PALLADIUM CATALYSED OXIDATION OF α-OLEFINS TO KETONES

BY

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DECLARATION

I hereby certify that this research is the result of my own investigation which has not already been accepted in substance for any degree and is not being submitted in candidature for any other degree.

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This thesis is dedicated to the memory of my brother
Mfanufikile (Mafiki) Wilfred Khuzwayo (1977-1993)
who was denied the opportunity to realise his own potential.

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ABBREVIATIONS

SYMBOL	DEFINITION
AIDS	Acquired Immune Defiency Syndrome
aq.	aqueous
atm	atmosphere(s)
d	doublet
DMF	N,N-dimethylformamide
EI	electron ionisation
g	grams
GC-MS	Gas Chromatography Mass Spectroscopy
h	hours
HIV	Human Immunodefiency Virus
K	rate constants
m	multiplet
m^3	ubic metre
M	molar
M	metal
ml	millilitre
min.	minutes
mol (mmol)	moles (millimoles)
NMR	nuclear magnetic resonance
p	*para*
Ph	phenyl
ppm	parts per million
q	quartet

R	alkyl / carbon based group
R.T.	Room Temperature
RX	alkyl halide
s	singlet
sat.	saturated
sec.	seconds
sec	secondary
t	*tert* (tertiary)
t	triplet
T-cells	T lymphocytes (thymus)
THF	tetrahydrofuran
TMS	tetramethylsilane / trimethylsilyl

SUMMARY

The aim of this research project was to investigate the oxidation reactions of olefins to ketones. Initial studies revolved around the oxidation reactions of terminal olefins to symmetrical dialkyl ketones. The inability to isolate pure products, and the consumption of large amounts of the expensive palladium catalyst for each run as well as the extremely low yields that resulted from these oxidation reactions, made it difficult to thoroughly investigate this oxidation system. It was then decided to embark on the investigation of oxidation reactions of α-olefins to methyl ketones. For these studies, six terminal olefins were oxidised to methyl ketones employing seven different oxidation reactions.

One of the most important and pioneering reactions in this field is the system employing $PdCl_2$ / $CuCl_2$ / O_2 for the oxidation of terminal olefins to methyl ketones, namely the Wacker oxidation reaction. Experimental results, however, indicated that high product contamination from by-products resulted from these oxidation reactions despite the fairly good yields of product from the Wacker oxidation system.

Some reaction systems that have been developed from the Wacker oxidation system were also investigated. The oxidation system employing $PdCl_2$ / *p*-benzoquinone for the oxidation of terminal olefins to ketones was studied. The oxidation reactions resulted in incomplete oxidation with higher olefins (1-decene, 1-nonene and 1-octene), and complete oxidation of lower olefins (1-heptene, 1-hexene and 1-pentene) under the same reaction conditions. The products from lower olefins oxidised under these reaction conditions were pure and high yielding.

Another system that proved efficient both with feasibility and good yields of products was the oxidation system employing $Pd(OAc)_2$ / H_2O_2 catalyst to oxidise terminal olefins to methyl ketones.

Phase transfer catalysis has been employed in organic chemistry to effect different reactions. In this case two types of phase transfer agents were employed to effect the oxidation of terminal olefins to ketones. The first oxidation system involved the use of a $PdCl_2$ / $CuCl_2$ / O_2 catalyst with a quaternary ammonium salt, cetyltrimethylammonium bromide (CTAB), to govern the course of the reaction. Reasonable yields were obtained, and moderate purity of products was also observed.

The second phase transfer catalysis system employed polyethylene glycol (PEG-200) as a phase transfer agent, and $PdCl_2$ / $CuCl_2$ / O_2 as a catalyst for oxidation of olefins to ketones. This oxidation system resulted in different isomers of a ketone from a terminal olefin. Pure methyl ketones were not isolable from the mixture of methyl and ethyl ketones.

The oxidation reactions of olefins to ketones employing $Pd(OAc)_2$ / p-benzoquinone in combination with electrolysis were also investigated. The unique feature about these reactions was the fact that cyclic olefins could also be oxidised under these conditions. Good yields were obtained, and high product purity was observed.

One of the important oxidation reactions investigated during the project was the reaction that used an alternative metal to the expensive palladium catalyst for the oxidation reactions to ketones. This oxidation system employs $CuCl_2$ / 18-C-6 / acetaldehyde as a catalyst for the oxidation of hydrocarbons to ketones and alcohols. It was discovered during the investigation that olefins can also be used as substrates and

are oxidised to the corresponding ketones. The use of olefins as substrates resulted in higher yields than the hydrocarbon oxidation reactions, and less contamination in the product mixture was also observed.

1. INTRODUCTION

1.1. THE FISCHER TROPSCH PROCESS

1.1.1. History

The preparation of liquid hydrocarbons by the hydrogenation of carbon monoxide on cobalt-based contact masses, under rather severe conditions (100 bar / 300-400°C), was disclosed in 1916 by Badische Anilin and Soda Fabrik.[1] In 1925, as a result of systematic studies carried out at the Kaiser Wilhelm Institut für Kohlenforschung, at Mühlheim / Ruhr, Fischer and Tropsch found that liquid hydrocarbons could be obtained at normal pressures (1 bar) by the interaction at 250-300°C of CO and H_2 on certain iron and cobalt catalysts.[1] This synthesis, known subsequently as the Fischer-Tropsch (F.T.) synthesis, aroused great industrial interest since it constituted an attractive alternative which is the production of liquid hydrocarbons (fuel) from coal.[1]

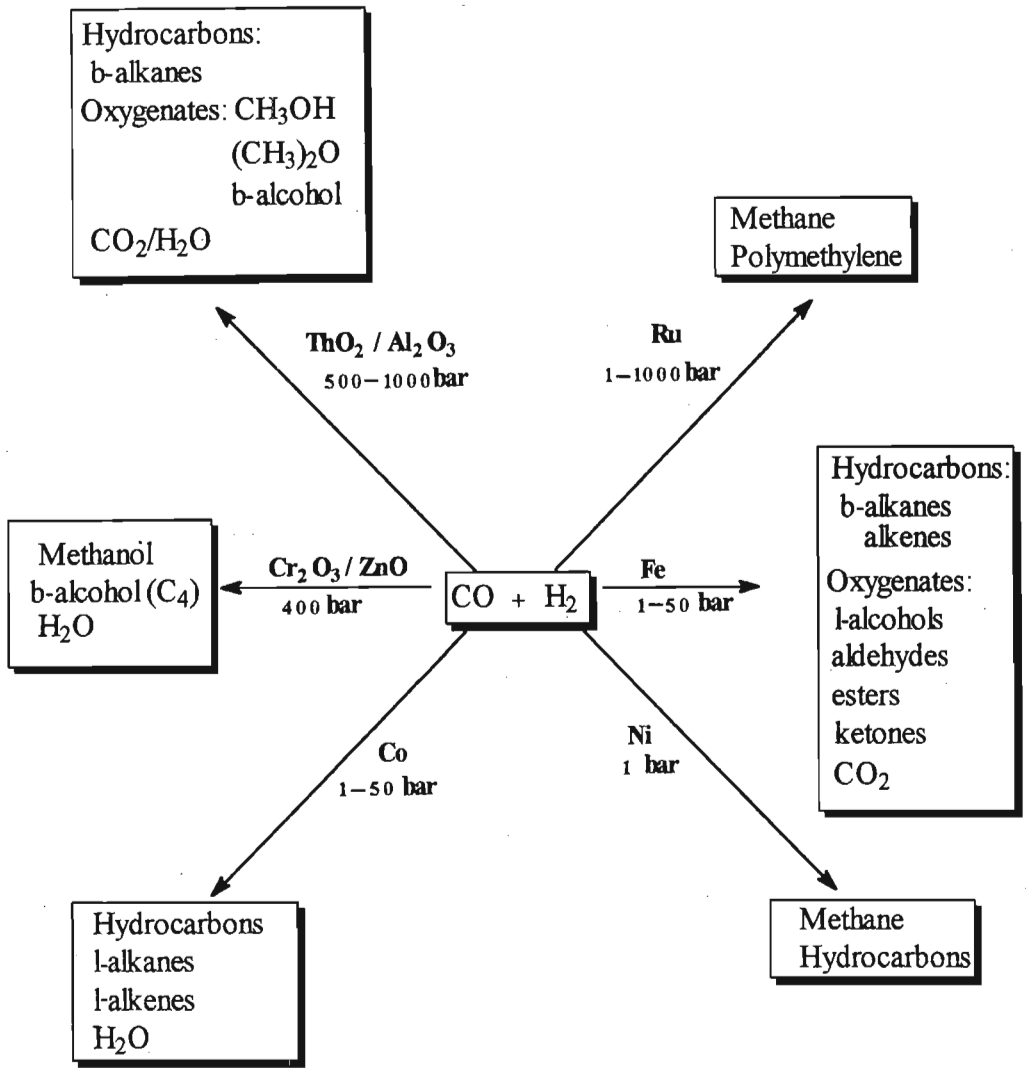
By 1941, nine F.T. plants with a production of 740 000 tons per year were operative in Germany. The shortage of cobalt during the World War II years prompted renewed interest in the iron catalysts and Ruhrchemie-Lurgi developed a medium-pressure industrial process based on iron catalysts.[3,4] The abundance and cheapness of petroleum, and thus of petroleum-derived olefins and hydrocarbon fuels in the 1950s and 1960s, led to the shut down in most countries of these coal-based F.T. synthesis units. A (F.T.) plant constructed in South Africa (Sasol) at about the same time (1954) has continued to produce gasoline, waxes, and oxygenated aliphatics. The Sasol plant gasifies inexpensive coal in Lurgi generators at elevated pressures. After purification, the syngas is sent to entrained and fixed-bed synthesis reactors containing iron catalysts.[2]

The economic uncertainties worldwide of the late 1970s, particularly with respect to the crude oil supplies, stimulated renewed interest in hydrocondensation of CO. The goals set included not only hydrocarbons for fuel (methane, gasoline, kerosene, diesel oil and waxes), but also certain key industrial chemicals (olefins, alcohols, acids and amines).[1,4,5]

1.1.2. Catalysts

The first catalysts used in the German normal and medium pressure F.T. synthesis unit were all derived from cobalt supported on silica.[1] Following World War II, considerable research was conducted in the United States on the iron catalysts.[2] There are appreciable differences in the activities and selectivities of the cobalt and iron catalysts. The iron catalysts tend to be more active, more robust and tend to have long active lives.[1] It must be stressed, however, that the performance of a given catalyst (selectivities, conversions) in production is dependent upon both the conditions in the reactor (temperature, pressure and flow rate) and the design of the reactor (fixed bed, fluidised bed).

Generally speaking, most of the Group VIII metals and certain oxides catalyse the hydrocondensation of carbon monoxide (Scheme 1). To date it is, however, only the first-row transition metals (Fe, Co, Ni) together with ruthenium and thoria (ThO_2), which are sufficiently active in the formation of alkanes, alkenes, alcohols, aldehyde, ketones and esters.[1]



l = linear , b = branched

Scheme 1

The overall products obtained under the usual F.T. synthesis conditions consist of a complex mixture of the following general types of hydrocarbons and oxygenated products: linear and methyl-branched alkanes together with cycloalkanes; linear terminal olefins accompanied by small amounts of *cis/trans* internal olefins; aromatic hydrocarbons, benzene, toluene, xylenes and mesitylenes; linear alcohols, aldehydes, esters and acids as well as ketones,[6,7,8] with carbon dioxide as the usual side product (Scheme 1).[6,9,10] The relative proportions of oxygenated and hydrocarbon products are

a function of the reaction conditions; alkali promoters, low temperatures, high pressures, low residence times and high recycle ratios all favour the formation of oxygenated products.[11,12] The presence of ammonia in the CO / H_2 feedstock leads, in the case of iron catalysts, to the formation of linear homologous primary amines, or at higher temperatures, directly to acetonitrile.[13]

1.1.3. Processes

The scale up of the laboratory experiments on the hydrocondensation of CO to industrial production units represents a major technical achievement;[3-6,14-16] the major problems which had to be solved include the following:

a) The dissipation of the heat occasioned by the exothermicity of the reaction (avoiding hot-spot leading to methanation, formation of volatile metal carbonyls and / or carbon deposition), *i.e.* design of sequential reactor, cooled reactors and / or gas recycle reactor.
b) Steering the reaction, by an adequate control of feedstock composition, gas-recycle, residence time, *etc.*, towards the desired range of hydrocarbon products, *i.e.* design of flexible reactors.
c) Prolonging the life of the catalyst by increasing its mechanical strength and by developing techniques permitting the periodic removal of accummulated hydrocarbon (wax) deposits.
d) Developing adequate product separation processes.
e) Eventual recycling of the catalyst.

The solutions proposed for overcoming the exothermicity of the F.T. synthesis include sequential water-cooled fixed-bed reactors, entrained fluid-bed reactors, fluidized reactors and liquid phase reactors.[3-6,16-18] The first industrial normal-pressure units employed multiple-stage, water cooled, fixed-bed lamellar reactors. The gas loading

(70-1000 m^3 gas / m^3 catalyst / h) and the conversions (70-75%) were controlled in the first reactor and the off-gas, after condensation of the products, was fed into a second reactor. No gas recirculation was employed and the final off-gases were burned as fuel.[3,4] Problems were encountered at the levels of the filling, the cleaning (from accummulated hydrocarbons) and the emptying of the spent catalyst; catalyst life was 3-6 months. The double-tube water-cooled pressure reactors used in the medium pressure F.T. units introduced several improvements. Thus under pressure (7-12 bar) with similar gas loadings (100-110 m^3 / m^3 / h) more liquid products were present in the reactor thus ensuring a better heat elimination and catalyst washing. The use of up to three consecutive reactors with a gas recycle in the first reactor permitted up to 12 and more months operation. This type of reactor was the basis of the Sasol's Arge high-load reactors.[1] These reactors operate at 20-25 bar / 220-250°C with a fresh gas loading of 500-600 m^3 / m^3 / h, a hot gas recycle and at conversions of 65-70%. Five such reactors with 40m^3 catalyst each, permit a daily production of 250 tones of primary C_{2+} products.[4]

Entrained bed reactors have also been used in the synthesis of hydrocarbons: the purified CO / H_2 is passed under pressure through the catalyst at 315-340°C and then into a settling reactor. The catalyst passes continuously between hot reaction and cooling zones and an intermediate settling chamber seperates hot gases and catalyst; the hot gases are cooled to condense out products (hydrocarbons and H_2O plus oxygenates). The final gases may be recycled to the reactor either directly or *via* a gas reforming unit; alternatively it can be used as a fuel.[4-6,18] The turbulent conditions of the process necessitates catalysts possessing high mechanical strength; thus alkali and copper promoted fused iron contact masses are usually employed.[4]

The technology as well as the catalyst used to effect the hydrocondensation of carbon monoxide determine the spectrum of the primary reaction products. Thus the hydrocarbon C number, the olefin content, the proportions of oxygenates and the quantity of methane, may be substantially modified by changing the pressure,

temperature, fresh gas loading and composition, residence time and ratio of fresh to recycled gas. This, together with the ever-present problem referred to earlier, has prompted extensive research in reactor design. Amongst the concepts developed (entrained and fluidized beds),[3-6,14,15,19] that of the liquid phase reactors has aroused particular interest in many countries (*e.g.* Germany, Great Britain, India, Japan and U.S.A.).[1] In the liquid phase F.T. synthesis, the catalyst is suspended in high-boiling F.T. products and the CO / H_2 mixture is blown through this suspension. Heat control is effected by internal water cooling. The flexibility of this three-phase technique permits a better control of the final product distribution, particularly of the olefin content; the formation of 50% of the hydrocarbons in the boiling range 15-150°C containing 86% olefins has been reported.[1] Carbon deposition is substantially reduced, as is coating of the catalyst, with the result that the overall lifetime of the catalyst is increased.[17]

1.1.4. Products, separation and uses

The rich variety of products which may be obtained with the F.T. synthesis imparts a certain specificity to the products isolation techniques associated with each type of process. With cobalt catalysts the products are essentially water and hydrocarbons, whilst with iron contact masses oxygenated compounds are also formed. The early F.T. syntheses were operated to produce liquid fuels and the conditions were set to give long-chain hydrocarbons and waxes.[3,20] The gases leaving the reactors were allowed to cool and condense, separating the water and hydrocarbon layers, and the uncondensed gases were scrubbed with water to remove acids and alcohols and the remainder was either processed (converted to CO), recycled or used as fuel. The hydrocarbon condensate was subjected to distillation as follows: The volatile C_3-C_4 fraction was either used as liquid gas or, if the olefin content was high, processed, by polymerisation, to polymer petrol or carbonylation to oxo products. The C_5-C_{10} fraction, boiling point 40-180°C, after alkali washing to remove the acids, constitutes

the basis for synthetic motor petrol (gasoline) with a low octane number (50-60). The octane number may be increased by additives (anti-knock agents or polymer petrol).[1]

In the case of products from iron catalyst, the octane number can be raised by transforming the alcohol present (on alumina or bauxite catalysts at 400-450°C) to give a new fuel richer in olefins, and aromatics. The fraction boiling at 180-320°C (C_{11}-C_{20}) formed the basis of a diesel fuel with a good octane number. These were also transformed into lubricating oils, detergents (by sulphochlorination and sulphoxidation) and plasticizers. The paraffins boiling above 320°C were processed by vacuum and / or steam distillation techniques and separated into different types of waxes (hard, soft and liquid). These in turn were either used in this form or transformed by oxidation or chlorination.

The aqueous phase obtained with iron-based F.T. processes was subjected to distillation, and certain alcohol (C_1-C_2) or alcohol mixtures (C_5), as well as ketones such as propanone and butanone, were separated.[3,4]

The industrial units can thus be operated to give shorter-chain products containing much higher proportion of olefins and particularly of linear terminal olefins. F.T. products thus become not only a source of fuel, but also a potential source of α-olefins, for plasticizer alcohols (C_6-C_{12}) and detergents alcohols (C_{12}-C_{18}), as well as long-chain carboxylic acids, lighter alcohols and ketones. This, together with the concomitant progress in other areas of catalysis (more active catalysts for the oxo synthesis, zeolites for the selective transformation of alcohols), permit alternative work-up procedures and uses for F.T. products.[1]

1.1.5. Industrial perspectives

Major current industrial objectives include selective CO hydrocondensation syntheses aimed at C_2-C_4 as well as medium-chain olefins suitable for the oxo syntheses of plasticizers (C_6-C_{12}) and detergents (C_{12}-C_{18}).[1] Modification of catalysts and reactors for the production of medium-chain olefins can be effected industrially, the selective synthesis of C_2-C_4 olefins requires the development of new catalysts. Promoters are employed to alter the selectivity of iron-based catalysts and these fall into two main groups:[1]

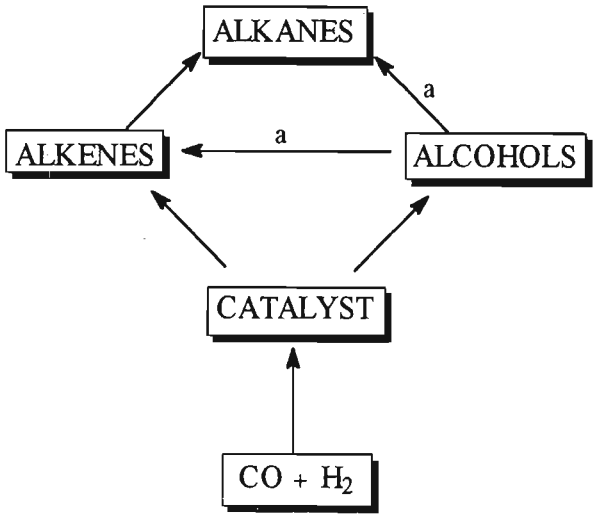
a) Structural promoters, which increase the active surface area, impede recrystallisation and impart added mechanical robustness to the contact mass.

b) Chemical promoters, which include copper and the alkali or alkaline earth metal oxides (K_2O), modify the activity and selectivity of the catalysts. Copper facilitates the processes of pretreatment of the iron contact mass and thus the activity of the catalyst.

The presence of alkali metal oxides tends to alter the product spectrum towards medium and long chain products, and increases the olefin content of the hydrocarbons, and also the alcohol content of the total products.[3-6,14,15] The nature of the cation appears to be important since it has been shown that their activity follows the sequence Rb > K > Na > Li; for economic reasons, K_2CO_3 is used industrially. The alkali promoters influence the texture of the catalyst (surface area and porosity). They increase the heat of chemisorption of CO as well as the quantity of CO adsorbed, whereas they decrease the heat of chemisorption of H_2 and the amount adsorbed.[3-6,14,15,21,22]

1.1.6. Mechanism and Model Reactions

The mechanisms of these hydrocondensation reactions are shrouded in the diversity of the products. This diversity implies that many parallel primary and subsequent reactions occur: CO dissociation, C-C bond formation, C-H bond formation, O-transformation, cyclization and isomerisation, to mention but a few.[1] It is thus illusory to look for a unique universal mechanism, although certain underlying principles may be common to all these syntheses. There is still some uncertainty concerning the primary reaction products in the F.T. synthesis and, more particularly, the sequence in which they are formed (scheme 2). Thus they could appear sequentially, *i.e.* alcohols, alkanes, alkenes, or they could be formed simultaneously from a common intermediate.[6,14,23-30,]



a = dehydroformylation

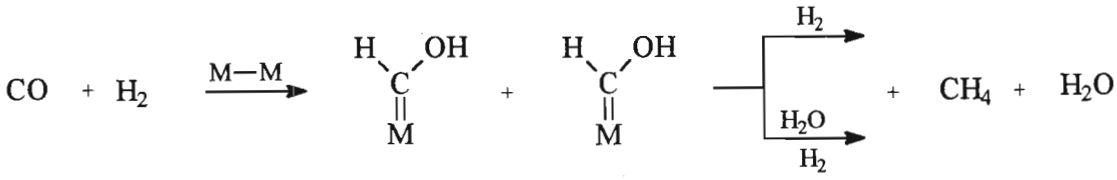
Scheme 2

This intricate synthesis may be likened to certain natural syntheses. Thus Fischer and Tropsch drew an analogy with Nature's Carbohydrate syntheses from CO_2 and H_2O.[31]

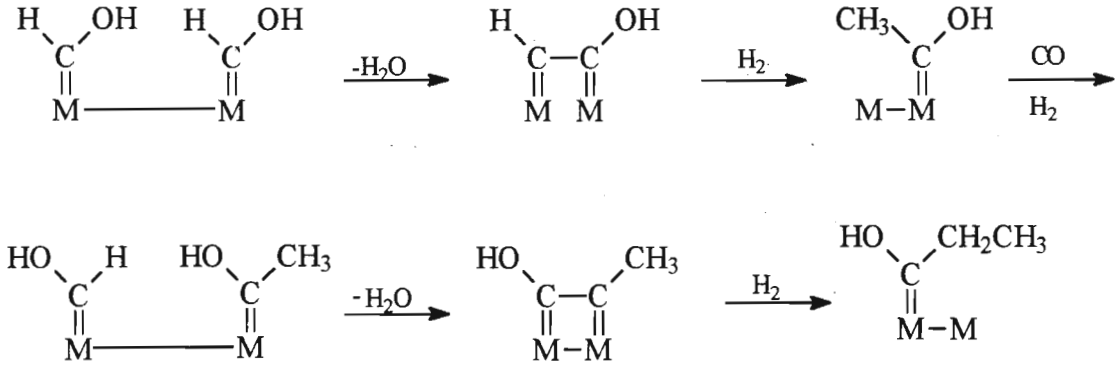
Other authors have proposed that primodial organic matter, including amino acids, could have originated in F.T. synthesis (CO, H_2 (H_2O), NH_3) on meteoritic iron.[32]

Storch, Golumbic and Anderson[6,14] proposed that the initial interaction of CO and H_2 on the catalyst surface led to oxygenated surface species (Schemes 3 and 4).

Chain initiation



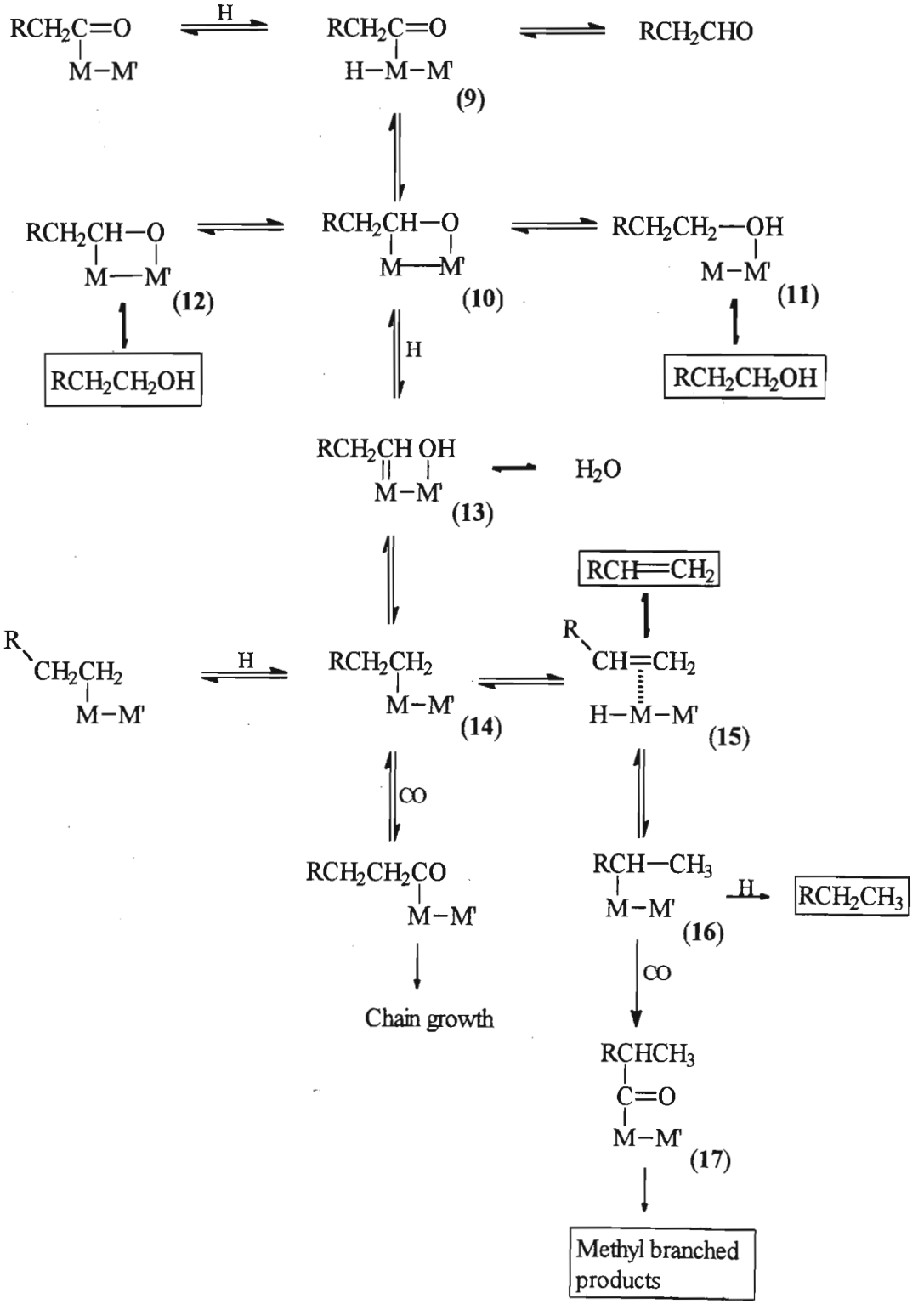
Chain-growth



Scheme 3

Product formation can be rationalised in terms of subsequent transformations of the acyl-metal species by a stepwise H-transfer reaction (Scheme 4).[28] The hydrido-acyl-metal intermediate (**9**) or the equivalent bidentate alkoxide (**10**) are the aldehydes precursors. The alcohols originate from the reduced forms of (**10**), namely (**11**) or the hydroxyalkyl complex (**12**). The intermediates (**10**) can also evolve towards the metal carbene complex (**13**) and hence the alkyl-metal compounds (**14**). The olefins are formed by β-metal hydride elimination in (**14**); the intermediate (η-olefins) metal

hydride (**15**) permits the passage, *via* the isoalkyl and acyl complexes (**16**) and (**17**), from the linear to the branched products. The alkanes result from the hydrogenolysis of the alkyl-metal intermediates or by reductive elimination in the corresponding hydrides. The alkyl-metal intermediates (**14**) and (**16**) ensure, by CO insertion, the chain propagation to homologous linear and branched products.[1]


RCH2C=O
M–M'
H
RCH2C=O
H–M–M'
(9)
RCH2CHO
RCH2CH–O
M—M'
(12)
RCH2CH2OH
RCH2CH–O
M—M'
(10)
RCH2CH2—OH
M–M'
(11)
RCH2CH2OH
H
RCH2CH OH
M–M'
(13)
H2O
RCH=CH2
R
CH2CH2
M–M'
H
RCH2CH2
M–M'
(14)
R
CH=CH2
H–M–M'
(15)
CO
RCH2CH2CO
M–M'
Chain growth
RCH–CH3
M–M'
(16)
H
RCH2CH3
CO
RCHCH3
C=O
M–M'
(17)
Methyl branched products

Scheme 4

In conclusion, the overall industrial objectives in the area of CO hydrocondensation have shifted to finding alternative and selective syntheses of petroleum derived intermediates. Thus, much laboratory research is aimed at the preparation of new catalysts which would permit the direct and selective transformation of CO / H_2 mixtures into olefins (C_2-C_3), linear terminal olefins (C_6-C_{20}), light alcohols (C_1-C_4), oxygenated C_2 and C_3 compounds and eventually, from CO / H_2 / NH_3, mixtures of amines and nitriles. Modification of classical iron-based contact masses and of reaction technology impart considerable flexibility to the F.T. synthesis and permit an accrued selectivity towards light and medium linear terminal olefins.[4-5,17-18,33-34] Increased selectivity towards C_2-C_3 olefins still remains a problem.

The aim of this section was to show the extent of olefin production in the F.T. processes. These olefins are then converted to many different marketable products. This research project concentrated on the production of ketones which are in turn reduced to secondary alcohols. Section 1.3. looks at these different synthesis processes. In order to present the syntheses systems, we need to look at palladium chemistry, as palladium was used as a catalyst for most of these reactions. Section 1.2. looks at the palladium chemistry and its use in organic syntheses.

1.2. INTRODUCTION TO PALLADIUM CHEMISTRY

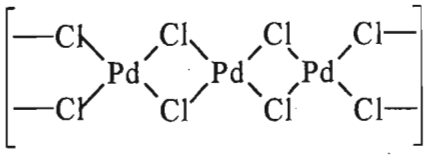
1.2.1. History

Palladium was discovered by W. H. Wollaston, who with S. Tennant, was studying, the refining of platinum from South America ores in 1805.[35] He named it after the small 'planet' Pallas which had been discovered a short time earlier. Palladium is a relatively rare element occurring to the extent of one part in about 10^{13} of the Earth Crust.[36]

Modern palladium chemistry developed very rapidly after the Wacker process had been invented in 1958.[35,37] Palladium-based reagents and catalysts have become indispensable tools for the synthetic organic chemist. Palladium compounds are convenient reagents since they are usually stable and easy to handle. Toxicity is also not a serious problem. On the other hand, palladium is a rather expensive metal with a high atomic weight. Therefore, stoichiometric consumption of palladium compounds is only tolerable in a few organic syntheses.[37]

Palladium enjoys two stable oxidation states, the +2 state and the zero-valent state, and it is the facile redox interchange between these two oxidation states which is responsible for the rich reaction chemistry that palladium complexes display. Each oxidation state has its own unique chemistry.[38]

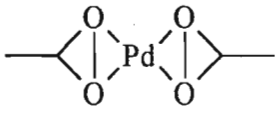
Palladium(II) complexes are electrophilic, and tend to react with electron-rich organic compounds, particularly olefins and arenes. The most common starting material for most palladium complexes is palladium(II) chloride (**18**), $[PdCl_2]_n$, a commercially available red-brown chloro-bridged oligomer, insoluble in most organic solvents.[38]



$[PdCl_2]_n$

(18)

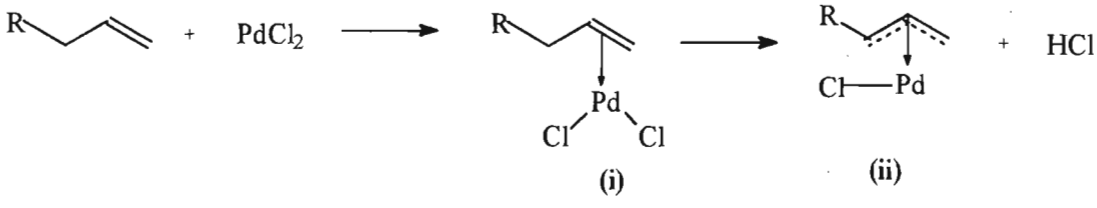
The other commonly used palladium(II) complex is palladium(II) acetate, $Pd(OAc)_2$, again commercially available and soluble in common organic solvents. This salt is prepared by dissolving metallic palladium in hot acetic acid containing a small amount of nitric acid. After evaporation of the solvent, $Pd(OAc)_2$, **(19)** is recrystallized from benzene.[35,38-40]



$[Pd(OAc)_2]$

(19)

Palladium(II) compounds form π-complexes (**i**) with olefins (Scheme 5). The electron density of olefins decreases by coordinating to palladium(II), enabling attack by various nucleophiles on the co-ordination olefin. The attack of nucleophiles with the concomitant formation of a carbon-palladium σ-bond (**ii**) is called a palladation reaction.[44]

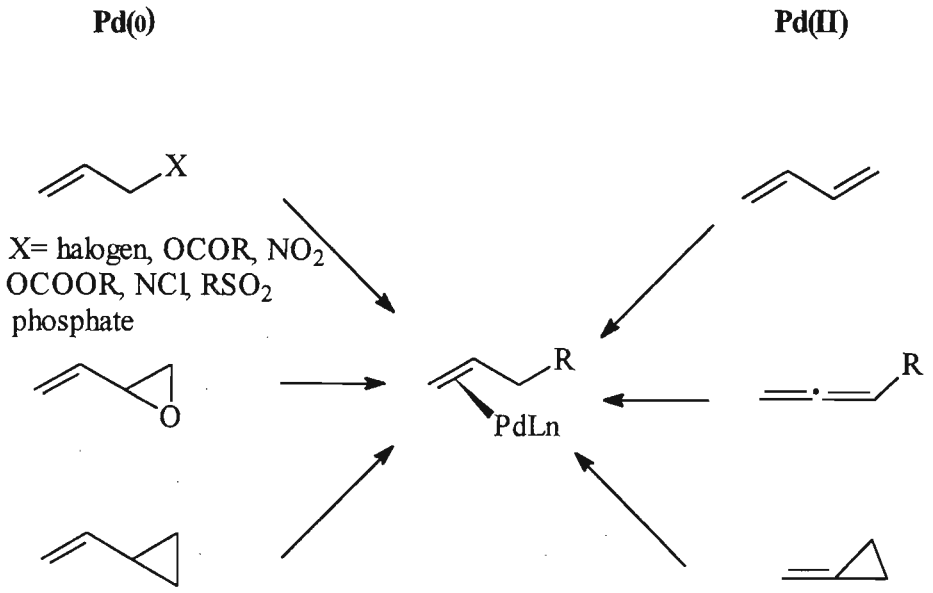


Scheme 5

Palladium(0) complexes are strong nucleophiles and bases, and most commonly are used to catalyse reactions involving organic halides, acetates and triflates. By far the most commonly used palladium(0) complex is $Pd(PPh_3)_4$, 'tetrakis' (triphenylphosphine)palladium(0). This complex is prepared by reacting freshly precipitated palladium oxide with PPh_3 in ethanol.[41-43]

1.2.2. Generation of η^3-palladium intermediates

Palladium(0) complexes catalyse a large range of synthetically important reactions of allylic substrates, which proceed *via* η^3-allyl intermediates. These intermediates are yellow crystalline solids and, in addition to being fairly air-stable and isolable, they can be quite reactive under the appropriate conditions. η^3-or π-Allyl palladium complexes may be easily formed from a variety of substrates containing at least one double bond (Scheme 6).[45]



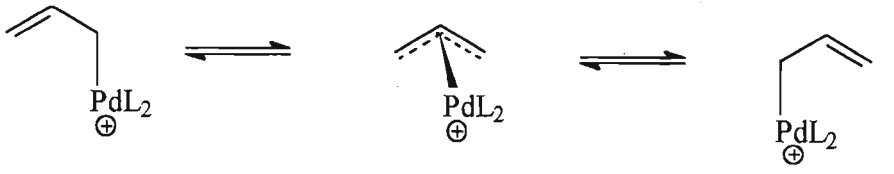
Scheme 6

Depending on the starting material, both palladium(0) and palladium(II) catalysis can occur.[46]

Allyl metal complexes can be made from a range of organic substrates in a number of ways. These include:

1) Oxidative addition of allylic substrate to metal(0) complexes. This is one of the most general syntheses as allylic substrates containing a wide variety of functional groups are tolerated.
2) Insertion of 1,3-dienes into a metal hydride (or metal alkyl)
3) Abstraction of the allylic proton from a π-olefin complex
4) Nucleophilic attack on a 1,3-diene metal complex
5) The reaction of a Grignard allyl compound with transition metal halides.

Many π-allyl systems are not static and undergo a number of dynamic processes, the most common being the π-σ allyl transformation. The wide range of reactivities exhibited by metal-allyl complexes is often attributed to the existence of this facile equilibrium. The π-allyl complex may also occur in equilibrium with its two canonical forms, *i.e.* two enantiomeric σ-allyl complexes (Scheme 7).[45]



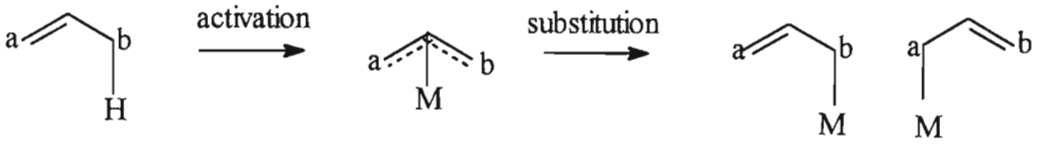
Scheme 7

Historically, η^3-allyl palladium complexes were first isolated over thirty years ago, when they were synthesised by the reaction of dienes with palladium(II) salts.[47]

1.2.3. Reactions of Nucleophiles with η^3-allyl complexes

The formation of carbon-carbon bonds with high selectivity presents a formidable challenge in organic synthesis. In 1965, Tsuji and co-workers [48] reported the reaction of π-allyl palladium chloride with a number of C-based nucleophiles and postulated that this reaction offered a new method of carbon-carbon bond formation.

The reaction of nucleophiles with η^3-allyl complexes may be divided into two categories:
Firstly, those involving nucleophilic attack at the metal centre itself followed by nucleophile migration to the organic ligand. Secondly, those which entail nucleophilic attack at a metal co-ordinated organic ligand. The latter reaction is essential to the rapidly developing field involving the use of transition metals in organic synthesis (Scheme 8).[49]



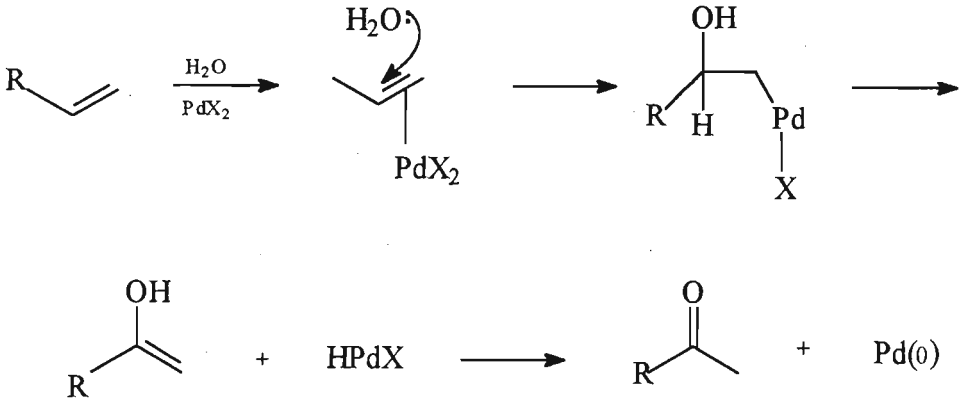
Scheme 8

The allyl-metal intermediate is formed from the olefin in the activated step. This approach is beneficial in that greater selectivity is afforded in the substitution step because the new carbon-carbon bond can be formed at either C(a) or C(b).

1.2.4. Heteroatom Addition to alkenes

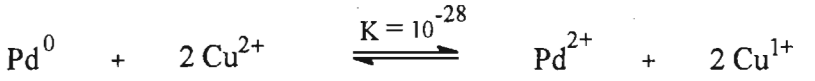
Undersatnding the nature of the conversion of ethylene to acetaldehyde by water in the presence of palladium stimulated many of the applications of organopalladium

chemistry o fine synthesis.[50-55] While the mechanism continued to serve as a contested question, kinetic studies suggesting a *cis* hydroxypalladation,[53] and stereochemical studies suggesting a *trans* hydroxypalladation,[54,55] synthetic applications remained unexplored. The power of this method, which, in part, stems from an unusual high chemoselectivity, has only recently been appreciated. Scheme 9 outlines the essence of the Wacker reaction. The formation of Pd(0) requires an oxidant to make the reaction catalytic. Copper(II) chloride is by far the most common oxidant. When used in conjuction with oxygen, even the copper salt is utilised catalytically. For fine organic synthesis, the most useful appear to be copper(II) chloride,[56-58] benzoquinone,[56,59] hydrogen peroxide and *t*-butyl hydroperoxide.[60]



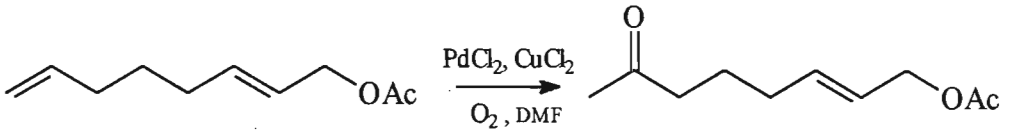
Scheme 9

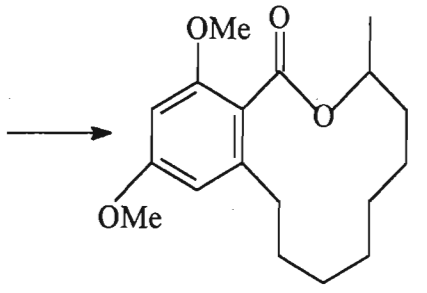
Reoxidation of Pd(0) *in situ* is not always easy. Palladium is more stable as the Pd(0) than as Pd(II). Therefore, the oxidation of Pd(0) with a base metal such as $CuCl_2$ seems to be rather exceptional and somewhat peculiar. A very small equilibrium constant calculated for the oxidation reaction of metallic palladium with free Cu(II) ion suggests the difficulty of oxidising Pd(0) with Cu(II) salts (Scheme 10).[61]



Scheme 10

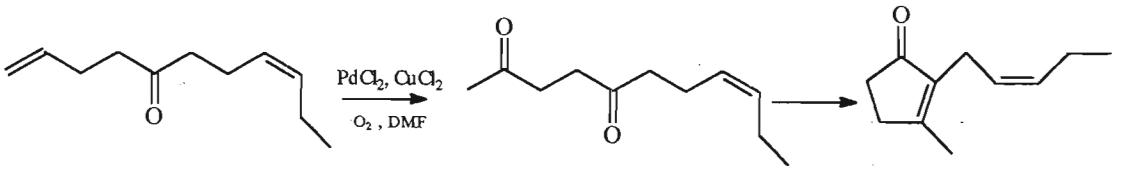
Terminal olefins react selectively in the presence of an internal double bond. The realisation of the power of the method has stimulated numerous applications in the synthesis of natural products in a very short time, some of which are listed below (Schemes 11 and 12).[62]





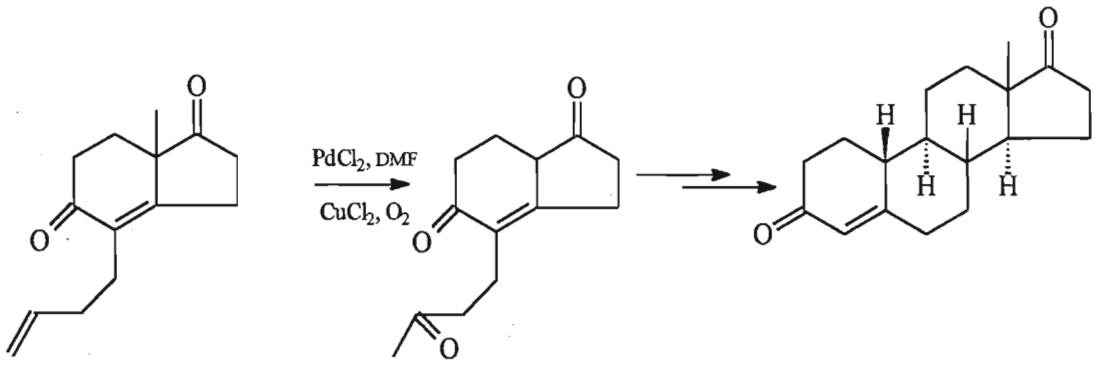
Lasioiplodin

79%



Jasmone

70%

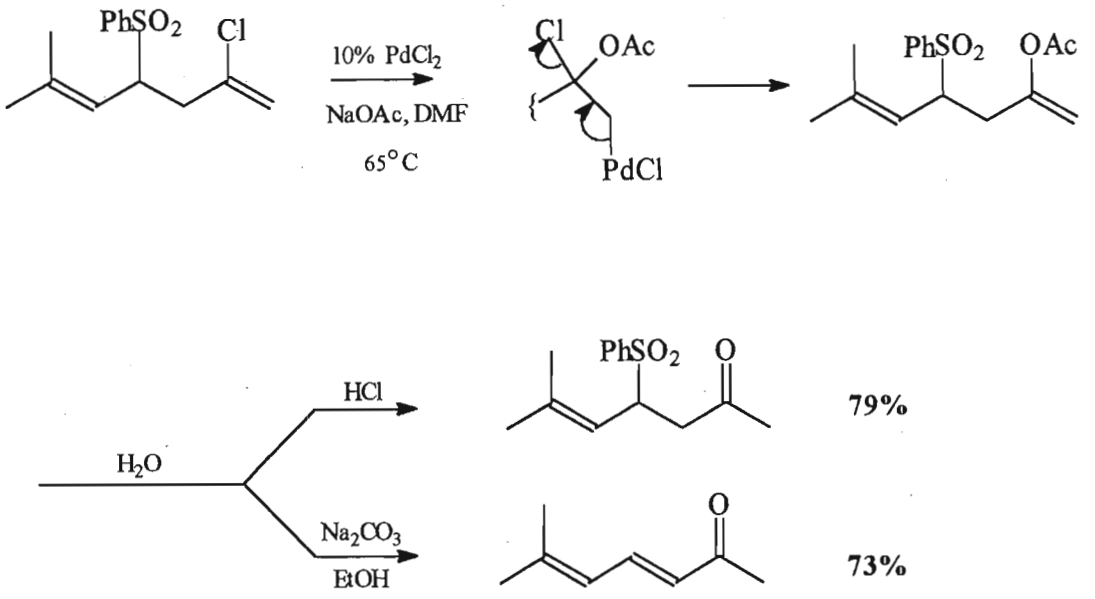


19-Nortestosterone

77%

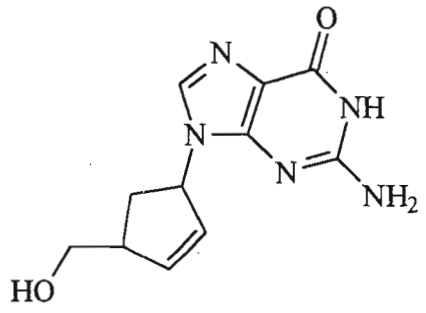
Scheme 11

One of the most promising applications of acetoxypalladation is the exchange reaction of heteroatom substituted alkenes.[63] The direct hydrolysis of vinyl chlorides to ketones previously required harsh acidic conditions. Exchange of the chloride for an acetate produces the vinyl acetate which can liberate the ketone under mild acid or base conditions (Scheme 12).[63]



Scheme 12

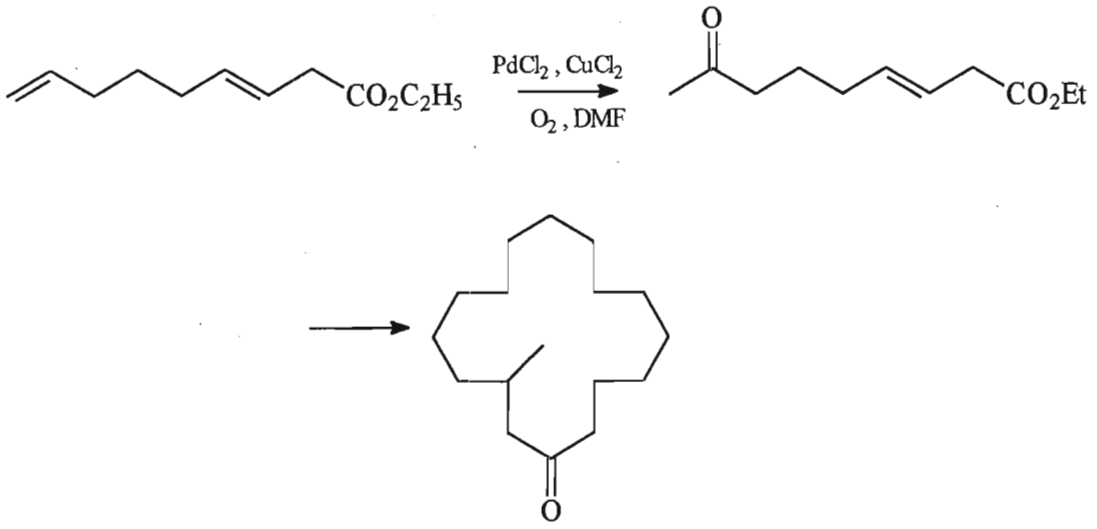
π-Allyl palladium chemistry has found application in many natural products syntheses. Jung and Rhee[64] have successfully employed π-allyl palladation complexes and their chemistry in the synthesis of an anti-viral agent (±)-carbovir (**20**).



(20)

Carbovir is currently being developed as an anti-retro-viral agent in the treatment of AIDS,[65] due to its ability to inhibit the infection and replication of HIV in T-cells at concentrations well below toxic level.[65] This π-allylic chemistry has also made a

tremendous contribution to the perfume industry. Muscone (3-methylcyclopentadecanone) can be synthesised *via* the π-allyl palladium intermediate (Scheme 13). This yellow liquid was previously extracted from the scent gland of the Tibetan musk deer.[66,67]



Muscone

87%

Scheme 13

This short introduction to palladium chemistry serves to ascertain the immense potential of palladium-mediated bond-forming transformations in organic synthesis. Palladium complexes have a very rich organic chemistry and are among the most readily available, easily prepared and easily handled of the transition metal complexes. Their real synthetic utility lies in the wide range of organic transformations promoted by palladium catalysts, and in the specificity and functional group tolerance of most of these processes.

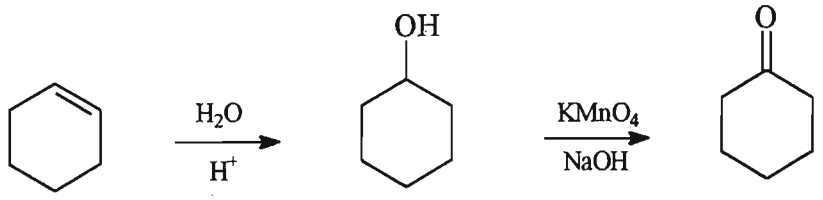
These include nucleophilic attack on palladium(II) olefin complexes, *e.g.* carbon nucleophiles and heteroatom nucleophiles (oxygen and nitrogen); palladium (II)-catalysed rearrangements; orthopalladation; transmetallation; palladium(0)-catalysed

insertion reactions; palladium(0)-catalysed reactions of allylic compounds; palladium(0)-catalysed telomerization of dienes and palladium(0)-copper(I)-catalysed coupling of aryl and vinyl halides with terminal alkynes. They permit unconventional transformations and give synthetic chemists wide latitude in their choice of starting materials. When utilised with skill and imagination, exceptionally efficient total syntheses can be achieved. The complexities and subtleties of organopalladium chemistry have hampered the adaptation of palladium mediated reactions in organic synthesis. It is such features, however, that give this field its attractiveness. Dramatic changes in selectivity can frequently be accomplished by seemingly minor modifications of experimental conditions, especially choice of ligands. As more is learned about the source of these effects, their predictability and therefore their applicability increases.

1.3. SYNTHESES OF KETONES FROM OLEFINS

1.3.1. Simple oxidation with potassium permanganate

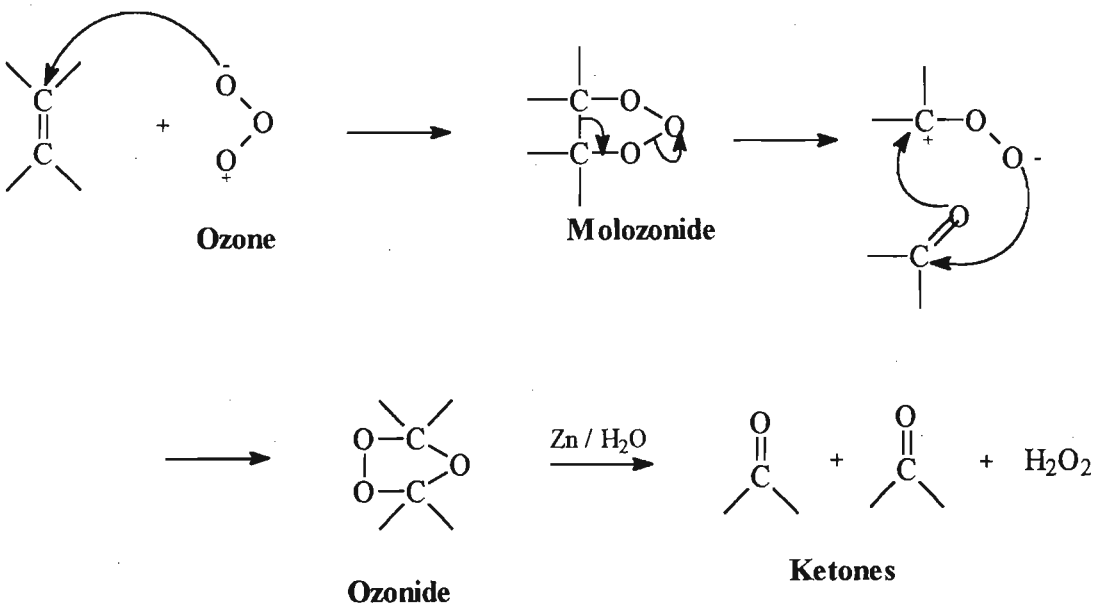
Oxidation of alkenes to ketones can be carried out using a powerful oxidising reagent such as potassium permanganate (Scheme 14).[68]



Scheme 14

1.3.2. Ozonolysis

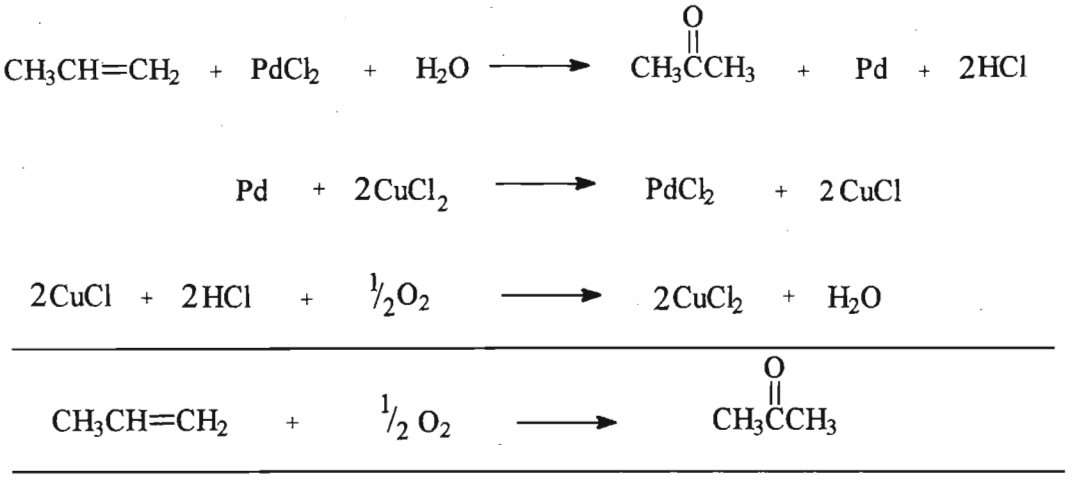
The very powerful oxidising agent ozone, O_3, readily attacks C=C bonds, rupturing not only the π-bond, but also the σ-link. The reaction termed ozonolysis, is carried out by passing ozone through a solution of the olefin in an inert solvent such as carbon tetrachloride or acetic acid. A molozonide is formed, and this rearranges exothermically to the more stable ozonide. Reduction is performed by adding to the ozonide solution a palladium or platinum catalyst and then passing in hydrogen gas to produce carbonyl compounds (Scheme 15). The other alternative is that the solvent can be removed carefully and the ozonide treated with zinc dust and water, yielding similar products.[68,69]



Scheme 15

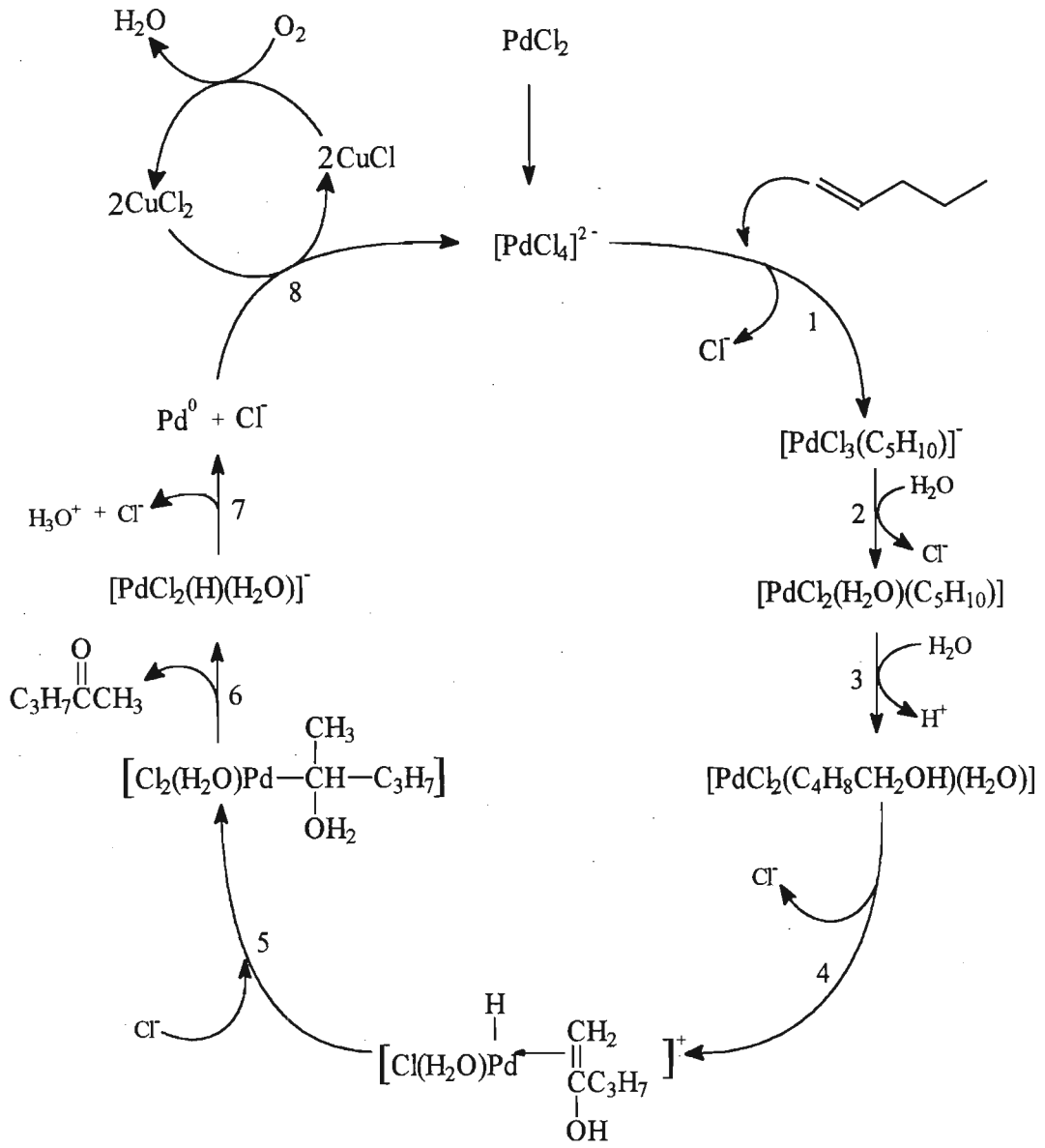
1.3.3. The original Wacker process

The oxidation of olefins to carbonyl compounds by oxygen and a solution of Pd(II) in aqueous hydrochloric acid is an important industrial process (the Wacker reaction). The palladium(II) is simultaneously reduced to the metal, but the reaction is rendered catalytic by addition of Cu(II) chloride in the presence of air or oxygen, whereby the palladium is continuously reoxidised to Pd(II) (Schemes 16 and 17).[35-37,70]



Scheme 16

The mechanism of this reaction has been very widely studied and it is now believed to proceed by an initial *trans*-hydroxy-palladation of the ethylene to form an unstable complex which then rapidly undergoes β-elimination with the transfer of a hydride ion from one carbon of the ethylene to the other, *via* the palladium. The hydride migration is required to explain the observation that when the reaction is conducted in deuterium oxide, no deuterium is incorporated in the carbonyl compound produced.[46]



Scheme 17

The proposed sequence of events as shown in Scheme 17 is as follows:[70]

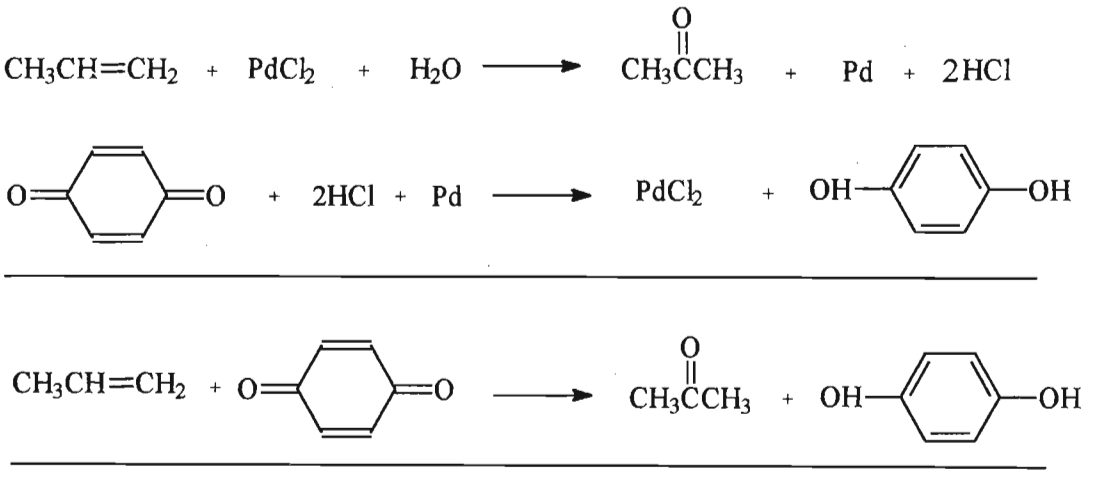
1. Uptake of α-olefin with a release of Cl^-, *i.e.* a substitution reaction rather than addition, to produce $[PdCl_3(C_5H_{10})]^-$
2. Substitution of Cl^- (another one) by H_2O to produce $[PdCl_2(H_2O)(C_5H_{10})]$

3. Nucleophilic attack of one H_2O molecule on the coordinated olefin. The H_2O coordinated is acidic and a proton is lost leaving the OH^- group.
4. Migration of the hydride to the palladium is accompanied by the loss of Cl^- and the formation of the hydroxy olefin.
5. Isomerisation, caused by migration of the H^- from the metal to the other carbon, forming a branched complex.
6. Elimination of a ketone by β-elimination from the hydroxyl group to the metal.
7. Reductive elimination of HCl with the formation of Pd(0).
8. Regeneration of a catalyst.

This reaction has been extended, with modification, to provide a good laboratory method for the oxidation of a wide range of terminal olefins to methyl ketones selectively.[35-38,70-79] The following reaction systems have been developed to eliminate the shortcomings of the original Wacker process.

1.3.4. $PdCl_2$ / *p*-Benzoquinone oxidation system

The essence of the Wacker process is the invention of the reoxidation process for palladium(0) by using copper(II) chloride as a co-catalyst. Copper salts are good reoxidants, but chlorination of carbonyl compounds takes place with copper(II) chloride.[73] For example, chloroacetaldehyde is the byproduct of the Wacker process.[37] Thus, a number of other reoxidants have been introduced. Benzoquinone was first used by Moisseev *et al.*[76-77] as a good reoxidant, but a stoichiometric amount is necessary.[50] This system avoids the use of co-metals as reoxidants. The reaction conditions are mild, and small amounts of the catalyst are used.[71-72] The reoxidant is consumed, and it is not regenerated (Scheme 18).



Scheme 18

1.3.5. Pd $(OAc)_2$ / H_2O_2 oxidation system.

The ability of hydrogen peroxide to reoxidise palladium(0) in the ethylene oxidation was reported.[38-39] Compared with palladium(II) chloride / copper(II) chloride, the rate of the oxidation was very high.[41] This process takes place in the absence of halogens and co-metals (Scheme 19).[79] It provides very high selectivity for methyl ketones and complete conversion of olefins. The system consumes very small amounts of palladium. It gives one isomer of the product.

$$CH_3CH{=}CH_2 + PdCl_2 + H_2O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_3 + Pd + 2HCl$$

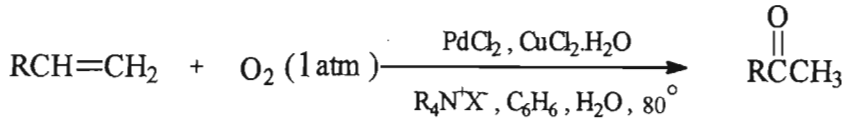
$$2HCl + Pd + H_2O_2 \longrightarrow PdCl_2 + 2H_2O$$

$$CH_3CH{=}CH_2 + H_2O_2 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_3 + H_2O$$

Scheme 19

1.3.6. $PdCl_2$ / $CuCl_2$ / O_2 / quaternary ammonium salts governed oxidation of olefins to ketones.

The system converts terminal olefins to ketones in good yields under mild conditions by means of phase transfer catalysis. Many applications of phase transfer catalysis in organic chemistry have been described in the literature during the past thirty years.[80-82] The use of such biphasic media for effecting reactions catalysed by metal complexes is a more recent development.[83-85] The advantages of such processes over conventional methods include significant enhancement of reaction rates, and simplicity both in execution and workup of the reaction. The quaternary ammonium salts govern the course of the reaction (Scheme 20).[84] The relative extractibility and solubility, in the organic phase, of ionic species derived from the different quaternary ammonium salts, may govern the course of the reaction.[84]

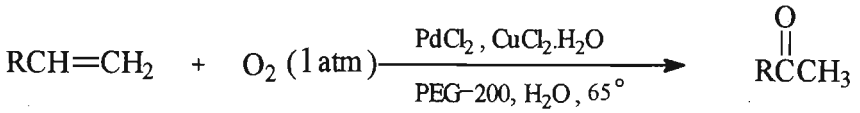


Scheme 20

1.3.7. $PdCl_2$ / $CuCl_2$ / O_2 / PEG-200 promoted oxidation of olefins to ketones.

This is also a phase transfer catalysis using polyethylene glycol (PEG-200) as a phase transfer agent (Scheme 21).[87,88] Ever since Pedersen's discovery of crown ethers and their cation-binding properties,[89] there has been considerable general interest in the corresponding oligoethylene glycols as less expensive analogous. PEGs have been used as catalysts in potassium permanganate[90] and potassium dichromate oxidations,[91,92] photocyanation of anisole,[93] carboxylate and other substitutions,[94,95] methylation of glycols,[96] ether and sulfide synthesis,[97] ester aminolysis,[98] base-catalysed condensation reaction,[99] elimination reactions,[100] and both enhancement of ester reduction[101] and retardation of ketone reduction with borohydride.[102]

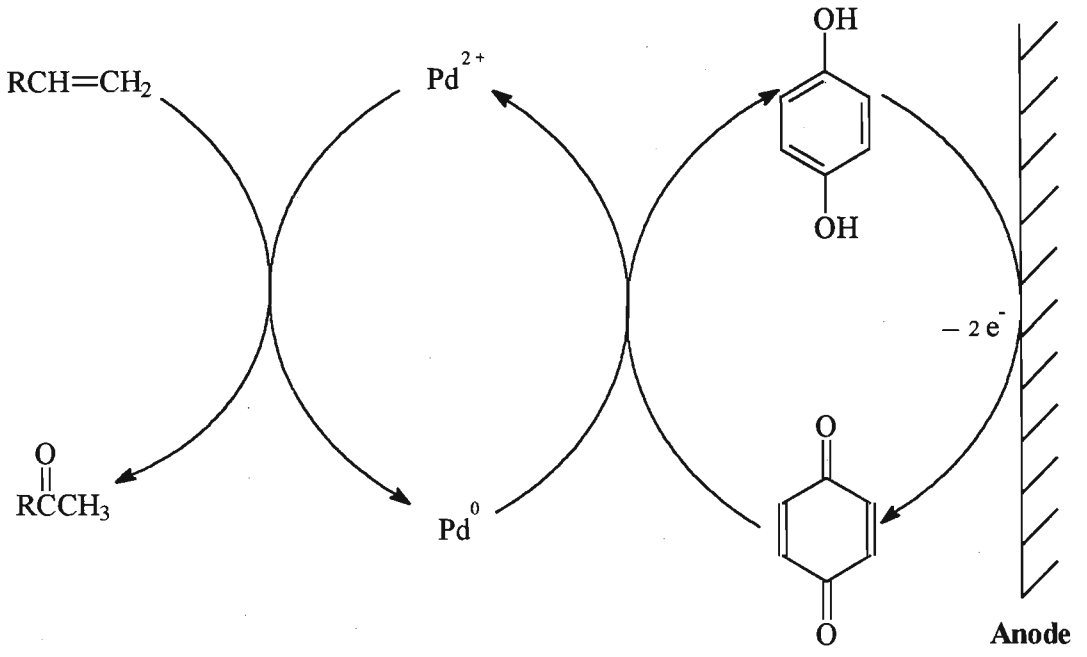
Recently, Santaniello, Manzocchi, and coworkers[103] have advocated the use of PEGs as solvents and catalysts for a variety of phase-transfer reactions. PEGs are cheap and thus very attractive. Alper and Januszkiewicz[88] have successfully used the PEGs in the oxidation of both terminal and internal olefins to ketones. These reactions give a variety of isomers, *e.g.* 2-heptanone and 3-heptanone from 1-heptene.



Scheme 21

1.3.8. $Pd(OAc)_2$ / *p*-benzoquinone oxidation in conbination with electrolysis.

This system employs $Pd(OAc)_2$ and benzoquinone in combination with anodic oxidation to oxidise 1-alkenes to methyl ketones efficiently. Cyclopentene and cyclohexene can also oxidised smoothly to the corresponding ketones in good yields.[104]



Scheme 22

This system overcomes some of the drawbacks observed with the Wacker system. As illustrated by Mimoun and coworkers[104] the drawbacks of the Wacker system ($PdCl_2$ / $CuCl_2$ / O_2 system) are the following:

- The reaction medium is not completely homogeneous when the reaction is carried out in aqueous DMF.
- Large amounts of Pd(II) and copper salts must be used. Sometimes nearly a stoichiometric amount of copper salt is necessary to complete the oxidation.

In contrast the electro-oxidation described above (Scheme 22) uses a good oxidant benzoquinone which is reduced to hydroquinone (Scheme 22). It is known that hydroquinone can be oxidised easily to benzoquinone electrochemically.[105] The concomitant oxidation of the olefins and the reduction of the benzoquinone regenerating Pd(II) signifies a further improvement on the Wacker process.[104,106] Large amounts of the reoxidant used in (section 1.3.5) are no longer required as the benzoquinone is regenerated electrochemically in this system.

1.3.9. $Pd(OAc)_2$ / PPh_3 / CF_3COOH oxidation of olefins to dialkyl ketones

The formation of dialkyl ketones was first reported by Roelen[107] in the first patent published on hydroformylation in 1942. In this paper it was reported that under carefully controlled conditions, the aldehyde produced from the process contained about 20% diethyl ketone. A process for the production of diethyl ketone was later (1955) patented by Naragon and coworkers.[108] In this process diethyl ketone are reported to be formed under very harsh conditions of temperature and pressure.

Much more research has been dedicated to the synthesis of these ketones by organic chemists employing different catalyst systems. Work on these reactions was also performed by Brown and Rathke[109] in 1964 and 1966. They reported that oxidation of organoborane intermediates in the presence of water produced dialkyl ketones in 95% yields. Later (1973), Brown[110] reported on the highly effective route to ketones *via* hydroboration. He investigated the transformation of esters of borinic acids under exceptionally mild conditions by α,α-dichloromethyl methyl ether (DCME) and lithium triethylcarboxide into an intermediate which can readily be oxidised to the corresponding symmetrical ketones in high yields (87%).

In 1975, Pelter and coworkers[111] reported a high yield ketone (65-87%) synthesis by reacting trialkylcyanoborates with acylating agents or N-phenyl benzimidoyl chloride. In 1982, Suzuki and coworkers[112] reported a synthesis of symmetrical ketones in 85% yield by the reaction of organoboranes with catechol dichloromethylene ether in the presence of methyllithium. In 1984, Zudin and coworkers[113] performed oxidation reactions that were last performed by Naragon in 1955,[108] the details of which are discussed below.

In 1990, Noels and coworkers[114] reported a direct catalytic access to symmetric ketones in 60% yield, from the coupling reaction of aldehydes with dicobaltoctacarbonyl in pyridine, under a pressure of syngas. In 1990, Periasamy and

coworkers[115] reported a reaction of $NaCo(CO)_4$ with R_2BI under carbon monoxide at atmospheric pressure at room temperature that resulted in dialkyl ketones in good yields of 61-85% after H_2O_2 / OH^- oxidation. In 1994, Kabalka and coworkers[116] reported a reaction of trialkylboranes with acyllithium reagents to yield ketones after oxidation with hydrogen peroxide. The ketones contained one alkyl group supplied by the alkyllithium reagent and one alkyl group supplied by the organoborane. In 1995, Periasamy and coworkers[117] reported synthesis of dialkyl ketones from olefins using $Ph(Et)_2N{:}BH_3$ / $CoCl_2$ / CO reagent system.

The work done by Zudin and coworkers[113] improved the work of Naragon, by using milder conditions for the formation of dialkyl ketones. They performed oxidation reactions of short chain olefins (ethylene and propylene) with $Pd(OAc)_2$ and PPh_3 in aqueous trifluoroacetic acid. They observed high selectivity (95-99%) in the ethylene reaction with propionic acid and traces of propionaldehyde as byproducts. In the case of propylene the main reaction products were isomeric dipropyl ketones, and the byproducts were butyric acids and small amounts of butyraldehydes and several unidentified products. They also found that the rate and selectivity (relative to the sum of the ketones and acids formed) of ketones formation in reactions(2) depend on the concentration of water in CF_3COOH (Scheme 23). Furthermore, the concentration of water also influences the distribution of isomers of dipropyl ketone. For example, at very low concentration of water the molar ratio of 2,4-dimethylpentan-3-one: 2-methylhexan-3-one: heptan-4-one in the product mixture was *ca* 1:2:1, while at 25-30 vol% this ratio was *ca* 1:5:1.[113]

$$2C_nH_{2n} + 2CO + H_2O \xrightarrow[30-70^\circ C,\ 1atm]{Pd^{2+},\ PPh_3} (CnH_{2n+1})_2CO + CO_2 \quad (1)$$

$$2C_nH_{2n} + CO + H_2 \xrightarrow[30-70^\circ C,\ 1atm]{Pd^{2+},\ PPh_3} (CnH_{2n+1})_2CO \quad (2)$$

Scheme 23

Zudin and coworkers[113] have worked out a mechanism for this reaction (Scheme 24). It is believed that a hydride complex of palladium is formed and that the catalytic cycle involves olefins insertion into a Pd-H bond and CO insertion into a Pd-C bond. Reaction (1) follows the route of formation of Pd-H bond in the (rate-determining) reduction of Pd(II) by CO followed by proton addition to the resulting Pd(0) species. Reaction (2) depicts the formation of Pd-H bond by heterolytic rupture of hydrogen by the Pd(II) complex.

$$L_2PdX_2 + CO + H_2O + L_2 \longrightarrow L_4Pd + CO + 2HX \quad (3a)$$

$$L_4Pd + HX \longrightarrow LmPd(H)X \quad (3b)$$

$$L_2PdX_2 + H_2 \rightleftharpoons LmPd(H)X + HX \quad (4)$$

$$LmPd(H)X + CnH_{2n} \rightleftharpoons LmPd(CnH_{2n+1})X \quad (5)$$

$$LmPd(CnH_{2n+1})X + CO \rightleftharpoons LmPd(COCnH_{2n+1})X \quad (6)$$

$$LmPd(COCnH_{2n+1})X + CnH_{2n} + HX \longrightarrow L_2PdX_2 + (CnH_{2n+1})_2CO \quad (7)$$

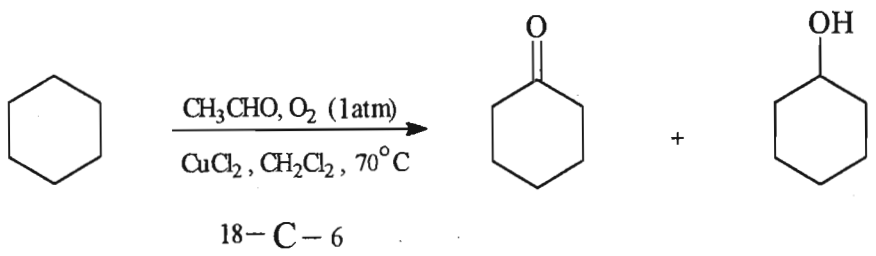
$$LmPd(COCnH_{2n+1})X + H_2O \longrightarrow LmPd(H)X + CnH_{2n+1}CO_2H \quad (8)$$

Scheme 24

Therefore, the catalytic formation of dialkyl ketones from reactions (1) and (2) may be represented in the set of equations (3)-(7). (L=PPh_3, X=CF_3COO, n=2 or 3, m=2 or 3). Byproducts (carboxylic acids) are formed according to reaction (8).[113]

1.3.10. $CuCl_2$ / 18-C-6 / O_2 oxidation of alkanes and olefins to ketones.

Copper like iron is predominantly contained in metalloenzymes that play important roles in biological dioxygenase metabolism. Much effort has been devoted to mimicking both iron and copper containing monooxygenases such as peptidylglycine α-amidating monooxygenases and cytochrome P-450[118-119] which catalyse the oxidation of aliphatic C-H bonds. It was as a result of these studies that the oxidation of alkanes with copper was developed.[120] It was discovered that novel copper salt-catalysed oxidation of alkanes with molecular oxygen (1 atm) proceeds efficiently at room temperature (Scheme 25). Copper-crown ether catalysed the oxidation of alkanes with molecular oxygen in the presence of aldehydes under mild conditions giving the corresponding ketones and alcohols efficiently.[121]

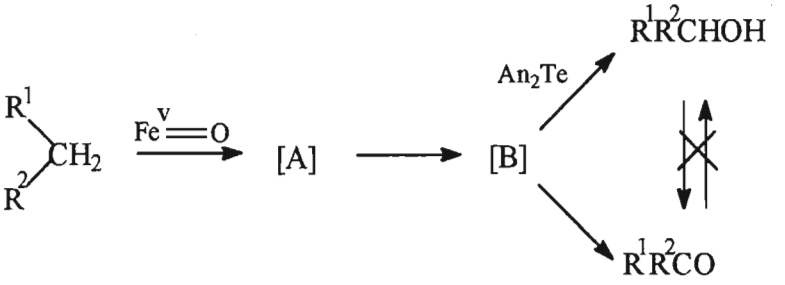


Scheme 25

Barton and coworkers[122] have succeeded in mimicking the iron enzymes and this is evident in the success of the Gif reaction that was developed in 1980s. The Gif reaction is the oxidation of hydrocarbons using molecular oxygen and a system comprising of hydrogen sulphide and iron powder in pyridine containing acetic acid and a little water. Selective oxidation of the inactivated carbon hydrogen bond is of industrial importance and is currently very relevant. Like the copper-crown reaction above, the Gif reaction results in a mixture of products, *i.e.* ketones and alcohols. The Gif system has an unusual substitution pattern (CH_2>CH>CH_3), and this is not

compatible with normal free radical attack.[123] Although optimal conditions have yet to be established, it is apparent that the choice of the solvent is important in controlling not only the yields, but also the ratio of products obtained.[124]

The mechanism of the reaction is thought to follow this pattern (Scheme 26).[125]



An_2Te = Dianisyl terruride

Scheme 26

There is good evidence for an intermediate A in this conversion. A can be efficiently captured by PhSeSePh, PhSSPh, $CHBr_3$ and CCl_4. This intermediate is thought to result from the insertion of an oxenoid (Fe^{v}=O) species into the C-H bond, and that it has an iron-carbon σ-bond (Fe^{v}-CHR^1R^2). Recent work has shown that there is also a second intermediate B, which affords a *sec.*-alcohol on hydrolysis and gives ketones under normal oxidation conditions. It has already been established that under Gif oxidation conditions, *sec.*-alcohols are not converted into ketones and ketones are not converted into *sec.*-alcohols.[126-127]

Addition of An_2Te to the Gif oxidation system resulted in a marked effect on the ratio of *sec.*-alcohols to ketone.[125] The simplest interpretation of this result is that the intermediate A is converted to the ketone in two steps (Scheme 26). The first step is the formation of a second intermediate B in which oxidation has taken place to the secondary alcohol level. Normally B is oxidised further to a ketone, but in the presence

of An_2Te this process is much less efficient. The secondary alcohol is released without further transformation. The most probable formulation of B is as an alkoxide of Fe(III).[128]

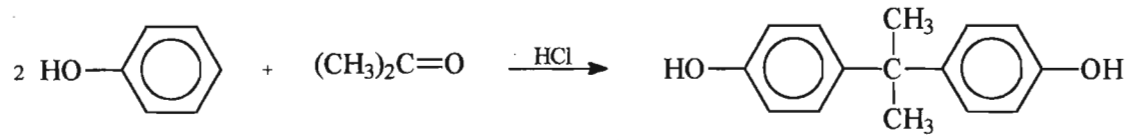
1.4. APPLICATION, USES AND MARKETABILITY OF KETONES AND THEIR PRODUCTS.

Sasol is continuously looking at ways to get a better market for surplus olefins produced in their F.T. process. To date they have developed many processes to market these olefins, *e.g.* production of acrylic acid, and in turn acrylates which are used as solvent; production of amines from the modified F.T. system; synthesis of ketones and aldehydes, which are in turn reduced to high quality alcohols and used for the production of chloro-alkali chemicals.[129-130] Ketones can be reduced to alcohols which have a good market locally and internationally. These alcohols can be marketed as high quality solvents, plasticizers and detergents.

The ability of the carbonyl group (C=O) to combine not only with a large variety of carbon frameworks but also with hetero atoms, result in the proliferation of carbonyl compounds throughout the organic chemical world. The carbonyl group is present in many substances of biological and commercial importance, and carbonyl compounds provide the essential ingredient for a large number of organic syntheses. The chemistry of carbonyl compounds, therefore, occupies a central place in the study of organic chemistry.[69]

Acetone is the most commercially important of the aliphatic ketones. It is produced by dehydrogenation of isopropyl alcohol, and as a coproduct in the synthesis of phenol by the oxidation of cumene. In addition to its use as a commercial solvent, it provides the starting material for a variety of derived products, including isobutyl methyl ketone and methyl methacrylate.[131]

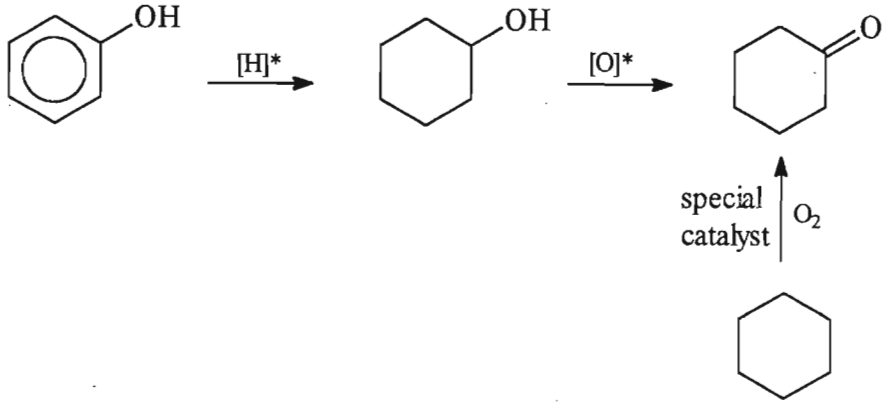
Acetone reacts with a phenol to form a compound known as bisphenol-A (Scheme 27).[131]



Scheme 27

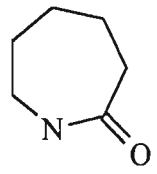
Bis-phenol-A can be converted to an "epoxy monomer" by the action of 2-chloromethyloxirane (epichlorohydrin), and polymerisation of the monomer can be induced by trifunctional amines such as diethylenetriamine to yield epoxy resins, useful in low molecular weight form as adhesives and in higher molecular weight form as surface coatings.[131]

A cyclic ketone of considerable commercial importance is cyclohexanone. It is prepared either by air oxidation of cyclohexane, using special catalysts, *e.g.* $CuCl_2$ / 18-C-6 / Acetaldehyde, or by the oxidation of cyclohexanol, which in turn, is prepared by the reduction of phenol (Scheme 28).[131]



Scheme 28

The main use of cyclohexanone is in the preparation of caprolactam, (hexanolactam. 6-amino caproic acid lactam) (**21**), which is the monomer in the production of the fiber Nylon-6.[131]

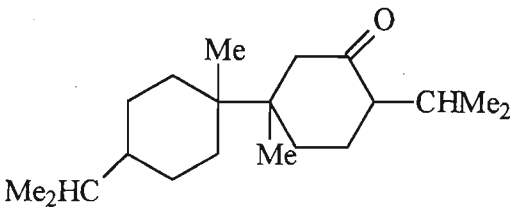


$C_6H_{11}NO$

(21)

Plasticizers, *e.g.* for PVC or rubber, are prepared by 2-stage polycondensation-esterification of the byproduct obtained in the oxidation of cyclohexane to cyclohexanone.[132] Other uses of cyclohexanone are in the synthesis of the following commercially important materials: Nylon, adipic acid, nitrocellulose lacquers, celluloid, artificial leather and printing inks.[132]

A number of C_4-C_9 aliphatic ketones were found to be acetylcholinesterase inhibitors. These ketones are transition state analogues of this enzyme.[133] Some cyclic ketones act as anti-asthmone (**22**) analogues or derivatives. These showed weak asthmatic relaxation effects. Apparently the cyclohexane ring with the carbonyl is associated with the anti-asthmatic action of this compound.[134]

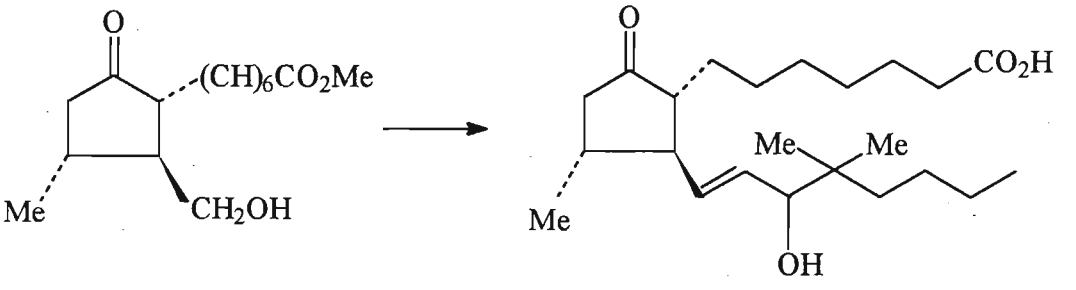


Antiasthmone

(22)

Aliphatic ketones have been used to modify casein amino acid *via* reductive alkylation at pH 9.0 to give stable non cross-linked lysine-modified derivatives. Solubility and emulsifying properties of alkylated caseins were changed by the process.[135] Some of the methyl ketones are useful starting material for the syntheses of important classes of Natural Products, these include carotenes, antibiotics, terpenoids, steroids, co-enzymes *etc.*[137-139] Among the many natural occurring ketones are several large ring compounds, including 3-methylcyclopentadecanone (muscone) (Scheme 14), isolated from the scent glands of the musk deer, and cycloheptadec-9-enone (civetone), isolated from the scent glands of the civet cat. These materials, along with cyclopentadecanone itself, find use in perfumery.[137]

Prostaglandins have been prepared from ketone intermediates[140] (Scheme 29).



Scheme 29

A major area of research at Sasol is the conversion of the surplus olefins to the more marketable products such as alcohols. It is economical to first synthesise ketones or aldehydes and then convert these to either primary or secondary alcohols.

The aim of this research project was thus:

- To investigate the one-pot synthesis of ketones from α-olefins (Wacker chemistry).
- To try and modify the Wacker system, so that improved selectivity and higher yields can be achieved.

- To investigate the processes that developed from the Wacker process, for example, using *p*-benzoquinone or hydrogen peroxide as reoxidants for the $PdCl_2$ catalyst.
- To try and optimise the conditions for some of these oxidation reaction systems.
- To further investigate oxidation to symmetrical dialkyl ketones, and improve the yields.
- To extend the range of olefins used for the synthesis of dialkyl ketones.
- To try and compare all these systems, in terms of their feasibility, product yields, purity of the products, and the cost associated with some of these reaction systems.

2. DISCUSSION

2.1. INTRODUCTION

The initial aim of this Masters project was to synthesise symmetrical dialkyl ketones from olefins. These ketones can in turn be reduced to alcohols, which can be used as solvents and for the preparation of surfactants.[141] As described earlier (Section 1.1.), Sasol produces a vast surplus of olefins from their Fischer-Tropsch process.[1]

Extensive research has been directed towards conversion of these olefins to useful products that have a better market value. For example, Sasol[142] has investigated the hydroformylation reaction for the conversion of olefins to alcohols. Lawson and coworkers[142] have successfully oxidised branched and linear olefins to alcohols under rather harsh hydroformylation conditions. To a lesser extent, Young and coworkers[143-145] have investigated the oxidation of olefins to dialkyl ketones, that may in turn be reduced to alcohols.

To date little success has been achieved in the synthesis of symmetrical dialkyl ketones from these olefins. Imyanitov and coworkers,[146] Wender and coworkers[147] as well as Murata and coworkers[148] have attempted to find reaction conditions favouring the predominant formation of dialkyl ketones from olefins, CO, and H_2. Zudin and coworkers[113] succeeded in finding mild conditions for the oxidation of ethylene and propylene to 3-pentanone and 4-heptanone, respectively. Work done by Young and coworkers[143-145] at Sasol (Sasolburg) has proved that this reaction works, but they restricted their work to ethylene, propylene and 1-pentene oxidation. The envisaged approach of this research programme was to further investigate the work done by Zudin and Young (discussed above) in this field, and to try and improve on these processes.

The rich chemistry associated with the synthesis of alkyl ketones from olefins, using palladium catalysts (Wacker chemistry), has received a great deal of attention, and it is well covered in the literature.[35-37] Our second aim was thus to investigate this Wacker oxidation system, and to study other oxidation systems that have been developed from the original Wacker system.

2.2. SYNTHESIS

2.2.1. The original Wacker system, $PdCl_2$ / $CuCl_2$ / O_2 system.

As described earlier (Section 1.3.4), the Wacker process is the most important and widely studied Palladium(II) catalysed oxidation of terminal olefins to ketones. This process, discovered by Smidt and coworkers in 1959,[36] actually consists of three separate reactions (Scheme 18, Section 1.3.4).[35-37]

Smidt and coworkers'[36] elaborate research and findings that copper(II) chloride reoxidises the palladium(0) to palladium (II) *in situ* opened the door to a valuable new commercial process.[36] Copper(II) chloride was regenerated by air oxidation of copper(I) chloride in aqueous solution. [149-150] The net reaction is an air oxidation of olefins to ketones (Scheme 18, Section 1.3.4).[36]

Because of the commercial importance of the reaction, the kinetics of the oxidation of olefins (more particularly ethylene) by palladium chloride in aqueous chloride media, have been studied by a number of researchers. Smidt and coworkers,[151-153] and Henry[149-150] agree that in the [Pd(II)] range from 0.005 to 0.04M, [Cl⁻] from 0.1 to 1.0M, and $[H^+]$ from 0.04 to 1.0M, the rate expression is as illustrated in Equation 1.[36]

$$\frac{-d[C_nH_{2n}]}{dt} = \frac{k[PdCl_4^{2-}][C_nH_{2n}]}{[Cl^-]^2[H^+]}$$

Equation 1

Outside these concentration ranges, and with other olefins, the mechanism may change.[111] Copper salts affect the free chloride concentration in an uncertain manner by forming Cu(I) and Cu(II) chloride species such as $CuCl_n^{(n-1)-}$ and $CuCl_n^{(n-2)-}$. The hydrogen ion concentration also changes during the course of a reaction, since the

regeneration of $PdCl_4^{2-}$ by $CuCl_2$ does not consume the hydrogen ion produced in the olefin oxidation step.[36]

The first step of our research programme was to investigate the Wacker process. As part of the investigation, we attempted the oxidation of 1-decene as performed by Tsuji.[37] 1-Decene was oxidised with palladium chloride in the presence of copper(II) chloride pretreated with oxygen, using water and DMF as the solvent system. 2-Decanone was extracted with ether, and fractional distillation of the product mixture gave pure 2-decanone (70%). These results are not very different from the results of Tsuji and coworkers' oxidation of 1-decene to 2-decanone affording 73% yield.

We also performed oxidation reactions of 1-nonene, 1-octene, 1-heptene, 1-hexene and 1-pentene employing the Wacker process ($PdCl_2$ / $CuCl_2$ / O_2), (Table 1). GC-MS analysis of the crude reaction mixture after the workup indicated that the desired ketone was the major product. There were some unidentified byproducts, which may be the chlorinated carbonyl, as suggested by Tsuji and coworkers.[37] Other reseachers[156-157] have identified chlorohydrin as one of the byproducts from the reaction of olefins with palladium(II) chloride and copper(II) chloride. Tsuji and coworkers[37] have performed the oxidation of different higher terminal olefins under the same reaction conditions, and they stipulate that oxidation of higher terminal olefins under these reaction conditions is slow and sometimes accompanied by undesired byproducts formed by the chlorination of carbonyl compounds by copper(II) chloride. Unfortunately, Tsuji and coworkers did not publish detailed results about which olefins were investigated and what yields were obtained, thus comparison in this regard will not be possible.

Table 1: Summary of methyl ketones and corresponding isolated yields from the oxidation reactions of corresponding α-olefins employing the original Wacker system.

KETONE	%YIELD
2-Pentanone	10
2-Hexanone	68
2-heptanone	69
2-Octanone	69
2-Nonanone	71
2-Decanone	70

Table 1 summarises our results of the oxidation of different aliphatic olefins. Good isolable yields are observed in the oxidations of higher olefins. The oxidation of 1-pentene gave very low yields. The reason for the observed decrease of the total yields with the decrease of the chain length is not known at this stage.

In an effort to improve the yields and purity of the products from the original Wacker system, to the original reagents was added a catalytic amount of *p*-benzoquinone, using 1-decene as a substrate. This was to assist the $CuCl_2$ in the reoxidation of Pd(0) to Pd(II), and to reduce the contamination in the product mixture. This approach, however, resulted in more contamination in the product mixture with the yields not changing significantly.

2.2.2. The $PdCl_2$ / *p*-benzoquinone oxidation system.

As discussed in Section 1.3.5., copper(II) chloride is not the only reoxidant that can be used to regenerate Pd(II) in the chloride-containing system. Thus, among others, benzoquinone has been used for this purpose in aqueous solution.[158] There are a number of procedures in the literature for the oxidation of olefins to ketones using *p*-benzoquinone as reoxidant for palladium(0).[71-72] Henry and coworkers[36] have stipulated that benzoquinone does not affect the free chloride concentration, and for these reasons, benzoquinone has been used as an oxidant in kinetic studies.[36] The fact that benzoquinone does not change the rate of oxidation indicates that the rate of reoxidation of Pd(0) to Pd(II) is faster than the rate of olefin oxidation. Another advantage of benzoquinone, as mentioned in mechanistic studies, is that the hydrogen ion concentration also does not change during the course of the run. Thus the HCl formed in the oxidation of olefins by $PdCl_4^{2-}$ is used up in the regeneration step.[36]

We attempted oxidation of 1-decene with palladium chloride in the presence of *p*-benzoquinone following the procedure based on a recent publication by Tsuji and coworkers.[37] GC-MS analysis of the product mixture after the workup indicated that there was incomplete oxidation of 1-decene under these reaction conditions. The quantity of 1-decene (50 mmol) given in Tsuji's procedure proved to be in excess in our experiments. When we used 1-decene (50 mmol) as a substrate, the product was a mixture of 1-decene (75%) and 2-decanone (25%) (relative percentages calculated by integration of GC-MS peaks). These results do not comply with findings of Tsuji and coworkers. They claim a 78% yield of 2-decanone after distillation and a complete conversion. No mention is made of any substrate being recovered in the product mixture. Thus, there is a large discrepancy between Tsuji and coworkers'[37] investigations and our investigations of the oxidation of 1-decene. We found that approximately 25 mmol of 1-decene were oxidised to 2-decanone per 1 mmol of $PdCl_2$ catalyst. Tsuji and coworkers'[37] results indicate that they were able to oxidise 100 mmol of olefin per 1 mmol of $PdCl_2$ catalyst.

We then successfully achieved complete oxidation of 1-decene by decreasing the quantity of olefin used. We achieved complete conversion of 1-decene to 2-decanone (80%) when 1-decene (1.75 g, 11.5 mmol) was used. Tsuji and coworkers[37] achieved obtained 2-decanone (78%) when they oxidised 1-decene (7.0 g, 50 mmol) under the same reaction conditions.

In an attempt to optimise the reaction conditions for the complete oxidation of 1-decene to 2-decanone, the effect of time and temperature (Table 2 and 3) were investigated. The investigations were performed using a quarter of the literature amount (12.5 mmol). These investigations proved that the temperature and time of the reaction do not affect the ketone yields. The yields presented in these tables are relative quantities in the product mixtures calculated by integration of GC-MS spectra.

Table 2 illustrates the effect of temperature on the product distribution for the oxidation of 1-decene to 2-decanone using the $PdCl_2$ / *p*-benzoquinone oxidation system. The reaction time (7 hours) as well as all other variables were maintained as per original oxidation of 1-decene to 2-decanone above for all of these investigations. The results show that little or no effect is observed with the increase of temperature on the 2-decanone yield. Elevated temperatures have, however, a significant effect on the isomerisation of 1-decene. From the table, it can be concluded that increasing the temperature increases the percentage of internal olefins in the product mixture from the oxidation process. These results comply with Tsuji and coworkers'[37] findings of the oxidation of olefins at different temperatures. They investigated the effect of temperature on the oxidation of 1-octene in *n*-propyl alcohol, and concluded that high temperatures facilitate double bond migration.[37]

Table 2: Summary of the effect of temperature on the palladium(II) chloride / *p*-benzoquinone catalysed oxidation of 1-decene (12.5 mmol) to 2-decanone and decene isomers. Percentages represent relative quantities calculated by intergration of GC-MS peaks.

Temperature °C	2-Decanone%	1-Decene %	2- and 3-Decene %
25	92	7	1
55	92	6	2
70	92	4	4
80	92	4	4

Table 3 illustrates the effect of time on the product distribution for the oxidation of 1-decene to 2-decanone using the $PdCl_2$ / *p*-benzoquinone oxidation system. The reaction temperature (65°C) as well as all other variables were maintained as per original oxidation of 1-decene to 2-decanone above for all of these investigations. Oxidations were performed at shorter (entry 1) and longer (entries 2-6) reaction times than the 7 hours that is stipulated by Tsuji and coworkers in their procedure.[112]

Table 3: Summary of the effect of time on the palladium(II) chloride / *p*-benzoquinone catalysed oxidation of 1-decene (12.5 mmol) to 2-decanone and 1-decene isomers. Percentages represent relative quantities calculated by intergration of GC-MS peaks.

Time (h)	2-Decanone	1-Decene %	2- and 3-Decene %
6	92	7	1
18	92	5	3
24	93	4	4
48	92	4	4
72	92	4	4
144	92	4	4
168	92	4	4

These results (Table 2 and 3) lead us to conclude that despite repeated attempts at trying to match Tsuji's findings, the conditions employed only realised a 25% oxidation yield.

We also attempted the oxidation of other olefins employing Tsuji's system. 1-Nonene was also oxidised to 2-nonanone, the product mixture indicating that incomplete oxidation had also occurred. GC-MS peak integration indicated that about 75% of the 1-nonene was recovered from a 1-nonene oxidation run. We then performed experiments to determine an exact amount of 1-nonene to result in complete conversion of 1-decene to 2-nonanone. We achieved complete conversion to 2-nonanone (89%), when 1-nonene (12 mmol) was used. Similarly, a mixture of 1-octene and 2-octanone was obtained when the literature quantity (50mmol) was used for the oxidation of 1-octene to 2-octanone. Complete conversion of 1-octene to 2-

octanone (85%) was achieved when a quarter (12.5 mmol) of the amount given in the literature (50 mmol) was used.

Following the successful oxidation of the higher olefins, we then extended this oxidation method to lower olefins, *e.g.* 1-heptene, 1-hexene and 1-pentene. Unlike the higher olefins, 100% conversion to 2-heptanone, 2-hexanone and 2-pentanone was achieved using the amount of α-olefin suggested in the literature (50 mmol), from 1-heptene, 1-hexene and 1-pentene, respectively (Table 4). The relative purity of the product obtained after the workup of the product mixture from this oxidation system, make the $PdCl_2$ / *p*-benzoquinone oxidation system the only system from which we obtained isolable yields of 2-pentanone (50%).

Table 4: Summary of methyl ketones and corresponding isolable yields synthesised by $PdCl_2$ / *p*-benzoquinone system from the corresponding α-olefins.

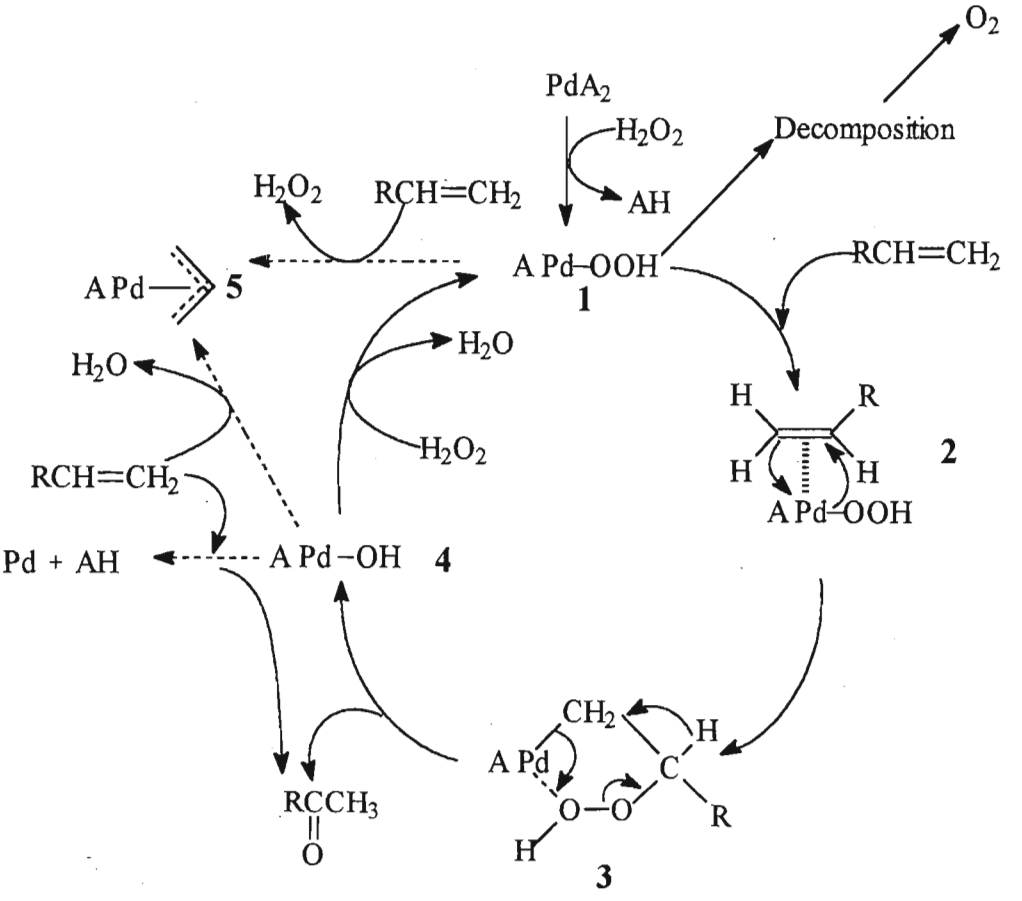
KETONE	%YIELD
2- Pentanone	50
2-Hexanone	71
2-heptanone	80
2-Octanone	85
2- Nonanone	89
2-Decanone	80

Table 4 illustrates the good yields obtained with this oxidation system. The yields do not follow any pattern as the chain length of an olefin is increased or decreased. The overall results from this oxidation system are higher than the yields obtained from the $PdCl_2$ / $CuCl_2$ system. Tsuji and coworkers[37] also obtained higher yields with the $PdCl_2$, *p*-benzoquinone oxidation of 1-decene (78%) than with $PdCl_2$ / $CuCl_2$ oxidation

of 1-decene (73%). We can therefore, conclude that replacing $CuCl_2$ / O_2 with *p*-benzoquinone gives improved results from the Wacker oxidation system. Economics of each of these systems on a small scale will be discussed and compared at a later stage in this section.

2.2.3. The $Pd(OAc)_2$ / hydrogen peroxide system.

One of the important achievements in the continued efforts to improve the Wacker system was the discovery of the $Pd(OAc)_2$ / hydrogen peroxide catalytic system.[77-78] Mimoun and coworkers[80] described a very efficient catalytic procedure for the oxidation of terminal olefins to methyl ketones by hydrogen peroxide using a palladium catalyst and operating in the absence of halogens and co-metals. Their thorough investigation of the system allowed them to suggest the mechanism depicted below (Scheme 38).[80]



A = OAc

Scheme 38

Palladium hydroperoxidic species **1**, obtained by addition of H_2O_2 to palladium compounds, appear to be the most likely active intermediates in this catalytic oxidation. PdOOH species undergo an oxygen transfer to olefins through a pseudocyclic hydroperoxy-palladation mechanism (**2** and **3**) of the coordinated olefin.[80] The involvement of such pseudocyclic peroxidic intermediates (**3**) is further supported by the exchange reaction between Na_2PdCl_4 and $CF_3CO_2HgCH_2CH(Ph)OOH$ affording acetophenone.[80]

The presence of a large excess of H_2O_2 is necessary not only to compensate its unavoidable Pd-catalysed decomposition, but also to regenerate PdOOH species from PdOH (**4**). At low H_2O_2 concentrations, PdOH species may undergo a hydroxypalladation of the olefin, affording the ketone and metallic palladium precipitation. The metallic palladium does not dissolve again in the solution when excess H_2O_2 is added. Furthermore, the presence of excess H_2O_2 is necessary to avoid the formation of π-allylic complexes (**5**) and for regeneration of the initial PdOOH species.[80] Mimoun and coworkers[116] also performed experiments with cyclic and internal olefins, and discovered that they are unreactive under these reaction conditions.

The experiments performed in our laboratory applying this system were consistent with the results obtained by Mimoun and coworkers.[80] The oxidations of 1-decene, 1-nonene, 1-octene 1-heptene and 1-hexene were performed in the presence of $Pd(OAc)_2$ and hydrogen peroxide in acetic acid. It was observed that during the initial stages of the oxidation process Pd(0) (black) precipitated out and dissolved back into the solution as the reoxidant hydrogen peroxide was added. After the workup of the product mixtures, fractional distillation was performed on the product residues to yield 2-decanone (83%), 2-nonanone (85%), 2-octanone (80%), 2-heptanone (77%) and 2-hexanone (57%), respectively. Mimoun and coworkers[80] obtained the following yields from the oxidations of some of the olefins that we also investigated: 2-decanone (95%) and 2-octanone (96%). The problem we experienced with this system was with the

isolation of the product from the acetic acid (solvent). This might explain the lower yields we obtained relative to the yields obtained by Mimoun and coworkers.[80]

The small discrepancy between our yields and those of Mimoun and coworkers[80] does not prevent us from agreeing with them that this palladium-catalysed synthesis of methyl ketone from terminal olefins using H_2O_2 appears to be the most useful in the synthetic methods. It provides very high selectivity to methyl ketones with complete conversions of the olefins, and only requires catalytic amounts of palladium (20-40 ppm).

Table 5: Summary of methyl ketones synthesised by $Pd(OAc)_2$ / hydrogen peroxide system from corresponding α-olefins.

KETONE	%YIELD
2-Hexanone	57
2-heptanone	77
2-Octanone	80
2- Nonanone	85
2-Decanone	83

Different solvents were also investigated with this reaction system, using 1-decene as a substrate. Relative percentage of the product in the product mixture was determined by integration of GC-MS spectra (Table 6). It was thought that acetic acid, being a strong acid donates a proton to the olefin during the oxidation. Other solvents (Table 6) with dielectric constant between that of acetic acid and of water were also investigated, but the role of the solvent in the whole reaction system is not clear.

From Table 6 it is shown that none of the solvent systems that were investigated furnished better results than the acetic acid (percentage yields calculated by integration of GC-MS spectra). In an attempt to optimise the conditions for the conversion of 1-decene to 2-decanone hydrogen peroxide was added over a longer period of time (1 hour). This did not improve the yields or the conversion rates.

Table 6: Solvents investigated in the $Pd(OAc)_2$ / H_2O_2 oxidation of 1-decene to 2-decanone. Percentages show relative quantities in the product mixture determined by intergration of GC-MS spectra.

SOLVENT	STARTING MATERIAL (OLEFIN)%	PRODUCT (KETONE)%
Acetic Acid	0	100
Ethylene Glycol	99	1
Methanol	25	75
Ethanol	93	7
Acetonitrile	100	0

The high cost of the palladium catalysts used in these industrially important reactions stimulated different researchers to investigate other cheaper metals as possible alternatives to the expensive and corrosive palladium catalysts. Muharashi and coworkers[120-121] have investigated the use of copper(II) chloride for the oxidation of alkene to ketone (section 2.2.4.). Barton and coworkers[122-128] investigation into the use of the iron for the oxidation of hydrocarbons have indicated the high possibility for iron to be an alternative metal to palladium for oxidation reactions.

The complete oxidation of olefins and high yields of ketones we observed with the $Pd(OAc)_2$ / H_2O_2 oxidation system, made this an ideal system to investigate the ability of copper salts to oxidise olefins. We investigated copper chloride for this purpose, while all other variables (temperature, solvent, reoxidant) were maintained as in the palladium oxidation reactions.

- For the first reaction, the amount of copper(II) chloride used was equal to the number of moles of palladium acetate used in palladium reactions (2.5×10^{-5} mol). This reaction was unsuccessful, as no traces of 2-decanone were detected, and only 1-decene was observed on the GC-MS spectra.

- The second reaction had twice the amount (5.0×10^{-5} mol) of copper(II) chloride, but no oxidation of the 1-decene occurred.

- The third reaction had (1 mol) copper chloride and was allowed to run for extended time. The reaction was spotted on a thin layer chromatography plate at different times, and even after 36 hours, 2-decanone did not form from 1-decene.

2.2.4. The $PdCl_2$ /$CuCl_2$ / O_2/ quaternary ammonium salt (CTAB) facilitated oxidation system.

Phase transfer catalysis has been known to organic chemists for about thirty years now. During 1980s Alper[84] and Cassar[85] made use of these biphasic media for effecting reactions catalysed by metal complexes. They discovered that the use of such processes has advantages over conventional methods, in that they significantly enhance reaction rates and simplicity both in execution and workup of the reaction.

Alper and coworkers[84] were the first to perform oxidation reactions of olefins to ketones under phase transfer conditions. They stipulated that a novel aspect of the

oxidation process is its dependence on the type of phase transfer agent. They also revealed that olefins are oxidised only by the use of large lipophilic phase transfer catalysts. These included tetradecyltrimethylammonium bromide (CTAB) and dodecyltrimethylammonium chloride (DTAC). In the latter case change of one methyl group to ethyl and chloride to bromide results in lower product yields and in the recovery of more substrate. With quaternary ammonium salts containing alkyl groups of shorter chain length than twelve carbons, little or no oxidation occurs. These include Aliquat 336 (tricaprylmethylammonium chloride), benzyltriethyl ammonium chloride, and tetrabutyl ammonium hydrogen sulfate.[84]

Their investigations also revealed that oxidation reactions do not appear to be dependent on the micelle character since attempted oxidation of 1-decene using sodium dodecyl sulphate in place of CTAB gave only a mixture of isomeric decenes. Instead, the relative extractibility and solubility in the organic phase, of ionic species derived from the different quaternary ammonium salts, may govern the course of the reaction.[84]

We performed oxidation reactions of different aliphatic olefins under the phase transfer conditions employing CTAB as phase transfer agent. Oxidation of α-olefins 1-decene 1-nonene, 1-octene and 1-heptene with palladium chloride and copper chloride in benzene and water resulted in methyl ketones 2-decanone, 2-nonanone, 2-octanone and 2-heptanone, respectively, being produced in good yields (Table 7).

Alper and coworkers[84] obtained 2-decanone (73%) from the oxidation reaction of 1-decene using CTAB as a phase transfer agent. This percentage yield is not very different from the yields we obtained with the oxidation of 1-decene to 2-decanone (69%), employing the same phase transfer agent CTAB. From our experience, this system proved to be a bit difficult to handle, iced water was pumped through the condenser to prevent the evaporation of benzene during the stirring of the reaction mixture at 80°C for 48 hours. Moreover, low yields of pure products resulted from the

oxidation of 1-hexene and 1-pentene. The formation of these lower olefins was only confirmed by GC-MS analysis.

Table 7: Summary of methyl ketones and corresponding isolable yields synthesised by $PdCl_2$ / quaternary ammonium salt oxidation system.

KETONE	%YIELD
2-heptanone	64
2-Octanone	70
2-Nonanone	70
2-Decanone	69

From the results (Table 7) it can be deduced that the oxidation system is efficient. Conclusions, however, cannot be drawn about the relationship between yields and chain length. Compared to the other oxidation processes described earlier on, in our opinion, this oxidation system is time consuming and is not as facile as Alper and coworkers[84] claim it to be.

2.2.5. The $PdCl_2$ /$CuCl_2$ /O_2/ polyethylene glycol-200 facilitated oxidation system.

The application of phase transfer catalysis to the palladium catalysed oxidation of olefins to ketones using quaternary ammonium salts was a good discovery, since the conditions are mild and the yields are good. However, Alper and coworkers[84] have shown that internal olefins fail to react under these reaction conditions.

Alper and coworkers'[88] intensive research on the phase transfer application to oxidation of olefins to ketones, yielded a new kind of phase transfer agent for these oxidations. PEGs have been employed as phase transfer agents for alkoxylation and reduction reactions.[88] It seemed conceivable to Alper and coworkers[88] that the application of PEGs to the palladium(II) catalysed olefin oxidation reactions would result in enhanced reactivity compared with the phase transfer process with quaternary ammonium salts. They performed the oxidation of 1-decene with $PdCl_2$ / $CuCl_2$ system in a mixture of PEG-400 and water, with 2-decanone being formed in 86% yield. Although 2-decanone was the predominant product, small amounts of isomeric decanones were also formed.

We attempted the oxidation of 1-decene following the procedure prescribed by Alper and coworkers.[88] Using PEG-200 for our oxidation reactions, we obtained 2-decanones (56%) (Table 8). This yield is lower than the yield of 2-decanone (68%) reported by Alper and coworkers employing PEG-400. These different results confirm Alper and coworkers'[88] findings that the yield of decanone decreases if the molecular weight of PEG decreases from PEG-400 to PEG-200 or increases to PEG-1000. Other terminal olefins, *i.e.* 1-nonene, 1-octene and 1-heptene were also oxidised under the same reaction conditions to the methyl ketones 2-nonanone, 2-octanone and 2-heptanone, respectively, in reasonable total isolable yields (Table 8).

Table 8: Summary of methyl ketones synthesised by $PdCl_2$ / PEG-200 reaction system from α-olefins

METHYL KETONE	% YIELD	ETHYL KETONE	%YIELD
2-Heptanone	50	3-Heptanone	7
2-Octanone	50	3-Octanone	5
2-Nonanone	45	3-Nonanone	12
2-Decanone	50	3-Decanone	6

GC-MS analysis of the isolated products indicated that there were at least two isomers of the methyl ketone formed. Relative percentage yields of the methyl ketones and the other isomer worked out by integration of GC-MS peaks (Table 8). The sum of the two isomers of each ketone gives the total isolable yield. Alper and coworkers[123] results also indicate that more than one isomer of each ketone was isolated, their detailed analysis indicated that the other isomer was a 3- ketone. Attempts at separating the isomers by fractional distillation failed as their boiling points were too close (Table 9).[159]

Table 9: Boiling points of the methyl and ethyl ketone isomers.[159]

METHYL KETONE	BOILING POINT (°C)	ETHYL KETONE	BOILING POINT (°C)
2-Heptanone	149-150	3-Heptanone	146-149
2-Octanone	173	3-Octanone	167-168
2-Nonanone	192	3-Nonanone	187-188
2-Decanone	211	3-Decanone	204-205

Alper and coworkers[88] performed experiments to compare rates of oxidation when PEGs are used to the rates when CTAB was used. They found that the rate of PEG-400 induced oxidation of 1-decene is 3.1 times faster than CTAB facilitated oxidation of the same substrate under the same conditions. They then concluded that PEG is superior for the oxidation of both terminal and internal olefins.

We agree with Alper and coworkers[88] that the system is very effective and attractive because of the low cost of PEGs, but the shortcomings of the quaternary ammonium salt facilitated oxidations are not overcome with the use of PEGs.

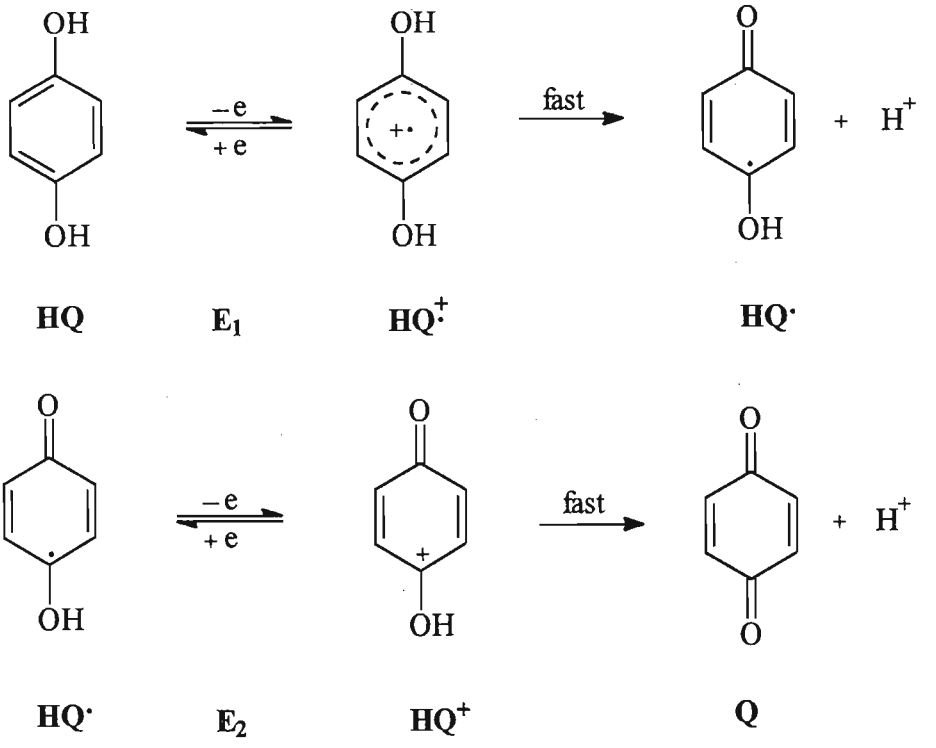
2.2.6. The $Pd(OAc)_2$ / p-benzoquinone / electrolysis oxidation system.

We decided to perform olefin oxidation reactions that involve electrochemistry, for the following reasons: The cost of electricity is low in South Africa at present, and the system seems to be the most economical at the moment. The amount of byproduct from this system is very low and this makes the system more environmentally friendly. The electrochemical regeneration of the benzoquinone makes the system even more useful, as the expensive reoxidant is not used up, and thus lesser quantities are used.[104]

The oxidation of hydroquinone is of fundamental importance in that the hydroquinone-benzoquinone redox couple is considered as the classical organic redox synthesis.[160] In order for us to investigate the oxidation of olefins with this system, it was necessary to first establish the electrochemical oxidation conditions for the conversion of hydroquinone to benzoquinone.

Parker[105] has investigated anodic oxidation of hydroquinone in acetonitrile, using rotating disc electrode voltammetry. He constructed a voltammogram of hydroquinone in acetonitrile and found an oxidation peak to benzoquinone at about 1V. He worked out the mechanism of this oxidation process as shown in Scheme 39.

The mechanism of this interesting reaction is still being debated. Parker[105] believes that it follows a pattern in Scheme 39. In his preliminary communication,[161] he suggested that the electron and proton transfers during the two electron oxidation of hydroquinone to benzoquinone occurred in rapid succession and that benzoquinone was the first observable species by rapid electrochemical techniques.



scheme 39

The initial electron transfer, E_1, is followed by rapid deprotonation to give the radical, hydroquinone (HQ•). The radical is more easily oxidised than hydroquinone ($E_1 > E_2$), and thus undergoes further electron transfer to give the protonated benzoquinone. Up to this point the steps cannot be separated by rapid electrochemical techniques.[105]

We then investigated the oxidation process of hydroquinone following Parker's[105] procedure. The voltage at which the hydroquinone is oxidised to benzoquinone was established by constructing a voltammogram of hydroquinone in acetonitrile and using $NaClO_4$ as a supporting electrolyte and a platinum electrode. This system proved to work efficiently. A voltammogram (Figure 1) shows the oxidation peak of the hydroquinone observed at O.976 mV. The peak height for the oxidation of hydroquinone is 26mV. These voltages conform with Parkers investigations of the system.

The results from the oxidation reactions performed with hydroquinone were then used for the oxidation of α-olefins to methyl ketones. As it has been established above in the $PdCl_2$ / benzoquinone oxidation systems (Section 1.3.5.) , during the oxidation of olefins to ketones Pd(II) is reduced to Pd(0), and the benzoquinone oxidises Pd(0) to back Pd(II). But a stoichiometric amount of the benzoquinone is needed for the complete oxidation of olefins. This electrolysis system (electrochemical regeneration of benzoquinone) avoids the use of such large amounts of benzoquinone, with the reaction being catalytic with respect to both palladium and benzoquinone.

Tsuji and coworker[104] performed the oxidations of both aliphatic and cyclic olefins using the benzoquinone system in combination with electrolysis. They reported high yields of ketones, cyclohexanone (83%) from cyclohexene and 2-decanone (63%) from 1-decene. Horowitz[106] described another method of using the chloropalladate ion as a reoxidant. In this system the reduced palladium was reoxidised electrochemically using the iron(II) / iron(I) couple as the transfer agent.

We performed oxidation of cyclohexene, employing Tsuji and coworker's[104] oxidation system, using $Pd(OAc)_2$, benzoquinone and Et_4NBF_4 as a supporting electrolyte in acetonitrile and water. Cyclohexanone (65%) was isolated. Oxidations of other olefins 1-decene, 1-nonene, 1-octene, 1-heptene, 1-hexene and cyclooctane were also performed. We obtained good yields (Table 10) from the oxidation reactions, the yields were slightly lower isolated yields than those of Tsuji and coworker.[104] This discrepancy cannot be explained, but there were slight differences between his experimental setup and ours. We used a platinum stationary electrode for the anodic oxidation of hydroquinone during the oxidation of the olefin to ketones, while they used a rotating disc electrode.

Table 10. The experimental time and corresponding isolated yields for electrolysis oxidation reactions for different cyclic and aliphatic olefins.

OLEFINS	TIME (h)	KETONE YIELD (%)
1-Hexene	1	60
Cyclohexene	1.5	58
1-Heptene	2	59
1-Octene	3	60
1-Nonene	5	59
1-Decene	7	62
Cyclooctene	12	0

Table 10 illustrates the times taken by each oxidation reaction to go to completion and the isolated yields of each of the ketones. Cyclooctene was resistant to oxidation. Reaction times shown in the Table 10 reflect the obstinacy associated with the oxidation of higher olefins.

An example of the calculation of the number of moles oxidised using a hypothetical time under these reaction conditions is shown below.[162] Knowing the quantity of an olefin to be oxidised, the time could then be calculated by changing the subject of the formula in the calculation below.

Quantity of electricity passed = it (coulombs)

i = current in amps.
t = time in secs.

Number of faradays passed = $\frac{it}{F}$

F = faraday = 96500 C/mol

Number of moles oxidised = number of faradays passed

EXAMPLE :

Instrument settings : Y– axis = 26 mV

Current passing per volt = 100 mA/V

$\therefore$ Current = 26×10^{-3} mA $\times$ 100

= 2.6 mA

Time taken (supposed) = 4h = 3600 $\times$ 4 sec.

$\therefore$ Q = it = 2.6 $\times$ 3.600 $\times$ 4 C

= 37440 C

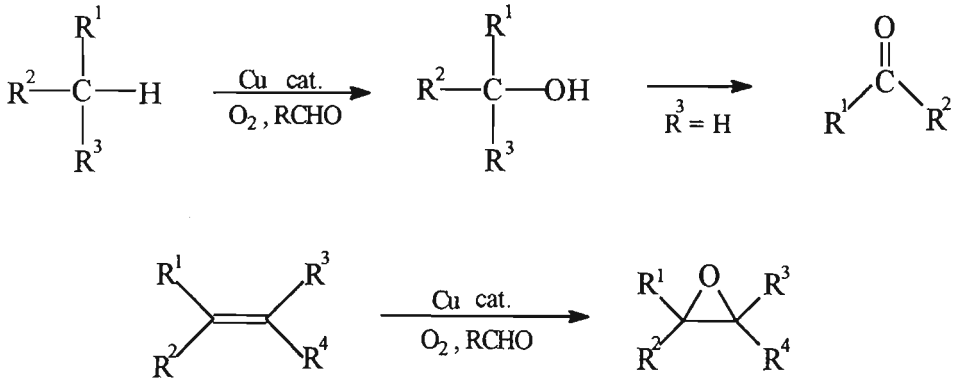
Number of faradays passed = $\frac{37440}{96500}$ = 0.3880 equivalents

Number of moles oxidised = 388.0 mmol.

The experimental time (Table 10) for each oxidation reaction was longer than the time that the calculation above predicted. This discrepancy was more obvious for higher olefins.

2.2.7. $CuCl_2$ / 18-C-6 / O_2 / oxidation of alkanes and olefins to ketones.

Copper, as well as iron, are predominantly contained in metalloenzymes that play important roles in biological dioxygen metabolism.[120] Murahashi and coworker's[120,121] and Barton and coworker's[122-128] efforts have been devoted to mimicking these enzymes for organic synthesis purposes. Barton and coworkers[122-128] have done extensive work on the oxidation of saturated hydrocarbons selectively to ketones. This system utilises pyridine and acetic acid as a solvent, and iron catalysts. Murahashi and coworkers[120,121] reported aerobic oxidation of alkanes in the presence of acetaldehyde catalysed by the copper-crown ether complex which was discovered as a result of these enzyme mimicking research projects. Murahashis'[120] first reported the use of copper salts in the absence of the crown ether to oxidise the alkanes to ketones in the presence of the aldehyde. When olefins were used as substrates under the same reaction conditions, epoxidation occurred (Scheme 40).[120]



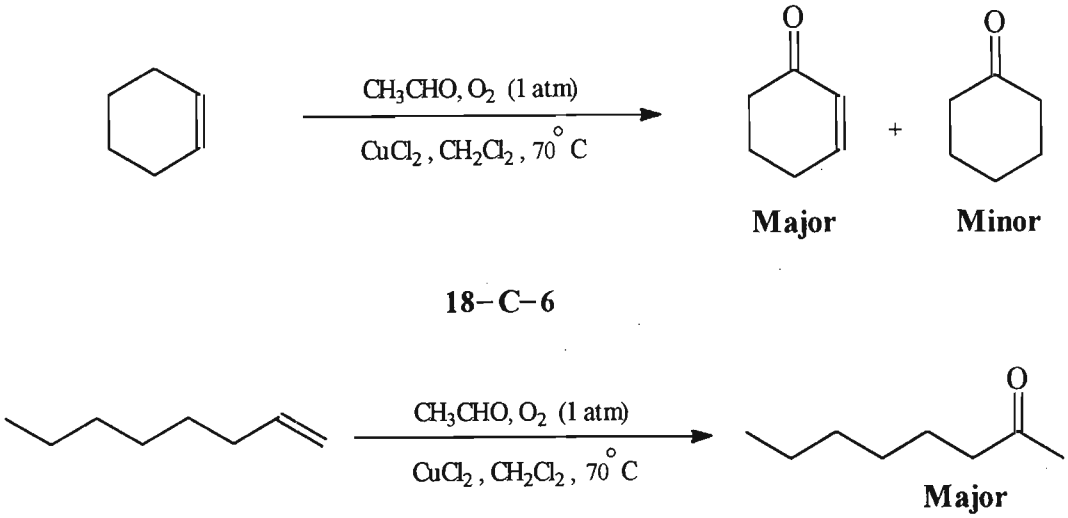
Scheme 40

In Murahashi and coworker's latest publication,[122] they described an oxidation reaction which is more like the oxidation reaction above,[121] only this one uses a crown ether to enhance the reaction. Hydrocarbons are oxidised to ketones and alcohols with the

$CuCl_2$ / 18-C-6 / acetaldehyde system. In this report no mention is made of the behaviour of olefins under these conditions. It was against this background that we decided to use olefins as substrates in the presence of the crown ethers. We performed oxidations following Murahashi's latest publication on these oxidation conditions.[117] The reactions were performed with alkanes, aliphatic and cyclic olefins as substrates. The products obtained varied from α,β-unsaturated to saturated ketones, yields obtained by integration of GC-MS peaks (Table 11).

The oxidation of cyclohexene with the $CuCl_2$, 18-C-6 and acetaldehyde gave unexpected results. The two major products for the reaction of cyclohexene under these conditions were α,β-unsaturated 2-cyclohexen-1-one (58%) and cyclohexanone (30%). Percentages reflect relative quantities in the product mixture calculated by intergration of GC-MS spectra. The aliphatic olefins and alkanes (aliphatic and cyclic) gave saturated 2-ketones in reasonable yields (Table 11). The olefins gave higher yields as well as cleaner products than the alkanes (aliphatic and cyclic). For most olefins was achieved, and because of the contamination low isolable yields of the desired products resulted. Murahashi's second paper[122] on this catalysis system suggests that alkanes react and form ketones and alcohols. Alcohols were evident in most of the product mixtures with the m/z = ketone + 2 in the MS spectrum. The suggested mechanism for this reaction is presented on page 41 section 1.3.10.

The NMR data for most of these products is not available because the products were contaminated by many other byproducts. The IR and GC-MS data were enough proof for the formation of a ketones rather than an epoxide. There is a strong and dominant peak at about 1712 cm^{-1} due to the C=O stretch in the IR spectra. There is no peak associated with the wavelength around 1250 cm^{-1} where the epoxide absorbs. The reasons for these differences between the aerobic oxidation in the presence of the crown ether and in its absence are not known as yet.



Scheme 41

Table 11: The distribution of products in the $CuCl_2$- 18-Crown-6 oxidation reaction

SUBSTRATE	KETONE (%)	ALCOHOL AND OTHER PRODUCTS (%)
n-Pentane	20	80
n-Hexane	40	60
n-Heptane	45	55
Cyclohexane	35	65
1-Pentene	45	55
1-Hexene	45	55
Cyclohexene	55	45
1-Heptene	57	43
1-Octene	40	60
Cyclooctene	0	100
1-Nonene	42	58
1-Decene	40	60

Table11 illustrates the relative quantities in percentages present in the product mixture. Isolation of the desired product was effected by fractional distillation and this method was fairly successful in separating the ketones from their corresponding alcohols and unreacted substrates by virtue of different boiling points.

The alternative copper salt was investigated with the 18-C-6 system. Use of $Cu(OAc)_2$ in place of $CuCl_2$ gave similar yields and distribution of products (Table 12).

Table 12: Showing the effect of copper salts to the yield of the ketones from cyclohexene.

COPPER SALT	KETONES%	Alcohol and other products(%)
$CuCl_2$	55	45
$Cu(OAc)_2$	56	44

A different host molecule to 18-C-6 was also investigated. The dibenzo-18-crown 6 gave slightly better results than the 18-crown 6. Relative percentages calculated by intergration of GC-MS peaks.

Table 13: Showing the improvement of the yield with the use of a different host ligand with cyclohexene.

HOST LIGAND	COST OF A HOST LIGAND ($/g)[159]	KETONE%
18-C-6	17.64	55
Dibenzo-18-C-6	2.64	60

The $CuCl_2$ / 18-C-6 / acetaldehyde system could be very useful in industry as it avoids the use of expensive and corrosive palladium metal complexes. The use of crown-ethers enhances the yields from the oxidation reactions, and during our investigation we observed that dibenzo 18-crown-6 gives slightly higher yields than 18-crown-6 (Table 13).

2.2.8. Synthesis of dialkyl ketones with $Pd(OAc)_2$ / PPh_3 oxidation system.

As described earlier (Section 1.3.10.), extensive research has been devoted to the synthesis of dialkyl ketones by many researchers[107-117] The investigations performed by Zudin and Coworkers[113] in the oxidation of olefins to symmetrical dialkyl ketones were outstanding. They investigated the oxidation of ethylene and propylene under mild reaction conditions (30-70°C, 1 atm), employing $Pd(OAc)_2$ and PPh_3 in aqueous trifluoroacetic acid. They obtained 3-pentanone and 4-heptanone with high selectivity (95-99%).

Research done at Sasol[143-145] confirmed the work done by Zudin. At present they can synthesise C_{11} to C_{21} alcohol *via* hydroformylation which involves drastic pressure and temperature conditions.[142] Young and coworkers[143-145] at Sasol extended the range of olefins used as substrate for the synthesis of dialkyl ketones. They performed oxidation reactions on ethylene, propylene and 1-pentene, and apparently could not isolate pure dialkyl ketones as they present GC-MS analysis only. We performed these oxidation reactions following a procedure given by Young and coworkers[143]. We extended the range of terminal olefins used by Young and coworkers[143] in the system even further. We successfully synthesised dialkyl ketones C_7, C_{11}, C_{13}, C_{15}, C_{17}, C_{19}, and C_{21} under these mild reaction conditions (30-70°C, 1 atm) from propylene, 1-pentene, 1-hexene, 1-heptane, 1-octene, 1-nonene and 1-decene, respectively (Table 14). This reaction system though has it shortcomings:

The products were always contaminated by the triphenylphosphine which was removed by allowing it to crystallise out of the solution. The problem we observed with this was that the triphenylphosphine was never totally removed from the solution. The yields given in Table 14 are with most of the triphenyl phosphine removed, but in some cases this was hardly achieved. Table 14, illustrates the yields of dialkyl ketones calculated by integration of GC-MS peaks. The observed pattern as in the table is that, yields decrese with the increasing chain length of the olefin. Long chain olefins

reacted slower than short chain olefins, and very small peaks were observed in the GC-MS spectra for their products.

Table 14. Showing the yields of the dialkyl ketones from the oxidation reactions of α-olefins.

OLEFIN	DIALKYL KETONE (%)	OTHER PRODUCTS (%)
Propylene	75	25
1-Pentene	70	30
1-Hexene	76	24
1-Heptene	30	70
1-Octene	10	90
1-Nonene	8	92
1-Decene	7	93

It was difficult to separate the desired product from all the contaminants, consequently, we could not perform detailed qualitative analysis, *e.g.* H-NMR and C-NMR on these products.

The preparation of the dialkyl ketones with the $Pd(OAc)_2$ and PPh_3 system resulted in the precipitation of Pd(0) metal. Large amounts of the catalyst were consumed by each reaction and the catalyst was not regenerated. We then decided to use some of reoxidants that were good for the oxidation reactions of terminal olefins to methyl ketones, to regenerate the catalyst. We investigated the following variables, to test whether Pd(II) can be regenerated under the reaction conditions, thus improving the yields of dialkyl ketones.

- Efficient reoxidants, benzoquinone and hydrogen peroxide were added in catalytic amounts to regenerate Pd(II). There was always black precipitation on the sides of the reactor.
- Higher pressures of CO / H_2 (2 atm) were used .
- Oxygen (1 atm) was also used as a reoxidant of Pd(0) to Pd(II).
- Oxidation reaction were performe at higher reaction temperatures.

Table 15. Showing the effect on the product yield (from 1-pentene) as the conditions were altered.

Additives	Dipentyl ketone yield (%)
Normal system	70
H_2O_2 (1 mmol)	50
p-benzoquinone (1 mmol)	30
CO / H_2 (2 atm)	71
Higher temperature (100°C)	71

The yields illustrated in Table 15 were also calculated by integration of GC-MS peaks. All these efforts did not bear any significant changes to the yields of dialkyl ketones.

The use of an alternative solvent to trifluoroacetic acid was also investigated. Research done at Sasol[143] showed that there is a potential for an alternative solvent to the expensive and corrosive trifluoroacetic acid. This solvent is acetonitrile, and research at Sasol indicated that it could not work on its own as a solvent, but it needed catalytic amounts of trifluoroacetic acid. However, lower yields were observed with this solvent system.

2.3. CONCLUSION AND FUTURE PROPOSALS.

The initial aim of this Masters project was to synthesise dialkyl ketones, and to improve on the systems that have been developed so far in this field. During this study we were drawn by the rich chemistry associated with the synthesis of alkyl ketones with palladium catalysts (Wacker chemistry).[35-37] We also explored cheaper systems that have been developed to minimise cost of oxidising olefins to ketones.

The initial goal was to a much lesser extent achieved, but extensive and intensive research was done on the existing alkyl ketones synthesis processes. Some novel synthesis were also brought to light during the investigations of existing systems. The synthesis of α,β-unsaturated cyclic ketones, using the $CuCl_2$ / 18-C-6 / acetaldehyde system, has to our knowledge not been reported. The synthesis of saturated aliphatic ketones from olefins using the same system has also not been reported.

The dialkyl ketone synthesis disclosed by Zudin and coworkers,[113] that was also investigated at Sasol by Young and coworkers[143-145] was extended to higher than C_3 olefins in our laboratory. To our knowledge Sasol has been able to synthesise the C_7-C_{21} alcohols under the harsh hydroformylation conditions. Now we have been able to synthesise the C_7-C_{21} symmetrical ketones (low yields), these ketones can in turn be reduced to secondary alcohols. The conditions under which these ketones are produced are much milder than the hydroformylation conditions. Our attempts to modify the system to afford better the yields and to avoid contamination of products were unsuccessful.

This was an elaborate research of oxidation reactions of olefins to ketones, and in order to draw a conclusion we need to compare and contrast the oxidation systems that we investigated.

2.3.1. Notable comparison of the oxidation systems.

- *The Wacker process*

This system gave good yields, although the product mixture which was contaminated, needed further purification by fractional distillation. The reactions took 24 hours to go to completion. Economically, this system is costly to run, 1 g of $PdCl_2$ oxidises only 5.5 g of the olefin (1-heptene).

- *The $PdCl_2$ / benzoquinone system*

This was one of the best systems, the yields were very good. The products were easily recovered from the product mixture. With the reaction time of only 7 hours and no apparent need for fractional distillation to purify the products , this system proves to be the most facile of them all. We have calculated the amount of olefin that can be oxidised by 1 g of a catalyst. 55.1 g of the olefin (1-heptene) were oxidised by 1 g of $PdCl_2$. This is a large amount of an olefin, and as far as we are concerned economically this system is cheaper that the $PdCl_2$ / $CuCl_2$ / O_2 system. $PdCl_2$ (1 g) cost about \$37.40 and benzoquinone (1 g) cost about \$2.17.[159] Thus, the oxidation of 1-heptene (55. 1 g) cost about \$50.42 in this system, whereas the oxidation of the same amount of olefin with the Wacker system cost about \$378.95. As far as we are concerned, the high cost of the benzoquinone does not affect the usefulness of this system, it is much cheaper to run than the Wacker oxidation system.

- *The $Pd(OAc)_2$ / H_2O_2 system*

The yields were good, but it proved to be a problem to get rid of the solvent. The complete conversion of olefins to ketones within a very short span of time (6 hours), denotes the high efficiency of this system. Economically, this system is cheaper than the Wacker system and more expensive than the benzoquinone system to run, 1 g of $Pd(OAc)_2$ (\$51.70)[159] oxidises 6.0 g of the olefin (1-heptene).

- *The $PdCl_2$ / quaternary ammonium salt system*

The yields were good, the solvent removal was a problem with this system as well. The reaction time was 48 hours, about 8 times the time taken by the benzoquinone and H_2O_2 systems. The oxygen was bubbled throughout the 48 hours making the system rather expensive to run. Economically, this system is cheaper than the Wacker and H_2O_2 system and more expensive tan the benzoquinone system to run, 1 g of $PdCl_2$ oxidises only 13.9 g of the olefin (1-heptene).

- *The $PdCl_2$ / PEG-200 system*

This system gave good yields, the main problem with this system was the different isomers of the ketones that resulted. Under the reaction conditions, the α-olefins isomerised to internal olefins. The PEG facilitated reaction oxidises internal olefins to corresponding ketones as well, and that is why there was a mixture of products. PEGs are cheap and thus this system is more attractive than the quaternary ammonium salts system. The economic analysis of this system are the same as done for the quaternary ammonium salts.

- *The $Pd(OAc)_2$ / benzoquinone / electrolysis system*

This is one of the greatest achievements with the efforts to minimise the cost associated with the operation of the systems to synthesise ketones from olefins. This system precludes the high cost of benzoquinone problem, because the benzoquinone is regenerated by electrolysis. The yields were very good and the product isolation was effortless. The reaction time varied according to the size of the olefin. Shorter chains took shorter time to get oxidised than long chain olefins. With much smaller amounts of benzoquinone used the system is more cost effective than the cheapest of the above.

- *The $CuCl_2$ / 18-C-6 / O_2 system*

Very low yields are associated with this reaction. But the reaction system is a good system for the synthesis of ketone without having to use expensive catalysts. The reaction period for this system was 24 hours, and products proved difficult to isolate .

Getting pure products in the reaction that gives extremely low yields, and the desired product being the minor in the product residue was very difficult. There is plenty of room for improvement in this field. With the cost of 18-C-6 being $17.60[159] per gram, and dibenzo 18-C-6 being $2.64[159] per gram, opposed to $37.40[159] per gram of palladium(II) chloride catalyst, this reaction can be useful in industry.

- *The $Pd(OAc)_2$/ PPh_3 system for the synthesis of dialkyl ketones*

This system resulted in very low yields of very contaminated products. The reactions of higher olefins gave lower and lower yields as the chain length was increased. These product could not be isolated and analysed. The reactions could not be scaled up, as each run consumed (1 g) of the expensive catalyst for the conversion of (1.87 g) of the olefin. This implies that employing this system cost 29 times the cost of operating the benzoquinone system which is approximately ($1462.18). The problem with the large amounts of the PPh_3 recovered in the product mixture makes the system even more difficult to operate.

There is still room for extensive and intensive research in this field for synthesis of ketones from olefins. There are many published research programmes that deal synthesis of dialkyl ketones as described above. The important one being the one that uses aldehydes with $Co(CO)_8$ as a catalyst.[114] This system looks feasible from the industrial point of view. The feed for this system could be from the hydroformylation process and the catalyst and other reagents could be added at the outlet of the plant and the system pressurised to give dialkyl ketones. The other rather expensive process is the system that use organoboranes or boric acid.[111,112,115] Future research programmes can look at these oxidation systems for the synthesis of dialkyl ketones and compare their yields and cost associated with each system.

The other system worth looking at, is the palladium (0)-catalysed oxidative addition and transmetallation The palladium (0)-catalysed coupling of aryl and vinyl halides and triflates with main group organometallics *via* oxidative addition -transmetallation

sequence (Scheme 12) has been very broadly developed and has an overwhelming amount of literature associated with it.[38]

The palladium(0) complexes are electron-rich, nucleophilic species prone to oxidation. These complexes undergo oxidative addition when an oxidising agent such as RX, adds to the metal. The metal is formally oxidised from Pd(0) to Pd(II) during the process. The α-vinylpalladium(II) complexes formed by this oxidative addition enjoy the rich chemistry, including olefin and CO insertion *etc.* Ketones, symmetrical and non-symmetrical, can be synthesised from these complexes by coupling the CO insertion with transmetallation (Scheme 12).

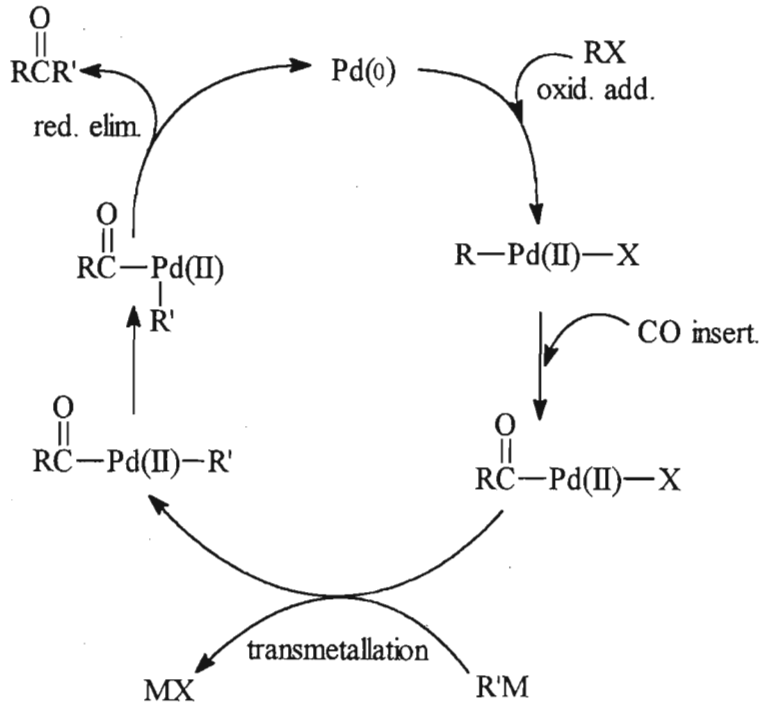
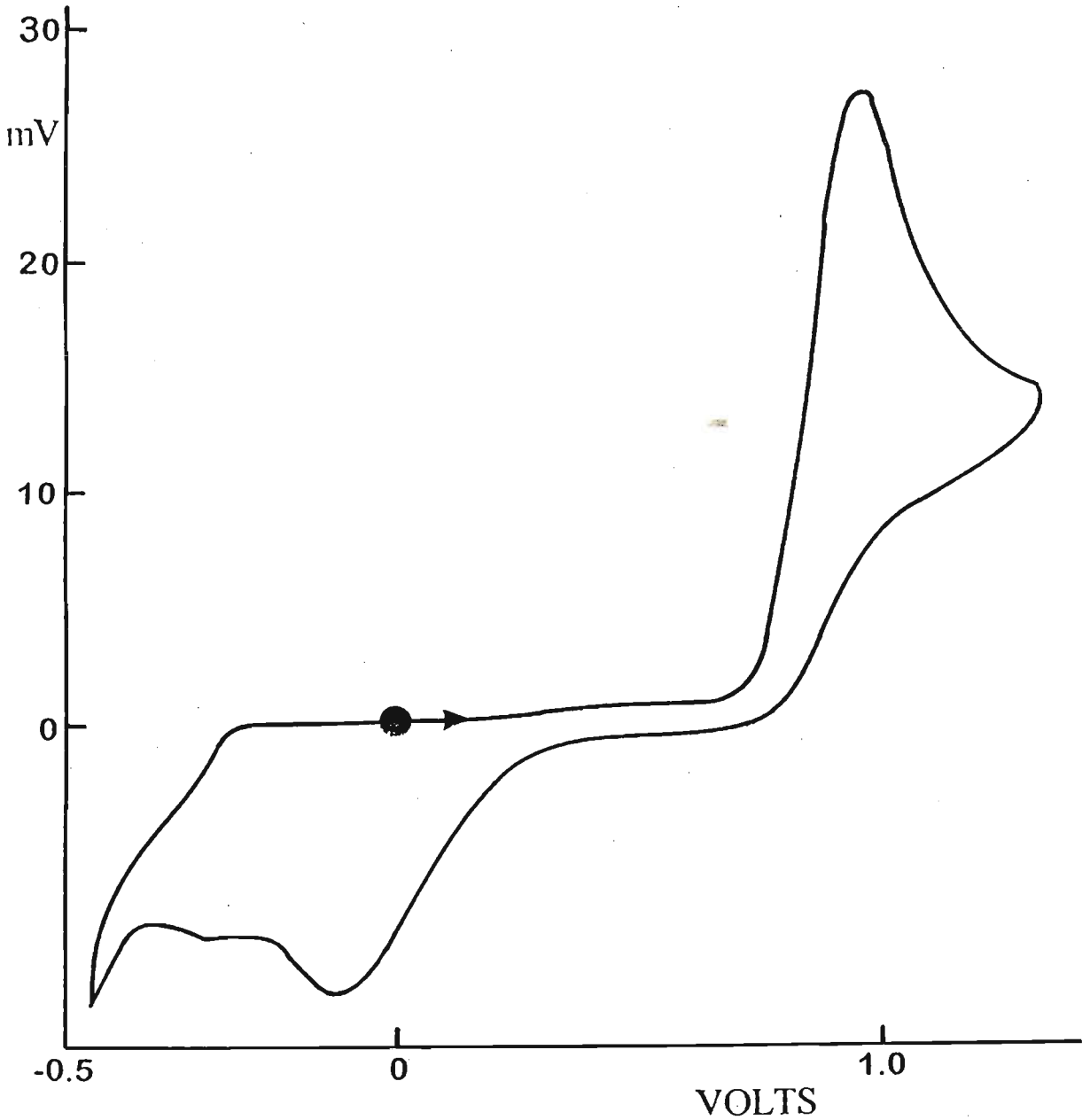
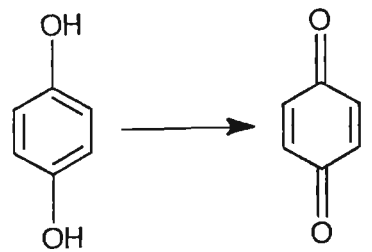


FIGURE 1.





3. EXPERIMENTAL

3.1. INSTRUMENTATION, AND GENERAL PROCEDURES.

NMR spectra were recorded on a Varian T-60 (^{1}H 60 MHz) and a Gemini 200 (^{1}H 200 MHz and ^{13}C 50 MHz), using $CDCl_3$ as a solvent and TMS as internal standard. Mass spectra were recorded on a Hewlett-Packard gas chromatography mass spectrometer (HP5988A). Infra Red (IR) spectra were recorded on a Shimadzu FTIR-4300 spectrometer, and were performed in $CHCl_3$ using KBr disks. Only characteristic peaks are indicated, in wavelength (cm^{-1}).

Merck plastic sheets pre-coated with silica gel Kieselgel 60 (F_{254}) were used for thin layer chromatography. An oxygen line was used for the reactions where oxygen had to be bubbled throughout the reaction time, and a balloon was used for reactions performed under an oxygen atmosphere. Purification of compounds was achieved by fractional distillation. All commercially obtained chemicals were used as is, unless indicated otherwise. Low reaction temperatures were maintained using ice water and liquid nitrogen.

In order to keep the content of this thesis as brief as possible, the physical data of the same molecule that was synthesised by different methods has only been presented once, in the first method used to synthesise that particular molecule.

3.2. SYNTHESES

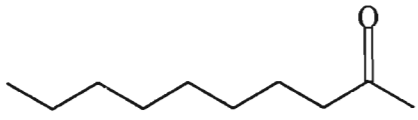
3.2.1. The $PdCl_2$ / *p*-benzoquinone oxidation of olefins to ketones[37]

General procedure.

In a 100 ml round bottom flask fitted with a magnetic stirrer, was placed a mixture of palladium (II) chloride (89 mg , 0.5 mmol), *p*-benzoquinone (5.94 g, 55 mmol), and 7:1 dimethylformamide / water (20 ml). To the solution was added α-olefin (50 mmol) over 10 minutes and the mixture was stirred at room temperature for 7 hours. The solution was poured into cold hydrochloric acid (3M, 100 ml) and extracted with ether (5 x 50 ml). The extracts were combined and washed with aqueous sodium hydroxide solution (10%, 3 x 50 ml) and a portion of brine (50 ml), and then dried over magnesium sulfate. After removal of the solvent the residue was distilled to give methyl ketones in yields stated below.

Oxidation of 1-decene to 2-decanone with palladium(II) chloride and p-benzoquinone

1-Decene (1.75 g, 12.5 mmol) was used as a substrate for this experiment.



2-decanone

$C_{10}H_{20}O$

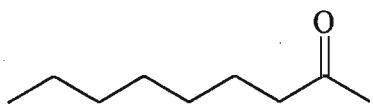
MW=156 g/mol

(1)

Yield: .1.40 g (80%).**B.P.** 207°C/760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS:** *m/z* (EI) 156 (M^+, 8%), 98 (6%), 96 (6%), 85 (7%), 71 (40%), 59 (40%), 58 (100%), 57 (19%), 55 (13%). **NMR** ^1H: δ_H (200 MHz) 0.885 [3H, t, CH_3CH_2-]; 1.272 [5xCH_2, m, $CH_3CH_2CH_2CH_2CH_2CH_2$-]; 1.567 [2H, m, -$CH_2CH_2C(O)$-]; 2.137 [3H, s, -$C(O)CH_3$]; 2.309 [2H, t, -$CH_2CH_2C(O)$-].^{13}C: δ_C (50 MHz) 14.1 [q, 1xCH_3, CH_3CH_2-]; 22.7 [t, 1xCH_2, CH_3CH_2-]; 23.9 [t, 1xCH_2, $CH_2CH_2C(O)$-]; 29.17 [t, 1xCH_3, $CH_3C(O)$-]; 29.21 [t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 29.4 [t, 1xCH_2, $CH_3CH_2CH_2CH_2CH_2$-]; 29.8 [t, 1xCH_2, -$C(O)CH_2CH_2CH_2CH_2$-]; 31.9 [t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 43.8 [t, 1xCH_2, $CH_2C(O)$-]; 209.4 [s, -C(O)-]

Oxidation of 1-nonane to 2-nonanone with palladium(II) chloride and p-benzoquinone

1-Nonene (1.6 g, 12.5 mmol) was used as a substrate for this experiment



2-nonanone

$C_9H_{18}O$

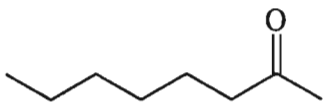
MW=142 g/mol

(2)

Yield: 1.42 g (89%). **B.P.** 200°C/ 760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** *m/z* (EI) 142 (M^+, 15%), 85 (9%), 84 (8%), 71 (44%), 59 (48%), 58 (100%), 57 (44%), 55 (18%). **NMR** ^1H: δ_H (200 MHz) 0.862 [3H, t, CH_3CH_2-]; 1.22 [4xCH_2, m, $CH_3CH_2CH_2CH_2CH_2$-]; 1.55 [2H, m, -$CH_2CH_2C(O)$-]; 2.137 [3H, s, -$C(O)CH_3$]; 2.42 . [2H, t, -$CH_2CH_2C(O)$-]. ^{13}C: δ_C (50 MHz) 14.10 [q, 1xCH_3, CH_3CH_2-]; 22.65 [t, 1xCH_2, CH_3CH_2-]; 23.89 [t, 1xCH_2, $CH_2CH_2C(O)$-]; 29.12 [q, 1xCH_3, $CH_3C(O)$-]; 29.18 [t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 29.86 [t, 1xCH_2, $CH_3CH_2CH_2CH_2CH_2$-]; 31.72 [t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 43.83 [t, 1xCH_2, $CH_2C(O)$-]; 209.49 [s, -C(O)-].

Oxidation of 1-octene to 2-octanone with palladium(II) chloride and p-benzoquinone

1-Octene (1.4 g, 12.5 mmol) was used as a substrate for this experiment



2-octanone

$C_8H_{16}O$

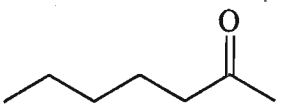
MW=128 g/mol

(3)

Yield: 1.2 g (85%). **B.P.** 175°C/760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** m/z (EI) 128 (M+, 9%), 85 (10%), 71 (17%), 59 (18%), 58 (100%). **NMR** ^1H: δ_H (200 MHz) 0.867 [3H, t, CH_3CH_2-]; 1.277 [3xCH_2, m, $CH_3CH_2CH_2CH_2$-]; 1.557 [2H, m, -$CH_2CH_2C(O)$-]; 2.130 [3H, s, -$C(O)CH_3$]; 2.418 [2H, t, -$CH_2CH_2C(O)$-]. ^{13}C: δ_C 50 MHz) 14.04 [q, 1xCH_3, CH_3CH_2-]; 22.51 [t, 1xCH_2, CH_3CH_2-]; 23.84 [t, 1xCH_2, $CH_2CH_2C(O)$-]; 28.87 [t, 1xCH_3, $CH_3C(O)$-]; 29.85[t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 31.62 [t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 43.82 [t, 1xCH_2, $CH_2C(O)$-]; 209.40 [s, -C(O)-]

Oxidation of 1-heptene to 2-heptanone with palladium(II) chloride and p-benzoquinone

1-Heptene (4.9 g, 50 mmol) was used as a substrate for this experiment



2-heptanone

$C_7H_{14}O$

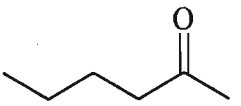
MW=114 g/mol

(4)

Yield: 3.9 g (80%).**B.P.** 152°C/760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** m/z (EI) 114 (M+, 51%), 98 (15%), 71 (29%), 59 (15%), 58 (100%). **NMR** ^1H: δ_H (200 MHz) 0.891 [3H, t, CH_3CH_2-]; 1.283 [2xCH_2, m, $CH_3CH_2CH_2$-]; 1.576 [2H, m, -$CH_2CH_2C(O)$-]; 2.136 [3H, s, -$C(O)CH_3$]; 2.422 [2H, t, -$CH_2CH_2C(O)$-]. ^{13}C: δ_C (50 MHz) 13.94 [q, 1xCH_3, CH_3CH_2-]; 22.49 [t, 1xCH_2, H_3CH_2-]; 23.58 [t, 1xCH_2, $CH_2CH_2C(O)$-]; 29.86 [t, 1xCH_3, $CH_3C(O)$-]; 31.39 [t, 1xCH_2, $CH_3CH_2CH_2CH_2$-]; 43.79 [t, 1xCH_2, $CH_2C(O)$-]; 209.36 [s, -C(O)-]

Oxidation of 1-hexene to 2-hexanone with palladium(II) chloride and p-benzoquinone

1-Hexene (4.2 g, 50 mmol) was used as a substrate for this experiment



2-hexanone

$C_6H_{12}O$

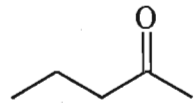
MW=100 g/mol

(5)

Yield: 3.0 g (71%). B.P. 127°C/ 760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** m/z (EI) 100 (M+, 27%), 85 (14%), 71 (11%), 59 (6%), 58 (100%), 57 (30%). **NMR** ^1H: δ_H (200 MHz) 0.891 [3H, t, CH_3CH_2-]; 1.318 [2H, m, CH_3CH_2-]; 1.563 [2H, q, -$CH_2CH_2C(O)$-]; 2.140 [3H, s, -$C(O)CH_3$]; 2.435 [2H, t, -$CH_2CH_2C(O)$-]. ^{13}C: δ_C (50 MHz) 13.88 [q, 1xCH_3, CH_3CH_2-]; 22.33 [t, 1xCH_2, CH_3CH_2-]; 25.99 [t, 1xCH_3, $CH_3C(O)$-]; 29.85 [t, 1xCH_2, $CH_2CH_2C(O)$-]; 43.51 [t, 1xCH_2, $CH_2C(O)$-]; 209.36 [s, -$C(O)$-]

Oxidation of 1-pentene to 2-pentanone with palladium (II) chloride and p-benzoquinone

1-Pentene (3.5 g, 50 mmol) was used as a substrate for this experiment



2-pentanone

$C_5H_{10}O$

MW=86 g/mol

(6)

Yield:1.8 g (50%). **B.P.** 105°C/760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** m/z (EI) 86 (M+, 100%), 71 (68%), 58 (55%), 55 (5%), 53 (5%). **NMR** ^1H: δ_H (200 MHz) 0.92 [3H, t, CH_3CH_2-]; 1.60 [3H, s, -C(O)CH_3]; 2.13 [2H, s, -$CH_2CH_2C(O)$-]; 2.41 [2H, t, -$CH_2CH_2C(O)$-]. ^{13}C: δ_C (50 MHz) 13.86 [q, 1xCH_3, CH_3CH_2-]; 22.33 [t, 1xCH_2, CH_3CH_2-]; 25.95 [t, 1xCH_3, $CH_3C(O)$-]; 43.70 [t, 1xCH_2, $CH_2C(O)$-]; 209.36 [s, -C(O)-]

Oxidation of propylene to acetone with palladium (II) chloride and p-benzoquinone

In a 100 ml round bottom flask fitted with a magnetic stirrer was placed a mixture of palladium (II) chloride (89 mg, 0.5 mmol), *p*-benzoquinone (5.94 g, 55 mmol), and 7:1dimethylformamide / water (20 ml). To the solution propylene was bubbled and the mixture was stirred in ice water for 7 hours. The solution was poured into cold hydrochloric acid (3M, 100 ml) and extracted with ether (5 x 50 ml). The extracts were combined and washed with aqueous sodium hydroxide solution (10%, 3 x 50 ml)

and a portion of brine (50 ml), and then dried over magnesium sulfate. After removal of the solvent, the residue was analysed using GC-MS analysis and no product peak was observed.

3.2.2. The original Wacker system employing $PdCl_2$ / $CuCl_2$ to oxidise olefins to ketones[37]

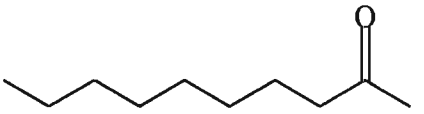
General procedure

In a 50 ml round bottomed two necked flask fitted with a magnetic stirrer and a rubber septum was placed a mixture of palladium(II) chloride (0.265 g, 1.5 mmol) and copper(I) chloride (1.485 g, 15 mmol) in water (1 ml) and dimethylformamide (7 ml). The mixture was stirred at room temperature under an oxygen atmosphere. The initial black solution gradually turned green due to oxygen absorption. After 1 hour, the α-olefin (15 mmol), dissolved in water (0.5 ml) and dimethylformamide (3.5 ml), was added slowly and the solution stirred vigorously at room temperature under an oxygen atmosphere.

The colour of the solution turned to black within 30 min of the reaction, then gradually returned to green. After 24 hours, the reaction mixture was poured into cold hydrochloric acid (100 ml) and extracted with ether (3M, 5 x 50 ml). The extracts were combined and washed with aqueous sodium hydroxide solution (10%, 3 x 50 ml) and a portion of brine (50 ml), and then dried over magnesium sulfate. The solvent was evaporated and the residue was fractional distilled to give methyl ketones.

Oxidation of 1-decene to 2-decanone with palladium(II) chloride / $CuCl_2$ / O_2

The olefin used was 1-decene (2.1 g, 15 mmol).



2-decanone

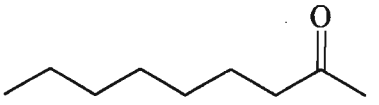
$C_{10}H_{20}O$

MW=156 g/mol

Yield: (70%)

Oxidation of 1-nonane to 2-nonanone with palladium(II) chloride / $CuCl_2$ / O_2

The olefin used was 1-nonene (1.89 g, 15 mmol).



2-nonanone

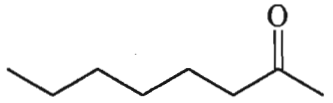
$C_9H_{18}O$

MW=142 g/mol

Yield: (71%)

Oxidation of 1-octene to 2-octanone with palladium(II) chloride / $CuCl_2$ / O_2

The olefin used was 1-octene (1.68 g, 15 mmol).



2-octanone

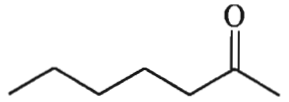
$C_8H_{16}O$

MW=128 g/mol

Yield: (69%).

Oxidation of 1-heptene to 2-heptanone with palladium(II) chloride / $CuCl_2$ / O_2

The olefin used was 1-heptene (1.47 g, 15 mmol).



2-heptanone

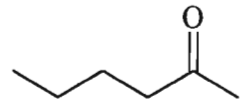
$C_7H_{14}O$

MW=114 g/mol

Yield: (69%).

Oxidation of 1-hexene to 2-hexanone with palladium(II) chloride / $CuCl_2$ / O_2

The olefin used was 1-hexene (1.26 g, 15 mmol).



2-hexanone

$C_6H_{12}O$

MW=100 g/mol

Yield: (68%).

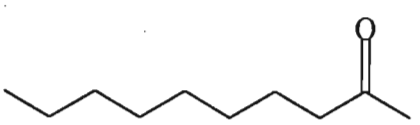
3.2.3. $Pd(OAc)_2$ / Hydrogen Peroxide oxidation of olefins to ketones[80]

General procedure

In a 100 ml round bottomed two necked flask fitted with a magnetic stirrer, a condenser, and a 50 ml dropping funnel (for introduction of H_2O_2), was placed a mixture of palladium(II) acetate (0.0056 g, 2.5 $x10^{-5}$ mol), hydrogen peroxide 30% (21.25 g, 0.1875 mol), acetic acid (solvent) (50 ml) and the α-olefin (0.0375 mol). The mixture was stirred at 80°C and the H_2O_2 was introduced dropwise into the mixture during 30 minutes at the reaction temperature. After 6 hours, the mixture was cooled and water was added. The product was extracted with ether (3 x 50 ml). The extracts were combined and dried over $MgSO_4$. After removal of the solvent, the residue was distilled to give methyl ketone.

Oxidation of 1-decene to 2-decanone with $Pd(OAc)_2$ / Hydrogen Peroxide

The olefin used for this run was 1-decene (5.26 g, 0.0375 mol).



2-decanone

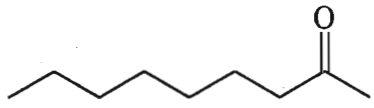
$C_{10}H_{20}O$

MW=156 g/mol

Yield: (83%)

Oxidation of 1-nonane to 2-nonanone with $Pd(OAc)_2$ / Hydrogen Peroxide

The olefin used for this run was 1-nonene (4.73, 0.0375 mol).



2-nonanone

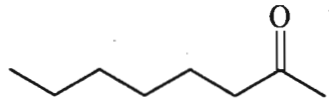
$C_9H_{18}O$

MW=142 g/mol

Yield: (85%)

Oxidation of 1-octene to 2-octanone with $Pd(OAc)_2$ / Hydrogen Peroxide

The olefin used for this run was 1-octene (4.21 g, 0.0375 mol).



2-octanone

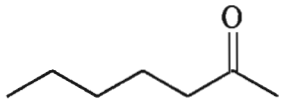
$C_8H_{16}O$

MW=128 g/mol

Yield: (80%).

Oxidation of 1-heptene to 2-heptanone with $Pd(OAc)_2$ / Hydrogen Peroxide

The olefin used for this run was 1-heptene (3.68 g, 0.0375 mol).



2-heptanone

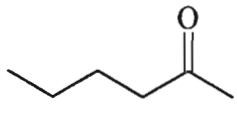
$C_7H_{14}O$

MW=114 g/mol

Yield: (77%).

Oxidation of 1-hexene to 2-hexanone with $Pd(OAc)_2$ / Hydrogen Peroxide

The olefin used for this run was 1-hexene (3.16 g, 0.0375 mol).



2-hexanone

$C_6H_{12}O$

MW=100 g/mol

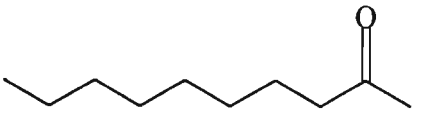
Yield: (57%).

3.2.4. $PdCl_2$ / $CuCl_2$ / O_2 /quaternary ammonium salt (CTAB) catalysed oxidation of olefins to ketones.[84] (PHASE TRANSFER CATALYSIS).

In a 100 ml two necked round bottomed flask was placed a mixture of palladium chloride (0.177 g, 1.0 mmol) and $CuCl_2.2H_2O$ (1.705 g, 10 mmol) in water (10 ml), and the mixture was stirred for 10 minutes. The α-olefin (25 mmol) was added followed by benzene (15 ml) and cetyltrimethylammonium bromide (0.72892 g, 2.0 mmol). Oxygen was bubbled through the solution at 80°C for 48 hours. After cooling to room temperature, ethyl acetate (15 ml) was added and the solution was filtered. The filtrate was dried over $MgSO_4$ and distilled affording methyl ketones in good yields.

Oxidation of 1-decene to 2-decanone with $PdCl_2$ / $CuCl_2$ / O_2 / CTAB

The olefin used for this run was 1-decene (3.51 g, 25 mmol).



2-decanone

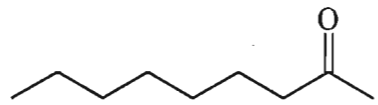
$C_{10}H_{20}O$

MW=156 g/mol

Yield: (69%)

Oxidation of 1-nonene to 2-nonanone with $PdCl_2$ / $CuCl_2$ / O_2 / CTAB

The olefin used for this run was 1-nonene (3.16 g, 25 mmol).



2-nonanone

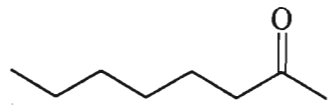
$C_9H_{18}O$

MW=142 g/mol

Yield: (70%)

Oxidation of 1-octene to 2-octanone with $PdCl_2$ / $CuCl_2$ / O_2 / CTAB

The olefin used for this run was 1-octene (2.81 g, 25 mmol).



2-octanone

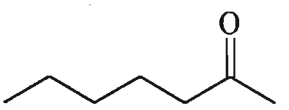
$C_8H_{16}O$

MW=128 g/mol

Yield: (70%).

Oxidation of 1-heptene to 2-heptanone $PdCl_2$ / $CuCl_2$ / O_2 / CTAB

The olefin used for this run was 1-heptene (2.46 g, 25 mmol).



2-heptanone

$C_7H_{14}O$

MW=114 g/mol

Yield: (64%).

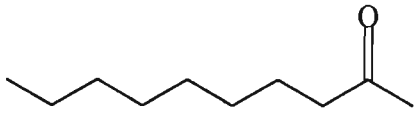
3.2.5. $PdCl_2$ / $CuCl_2$ / O_2 / PEG-200 oxidation of α-olefin to ketones [88] (PHASE TRANSFER CATALYSIS)

General procedure

In a 100 ml two-necked round bottom flask fitted with a magnetic stirrer, was placed a mixture of palladium (II) chloride (0.177 g , 1 mmol), $CuCl_2$-$2H_2O$ (0.269 g , 2 mmol), PEG-200 (20 ml), water (2 ml) and α-olefin (25 mmol). Oxygen was bubbled through the stirred reaction mixture at 65°C for 48 hours. When the reaction was complete, water (25 ml) was added. The product was extracted with hexane (3 x 50 ml), and the combined extracts were dried over $MgSO_4$. After the solvent was removed, the residue was distilled to give 2-ketone and 3-ketone,the yields are stated below.

Oxidation of 1-decene to 2-decanone with $PdCl_2$ / $CuCl_2$ / O_2 / PEG-200

The olefin used for this run was 1-decene (3.51 g, 25 mmol).



2-decanone

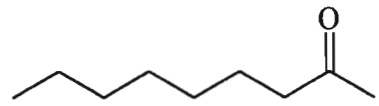
$C_{10}H_{20}O$

MW=156 g/mol

Yield: (60%)

Oxidation of 1-nonane to 2-nonanone with $PdCl_2$ / $CuCl_2$ / O_2 / PEG-200

The olefin used for this run was 1-nonene (3.16 g, 25 mmol).



2-nonanone

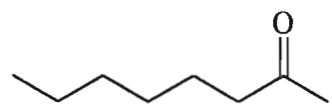
$C_9H_{18}O$

MW=142 g/mol

Yield: (61%)

Oxidation of 1-octene to 2-octanone with $PdCl_2$ / $CuCl_2$ / O_2 / PEG-200

The olefin used for this run was 1-octene (2.81 g, 25 mmol).



2-octanone

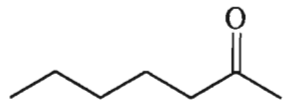
$C_8H_{16}O$

MW=128 g/mol

Yield: (55%).

Oxidation of 1-heptene to 2-heptanone with palladium (II) chloride and PEG-200.

The olefin used for this run was 1-heptene (2.46 g, 25 mmol).



2-heptanone

$C_7H_{14}O$

MW=114 g/mol

Yield: (58%).

3.2.6. Aerobic oxidation ($CuCl_2$ / 18-C-6 / CH_3CHO) of alkanes and alkenes to ketones.[121]

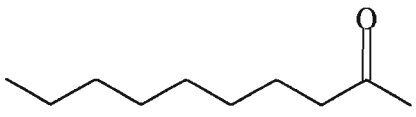
General procedure

A mixture of copper chloride (1.00×10^{-4} mmol) and 18-crown-6 (1.00×10^{-4} mmol) in dichloromethane (5 ml) was stirred for 20 minutes in an autoclave (100 ml). An alkane or alkene (40 mmol) and acetaldehyde (4.00 mmol) was added to the reaction mixture. The reaction mixture was flushed with molecular oxygen (1 Atm), and reacted by stirring at 70°C for 24 hours.

When the reaction was complete, the solvent was removed and the residue was extracted with ether(3 x 25 ml). The ether extracts were combined and washed with saturated sodium bicarbonate (2 x 25 ml) and brine (25 ml). The product mixture was analysed by GC-MS, and it consisted the desired product presented below and some by-products.

Aerobic oxidation of 1-decene to 2-decanone with $CuCl_2$ / 18-C-6 / CH_3CHO

The olefin used for this run was 1-decene (5.6 g, 40 mmol).



2-decanone

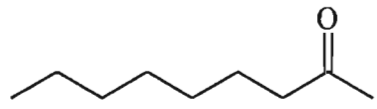
$C_{10}H_{20}O$

MW=156 g/mol

Yield: (58%)

Aerobic oxidation of 1-nonene to 2-nonanone with $CuCl_2$ / 18-C-6 / CH_3CHO

The olefin used for this run was 1-heptene (5.1 g, 40 mmol).



2-nonanone

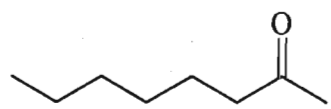
$C_9H_{18}O$

MW=142 g/mol

Yield: (57%)

Aerobic oxidation of 1-octene to 2-octanone with $CuCl_2$ / 18-C-6 / CH_3CHO

The olefin used for this run was 1-octene (4.5 g, 40 mmol).



2-octanone

$C_8H_{16}O$

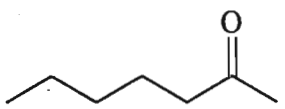
MW=128 g/mol

Yield: (58%).

Aerobic oxidation of 1-heptene and n-heptane to 2-heptanone with $CuCl_2$ / 18-C-6 / CH_3CHO

The olefin used for this run was 1-heptene (3.9 g, 40 mmol).

The alkane used for this run was n-heptane (4.0 g, 40mmol)



2-heptanone

$C_7H_{14}O$

MW=114 g/mol

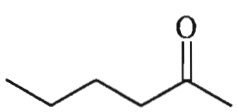
Yield:(56%), from 1-heptene.

Yield:(30%), from n-heptane.

Aerobic oxidation of 1-hexene and n-hexane to 2-hexanone $CuCl_2$ / 18-C-6 / CH_3CHO

The olefin used for this run was 1-hexene (3.4 g, 40 mmol).

The alkane used for this run was n-hexane (3.5 g, 40mmol)



2-hexanone

$C_6H_{12}O$

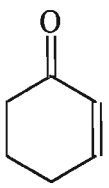
MW=100 g/mol

Yield: (55%), from 1-hexene.

Yield:(30%), from n-hexane.

Aerobic oxidation of cyclohexene to cyclohex-2-en-one with $CuCl_2$ / 18-C-6 / CH_3CHO

The olefin used for this run was clohexenene (3.3 g, 40 mmol).



cyclohex-2-en-one

C_6H_8O

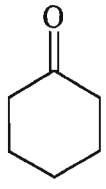
MW=96 g/mol

(8)

Yield: 1.47 g (45%). **B.P.** 170°C/760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** m/z (EI) 96 (M+, 30%), 68 (100%), 55 (9%), 53 (10%), 51 (7%). **NMR** ^1H: δ_H (200 MHz) 2.032 [2H, q -CH_2**H_2**CH_2C(O)-]; 2.397 [2x2H_2, m, -**H_2**C(O)- and -CH_2CH=CH-]; 6.031 [H, d, -C(O)**H**=CH-]; 7.015 [H, d, -C(O)CH=**H**-]. ^{13}C: δ_C (50 MHz) 22.73 [t, 1xCH_2, -CH_2**CH_2**CH_2-]; 25.67 [t, 1xCH_2, -**CH_2**CH=CH-]; 38.11 [t, 1xCH_2, -**CH_2**C(O)-]; 129.88 [d, 1xCH, -CH=**C**HC(O)-]; 150.83 [d, 1xCH, -**C**H=CHC(O)-]; 199.84 [s, **C**(O)-].

Aerobic oxidation of cyclohexane to cyclohexanone with $CuCl_2$ / 18-C-6 / CH_3CHO

An alkane used for this run was cyclohaxane (3.4 g, 40 mmol).



cyclohexanone

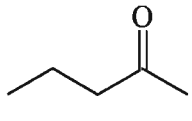
$C_6H_{10}O$

MW=98 g/mol

(7)

Yield: 1.97 g (58%). B.P. 160°C/760 mmHg. **IR:** ν_{max} 1710 cm^{-1} (C=O). **GC-MS** m/z (EI) 98 (M+, 68%), 83 (13%), 70 (31%), 69 (44%), 58 (13%), 55(100%). **NMR** ^1H: δ_H (200 MHz) 1.744 [2H, m -CH2CH$_2$C**H**$_2$CH$_2$CH$_2$-]; 1.866 [2x2H$_2$, m, -CH2C**H**$_2$CH$_2$C**H**$_2$CH$_2$-]; 2.340 [x2H, m, C**H**$_2$CH$_2$CH$_2$CH$_2$C**H**$_2$-]. ^{13}C: δ_C (50 MHz) 25.01 [t, 1xCH$_2$, -CH2CH$_2$**C**H$_2$CH$_2$CH$_2$-]; 27.05 [t, 2xCH$_2$, -CH2**C**H$_2$CH$_2$CH$_2$CH$_2$O-]; 42.00 [t, 2xCH$_2$, -**C**H$_2$CH$_2$CH$_2$CH$_2$CH$_2$-]; 212.11 [s, -**C**(O)-]

Aerobic oxidation of 1- pentene to 2-pentanone with $CuCl_2$ / 18-C-6 / CH_3CHO



2-pentanone

$C_5H_{10}O$

MW=86 g/mol

Yield: (25%).

3.2.7. $PdCl_2$ / *p*-Benzoquinone system coupled with electrolysis, a complete catalytic system for conversion of olefins to ketones

Oxidation of the hydroquinone to benzoquinone[105]

The voltage at which the hydroquinone is oxidized to benzoquinone was investigated using the reaction conditions below:

Cyclic voltammograms of hydroquinone (2.0 mM) in acetonitrile containing 2,6-lutidine (0 mM; 0.4 mM; 0.8 mM; 1.2 mM and 2.0 mM) were constructed. A supporting electrolyte used was $NaClO_4$ (0.1 M). From these series of experiments the voltage at which the hydroquinone gets oxidised to benzoquinone was deduced to be 0.976 V, (Figure 1, Section 2)

Oxidation of olefins[104]

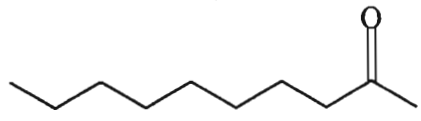
Olefins were then to be oxidised using palladium acetate, and the palladium would be reoxidised by the benzoquinone, which is electrochemically reoxidized back to benzoquinone to complete the cycle.

General procedure

An anodic solution (100 ml) containing cyclohaxene (0.822 g, 10 mmol), $Pd(OAc)_2$ (0.0449 g, 0.2 mmol), and supporting electrolyte (0.3M Et_4NBF_4) was electrolysed using a Platinum anode at constant voltage of 0.976 V in a divided cell at room temperature. The reaction time was highly determined by the length of the olefin. The lower aliphatic and cyclic olefins took less than two hours for the reactions to go to completion, but higher olefins took much longer. Cyclooctene was found to be resistant to oxidation under these conditions, but aliphatic olefins were all successfully oxidized to corresponding ketones in yields ranging from 58-62%.

Oxidation of 1-decene to 2-decanone with $Pd(AOc)_2$ / p-benzoquinone / electrolysis

The olefin used for this run was 1-decene (1.4 g, 10 mmol).



2-decanone

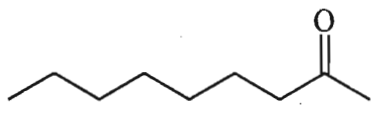
$C_{10}H_{20}O$

MW=156 g/mol

Yield: (62%)

Oxidation of 1-nonane to 2-nonanone with $Pd(AOc)_2$ / p-benzoquinone / electrolysis

The olefin used for this run was 1-nonene (1.3 g, 10 mmol).



2-nonanone

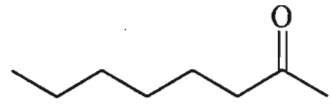
$C_9H_{18}O$

MW=142 g/mol

Yield: (59%)

Oxidation of 1-octene to 2-octanone with $Pd(AOc)_2$ / p-benzoquinone / electrolysis

The olefin used for this run was 1-octene (1.1 g, 10 mmol).



2-octanone

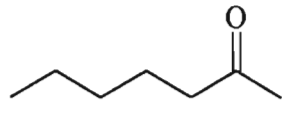
$C_8H_{16}O$

MW=128 g/mol

Yield: (60%).

Oxidation of 1-heptene to 2-heptanone with $Pd(AOc)_2$ / p-benzoquinone / electrolysis.

The olefin used for this run was 1-heptene (1.0 g, 10 mmol).



2-heptanone

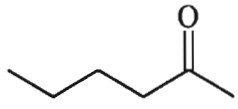
$C_7H_{14}O$

MW=114 g/mol

Yield: (59%).

Oxidation of 1-hexene to 2-hexanone with $Pd(AOc)_2$ / p-benzoquinone / electrolysis

The olefin used for this run was 1-hexene (0.8 g, 10 mmol).



2-hexanone

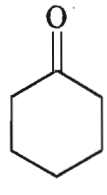
$C_6H_{12}O$

MW=100 g/mol

Yield: (60%).

Oxidation of cyclohexene to cyclohexanone with $Pd(AOc)_2$ / p-benzoquinone / electrolysis

The olefin used for this run was cyclohexene (0.8 g, 40 mmol).



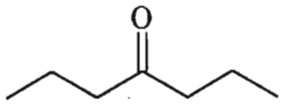
cyclohexanone

$C_6H_{10}O$

MW=98 g/mol

Yield: (58%).

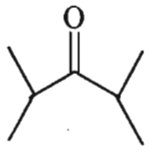
3.2.8. Synthesis of dipropyl ketones (C_7 ketones), with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)[113]



4-Heptanone

$C_6H_{12}O$

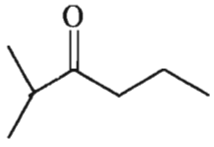
MW=100 g/mol



2,4-Dimethylpent-3-one

$C_6H_{12}O$

MW=100 g/mol



2-Methylhexan-3-one

$C_6H_{12}O$

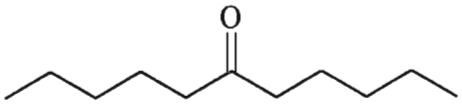
MW=100 g/mol

Yield: (75%)

Triphenylphosphine (10 mmol, 2.632 g), palladium acetate (1 mmol, 0.2245 g), trifluoroacetic acid (19 ml) and water (1 ml) were charged into a 100 ml Parr reactor.

The reactor was then pressurised to (1 Atm) with a 2:1:1 propylene, carbon monoxide and hydrogen gas mixture. The reactor was then heated to 80°C and stirred for one hour. After cooling ,the products were collected and the solvent was distilled off. GC-MS analysis showed the formation of C_7 ketones. Isolation of pure product was unsuccessful.

Synthesis of 6-undecanone (C_{11} ketone), and higher aliphatic dialkyl ketones with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)[113]



6-Undecanone

$C_{11}H_{22}O$

MW=171 g/mol

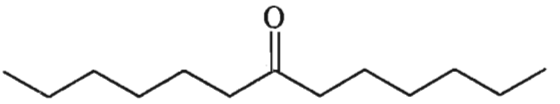
Yield: (70%)

General procedure

Triphenylphosphine (10 mmol, 2.632 g), palladium acetate (1 mmol, 0.2245 g), trifluoroacetic acid (19 ml) and water (1 ml) were charged into a 100 ml Parr reactor. In order to maintain the ratio of olefin: CO: H_2 at 2:1:1, 1-pentene (4.285 mmol, 0.300 g , 0.548 ml) were charged into the reactor. The reactor was then pressurised with a CO + H_2 mixture to (1 Atm) then heated to 90°C and stirred at this temperature for three hours. After cooling, the product mixture was collected and the solvent (trifluoroacetic acid) was distilled off. GC-MS analysis of the residue mixture indicated the formation of C_{13} dialkyl ketones. Isolation of any pure dialkyl ketone was unsuccessful.

Synthesis of 8-tridecanone ketone (C_{13} ketone) with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)

The olefin used for this run was 1-hexene (0.360 g, 4.285 mmol).



7-Tridecanone

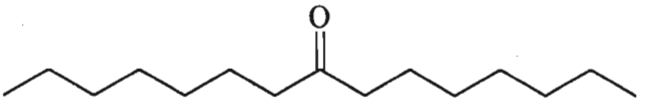
$C_{13}H_{26}O$

MW=198 g/mol

Yield: (76%)

Synthesis of 8-pentadecanone ketone (C_{15} ketone) with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)

The olefin used for this run was 1-heptene (0.420 g, 4.285 mmol).



8-Pentadecanone

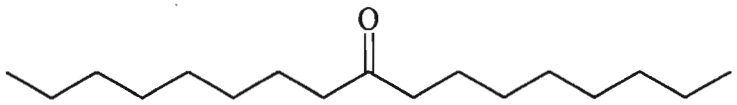
$C_{15}H_{30}O$

MW=226 g/mol

Yield: (30%)

Synthesis of 9-heptadecanone ketone (C_{17} ketone) with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)

The olefin used for this run was 1-octene (0.480 g, 4.285 mmol).



9-Heptadecanone

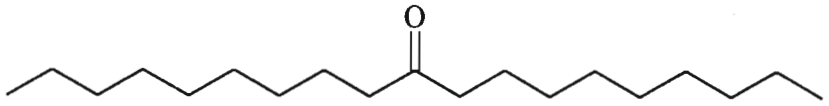
$C_{17}H_{34}O$

MW=254 g/mol

Yield: (10%)

Synthesis of 10-nonadecanone ketone (C_{19} ketone) with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)

The olefin used for this run was 1-nonene (0.540 g, 4.285 mmol).



10-Nonadecanone

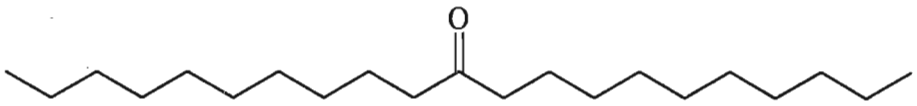
$C_{19}H_{38}O$

MW=282 g/mol

Yield: (8%)

Synthesis of 11-heneicosanone ketone (C_{21} ketone) with $Pd(OAc)_2$ / PPh_3 / CF_3COOH)

The olefin used for this run was 1-decene (0.600 g, 4.285 mmol).



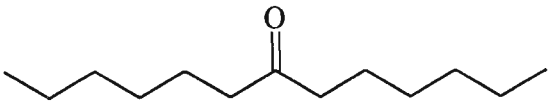
11-Heneicosanone

$C_{21}H_{42}O$

MW=310 g/mol

Yield: (7%)

Synthesis of 7-tridecanone ketones in a solvent other than trifluoroacetic acid



7-Tridecanone

$C_{13}H_{26}O$

MW=198 g/mol

Yield: (15%)

General procedure

Triphenylphosphine (10 mmol, 2.632 g), palladium acetate (1 mmol, 0.2245 g), acetonitrile (18 ml), trifluoroacetic acid (1 ml) and water (1 ml) were charged into a 100 ml Parr reactor. In order to maintain the ratio of olefin: CO: H_2 at 2:1:1, 1-hexene (4.285 mmol, 0.369 g , 0.548 ml) were charged into the reactor. The reactor was then pressurised with a CO + H_2 mixture to (1 Atm) then heated to 90^0C and stirred at this temperature for three hours. After cooling, the product mixture was collected and the solvent (trifluoroacetic acid) was distilled off. GC-MS analysis of the residue mixture indicated the formation of C_{13} dialkyl ketone(7-Tridecanone). A pure product was not isolable.

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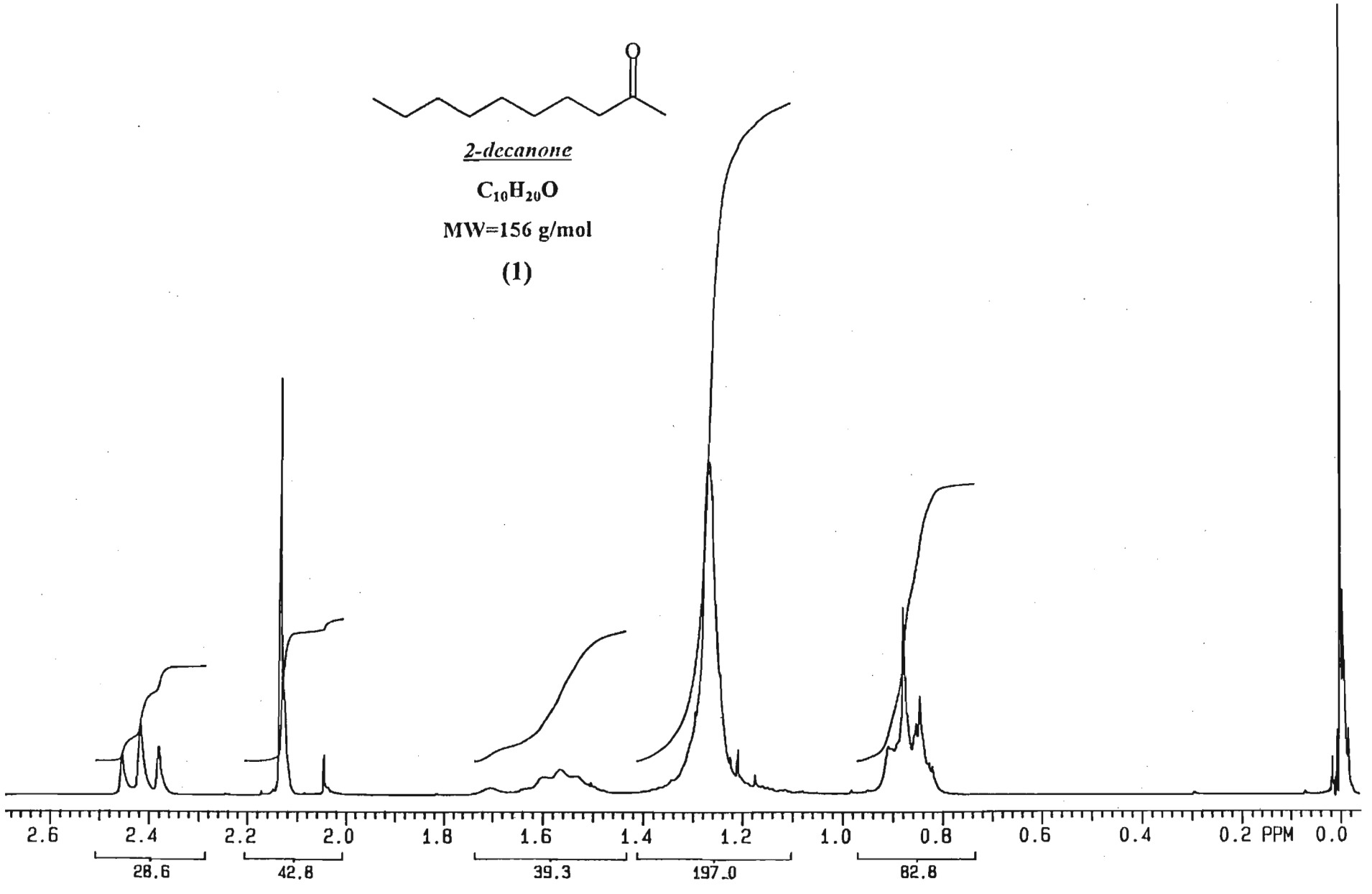
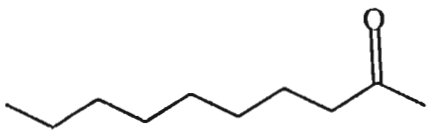
5. APPENDIX

^{1}H and ^{13}C NMR Spectra

and

IR Spectra


2-decanone
C10H20O
MW=156 g/mol
(1)
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2 PPM
0.0
28.6
42.8
39.3
197.0
82.8

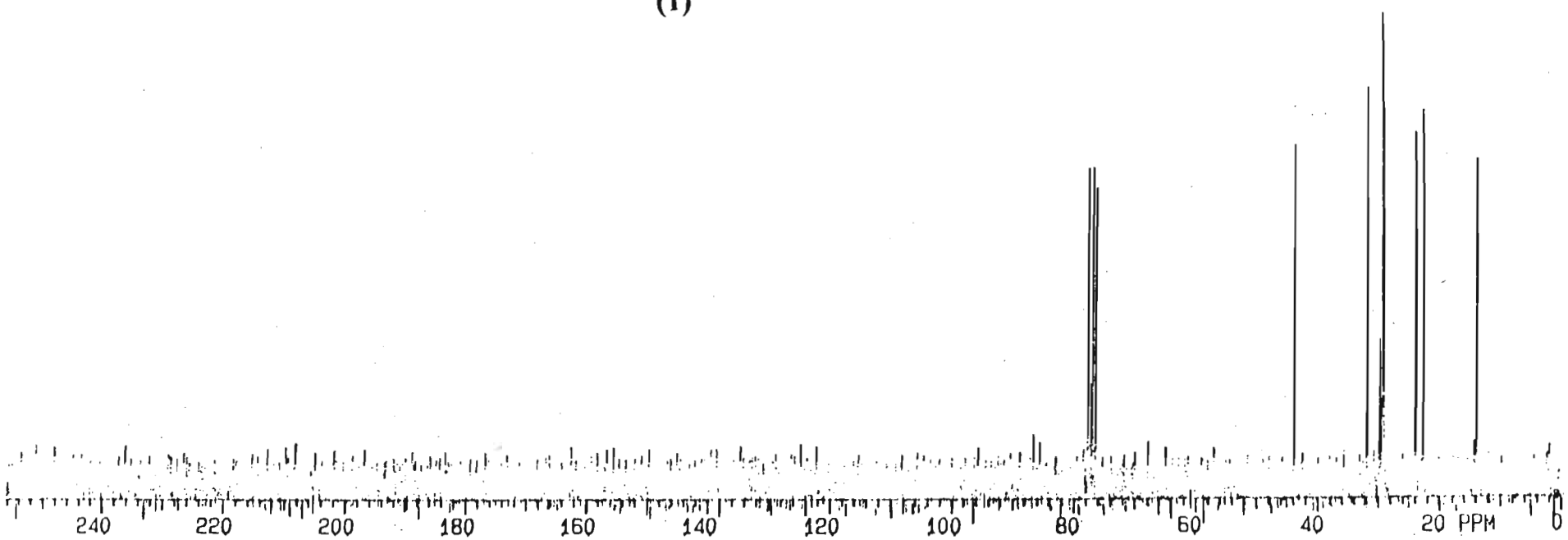


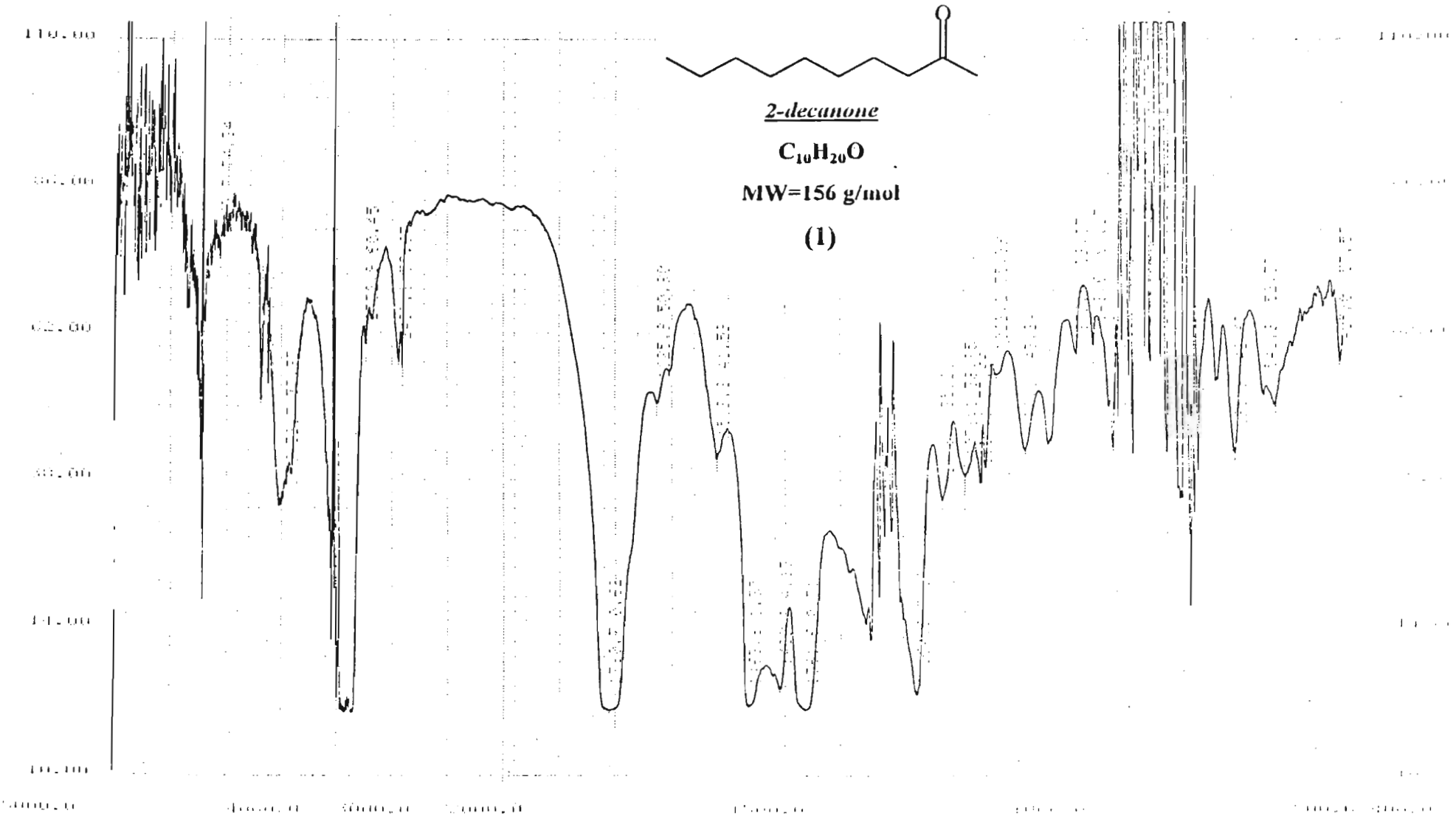
2-decanone

$C_{10}H_{20}O$

MW=156 g/mol

(1)





2-decanone

$C_{10}H_{20}O$

MW=156 g/mol

(1)

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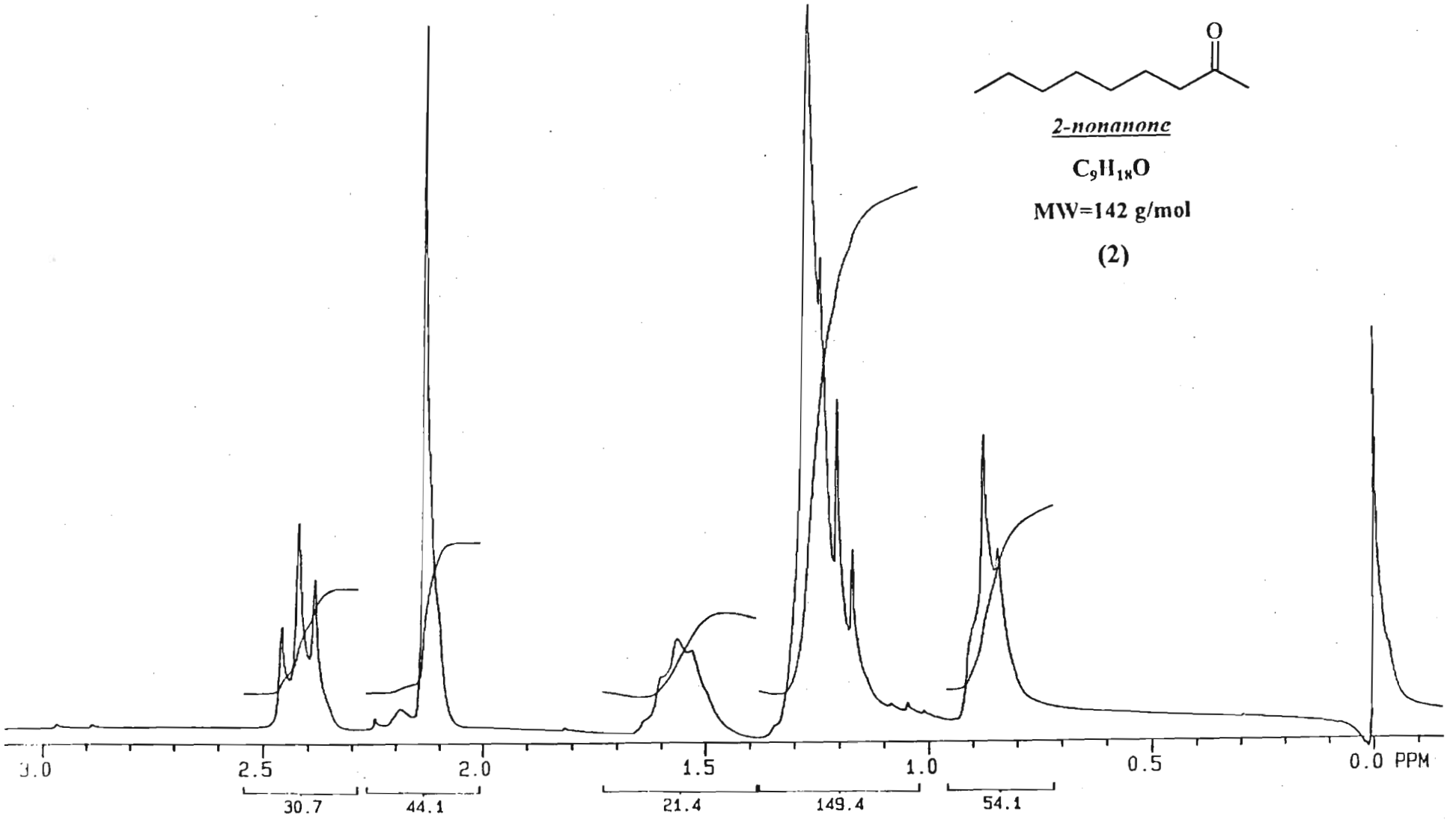
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2-nonanone
C9H18O
MW=142 g/mol
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2.5
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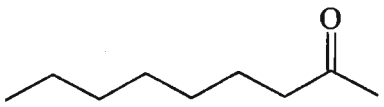
1.5
1.0
0.5
0.0 PPM
30.7
44.1
21.4
149.4
54.1

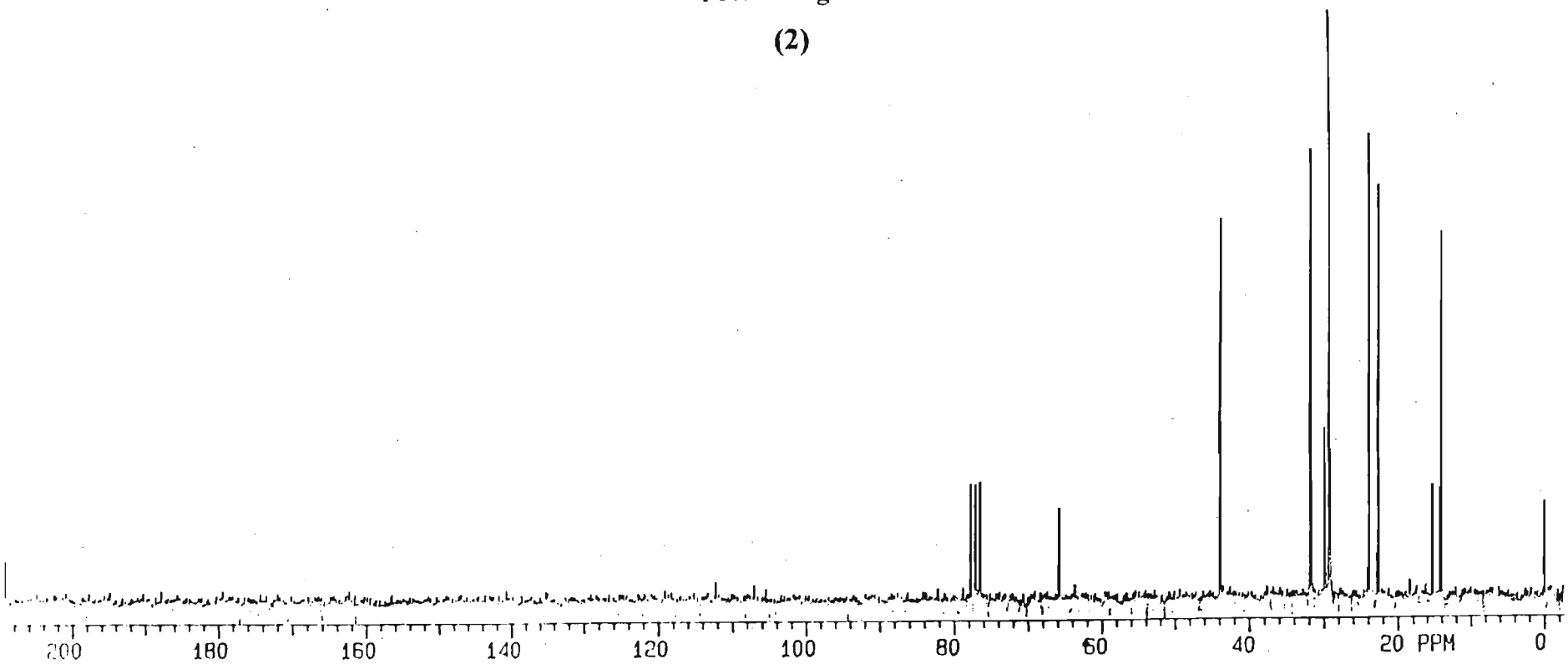


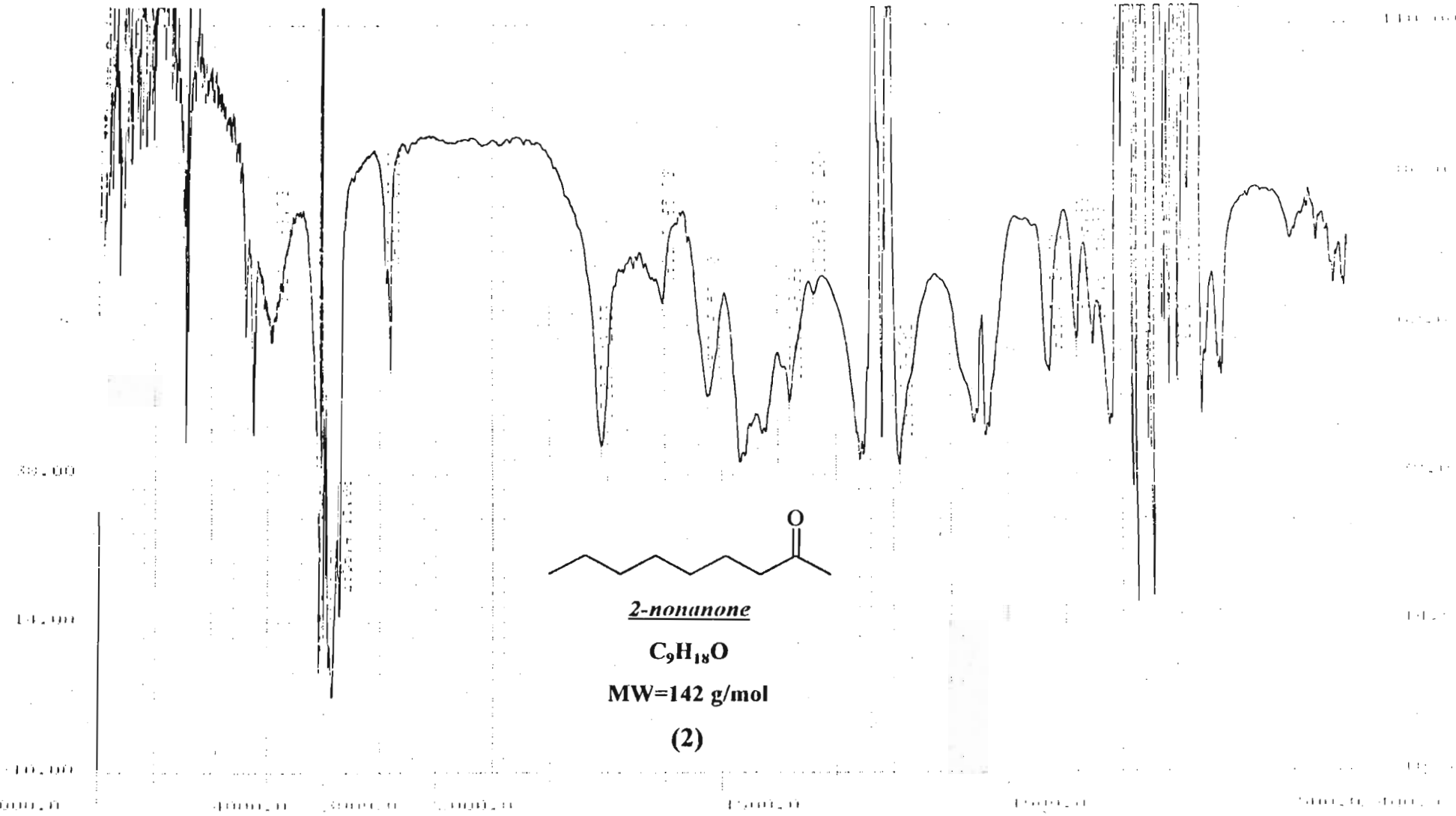
2-nonanone

$C_9H_{18}O$

MW=142 g/mol

(2)





2-nonanone

$C_9H_{18}O$

MW=142 g/mol

(2)

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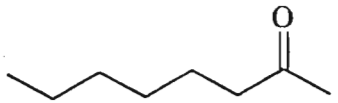

2-octanone

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MW=128 g/mol

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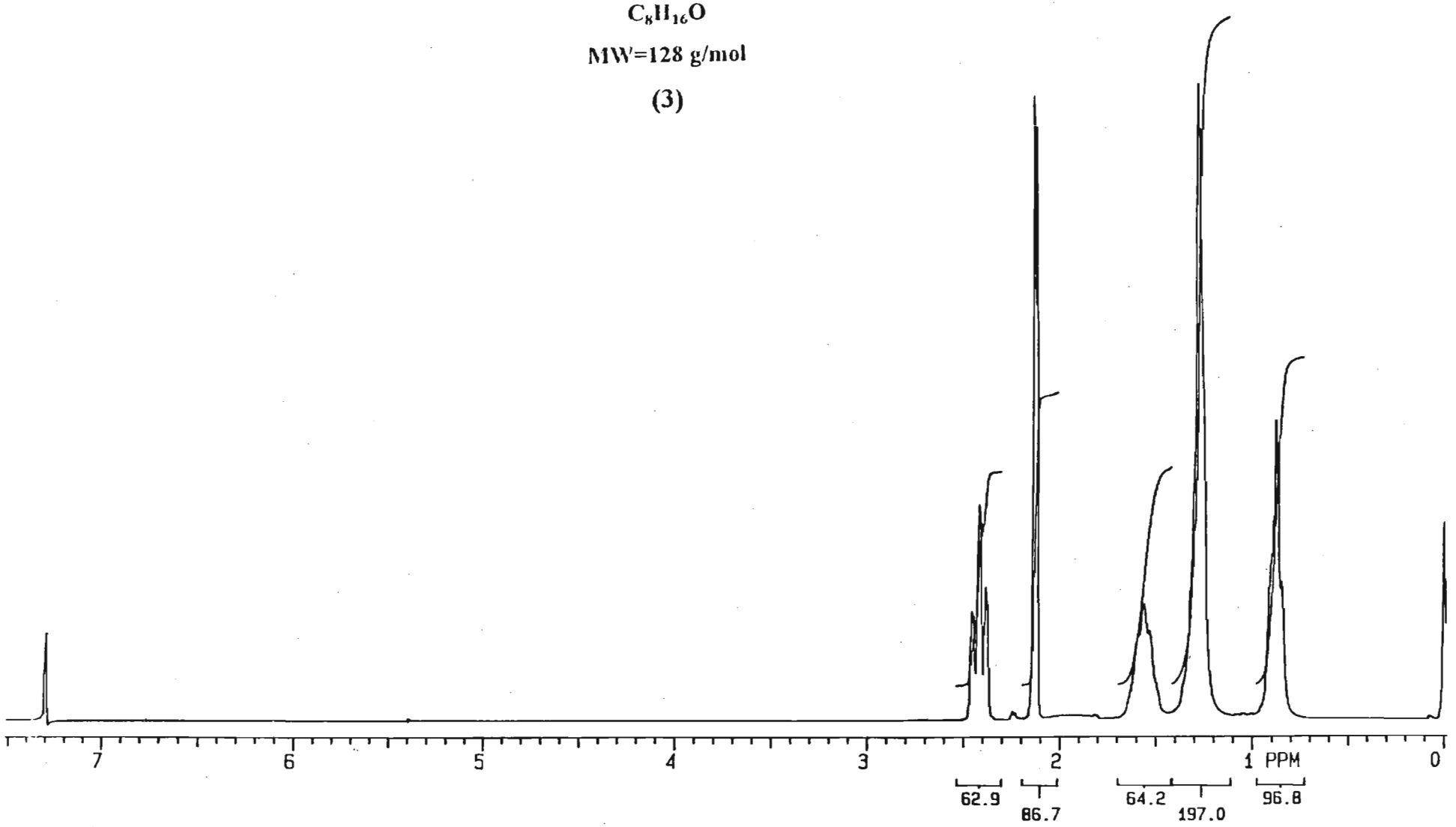
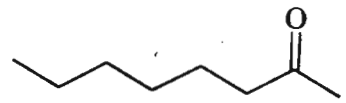


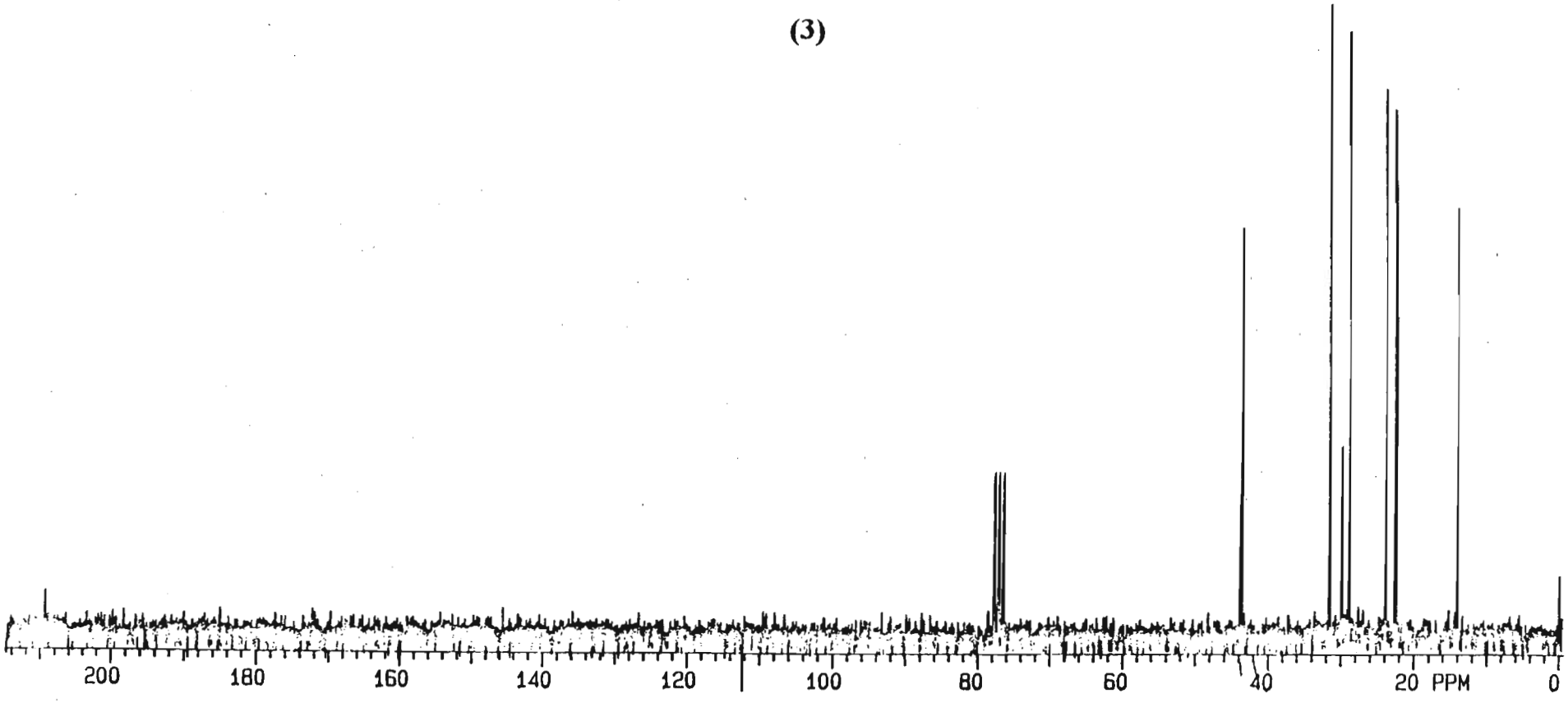


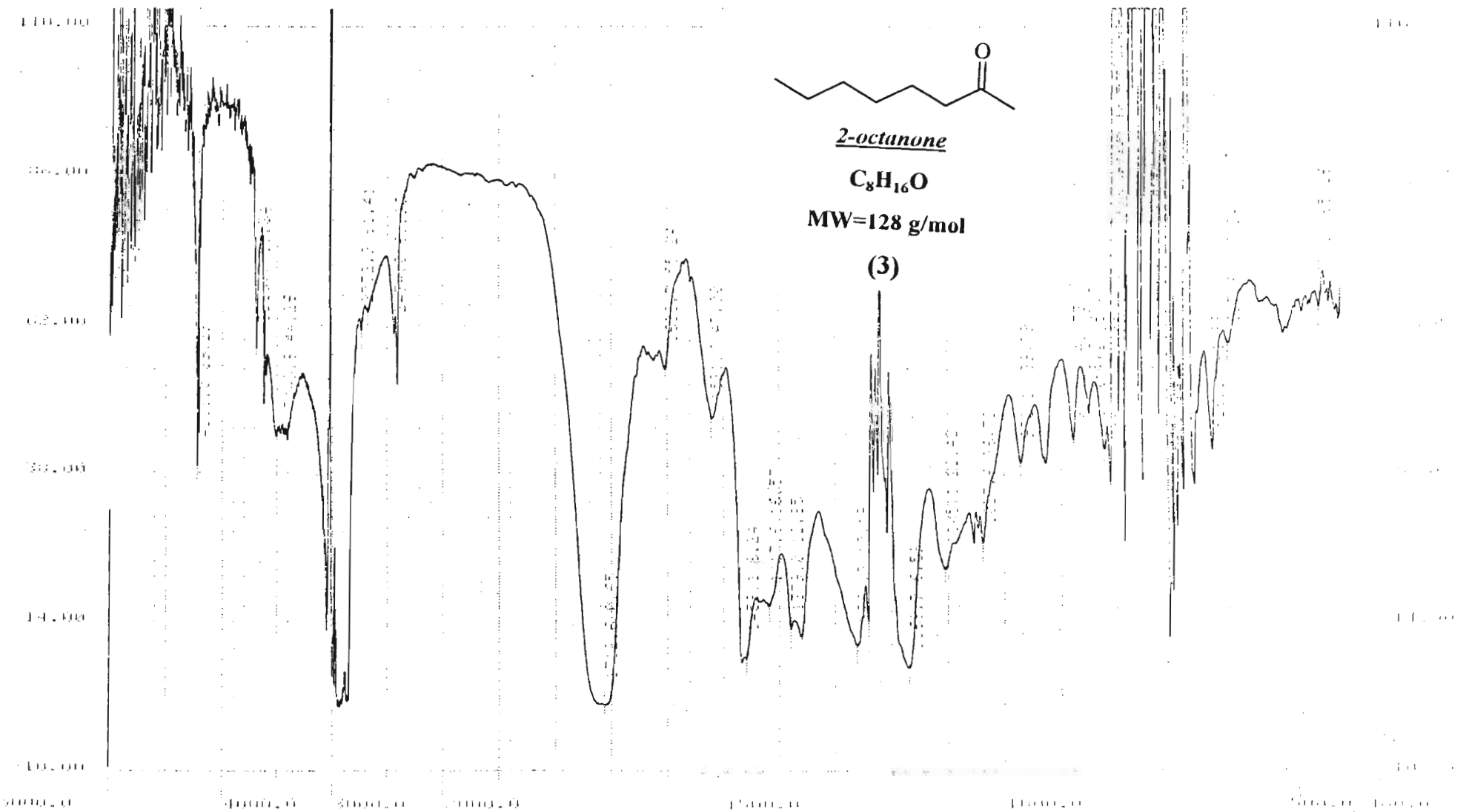
2-octanone

$C_8H_{16}O$

MW=128 g/mol

(3)





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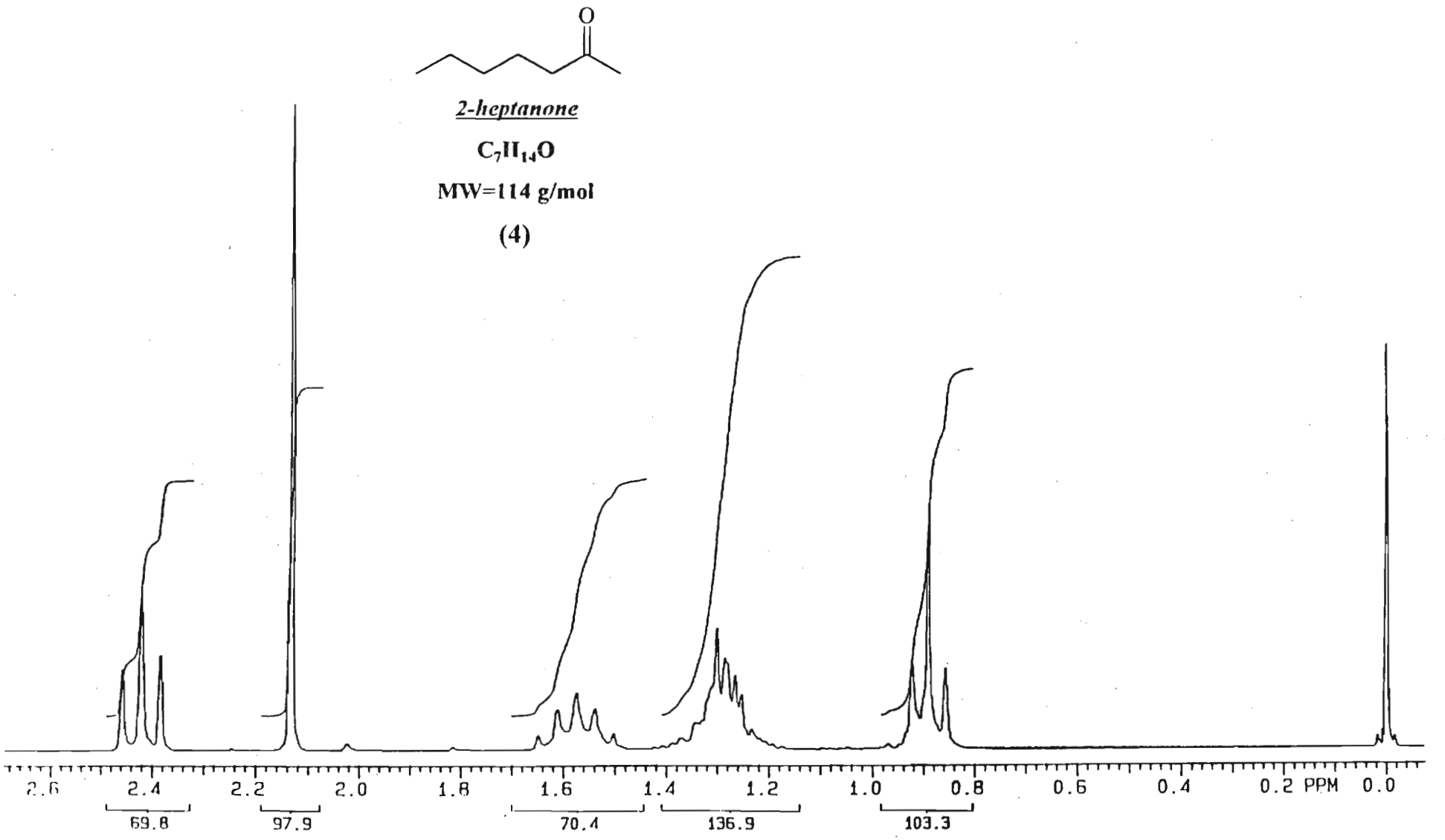
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2-heptanone
C7H14O
MW=114 g/mol
(4)
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2.0
1.8
1.6
1.4
1.2
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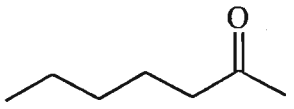
70.4
136.9
103.3

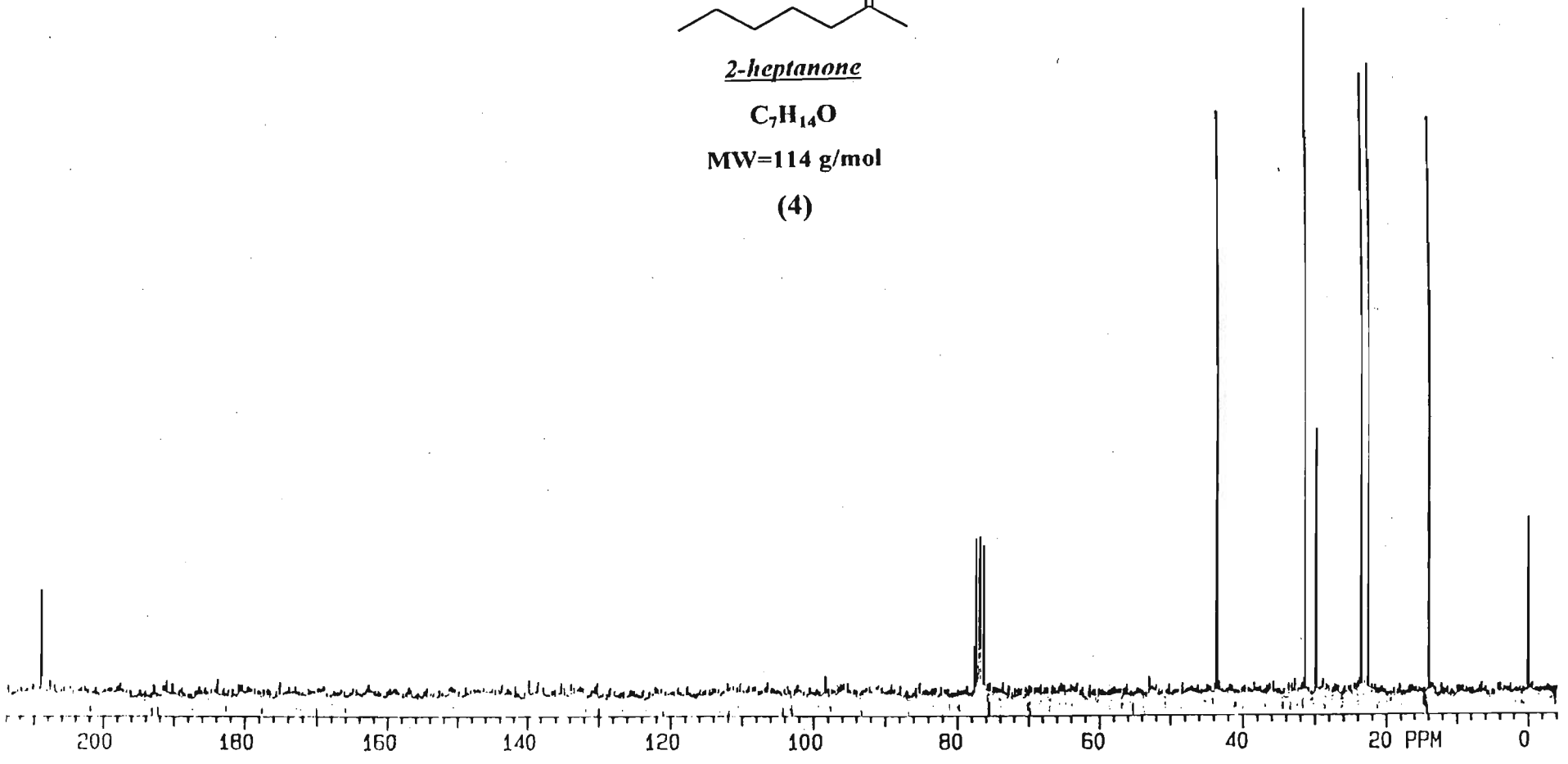


2-heptanone

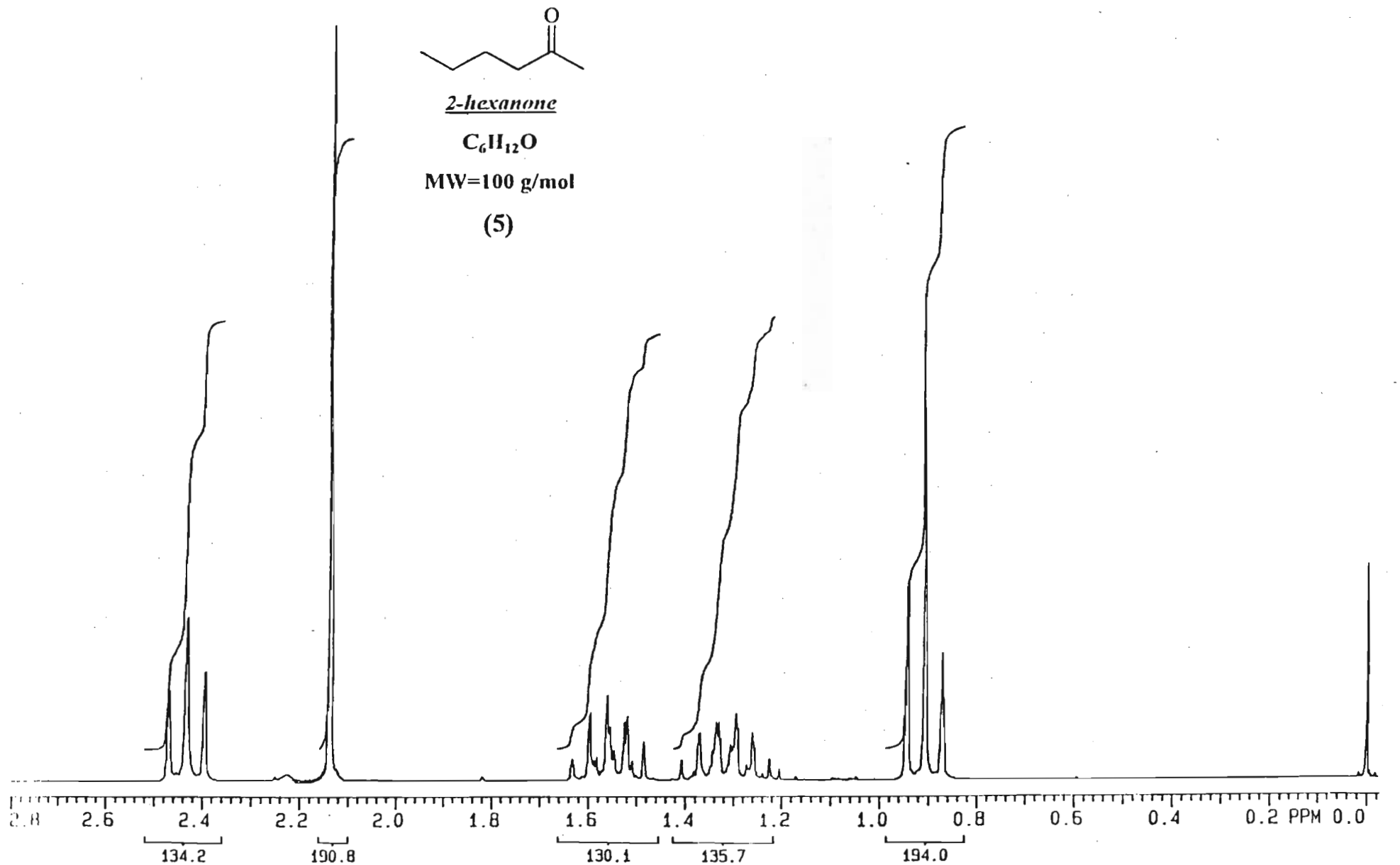
$C_7H_{14}O$

MW=114 g/mol

(4)



2-heptanone
C7H14O
MW=114 g/mol
(4)


O
2-hexanone
C6H12O
MW=100 g/mol
(5)
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2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2 PPM 0.0
134.2
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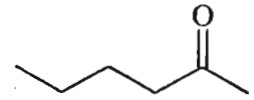

2-hexanone

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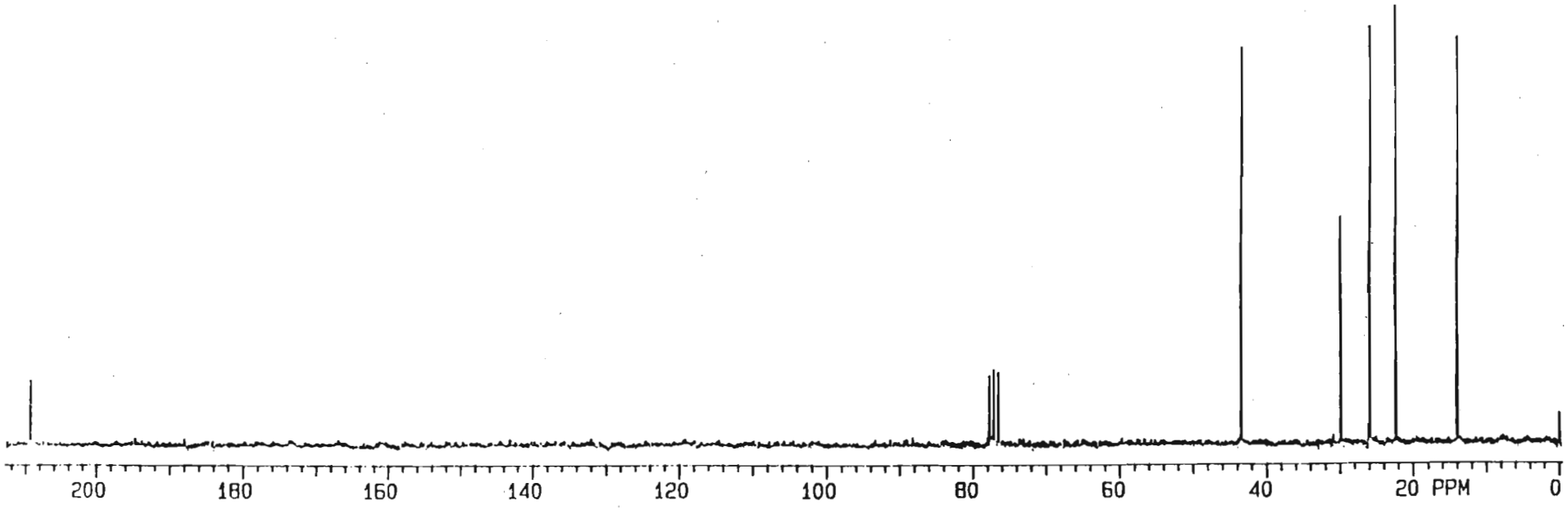
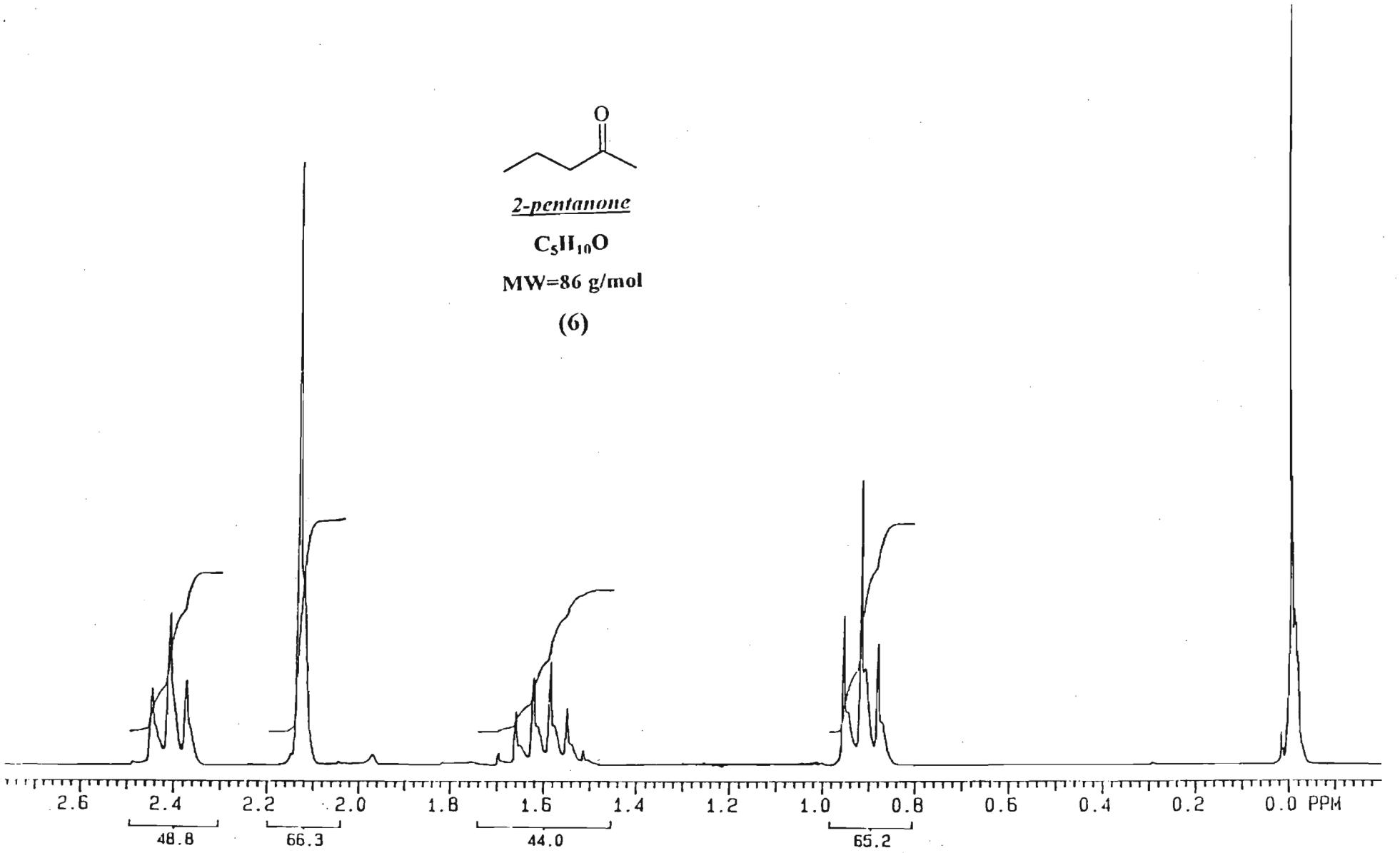
(5)

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C5H10O
MW=86 g/mol
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2.2
2.0
1.8
1.6
1.4
1.2
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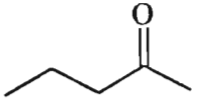

2-pentanone

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MW=86 g/mol

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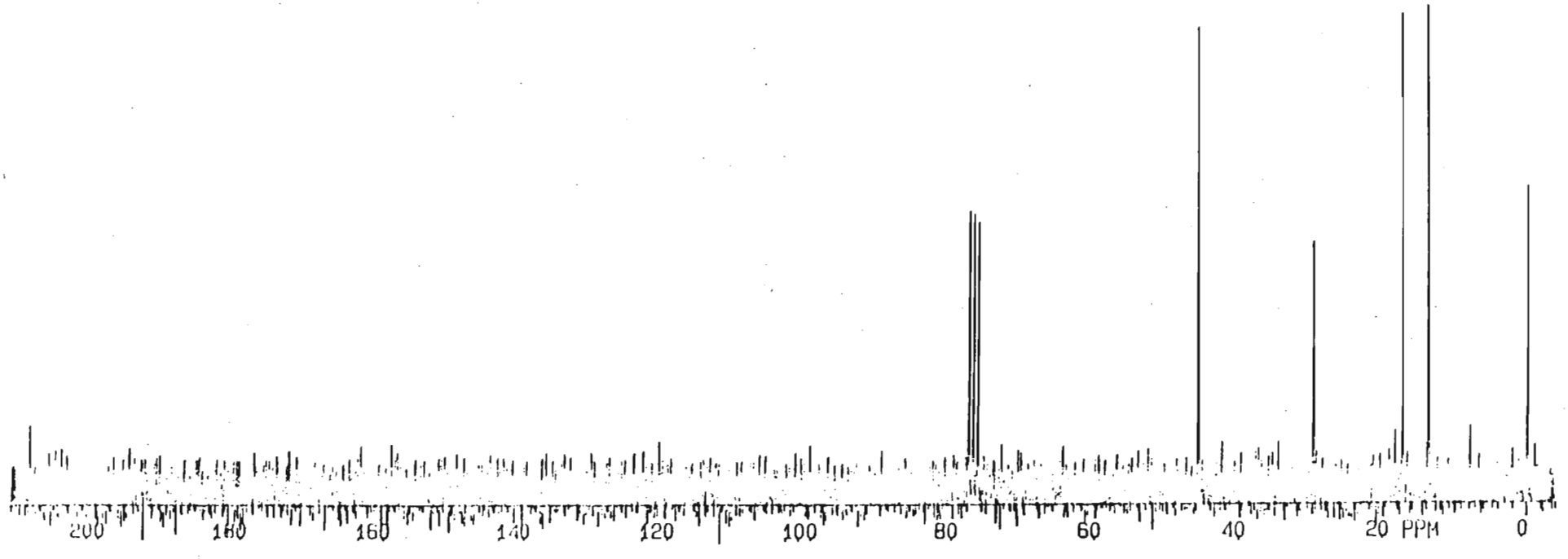

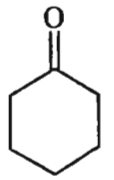

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MW=98 g/mol

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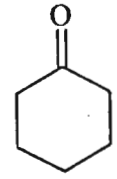

cyclohexanone

$C_6H_{10}O$

MW=98 g/mol

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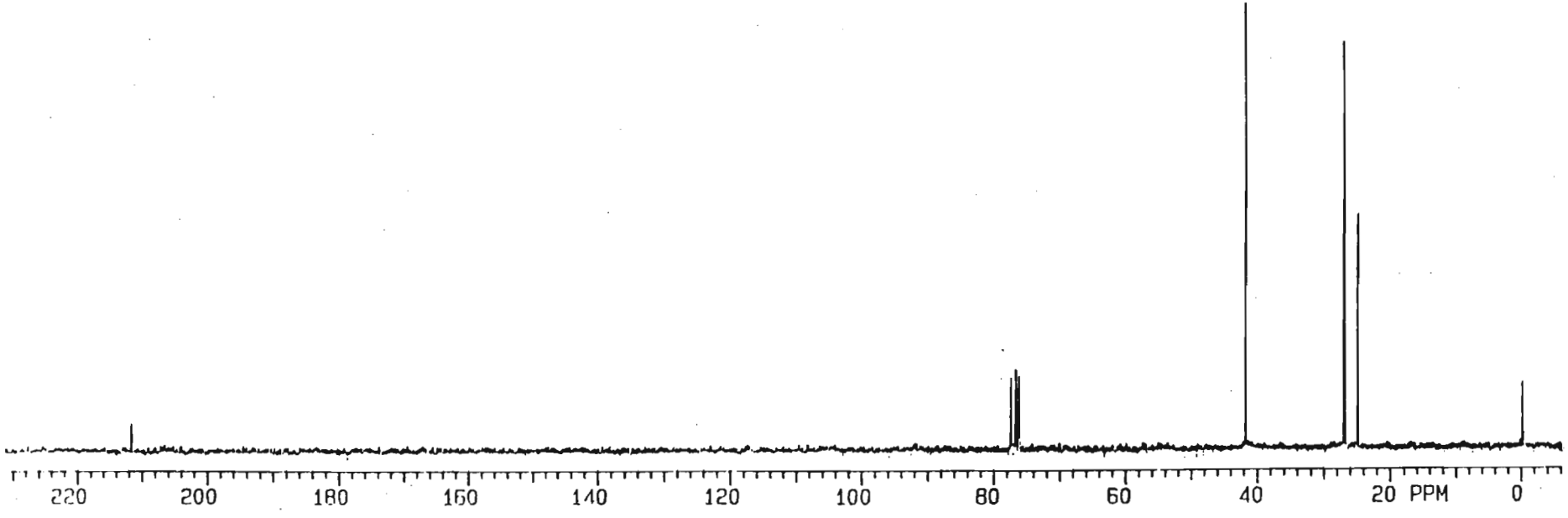
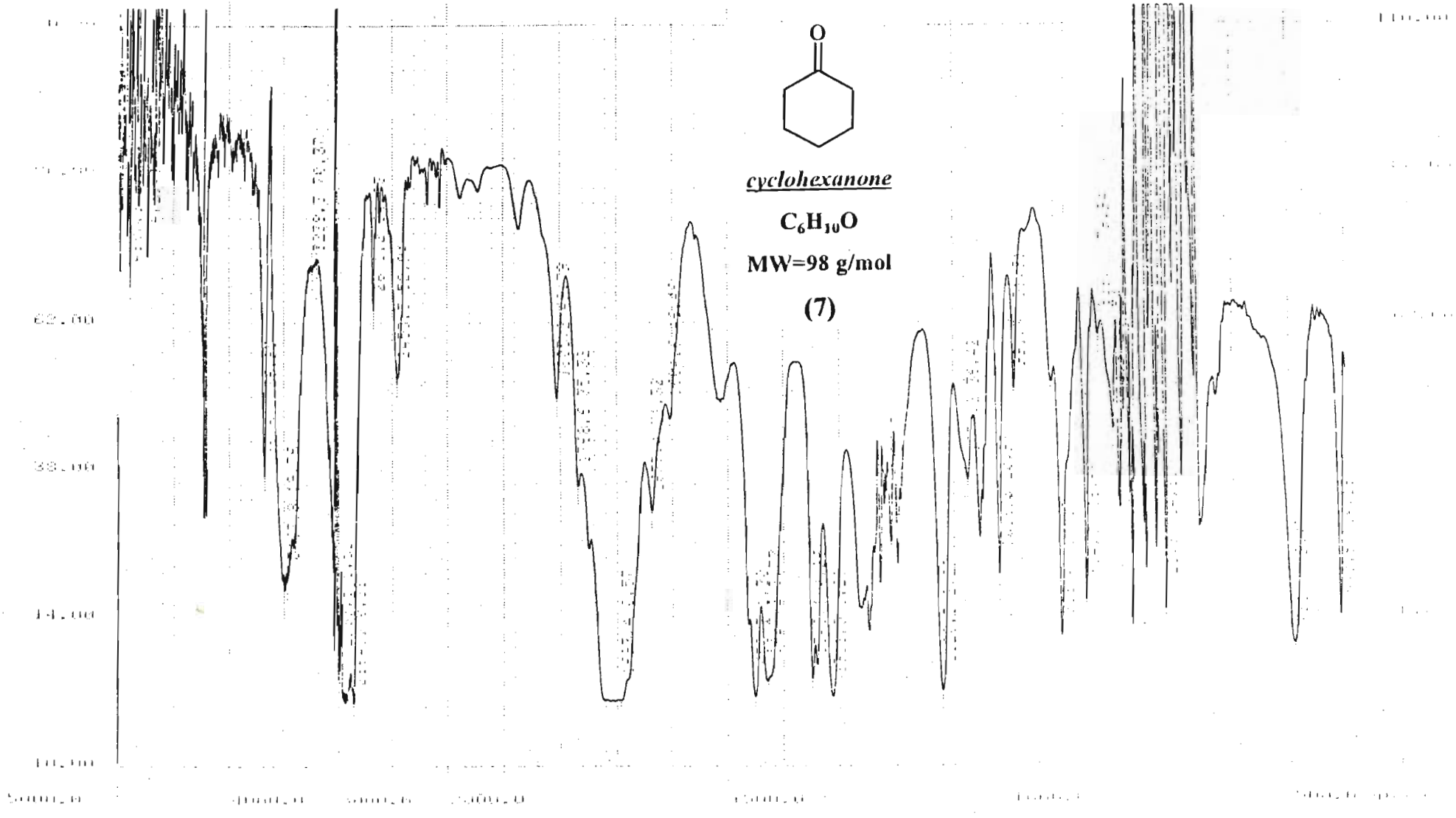
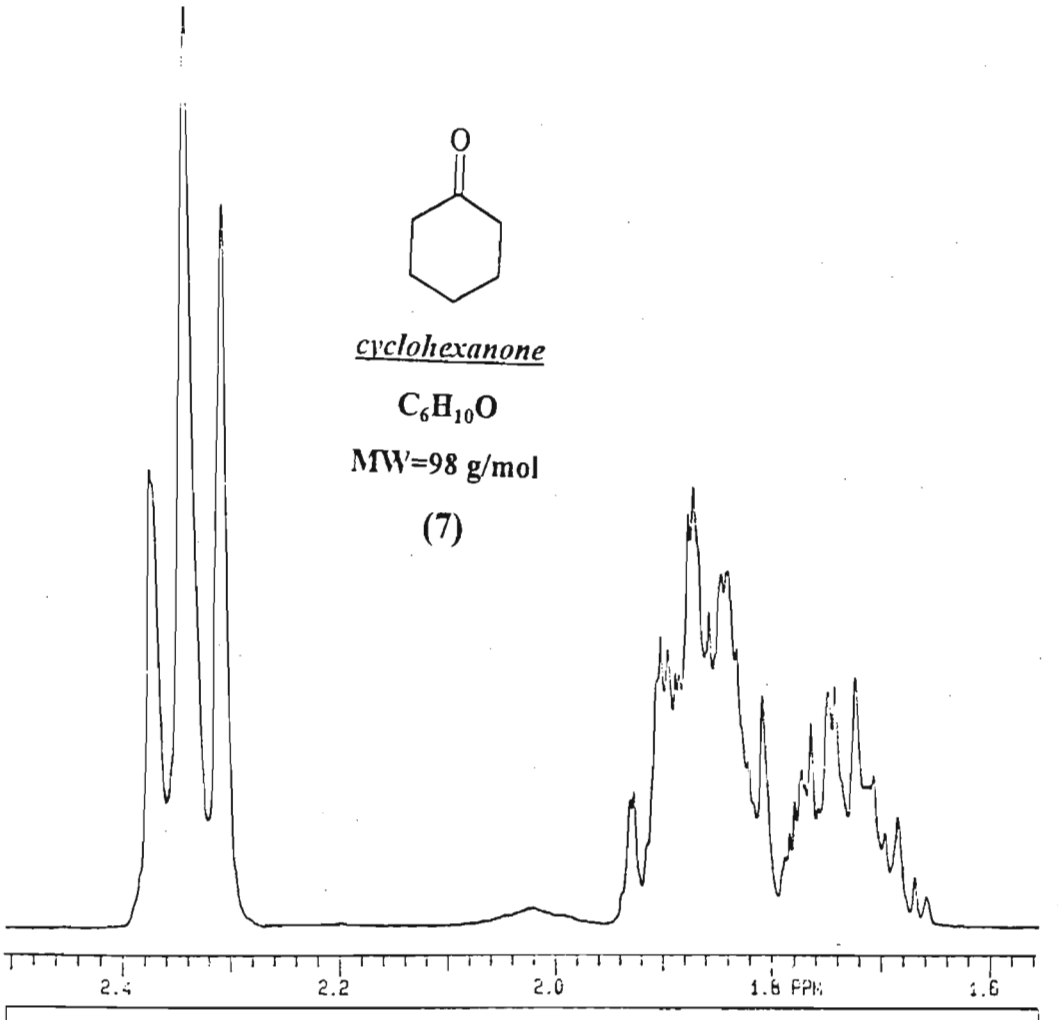




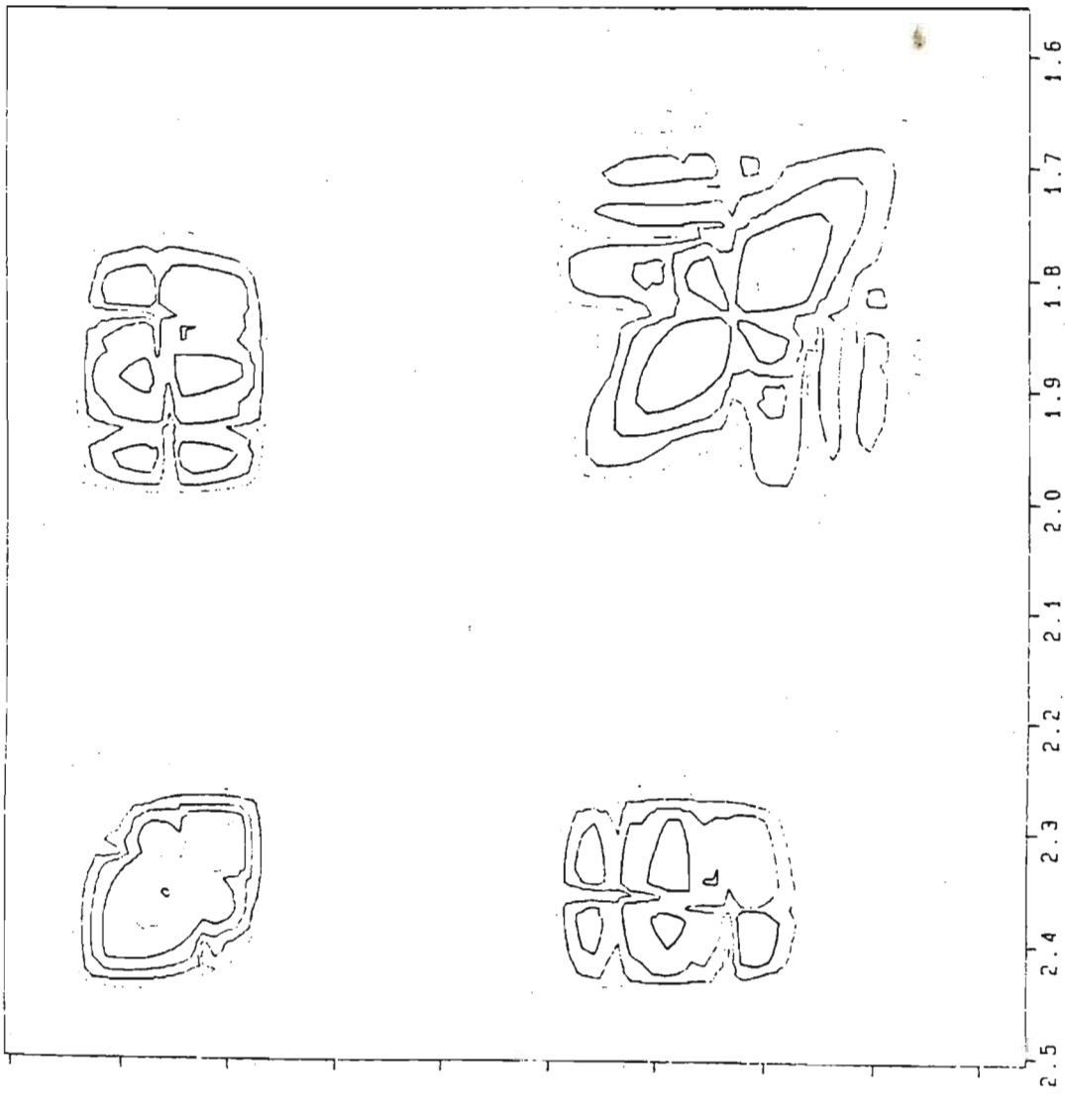


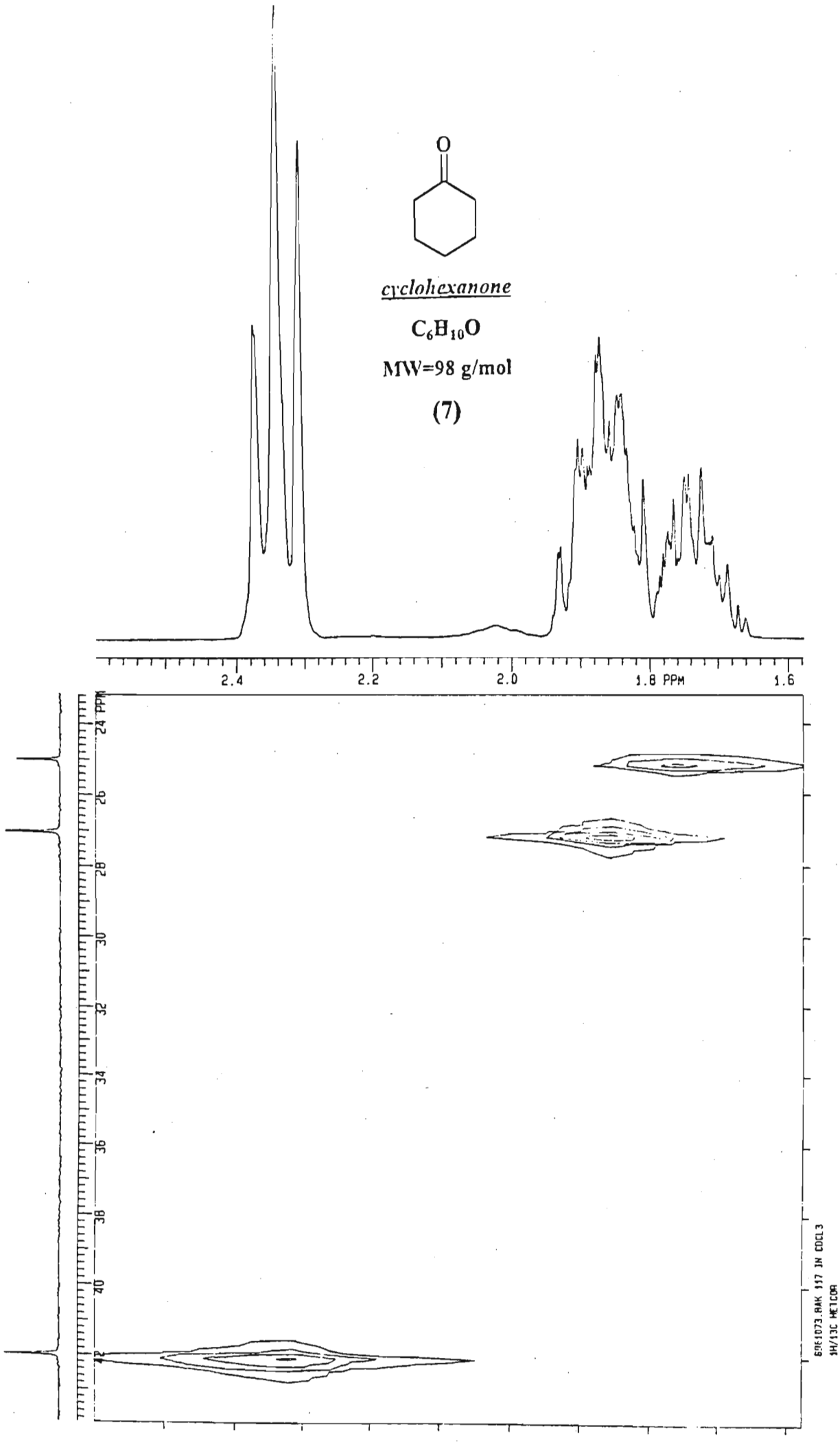
cyclohexanone

$C_6H_{10}O$

MW=98 g/mol

(7)

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MW=98 g/mol
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2.2
2.0
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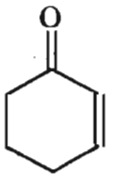
1H/13C METCOR

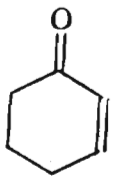


cyclohex-2-en-one

C_6H_8O

MW=96 g/mol

(8)

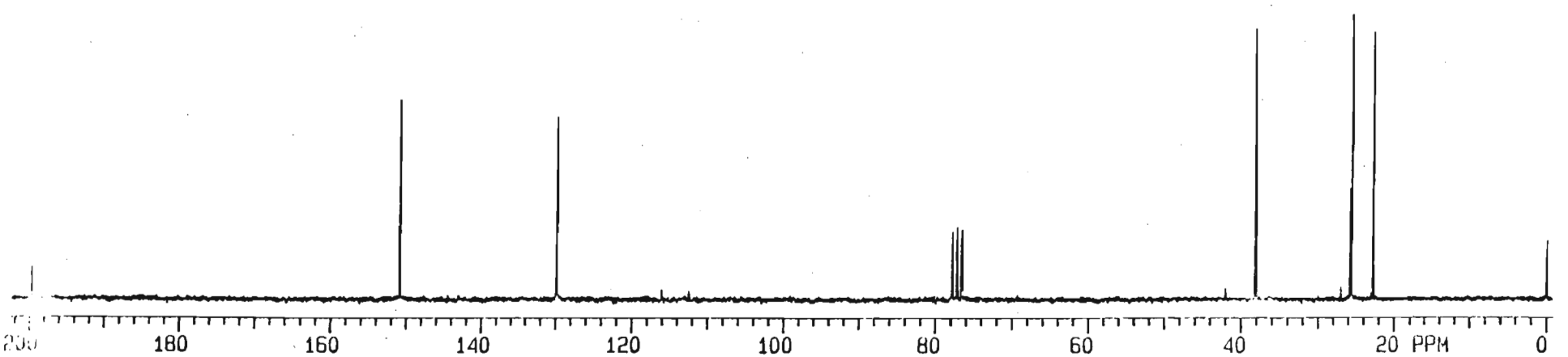


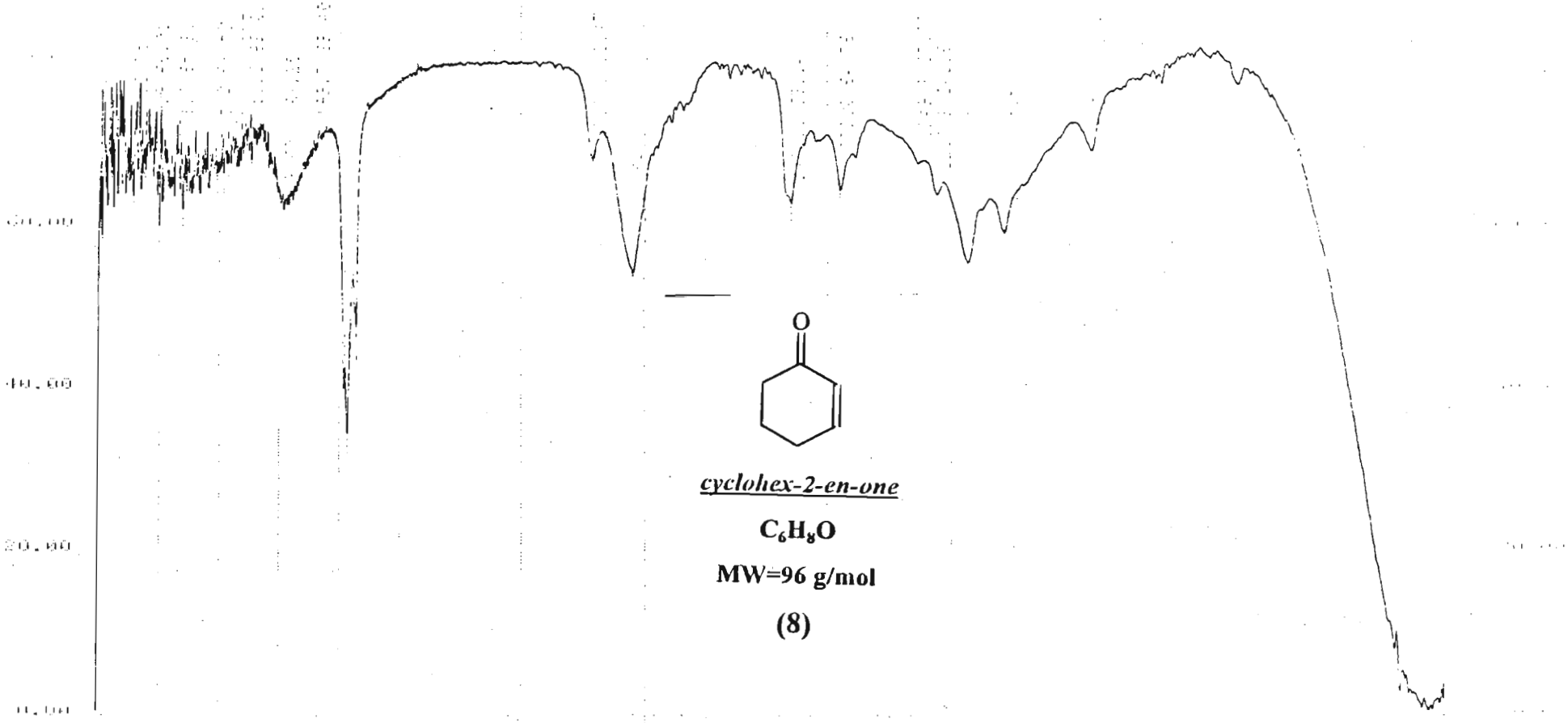
cyclohex-2-en-one

C_6H_8O

MW=96 g/mol

(8)



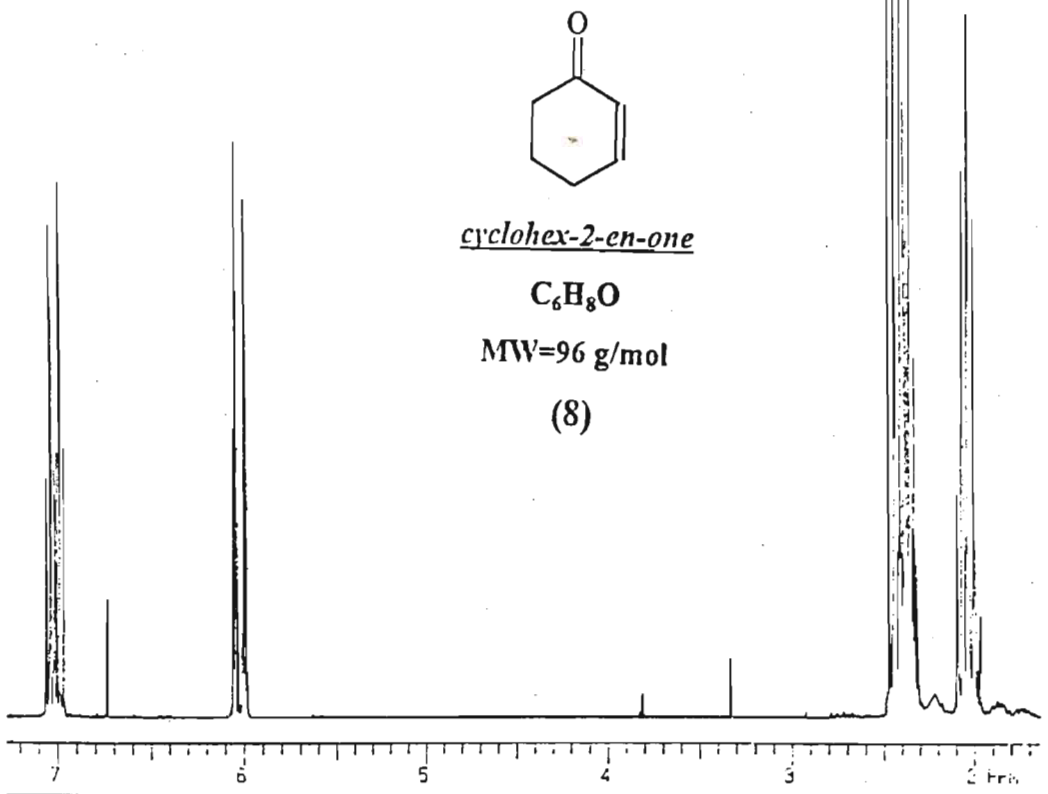


cyclohex-2-en-one

C_6H_8O

MW=96 g/mol

(8)



cyclohex-2-en-one

C_6H_8O

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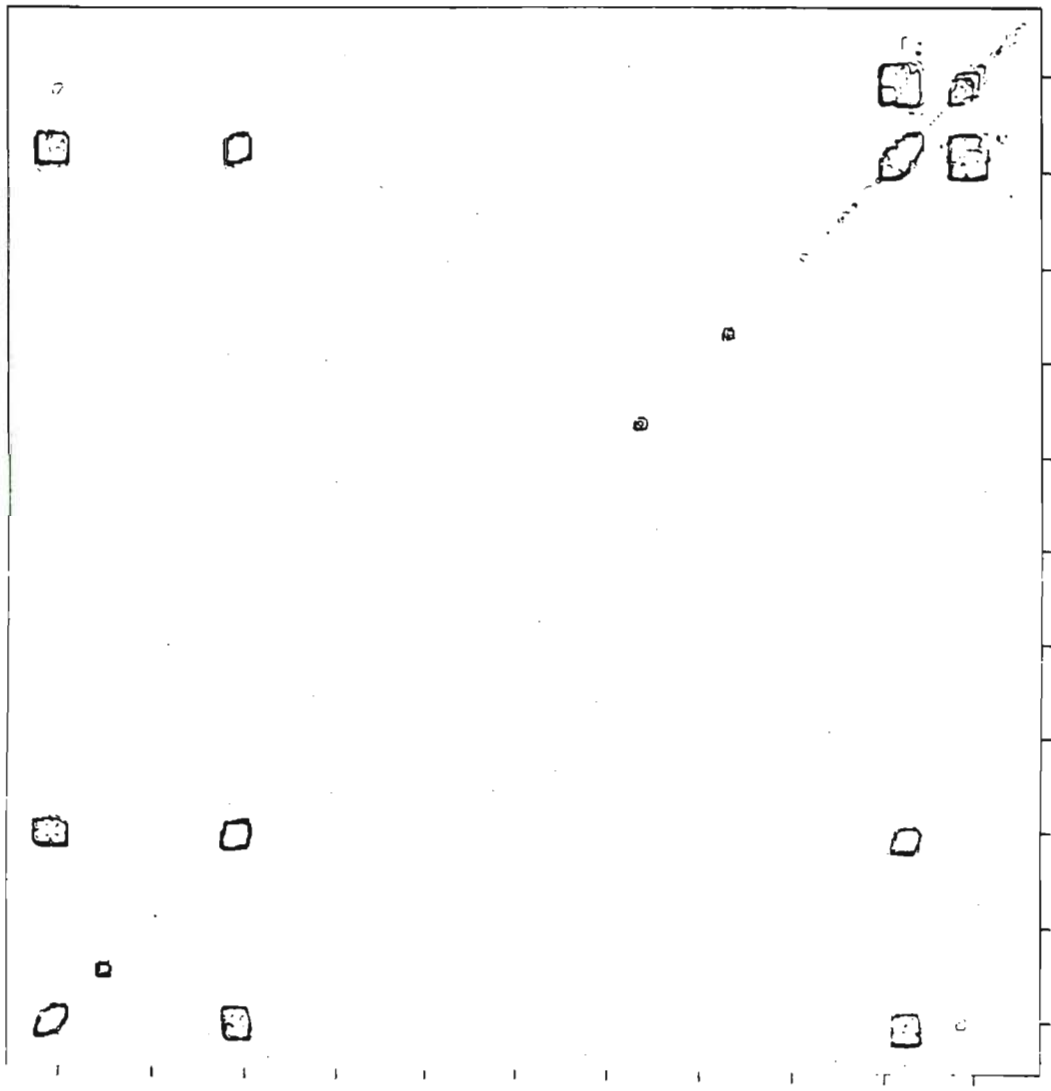
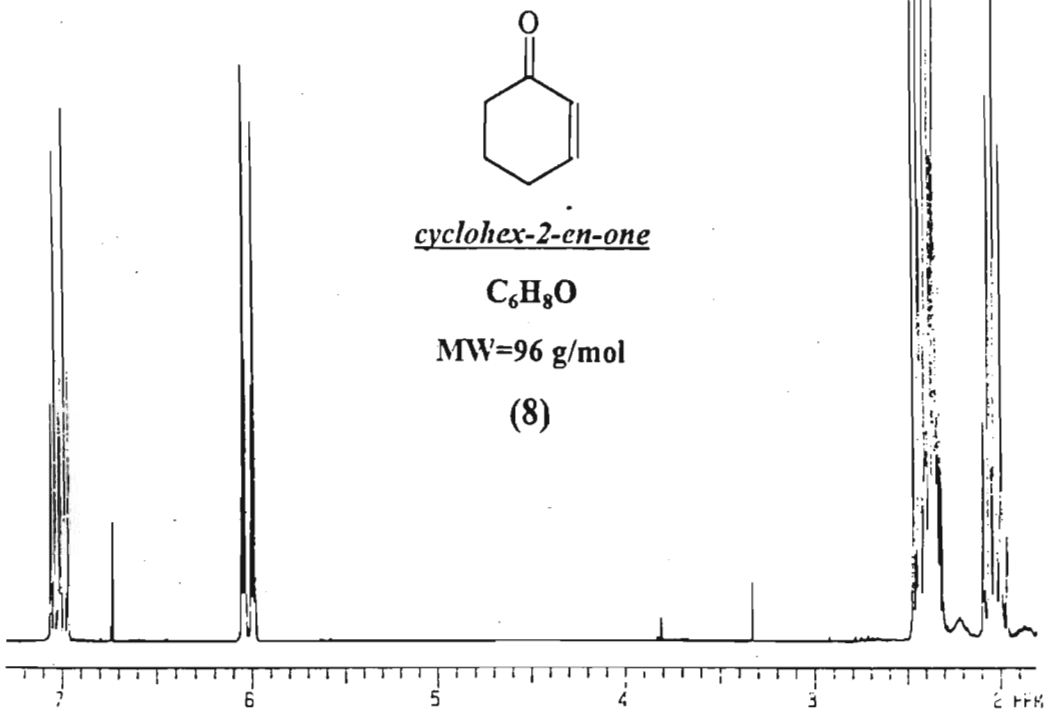
(8)





cyclohex-2-en-one

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(8)