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Conjugate addition of allylic groups to α,β-unsaturated carbonyl compounds via (η^3-allyl)$Fe(CO)_2NO$ complexes

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Abstract

(η^3-Allyl)$Fe(CO)_2NO$ complexes undergo conjugate addition to α,β-unsaturated carbonyl compounds to give the corresponding δ,ϵ-unsaturated carbonyl compounds in good yields. The reaction of (η^3-1- or 2-trimethylsiloxyallyl) $Fe(CO)_2NO$ complexes with α,β-unsaturated ketones affords 1,6- or 1,5-diketones, respectively. (η^3-1-Acetonylallyl)$Fe(CO)_2NO$ complexes also react with α,β-unsaturated carbonyl compounds to give 1,8-dicarbonyl compounds. The mechanisms and reactivity of these conjugate addition reactions are discussed.

Key words: Iron; Carbonyl; Allyl; Silicon; Nitrosyl; Ketone

1. Introduction

Conjugate addition of carbon nucleophiles to α,β-unsaturated carbonyl compounds is an important reaction in organic synthesis. Many methods have been developed for this reaction [1]. It is known that organometallic compounds, such as organocuprates [2] and organozinc compounds [3], can serve as useful carbon nucleophiles for the selective conjugate addition to α,β-unsaturated ketones. However, these methods have their inherent limitation in applicability. For example, the preparation of organocuprates with some functionalized substituents is often a difficult task [4]. In the field of transition-metal chemistry, it is also known that π-allyl nickel complexes undergo conjugate addition to α,β-unsaturated esters to give a mixture of $\Delta^{5,6}$- and $\Delta^{2,3}$, $\Delta^{5,6}$-unsaturated esters [5]. Yamashita *et al.* reported the synthesis of 1,4-dicarbonyl compounds from organotetracarbonylferrates and α,β-unsaturated carbonyl compounds. This reaction involves insertion of CO in the ferrate complexes and subsequent conjugate addition of an acyl group to α,β-unsaturated carbonyl compounds [6].

(η^3-Allyl)$Fe(CO)_2NO$ complexes are neutral species and undergo various types of reactions. Recently, we have demonstrated that iron complexes of this type can be utilized as useful intermediates for a variety of organic transformations [7–10,14]. The allylic ligands of these complexes react with carbon electrophiles, such as allylic halides and acyl halides, at the less hindered site to give 1,5-dienes and β,γ-unsaturated carbonyl compounds, respectively [7]. These reactions proceed via oxidative coupling of the organic halides on the iron atom of the complexes [7]. The allylic ligands of the iron complexes also react with carbon nucleophiles, such as $NaCH(CO_2Et)_2$, at the less hindered site [10]. This reaction proceeds via a direct attack of the nucleophiles toward the allylic ligands [10]. These results indicate that (η^3-allyl)$Fe(CO)_2NO$ complexes react with both carbon electrophiles and nucleophiles, though via different pathways.

We report here that these iron complexes react smoothly with α,β-unsaturated carbonyl compounds to give δ,ϵ-unsaturated carbonyl compounds in high yields. We also report that (η^3-1-and 2-trimethylsiloxyallyl)Fe-

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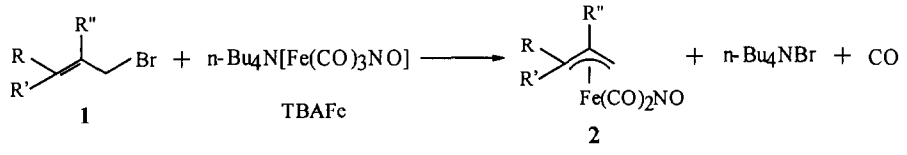
$(CO)_2NO$ complexes and $(\eta^3$-1-acetonylallyl)$Fe(CO)_2$-NO complexes react regioselectively with α,β-unsaturated carbonyl compounds to give 1,5-, 1,6-, and 1,8-dicarbonyl compounds, respectively. The mechanisms and reactivity of these reactions are discussed.

2. Results and discussion

2.1. Synthesis of δ,ϵ-unsaturated carbonyl compounds

We have reported previously that the reaction of 3-halo-1-alkenes **1** with 1 equiv. of $^nBu_4N^+$ $[Fe(CO)_3$-



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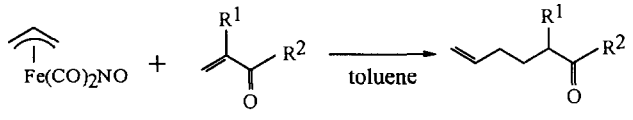
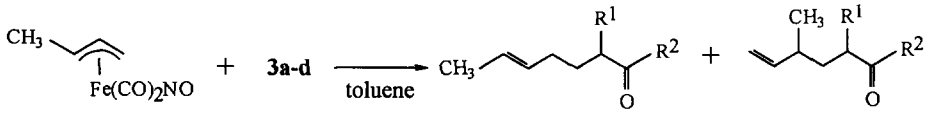


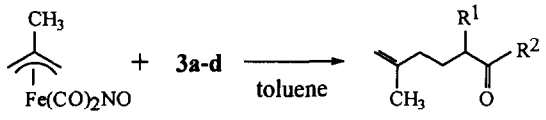
2a **3a-d** **4a-d**

in **3a-d** and **4a-d**:
a: R^1=H, R^2=C_6H_5, **b**: R^1=CH_3, R^2=C_6H_5, **c**: R^1=H, R^2=p-$CH_3C_6H_4$, **d**: R^1=H, R^2=C_2H_5



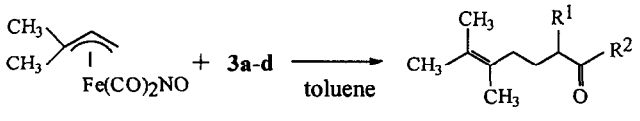
2b **5a-d** **6a-d**

in **5a-d** and **6a-d**:
a: R^1=H, R^2=C_6H_5, **b**: R^1=CH_3, R^2=C_6H_5, **c**: R^1=H, R^2=p-$CH_3C_6H_4$, **d**: R^1=H, R^2=C_2H_5



2c **7a-d**

in **7a-d**:
a: R^1=H, R^2=C_6H_5, **b**: R^1=CH_3, R^2=C_6H_5, **c**: R^1=H, R^2=p-$CH_3C_6H_4$,
d: R^1=H, R^2=C_2H_5



2d **8a-d**

in **8a-d**:
a: R^1=H, R^2=C_6H_5, **b**: R^1=CH_3, R^2=C_6H_5, **c**: R^1=H, R^2=p-$CH_3C_6H_4$,
d: R^1=H, R^2=C_2H_5

Scheme 1.

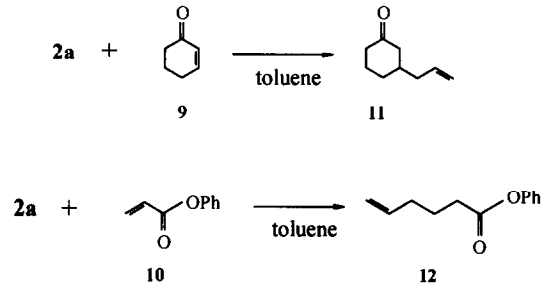
$NO]^-$(TBAFe) gives the $(\eta^3$-allyl)$Fe(CO)_2NO$ complexes **2** in high yields [7]. In this investigation, we found that these iron complexes react with α,β-unsaturated carbonyl compounds in toluene to give δ,ε-unsaturated carbonyl compounds, and this reaction can be accomplished in a single pot without isolating the allyl iron complexes.

The actual reaction was performed as follows: a toluene solution containing allyl bromide (**1a**) and 1 equiv. of TBAFe was stirred at room temperature for 2 h, and an excess of phenyl vinyl ketone (**3a**) was then added. The resulting mixture was stirred for a further 15 h at 80°C. Hydrolysis of the reaction mixture with hydrochloric acid gave 1-phenyl-5-hexen-1-one (**4a**) in 48% isolated yield. The iron complex **2a** also reacted with α,β-unsaturated ketones **3b–d** similarly, giving δ,ε-unsaturated ketones **4b–d** (Scheme 1). The yields of products were significantly improved by adding a small amount (0.1 equiv.) of chlorotrimethylsilane (TMSCl) or iodotrimethylsilane (TMSI) to the reaction mixtures, prior to the addition of α,β-unsaturated carbonyl compounds. The results are given in Table 1. It has been reported that the conjugate addition of organocupper compounds to α,β-unsaturated ketones is facilitated by adding Lewis acids such as TMSCl and

TABLE 1. Preparation of δ,ε-unsaturated carbonyl compounds [a]

Iron complex	α,β-Unsaturated carbonyl	Additive	Products (Yield/% [b])
2a	**3a**	none	**4a** (48)
2a	**3a**	$BF_3 \cdot Et_2O$	**4a** (trace)
2a	**3a**	TMSCl	**4a** (58)
2a	**3a**	TMSI	**4a** (86)
2a	**3b**	TMSCl	**4b** (53)
2a	**3b**	TMSI	**4b** (63)
2a	**3c**	TMSI	**4c** (78)
2a	**3d**	TMSI	**4d** (76)
2b	**3a**	TMSI	**5a** (43) **6a** (26)
2b	**3b**	TMSI	**5b** (63) **6b** (17)
2b	**3c**	TMSI	**5c** (53) **6c** (26)
2b	**3d**	TMSI	**5d** (48) **6d** (20)
2c	**3a**	TMSI	**7a** (52)
2c	**3b**	TMSI	**7b** (43)
2c	**3c**	TMSI	**7c** (58)
2c	**3d**	TMSI	**7d** (40)
2d	**3a**	TMSI	**8a** (69)
2d	**3b**	TMSI	**8b** (65)
2d	**3c**	TMSI	**8c** (72)
2d	**3d**	TMSI	**8d** (64)
2a	**9**	none	**11** (38)
2a	**10**	TMSI	**12** (68)

[a] Allyl bromides: 2 mmol, TBAFe: 2 mmol, **3**: 4 mmol, TMSI: 0.2 mmol, toluene: 10 cm^3, temp: 80°C, time: 15 h.
[b] Isolate yields based on allyl bromides used.

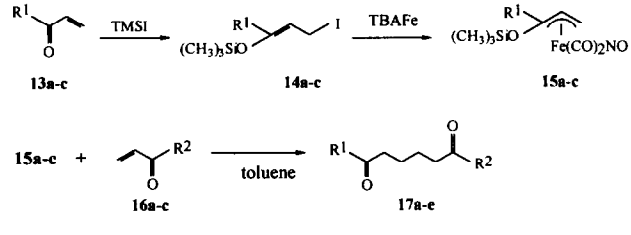


Scheme 2.

$BF_3 \cdot$ etherate to the reaction systems [11]. However, in our case the addition of $BF_3 \cdot$ etherate suppressed the reaction (Table 1).

The reaction of the iron complex **2b** with **3a–d** in toluene gave isomeric mixtures of δ,ε-unsaturated ketones **5a–d** and **6a–d**. In these cases, the reaction occurred preferentially at a less hindered site of the allylic ligand of **2b**, and the formation of **5a–d** predominated. The reaction of the iron complex **2c** with **3a–d** under similar conditions afforded solely the unsaturated ketones **7a–d** in moderate yields. From the iron complex **2d** and **3a–d**, only **8a–d** were obtained and no other regioisomers were isolated, indicating that the reaction occurred exclusively at a less hindered site of the allylic ligand. The results are included in Table 1.

The iron complex **2a** reacted also with 2-cyclohexen-1-one (**9**) and phenyl acrylate (**10**) to give the corresponding ketone **11** and ester **12**, respectively, in moderate yields (Scheme 2). The results are also given in Table 1. However, the iron complexes did not react with aldehydes and ketones, such as propanal, benzaldehyde, acetophenone and 2-butanone, not even in the presence of TMSI. Furthermore, there was no indication that the allylic ligands of iron complexes are added to the carbonyl carbon of any of the compounds studied. These results suggest that the allylic ligands act as very soft nucleophiles.



Scheme 3.

TABLE 2. Preparation of 1,6-diketones [a]

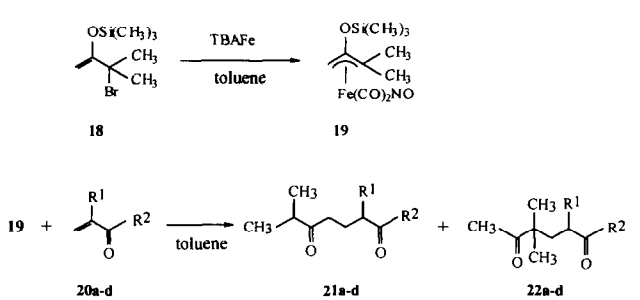
Complex	α,β-Unsaturated ketone	Product (Yield/% [b])	
15a	**16a**	**17a**: $R^1 = C_6H_5$ $R^2 = C_6H_5$	(93)
15b	**16b**	**17b**: $R^1 = p\text{-}CH_3C_6H_4$ $R^2 = p\text{-}CH_3C_6H_4$	(83)
15c	**16c**	**17c**: $R^1 = C_2H_5$ $R^2 = C_2H_5$	(56)
15c	**16a**	**17d**: $R^1 = C_2H_5$ $R^2 = C_6H_5$	(46)
15a	**16b**	**17e**: $R^1 = C_6H_5$ $R^2 = p\text{-}CH_3C_6H_4$	(81)

[a] Complexes **15**: 2 mmol, **16**: 2 mmol, toluene: 10 cm^3, temp: 80°C, time: 15 h.
[b] Isolated yields based on complexes **15** used.

2.2. Synthesis of 1,6-diketones

We have shown that (η^3-1-trimethylsiloxyallyl)-$Fe(CO)_2NO$ complexes can be prepared in high yields by the reaction of TBAFe with 1 equiv. of 3-iodo-1-trimethylsiloxy-1-alkenes, that are derived from α,β-unsaturated ketones and TMSI [10]. We now found that the iron complexes **15a–c**, which had been prepared from 3-iodo-1-trimethylsiloxy-1-alkenes **14a–c** and TBAFe, react with α,β-unsaturated ketones **16a–c** in toluene at 80°C for 15 h to give the 1,6-diketones **17a–e** in good yields (Scheme 3). The results are shown in Table 2. In these cases, the addition of the 1-siloxyallylic ligands of the iron complexes again occurred at their less hindered sites. The regioselectivity in this reaction was extremely high, so that only a single product was obtained in every case. The reaction could be carried out in a single pot, starting with α,β-unsaturated ketones **13a–c** without isolating any of intermediates.

The above results indicate that the (η^3-1-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes serve as a β-acyl carbanion equivalent synthon (homoenolate). The homoenolate equivalent synthon had also been generated from trimethylsiloxycyclopropanes by using palladium complexes as a catalyst [12,13].



in **20a-d**, **21a-d**, and **22a-d**:
a: R^1=H, R^2=C_6H_5, **b**: R^1=CH_3, R^2=C_6H_5, **c**: R^1=H, R^2=p-$CH_3C_6H_4$, **d**: R^1=H, R^2=C_2H_5

Scheme 4.

TABLE 3. Preparation of 1,5-diketone [a]

α,β-Unsaturated ketone	Products (Yields/% [b])	
20a	**21a** (46)	**22a** (12)
20b	**21b** (38)	**22b** (4)
20c	**21c** (42)	**22c** (8)
20d	**21d** (36)	**22d** (8)

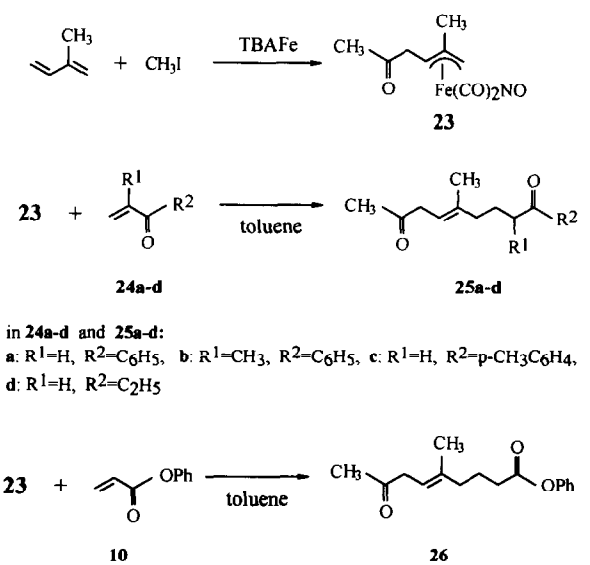
[a] **18**: 2 mmol, TBAFe: 2 mmol, **20**: 4 mmol, toluene: 10 cm^3 temp: 80°C, time: 15 h.
[b] Isolated yields based on **18** used.

2.3. Synthesis of 1,5-diketones

The (η^3-1,1-dimethyl-2-trimethylsiloxyallyl)$Fe(CO)_2$-NO complex (**19**) was prepared from 3-bromo-3-methyl-2-trimethylsiloxy-1-butene (**18**) and TBAFe by the method previously reported [10]. The reaction of **19** with α,β-unsaturated ketones **20a–d** in toluene at 80°C for 15 h gave isomeric mixtures of 1,5-diketones **21a–d** and **22a–d** (Scheme 4). In this reaction, the allylic ligands of **19** reacted preferentially at the less hindered sites and the formation of **21a–d** predominated. The results are given in Table 3. These results suggest that (η^3-2-trimethylsiloxyallyl)$Fe(CO)_2NO$ complexes serve as a soft α-acyl carbanion equivalent synthon.

2.4. Synthesis of 1,8-dicarbonyl compounds

The (η^3-1-acetonylallyl)$Fe(CO)_2NO$ complex (**23**) was prepared from 2-methyl-1,3-butadiene, iodomethane and TBAFe by the method previously reported [7,14]. The reaction of **23** with α,β-unsaturated ketones **24a–d** in toluene at 80°C for 15 h gave 1,8-diketones **25a–d** in moderate yields (Scheme 5). The iron complex **23** reacted also with phenyl acrylate (**10**) to



in **24a-d** and **25a-d**:
a: R^1=H, R^2=C_6H_5, **b**: R^1=CH_3, R^2=C_6H_5, **c**: R^1=H, R^2=p-$CH_3C_6H_4$, **d**: R^1=H, R^2=C_2H_5

Scheme 5.

TABLE 4. Preparation of 1,8-dicarbonyl compound [a]

α,β-Unsaturated carbonyl	Products (Yields/% [b])
24a	**25a** (38)
24b	**25b** (32)
24c	**25c** (41)
24d	**25d** (48)
10	**26** (32)

[a] Complexes **23**: 3 mmol, **24** and **10**: 5 mmol, toluene: 10 cm^3 temp: 80°C, time: 15 h.
[b] Isolated yields based on **23** used.

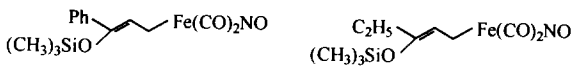
give the corresponding ester **26** in moderate yield (Scheme 5). The results are shown in Table 4. In these reactions, the allylic ligand of the iron complex reacted regioselectively with α,β-unsaturated carbonyl compounds at the less hindered site, giving single products without containing any regioisomers.

The significant feature of the conjugate addition reactions to α,β-unsaturated carbonyl compounds by the use of (η^3- allyl)$Fe(CO)_2NO$ complexes is that the reactions are tolerant for a wide variety of functional groups on the allylic ligands of iron complexes, and could consequently find wide application in organic synthesis.

2.5. Mechanistic consideration

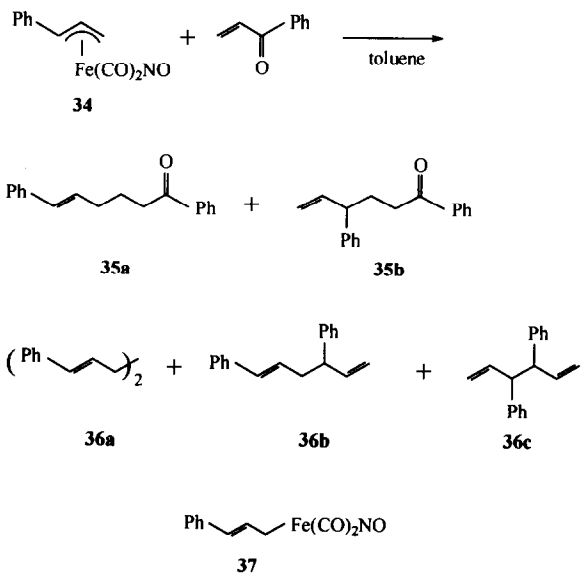
A possible mechanism for the conjugate addition reactions described in the preceding sections is shown in Scheme 6. The key step is the α,β-unsaturated carbonyl compound-induced conversion of η^3-allylic iron complexes **27** into η^1-allylic iron complexes **29**. Insertion of the η^1-allylic groups into the activated carbon–carbon double bond of α,β-unsaturated carbonyl compounds, followed by acid hydrolysis of enolate complexes **30**, gives δ,ε-unsaturated carbonyl compounds **31**. A similar mechanism had been proposed for reactions involving η^3-allyl nickel complexes [15].

Although we do not have unequivocal evidence for this mechanism at present, this mechanism explains all the experimental results that we have collated so far. Firstly, the addition of TMSI to the reaction systems facilitated the conjugate addition reactions (Table 1). This can be accounted for on the basis of the reasonable assumption that the electrophilicity of α,β-unsaturated carbonyl compounds can be enhanced by coordination of TMSI to the carbonyl oxygen (see 29 in Scheme 6). Secondly, the reactivity of the iron complex **15a** in the conjugate addition to phenyl vinyl ketone was higher than that of the iron complex **15c** (Table 2). This can be understood by considering the reactivity of these complexes in the conversion into their η^1-allylic iron complexes. The conversion of **15a** into η^1-complex **32** is supposed to occur more efficiently than the conversion of **15c** into the corresponding η^1-complex **33**: note that **32** is thermodynamically more stable than **33**.

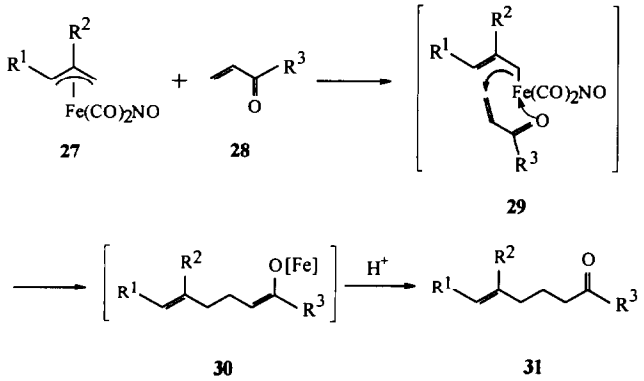


32 **33**

In this connection, it may be important to note that the reaction of (η^3-1-phenylallyl)$Fe(CO)_2NO$ (**34**) with phenyl vinyl ketone (**3a**) in toluene under similar conditions as above gave a small amount (10%) of conjugate addition products **35a–b** (**35a**:**35b** = 7:5), accompaning the formation of a large amount (89%) of



Scheme 7.



Scheme 6.

1,5-dienes **36a–c** (**36a**:**36b**:**36c** = 45:41:3). The major products **36a–c** are produced supposedly via the η^1-allyl iron complex **37** (Scheme 7). This result also suggests that the phenyl substituent at 1-position of the allylic ligands promotes the conversion of a η^3- into a η^1-complex.

The other noteworthy result is that the reactivity of η^3-allylic iron complexes was suppressed by adding phosphines and phosphites into the reaction systems. For example, in the reaction of **2a** with **3b** in toluene at 80°C for 15 h, the yield of **4b** was lowered markedly by the addition of an equivalent amount of PPh_3 or $P(OPh)_3$ to **2a**: the yield of **4a** was 38% in the absence of any additives, but it fell to 6% in the presence of PPh_3 and to 3% in the presence of $P(OPh)_3$. These results can be explained in terms of (η^3-allyl)$Fe(CO)_2$-NO complexes being stabilized by replacement of one of two CO ligands by a phosphorus ligand. In fact, (η^3-C_3H_5)$Fe(CO)_2NO$ (**2a**) was decomposed with evolution of CO at much faster rate than (η^3-C_3H_5)$Fe(CO)(NO)(PPh_3)$ upon heating the iron complexes in toluene at 80°C. Thus, the results obtained so far for the conjugate addition reactions are consistent with the mechanism shown in Scheme 6.

3. Experimental details

3.1. General

IR spectra were obtained with a Jasco FT/IR-8900 spectrometer. NMR spectra were recorded on a Jeol EX90A spectrometer. Samples were dissolved in $CDCl_3$ and chemical shift values (ppm) were relative to tetramethylsilane. Elemental analyses were carried out on a Yanaco MT-3 CHN corder. GLC analyses were performed with a Shimadzu GC 14B chromatograph using a column (3 mm i.d. × 1 m) packed with SE 30 (10%).

3.2. Material

Tetrabutylammonium tricarbonylnitrosylferrate (TBAFe), $^nBu_4N[Fe(CO)_3NO]$, was prepared by modifying the method previously reported [7].

A solution of $Fe(CO)_5$ (60 mmol) in CH_2Cl_2 (20 cm^3) was added to a mixture of $NaNO_2$ (60 mmol) and $^nBu_4NBr$ (60 mmol) in water (20 cm^3). The resulting mixture was stirred under argon at room temperature for 2 h. The organic layer was separated, washed with water, and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave $^nBu_4N[Fe(CO)_3NO]$ (TBAFe) as yellow crystals in 86% yield; mp 56–56.5°C. IR (KBr) 1980, 1850 cm^{-1} (CO), 1630 cm^{-1} (NO).

3-Bromo-3-methyl-2-trimethylsiloxy-1-butene (**18**) [16], phenyl vinyl ketone (**3a**) [17], *p*-tolyl vinyl ketone (**3c**) [17], 2-methyl-1-phenyl-2-propen-1-one (**3b**) [17],and phenyl acrylate (**10**) [18] were prepared by the methods reported in the literature. Other chemicals were purchased and purified under argon prior to use.

3.3. Preparation of δ,ε-unsaturated ketones and esters. A typical procedure

A mixture of 3-bromo-1-propene **1a** (2 mmol) and TBAFe (2 mmol) in toluene (10 cm^3) was stirred at room temperature for 3 h under argon. During this period, (η^3-allyl)$Fe(CO)_2NO$ (**2a**) was formed with evolution of one molar equiv. (2 mmol) of CO to TBAFe. To this solution, phenyl vinyl ketone (**3a**, 4 mmol) and iodotrimethylsilane (TMSI, 0.2 mmol) was added. The resulting mixture was then heated at 80°C for 15 h, cooled, hydrolyzed with 4 M hydrochloric acid, and extracted with ether (30 cm^3). The ether extract was washed successively with 1 M aqueous NaOH (30 cm^3) and water, and dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel. Elution with hexane–ethyl acetate (97.5/2.5) gave 1-phenyl-5-hexen-1-one (**4a**) in 86% yield.

4a: oil; IR (neat) 3045, 2935, 1680, 990, 910, 748, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.65–2.40 (4H, m), 2.88 (2H, t, J = 7.0 Hz), 4.84–5.10 (2H, m), 5.50–5.88 (1H, m), 7.47–7.51 (3H, m), 7.90–8.00 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.3, 33.1, 37.7, 115.2, 128.0, 128.5, 132.8, 136.0, 138.0, 200.2. Found; C, 82.49; H, 7.92%; Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

4b: oil; IR (neat) 3045, 2978, 2935, 1676, 990, 910, 750, 688 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (3H, d, J = 7.0 Hz), 1.77–2.29 (4H, m), 3.50 (1H, m), 4.94–5.10 (2H, m), 5.48–5.85 (1H, m), 7.39–7.47 (3H, m), 7.90–8.00 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.3, 31.5, 32.6, 39.8, 115.2, 128.3, 128.6, 132.8, 136.8, 138.1, 200.2. Found; C, 82.56; H, 8.57%; Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

4c: oil; IR (neat) 3045, 2935, 1680, 990, 910, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63–2.32 (4H, m), 2.40 (3H, s), 2.95 (2H, t, J = 7.0 Hz), 4.92–5.06 (2H, m), 5.48–5.89 (1H, m), 7.24 (2H, d, J = 8.13 Hz); 7.85 (2H, d, J = 8.13 Hz); ^{13}C NMR ($CDCl_3$) δ 23.5, 24.7, 33.3, 35.4, 115.5, 126.7, 131.4, 134.2, 138.8, 143.5, 199.2. Found; C, 82.61; H, 8.71%; Calcd for $C_{13}H_{16}O$: C,82.93; H, 8.57%.

4d: oil; IR (neat) 2978, 2935, 1726, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (3H, t, J = 7.0 Hz), 1.62–2.51 (8H, q, J = 7.0 Hz), 4.90–5.09 (2H, m), 5.58–5.86 (1H, m); ^{13}C NMR ($CDCl_3$) δ 12.4, 21.9, 31.2, 46.6, 47.1, 114.2, 138.6, 210.2. Found; C, 75.87; H, 11.21%; Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

5a: oil; IR (neat) 3045, 2935, 1686, 960, 748, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (3H, m), 1.72–2.10 (4H, m), 2.86 (2H, t, J = 7.0 Hz), 5.24–5.41 (2H, m, $J(H–H)$ = 15.6 Hz), 7.21–7.31 (3H, m), 7.72–7.83 (2H,

m); ^{13}C NMR ($CDCl_3$) δ 20.2, 24.8, 32.3, 37.6, 121.6, 128.1, 128.6, 132.8, 136.7, 138.4, 202.0. Found; C, 82.72; H, 8.61%; Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

5b: oil; IR(neat) 3045, 2978, 2935, 1685, 965, 750, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (3H, d, J = 7.0 Hz), 1.68 (3H, m), 1.76–2.10 (4H, m), 3.45 (1H, m), 5.32–5.44 (2H, m, J(H–H) = 15.7 Hz), 7.22–7.35 (3H, m), 7.72–7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.3, 20.2, 30.4, 32.8, 39.7, 123.5, 128.0, 128.5, 132.8, 133.2, 136.5, 204.5. Found; C, 83.31; H, 8.93%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

5c: oil; IR (neat) 3045, 2935, 1678, 965, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.68 (3H, m), 1.78–2.26 (4H, m), 2.42 (3H, s), 2.90 (2H, t, J = 7.0 Hz), 5.32–5.42 (2H, m, J(H–H) = 15.6 Hz), 7.25 (2H, d, J = 8.04 Hz), 7.89 (2H, d, J = 8.04 Hz); ^{13}C NMR ($CDCl_3$) δ 20.4, 22.3, 24.8, 32.1, 39.0, 125.6, 128.1, 128.5, 129.2, 134.2, 143.8, 199.2. Found; C, 83.41; H, 8.79%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

5d; oil; IR (neat) 2978, 2935, 1736, 965 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (3H, t, J = 7.0 Hz), 1.68 (3H, m), 1.72–2.42 (8H, m), 5.30–5.45 (2H, m, J(H–H) = 15.2 Hz); ^{13}C NMR ($CDCl_3$) δ 12.4, 17.8, 21.9, 31.2, 46.6, 47.1, 123.9, 129.2, 210.2. Found; C, 76.93; H, 11.52%; Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

6a: oil; IR (neat) 3045, 2935, 1684, 990, 910, 748, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (3H, d, J = 7.0 Hz), 1.70–2.15 (3H, m), 2.81 (2H, t, J = 7.0 Hz), 4.90–4.98 (2H, m), 5.52–5.60 (1H, m), 7.20–7.35 (3H, m), 7.71–7.79 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.9, 24.7, 33.7, 36.2, 115.7, 128.5, 129.0, 132.0, 136.0, 138.4, 203.0. Found; C, 82.69; H, 8.46%; Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

6b: oil; IR (neat) 3045, 2978, 2935, 1680, 990, 910, 750, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12–1.20 (6H, m), 1.78–2.35 (3H, m), 3.45 (1H, m), 4.92–5.06 (2H, m), 5.62–5.81 (1H, m), 7.20–7.34 (3H, m), 7.70–7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.9, 22.3, 32.0, 36.2, 40.5, 115.7, 128.0, 128.5, 132.8, 136.5, 139.9, 204.0. Found; C, 83.04; H, 8.82%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

6c: oil; IR (neat) 3045, 2935, 1680, 990, 910, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (3H, d, J = 7.0 Hz), 1.78–2.42 (3H, m), 2.38 (3H, s), 2.90 (2H, t, J = 7.0 Hz), 4.92–5.03 (2H, m), 5.62–5.81 (1H, m), 7.25 (2H, d, J = 8.04 Hz), 7.89 (2H, d, J = 8.04 Hz); ^{13}C NMR ($CDCl_3$) δ 17.8, 22.3, 24.6, 36.2, 37.7, 113.5, 128.1, 128.8, 129.9, 139.9, 143.9, 199.2. Found; C, 83.40; H, 8.77%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

6d: oil; IR (neat) 2978, 2935, 1735, 990, 910 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (3H, t, J = 7.0 Hz), 1.21 (3H, d, J = 7.0 Hz), 1.69–2.38 (7H, m), 4.82–5.10 (2H, m), 5.51–5.80 (1H, m); ^{13}C NMR ($CDCl_3$) δ 12.4, 22.3, 23.0, 32.7, 46.5, 47.1, 112.0, 146.9, 211.2. Found; C, 77.30; H, 11.50%; Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

7a: oil; IR (neat) 3045, 2935, 1680, 748, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67 (3H, br s), 1.78–2.20 (4H, m), 2.89 (2H, t, J = 7.0 Hz), 4.61–4.72 (2H, m), 7.28–7.40 (3H, m), 7.75–7.80 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.0, 22.3, 37.2, 37.9, 110.7, 128.0, 128.6, 132.9, 136.0, 145.1, 200.3. Found; C, 82.98; H, 8.76%; Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

7b: oil; IR (neat) 3045, 2978, 2935, 1680, 750, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.12 (3H, d, J = 7.0 Hz), 1.67 (3H, br s), 1.80–2.25 (4H, m), 3.50 (1H, m), 4.60–4.70 (2H, m), 7.28–7.35 (3H, m), 7.72–7.80 (2H,m); ^{13}C NMR ($CDCl_3$) δ 17.3, 22.0, 31.5, 32.6, 39.8, 110.7, 128.0, 128.7, 132.9, 136.6, 145.1, 200.3. Found; C, 83.36; H, 8.71%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

7c: oil; IR (neat) 3045, 2935, 1680, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.56 (3H, br s), 1.87–2.25 (4H, m), 2.41 (3H, s), 2.92 (2H, t, J = 7.0 Hz), 4.62–4.72 (2H, m), 7.25 (2H, d, J = 8.05 Hz), 7.98 (2H, d, J = 8.05 Hz); ^{13}C NMR ($CDCl_3$) δ 21.7, 22.2, 25.4, 31.6, 39.4, 111.0, 129.2, 130.1, 134.0, 145.1, 145.5, 199.2. Found; C, 83.09; H, 8.87%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

7d: oil; IR (neat) 2978, 2935, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (3H, t, J = 7.0 Hz), 1.60 (3H, br s), 1.80–2.35 (8H, m), 4.60–4.65 (2H, m); ^{13}C NMR ($CDCl_3$) δ 12.4, 22.0, 22.5, 32.5, 46.5, 47.1, 109.0, 147.0, 210.8. Found; C, 77.24; H, 11.43%; Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50%.

8a: oil; IR (neat) 3045, 2935, 1680, 748, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.66 (6H, br s), 1.78–2.27 (4H, m), 2.89 (2H, t, J = 7.0 Hz), 5.25–5.32 (1H, m), 7.22–7.33 (3H, m), 7.70–7.84 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.6, 23.4, 26.1, 29.8, 38.6, 124.0, 128.3, 128.5, 132.0, 132.8, 136.0, 203.7. Found; C, 83.05; H, 8.89%; Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97%.

8b: oil; IR (neat) 3045, 2978, 2935, 1680, 750, 688 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (3H, d, J = 7.0 Hz), 1.66 (6H, br s), 1.78–2.27 (4H, m), 3.48 (1H, m), 5.25–5.33 (1H, m), 7.24–7.44 (3H, m), 7.78–7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.3, 17.5, 23.1, 26.1, 29.3, 41.6, 124.4, 128.0, 128.3, 131.6, 132.8, 136.0, 203.5. Found; C, 83.32; H, 9.05%; Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32%.

8c: oil; IR (neat) 3045, 2935, 1680, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.69 (6H, br s), 1.78–2.28 (4H, m), 2.40 (3H, s), 2.86 (2H, t, J = 7.0 Hz), 5.35–5.40 (1H, m), 7.25 (2H, d, J = 8.06 Hz), 8.85 (2H, d, J = 8.06 Hz); ^{13}C NMR ($CDCl_3$) δ 17.0, 22.1, 23.4, 26.1, 29.5, 37.6, 124.0, 128.2, 129.2, 130.2, 132.5, 147.5, 202.5. Found; C, 83.43; H, 9.21%; Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32%.

8d: oil; IR (neat) 2978, 2935, 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (3H, t, J = 7.0 Hz), 1.66 (6H, br s), 1.75–2.39 (8H, m), 5.15–5.25 (1H, m); ^{13}C NMR

($CDCl_3$) δ 12.5, 17.1, 21.9, 25.5, 31.0, 46.5, 47.1, 124.6, 131.6, 210.8. Found; C, 77.94; H, 11.53%; Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76%.

11: oil; IR (neat) 3040, 2940, 1736, 1196, 1135, 992, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20–2.30 (11H, m), 4.86–4.92 (2H, m), 5.62–5.54 (1H, m); ^{13}C NMR ($CDCl_3$) δ 24.8, 30.5, 38.5, 40.5, 41.1, 47.4, 116.5, 135.4, 211.2. Found; C, 78.34; H, 10.15%; Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21%.

12: oil; IR (neat) 2950, 2915, 1708, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87–1.99 (2H, m), 2.17 (2H, q, $J = 7.0$ Hz), 2.72 (2H, t, $J = 7.0$ Hz), 4.85–5.06 (2H, m), 5.40–5.60 (1H, m), 7.16–7.24 (5H, m); ^{13}C NMR ($CDCl_3$) δ 23.6, 32.0, 34.6, 115.7, 121.6, 125.7, 125.8, 138.5, 150.7, 171.6. Found; C, 75.41; H, 7.02%; Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%.

3.4. Preparation of 1,6-diketones

3.4.1. Symmetrical 1,6-diketones

A mixture of an α,β-unsaturated ketone **13a** (4 mmol) and TMSI (2.5 mmol) in toluene (10 cm^3) was stirred at room temperature for 3 h under argon. TBAFe (2 mmol) was added and the resulting mixture was stirred at room temperature for a further 3 h. During this period, (η^3-1-trimethylsiloxyallyl)iron complex **15a** was formed with evolution of 1 equiv. (2 mmol) of CO to TBAFe. The resulting mixture was heated at 80°C for 15 h, cooled, treated with 4 M hydrochloric acid, and then extracted with ether (30 cm^3). The extract was washed with 1 M aqueous NaOH solution (30 cm^3) and water, and then dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on silica gel. Elution of hexane–ethyl acetate (95/5) gave 1,6-diketone (**17**) in good yields.

3.4.2. Unsymmetrical 1,6-diketones

A mixture of ethyl vinyl ketone (**13c**, 2 mmol) and TMSI (2.5 mmol) in toluene (10 cm^3) was stirred at room temperature for 3 h under argon. TBAFe (2 mmol) was added and the resulting mixture was stirred at room temperature for 3 h. During this period, (η^3-1-trimethylsiloxyallyl)iron complex **15c** was formed with evolution of 1 equiv. (2 mmol) of CO to TBAFe. Then, phenyl vinyl ketone (**16a**, 2 mmol) was added to the above mixture without isolating **15c**. The resulting mixture was heated at 80°C for 15 h, cooled, treated with 4 M hydrochloric acid, and then extracted with ether (30 cm^3). The extract was washed with 1 M aqueous NaOH solution (30 cm^3) and water, and then dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on silica gel. Elution of hexane–ethyl acetate (95:5) gave the 1,6-diketone **17d** in moderate yield.

17a: mp 110°C; IR (KBr) 3035, 2937, 1683, 1596, 731, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (4H, m), 2.93 (4H, m), 7.35–7.45 (6H, m), 7.84–8.87 (4H, m); ^{13}C NMR ($CDCl_3$) δ 23.8, 38.3, 127.9, 128.2, 132.5, 136.8, 199.9. Found; C, 81.25; H, 6.62%; Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81%.

17b: mp 151–152°C; IR (KBr) 3035, 2975, 1680, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80–1.87 (4H, m), 2.41 (6H, s), 3.00 (4H, m), 7.25 (4H, d, $J = 8.05$ Hz), 8.86 (4H, d$J = 8.05$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.4, 23.9, 38.3, 128.5, 128.6, 134.5, 143.8, 199.8. Found; C, 81.87; H, 7.60%; Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%.

17c: mp 52°C; IR (KBr) 2973, 1708, 1459 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (6H, t, $J = 7.46$ Hz), 1.54–1.59 (4H, m), 2.38–2.46 (8H, m); ^{13}C NMR ($CDCl_3$) δ 8.40, 23.34, 35.85, 42.04, 211.3. Found; C, 70.71; H, 10.49%; Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

17d: mp 84°C; IR (KBr) 3050, 2975, 2935, 1708, 1680, 765, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (3H, t, $J = 7.0$ Hz), 1.66–1.82 (4H, m), 2.28 (2H, q, $J = 7.0$ Hz), 2.46 (2H, t, $J = 7.0$ Hz), 2.93 (2H, t, $J = 7.0$ Hz), 7.35–7.45 (3H, m), 7.84–7.88 (2H, m); ^{13}C NMR ($CDCl_3$) δ 8.80, 23.4, 23.8, 35.9, 38.3, 42.5, 128.4, 128.6, 132.9, 136.9, 200.2, 211.0. Found; C, 77.39; H, 8.36%; Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

17e: mp 122°C; IR (KBr) 3045, 2935, 1680, 810, 765, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60–1.78 (4H, m), 2.41 (3H, s), 2.93 (2H, t, $J = 7.0$ Hz), 3.00 (2H, t, $J = 7.0$ Hz), 7.25 (2H, d, $J = 8.05$ Hz), 7.36–7.45 (3H, m), 7.84–7.87 (2H, m), 8.76 (2H, d, $J = 8.05$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.4, 23.8, 23.9, 38.3, 38.5, 127.9, 128.2, 128.5, 128.6, 132.5, 134.5, 136.8, 143.8, 199.8, 199.9. Found; C, 81.14; H, 7.09%; Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%.

3.5. Preparation of 1,5-diketones

A mixture of 3-bromo-3-methyl-2-trimethylsiloxy-1-butene (**18**, 2 mmol) and TBAFe (2 mmol) in toluene (10 cm^3) was stirred at room temperature for 3 h under argon. During this period, (η^3-2-trimethylsiloxyallyl) iron complex **19** was obtained with evolution of 1 equiv. (2 mmol) of CO to TBAFe. To this solution, phenyl vinyl ketone (**20a**, 4 mmol) was added. The resulting mixture was heated at 80°C for 15 h, cooled, hydrolyzed with 4 M hydrochloric acid, and then extracted with ether (30 cm^3). The ether extract was washed successively with 1 M aqueous NaOH solution (30 cm^3) and water, and then dried over Na_2SO_4. The solvent was evaporated, and the residue was chromatographed on silica gel. Elution of hexane–ethyl acetate (95:5) gave 6-methyl-1-phenylheptane-1,5-di-

one (**21a**) and 4,4-dimethyl-1-phenylhexane-1,5-dione (**22a**) in moderate yields.

21a: oil; IR (neat) 3045, 2980, 2935, 1720, 1680, 765, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12 (6H, d, $J = 7.0$ Hz), 2.00–2.12 (2H, m), 2.44 (2H, t, $J = 7.0$ Hz), 2.80 (1H, m), 3.70 (2H, t, $J = 7.0$ Hz), 7.30–7.52 (3H, m), 7.80–7.93 (2H, m); ^{13}C NMR ($CDCl_3$) δ 18.2, 33.9, 40.3, 41.6, 46.1, 128.6, 128.7, 132.9, 136.1, 200.2, 212.0. Found; C, 77.35; H, 8.13; Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

21b: oil; IR (neat) 3045, 2980, 2935, 1720, 1680, 766, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14–1.24 (9H, m), 2.08 (2H, q, $J = 7.0$ Hz), 2.44 (2H, t, $J = 7.0$ Hz), 2.86 (1H, m), 3.85 (1H, m), 7.27–7.45 (3H, m), 7.82–7.98 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.3, 18.2, 33.9, 40.3, 41.6, 46.5, 128.4, 128.6, 132.7, 136.5, 200.2, 212.3. Found; C, 77.24; H, 8.61%; Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

21c: oil; IR (neat) 3045, 2975, 2935, 1720, 1680, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (6H, d, $J = 7.0$ Hz), 2.06–2.19 (2H, m), 2.38 (2H, t, $J = 7.0$ Hz), 2.41 (3H, s), 2.78 (1H, m), 3.02 (2H, t, $J = 7.0$ Hz), 7.21 (2H, d, $J = 8.10$ Hz), 8.08 (2H, d, $J = 8.10$ Hz); ^{13}C NMR ($CDCl_3$) δ 18.2, 22.4, 24.0, 40.3, 41.6, 46.5, 128.5, 128.6, 134.5, 143.2, 200.2, 212.2. Found; C, 77.81; H, 8.59%; Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

21d: oil; IR (neat) 2980, 2935, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (3H, t,$J = 7.0$ Hz), 1.13 (6H, d, $J = 7.0$ Hz), 1.89–2.00 (2H, m), 2.10 (2H, q, $J = 7.0$ Hz), 2.45 (4H, m), 2.78 (1H, m); ^{13}C NMR ($CDCl_3$) δ 8.0, 18.2, 31.8, 35.5, 40.2, 40.3, 41.6, 210.7, 212.1. Found; C, 70.70; H, 10.48%; Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

22a: oil; IR (neat) 3045, 2980, 2935, 1720, 1680, 765, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (6H, s), 2.10 (3H, s), 2.24 (2H, t,$J = 7.0$ Hz), 3.72 (2H, t,$J = 7.0$ Hz), 7.30–7.52 (3H, m), 7.80–7.98 (2H, m); ^{13}C NMR ($CDCl_3$) δ 28.0, 29.4, 34.0, 44.6, 45.8, 128.0, 128.5, 132.9, 136.5, 200.0, 206.8. Found; C, 77.08; H, 8.45%; Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

22b: oil; IR (neat) 3045, 2980, 2935, 1728, 1678, 765, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (6H, s), 1.13 (3H, d, $J = 7.0$ Hz), 2.10 (3H, s), 2.26 (2H, d, $J = 7.0$ Hz), 3.85 (1H, m), 7.26–7.45 (3H, m), 7.78–7.95 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.8, 28.0, 29.2, 34.5, 45.8, 46.5, 128.2, 128.6, 132.8, 136.0, 200.0, 206.8; Found; C, 77.39; H, 8.77%; Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

22c: oil; IR (neat) 3045, 2975, 2935, 1730, 1680, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (6H, s), 2.09 (3H, s), 2.12 (2H, t, $J = 7.0$ Hz), 2.40 (3H, s), 3.02 (2H, t, $J = 7.0$ Hz), 7.20 (2H, d, $J = 8.12$ Hz), 8.02 (2H, d, $J = 8.12$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.4, 28.0, 29.0, 39.5, 44.0, 45.8, 128.5, 128.6, 134.6, 143.0, 200.0, 212.0. Found; C, 77.75; H, 8.50%; Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68%.

22d: oil; IR (neat) 2980, 2935, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (3H, t, $J = 7.0$ Hz), 1.09 (6H, s), 2.02 (3H, s), 2.09–2.28 (4H, m), 2.45 (2H, t, $J = 7.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 8.0, 28.0, 29.4, 32.0, 35.5, 40.2, 45.5, 206.8, 210.5. Found; C, 70.85; H, 10.80; Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

3.6. Preparation of 1,8-dicarbonyl compounds

A mixture of iodomethane (4.5 mmol), 2-methyl-1,3-butadiene (3 mmol) and TBAFe (3 mmol) in toluene (10 cm^3) was stirred at room temperature for 3 h, and then α,β-unsaturated ketone **24a** (5 mmol) and TMSI (0.2 mmol) were added. The resulting mixture was further stirred at 80°C for 20 h, acidified with 4 M hydrochloric acid, and extracted with ether (30 cm^3). The ether extract was washed with water, dried (Na_2SO_4), and concentrated. The residue was purified by chromatography on silica gel with hexane–ethyl acetate (95 : 5), giving 4-nonene-2,9-dione derivative **25a** in moderate yield.

25a: oil; IR (neat) 3058, 2960, 1756, 1682, 700, 666 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 1.70$ (3H, br s), 1.70–2.33 (9H, m), 3.41 (2H, t, $J = 7.0$ Hz), 5.42–5.47 (1H, m), 7.26–7.58 (3H, m), 7.90–8.01 (2H, m); ^{13}C NMR ($CDCl_3$) δ 23.9, 24.8, 27.4, 29.6, 31.1, 43.0, 128.1, 129.6, 130.0, 134.2, 135.1, 137.9, 199.8, 206.2. Found; C, 78.73; H, 8.31%; Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25%.

25b: oil; IR (neat) 3050, 2970, 1750, 1680, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (3H, d, $J = 7.0$ Hz), 1.65 (3H, br s), 1.79–2.20 (4H, m), 2.10 (3H, s), 2.58 (2H, d, $J = 7.0$ Hz), 3.45 (1H, m), 5.32 (1H, t, $J = 7.0$ Hz), 7.32–7.49 (3H, m), 7.78–7.85 (2H, m); ^{13}C NMR ($CDCl_3$) δ 17.3, 22.0, 23.6, 29.5, 31.5, 39.8, 49.3, 125.6, 128.0, 128.6, 132.6, 136.5, 137.0, 199.6, 206.8. Found; C, 79.09; H, 8.68%; Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%.

25c: oil; IR (neat) 3045, 2970, 1745, 1682, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.65 (3H, br s), 1.78–2.20 (4H, m), 2.10 (3H, s), 2.40 (3H, s), 2.58 (2H, d, $J = 7.0$ Hz), 3.39 (2H, t, $J = 7.0$ Hz), 5.32 (1H, t, $J = 7.0$ Hz), 7.25 (2H, d, $J = 8.05$ Hz), 7.84 (2H, d,$J = 8.05$ Hz); ^{13}C NMR ($CDCl_3$) δ 22.0, 22.3, 23.5, 28.3, 32.2, 39.3, 49.0, 125.6, 128.1, 128.8, 132.9, 137.0, 145.1, 199.2, 206.8. Found; C, 79.05; H, 8.84%; Calcd for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58%.

25d: oil; IR (neat) 2967, 2930, 1712, 1452, 1377 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (3H, t, $J = 7.0$ Hz), 1.64 (3H, br s), 1.78–2.60 (11H, m), 2.40 (4H, q, $J = 7.0$ Hz), 5.29–5.34 (1H, m); ^{13}C NMR ($CDCl_3$) δ 7.6, 23.2, 25.0, 29.4, 29.5, 33.6, 46.1, 46.9, 119.3, 133.6, 213.9, 214.1. Found; C, 73.55; H, 10.14%; Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%.

26: oil; IR (neat) 3044, 3014, 2962, 2928, 1756, 1197, 1136, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (3H, br

s), 1.77–2.59 (9H, m), 2.70 (2H, t, $J = 7.2$ Hz), 5.39–5.46 (1H, m), 7.18–7.47 (5H, m). ^{13}C NMR ($CDCl_3$) δ 23.4, 25.3, 27.5, 29.1, 32.0, 39.3, 118.9, 120.6, 125.6, 132.0, 133.7, 150.8, 174.4, 205.0. Found; C, 78.76; H, 7.59%; Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%.

3.7. Reaction of (η^3-1-phenylallyl)Fe(CO)$_2$NO with pheny vinyl ketone

A mixture of 3-chloro-1-phenyl-1-propene (2 mmol) and TBAFe (2 mmol) in toluene (10 cm^3) was stirred at room temperature for 3 h under argon, and phenyl vinyl ketone (4 mmol) and TMSI (0.4 mmol) were then added. The resulting mixture was heated at 80°C for 15 h, cooled hydrolyzed with 4 M hydrochloric acid, and then extracted with ether. The ether extract was washed successively with 1 M aqueous NaOH solution and water, and dried over Na_2SO_4. After removal of the solvent, the residue was subjected to GLC using a column pached with SE 30 (10%). The products (**35a,b** and **36a–c**, see text) were identified by comparison of their retention times with those of the respective authentic specimens [7] and analyzed quantitatively by using biphenyl as an internal standard.

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