Metal-carbonyl-Induced Reaction of Isoxazoles. Ring Cleavage and Reduction by Hexacarbonylmolybdenum, Pentacarbonyliron, or Nonacarbonyldi-iron

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In the presence of $[Mo(CO)_6]$ and water the isoxazoles (**1a—f**) undergo thermally induced reductive cleavage of the N–O bond to give β-amino enones in good yield. Similar results were obtained by the use of $[Fe(CO)_5]$ and water with photoirradiation, or of $[Fe_2(CO)_9]$ and water with heating. A mechanism involving an *N*-complexed isoxazolepentacarbonylmolybdenum or isoxazoletetracarbonyliron, and a $[Mo(CO)_5]$- or $[Fe(CO)_4]$-complexed (β-oxo vinyl)nitrene intermediate is proposed for the reactions. The complexed nitrene moiety could be reduced by the central metal in the presence of water to give amine. Furthermore, treatment of 2-benzoyl-3-phenyl-2*H*-azirine (**8a**), which is an isomer of 3,5-diphenylisoxazole, with the metal carbonyls and water also resulted in the formation of a β-amino enone possibly *via* the corresponding complexed (β-oxo vinyl)nitrene. An *N*-complexed isoxazole-pentacarbonylmolybdenum intermediate was prepared by the photoreaction of $[Mo(CO)_6]$ with 3,5-dimethylisoxazole. Its characterization, and chemical transformations, have been carried out to investigate the proposed mechanism.

Recently much attention has been focussed on azirines, which undergo a variety of interesting and useful ring cleavage reactions in the presence of transition-metal carbonyls [2] such as $[Fe_2(CO)_9]$,[3] $[Co_2(CO)_8]$,[4] and $[M(CO)_6]$ (M = Mo,[5—7] Cr,[6] and W[6]). Among these ring cleavage reactions, the $[Mo(CO)_6]$-induced efficient intramolecular reaction of 2-formyl-3-phenyl-2*H*-azirine to give 3-phenylisoxazole stands in contrast to the photochemical and thermal behaviour of isoxazoles.[6] 3,5-Diarylisoxazoles undergo photochemically induced N–O bond cleavage to give oxoazirines, which recyclize to the starting isoxazoles or oxazoles, depending on the wavelength of further irradiation.[8] Heating of isoxazoles has also been noted to induce N–O bond cleavage to give oxoazirines.[9]

We have an interest in this N–O bond cleavage in isoxazoles and related compounds. In isoxazoles the nitrogen–oxygen linkage appears to be antibonding in character (LUMO shown as **A** in the Figure),[10] and this seems to be responsible for the
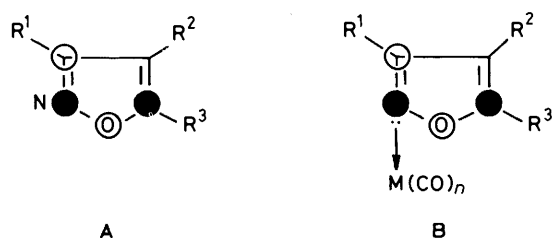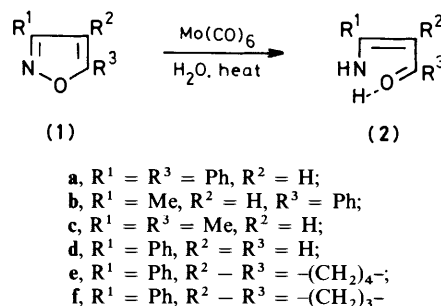

Figure.

facile photochemical N–O bond cleavage. Considering the isoxazoles *N*-complexed (**B**) to the above mentioned metal carbonyls, a possible delocalization of a π-d electron from the central metal to the π^* (LUMO) of the isoxazole is expected to facilitate the N–O bond cleavage under mild conditions, as distinct from the purely thermal[9] process. This paper describes the thermally induced reaction of isoxazoles (**1a—f**) and 2-benzoyl-3-phenyl-2*H*-azirine (**8a**) with $[Mo(CO)_6]$ or $[Fe_2(CO)_9]$, or with $[Fe(CO)_5]$ when photoirradiated in the presence of water to give β-amino enones in good yields.

Results and Discussion

The thermally induced reaction of isoxazoles (**1a—f**) with $[Mo(CO)_6]$ in moist acetonitrile containing an equivalent amount of water and subsequent purification by t.l.c. of the product afforded the β-amino enones (**2a—f**) in good yield (see Scheme 1 and Table 1, entries 1—6); the β-amino enones (**2a—f**)

a, $R^1 = R^3 = Ph$, $R^2 = H$;
b, $R^1 = Me$, $R^2 = H$, $R^3 = Ph$;
c, $R^1 = R^3 = Me$, $R^2 = H$;
d, $R^1 = Ph$, $R^2 = R^3 = H$;
e, $R^1 = Ph$, $R^2 - R^3 = -(CH_2)_4-$;
f, $R^1 = Ph$, $R^2 - R^3 = -(CH_2)_3-$

Scheme 1.

are inert under the reaction conditions. Almost all the β-amino enones are known compounds and were identified by comparison of their spectral data with those of authentic specimens, which were obtained by the catalytic hydrogenation of the corresponding isoxazoles.[11] In the present reactions, stoicheiometric amounts of $[Mo(CO)_6]$ were not required, and a molar ratio of 1.0:0.5 for (**1a—f**) to $[Mo(CO)_6]$ resulted in the complete consumption of the starting material (Table 1, entries 1—6). However, using a molar ratio of 1.0:0.33 or 1.0:0.2 for (**1a**) to $[Mo(CO)_6]$ gave a lower yield of (**2a**), together with unchanged starting material even after prolonged heating (Table 1, entries 7 and 8).

The present reactions are best explained by the mechanism shown in Scheme 2 in which initially there is complex formation between (**1**) and $[Mo(CO)_6]$ to give (**3**); subsequent N–O bond cleavage then gives the (β-oxo vinyl)nitrene complex (**4**).[8] Previously, it was suggested that the $[Mo(CO)_5]$-complexed 1-phenylvinylnitrene, derived by heating α-azidostyrene (or 3-phenyl-2*H*-azirine) with $[Mo(CO)_6]$, was reduced to the corresponding enamine.[7] On the basis of the previous study, the

Table 1. Reductive cleavage of isoxazoles (1a—f) and an azirine (8a) in the presence of [Mo(CO)$_6$]

Entry	Compd.	Molar ratio of [Mo(CO)$_6$]	Reaction conditions[a]	Reaction time (h)	Product yield (%)
1	(1a)	0.5	i	4	(2a) (90)
2	(1b)	0.5	i	4	(2b) (80)
3	(1c)	0.5	i	4	(2c) (91)
4	(1d)	0.5	i	4	(2d) (89)
5	(1e)	0.5	i	24	(2e) (77)
6	(1f)	0.5	i	24	(2f) (84)
7	(1a)	0.33	i	24	(2a) (70), (1a) (14)
8	(1a)	0.20	i	24	(2a) (57), (1a) (31)
9	(1a)	2.0[b]	ii	6	(1a) (81)
10	(8a)	1.0	ii, iii	40	(1a) (94)
11	(8a)	1.0	ii	40	(2a), (28), (1a) 50)

[a] i, Refluxed in moist acetonitrile containing an equivalent amount of water; ii, Ambient temperature; iii, anhydrous conditions. [b] [Mo(CO)$_3$(MeCN)$_3$] was prepared *in situ*.
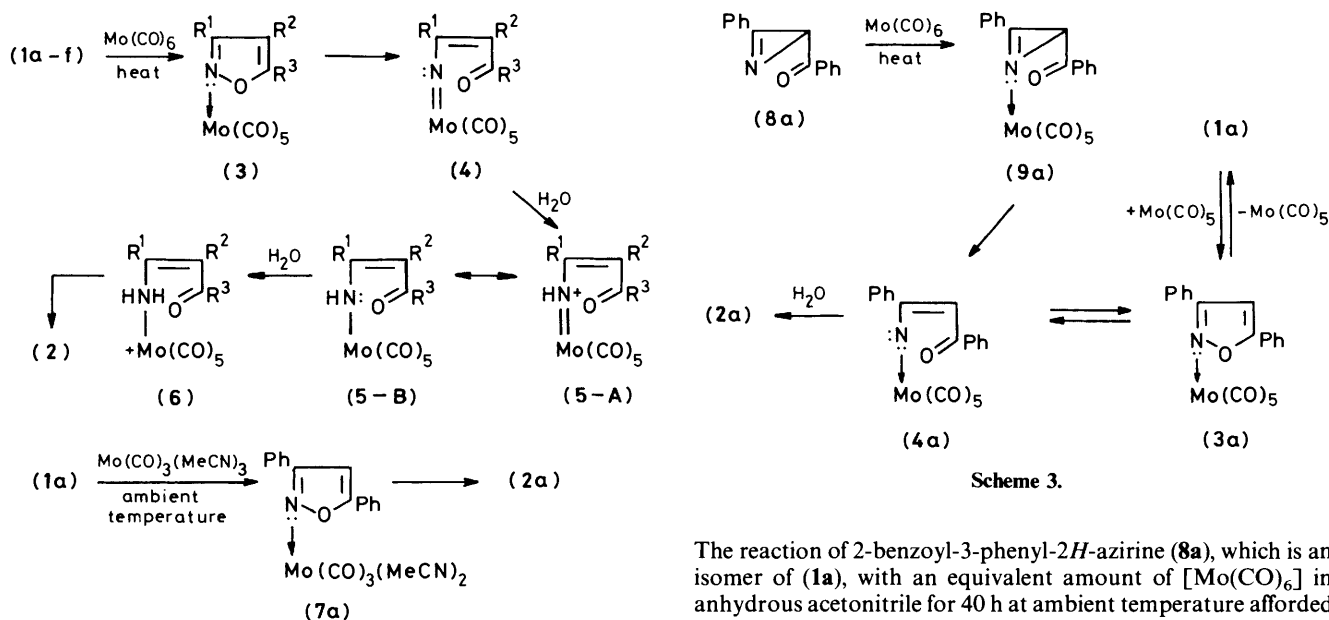
Scheme 2.

Scheme 3.

protonation of the nitrogen atom of compound (4) could give compound (5) in the presence of water. The structure (5-B) is a contributor to the resonance hybrid of (5). The further protonation of compound (5) giving compound (6) followed by decomplexation, would give the β-amino enone (2). Thus, the mechanism of the [Mo(CO)$_6$]-induced N–O bond cleavage under mild conditions is very similar to the photochemically induced process.[8] This fact also suggests the delocalization of the π-d electron from molybdenum to the π* orbital (LUMO) of isoxazole in (3) (see **B** in the Figure). Furthermore, the *in situ* preparation of [Mo(CO)$_3$(MeCN)$_3$],[12] and the subsequent reaction of (1a) at ambient temperature gave (2a) in 81% yield (Table 1, entry 9). This suggests that the ligand-exchange reaction of [Mo(CO)$_3$(MeCN)$_3$] with (1a) to give (7a) proceeds under mild conditions compared with those required for the reaction of [Mo(CO)$_6$] with (1a). The facile N–O bond cleavage of (7a) occurs even at ambient temparature, suggesting considerable delocalization of the π-d electron of the [Mo(CO)$_3$(MeCN)$_2$]-complexed (7a) compared with that of the [Mo(CO)$_5$]-complexed (3).

Further support for the intermediacy of the complexed (β-oxo vinyl)nitrene (4) was obtained as illustrated in Scheme 3.

The reaction of 2-benzoyl-3-phenyl-2*H*-azirine (8a), which is an isomer of (1a), with an equivalent amount of [Mo(CO)$_6$] in anhydrous acetonitrile for 40 h at ambient temperature afforded (1a) in excellent yield, while in moist acetonitrile, both the β-amino enone (2a) and the isoxazole (1a) were obtained (Table 1, entries 10 and 11). The formation of (1a) from (8a) probably proceeds *via* the nitrene complex (4a), which undergoes rapid ring closure to (3a) and decomplexation to give (1a), as suggested by Alper *et al.*[6] This seems to suggest that the equilibrium between (3a) and (4a) is largely shifted to (3a) at ambient temperature. In the presence of water, the protonation–reduction reaction which gives the β-amino enone (2a) competes with the ring closure reaction which gives (1a). Thus, the (β-oxo vinyl)nitrene species (4) seems to be a reasonable precursor of the β-amino enones in the present reaction. A molar ratio of 1.0:0.5 for (1) and [Mo(CO)$_6$] is enough to complete the reaction of (1a—f). This suggests that the resulting [Mo^{2+}(CO)$_5$] species also participate in the ring cleavage and reduction of the isoxazoles.

Evidence for the existence of complex (3) was also obtained. Benzazolepentacarbonyl complexes such as [M(CO)$_5$L] (M = Cr, Mo, W; L = benzimidazole, benzothiazole, and benzoselenazole) have been prepared by photochemical reaction of the metal carbonyls with the corresponding heterocyclic compounds in tetrahydrofuran (THF).[13] According to this procedure, photoirradiation of [Mo(CO)$_6$] with (1c) in THF afforded a yellow crystalline complex (3c), the structure of which was assigned on the basis of spectral evidence (Table 2; see also Experimental section). Of especial significance was the

Table 2. ^1H, ^{13}C, and ^{14}N Chemical shifts (p.p.m.) of the isoxazole (1c) and its pentacarbonylmolybdenum complex (3c) in $(CD_3)_2CO$

Compd.	^1H n.m.r.^{a}	^{13}C n.m.r.^{a,b}	^{14}N n.m.r.^{c}
(1c)	1.68 (3 H, s)	17.7, 18.6	−4
	1.84 (3 H, s)^d	106.8, 162.2	
	5.41 (1 H, s)^d	171.3	
(3c)	1.98 (3 H, s)	18.3, 20.6	−70
	2.00 (3 H, s)^d	109.3, 153.8	
	5.83 (1 H, s)^d	173.4, 202.7	
		205.1	

^{a} Tetramethylsilane as an internal standard. ^{b} Recorded on a JNM-FX90Q spectrometer. ^{c} Recorded on a JNM-GX400 spectrometer, nitromethane as external standard. ^{d} Appeared as a broad singlet.

^{14}N n.m.r. spectrum of (3c), which exhibited a signal −70 p.p.m. to higher field than that for (1c) at −4 p.p.m.; also the signals observed in the ^1H n.m.r. and ^{13}C n.m.r. spectra of (3c), were lowfield compared with those of (1c). These data clearly indicate co-ordination of the nitrogen atom.[14] Complex (3c) is unstable, a parent ion peak being absent in its mass spectrum; satisfactory elemental analyses were, however, obtained. In $(CD_3)_2CO$ solution, (3c) gradually decomposed at ambient temperature and afforded a mixture of (1c) (30%), (2c) (37%), and (3c) (33%) after 24 h. Furthermore, heating of a solution of (3c) in boiling moist acetonitrile gave the β-amino enone (2c) in
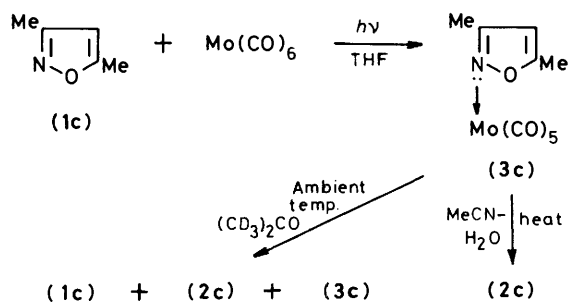
Scheme 4.

81% yield. These observations provide evidence for the intermediacy of the complex (3) and for the equilibrium between (3) and (1) as well as (3) and (4) in solution (see also Scheme 3).

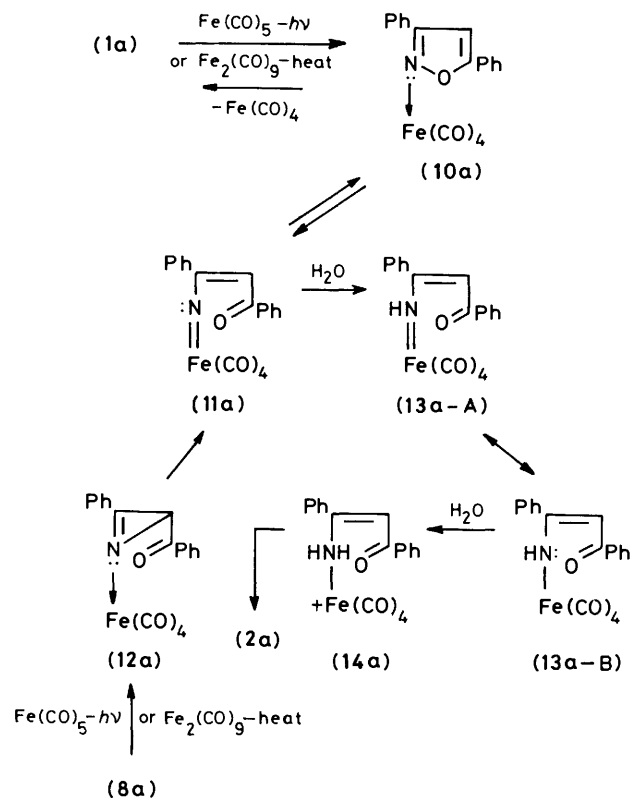Similarly to the $[Mo(CO)_6]$-induced reaction, $[Fe(CO)_5]$ or $[Fe_2(CO)_9]$ also causes the reaction of isoxazoles (1a—d) and an azirine (8a) (see Table 3).

Photoirradiation of (1a—d) with $[Fe(CO)_5]$ in moist acetonitrile afforded the β-amino enones (2a—d) in good yields (entries 1—4). Photoirradiation of (1c) under similar conditions in the absence of $[Fe(CO)_5]$ for 6 h gave no (2c), and (1c) was recovered quantitatively. Therefore, it is clear that both light and $[Fe(CO)_5]$ are indispensable for the present reactions. Similar transformations were also effected by use of daylight through a Pyrex filter (entries 5—7). Photoirradiation of $[Fe(CO)_5]$ has been shown to give $[Fe(CO)_4]$ species in low-temperature matrices.[15] In solution and in the absence of a nucleophile, $[Fe(CO)_4]$ reacts efficiently to give $[Fe_2(CO)_9]$,[16] while in the presence of a nucleophile such as pyridine, an $[Fe(CO)_4(pyridine)]$ complex is formed.[17] Therefore, the photochemically generated $[Fe(CO)_4]$ species is probably responsible for the present reactions.

The free or solvated $[Fe(CO)_4]$ species is generally assumed

to be the common reactive intermediate in the thermolysis ($\geqslant 80$ °C) or photolysis of $[Fe(CO)_5]$ and the thermolysis of $[Fe_2(CO)_9]$ ($\geqslant 20$ °C).[18] Consistent with this theory, heating of (1a—d) with $[Fe_2(CO)_9]$ in aqueous acetonitrile also gave the corresponding β-amino enones (2a—d) in good yield (entries 8—11). Thus the $[Fe(CO)_4]$-complexed isoxazole, which is similar to (3) in Scheme 2, seems to be a reasonable intermediate in the present reactions; this type of complex was not isolated, however.

The reactions of (1) to give (2) are illustrated in Scheme 5, (1a)

Scheme 5.

being used as an example. These mechanistic paths are almost the same as those for the $[Mo(CO)_6]$-induced reactions (Scheme 2). Photoirradiation of the azirine (8a) with $[Fe(CO)_5]$, or heating of $[Fe_2(CO)_9]$ in moist acetonitrile, also afforded the β-amino enone (2a) together with the isoxazole (1a) (Table 3, entries 14 and 15). Thus, it seems probable that the reaction of (8a) as well as (1a) proceeds via a common nitrene complex (11a). According to our previous studies,[19] the nitrogen-containing moiety of $[Fe(CO)_4]$-complexed 1-phenyl-vinylnitrene could undergo reduction by the iron-containing moiety to give the imine or enamine (major path), or carbonyl insertion (minor path) to give 1-phenylvinyl isocyanate. The isocyanate could then give the imine or enamine in the presence of water. Thus, the reduction–protonation reaction of (11a), which is similar to (4), would also give (2a). In the photoirradiation or heating of (1a) under anhydrous conditions (Table 3, entries 12 and 13), however, (2a) was obtained in low yield along with a mixture of other products, in both cases. The mixture does not appear to contain the $[Fe(CO)_n]$ moiety, and thus the structure was not elucidated. Even in the reaction under anhydrous conditions, the possibility of the presence of some water cannot be ruled out.

In conclusion, since the reductive cleavage of isoxazoles by

Table 3. Reductive cleavage of isoxazoles (1a—d) and an azirine (8a) in the presence of [Fe(CO)$_5$] or [Fe$_2$(CO)$_9$]

Entry	Compd.	Metal carbonyl[a]	Solvent	Reaction conditions[b]	Reaction time (h)	Product yield (%)
1	(1a)	i	MeCN–H$_2$O	A	24	(2a) (68)
2	(1b)	i	MeCN–H$_2$O	A	24	(2b) (76)
3	(1c)	i	MeCN–H$_2$O	A	6	(2c) (72)
4	(1d)	i	MeCN–H$_2$O	A	24	(2d) (65)
5	(1a)	i	MeCN–H$_2$O	B	24	(2a) (74)
6	(1b)	i	MeCN–H$_2$O	B	24	(2b) (79)
7	(1c)	i	MeCN–H$_2$O	B	24	(2c) (65)
8	(1a)	ii	MeCN–H$_2$O	C	5	(2a) (66)
9	(1b)	ii	MeCN–H$_2$O	C	5	(2b) (79)
10	(1c)	ii	MeCN–H$_2$O	C	5	(2c) (71)
11	(1d)	ii	MeCN–H$_2$O	C	5	(2d) (79)
12	(1a)	i	PhH	A	24	(2a) (56)[c]
13	(1a)	ii	PhH	C	5	(2a) (41)[c]
14	(8a)	i	MeCN–H$_2$O	B	5	(2a) (43), (1a) (39)
15	(8a)	ii	MeCN–H$_2$O	C	0.7	(2a) (57), (1a) (31)

[a] i, 1.2 mol equiv. [Fe(CO)$_5$] used; ii, 1.0 mol equiv. [Fe$_2$(CO)$_9$] used. [b] A: Irradiated with RPR-350 nm lamps through a Pyrex filter; B: Exposed to weak daylight through a Pyrex filter; C: heated at 50 °C. [c] Accompanied by a mixture of products (ca. 10—17%) whose structures have not been elucidated.

catalytic hydrogenation is widely applicable in synthesis,[11] the present reactions could serve as a convenient method for the preparation of β-amino enones. Furthermore, the behaviour of a series [5,19] of the postulated complexed nitrene species, such as (4) and (11) could also be interesting with regard to the chemistry of a variety of dinitrogen complexes of low-valency transition-metals.[20]

Experimental

I.r. spectra were recorded on a Shimadzu IR-400 spectrometer. ^{1}H N.m.r. spectra were recorded on a Hitachi R-24 or JEOL JHM-PMX60PS spectrometer and chemical shifts are given relative to internal SiMe$_4$. [Fe(CO)$_5$] and [Mo(CO)$_6$] (Strem Chemicals, Inc.) were commercial samples. [Fe$_2$(CO)$_9$] was prepared by the standard method.[16] M.p.s are uncorrected.

Preparation of the Isoxazoles (1a—f).—3,5-Diphenylisoxazole (1a) was prepared by 1,3-dipolar cycloaddition of benzonitrile oxide with phenylacetylene according to the method of Lee,[21] and had m.p. 140—141 °C (lit.,[21] 141—142 °C); δ$_H$(CDCl$_3$) 6.20 (1 H, s), 6.70—7.00 (6 H, m), and 7.10—7.40 (4 H, m).

3-Methyl-5-phenylisoxazole (1b) was prepared according to a literature methods,[22] and had b.p. 82 °C at 3 Torr; m.p. 61.5—62.5 °C; δ$_H$(CCl$_4$) 2.22 (3 H, s), 6.24 (1 H, s), 7.20—7.50 (3 H, m), and 7.50—7.80 (2 H, m).

3,5-Dimethylisoxazole (1c) was prepared from acetylacetone and hydroxylamine hydrochloride by a standard method[23] and had b.p. 140—142 °C at 760 Torr; δ$_H$(CCl$_4$) 2.10 (3 H, s), 2.22 (3 H, s), and 5.61 (1 H, s).

3-Phenylisoxazole (1d) was prepared by 1,3-dipolar cycloaddition of benzonitrile oxide to bromoethylene and subsequent dehydrobromination:[24] b.p. 103—105 °C at 6 Torr; δ$_H$(CCl$_4$) 6.51 (1 H, d, J 1.8 Hz), 7.20—7.45 (3 H, m), 7.60—7.82 (2 H, m), and 8.39 (1 H, d, J 1.8 Hz).

3-Phenyl-4,5,6,7-tetrahydro-2,1-benzisoxazole (1e) was prepared by 1,3-dipolar cycloaddition of benzonitrile oxide to 1-pyrrolidin-1-ylcyclohexene and the subsequent acid-catalysed elimination of pyrrolidine:[25] m.p. 50—53 °C (lit.,[25] 53—54 °C); δ$_H$(CCl$_4$) 1.49—2.01 (4 H, m), 2.38—2.82 (4 H, m), and 7.12—7.76 (5 H, m).

3-Phenylcyclopent[c]isoxazole (1f) was prepared by 1,3-dipolar cycloaddition of benzonitrile oxide to 1-pyrrolidin-1-

ylcyclopentene and the subsequent Hofmann elimination of pyrrolidine:[25] m.p. 82—83 °C (lit.,[25] 83—84 °C); δ$_H$(CCl$_4$) 2.76 (6 H, m) and 7.18—7.84 (5 H, m).

General Procedure for the Thermal Reaction of the Isoxazoles (1a—f) *with* [Mo(CO)$_6$].—A solution of the isoxazoles (1) (1 mmol), water (1 mmol), and the appropriate amount of [Mo(CO)$_6$] in acetonitrile (20 ml) was refluxed for the period indicated in Table 1. After the reaction was complete, hexane (30 ml) was added and the reaction mixture was then filtered through Celite. The filtrate was concentrated, and the residue was purified by t.l.c. on silica gel, using benzene as a developer, to give the products. The reaction conditions and the yields of the β-amino enones are summarized in Table 1. The β-amino enones were identifed by comparison of their physical data with those of authentic specimens, which had been obtained by catalytic hydrogenation of the corresponding isoxazole derivatives.[11] For (2a): m.p. 85—87 °C (lit.,[26] m.p. 86—87 °C). For (2b): m.p. 142—143 °C (lit.,[11] 143 °C). For (2c):[26] b.p. 95 °C at 5 Torr; δ$_H$(CCl$_4$) 1.84 (3 H, s), 1.86 (3 H, s), 4.83 (1 H, s), 6.8—7.3 (1 H, br s), and 9.3—9.8 (1 H, br s). For (2d): m.p. 73—74 °C (lit.,[27] 73—74.5 °C). For (2e), 2-(α-aminobenzylidene)-cyclohexane: m.p. 103—105 °C (from hexane–CCl$_4$, 1:1); ν$_{max.}$ 3 051s, 3 395—3 285w, 3 084w, 2 941s, 2 874m, 1 609s, 1 569s, 1 514s, 1 464s, 1 420m, 1 321s, 1 282s, 1 156s, 1 133s, 1 070m, 1 020w, 919w, and 872w; δ$_H$(CCl$_4$) 1.21—1.82 (1 H, m), 1.19—2.30 (4 H, m), 7.27 (5 H, s); m/z 201 (M^+, 84%) and 200 (100) (Found: C, 77.8; H, 7.4; N, 7.05. C$_{13}$H$_{15}$NO requires C, 77.58; H, 7.51; N, 6.96%). For (2f), 2-(α-aminobenzylidene)cy-clopentanone: m.p. 115—116 °C; ν$_{max.}$(CHCl$_3$) 3 472m, 3 550—3 100w, 2 958m, 1 637s, 1 594s, 1 579s, 1 518m, 1 508s, and 1 250s; δ$_H$(CDCl$_3$) 1.60—1.90 (2 H, m), 2.20—2.70 (4 H, m), 7.41 (5 H, br s); m/z 187 (M^+, 100) (Found: C, 79.55; H, 7.05; N, 7.3. C$_{12}$H$_{13}$NO requires C, 79.97; H, 7.00, N, 7.48%).

Reaction of (1a) *with* [Mo(CO)$_3$(MeCN)$_3$].—A solution of [Mo(CO)$_3$(MeCN)$_3$] was prepared from [Mo(CO)$_6$] (528 mg, 2 mmol) in anhydrous acetonitrile (5 ml) under reflux for 4 h under a nitrogen atmosphere.[12] The solution was cooled to ambient temperature, and (1a) (221 mg, 1 mmol) and water (18 mg, 1 mmol) were added; the mixture was then stirred for 6 h. Work-up similar to that described above gave (2a) (180 mg, 81%) (Table 1, entry 9).

Preparation of 2-Benzoyl-3-phenyl-2H-azirine (**8a**).—This was prepared by photoirradiation of (**1a**) according to the method of Ullman *et al.*[8] and had $v_{max.}$(film) 1 776s and 1 667s; δ_H(CCl$_4$) 3.62 (1 H, s) and 7.20—8.20 (10 H, m).

General Procedure for the Reaction of the Azirine (**8a**) *with* [Mo(CO)$_6$].—A solution of (**8a**) (111 mg, 0.5 mmol) and [Mo(CO)$_6$] (132 mg, 0.5 mmol) in acetonitrile (20 ml) was stirred either at ambient temperature or under reflux either in the presence or in the absence of water. The reaction mixture was concentrated and the resulting residue was separated by t.l.c. on silica gel, using benzene as developer, to give the products. The reaction conditions and the yields of the products are summarized in Table 1 (entries 10 and 11).

Preparation of 3,5-Dimethylisoxazolepentacarbonylmolybdenum (**3c**) *by Photoirradiation.*—A solution of (**1c**) (1.97 g, 20 mmol) and [Mo(CO)$_6$] (2.64 g, 10 mmol) in anhydrous THF (100 ml) was irradiated with a Rayonet Photoreactor fitted with RPR-350 nm lamps through a Pyrex filter for 21 h at *ca.* 10 °C. The reaction mixture was concentrated and the residue was chromatographed on silica gel. The fraction eluted with hexane contained 710 mg (36%) of [Mo(CO)$_6$]. The fraction eluted with benzene was recrystallized from hexane to give yellow crystals of (**3c**) {835 mg, 25% yield based on [Mo(CO)$_6$] used}, m.p. 42—45 °C (decomp.); $v_{max.}$ (hexane 2 087w, 1 968m, and 1 928s; $\lambda_{max.}$(MeCN) (log ε) 228 (4.56), 249 (4.68), 300sh (3.36), and 374 (3.52) (Found: C, 36.3; H, 2.2; N, 4.1. C$_{10}$H$_7$NO$_6$Mo requires C, 36.06; H, 2.12; N, 4.20%); the ^{1}H, ^{13}C, and ^{14}N n.m.r. spectra are summarized in Table 2.

Thermal Reaction of (**3c**) *with Water.*—A solution of (**3c**) (333 mg, 1 mmol) and water (18 mg, 1 mmol) in anhydrous acetonitrile (3 ml) was refluxed for 1 h. After the evaporation of the solvent, the residue was purified by t.l.c. on silica gel using chloroform–ethyl acetate (1 : 1) to give the β-amino enone (**2c**) (80 mg, 81%).

General Procedure for the Photoirradiation of the Isoxazoles (**1a**—**d**) *with* [Fe(CO)$_5$].—A solution of the isoxazole (**1**) (1 mmol) and [Fe(CO)$_5$] (236 mg, 1 mmol) in acetonitrile (20 ml) containing water (18 mg, 1 mmol) or in anhydrous benzene (20 ml) was irradiated with a Rayonet Photoreactor fitted with RPR-350 nm lamps or exposed to weak daylight through a Pyrex filter for an adequate period. After the reaction was complete, hexane was added and the reaction mixture was filtered through Celite. The filtrate was concentrated and the resulting residue was separated by t.l.c. using dichloromethane as developer to give the products. The reaction conditions and the yields of the products are summarized in Table 3 (entries 1—7).

General Procedure for the Thermal Reaction of the Isoxazoles (**1a**—**d**) *with* [Fe$_2$(CO)$_9$].—A solution of the isoxazoles (**1**) (1 mmol) and [Fe$_2$(CO)$_9$] (366 mg, 1 mmol) in acetonitrile (20 ml) containing water (18 mg, 1 mmol) or in anhydrous benzene was heated at 50 °C for the appropriate period. After the reaction was complete, hexane was added to the mixture which was then filtered through Celite. The filtrate was concentrated and the resulting residue was separated by t.l.c. on silica gel using dichloromethane as developer to give the products. The reaction conditions and the yields of the products are summarized in Table 3 (entries 8—11).

Photoirradiation of the Azirine (**8a**) *with* [Fe(CO)$_5$].—A solution of (**8a**) (11 mg, 0.5 mmol) and [Fe(CO)$_5$] (117 mg, 0.6 mmol) in acetonitrile (20 ml) containing water (9 mg, 0.5 mmol) was exposed to daylight for 4 h. After the reaction was complete, hexane (20 ml) was added and the mixture filtered through

Celite. The filtrate was concentrated and the resulting residue was separated by t.l.c. on silica gel using benzene as developer to give (**1a**) (43 mg, 39%) and (**2a**) (48 mg, 43%) (Table 3, entry 14).

Photoirradiation of the Azirine (**8a**) *in the Absence of* [Fe(CO)$_5$].—A solution of (**8a**) (110 mg, 0.5 mmol) and water (9 mg, 0.5 mmol) in acetonitrile (20 ml) was exposed to daylight through a Pyrex filter for 4 h. The reaction mixture was concentrated and the residue was purified by t.l.c. on silica gel using benzene as developer to give (**1a**) (23%) and (**8a**) (76 mg, 69%).

Thermal Reaction of the Azirine (**8a**) *with* [Fe$_2$(CO)$_9$].—A solution of (**8a**) (110 mg, 0.5 mmol) and [Fe$_2$(CO)$_9$] (183 mg, 0.5 mmol) in acetonitrile (20 ml) containing water (9 mg, 0.5 mmol) was heated at 50 °C for 40 min. After the reaction was complete, hexane (20 ml) was added to the reaction mixture which was then filtered through Celite. The filtrate was concentrated and the residue was separated by t.l.c. on silica gel using benzene as developer to give (**1a**) (34 mg, 31%) and (**2a**) (63 mg, 57%) (Table 3, entry 15).

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