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Iron-Catalyzed Nucleophilic Substitution of Allylic Acetate

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This paper is dedicated to Prof. J.-E. Bäckvall on account of his 60th birthday.

Abstract: The combination of diiron nonacarbonyl and dimethylamine gives an active catalyst for displacement of allylic acetate by diethyl methylmalonate. It was found that among a series of amines, only dimethylamine and morpholine were efficient promoters of the reaction. Solvents such as dimethylformamide (DMF) and *N*-methylformamide were much superior to tetrahydrofuran, dichloromethane, and ethanol.

Keywords: allylic substitution; π-allyl-iron complexes; amine-iron carbonyl complexes; diiron nonacarbonyl; homogeneous catalysis

Introduction

While a number of metal complexes, in particular of palladium(II), have been extensively used as catalysts in π-allyl chemistry, there are relatively few reports on the use of iron catalysts.[1] In early studies, $[Fe(CO)_3NO]^-$ with sodium and tetrabutylammonium counterions was reported to function as catalyst for the nucleophilic displacement of allylic halide, allylic carbonate, and, less efficiently, allylic acetate by malonate ion.[1a–c] In this reaction, an atmosphere of CO was required, but in the more recent study, phosphines were added instead.[1d,e] It had earlier been shown that preformed cationic π-allyl-iron carbonyl complexes react with a series of different nucleophiles[2] and around 1985 the first report on the use of $Fe_2(CO)_9$ as catalyst for nucleophilic displacement of allylic acetate by malonate anion appeared.[3] In connection with early studies on the regiochemistry of nucleophilic attack on unsymmetric π-allyl systems, we decided to investigate in more detail the regiochemistry of the attack on π-allyl-iron carbonyl systems.[4]

Results and Discussion

In the initial experiments we tried to replace the acetate of (*Z*)-hex-2-enyl acetate (**1**) by the anion of diethyl methylmalonate, using $Fe_2(CO)_9$ as catalyst in refluxing THF, as described for crotyl acetate and dimethyl methylmalonate.[3] Much to our surprise, no product could be detected even after six days. However, by changing the solvent to DMF, we obtained complete reaction after 2 days at room temperature. Also other substrates were studied and the results were excellent and reproducible until we started using a new batch of solvent and the reaction failed again. However, we were aware that DMF can contain small amounts of dimethylamine, probably from slow decomposition of the solvent itself. We therefore added dimethylamine and were now able to observe facile reaction.[4] According to the exploratory study, using 10 mol% of catalyst, and between 1 and 8 molar equivalents of dimethylamine, optimal yield and rate was obtained with 2–4 equivalents (Table 1).

Earlier studies, which used $[Fe(CO)_3NO]^-$ as precatalyst, showed that the leaving group was displaced by the nucleophile with retention of stereo- and regiochemistry. This suggests direct displacement of the leaving group or possibly reaction of an intermediate σ-complex.[1a–c] However, in a more recent study, where the active catalyst was generated by addition of phosphines, the major product was formed from internal addition of the nucleophile, irrespective of the structure of the substrate.[1d,e] This is similar to results obtained with iridium catalysts.[5] By contrast, the early study of preformed π-allyl-iron carbonyl complexes suggested predominant terminal attack of the nucleophile.[2] Also the catalytic reaction using the iron carbonyl complex $Fe_2(CO)_9$ would therefore be expected to give this result. Accordingly, studies of

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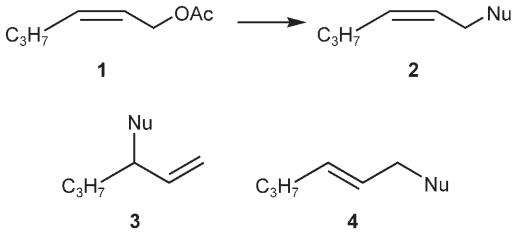
Table 1. The effect of the dimethylamine/$Fe_2(CO)_9$ ratio on the catalytic alkylation of (*Z*)-hex-2-enyl acetate (**1**), using 10% catalyst.



Entry	Amine/catalyst ratio	Relative yields [%]			Total yield [%][a]
		2	**3**	**4**	
1	1	89	2	9	76
2	2	91	1	8	100
3	4	91	1	8	99[b]
4	8	90	1	9	92[b]

[a] Yield after 2 days.
[b] Yield after18 h.

Table 2. The effect of different reaction conditions on the dimethyl amine promoted catalytic reaction of (*Z*)-hex-2-enyl acetate with malonate.

Entry	Catalyst	Relative yields (%)			Total yield (%)[a]
		2	**3**	**4**	
1	10% $Fe_2(CO)_9$, r.t.	91	1	8	100
2	5% $Fe_2(CO)_9$, r.t.	91	1	8	66
3	5% $Fe_2(CO)_9$, −5 °C	92	1	7	52
4	5% $Fe_2(CO)_9$, 60 °C	56	25	19	100
5	5% $Fe_2(CO)_9$, r.t., No light	91	1	8	97
6	10% $Fe_2(CO)_9$, r.t., CO atm	94	1	5	7
7	20% $Fe(CO)_5$, r.t.	79	8	13	68[b]

[a] Yield after 2 days.
[b] Yield after 3 days.

(*E*)-but-2-enyl acetate (**8**) as substrate and either $Fe_2(CO)_9$,[3] or the combination of $Fe_2(CO)_9$ and dimethylamine as catalyst, gave *ca.* 70% terminal attack by diethyl methylmalonate. This may be compared with the palladium-catalyzed reaction, which gave exclusively the terminal product.[6] (*E*)-Hex-2-enyl acetate (**11**) gave a similar result.[6] However, with (*Z*)-hex-2-enyl acetate (**1**) the palladium-catalyzed reaction of gave a complicated mixture, depending on the added ligands and usually extensive formation of (*E*)-product,[6] By contrast, with the iron catalyst, predominant terminal attack was observed, with retention of the (*Z*)-stereochemistry.[4] A more extensive study of the iron-catalyzed reaction was therefore initiated.

In the initial experiments, with 10% of catalyst at room temperature, (*Z*)-hex-2-enyl acetate (**1**) was used as substrate. The main product was found to be the (*Z*)-compound **2**, accompanied by small amounts of its two isomers **3** and **4**, in a ratio **2:3:4** of *ca.* 90:2:8, independent of the relative dimethyl amine/catalyst ratio (see Table 1). With only 5 mol% of catalyst, the reaction gave considerably lower yield. The yield decreased even further if the temperature was lowered to −5 °C. The ratio between the products **2**, **3** and **4** was independent of whether 5% or 10% catalyst loading was used (Table 2). However, when the temperature was raised to 60 °C the selectivity for the (*Z*)-product went down.

Because of the well known fact that light can dissociate coordinated carbon monoxide, an experiment was preformed with aluminium foil wrapped around the flask. The results indicate that exclusion of light had a positive effect on the yield (Table 2, entries 2 and 5). In contrast to the reaction with the catalyst $[Fe(CO)_3NO]^-$ where CO was required to get any reaction,[1d,e] CO essentially inhibited the reaction catalyzed by $Fe_2(CO)_9$. Finally, $Fe(CO)_5$ was tried in order to investigate if this cheap chemical could be used as catalyst. The reaction turned out to be slower than with $Fe_2(CO)_9$ and to give lower selectivity for the (*Z*)-product Table 2, entries 6 and 7).

A number of different amines was also studied and we were surprised to find that dimethylamine was by far the most efficient promotor, with morpholine as second best. Among a number of other potenital ligands, phenanthroline, triphenylphosphine and *n*-butyl isonitrile were found to strongly inhibit the catalysis (Table 3).

With diethylamine, there was a sharp decrease in the yield to 50%, suggesting that steric factors are important. This hypothesisis was supported by the results of using morpholine, a secondary amine with low steric requirements, which gave a yield comparable with that of dimethylamine. However, other factors are also important as shown by the low yields, *ca.* 20%, with primary amines (Table 3, entry 8). With diamines and tertiary amines further reduction of the yield to <10% was observed. The conclusion from the study was that the yield decreases in the order $R_2NH > RNH_2 > R_3N \approx NH_3$, where the alkyl groups influence the yield in the order Me > Et > Bu.

A series of other ligands, which have little in common with amines, e.g., *n*-butyl isonitrile, which probably acts as a CO equivalent, phenanthroline, and triphenylphosphine, were also studied, giving *ca.* 10% of product (Table 3). In the earlier study, which used $Fe_2(CO)_9$ alone as catalyst, it was suggested that the active catalyst was the adduct of malonate and $Fe(CO)_4$.[3] Since in our hands malonate alone gave no displacement product, a possible explanation is

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Table 3. The effect of amines and other potential promoters for the $Fe_2(CO)_9$-catalyzed alkylation of (*Z*)-hex-2-enyl acetate.

Entry	Ligand	Relative yields [%]			Yield [%][a]
		2	**3**	**4**	
1	NH_3	96	4	0	6[b]
2	$MeNH_2$	97	2	1	24[b]
3	Me_3N	89	8	2	15
4	$EtNH_2$	94	6	1	22
5	Et_2NH	75	23	3	50
6	Et_3N	77	14	9	6
7	$BuNH_2$	90	8	2	16
8	Morpholine	95	3	2	94[b]
9	Diaminoethane	92	8	0	4
10	Bis(*N,N'*-dimethylamino)-ethane	88	12	0	8
11	Phenantroline	91	9	0	6
12	Ph_3P	86	13	1	8
13	*n*-BuNC	88	11	1	11

[a] Yield after 2 days.
[b] Yield after 4 days.

that a combination of this adduct and ligands such as triphenylphosphine yields a catalyst with rather poor activity. With secondary and perhaps primary amines, which give a more active catalyst, a different mechanism seems reasonable, see below.

The same regiochemistry was observed for all the amines, giving essentially complete preference for terminal attack (>90%). The stereocontrol was also very high (except for the ethylamines) yielding *ca.* 90% retention of the double bond. This is in contrast to the palladium-catalyzed reaction which, depending on the added ligands, gave extensive isomerization of the double bond and also the product from internal addition of the nucleophile.[6] The value for retention of the (*Z*)-double bond in the iron carbonyl-catalyzed reaction is the highest observed in metal-catalyzed alkylation, although some catalysts based on $Mo(CO)_6$ and added phenanthroline ligands, also yield high retention of the stereochemistry of the double bond.[7]

In terms of yields, the solvents can be rated as DMF > CH_3CN > NMF > THF > CH_2Cl_2 > EtOH (Table 4). There is no obvious explanation for the order, but a common problem is the low solubility of $Fe_2(CO)_9$ in any solvent. With the exceptions of ethanol, the solvents with high polarity gave the highest yields. NMF appears to be a special case, since it gave the most rapid reaction but with a yield of only *ca.* 70% after complete conversion.

To survey the scope and limitations of the reaction, a number of different allylic acetates was examined, generally giving good yields of displacement product (Table 5).

Hex-1-en-3-yl acetate (**12**) gave >90% of the (*E*)-product (Table 5, entry 4). This observation is of interest, because it tells us that the reaction probably proceeds through a π-allyl intermediate, in contrast to the reactions with the $Bu_4N[Fe(CO)_3NO]$ catalyst.[1a–c] In addition, the similarity in the product patterns in the reactions of **11** and **12** (Table 5, entries 2 and 4) indicates that both proceed *via* the *syn* complex.

The reaction is sensitive to steric effects and the sluggish reaction of the nucleophile at the internal position is illustrated the reaction of pent-3-en-2-yl acetate (Table 5, entry 7). To obtain reasonable yields, it was necessary to raise the temperature to 60 °C for three days. In addition, the simple cyclic acetate **23** failed to react.

Changing the leaving group on the (*Z*)-hexenyl from acetate to trifluoroacetate had a dramatic impact on the reaction time, 1 h in place of 18 h, indicating that the rate-determining step for the reaction is the oxidative addition (Table 2, entry 1, Table 5, entry 1)

An interesting synthon is (*Z*)-2-butene-1,4-diol which is inexpensive and commercially available. Its special feature is that it contains a *cis* double bond and two terminal functional groups. The diacetate **15**

Table 4. The effect of solvent on the iron-catalyzed alkylation of (*Z*)- hex-2-enyl acetate.

Entry	Solvent	Equivs. of cat.	Equivs. of Me_2NH	Relative yields [%]			Yield [%][a]
				2	**3**	**4**	
1	CH_2Cl_2	0.1	0.4	21	57	22	24
2	THF	0.1	0.4	47	33	20	47
3	EtOH	0.1	0.4	67	24	9	15
4	CH_3CN	0.1	0.4	47	3	50	77
5	NMF[b]	0.05	0.05	93	3	4	63[c]
6	NMF	0.05	0.1	93	3	4	70[c]
7	NMF	0.05	0.4	92	3	5	65[c]

[a] Yield after 48 h.
[b] NMF = *N*-methylformamide.
[c] Yield after 4 h.

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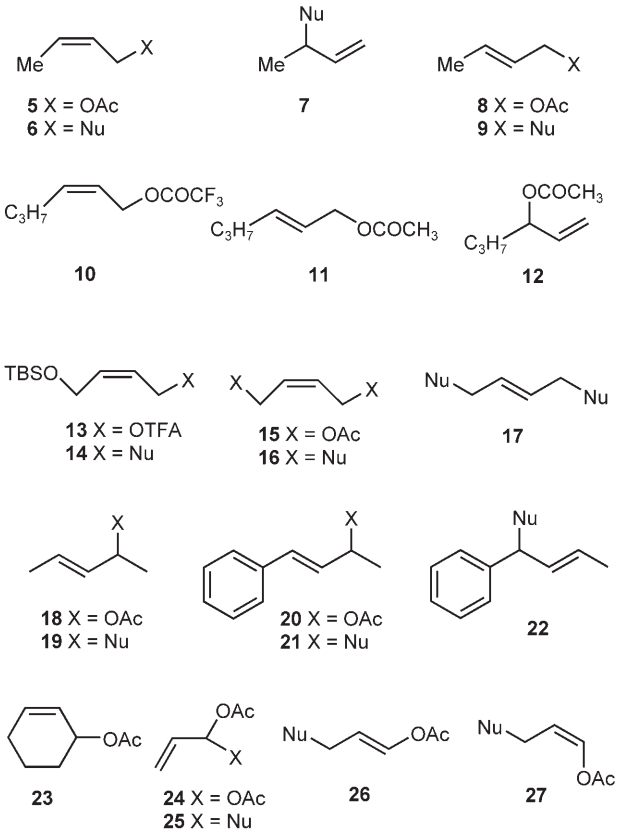
Table 5. Products and yields in the iron carbonyl-catalyzed reaction of a series of allylic acetates with sodium diethyl methylmalonate.



Entry	Substrate	Product [%][a]			Yield [%]
1	**10**	**2** (92)	**3** (5)	**4** (2)	90[b]
2	**11**	**2** (2)	**3** (7)	**4** (91)	100[c]
3	**8**	**6** (0)	**7** (23)	**9** (77)	100
4	**12**	**2** (2)	**3** ((7)	**4** (91)	92
5	**13**	**14**			95[d]
6	**15**	**16** (80)[d]	**17** (20)[d]		100
7	**18**	**19**			50[c]
8	**20**	**21** (76)	**22** (24)		74
9	**23**				n.r.
10	**24**	**25** (52)	**26** (22)	**27** (26)	74

[a] Determined by GC.
[b] Yield after 1 h.
[c] Reaction time 3 days at 60 °C.
[d] Determined by ^{1}H and ^{13}C NMR.

can be converted to the diacetate **16** which in principle should be readily further functionalized, Similarly, the protected mono-trifluoroacetate **13** gave exclusively the *Z*-product **14** from terminal substitution (Table 5, entry 5). After deprotection of the TBS group, the alcohol should be readily further functionalized.

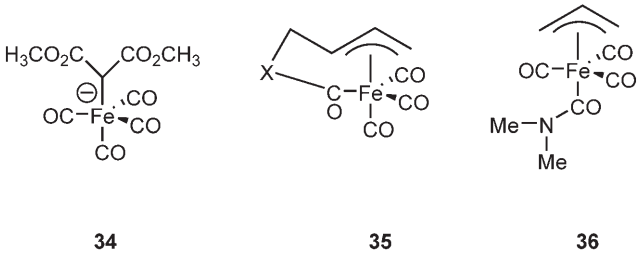
The structure of the catalytically active species in the reaction is of interest, particularly for the development of a catalyst for asymmetric synthesis. Since both $Fe(CO)_5$ and $Fe_2(CO)_9$ work as pre-catalysts, with the latter being considerably more active, a species such as $Fe(CO)_4$(solvent) is perhaps first formed.[8] This assumption is supported by the fact that added CO inhibits the reaction. In an attempt to elucidate the intermediates formed, a ^{13}C NMR experiment was performed. An inverse gated-decoupled experiment allowed integration of the ^{13}C peaks, thus giving the relative amount of the different carbons.[9] The decomposition process of the different complexes was monitored by ^{13}C NMR over a long period of time to permit an assignment of which peaks belong to the same complex.

The spectra contained four different carbonyls and two different coordinated dimethylamines. After matching the carbonyls with the amines, it was found that the most abundant complex was $Fe(CO)_3(Me_2NH)_2$ (**30**). The other major ^{13}C peak in the spectrum was assigned to $Fe(CO)_4(Me_2NH)$ (**31**). In addition, two minor carbonyl peaks were observed in a ratio of 1:1, either belonging to one species, containing two inequivalent carbon monoxides or two different species. It was also noted that non-deuteriated DMF had been formed. This suggests that hydride species such as **28** or **32** are generated. The anionic complexes **29** and **33**, which could then be formed by deprotonation, are attractive intermediates since they should be sufficiently strong nucleophiles to give π-allyliron complexes by reaction with allyl acetates.

An anionic structure **34** was also suggested as intermediate in the earlier study of iron carbonyl-catalyzed displacement of allylic acetate by malonate.[3b] Since in our hands a second ligand seems to be required, it may be that the steric bulk of the diethyl methylmalonate leads to an inefficient reaction in the next step.

Nucleophilic attack by alkyllithium on iron carbonyls is known from the literature,[10] and generally results in addition to one carbonyl as in **28** and **32**. It has also been shown in one case that an amine can in fact act as such a nucleophile.[11] After deprotonation this will give the postulated nucleophilic species **29** or **33** (Scheme 1). Intermediates of similar structures are known from the literature which gives credibility to the postulated structure.[12]

It is interesting also to note that complexes such as the lactone and lactam complexes **35** which are useful synthetic intermediates,[13] have structures closely related to the intermediate **36**, which is formed on oxi-



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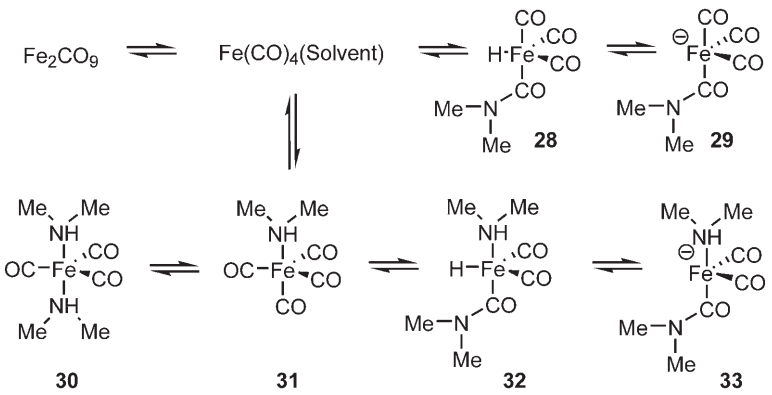

Scheme 1. Postulated structures of the nucleophiles generated from $Fe_2(CO)_9$ and dimethylamine.

dative addition of **29** to allyl acetate. However, complexes related to **35** do not seem to react with nucleophiles, perhaps because they are not sufficiently positively charged.

Conclusions

The results show that the amine-promoted iron-catalyzed alkylation is applicable to a variety of allylic acetates, but that it is more sensitive to steric effects than the corresponding palladium-catalyzed reaction. As might be expected, a better leaving group such as trifluoroacetate, leads to a much more rapid reaction. In contrast to the palladium-catalyzed reaction, the substrate configuration, (*Z*) or (*E*), is retained in the displacement reactions, providing a useful complement to the palladium-catalyzed reaction.

Further work is required to establish the mechanism of allylic displacement catalyzed by iron carbonyls and also the scope of the reaction. Since Enders and others have shown that chiral induction is possible in stoichiometric reactions of π-allyl-iron carbonyls,[14] the present exploratory study suggests that it should be possible to develop an asymmetric catalytic version, using catalysts based on iron carbonyls.

Experimental Section

Anhydrous DMF was purchased from Aldrich. Prior to use, the DMF was sonificated under vacuum in order to remove any trace amounts of the degradation product dimethylamine, to avoid any background reaction. All other solvents and reagents were commercial products, purified by standard techniques. The product mixtures were analyzed using a gas chromatograph (Varian 3700) equipped with a an autoinjector (Varian 8000 Autosampler). The used column was a 15 m × 0.15 mm dimethylpolysiloxane (100%) capillary column. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker model AM 400 spectrometer.

General Procedure for Iron-Catalyzed Alkylation

An oven-dried flask equipped with a magnetic stirrer was used. An aluminium foil was wrapped around the flask to cut out light. $Fe_2(CO)_9$ (36 mg, 0.1 mmol) was then added and the crystals were ground for 15 min with a magnetic stirrer at the high speed under N_2, in order to increase the dissolution rate of the catalyst. The allylic acetate (1 mmol), the internal standard dodecane (70 mg), DMF (1 mL) and the amine (0.4 mmol) were added, followed by a standard solution of sodium diethyl methylmalonate in DMF solution (1 M, 2 mL, 2 mmol). The gaseous amines were condensed in a flask at −78 °C and diluted with DMF. The appropriate amount of the stock solution was then charged into the reaction flask.

The reaction was monitored by GC at regular time interval (1, 2, 5, 18 h, and 2 days) by working up a small aliquot in diethyl ether and water.

Analytical Evaluation of the GC Results

The relative ratios cited in the Tables are based upon the relative area % obtained from the gas chromatograms. The cited yields are calculated from a response curve, obtained by authentic samples of the product, and the internal standard dodecane.

Preparation of Allylic Acetates

The following alcohols and acetates were bought from Aldrich and used as received: 1-hexen-3-ol, (*Z*)-2-hexen-1-ol, (*E*)-2-hexen-1-ol, cyclohexenyl acetate, and 1,1-diacetoxy-2-propane. Methyl-1-penten-3-ol was prepared by Grignard reaction between methylmagnesium bromide and acrolein. (*Z*)-Hex-2-enyl trifluoroacetate,[6] 1-(*tert*-butyldimethylsiloxy)-(*Z*)-but-2-en-4-ol,[15] 1-(*tert*-butyldimethylsiloxy)-(*Z*)-but-2-en-4-yl trifluoroacetate,[6] and 1-phenylbut-1-en-3-yl acetate,[6] were prepared according to literature procedures. The alcohols were converted to the acetates in good yields using standard procedures.

(*Z*)-Hex-2-enyl acetate: ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 5.66–5.45 (m, 2H), 4.58 (d, $J = 6.4$ Hz, 2H), 2.05 (app. q, $J =$ 7.1 Hz, 2H), 2.02 (s, 3H), 1.37 (app. sextet, $J = 7.3$ Hz, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta =$ 171.0, 135.1, 123.5, 60.4, 29.5, 22.5, 21.0, 13.6.

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(*E*)-Hex-2-enyl acetate: ^{1}H NMR: $\delta = 5.74$ (br dt, $J = 15.4$, 6.6 Hz, 1H), 5.56 (br dt, $J = 15.4$, 7.3 Hz, 1H),4.88 (d, $J =$ 6.3 Hz, 2H), 2.12 (app. q, $J = 7.3$ Hz, 2H), 1.38 (app. sextet, $J = 7.3$ Hz, 2H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$): $\delta = 170.8$, 136.4, 123.6, 65.3, 34.2, 22.0, 21.0, 13.6.

Identification of the Products

The products from the reaction with diethyl methylmalonate were compared with synthetic samples prepared according to ref.[6]

Product 2: ^{1}H NMR: δ05.53 (m, 1H), 5.24 (m, 1H), 4.15 (q, $J = 7.0$ Hz, 4H), 2.61 (d, $J = 7.35$ Hz, 2H), 2.00 (q, $J =$ 7.3 Hz, 2H), 1.37 (app. sextet, $J = 7.5$ Hz, 2H), 1.35 (s, 3H), 1.22 (t, $J = 7.1$ Hz, 6H), 0.88 (t, $J = 7.2$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ0172.1, 133.7, 122.0, 61.0, 53.5, 33.1, 29.3, 22.6, 19.6,14.0, 13.8.

Product 3: ^{1}H NMR: δ05.55 (ddd, $J_1 = 17.2$ Hz, $J_2 =$ 10.3 Hz, $J_3 = 6.3$ Hz, 1H), 5.08–5.00 (m, 2-H), 4.16 (q, $J =$ 7.0 Hz 4H), 2.69 (t, $J = 10.0$ Hz, 1H), 1.37 (m, 2H), 1.36 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 6H), 0.87 (t, $J = 7.2$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ0171.4, 137.2, 118.1, 57.6, 48,7, 48.5, 32.0,20.8, 19.6, 17.0, 14.0.

Product 4: ^{1}H NMR: δ05.46 (br, dt, $J_1 = 15.0$ Hz, $J_2 =$ 6.6 Hz, 1H), 5.25 (br, dt, $J_1 = 15.4$ Hz, $J_2 = 7.3$ Hz, 1H), 4.14 (q, $J = 7.0$ Hz, 4H), 2.51 (d, $J = 7.3$ Hz, 2H), 1.93 (q, $J =$ 6.5 Hz, 2H), 1.33 (s, 3H), 1.32 (app. sextet, $J = 7.5$ Hz, 2H), 1.20 (t, $J = 7.0$ Hz, 6H), 0.83 (t, $J = 7.3$ Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$): δ0172.0, 135.2. 123.8, 61.0, 53.7, 38.8, 34.6, 22.4, 19.6, 14.0, 13.5.

Identification of Products by ^{1}H NMR

In the case where no pure samples of the three isomers were available, identification by ^{1}H NMR was used. Identification of the (*E*) and (*Z*) product was done by observing the coupling constant for the double bond [(*E*) product $J \approx 15$ Hz and for (*Z*) $J \approx 11$ Hz]. The product derived from internal attack of the nucleophile was determined by the characteristic pattern from the terminal protons in the double bond. Integration of the ^{1}H NMR signals gave an approximate product distribution that was more accurately determined by GC.

Preparation of Samples for ^{13}C NMR

$Fe_2(CO)_9$ was mixed in DMF-d_7 and dimethylamine was bubbeled through (an excess). The solution was stirred for 45 min under a nitrogen atmosphere. The dark brown solution was filtered through a small plug of celite in a Pasteur pipette into a NMR tube.

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