



The photochemical dimerization of norbornadiene using chromium carbonyls  
by Brian Kellog Hill

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of  
DOCTOR OF PHILOSOPHY in Chemistry  
Montana State University  
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Abstract:

Norbornadiene has previously been shown to undergo dimerization photochemically with Group VI and VIII and thermally with Group VIII unsubstituted metal carbonyls. Furthermore, diene-iron-tricarbonyls cause the reaction to be more stereospecific and give only two products instead of the usual eleven obtained using the unsubstituted metal carbonyls. To learn if this change in products was generally characteristic of unsubstituted and substituted metal carbonyls a series of chromium carbonyls were investigated. The products of the chromium metal carbonyls were three trans dimers, a saturated cage dimer and one ketone insertion product. A possible mechanism for the photochemical dimerization of norbornadiene using chromium hexacarbonyl and substituted chromium carbonyl as sensitizers was determined. A common intermediate for the reactions has been proposed.

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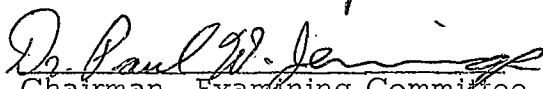
DOCTOR OF PHILOSOPHY

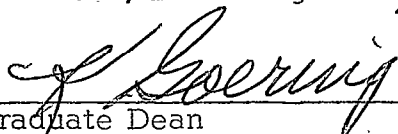
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TABLE OF CONTENTS

|                                                                                          | Page |
|------------------------------------------------------------------------------------------|------|
| LIST OF TABLES .....                                                                     | vi   |
| LIST OF FIGURES .....                                                                    | vii  |
| ABSTRACT .....                                                                           | x    |
| INTRODUCTION .....                                                                       | 1    |
| DISCUSSION .....                                                                         | 25   |
| Procedure for Determining Products and Product Ratios .....                              | 27   |
| Isolation of Intermediates Using Chromium Hexacarbonyl .....                             | 34   |
| Isolation of Intermediates for Benzene, Toluene or Mesitylene Chromium Tricarbonyl ..... | 41   |
| Other Investigations .....                                                               | 56   |
| CONCLUSION .....                                                                         | 60   |
| EXPERIMENTAL .....                                                                       | 70   |
| Reagents .....                                                                           | 70   |
| Instruments .....                                                                        | 71   |
| Light and Reaction Systems .....                                                         | 72   |
| Photoreaction for Determining Products and Product Ratios .....                          | 73   |
| Isolation of Photoreaction Intermediates .....                                           | 81   |
| Photochemical Time Study .....                                                           | 85   |
| Beer's Law .....                                                                         | 86   |
| Infrared Study .....                                                                     | 86   |
| Thermal Reaction of Chromium Hexacarbonyl and Norbornadiene .....                        | 86   |
| Irradiation of Norbornadiene Without Metal Carbonyl .....                                | 87   |
| Photoreaction of Norbornene .....                                                        | 87   |

|                                                                                      | Page |
|--------------------------------------------------------------------------------------|------|
| EXPERIMENTAL (continued)                                                             |      |
| Thermal Reaction of Pyridine Chromium Pentacarbonyl<br>and Norbornadiene . . . . .   | 87   |
| Thermal Reaction of Dipyridine Chromium<br>Tetracarbonyl and Norbornadiene . . . . . | 88   |
| Isolation of Carbonyl Polymer . . . . .                                              | 89   |
| LITERATURE CITED . . . . .                                                           | 90   |

## LIST OF TABLES

|                                                                            | Page |
|----------------------------------------------------------------------------|------|
| I. Transition Complexes With Norbornadiene . . . . .                       | 14   |
| II. Dimers, Trimers and Ketones of Norbornadiene . . . . .                 | 15   |
| III. Metal Carbonyl Reactant Templates . . . . .                           | 25   |
| IV. Experimental Procedure for Product Identification . . . . .            | 28   |
| V. Product Ratios of Norbornadiene Dimers . . . . .                        | 32   |
| VI. Peak Assignments for the Mass Spectrum of the Red<br>Complex . . . . . | 50   |

## LIST OF FIGURES

|                                                                                                                                             | Page |
|---------------------------------------------------------------------------------------------------------------------------------------------|------|
| 1. Pictorial Representation of the Bond Between<br>Platinum and Ethylene . . . . .                                                          | 4    |
| 2. Pictorial Representation of a Metal Carbonyl Bond . . . . .                                                                              | 7    |
| 3. Structure of a Bridged and Triple Bridged Carbonyl . . . . .                                                                             | 8    |
| 4. Non-concerted Mechanism for the Formation of<br>Norbornadiene Dimers . . . . .                                                           | 23   |
| 5. Nuclear Magnetic Resonance Spectra of<br>Norbornadiene Dimers . . . . .                                                                  | 29   |
| 6. Nuclear Magnetic Resonance Spectrum of<br>Norbornadiene Cage Dimer . . . . .                                                             | 30   |
| 7. Infrared Spectrum of Chromium Hexacarbonyl<br>Solution at Zero Time of Irradiation . . . . .                                             | 36   |
| 8. Infrared Spectrum of Chromium Hexacarbonyl<br>Solution after Two Hours of Irradiation . . . . .                                          | 36   |
| 9. Infrared Spectrum of Chromium Hexacarbonyl<br>Solution after Six Hours of Irradiation . . . . .                                          | 37   |
| 10. Infrared Spectrum of Chromium Hexacarbonyl<br>Solution after Two Hours of Irradiation and Six<br>Hours in the Dark . . . . .            | 39   |
| 11. Infrared Spectrum of Mesitylene Chromium<br>Tricarbonyl Solution at Zero Time of Irradiation . . . . .                                  | 43   |
| 12. Infrared Spectrum of Mesitylene Chromium<br>Tricarbonyl Solution after 30 Minutes of Irradiation . . . . .                              | 43   |
| 13. Infrared Spectrum of Mesitylene Chromium<br>Tricarbonyl Solution after One Hour of Irradiation . . . . .                                | 44   |
| 14. Infrared Spectrum of Mesitylene Chromium<br>Tricarbonyl Solution after 3 1/2 Hours of Irradiation . . . . .                             | 44   |
| 15. Infrared Spectrum of Mesitylene Chromium<br>Tricarbonyl Solution after 30 Minutes of Irradiation<br>and Six Hours in the Dark . . . . . | 45   |

|                                                                                                                                           | Page |
|-------------------------------------------------------------------------------------------------------------------------------------------|------|
| 16. Mass Spectrum of Norbornadiene Chromium<br>Tetracarbonyl . . . . .                                                                    | 47   |
| 17. Infrared Spectrum of Red Complex . . . . .                                                                                            | 48   |
| 18. Mass Spectrum of Red Complex . . . . .                                                                                                | 49   |
| 19. Infrared Spectrum of Benzene Chromium Tricarbonyl<br>at Zero Time of Irradiation . . . . .                                            | 52   |
| 20. Infrared Spectrum of Benzene Chromium Tricarbonyl<br>after 30 Minutes of Irradiation . . . . .                                        | 52   |
| 21. Infrared Spectrum of Benzene Chromium Tricarbonyl<br>after One Hour of Irradiation . . . . .                                          | 53   |
| 22. Infrared Spectrum of Benzene Chromium Tricarbonyl<br>after 3½ Hours of Irradiation . . . . .                                          | 53   |
| 23. Infrared Spectrum of Toluene Chromium Tricarbonyl<br>at Zero Time of Irradiation . . . . .                                            | 54   |
| 24. Infrared Spectrum of Toluene Chromium Tricarbonyl<br>after 30 Minutes of Irradiation . . . . .                                        | 54   |
| 25. Infrared Spectrum of Toluene Chromium Tricarbonyl<br>after One Hour of Irradiation . . . . .                                          | 55   |
| 26. Infrared Spectrum of Toluene Chromium Tricarbonyl<br>after 3½ Hours of Irradiation . . . . .                                          | 55   |
| 27. Plot of Peak Height of Gas Chromatograph and<br>Intensity of Infrared Bands versus Time,<br>Chromium Hexacarbonyl . . . . .           | 58   |
| 28. Plot of Peak Height of Gas Chromatograph and<br>Intensity of Infrared Bands versus Time,<br>Mesitylene Chromium Tricarbonyl . . . . . | 58   |
| 29. Possible Ways for Chromium to Bond to<br>Norbornadiene . . . . .                                                                      | 60   |
| 30. Formation of Norbornadiene Chromium Tetracarbonyl<br>from Chromium Hexacarbonyl . . . . .                                             | 63   |

|                                                                                                    | Page |
|----------------------------------------------------------------------------------------------------|------|
| 31. Formation of Norbornadiene Chromium Tetracarbonyl<br>from Arene Chromium Tricarbonyl . . . . . | 65   |
| 32. Formation of Dimers Using Dinorbornadiene<br>Chromium Tetracarbonyl . . . . .                  | 67   |
| 33. Formation of Cage Dimer using Dinorbornadiene<br>Chromium Tricarbonyl . . . . .                | 68   |

## ABSTRACT

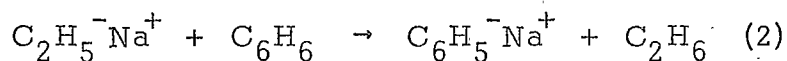
Norbornadiene has previously been shown to undergo dimerization photochemically with Group VI and VIII and thermally with Group VIII unsubstituted metal carbonyls. Furthermore, diene-iron-tricarbonyls cause the reaction to be more stereospecific and give only two products instead of the usual eleven obtained using the unsubstituted metal carbonyls. To learn if this change in products was generally characteristic of unsubstituted and substituted metal carbonyls a series of chromium carbonyls were investigated. The products of the chromium metal carbonyls were three trans dimers, a saturated cage dimer and one ketone insertion product. A possible mechanism for the photochemical dimerization of norbornadiene using chromium hexacarbonyl and substituted chromium carbonyl as sensitizers was determined. A common intermediate for the reactions has been proposed.

## INTRODUCTION

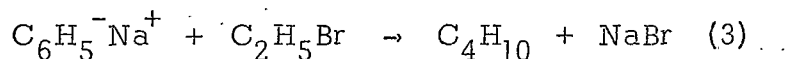
An investigation of the periodic table will reveal that 86 of the 104 characterized elements have an electronegativity of less than 2.2 (1) and that these 86 elements comprise either the metal or the metalloid elements. Since the electronegativity of carbon is 2.5 (1) and the electronegativity of either the metals or the metalloids is 2.2 (1) or less, it should be expected that bonds will be formed between carbon and either metal or metalloid elements. Because of the varying differences in electronegativities, it should be expected that there will be a variation in the bond characters from ionic (where the difference in electronegativity is large) to covalent (where the difference in electronegativity is small). In addition to ionic and covalent bonds, a third type of bond, the synergic bond, can be formed and will be discussed. The area of chemistry which involves compounds with bonds between either metal or metalloids and carbon is called organometallics.

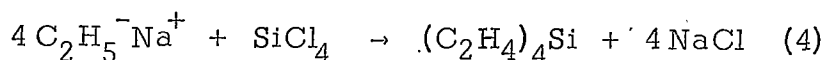
Since the alkali and alkaline earth metals have the largest difference in electronegativity with respect to carbon, they form mostly ionic bonds with the bond's covalent character decreasing as the difference in electronegativity increases.

As a result of the ionic character of the bond, the organometallic complexes of the alkali and alkaline metals show the replacement reaction so commonly encountered in the inorganic chemistry of ionic compounds.



Another type of ionic reaction is the double decomposition reaction:

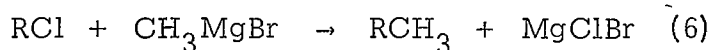




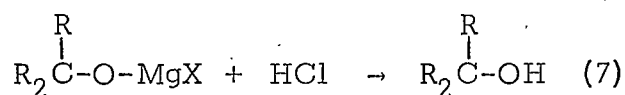
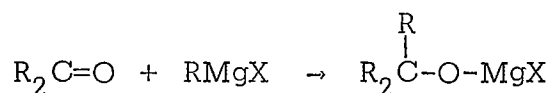
The last reaction also provides a useful synthesis of an organometallic compound of a metalloid.

Another manifestation of the ionic bond is that the compounds are electrical conductors and during electrolysis yield hydrocarbons at the anode and metals at the cathode (5).

Organometallic complexes of the alkaline earth metals, such as the Grignard reagent, are commonly used in the synthesis of organic compounds to attach a hydrocarbon to another molecule. Using the Grignard reagent this is accomplished by replacing a halogen with a hydrocarbon molecule.



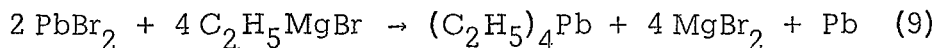
Another use of the Grignard reagent is the conversion of carbonyls to hydroxyls:



These reactions may be thought of as the magnesium ion giving up the organic ligand for a more electronegative element. Thus when phenyllithium is used in place of phenylmagnesium bromide in a Grignard reaction, the phenyllithium reacts 100 times faster because lithium has a lower electronegativity than magnesium (8).

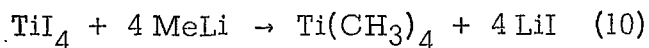
When the electronegativity difference with respect to carbon is less than 1.2 the covalent character of the organometallic bond is more important in determining the bond characteristics than is the ionic bond character. Thus the organometallic covalent compounds are formed by metalloids. The organometallic metalloid complexes are unassociated stable compounds, unreactive to air and water, which resist change in mild acid and base solutions. An example of this type of compound is tetramethylsilane. However, there are some differences from strictly organic reactions due to: a) the ability of the organometallic metalloid complex to use the unfilled d orbitals of the metalloid; and b) the varying electron donating ability of the metalloid with respect to carbon.

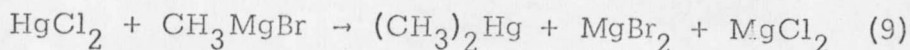
The covalently bonded organometallic metalloids are usually prepared by the reaction of the halide of the metalloid with the sodium salt of the organic ligand, as shown previously, or with the Grignard reagent and a halide of the metalloid.



In addition to the covalent complexes formed with the metalloids, there are also covalent complexes formed using transition metals. These covalently bonded transition metal organometallic complexes are characterized by low thermal stability and reactivity to air and water.

To prepare a covalently bonded alkyl or aryl transition metal organometallic complex, a reaction is usually run with the transition metal halide, with methyllithium or with methylmagnesium bromide.





The third type of bond, the synergic bond, consists of two parts as represented in Figure 1. First of all, there is a donation of pi electrons

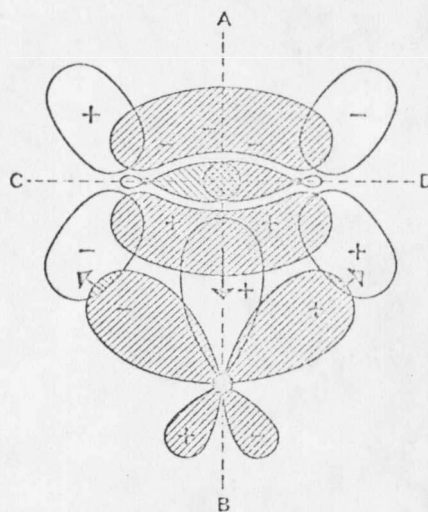
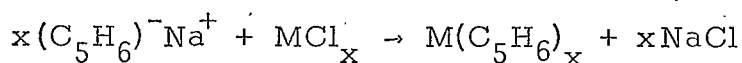


Fig. 1. Pictorial representation of the bond between platinum and ethylene. The dotted line on the C-D axis represents the symmetry axis of the  $\sigma$ -bond and the two hatched spaces above and below the  $\sigma$ -bond represent the  $\pi$ -orbital of ethylene. Both  $\sigma$ - and  $\pi$ -bonds are occupied by two electrons. Around the platinum, shown as a small circle in the lower part of the diagram on the A-B axis, are shown a hybrid empty  $dsp_2$ -orbital (upward ellipse) superimposed on the occupied  $\pi$ -orbital of ethylene, forming a dative  $\sigma$ -bond. The hatched area around the platinum atom represents the occupied  $d_{xz}$ -orbital (on the plane of the diagram) which is overlapping the  $\pi$ -antibonding orbital of ethylene giving  $\pi$ -back-donation. The arrows indicate the direction of transfer of the electron charge due to the bonding. (11)

from the ligand to the vacant orbital of the metal. The second part consists of the back-bonding or flow of electrons from the filled d orbital of the metal to the antibonding orbital of the double bond. Although this antibonding orbital of the double bond is antibonding with respect to the carbon-carbon bond, it is a bonding orbital with respect to the

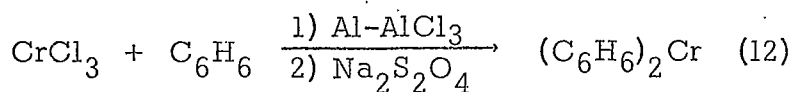
carbon-metal bond and thus the back-bonding adds to the stability of the complex. The number of double bonds that can be bonded to a single metal atom by a synergic bond is limited by the number of ligands that can be arranged so the geometry of the ligand orbital matches with a vacant bonding orbital of the metal, by the amount of back-donation that can occur, and finally by the steric factors of the ligand.

One method of preparing compounds containing the synergic bond is the double decomposition reaction outlined below:



The metal can be vanadium, chromium, manganese, iron, ruthenium, cobalt or nickel.

Another double bond system that can be used is benzene. Thus dibenzene chromium can be prepared as follows:

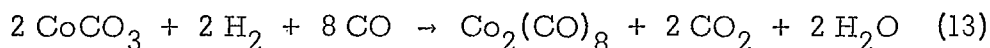


The organic ligand can also be a chain system where the double bonds are conjugated, as in butadiene, or non-conjugated, as in ethylene, or any of the many derivatives of these systems.

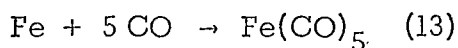
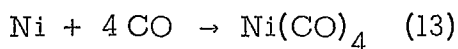
Synergic bonds are not limited to bonds between pi electrons and metals, but can also exist with other molecules which can donate a lone pair of electrons to a vacant metal orbital and accept some back-donation from the metal d orbital. One such molecule is carbon monoxide. When carbon monoxide is the only ligand the complex is called a metal carbonyl. Metal carbonyls are known for transition elements from

Group VB to VIII. When a metal carbonyl contains a metal with an even atomic number it may contain one or more than one metal atom(s) per complex, but a metal carbonyl complex containing a metal with an odd atomic number forms complexes which contain more than one metal atom per complex except for vanadium hexacarbonyl, which has an odd atomic number but still has only one metal atom per complex. In all cases the most stable state of the metal carbonyl of each transition metal has the electron configuration of the noble gas of whichever period it is a part.

The metal carbonyls of Groups VB to VIII are generally prepared by the action of carbon monoxide, in the presence of a reducing agent, on the metal salt at high temperature and pressure.



Only two metal carbonyls can be formed directly from the pure metal and carbon monoxide.



The carbonyl molecule is known to bond to metals in three different ways: terminal, double bridging and (rarely) triple bridging. The molecular orbital picture of the bonding between the terminal carbonyl and the metal is again divided into two parts. The carbonyl donates two sigma electrons to the empty metal hybridized orbital and the metal donates electrons from its filled d orbitals to the carbonyl antibonding orbital. This bond, as before, is synergic since the drift of electrons from the carbonyl to the metal makes the carbonyl more positively charged, which

in turn makes it a better acceptor of electrons from the metal d orbital, thus cancelling the positive charge, as shown in Figure 2.

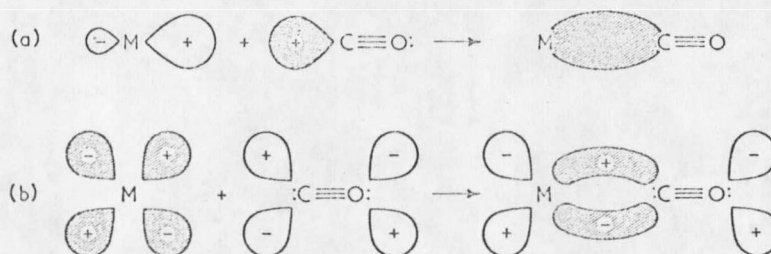


Fig. 2. (a) The formation of the metal-carbon  $\sigma$ -bond using an unshared pair on C atom. (b) The formation of the metal-carbon  $\pi$ -bond. The other orbitals on the CO are omitted for clarity. (14)

In the case of double bridging carbonyls, the carbonyl group contributes one electron to each of the two metal atoms to form normal sigma bonds with the metal also donating one electron. The carbonyl will also accept some back-donation from the metal into its antibonding orbital. In all the cases where there are bridging metal carbonyls, either double or triple, there is also a metal-metal bond, as shown in Figure 3. This bond is present because the carbonyl holds the two metals so close that there is an overlap of orbitals and it also allows the metals to achieve a complete shell of electrons, thus adding to the stability of the complex.

A very important aspect of metal carbonyls is that sigma substituted transition metal carbonyls are much more stable than are the sigma substituted transition metals alone (16). The increase in stability may be due to the removal of the excess electron density, which is caused by the

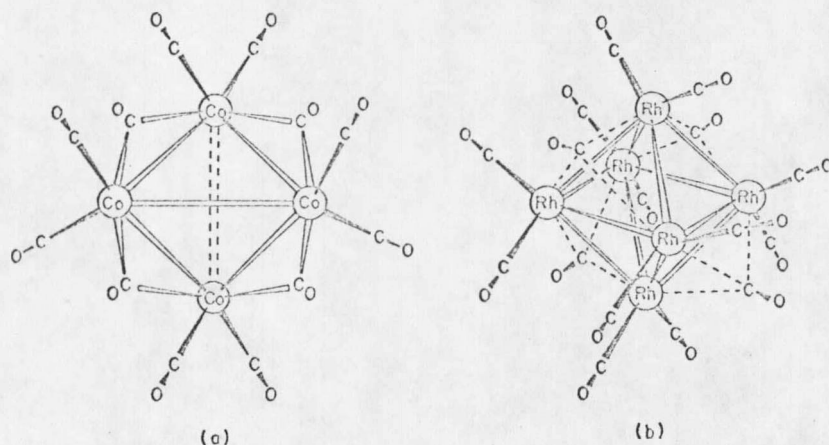
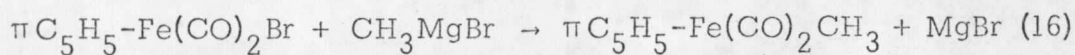


Fig. 3. (a) The  $D_{2d}$  structure proposed for  $Co_4(CO)_{12}$  in solution on the basis of its infrared spectrum. (b) The structure (symmetry  $T_d$ ) of  $Rh_6(CO)_{16}$  determined entirely by X-ray crystallography. (15)

sigma bonded organic ligands, by back-donation of electrons from the metal to the carbonyl antibonding orbitals.

The more stable sigma substituted transition metal carbonyls are prepared by the use of the Grignard reagent with the halide of the metal complex.



The sodium salt of the complex can also be made to react with an organic halide.

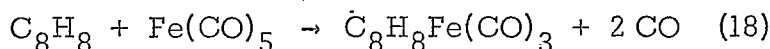
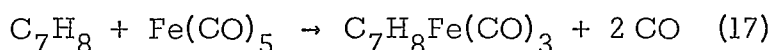
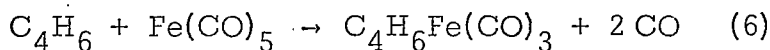


An even larger group of organometallic metal carbonyls are the pi substituted transition metal carbonyls. Here again the presence of the

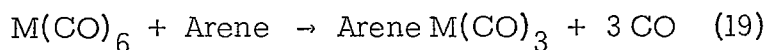
carbonyls adds stability to the complex. For example, dibenzene chromium is readily oxidized in air to the derivative of the dibenzene chromium cation, while the corresponding complex, benzene chromium tricarbonyl, is stable in air.

This increase in stability of pi substituted transition metal carbonyls may again be due to the ability of the carbonyl to accept more back-donation from the metal than the pi substituted ligand can accept.

The pi substituted transition metal carbonyls can usually be prepared thermally from the metal carbonyl and the desired ligand:



Although the reactions of iron pentacarbonyl parallel those of most of the transition metal carbonyls, there is one more important type which is not possible with iron pentacarbonyl. This is the reaction of aromatic compounds such as benzene, toluene, aniline with a Group VI metal hexacarbonyl.



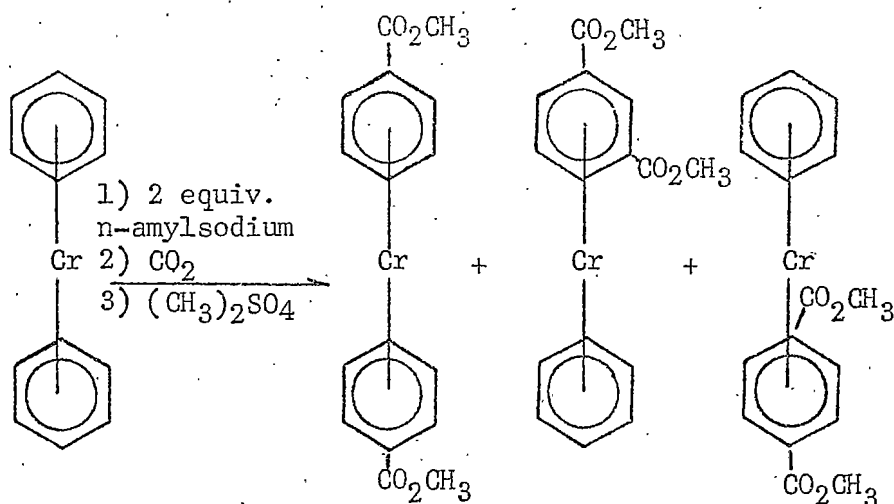
The fact that the arene is connected to the metal by its aromatic pi system creates an electron deficiency in the arene and causes it to be less prone to electrophilic attack than the free arene (20).

That complexing with a metal carbonyl does decrease the electron availability is shown by a comparison of the acid strength of benzoic acid

with that of benzoic acid chromium tricarbonyl. The  $pK_a$  of the benzoic acid chromium tricarbonyl is 4.77, compared to  $pK_a$  5.68 for benzoic acid. Thus we see that benzoic acid chromium tricarbonyl will act much the same as nitrobenzoic acid, which has a  $pK_a$  of 4.48 (20).

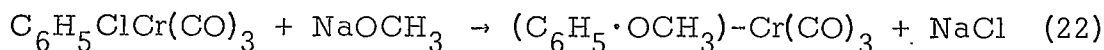
In addition to causing the arene ring to be less reactive toward electrophile in general, arene metal carbonyls are also unstable to strong acids and thus are not able to withstand the reaction conditions for nitration and sulfonation (20).

It is still possible, though, to add many substituents such as halide, nitrate, hydroxide and amine indirectly to an arene ring when it is attached to a metal. One successful method is to treat the arene metal with an alkali metal reagent such as *n*-amyl sodium. This metalated species can then attack an electrophilic molecule to form a substituted arene metal (21).

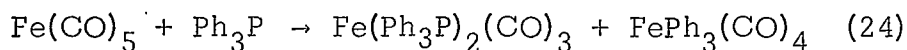


By the same reasoning which was used to explain the decrease in reactivity of arene metal carbonyls, it is evident that the nucleophilic

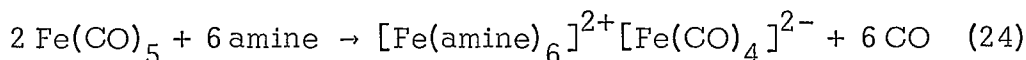
attack on the arene will be enhanced. This idea is also supported by the nucleophilic displacement reaction of functional groups which have been described to proceed in the pi complexed arene but do not proceed in an uncomplexed arene (22).



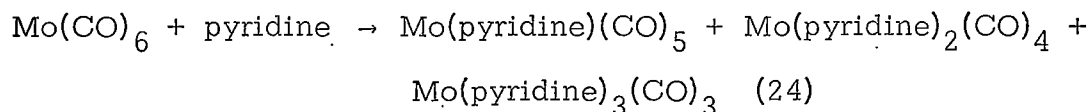
Another important reaction of metal carbonyls is the displacement of the carbonyl group by another sigma donor. The sigma donor with the ability to accept back-bonding such as  $\text{CN}^-$ ,  $\text{AsPh}_3$ ,  $\text{SbPh}_3$ ,  $\text{SR}_2$ ,  $\text{PX}_3$ , or  $\text{P(OR)}_3$  can displace one or more carbonyls (23).



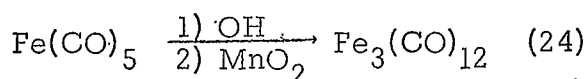
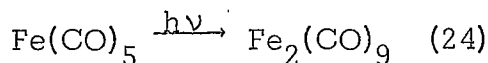
In the presence of amine, nitrogen or oxygen ligands, iron pentacarbonyl will undergo a dissociation reaction:



while molybdenum hexacarbonyl will form a series of sigma complexes:



A different type of reaction is the formation of polynuclear complexes of the starting metal carbonyl. In the case of iron, there are two polynuclear complexes known:

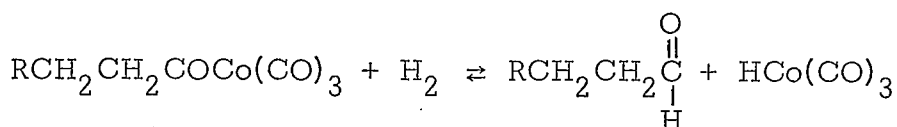
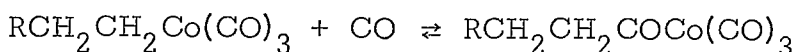
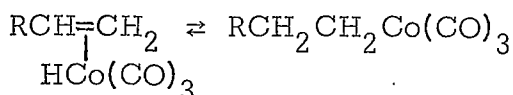
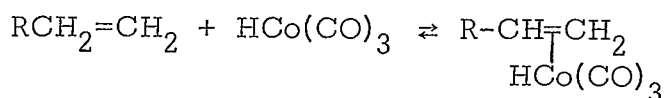
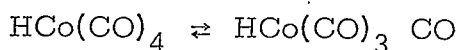
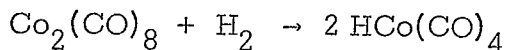


In many cases where iron pentacarbonyl is one of the reactants, the actual reacting species may be one of the polynuclear complexes shown above.

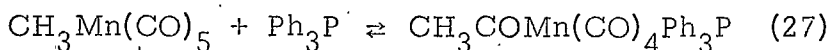
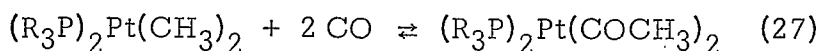
Another type of reaction is the transfer of a carbonyl group from the transition metal to a ligand attached to the metal carbonyl. This reaction is demonstrated by the oxo process reported first by Roelen in 1938 (25). All Group VIII transition metals have been shown to undergo this type of reaction (25). This reaction is used commercially with dicobalt octacarbonyl to make aldehydes at pressures of 100 to 200 atmospheres with a 1:1 mixture of hydrogen and carbon monoxide and at a temperature between 100°C and 150°C. At lower pressure and temperatures the yield is correspondingly lower.

A mechanism has been proposed for this reaction by Heck and Breslow and is outlined below (26).

## Oxo Process



The most important step of the oxo reaction is the carbonyl insertion between the metal and the hydrocarbonyl ligand. Similar reactions are observed in the metal alkyl complexes such as those listed below:



### Complexes of Norbornadiene and Transition Metals

The first reported complex between norbornadiene (bicyclo[2.2.1]heptadiene-2,5) and a transition metal was reported by Burton, Green, Abel and Wilkinson in 1958 (28). They reported the thermal reaction of norbornadiene with iron pentacarbonyl, forming norbornadiene iron tricarbonyl. This reaction showed that norbornadiene

could be used as a ligand but was also the first case of a "non"-conjugated diene system forming such a metal pi complex.

Since this first report of a norbornadiene transition metal complex, norbornadiene has been shown to form complexes with eleven other transition metals.

A total of eighteen complexes have been identified and are listed in Table I.

Table I

## Transition Metal Complexes with Norbornadiene

|                             |                           |
|-----------------------------|---------------------------|
| $C_7H_8Fe(CO)_3$ (28)       | $C_7H_8PtCl_3$ (30)       |
| $Co_2(CO)_4(C_7H_8)_2$ (29) | $C_7H_8Mo(CO)_4$ (31)     |
| $Co_2(CO)_6C_7H_8$ (29)     | $C_7H_8Cr(CO)_4$ (32)     |
| $C_7H_8PdCl_2$ (30)         | $C_7H_8W(CO)_4$ (32)      |
| $[C_7H_8RhCl]_2$ (30)       | $C_7H_8IrCl$ (33)         |
| $C_7H_8(AgNO_3)_2$ (30)     | $C_7H_8Au_2Cl_4$ (34)     |
| $C_7H_8RuCl_2$ (30)         | $(C_7H_8)_2Au_2Cl_4$ (34) |
| $C_7H_8RuBr_2$ (30)         | $(C_7H_8)_3Au_2Cl_4$ (34) |
| $C_7H_8(CuBr)_2$ (30)       | $C_7H_8CuCl$ (35)         |

Dimer and Trimer of Norbornadiene

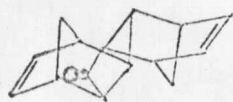
There are, if one considers stereochemistry, over a hundred different ways to form dimers and trimers of norbornadiene and, if one includes

the possible ketones, the number of compounds will be much larger. This problem of so many possible isomers is not a serious one in the metal carbonyl catalyzed dimerization of norbornadiene since steric factors eliminate many of the possible structures and thus far eleven compounds have been found.

The structures of the compounds that have been found are shown in Table II with their stereochemistry indicated if it has been determined.

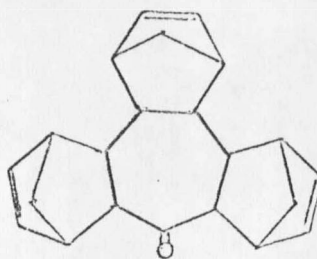
Table II

Dimers and Trimers of Ketones of Norbornadiene



I

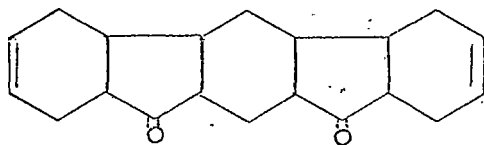
m.p. 85°C (31, 36)



II

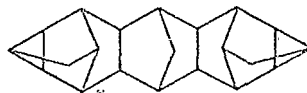
m.p. 196°C (36)

Table II (cont.)



III

m.p. 218°C (36)



IV

m.p. 176°C (37)

n.m.r. .87, 1.23, 1.67, 1.89, 2.08



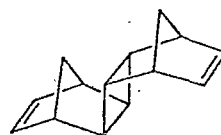
V

exo trans exo pentacyclo-(8.2.1.1<sup>4,7,0<sup>2,9</sup>,0<sup>3,8</sup></sup>)

tetradecadiene (38)

m.p. 67°C

n.m.r. 1.23, 1.32, 1.69, 2.62, 5.97

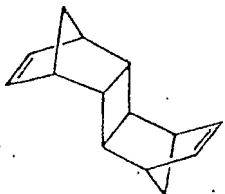


VI

exo trans endo pentacyclo-(8.2.1.1<sup>4,7,0<sup>2,9</sup>,0<sup>3,8</sup></sup>)

tetradecadiene (38)

m.p. oil

n.m.r. 1.13, 2.00, 2.54, 2.80,  
5.82, 6.20

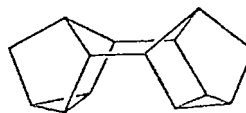
VII

endo trans endo pentacyclo-(8.2.1.1<sup>4,7,0<sup>2,9</sup>,0<sup>3,8</sup></sup>)

tetradecadiene (38)

m.p. 92°C

n.m.r. 1.02, 1.55, 1.85, 2.72, 6.25



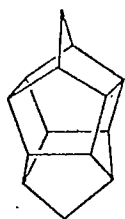
VIII

endo cis endo heptacyclo-(5.3.1.1<sup>3,6,4<sup>4,12</sup>,1<sup>9,11</sup>,0<sup>3,5</sup>,0<sup>8,10</sup></sup>)

tetradecane (39)

m.p. 65°C

Table II (cont.)



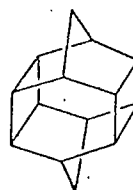
IX

heptacyclo-  
(5.5.1.1<sup>4,10</sup>.0<sup>2,6</sup>.0<sup>3,11</sup>.0<sup>5,9</sup>.0<sup>8,12</sup>)

tetradecane (39, 40)

m.p. 165°C

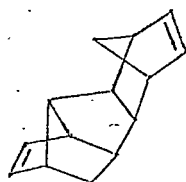
n.m.r. 1.79, 2.45



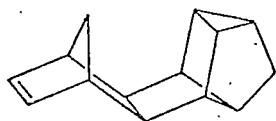
X

heptacyclo-  
(7.4.10<sup>2,8</sup>.0<sup>3,7</sup>.0<sup>4,12</sup>.0<sup>6,11</sup>.0<sup>10,13</sup>)

tetradecane (39, 40)

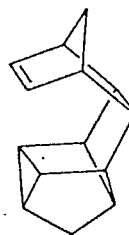


XI



XII

n.m.r. .80, 1.28, 1.88, 2.37, 2.55,  
6.05 (37)



XIII

n.m.r. .35, 1.15, 1.53, 1.78, 2.00,  
2.58, 5.30 (37)

## Metal Carbonyl Catalyzed Dimerization of Norbornadiene

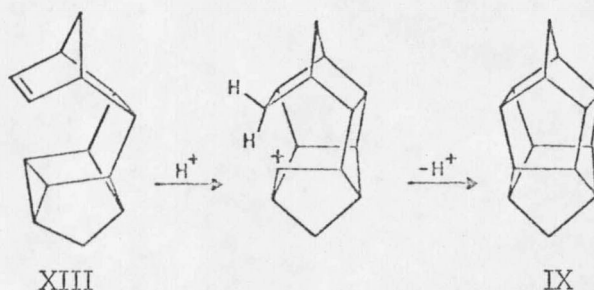
### Thermal Dimerization

The metal carbonyl catalyzed thermal dimerization of norbornadiene was first reported by Petit in 1958 (31). Petit found when norbornadiene was refluxed with iron pentacarbonyl for fifteen hours and then fractionally distilled the products were norbornadiene iron tricarbonyl and a ketone dimer. The ketone was obtained as white needles from alcohol, melting point  $82^{\circ}\text{C}$  (I).

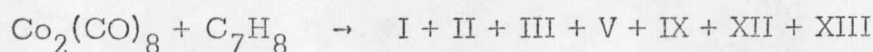
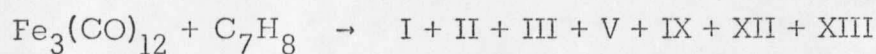
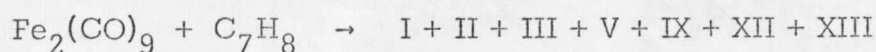
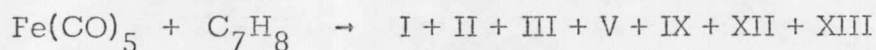
Bird, Cookson and Hudac (41) in the following year showed that norbornadiene and iron pentacarbonyl reacted to give, in addition to norbornadiene iron tricarbonyl, three ketones (I, II, III). Bird, Cookson and Hudac (41) also reported that nickel tetracarbonyl dimerized norbornadiene to give two hydrocarbons, which were tentatively assigned to compounds VII and XI. The compound assigned to structure XI was later changed to structure VI by Cannell (42), based on nuclear magnetic resonance studies.

Limal and Shim (40) in 1961 were able to show that a saturated hydrocarbon dimer of norbornadiene was formed when a mixture of iron pentacarbonyl and norbornadiene was irradiated with a sun lamp. Cookson (41) had shown the same dimer was formed thermally from iron enneacarbonyl in norbornadiene. Since the photoreaction of iron pentacarbonyl forming iron enneacarbonyl was known (43), Limal and Shim postulated that the light caused the formation of iron enneacarbonyl which then catalyzed the thermal reaction of norbornadiene hydrocarbon to give

the saturated dimer. There was some difficulty in deciding if the saturated dimer was structure IX or X. It was finally concluded by Katz and Acton (44), on the basis that an identical cage could be formed from XIII and hydroiodic acid, that the correct cage structure was IX.



Bird, Colinese, Cookson, Hudec and William (41), in their paper describing the formation of a saturated carbonyl from iron enneacarbonyl, also discuss the following thermal reactions of norbornadiene:



An insight into the mechanism of the thermal dimerization reaction of norbornadiene using metal carbonyl as a catalyst is provided by using iron dicarbonyl dinitrosyl as the catalyst (45). From the large number of iron dinitrosyl complexes that can be prepared using iron dicarbonyl dinitrosyl, it is evident that the carbonyl groups can be replaced more easily than the nitrosyl group. In the reaction of iron dicarbonyl

dinitrosyl and norbornadiene the appearance of an infrared peak at  $1745\text{ cm}^{-1}$  indicates the formation of a complex between iron dinitrosyl and norbornadiene. It has been proposed (45) that the complex between two norbornadienes and iron dinitrosyl may be formed by having one of the double bonds on each norbornadiene replace one carbon monoxide.

If the complex is formed by successive replacement of the carbon monoxide ligand by the double bond of norbornadiene, the replacement of the carbon monoxide by triphenylphosphine should stop the formation of the complex since triphenylphosphine ligands are not replace by double bonds (45). The reaction of iron dinitrosyl bistrisphenylphosphine has been tried and no dimer products are formed under similar reaction conditions used for the iron dinitrosyl dicarbonyl reaction.

The dimerization can then be visualized as occurring intramolecularly between two norbornadienes attached to an iron dinitrosyl in a sterically critical tetrahedral complex structure. Although only one pi bond from each norbornadiene molecule is formally involved, the lack of a dimer when norbornene is used (45) suggests the second pi bond of norbornadiene also contributes to the transition state.

In the case of cobalt tricarbonyl nitrosyl (45) there is the possibility of replacing three ligands instead of just two. If all three carbonyls were replaced, this would allow for one norbornadiene to be doubly bonded to the transition metal and one singly bonded. From this intermediate one would expect one of the major products to be a nortricyclene type dimer (XII, XIII). The major products are a

nortricyclene type dimer and the exo trans exo dimer (V) in addition there is a trace of dimer VI found.

The formation of an exo trans exo dimer and a nortricyclene type dimer in the reaction of cobalt tricarbonyl nitrosyl (45) demonstrates another interesting fact. According to the Woodward-Hoffman rules (46, 47, 48), the formation of exo trans exo type dimers should be thermally forbidden where the formation of nortricyclene type dimers should be thermally allowed (46, 47, 48). The fact that both types of dimers are formed thermally in the presence of a transition metal catalyst indicates that the Woodward-Hoffman symmetry restrictions do not apply (46, 47, 48). This change in restriction may be due to the mixing of the ethylene carbon's  $2p\pi$  orbital with the metal d orbital. The atomic d orbitals of the metal allow the electrons of the hydrocarbon ligand and the metal electrons to mix and fill the required region of space for dimerization of the ligand to occur. That both types of dimer are formed is further evidence of a transition state involving two norbornadienes and a transition metal. The role of the metal in this case is therefore the removal of the symmetry restrictions and the lowering of the activation energy.

Another possible way to explain the formation of the thermally forbidden exo trans exo dimer in the thermal experiment is to invoke a non-concerted mechanism. The non-concerted mechanism is proposed for the formation of dimer products using rhodium on carbon as the catalyst. Katz and Mrowca (37) investigated this reaction and found the thermal

products to be XII, XIII, IV and a trace of V. The rhodium-carbon catalyst is very effective, giving products quantitatively and quickly at room temperature.

Katz and Acton (44) have investigated the reaction of rhodium on carbon further and have reported a formal relationship between two pairs of the reported hydrocarbon dimers. They further suggest that in the metal catalyzed cycloaddition reactions an intermediate is produced in which only one carbon to carbon bond is formed uniting the two norbornadienes. Rotation can occur about this single bond before the second bond closes. This mechanism allows the Diels-Alder product and the other hydrocarbon dimer to arise from the same intermediate. If the second bond closes without rotation about the initial bond the products are V, VI and VII. If rotation of  $90^\circ$  occurs about the initial bond the products are XII and XIII (Figure 4).

A reaction of 30% palladium on carbon gives a .1% yield of dimer I while both .5% platinum on charcoal and the nickel catalyst failed to give any product when run under similar reaction conditions (44).

Two other metal carbonyls have been shown to catalyze a thermal reaction of norbornadiene. Molybdenum hexacarbonyl (50) and tungsten hexacarbonyl (50) have both been shown to act as catalysts for the polymerization of norbornadiene. The polymer that is formed is a white solid, stable to greater than  $350^\circ\text{C}$  at atmospheric pressure and is formed when norbornadiene is refluxed in toluene for 21 hours with either molybdenum or tungsten hexacarbonyl. The reaction mixture of metal hexacarbonyl

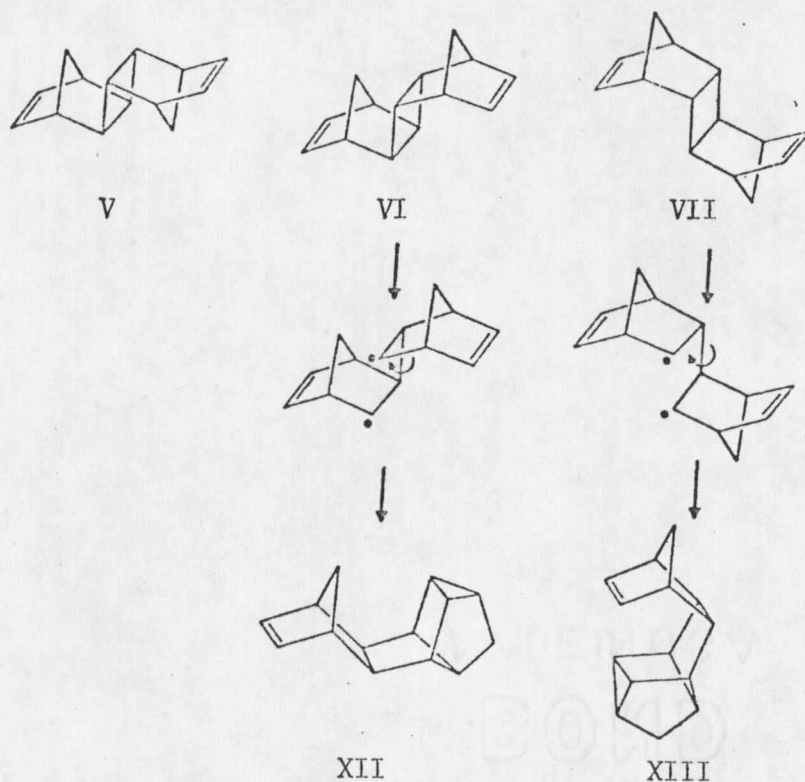


Fig. 4. Non-concerted mechanism proposed for the formation of dimer products using rhodium on carbon as the catalyst (44).

and norbornadiene should be anhydrous and free of oxygen for the highest yield.

#### Photochemical Dimerization

The photochemical reactions of norbornadiene and metal carbonyls have not been studied as extensively as the correspondingly thermal reactions. The fact that light would cause dimerization was first reported in 1958 by Petit (31). Petit showed that iron pentacarbonyl and norbornadiene in sunlight for five hours gave norbornadiene iron tricarbonyl, a ketone (I) and a solid hydrocarbon dimer with a melting point of 67-68°C (V).

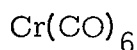
It has now been shown (51) that if substituted or unsubstituted butadiene iron tricarbonyls are used as a catalyst for the photochemical dimerization of norbornadiene, the products are exo trans exo (V) and endo trans endo (VII). This change of photochemical products from the use of iron pentacarbonyl as the catalyst suggests that changes in the number of carbonyls or stereochemistry or both may be an important factor in determining the final reaction products.

The following investigation was initiated to determine: a) the photochemical mechanism of the dimerization of norbornadiene using metal carbonyls; b) the effect of the steric factors of the ligand on the product identities and the product ratios; c) the effect of the number of carbonyls on the product identities and the product ratios.

## DISCUSSION

To begin the investigation of the steric effects and the effect of the number of carbonyls on metal carbonyl catalyzed dimerization of norbornadiene and to determine the photochemical mechanism of this reaction, it was necessary to choose a transition metal carbonyl to act as a reactant template. The transition metal should be able to form stable complexes not only with carbonyls but also with organic ligands which would allow for a variation in steric factors. Chromium was the transition metal chosen because it forms chromium hexacarbonyl, norbornadiene chromium tetracarbonyl and also a series of benzene-substituted chromium tricarbonyls. In addition, the number of carbonyls could be varied even further since there is the air-unstable dicumene chromium. The following series of chromium complexes were chosen as the photochemical reactant templates.

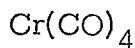
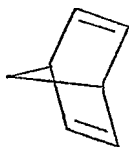
Table III  
Metal Carbonyl Reactant Templates



Chromium hexacarbonyl

Infrared spectrum  $1988\text{ cm}^{-1}$  (52)

Ultraviolet spectrum 230 (log  $\epsilon$  4.78), 280  
(log  $\epsilon$  4.07), 318  
(log  $\epsilon$  3.49) (53)

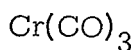
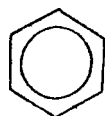


Norbornadiene chromium tricarbonyl

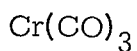
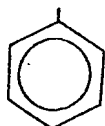
Infrared spectrum 1913, 1944, 1958,  $2033\text{ cm}^{-1}$

Nuclear magnetic resonance 4.42, 3.73, 1.30 (54)

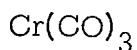
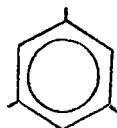
Table III (cont.)



Benzene chromium tricarbonyl

Infrared spectrum 1910, 1983  $\text{cm}^{-1}$ 
 Ultraviolet spectrum 218 ( $\log \epsilon$  4.43),  
 264 ( $\log \epsilon$  3.92),  
 316 ( $\log \epsilon$  4.05) (53)


Toluene chromium tricarbonyl

Infrared spectrum 1900, 1971  $\text{cm}^{-1}$ 
 Ultraviolet spectrum 218 ( $\log \epsilon$  4.05),  
 261 ( $\log \epsilon$  3.97),  
 318 ( $\log \epsilon$  4.12) (53)


Mesitylene chromium tricarbonyl

Infrared spectrum 1889, 1963  $\text{cm}^{-1}$ 
 Ultraviolet spectrum 215 ( $\log \epsilon$  4.48),  
 253 ( $\log \epsilon$  4.02),  
 312 ( $\log \epsilon$  4.08) (56)


Dicumene chromium

The infrared bands between 1850-2050  $\text{cm}^{-1}$  are characteristic of all metal carbonyls and are assigned to the carbon-oxygen stretching frequency (57).

The ultraviolet spectra are also very characteristic of the metal carbonyls. The 230 m $\mu$  and 280 m $\mu$  bands are attributed to the metal to ligand charge transfer ( $1_{A_{1g}} \rightarrow 1_{T_{1g}}$ ) (58). The band in the 320 m $\mu$  region is due to the d  $\rightarrow$  d transition and is very difficult to locate since the ligand to metal charge transfers are intense in this region of the ultraviolet. The reason the d  $\rightarrow$  d transitions are in this region and not at longer wavelengths is that the carbonyls cause a large crystal field splitting (59).

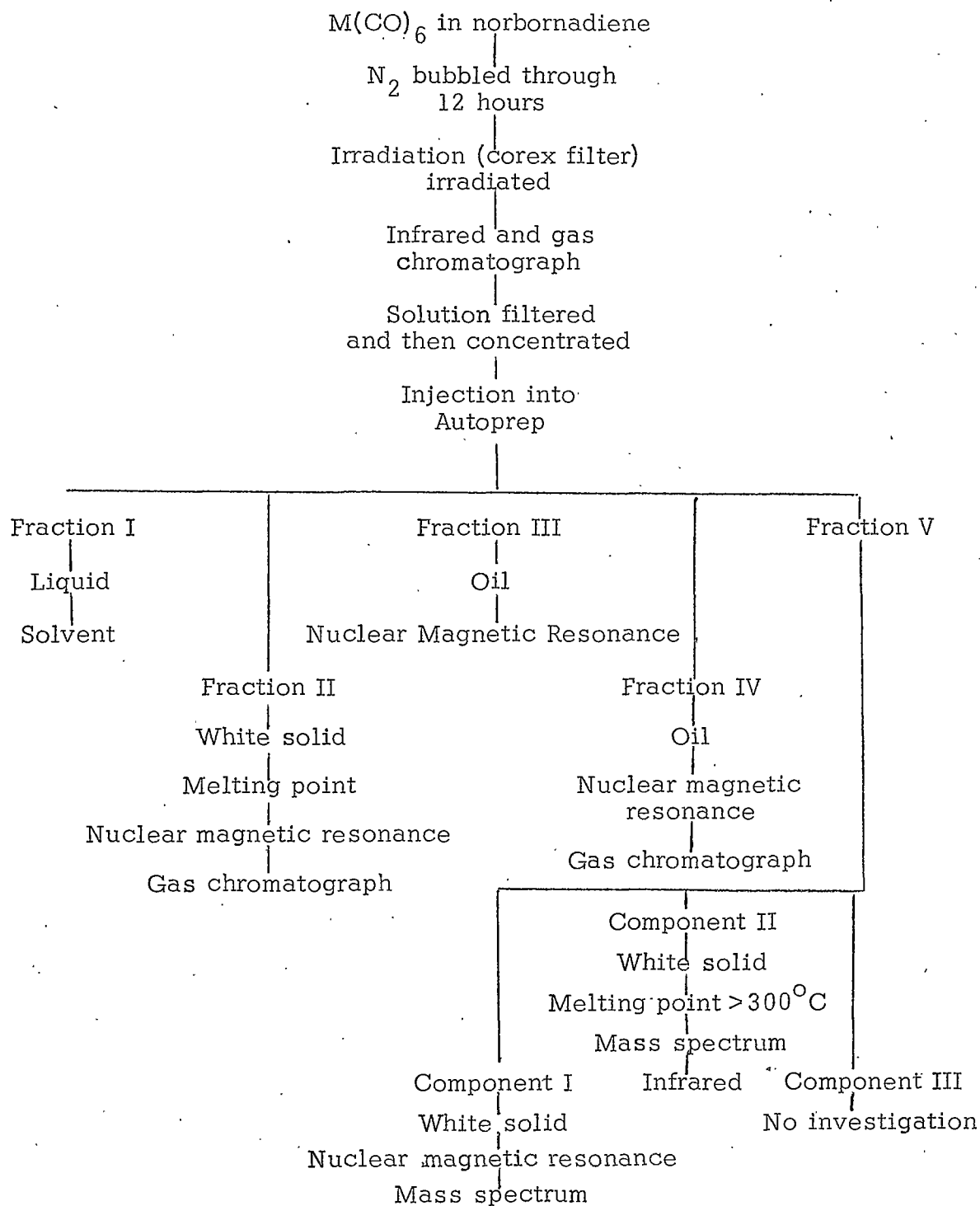
The initial experiments were to determine if the chromium complexes could act as photochemical reactant templates and to determine the photochemical products, if any.

#### Procedure for Determining Products and Product Ratios

The general procedure (Table IV) was to make a solution of the metal carbonyl in 70 ml of freshly distilled norbornadiene. This solution was put into the large reaction vessel and purified nitrogen was bubbled through the solution for 12 hours. The irradiation was started and the sample irradiated using a corex filter for approximately 24 hours. Infrared and gas chromatographs were run on the total reaction product. The reaction mixture was then filtered through activated alumina and washed with hexane. This solution was concentrated to remove the hexane and then run through the Aerograph Autoprep and separated. Integration of the peaks using a Sargent Model SR recorder gave the product ratios. Five separate fractions were collected and identified. Fraction five contained three components.

Table IV

## Experimental Procedure for Product Identification



Fraction one represented all the material that came off the 30% SE-30 column before the first dimer, which was detected 88 minutes after the initial injection. Fraction one was shown by gas chromatography to contain only the remaining solvent. Fraction two was collected as a white solid with a melting point of 67-68°C. A comparison of the nuclear magnetic resonance spectrum (Figure 5), melting point, and a gas chromatogram with an authentic sample of exo trans exo proved this fraction

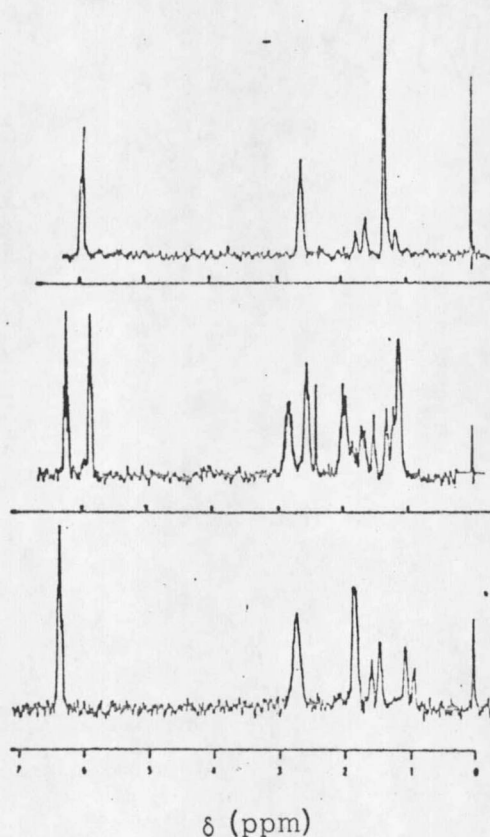


Fig. 5.  $H^1$  magnetic resonance spectra (60 Mc.) of norbornadiene dimers: top, exo trans exo; center, exo trans endo; bottom, endo trans endo. (38)

was the exo trans exo dimer (V). The third fraction was an oil. The nuclear magnetic resonance spectrum of this sample (Figure 5) compared with the nuclear magnetic resonance spectrum of a known sample of hydrocarbon dimer exo trans endo showed this fraction was the exo trans endo dimer (VI). The fourth fraction was also collected as an oil. A comparison of the nuclear magnetic resonance spectrum (Figure 5) and the gas chromatogram showed this fraction was the endo trans endo dimer (VII) with a very small amount of exo trans endo dimer. The fifth fraction was found to contain three components. Rechromatography of this fraction on the Autoprep under the same conditions as before permitted the separation of the three components. The first and major component of the fifth fraction was collected as a white solid. The nuclear magnetic resonance spectrum (Figure 6) was compared to the nuclear magnetic resonance spectrum of the cage compound (IX) proposed by Katz and Acton (44) and found to be identical. Although the nuclear magnetic resonance spectra are identical, it is necessary to point out that the other cage compound (X) would also have only two peaks in a ratio of 3:1 in

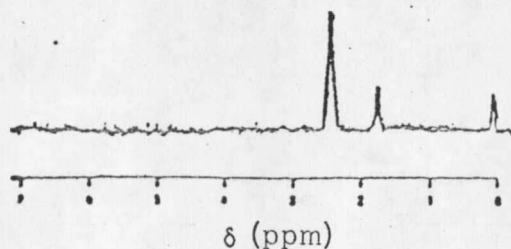


Fig. 6.  $H^1$  magnetic resonance spectrum (100 Mc.) of norbornadiene cage dimer.

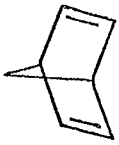
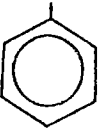
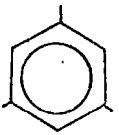
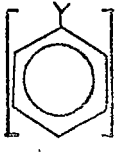
the same region of the nuclear magnetic resonance spectrum (40, 41). Since this is so, it may not be possible to distinguish between the two cage compounds by the nuclear magnetic resonance spectrum alone. Thus the assignment of the cage compound in component one of fraction five to structure IX is only tentative.

The second component of the fifth fraction was a polymer (50). This compound, isolated in large yield in a later reaction described in the experimental section, was shown to be stable to greater than 300°C. It was assigned to be a carbonyl-containing polymer because the infrared spectrum contained a  $1715\text{ cm}^{-1}$  peak not observed in the hydrocarbon dimer. The mass spectrum showed peaks to a molecular weight of over 1000. The third component of the fifth fraction was such a minor product it was not investigated further.

Integration of the peaks of the gas chromatograms led to the product percentages listed in Table V. It is assumed for these calculations that the three dimers and the single cage compound represented the total reaction product. This assumption was necessary since it was evident from the comparison of the gas chromatogram of the total reaction products and of the filtered sample that most of the carbonyl-containing polymer was removed from the sample during the filtration through activated alumina. The filtration which was used to remove the solid particles and the carbonyl compounds was accomplished by filtering the total reaction sample through a Büchner funnel filled with activated

Table V

## Product Ratios of Norbornadiene Dimers

|                                                                                                       |  | <u>Exo trans</u><br><u>exo</u> | <u>Exo trans</u><br><u>endo</u> | <u>Endo trans</u><br><u>endo</u> | Cage |
|-------------------------------------------------------------------------------------------------------|--|--------------------------------|---------------------------------|----------------------------------|------|
| $\text{Cr(CO)}_6$                                                                                     |  | 36                             | 21                              | 29                               | 14   |
|  $\text{Cr(CO)}_4$   |  | 52                             | 20                              | 23                               | 5    |
|  $\text{Cr(CO)}_3$   |  | 36                             | 24                              | 33                               | 7    |
|  $\text{Cr(CO)}_3$ |  | 49                             | 22                              | 22                               | 7    |
|  $\text{Cr(CO)}_3$ |  | 39                             | 26                              | 26                               | 9    |
|  $\text{Cr}$       |  | 0                              | 0                               | 0                                | 0    |

alumina. The hydrocarbon dimers were eluted off the alumina with hexane; some polymer was also eluted by the hexane.

These percentages are based on one series of reactions which were run and treated as identically as possible. The relative values based on the integration are consistent with the relative values based on the peak height of the gas chromatogram taken of the total reaction product.

The variations in percentages are larger than expected from subsequent experimental results discussed later in this thesis. Some of the variations may be due to the chromatographic separation. In the case of norbornadiene chromium tetracarbonyl, with two identical samples there is a maximum variation in the percentage values of five percent in the value for exo trans exo.

Another error is possible. Since the cage compound is formed in such small amounts, its peak on the gas chromatogram is only slightly above the base line and therefore the starting and final points of the integration must be estimated. In addition, a correction for the amount of carbonyl polymer must be estimated.

The first observation based on these experimental results is that the carbonyl group may have to be present since dicumene chromium does not act as a photochemical to give any dimer hydrocarbon products.

In all cases (except dicumene chromium) identical products are formed and similar percentages are obtained. The fact that the products are identical is interpreted to mean that all the hydrocarbon dimers are coming from an intermediate which contains the same number of carbonyl groups. It has been shown (45, 51) that the hydrocarbon dimer products of norbornadiene vary with the number of replaceable carbonyl groups.

Another conclusion drawn from Table V is that the steric factors of the organic ligands benzene, toluene and mesitylene do not affect the number of final products or affect greatly the product percentages. In addition, comparing chromium hexacarbonyl with benzene or mesitylene chromium tricarbonyl indicates that the steric effects of the organic ligand compared to a carbonyl does not affect the final products or affect greatly the product percentages. Since the steric difference between carbonyl, benzene, toluene and mesitylene are large, one might expect there to be a large variation in the nature of the products if the organic ligand was present when the actual dimerization occurred on the metal, as is believed to occur. Since there is no variation in the type of products, the indication is that benzene, toluene and mesitylene are lost prior to the actual formation of all the hydrocarbon dimers. It will be proposed that the cage dimer is not formed from the dimerization of norbornadiene attached directly to the chromium, but rather that an intermediate similar to dimer XI is formed which then reacts to form the cage compound. This same dimer is proposed by Katz and Acton (44) to give the cage compound by the reaction with hydroiodic acid.

#### Isolation of Intermediates Using Chromium Hexacarbonyl

A 0.0143 M chromium hexacarbonyl solution in norbornadiene was put into the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. An infrared spectrum of the solution was taken and the irradiation, using a pyrex filter, was started. Infrared spectra were taken at half-hour intervals for seven hours. After a total irradiation

time of ten hours another infrared spectrum was taken and compared to the one taken at seven hours. The comparison showed no further change had occurred so the irradiation was stopped.

Infrared spectra and gas chromatograms taken during the course of the reactions indicated that the chromium hexacarbonyl was changed rapidly to a second metal carbonyl. Secondly, the hydrocarbon dimer products did not appear in the gas chromatograms until after the appearance of the second metal carbonyl and stopped increasing in amount when the second metal carbonyl peak was no longer present in the infrared spectra (Figure 27). The infrared spectra and gas chromatograms indicated further that the second metal carbonyl was identical to norbornadiene chromium tetracarbonyl.

Another solution, similar in composition, was prepared and irradiated as described above. After two hours of irradiation, the carbonyl band of chromium hexacarbonyl had disappeared completely from the infrared spectrum, and the infrared bands of the second metal carbonyl were still evident (Figures 7, 8). The irradiation was continued and the infrared spectrum showed that all the metal carbonyl was absent after six hours (Figure 9).

Another solution was irradiated for two hours. The irradiation was stopped and the reaction mixture was allowed to stand under nitrogen for 19 hours with infrared spectra taken at 2-hour intervals. A peak at  $1988\text{ cm}^{-1}$  in the infrared spectrum appeared (chromium hexacarbonyl,  $1988\text{ cm}^{-1}$ ) after irradiation was stopped for six hours and grew to a

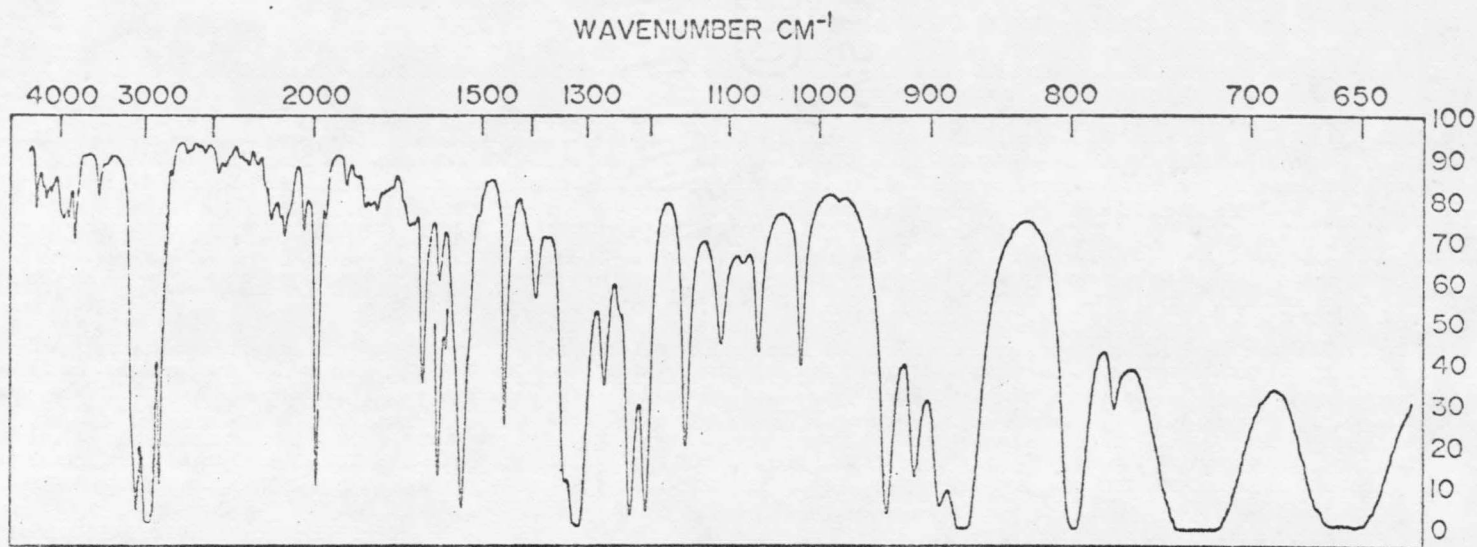


Fig. 7. 0 time of irradiation for chromium hexacarbonyl.

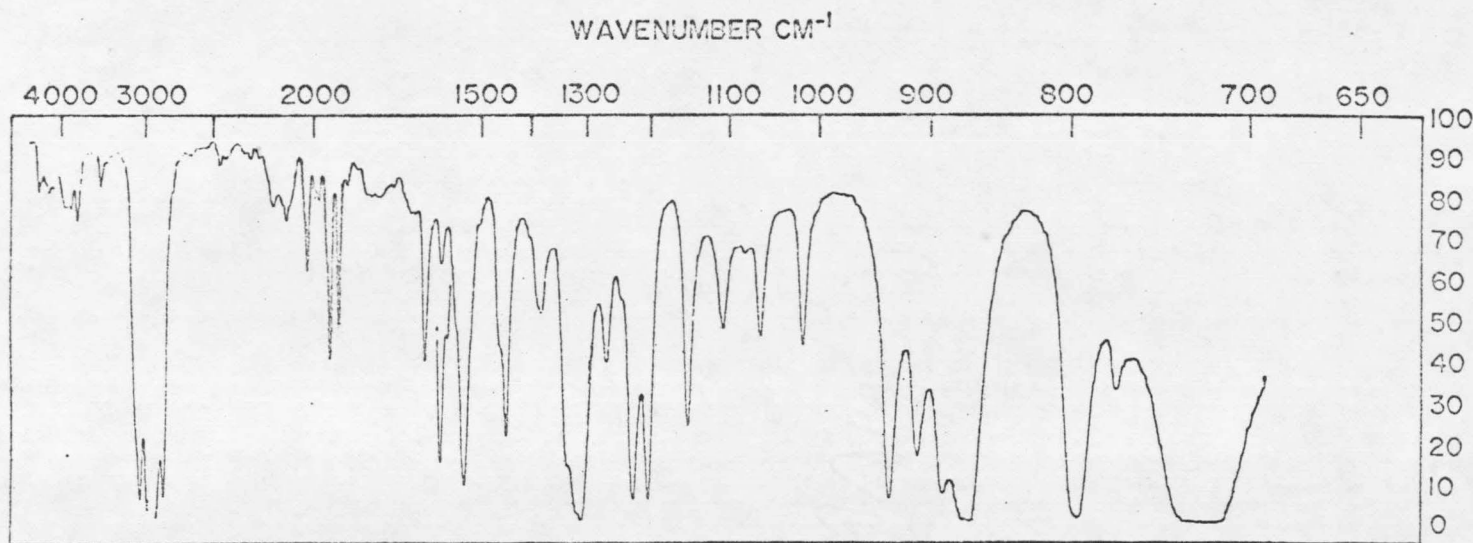


Fig. 8. 2 hours of irradiation for chromium hexacarbonyl.

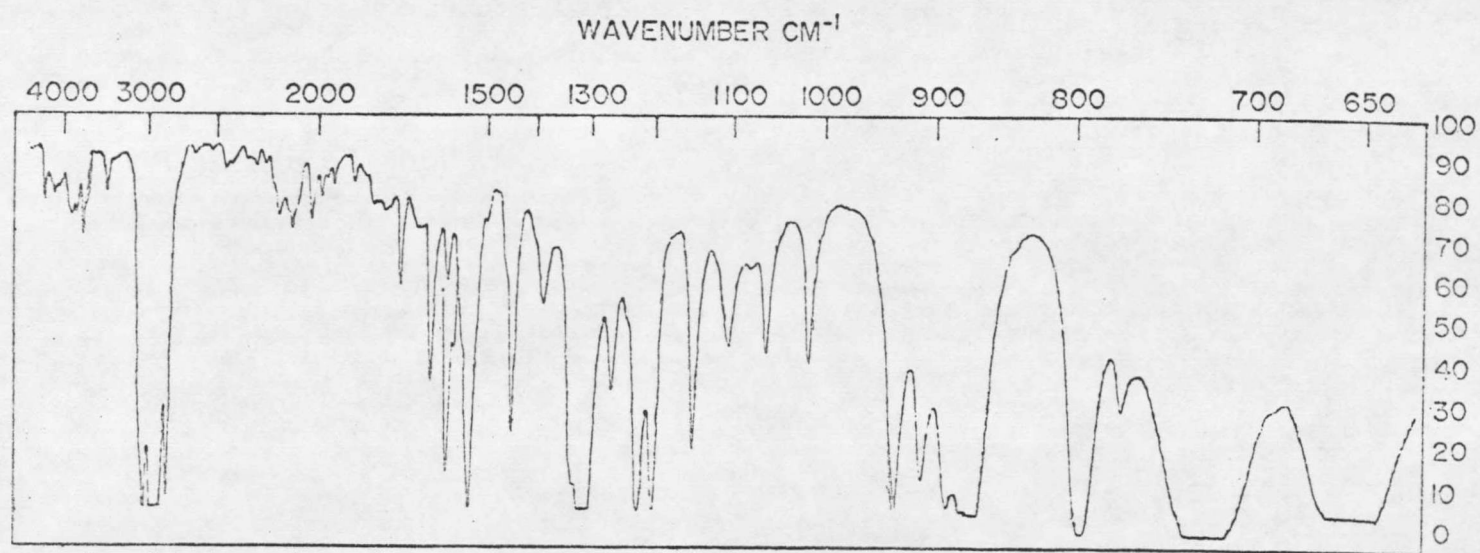


Fig. 9. 6 hours of irradiation for chromium hexacarbonyl.

maximum height of one-half its original intensity and the infrared peaks due to the second metal carbonyl remained unchanged (Figure 10).

The reappearance of the chromium hexacarbonyl infrared band may be due to the reformation of chromium hexacarbonyl from chromium pentacarbonyl and from norbornadiene chromium pentacarbonyl which could lose the norbornadiene to form chromium pentacarbonyl. It has been reported (60) that chromium hexacarbonyl when irradiated with ultraviolet light forms chromium pentacarbonyl which is also proposed to be an intermediate in the formation of chromium hexacarbonyl derivatives formed through the replacement of one or more carbonyl groups by ligands such as nitrides and olefins. In the same paper (60) it was also reported that when the irradiation was stopped the chromium pentacarbonyl reverted substantially back to chromium hexacarbonyl. Interfering peaks from the norbornadiene and second metal carbonyl did not allow the chromium pentacarbonyl peak to be identified.

To check the stability of the second intermediate metal carbonyl further, a solution of chromium hexacarbonyl and norbornadiene was heated to 70°C for five hours without any changes observed in the infrared spectrum of either chromium hexacarbonyl or the second metal carbonyl. This solution was cooled to room temperature and the solution irradiated for an additional 30 minutes. The peak at 1988 cm<sup>-1</sup> in the infrared spectrum again disappeared. The reaction mixture was removed from the reaction vessel and the solvent quickly evaporated in a roto evaporator to a volume of 5 ml. This concentrated solution was

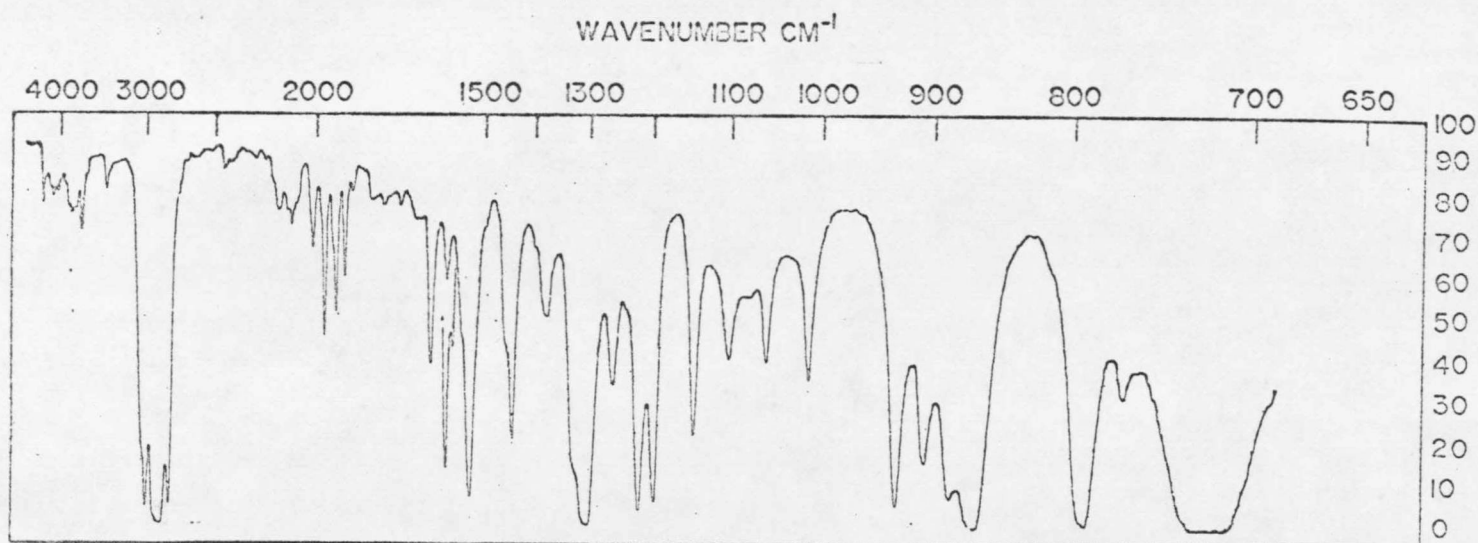


Fig. 10. 2 hours of irradiation and then 6 hours in the dark for chromium hexacarbonyl.

chromatographed on an activated silica gel column. Hexane was added to remove any hydrocarbon dimers and until a bright yellow band started to be eluted from the column. The hexane fraction was evaporated and shown by infrared spectrum not to contain any metal carbonyls. Benzene was added to the column and the bright yellow band collected. The benzene was removed and the remaining yellow solid sublimed. Infrared and nuclear magnetic resonance spectra were taken of this yellow metal carbonyl (m.p.  $92-93^{\circ}\text{C}$ ) and compared to the infrared and nuclear magnetic resonance spectra of an authentic sample of norbornadiene chromium tetracarbonyl. The spectra were identical and the melting point of the yellow solid was identical to that reported for norbornadiene chromium tetracarbonyl.

In conclusion, this experiment showed that chromium hexacarbonyl changed rapidly to a second metal carbonyl, which was isolated and shown to be norbornadiene chromium tetracarbonyl. It was indicated by the reappearance of the chromium hexacarbonyl infrared band at  $1988\text{ cm}^{-1}$  that an intermediate metal carbonyl, chromium pentacarbonyl, was formed during the reaction sequence of chromium hexacarbonyl going to norbornadiene chromium tetracarbonyl. It was also found that the hydrocarbon dimers were not found until norbornadiene chromium tetracarbonyl was present and the dimer stopped being formed when norbornadiene chromium tetracarbonyl was absent.

Because norbornadiene chromium tetracarbonyl, when used as the reactant template, gives the same products as the other reactant

templates used, and because formation of dimers in the chromium hexacarbonyl appears to depend upon the presence of norbornadiene chromium tetracarbonyl it was decided to check if norbornadiene chromium tetracarbonyl was the common intermediate of all the reactions indicated by the products and percentage products experiments.

#### Isolation of Intermediates for Benzene, Toluene or Mesitylene

##### Chromium Tricarbonyl

Solutions of benzene, toluene and mesitylene chromium tricarbonyl in norbornadiene, 0.0143 M, were prepared and put into the photo reactor. Nitrogen was bubbled through the solutions for 12 hours. An infrared spectrum was then taken just before the irradiation, with a pyrex filter, was started and at half-hour intervals for three hours. A final infrared spectrum was taken after five and one-half hours of total irradiation time. The initial yellow solution turned red immediately after the irradiation was started.

From a comparison of the infrared spectra in the metal carbonyl region for the benzene, toluene and mesitylene chromium tricarbonyl reactions it was concluded that there were three different metal carbonyls present during the course of the reactions (Figure 28), and also that the three reactions were undergoing similar changes. The first metal carbonyl was the starting material, the second metal carbonyl was a red complex and was found in small amounts immediately after the irradiation was started. The third complex was not seen in the infrared spectrum until the solution had been irradiated for approximately 30 minutes.

The mesitylene chromium tricarbonyl reaction was repeated to determine what metal carbonyls formed after the irradiation was started. The solution was irradiated for 30 minutes, at which time the peak in the infrared spectrum due to mesitylene chromium tricarbonyl had vanished but the second metal carbonyl complex, the red complex, infrared bands were present (Figures 11, 12). The irradiation was continued and the peaks of a third metal carbonyl appeared (Figure 13). The irradiation was continued and after a total of three and one-half hours of irradiation the metal carbonyl bands were absent (Figure 14).

Another similar solution was irradiated as before for 30 minutes. The irradiation was stopped and half the solution was allowed to stand in the dark for 24 hours. An infrared spectrum was taken after six hours and the spectrum showed that the peaks due to mesitylene chromium tricarbonyl had reappeared and the infrared bands due to the red complex had decreased in intensity (Figure 15). An infrared spectrum was also taken after 24 hours, and comparison with the one taken at six hours (Figure 15) showed no further change had occurred. The second half of the reaction mixture was removed from the reaction vessel and taken rapidly to dryness in a roto evaporator. The water bath for the roto evaporator was kept at room temperature. The residue after the solvent was removed was a red-yellow solid. The red-yellow solid was put into a sublimator immediately and heated to  $35^{\circ}\text{C}$ . A yellow solid was collected on the sublimator cold finger and the red solid material remained behind. The red solid was heated to  $70^{\circ}\text{C}$  in the sublimator but it remained in the

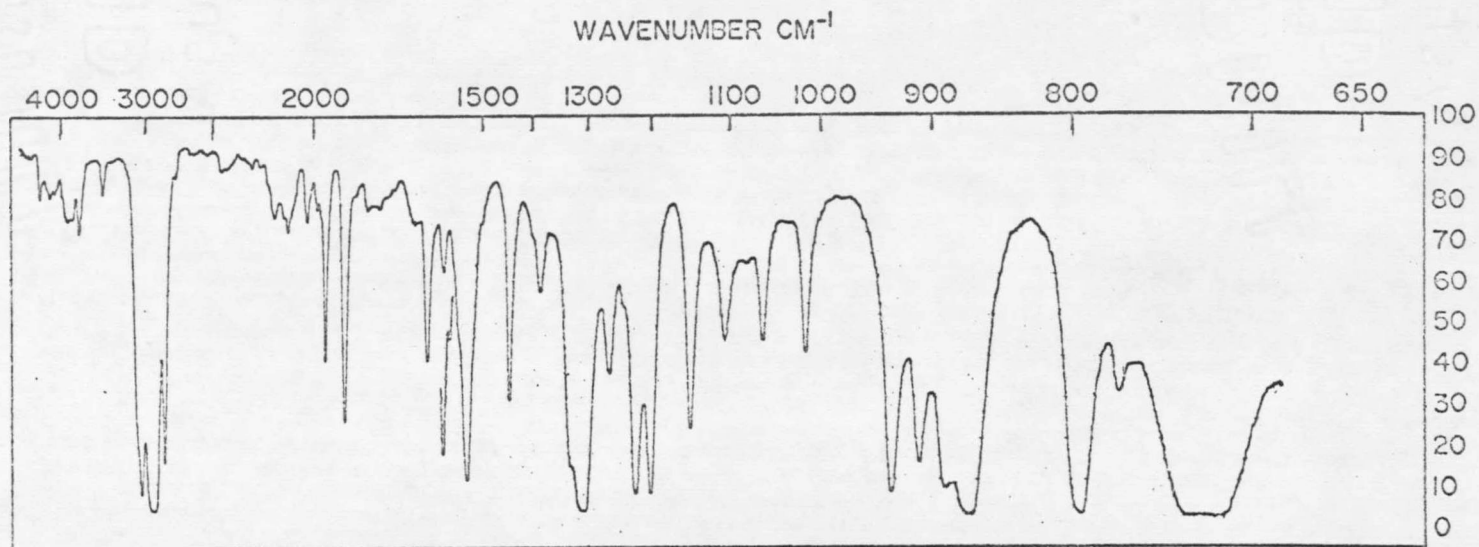


Fig. 11. 0 time of irradiation for mesitylene chromium tricarbonyl.

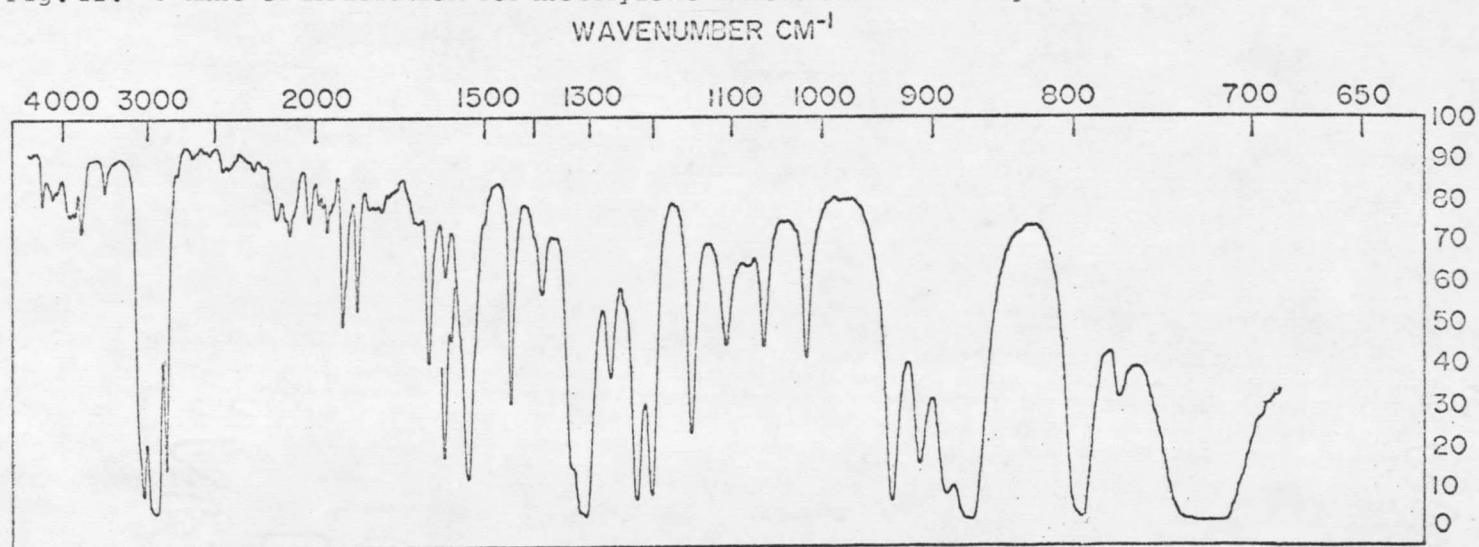


Fig. 12. 30 minutes of irradiation for mesitylene chromium tricarbonyl.

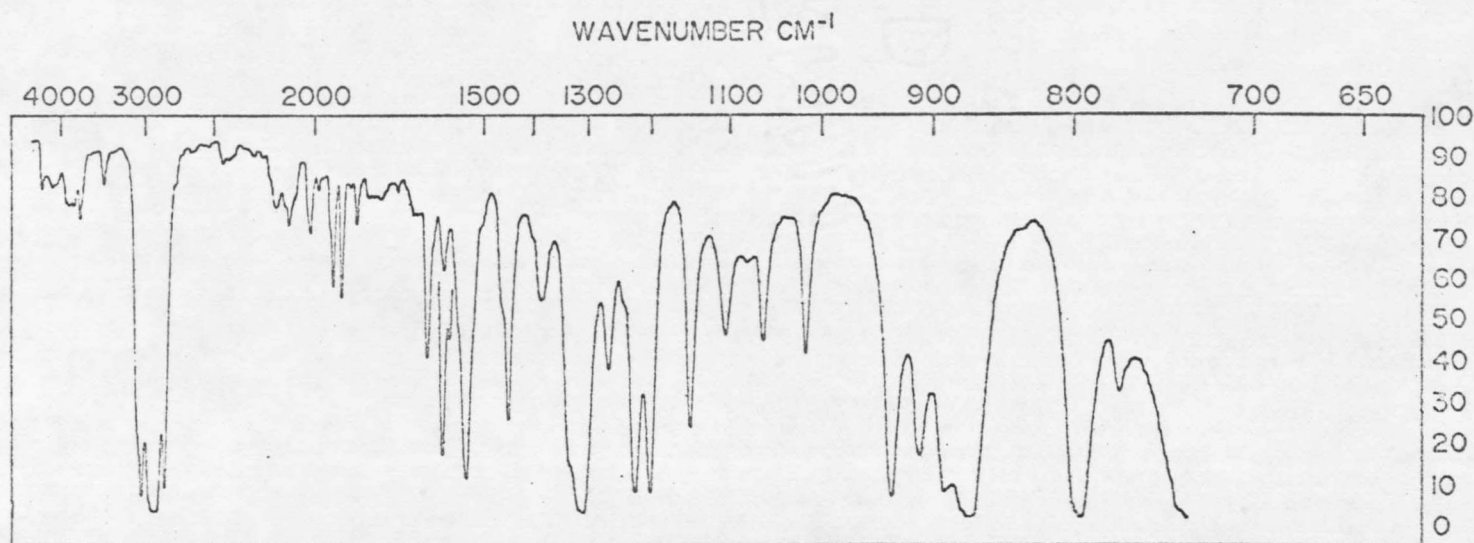


Fig. 13. 1 hour of irradiation for mesitylene chromium tricarbonyl.

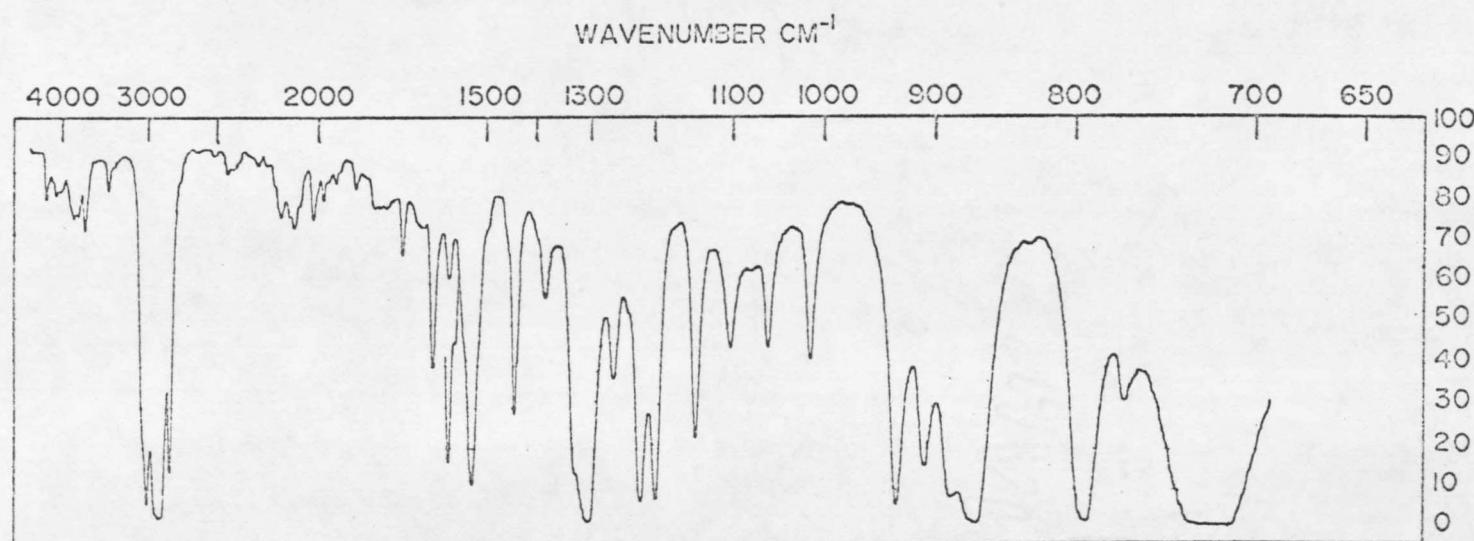


Fig. 14.  $3\frac{1}{2}$  hours of irradiation for mesitylene chromium tricarbonyl.

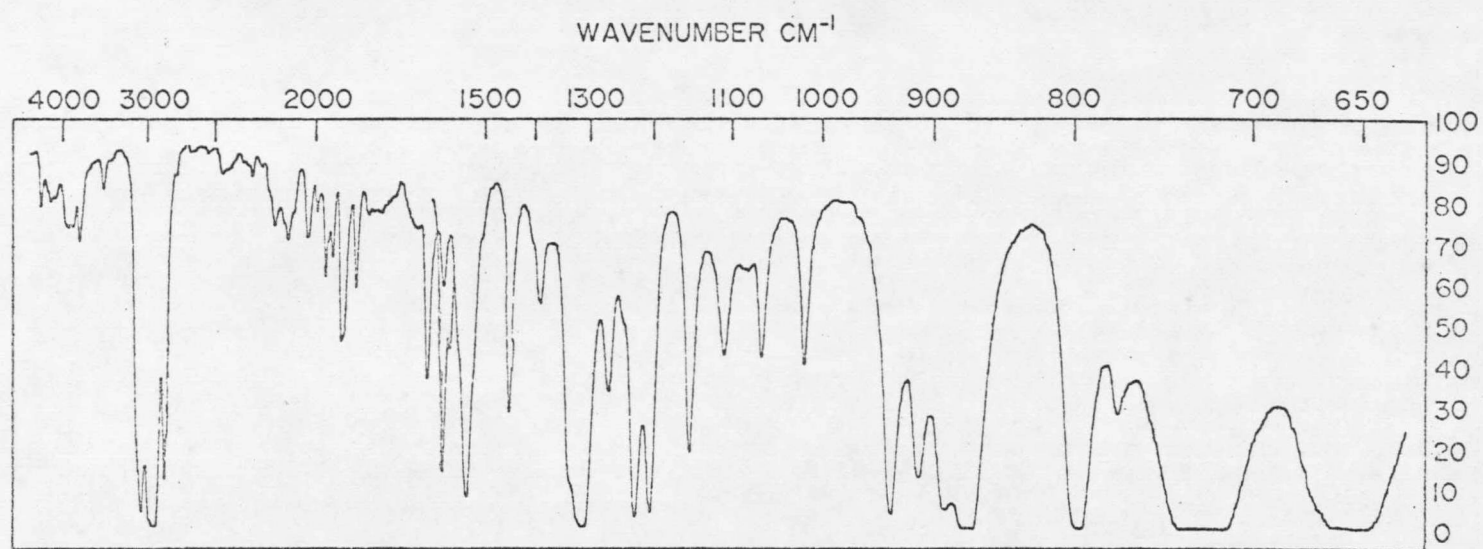


Fig. 15. 30 minutes of irradiation and then 6 hours in the dark for mesitylene chromium tricarbonyl.

bottom unchanged. An infrared spectrum, a mass spectrum (Figure 16) and a nuclear magnetic resonance spectrum were taken of the sublimed yellow solid material and all were identical to the corresponding spectra of an authentic sample of norbornadiene chromium tetracarbonyl. The infrared spectrum also was identical to the infrared spectrum of the third metal complex found in the reaction mixture.

The red complex (the residue from the sublimator) was very unstable and decomposed in the air and in solvents (such as hexane, petroleum ether, carbon tetrachloride, chloroform, N,N-dimethylformamide, dimethyl sulfoxide, benzene, ethanol and methanol) even when the air was replaced by deoxygenated nitrogen. An infrared spectrum of the red solid was taken using potassium bromide (Figure 17) and this showed the red material was a metal carbonyl complex and identical to the second metal carbonyl complex, the red complex, in the reaction of mesitylene chromium tricarbonyl. Because of its instability in solvents, a nuclear magnetic resonance spectrum was not possible so a mass spectrum was taken (Figure 18). The mass spectrum had a parent peak of 348 atomic mass units, which is correct for a complex containing mesitylene, norbornadiene and three carbonyls.

The next major peak below 348 is 256, which can be assigned to either norbornadiene chromium tetracarbonyl or mesitylene chromium tricarbonyl. The mass spectrum of the red complex does not have a significant peak at 228, in contrast to the mass spectrum of norbornadiene chromium tetracarbonyl. The mass spectrum of the red complex has large

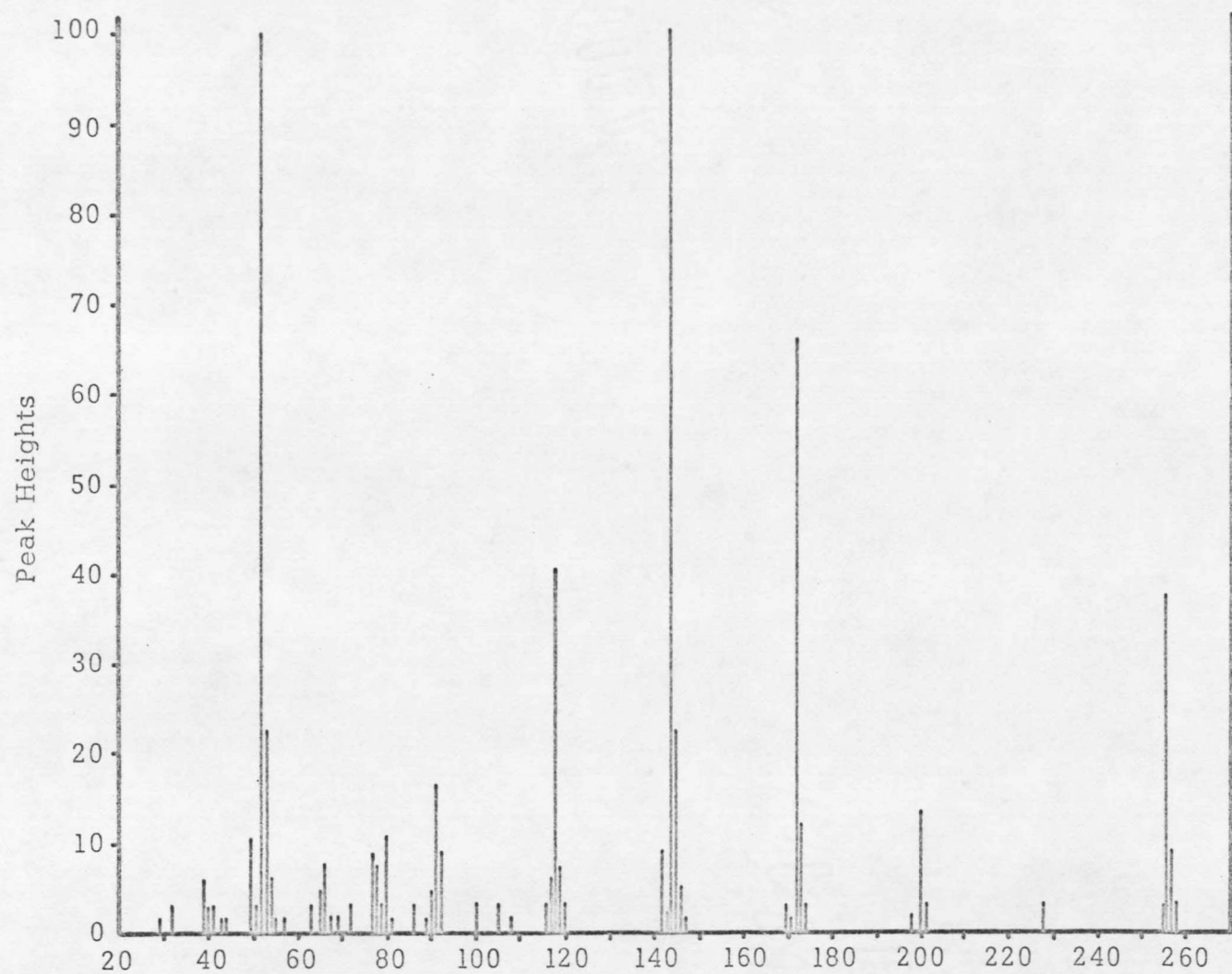


Fig. 16. Mass spectrum of norbornadiene chromium tetracarbonyl.

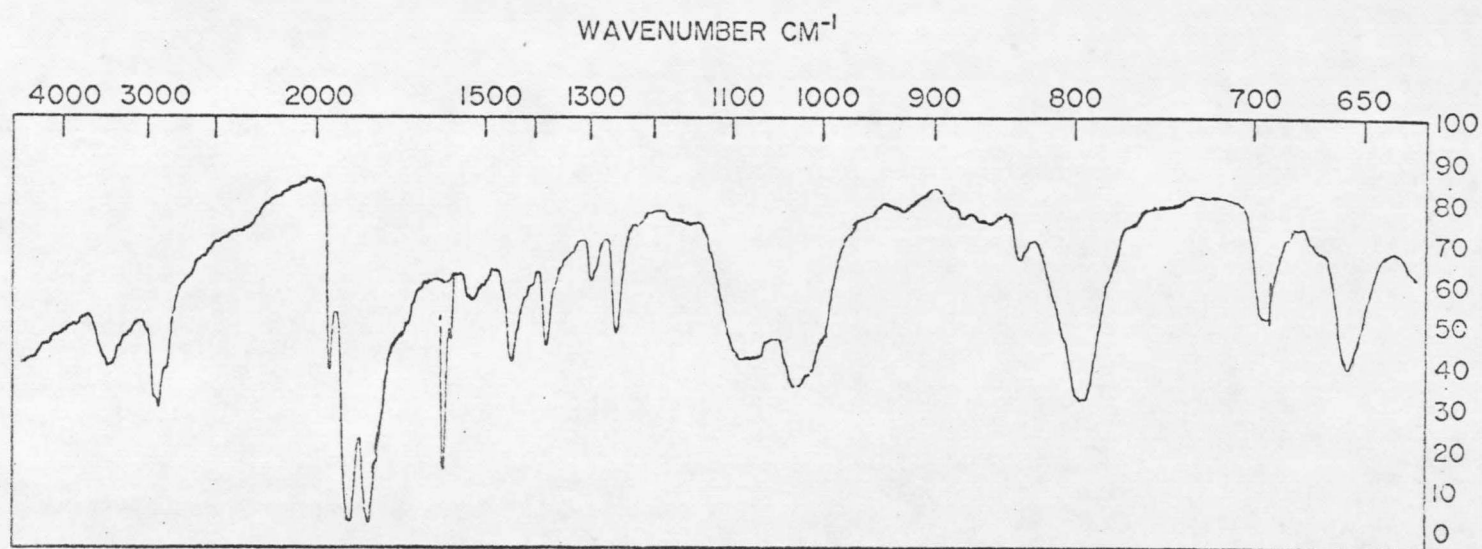


Fig. 17. Infrared spectrum of red complex.

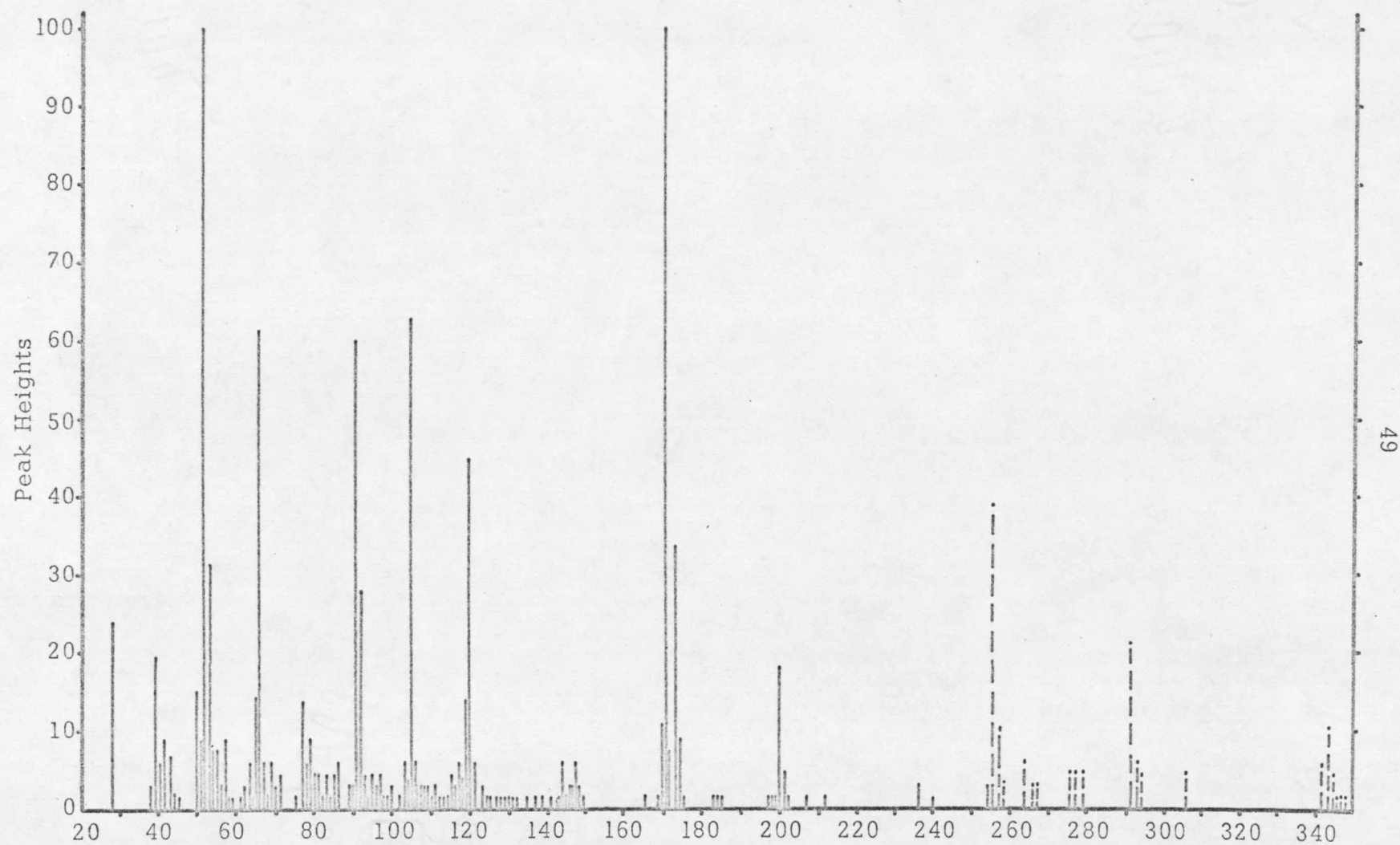
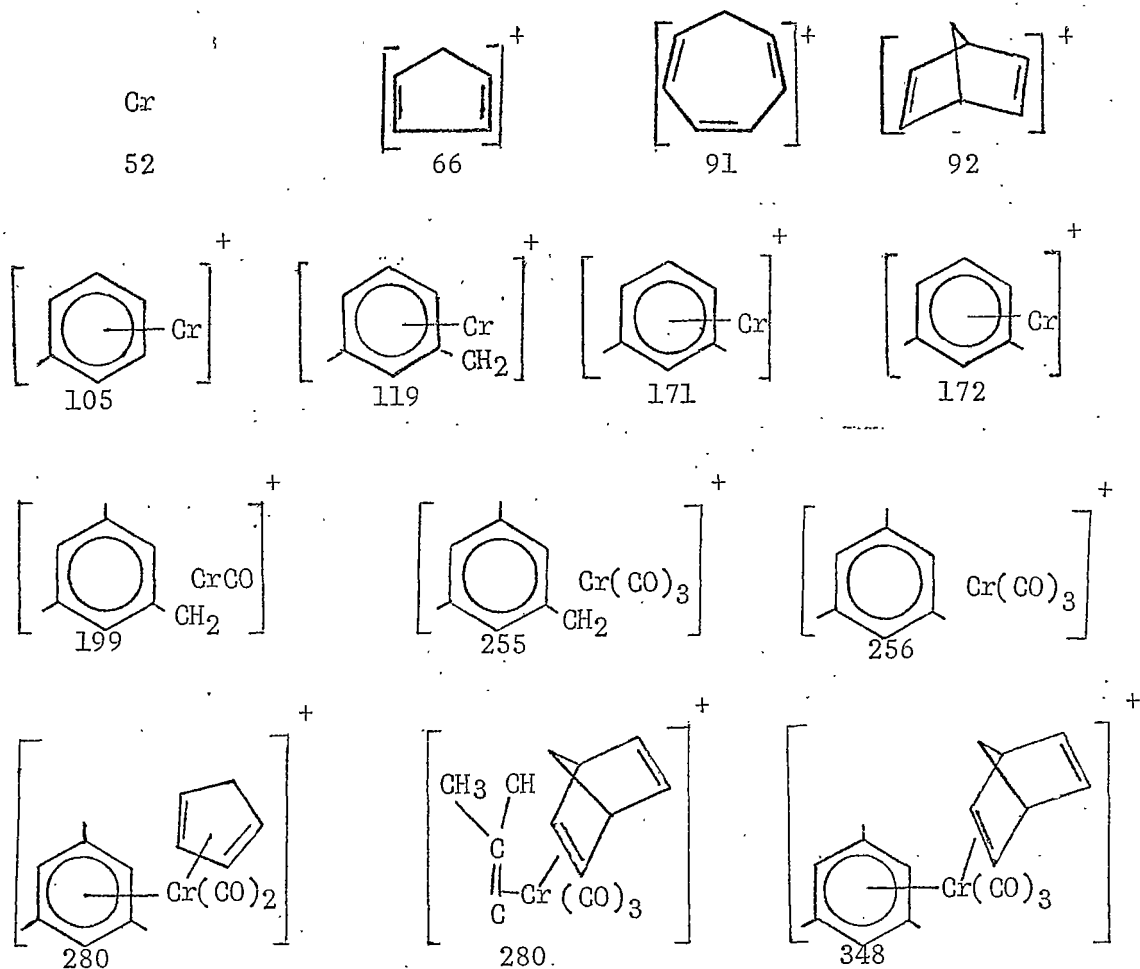


Fig. 18. Mass spectrum of red complex.

peaks at 105, 119, 171, 172 (Table VI) which are not present as large peaks in the mass spectrum of norbornadiene. Thus the 256 peak is assigned to mesitylene chromium tricarbonyl. A final point about the mass spectrum of the red complex is demonstrated in the peaks which contain a mesitylene group. From the peak height it is evident that the

Table VI

Peak Assignments for the Mass Spectrum of the Red Complex



larger peaks contain a mesitylene which has lost one hydrogen and formed possibly a dimethyl tropylium ion. This would correspond to the benzyl ion losing a hydrogen to form the tropylium ion, which it does because of increased resonance stability of the tropylium ion as compared to the benzyl ion. To check the thermal stability of the red complex a reaction was run and the red complex isolated, keeping the temperature below 35°C. Mass spectra were then taken of the sample at 20°C, 25°C, 50°C, 70°C, 90°C, 115°C, and the red complex showed no thermal decomposition.

Both benzene and toluene chromium tricarbonyl also formed a red complex and had infrared spectra changes similar to the mesitylene chromium tricarbonyl reaction (Figures 19-26).

The infrared spectra of the benzene, toluene and mesitylene chromium tricarbonyl reactions demonstrates the presence of norbornadiene chromium tetracarbonyl in all cases. In addition, the fact that the mesitylene chromium tricarbonyl infrared bands are completely gone in 30 minutes but reappear upon standing in the dark indicates there must be an intermediate found on the path of the reaction of the mesitylene chromium tricarbonyl going to norbornadiene chromium tetracarbonyl. This is so since norbornadiene chromium tetracarbonyl will not revert back to mesitylene chromium tricarbonyl in the presence of the mesitylene, as is indicated by the constant intensity of the infrared band due to norbornadiene chromium tetracarbonyl when mesitylene is present. The intermediate that reverts back to the starting material is proposed to

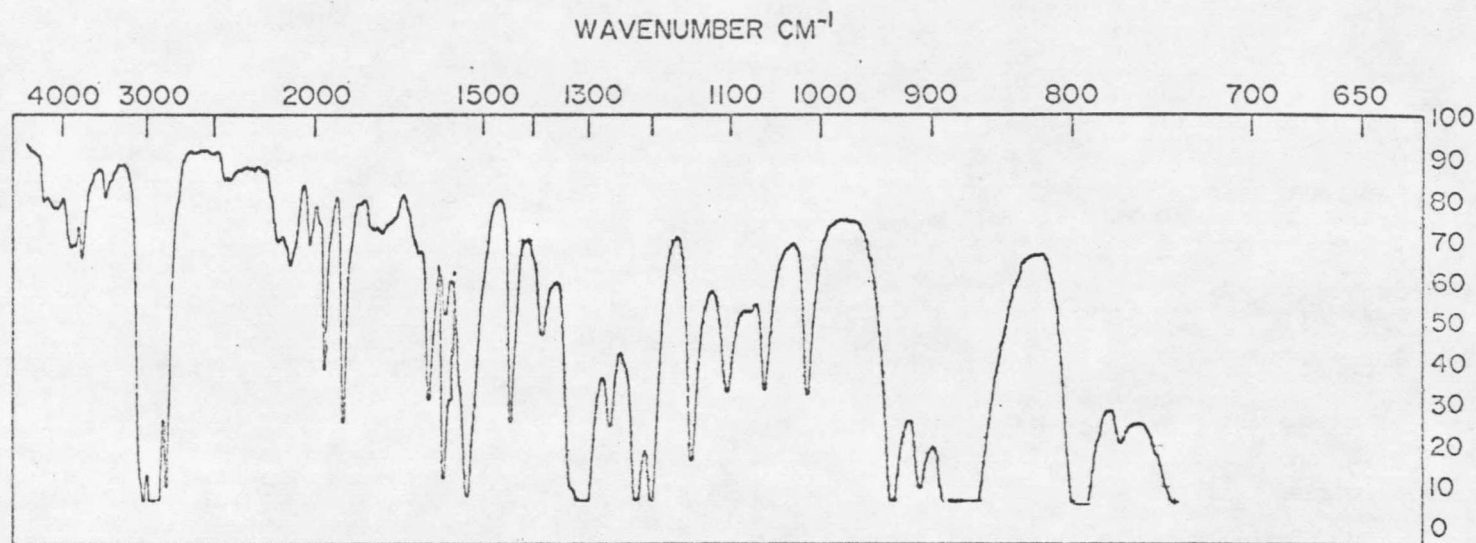


Fig. 19. 0 time of irradiation for benzene chromium tricarbonyl.

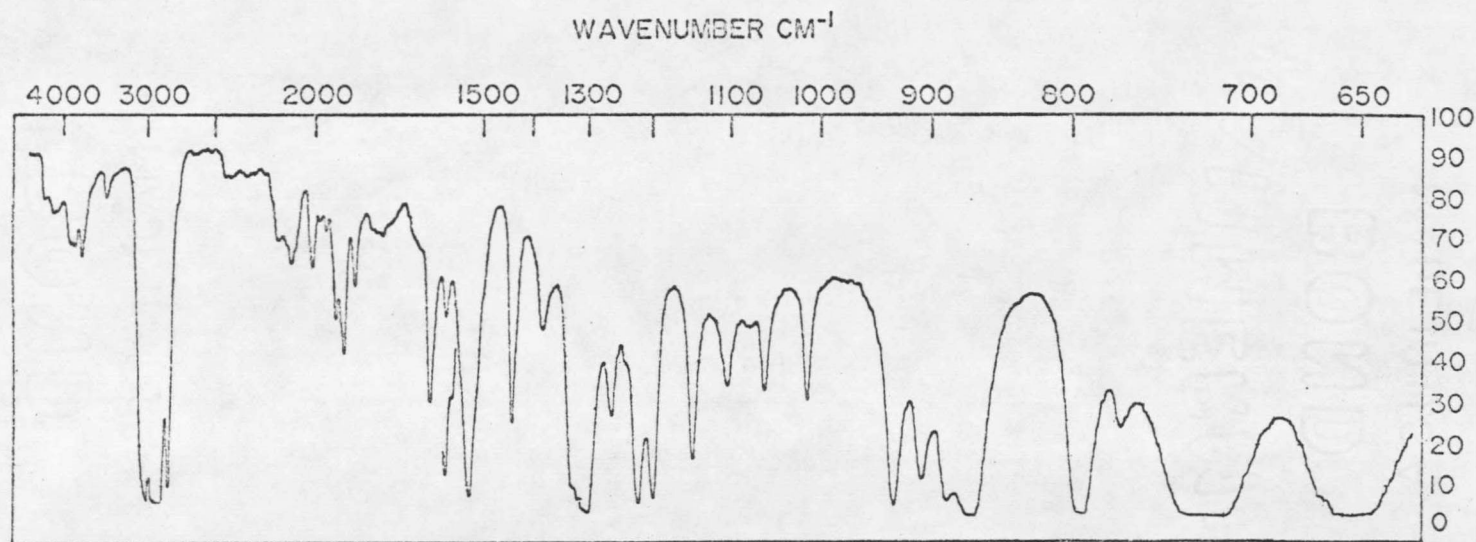


Fig. 20. 30 minutes of irradiation for benzene chromium tricarbonyl

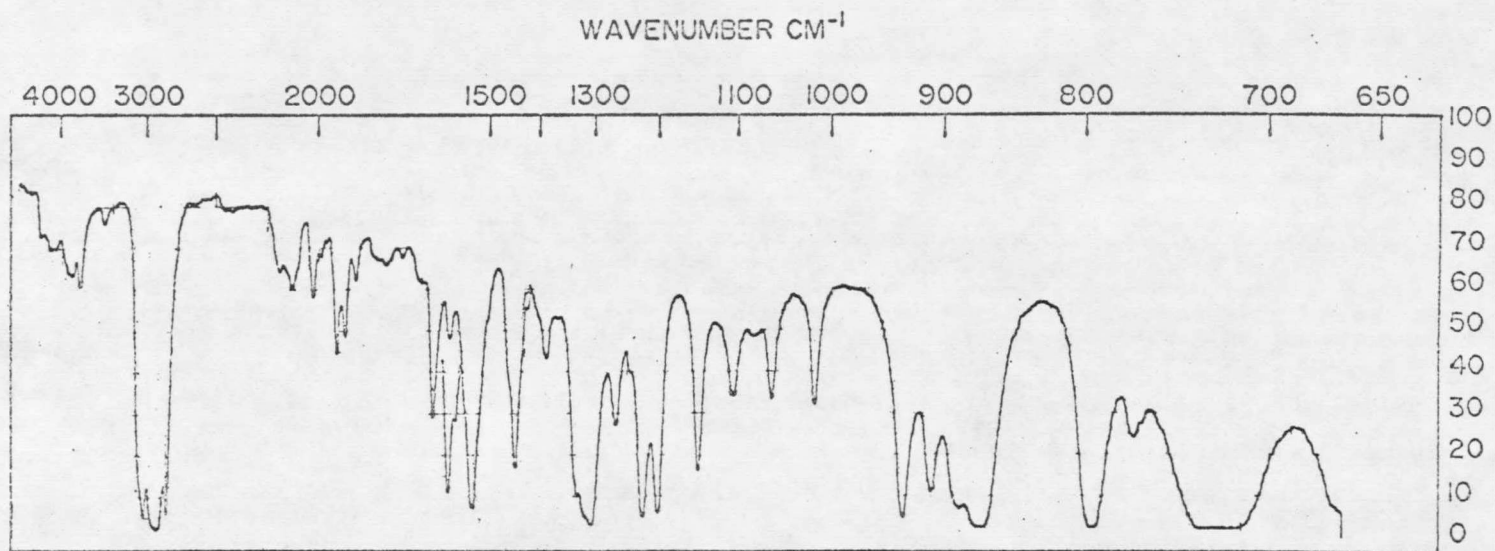


Fig. 21. 1 hour of irradiation for benzene chromium tricarbonyl.

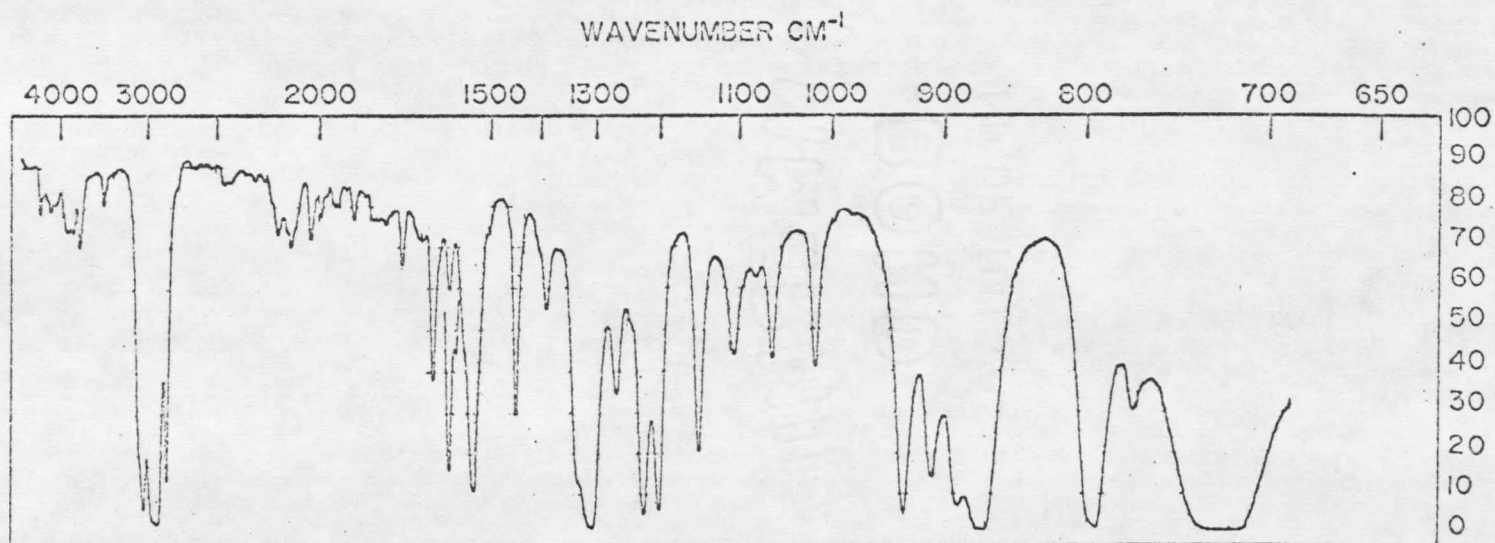


Fig. 22. 3 1/2 hours of irradiation for benzene chromium tricarbonyl.

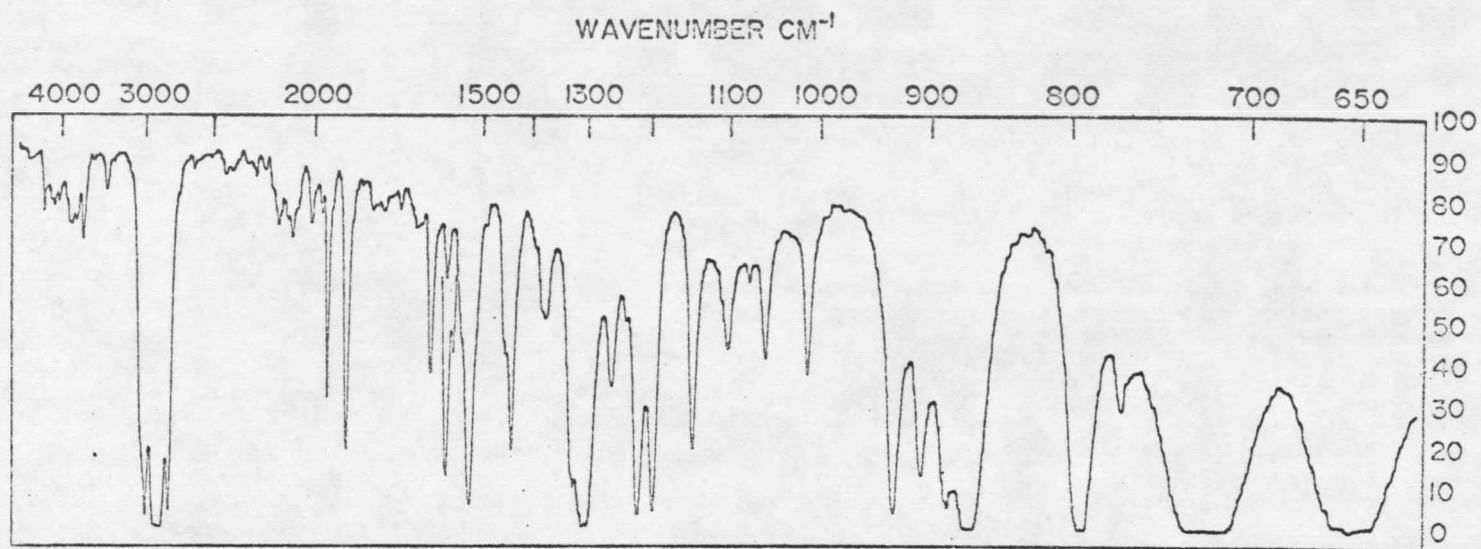


Fig. 23. 0 time of irradiation for toluene chromium tricarbonyl.

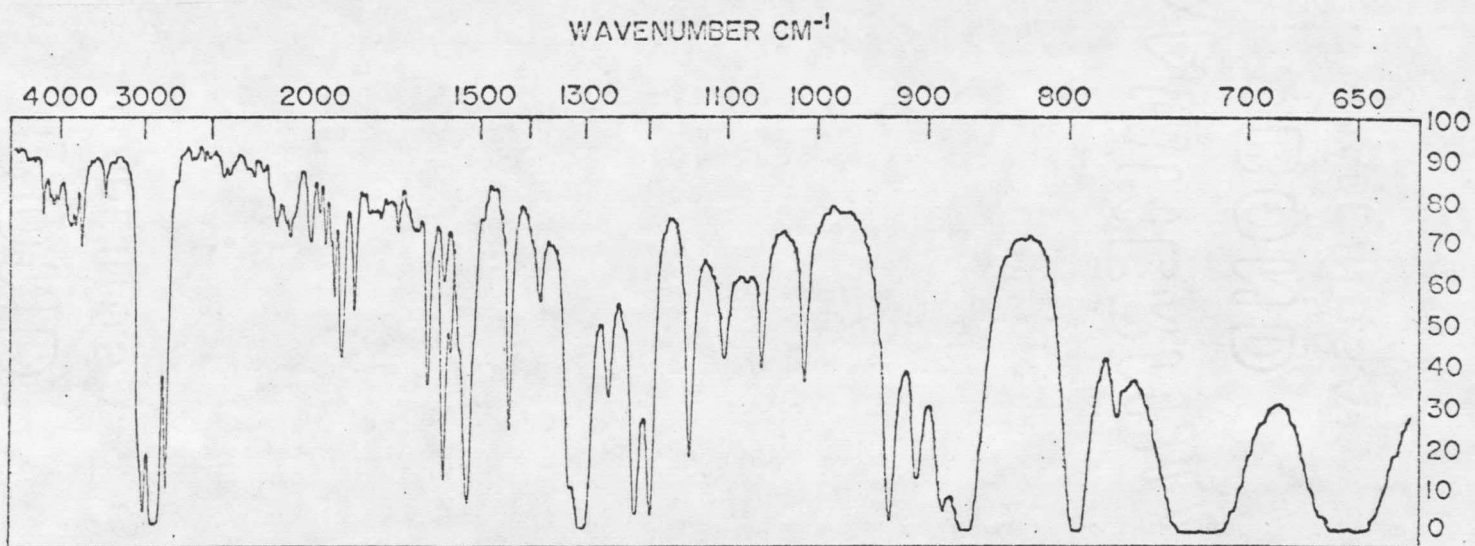


Fig. 24. 30 minutes of irradiation for toluene chromium tricarbonyl.

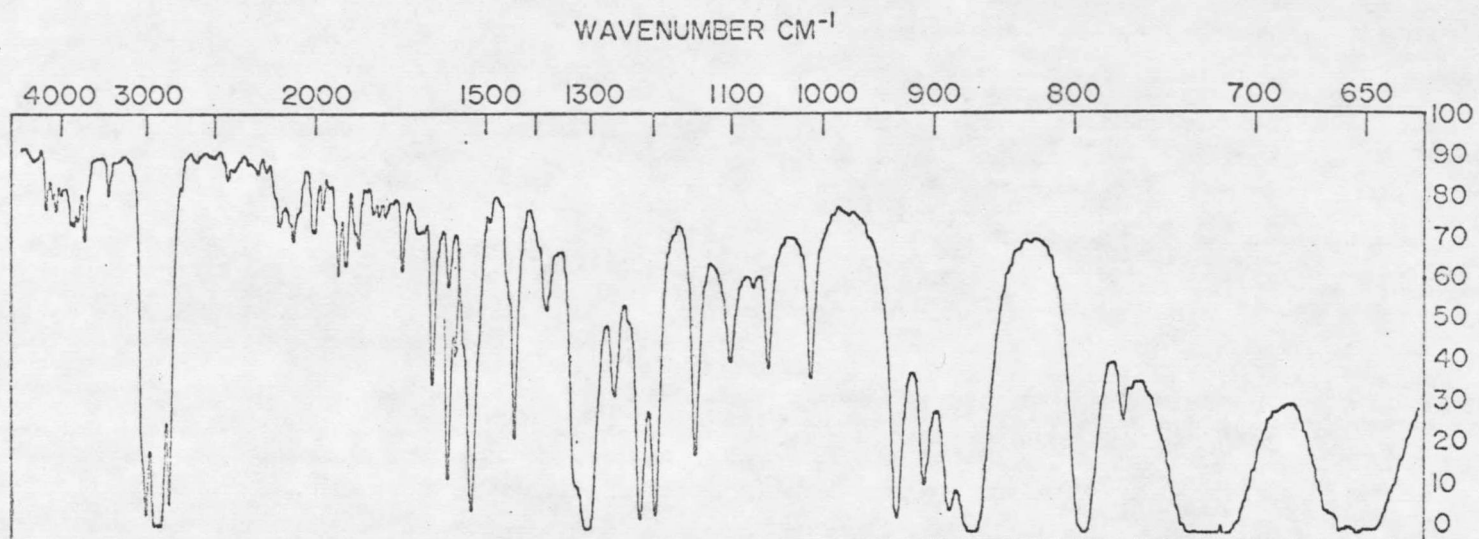


Fig. 25. 1 hour of irradiation for toluene chromium tricarbonyl.

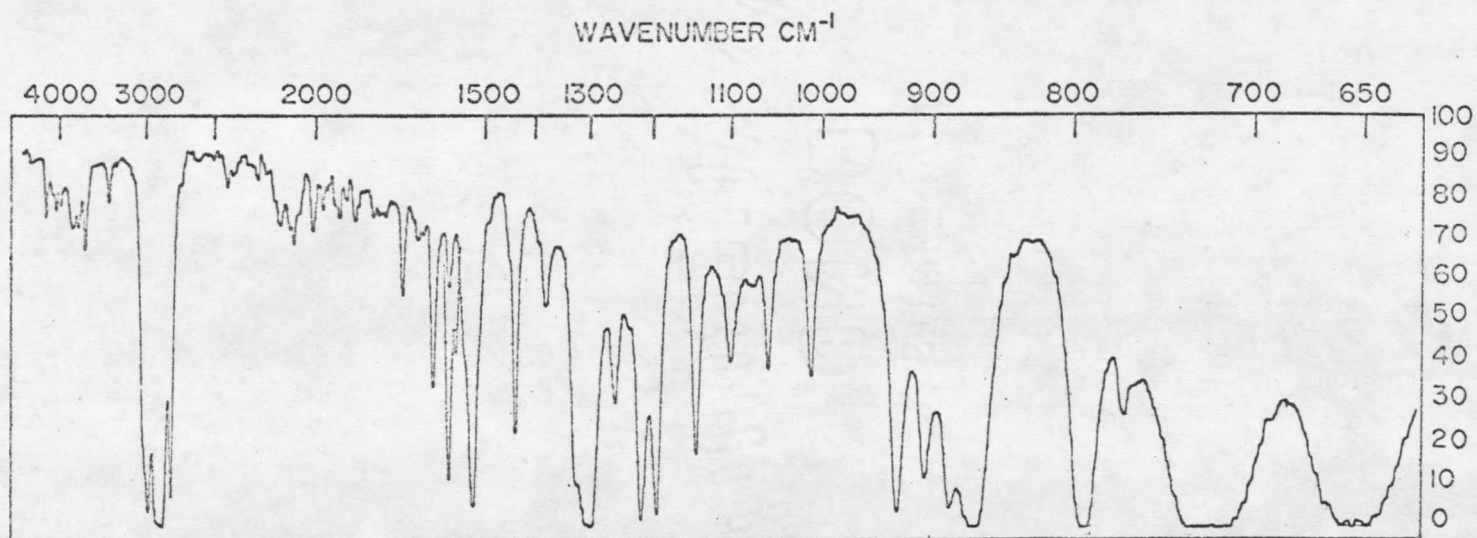


Fig. 26. 3 1/2 hours of irradiation for toluene chromium tricarbonyl.

be the red complex. The intermediate contains either benzene, toluene or mesitylene and norbornadiene chromium tricarbonyl.

#### Other Investigations

In the case of the chromium reaction with norbornadiene, the last traces of norbornadiene chromium tetracarbonyl are not gone from the infrared spectrum until a total reaction time of six hours. In the case of benzene, toluene or mesitylene, the last indications of norbornadiene chromium tetracarbonyl are gone in three and one-half hours. Taken by itself this would indicate that chromium hexacarbonyl reacts slower than benzene, toluene or mesitylene chromium tricarbonyl. However, each chromium hexacarbonyl can form one norbornadiene chromium tetracarbonyl, but this one-to-one ratio is not possible for the benzene, toluene and mesitylene chromium tricarbonyl since they must gain a carbonyl which must come from the decomposition of the starting material. Thus there is less chromium tetracarbonyl formed in the arene chromium tricarbonyls if equal molar solutions are used in each case as they were in these experiments. To check the times of the reactions more carefully a time study was carried out.

For the time study the procedure was to make a 70-ml solution of the metal carbonyl in norbornadiene. Nitrogen was bubbled through the solution for 12 hours and the sample irradiated using a corex filter. A sample was removed just before the irradiation was started and at one-hour intervals thereafter until no change appeared to be occurring by the

gas chromatographic analysis, after which time samples were removed at longer intervals.

A plot showing the time versus hydrocarbon dimer products found as determined solely by peak height indicates the mesitylene chromium tricarbonyl does react faster than chromium hexacarbonyl (Figures 27, 28). Equally as important, the data indicate an induction period, and thus suggest that the actual reactant template for the dimerization is formed after the sample has been irradiated. The idea of an induction period is supported by the Beer's Law and infrared spectra studies described below.

In the Beer's Law experiment the ultraviolet spectrum of chromium hexacarbonyl in a 1:100 solution of norbornadiene and cyclohexane was compared with the ultraviolet spectrum of a saturated solution of chromium hexacarbonyl in hexane. The object was to see if there were any changes in the absorption spectrum of chromium hexacarbonyl that would indicate there was a bond between the chromium hexacarbonyl and the norbornadiene prior to irradiation. From comparison of the ultraviolet spectra, it was concluded that norbornadiene and chromium hexacarbonyl either did not form a ground state complex or formed a complex in very low concentration.

Another experiment used to show there was no ground state complex was an infrared spectrum study. In this study two solutions of norbornadiene and chromium hexacarbonyl were compared to the infrared spectrum of chromium hexacarbonyl in carbon tetrachloride and an

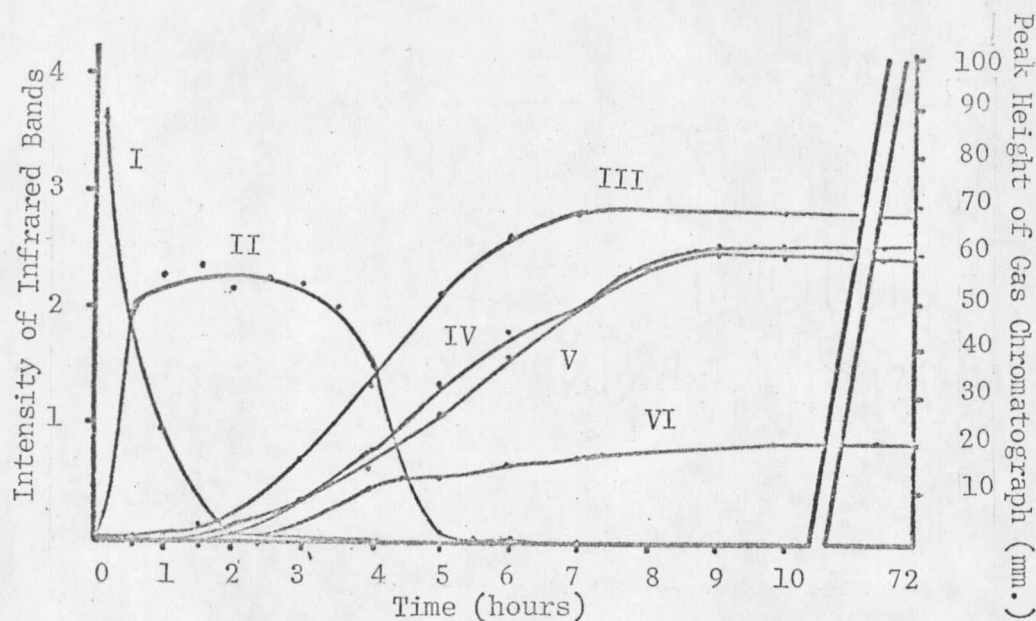


Fig. 27. Plot of peak heights of products versus time and plot of infrared bands intensity of the metal carbonyls versus time: I) chromium hexacarbonyl, II) norbornadiene chromium tetracarbonyl, III) exo trans exo dimer, IV) endo trans endo dimer, V) exo trans endo dimer, VI) cage dimer.

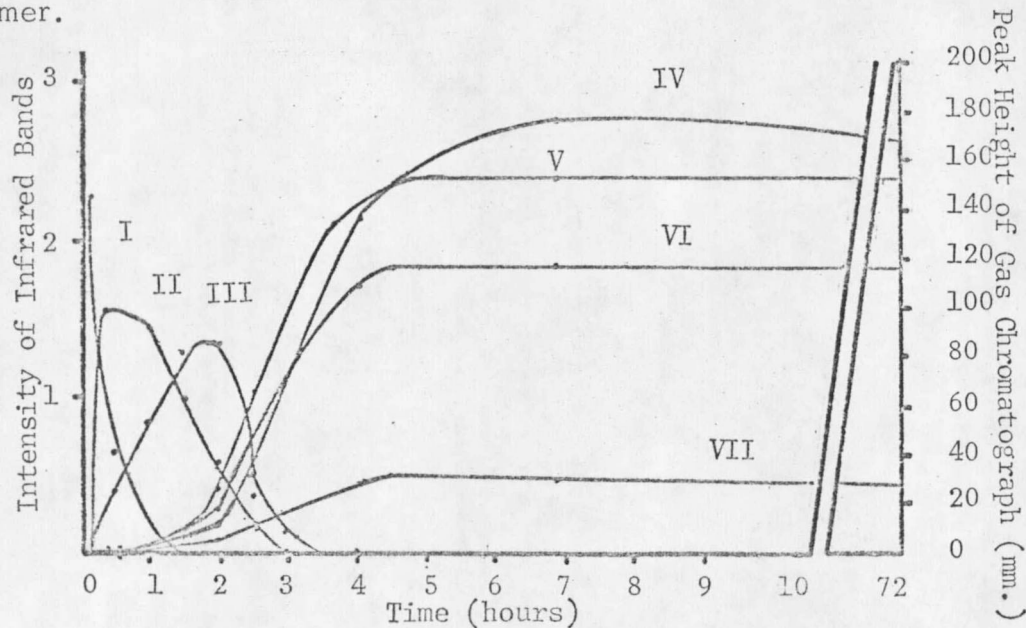


Fig. 28. Plot of peak heights of products versus time and plot of infrared bands intensity of the metal carbonyls versus time: I) mesitylene chromium tricarbonyl, II) red complex, III) norbornadiene chromium tetracarbonyl, IV) exo trans exo, V) endo trans endo, VI) exo trans endo, VII) cage dimer.

infrared spectrum of pure norbornadiene. The reason for the comparison was to see if there was any shift of the chromium hexacarbonyl bond due to bonding with norbornadiene. A comparison showed no shift and it was concluded that there was no bonding between norbornadiene and chromium hexacarbonyl in the ground state or if there was any it was in very low concentrations.

Furthermore, to examine the thermal reaction a solution of norbornadiene and chromium hexacarbonyl was heated to various temperatures ( $57^{\circ}\text{C}$ ,  $83^{\circ}\text{C}$ ,  $89^{\circ}\text{C}$ ) for 24 hours at each temperature. The solutions were analyzed by gas chromatography at 24-hour intervals to see if there was a thermal reaction from a ground state complex. The gas chromatogram did not show any dimers over the 3-day period and the infrared peak of chromium hexacarbonyl at  $1988\text{ cm}^{-1}$  indicates all the starting material was recovered.

Another point demonstrated by the time study was the necessity of the presence of a metal carbonyl. This is shown by the curve becoming a horizontal line, indicating no increase in dimer products at a time corresponding to the disappearance of the metal carbonyl bonds in the infrared spectrum (Figures 27, 28).

To substantiate the idea of the necessity of the presence of a metal carbonyl, norbornadiene was irradiated with  $>280\text{ m}\mu$  light and also with light of  $<280\text{ m}\mu$  and no hydrocarbon dimer products were detected by the gas chromatograph.

## CONCLUSION

Thus far the interpretation of the data has indicated the presence of a common intermediate which is formed after the solution has been irradiated. This common intermediate is proposed to be norbornadiene chromium tetracarbonyl since this is the only metal carbonyl isolated from all the reactions where products are formed. In addition, the appearance of the dimer corresponds to the appearance of norbornadiene chromium tetracarbonyl and when norbornadiene chromium tetracarbonyl is absent no dimer products are formed.

It is necessary at this point to digress for a moment to discuss how the norbornadiene could be attached to the chromium in the dimerization reaction. There are several possibilities. It can either be bonded exo or endo when it is a single bond and must be endo when both bonds are bonded to the same metal (Figure 29).

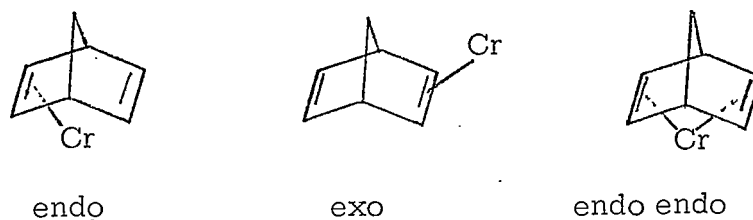


Fig. 29. Possible ways for chromium to bond to norbornadiene.

Electrophilic attack on the norbornadiene is usually exo (60) and in the silver complex,  $C_7H_8(AgNO_3)_2$  (30), the silver has been shown by X-ray crystal structure to exist on the exo side. Thus it would seem that the exo side is the preferred side.

If the norbornadiene should bond only *exo* to chromium it is difficult to rationalize how norbornadiene chromium tetracarbonyl could exist since all the norbornadiene chromium bonds are *endo* to norbornadiene. On the other hand, if norbornadiene would bond only *endo* to chromium it would be difficult to rationalize how the *exo trans endo* dimer is formed, especially since the *exo trans endo* dimer is found in large amounts in all the chromium cases. Another possibility is that neither of the norbornadienes is bonded to the metal when the dimerization occurs, but this is tentatively excluded because the products vary with different metals. Thus if the only purpose of the metal was to excite a non-attached norbornadiene, all the cases where norbornadiene was excited, the norbornadiene would be similar and one could expect identical products but, as already stated, the products do vary with different metals.

Another possibility is that only one norbornadiene is bonded to the metal with only one double bond and the dimerization may then occur between the double bond not attached to the metal and a norbornadiene from the solution. This idea has been proposed (51) and is currently under investigation. In the case of chromium carbonyls, it is difficult to see how this single bonded norbornadiene mechanism is occurring since it would be necessary to form norbornadiene chromium tetracarbonyl (isolated) and then have this norbornadiene chromium tetracarbonyl revert back to norbornadiene chromium pentacarbonyl before the reaction would go to products.

One remaining possibility is that both norbornadienes are attached to the metal and they can be attached either *exo* or *endo* and can change from *exo* to *endo* or from *endo* to *exo*. The validity of this statement is shown by the following case. A reaction of neat norbornadiene with norbornadiene chromium tetracarbonyl and the reaction with the various metal carbonyls yield identical products and in similar ratios. Thus, unless it is proposed that the norbornadiene came off completely and two other norbornadienes replace it and went on only *exo*, at least one of the norbornadienes attached to the chromium will be bonded *endo* since this norbornadiene came from the *endo* bonded norbornadiene chromium tetracarbonyl.

But the reaction yielded the *exo trans exo* dimer in the largest yield, which indicates that both the norbornadienes were *exo* bonded to the chromium. Thus we must conclude either the *exo trans exo* can be formed from two norbornadienes, one of which must be bonded *endo*, or that there is some type of mechanism that allows the norbornadiene which is bonded to the chromium to change from *endo* to *exo*. Another point favoring the mechanism of having both the norbornadienes bonded to the chromium is that the metal orbital can be used to lower the symmetry restrictions and the activation energy (46, 47, 48).

The author has chosen to interpret the data using the last possibility and the mechanistic consequences are discussed below.

In the case of chromium hexacarbonyl, the formation of norbornadiene chromium tetracarbonyl is proposed to be formed by the reaction sequence shown in Figure 31.

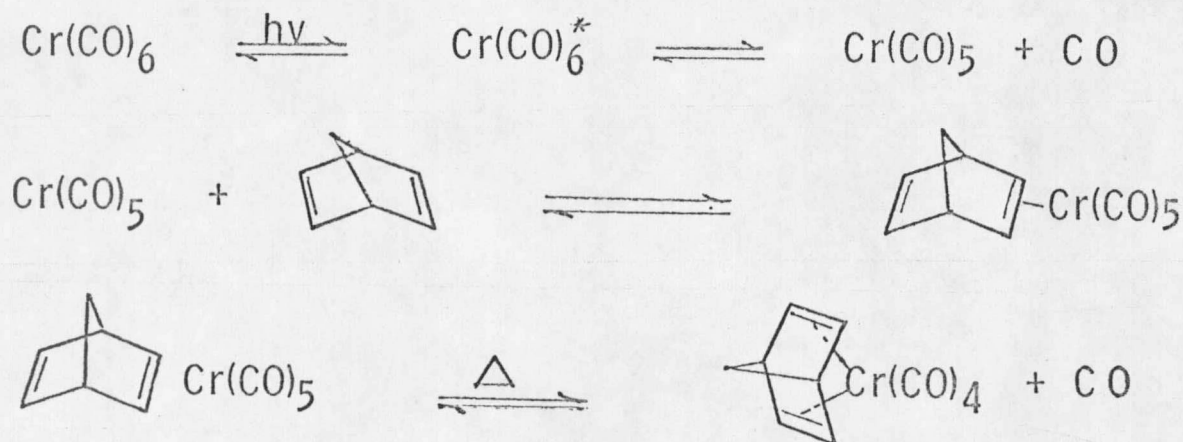


Fig. 30. Formation of norbornadiene chromium tetracarbonyl from chromium hexacarbonyl.

The photochemical reaction of chromium hexacarbonyl going to chromium pentacarbonyl is well known and the reverse process has been shown to occur when the irradiation is stopped. In the experiment demonstrating this, the only carbon monoxide present was what was given up by the chromium hexacarbonyl (61, 62). Chromium pentacarbonyl is reported to have the characteristics of an electron deficient molecule and will thus bond to many molecules which will donate electrons to this electron deficient system (61, 62). Since all the reactions are run in neat norbornadiene, which is known to be able to donate its pi electrons to metal species (Table I), it is reasonable that norbornadiene will act as an electron donor and norbornadiene chromium pentacarbonyl will be formed.

The second pi bond of the attached norbornadiene will then displace another carbonyl (45) and the stable norbornadiene chromium tetracarbonyl will be formed. This displacement of a carbonyl by a double bond is shown to occur generally in metal carbonyls (45). The fact that norbornadiene chromium tetracarbonyl can be formed thermally from chromium pentacarbonyl as in the last reaction step is demonstrated by the reaction of N-pyridine chromium pentacarbonyl. When N-pyridine chromium pentacarbonyl is heated to reflux with norbornadiene and methyl iodide in tetrahydrofuran the products are norbornadiene chromium tetracarbonyl and N-methyl pyridinium iodide salt. Even in the case of di-N-dipyridine chromium tetracarbonyl, run under similar conditions, the only products of this reaction are norbornadiene chromium tetracarbonyl and N-methyl pyridinium iodide.

In the benzene, toluene and mesitylene chromium tricarbonyl reactions the infrared spectra and mass spectra indicate what the intermediate is prior to the formation of norbornadiene chromium tetracarbonyl and the proposed mechanism is shown in Figure 31. Light is absorbed and a benzene ring to chromium metal bond is broken. Again we have an electron-deficient metal carbonyl in neat norbornadiene. The norbornadiene donates its pi electron from one double bond, forming norbornadiene benzene chromium tricarbonyl, which is then isolated as the red complex. The red complex is tentatively assigned this structure instead of the structure where the norbornadiene is doubly bonded and the benzene ring singly bonded because the mass spectrum indicates that most of the

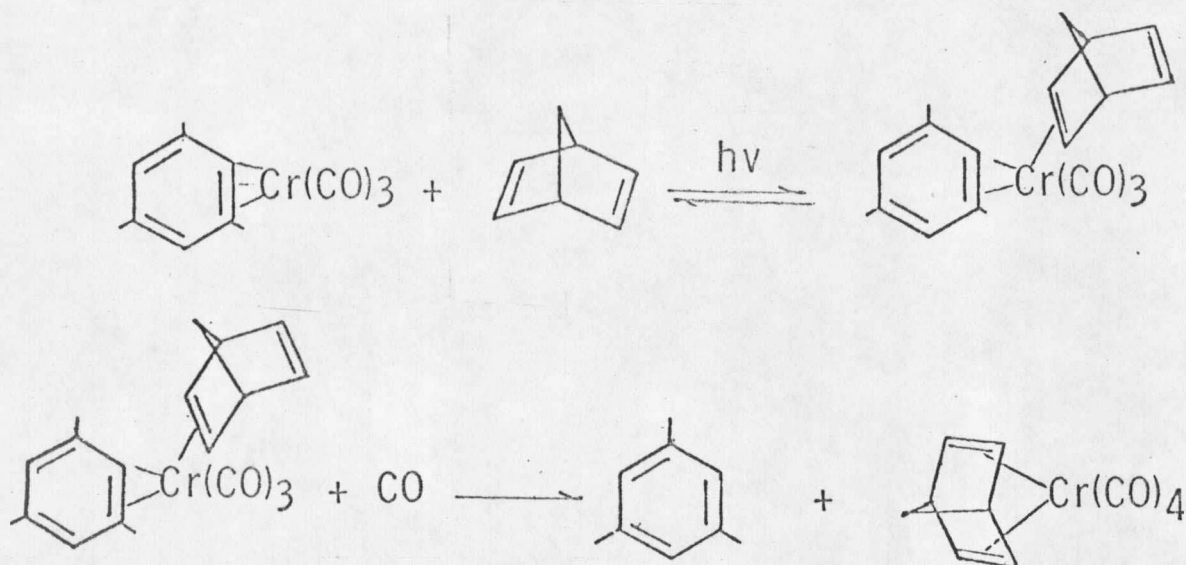


Fig. 31. Formation of norbornadiene chromium tetracarbonyl from arene chromium tricarbonyl.

larger peaks contain the benzene ring, indicating it is held better than the norbornadiene. This molecule would then, when irradiated, change to having the norbornadiene doubly bonded and the benzene ring singly bonded. The benzene ring could then come off and the norbornadiene chromium tricarbonyl remaining will form norbornadiene chromium tetracarbonyl by picking up a carbonyl from the solution. Carbon monoxide is soluble in water to 2.3 volumes per 100 ml of water (63), which is approximately 0.001  $\text{M}$ . It is appreciably more soluble in organic solvents (63). This carbonyl, which is picked from the solution, can come from the decomposition of starting material and also from the metal carbonyl left after dimers are formed. The norbornadiene chromium tricarbonyl could also form dinorbornadiene chromium tricarbonyl if the

norbornadiene chromium tricarbonyl picked another norbornadiene molecule from the solution instead of a carbonyl.

Because the norbornadiene is present in such large amounts it would seem reasonable that the norbornadiene chromium tricarbonyl would bond with norbornadiene instead of the carbon monoxide, but the results indicate norbornadiene chromium tetracarbonyl is formed. One possible explanation is that since carbonyl is much smaller sterically it is favored. In addition, if norbornadiene does attach itself to the norbornadiene chromium tricarbonyl the result is a stable molecule, norbornadiene chromium tetracarbonyl, whereas if a norbornadiene attaches itself to norbornadiene chromium tricarbonyl the product, dinorbornadiene chromium tricarbonyl, has not been isolated and is only postulated as a transient intermediate.

Once the stable norbornadiene chromium tetracarbonyl is formed, light must be absorbed to cause the reaction to continue. That irradiation is necessary is shown by the thermal reaction of norbornadiene chromium tetracarbonyl in neat norbornadiene at 65°C for 12 hours, which does not give any dimer product, and the starting material can be recovered from the solution. Thus it is proposed that absorption of light causes the chromium to lose another carbonyl and form a transient dinorbornadiene chromium tricarbonyl, or the absorption of light will break a norbornadiene chromium bond, resulting in the formation of a dinorbornadiene chromium tetracarbonyl which will act as a transient intermediate.

In the latter case (Figure 32), using dinorbornadiene chromium tetracarbonyl, the two norbornadienes would be situated so as to give as products V, VI and VII similar to the products from the thermal reaction of iron dicarbonyl, dinitrosyl and norbornadiene (45). These products are visualized as being formed when the  $2p\pi$  orbitals of norbornadiene are mixed with the chromium d orbitals. Once this mixing has occurred the thermal restriction rules proposed by Woodward and Hoffman no longer apply (46, 47, 48), and the dimerization will proceed to product thermally. The metal thus has a dual role of removing the symmetry restriction and lowering the activation energy (46, 47, 48). It should be pointed out here that in the thermal dimerization of norbornadiene using metal carbonyls it is postulated (45) that one pi bond from each norbornadiene is formally involved, but it has also been suggested that the second pi bond of the norbornadiene also contributes to the transition state (45). A photochemical reaction using chromium hexacarbonyl and norbornene dissolved

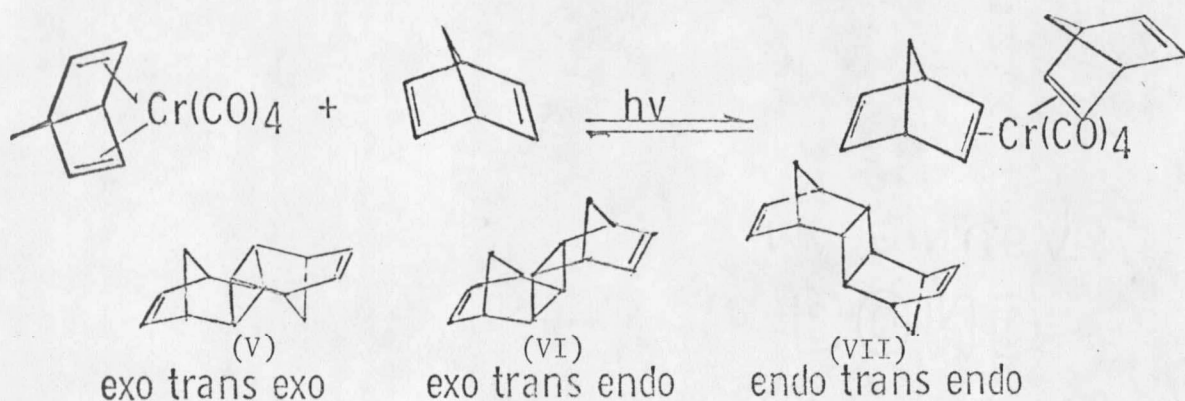


Fig. 32. Formation of dimers using dinorbornadiene chromium tetracarbonyl.

in hexane was run and no dimer products were detected in the gas chromatogram, indicating the second bond is necessary either to form the norbornadiene chromium tetracarbonyl or in formation of the first bond of norbornadiene to the metal carbonyl.

In the former case, where a carbonyl is lost and replaced by a norbornadiene forming dinorbornadiene chromium tricarbonyl, the product resulting from this intermediate is thought to be a Diels-Alder type dimer XIII similar to cobalt tricarbonyl nitrosyl and norbornadiene. The Diels-Alder type dimer should then close photochemically to form the cage compound found in small yield in all the reactions (Figure 33).

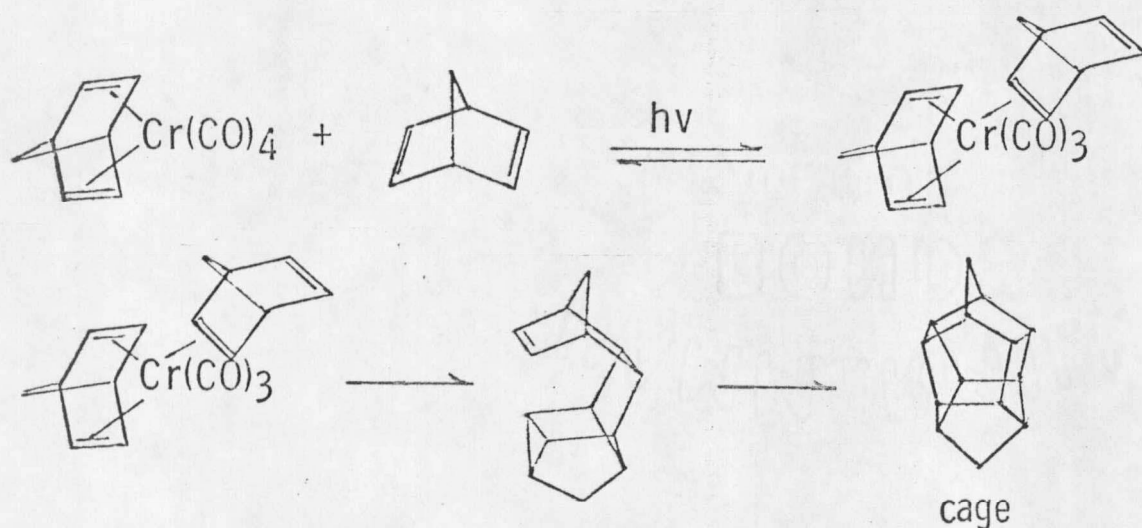


Fig. 33. Formation of dimer using dinorbornadiene chromium tricarbonyl.

It should be pointed out that, although it is possible to form the two dinorbornadiene species without having to form norbornadiene chromium tetracarbonyl, the experimental results show norbornadiene chromium tetracarbonyl is formed. In addition, when norbornadiene

chromium tetracarbonyl is used as the starting reactant template it gives the expected products in a similar ratio to the other reactant templates. Furthermore, dimers are not seen in the gas chromatogram until norbornadiene chromium tetracarbonyl is present in infrared spectra and they stop when it is absent.

## EXPERIMENTAL

### Reagents

Chromium hexacarbonyl, benzene chromium tricarbonyl, toluene chromium tricarbonyl, mesitylene chromium tricarbonyl and dicumene chromium were obtained from Alfa Inorganics, Inc., and except for dicumene chromium, were used without further purification. Dicumene chromium, a black viscous liquid, was distilled under vacuum (130-133°/0.1-0.2 mm) and used immediately.

Norbornadiene chromium tetracarbonyl was prepared as described by Bennett, Pratt and Wilkinson (64) by treatment of chromium hexacarbonyl with norbornadiene at elevated temperatures. It was found to be formed in higher yield (50%) when norbornadiene and chromium hexacarbonyl were irradiated for 24 hours ( $>280\text{ m}\mu$ ) in a sealed tube from which the air was removed. In both methods the product was purified by sublimation.

The nitrogen used in all reactions in the deoxygenating procedure was purified by passing it through BSTS catalyst (BASF Colors & Chemicals, Inc.), which removed the oxygen and water.

Norbornadiene was obtained from Frinton Laboratories. Purification was accomplished by sitting it over activated neutral alumina for several hours and then distilling it just prior to using it.

Norbornene was obtained from Aldrich Chemical Company, Inc., and was used as received.

### Instruments

Infrared spectra were obtained using either a Beckman IR-4 or a Beckman IR-5-A infrared spectrophotometer. Spectra were run in solution using matched liquid infrared cells with sodium chloride windows. Each spectrum was standardized with the polystyrene absorption peak at  $1601.8\text{ cm}^{-1}$ .

Nuclear magnetic resonance spectra were obtained in solution using a Varian model A-60, except for the cage compound which was run using a Varian model AH-100.

Ultraviolet spectra were obtained in solution using matched quartz cells on a Cary Model 14.

The gas chromatograph used for product identification was an F & M Model 400 gas chromatograph. The column was a glass, 4', 5% SE-30 on Gas Chrom-Z (100-120 mesh). The temperature program of  $75^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  ( $7.5^{\circ}/\text{min}$ ) with a flow rate of 40 ml helium per minute was used for best separation. The three dimer compounds and single cage compound were detected between  $120\text{--}135^{\circ}\text{C}$  and the carbonyl product was detected between  $158\text{--}160^{\circ}\text{C}$ .

For product isolation an Aerograph model A-700 Autoprep was used. A  $1/4$ -inch outer diameter 20-foot aluminum column packed with 30% SE-30 on Gas Chrom-Z (100-120 mesh) was used. The chromatographic conditions were: column,  $180^{\circ}\text{C}$ ; collector,  $225^{\circ}\text{C}$ ; detector,  $260^{\circ}\text{C}$ ; injector,  $250^{\circ}\text{C}$ ; flow rate, 300 ml helium per minute. Under these conditions the first dimer appeared in 88 minutes.

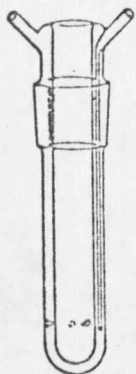
The samples to be chromatographed on the Aerograph Autoprep were filtered through a Büchner funnel filled with activated neutral alumina to remove solid particles and carbonyl polymers. The alumina was washed with hexane to elute all the dimer and cage compounds, leaving behind the chromium oxide and most of the carbonyl insertion product. The solutions were concentrated and injected into the Aerograph. Products were easily separated and integration of peak areas using a Sargent model SR recorder afforded a method to determine dimer product percentages.

Mass spectra were obtained for the cage compound from Purdue University on a Hilachi RMU-6A. All other mass spectra data were obtained on the Varian Mat CH5.

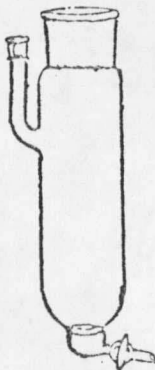
#### Light and Reaction Systems

In all cases the light source for the photochemical reaction was a Hanovia Type A 450-watt high pressure mercury arc.

Samples were irradiated in a reaction vessel constructed of a Pyrex glass vessel that would accommodate a quartz or Pyrex water-cooled immersion well suitable for holding the lamp and a circular filter. The bottom of the reaction vessel had a filtered disk to allow nitrogen to bubble through the reaction mixture out a condensor connected to a side arm and through a nitrogen bubbler. Nitrogen was bubbled through the reaction mixture 12 hours before the irradiation was started to remove dissolved oxygen.



Immersion Well



Reaction Vessel



Lamp

#### Photoreaction for Determining Products and Product Ratios

##### Chromium Hexacarbonyl

To 70 ml of purified norbornadiene 0.7483 g (0.0035 mole) of chromium hexacarbonyl was added. This solution was placed in the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. The light, with a corex filter, was then turned on and the irradiation was run for 33 hours. The nitrogen was bubbled through the solution during the complete reaction. A gas chromatogram was taken of the total reaction product, which was then filtered through a Büchner funnell filled with activated neutral alumina to remove the solid material (decomposition product) and most of the carbonyl polymer. The alumina was washed with hexane until no dimers were in the filtrate. The hexane solution was then concentrated to a viscous liquid. The viscous liquid was injected into the Aerograph Autoprep and five fractions were

collected. The fifth fraction contained three components. The integration of the peaks of the gas chromatogram were recorded using a Sargent model SR recorder.

Fraction 1 — Identified as the unremoved solvent.

Fraction 2 — Nuclear magnetic resonance 1.23, 1.32, 1.69, 2.62, 5.97.

Gas chromatogram peak percentage 36%

Melting point 67-68°C.

Fraction 3 — Nuclear magnetic resonance 1.13, 2.00, 2.54, 2.80, 5.82, 6.20.

Gas chromatogram peak percentage 21%

Fraction 4 — Nuclear magnetic resonance 1.02, 1.55, 1.85, 2.72, 6.35.

Gas chromatogram peak percentage 29%

Fraction 5 — Component 1

Nuclear magnetic resonance 1.79, 2.45.

Gas chromatogram peak percentage 14%

Component 2

Melting point > 300°C.

Component 3

Not investigated.

#### Norbornadiene Chromium Tetracarbonyl

To 70 ml of purified norbornadiene 0.2446 g (0.0009 mole) of norbornadiene chromium tetracarbonyl was added. This solution was

placed in the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. The light, with a corex filter, was then turned on and the irradiation was run for 24 hours. The nitrogen was bubbled through the solution during the complete reaction. A gas chromatogram was taken of the total reaction product, which was then filtered through a Büchner funnel filled with activated neutral alumina to remove the solid material (decomposition product) and most of the carbonyl polymer. The alumina was washed with hexane until no dimers were in the filtrate. The hexane solution was then concentrated to a viscous liquid. The viscous liquid was injected into the Aerograph Autoprep and five fractions were collected. The fifth fraction contained three components. The integration of the peaks of the gas chromatogram were recorded using a Sargent model SR recorder.

Fraction 1 — Identified as the unremoved solvent.

Fraction 2 — Nuclear magnetic resonance 1.23, 1.32, 1.69, 2.62, 5.97.

Gas chromatogram peak percentage 52%

Melting point 67-68°C.

Fraction 3 — Nuclear magnetic resonance 1.13, 2.00, 2.54, 2.80, 5.82, 6.20.

Gas chromatogram peak percentage 20%

Fraction 4 — Nuclear magnetic resonance 1.02, 1.55, 1.85, 2.72, 6.35.

Gas chromatogram peak percentage 20%

Fraction 5 — Component 1

Nuclear magnetic resonance 1.79, 2.45.

Gas chromatogram peak percentage 5%.

## Component 2

Melting point  $> 300^{\circ}\text{C}$ .

## Component 3

Not investigated.

## Benzene Chromium Tricarbonyl

To 70 ml of purified norbornadiene 0.5842 g (0.0027 mole) of benzene chromium tricarbonyl was added. This solution was placed in the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. The light, with a corex filter, was then turned on and the irradiation was run for 24 hours. The nitrogen was bubbled through the solution during the complete reaction. A gas chromatogram was taken of the total reaction product, which was then filtered through a Büchner funnel filled with activated neutral alumina to remove the solid material (decomposition product) and most of the carbonyl polymer. The alumina was combined with hexane until no dimers were in the filtrate. The hexane solution was then concentrated to a viscous liquid. The viscous liquid was injected into the Aerograph Autoprep and five fractions were collected. The fifth fraction contained three components. The integration of the peaks of the gas chromatogram were recorded using a Sargent model SR recorder.

Fraction 1 — Identified as the unremoved solvent.

Fraction 2 — Nuclear magnetic resonance 1.23, 1.32, 1.69, 2.62, 5.97.

Gas chromatogram peak percentage 36%.

Melting point 67-68°C.

Fraction 3 — Nuclear magnetic resonance 1.13, 2.00, 2.54, 2.80, 5.82, 6.20.

Gas chromatogram peak percentage 24%.

Fraction 4 — Nuclear magnetic resonance 1.02, 1.55, 1.85, 2.72, 6.35.

Gas chromatogram peak percentage 33%.

Fraction 5 — Component 1

Nuclear magnetic resonance 1.79, 2.45.

Gas chromatogram peak percentage 7%.

Component 2

Melting point > 300°C.

Component 3

Not investigated.

#### Toluene Chromium Tricarbonyl

To 70 ml of purified norbornadiene 0.1123 g (0.0004 mole) of toluene chromium tricarbonyl was added. This solution was placed in the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. The light, with a corex filter, was then turned on and the irradiation was run for 24 hours. The nitrogen was bubbled through the solution

during the complete reaction. A gas chromatogram was taken of the total reaction product, which was then filtered through a Büchner funnel filled with activated neutral alumina to remove the solid material (decomposition product) and most of the carbonyl polymer. The alumina was washed with hexane until no dimers were in the filtrate. The hexane solution was then concentrated to a viscous liquid. The viscous liquid was injected into the Aerograph Autoprep and five fractions were collected. The fifth fraction contained three components. The integration of the peaks of the gas chromatogram were recorded using a Sargent model SR recorder.

Fraction 1 — Identified as the unremoved solvent.

Fraction 2 — Nuclear magnetic resonance 1.23, 1.32, 1.69, 2.62, 5.97.

Gas chromatogram peak percentage 49%.

Melting point 67-68°C.

Fraction 3 — Nuclear magnetic resonance 1.13, 2.00, 2.54, 2.80, 5.82, 6.20.

Gas chromatogram peak percentage 22%.

Fraction 4 — Nuclear magnetic resonance 1.02, 1.55, 1.85, 2.72, 6.35.

Gas chromatogram peak percentage 22%.

Fraction 5 — Component 1

Nuclear magnetic resonance 1.79, 2.45.

Gas chromatogram peak percentage 7%.

## Component 2

Melting point  $> 300^{\circ}\text{C}$ .

## Component 3

Not investigated.

## Mesitylene Chromium Tricarbonyl

To 70 ml of purified norbornadiene 0.1045 g. (0.0004 mole) of mesitylene chromium tricarbonyl was added. The solution was placed in the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. The light, with a corex filter, was then turned on and the irradiation was run for 24 hours. The nitrogen was bubbled through the solution during the complete reaction. A gas chromatogram was taken of the total reaction product, which was then filtered through a Büchner funnel filled with activated neutral alumina to remove the solid material (decomposition product) and most of the carbonyl polymer. The alumina was washed with hexane until no dimers were in the filtrate. The hexane solution was then concentrated to a viscous liquid. The liquid oil was injected into the Aerograph Autoprep and five fractions were collected. The fifth fraction contained three components. The integration of the peaks of the gas chromatogram were recorded using a Sargent model SR recorder.

Fraction 1 — Identified as the unremoved solvent.

Fraction 2 — Nuclear magnetic resonance 1.23, 1.32, 1.69, 2.62, 5.97.

Gas chromatogram peak percentage 39%

Melting point 67-68°C.

Fraction 3 — Nuclear magnetic resonance 1.13, 2.00, 2.54, 2.80, 5.82, 6.20.

Gas chromatogram peak percentage 26%.

Fraction 4 — Nuclear magnetic resonance 1.02, 1.55, 1.85, 2.72, 6.35.

Gas chromatogram peak percentage 26%.

Fraction 5 — Component 1

Nuclear magnetic resonance 1.79, 2.45.

Gas chromatogram peak percentage 9%.

Component 2

Melting point > 300°C.

Component 3

Not investigated.

#### Dicumene Chromium

To 70 ml of purified norbornadiene 0.4 ml ( $\approx 0.0012$  mole) of dicumene chromium was added. This solution was placed in the photo reactor and purified nitrogen was bubbled through the solution for 12 hours. The light, with a corex filter, was then turned on and the irradiation was run for 24 hours. The nitrogen was bubbled through the

solution during the complete reaction. A gas chromatogram was taken of the reaction mixture after 24 hours, and showed no hydrocarbon dimers.

### Isolation of Photoreaction Intermediates

#### Chromium Hexacarbonyl

To 70 ml of purified norbornadiene 0.1920 g (0.0009 mole) of chromium hexacarbonyl was added and the solution was put into the photo reactor. Purified nitrogen was bubbled through the solution for 12 hours. An infrared spectrum was then taken (infrared spectrum  $1988\text{ cm}^{-1}$ , Figure 7) and the light, with a pyrex filter, was turned on. Infrared spectra were taken at one-half hour intervals for seven hours (infrared spectra after two hours  $2033, 1959, 1944, 1913\text{ cm}^{-1}$ , Figure 8). After a total irradiation time of ten hours another infrared spectrum was taken and compared to the one taken at six hours. The comparison showed no change so the irradiation was stopped (infrared spectrum after six hours, no metal carbonyl bands, Figure 9).

Another reaction solution, in which 0.2007 g (0.0009 mole) of chromium hexacarbonyl was added to 70 ml of purified norbornadiene, had purified nitrogen bubbled through as before. An infrared spectrum was taken (infrared spectrum at zero time  $1988\text{ cm}^{-1}$ ) and the light, with a pyrex filter, was turned on. The reaction was run for two hours, then the irradiation was stopped and an infrared spectrum taken (infrared spectrum after two hours  $2033, 1959, 1944, 1913\text{ cm}^{-1}$ ). The reaction solution was allowed to stand under nitrogen for 19 hours. Infrared spectra were taken at two-hour intervals and reached a maximum change in six hours after

irradiation was stopped (infrared spectrum after six hours 2033, 1988, 1959, 1944,  $1913\text{ cm}^{-1}$ , Figure 10). After the solution sat for 19 hours it was heated to  $70^{\circ}\text{C}$  for five hours with no apparent change occurring in the infrared spectrum. The solution was then cooled to room temperature and the light, with a pyrex filter, turned on for 30 minutes before an infrared spectrum was taken (infrared spectrum after 30 minutes 2033, 1959, 1944,  $1913\text{ cm}^{-1}$ ). The reaction mixture was removed from the photo reactor and roto evaporated to a volume of 5 ml. The 5-ml concentrate was chromatographed on an activated silica gel column. Hexane was added to remove any hydrocarbon dimers and until a bright yellow band started to be eluted. An infrared spectrum was taken of all the hexane fractions after they were combined and concentrated, but the infrared spectrum showed no metal carbonyl bands. Benzene was added to the silica gel column and the bright yellow band collected. The benzene was removed and roto evaporated. The residue was sublimed and an infrared spectrum (infrared spectrum 2033, 1959, 1944,  $1913\text{ cm}^{-1}$ ) and nuclear magnetic resonance spectrum (nuclear magnetic resonance spectrum 4.42 [4H], 3.63 [2H], 1.30 [2H]) were taken.

#### Benzene Chromium Tricarbonyl

To 70 ml of purified norbornadiene 0.2135 g (0.0010 mole) of benzene chromium tricarbonyl was added and the solution was put into the photo reactor. Purified nitrogen was bubbled through the solution for 12 hours. An infrared spectrum taken (infrared spectrum 1976,  $1905\text{ cm}^{-1}$ , Figure 19), and the light, with a pyrex filter, was turned on. Infrared

spectra of the reaction solution were taken at half-hour intervals for 3 1/2 hours (infrared spectrum after 30 minutes 2030, 1960, 1944, 1905, 1861  $\text{cm}^{-1}$ , Figure 20; infrared spectrum after one hour 2030, 1960, 1944, 1907, 1961  $\text{cm}^{-1}$ , Figure 21). After a total reaction time of 5 1/2 hours an infrared spectrum was taken and compared to the infrared spectrum taken at 3 1/2 hours. No change was observed. The irradiation was stopped (infrared spectrum after 3 1/2 hours, no metal carbonyl bands, Figure 22).

#### Toluene Chromium Tricarbonyl

To 70 ml of purified norbornadiene 0.2273 g (0.0010 mole) of toluene chromium tricarbonyl was added and the solution was put into the photo reactor. Purified nitrogen was bubbled through the solution for 12 hours. An infrared spectrum was taken (infrared spectrum 1971, 1900  $\text{cm}^{-1}$ , Figure 23), and the light, with a pyrex filter, was turned on. Infrared spectra of the reaction solution were taken at half-hour intervals for 3 1/2 hours (infrared spectrum after 30 minutes 2030, 1971, 1960, 1944, 1907, 1860  $\text{cm}^{-1}$ , Figure 24; infrared spectrum after one hour 2030, 1960, 1942, 1910, 1860  $\text{cm}^{-1}$ , Figure 25). After a total reaction time of 5 1/2 hours an infrared spectrum was taken and compared to the infrared spectrum taken at 3 1/2 hours. No change was observed and the irradiation was stopped (infrared spectrum after 3 1/2 hours, no metal carbonyl bands, Figure 26).

#### Mesitylene Chromium Tricarbonyl

To 70 ml of purified norbornadiene 0.2588 g (0.0010 mole) of mesitylene chromium tricarbonyl was added and this solution was put into the photo reactor. Purified nitrogen was bubbled through the

solution for 12 hours. An infrared spectrum was then taken (infrared spectrum 1963, 1889  $\text{cm}^{-1}$ , Figure 11) and the light, with a pyrex filter, was turned on. Infrared spectra were taken of the reaction solution at one-half intervals (infrared spectrum after 30 minutes 1908, 1860  $\text{cm}^{-1}$ , Figure 12; infrared spectrum after two hours 2030, 1960, 1940, 1909, 1860  $\text{cm}^{-1}$ , Figure 13). After a total irradiation time of 5 1/2 hours an infrared spectrum was taken and compared to the infrared spectrum taken after 3 1/2 hours. The comparison showed no change in the metal carbonyl region of the infrared spectra so the irradiation was stopped (infrared spectrum after 3 1/2 hours, no metal carbonyl bands, Figure 14).

Another reaction solution of 0.2247 g (0.0009 mole) of mesitylene chromium tricarbonyl was run as before. After a total irradiation time of 30 minutes the irradiation was stopped and the solution was divided into two parts. One part was allowed to stand in the dark. An infrared spectrum was taken after six hours (infrared spectrum 1963, 1910, 1889, 1960  $\text{cm}^{-1}$ , Figure 15). The other half of the reaction mixture was taken to dryness in a roto evaporator using water at room temperature for the water bath. The residue after the solvent was removed was a red-yellow solid. The red-yellow solid was put into a sublimator and heated to 35°C. A yellow solid was collected and the red solid remained at the bottom of the sublimator. The red solid was heated to 70°C in the sublimator but remained unchanged in the bottom of the sublimator.

The reaction was rerun and more of the yellow solid collected. A nuclear magnetic resonance spectrum (nuclear magnetic resonance

spectrum 4.42 [4H], 3.73 [2H], 1.30 [2H]), an infrared spectrum (infrared spectrum 2033, 1959, 1944, 1913  $\text{cm}^{-1}$ ), and a mass spectrum (mass spectrum, Figure 16) were taken of the yellow solid.

The red complex was also collected and an infrared spectrum (infrared spectrum 1870, 1820  $\text{cm}^{-1}$ , Figure 17) was taken of the red complex using a potassium bromide pellet. The red complex decomposed in many solvents even when the oxygen was removed by bubbling nitrogen through the solvent. The solvents were hexane, petroleum ether, carbon tetrachloride, chloroform, dimethyl formamide, dimethyl sulfoxide, benzene, ethanol and methanol.

Another similar reaction was run and the red solid collected and purified without heating above 35°C. It was purified by subliming the yellow solid away at 35°C. To check the red complex for thermal stability, a mass spectrum was run at 20°C, 25°C, 50°C, 70°C, 90°C and 115°C.

#### Photochemical Time Study

For the time studies solutions of norbornadiene and either chromium hexacarbonyl 0.2707 g (0.0012 mole) or mesitylene chromium tricarbonyl 0.2776 g (0.0011 mole) were used. In each of these studies purified nitrogen was bubbled through the solution for 12 hours and then the light, using a corex filter, was turned on.

In the case of chromium hexacarbonyl, gas chromatograms of samples of the reaction solution were taken at one-hour intervals for 14 hours and then at longer intervals for a total time of three days. A plot

showing peak heights of the hydrocarbon dimer versus time is shown in Figure 27.

In the case of mesitylene chromium tricarbonyl, gas chromatograms were taken every half-hour for 2 1/2 hours and then at longer intervals for a total of three days. A plot showing peak heights versus time is shown in Figure 28.

#### Beer's Law

For the study a solution of 1 ml of norbornadiene in 99 ml of cyclohexane was prepared. To this chromium hexacarbonyl was added until a saturated solution was made. Another saturated solution of chromium hexacarbonyl was also prepared in cyclohexane but no norbornadiene was added. The ultraviolet spectra were run on these two solutions and compared.

#### Infrared Study

Two solutions of chromium hexacarbonyl in norbornadiene were prepared. One solution contained 0.0378 g (0.0017 mole) chromium hexacarbonyl in 10 ml of norbornadiene and one contained 0.0537 g (0.0024 mole) chromium hexacarbonyl in 10 ml of norbornadiene. The infrared spectra of these solutions were compared in the metal carbonyl region to the infrared spectrum of chromium hexacarbonyl in carbon tetrachloride.

#### Thermal Reaction of Chromium Hexacarbonyl and Norbornadiene

For this study 0.02625 g (0.0012 mole) of chromium hexacarbonyl was placed in the large photoreactor with 70 ml of norbornadiene.

Purified nitrogen was bubbled through the solution. The solution was then heated, by means of a heating tape wrapped around the reaction vessel, to 57°C for 24 hours. The same solution was then heated to 83°C for 24 hours and finally it was heated to 89°C for 24 hours. Infrared spectra were taken every 24 hours (infrared spectrum at zero time 1988 cm<sup>-1</sup>; infrared spectrum of the final solution 1988 cm<sup>-1</sup>). A gas chromatogram was taken every 24 hours.

#### Irradiation of Norbornadiene Without Metal Carbonyl

For this study 70 ml of purified norbornadiene which had nitrogen bubbled through it was irradiated with light, using a quartz filter, for six hours. A gas chromatogram was taken after this six hours and showed no hydrocarbon dimers present. The same sample was then irradiated with light, using a corex filter, for 12 more hours. A gas chromatogram was then taken and showed no hydrocarbon dimers.

#### Photoreaction of Norbornene

In this study 6.984 g (0.0743 mole) of norbornene was dissolved in 70 ml of cyclohexane and 0.2723 g (0.0012 mole) of chromium hexacarbonyl was added. Nitrogen was bubbled through the solution for seven hours. Then the solution was irradiated, using a corex filter, for 24 hours. A gas chromatogram was taken and showed no hydrocarbon dimers had been formed.

#### Thermal Reaction of Pyridine Chromium Pentacarbonyl and Norbornadiene

For this reaction, 0.2303 g (0.0008 mole) of pyridine chromium pentacarbonyl (65) was added to a solution made of 5 ml norbornadiene,

5 ml methyl iodide and 15 ml tetrahydrofuran. Nitrogen was bubbled through the solution for several hours, then the solution was heated to reflux for 12 hours. An infrared spectrum (infrared spectrum 2030, 1960, 1940,  $1910\text{ cm}^{-1}$ ) was then taken of the solution. The total reaction mixture was then filtered. The residue was a tan solid (N-methyl pyridinium iodide salt). The yellow filtrate was concentrated and a gas chromatogram taken, which showed no hydrocarbon dimers. The filtrate was then taken to dryness and the residue of the filtrate sublimed. An infrared spectrum (infrared spectrum 2030, 1960, 1940,  $1910\text{ cm}^{-1}$ ), nuclear magnetic resonance spectrum (nuclear magnetic resonance spectrum 4.42 [4H], 3.73 [2H], 1.30 [2H]), and a mass spectrum (mass spectrum, Figure 16) were taken of the yellow sublimed residue.

#### Thermal Reaction of Dipyrindine Chromium Tetracarbonyl and Norbornadiene

To 10 ml of norbornadiene, 5 ml of methyl iodide and 15 ml of tetrahydrofuran, 0.1039 g (0.0003 mole) of dipyrindine chromium tetracarbonyl (65) were added. Nitrogen was bubbled through the solution for several hours and then the solution was heated to reflux for 12 hours. The reaction solution was then filtered. The residue was a tan solid (N-methyl pyridinium iodide salt). The filtrate was taken to dryness and the yellow solid remaining was sublimed. An infrared spectrum was taken (infrared spectrum 2030, 1960, 1940,  $1908\text{ cm}^{-1}$ ) of the yellow sublimed solid.

### Isolation of Carbonyl Polymer

Reactions of benzene, mesitylene chromium tricarbonyl and chromium hexacarbonyl were run as described in the isolation of reaction intermediates. The total reaction products were combined and concentrated to less than 5 ml. This concentrated solution was chromatographed on activated neutral alumina. Hexane was added until no more hydrocarbon dimers were left on the column. The column was then washed with 50% hexane-50% benzene until a dull yellow band started to be eluted. Then 50% benzene and 50% ether solutions were added to the column and the dull yellow band collected. The 50% benzene and 50% ether fraction was concentrated to a yellow viscous liquid. The yellow oil was redissolved in 100% ether and then methanol was added until a white precipitate appeared.

An infrared spectrum was taken of the dried white solid. The distinguishing feature of this infrared spectrum was a strong peak at  $1715\text{ cm}^{-1}$ . A gas chromatogram was taken on the F&M and the only peak came at  $158\text{--}160^{\circ}\text{C}$ . Then a mass spectrum was taken and it showed the white solid had a mass peak of at least 1000. Finally a melting point was taken and it showed the compound was stable to at least  $300^{\circ}\text{C}$ .

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