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Metal Carbonyl-Induced N-O Bond Cleavage of the Oxime Group

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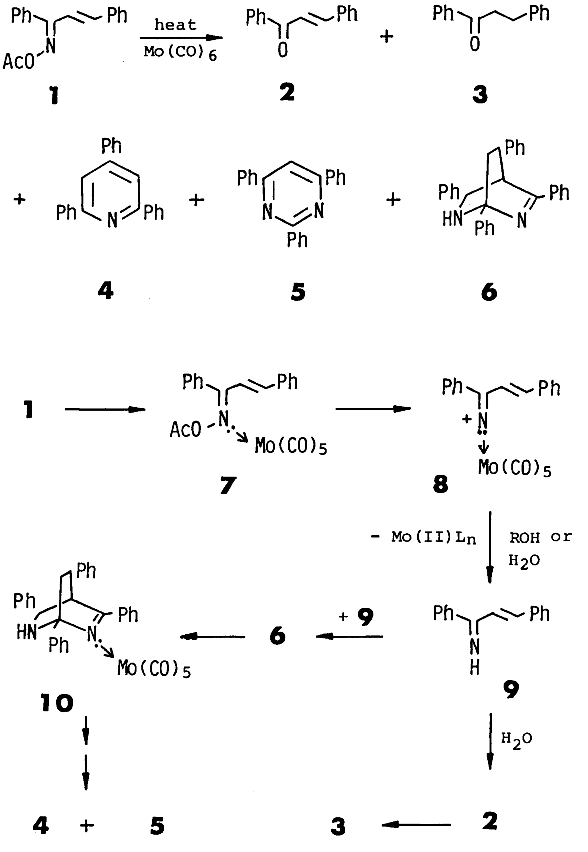
Synopsis. The reaction of [Mo(CO)$_6$] or [Fe$_2$(CO)$_9$] with oxime *O*-acetate of 1,3-diphenyl-2-propen-1-one undergoes a reductive N–O bond cleavage to give an imine which dimerises and/or is hydrolyzed to ketones. The dimer, so formed, undergoes fragmentations to give pyridine and pyrimidine derivatives. Similarly, the reaction of [Mo(CO)$_6$] with several oxime *O*-acetates, oximes, and an oxime ether were shown to give the corresponding ketones. A reaction of oxime *O*-acetates with [Cr(CO)$_6$] or with [W(CO)$_6$] to give the corresponding ketones was also shown to proceed very slowly.

In relation to the synthetic and mechanistic interests of a [Mo(CO)$_6$]-, [Fe$_2$(CO)$_9$]-, or [Fe(CO)$_5$]-induced reductive N–O bond cleavage of isoxazoles[1] and 2-isoxazolines,[2,3] we previously showed that oxime *O*-acetates, oximes, and oxime ethers can be converted to the corresponding ketones in the presence of [Fe$_2$(CO)$_9$] or [Fe(CO)$_5$] under thermal conditions or under photoirradiations.[4] The postulated mechanism involves the imine intermediate. In connection with this study, we report here that a [Mo(CO)$_6$]-induced reaction of oxime *O*-acetate of 1,3-diphenyl-2-propen-1-one gives the imine intermediate. The deoximation of several oxime derivatives using group VI metal carbonyls [M(CO)$_6$: M=Mo, Cr, and W] are described.

The thermal reaction of oxime *O*-acetates **1** with [Mo(CO)$_6$] in ethanol or in mosit acetonitrile under reflux afforded 1,3-diphenyl-3-propen-1-one (**2**), 1,3-diphenyl-1-propanone (**3**), 2,4,6-triphenylpyridine (**4**),[5] 2,4,6-triphenylpyrimidine (**5**),[6] (Table 1, Entries 1 and 2). The detailed reaction conditions and the yields of the products, all of which are known compounds, are summarized in Table 1.

The present reaction can be explained by the mechanism shown in Scheme 1. From an analogy of the [Mo(CO)$_6$]-induced N–O bond cleavage of isoxazoles[1] and 2-isoxazolines,[3] and the [Fe$_2$(CO)$_9$]-induced deoximation reaction of oxime derivatives,[4] the initial step of the reaction was shown to be a complexation of **1** to give **7**.[4] The subsequent N–O bond cleavage gives complex **8**, the nitrogen moiety of which would be reduced by the central molybdenum followed by protonation to give the imine **9** in a protic media.[4] The hydrolysis of **9** would result in the formation of **2** even by stray water. Under the present conditions, **2** was reduced to give **3** (see Experimental).

The imine **9** has been known to dimerise to give a bicyclic dimer **6**, the thermal reaction of which at 190 °C gives **4** and **5** in the presence of sulfur.[7] The thermal reaction of **6** in ethanol under reflux for 24 h afforded **4** (5%) and a trace of **5**; the starting material **6** was recovered in 95% yield. However, the

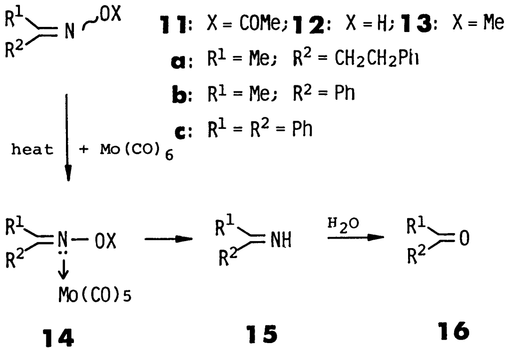


Scheme 1.

Table 1. Experimental Results Obtained in the Reaction of **1**

Entry	Solvent	Reaction Conditions[a]	Reaction Time/h	Product (yield/%) **2**	**3**	**4**	**5**	**6**
1	EtOH	A	24	0	7	31	6	15
2	MeCN-H$_2$O	A	7	5	6	39	1	9
3	EtOH	B	1.5	6	0	2	0	29

a) A: A molar equivalent amount of [Mo(CO)$_6$] was used, being heated under reflux. B: 1.2 Molar equivalent amount of [Fe$_2$(CO)$_9$] was used, being heated under reflux.



Scheme 2.

fragmentation reaction of **6** was accelerated in the presence of $[\mathrm{Mo(CO)_6}]$, resulting in the formation of **4** (42%), **5** (1%), and **6** (48%) under reflux in ethanol for 24 h. A possible explanation of this fact is a complexation of the $[\mathrm{Mo(CO)_5}]$ species to the nitrogen atom of **6** to give **10**. Previously, it was suggested that $[\mathrm{Mo(CO)_5}]$ and $[\mathrm{Fe(CO)_4}]$ species can coordinate to the oxygen atom of an epoxide ring to facilitate a C–O bond cleavage.[8] The metal carbonyl species also seems to exhibit the nature of a Lewis acid. In a similar fashion, $[\mathrm{Mo(CO)_5}]$ in a possible intermediate **10** might facilitate the elimination of styrene or benzaldimine from **6**, followed by dehydrogenation to give **4** and **5**.

In relation to a previous study,[4] a reaction of **1** with $[\mathrm{Fe_2(CO)_9}]$ in ethanol was carried out. The reaction proceeded very fast compared to an $[\mathrm{Mo(CO)_6}]$-induced reaction, and **2**, **4**, and **6** were obtained in rather low yields (Table 1, Entry 3). Thus, the reaction is very similar to an $[\mathrm{Mo(CO)_6}]$-induced reaction (Scheme 1). The reduction of **2** to give **3** was not observed in this case.

Thermal reactions of oxime O-acetates **11a—c**, oximes **12a—c**, and an oxime ether **13c** in the presence of $[\mathrm{Mo(CO)_6}]$ afforded the corresponding ketones **16a—c**. Reaction pathways similar to that in Scheme 1 are depicted in Scheme 2. The reaction conditions and yields of the products are summarized in Table 2. The reactions of oxime *O*-acetates **11a—c** proceeded fast and the starting materials were completely consumed to give **16a—c** in good yields (Table 2, Entries 1—3). However, the reaction of the oximes and the oxime ether generally proceeded slowly and the starting materials were recovered (Entries 5—7). Thus, oxime *O*-acetates are labile compared to oximes and the oxime ether.[4] On the other hand, the reaction of **11a** with $[\mathrm{W(CO)_6}]$ or with $[\mathrm{Cr(CO)_6}]$ did not occur and **11a** was recovered (Table 2, Entry 8 or 10). Similarly, the reaction of **11c** proceeded very slowly and the corresponding ketone **16c** was obtained in low yield in addition to **11c** (Table 2, Entries 9 and 11). In the deoximation reactions of oxime derivatives, $[\mathrm{Mo(CO)_6}]$ was shown to be effective compared to $[\mathrm{W(CO)_6}]$ and $[\mathrm{Cr(CO)_6}]$ under the present conditions.

Ketimine and aldimine complexes of pentacarbonylchromium have been synthesized.[9] Furthermore, recent work by Shvo et al. clarified that ketimine and aldimine complexes of pentacarbonyltungsten can be obtained in yields ranging from 10 to 20% from a reaction of $[\mathrm{W(CO)_5THF}]$ with ketoximes and aldoximes.[10] Under the present reaction conditions, no ketimine complex of the group VI metal carbonyls was obtained.

Table 2. Deoximation of **11a—c**, **12a—c**, and **13c**[a]

Entry	Compound	Reaction Time/h	Product yield/%	Recovery/%
1	**11a**	24	**16a** (77)	0
2	**11b**	20	**16b** (60)	0
3	**11c**	10	**16c** (85)	0
4	**12a**	22	**16a** (77)	0
5	**12b**	48	**16b** (55)	13
6	**12c**	144	**16c** (81)	16
7	**13c**	27	**16c** (56)	32
8[b]	**11a**	24	**16a** (0)	90
9[b]	**11c**	14	**16c** (5)	94
10[c]	**11a**	24	**16a** (0)	98
11[c]	**11c**	14	**16c** (2)	96

a) The reactions were carried out in moist acetonitrile under reflux by using an equivalent amount of $[\mathrm{Mo(CO)_6}]$. b) The reactions were carried out by using an equivalent amount of $[\mathrm{W(CO)_6}]$. C) The reactions were carried out by using an equivalent amount of $[\mathrm{Cr(CO)_6}]$.

Experimental

General Procedure for the Reaction of 1,3-Diphenyl-2-propen-1-one Oxime O-Acetate 1 with $[\mathrm{Mo(CO)_6}]$ or with $[\mathrm{Fe_2(CO)_9}]$. A solution of **1** (265 mg, 1 mmol) with $[\mathrm{Mo(CO)_6}]$ (264 mg, 1 mmol) or with $[\mathrm{Fe_2(CO)_9}]$ (437 mg, 1.2 mmol) in ethanol (3 cm^3) or in acetonitrile (3 cm^3) containing water (ca. 1 mmol) was heated under reflux until **1** was completely consumed. After removing the solvent, the residue was dissolved in benzene (10 cm^3) and filtered through Celite to remove any insoluble material. The filtrate was concentrated and the resulting residue was separated by TLC on silica gel using benzene–hexane (1/1) as a developer to give the products. The results are summarized in Table 1.

Reduction of 1,3-Diphenyl-2-propen-1-one 2 with $[\mathrm{Mo(CO)_6}]$. A solution of **2** (104 mg, 0.5 mmol and $[\mathrm{Mo(CO)_6}]$ (264 mg, 1 mmol) in ethanol (2 cm^3) was heated under reflux for 24 h under a nitrogen atmosphere. After hexane was added to the reaction mixture, it was filtered through Celite to remove any insoluble material. The filtrate was concentrated and the resulting residue was separated by TLC on silica gel using benzene-hexane (1/1) as a developer to give **3** (58 mg, 55%) and **2** (15 mg, 14%).

Thermal Reaction of 6. A solution of **6** (42 mg, 0.1 mmol) in ethanol (1 cm^3) was heated under reflux for 24 h. After the solvent was evaporated, the residue was separated by TLC on silica gel using benzene–dichloromethane (1/1) as a developer to give **2** (2 mg, 5%), a trace of **3**, and **6** (40 mg, 95%).

Thermal Reaction of 6 in the Presence of $[\mathrm{Mo(CO)_6}]$. A solution of **6** (42 mg, 0.1 mmol) and $[\mathrm{Mo(CO)_6}]$ (27 mg, 0.1 mmol) in ethanol (1 cm^3) was heated under reflux for

24 h. After the solvent was evaporated, the resulting residue was separated by TLC on silica gel using benzene-dichloromethane as a developer to give **2** (13 mg, 42%), **3** (1 mg, 2%), and **6** (20 mg, 48%).

General Procedure for the Deoximation Reaction of Oxime *O*-Acetates 11a—c, Oximes 12a—c, and Oxime Ehter 13c with [Mo(CO)$_6$]. A solution of oxime derivatives **11a—c**, **12a—c**, or **13c** (1 mmol) with [Mo(CO)$_6$] (264 mg, 1 mmol) in acetonitrile (2 cm^3) containing water (ca. 1 mmol) was heated under reflux for various periods of time. After the solvent was evaporated, the residue was dissolved in benzene (10 cm^3) and filtered through Celite to remove any insoluble material. The filtrate was concentrated and the resulting residue was separated by TLC on silica gel using benzene–dichloromethane (1/1) as a developer to give the products. The reaction conditions and the yields of the products are summarized in Table 2 (Entries 1—7).

General Procedure for the Deoximation Reaction of Oxime *O*-Acetate 11a,c with [W(CO)$_6$] or with [Cr(CO)$_6$]. A solution of oxime *O*-acetate **11a,c** (1 mmol) with [W(CO)$_6$] (352 mg, 1 mmol) or with [Cr(CO)$_6$] (220 mg, 1 mmol) in acetonitrile (2 cm^3) containing water (ca. 1 mmol) was heated under reflux for various periods of time. After the solvent was evaporated, the residue was dissolved in benzene (10 cm^3) and filtered through Celite to remove a insoluble material. The filtrate was concentrated and the resulting residue was separated by TLC on silica gel using benzene-dichloromethane as any developer to give the products. The reaction conditions and the yields of the products are summarized in Table 2 (Entries 8—11).

References

1) M. Nitta and T. Kobayashi, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1401.

2) M. Nitta and T. Kobayashi, *J. Chem. Soc., Perkin Trans. 1*, **1984**, 2103.

3) M. Nitta, A. Yi, and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **58**, 991 (1985).

4) M. Nitta, I. Sasaki, H. Miyano, and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **57**, 3358 (1984).

5) O. Tsuge, M. Tashiro, and K. Yamada, *Kogyo Kagaku Zasshi*, **71**, 1667 (1968).

6) A. L. Weis and V. Rosenbach, *Tetrahedron Lett.*, **22**, 1453 (1981).

7) A. R. Forrester, M. Gill, and R. H. Thomson, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 616.

8) H. Alper, D. D. Roches, J. Durst, and R. Legault, *J. Org. Chem.*, **41**, 3611 (1976); T. Kobayashi and M. Nitta, *Chem. Lett.*, **1982**, 325; M. Nitta and T. Kobayashi, *Chem. Lett.*, **1985**, 877.

9) E. O. Fisher and I. Knaus, *Chem. Ber.*, **103**, 1262 (1970).

10) D. Czarkie and Y. Shvo, *J. Organomet. Chem.*, **280**, 123 (1985).