INVESTIGATION OF THE PHOTOCHEMICAL KETONE COORDINATION TO TUNGSTEN HEXACARBONYL

by

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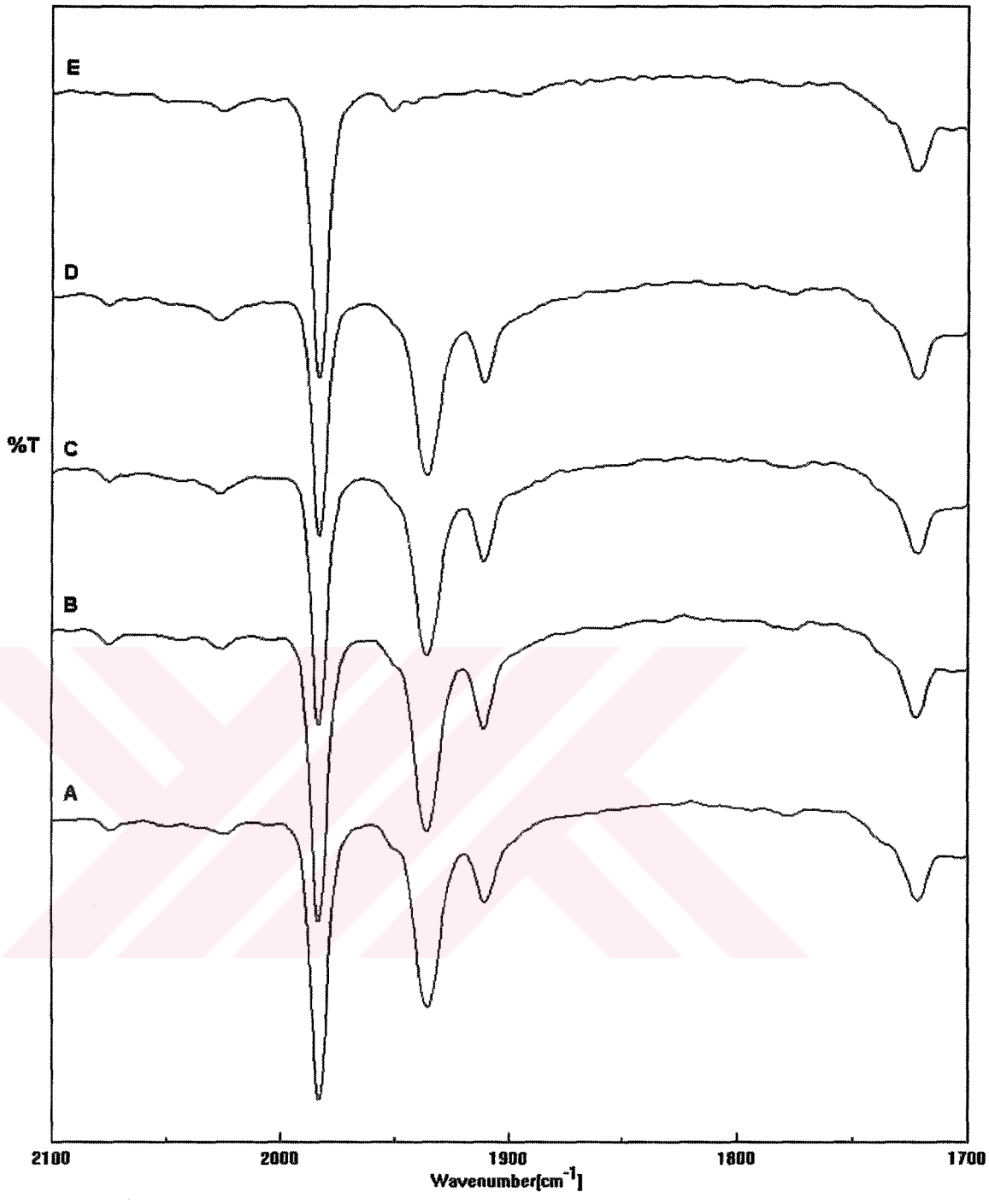

Figure 3.1.1 The spectral changes in the irradiation done with 3-methylcyclohexanone in 15 minutes (A), 30 minutes (B), 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

Approval of the Graduate School of Natural Sciences

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality as a thesis for the degree of Master of Science.

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ABSTRACT

INVESTIGATION OF THE PHOTOCHEMICAL KETONE COORDINATION TO TUNGSTEN HEXACARBONYL

Altıntaş, Bahadır

Master of Science, Department of Chemistry

Supervisor: Assoc. Prof. Dr. Çetin BOZKURT

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Some ketones can be converted to aldol condensation products by acid or base catalyst. It was found that this type of condensation can be achieved stochiometrically by a photochemical reaction. Irradiation of $W(CO)_6$ in CCl_4 gives species that converts cyclic ketones to their condensation products.

The condensation reactions of 3-methylcyclohexanone, 2-acetylcyclopentanone,2-methycyclohexanone, 4-ethylcyclohexanone,3-heptanone, 4-heptanone, cycloheptanone and cyclooctanone have been

investigated by $W(CO)_6/CCl_4$/UV system. FT-IR studies of these reactions indicates that the active intermediate is ketone coordinated to $W(CO)_5$. And this research shows that aldol type condenstions of ketone depends on the size of the ketone and the number of the carbon atom that substituent is bonded.

Keywords: Metal carbonyl, photochemistry, ketones, aldol condensation

ÖZET

KETONLARIN FOTOKİMYASAL OLARAK TUNGSTEN HEKZAKARBONİL İLE KORDİNASYONLARININ İNCELENMESİ

Altıntaş, Bahadır

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Tez Danışmanı: Doç.Dr. Çetin BOZKURT

Ağustos 2003, 51 sayfa

Bazı ketonlar asit ya da baz katalizörler ile aldol tipi kondenzasyon ürünlerine dönüştürülebilirler. Bu tip kondenzaysonların stökiyometrik olarak fotokimyasal reaksiyonlarla da gerçekleşebildiği bulunmuştur. $W(CO)_6$ in CCl_4 içinde ışınlanması, ketonları kondenzasyon ürünlerine dönüştüren ürünler vermektedir.

$W(CO)_6/CCl_4/UV$ sistemi ile, 3-metilsiklohekzanon, 2-asetilsiklopentanon, 2-metilsiklohekzanon, 4-etilsiklohekzanon, 3-heptanon, 4-heptanon, sikloheptanon ve siklooktanonun kondenzasyon reaksiyonları

incelenmiştir. Bu reaksiyonların FT-IR çalışmları, aktif ara ürünün ketona koordine $W(CO)_5$ olduğunu belirtmektedir. Bu çalışma ketonların aldol tipi kondenzasyonunun ketonun büyüklüğüne ve ekli grubun bağlanmış olduğu karbon atomunun numarasına bağlı olduğunu göstermektedir.

Anahtar kelimeler: Metal karbonil, fotokimya, ketonlar, aldol kondenzasyonu.

ACKNOWLEDGEMENTS

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I would also shout my thanks to all the people at the Abant Izzet Baysal University, Department of Chemistry. And the last but not the least, I express my thanks to everyone who supports me on my way.

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1. INTRODUCTION

Metal carbonyls may be considered as part of the surface of a transition metal cut from the surface stabilized by carbon monoxide molecules. There are reactions which are catalyzed by metal surfaces and also catalyzed by soluble metal carbonyls and related complexes. That is why there are too many researches on metal carbonyls. Using of the metal carbonyls as a catalyts in organic synthesis has been widely investigated. [1]

It has been known that there are many metal carbonyl catalyzed reactions. Generally the catalytic species are coordinatively unsaturated carbonyl complexes which are generated from metal carbonyls by the action of heat or light. Photolysis of a metal carbonyl by ultraviolet light creates coordinatively unsaturated species in solution.

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO$$

The coordinatively unsaturated species that produced by irradiation can give two kinds of reactions.

i. The substracted carbonyl can bond again to the metal.

$$M(CO)_5 + CO \longrightarrow M(CO)_6$$

or

ii. Another ligand can coordinate the metal carbonyl

$$M(CO)_5 + L \longrightarrow M(CO)_5L$$

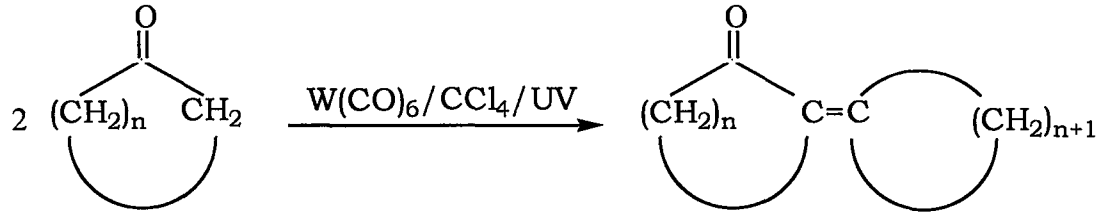
It has been known that metal carbonyl complexes are catalysts for olefin metathesis reactions.[2]

Irradiation of tungsten hexacarbonly in carbon tetrachloride leads olefin metathesis reaction. Olefin metathesis reactions consist the exchange of alkylidene groups around the double bond of olefin [3]. New olefins can be produced which is difficult to obtain by other methods.

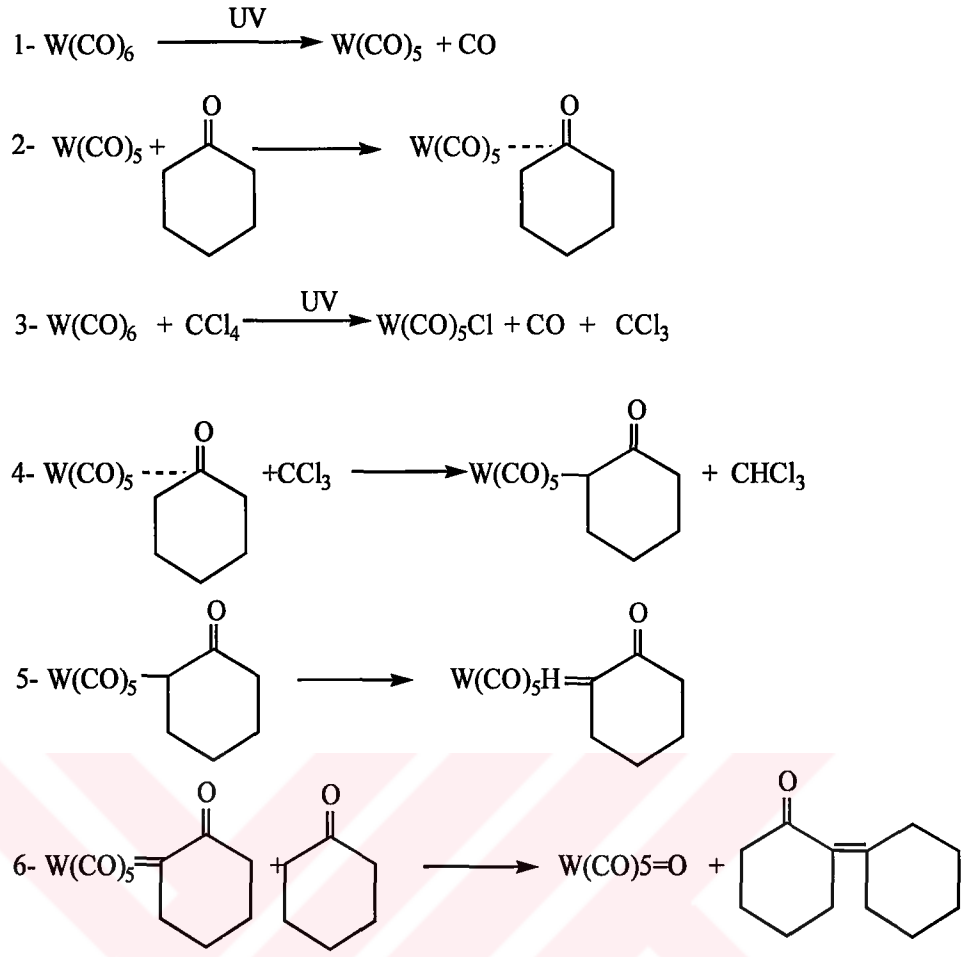
$$2R_1\text{-}CH{=}CH\text{-}R_2 \xrightarrow{W(CO)_6/CCl_4/UV} R_1\text{-}CH{=}CH\text{-}R_1 + R_2\text{-}CH{=}CH\text{-}R_2$$

In the metathesis by $W(CO)_6/CCl_4/UV$ system, it has been reported that generated catalyst species may be $W(CO_5)Cl$, $W(CO)_4Cl_2$,$(CO)_4W{=}CCl_2$ and $(CO)_3Cl_2W{=}CCl_4$ [4].

The role of the active catalyst is not completely understood in the photochemical metathesis reactions, so there has been many research on this subject [4,5]. Carbene mechanism [6] that is also acceptable for olefin metathesis reactions, has also been used for the related reactions catalyst by $W(CO)_6/CCl_4/UV$ system. Some evidence for the existence of carbene intermediates has been reported using benzaldehyde as a carbene-trap for the metathesis of linear olefins. When cyclohexanone was applied as the carbene-trap, the only reaction product observed was the partially deoxygenated dimer of ketone [7].



The reaction of the $W(CO)_6/CCl_4/UV$ system with cyclic ketones has been investigated and the following mechanism was proposed for the formation of Wittig type aldol products [8].



In this study, the effect of $W(CO)_6/CCl_4/UV$ system on linear(4-heptanone, 3-heptanone) ,cyclic(cycloheptanone, cyclooctanone) and substituted cyclic(2-methycyclohexanone,3-methycyclohexanone, 4-ethylcyclohexanone, 2-acetylcyclopentanone) ketones were investigated.

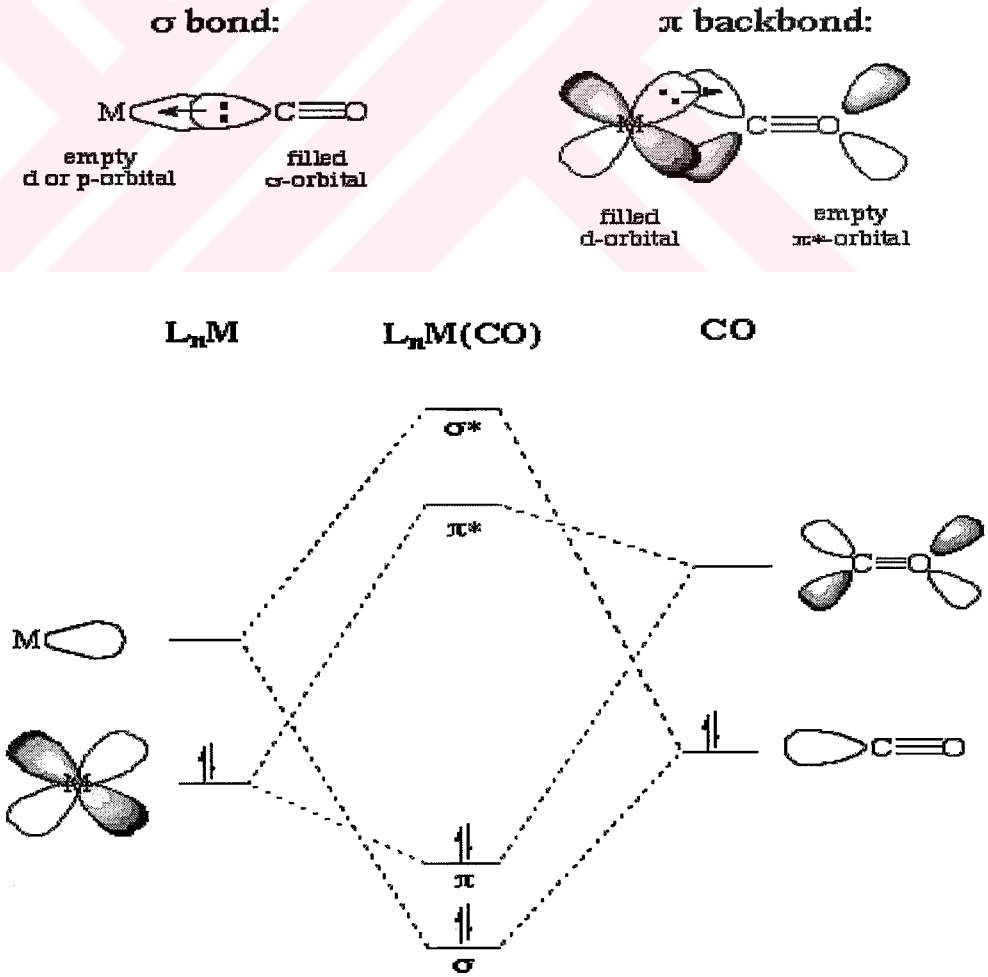
1.1 Properties of Metal Carbonyls

Carbon monoxide is the most common ligand in organometallic chemistry. It may serve as the only ligand binary carbonyls such as $Ni(CO)_4$, $W(CO)_6$ and $Fe_2(CO)_9$ or more commonly in combination with other ligands, both organic and inorganic. CO may bond to a single metal or it may serve as a bridge between two or more metals [9].

The first discovered metal carbonyl is nickel carbonyl,$Ni(CO)_4$, by Mond in 1890. from that date, iron, cobalt,molybdenum and chromium carbonyls were synthesized until 1926. Nowadays, there are wide range of metal carbonyls synthesized.

The applications of transition metals in catalytic organic reactions have a lot of industrial importance. Most organic chemicals are produced in bulk quantities by using transition metal complexes as homogeneous catalyst. Most commonly known six coordinated metal carbonyls are $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$. [10]

Bonding of the metal and carbonyl ligand can be described with molecular orbital terms where it is believed that this type of bond is a combination of δ- and π- bonding.



The two components of this bonding are synergistic. The more sigma donation by the carbonyl (or other δ-donors on the metal center), the stronger the π-backbonding interaction. Notice that although this involves the occupation of a π* orbital on the CO, it is still a bonding interaction as far as the metal center is concerned. There is a fundamental similarity between the nature of carbonyl-metal bonding and that of alkenes, acetylenes, phosphines, and dihydrogen.

This occupation of the π* on CO does lead to a decreased bond order in the carbon monoxide molecule itself. As we might expect, as the π-backdonation becomes stronger, the CO bond order should decrease from that of the free ligand. Two consequences that we might expect if the CO bond order was reduced would be a lengthening of the C-O bond and a decrease in the carbonyl stretching frequency in the IR. Both of these hold true.

Metal carbonyls can be made in a variety of ways. Here are just a few examples:

For Ni and Fe, the homoleptic or binary metal carbonyls can be made by the direct interaction with the metal (Equation 1).

In other cases, a reduction of a metal precursor in the presence of CO (or using CO as the reductant) is used (Equations 2-3).

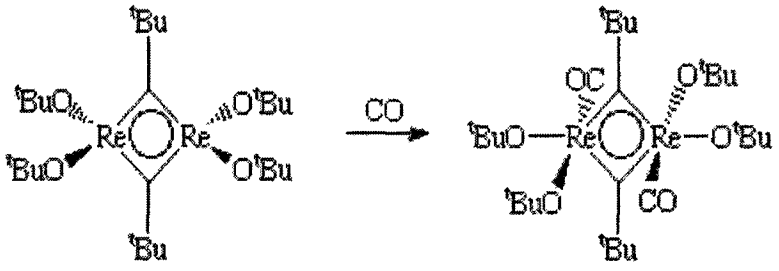
Carbon monoxide also reacts with various metal complexes, most typically filling a vacant coordination site (Equation 4) or performing a ligand substitution reactions (Equation 5).

Occasionally, CO ligands are derived from the reaction of a coordinated ligand through a deinsertion reaction (Equation 6).

$$Ni^0 + xs\ CO \xrightarrow{25\ ^\circ C} Ni(CO)_4 \quad (1)$$

$$WMe_6 + xs\ CO \longrightarrow W(CO)_6 + 3\,Me_2CO \quad (2)$$

$$Re_2O_7 + xs\ CO \longrightarrow (OC)_5Re{-\!\!-}Re(CO)_5 + 7\,CO_2 \quad (3)$$



(4)

$$[Ru(NH_3)_5H_2O]^{2+} \xrightarrow{CO} [Ru(NH_3)_5(CO)]^{2+} \quad (5)$$

$$RhCl(PPh_3)_3 + RCHO \longrightarrow RhCl(CO)(PPh_3)_2 + RH \quad (6)$$

1.2 Photochemical Reactions of Metal Carbonyls

Photochemistry of metal carbonyls may be done by the interaction of visible and ultraviolet light with metal complexes, largely but not exclusively in solution and largely but not exclusively in at room temperature.

Several light sources has been used over the years such as mercury arcs and the sun light. Among these, mercury arcs in various forms (very low pressure for the resonance lines at 185 and 254nm, medium pressure "point" sources, and high pressure high intensity lamps) have remained important. They have an advantage over other sources in that they have a more or less line spectrum so that it is relatively easy to obtain monochromatic light. Xenon arcs give intense light in the visible region but their spectra are nearly continuous.

Laser is a new light source for many photochemical reactions. Inorganic photochemistry has greatly benefited from these developments far more than organic photochemistry. Since organic molecules generally require UV light and such lasers are only more recent on the scene.

The common used lasers are rare gas ion laser. This type of laser may be named as "Continuous Wave Laser" with the wavelengths grouped near the green and blue region of the spectrum. This type of laser has extremely high intensity. A dye laser excited by an ion laser provides, with some loss of intensity, all wavelengths from 300 to 1030 nm. Helium-cadmium laser has much lower intensity within the wavelengths at 442 nm and 325 nm. Helium-neon laser also has little use in photochemistry.

The other useful lasers are intermittent. Ruby laser (694 nm or doubled) and neodymium laser lasers (1060 nm, doubled at 530 nm, triplet to 353 nm, and quadrupled to 265 nm) provide intense bursts of light.

Excimer lasers are use a mixture of a rare gas and fluorine or hydrogen chloride. They give intense 15 ns pulses at UV wavelengths, such as 193, 22, 249 and 303 nm, depending on filling gases.

1.3 Energy-Transfer Process of Excited States of Coordination Compounds

An electronically excited state *D, obtained a molecule D absorbs a photon of suitable energy,

$$D + h\nu \longrightarrow {}^*D$$

is virtually a new chemical species which it's chemical and physical properties different from those of the corresponding ground state molecule.

A distinctive feature of an electronically excited state is its potential to transfer energy to another species.

$$^*D + A \longrightarrow D + {}^*A$$

This is simply called as energy transfer. Energy transfer may be radiative or nonradiative.

Radiative state consists of the emission of a quantum of light by the donor excited state which is followed by absorption of the emitted photon by the acceptor.

$$^*D \longrightarrow D + h\nu$$

$$h\nu + A \longrightarrow {}^*A$$

Nonradiative energy transfer occurs when there is some interaction between *D and A.

If energy transfer is considered as the only quenching process, the competition for the excited donor is represented by the equations below.

$$^*D \longrightarrow D + h\nu \qquad (1)$$

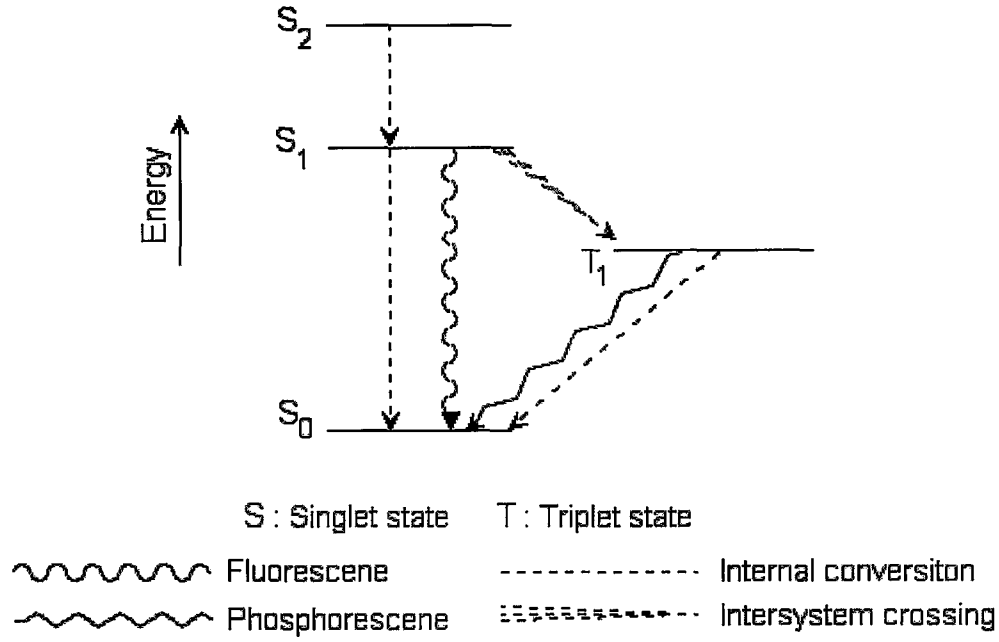
$$^*D \longrightarrow D + \text{heat} \qquad (2)$$

$$^*D \longrightarrow \text{Product} \qquad (3)$$

$$^*D + A \longrightarrow D + {}^*A \qquad (4)$$

Eq. 1 indicates Radiative , Eq.2 indicates nonradiative and Eq. 3 indicates reactive pathways. Eq. 4 indicates energy transition to another species.

Photophysical relaxation pathways for decay of excited states may be given by Jablonski Diagram.



The ground state denoted by S_0 and excited states by S_1 ,S_2 and T_1, although there are higher singlet and triplet states. Radiative pathways are indicated by solid wave-arrows and non radiative pathways use broken-arrows. A nonradiative relaxation between two states of the same multiplicity (e.g. S_2 to S_1) is called an interconversion while relaxation between states of different multiplicity (e.g. S_1 to T_1) is an intersystem crossing. A radiative or emissive transition between states of the same multiplicities (e.g. S_1 to S_0) is referred to as a fluorescence. If an emissive transition involves a change of multiplicity (e.g. T_1 to S_0), it is referred to as a phosphorescence. [11]

1.4 Stretching Modes of Metal Carbonyls

$\underline{M(CO)_4}$:

Two common structure is given for $M(CO)_4$ species if all the carbonyl ligands are identical. The first of these is tetrahedral and the second is square planar. If the structure is as $M(CO)_4L$ where L is any ligand, there are two possibilities for stretching bond. If L is in the axial position, it has 3 modes and in if it is in the equatorial position it has four stretching mode.

Another structure is $M(CO)_4L_2$ which has two identical ligand. There is also two possibilities for stretching modes of this structure. First case is when these two ligand in trans position, it has one stretching mode, and when they are in cis position it has four stretching modes as well.

$M(CO)_5$:

If five carbonyl group is identical the structure is trigonalbipyramidal and it has two stretching modes in IR. In other case if the structure is $M(CO)_5L$ there are three stretching modes and three peaks can be observed by IR.

$M(CO)_6$:

The structure of this type of metal carbonyl is octahedral and there is only one stretching mode from six identical carbonyl group and only one peak can be observed by IR. [12]

Spectroscopic Features of Carbonyl Complexes

In the IR, typical stretching frequencies are:

- Uncoordinated or "free" CO: 2143 cm^{-1}
- Terminal M-CO: 2125 to 1850 cm^{-1}
- Doubly bridging (μ-2): 1850 to 1750 cm^{-1}
- Triply bridging (μ -3): 1675 to 1600 cm^{-1}
- Semibridging: somewhere between terminal and μ-2.

1.5 Photochemistry of Tungsten hexacarbonyl

Oxidation of tungsten hexacarbonyl in carbon tetrachloride has been reported by a simple photochemical experiment [13].

Tungsten hexacarbonyl itself affords to phosgene by an even simpler method. Transformation can be occur under an oxygen atmosphere and is completely inhibited when air is excluded from the reaction system. By-products include the oxides of tungsten which are finally converted into WO_3 in the presence on an excess of oxidant.

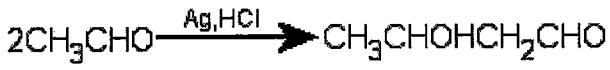
By a reversible reaction between O_2 and $W(CO)_6$ to produce highly activated oxidizing agent of unknown structure or stochiometry, phosgene formation is initiated. This species abstracts the chlorine from CCl_4, generating the trichloromethyl radical which only reacts with O_2 to yield phosgene.

Another photochemical reaction of $W(CO)_6$ leads to the formation of oxygenation products (alkyl hydroperoxide, alcohol and ketone)[14].

As we mentioned before, $W(CO)_6$ has been used for catalysis of a lot of olefin metathesis reactions[4]. It was found the $W(CO)_6$ can be used for aldol type condensation reactions [8].

1.6 Aldol Type Condensations

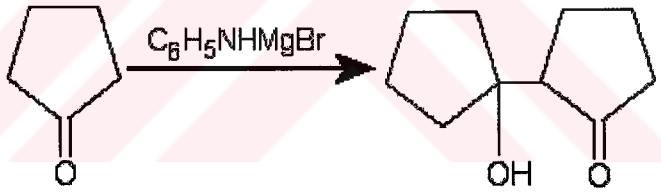
Aldol type condensation takes its name from aldol(3-hydroxybutanal), a name introduced by Wurtz who was first prepared this β-hydroxy aldehyde from acetaldehyde in 1872.



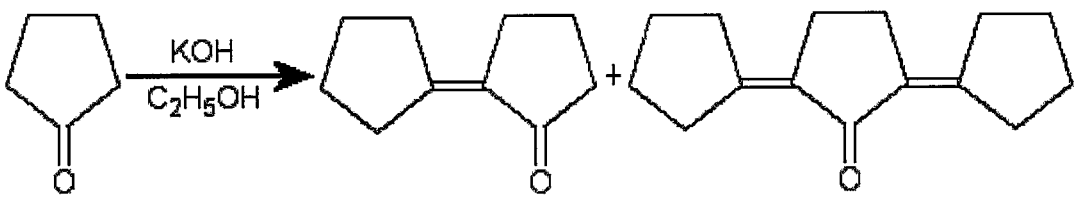
The aldol condensation includes reactions producing β-hydroxy aldehydes(β-aldols) or β-hydroxy ketones(β-ketols) by self condensations or mixed condensations of aldehydes or ketones.

The Claisen-Schmidt condensation is an aldol condensation discovered by Schmidt in 1880 and developed by Claisen(1881-1889). It is most often take to be the condensation of an aromatic aldehyde with an aliphatic aldehyde or ketone to yield α,β-unsaturated aldehyde or ketone, usually in the presence of a basic catalyst.

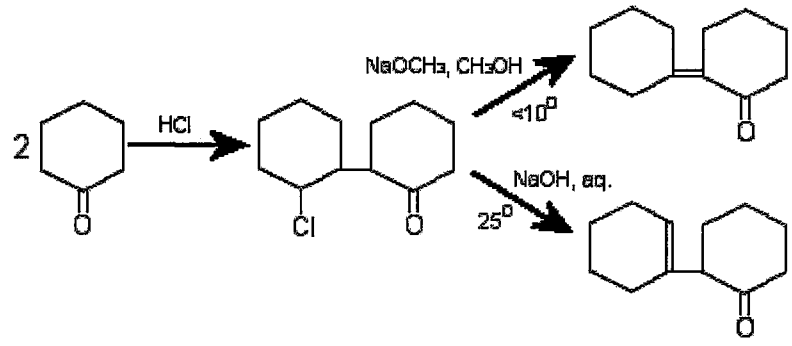
Self condensation of acyclic ketones proceeds normally; cyclopentanone, cyclohexanone and cycloheptanone form ketols or α,β-unsaturated ketones. Ketol formation is favored with anilinemagnesium bromide in ether. 2-cyclobutylidenecyclobutanone has been prepared from cyclobutanone and its enamines.



Acid catalyst favor the monosubstituted unsaturated ketone. With cyclohexanones the double bond in the product mat appear in the endocyclic β,γ position as well as the α,β positions. The use of ethanolic potassium hydroxide as a catalyst leads to mixtures of mono and bis-condensation products.



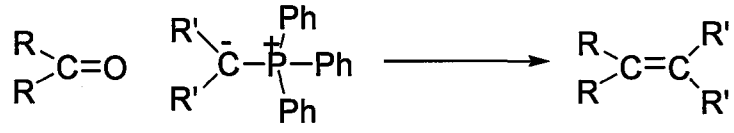
The intermediate β-chloroketone,2-(1chlorocyclohexyl)cyclohexanone prepared from cyclohexanone and hydrochloric acid, maybe dehydorgenated to the α,β-unsaturated ketone (methanolic sodium methoxide at low temperature, <10°) or the endocylic β,γ-isomer (with aqueous sodium hydroxide at room temperature) [15]



The reactions in this study produces aldol type condensation product and the mechanism is the same as Wittig type reactions.

1.7 Wittig type reactions

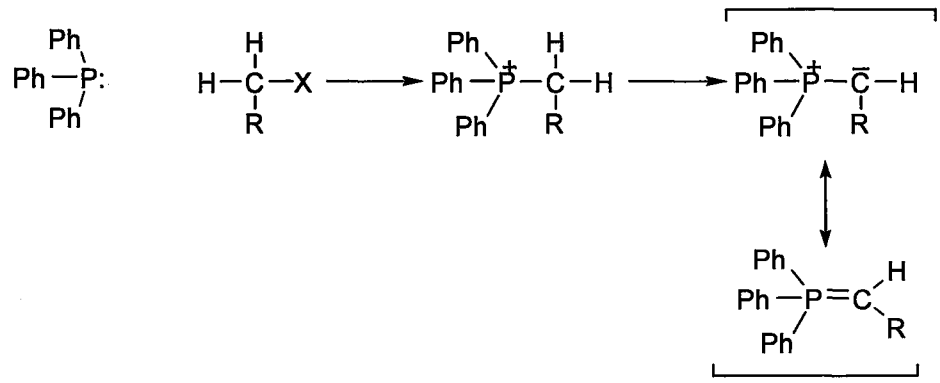
In 1954 Wittig discovered that the addition of a phosphorus stabilized anion to a carbonyl compound did not generate an alcohol, but an alkene! (Nobel prize in 1979).



$Ph_3P=O$

The phosphorus stabilized anion is called an ylide, which is a molecule that is overall neutral, but exists as a carbanion bound to a positively charged heteroatom.

Phosphorus ylides are produced from the reaction of triphenylphosphine



and alkyl halides.

This two step reaction starts with the nucleophilic attack of the Phosphorus on the (usually primary) alkyl halide. This generates an alkyl triphenylphosphonium salt.

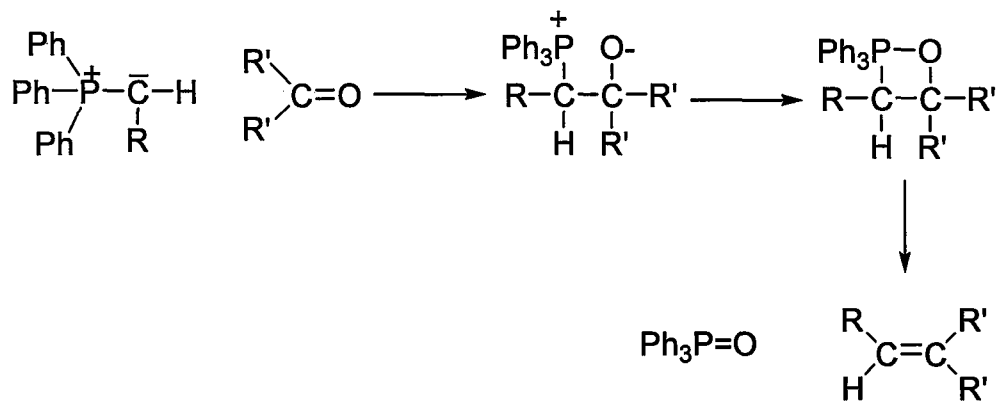
Treatment of this salt with a strong base removes a proton from the carbon bound to the phosphorus, and generates the ylide.

The ylide is a resonance form of a C=P double bond.

The double bond resonance form requires 10 electrons around the P atom. This is achievable through use of its d electrons (3rd row element), but the π bond to carbon is weak, and this is only a minor contributor.

The carbanionic character of the ylide makes it a very powerful nucleophile, and so it reacts rapidly with a carbonyl group.

This produces an intermediate which has charge separation - a betaine.



Betaines are unusual since they have a negatively charged oxygen and a positively charged phosphorus.

Phosphorus and oxygen always form strong bonds, and these groups therefore combine to generate a four membered ring - an oxaphosphetane ring.

This 4 membered ring quickly collapses to generate an alkene and (very stable) triphenyl phosphine oxide.

The elimination of $Ph_3P=O$ is the driving force of this reaction.

This is a good general route to make new C=C double bonds starting from carbonyl compounds.

1.8 Theory Of Used Techniques

1.8.1 Fourier Transform Infrared (FT/IR)

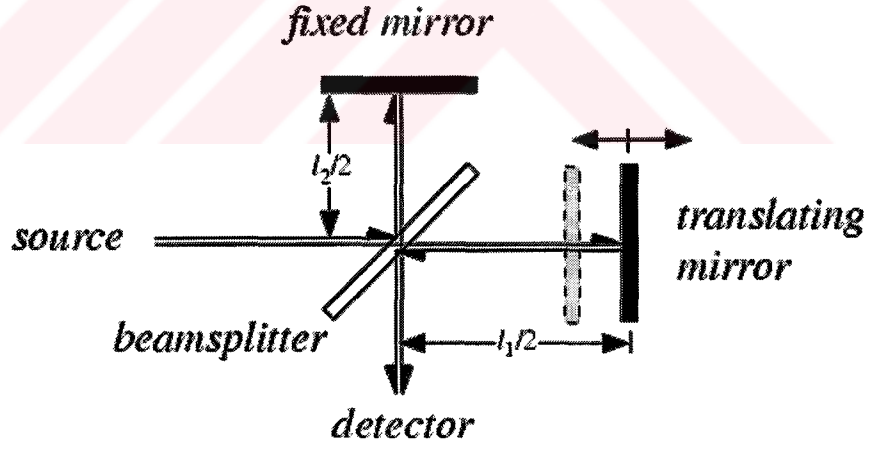


Figure 1.8.1.1. A simple schematic presentation of Fourier transform spectrometer

A Fourier transform spectrometer (abbreviated FTS) is a Michelson interferometer with a movable mirror. By scanning the movable mirror over some distance, an interference pattern is produced that encodes the

spectrum of the source (in fact, it turns out to be its Fourier transform). Fourier transform spectrometers have a multiplex advantage over dispersive spectral detection techniques for signal, but a multiplex disadvantage for noise.

In its simplest form, a Fourier transform spectrometer consists of two mirrors located at a right angle to each other and oriented perpendicularly, with a beam splitter placed at the vertex of the right angle and oriented at a 45° angle relative to the two mirrors. Radiation incident on the beam splitter from one of the two "ports" is then divided into two parts, each of which propagates down one of the two arms and is reflected off one of the mirrors. The two beams are then recombined and transmitted out the other port. When the position of one mirror is continuously varied along the axis of the corresponding arm, an interference pattern is swept out as the two phase-shifted beams interfere with each other.

The invention of the Fourier transform spectrometer coincides with A. Michelson's 1880 invention of the Michelson interferometer. In this device, the arms are kept the same length, but interference occurs if the phase velocity in the two arms differs, because the resulting phase advancement experienced by the beams traveling down the two arms is then also different. Using increasingly refined versions of Michelson's original device, Michelson and Morley searched for evidence of the Earth's motion through ether, the medium believed at the time to permeate space and allow the propagation of light through interplanetary space. If a relative motion between the ether and Earth had been present, the speed of light in the two perpendicular arms

would have been different, and the resulting optical paths would therefore also have been different.

As a result, an observable change in the brightness (or "visibility") of the recombined interfering beams would have occurred. The absence of a change in the observed visibility for any orientation or time or year marked the death knell for the ether theory and paved the way for the (initially skeptical) acceptance of Albert Einstein's theory of special relativity, along with its sometimes counterintuitive implications.

Michelson was fully aware of the spectroscopic potential of his interferometer (Michelson 1891, 1892), but the lack of sensitive detectors (and nonexistence of Fourier transform algorithms capable of being carried out by human calculators) proved insurmountable barriers for its practical implementation. In fact, Michelson's only detector consisted of his own two eyes, and it was not until two decades after the interferometer's invention that Rubens and Wood (1911) published the first true interferogram, recorded with a microradiometer. Because of the continued difficulty in computing Fourier transforms, these early investigators were unable to invert their interferograms directly, but instead guessed a spectrum, computed the inverse Fourier transform, and then compared it to their measured interferogram. The guessed spectrum was then modified to bring it into better agreement with the data, and the process was continued until sufficient agreement was obtained (or the patience of the spectrum guesser wore thin!).

Practical Fourier transform spectroscopy began to come into its own only in the early 1950s when experimental groups at Johns Hopkins University, the Air Force Cambridge Research Laboratories, and elsewhere built and tested high resolution spectrometers. The first astronomical application of Fourier transform spectroscopy occurred in the late 1950's and early 1960s when P. and J. Connes (and others) obtained high resolution and high-quality spectra of the planets. These developments were greatly aided by the publication of Cooley and Tukey's seminal paper on the "fast Fourier transform" algorithm. The Cooley and Tukey (1965) algorithm allowed Fourier transforms to be computed efficiently using a recursive algorithm which could be implemented easily on primitive electronic computers, reducing the computation time by several orders of magnitude and making the timely transformation of long interferograms feasible. (As a historical sidebar emphasizing the often surprising applicability of pure mathematics to real-world problems, it should be noted that the critical factorization step used by Cooley and Tukey in their algorithm had already been recognized and described by Gauss as early as 1805! (Strang 1993).)

Today, commercial Fourier transform spectrometers are widely available. Aided by fast computers which perform Fourier transforms in a flash, visible, infrared, and microwave Fourier transform spectrometers are common laboratory instruments used for spectroscopy in many diverse disciplines.

1.8.2 Gas Chromatography-Mass Spectrometry

The appearance of a chromatographic peak at a particular retention time suggests but does not guarantee the presence of a particular compound. The probability of positive identification will depend on factors like the type and complexity of the sample and sample preparation procedures employed. A gas chromatogram of an injected blood sample diluted with a solution of an internal standard (to verify retention time and relative peak area) that gives a large peak expected for alcohol strongly suggests the presence of blood alcohol since there are few nontoxic compounds that would likely interfere. Usually, there is indication of alcohol ingestion, and the key legal question is what is the concentration? However, the appearance of a GC peak for cocaine may not be so straightforward in confirming the presence of this drug. Hence, confirmatory evidence is usually sought. Spectral information, such as infrared or ultraviolet spectrometry, may be sought. A very powerful tool is the combination of gas chromatography with mass spectrometry, a technique known as gas chromatography-mass spectrometry (GC-MS).

Following the first experiences of J. J. Thomson (1912), mass spectrometry has undergone countless improvements. Since 1958, the chromatography-mass spectrometry coupling has revolutionized the analysis of volatile compounds. Combined with the development of the coupling with other separation techniques such as GC and HPLC, the hyphenated instruments allow to obtain significant information from mixtures of natural or synthetic compounds.

1.8.3 The Fundamental Mass Spectrometry

Mass spectrometry is a sophisticated instrumental technique that produces, separates, and detects ions in the gas phase. The basic components of a mass spectrometer are shown in Figure 1. A sample with a moderately high vapor pressure is introduced in an inlet system. operated under vacuum (10^{-4} to 10^{-7} torr) and at high temperature (up to 300 degree C). It vaporizes and is carried to the ionization source. Nonvolatile compounds may be vaporized by means of a spark or other source. Analyte molecules are typically neutral and must be ionized. This is accomplished by various means but typically is done by bombarding the sample with high-energy electrons in an electron-impact source. The electrons produce a positive ion, for example:

$$M + e^- \longrightarrow M^- + 2e^-$$

M is the analyte molecule and M^+ is called the molecular ion or parent ion. The M^+ ions are produced in different energy states and the internal energy (rotational, vibrational, and electronic) is dissipated by fragmentation reactions, producing fragments of lower mass which are themselves ionized or converted to ions by further electron bombardment. The fragmentation pattern is fairly consistent for given conditions (electron beam energy). Only a small amount or none of the parent ion may remain.

Most of the ions have a charge corresponding to the loss of only one electron. Multiply charged ions can also be obtained. The ions are separated in the spectrometer by being accelerated through a mass separator. The

total charge of the ions will be represented by q, the electron charge by e and the number of charges on the ions by z:

$$q = ze \text{ and } e = 1.0 \times 10^{-19} \text{ coulomb}$$

where m/z (or m/e) represents the mass to charge ratio. When the mass is given in dalton (Da) and the charge in number of electron charges, m/z is given in thomson (Th). Sometimes, m is given as the mass number and z as the charge number, both of which are unitless.

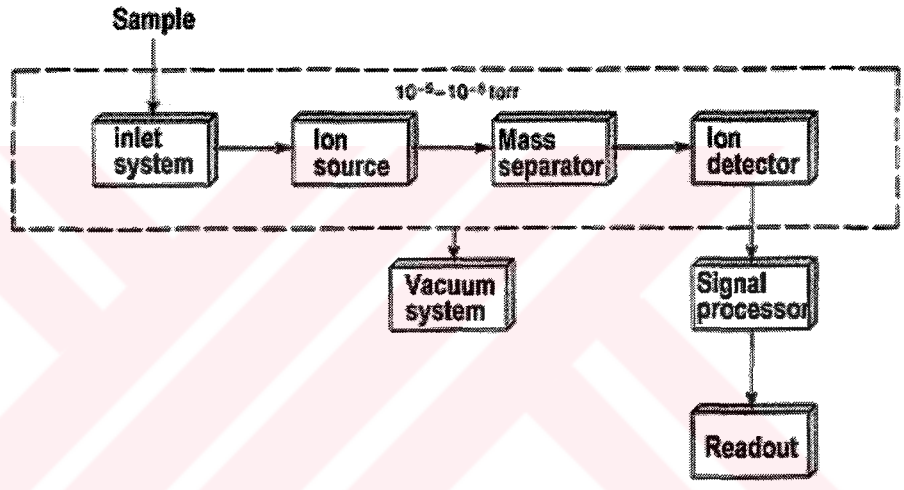


Figure 1.8.3.1. Components of a mass spectrometer

Separation is actually accomplished based on the mass-to-charge (m/e) ratios of the ions. Various spectrometers are based on magnetic sectors in which ions pass through a magnetic field and are deflected based on their m/e ratio; time-of-flight in which they traverse a long flight tube and arrive at a detector at different times based on their relative kinetic energies after being accelerated through an electrical field (the lighter ones arrive first); or quadrapoles in which the ions pass through an area with four hyperbolic magnetic poles, created by a radio frequency field, and certain ions take a

stable path" through the field and others take an "unstable path" and are not detected- the radiofrequency field is scanned rapidly to detect all the ions. The quadrapole mass spectrometer is ideally suited as a gas chromatography detector because it is compact and relatively inexpensive, and a complete scan is achieved in the duration of a GC peak, simply by scanning a voltage. The resolution is more limited than with other mass analyzers, but this is not usually a problem when combined with the gas chromatography information.

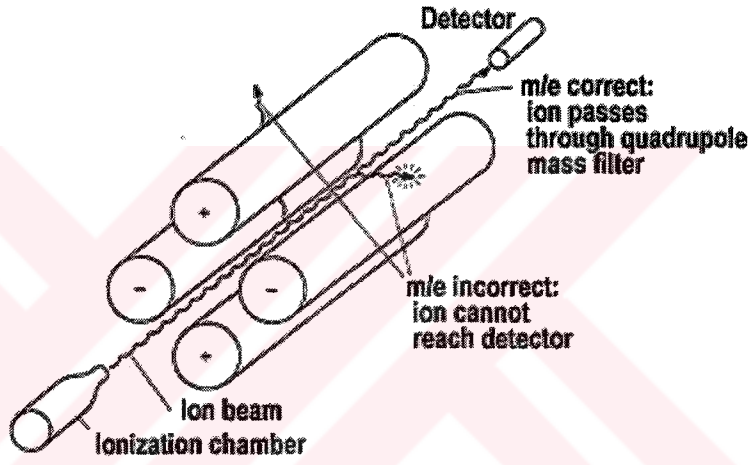


Figure 1.8.3.2. Quadrapole Mass Analyzer

The separated ions are detected by means of an electron multiplier, which is similar in design to photomultiplier tubes. Detection sensitivities at the nanogram level are common.

1.8.4 Mass Spectra

The effluent from a gas chromatograph may be connected to the sample inlet system of a mass spectrometer, forming a GC-MS system. The mass spectrometer then serves as the GC detector with high sensitivity and

selectivity. The mass spectrometer may be operated in various modes. In the total ion current (TIC) monitoring mode, it sums the currents from all fragment ions as a molecule (or molecules) in a GC peak passes through the detector, to provide a conventional looking gas chromatogram of several GC peaks. In the selective ion mode (SIM), a specific m/e ratio is monitored, and so only molecules that give a molecular or fragment ion at that ratio will be sensed. The mass spectrum of each molecule detected is stored in the system's computer, and so the mass spectrum corresponding to a given GC peak can be read out. The mass spectrum is generally characteristic for a given compound (if only one compound is present under the GC peak), giving a certain "fingerprint" of peaks at various (m/e) ratios. Certain peaks will dominate in intensity.

The fragmentation pattern often exhibits peaks corresponding to loss of specific groups in the molecule, for example, $-CO_2$ or -NH, which lends further credence to the presence of a given molecule or which can be used to gain structural information about a molecule. Manufacturers of mass spectrometers provide computer libraries of mass spectra of thousands of compounds, and spectral computer searches can be made to match an unknown spectrum.

The connection of capillary gas chromatography with mass spectrometry provides an extremely powerful analytical tool. Capillary GC, with thousands of theoretical plates, can resolve hundreds of molecules into separate peaks, and mass spectrometry can provide identification. Even if a

peak contains two or more compounds, identifying peaks can still provide positive identification, especially when combined with retention data.

2. EXPERIMENTAL STUDIES

2.1.Tungsten Hexacarbonyl

$W(CO)_6$ was purchased from Aldrich Chemical Company and used as is without purifying. Because when it was purified, it was found that it does not effect the experiment result.[16]

2.2. Solvents

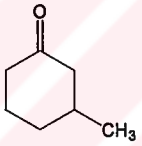
n-hexan(Merck): Purified under nitrogen athmosphere by franctional distillation.

Carbon tetrachloride(May & Baker): Used directly because its factory standards were enough for the experiments.

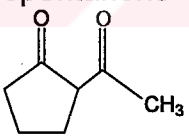
2.3. Ketones

All from Merck, reagent grade

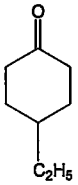
3-methyl cyclohexanone



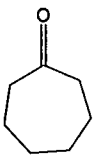
2-acetyl cyclopentanone



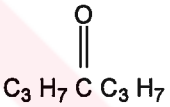
4-ethyl cyclohexanone



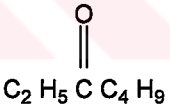
Cycloheptanone



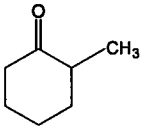
4-heptanone



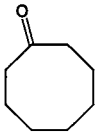
3-heptanone



2-methyl cyclohexanone



Cyclooctanone



2.4. Irradiation Apparatus

For the irradiation , Heraeus Laboraty-UV-Rector system/2 has been used. TW150 model medium pressure mercury lamp has been used as an UV source.

All the materials in the framework of the lamp are made of pyrex except the outer case is made borosilicate.

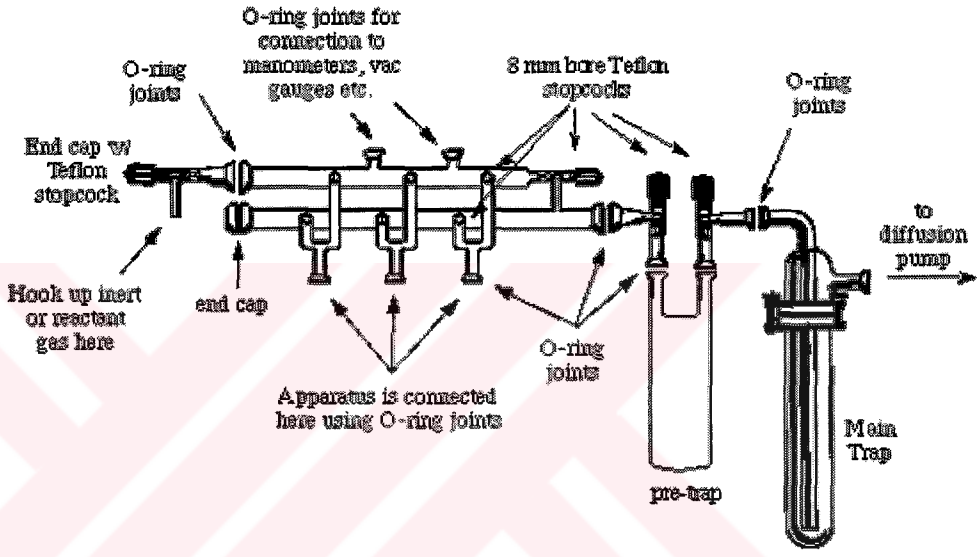


Figure 2.4.1 : A typical Schlenk system

2.5. Experimental Procedure

Solvent n-hexane was distilled under nitrogen atmosphere by fractional distillation. And solvent is collected in a schlenk flask.

Figure 2.5.1 : Schlenk type storage flask

All manipulations were made under nitrogen atmosphere. Necessary amount of $W(CO)_6$ (respect to keton/$W(CO)_6$ ratio that 1/5) was taken and dissolved in 150 mL solvent (n-hexan) with magnetic stirrer. When dissolution is completed, necessary amount of cyclicketon was taken and added to reactor that filled with solution of n-hexane and $W(CO)_6$. At the same time UV lamb was turned on and irradiation was started. After that in every 15 minutes, IR of the solution was taken to follow the reaction.

In the first few minutes, color of the solution turned into yellow from colorless which provides the formation of the pentacarbonyl derivatives of tungsten.

After 30 minutes of irradiation, 1 mL of CCl_4 was added to solution. Color of the solution turned into green and small precipitates were observed. And then , irradiation was continued for 30 minute more.

After one hour of irradiation, it was stopped. The green-blue solution was kept for a day and again IR was taken. Solution is kept for further analysis with GC-MS in the dark.

3. RESULTS

3.1. 3-methylcyclohexanone

At the beginning of the irradiation, the color of the solution was yellow. This color got intense by time, and after 15 minute the first IR was taken.Three main peaks, 2075.03cm^{-1}, 1982.46cm^{-1}, 1935.22cm^{-1}, 1909.18 cm^{-1} ,were observed in IR spectra. The peak at 1982.46 cm-1 corresponds to $W(CO)_6$, and the intensity of this peak decreases by the time(Figure 3.1.1). At the 30th minute, IR was taken again and CCl_4 was added to the solution. The color of the solution started to become green to yellow and precipitation was observed. IR was taken at 45th and 60th minute. The Color of the solution became dark green-blue. Irradiation was stopped and the solution was kept for one week and IR was taken again. The only remaining peak was the peak of $W(CO)_6$ at 1982.46 cm^{-1} which corresponds to excess $W(CO)_6$.

GC studies were done for the solution obtained above (Figure 3.1.2). And it shows that there maybe the product as we wish in the solution. So mass spectra was taken for this solution (Figure 3.1.3). It gives the similar peaks as the product we expected.

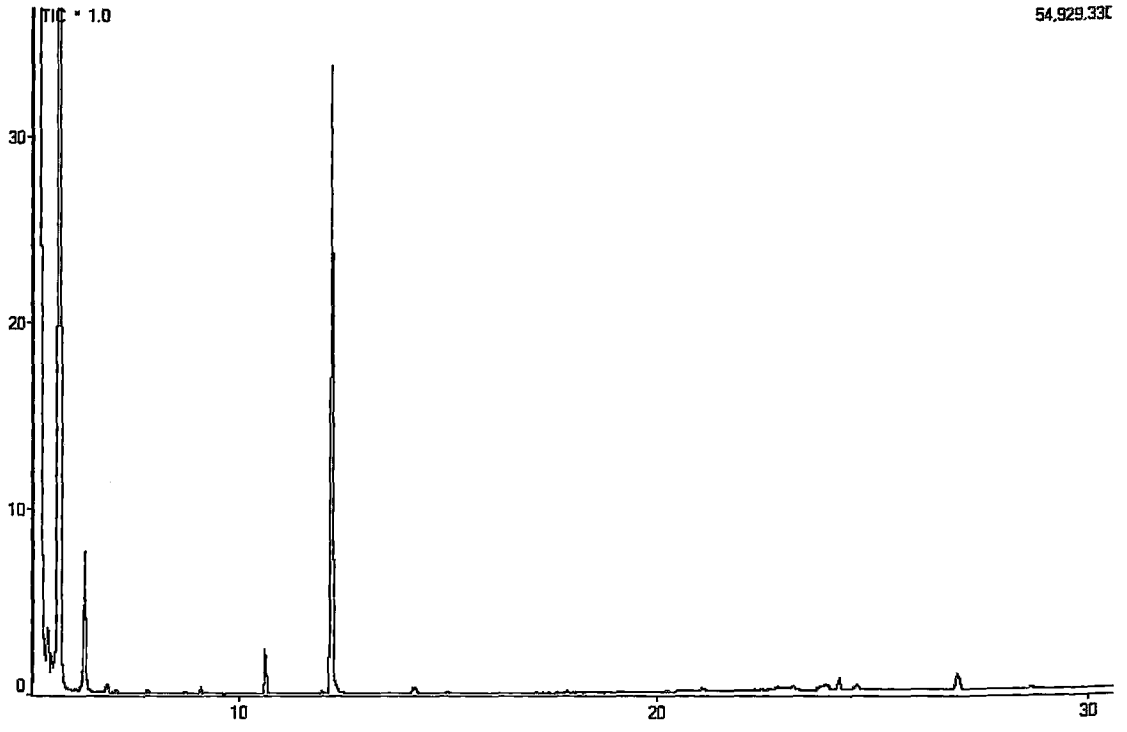


Figure 3.1.2: GC spectrum for 3-methylcyclohexanone product

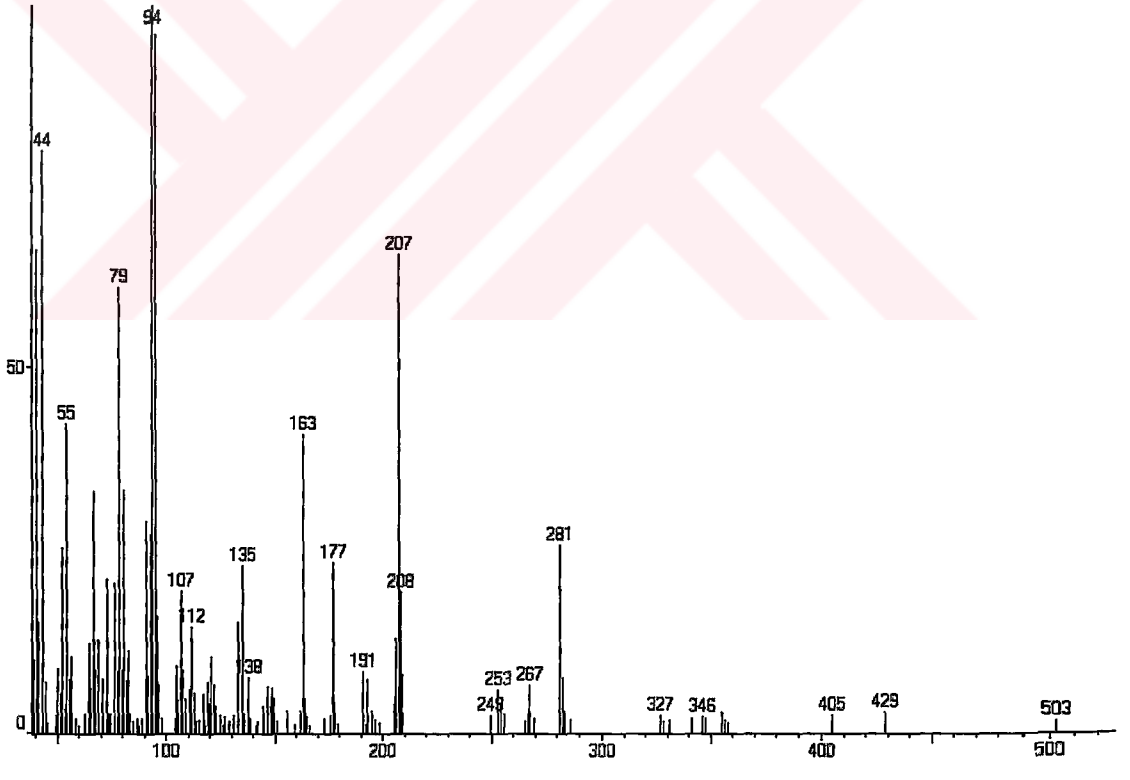


Figure 3.1.3: Mass spectrum for 3-methylcyclohexanone product

3.2. 4-ethylcyclohexanone

In the first 15 minutes, the color of the solution was yellow. The IR spectrum after 15 minutes shows the peaks at 1983.43, 1936.18, 1911.11 cm^{-1}. The intensities of the peaks decrease by time (Figure 3.2.1.).

After 30 minutes of irradiation, Ir was taken and CCl_4 was added to the solution. The color of the solution became green and small precipitates observed. The size of these precipitates was grown by time. IR was taken in 45^{th} minute and the peaks are still had the same wave number but intensities were decreasing. The last IR was taken at 60^{th} minute and green-blue solution was kept for the next day.

1 day later, solution was completely blue and when IR was taken only the peak at ~1983 cm^{-1} was remained.

GC studies for this product gives that the product we expected is formed (Figure 3.2.2.) and mass spectrum for this product was taken to prove.(Figure 3.2.3.)

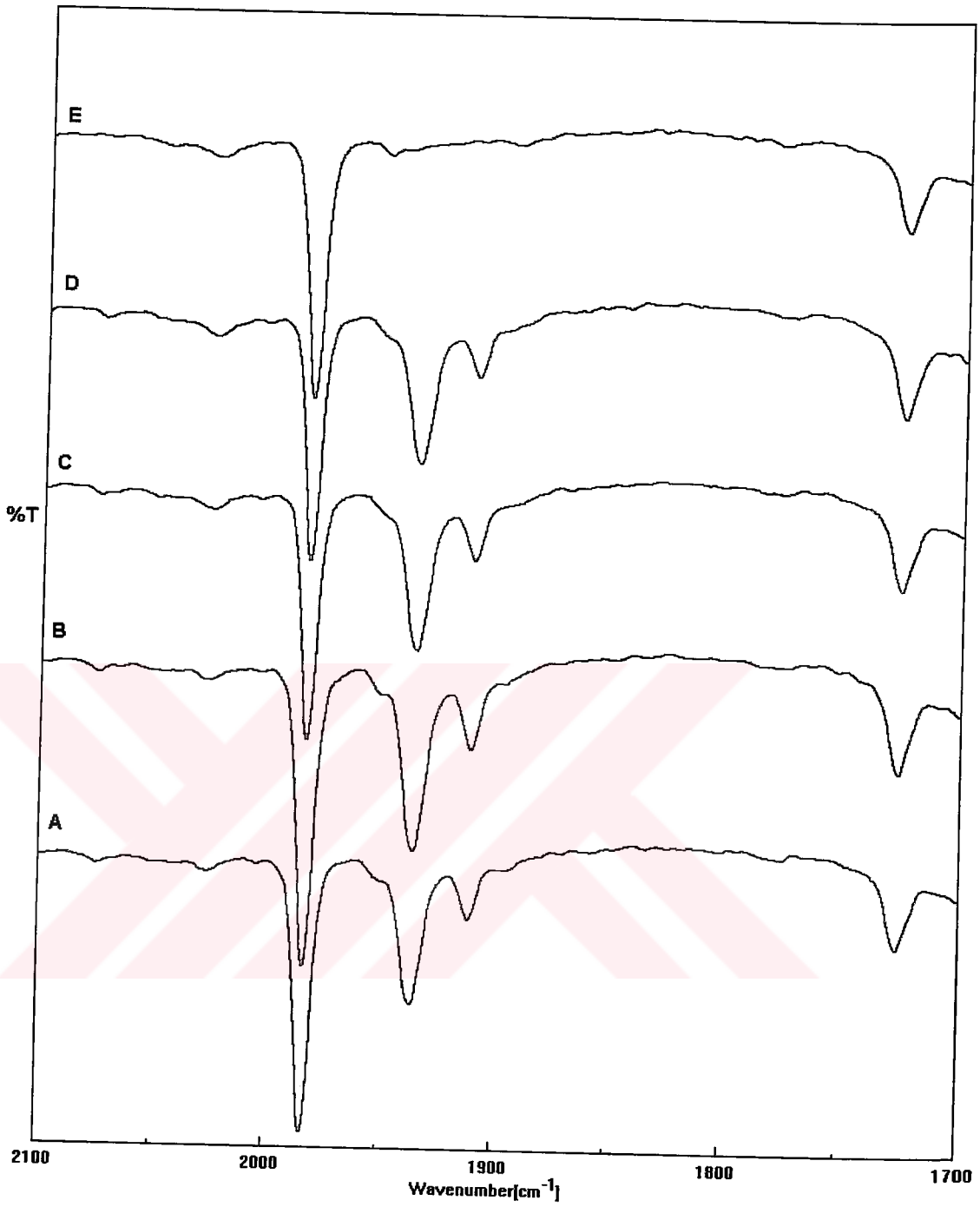


Figure 3.2.1. : The spectral changes in the irradiation done with 4-ethylcyclohexanone in 15 minutes (A), 30 minutes (B), 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

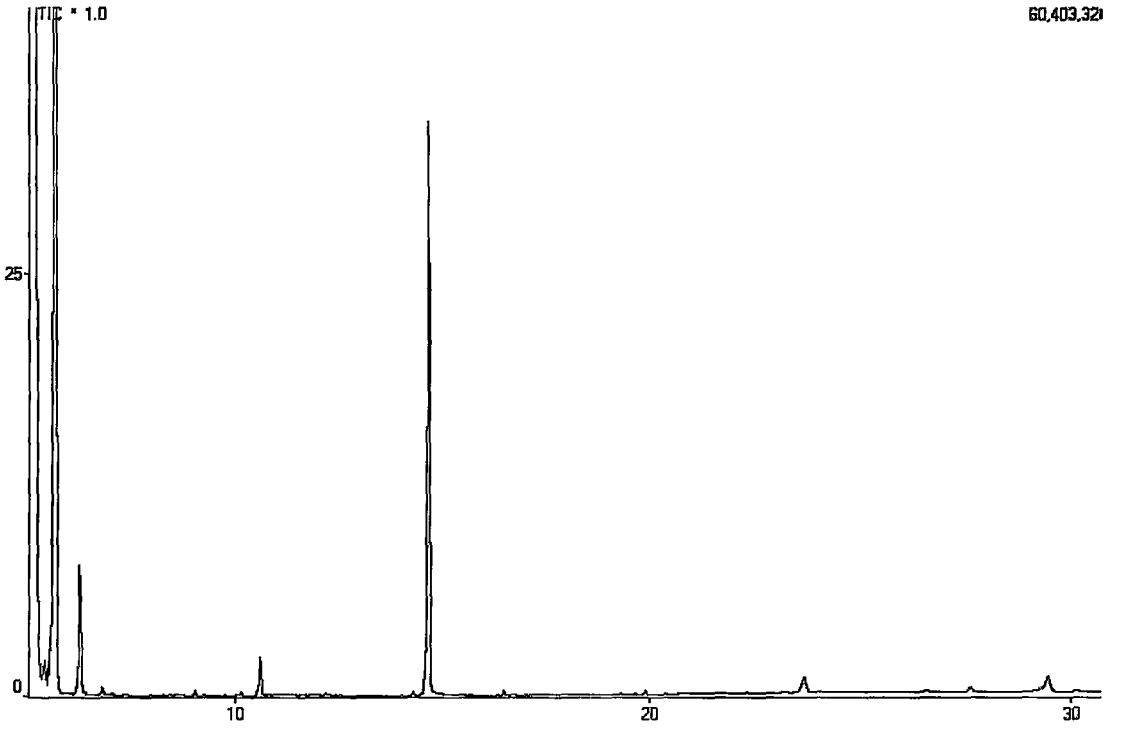


Figure 3.1.2.: GC spectrum for 4-ethylcyclohexanone product

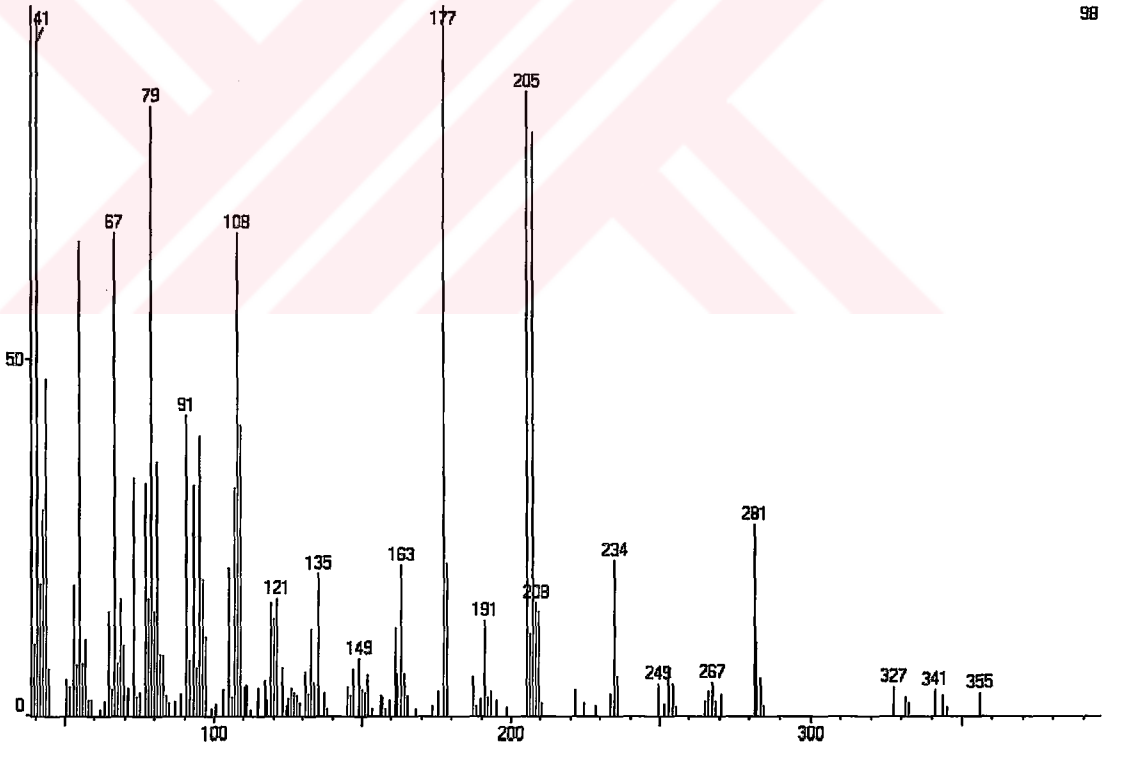


Figure 3.2.3.: Mass Spectrum for 4-ethylcyclohexanone product

3.3. 2-acetylcyclopentanone

At the beginning of the irradiation, the color of the solution was yellow. After 15 minutes of irradiation, IR was taken and the observed peaks were at 2024.89, 1982.46, 1934.25 and 1910.15 cm^{-1}. the color of the solution was yellow. At the 30^{th} minute, IR was taken again and CCl_4 was added. The color of the solution became green when small precipitates were forming. at the 45^{th} and 60^{th} minutes, Ir was taken and blue-green solution was kept for a day. IR was taken next day and it was seen that only peak for $W(CO)_6$ remained (Figure 3.3.1.). The color of the solution turned into completely blue.

GC spectrum shows that there is not product we expected and we do not need to take mass spectrum.

3.4. Cycloheptanone

The first observed color of the solution was yellow. Ir was taken at 15^{th} minute and the peaks at 2075.03, 2024.98, 1983.43, 1935.22, 1911.11 cm^{-1} were observed. The intensities of theses peaks was decreasing by the time (Figure 3.4.1). after 30 minutes irradiation, IR was taken again an CCl4 was added to the solution. Green precipitates were observed. The solution became darker and the color of the solution turned in to blue in next 30 minutes. Ir spectra were taken at 45^{th} and 60^{th} minutes. And solution was kept for a day. IR was taken after a day and the only remaining peak was the peak of $W(CO)_6$'s peak at 1983.43.

It was obtained that there is not the product we expected from the GC analysis so mass spectrum were not taken for this experiment.

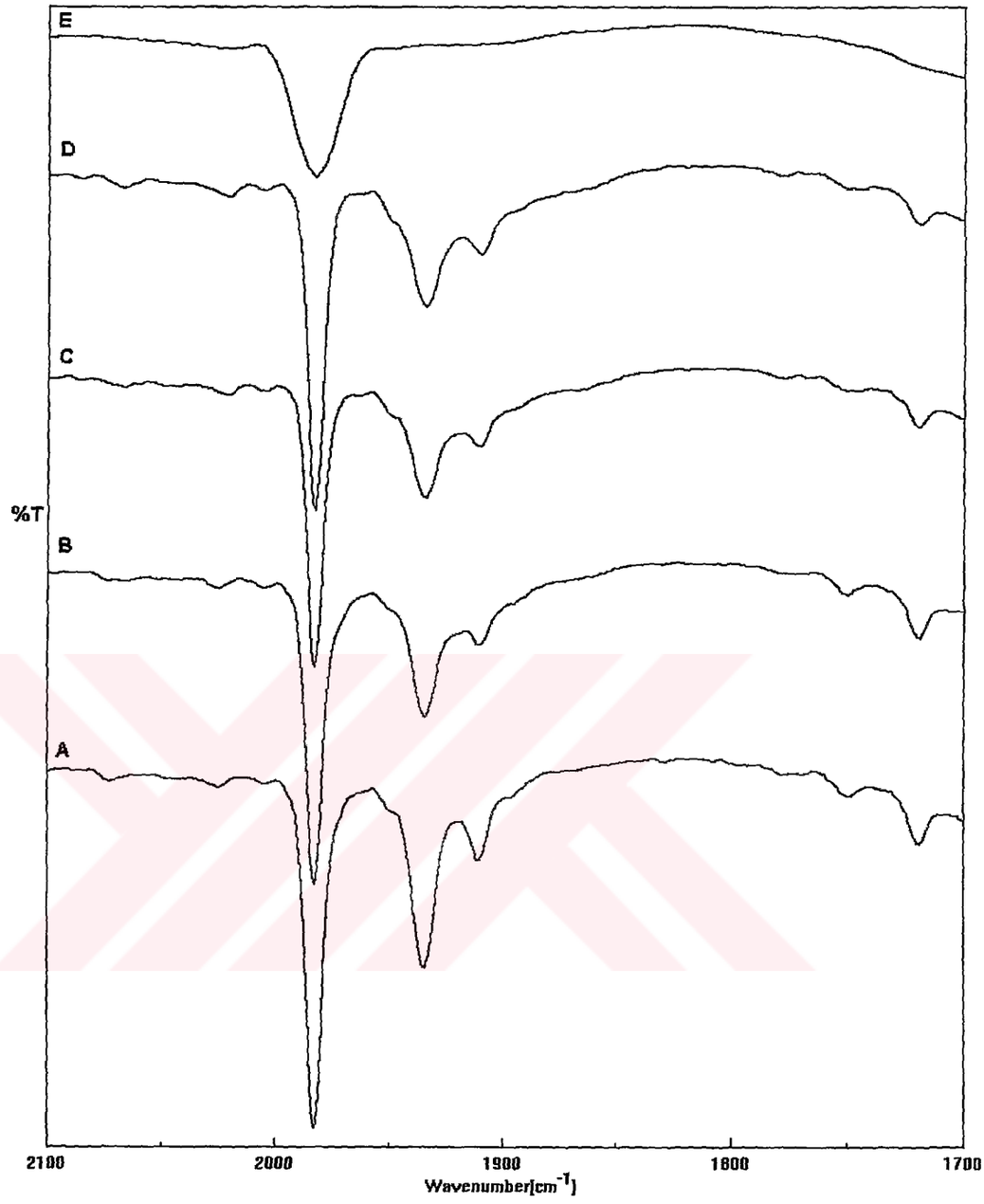


Figure 3.3.1. : The spectral changes in the irradiation done with 2-acetylcyclopentanone in 15 minutes (A), 30 minutes (B), 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

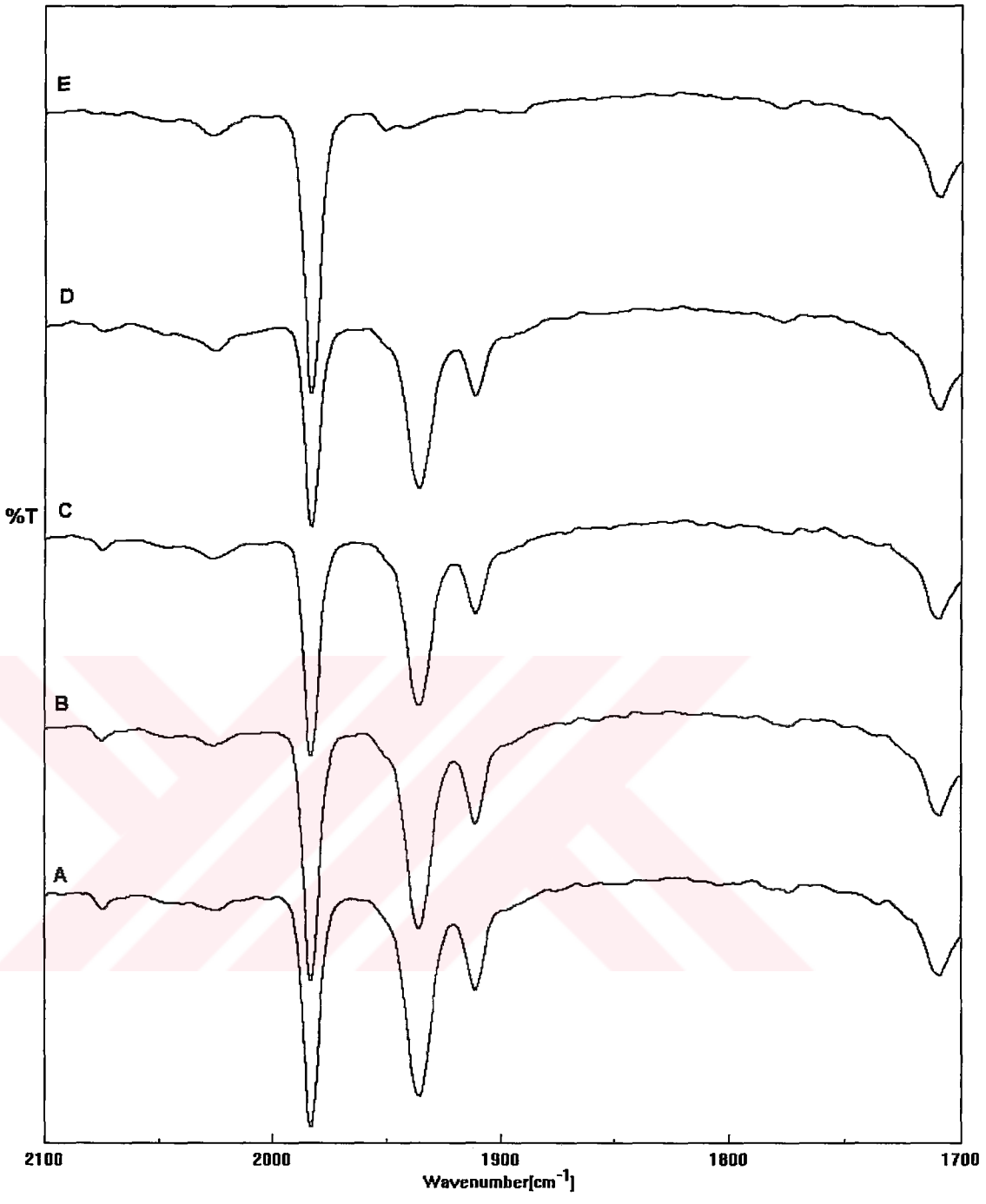


Figure 3.4.1. : The spectral changes in the irradiation done with cycloheptanone in 15 minutes (A), 30 minutes (B), 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

3.5. 4-heptanone

As we can see in the IR spectrum, peaks for this experiment are not intense as other cyclic ketones. Two main peaks were obtained at 1982.46 and 1940.04 cm^{-1} in the first IR at 15^{th} minute. The color of the solution was yellow as well. Intensity of the peaks were decreasing by time (Figure 3.5.1.). After taking IR in every 30^{th} minute, CCl_4 was added and color changed into green and small precipitates were observed. At the 45^{th} and 60^{th} minutes, IR was taken and the color of the solution turned into blue and darker at the end of the reaction. The solution kept for nest day to take IR again. The next day IR of the dark blue solution was taken and it was seen that a peak at 1982.46 remained only.

In the GC studies, there was not the product as we expected and no need to take mass spectum of this product.

3.6. 3-heptanone

The results were exactly the same as 4-heptanone's results but the wavenumber of the peaks were a little bit different (Figure 3.6.1.). In the first IR spectrum at 15^{th} minute two main peaks at 1982.46 and 1936.18 cm^{-1} were obtained. After 30^{th} minute CCl_4 was added and color was changed to green and also precipitates were observed. next day, the color was completely changed to blue and one peak at ~1982cm^{-1} was remained at IR spectrum.

GC studies showed that there is not any product we expected, so we did not need to take mass spectrum for this product.

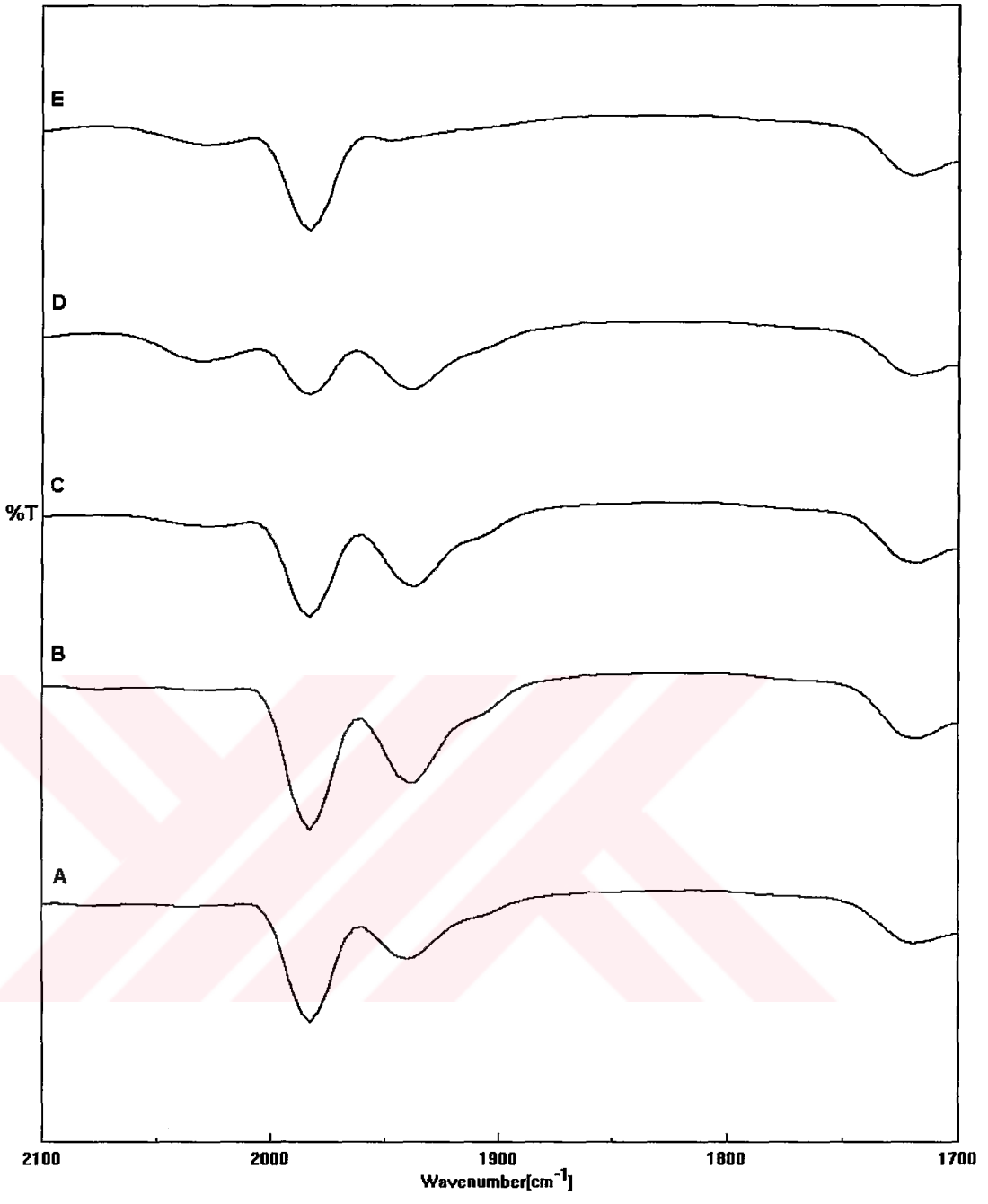


Figure 3.5.1: The spectral changes in the irradiation done with 4-heptanone in 15 minutes (A), 30 minutes (B), and 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

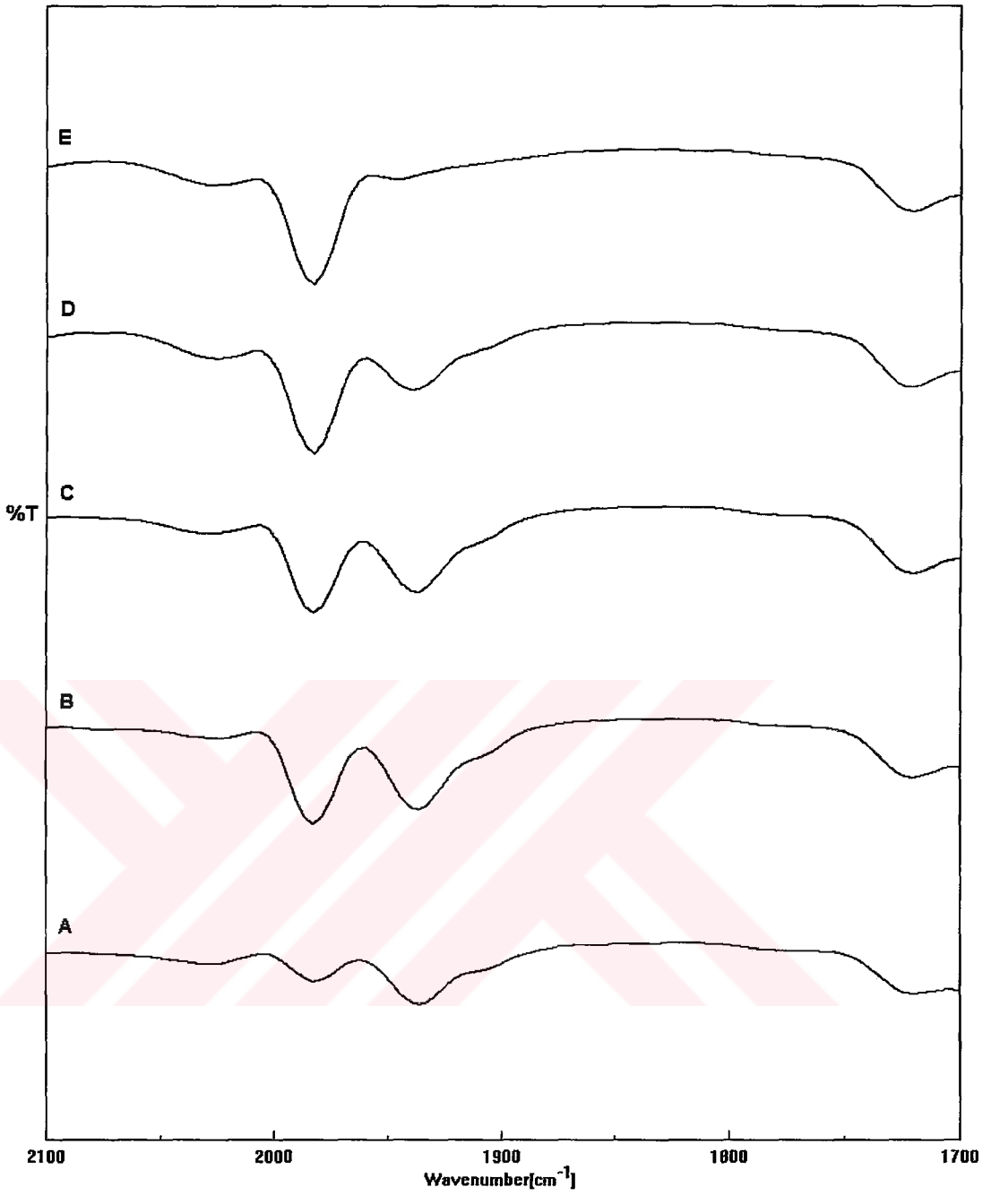


Figure 3.6.1: The spectral changes in the irradiation done with 3-heptanone in 15 minutes (A), 30 minutes (B), and 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

3.7 2-methylcyclohexanone

In the first 15 minutes, the color of the solution was yellow and at the 15th minute Ir was taken. The peaks at 2025.85, 1982.46, 1936.18, 1910.15 cm^{-1} were obtained (Figure 3.7.1). The intensity of the color was getting darker until 30th minute. At the 30th minute, IR was taken again and CCl_4 was added to the solution. The color changed into green instantly and precipitation started. IR was taken at the 45th and 60th minutes and green-blue solution kept for next day. The other day, IR was taken and the only remaining peak was $W(CO)_6$'s peak at ~1982 cm^{-1}.

It was found in GC studies that there is not the product we tried to produce so mass spectrum was not taken.

3.8 Cyclooctanone

After 15 minutes of irradiation, IR was taken and five peaks at 2075.03, 2025.85, 1982.46, 1936.18, 1910.15 cm^{-1} were obtained (Figure 3.8.1.). The color of the solution was light yellow. After taking IR at 30th minute, CCl4 was added and the color started to change into green while small precipitates was forming. The color of the solution was completely blue after 60th minute. The solution kept for the next day. Ir was was taken after one day and the remaining peak was the peak of $W(CO)_6$ at 1982.46 cm^{-1}.

GC spectrum shows that there is not product we expected and we do not need to take mass spectrum.

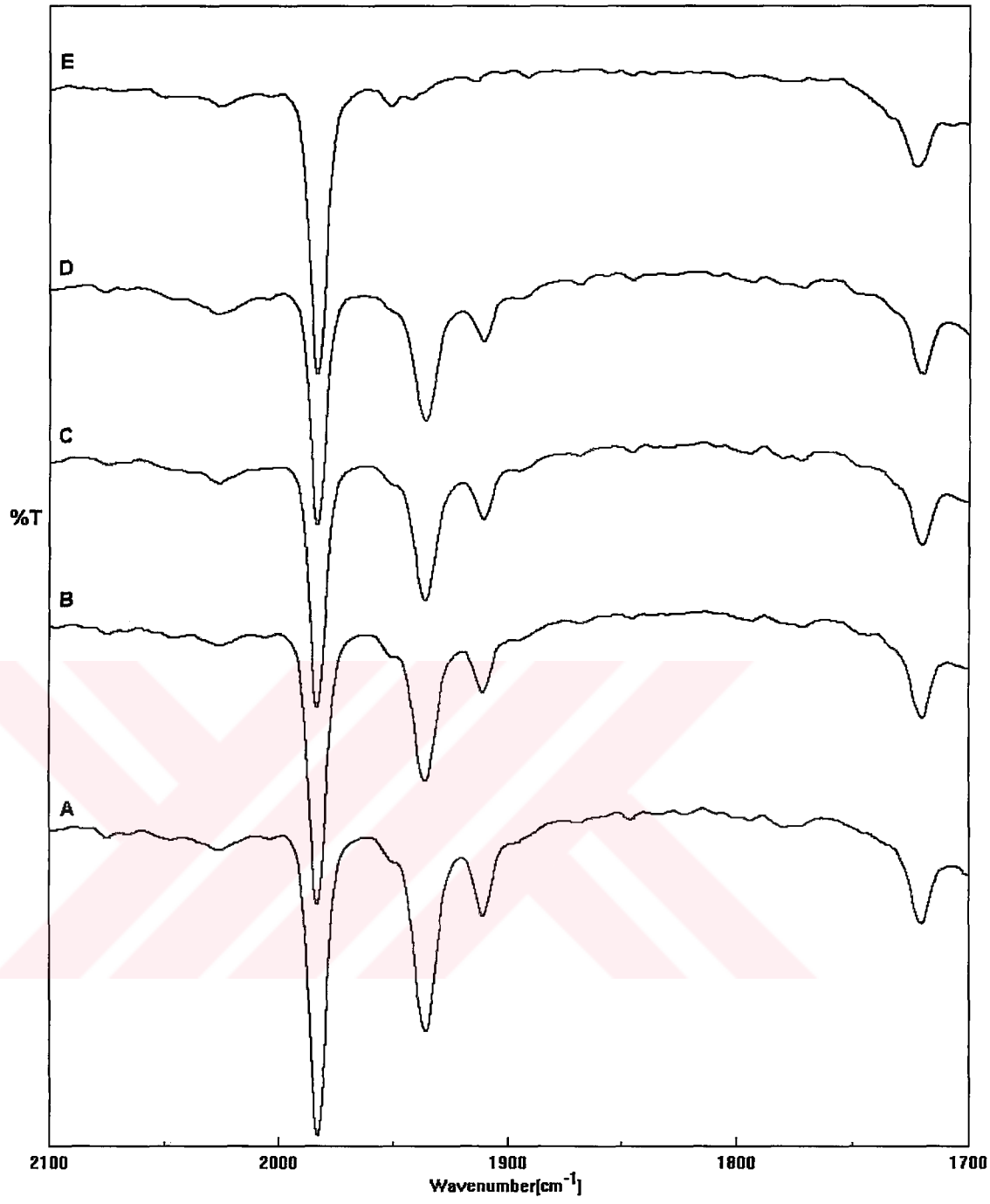


Figure 3.7.1. : The spectral changes in the irradiation done with 2-methylcyclohexanone in 15 minutes (A), 30 minutes (B), 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

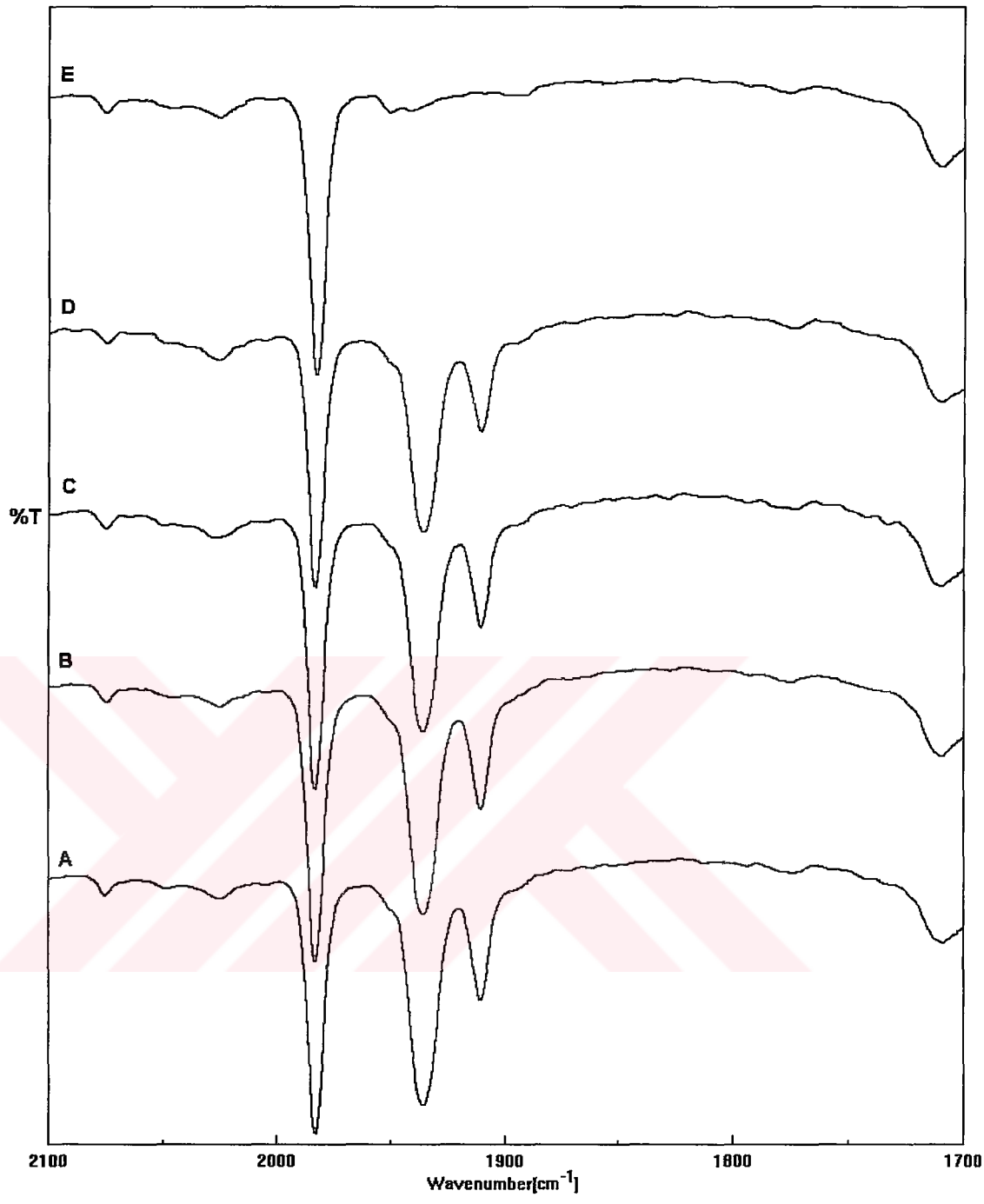
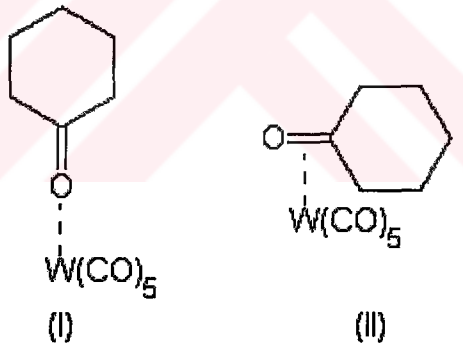


Figure 3.8.1. : The spectral changes in the irradiation done with cyclooctanone in 15 minutes (A), 30 minutes (B), 45 minutes (C), 60 minutes (D) and 1 day (E) time intervals.

4. DISCUSSION

If a keton added to the $W(CO)_6/CCl_4/UV$ system, it has been seen that the intensity of the vibrational frequency of $W(CO)_6$ which has O_h symmetry at 1982 cm^{-1} was decreasing and three different peaks at 2025, 1934 and 1910 cm^{-1} was appeared. In the $W(CO)_5L$ complex which has C_{4v} symmetry, there are $(A_1)^1$, $(A_1)^2$,B_2 and E vibrational modes and they are all IR active and Raman active. In general, $(A_1)^1$ vibration is shifted to higher wavelength with increasing σ donor or π acceptor property of the L which is a weak or not a carbonyl ligand [12]. All these results shows that the coordination of $W(CO)_5$ and keton was occured.

This coordination can be occurring in two ways. The first of them is, coordination may be done on unpaired electrons of oxygen atom(I) and the second way is, coordination may be done on C=O double bond(II).



(I) (II)

Figure 4.1.: Two different ways of bonding of $W(CO)_5$ to a ketone.

But increasing carbon number in the cyclic ketone, there is not any change in the vibrational frequency of the carbonyl group. But normally, if there is a coordination from C=O double bond, a change in frequency of carbonyl group is expected. On the other hands, if there is a coordination from double bond, it is impossible for carbonyl groups in equatorial plane to keep this situation when the number of the ring gets higher.

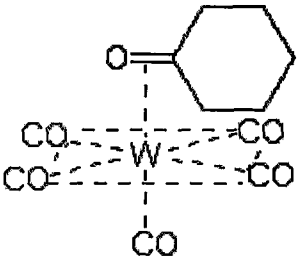
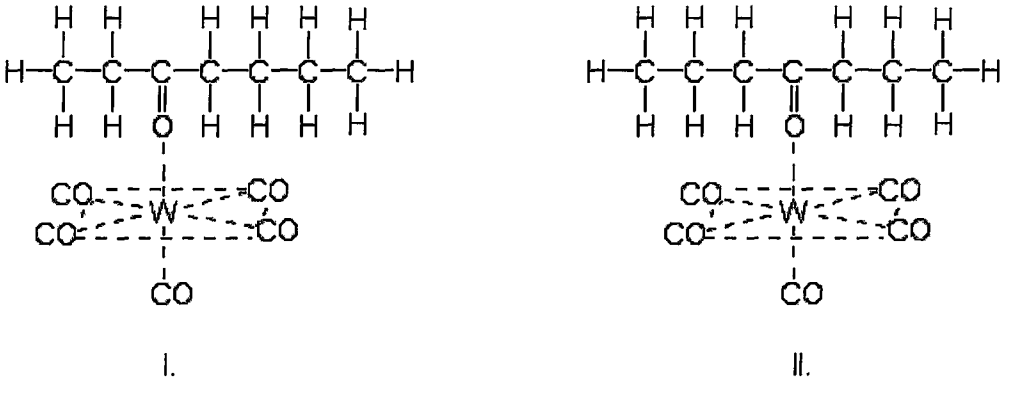


Figure 4.2.: Illustration of equatorial carbonyl groups after bonding on C=O double bond to a ketone.

For these reasons, we can say that coordination can be occurring from the unpaired electrons of oxygen atom.

In the linear ketones, wittig type reaction could not be observed with $W(CO)_6/CCl_4/UV$ system. Since wittig type reaction goes on ketones' α hydrogens, the steric effect becomes very important. The most acceptable reason for this type of ketones does not give a reaction is steric hindrance around the α hydrogen. So this hydrogens can not be substracted from the keton and reaction does not occur. Because, as you can see in the open structure of 3-heptanone (Figure 4.3 (I)) and 4-heptanone (Figure 4.3 (II)), it has a steric hindrance and it makes difficult to $W(CO)_5$ coordination to this ketone.



I. II.

Figure 4.3.: Coordination of $W(CO)_5$ to 3-heptanone and 4-heptanone

For cyclic ketones which have more then 6 membered ring, there is no reaction observed in $W(CO)_6/CCl_4/UV$ system. This may be caused by steric effect as mentioned before.

It has been known that tungsten hexacarbonyl complexes with lack of coordination form pentacarbonyl derivative in various solvents. In CCl_4 solutions, unsaturated $W(CO)_5....CCl_4$ complexes is formed [4]. It was found that the formation of these type of complexes spectroscopically but in the experiments done with $W(CO)_6/CCl_4/UV$ systems, complexes could not be isolated [5].

In the experiments for substituted cyclic ketones, it has been seen that there is no reaction with the ketone which has substituted from α position. This is basically explained by mechanism of aldol condensations.

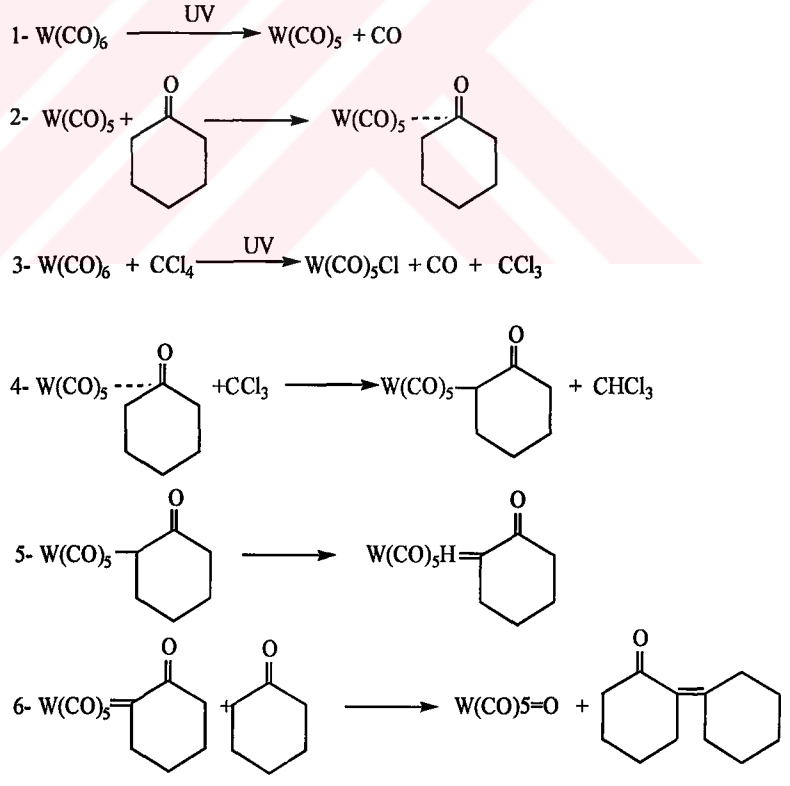


Figure 4.4. : Reaction mechanism of $W(CO)_6$ with ketones in UV/CCl_4 system.

For a ketone to go into self-condensation, there must be empty α position so the ketone may dimerize itself by substracting the α hydrogen. But if there is substituent in the α position it is impossible to substract the substituent and α hydrogen from there. So it could not be observed reaction for 2-methylcyclohexanone and 2-acetylcyclopentanone.

But for the other positions of substituents, e.g. 3-methylcyclohexanone and 4-ethylcyclohexanone, the condensation can occur with $W(CO)_6/CCl_4/UV$ system. Their α hydrogen can easily be served to go self condensation reaction.

Aldol condensations occur in a basic medium. A base takes ketones a hydrogen and an other ketone bonded from α position. Due to cyclic and acyclic ketones have nearly the same acidity in CCl_4, steric effect is more important then acidity for a ketone to go condensation reaction. If a ketone have less crowd around it, it's easier to give product. Increasing branching or ring size causes less difficulty in reaction to occur.

But if we consider these reactions as a radicalic reaction, it must give product for any ketone with independence of ketone size or branching. As we can see from the experiments, there is no product for every ketone especially for big ketones and highly branched ketones like cyclooctanone, cycloheptanone, 2-acetylcyclopentanone,4-heptanone and 3-heptanone. This shows us that the reactions are not radicalic and there is not any radicalic intermediate product of CCl_4.

Instead of radicalic reaction, we can consider about other coordination types of tungsten with seven ligands. It has been known that tungsten can

make WL_7 type coordinations [17]. So we can think that tungsten can coordinate to ketone from oxygen and coordinate to CCl_4.

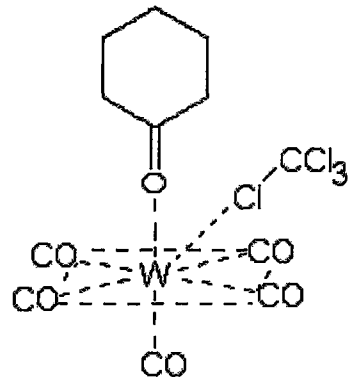


Figure 4.5.: Coordination of $W(CO)_5$ with CCl_4 and a ketone

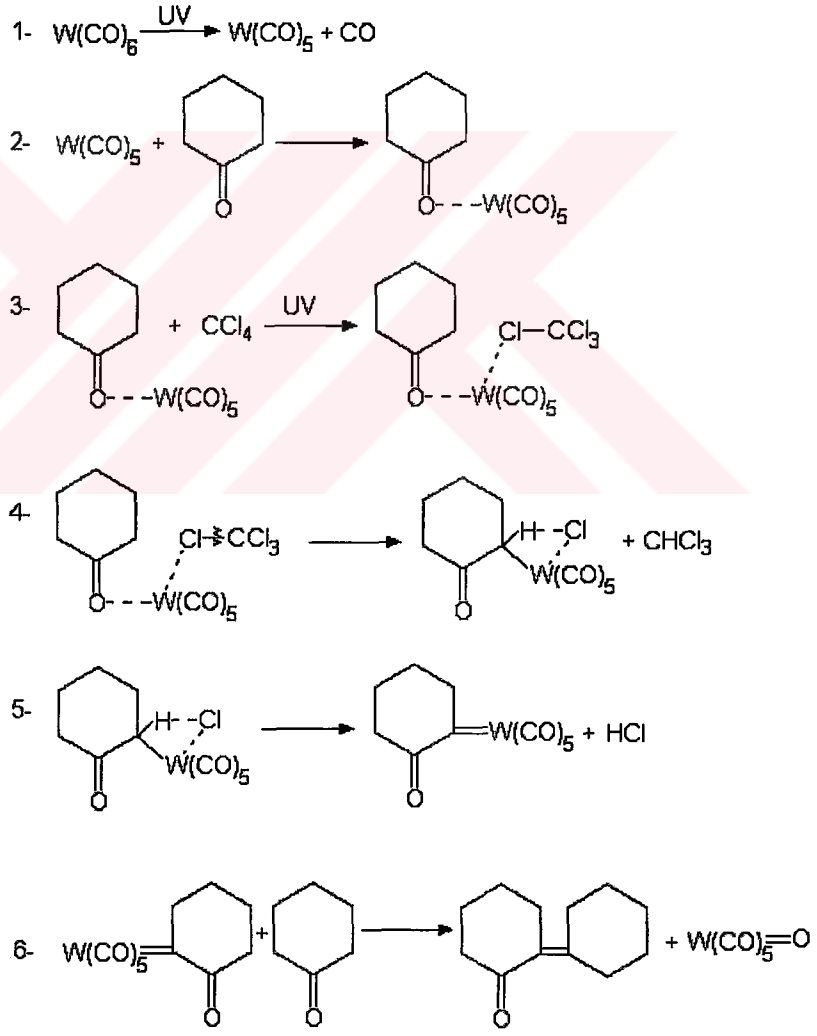


Figure 4.6 : A new mechanism of $W(CO)_6$ with ketones in UV/CCl_4 system

The proposed mechanism for this type of coordination is given in Figure 4.6

As shown in Figure 4.6, there is no any radicalic product of $W(CO)_5$ and CCl_4. Instead of the mechanism given before (Figure 4.4), there is a coordination of $W(CO)_5$ with 7 ligands as given in Figure 4.5. At the step 4^{th} there is a coordination of CCl_4 to $W(CO)_5$ and this is followed by the cleavage of $Cl\text{-}Cl_3$ (step 5) and substracting of HCl (step 6) to produce metal-carbene. This is a new mechanism for aldol condensations of ketone in $W(CO)_6/CCl_4$/UV system.

5. CONCLUSION

In these study condensation reactions of linear, cyclic and substituted cyclic ketones in $W(CO)_6/CCl_4/UV$ catalyst system were studied.

It was found that every ketone coordinate with tungsten hexacarbonly from its unpaired electrons of oxygen atom.

Linear ketones ,3-heptanone and 4-heptanone, did not give any aldol condensation product due to steric effect of ketone.

From the experiments done with cyclic ketones, cycloheptanone and cyclooctanone, it was found that there is no condensation product. It is probably caused by size of ketone. Bigger ring size causes higher steric effect.

For the substituted cyclic ketones, it was found that while 3-methyl cyclohexanone and 4-ethylcyclohexanone give condensation product, 2-ethylcyclohexanone and 2-acetylcyclopentanone did not give product. The reason of this should be the substituent at the ketones α carbon. In 2-methylcyclohexanone and 2-acetylcyclopentanone, due to filled α carbon, the condensation could not be occurred. Otherwise, 3-methylcyclohexanone and 4-ethlycyclohexanone have not any substituent at α carbon and they can give product.

6. REFERENCES

[1] Werder Irwins, Organic sythesis via metal carbonyls, Interscience Publishers, Vol.1, 1968

[2] Herndan James W., The chemistry of the carbon-transition metal double and triple bond: annual survey covers the year 1997, Coordination Chemistry Reviews, 181, 177-242,1999

[3] Casey,C.P.and Burkhardt, T.J., Reactions of (Diphenylcarbene) penta carbonyl tungsten(O) with Alkenes, Role of metal –Carbene Complexes in Cyclopropanation and Olefin Metathesis Reactions, J.Am. Chem. Soc., 6, 7808-9, 1974

[4] Szymanska-Buzar T., J. of Mol. Catal., v48, 43, 1988

[5] Schilder P G. M., Stufkens D. J., Oskam A. And Mol J.C., Metathesis of 2-pentene with the W(CO)6/CCl4/UV system, Role and Physical Properties of the Photogenerated Precipitate, J. Organometall. Chem., 426 ,351-359. 1992

[6] Herisson J. L. and Chauvin Y., Makromol. Chem., 141, 161, 1970.

[7] Bozkurt Ç., Tekin H.N., Imamoglu Y., The formation and structure of the active carbene in the photochemical metathesis reactions, Hacettepe Bulletin Of Natural Sciences And Engineering, volume 24 series A and C, 1995

[8] Bozkurt Ç., Aldol-type condensation reactions of cyclic ketones by the $W(CO)_6/CCl_4$/UV system, Journal Of Organometallic Chemistry 603, 252-255, 2000

[9] Spessard O. Gary, Miessler L. Gary, Organometallic Chemistry, Patience-Hall, pp 61,1997

[10] Yılmaz F., M.S. Thesis, Abant Izzet Baysal University,Bolu, 2001

[11] Journal Of Chemical Education, Volume 60, Number 10, 1983

[12] Braterman P. S., Metal Carbonyl SpectraAcademic Press,1975

[13] Silverman Richard B. and Olofson R. A., The Oxidation of tungsten carbonyl in carbon tetrachloride, Chemical Communications, 1313, 1968

[14] Shul'pin G. B. And Druzhinina A. N., Oxidation of saturated hydrocarbons by air in acetonitrile in the presence of molybdenum or tungsten carbonyls during light irradiation, Petrol Chem. Vol. 33, No. 3, pp. 247-251, 1993

[15] Blatt A. H., Adams R., Organic Reactions, Volume 16, pp 19-21

[16] Şilikçi Ö. Y., M.S. Thesis, Abant Izzet Baysal University, Bolu, 2000

[17] Wender & Pino,Organic systhesis of metal carbonyls, Interscience publishers, pp.222, 1968