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Deoximation of Oxime *O*-Acetates, Oximes, and Oxime Ethers by Nonacarbonyldiiron or Pentacarbonyliron. An Electronic Effect for the N-O Bond Cleavage[1]

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Synopsis. The reaction of $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$ with oxime *O*-acetates, oximes, and oxime ethers under photoirradiation or thermal conditions undergoes deoximation to give the corresponding ketones. The oxime *O*-acetate was found to be the most reactive class of these compounds. A proposed mechanism involves an initial complexation of the $[Fe(CO)_4]$ species to the nitrogen atom of the oxime group, and the subsequent N–O bond cleavage to give an imido complex. Then the imido complex could collapse to the corresponding ketone via an imine intermediate in protic media.

Previous works in this series have included the papers involving a system which formally contains a C=N–O group.[2,3] The reaction of substituted 2-isoxazolines with $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$ in methanol under thermal conditions or photoirradiation has been shown to undergo the N–O and C_4–C_5 bond cleavages to give two fragments of aldehydes and the complexed nitrenes, which could collapse to ketones in protic media.[2,4] Under similar reaction conditions, substituted isoxazoles could undergo a reductive cleavage of the N–O bond to give β-amino enones in good yields.[3] Although the transformation of oximes to the corresponding ketones has been accomplished thermally by $[Fe(CO)_5]$–$BF_3 \cdot OEt_2$[5] or $[Fe(CO)_5]$[6] in anhydrous solvent, the role of $BF_3 \cdot OEt_2$ or the electronic factor controlling the N–O bond cleavage is ambiguous.

In this paper we report on the deoximation of oxime *O*-acetates **1a—d**, oximes **2a—d**, and oxime ethers **3a,c** by $[Fe_2(CO)_9]$ or $[Fe(CO)_5]$ in methanol under thermal conditions or photoirradiation, and suggest that the greater pertinence of the N–O bond cleavage for the oxime *O*-acetates may lead to the corresponding ketones **4a—d**. The reaction conditions and the yields of the products are summarized in Table 1.

Thermal reaction of oxime O-acetates **1a—d** with $[Fe_2(CO)_9]$ in methanol at 60 °C for 1 h afforded the corresponding ketones **4a—d** in good yields (Table 1, entries 1—4). Similarly, photoirradiation of **1a—d** with $[Fe(CO)_5]$ in methanol at the ambient temperature afforded the ketones and the remainder being unreacted starting materials (entries 5—8). On the other hand, thermal reaction of oximes **2a—d** (entries 9—12) or oxime ether **3a** (entry 17) with $[Fe_2(CO)_9]$ proceeded slowly and afforded the corresponding ketones, along with the unreacted starting materials. Furthermore, photoreaction of **2a—d** (entries 13—16) or **3c** (entry 18) with $[Fe(CO)_5]$ also proceeded very slowly as compared to the cases of **1a—d** (5—8). The oximes of conjugated ketones (entries 13 and 14) seem to be less reactive than those of nonconjugated ketones (entries 15 and 16). Regarding the reaction time and the yields of the

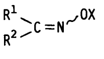
TABLE 1. DEOXIMATION OF OXIME *O*-ACETATES **1**, OXIMES **2**, AND OXIME ETHERS **3**

Entry	Compound	Reaction conditions[a]	Reaction time/h	Product[b]	
				Ketone **4**	Recovery
1	**1a**	A	1	94	0
2	**1b**	A	1	87	0
3	**1c**	A	1	91	0
4	**1d**	A	1	82	0
5	**1a**	B	22	82	10
6	**1b**	B	22	53	23
7	**1c**	B	16	76	11
8	**1d**	B	18	53	27
9	**2a**	A	1	32	64
10	**2b**	A	4	30	51
11	**2c**	A	1	67	19
12	**2d**	A	1	60	24
13	**2a**	B	60	65	26
14	**2b**	B	48	28	61
15	**2c**	B	22	89	0
16	**2d**	B	48	81	0
17	**3a**	A	4	15	80
18	**3c**	B	24	65	6

a) A: A molar equivalent quantity of $[Fe_2(CO)_9]$ was used, being heated at 60 °C. B: 2 Molar equivalent quantity of $[Fe(CO)_5]$ was used, being photoirradiated. b) Isolated yield based on the starting material used. c) Isolated yield of the unreacted starting material.

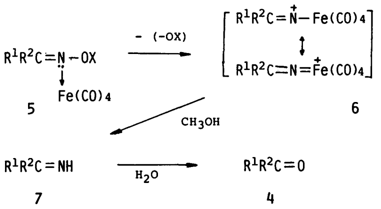
ketones, the oxime *O*-acetates are very labile as compared to the oximes or oxime ethers under both the thermal and photoirradiation conditions. Therefore, the deoximation of oxime *O*-acetates by [$Fe_2(CO)_9$] under thermal conditions appears most promising.

The present reactions are best explained by the mechanism shown in Scheme 1. Free or solvated [$Fe(CO)_4$] species have been generally assumed to be the reactive common intermediate in the photolysis[7] or thermolysis (≥80 °C) of [$Fe(CO)_5$] and thermolysis (≥20 °C) of [$Fe_2(CO)_9$].[8] Therefore, thermally or photochemically generated [$Fe(CO)_4$] species could be a reasonable intermediate in the present deoximation reactions.[2,3] The initial step could be a complexation to give **5**. The subsequent N–O bond cleavage could give imido complex **6**.[2] In methanol, the nitrogen moiety of **6** could be reduced by iron moiety,[2,4] and the subsequent protonation could give an imine such as **7**,[6] which could collapse to the ketones by stray water or under workup conditions.



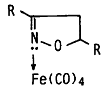
1 - 3

1: $X = COCH_3$; 2: $X = H$; 3: $X = CH_3$
a: $R^1 = R^2 = Ph$
b: $R^1 = CH_3$, $R^2 = Ph$
c: $R^1 = CH_3$, $R^2 = CH_2CH_2Ph$
d: $R^1 = R^2 = CH_2Ph$



Scheme 1.

2-Isoxazoline is a cyclic ether of oximes, and it undergoes facil N–O and C-4–C-5 bond cleavages to give an aldehyde and a complexed nitrene intermediate which collapses to the corresponding ketone.[2] However, the reactions of oximes **2a-d** as well as oxime ethers **3a,c** are not completed after prolonged heating or photoirradiation (Table 1). Regarding the rigid *N*-complexed C=N–O group (formal hetero-analogue of an allylic anion) of **8** (R=Phenyl or Alkyl), the delocalization of π-d electron from the iron to the π^* orbital of the C=N–O group was suggested to weaken the N–O bond.[2]



8 R = Ph or Alkyl

This electronic effect allowing a facile N–O bond cleavage seems to be reduced by a free rotation across the N–O bond in the cases of oximes and oxime ethers as well as oxime *O*-acetates. The higher reactivity of oxime *O*-acetate as compared to oximes or oxime ethers could be ascribed to the large leaving ability of the OAc group as compared to the OH or OR group.

The reductive[9] or oxidative[10] transformation of oximes to the corresponding ketones has been accomplished. The reductive deoximation of oxime *O*-acetates has also been accomplished by chromium(II) acetate.[11] The present reaction of oxime *O*-acetates could also serve as a convenient method for the deoximation reaction.

Experimental

[$Fe(CO)_5$] (Strem Chemical Inc.) is a commercial sample. [$Fe_2(CO)_9$] was prepared by the standard method.[12] All of the reactions were carried out under a dry nitrogen atmosphere. The photoirradiation was carried out using Rayonet Photoreactor fitted with RPR-350 lamps through a Pyrex filter. The oximes and oxime O-acetates were prepared by the standard method. The oxime ethers were prepared by a phase transfer method.[13]

General Procedure for the Deoximation of Oxime O-Acetates ***1a—d****, Oximes* ***2a—d****, and Oxime Ether* ***3a*** *with [$Fe_2(CO)_9$] under Thermal Conditions.* A solution of **1a—d**, **2a—d**, or **3a** (1 mmol) and [$Fe_2(CO)_9$] (437 mg, 1 mmol) in 10 cm³ of anhydrous methanol was heated at 60 °C for an adequate period. After removal of the methanol, the residue was dissolved in 30 cm³ of a benzene-hexane mixture (2/1) and filtered through Celite to remove insodluble materials. Then the filtrate was concentrated and the resulting residue was separated by TLC on silica gel using benzene as the eluent to give the corresponding ketones and unreacted starting materials. The results are summarized in Table 1.

General Procedure for the Deoximation of Oxime O-Acetates ***1a—d****, Oximes* ***2a—d****, and Oxime Ether* ***3c*** *with [$Fe(CO)_5$] under Photoirradiation.* A solution of **1a—d**, **2a—d**, or **3c** (1 mmol) and [$Fe(CO)_5$] (392 mg, 2 mmol) in 10 cm³ of anhydrous methanol was irradiated for an adequate period. After the methanol was evaporated, the residue was dissolved in 30 cm³ of a benzene-hexane mixture (2/1). Then the solution was filtered through Celite to remove insoluble materials. After evaporating the filtrate the resulting residue was separated by TLC on silica gel using benzene as the eluent to give the corresponding ketones and unreacted starting materials. The results are summarized in Table 1.

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