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# A comparative study on aldol-type condensation reactions of cyclic, acyclic and substituted cyclic ketones by the $W(CO)_6/CCl_4$/UV system

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**Aldol-type condensation reactions of a number of cyclic, acyclic and substituted cyclic ketones were investigated using the $W(CO)_6/CCl_4$/UV system. The progress of the reactions was followed by IR and GC-MS techniques. The cyclic ketone derivatives with $\beta$- and $\gamma$-substituent gave the expected condensation products. However, the $\alpha$-substituted cyclic, acyclic and unsubstituted cyclic ketones with rings larger than six did not. Formation of [W]–ketone complexes with all of the ketones used was observed by FTIR. With respect to our studies, a mechanism involving an intermediate seven-coordinate tungsten complex has been proposed. Copyright © 2005 John Wiley & Sons, Ltd.**

**KEYWORDS:** photochemistry; metal carbonyls; tungsten hexacarbonyl; aldol condensation; ketones; cyclic ketones; seven coordination; metal–carbene complexes

## INTRODUCTION

In our previous study we reported that cyclic ketones can be converted to their aldol-type condensation products, when they are irradiated by UV light with $W(CO)_6$ and $CCl_4$.[1] The condensation products of cyclic ketones with ring sizes of 5, 6, 7 and 8 were investigated using this photochemical system and a metal–carbene intermediate mechanism has been proposed (Scheme 1).

In this work, we have further examined the mechanism in a comparative manner by employing the acyclic ketones (2-heptanone, **I**; 3-heptanone, **II**; 4-heptanone, **III**), cyclic ketones (cycloheptanone, **IV**; cyclooctanone, **V**, cyclododecanone, **VI**) and substituted cyclic ketones (2-acetylcyclopentanone, **VII**; 2-methylcyclohexanone, **VIII**; 3-methylcyclohexanone, **IX**; 4-ethylcyclohexanone, **X**; Scheme 2).

## EXPERIMENTAL

The reactions were carried out in a quartz photochemical reactor (Hereaus Laboratory-UV-Reactor System/2) with a mercury lamp (TQ 150) as the light source. All manipulations were performed under argon using standard Schlenk techniques at room temperature.

A 200 ml solution of $W(CO)_6$ ($5.0 \times 10^{-3}$ mol $l^{-1}$) in *n*-hexane was irradiated for 10 min. Then the ketone ($5.0 \times 10^{-2}$ mol $l^{-1}$) was added under continuous irradiation. $CCl_4$ (0.150 mol $l^{-1}$) was then introduced 30 min after addition of the ketone. FTIR and GC-MS data of the mixtures were periodically recorded by withdrawing samples for analysis.

The ketones were purchased from Merck and used without purification. $W(CO)_6$ was purchased from Aldrich. Carbon tetrachloride (May & Baker) and *n*-hexane (Merck) were distilled and stored under argon atmosphere.

FTIR spectra were recorded on a Jasco 430 spectrometer. GC-MS analyses were performed using the combined system Shimadzu GC-MS QP5050A connected to a computer preloaded with NIST and Wiley Mass Library software.

## RESULTS AND DISCUSSION

The most important photochemical reaction of the carbonyls of the group VIB metals (Cr, Mo and W) is the dissociation of one or more carbonyls to give coordinatively unsaturated species, $M(CO)_n$ ($n < 6$).[2] The chemistry of these unsaturated species can be directly monitored by IR spectroscopy during the reaction course.[3]

When $W(CO)_6$ was irradiated in *n*-hexane, three absorption peaks arose in the carbonyl stretching region of the IR spectrum due to formation of a pentacoordinated tungsten compound. These three peaks, appearing at 2078, 1961 and 1946 $cm^{-1}$, indicate the formation of solvent-stabilized

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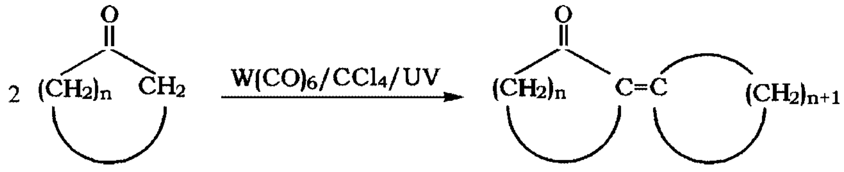
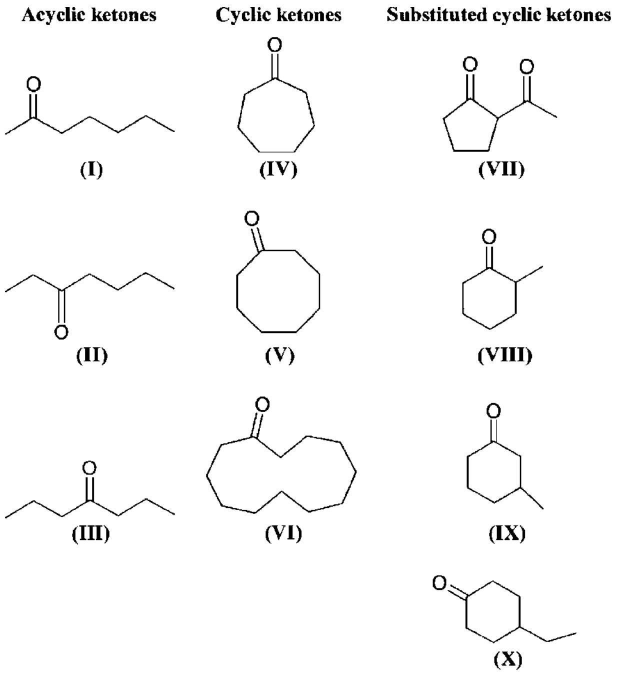


Scheme 1.



Scheme 2.

$W(CO)_5$ ($C_{4v}$) species.[4] Addition of ketone to this solution resulted in the disappearance of these peaks, but another three peaks at ~2075 ($A^1{}_1$), ~1935 (E) and ~1910 cm$^{-1}$ ($A_1{}^2$) arose in the carbonyl region of the IR spectrum. The intensities and the frequencies of these bands are consistent with the formation of $W(CO)_5$–ketone adducts.[5] The carbonyl stretching region of the IR spectra of the reaction mixtures of all studied ketones displayed nearly the same features (Fig. 1) and the measured absorption frequencies are given in Table 1. The IR data reveal the formation of an oxygen-bound $W(CO)_5$–ketone adduct for all of the employed ketones. The CO stretching bands given in Table 1 are close in frequency to the literature values.[5,6]

**Table 1.** IR frequencies (cm$^{-1}$) of $W(CO)_5$–ketone adducts

| Ketones | No. | $A_1{}^1$ | E | $A_1{}^2$ | Keton CO |
|---|---|---|---|---|---|
| 2-Heptanone | **I** | 2075 | 1938 | 1911 | 1720 |
| 3-Heptanone | **II** | 2076 | 1934 | 1911 | 1720 |
| 4-Heptanone | **III** | 2075 | 1936 | 1912 | 1720 |
| Cycloheptanone | **IV** | 2075 | 1935 | 1911 | 1709 |
| Cyclooctanone | **V** | 2074 | 1931 | 1907 | 1710 |
| Cyclododecanone | **VI** | 2075 | 1934 | 1911 | 1711 |
| 2-Acetylcyclopentanone | **VII** | 2074 | 1934 | 1910 | 1719 |
| 2-Methylcyclohexanone | **VIII** | 2075 | 1936. | 1910 | 1725 |
| 3-Methylcyclohexanone | **IX** | 2075 | 1935. | 1911 | 1721 |
| 4-Ethylcyclohexanone | **X** | 2075 | 1936. | 1911 | 1725 |

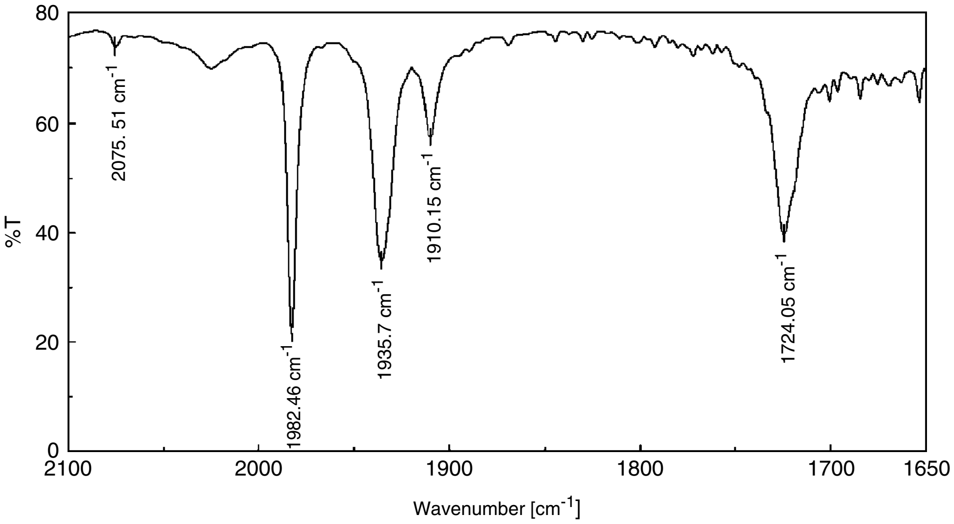


**Figure 1.** A typical FT-IR spectrum for $W(CO)_5$–ketone adducts.

When $CCl_4$ was introduced into the reaction mixture, the three carbonyl peaks due to the tungsten carbonyl–ketone adduct ($C_{4v}$) disappeared slowly, and complete disappearance was noted after one day. A blue solution containing solid particles was eventually obtained, which indicates the formation of oxidized non-soluble W-species.[7]

We analyzed these reaction mixtures using GC-MS to check for the existence of any aldol-type product of the used ketone. According to the GC-MS results, aldol-type condensation products were formed only from **IX** and **X.** Other ketones did not give the expected partially deoxygenated dimers. Mass spectrometric data of the aldol-type products of 3-methylcyclohexanone and 4-ethylcyclohexanone were obtained by electron impact (EI) ionization using a GC-MS system (Table 2.).

Different fragment ions obtained at different masses were defined, such as [$M-CH_3$], [$M-CHO$], [$M-C_3H_7$], [$M-C_3H_7-CO$] and [$M-C_3H_7-CO-C_3H_3$] at 191, 177, 163, 135 and 94 amu for 3-methylcyclohexanone, and [$M-C_2H_5$], [$M-C_2H_5-CO$], [$M-C_2H_5-C_3H_6$], [$M-C_2H_5-C_3H_7-CO$], [$M-C_2H_5-C_3H_5-CO-C_3H_3$] and [$M-C_2H_5-C_3H_6-CO-C_3H_3$] at 205, 177, 163, 135, 95 and 94 amu for 4-ethylcyclohexanone, respectively.

For the compound 3-methylcyclohexanone, the peak at 163 amu could not be seen when the addition was carried out at the 2 position. Therefore, addition occurred at the 6 position due to steric hindrance at the 2 position.

According to our new results, it is clear that the $W(CO)_6/CCl_4/h\nu$ system can convert cyclic ketones with five and six carbon-containing rings and their derivatives with unsubstituted $\alpha$-carbons to the their aldol-type condensation products.

Substantial evidence for the formation of chlorinated substances by irradiation of $W(CO)_6$ with $CCl_4$ in the presence of organic molecules has been reported.[8–11] A radical mechanism for this reaction would be justified if the ketone reactions had given aldol-type products no matter what the ketone was. However, the expected products did not form from the acyclic, larger size cyclic and $\alpha$-substituted cyclic ketones, suggesting that a different mechanism should be considered other than a free radical one.

**Table 2.** Mass spectrometric data of the products of IX and X

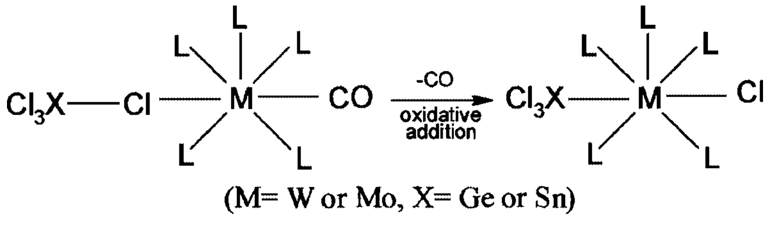
| Aldol products of ketones | Mass and intensities of the molecular and fragment ions |
|---|---|
| **IX** | 206 (22), 191 (17), 177 (28), 163 (45), 135 (30), 112 (24), 94 (100) |
| **X** | 234 (28), 205 (88), 191 (20), 177 (100), 163 (27), 135 (26), 95 (42), 94 (9) |

On the other hand, coordination of $CCl_4$ to the pentacarbonyl tungsten fragment has been well documented by flash photolysis experiments. Formation of this intermediate can be realized by following the absorptions at 2088, 1973 and 1943 cm$^{-1}$ in the IR spectra of $(CO)_5W\ldots CCl_4$.[12] We did not observe these peaks in our experiments, but the formation of $HCCl_3$ and $C_2Cl_6$ resulting from the Cl–C bond breakage of $CCl_4$ has been well established by GC-MS analysis. Since a free radical mechanism has now been eliminated, we may suggest another mechanism than a seven-coordinated intermediate **2**.

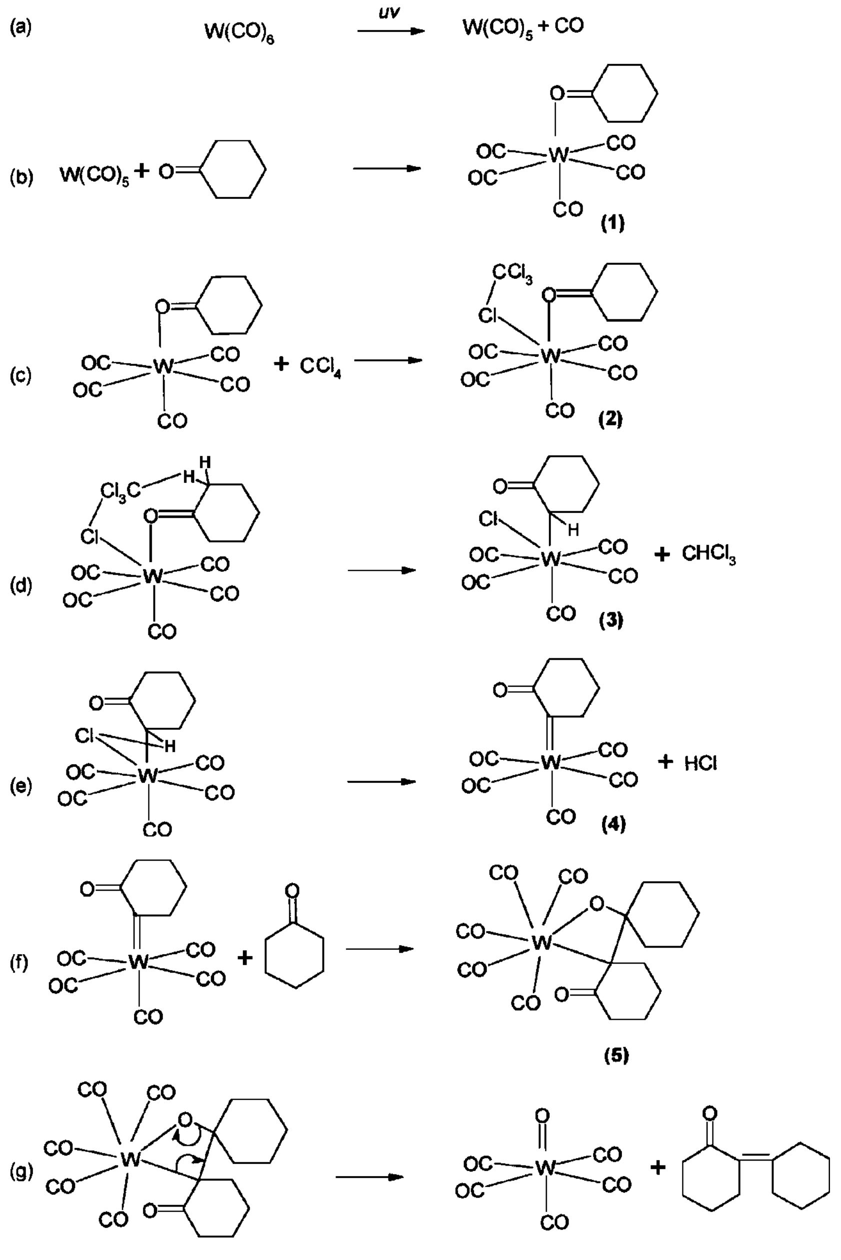
A number of seven-coordinate compounds containing W–Sn, Mo–Sn or Mo–Ge bonds have been prepared by reaction of tungsten or molybdenum carbonyls (or mixed carbonyls) with $SnCl_4$ or $GeCl_4$.[13–19] All of these seven coordinate complexes, derived from the reaction of a GroupVIB carbonyl and a GroupIVA tetrachloride, are well-defined stable compounds and some of them also exhibit catalytic activities in polymerization reactions.[20–22] Without experimental evidence, these reactions were regarded as dissociative substitutions proceeding through CO elimination and oxidative addition of the halide.[17] The interaction of another Group IVA tetra halide, $CCl_4$, with carbonyl complexes remain obscure, since no stable intermediate nor product has been defined, even with advanced techniques like matrix isolation, flash photolysis.[3–7,12]

An alternative associative mechanism for the initiation step of interaction between Group IVA halide and Group VIB carbonyl (or mixed carbonyl) can also be rationalized with our experimental findings, considering the formation of **2.** According to this associative mechanism, a seven-coordinate intermediate formed by addition of the halide to the carbonyl may then eliminate one CO group to give an oxidative addition product as isolated with Ge or Sn halides (Scheme 3).

In the case of $CCl_4$, no oxidative addition products have been reported as yet. However, the seven-coordinate intermediate formed in the coordination of cyclic ketones to $W(CO)_6$ within the $W(CO)_6/CCl_4/h\nu$ system appears to



Scheme 3.



**Scheme 4.**

be a key compound in proposing the mechanism. All the results obtained could be explained by the existence of this intermediate in the proposed mechanism (Scheme 4).

1. Aldol-type reactions of the cyclic ketones proceeded slowly, namely one day, after the addition of $CCl_4$ into the reaction mixture, as might be expected from the relative stability of six coordinated tungsten against the formation of a seven-coordinate complex.
2. Formation of $[W(CO)_5$–ketone] complexes for all of the studied ketones was observed by FTIR spectroscopy. However, substitution at the $\alpha$-position of the cyclic ketones may create steric hindrance in the $[W(CO)_5$–ketone] complex to prevent the coordination of $CCl_4$ to complete seven coordination of tungsten as given in Scheme 3. Therefore the ketones containing substituents in the $\alpha$-position (**VII, VIII**) could not be converted to the aldol-type products by this system.
3. The $\alpha$-hydrogen acidities of the cyclic ketones are not expected to have any significant influence on the aldol-type condensation reactions since the $\alpha$-hydrogen acidities of larger ring and acyclic ketones have been demonstrated to be of similar magnitude to five- or six-membered cyclic ketones.[23,24] Therefore sterical factors should be considered in explaining the failure of larger-size cyclic and acyclic ketones in giving the aldol condensation products. In addition, 3-methylcyclohexanone has two unequivalent

$\alpha$-hydrogens, which may give rise to two different aldol products; however, according to the mass spectra data only the sterically less hindered hydrogen at the 6 position has been involved in the reaction.

When $CCl_4$ is coordinated to the metal, Cl–C bond dissociation may occur easily.[25,26] Reactions through $\alpha$-hydrogen abstraction of cyclic ketones by transition metal compounds have been reported in the literature.[27] Therefore, a possible $\sigma$-bonded tungsten ketone complex, **3**, and $HCCl_3$ could be obtained from **2** (Scheme 4).

The seven-coordinate complex **3** may give a carbene with further $\alpha$-hydrogen abstraction by the coordinated Cl with evolution of HCl.[28,29] HCl gas released was detected by passing the exhausted argon from the reactor over a wetted litmus paper. HCl evolution was detected for each reaction, leading to aldol-type condensation products, but not in the other cases. Therefore, a carbene intermediate, **4**, may be formed following HCl elimination from **3**.

Metal–carbene complexes are powerful oxygen abstractors from ketones.[30,31] Recently, the efficiency of $W(CO)_n$ species on the oxygen abstraction of O from the C=O group was reported.[32] Oxygen abstraction from a ketone by **4** should initially include the coordination of a second ketone, whereas a similar mechanism has been proposed for the metathesis reactions of olefins by a tungsten–carbene complex.[33] Following the coordination of the second ketone, subsequent formation of a metallo-oxo-cyclobutane, **5**, takes place. Oxygen containing metallacycles has been well documented.[34,35] In the last step of oxygen abstraction, the metallo-oxo-cyclobutane converts into an aldol-type product via the formation of a W=O bond.

## CONCLUSION

All attempts to observe the intermediates in our study failed. Nevertheless, a plausible mechanism been proposed to explain the formation of aldol-like products from cyclic ketones by $W(CO)_6/CCl_4/h\nu$ (Scheme 4).

In the final step of the mechanism, two products appear. One of them is the partially deoxygenated dimer of the ketone, the formation of which has been shown by GC-MS analysis. The other is the oxygenated tungsten carbonyl, which readily undergoes further oxidation[7] or polymerization reactions[36] that preclude any experimental evidence. Mechanistic studies are in progress.

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