flask containing a mixture of dry ice and acetone. This was done in order to preserve any of the organic material that may have been evaporated with the ether. None appeared to have done this. A few grams of anhydrous  $\text{Na}_2\text{SO}_4$  was added to the remaining organic "Product" in order to remove any water present.

A Vapour Phase Chromatograph (VPC) was compared with one obtained from unreacted cyclooctatetraene in order to determine if the cyclooctatetraene had indeed been reacted in its entirety or at least in part. Column R was used with 10 lbs. of pressure; the temperature was set at 104°C and the column was allowed to equilibrate for three hours before use. A two microliter sample of unreacted cyclooctatetraene was introduced; it came off at the four minute mark. There was a small amount of an impurity which appeared at the 1.6 minute mark. It was initially assumed that this impurity was benzene. A two microliter sample of pure benzene was run through the column and it came off at the 7 min. mark. Thus, the impurity was not benzene.

A two microliter sample of the organic product was introduced and four distinct peaks were produced: 2, 4.1, 7.2 and 11 min. marks. The 7.2 and 11 min. peaks were the



most prominent ones and were in a ratio of 1:8 respectively. The 2 min. peak was assumed to be petroleum ether remaining in the product and the 4.1 min. peak to be unreacted cyclooctatetraene. The 7.2 and 11 min. peaks were assumed to be the trienes; Sanne and Schlichting obtained a 1:10 ratio for the 1,3,5 - and 1,3,6 - cyclooctatrienes produced. It was guessed that the impurity in the "pure" cyclooctatetraene was the 1,3,5 - cyclooctatriene.

Since the only reported boiling points found for the two isomeric trienes were at 58 mm Hg of pressure, the distillation of the product was run at this pressure. The distillation was achieved by means of a Nester-Faust spinning band distillation column with a Cartesian Manostat to regulate the pressure produced by an aspirator. The manostat was set to read a pressure of 58 mm of Hg; the pot was heated by means of a heating mantle. The system<sup>was</sup> allowed to equilibrate for two hours after the vapours condensing at the top of the column read 58°C. The temperature of the vapours being drawn off was 57-59°C. The reflux ratio of the drawn off liquid was 4.5:1. The refractive index of the distilled product was 1.5292 and 10.4 gr. were collected. A polymeric residue was found in the pot as predicted.

A check on the manostat with a manometer showed that when it was set to read 58mm of Hg, it was actually reading 39 mm of Hg according to the manometer.

A VPC was again run under the same conditions as set forth previously. The undistilled product was again re-run and a completely different spectrum was obtained. It thus appeared that over a period of three weeks the undistilled product had changed its composition. For the distilled product, 2.6 and 13 min. peaks were obtained; the 13 min. peak being the much more prominent. Neither of these peaks corresponded to any of the peaks seen in any of the previous spectra.

Nuclear Magnetic Resonance (NMR) spectra were run on both cyclooctatetraene and the distilled product. Conditions for these spectra were:

Filter bandwidth:	4 cps
R. F. Field:	.01 mG
Sweep time:	250 sec
Sweep width:	500 cps
Sweep offset:	000 cps
Spectrum Ampl.:	.16
Integral Ampl.:	off

For the pure cyclooctatetraene, a single peak was seen at 5.7 ppm; the same identical peak was obtained with the distilled product. These spectra strongly point to the fact that the distilled product was unreacted cyclooctatetraene.

An elemental analysis of the distilled product was performed by the Microanalytical Laboratory of Oxford, England.



Their results were:

91.94% C	8.28% H
92.12% C	8.10% H

These agree quite closely with the calculated values for the carbon and hydrogen percentages in cyclooctatetraene - 92.4% C and 7.1% H.

The reaction was re-run in an inert atmosphere; it was assumed that the product was formed but reacted with the atmosphere upon standing. To the three-neck flask apparatus was added 24.7 gr cyclooctatetraene, 38 gr methanol, 8 gr water and 18 gr zinc dust. Nitrogen was bubbled in through the water condenser. The mixture was heated to 65°C with stirring and then .08 gr  $\text{CuSO}_4$  was added. This mixture was heated for one hour, keeping the temperature below 70°C. During the course of two hours, 8 gr of 10% NaOH were added and the temperature kept below 80°C. At the end of the two hours, 320 ml water were added and the flask flushed with nitrogen. The flask was chilled in an ice bath to approximate room temperature for the mixture; 20%  $\text{H}_2\text{SO}_4$  was added until the solution was neutral to litmus. The mixture was steam distilled to remove the organic layer; this layer was separated from a saturated NaCl solution and the water removed with anhydrous  $\text{Na}_2\text{SO}_4$ .

The organic product had the appearance and odour of cyclooctatetraene; its index of refraction was 1.530. Because most of the zinc still remained in the reaction flask and the refractive index of the sample approximated

that of cyclooctatetraene, it was assumed that no reaction had occurred.

It was presumed that there was not a favourable concentration of hydroxide ions for the reaction to occur. Again the reaction was tried with an increased amount of base. The same apparatus and reaction conditions were maintained: 20 gr cyclooctatetraene, 30 gr methanol, 6.4 gr water and 16 gr zinc dust. This time 1.28 gr 40% NaOH were added during the course of two hours. While the NaOH was being added, a gas was being evolved from the stirred mixture; it was assumed that this evolved gas was hydrogen. Water (260 ml) was added to the flask and the same separation of the organic layer was performed. As in the previous experiment, the organic "product" had the appearance and odour of cyclooctatetraene; its refractive index was 1.532. Once again, not an unfrequent assumption, no reaction occurred.

It was then suggested that proper mixing of the three phases in the flask was not being achieved and that this was the source of the trouble. A mechanical stirrer was inserted in the middle neck of the flask; the thermometer and water condenser containing the glass tubing for the bubbling of nitrogen were placed in the two side necks. The same reaction conditions were established as previously; 20 gr cyclooctatetraene, 30 gr of methanol, 16 gr zinc dust and 30 gr of water were initially added to the flask. Over two hours, 20 gr of 40% NaOH was added with stirring after the temperature had reached 70°C. No evolution of hydrogen was



detectable under these conditions. After reaction, the mixture was neutralized with 20%  $H_2SO_4$  and the organic layer steam distilled; the product was then separated from a saturated NaCl solution and dried with anhydrous  $Na_2SO_4$ .

The product had a less intense yellow coloring than cyclooctatetraene and the odours of the two did not appear to be identical. The refractive index of the sample was 1.515. At all times the sample was kept under a nitrogen atmosphere.

A VPC was run on the dried organic product. Column X was used with 10 lbs. of pressure; the temperature was set at  $104^{\circ}C$ . and the column was allowed to equilibrate for three hours before use. A two microliter sample of pure cyclooctatetraene was introduced and showed a major peak at 27.6 min. A two microliter product sample was introduced and gave significant peaks at 27.2, 31 and 35 min. markings. The predominant peak was at 31 min. It was assumed that this is the 1,3,6 - cyclooctatriene peak; the 35 min. peak is the 1,3,5 - cyclooctatriene peak and the 27.2 peak corresponds to cyclooctatetraene.

The product was then fractionally distilled on the spinning band column with the Cartesian Manostat to regulate pressure. The manostat was properly adjusted so that it read 58 mm of Hg in accord with a manometer. The pot and column heating variacs were adjusted and the vapours were allowed to condense at a temperature of about  $64^{\circ}C$ .; the system was allowed to reflux and equilibrate for two hours. The

condensing vapours being drawn off had a temperature of 64-65°C.; the reflux ratio was 6:1. The refractive index of the collected product was 1.509. Once again a polymeric residue was found in the pot.

A NMR spectrum was run on the collected product under the following conditions:

Filter bandwidth:	4 cps
R. F. Field:	.005 mG
Sweep time:	250 sec
Sweep width:	500 cps
Sweep offset:	000 cps
Spectrum Ampl.:	1.6
Integral Ampl.:	80 (.5)

It showed much splitting in the 5.5 - 6.3 ppm and 2.2 - 2.5 ppm regions. There was presumably a small amount of impurity present which was detectable in the 3.3 - 25 ppm region.

The integral spectrum showed the hydrogens to be in a ratio of 3:2 as they should be with the 1,3,6 - cyclooctatriene; this ratio is obtained if the impurity afore mentioned is disregarded.

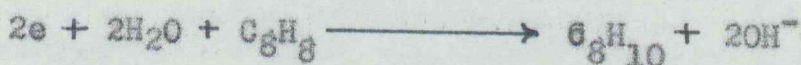
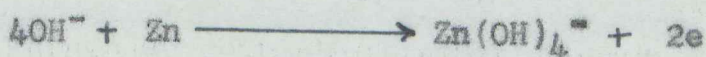
A NMR spectrum was run on the liquid remaining in the pot. The same conditions were used as in the previous spectrum. It showed prominent peaks at 2.3, 5.7, and 5.85 ppm with very little splitting. The 5.7 ppm peak corresponds to the cyclooctatetraene spectrum peak; the other two are presumably the peaks for 1,3,5 - cyclooctatriene.



CONCLUSION

It appears that finally the synthesis of 1,3,6 - cyclo-octatriene has been achieved. The investigation has proven that what at first appears to be a rather straight-forward reaction on paper can become a time consuming and frustrating laboratory experiment.

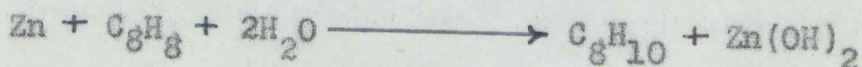
The most prominent conclusion that can be drawn is that the synthesis of 1,3,6 - cyclooctatriene as outlined by Sanne and Schlichting is best carried out with a mechanical stirrer so that one obtains proper mixture of the reactants. The presumed oxidation-reduction reactions which occur under these conditions are:



The overall reaction is:



or



It should be noted that a NMR spectrum with proper interpretation is a very powerful analytical device.

SUGGESTIONS FOR FURTHER WORK

There is much experimental work remaining before fruition of the original proposal of production of the cyclooctatrieneium dicarbonium ion is achieved. The first consideration should be proper preservation of the 1,3,6 - cyclooctatriene. At all times it should be stored and worked with under nitrogen. Sanne and Schlichting (20) report the reaction of the isomeric trienes with iron carbonyl and cyclopentadienyl-cobalt-dicarbonyl; it thus may be possible to preserve and stabilize the triene through these metal complexes.

The next major project is the dibromination of the 1,3,6 - cyclooctatriene at the 5- and 8- positions with N-bromosuccinimide. Allendoerfer and Reiger (22) studied the cyclooctatrieneium dianion and used the polar aprotic solvents N,N - dimethylformamide and dimethyl sulfoxide to avoid the unwanted effects of water and alkali metal ions. The cyclooctatrieneium dicarbonium ion should also be prepared in these aprotic solvents.



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