SYNTHETIC APPLICATIONS OF SENSITIZED PHOTOREDUCTION OF

BIS(ACETYLACETONATO)NICKEL(II)

by

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SYNTHETIC APPLICATIONS OF

SENSITIZED PHOTOREDUCTION OF

BIS (ACETYLACETONATO) NICKEL (II)

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ABSTRACT

Synthetic Applications of

Sensitized Photoreduction of Ni(acac)$_2$

The photoreduction of bis(acetylacetonato)nickel(II),
Ni(acac)$_2$, sensitized by triplet excited state acetone in a
2-propanol/benzene mixture or in THF can serve to catalytically
hydrogenate olefins *in situ* under hydrogen. Under these photohy-
drogenation conditions, the vinyl group in 4-vinylcyclohexene
was reduced while the ring double bond remained unaffected.
Other olefins such as norbornene, 5-methylene-bicyclo[2.2.1]-
heptene, 1,7-octadiene, and dicyclopentadiene were re-investi-
gated under modified conditions. In agreement with previous
discoveries, bicyclic dienes were hydrogenated at the more
strained double bonds. The requirement of light in the catalytic
hydrogenation was established by the observation of the
cessation of hydrogenation when irradiation was interrupted or
by the addition of large excess of Ni(acac)$_2$. The hydrogenation
of dicyclopentadiene and 1,5-COD was completely stopped in the
presence of four equivalents of P(n-Bu)$_3$. Intramolecular
cycloaddition of dicyclopentadiene can be sensitized by excited
state acetone, xanthone, and benzene with different efficiencies
to give a caged product.

The sensitized photolysis of Ni(acac)$_2$ under carbon monoxide
was applied to the carbonylation of organic halides under mild
conditions. Organic substrates such as bromo- and iodo- benzene,

1-bromonaphthalene, crotyl bromide, and cyclohexyl iodide were carbonylated, probably by $Ni(CO)_4$ generated *in situ*, either under photolysis at room temperature or under refluxing in the dark.

In order to distinguish between homogeneous and heterogeneous reactions, selective poisoning of colloidal and solid nickel was conducted by the addition of mercury(0). The results were unfortunately ambiguous. A mixture of a photolysate from the sensitized reduction of $Ni(acac)_2$ and an olefin was shaken under a low hydrogen pressure in the dark but gave no hydrogenation products. On the basis of the experimental results the question of homogeneous vs heterogeneous catalytic processes could not be decided.

DEDICATION

To my parents

ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS

acacH	acetylacetone (2,4-pentanedione)
1,5-COD	*cis,cis*-cycloocta-1,5-diene
1,4-COD	*cis,cis*-cycloocta-1,4-diene
COE	cyclooctene
COA	cyclooctane
dct	dibenzo[*a,e*]cyclooctatetraene
hfacH	hexafluoroacetylacetone
MDOB	methylenedioxybenzene
Ni(acac)$_2$	bis(acetylacetonato)nickel
P(n-Bu)$_3$	n-tributylphosphine
SH	hydrogen atom donor
tfacH	trifluoroacetylacetone
THF	tetrahydrofuran
xanthone	xanthen-9-one

CHAPTER ONE

INTRODUCTION

1-1. Metal β-Diketonates and Their Photochemistry

Complexes of β-diketonates are among the most widely studied coordination compounds,[1-3] having the generalized formula shown below.[4-8]
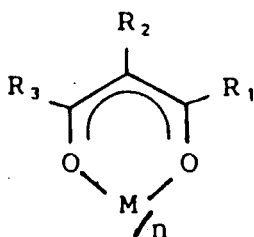
$(R_1, R_2, R_3 = $ alkyl, aryl, $etc.$; $n = 1-4)$

The most common β-diketonate ligand is the anion of 2,4-pentanedione $(R_1, R_3 = CH_3, R_2 = H)$, or acetylacetonate (acac), which has been found to form coordination complexes with virtually every metal.

In the last twenty five years, a number of books[9-13] and reviews[14-16] describing the photochemistry of inorganic compounds, including those of metal β-diketonates, have been published. Studies have established the general photoreactivity pattern of the first-row transition metal β-diketonates.[17-23] Thus, irradiation of metal β-diketonates has been found to cause either stereochemical rearrangement of the ligands[17-19] or

reduction of the central metal.[20-23] There are two types of photoreduction depending on the central metal of the complexes. For Mn, Co, and Fe chelates, photolysis leads to one-electron reduction (Equation 1-1).[20,21]

$$M(AA)_3 \xrightarrow[\text{EtOH}]{h\nu} M(AA)_2(EtOH)_2 + HAA \qquad \text{1-1}$$
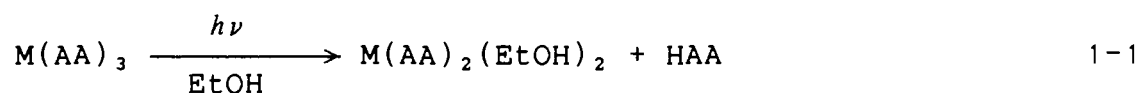
(M = Mn or Co, AA = tfac; M = Fe, AA = hfac)

For the chelates of nickel and copper, further thermal reduction generates the M^0 state (Equation 1-2).[22,23]

$$M(AA)_2 \xrightarrow[\text{EtOH}]{h\nu} M(AA) + HAA \longrightarrow M^0 + 2HAA \qquad \text{1-2}$$
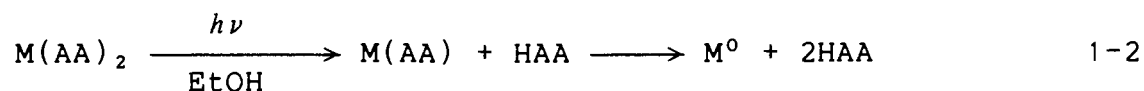
(M = Ni or Cu, AA = acac)

1-2. Sensitized Photoreduction of Ni(acac)$_2$

In solution, transition metal complexes quench the triplet excited states of aromatic ketones with high efficiency.[24-34] The mechanism of the interaction between transition metal chelate quenchers and organic sensitizers has been studied extensively by kinetic flash photolysis. These studies have led to several different proposals, including the catalyzed intersystem crossing mechanism,[24] the energy transfer via an exciplex formation,[26-29] and the combination of energy transfer and electron transfer.[25,30-38]

Bis(acetylacetonato)nickel(II), Ni(acac)$_2$, has an intense intraligand absorption at 295 nm (Figure 1-1) and three weak d-d transition absorptions at 400, 650, and 745 nm.[39] Direct irradiation of Ni(acac)$_2$ in alcohols on the low energy shoulder of the maximum absorption at 312 nm gave no detectable photochemical reaction, but excitation on the high energy side at 254 nm caused slow photoreaction.[22] In comparison, sensitized photolysis was more efficient. It is now known that xanthone, benzophenone, or acetone can sensitize the photoreduction of Ni(acac)$_2$ in H-atom donating solvents to give metallic nickel.[40,41]

The quenching of triplet excited state ketones by Ni(acac)$_2$ has been suggested to proceed via the following mechanism (Scheme 1-1).[40]

Scheme 1-1

$$*R_2C=O + Ni(acac)_2 \longrightarrow [*R_2C=O \text{ -- } Ni(acac)_2] \longrightarrow$$

$$[R_2C=O^{\cdot -} \text{ --- } Ni(acac)^+ \text{ --- } acac\cdot] \longrightarrow$$

$$R_2C=O + Ni(acac) + acacH + S\cdot$$
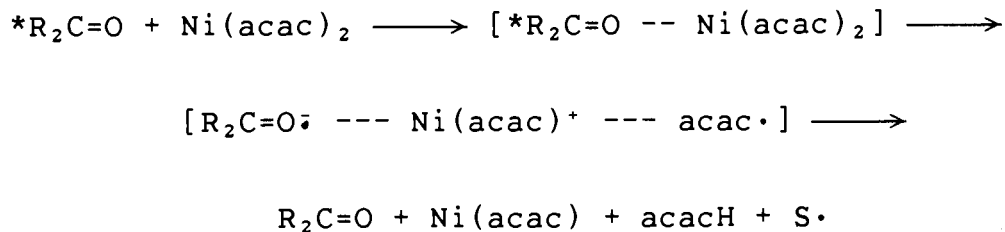
Photoreduction of Ni(acac)$_2$ is believed to form paramagnetic (d^9) nickel(I) intermediates.[22] The sensitized photoreduction of Ni(acac)$_2$ exhibited a signal at g = 2.186 with ΔH_{pp} = 46 gauss of the transient Ni(I) complex. In the dark, the decay of the
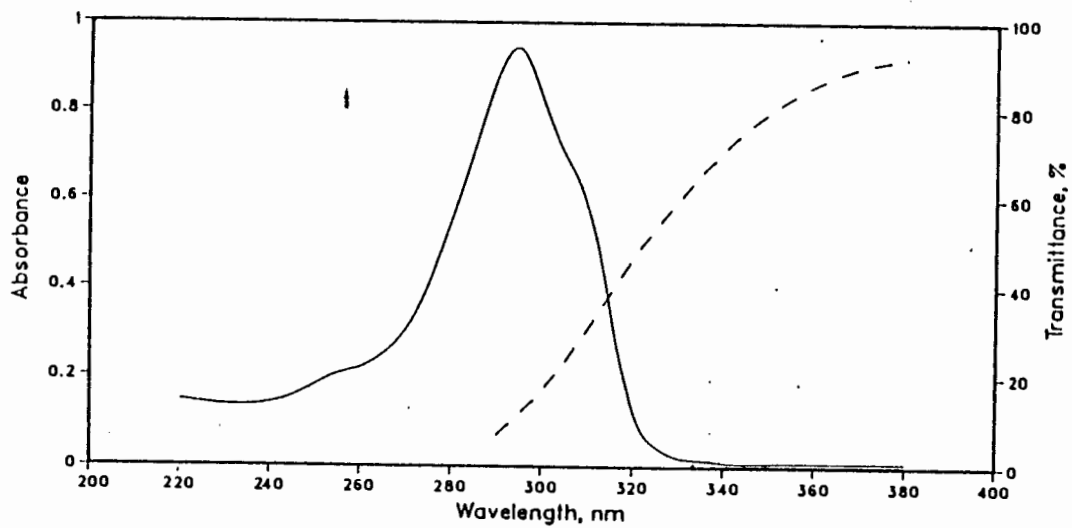
Figure 1-1. Uv spectrum of Ni(acac)$_2$ (3.4 x 10^{-4} M) in methanol, cell length 0.1 cm. Dashed line is the Pyrex filter transmittance.

transient signal followed first order kinetics.[42] It was found
that xanthone sensitized photolysis of $Ni(acac)_2$ in benzene
under hydrogen gave a Ni-H signal at -15.2 ppm in the ^1H NMR
spectrum.[43]

1-3. Hydrogenation and Carbonylation of Organic Compounds Catalyzed by Transition Metal Complexes

Homogeneous hydrogenation of unsaturated organic compounds,
catalyzed by soluble transition metal complexes, is an important
class of organometallic reactions.[44-48] Numerous soluble
transition metal complexes catalyze hydrogenation of olefins.
Most of them can be roughly classified into the following four
classes:

1. Wilkinson's catalyst, $RhCl(PPh_3)_3$ and the closely related
   $[Rh(diene)(PR_3)_2]^+$ complexes.[49-53]
2. Mixtures of platinum and tin chlorides.[54-56]
3. Anionic cyanocobalt complexes.[57,58]
4. Ziegler catalysts prepared from a transition metal salt and
   an alkylaluminum compound.[59-61]

In general, evidence concerning the mechanisms indicates
that the formation of metal hydrides is an obligatory step in
homogeneously catalyzed hydrogenation.[44-48] Usually the olefin
and H_2 are brought together as ligands in the coordination
sphere of the metal. A rearrangement of the complex 1 to a metal
alkyl is followed by some sort of M-C bond cleavage process.

Catalysts differ in the mode of cleaving H_2 to form the metal
hydride and the cleavage of the metal-alkyl bond to form the
alkane.

$$\begin{matrix} C \\ \| \\ C \end{matrix}\text{-M-H} \longrightarrow \text{M-C-C-H}$$

1

Heterogeneous catalysts are usually more convenient for
practical application in hydrogenation, but homogeneous
catalysts are more sensitive toward steric effects and thus, are
much more selective in the reduction of less- hindered olefins,
such as terminal versus internal, cis versus trans, 1,1- versus
1,2-disubstituted, and disubstituted versus trisubstituted. For
example, in the presence of the Wilkinson's catalyst,
$RhCl(PPh_3)_3$, the rate difference between the two extremes in the
following monoolefin series is about 50-fold.[49-53]

Hydrogenolysis reactions are rarely observed among homogene-
ous catalysts, whereas heterogeneous catalysts frequently cleave
carbon-heteroatom bonds. Asymmetric homogeneous catalytic
hydrogenation has been extensively reviewed.[62-68] By contrast,
heterogeneous asymmetric hydrogenation is not as effective and

very little is known.[69]

Hydrogenation reactions via photogenerated catalysts invariably involve photoinduced dissociation of a ligand and generation of coordinatively unsaturated species.[46] For example, with UV irradiation, $Fe(CO)_5$ is an effective catalyst for hydrogenation of olefins under ambient conditions (Equation 1-3),[70,71] in contrast to more severe thermal conditions ($150°C$, 10 atm).

$$\diagup\!\!\!\!\diagup \diagdown\!\!\!\!\diagdown \quad \xrightarrow[H_2]{h\nu, \ Fe(CO)_5} \quad \diagup\!\!\!=\!\!\!\diagdown \qquad\qquad 1-3$$
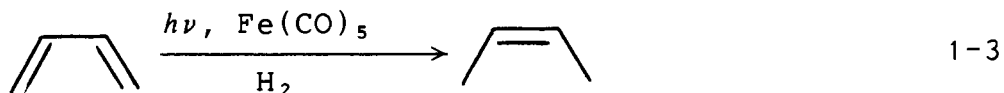
Previous work in this lab has shown that sensitized photolysis of $Ni(acac)_2$ under hydrogen can cause catalytic hydrogenation of olefins added *in situ*.[42] Hydrogenation under mild conditions showed the usual chemical selectivity.[42] For example, xanthone-sensitized photolysis of $Ni(acac)_2$ in the presence of 1,5-COD caused catalytic isomerization and hydrogenation at room temperature. Under similar conditions, oct-1-en-3-ol was reduced to form 3-octanol without forming 3-octanone.[42]

The carbonylation of organic halides with CO in the presence of a transition metal complex has been extensively studied.[72,73] Under suitable conditions, most classes of organic halides can be carbonylated in the presence of nickel catalysts. Hetero-geneous catalysts such as NiI_2 on SiO_2 have been used for

carbonylation of chlorobenzene to produce benzoic acid in high yield (Equation 1-4).[74]

$$PhCl + CO + H_2O \xrightarrow[\text{NiI}_2]{>290°C, \ 450 \ atm} PhCO_2H + HCl \qquad 1-4$$
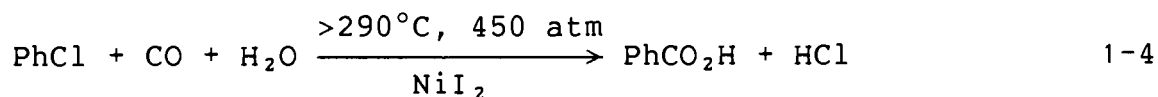
Common homogeneous catalysts such as nickel tetracarbonyl, its derivatives and precusors, have been frequently used. $Ni(CO)_4$ may be prepared by reducing nickel salts with metal power in the presence of CO.[75,76] The anionic nickel tricarbonyl halides and polynuclear nickel carbonyl anions are also active.[73] The reaction can be carried out in a stoichiometric manner using nickel tetracarbonyl as the source of CO.[77]

In 1963, Bauld first reported that $Ni(CO)_4$ reacts with aryl iodide in alcoholic solvent under a CO atmosphere to give corresponding esters.[78] It is proposed that the primary products of the carbonylation of aryl halides are presumably aroyl halides which react further in the presence of water, alcohols or amines to give carboxylic acids, esters, amides or nitriles (Equation 1-5).[72]

$$ArX + CO \xrightarrow{[Ni]} ArCOX \xrightarrow{\begin{array}{l} H_2O \longrightarrow ArCO_2H \\ ROH \longrightarrow ArCO_2R \\ R_2NH \longrightarrow ArCONR_2 \end{array}} \qquad 1-5$$
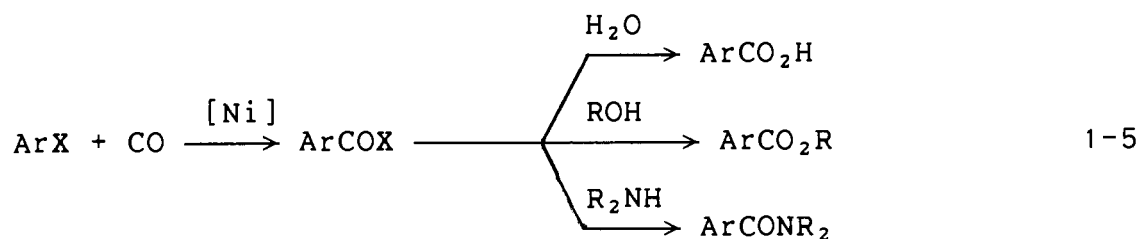
In general, the course of carbonylation reactions is favored by the addition of a base. With stoichiometric amounts of alkali metal carbonates or orthophosphates, aryl halides are readily transformed to anhydrides at 250-375°C under >500 atm CO pressure in the presence of $Ni(CO)_4$ (Equation 1-6).[79] Hegedus[80]

$$2 \ PhBr + CO \xrightarrow[\text{Ni(CO)}_4]{\text{Na}_2\text{CO}_3} (PhCO)_2O \qquad \qquad 1-6$$
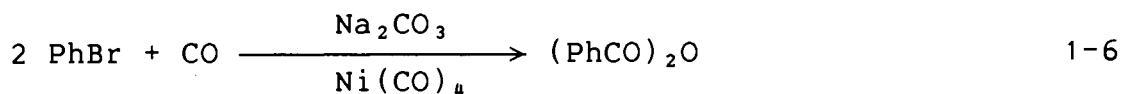
and Mizoroki[75] pointed out the importance of the presence of a base in the carbonylation of aromatic halides at atmospheric pressure. It has been suggested that the function of the base is to neutralize the hydrogen halide produced in the reaction[75] and/or to generate nickel carbonyl anionic species thought to be responsible for the carbonylation.[80,81]

The carbonylation of allyl halides has generally been carried out using $Ni(CO)_4$ as the catalyst precusor.[82] On the other hand, alkyl halides can not be directly carbonylated in the presence of $Ni(CO)_4$. Efficient carbonylation of alkyl iodides[80] and ω-iodoalkynes[83] has been observed using the $Ni(CO)_4$ and t-butoxide reagent (Equation 1-7). Under harsher conditions ($ca.$ 300°C) it is possible to carbonylate alkyl halides catalytically.[84]

$$RC{\equiv}C(CH_2)_3I \xrightarrow[t\text{-}C_4H_9O^-/t\text{-}C_4H_9OH]{\text{Ni(CO)}_4, \ CO} RC{\equiv}C(CH_2)_3CO_2(t\text{-}C_4H_9) \qquad 1-7$$
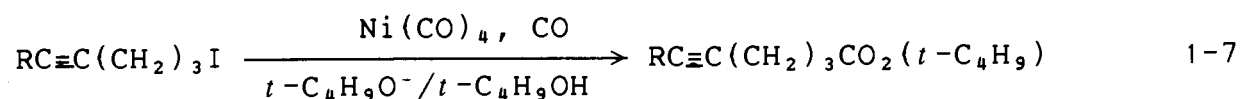
Photochemical behavior of transition metal carbonyls has been well studied with current interest in the photogeneration of catalytically active species in homogeneous catalysis.[12] Recently significant progress has been made in the area of photochemical carbonylation by transition metal complexes.[85,86] Mirbach and coworkers have reported the photochemical hydroformylation of olefins with cobalt and rhodium catalysts under high pressure (Equation 1-8).[87] Watanabe *et al.*[88] have reported the photochemical carbonylation of alkyl iodides catalyzed by various group VII and VIII metal carbonyls including $Ni(CO)_4$ under atmospheric pressure of carbon monoxide.

$$RCH=CHR' \xrightarrow[\text{catalyst}]{h\nu,\ CO/H_2} RCH(CHO)CH_2R' + RCH_2CH(CHO)R' \qquad 1-8$$
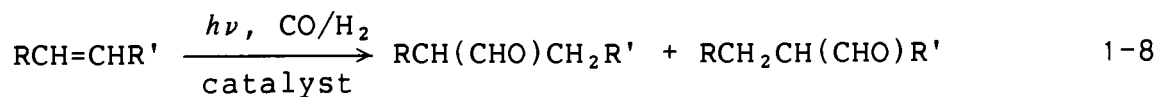
Sensitized photolysis of $Ni(acac)_2$ under carbon monoxide in H-atom donors (alcoholic solvents or H_2) results in the production of $Ni(CO)_4$ (Equation 2-12).[42] Preparation of $Ni(CO)_4$ by

$$Ni(acac)_2 + CO \xrightarrow[\text{H-atom donor}]{h\nu,\ sen.} Ni(CO)_4 \qquad 2-12$$
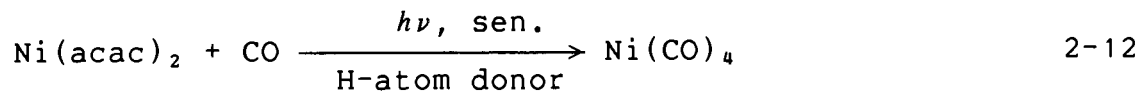
sensitized photolysis of $Ni(acac)_2$ under an atmosphere of CO, followed by *in situ* irradiation in the presence of organic compounds shows promise for carbonylation of these compounds. For example, the formation of a lactone by irradiation of $Ni(acac)_2$ and phenylacetylene in acetone/2-propanol under carbon

monoxide has been reported.[42]

1-4. Homogeneity versus heterogeneity

A problem that is encountered frequently in studies of
catalysis by transition metal compounds is distinguishing
between homogeneous and heterogeneous reactions. For a reaction
catalyzed by a transition metal compound, the metal itself may
have been precipitated under the reaction conditions. Either the
metal powder, film or colloid (especially in polar solvents) may
form even if the catalyst is prepared from a soluble metal
complex.[89] For example, sensitized photoreduction of $Ni(acac)_2$
under hydrogen in the presence of an olefin can cause the
hydrogenation of the olefin.[42] Li reported that when xanthone
was used as a sensitizer in benzene, the reaction solution was
clear and homogeneous; when acetone was used as a sensitizer in
2-propanol, a black precipitate of metallic nickel appeared in
the course of the reaction producing a dark, cloudy solution.[42]
A number of methods have been proposed for detecting
catalytically active components.[90-96]

Maitlis[90] used a filtration method to see if catalytic
activity resides in the filterable fraction of a catalytic
system. This is not applicable to cases where a colloidal
suspension has been formed, since the colloid can not be
filtered. The test would not be applicable to systems in which
only freshly precipitating metal or the colloidal precusor is

active. It is also inconvenient to use in cases where air
sensitivity or extreme conditions of temperature or pressure
make filtration difficult.

Collman[91] has used a polystyrene-based substrate into which
only soluble species can enter. This would not be expected to be
applicable to cases where polymer-anchored catalysts are used.
Others have looked for evidence of a cross-over from homogeneous
to heterogeneous operation by studying catalytic rates and prod-
uct distributions.[96] Dynamic light scattering has been used to
detect and characterize colloids but does not give information
as to whether any particular component is catalytically active
or not.[92,93]

Crabtree[94] has proposed a test for homogeneity based on the
use of dibenzo[a,e]cyclooctatetraene (dct,2), a selective poison
for homogeneous catalysts. It was suggested that dct would
poison homogeneous catalysts by binding to the metal to form

2
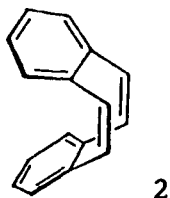
catalytically inert complexes. On the other hand, it might
affect a heterogeneous catalyst to a far lesser extent because
binding to a surface would be expected to be weak in view of the
tub conformation of dct. In contrast, Whitesides[95] has used

liquid mercury as a heterogeneous catalyst poison[97] to selectively suppress the catalytic activity of bulk metal by either physisorption or amalgamation. In certain circumstances, the addition of mercury(0) might not influence the homogeneously catalyzed reaction. In hydrogenation reactions, the reactivities and selectivities of catalysts may be considered as indirect evidence for distinguishing between homogeneous and heterogeneous catalytic processes but can not be used as a criterion.

CHAPTER TWO

RESULTS

2-1. Photohydrogenation of Olefins in the Presence of Ni(acac)$_2$

Triplet acetone sensitized photolysis of Ni(acac)$_2$ was applied to the hydrogenation of olefins. Two types of olefins (cyclic and linear) were subjected to photohydrogenation.

Hydrogenation of norbornene (3) in acetone/2-propanol in the presence of Ni(acac)$_2$ gave norbornane (4) and formed a metallic nickel in one hour.[42] Photolysis of Ni(acac)$_2$ and 3 in acetone/ THF (4:1 by volume) under H$_2$ for 10 hours gave a hydrogenated product norbornane, 4, with 79% conversion of 3 (Equation 2-1). Trace amounts of metallic nickel appeared in about 6 hours. The reaction was monitored by GC with respect to an internal
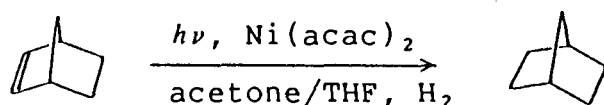
$$\text{3} \xrightarrow[\text{acetone/THF, H}_2]{h\nu,\ \text{Ni(acac)}_2} \text{4} \qquad\qquad 2\text{-}1$$

time(hr)	3 %	4 %
0	100	–
2	99	1
4	90	9
7	57	43
10	21	79

standard and the results shown above suggest that the
hydrogenation of 3 did not occur until after 2 hours of
irradiation.

Li reported that 5-methylene-bicyclo[2.2.1]heptene (5) was
hydrogenated to give 5-methylene-bicyclo[2.2.1]heptane (6) by
xanthone sensitized photolysis of Ni(acac)$_2$ in benzene.[42] A
solution of 5 and Ni(acac)$_2$ in acetone/2-propanol/benzene (2:2:1
by volume) was irradiated under H$_2$ for 5 hours to give the
hydrogenated product, 6, in 61% total yield with 84% conversion
of 5 (Equation 2-2). The fully saturated product was not found
at this stage. Metallic nickel appeared in about 3 hours. The

$$\text{5} \xrightarrow[\text{acetone/2-propanol/benzene}]{h\nu,\ \text{Ni(acac)}_2,\ \text{H}_2} \text{6} \qquad 2\text{-}2$$
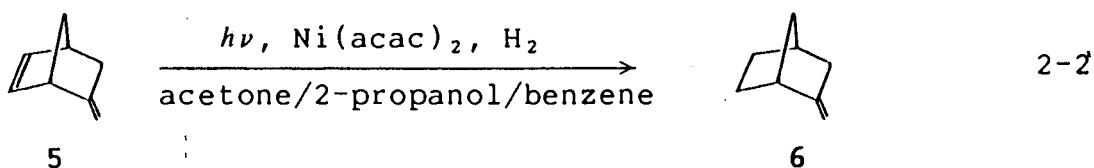
similar photohydrogenation of 5 in the presence of Ni(acac)$_2$ in
acetone/THF (4:1 by volume) under H$_2$ yielded 93% of 6 with a 98%
conversion of 5 in 3 hours. Trace amounts of metallic nickel
formed during irradiation while the fully saturated product was
not found.

Photohydrogenation of 4-vinylcyclohexene, 7, in acetone/
2-propanol/benzene (2:2:1 by volume) for 6 hours yielded 4-ethyl
cyclohexene, 8, in a 56% yield with 58% conversion of 7

(Equation 2-3). Metallic nickel was observed in about 3 hours.

$$\text{7} \quad \xrightarrow[\text{acetone/2-propanol/benzene}]{h\nu, \; Ni(acac)_2, \; H_2} \quad \text{8} \qquad 2\text{-}3$$
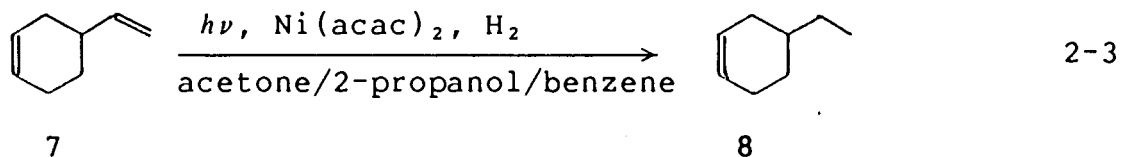
Product **8** gave a molecular ion peak of m/e 110 in the GC-MS

spectrum, indicative of the reduction of one of the double

bonds. The ^{1}H NMR spectrum showed two typical olefinic proton

signals at δ 5.6 ppm but no ABX pattern of the vinyl proton

signals at 5.9 and 5.0 ppm.[98] Under similar conditions

photohydrogenation of 7 in acetone/THF (4:1 by volume) for 7

hours gave 91% of **8** with a 94% conversion of 7. The fully

hydrogenated product was not found at this stage. Trace amounts

of black precipitate appeared in about 5 hours.

It was found that octa-1,7-diene, **9**, was hydrogenated to

give 1-octene (**10**) and octane (**11**) by xanthone sensitized

photolysis of Ni(acac)$_2$.[42]

$$\text{9} \quad \xrightarrow[\text{acetone/2-propanol/benzene}]{h\nu, \; Ni(acac)_2, \; H_2} \quad \text{10} \qquad 2\text{-}4$$

$$+ \quad \text{11}$$
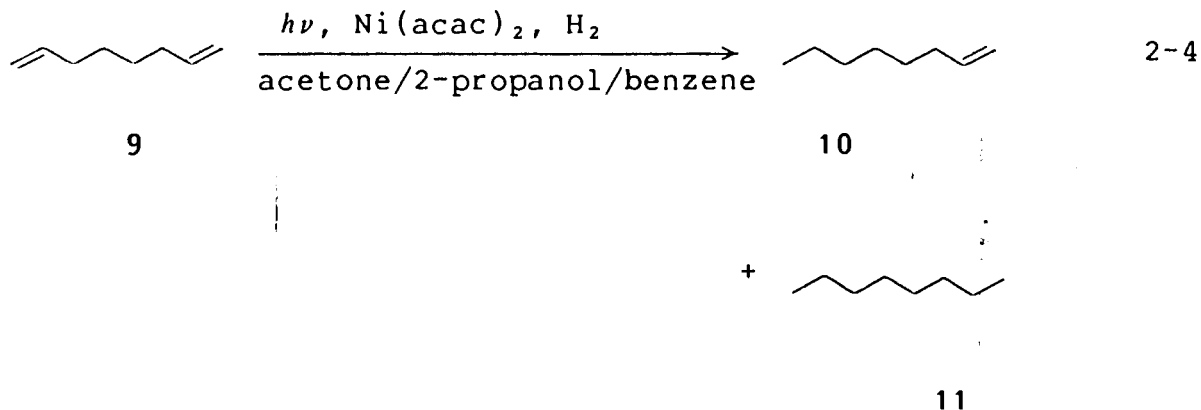
A solution of Ni(acac)$_2$ and **9** in acetone/2-propanol/benzene (3:1:2 by volume) was irradiated under H$_2$ for 5 hours to form 1-octene, **10**, (49%) and octane, **11**, (21%) with a 70% conversion of **9** (Equation 2-4). No isomerized product was found.

2-2. Photohydrogenation of Dicyclopentadiene, 12, in the Presence of Ni(acac)$_2$

2-2-1. Photohydrogenation of 12: reaction patterns

Photohydrogenation of dicyclopentadiene (3a,4,7,8a-tetrahydro-4,7-methano-indene, **12**) was observed by sensitized photolysis of Ni(acac)$_2$ under hydrogen.[42] Dicyclopentadiene **12** was used as a model compound to study suitable conditions for photohydrogenation, particularly the best solvent mixture for the catalytic processes.

Photohydrogenation of dicyclopentadiene, **12**, in acetone/THF (4:1 by volume) for 8 hours produced 3a,4,5,6,7,8a-hexahydro-4,7-methano-indene, **13**, with 73% yield. A photocycloaddition product, pentacyclo[5.2.1.0^{26}.0^{39}.0^{48}.]decane,[99] **14**, was also found in a 2% yield with a 76% conversion of **12** (Equation 2-5). A trace amount of black precipitate appeared in the later stage of irradiation, while no evidence was found for the fully hydrogenated product. Photolysis of Ni(acac)$_2$ and **12** in acetone/2-propanol/benzene (1:1:8 by volume) under H$_2$ for 2

hours gave 13 (58%) and 14 (15%) with 76% conversion of 12.

A solution of Ni(acac)$_2$ and 12 in acetone/2-propanol/benzene (12:3:10 by volume) was irradiated at >290 nm under H$_2$ for 10 hours to produce 13 (89%), 14 (7%) and the fully hydrogenated product 15 (4%) (Equation 2-5). The color of the reaction
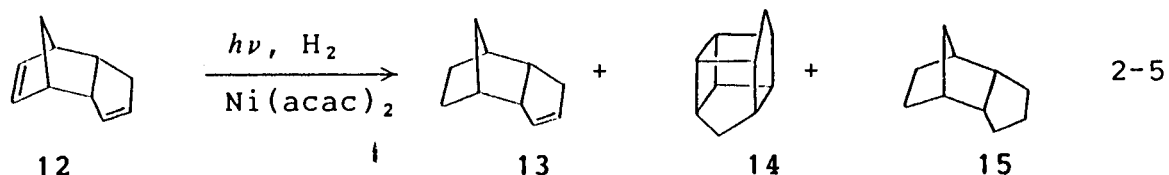
mixture changed gradually from green to yellow upon irradiation, and some precipitation of metallic nickel appeared in 4 hours. The transformation of the compounds was followed by GC (Figure 2-1). The formation of 15 could only be detected after 8 hours of irradiation when 12 was totally consumed, while the cage product 14 was observed in the initial stage.

Similar photohydrogenation of 12 in acetone/THF (4:1 by volume) under H$_2$ for 9 hours gave 13 (97%), 14 (1%), and 15 (1%) with 99% conversion of 12. The solution changed gradually from green to yellow in 4 hours and a trace amount of black precipi- tate appeared after 7 hours of irradiation. The course of the reaction was monitored by GC analysis (Figure 2-2). Under the conditions shown in Figure 2-2, the formation of cage pruduct 14 was only a trace amount without showing in the figure. The fully hydrogenated product 15 appeared when almost all of 12 had been
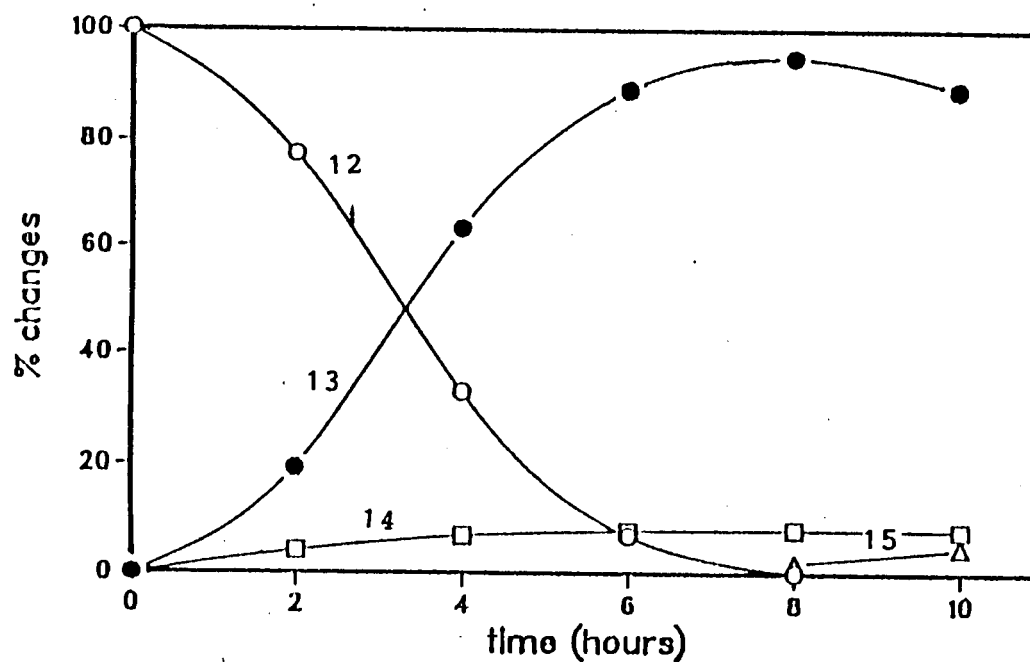
Figure 2-1. Photohydrogenation of 12 (0.029 M) in the presence of Ni(acac)$_2$ (0.0056 M) in acetone/2-propanol/benzene (12:3:10 by volume) through a Pyrex filter under H$_2$ at room temperature.
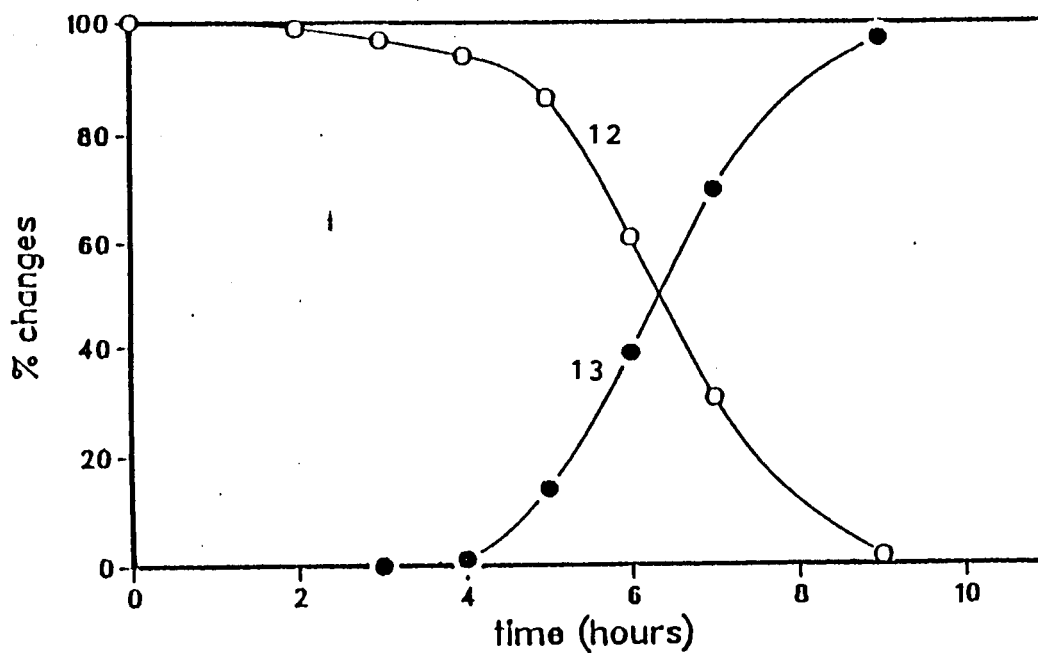
Figure 2-2. Photohygrogenation of **12** (0.051 M) in the presence of Ni(acac)$_2$ (0.001 M) in acetone/THF (4:1 by volume) through a Pyrex filter under H$_2$ at room temperature.

consumed. A long induction period was required for the reaction of the starting material 12 and the formation of hydrogenated product 13. It appeared that Ni(acac)$_2$ totally quenched triplet acetone in the initial stage of photolysis, which suggested that photoreduction of Ni(acac)$_2$ preceded and was more efficient than the photohydrogenation of 12.

In comparison, irradiation of similar solutions of 12 in the presence of Ni(acac)$_2$ in acetone/2-propanol/benzene and in acetone/THF under N$_2$ for the same period of time were also carried out (Table 2-1). In both cases, most of the starting material 12 was recovered with certain amounts of cage product 14. Trace amounts of hydrogenated product 13 were also found and are likely due to the known hydrogen abstraction reactions.[100] A small amount of nickel precipitate was found during the photolysis.

Triplet state sensitized cycloaddition of 12 to form the cage product 14 (Equation 2-6) is a known reaction.[99]

$$\text{12} \xrightarrow{h\nu/\text{sen.}} \text{14} \qquad \qquad 2\text{-}6$$
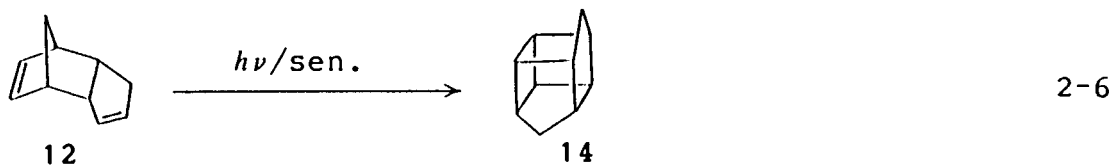
It was found that 12 can be sensitized by acetone and benzene to undergo intramolecular addition to give 14. Irradiation of 12 in acetone/2-propanol/benzene and acetone/THF in the absence of Ni(acac)$_2$ under N$_2$ at >290 nm produced 14 but not the

Table 2-1

Photolysis of **12** (0.05 M) and Ni(acac)$_2$ (0.005 M) through a Pyrex filter under N$_2$ for 12 hours.

Solvents	12(%)	13(%)	14(%)
acetone/2-propanol/benzene (12:3:10 by volume)	70	4	26
acetone/THF (4:1 by volume)	89	5	6

hydrogenated product (Table 2-2).

When benzene was used as the sensitizer, the sensitized cycloaddition of **12** was more efficient. Irradiation of **12** in benzene under nitrogen through Corex filter for 3 hours gave **14** (90%) with 90% conversion of **12**. Solution of **12** and Ni(acac)$_2$ in benzene and in benzene/H-atom donors were irradiated under N$_2$ through a Corex filter. The formation of cage product **14** was still effective in the presence of a small amount of Ni(acac)$_2$. A trace amount of hydrogenated product **13** formed in benzene/ 2-propanol, benzene/ethanol, and benzene/THF due to the hydrogen abstraction reaction (Table 2-3).[100]

The benzene sensitized intramolecular addition of 4-vinyl cyclohexene, **7**, was attempted but no cyclization product was found.

2-2-2. Photohydrogenation of **12**: effect of [Ni(acac)$_2$]

As described above, hydrogenation product **13** was contaminated by sensitized photocycloaddition product **14**, particularly in the acetone/2-propanol/benzene system. The formation of **14** was suppressed by introducing a large amount of Ni(acac)$_2$ in order to competitively quench triplet state acetone. Solutions containing **12** at the same concentration mixed with various amount of Ni(acac)$_2$ in acetone/2-propanol/benzene (12:3:10 by volume) were photolytically hydrogenated for 6 hours to give

Table 2-2

Photolysis of **12** (0.05 M) through a Pyrex filter for
6 hours under N_2 at room temperature.

Solvents	12(%)	14(%)
acetone/2-propanol/benzene (12:3:10 by volume)	23	76
acetone/THF (4:1 by volume)	77	9

Table 2-3

Photolysis of **12** (0.02 M) in the presence of Ni(acac)$_2$
(0.001 M) through a Corex filter under N_2 for 6 hours
at room temperature.

Solvents (v:v=4:1)	12(%)	13(%)	14(%)	Observations
benzene	3	0	97	green
benzene/methanol	13	0	86	yellow, trace ppt
benzene/ethanol	39	3	58	yellow, trace ppt
benzene/2-propanol	27	6	67	yellow, ppt
benzene/THF	53	3	44	yellow, trace ppt

different yields of hydrogenated product 13 and cage product 14
(Table 2-4). Apparently, at a relatively high concentration of
Ni(acac)$_2$, the formation of 14 was suppressed but the photo-
hydrogenation of 12 to 13 was also retarded. Similar photohydro-
genation of 12 in acetone/THF (4:1 by volume) remedied this
problem showing the formation of only trace amounts of the cage
product 14 (Table 2-5). Observed as in
acetone/2-propanol/benzene system, the formation of hydrogenated
product 13 was slowed down at a relatively high concentration of
Ni(acac)$_2$. The retardation of the hydrogenation is probably due
to the absorption of light by large amount of Ni(acac)$_2$ and the
preferential quenching of triplet state acetone by Ni(acac)$_2$.
Photolysis may be required to promote the catalytic
hydrogenation of 12 to 13. Alternatively, it might result from
the formation of polynuclear nickel complexes in high
[Ni(acac)$_2$] solution.

2-2-3. Photohydrogenation of 12: the role of irradiation

The effect of light on the photohydrogenation of 12 is
illustrated by the following reaction patterns. Photolysis of
Ni(acac)$_2$ and 12 in acetone/THF (4:1 by volume) was carried out
under hydrogen for 6 hours. At which time the irradiation was
interrupted for one hour. It was found by GC analysis that no
changes of 12 and 13 occurred in the dark period (Figure 2-3).
Resuming irradiation resulted in continued hydrogenation of 12

Table 2-4

Effect of Ni(acac)$_2$ concentration on photohydrogenation
of 12 (0.05 M) in acetone/2-propanol/benzene under H$_2$
for 6 hours at room temperature.

[12] : [Ni(acac)$_2$]	12(%)	13(%)	14(%)	Observations
1 : 1	99	0	2	green
1 : 0.5	99	0	2	green
1 : 0.2	68	27	4	yellow-green
1 : 0.1	59	35	8	yellow, trace ppt
1 : 0.04	54	39	9	dark, ppt
1 : 0.02	41	44	17	dark, ppt
1 : 0	24	0	76	−

Table 2-5

Effect of Ni(acac)$_2$ concentration on photohydrogenation of 12 (0.05 M) in acetone/THF under H$_2$ for 6 hours at room temperature.

[12] : [Ni(acac)$_2$]	12(%)	13(%)	14(%)	Observations
1 : 1	98	0	1	green
1 : 0.5	97	1	1	green
1 : 0.2	34	64	1	yellow
1 : 0.1	23	76	2	yellow, trace ppt
1 : 0.02	0	92	2	yellow, ppt*
1 : 0	77	0	9	-**

* The saturated product 8 was obtained in 5%.

** The corresponding oxetanes (10%) were detected by GC-MS.
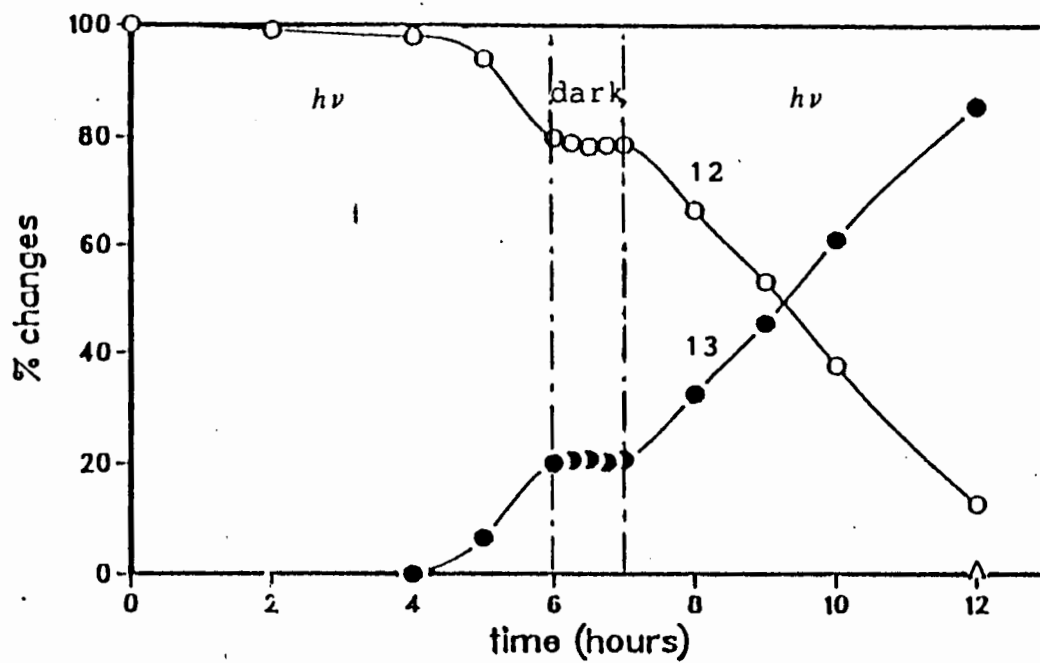
Figure 2-3. Photohydrogenation of **12** under the same conditions as in Figure 2-2 except the irradiation was interrupted in the period of 6-7 hours.

to 13. Undoubtly irradiation was the key to the promotion of catalytic hydrogenation. A long induction period was required for the hydrogenation as shown in Figures 2-3 and 2-2, which indicated that the sensitized photoreduction of Ni(acac)$_2$ precedes the photohydrogenation with a greater efficiency.

2-2-4. Photohydrogenation of 12 and 1,5-COD: effect of P(n-Bu)$_3$

Irradiation of 12 in acetone/THF (4:1 by volume) in the presence of Ni(acac)$_2$ under H$_2$ for 6 hours gave a yellow solution with the formation of hydrogenated product 13. P(n-Bu)$_3$ (4 equivalents of Ni(acac)$_2$) was added to the solution during the irradiation. The solution became green and no formation of 13 from 12 was observed on continued irradiation (Figure 2-4).

It has been previously observed that photolysis of a benzene solution of Ni(acac)$_2$ and xanthone containing 1,5-COD under H$_2$ gives the isomerized product, 1,4-COD, and the hydrogenated products, cyclooctene (COE) and cyclooctane (COA) (Equation 2-7).[42]

$$1,5\text{-COD} \xrightarrow[\text{Ni(acac)}_2,\ H_2]{h\nu/\text{xanthone}} 1,4\text{-COD} + \text{COE} + \text{COA} \qquad 2\text{-}7$$
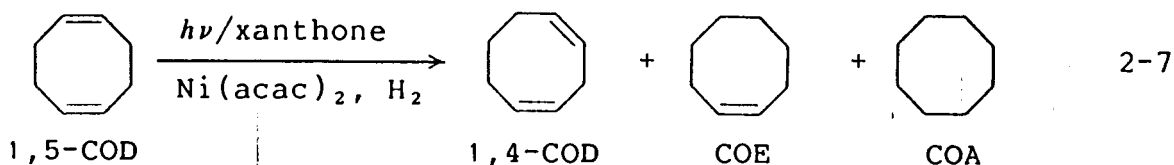
The effect of P(n-Bu)$_3$ on the photohydrogenation of 1,5-COD is shown by the following reaction patterns. After both 1,4-COD and COE were found in 2 hours, 4 equivalents of P(n-Bu)$_3$ on the
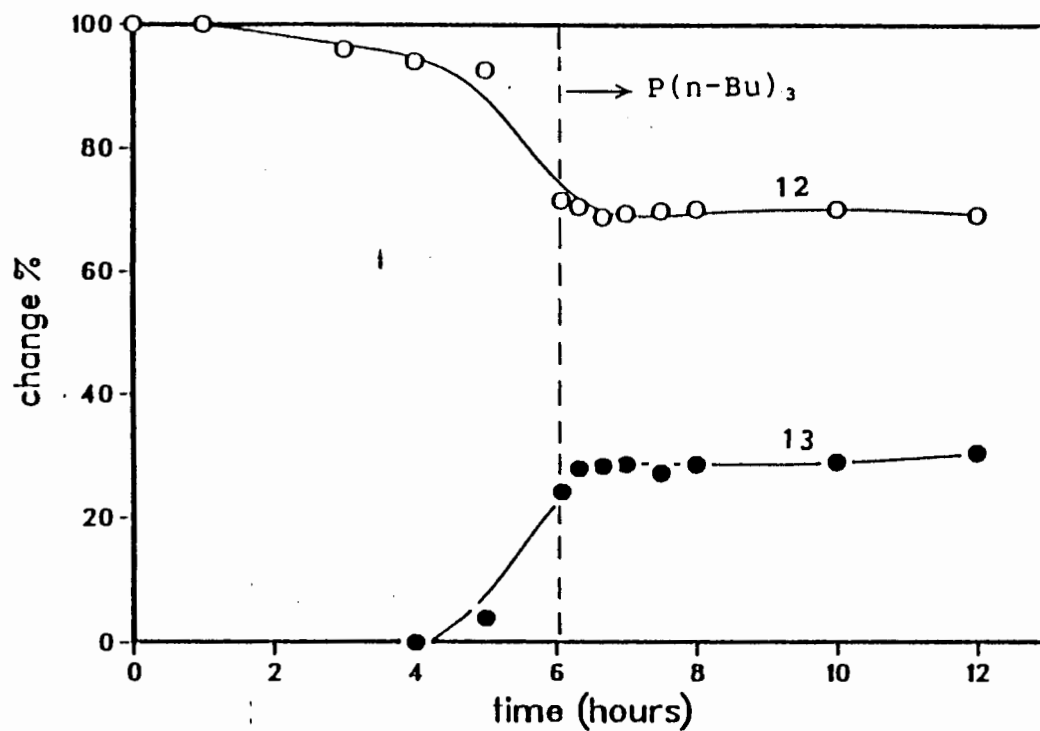
Figure 2-4. Photohydrogenation of 12 under the same conditions as in Figure 2-2 except the adding of P(n-Bu)$_3$ (4 times of Ni(acac)$_2$) after 6 hours of irradiation.

basis of the amount of Ni(acac)$_2$ was added without interrupting

irradiation. It was found by GC analysis that the changes of

1,5-COD and the products retarded, and eventually stopped

(Figure 2-5). COA was not found under prolonged irradiation. A

small decrease in the amount of 1,5-COD in later stage of

prolonged photolysis may be due to the reaction of 1,5-COD and

xanthone to form the corresponding oxetanes.[100]

2-3. Homogeneous versus Heterogeneous Catalytic Processes

2-3-1. Photohydrogenation of olefins in the presence of Hg(0)

In the studies of photohydrogenation of olefins in the

presence of Ni(acac)$_2$, the precipitation of Ni(0) metal always

occurred. This raised the question of whether the photohydro-

genation involves homogeneous or heterogeneous catalysis,

because heterogeneous hydrogenation of olefins catalyzed by

nickel metal is well known.[101] Previous studies has utilized the

technique of selective poisoning,[95] in which mercury was added

to a reaction mixture to selectively suppress the catalytic

reactivity of the bulk colloidal and/or solid metal. It is

believed that mercury does not influence the homogeneous,

nonheterogeneous catalyzed reactions of the organometallic

species of interest. Some successful examples of the use of

mercury(0) to poison undesired heterogeneous transition metal

catalyzed reactions have been described.[94,95]
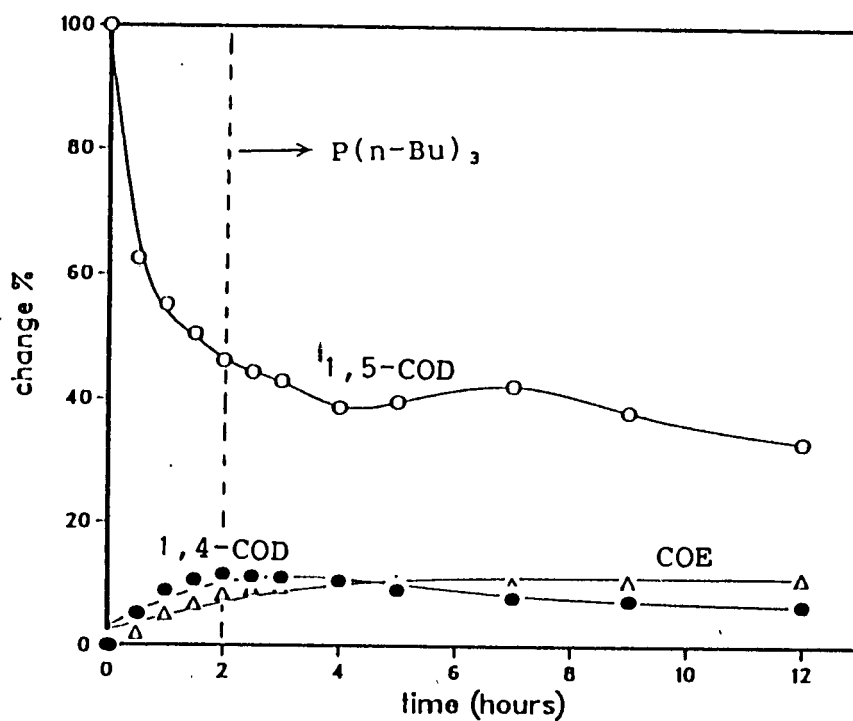
Figure 2-5. Photohydrogenation of 1,5-COD (0.023 M) in the presence of Ni(acac)$_2$ (0.004 M) and xanthone (0.005 M) in benzene under H$_2$ through a Pyrex filter at room temperature. P(n-Bu)$_3$ (0.016 M) was added after 2 hours of irradiation.

The data in Table 2-6 and Table 2-7 summarize the photo-
hydrogenation of **12** in the presence and the absence of mercury.
In the solvent systems of acetone/2-propanol/benzene and
xanthone/benzene, the formation of hydrogenated product **13** was
completely suppressed by the presence of mercury (Table 2-6). In
acetone/THF, the photohydrogenation of **12** was significantly
slowed, but not halted, by the presence of mercury (Table 2-7).

The effect of mercury(0) on the photohydrogenation of
norbornene, **3**, in acetone/THF was examined (Table 2-8). Before
photolysis these solutions were slightly green in color and the
mercury was bright and shiny. In the absence of mercury, the
inside wall of the tube was covered with a black solid and the
color of the reaction solution turned yellow and contained a
suspended black precipitate after 6 hours of photolysis. In
contrast, the inside wall of the tube containing mercury was
clean and the solution was clear and yellow with a small amount
of black solid. The mercury was covered with a dusty film. The
photohydrogenation of **3** in the presence of Hg(0) for the same
period of time gave 18% of **4** with 27% conversion of **3**. Thus,
mercury is apparently able to suppress but not halt the
photohydrogenation of **3** in acetone/THF.

Photohydrogenation of 1,5-COD in the presence and the
absence of mercury was also investigated (Table 2-9). Mercury(0)
does not significantly change the course of the transformation
of 1,5-COD to 1,4-COD and COE. Reaction solutions in xanthone/

Table 2-6

Photohydrogenation of **12** (0.03 M) in the presence of
Ni(acac)$_2$ (0.005 M) under H$_2$ at room temperature in the
presence and absence of Hg(0).

Solvents	time (hr)	Hg:Ni(acac)$_2$ mole ratios	**12**	**13** (%)	**14**	Observations
A/P/B*						
(12:3:10)	4	0	7	60	18	yellow, ppt
		1300:1	74	1	21	yellow, tract ppt
(2:3:20)	3	0	86	4	9	yellow
		1100:1	94	0	6	yellow
Benzene**	5	0	3	66	13	yellow
		550:1	51	0	17	yellow***

* A= acetone, P= 2-propanol, B= benzene; ratios by volume.

** xanthone= 0.007 M.

*** The corresponding oxetanes (15%) were detected by GC-MS.

Table 2-7

Photohydrogenation of **12** (0.067 M) in the presence of
Ni(acac)$_2$ (0.005 M) in acetone/THF (4:1 by volume) under H$_2$
at room temperature in the presence and absence of Hg(0).

time (hr)	Hg:Ni(acac)$_2$ mole ratios	**12**	**13** (%)	**14**	Observations
1	0	>98	0	1	yellow-green
	820:1	98	1	1	yellow-green
3	0	60	29	1	yellow
	1030:1	88	2	2	yellow
5	0	32	57	1	yellow, trace ppt
	740:1	83	4	2	yellow

Table 2-8

Photohydrogenation of norbornene, **3** (0.13 M) in the
presence of Ni(acac)$_2$ (0.005 M) in acetone/THF (4:1 by volume)
under H$_2$ at room temperature in the presence and absence of
Hg(0).

Irradiation time(hr)	Hg:Ni(acac)$_2$ mole ratios	3 (%)	4	Observations
2	0	68	23	yellow, trace ppt
	900:1	84	5	yellow, no ppt
4	0	36	53	dark yellow, ppt
	750:1	77	13	yellow, no ppt
6	0	26	66	dark, ppt
	590:1	73	18	yellow, trace ppt

Table 2-9

Photohydrogenation of 1,5-COD (0.06 M) in the presence of Ni(acac)$_2$ (0.006 M) under H$_2$ at room temperature in the presence and absence of Hg(0).

Solvents (v:v:v)	time (hr)	Hg:Ni(acac)$_2$ mole ratios	1,5-COD (%)	1,4-COD (%)	COE (%)	Observations
A/P/B*	6	0	80	7	4	yellow, ppt
(12:3:10)		600:1	90	5	3	yellow, trace ppt
A/T*	5	0	61	12	8	yellow, ppt
(4:1)		1090:1	72	8	5	yellow, trace ppt
X/B**	6	0	80	11	4	yellow
		560:1	84	11	3	yellow

* A= acetone, P= 2-propanol, B= benzene, T= THF.

** X= xanthone (0.009 M), B= benzene.

benzene system changed from green to yellow but remained clear
and appeared to be homogeneous whether Hg(0) was present or not.
On the other hand, in the absence of added mercury, reaction
solutions in acetone/2-propanol/benzene was yellow with a
suspended black precipitate; and in the presence of Hg(0), the
reaction solutions was clear and the mercury beads looked gray.
Similar results were observed in the solvent system of
acetone/THF as in acetone/2-propanol/benzene (but with less
black precipitate in the absence of mercury).

2-3-2. Sensitized cycloaddition of 12 in the presence of Hg(0)

Some energy levels of electronic excited states UV-visible
transitions of the excited mercury atom are shown with the
corresponding wavelengths (Equations 2-8 to 2-10).[102]

$$6s \ {}^1S_0 \longrightarrow 6p \ P_1 \qquad 1849.57 \ \text{Å} \qquad\qquad 2\text{-}8$$

$$6s \ {}^1S_0 \longrightarrow 6p \ {}^3P_1 \qquad 2536.52 \ \text{Å} \qquad\qquad 2\text{-}9$$

$$6p \ {}^3P_1 \longrightarrow 7s \ {}^3S_1 \qquad 4358.35 \ \text{Å} \qquad\qquad 2\text{-}10$$

It is also known that the triplet state Hg ($6p \ {}^3P_1$) is
readily formed by UV irradiation of mercury vapor and plays an
important role in photosensitization.[103-105] It was necessary to
test whether the added mercury could have some effect on the
incident light. In our system, a Pyrex filter (cut-off 290 nm)
was used.

To study the role of Hg(0) in the photohydrogenation reaction, the well-defined system of the sensitized photocyclo-addition of dicyclopentadiene 12 (Equation 2-6) was examined. Direct photolysis (through Pyrex filter) of solutions of 12 in 2-propanol and in benzene under N_2 in the presence and absence of mercury gave no cyclization product 14. In the presence of mercury, sensitized photoaddition of 12 in acetone and in acetone/2-propanol/benzene produced cage product 14 in nearly identical yields with those observed from in the absence of mercury (Table 2-10). It is clearly indicated that mercury(0) is neither a sensitizer nor a quencher in the system of photohydro-genation.

2-3-3. The hydrogenation of olefins in the dark

Olefins can be reduced with a variety of heterogeneous catalysts.[101] Catalysts such as Raney nickel can catalyze the hydrogenation of olefins under mild conditions.[106-108]

Photohydrogenation of olefins produced metallic nickel in the forms of a powder, film (see Experimental Section) or, in some cases, colloidal metal.[42] These freshly generated nickel(0) species may be active in catalyzed hydrogenation of olefins. The retardation in photohydrogenation by mercury may be due to the quenching of catalytic activity of the heterogeneous nickel species generated in the reaction. In order to consider the possibility of heterogeneous catalytic processes, the catalytic

Table 2-10

Sensitized intramolecular cycloaddition of **12** (0.05 M)
through Pyrex filter under N_2 at room temperature for 1 hour
in the presence and absence of Hg(0).

Solvent(s)	Mercury	12(%)	14(%)
2-propanol(P)	present	>99	0
	absent	>99	0
benzene(B)	present	99	1
	absent	98	1
acetone(A)	present	82	16
	absent	78	17
A/P/B	present	79	16
(12:3:10)	absent	83	13

reactivities of the newly generated metallic and/or colloidal nickel were tested in the presence of olefins under hydrogen pressure.

The heterogeneous nickel species were produced by photolysis of a solution of $Ni(acac)_2$ under H_2 for about 2 hours. The photolysate was removed to a pressure reactor under N_2 and mixed with a solution of olefin (N_2 saturated). The reactor was connected to a system under 40-50 psi hydrogen pressure and shaken in the dark. The reaction was followed by monitoring the barometer readings of H_2 pressure, and by GC analysis of the final sample. The solvent systems used were acetone/THF, acetone/THF/diglyme, acetone/2-propanol/diglyme, and xanthone /benzene/2-propanol.

Photolysis of $Ni(acac)_2$ in acetone/THF (4:1 by volume) resulted in a dark yellow solution with a small amount of black precipitate. In a similar solution, some diglyme was added to stablize the newly generated colloidal nickel. Irradiation of $Ni(acac)_2$ in acetone/THF/diglyme (8:2:1 by volume) gave a cloudy yellow solution but no black precipitate was observed. The photolysates were mixed with olefins and kept in the dark under H_2 pressure for 16-24 hours. The H_2 pressure did not decrease and GC analysis showed almost complete recovery of the starting materials without hydrogenated product.

According to previous discovery,[42] the ESR signal of colloi-
dal Ni(0) has been observed through photolysis of Ni(acac)$_2$ in
acetone/2-propanol (19:1 by volume) and benzene/2-propanol (19:1
by volume, in the presence of xanthone) under H$_2$. Irradiation of
Ni(acac)$_2$ in acetone/2-propanol/diglyme (8:2:1) under H$_2$ gave a
dark green solution without precipitation. After mixing with a
solution of dicyclopentadiene (12) under H$_2$ pressure (40 psi) in
the dark for 16 hours, >96% of 12 was recovered and a small
amount of black metal powder was found. No hydrogen was consumed
by barometer readings. Re-irradiation of the mixture under H$_2$
stream for 2 hours yielded hydrogenation product 13 (7%) and
cage product 14 (1%) with 18% conversion of 12.

Photolysis of Ni(acac)$_2$ in benzene/2-propanol (19:1 by
volume, in the presence of xanthone) under H$_2$ gave a dark yellow
solution without precipitation. After mixing with 12 in the dark
under H$_2$ (48 psi) for 24 hours, no change in hydrogen pressure
was observed and >98% of 12 was recovered.

2-4. Photochemical Carbonylation of Organic Halides by Photolysis of Ni(acac)$_2$ under CO

2-4-1. Carbonylation of aryl halides and their relative reactivities

Irradiation of Ni(acac)$_2$ in acetone/2-propanol under CO for
4 hours changed the color from green to yellow. Iodobenzene, 16,

was added to the solution ([16]:[Ni(acac)$_2$]= 8:3) and following

12 hours of photolysis the solution became brown. One product

was isolated from the photolysate and determined as 2-propyl

benzoate, 17 (74% based on the amount of 16, Equation 2-11). A

similar mixture of 16 and Ni(CO)$_4$ (generated *in situ*) was

refluxed (50-60°C) in the dark for 24 hours to give 30% yield of

17.

$$ \underset{\textbf{16}}{\text{I}\bigcirc} \quad \xrightarrow[\text{2-propanol, CO}]{h\nu/\text{acetqne, Ni(acac)}_2} \quad \underset{\textbf{17}}{\overset{\text{CO}_2\text{CH(CH}_3)_2}{\bigcirc}} \qquad \text{2-11} $$
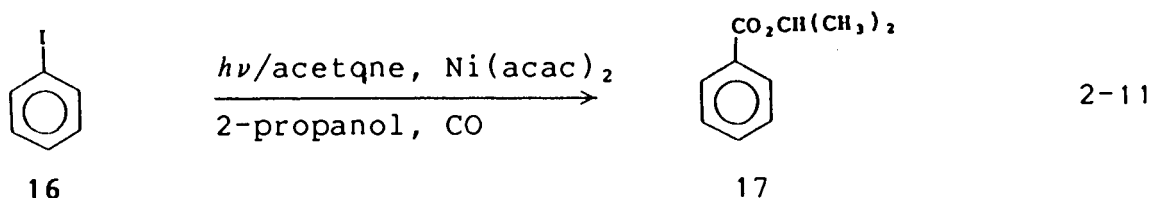
Photolysis of Ni(acac)$_2$ in acetone/methanol under CO for 6

hours gave a colorless solution. Bromobenzene, 18, was added to

the solution ([18]:[Ni(acac)$_2$]= 3:1) and the mixture was

contineously irradiated for 12 hours to yield a yellowish-brown

solution. The starting material 18 (50%) was recovered and a

product methyl benzoate, 19 (26% based on 18, Equation 2-12) was

isolated. A similar mixture of 18 and the photolysate of

$$ \underset{\textbf{18}}{\overset{\text{Br}}{\bigcirc}} \quad \xrightarrow[\text{methanol, CO}]{h\nu/\text{acetone, Ni(acac)}_2} \quad \underset{\textbf{19}}{\overset{\text{CO}_2\text{CH}_3}{\bigcirc}} \qquad \text{2-12} $$
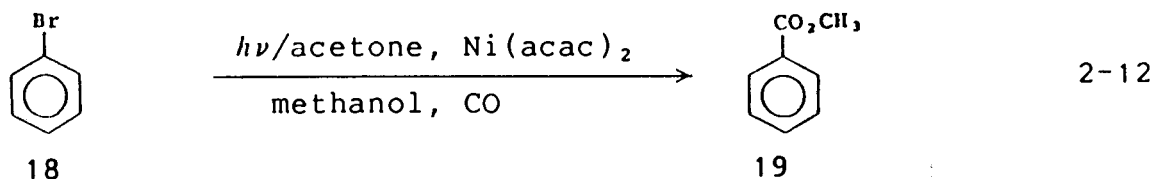
Ni(acac)$_2$ under CO was stirred in the dark at room temperature

for 24 hours. The carbonylated product 19 was not obtained. In

another experiment, chlorobenzene, 20, was added after 4 hours

of photolysis of Ni(acac)$_2$ in acetone/methanol under CO. Irradiation of the mixture for 12 hours resulted in a slightly yellow solution and GC analysis showed >97% recovery of **20**.

The reactivities of different aryl halides toward carbonylation were examined. Two mixtures were tested: iodobenzene/bromobenzene and chlorobenzene/bromobenzene. Equimolar quantities of the two halides were mixed and carbonylated. The reaction was stopped at a relatively low degree of conversion (*ca.* 30%) to avoid a significant change in the concentrations of the two halides. Irradiation of Ni(acac)$_2$ in acetone/methanol under CO for 4 hours gave a colorless solution. A mixture of **16** and **18** ([**16**]:[**18**]:[Ni(acac)$_2$]= 1:1:1) was added and the solution became yellow after 6 hours of photolysis. GC analysis of the photolysate showed the recovery of **16** (69%) and that of **18** (97%) with the formation of methyl benzoate, **19** (25% based on **16**). Under similar conditions, a mixture of **18** and **20** ([**18**]:[**20**]:[Ni(acac)$_2$]= 1:1:1) was irradiated for 6 hours to give the recovery of **18** (77%) and that of **20** (98%) with the formation of **19** (12% based on **18** charged).

2-4-2. Carbonylation of iodobenzene, 16: thermal and photochemical decomposition of Ni(CO)$_4$

Gaseous nickel tetracarbonyl decomposes under thermal and photochemical conditions.[109] As the decomposition is required to create a coordinatively unsaturated position,[48] it is important

to investigate whether the light energy is necessary in the carbonylation reaction.

$Ni(CO)_4$ is produced by irradiation of $Ni(acac)_2$ and xanthone in methanol under a slow stream of CO (Equation 2-13) and collected in traps.[42]

$$Ni(acac)_2 + CO \xrightarrow[\text{MeOH}]{h\nu/\text{xanthone}} Ni(CO)_4 \qquad\qquad 2\text{-}13$$
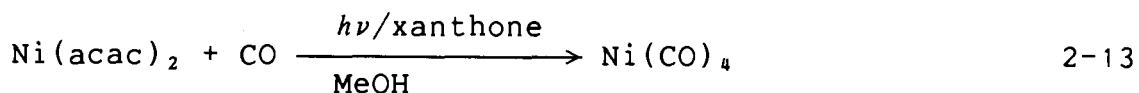
A mixture of the collected $Ni(CO)_4$ and **16** in methanol was stirred in the dark under CO at room temperature (*ca.* 20°C) for 12 hours. The solution became slightly yellow and GC analysis showed >98% recovery of **16** without the formation of the carbonylated product **19**. The same mixture was refluxed under CO in the dark for 12 hours to give a yellowish brown solution. The carbonylated product **19** (8%) was found with a 13% conversion of **16**.

Direct photolysis (Pyrex filter) of a mixture of the collected $Ni(CO)_4$ and **16** in methanol under CO at room temperature for 12 hours gave a yellow solution. GC analysis of the photolysate showed the formation of carbonylated product **19** (10%) and 85% recovery of **16**.

Irradiation of a solution of the collected $Ni(CO)_4$ and **16** in acetone/methanol through a Pyrex filter under CO for 12 hours yielded a yellowish brown solution. GC analysis showed the

formation of **19** (14%) with 19% conversion of **16**.

2-4-3. Carbonylation of **16**: in the presence of K_2CO_3

Irradiation of a solution of Ni(acac)$_2$ in acetone/methanol under CO for 4 hours gave a colorless solution. The mixture of the photolysate and iodobenzene, **16** ([**16**]:[Ni(acac)$_2$]= 1:1) was irradiated for additional 12 hours to give a brown solution. The transformation of **16** to carbonylated product **19** was demonstrated by GC analysis as shown in Figure 2-6.

As mentioned in Section 1-3, the yields of the carbonylated products are enhanced by the presence of a base.[75,81] The results of photolysis of mixtures of Ni(acac)$_2$ and **16** ([**16**]:[Ni(acac)$_2$]= 10:1) in acetone/methanol under CO for 12 hours in the presence and the absence of K_2CO_3 are given in Table 2-11. The photochemical carbonylation of **16** by photolysis of Ni(acac)$_2$ under CO produced more of the carbonylated product **19** in the presence of K_2CO_3 than that formed in the absence of K_2CO_3.

In comparison, a mixture of Ni(acac)$_2$, **16**, and K_2CO_3 in acetone/methanol was stirred under CO in the dark at room temperature for 12 hours. No carbonylated product was found. Under similar condition, a mixture of Ni(CO)$_4$ (generated *in situ* by photolysis of Ni(acac)$_2$ under CO), **16**, and K_2CO_3 in acetone/ methanol was stirred under CO in the dark for 12 hours. A trace
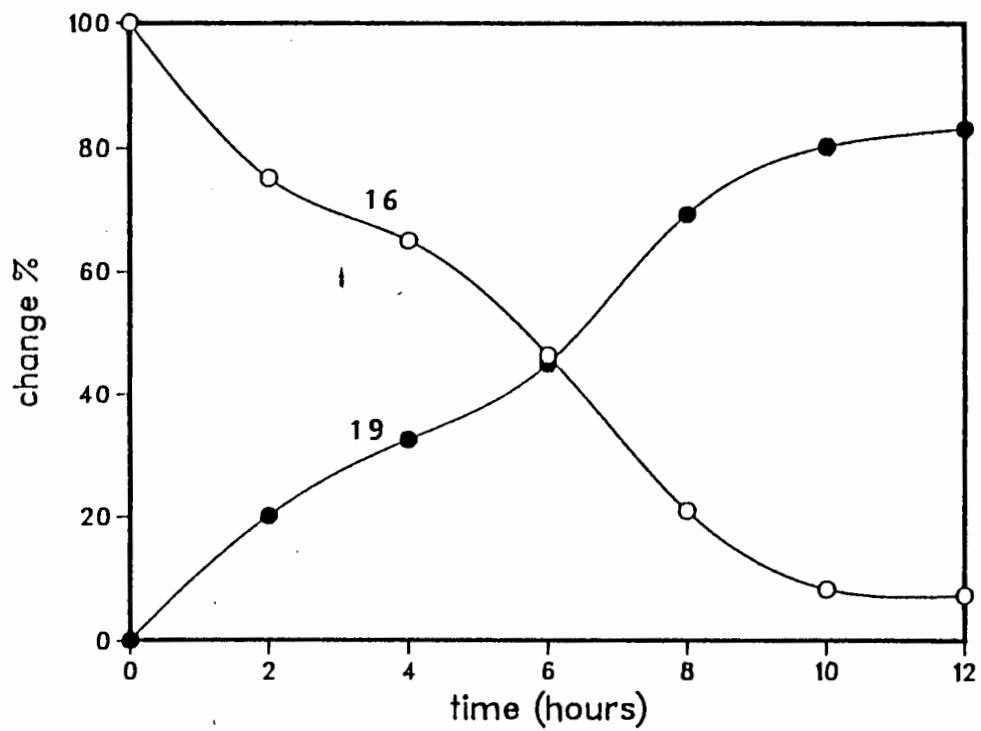
Figure 2-6. Photochemical carbonylation of **16** (3.0 mmol) in the presence of Ni(acac)₂ (3.0 mmol) in acetone/methanol (4:1 by volume) under CO at room temperature.

Table 2-11

Photochemical carbonylation of iodobenzene, 16 in the presence of $Ni(acac)_2$ in acetone/methanol (4:1 by volume) under CO in the presence and absence of K_2CO_3.*

$Ni(acac)_2$: 16 : K_2CO_3 molar ratios**	16(%)	19(yield%) based on 16	based on $Ni(acac)_2$
1 : 10 : 0	86	8.5	85
1 : 10 : 10	13	59.2	592

* 12 hours of irradiation, light source 450-Watt/Pyrex filter.

** $Ni(acac)_2$, 0.3 mmol; 15, 3.0 mmol; K_2CO_3, 3.0 mmol.

amount of carbonylated product **19** (<2%) was found with 97%

recovery of **16**.

2-4-4. Photochemical carbonylation of other organic halides

Irradiation of a mixture of $Ni(CO)_4$ (generated *in situ* by

photolysis of $Ni(acac)_2$ under CO), 1-bromonaphthalene, **21**, and

K_2CO_3 in acetone/methanol under an atmosphere of CO at room

temperature yielded methyl 1-naphthoate, **22** (41%) and

naphthalene, **23** (7%) with a 75% conversion of the starting

material **21** (Equation 2-14). The structures of the two products

$$\text{21} \quad \xrightarrow[\text{acetone/methanol, CO}]{h\nu,\ Ni(acac)_2} \quad \text{22} \quad + \quad \text{23} \qquad 2\text{-}14$$
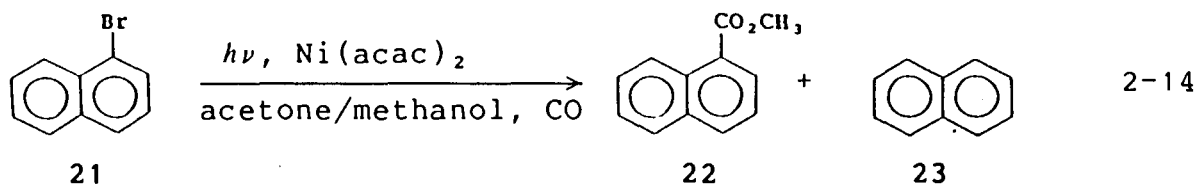
were determined by GC-MS spectra and by GC coinjection with

authentic samples. The carbonylated product **22** was isolated in

27% yield.

Under similar conditions, photolysis of a mixture of

iodocyclohexane, **24**, K_2CO_3, and $Ni(CO)_4$ (generated *in situ*) in

acetone/methanol under CO for 8 hours produced a product

determined as methyl cyclohexanecarboxylate, **25** (16%) with 82%

recovery of **24** (Equation 2-15). The carbonylated product **25** was

isolated in 9% yield.

$$\text{24} \xrightarrow[\text{acetone/methanol, CO}]{h\nu, \ \text{Ni(acac)}_2} \text{25} \qquad \text{2-15}$$
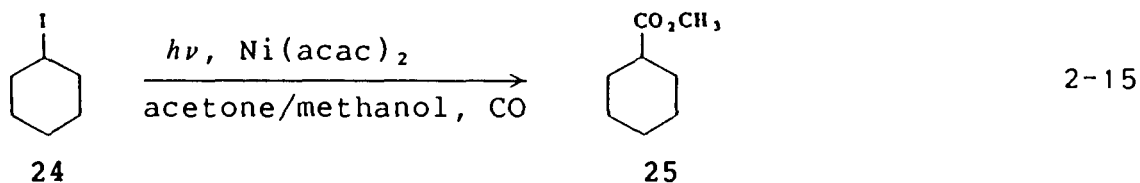
Irradiation of a mixture of crotyl bromide (26), K_2CO_3 and Ni(CO)$_4$ (generated *in situ*) in acetone/methanol under CO for 8 hours gave methyl 4-pentenoate, 27 (32% isolated yield) (Equation 2-16). 4-hydroxy-4-methyl-2-pentanone (28) was also isolated as a product of acetone self-condensation (Equation 2-17).

$$\text{26} \xrightarrow[\text{acetone/methanol, CO}]{h\nu, \ \text{Ni(acac)}_2} \text{27} \qquad \text{2-16}$$

$$\xrightarrow{K_2CO_3} \text{28} \qquad \text{2-17}$$
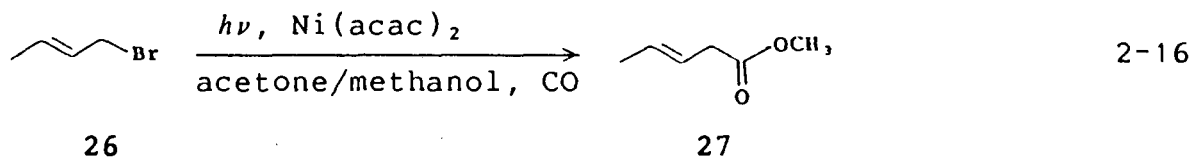
CHAPTER THREE

DISCUSSION

3-1. Photohydrogenation of Olefins by Photolysis of Ni(acac)$_2$ under H$_2$

Previous work has shown that sensitized photoreduction of Ni(acac)$_2$ under hydrogen can catalyze the hydrogenation of olefins *in situ*. This work was done under modified conditions using acetone as a sensitizer. The photohydrogenation can be run in different kinds of apparatus with a variety of configurations (3 ml to 300 ml scale).

In agreement with the previous observation,[42] bicyclic dienes (5 and 12) were reduced at the more strained C=C bonds exclusively and hydrogenation of the second olefinic bonds (i.e. those of 6 and 13) did not occur before the diene 5 and 12 were consumed. An unconjugated linear diene (9) was hydrogenated to give monoene and alkane without selectivity. The photohydrogenation of 4-vinylcyclohexene (7) showed the exclusive reduction of the external vinyl group without affecting the cyclic double bond. Similar selective hydrogenation of 7 has been reported by using heterogeneous catalysts, such as P-1 Ni$_2$B prepared by NaBH$_4$ and Ni(OAc)$_2$ (aq),[110] Urushibara type nickel catalysts prepared by NiCl$_2 \cdot$H$_2$O powder and zinc dust,[111] and designated NiC catalyst prepared by NaH and Ni(OAc)$_2$ in THF.[112]

Such selectivity is an advantage over Raney nickel catalyzed hydrogenation, where both double bonds of 7 were completely hydrogenated.[106-108]

It has been proposed[113] that the overall photohydrogenation reaction can be divided into three inter-related consecutive chemical events. In the first step, a triplet excited state acetone sensitizes the photoreduction of $Ni(acac)_2$ in the presence of a H-atom donor and a ligand to give the $Ni(acac)L_2$ complexes. Then the $Ni(acac)L_2$ complexes, having a 17-electron valence shell configuration, react rapidly with hydrogen to form the monohydridonickel complexes, $H-Ni(acac)L_2$, with a stable 18-electron configuration. Finally light promotes olefin hydrogenation catalyzed by the $H-Ni(acac)L_2$ complexes.

The photoreduction of $Ni(acac)_2$ in the presence of an olefin (using ethene C_2H_4 as a model) should form a soluble $Ni(I)$ complex, $Ni(acac)(C_2H_4)_2$ (Equation 3-1).

$$Ni(acac)_2 + CH_2=CH_2 \xrightarrow[SH]{h\nu} Ni(acac)(C_2H_4)_2 + acacH \qquad 3-1$$
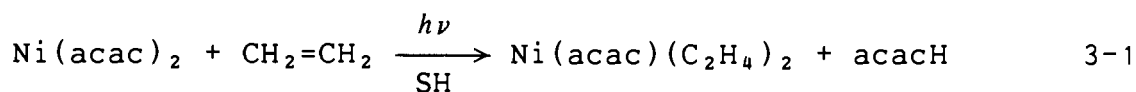
30

The formation of nickel hydrides is the major reaction pathway in catalytic hydrogenation and other related processes.[109,114] The interaction between $Ni(I)$ complexes and hydrogen to form nickel hydrides was shown by ^1H NMR studies in this lab.[43] Since $Ni(acac)L_2$ complexes have the 17-electron

configuration, the reaction of $Ni(acac)(C_2H_4)_2$ (**30**) with hydrogen will generate the 18-electron $H-Ni(acac)(C_2H_4)_2$ complex, as shown in Equation 3-2.

$$Ni(acac)(C_2H_4)_2 + H_2 \longrightarrow H-Ni(acac)(C_2H_4)_2 \qquad 3-2$$
$$\textbf{30} \qquad\qquad\qquad \textbf{31}$$
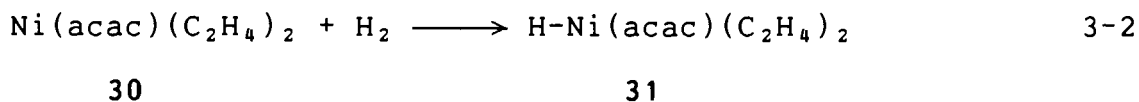
It is proposed that Ni(I) species follow a bimolecular disproportionation reaction as shown in Equation 3-3.[42]

$$2 \ Ni(acac)L_2 \longrightarrow NiL_4 + Ni(acac)_2 \qquad 3-3$$
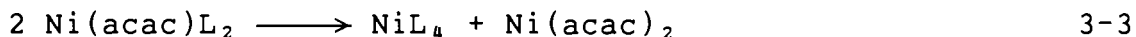
Photoinitiated dissociation of complexed ligands is a well known reaction.[9,14] The decomposition of NiL_4 is believed to lead to the formation of colloidal and metallic nickel (Equation 3-4) under irradiation.[42]

$$NiL_4 \longrightarrow \text{"Colloidal Ni"} \longrightarrow \text{"Ni metal"} \qquad 3-4$$
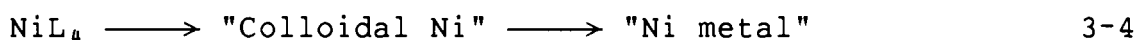
As mentioned earlier, photohydrogenation of olefins proceeds smoothly while the photolysates are clear, or homogeneous. ESR isotropic signals of Ni(I) as well as ^1H NMR signals of Ni-H and Ni-CH have been previously detected,[42] and it has been suggested that Ni complexes **31** and **32** act as catalytic carriers in the homogeneous phase using photoexcitation as the driving force (Scheme 3-1).[113] However, there is the possibility that metallic and colloidal nickel formed in the process can also act as

heterogeneous catalysts in hydrogenation. This point will be discussed later.

Scheme 3-1

$$H-Ni(acac)(C_2H_4)_2 \qquad CH_3CH_2-Ni(acac)(C_2H_4)$$

$$31 \qquad\qquad\qquad 32$$

$$h\nu$$

$$C_2H_6 \qquad\qquad H_2 + C_2H_4$$
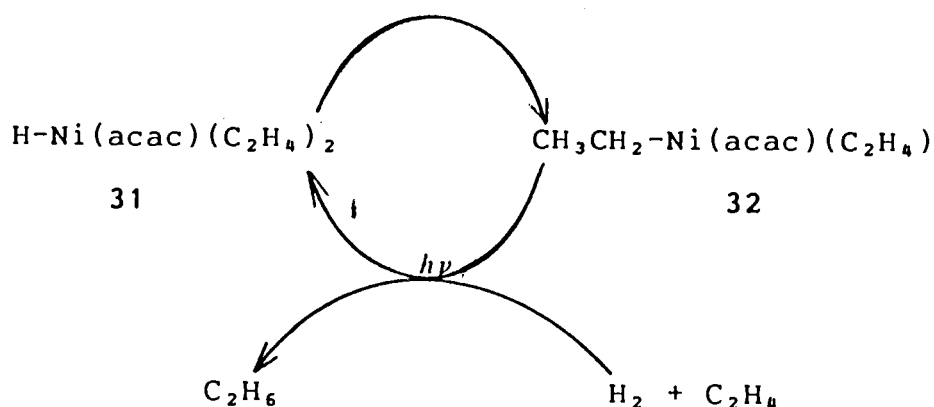
The proposed mechanism of homogeneous photohydrogenation with nickel hydride complexes (Scheme 3-1) is similar to the commonly accepted mechanism which involves intramolecular addition of Ni-H bond across a coordinated olefinic bond, and hydrogenolysis to regenerate Ni-H complex 31. The data shown in Tables 2-4 and 2-5 indicate that the hydrogenation of olefins is quenched by high concentration of $Ni(acac)_2$. Also Figure 2-3 clearly shows the importance of light on the catalytic process. Photoexcitation of 32 may be involved by either a direct or sensitized route, to promote the transformation of $32 \rightarrow 31$.

On the basis of the proposed mechanism the observed chemical selectivity of hydrogenation can be explained by:

1. functional groups such as carbonyl, ester, cyano, and amide
    groups are difficult to reduce due to weak coordination
    properties with nickel centers;

2. stronger coordinating carbon-carbon double bonds should be
    preferentially hydrogenated; e.g., norbornene type versus
    other olefinic bonds in intramolecular competition in 5 and
    12, and terminal double bond versus internal double bond in
    photohydrogenation of 7.

The selective coordination of the norbornene type double bond on
12 to nickel center is similar to that in Cu(I) catalyzed photo-
dimerization of 12, in which 12 is an exo-monodentate ligand in
33 and shows little tendency to act as an endo-tetrahepto
chelating ligand as in 34.[115]

33   34
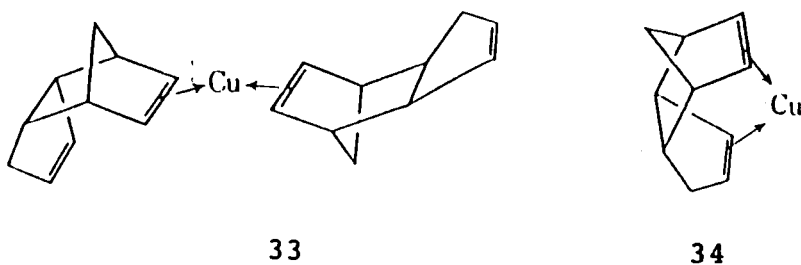
    The hydrogenation of dicyclopentadiene 12 is inhibited by
the presence of four equivalents of P(n-Bu)$_3$. As the coordina-
tion of the olefinic bond with nickel metal center is required
prior to reduction, obviously P(n-Bu)$_3$, being a better
coordinating ligand, should have displaced the olefin from 30
and 31 (Equations 3-5 and 3-6) or quenched other processes
required for the photohydrogenation. The addition of P(n-Bu)$_3$

eventually stopped the photohydrogenation and isomerization of
1,5-COD. The continued olefin transformation in the initial
stage following adding $P(n\text{-}Bu)_3$ implied the presence of a
catalytic process. The addition of $P(n\text{-}Bu)_3$ may stop the
catalytic process through several different reaction pathways.

$$Ni(acac)(C_2H_4)_2 \xrightarrow[-\ C_2H_4]{+\ P(n\text{-}Bu)_3} Ni(acac)[P(n\text{-}Bu)_3]_2 \qquad 3\text{-}5$$

30

$$H\text{-}Ni(acac)(C_2H_4)_2 \xrightarrow[-\ C_2H_4]{+\ P(n\text{-}Bu)_3} H\text{-}Ni(acac)[P(n\text{-}Bu)_3]_2 \qquad 3\text{-}6$$
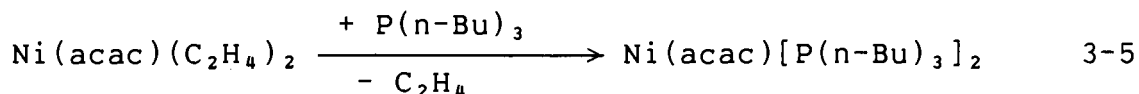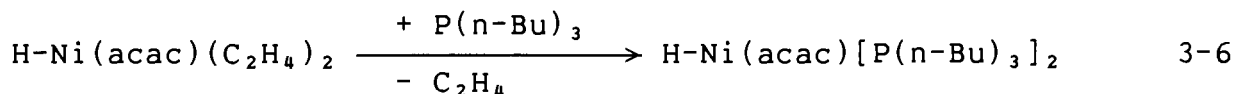
31

The efficiency of hydrogenation depends on many factors,
especially the rate of photon input. Precipitation of metallic
nickel further complicates the quantitative studies of this
process and prevents measurements of quantum yields and turn
over rates. The observed reactivity difference is a complex
resulting effect of various factors, such as the ability of
olefins to coordinate, the facility of the nickel complex **32** to
undergo hydrogenolysis, and other steric or excitation factors,
etc. Therefore one should be cautious in using reactivity
difference in mechanistic discussions.

The photohydrogenation studied depends on an acetone
sensitized process as the key step in driving the reaction.
Acetone is volatile and easily removed from the system after the

reaction. The high triplet excited state energy (78 Kcal/mol) makes acetone a good sentizer, although there are some minor drawbacks, e.g., low absorptivity at >300 nm and self-quenching reaction of its triplet state (k_{sq} = 3 x 10^6 M^{-1}s^{-1}).[116] Any substrate that can quench triplet excited ketones with diffusion controlled rate is not suitable, since it can compete effectively to inhibit generation of the catalytic species **31** and **32**. Conjugated dienes and α,β-unsaturated carbonyl compounds are among those substrates that could not be used because of the low triplet excited state energy.[117] However it is well known that the former can be reduced to monoolefins by thermal catalytic process of Ni-H complexes.[118] Acetone performs satisfactorily as a sensitizer relative to xanthone, particularly acetone's low reactivity to form the corresponding oxetanes[42,100] with olefins under the photohydrogenation conditions.

It is interesting to note that dicyclopentadiene **12** can be sensitized by acetone, xanthone, or benzene to undergo photo-cyclization to give the caged compound **14**. While sensitization by benzene is most efficient, sensitization by triplet excited state acetone does not compete efficiently with the sensitization of the reduction of Ni(acac)$_2$ and catalytic hydrogenation, particularly in THF. Also the formation of metallic nickel is significantly retarded and suppressed in THF. The patterns displayed in Figures 2-1 and 2-2 suggest that Ni(acac)$_2$ totally quenches excited state acetone in the first stage of photolysis

in THF but not in benzene. This may arise from modifications of Ni-complexes through loose coordination with solvent molecules.

3-2. Homogeneity versus Heterogeneity

As catalytic reactions of transition metals and their derivatives figure prominently in chemical industry, there is considerable interest in homogeneous versus heterogeneous catalysis, particularly for hydrogenation.[90-96] Characterization and identification of colloidal and solid metals in reaction mixtures is difficult. In recent years several proposals have focused on the identification of homogeneous versus heterogeneous reaction processes.[90-96] Further study on mechanism is required to test these proposals.

Selective poisoning with mercury(0) is a useful but not a widely applicable technique for differentiating homogeneous and heterogeneous reactions involving transition metal compounds.[95] This technique involves formation of mercury amalgams with active metallic powder. Mercury forms amalgams with bulk nickel to give $NiHg_4$ and $NiHg_3$ species,[119-120] and may also adsorb on the nickel surface.[121] Similarly, mercury may affect the catalytic activity of colloidal nickel through amalgamation.

The reaction pattern displayed in Figure 2-3 along with the results of the olefin hydrogenation at 40-50 psi pressure in the dark, suggest that the metallic and/or colloidal nickel(0)

formed in the reaction are not active in catalytic hydrogenation of olefins. If a heterogeneous process occurs, it could be an unknown heterogeneous hydrogenation requiring light promotion.

The results of photohydrogenation of olefins in the presence of Hg(0) indicate that in solvent systems containing benzene, the hydrogenation of olefin is essentially inhibited. In solvent systems containing THF, the hydrogenation is slowed, but not halted by the presence of Hg(0). The hydrogenation of 1,5-COD is not affected by the presence of Hg(0). Mercury does *not always* significantly change the course of the photohydrogenation. Sensitized photocyclization of dicyclopentadiene (12) confirms that mercury does not act as a sensitizer nor a quencher in the system.

This work can not clearly distinguish between homogeneous and heterogeneous processes. Further study on this question may apply other methods, such as the use of polymer-anchored organic substrates, or the use of a selective poison for homogeneous catalysts (e.g., dct). An interpretation of these observations is offered in Scheme 3-2 based on the homogeneous mechanism. There is a competition between transformation of Ni(acac)L_2 (30) to Ni-H complex 31 and the bimolecular decay of Ni(I) complexes (Equations 3-2 and 3-3). Following the disproportionation of Ni(I) complexes, the decomposition of NiL$_4$ to form colloidal and metallic nickel is facilitated by irradiation. The presence of mercury(0) favors the decomposition of NiL$_4$ through amalgamation

and/or physical adsorption with the bulk nickel. The formation

of Ni-H species might be suppressed by the side reaction of

Ni(acac)L$_2$ → NiL$_4$ which is possibly favored by the presence of

mercury.

Scheme 3-2

Ni(acac)$_2$ $\xrightarrow{\textit{hv}, \text{ L}}$ Ni(acac)L$_2$ $\underset{}{\overset{H_2}{\rightleftharpoons}}$ Ni-H $\longrightarrow$ hydrogenation

$\updownarrow$

NiL$_4$ + Ni(acac)$_2$

$\downarrow$

"colloidal Ni" and/or "Ni metal"

$\downarrow$ Hg(0)

NiHg$_4$ etc.
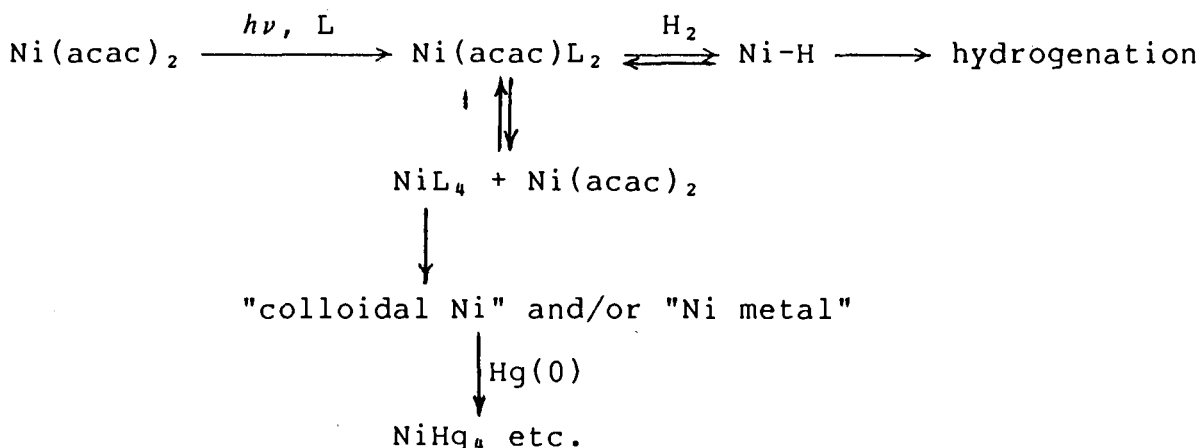
In benzene, the Ni(acac)L$_2$ complex is unstable and

disproportionation and decomposition occurs before reaction with

H$_2$. As a result, no Ni-H complex is formed and photohydrogena-

tion stops. In THF, the Ni(I) species can be stabilized by

coordination of THF, e.g., ESR signal has been detected for

Ni(acac)(THF)$_2$ species.[42,43] The decay of Ni(I) still competes

with the formation of Ni-H in the presence of mercury, so the

hydrogenation proceeds more slowly. In the presence of 1,5-COD,

the Ni(I) complex and Ni-H species are much better stablized by

1,5-COD than by THF or benzene, e.g., ESR signals of Ni(I) and

^{1}H NMR signals of Ni-H and Ni-CH can be detected in the presence

of 1,5-COD.[42] Thus photohydrogenation proceeds smoothly whether mercury is present or not.

3-3. Photochemical Carbonylation of Organic Halides

The carbonylation of organic halides in the presence of $Ni(CO)_4$ has been extensively studied.[72,73] The present study provides a method that can generate $Ni(CO)_4$ *in situ* by photo-reduction of $Ni(acac)_2$ under atmospheric CO and photochemically carbonylate organic halides at room temperature.

The mechanistic scheme (using $Ni(CO)_4$) for carbonylation of aromatic halides may involve several processes which are well established in organometallic chemistry (Equations 3-7 to 3-9):

(1). Oxidative addition:

$$R-X + Ni(CO)_4 \longrightarrow R-Ni(CO)_2X + 2CO \qquad \text{3-7}$$
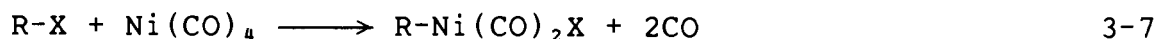
(2). Carbon monoxide insertion:

$$R-Ni(CO)_2X + CO \longrightarrow R-CO-Ni(CO)_2X \qquad \text{3-8}$$
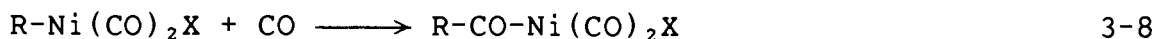
(3). Reductive elimination:

$$R-CO-Ni(CO)_2X + 2CO \longrightarrow R-COX + Ni(CO)_4 \qquad \text{3-9}$$

The reactivities of different halides toward photocarbonylation follow the decreasing order of I > Br > Cl. These

differences of reactivity of various halides are characteristic of oxidative addition reactions of organic halides with transition metal complexes such as those of cobalt,[123,124] and consistent with the reactivity order measured under thermal conditions.[81]

A vacant site on the nickel center is required prior to oxidative addition of R-X. Experimental values of Ni-CO binding energies for the sequence $Ni(CO)_x$ (x = 1-4) have been obtained.[125] The results are 29 (±15), 54 (±15), 13 (±10), and 25 (±2) Kcal/mol for the first, second, third, and fourth carbonyl, respectively. The results indicate that the dissociation of the first carbonyl is much easier than that of the second one. Indeed, the thermal decomposition of $Ni(CO)_4$ occurs at above 36°C (Equation 3-10), and under irradiation the photodecomposition is also possible.[109] Photolysis of $Ni(CO)_4$ in a gas matrix at low temperature has been reported to form $Ni(CO)_3$.[126,127] It is known that the exchange reaction between $Ni(CO)_4$ and ^{14}CO proceeds via the SN1 mechanism at a very fast rate under mild conditions.[126] The coordination of an organic halide to $Ni(CO)_3$ competes with the rapid recombination of $Ni(CO)_3$ and CO, and eventually results in the formation of carbonylated products. The role of the light energy is to aid the dissociation of $Ni(CO)_4$ to create a coordinatively unsaturated position on the metal center.
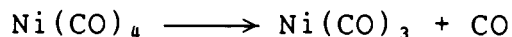
$$Ni(CO)_4 \longrightarrow Ni(CO)_3 + CO \qquad\qquad 3\text{-}10$$

The thermal decomposition of $Ni(CO)_4$ in the presence of iodobenzene (15) under CO produced carbonylated product methyl benzoate (18) in a similar yield to that observed from photochemical decomposition of $Ni(CO)_4$. In the presence of acetone, the yield of 18 by photochemical decomposition of $Ni(CO)_4$ seems to be about 4% more than that in the absence of acetone. This difference in yields is within experimental error.

The product yields are increased by adding K_2CO_3. The base may play a role in reducing the concentration of hydrogen halides formed during the carbonylation;[81] or generating anionic complexes (nickelates),[75] which were considered active in the carbonylation:[72,128]

$$[Ni_2(CO)_6]^{2-}, \; [Ni_3(CO)_8]^{2-}, \; [Ni_4(CO)_9]^{2-},$$

$$[Ni_5(CO)_9]^{2-}, \; [Ni_4H(CO)_9]^{-}, \; [Ni_5H(CO)_9]^{-}.$$
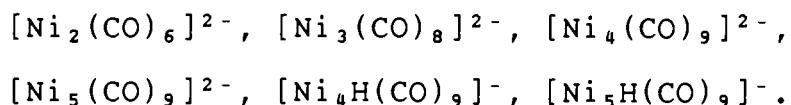
However, the chemistry of these anionic complexes is not well understood and further complicated by equilibria between the different species. A disadvantage in using K_2CO_3 is that acetone can undergo self-condensation reactions.

CHAPTER FOUR

EXPERIMENTAL

4-1. General Conditions

Unless otherwise specified, the experimental procedures were used under the following conditions. Melting points (m.p.) were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer 559 B spectrophotometer using a Nujol mull or KBr pellet. Ultraviolet (UV) and visible (Vis) spectra were recorded on a Varian Cary-210 spectrophotometer. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WM-400, or a Bruker SY-100 spectrometer. Chemical shifts (δ) are reported in parts per million relative to tetramethylsilane (TMS) and coupling constants (J) in Hz. The coupling patterns are presented as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). ^{13}C NMR spectra were recorded on the Bruker WM-400 spectrometer and are also reported relative to TMS. Mass spectra (MS) were obtained on a Hewlett-Packard 5985 GC/MS system, and gas chromatography-mass (GC-MS) spectra on the same system, equipped with a DB-1 capillary column (30 m x 0.25 mm), by electron impact ionization. Gas chromatography (GC) was performed on a Hewlet-Packard 5792A gas chromatograph equipped with an OV-1 (12 m x 0.20 mm) or an HP-1 (25 m x 0.20 mm)

capillary column, and output was processed with a Hewlett-Packard 3390A chart integrator.

4-2. Chemicals

Ni(acac)$_2$ (Harsaw) was recrystallized from methanol and dried under vacuum (0.5 mm Hg) for at least 2 hours. Xanthone (Aldrich) was recrystallized from ethanol. Oct-1,7-diene (Aldrich), norbornene (Aldrich), 5-methylene-bicyclo[2.2.1]-heptene (Aldrich), dicyclopentadiene (3a,4,7,8a-tetrahydro-4,7-methano-indene) (Aldrich), 4-vinylcyclohexene (Aldrich), butyl vinyl ether (Fisher), 1,5-COD (Aldrich), iodobenzene (Aldrich), bromobenzene (Aldrich), chlorobenzene (Aldrich), 1-bromo naphthalene (Aldrich), crotyl bromide (Aldrich), and cyclohexyl iodide (Aldrich) were distilled and stored under nitrogen prior to use. Tri-n-butylphosphine (Aldrich) was distilled prior to use. For photochemical reactions, reagent grade benzene, 2-propanol, acetone, ethanol, methanol, and tetrahydrofuran were distilled prior to use. Nitrogen (Union Carbide), hydrogen (Union Carbide), and carbon monoxide (Union Carbide) gases were used as received. For determination of products, authentic compounds norbornane (Aldrich), 1-octene (Aldrich), octane (Aldrich), 1,4-COD (Columbian Carbon), COE (Columbian Carbon), methyl benzoate (MCB), naphthalene (Allied Chemical), and methyl 1-naphthoate (Eastman) were used as received; authentic compounds 5-methylene-bicyclo[2.2.1]heptane,

3a,4,5,6,7,8a-hexahydro-4,7-methanoindene, and pentacyclo-
[5.2.1.0.0.0]decane were provided by H. Li of this lab.[42]

4-3. Photolysis Methods

Unless otherwise specified, photochemical reactions were
carried out in glassware made of Pyrex (cut-off 290 nm) with a
200-Watt or 450-Watt Hanovia medium-pressure mercury lamp as the
light source. Three photolysis methods were used depending on
reaction size and purpose.

Method I (300 ml-scale)

A cylindrical photocell (300 ml) was fitted with a side arm
at the top and a gas inlet extended to the bottom. A Pyrex
water-cooled lamp housing was inserted into the cell and the
side connected to a condenser. A slow stream of the applied gas
was allowed to bubble through the reaction solution from the gas
inlet, and escape from a gas trap at the top of the condenser.
During the irradiation, the solution was magnetically stirred.
To monitor the reaction, samples were withdrawn at intervals for
analysis without interrupting irradiation.

Method II (30 ml-scale)

The apparatus used in this method consists of a flat
cylindrical cell and a lamp housing jacket cooled by running

water. The cell has a side arm for use as a gas inlet, and a ground glass joint connected to a condenser. A gas trap was fitted on top of the condenser. The cell was placed 3 cm from the lamp jacket surface. After purging with gas for 20 minutes the reaction solution was irradiated under a constant gas flow. Samples were taken for analysis as in Method I.

Method III (3 ml-scale)

This method employed the same lamp housing jacket as Method II and several (normally 6-8) test tubes. The reaction solution was distributed into the tubes, capped with septa and wired up. Each solution was freed of oxygen by bubbling nitrogen (or hydrogen) through for 15 minutes using a long needle as an inlet and a short needle as an outlet. The needles were removed and septa sealed with *Parafilm wax paper. These tubes were placed around the lamp jacket, 3 cm away from the jacket surface. The whole system was immersed in a cold water bath. At intervals one of the tubes was removed and the photolysate was analyzed by GC.

4-4. Acetone Sensitized Photolysis of Ni(acac)$_2$ in the Presence of Olefins under H$_2$

4-4-1. Norbornene, 3

A solution of Ni(acac)$_2$ (0.03 g, 0.12 mmol) and 3 (0.11 g, 1.22 mmol) in acetone/THF (30 ml, 4:1 by volume) was irradiated

under H_2 (Method II) for 10 hours to give a yellow photolysate and trace black precipitate. GC analysis (50° isothermal) of the photolysate showed the peak of 3 (Rt = 2.26 min, 21%) and that of norbornane, 4 (Rt = 2.58 min, 79%), m/e (%): 96 (15, M^+), 81 (92), 68 (70), 67 (100), 54 (35), and 41 (19). The formation of 4 was confirmed by GC coinjection with an authentic sample.

4-4-2. 5-Methylene-bicyclo[2.2.1]heptene, 5

A solution of Ni(acac)$_2$ (0.04 g, 0.16 mmol) and 5 (0.18 g, 1.68 mmol) in acetone/2-propanol/benzene (30 ml, 2:2:1 by volume) was irradiated under H_2 (Method II) to become dark green in 3 hours. A black precipitate was formed after photolysis for 5 hours. GC analysis (50° isothermal) of the photolysate showed peaks corresponding to 5 (16%) and 2-methylene-bicyclo[2.2.1]-heptane, 6 (Rt = 2.98 min, 61%), m/e (%): 108 (32, M^+), 93 (55), 79 (100), 66 (50), 51 (8), 41 (10). The two compounds were confirmed by GC coinjection with authentic samples.

A solution of Ni(acac)$_2$ (0.033 g, 0.13 mmol) and 5 (0.085 g, 0.80 mmol) in acetone/THF (30 ml, 4:1 by volume) was irradiated under hydrogen (Method II) for 3 hours. The solution turned dark yellow with trace black precipitate. GC analysis (50° isothermal, 20 psi) of the photolysate showed the peaks corresponding to 5 (Rt = 2.25 min, 2%) and 6 (Rt = 2.46 min, 93%) as determined by GC coinjection with authentic samples.

4-4-3. 4-Vinylcyclohexene, 7

A solution of Ni(acac)$_2$ (0.39 g, 1.5 mmol) and 7 (1.70 g, 15.0 mmol) in acetone/2-propanol/benzene (300 ml, 2:2:1 by volume) was irradiated under H$_2$ (Method I) for 6 hours. A black precipitate formed during irradiation. GC analysis (50° isothermal) of the photolysate showed peaks of 7 (42%) and a product (Rt = 3.46 min, 56%). The photolysate was concentrated to 2.5 ml by distillation. Hexane (15 ml) was added, and the solution was passed through a basic alumina column (20 g) to give a colorless filtrate. The filtrate was concentrated to give a residue (0.5 ml). Seperation through the preparative GC (stainless steel column, 3 ft x 0.25 in, 10% Carbowax 20 M on Anakrom Q, 80-10 mesh; 60° isothermal, 15 psi) yielded a colorless liquid containing >85% of 4-ethylcyclohexene (8) (Rt= 3.46 min). GC-MS spetrum of 8 , m/e (%): 110 (20, M$^+$), 95 (17), 81 (100), 67 (30), 54 (40), and 41 (25). ^{1}H NMR (CDCl$_3$) δ: 0.9-2.3 (m, 12H), 5.65 (m, 2H).

A solution of Ni(acac)$_2$ (0.026 g, 0.10 mmol) and 7 (0.10 g, 0.97 mmol) in acetone/THF (30 ml, 4:1 by volume) was irradiated under H$_2$ (Method II) for 7 hours to give a dark solution with trace black precipitate. GC analysis (50° isothermal, 20 psi) of the photolysate showed peaks of 7 (Rt = 3.11 min, 6%) and 8 (Rt = 3.42 min, 91%) as confirmed by GC coinjection with authentic samples.

4-4-4. Oct-1,7-diene, 9

A solution of Ni(acac)$_2$ (0.034 g, 0.13 mmol) and **9** (0.13 g, 1.20 mmol) in acetone/2-propanol/benzene (30 ml, 3:1:2 by volume) was irradiated under H$_2$ (Method II, Section 4-3) for 5 hours. A black precipitate was formed during irradiation. GC analysis (50°C isothermal, 20 psi) of the photolysate showed the presence of **9** (30%) as well as two new components: 1-octene, **10**, (Rt = 2.65 min, 49%), m/e (%): 112 (15, M$^+$), 97 (6), 83 (50), 70 (100), 55 (82), 43 (52), 41 (80); and octane, **11**, (Rt = 2.79 min, 21%), m/e (%): 114 (14, M$^+$), 85 (98), 71 (48), 57 (52), 43 (100), 41 (70). The two products were confirmed by GC coinjection with authentic samples.

In a related experiment, a solution of the same concentrations of Ni(acac)$_2$ and **9** in acetone/benzene (3:2 by volume) was photolyzed under hydrogen for 5 hours showing no color change. GC analysis (50° isothermal) using cyclooctene as an internal standard showed a 97% recovery of **9**.

4-4-5. Dicyclopentadiene, 12

A solution of Ni(acac)$_2$ (0.026 g, 0.10 mmol) and **12** (0.12 g, 0.88 mmol) in acetone/2-propanol/benzene (30 ml, 4:1:8 by volume) was photolyzed under H$_2$ (Method II) for 2 hours to yield a dark yellow solution containing a trace of black precipitate. GC analysis (70° isothermal, 20 psi) showed the peaks of

3a,4,5,6,7,8a-hexahydro-4,7-methanoindene, **13** (Rt = 6.47 min, 58%), m/e (%): 134 (40, M$^+$), 119 (10), 91 (40), 77 (23), 66 (100),53 (5); and pentacyclo[5.2.1.0^{16}.0^{39}. 0^{48}]decane, **14** (Rt = 5.46 min, 15%), m/e (%): 132 (5, M$^+$), 117 (15), 91 (12), 78 (10), 66 (100), 51 (3); in addition to that of the unreacted **12** (24%). The two products were confirmed by GC coinjection with authentic samples.

A solution of Ni(acac)$_2$ (0.004 g, 0.014mmol) and **12** (0.11 g, 0.87 mmol) in acetone/THF (30 ml, 4:1 by volume) was irradiated under H$_2$ (Method II) for 8 hours to yield a dark solution. GC analysis (70° isothermal, 20 psi) showed the peaks of **13** (Rt = 6.19 min, 73%) and **14** (Rt = 5.23 min, 2%), in addition to that of the unreacted **12** (Rt = 4.92 min, 24%). The three components were confirmed by GC coinjection with authentic samples.

4-5. Photohydrogenation of 12 in the Presence of Ni(acac)$_2$

4-5-1. General description

A 200-Watt lamp was used as the light source. For reactions where conversions of the starting material and the yields of the products were required, a zero-hour sample (2 ml) was always kept in the dark as a control sample. Unless otherwise stated, yields are reported in absolute percentage (%) as determined by GC analysis. The absolute yields were calculated based on the peak intensities relative to a given quantity of internal stand-

ard. Olefins and their corresponding products are identified on GC by coinjection with authentic samples. A typical GC analysis (OV-1 capillary column, 25 m x 0.22 mm; column temperature, 70°C isothermal; injector temperature, 250°; detector temperature, 250°; column pressure, 20 psi) gave the following retention times: **12**, 4.95 min; **13**, 6.47 min; **14**, 5.46 min; methylenedioxy-benzene (MDOB, the internal standard), 4.23 min.

4-5-2. In acetone/2-propanol/benzene : reaction pattern

A solution of Ni(acac)$_2$ (0.036 g, 0.14 mmol) and **12** (0.096 g, o.73 mmol) in acetone/2-propanol/benzene (25 ml, 12:3:10 by volume) was irradiated under H$_2$ (Method II). The green solution turned dark yellow in two hours. Some black precipitate appeared after 4 hours of irradiation. The reaction was monitored by GC every 2 hours in 10 hours. Each sample (1 ml) was chromatog-raphed on a basic alumina column (4 g), washed with acetone, mixed with MDOB (0.03 M, 1 ml) and diluted with acetone to a total volume of 5 ml in a volumetric flask. The variation in percent yields of the products and in **12** are plotted in Figure 2-1.

4-5-3. In acetone/2-propanol/benzene : various amount of Ni(acac)$_2$

Solutions (5 ml each) containing **12** (0.052 M) and Ni(acac)$_2$ of various ratios ([Ni(acac)$_2$]: 0.050, 0.025, 0.010, 0.005,

0.002, and 0.001 M) were prepared in acetone/2-propanol/benzene (12:3:10 by volume). The tubes containing the solutions were capped with rubber septa and purged with H_2 for 20 minutes. They were arranged at the same distance, 5 cm, around the lamp housing jacket and irradiated (Method III) for 6 hours at room temperature. The photolysates were analyzed by GC as described in 4-5-2 and the results are given in Table 2-4.

A similar solution (5 ml) of **12** (0.05 M) and Ni(acac)$_2$ (0.005 M) in acetone/2-propanol/benzene (12:3:10 by volume) was saturated with nitrogen for 20 minutes and irradiated for 12 hours at room temperature. The photolysate was analyzed by GC (Table 2-1).

4-5-4. In acetone/THF : reaction pattern

A solution of Ni(acac)$_2$ (0.08 g, 0.30 mmol) and **12** (2.01 g, 15.2 mmol) in acetone/THF (300 ml, 4:1 by volume) was irradiated under H_2 (Method I). The green solution became yellow in 4 hours. Trace amount of black precipitate appeared after 7 hours of irradiation. The reaction was followed by GC every hour for 9 hours. Each sample (1 ml) was filtered through a basic alumina column (4 g), washed with acetone, mixed with MDOB (0.03 M, 1 ml) and diluted with acetone to a total volume of 5 ml in a volumetric flask. The variation in percent yields of the products and in **12** are plotted in Figure 2-2.

4-5-5. In acetone/THF : various amount of Ni(acac)$_2$

Solutions (5 ml each) containing 12 (0.052 M) and Ni(acac)$_2$ of various ratios ([Ni(acac)$_2$]: 0.050, 0.025, 0.010, 0.005, and 0.0005 M) were prepared in acetone/THF (4:1 by volume). The tubes containing the solutions were treated as described in 4-5-3. All the solutions were irradiated (Method III) for 6 hours at room temperature. The photolysate were analyzed by GC as described above to give the data shown in Table 2-5.

A similar solution (5 ml) of 12 (0.05 M) and Ni(acac)$_2$ (0.005 M) in acetone/THF (4:1 by volume) was saturated with N$_2$ and irradiated for 12 hours at room temperature. The photolysate was analyzed by GC (Table 2-1).

4-5-6. In acetone/THF : the role of irradiation

A solution of Ni(acac)$_2$ (0.08 g, 0.30mmol) and 12 (2.01 g, 15.2 mmol) in acetone/THF (300 ml, 4:1 by volume) was irradiated under hydrogen (Method I). The reaction was monitored by GC every 60 minutes in the first 6 hours. Then the light source was cut off and the yellow photolysate was kept in the dark under H$_2$ stream for 1 hour; during that period the color of the solution gradually turned back to green. Monitoring of the solution by GC analysis every 15 minutes showed no peak intensity changes relative to the internal standard (MDOB) for 12 and hydrogenated product 13 within this dark period. The solution was re-irradi-

ated, and the reaction followed by GC analysis again to show the further changes of **12** and **13** (Figure 2-3). The photolysate was yellow with trace amount of black precipitate after 5 hours of re-irradiation.

4-5-7. In acetone/THF : effect of P(n-Bu)₃

A solution of Ni(acac)$_2$ (0.08 g, 0.31 mmol) and **12** (2.19 g, 16.6 mmol) in acetone/THF (300 ml, 4:1 by volume) was irradiated under H$_2$ (Method I). After 6 hours of irradiation, tributyl-phosphine, P(n-Bu)$_3$ (0.31 g, 1.53 mmol), was added to the solution while the light was still on. The yellow photolysate turned green after the adding of P(n-Bu)$_3$ and no further color change was observed on prolonged irradiation. The reaction was monitored by GC every 60 minutes in the first 6 hours, every 20 minutes in the next 2 hours, and every 120 minutes in the last 4 hours. The variations in percentage yields of **12** and **13** are plotted in Figure 2-4. No precipitation was observed during the reaction.

4-5-8. Photohydrogenation of 1,5-COD in the presence of xanthone in benzene : effect of P(n-Bu)₃

A solution of Ni(acac)$_2$ (0.31 g, 1.2 mmol), 1,5-cyclo-octadiene (1,5-COD, 0.75 g, 6.9 mmol) and xanthone (0.31 g, 1.6 mmol) in benzene (300 ml) was irradiated under H$_2$ (Method I). After 2 hours of irradiation, P(n-Bu)$_3$ (1.0 g, 4.9 mmol) was

added to the solution without interrupting the irradiation. The yellow photolysate turned green after the adding of P(n-Bu)₃ and became yellowish green on further irradiation. No precipitate was observed. The reaction was followed by GC every 30 minutes in the first 3 hours, every 60 minutes in the next 2 hours, and every 120 minutes in the last 7 hours. The variations in percent yields of the isomerized and hydrogenated products and 1,5-COD are plotted in Figure 2-5.

4-5-9. Sensitized cycloaddition of 12

A solution of **12** (0.02 M) in benzene (4 ml) was saturated with nitrogen and irradiated through a Corex filter (cut-off 250 nm) for 3 hours. The photolysate analyzed by GC (70° isothermal, 20 psi) showed the peaks of **12** (9.6%) and cage product **14** (90.1%).

In a related experiment, solutions (4 ml each) of **12** (0.05 M) in acetone/2-propanol/benzene (12:3:10 by volume) and acetone/THF (4:1 by volume) were saturated with N₂ and irradiated through a Pyrex filter for 3 hours. The photolysates were analyzed by GC (Table 2-2).

Solutions (4 ml each) containing **12** (0.02 M) and Ni(acac)₂ (0.001 M) were prepared in different mixtures of solvents (benzene, benzene/methanol, benzene/ethanol, benzene/2-propanol, and benzene/THF). The tubes containing the solutions were capped

with rubber septa and purged with N_2 for 20 minutes. They were arranged about 5 cm away around the lamp housing jacket and irradiated through a Corex filter for 6 hours. The photolysates were analyzed by GC with respect to an internal standard (MDOB, 0.03 M). The results are listed in Table 2-3.

4-6. Catalytic Processes : Homogeneous vs Heterogeneous

4-6-1. General description

Warning: Mercury is a general protoplasmic poison. The maximum allowed concentration of mercury vapor in air is 0.01 ppm. Safe handling of mercury demands good ventilation, sealing of mercury containers, scrupulous attention to cleanliness of apparatus, clothing, hands, etc., rapid and thorough removal of spillages, and regular monitoring of the laboratory atmosphere.

For photohydrogenation of olefins in the presence and the absence of mercury, the experiments employed the same method as described in Method III, Section 4-3. All the tubes containing Hg(0) (added in the form of small drops of metallic mercury) were placed on a stirrer and the reaction mixtures were vigorously stirred during irradiation. The photolysates were analyzed by GC as described in Section 4-5-2.

The pressured experiments were run under the following procedures: a solution of $Ni(acac)_2$ in certain solvents was

irradiated under hydrogen (Method II). The photolysate was removed into a thick bottle (500 ml, Parr 666A, tested up to 120 psi) under nitrogen, mixed with a solution of olefin (saturated with N_2). The bottle was connected to a pressured system. The whole system was vacummed twice, then filled with H_2. The thick bottle was shaken in the dark at room temperature. The reaction was monitored by the reading of H_2 pressure on barometer and by GC analysis of the reaction mixtures.

4-6-2. Photohydrogenation of 12 in the presence of Hg(0) : in acetone/2-propanol/benzene

A solution of Ni(acac)$_2$ (0.005 M) and 12 (0.034 M) and large excess mercury (Hg:Ni(acac)$_2$ = 1300:1 mole ratio) in acetone/ 2-propanol/benzene (4 ml, 12:3:10 by volume) was purged with H_2 for 20 minutes and irradiated for 4 hours. The light green solution became yellow and dark with trace amount of precipitate after irradiation. No change was observed on the surface of mercury. The solution turned back to green as soon as opened to air. The photolysates were analyzed by GC with respect to a internal standard (MDOB, 0.05 M). The results are shown in Table 2-6.

In a control experiment, a similar solution without mercury was irradiated under H_2. After about 30 minutes of irradiation, the solution turned yellowish green and became darker. Some black precipitate appeared after 4 hours of irradiation. Yellow-

ish green photolysate gradually became green after opened to air. The photolysates were analyzed by GC (Table 2-6).

In a separate experiment, a solution of Ni(acac)$_2$ (0.005 M) and **12** (0.03 M) and large excess mercury (Hg:Ni(acac)$_2$= 1100:1) in acetone/2-propanol/benzene (4 ml, 2:3:20 by volume) was irradiated under H$_2$ for 3 hours. No precipitate was observed after irradiation. The results are listed in Table 2-6.

In a control experiment, a similar solution without Hg(0) was irradiated under H$_2$ for 3 hours. The results are given in Table 2-6.

4-6-3. Photohydrogenation of 12 in the presence of Hg(0) : in acetone/THF

Solutions (4 ml each) containing Ni(acac)$_2$ (0.005 M) and **12** (0.067 M) and large excess Hg(0) were prepared in acetone/THF (4:1 by volume) and irradiated under H$_2$ as described above. The photolysates were analyzed by GC with respect to an internal standard (MDOB, 0.05 M). The results are given in Table 2-7.

In a control experiment, similar solutions in the absence of Hg(0) were irradiated under H$_2$. The photolysates were analyzed by GC (Table 2-7).

4-6-4. Photohydrogenation of 12 in the presence of Hg(0) : in xanthone/benzene

A solution of Ni(acac)$_2$ (0.005 M), xanthone (0.007 M) and **12** (0.03 M) in benzene (4 ml) with large excess mercury (Hg:Ni(acac)$_2$= 550:1 mole ratio) was irradiated under H$_2$ as described above. The green solution became yellow-orange and remained clear after 5 hours of irradiation. The photolysates were analyzed by GC (Table 2-6).

In a control experiment, a similar solution in the absence of Hg(0) was irradiated under H$_2$ for 5 hours to give an clear orange solution. The results are given in Table 2-6.

4-6-5. Photohydrogenation of 1,5-COD in the presence of Hg(0) : in acetone/2-propanol/benzene

A solution of Ni(acac)$_2$ (0.006 M) and 1,5-COD (0.06 M) in acetone/2-propanol/benzene (3 ml, 12:3:10 by volume) in the presence of large excess mercury (Hg:Ni(acac)$_2$=600:1 mole ratio) was irradiated under H$_2$ as described above. The solution became dark yellow and some precipitate appeared after 6 hours of irradiation. Mercury turned to small beads while stirring and looked gray on the surface after irradiation. The photolysates were analyzed by GC (Table 2-9).

In a control experiment, a similar solution without Hg(0) was irradiated under the same condition for 6 hours. The green

solution turned dark yellow and some black precipitate was found. The results are given in Table 2-9.

4-6-6. Photohydrogenation of 1,5-COD in the presence of Hg(0) : in acetone/THF

Solutions (3 ml each) containing Ni(acac)$_2$ (0.006 M) and 1,5-COD (0.06 M) in acetone/THF (4:1 by volume) with large excess Hg(0) were irradiated under H$_2$ as described above. The solution looked yellow with a trace amount precipitate after 6 hours. Mercury beads were covered with dusty films. The photolysates were analyzed by GC (Table 2-9).

In a control experiment, similar solutions in the absence of Hg(0) were irradiated under the same conditions. The solution turned yellow with a small amount of precipitate. The results are listed in Table 2-9.

4-6-7. Photohydrogenation of 1,5-COD in the presence of Hg(0) : in the presence of xanthone in benzene

A solution of Ni(acac)$_2$ (0.006 M), xanthone (0.009 M) and 1,5-COD (0.06 M) in benzene (3 ml) in the presence of large excess mercury (Hg:Ni(acac)$_2$=560:1) was irradiated under H$_2$ for 6 hours. The green solution became yellow and remained clear after irradiation. No change was observed on the surface of Hg(0). GC analysis of the photolysate is shown in Table 2-9.

In a control experiment, a similar solution without Hg(0) was irradiated under the same conditions. The green solution looked yellow and clear after irradiation. The results are given in Table 2-9.

4-6-8. Photohydrogenation of norbornene, 3, in the presence of Hg(0) : in acetone/THF

Solutions (3 ml each) containing Ni(acac)$_2$ (0.005 M) and **3** (0.13 M) in acetone/THF (4:1 by volume) with large excess Hg(0) were irradiated as described above. The photolysates were analyzed by GC with respect to an internal standard (1,5-COD, 0.05 M). The results are given in Table 2-8.

In a control experiment, similar solutions in the absence of Hg(0) were irradiated under the same conditions. The photolysates were analyzed by GC (Table 2-8).

4-6-9. Photocycloaddition of 12 in the presence of Hg(0)

Solutions (3 ml each) containing **12** (0.05 M) and large excess Hg(0) in different solvents (or solvent mixtures) were irradiated through a Pyrex filter under N$_2$ for 1 hour. The photolysate were analyzed by GC (Table 2-10).

In a control experiment, similar solutions without Hg(0) were irradiated under the same conditions. The results are given in Table 2-10.

4-6-10. Hydrogenation of 12 under pressure in the dark

A solution of Ni(acac)$_2$ (0.14 mmol) in acetone/THF (30 ml, 4:1 by volume) was irradiated (Method II) under hydrogen for 1 hour. The green solution turned yellow with a trace amount of black suspension. The photolysate was removed into a thick bottle (500 ml, 120 psi) under a N$_2$ atmosphere in the dark, mixed with a solution of 12 (2.27 mmol) in acetone/THF (20 ml, 4:1 by volume, saturated with N$_2$). The initial hydrogen pressure in the system was 50 psi and after 24 hours in the dark, the final reading of the pressure was 49 psi. GC analysis of the mixture showed trace hydrogenated product 13 (1%) with 98% recovery of 12.

In a separate experiment, a solution of Ni(acac)$_2$ (0.05 mmol) in acetone/THF/diglyme (30 ml, 8:2:1 by volume) was irradiated under H$_2$ for 2 hours. The green solution looked yellow and cloudy but no precipitate was observed. The photolysate was mixed with a solution of 12 (1.9 mmol) in acetone (7 ml) as described above. The hydrogen pressure (40 psi) of the system remained the same after 16 hours in the dark.

A solution of Ni(acac)$_2$ (0.14 mmol) in acetone/2-propanol/ diglyme (30 ml, 8:2:1 by volume) was irradiated under H$_2$ for 2 hours. The green solution turned dark after irradiation but no precipitate was found. The photolysate was mixed with a solution

of **12** (1.89 mmol) in acetone (10 ml) as described above. After
16 hours in the dark under hydrogen pressure (40 psi), a trace
of black precipitate was found on the bottom of the bottle and
the solution looked green. GC analysis showed >96% recovery of
12 and no hydrogenated product was found. The solution was then
removed into a flat cell and irradiated under H_2 (Method II) for
2 hours. The solution became dark green with trace amount of
black precipitate. GC analysis showed the formation of **13** (7%)
and cage product **14** (1%) with 18% conversion of **12**.

In a separate experiment, a solution of Ni(acac)$_2$ (0.40
mmol) and xanthone (0.66 mmol) in benzene/2-propanol (40 ml,
19:1 by volume) was irradiated under H_2 for 1 hour. The solution
looked dark but no precipitation was observed after irradiation.
The photolysate was mixed with a solution of **12** (1.52 mmol) in
benzene (10 ml). The mixture was shaken in the dark under
hydrogen pressure (48 psi) for 24 hours. GC analysis showed a
98% recovery of **12** without the formation of hydrogenated product
13.

4-6-11. Hydrogenation of 1,5-COD under pressure in the dark

A solution of Ni(acac)$_2$ (0.18 mmol) in acetone/THF/diglyme
(30 ml, 8:2:1 by volume) was irradiated under H_2 for 2 hours.
The light green solution turned slightly cloudy without a
precipitation. The photolysate was mixed with a solution of
1,5-COD (2.96 mmol) in acetone (10 ml) and shaken in the dark

under hydrogen pressure (48 psi). After 24 hours no change on hydrogen pressure was observed, and 97% of 1,5-COD was recovered without the formation of hydrogenated and isomerized products according to GC analysis.

4-6-12. Hydrogenation of 3 under pressure in the dark

A solution of $Ni(acac)_2$ (0.14 mmol) in acetone/THF (30 ml, 4:1 by volume) was irradiated under H_2 for 2 hours to give a dark green solution with some black precipitate. The photolysate was mixed with a solution of 3 (4.4 mmol) in acetone (10 ml) and shaken in the dark under hydrogen pressure (38 psi) for 16 hours. GC analysis showed complete recovery of 3.

4-7. Photochemical Carbonylation of Organic Halides in the Presence of $Ni(acac)_2$ under CO

4-7-1. General description

Warning: Nickel tetracarbonyl is extremely poisonous. The threshold limit — the concentration to which a worker may be safely exposed day after day — is 0.001 ppm. Manipulation must be carried out in a fumehood with very good ventilation.

A 450-Watt lamp was used as the light source. For preparative experiments, large scale apparatus (Method I, Section 4-3) was used. The products were separated either by preparative GC

(stainless steel column, 3 ft x 0.25 in, 10% Carbowax 20 M on Anakrom Q, 80-10 mesh) or by column chromatography (Silica gel 60, 230-400 mesh). The structures of the products were determined by MS, IR, NMR and GC coinjection with authentic samples. Reactivity studies employed the 30 ml scale apparatus (Method II, Section 4-3). The percentages of the starting materials and products were determined by GC with respect to an internal standard.

4-7-2. Carbonylation of iodobenzene, 16

A soluiton of Ni(acac)$_2$ (0.02 M, 6.0 mmol) in acetone/ 2-propanol (300 ml, 4:1 bylume) was placed in a immersion type photocell and purged with CO for 20 minutes. The solution was irradiated with a 450-Watt lamp under a slow stream of CO. After 4 hours of irradiation the solution became colorless. Then iodobenzene 16 (3.5 g, 17.4 mmol) was added and the solution was divided into two portions (150 ml each).

Portion a: the 150 ml solution of 16 (8.7 mmol) and nickel species (3.0 mmol total) was irradiated under a slow bubble of N$_2$ through a Pyrex filter for 12 hours. The colorless solution turned brown after irradiation and became dark brown after open to air. The photolysate was passed through N$_2$ stream for 2 hours in order to eliminate the remaining Ni(CO)$_4$. Solvents were removed under reduced pressure at room temperature. The residue was mixed with 50 ml ether, washed by Na$_2$S$_2$O$_3$ (5%, 3 x 10 ml),

Na_2CO_3 (5%, 3 x 10 ml), and H_2O (2 x 10 ml), and dried over anhydrous $MgSO_4$. Ether was removed and the mixture was separated with column chromatography using ethyl acetate/hexane (1:9 by volume) as eluent. A colorless liquid (1.05 g) was obtained and determined as 2-propyl benzoate, 17 (74% yield based on 16), GC-MS m/e (%): 164(25, M^+), 149(5), 123(35), 122(25), 105(100), 77(30), 59(10); IR (cm^{-1}): 2960(s), 2890(s), 1725(vs), 1460(s), 1380(m), 1290(s), 1110(s), 725(s); ^1H NMR($CDCl_3$) δ: 1.38(d, J= 6.4Hz, 6H), 5.28(septet, J= 6.4 Hz, 1H), 7.51-8.07(m, 5H).

Portion b: the other 150 ml solution of 16 (8.7 mmol) and nickel species (3.0 mmol total) was stirred at 50-60°C in the dark under a slow bubble of nitrogen for 24 hours. The reaction mixture looked dark brown and was treated in a similar manner to that described above. Chromatography gave a recovery of 16 (0.53 g) and the carbonylated product 17 (0.45 g, 30% based on 16 charged) as determined by GC analysis.

In a separate experiment, a solution of Ni(acac)$_2$ (0.76 g, 3.0 mmol) in acetone/methanol (300 ml, 4:1 by volume) was purged with CO for 20 minutes and irradiated under CO stream for 4 hours to yield a colorless solution. 16 (0.65 g, 3.0 mmol) was added in and the mixture was irradiated under slow CO bubbles for 12 hours to give a brown solution. The reaction was monitored by GC every 2 hours. Each sample (2 ml) was mixed with 0.1 N HCl (0.5 ml), extracted with ether (2 x 3 ml), washed with 5% $Na_2S_2O_3$ (2 ml), H_2O (2 x 2 ml), dried with anhydrous $MgSO_4$,

and diluted with ether to a total volume of 10 ml in a volumet-
ric flask. The variations in percentages of **16** and the product
methyl benzoate (**19**) are plotted in Figure 2-7.

4-7-3. Carbonylation of bromobenzene, 18, and chlorobenzene, 20

A solution of Ni(acac)$_2$ (5.5 mmol) in acetone/methanol (300
ml, 4:1 by volume) was irradiated under CO for 6 hours to give a
colorless solution. Then bromobenzene **18** (14.5 mmol) was added
and the mixture was divided into two portions.

Portion a: 250 ml of the above solution of **18** (12.1 mmol)
and nickel species (4.6 mmol total) was irradiated under a slow
bubble of N$_2$ for 12 hours. The colorless solution turned
yellow-brown. The mixture was treated as described above and
distillation at reduced pressure gave two fractions: fraction 1
(1.20 g), b.p. 40-60°C (10 mmHg); fraction 2 (0.64 g), b.p.
70-90°C (10 mmHg). Chromatography of fraction 1 gave **18** (0.94 g,
determined by GC coinjection) and that of fraction 2 gave methyl
benzoate **19** (0.42 g, 26% yield based on **18** charged) as deter-
mined by spectra data and GC coinjection with an authentic
sample. MS m/e(%): 136 (35, M$^+$), 105 (100), 77 (47), 51 (7). IR
(cm^{-1}): 2970(m), 1725(vs), 1608(m), 1460(s), 1440(s), 1285(vs),
1120(s), 730(s); ^{1}H NMR δ: 3.94(s, 3H), 7.50-8.07(m, 5H).

Portion b: in the dark, 50 ml of the remained solution of **18**
(2.4 mmol) and nickel species (0.9 mmol total) was stirred at

room temperature under slow bubbling of nitrogen for 24 hours. The colorless solution turned yellow and was treated as described above to give a 80% recovery of **18** (0.30 g) and trace amount of **19** (<1%) was detected by GC analysis.

In a separate experiment, a solution of Ni(acac)$_2$ (0.075 g, 0.29 mmol) in acetone/methanol (30 ml, 4:1 by volume) was purged with CO for 15 minutes and irradiated for 4 hours under a CO stream to give a colorless solution. Then chlorobenzene **20** (0.11 g, 0.98 mmol) was added in and the mixture was irradiated under a slow bubble of N$_2$ for 12 hours. The mixture looked slightly yellow after irradiation and GC analysis (60° isothermal, 20 psi) showed >95% recovery of **20**.

4-7-4. Relative reactivity: 16/18/20

A solution of Ni(acac)$_2$ (0.077 g, 0.30 mmol) in acetone/ methanol (30 ml, 4:1 by volume) was purged with CO for 15 minutes and irradiated under CO bubbles for 4 hours to give a colorless solution. A mixture of iodobenzene **16** (0.061 g, 0.30 mmol) and bromobenzene **18** (0.047 g, 0.30 mmol) was added in and the solution was irradiated under slow bubbling N$_2$ for 6 hours to yield a yellow solution. GC analysis (85° isothermal, 20 psi) of the photolysate showed the recovery of **16** (69%) and that of **18** (97%), in addition to the formation of the carbonylated product **19** (25% yield based on the amount of **16**) as determined by GC coinjection with authentic sample.

In a related experiment, a soluiton of Ni(acac)$_2$ (0.077 g, 0.30 mmol) in acetone/methanol (30 ml, 4:1 by volume) was irradiated under CO for 4 hours to give a colorless solution. A mixture of **18** (0.047 g, 0.30 mmol) and chlorobenzene **20** (0.034 g, 0.30 mmol) was added and the solution was irradiated under slow N$_2$ bubbles for 6 hours to yield a yellowish green solution. GC analysis (70° isothermal, 20 psi) of the photolysate showed the recovery of **18** (77%) and that of **20** (98%) with the formation of **19** (12% based on **18**).

4-7-5. Carbonylation of 16: photochemical and thermal decomposition of Ni(CO)$_4$

A solution of Ni(acac)$_2$ (0.77 g, 3.0 mmol) and xanthone (0.88 g, 4.1 mmol) in methanol (300 ml) was placed in an immersion type photocell with the gas outlet connected to a series of two traps; the traps were immersed in a dry ice-acetone cooling bath (Figure 4-1). The green solution was irradiated with a 450-Watt lamp under a slow stream of CO. During the photolysis, the flow of the photocell cooling water was adjusted to maintain the photolysate temperature at 40-50°C. After 8 hours of irradiation, a corlorless solution (about 25 ml) was collected in the traps. Methanol (50 ml) was added into the traps and totally 75 ml solution was collected and stored in the dark at low temperature.
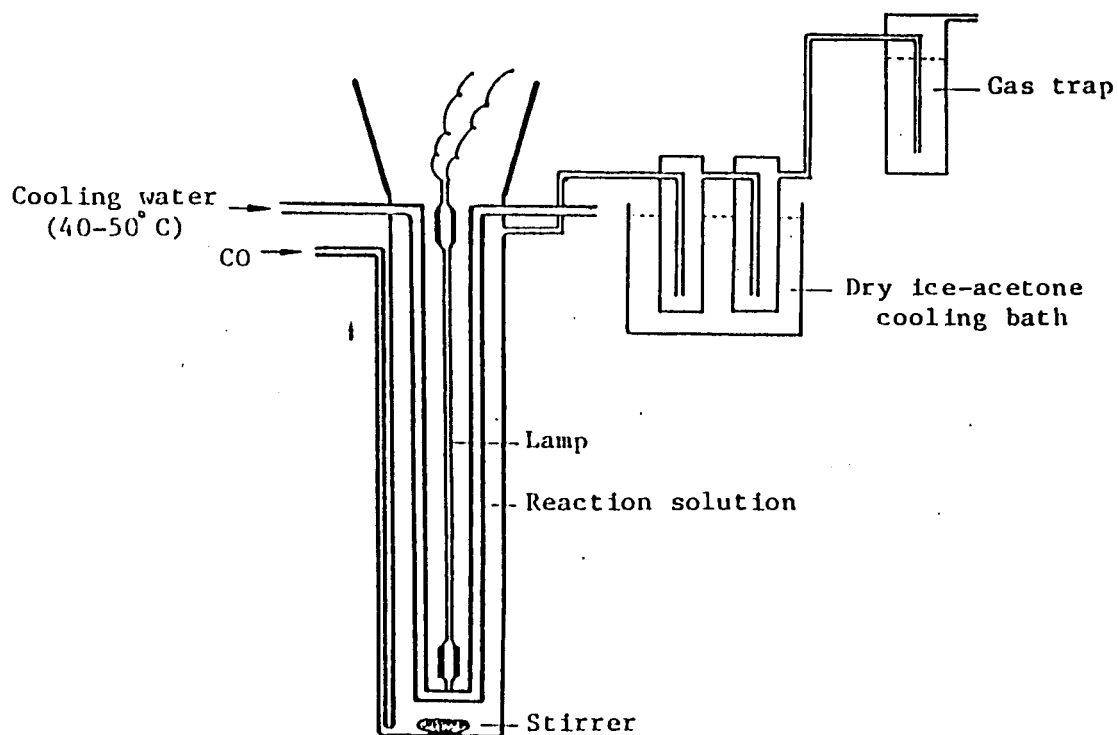
Figure 4-1. Immersion-type photocell connected with a double trap for preparation of Ni(CO)₄.

The collected solution (25 ml) was mixed with a solution of 16 (0.25 g, 1.23 mmol) in methanol (5 ml). The mixture was placed in a photocell (Pyrex) and irradiated under slow CO bubbling for 12 hours to give a yellow solution. GC analysis (100° isothermal, 20 psi) of the photolysate showed peaks corresponding to 16 (85%) and the carbonylated product 19 (10%) as confirmed by GC coinjection with authentic samples.

In a related experiment, another portion of the above collected solution (25 ml) was mixed with a solution of 16 (0.25 g, 1.23 mmol) in acetone (5 ml) and the mixture was irradiated under the same conditions for 12 hours to give a yellowish brown solution. GC analysis of the photolysate showed the formation of 19 (14%) with a recovery of 16 (82%).

The last portion of the above collected solution (25 ml) was mixed with a solution of 16 (0.25 g, 1.23 mmol) in methanol (5 ml). The mixture was placed in a 50 ml three-neck round bottom flask and stirred under a slow stream of CO at room temperature (about 20°C) for 12 hours. The solution become slightly yellow and GC analysis showed >98% recovery of 16. No carbonylated product was found. Then the temperature was raised to 50-60°C and the solution was refluxed under a slow stream of CO for 12 hours. The solution turned brown and GC analysis showed the formation of the carbonylated product 19 (8%) with a 13% conversion of 16.

4-7-6. Carbonylation of 16 in the presence of K_2CO_3

A mixture of Ni(acac)$_2$ (0.078 g, 0.30 mmol), 16 (0.61 g, 3.00 mmol), and K_2CO_3 (0.42 g, 3.00 mmol) in acetone/methanol (30 ml, 4:1 by volume) was purged with CO for 20 minutes and irradiated under slow CO bubbles. The suspension became cloudy after 12 hours of irradiation. The photolysate was mixed with HCl (0.1 N, 10 ml), extracted with ether, washed with $Na_2S_2O_3$ (5%) and H_2O, dried over anhydrous $MgSO_4$. GC analysis of the ether solution showed the peaks corresponding to 16 (23%) and the product 19 (59%) as confirmed by GC coinjection with authentic samples.

In control experiments, the similar solution in the absence of K_2CO_3 was irradiated under CO bubbles for 12 hours to give a yellow solution. The photolysate was treated as described above and GC analysis showed the formation of 19 (9%) and the recovery of 16 (86%). A similar solution of Ni(acac)$_2$ (0.077 g, 0.3 mmol), 16 (0.63 g, 3.0 mmol), and K_2CO_3 (0.42 g, 3.0 mmol) in acetone/methanol (30 ml, 4:1 by volume) was stirred under a slow stream of CO for 12 hours in the dark at room temperature. No color change was observed. The mixture was treated and analyzed as described above. GC analysis showed >96% recovery of 16. Carbonylated product was not found.

In a related experiment, a solution of Ni(acac)$_2$ (0.076 g, 0.3 mmol) in acetone/methanol (30 ml, 4:1 by volume) was purged

with CO for 20 minutes and irradiated under CO bubbles for 4
hours to give a yellow solution. The photolysate was mixed with
16 (0.61 g, 3.0 mmol) and K_2CO_3 (0.40 g, 3.0 mmol) and stirred a
slow stream of CO for 12 hours in the dark at room temperature.
The mixture was treated as described above and GC analysis
showed the recovery of 16 (97%) and a trace of carbonylated
product 19 (1.6%).

4-7-7. Carbonylation of 1-bromonaphthalene, 21

A solution of Ni(acac)$_2$ (0.79 g, 3.1 mmol) in acetone/
methanol (300 ml, 4:1 by volume) was irradiated under CO stream
for 6 hours to give a colorless solution. Then 21 (6.24 g, 30.6
mmol) and K_2CO_3 (2.84 g, 20.6 mmol) were added into the
solution. The mixture was contineously stirred and irradiated
under CO for 12 hours. The mixture became red-brown with some
cloudy suspension after irradiation. GC analysis (150°C
isothermal, 20 psi) showed peaks corresponding to 21 (Rt= 4.15
min, 35%), methyl 1-naphthoate, 22 (Rt= 6.40 min, 41%), and
naphthalene, 23 (Rt= 2.22 min, 7%). The two products were
determined by GC-MS and GC coinjection with authentic samples.
22, m/e(%): 186(60, M$^+$), 155(100), 127(82), 101(5), 77(10); 23,
m/e(%): 128(100, M$^+$), 102(5), 64(10), 51(10). The photolysate
was passed through N_2 for 2 hours to eliminate the remained
Ni(CO)$_4$. Solvents were removed under reduced pressure. The
residue was mixed with 0.2 N HCl (100 ml) and extracted with

ether (3 x 20 ml). The ether extracts were treated with 5% $Na_2S_2O_3$ (2 x 5 ml), 10% $NaHCO_3$ (2 x 5 ml) and H_2O (2 x 5 ml), dried over anhydrous $MgSO_4$, concentrated, and column chromatography (Silica gel, 230-400 mesh, 10% ethyl acetate/hexane) of the residue gave 1.5 g of **22** (27% based on **21** charged) as a colorless liquid confirming by GC coinjection with an authentic sample.

4-7-8. Carbonylation of iodocyclohexane, 24

A solution of $Ni(acac)_2$ (0.77 g, 3.0 mmol) in acetone/methanol (300 ml, 4:1 by volume) was irradiated under CO for 6 hours to give colorless solution. Then **24** (6.27 g, 30 mmol) and K_2CO_3 (4.10 g, 30.0 mmol) were added to the solution and the mixture was stirred and irradiated under CO for 8 hours, during which period a cloudy suspension developed. GC analysis (100° isothermal, 20 psi) of the photolysate showed peaks corresponding to **24** (Rt= 2.91 min, 82%) and a product identified as methyl cyclohexanecarboxylate, **25** (Rt= 3.01 min, 16%). The reaction mixture was treated as described above and column chromatography yielded 3.3 g of **24** (53% recovery) and 0.32 g of the carbonylated product **25** (9% based on the amount of **24**) as a colorless liquid. **25**, m/e(%): 142(60, M$^+$), 111(32), 87(100), 83(80), 74(45), 55(98), 41(40); IR (cm^{-1}): 2950(vs), 2880(s), 1740(vs), 1460(s), 1440(s), 1380(m), 1260(s), 1205(s), 1180(s), 1050(m), 770(m); ^1H NMR δ: 3.68(d, J= 0.8Hz, 3H), 2.29-1.36(m,

11H).

4-7-9. Carbonylation of crotyl bromide, 26

A solution of Ni(acac)$_2$ (0.77 g, 3.0 mmol) in acetone/
methanol (300 ml, 4:1 by volume) was irradiated under CO for 6
hours to give a colorless solution. Then 26 (4.20 g, 31.0 mmol)
and K$_2$CO$_3$ (4.10 g, 30.0 mmol) were added to the solution and the
mixture was stirred and irradiated under CO for 8 hours. During
the irradiation a white cloudy suspension developed. GC analysis
showed peaks corresponding to 26 (Rt= 1.99 min, 25% recorvered)
and two major compounds: 27 (Rt= 3.73 min) and 28 (Rt= 4.79
min). The reaction mixture was treated as described above and
column chromatography yielded 1.1 g of 27 and 1.0 g of 28. The
two compounds were determined as methyl-3-pentenoate (27) and
4-hydroxy-4-methyl-2-pentanone (28). 27 (32% yield), m/e (%):
114(30, M$^+$), 84(15), 83(10), 72(20), 59(40), 55(100), 39(15); IR
(cm^{-1}): 2960(m), 1735(s), 1660(s), 1410(m), 1290(m), 1110(m),
1040(m), 970(w); ^{1}H NMR δ(CDCl$_3$): 1.67(m, 3H), 2.98(m, 2H),
3.60(s, 3H), 5.50(m, 2H). 28, m/e (%): 115(15, M-1), 100(10),
73(100), 43(28); CI (chemical ionization) m/e (%): 117(50, M+1),
99(100); IR (cm^{-1}): 3444(s, broad), 2974(s), 2933(m), 1700(vs),
1366(s), 1183(m), 956(m); ^{1}H NMR δ(CDCl$_3$): 1.23(s, 6H), 2.17(s,
3H), 2.63(s, 2H), 3.80(s, 1H).

REFERENCES

1. R. C. Mehrotra, R. Bohra, and D. P. Gaur. *Metal β-Diketonates and Allied Derivatives.* Academic Press, London, 1978

2. J. P. Fackler, Jr. *Prog. Inorg. Chem.* 7, 361 (1966).

3. D. W. Barnum. *J. Inorg. Nucl. Chem.* **21**, 221 (1961); **22**, 183 (1961).

4. E. C. Lingafelter and R. L. Braum. *J. Am. Chem. Soc.* **88.** 2951 (1966).

5. R. H. Holm and F. A. Cotton. *J. Am. Chem. Soc.* **80**, 5658 (1958).

6. R. L. Lintvedt and H. F. Holtzclaw, Jr. *Inorg. Chem.* **5**, 239 (1966).

7. F. A. Cotton and R. H. Holm. *J. Am. Chem. Soc.* **82**, 5005 (1960).

8. J. P. Fackler, Jr. and F. A. Cotton. *J. Am. Chem. Soc.* **82**, 2979 (1960).

9. P. L. Lintvedt. *Concepts of Inorganic Photochemistry.* Ed. A. W. Adamson and P. D. Fleischauer, John Wiley & Sons, New York, 1975.

10. V. Balzani and V. Carassiti. *Photochemistry of Coordination Compounds.* Academic Press, London, 1970.

11. M. S. Wrighton. *Inorganic and Organometallic Photochemistry.* ACS. Vol 168, Washington, DC, 1978.

12. G. L. Geoffroy and M. S. Wrighton. *Organometallic Photochemistry*. Academic Press, New York, 1979.

13. G. J. Ferraudi. *Elements of Inorganic Photochemistry,* John Wiley & Sons, New York, 1988.

14. Symposium: Inorganic Photochemistry - State of the Art *J. Chem. Educ.* **60**, 784 (1983).

15. L. G. Vanquickenborne and A. Ceulemans. *Coord. Chem. Rev.* **48**, 157 (1983).

16. H. Henning and D. Rehorek. *Coord. Chem. Rev.* **61**, 1 (1985), and references therein.

17. C. Kutal, D. B. Yang, and G. Ferraudi. *Inorg. Chem.* **19**, 2907 (1980).

18. G. Ferraudi, D. B. Yang, and C. Kutal. *J. Chem. Soc. Chem. Commun.* 1050 (1979).

19. D. B. Yang and C. Kutal. *J. Chem. Soc. Chem. Commun.* 363 (1978).

20. H. D. Gafney, R. L. Lintvedt, and I. S. Jaivorwsky. *Inorg. Chem.* **9**, 1728 (1970).

21. N. Filipescu and H. Way. *Inorg. Chem.* **8**, 1863 (1969)

22. H. D. Gafney and R. L. Lintvedt. *J. Am. Chem. Soc.* **92**, 6996 (1970).

23. H. D. Gafney and R. L. Lintvedt. *J. Am. Chem. Soc.* **93**, 1623 (1971).

24. G. Porter and M. R. Wright. *Discuss. Faraday Soc.* **27**, 18 (1959).

25. G. L. J. Gijeman, F. Kaufman, and G. Porter. *J. Chem. Soc.*

Faraday Trans. II. **69**, 727 (1973).

26. A. J. Fry, R. S. H. Liu, and G. S. Hammond. *J. Am. Chem. Soc.* **88**, 4783 (1966).

27. G. S. Hammond and R. P. Foss. *J. Phys. Chem.* **68**, 3739 (1964).

28. F. Wilkinson and A. Farmilo. *J. Chem. Soc. Faraday Trans. II.* 604 (1976).

29. F. Wilkinson. *Pure Appl. Chem.* **41**, 661 (1975).

30. a). F. Wilkinson and C. Tsiamis. *J. Chem. Soc. Faraday Trans. II.* 77, 1681 (1981). b). F. Wilkinson and C. Tsiamis. *J. Am. Chem. Soc.* **105**, 767 (1983).

31. V. Balzani, F. Bolletta, and L. Moggi. *Spectr. Letters* **11**, 525 (1978).

32. V. Balzani, F. Bolleta, and F. Scandola. *J. Am. Chem. Soc.* **102**, 2152 (1980).

33. J. A. Bell and H. Linschitz. *J. Am. Chem. Soc.* **85**, 528 (1963).

34. Y. L. Chow, G. E. Buono-Core, B. Marciniak, and C. Beddard. *Can. J. Chem.* **61**, 801 (1983).

35. Y. L. Chow and G. E. Buono-Core. *Can. J. Chem.* **61**, 795 (1983).

36. Y. L. Chow, G. E. Buono-Core, and Yuquan Shen. *Organometallics* **3**, 702 (1984).

37. Y. L. Chow and G. E. Buono-Core. *J. Am. Chem. Soc.* **104**, 3771 (1982).

38. Y. L. Chow, G. E. Buono-Core, B. Marciniak, and H. Li. *J.*

Chem. Soc. Perkin Trans. II. 365 (1986).

39. G. Maki. *J. Chem. Phys.* **29**, 162 (1958).

40. Y. L. Chow, G. E. Buono-Core, C. W. B. Lee, and J. C. Scaiano. *J. Am. Chem. Soc.* **108**, 7620 (1986).

41. Y. L. Chow and G. E. Buono-Core. *J. Chem. Soc. Chem. Commun.* 592 (1985).

42. H. Li. *Ph.D. Thesis*, Simon Fraser University, 1988.

43. Y. L. Chow and H. Li. *Can. J. Chem.* **64**, 2229 (1986).

44. F. J. McQuillin. *Homogeneous Hydrogenation in Organic Chemistry.* D. Reidal, 1976.

45. B. R. James. *Comprehensive Organometallic Chemistry.* vol. **8**, Ed. G. Wilkinson, F. G. A. Stone, and E. Abel. New York 1982. p256.

46. B. R. James. *Adv. Organomet. Chem.* 17, 319 (1979).

47. B. R. James. *Homogeneous Hydrogenation.* Wiley, New York, 1973.

48. G. W. Parshall. *Homogeneous Catalysis. The Application and Chemistry of Catalysis by Soluble Transition Metal Compounds.* John Wiley and Sons, New York, 1980.

49. J. A. Osborn, F. H. Jardine, J. F. Young, and G. Willkinson. *J. Chem. Soc. A,* 1711 (1966).

50. R. E. Ireland and P. Bey. *Organic Synthesis,* **53**, 63 (1973).

51. W. Voelter and C. Djerassi. *Chem. Ber.* **101**, 58 (1968).

52. F. N. Jones. US Patent 3,459,785 (1969).

53. R. R. Schrock and J. A. Osborn. *J. Am. Chem. Soc.* **98**, 2134, 2143, 4450 (1976)

54. a) R. D. Cramer, E. L. Jenner, R. V. Lindsey, and U. G. Stolberg. *J. Am. Chem. Soc.* **85**, 1691 (1963). b). I. Yasumori and K. Hirabayashi. *Trans. Faraday Soc.* **67**, 3283 (1971).

55. Esso Research and Engineering Co. *Brit. Patent* 842,140 July 20, 1960.

56. a). R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg. *J. Am. Chem. Soc.* **87**, 658 (1965). b). J. C. Bailar. *J. Am. Oil. Chem. Soc.* **47**, 475 (1970).

57. a). J. Kwiatek, I. L. Mador, and J. K. Seyler. *Advances in Chemistry Series,* ACS, **37**, 201 (1963). b). J. Kwiatek. *Catal. Rev.* **1**, 37 (1967).

58. M. S. Spenser and D. A. Dowden. US Patent 3,009,969 (1961).

59. A. F. Halasa. US Patent 3,872,072 (1975).

60. M. F. Sloan, A. S. Matlack, and D. S. Breslow. *J. Am. Chem. Soc.* **85**, 4014 (1963).

61. J. C. Falk and J. Van Fleet. *Organic. Synthesis,* **53**, 1888 (1973).

62. H. B. Kagan and J. C. Frian. *New Approaches in Asymmetric Synthesis,* in *Topics in Stereochemistry,* vol. 10, ed. N. L. Allinger and E. L. Eliel, 1977.

63. J. D. Morrison, W. F. Masler, and M. K. Newberg. *Adv. in Catal.* **25**, 81 (1976).

64. H. B. Kagan. *Pure and Appl. Chem.* **43**, 401 (1975).

65. J. D. Morrison, W. F. Masler, and S. Hathaway. *Catalysis in Organic Synthesis,* R. N. Rylander and H. Greenfield, eds.,

Academic Press, 1976.

66. L. Marko and R. Heil. *Catal. Rev.* **8**, 269 (1974).

67. B. Bogdanovic. *Angew. Chem. Int. Ed. Engl.* **12**, 954 (1973).

68. W. S. Knowles. *Acc. Chem. Res.* **16**, 106 (1983).

69. Y. Izumi. *Angew. Chem. Int. Ed. Engl.* **10**, 871 (1971).

70. M. A. Schroeder and M. S. Wrighton. *J. Am. Chem. Soc.* **98**, 551 (1976).

71. M. S. Wrighton, D. S. Ginley, M. A. Schroeder. *Pure Appl. Chem.* **41**, 671 (1975).

72. I. Wender and D. Pino, eds., *Organic Synthesis via Metal Carbonyls*, Wiley-Interscience, vol.I, 1968; vol. II, 1977.

73. M. Ryang. *Organomet. Chem. Rev. A,* **5**, 67 (1970).

74. S. K. Palit and N. Tripathy. *J. Appl. Chem.* **19**, 301 (1969).

75. M. Nakayama and T. Mizoroki. *Bull. Chem. Soc. Jap.* **43**, 569 (1970).

76. G. P. Chiosoli, M. Dubini, M. Ferraris, F. Guerrieri, S. Merzoni, and G. Mondelli. *J. Chem. Soc.* C2889 (1968).

77. M. Nakayama and T. Mizoroki. *Bull. Chem. Soc. Jap.* **44**, 508 (1971).

78. N. L. Bauld. *Tetrahedron Lett.* 1841 (1963).

79. W. W. Prichard. *J. Am. Chem. Soc.* 78, 6137 (1956).

80. E. J. Corey and L. S. Hegedus. *J. Am. Chem. Soc.* **91**, 1233 (1969).

81. L. Cassar and M. Foa. *J. Organomet. Chem.* **51**, 381 (1973).

82. P. W. Jolly and G. Wilke. *The Organic Chemistry of Nickel,* II. Academic Press, New York, 1974.

83. J. K. Crandall and W. J. Michaely. *J. Organometal. Chem.* **51**, 375 (1973).

84. D. R. Levering and A. L. Glasebrook. *J. Org. Chem.* **23**, 1836 (1958).

85. A. J. Kunin and R. Eisenberg. *J. Am. Chem. Soc.* **108**, 535 (1986).

86. T. Sakakura and M. Tanaka. *J. Chem. Soc. Chem. Commun.* 758 (1987).

87. a). M. J. Mirbach, M. F. Mirbach, A. Saus, N. Topalsavoglou, and T. N. Psu. *J. Am. Chem. Soc.* **103**, 7590, 7594 (1981). b). A. Saus, T. N. Psu, M. Mirbach, and M. F. Mirbach. *J. Mol. Catal.* **18**, 117 (1983).

88. T. Kondo, Y. Tsuji, and Y. Watanabe. *Tetrahedron Lett.* 3833 (1988).

89. W. P. Dunsworth and F. F. Nord. *J. Am. Chem. Soc.* **72**, 4197 (1980).

90. J. E. Hamlin, K. Hirai, A. Millan, and P. M. Maitlis. *J. Mol. Catal.* **7**, 543 (1980).

91. J. P. Collman, K. M. Kosydov, M. Bressan, W. Lamanna, and T. Garret. *J. Am. Chem. Soc.* **106**, 2569 (1984).

92. R. H. Crabtree, M. F. Mellea, J. M. Mihelcic, and J. M. Quirk. *J. Am. Chem. Soc.* **104**, 107 (1982).

93. R. H. Crabtree, P. C. Demou, D. Eden, J. M. Mihelcic, C. A. Parnell, J. M. Quirk, and G. M. Morris. *J. Am. Chem. Soc.* **104**, 6994 (1982).

94. D. R. Anton and R. H. Crabtree. *Organometallics* **2**, 855

(1983).

95. G. M. Whitesides, M. Hackett, R. L. Brainard, J.-P. P. M. Lavalleye, A. F. Sowinski, A. N. Izumi, S. S. Moore, D. W. Brown, and E. M. Staudt. *Organometallics* **4**, 1819 (1980).

96. R. M. Laine. *J. Mol. Catal.* **14**, 137 (1982).

97. C. Paal and W. Hartmann. *Chem Ber.* **51**, 711 (1918).

98. a). Sadtler NMR Spectra, No. 8171M. b). S. R. Heller and G. W. A. Milne. *EPA/NIH Mass Spectral Database,* vol.1, US Goverment Printing Office, Washington D. C., 1978, p125.

99. a). G. O. Schenck and R. Steinmetz. *Chem. Ber.* **96**, 520 (1963). b). C. C. Ladwig and R. S. H. Liu. *J. Am. Chem. Soc.* **98**, 8093 (1976).

100. a). D. O. Cowan and R. L. Drisko. *Elements of Organic Photochemistry.* Plenum, New York, 1976. b). H. A. J. Carless. *Synthetic Organic Photochemistry.* ed. W. M. Horspool, Plenum Press, New York, 1984.

101. P. N. Rylander. *Organic Synthesis with Noble Metal Catalysts,* Acad. Press, New York, 1973.

102. G. V. Samsonov. *Handbook of Physicochemical Properties of the Elements*, Oldbourne, London, 1968.

103. A. B. Callear. *Chem. Rev.* **87**, 335 (1987).

104. H. E. Gunning and O. P. Strausz. *Advances in Photochemistry,* Vol. 1, ed. W. A. Noyes, G. S. Hammond, and J. N. Pitts, Interscience, New York, 1963.

105. R. J. Cvetanovic. *Progress in Reaction Kinetics,* Vol. 2, ed. G. Porter, Pergamon, Oxford, 1964.

106. H. Adkins and H. R. Billica. *J. Am. Chem. Soc.* **70**, 695 (1948).

107. H. A. Smith, W. C. Bedoit, Jr., and J. R. Fuzek. *J. Am. Chem. Soc.* **71**, 3769 (1948).

108. R. Paul, P. Buisson, and N. Joseph. *Ind. Eng. Chem.* **44**, 1006 (1952).

109. P. W. Jolly and G. Wilke. *The Organic Chemistry of Nickel,* I. Academic Press, New York, 1974.

110. C. A. Brown. *J. Org. Chem.* **35**, 1900 (1970).

111. M. Kajitani, Y. Sasaki, J. Okata, K. Ohmura, A. Sugimori, and Y. Urushibara. *Bull. Chem. Soc. Jap.* **47**, 1203 (1974).

112. J. J. Brunet, P. Gallois, and P. Caubere. *Tetrahedron Lett.* 3955 (1977).

113. Y. L. Chow, H. Li, and M. S. Yang. submitted for publish.

114. R. H. Crabtree. *The Organometallic Chemistry of the Transition Metals,* John Wiley & Sons, New York, 1988.

115. R. G. Salomon and J. K. Kochi. *J. Am. Chem. Soc.* **95**, 1189 (1973); **96**, 1137 (1974).

116. I. Naito and W. Schnabel. *Bull. Chem. Soc. Jap.* **57**, 771 (1984).

117. N. J. Turro. *Mordern Molecular Photochemistry,* the Benjamin/Cummings, Menlo Park, Calif., Chap. 9.

118. M. Sakai, F. Harada, Y. Sakakibara and N. Uchino. *Bull. Chem. Soc. Jap.* **55**, 343 (1982).

119. M. Z. Hasson, D. F. Untereker, and S. Brunkenstein. *J. Electroanal. Chem. Interfacial Electrochem.* **42**, 161 (1973).

120. a). G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsky. *J. Am. Chem. Soc.* **94**, 5258 (1972). b). G. M. Whitesides. *Pure Appl. Chem.* **53**, 287 (1981).

121. A. A. Sutyagina and G. D. Vovchenko. *Surf. Tech.* **13**, 257 (1981).

122. K. Tamao and M. Kumada. *The Chemistry of the Metal-Carbon Bond*, Vol. 4, ed. F. R. Hartley, John Wiley & Sons, New York, 1987.

123. G. N. Schrauzer and E. Deutsch. *J. Am. Chem. Soc.* **91**, 3341 (1969).

124. P. G. Chock and J. Halpern. *J. Am. Chem. Soc.* **91**, 582 (1969).

125. A. E. Stevens, C. S. Feigerle, and W. C. Lineberger. *J. Am. Chem. Soc.* **104**, 5026 (1982).

126. A. J. Rest and J. J. Turner. *J. Chem. Soc. Chem. Commun.* 1026 (1960).

127. A. J. Rest. *J. Organometal. Chem.* **40**, C76 (1972).

128. a). R. B. King. *Adv. in Organomet. Chem.* **2**, 157 (1964). b). T. A. Manual. *ibid.* **3**, 181 (1965).