

Metal-carbonyl-induced Reaction of 2-Isoxazolines. Ring Cleavage and Reduction by Pentacarbonyliron or Nonacarbonyliron¹

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3,5-Disubstituted 2-isoxazolines (**1a**–**f**) undergo N–O and C–4–C–5 bond-cleavage reaction with pentacarbonyliron and photoirradiation in methanol to give two fragments (aldehydes and ketones). The ketones could be derived from reduction of the complexed 1-substituted vinylnitrene intermediate and subsequent hydrolysis. Substituent effects have a significant influence on the course of the reaction. 2-Isoxazolines (**1h** and **i**) having no substituent at C-5 undergo N–O bond cleavage to give β -hydroxy- and β -methoxy-ketones, in addition to the above mentioned cleavage of the N–O and C–4–C–5 bonds. Furthermore, 2-isoxazolines (**1j** and **k**) bearing a substituent such as an acetoxy or ethoxy group at C-5 undergo N–O bond cleavage, and concomitant elimination of the substituent acetoxy or ethoxy group, leading to β -aminoenones. However, in the case of 2-isoxazolines (**1l** and **m**) bearing a piperidin-1-yl group at C-5, the N–O and C–4–C–5 bond-cleavage reactions predominate over the elimination of the C-5-substituent. Mechanisms are also proposed for the formation of the β -substituted ketones. Similar reactions were also effected thermally for several 2-isoxazolines with nonacarbonyliron.

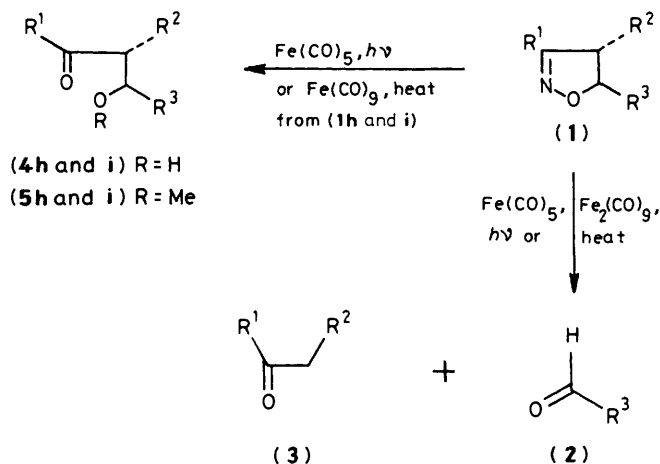
2-Isoxazoline (4,5-dihydroisoxazole) ring systems have been of great interest in recent years. 5-Substituted 2-isoxazolines are readily accessible under mild conditions by 1,3-dipolar cycloaddition of nitrile oxides to monosubstituted or 1,1-disubstituted olefins with complete regioselectivity,² and they have been used for the synthesis of β -aminoalcohols,³ α,β - or β,γ -unsaturated oximes,⁴ and β -hydroxyketones.⁵ The versatility of silyl nitronates and the derived 2-isoxazolines as precursors for a number of classes of compounds was also demonstrated recently.⁶

Previously we have reported that $[\text{Fe}(\text{CO})_5]$, $[\text{Fe}_2(\text{CO})_9]$, or $[\text{Mo}(\text{CO})_6]$ cause an efficient reductive cleavage of the N–O bond of isoxazoles to give β -aminoenones under mild conditions in the presence of water.^{7,8} The easy, metal-carbonyl-prompted N–O bond cleavage of isoxazoles has a strong resemblance to the photochemically⁹ or thermally¹⁰ induced N–O bond cleavage of isoxazoles leading to ketoazirines. The photoreactions of 2-isoxazolines were also studied by Schmid,¹¹ Matsuura,¹² and Mukai,¹³ who showed that N–O bond fission occurs upon irradiation. A special kind of 2-isoxazoline ring system is also known to undergo a thermally induced N–O bond cleavage to give an azirine ring.¹⁴ These findings prompted us to investigate the metal-carbonyl-induced reactions of 2-isoxazolines and to find out whether the ring could be cleaved in a synthetically useful manner. This paper describes the reactions of 2-isoxazolines with $[\text{Fe}(\text{CO})_5]$ under photoirradiation, or with $[\text{Fe}_2(\text{CO})_9]$ under thermal conditions.

Results and Discussion

The photoirradiation of 2-isoxazolines (**1a**–**g**) with 2 equivalents of $[\text{Fe}(\text{CO})_5]$ in anhydrous methanol, for an adequate period, and separation by t.l.c. affords aldehydes (**2**) and ketones (**3**) as shown in Scheme 1. The yields for (**2**) and (**3**), and the reaction times, are listed in Table 1. An equivalent amount of $[\text{Fe}(\text{CO})_5]$ was not enough to complete the present reaction. The reaction seems to be very selective and other products were not detected. Independent irradiation of acetophenone or benzaldehyde with $[\text{Fe}(\text{CO})_5]$ gives less than 85% recovery after irradiation for 24 h. Thus the rather low yields of aldehydes or ketones might be ascribed to their instability under the present conditions.

The photoreactions of 2-isoxazolines such as (**1a**),¹¹ (**1b**)¹²



Scheme 1. **a**, $\text{R}^1 = \text{R}^3 = \text{Ph}$, $\text{R}^2 = \text{H}$; **b**, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Ph}$; **c**, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{hexyl}$; **d**, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$; **e**, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{hexyl}$; **f**, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{vinyl}$; **g**, $\text{R}^1 = \text{mesityl}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Ph}$; **h**, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{R}^3 = \text{H}$; **i**, $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{H}$.

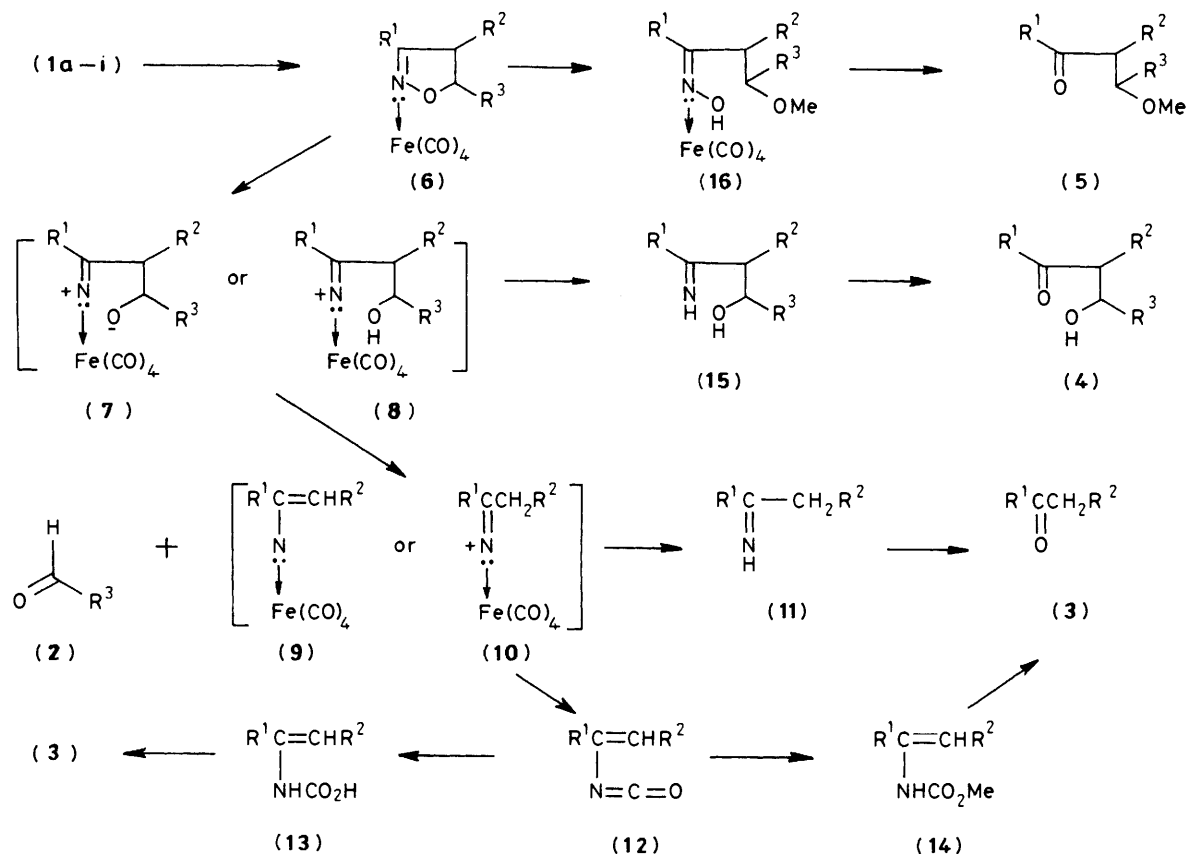
and other derivatives¹³ have been shown to undergo N–O bond cleavage. Since the irradiation of (**1a**) without $[\text{Fe}(\text{CO})_5]$ under the present conditions gave no product and (**1a**) was recovered quantitatively, the present irradiation conditions (RPR-350 nm lamps) would not be effective for an excitation of (**1a**). Therefore the photoirradiation could be necessary for the generation of $[\text{Fe}(\text{CO})_4]$ species from $[\text{Fe}(\text{CO})_5]$.¹⁵ The free or solvated $[\text{Fe}(\text{CO})_4]$ species is generally assumed to be the common reactive intermediate in thermolysis ($\geq 80^\circ\text{C}$) or photolysis of $[\text{Fe}(\text{CO})_5]$ and thermolysis of $[\text{Fe}_2(\text{CO})_9]$ ($\geq 20^\circ\text{C}$).¹⁶ Consistent with this notion, heating compounds (**1a**–**c**) with $[\text{Fe}_2(\text{CO})_9]$ in anhydrous methanol also gave the corresponding aldehydes (**2**) and ketones (**3**). The results are summarized in Table 1. Thus the $[\text{Fe}(\text{CO})_4]$ -complexed 2-isoxazoline could be a reasonable intermediate in the ring-cleavage reaction.

The substituent at C-3 did not seem to affect the reaction pathway. Thus the irradiation of (**1d**) with $[\text{Fe}(\text{CO})_5]$ in a similar way afforded the corresponding aldehyde and ketone.

Table 1. Reaction of the 2-isoxazolines (**1a**–**i**) with $[\text{Fe}(\text{CO})_5]$ or $[\text{Fe}_2(\text{CO})_9]$

	2-Isoxazoline			Conditions		Product		
	R ¹	R ²	R ³	<i>hν</i> ^a or heat ^b	<i>t</i> (h)	Aldehyde (2)	Ketone (3)	Others
(1a)	Ph	H	Ph	<i>hν</i>	24	57	69	—
(1b)	Ph	Ph	Ph	<i>hν</i>	10	62	96	—
(1c)	Ph	H	hexyl	<i>hν</i>	24	52	86	—
(1d)	Me	H	Ph	<i>hν</i>	2	39 (53) ^d	<i>e</i> (57) ^d	—
(1e)	Me	H	hexyl	<i>hν</i>	6	53 (61) ^d	<i>e</i> (54) ^d	—
(1f)	Ph	H	vinyl	<i>hν</i>	24	<i>e</i> (54) ^d	75 (78) ^d	—
(1g)	mesityl	H	Ph	<i>hν</i>	6	58	91 ^f	—
(1h)	Ph	H	H	<i>hν</i>	19	<i>e</i>	35	(4h) 53 (5h) 6
(1i)	Ph	Me	H	<i>hν</i>	5	<i>e</i>	45	(4i) 21 (5i) 17
(1a)				heat	6	73	81	—
(1b)				heat	3	42	84	—
(1c)				heat	4	<i>e</i>	53	(4h) 17 (5h) 13

^a Photoirradiation carried out with 2.0 mol equiv. of $[\text{Fe}(\text{CO})_5]$ in anhydrous methanol. ^b Reaction carried out with 1.0 mol equiv. of $[\text{Fe}_2(\text{CO})_9]$ in anhydrous methanol under reflux. ^c Based upon isolated products. ^d Yield of isolated 2,4-dinitrophenylhydrazone. ^e Isolation not carried out. ^f Yield of isolated mesityl methyl ketimine.

**Scheme 2.**

The volatile aldehydes and ketones were isolated by treatment of the photolysate with 2,4-dinitrophenylhydrazine to give the corresponding 2,4-dinitrophenylhydrazones. Furthermore the irradiation of **(1g)**, which has a bulky mesityl group at C-3, gave benzaldehyde and mesityl methyl ketimine instead of mesityl methyl ketone. Thus the present reaction seems to be general for the 3,5-disubstituted 2-isoxazolines and involves an imine or enamine intermediate.

The substituent at C-5 seems to be important for the N–O and C-4–C-5 bond cleavages giving **(2)** and **(3)**. The photoirradiation of **(1h)**, which has no substituent at C-5, with $[\text{Fe}(\text{CO})_5]$ gave acetophenone, along with 3-hydroxy-1-phenylpropan-1-one (**4h**) and 3-methoxy-1-phenylpropan-1-one (**5h**). In a similar way, 4-methyl-3-phenyl-2-isoxazoline (**1i**) afforded propiophenone, 3-hydroxy-2-methyl-1-phenylpropan-1-one (**4i**), and 3-methoxy-2-methyl-1-phenylpropan-1-one (**5i**). Thus

absence of the substituent at C-5 seems to prevent C-4-C-5 bond cleavage, which is the main photolytic pathway of the 3,5-disubstituted 2-isoxazolines (**1a-g**).

The present reactions in Table 1 are best explained by the mechanism in Scheme 2. The isolated mesityl methyl ketimine is good evidence for the intervention of an imine or enamine intermediate. As we described in a previous communication,⁸ the initial step could be an *n*-donor complexation of (**1**) to the $[\text{Fe}(\text{CO})_5]$ species,^{15,16} which is generated photochemically from $[\text{Fe}(\text{CO})_5]$ or thermally from $[\text{Fe}_2(\text{CO})_9]$, to give (**6**). The subsequent ring cleavage of (**6**) could give (**7**) [or (**8**)], of which reverse enamine alkylation could give aldehyde (**2**) and the nitrene complex (**9**) [or its protonated species (**10**)]. The factor allowing easy N-O bond cleavage could be ascribed to the delocalization of π -*d* electrons from the iron to the π^* orbital of the C=N-O moiety of the 2-isoxazolines. A complexed nitrene such as (**9**) has been suggested to be involved in the reaction of azirines with $[\text{Fe}(\text{CO})_5]$ or $[\text{Fe}_2(\text{CO})_9]$.¹⁷

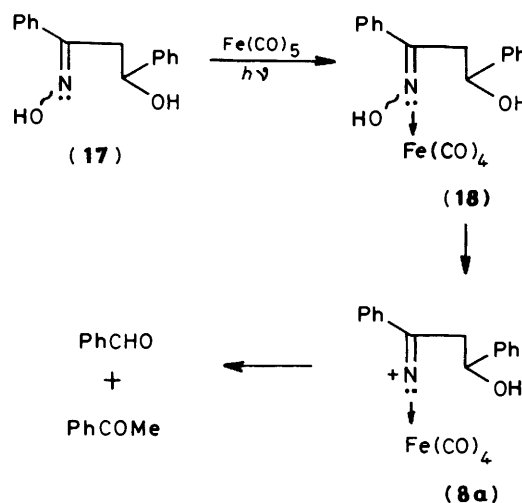
Previously, it was also shown that the postulated 1-phenylvinyl nitrene complex (**9a**; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$) could be derived from the reaction of α -azidostyrene, as well as 3-phenyl-2*H*-azirine, with $[\text{Fe}_2(\text{CO})_9]$ and heat.¹⁸ In methanol or in the presence of water, the nitrogen moiety of (**9a**) could undergo reduction by the iron moiety to give the imine or enamine (**11a**) (main pathway) and carbonyl insertion (minor pathway) to give 1-phenylvinyl isocyanate (**12a**). In the presence of water (**12a**) could collapse to (**3a**) via (**13a**), while in methanol, methyl 1-phenylvinyl carbamate (**14a**) is isolated. It is also suggested that the carbonyl insertion and elimination of the nitrogen molecule occurs simultaneously from the $[\text{Fe}(\text{CO})_4]$ -complexed α -azidostyrene to give (**12a**). The imine (**11a**) would be hydrolysed to give acetophenone in good yield in the presence of water or under work-up conditions. Thus (**9a**) [or its protonated species (**10a**)] seemed to be very labile in protic media or even in the presence of traces of water. Furthermore, (**14a**) could also be hydrolysed on t.l.c. plates to give acetophenone.¹⁸

On the basis of the previous study described above,¹⁸ the formation of ketones (**3**) in the present reaction could follow via (**9**) [or (**10**)] and (**11**), as well as (**14**). The photolysate of (**1a**) and $[\text{Fe}(\text{CO})_5]$ was analysed by g.l.c. (5% FFAP; 160 °C) and was shown to contain (**14a**) along with the corresponding aldehyde and ketone. However, (**14a**) decomposed under work-up conditions and it was not isolated. An intermediate (**13**) should not be ruled out in the presence of traces of water (*vide infra*).

In the case of (**1h**) or (**1i**), the energy barrier causing the C-4-C-5 bond cleavage to give (**2**) and complexed nitrene (**9**) [or (**10**)] might be high as compared with those of (**1a-g**), because of the absence of a substituent at C-5. Then, the pathway giving (**2**) and (**9**) could compete with the pathway giving (**4h**) or (**4i**)

via (**15**), which is derived from the reduction of the nitrogen moiety of (**7**) [or (**8**)] by the iron moiety. The formation of (**5h**) or (**5i**) seems to involve a nucleophilic attack of methanol on the less hindered secondary carbon atom C-5 of the complexed 2-isoxazoline (**6h** and **6i**) to give the complexed oxime (**16**), which could then undergo N-O bond cleavage to give (**5h**) or (**5i**) via reduction and subsequent hydrolysis of the complex similar to (**8**). Although the transformation of oximes into the corresponding ketones has been accomplished thermally by $[\text{Fe}(\text{CO})_5]$ ¹⁹ or $[\text{Fe}(\text{CO})_5]\text{-BF}_3\text{-OEt}_2$ ²⁰ under anhydrous conditions, the transformation was also possible under the present reaction conditions.²¹

Irradiation of (**4h**) or (**4i**) with $[\text{Fe}(\text{CO})_5]$ in methanol could not cause the reverse aldol-type reaction giving acetophenone or propiophenone along with formaldehyde, and (**4h**) or (**4i**) were recovered quantitatively. However, irradiation of 3-hydroxy-1,3-diphenylpropan-1-one oxime (**17**) with $[\text{Fe}(\text{CO})_5]$ in a similar way afforded acetophenone and benzaldehyde in 86 and 60% yield respectively, via the complex (**18**), as shown in Scheme 3. Thus the reverse enamine alkylation process of (**7**) [or (**8**)] to (**9**) [or (**10**)] could also be assessed.



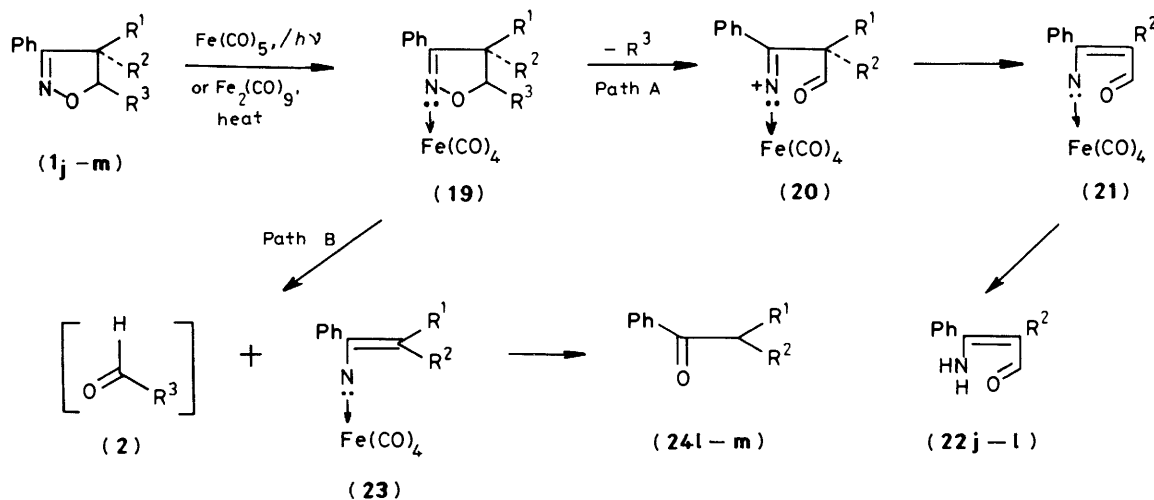
Scheme 3.

In a similar manner to the above reactions, we investigated the $[\text{Fe}(\text{CO})_5]$ - or $[\text{Fe}_2(\text{CO})_9]$ -induced reaction of 2-isoxazolines (**1j-m**) bearing a substituent such as OAc, OEt, or pyrrolidin-1-yl group at C-5. The reaction conditions and the products are summarized in Table 2. The reaction of (**1j** and **k**) follows path

Table 2. Reaction of the 2-isoxazolines (**1j-m**) with $[\text{Fe}(\text{CO})_5]$ or $[\text{Fe}_2(\text{CO})_9]$

	2-Isoxazoline			Conditions		Product yield (%) ^d	
	R ¹	R ²	R ³	<i>hν</i> or heat	<i>t</i> (h)	β-Aminoenone (22)	Ketone (24)
(1j)	H	H	OAc	<i>hν</i> ^a	6	80	0
(1k)	H	H	OEt	<i>hν</i> ^a	24	76	0
(1l)	H	Et	pyrrolidin-1-yl	<i>hν</i> ^a	24	35 ^e	51
(1m)	Me	Me	pyrrolidin-1-yl	<i>hν</i> ^a	20	0	72
(1j)				<i>hν</i> ^b	6	83	0
(1k)				<i>hν</i> ^b	24	85	0
(1j)				heat ^c	3	79	0
(1k)				heat ^c	3	73	0

^a Photoirradiation carried out with 2.0 mol equiv. of $[\text{Fe}(\text{CO})_5]$ in anhydrous methanol. ^b Photoirradiation carried out with 2.0 mol equiv. of $[\text{Fe}(\text{CO})_5]$ in anhydrous benzene. ^c Reaction carried out with 1.0 mol equiv. of $[\text{Fe}_2(\text{CO})_9]$ in anhydrous methanol under reflux. ^d Based upon isolated products. ^e *cis/trans* Mixture in the ratio 1:1.



Scheme 4. j, $R^1 = R^2 = \text{H}$, $R^3 = \text{OAc}$; k, $R^1 = R^2 = \text{H}$, $R^3 = \text{OEt}$; l, $R^1 = \text{H}$, $R^2 = \text{Et}$, $R^3 = \text{pyrrolidin-1-yl}$; m, $R^1 = R^2 = \text{Me}$, $R^3 = \text{pyrrolidin-1-yl}$.

A in Scheme 4 to afford β -aminoenones (**22**) in good yield. The compounds (**22**) could arise [via (**21**)] from N–O bond cleavage and subsequent elimination of the OAc or OEt group from the complex (**19**) to give complex (**20**), which is similar to (**8**) in Scheme 2. An alternative pathway is the elimination of HOAc or EtOH from (**1j** or **k**) giving 3-phenylisoxazole and the subsequent reductive cleavage of the isoxazole ring to give (**22**).⁸ It was shown that reaction of 3-phenylisoxazole with $[\text{Fe}(\text{CO})_5]$ under photoirradiation gives (**22**; $R^2 = \text{H}$) in good yield. Since the present reaction of (**1j** and **k**) giving (**22**) proceeded very fast as compared with that of 3-phenylisoxazole to give (**22**; $R^2 = \text{H}$), the intermediacy of 3-phenylisoxazole was ignored and the possibility of path A was assessed. Furthermore, these results seem to suggest the delocalization of a π -d electron from the iron to the π^* orbital of the C=N–O moiety and the ready elimination of either the OAc or the OEt group as an anion. On the other hand, the 2-isoxazoline (**11**) could follow both path A and path B. This fact might be ascribed to the low leaving ability of the pyrrolidin-1-yl group, as compared with OAc or OEt, and/or to the presence of the substituent at C-4. The 2-isoxazoline (**1m**) having two methyl groups at C-4 follows only path B to give (**24**).

The reactions in Table 2 were also shown to proceed in anhydrous benzene solution. Thus traces of water seem to be enough for the conversion of complex (**20**) or complexed nitrene species (**23**) into imine or enamine via the simple reduction and/or via an organic isocyanate such as (**12**) in Scheme 2.

The alkylation of 2-isoxazolines at C-4 has been reported.²² The reaction in Table 1 might serve as a method for the construction of functionalized carbon skeletons. Furthermore, β -aminoenones were obtained in good yield from 2-isoxazolines such as (**1j** and **k**) (Table 2). Since 2-isoxazolines, such as (**1j** and **k**) are easily accessible by 1,3-dipolar cycloaddition of nitrile oxides with enamines or alkyl vinyl ether derivatives with complete regioselectivity, this reaction might also serve as a convenient method for the preparation of various β -aminoenones.

Experimental

I.r. spectra were recorded on a Shimadzu IR-400 spectrophotometer. N.m.r. spectra were recorded on a Hitachi R-24 or JEOL JNM-PMX60SI spectrometer and chemical shifts are given in p.p.m. (δ) relative to internal SiMe_4 standard. $[\text{Fe}(\text{CO})_5]$ (Strem Chemicals, Inc.) was a commercial sample. $[\text{Fe}_2(\text{CO})_9]$

was prepared by the standard method.²³ Solvents were purified and dried by the standard methods.

General Procedure for the Preparation of 2-Isoxazolines.—The desired 2-isoxazolines were synthesized by the 1,3-dipolar cycloaddition of the corresponding nitrile oxides with olefins. The 2-isoxazolines (**1a** and **b**), (**1e–j**), and (**11**) are known compounds and were identified on the basis of their physical data. Several unknown 2-isoxazolines were prepared in a similar way and characterized as follows.

Preparation of the 2-isoxazoline (1c). A solution of triethylamine (3 ml) in ether (10 ml) was added dropwise to a stirred solution of benzohydroximoyl chloride (1.53 g, 10 mmol) and oct-1-ene (5 ml) in ether (40 ml) during 2 h at 0 °C. After the addition was completed, the reaction mixture was stirred for 24 h and then poured into water (50 ml) and extracted with ether. The extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was recrystallized from hexane to give 4-hexyl-3-phenyl-4,5-dihydroisoxazole (**1c**) (1.95 g, 85% yield based on benzohydroximic acid chloride), m.p. 47–48 °C (from hexane); δ_{H} 0.80–1.00 (3 H, m), 1.10–1.80 (2 H, m), 2.95 (1 H, dd, J 16.2 and 8.5 Hz), 3.32 (1 H, dd, J 16.2 and 10.0 Hz), 4.65 (1 H, m), and 7.25–7.70 (5 H, m); m/z 231 (57%, M^+) and 146 (100) (Found: C, 77.5; H, 9.2; N, 5.8. $\text{C}_{15}\text{H}_{21}\text{NO}$ requires C, 77.85; H, 9.15; N, 6.05%).

Preparation of the 2-isoxazoline (1k). A solution of triethylamine in ether (10 ml) was added dropwise to a stirred solution of benzohydroximoyl chloride (5.0 g, 32 mmol) and ethyl vinyl ether (7.2 g, 109 mmol) in ether (100 ml) during 2 h at 0 °C. After the addition was completed, the reaction mixture was stirred for another 10 h at 0 °C and then poured into water (100 ml) and extracted with ether. The extract was dried over MgSO_4 and evaporated. The residue was distilled to give 5-ethoxy-3-phenyl-4,5-dihydroisoxazole (**1k**) (5.07 g, 83%), b.p. 137 °C at 5 Torr; δ_{H} 1.13 (3 H, t, J 7.4 Hz), 3.10 (1 H, dd, J 17.0 and 3.0 Hz), 3.18 (1 H, dd, J 17.0 and 2.4 Hz), 3.65 (2 H, q, J 7.4 Hz), 5.48 (1 H, dd, J 3.0 and 2.4 Hz), and 7.20–7.70 (5 H, m); m/z 191 (100%, M^+) (Found: C, 68.7; H, 6.5; N, 7.0. $\text{C}_{11}\text{H}_{13}\text{NO}$ requires C, 69.09; H, 6.85; N, 7.33%).

Preparation of the 2-isoxazoline (1m). To a stirred solution of benzohydroximoyl chloride (3.12 g, 20 mmol) in ether (100 ml) was added 14% aqueous sodium hydroxide (16 ml) at 0 °C. After the mixture had been stirred for 10 min, the ether layer was separated and dried over Na_2SO_4 at 0 °C. The ether layer

(containing benzonitrile oxide) was then filtered and 2-methyl-1-pyrrolidin-1-ylprop-1-ene (2.5 g, 20 mmol) was added to the solution. After the mixture had been stirred for 24 h at 0 °C, it was concentrated. The resulting residue was chromatographed on silica gel. The fraction eluted with chloroform gave 4,4-dimethyl-3-phenyl-5-pyrrolidin-1-yl-4,5-dihydroisoxazole (690 mg, 14%), m.p. 85–86 °C (from hexane); δ_{H} 1.25 (3 H, s), 1.36 (3 H, s), 1.50–1.85 (4 H, m), 2.50–2.80 (4 H, m), 4.95 (1 H, s), and 7.10–7.70 (5 H, m); m/z 244 (3%, M^+) and 145 (100) (Found: C, 73.5; H, 8.05; N, 11.6. $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}$ requires C, 73.73; H, 8.25; N, 11.48%).

General Procedure for the Reaction of the 2-Isloxazolines (1a–i) with $[\text{Fe}(\text{CO})_5]$.—A solution of the 2-isloxazoline (1) (1 mmol) and $[\text{Fe}(\text{CO})_5]$ (2 mmol) in anhydrous methanol (20 ml) was irradiated in a Pyrex vessel under dry nitrogen with Rayonet RPR-350 nm lamps for 5–24 h at ambient temperature. After removal of the methanol, hexane (30 ml) was added to the residue and the mixture was filtered through Celite to remove insoluble material. The filtrate was concentrated, and the resulting residue was separated by t.l.c. on silica gel to give the products. The reaction times and the yields are summarized in Table 1. All of the reaction products are known compounds and were identified on the basis of physical data.

Isolation of the Corresponding 2,4-Dinitrophenylhydrazones of the Volatile Photoproducts in the Reaction of (1d–f).—After the photoreaction was carried out as described in the general procedure, the solution of photolysate was filtered through Celite. To the filtrate were added 2,4-dinitrophenylhydrazine (2 mmol) and conc. hydrochloric acid (2 drops). After having been stirred for 30 min, the reaction mixture was filtered through Celite and the filtrate was concentrated. The resulting residue was separated by t.l.c. on silica gel using benzene as developer to give the following 2,4-dinitrophenylhydrazones (2,4-DNP) of the corresponding aldehydes and ketones: acetone 2,4-DNP (m.p. 124–126 °C); benzaldehyde 2,4-DNP (m.p. 235–236 °C); heptanal 2,4-DNP (m.p. 105–106 °C); acrylaldehyde 2,4-DNP (m.p. 163–164 °C); acetophenone 2,4-DNP (m.p. 247–248 °C). Each of the above 2,4-DNPs was identified on the basis of the physical data of an authentic specimen.

Photoirradiation of (1a) in the Absence of $[\text{Fe}(\text{CO})_5]$.—A solution of (1a) (112 mg, 0.5 mmol) in anhydrous methanol (20 ml) was irradiated in a Pyrex vessel under dry nitrogen with Rayonet RPR-350 nm lamps for 24 h. After removal of the methanol, the resulting residue was purified by t.l.c. on silica gel using benzene as developer to give (1a) (103 mg, 92%).

Thermal Reaction of the 2-Isloxazoline (1a–c) with $[\text{Fe}_2(\text{CO})_9]$.—A solution of a 2-isloxazoline (1) (1 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (1 mmol) in anhydrous methanol (10 ml) was refluxed for 3–6 h under dry nitrogen. The reaction mixture was filtered through Celite and the filtrate was concentrated. The resulting residue was separated by t.l.c. on silica gel using chloroform as developer to give the products which are summarized in Table 1.

Photoirradiation of 3-Hydroxy-1,3-diphenylpropan-1-one Oxime (17) with $[\text{Fe}(\text{CO})_5]$.—A solution of (17) (241 mg, 1 mmol) and $[\text{Fe}(\text{CO})_5]$ (392 mg, 2 mmol) in anhydrous methanol (20 ml) was irradiated in a Pyrex vessel under dry nitrogen with Rayonet RPR-350 nm lamps for 24 h. The photolysate was filtered through Celite and the filtrate was concentrated. The resulting residue was separated by t.l.c. on silica gel using chloroform as developer to give (17) (96 mg, 40% recovery), benzaldehyde (40 mg, 37%) and acetophenone (62 mg, 52%).

General Procedure for the Photoirradiation of the 2-Isloxazolines (1j–m) with $[\text{Fe}(\text{CO})_5]$.—A solution of (1) (1 mmol) and $[\text{Fe}(\text{CO})_5]$ (2 mmol) in anhydrous methanol (20 ml) or in anhydrous benzene (20 ml) was irradiated in a Pyrex vessel under dry nitrogen with Rayonet RPR-350 nm lamps for 6–24 h at ambient temperature. The reaction mixture was filtered through Celite, and the filtrate was concentrated. The residue was separated by t.l.c. on silica gel using chloroform or ethyl acetate as developer to give the products summarized in Table 2. One of the products for the reaction of (1l) is the *cis/trans* (1:1) mixture of β -aminoenones (22l), which is an unknown compound. It was identified on the basis of the following physical data: m.p. 131–133.5 °C (from ethanol); δ_{H} 0.89 and 1.00 (each 3 H, t, J 7.0 Hz), 2.07 and 2.30 (each 2 H, q, J 8.0 Hz), 3.20–3.50 and 4.80–5.20 (each 1 H, br s), 7.33 (5 H, br s), and 8.90 and 9.22 (each 1 H, s); ν_{max} (CHCl_3) 3 424, 3 174, 2 958, 1 610, 1 584, 1 487, and 1 369 cm^{-1} ; m/z 175 (79%, M^+) and 174 (100) (Found: C, 75.7; H, 7.4; N, 7.75. $\text{C}_{11}\text{H}_{13}\text{NO}$ requires C, 75.40; H, 7.48; N, 7.99%).

Thermal Reaction of (1j and k) with $[\text{Fe}_2(\text{CO})_9]$.—A solution of (1) (1 mmol) and $[\text{Fe}_2(\text{CO})_9]$ (364 mg, 1 mmol) in anhydrous methanol (10 ml) was refluxed for 3 h. The reaction mixture was filtered through Celite and the filtrate was concentrated. The residue was separated by t.l.c. on silica gel using ethyl acetate as developer to give the products summarized in Table 2.

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