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Note

Aldol-type condensation reactions of cyclic ketones by the $W(CO)_6/CCl_4/UV$ system

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Abstract

The cyclic ketones can be converted to their aldol-type condensation products by the $W(CO)_6/CCl_4/UV$ system. The reaction was monitored by recording the IR and GC-MS spectra of the reaction mixture. The results support a mechanism that includes an intermediate carbene complex of tungsten. © 2000 Elsevier Science S.A. All rights reserved.

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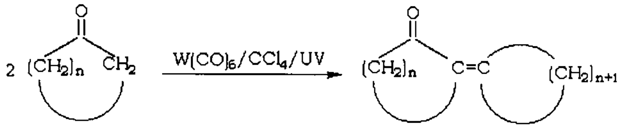
1. Introduction

It has been known that olefin metathesis reactions can be catalyzed by the species that are generated photochemically from hexacarbonyl tungsten and carbon tetrachloride [1,2]:

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

The nature of the active catalyst has not been fully understood in photochemical metathesis reactions though there has been substantial research on this subject [3,4]. The carbene mechanism [5] which is commonly accepted for olefin metathesis reactions, has also been considered for the related reactions catalyzed by the $W(CO)_6/CCl_4/UV$ system. We obtained some evidence for the existence of carbene intermediates in a previous study using benzaldehyde as a carbene-trap for the metathesis of linear olefins [6]. Surprisingly when cyclohexanone was applied as the carbene-trap, the only reaction product observed was the partially deoxygenated dimer of the ketone.

It is therefore of interest to examine the Wittig-type reactions of cyclic ketones in this photochemical system.



This paper describes our results with several cyclic ketones with $n = 3$–6.

2. Experimental

2.1. Reagents

$W(CO)_6$ (Merck) was used without further purification. Cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone, all from Merck); CCl_4 and *n*-hexane were distilled under argon atmosphere.

2.2. Typical reaction procedure

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 standart Schlenk techniques at room temperature.

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

Irradiation was stopped at 30 min after the addition of CCl_4. The reaction mixture obtained was concentrated by vacuum to ca. 2 ml and separated through a silicagel column with *n*-hexane–diethlyether (1:1) eluent. The condensation product thus isolated was further analyzed.

Additional experiments were performed to determine the effect of the W/ketone ratio on the reaction. Samples withdrawn were analysed by GC using the external standard method.

2.3. Physical measurements

FTIR spectra were recorded on a JASCO 430 spectrometer. GC-MS analyses were performed using combined system HP 5890 GC (30 m, $\varnothing = 0.2$ mm, capillary column coated with Hp-1% dimethylpolysiloxan gum, heating from 50 to 250°C with 10°C min^{-1}, carrier gas He, 10 ml min^{-1}) and HP 5971 mass spectrometer connected to a HP 486/33 N computer preloaded with HPG 1034 MS Chem. Station Software.

Table 1
Physical data for **I** and **II**

	I	II
IR frequencies (cm^{-1}) (KBr pellet)	3430–3300wb; 2932s; 2858s; 1728vs; 1600w	3410–3300wb; 2936s; 2854s; 1729vs; 1600w
Maxima of mass signals (*m*/*z*)	178, 149, 135, 121, 107, 79, 67	150, 149, 122, 107, 79, 67
Elemental analysis	Found: C, 78.0; H, 9.67%. Calc.: C, 80.9; H, 10.1%	Found: C, 77.9; H, 9.41%. Calc.: C, 80.0; H, 9.33%
M.p. (°C)	54–55	49–51

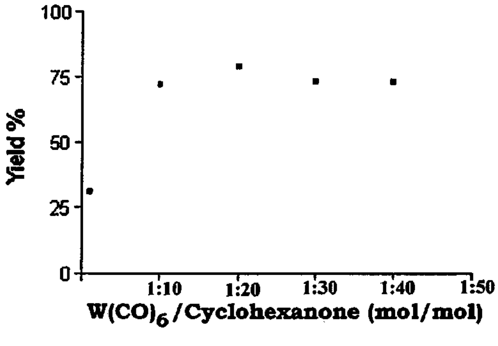


Fig. 1. Variation of the yield of **II** with the $W(CO)_6$/cyclohexanone ratio:

$$\text{Yield} = \frac{\text{No. of moles of } \mathbf{II}}{\text{No. of initial moles of } W(CO)_6} \times 100.$$

3. Results and discussion

GC-MS studies revealed that the expected condensation reactions with the cyclic ketones used have occurred. The condensation products of cyclopentanone and cyclohexanone (2-cyclopentylidencyclopentanone (**I**) and 2-cyclohexylidencyclohexanone (**II**)) have been isolated while those of the high boiling cycloheptanone and cyclooctanone (2-cycloheptylidencycloheptanone (**III**) and 2-cyclooctylidencyclooctanone (**IV**)) could not have been separated through the column.

The characteristic properties of **I** and **II** were eventually investigated (Table 1) and found to be identical with authentic samples [7].

We have focused our studies on cyclohexanone condensation to obtain some information about the mechanistic pathways of this photochemical process. In order to determine the role of the amount of $W(CO)_6$ on the conversion of cyclohexanone to **II**, the concentration of $W(CO)_6$ was kept constant and that of cyclohexanone was varied. Formation of **II** has been found to increase with the $W(CO)_6$/cyclohexanone ratio from 1/1 to 1/10 (Fig. 1) but never exceeding the initial concentration of $W(CO)_6$. This trend clearly indicates that the reaction does not follow a catalytic pathway.

When CCl_4 was replaced by $CHCl_3$ or CH_2Cl_2 no condensation product was observed which emphasizes the role of CCl_4 as a reagent rather than a solvent.

Fig. 2 shows the changes in the IR spectra of the $W(CO)_6$ solution in *n*-hexane upon irradiation and the addition of the cyclohexanone. The peak at ca. 1981 cm^{-1} in curve (a) represents the characteristic carbonyl stretching in $W(CO)_6$ (O_h). Irradiation leads to the photodissociation of $W(CO)_6$ and the peaks appearing at 2078, 1961, and 1946 cm^{-1} suggest that the formation of the coordinatively unsaturated $W(CO)_5$ (C_{4v}) intermediate (curve (b)). The light yellow color observed at this stage supports the existence of $W(CO)_5$ [8]. Introduction of cyclohexanone to this solution upon continuous irradiation resulted in the appearance of three new bands at 2075 (w), 1933 (s), and 1909 (m) cm^{-1} and in the disappearance of the former bands (curve (c)). The presence of new peaks is consistent with the $M(CO)_5L$ structure [9] which can be assigned as the $W(CO)_5$–cyclohexanone adduct characterized by 2075 (A_1^1), 1933 (E), and 1909 (A_1^2) frequencies. The intensities and positions of these bands are parallel to those reported for the $W(CO)_5$–acetone adduct [10]. Upon photolysis for 30 min, the peaks related to the adduct intensified while the peak at 1981 cm^{-1} corresponding

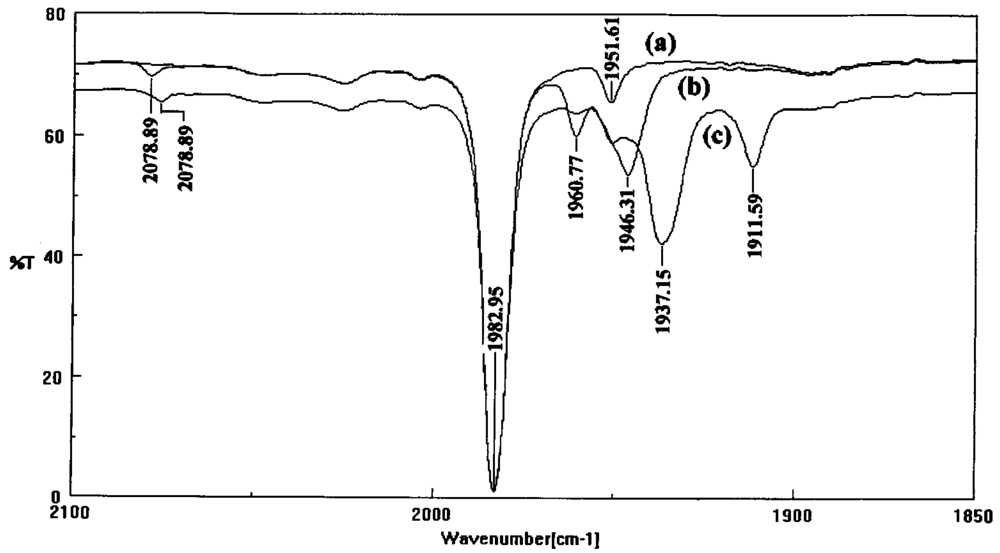


Fig. 2. The changes in the IR spectra of the $W(CO)_6$ solution in *n*-hexane upon irradiation. (a) $W(CO)_6$ solution, (b) after photolysis of the solution, (c) after the addition of the cyclohexanone.

to unreacted $W(CO)_6$ weakened. GC-MS analysis of the reaction mixture at this step showed that no condensation reaction takes place. The IR data of the other cyclic ketones studied are more or less the same as recorded for the $W(CO)_5$–cyclohexanone adduct [11]. No change was observed in the peak at 1951 cm^{-1} through photolysis and also upon addition of different cyclic ketones which led us to consider it related to an unidentified impurity.

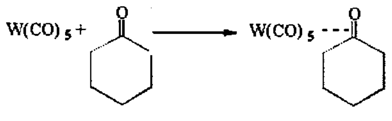
Addition of CCl_4 caused a reduction in the intensities and all three bands disappeared after 30 min of irradiation without the appearance of any extra band due to the formation of a new intermediate. Meanwhile, a blue precipitate was observed and the IR spectrum of this precipitate showed no absorption related to a carbonyl complex, as reported previously for photocatalytic metathesis reactions [4].

GC-MS analysis of the solution containing CCl_4 indicated the formation of **II**, $CHCl_3$, and C_2Cl_6.Chloroform and hexachloroethane are known to be derived from CCl_4 in olefin metathesis reactions catalyzed by the $W(CO)_6/CCl_4/UV$ system [6,12]; however, the observation of **II** from refers to a novel field of chemistry for the application of metal carbonyls.

4. Conclusion

Irradiation of $W(CO)_6$ produces initially the coordinatively unsaturated complex $W(CO)_5$ (1) which coordinates the ketone in the second step (2).

$$W(CO)_6 \xrightarrow{UV} W(CO)_5 + CO \qquad (1)$$

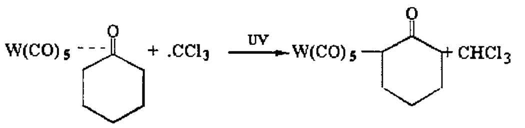


(2)

Addition of CCl_4 to the system yields $CHCl_3$ and C_2Cl_6 by radicalic reactions (4, 5) and **II** (5).

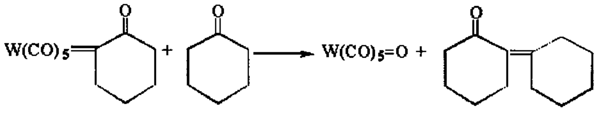
$$W(CO)_6 + CCl_4 \xrightarrow{UV} W(CO)_5Cl + CO + CCl_3 \qquad (3)$$

$$2CCl_3 \xrightarrow{UV} C_2Cl_6 \qquad (4)$$



(5)

Reaction 6, representing the formation of **II**, is quite similar to the well-known Wittig-type reactions of organic carbonyl compounds with Schrock-type alkylidene complexes [13].



(6)

Though we have not detected carbenic complexes of tungsten pentacarbonyl spectroscopically, it is plausible to propose that the active species that yield **II** are in carbene nature. The W-alkyl complex described in reaction 5, may give the proposed carbene by α-H abstraction in a way similar to the formation of the initiative carbenes in olefin metathesis reactions [14].

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