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Ferrocene Promoted Addition of Methyl 2,2-Dichloro-Carboxylates to 1-Alkenes

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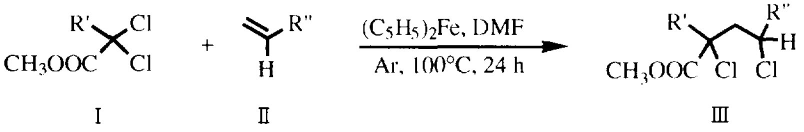
***Abstract*:** The Kharasch addition of methyl 2,2-dichlorocarboxylates to 1-alkenes is promoted by ferrocene in DMF at 100°C, affording 1:1 adducts in satisfactory yields.

INTRODUCTION

The reaction of alkenes with halogenated compounds, mainly polyhaloalkanes, involving the homolytic cleavage of a carbon-halogen bond, is a well investigated procedure ("Kharasch addition") to synthesize C-C bonds.[1] These reactions are generally initiated by organic peroxides,[2] alkylmetal hydrides[1c,3] or transition metal salts or complexes.[1b,4] Fe(II) salts and complexes are efficient catalysts,[5] but they generally have stability and also toxicity problems, owing to the frequently used alkylphosphines or carbonyl ligands.

In a continuation of our studies on the Halogen Atom Transfer Radical Addition (HATRA),[6] we found that ferrocene, a cheap and stable iron(II) complex,[7] efficiently promotes the addition of methyl 2,2-dichlorocarboxylates to 1-alkenes (Scheme 1).



Scheme 1

RESULTS AND DISCUSSION

Ferrocene is a strong one electron reducing agent, forming a charge transfer complex with various polyhalomethanes;[8] though being used in the presence of CCl_4 to initiate the radical polymerization of various acrylic monomers,[9] it has never been reported, as far as we know, as a catalyst in the Kharasch addition of halogenated compounds to olefins.

The reaction conditions have been optimized by reacting methyl 2,2-dichloropropanoate with 1-octene in the presence of ferrocene (10 mol/mol%) at different temperature and with different solvents. The better results have been obtained in dimethylformamide (DMF) at 100° C (table 1, entry 2); at 80° C the reaction completely fails (table 1, entry 3), whereas other solvents such as n-hexane, 1,2-dimethoxyethane, isopropyl alcohol, 1,2-dichloroethane, formamide, acetonitrile or di-n-propyl ether give poor conversions. Working with a number of alkenes and esters in DMF at 100°C, the results reported in the Table 1 are obtained.

Table 1. The addition of **I** to **II** initiated by $(C_5H_5)_2Fe$.

entry	R'	R''	Conversion (mol/mol %)[a]	1:1 Adduct **III** Yield (mol/mol%)[b]
1	H-	$CH_3(CH_2)_4CH_2$-	15	10
2	CH_3-	$CH_3(CH_2)_4CH_2$-	98	72
3[d]	CH_3-	$CH_3(CH_2)_4CH_2$-	10	traces
4	CH_3-	$CH_3(CH_2)_6CH_2$-	98	70
5	CH_3-	CH_2=CH_2-$(CH_2)_4$-	99	59[h]
6	CH_3-	$CH_3OOC(CH_2)_7CH_2$-	98	63
7	CH_3-	C_6H_5-CH_2-	96	60
8	CH_3-	3-cyclohexenyl-	95	53[h]
9	CH_3-	C_6H_5-	99	60[i]
10	CH_3-	CH_3OOC-	97	0[j]
11	C_6H_5-	$CH_3(CH_2)_4CH_2$-	95	0
12	C_6H_5-CH_2-	$CH_3(CH_2)_4CH_2$-	96	66
13	n-C_4H_8-	$CH_3(CH_2)_4CH_2$-	98	70
14	i-C_3H_7-	$CH_3(CH_2)_4CH_2$-	95	69

[a]Conversion monitored by GC. [b]Isolated yield based on I. The products are 1:1 mixtures of diastereoisomers. [d]Reaction temperature: T = 80°C. [h]Oligomers and/or telomers (>10 mol/mol%) are detected. [i]20 mol/mol% of 1:2 ester:alkene adduct is also isolated. [j]Only trace amounts of the 1:1 adduct are detected.

The reaction is very clean; isolated yields, which are usually good, are decreased by the side reaction of α-alkoxy-carbonyl radical addition to the cyclopentadienyl ring producing ferrocenyl radicals, which should decompose into inorganic iron salts and Cyclopentadienyl-derivatives.[10]

Dimerization by-products are not detected on using ferrocene; only little amounts of polymers or telomers (< 3 mol/mol%) and of the dehalogenated starting ester (< 5 mol/mol%) are found, especially from the more complex substrates. With the easy polimerizable methyl acrylate (table 1, entry 10), an extensive polimerization is observed but from styrene (table 1, entry 9) the 1:1 adduct is formed in satisfactory yield.

Non terminal alkenes, such as cyclohexene for example, are quite unreactive; 4-vinylcyclohexene, indeed, chemospecifically reacts at the monoalkylated olefinic bond (table 1, entry 8). Methyl 2,2-dichloro-2-phenylethanoate (table 1, entry 7) gives no addition reaction, likely owing to the stability of the intermediate benzylic radical, dimeric by-product being mostly observed.[6] Poor conversion is observed from methyl dichloroacetate (table 1, entry 1).

2-Br-2-Cl-esters give rise to radicals more quickly than the corresponding 2,2-dichloro esters, likely owing to the very easy cleavage of the C-Br bond.[11] Thus, methyl 2-Br-2-Cl-exanoate add easily to 1-octene, also at a lower temperature (80°C), but the reaction mixture is complicated by an extensive halogen scrambling in the products.

This HATRA transformation is not promoted by light (table 2, entry 2) and is only moderately inhibited by air (table 2, entry 3), p-dinitrobenzene (table 2, entry 4) or hydroquinone (table 2, entry 5), seemingly ruling a free radical chain process out. The oligo- and poly-merization of methyl acrylate (table 1, entry 10) may be instead rationalized by a ferrocene initiating free radical reaction.[9]

Table 2. The addition of methyl 2,2-dichloropropanoate to 1-octene initiated by $(C_5H_5)_2Fe$.

entry	R'	R''	Conversion (mol/mol %)[a]	1:1 Adduct **III** Yield (mol/mol%)[b]
1	CH_3-	$CH_3(CH_2)_4CH_2$-	98	72
2[c]	CH_3-	$CH_3(CH_2)_4CH_2$-	96	70
3[e]	CH_3-	$CH_3(CH_2)_4CH_2$-	98	57
4[f]	CH_3-	$CH_3(CH_2)_4CH_2$-	86	48
5[g]	CH_3-	$CH_3(CH_2)_4CH_2$-	98	50

[a] Conversion monitored by GC. [b] Isolated yield based on **I**. All the products are 1:1 mixtures of diastereoisomers. [c] Reaction carried out in the dark. [e] Reaction carried out in air atmosphere. [f] Reaction in the presence of 10 mol/mol% of p-dinitrobenzene. [g] Reaction performed in the presence of 10 mol/mol% of hydroquinone.

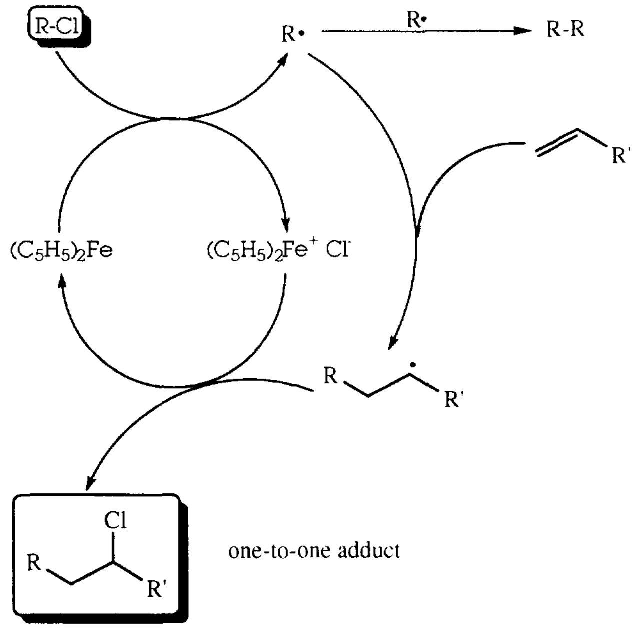
Other metallocene complexes, i.e. decamethylferrocene, ruthenocene, chromocene and nickelocene, have been tested; only ferrocene however, efficiently promotes the HATRA reactions, the other ones showing poor (table 3, entries 2 and 3) or no activity (table 3, entries 4, 5 and 6).

Table 3. The addition of methyl 2,2-dichloropropanoate to 1-octene initiated by different metallocene.

	Catalyst	Conversion (mol/mol %)[a]	1:1 Adduct **III** Yield (mol/mol%)[b]
1	Ferrocene	98	72
2	Decamethylferrocene	80	35
3	Chromocene	45	29
4	Ruthenocene	-	-
5	Nickelocene	-	-
6	Cobaltocene	-	-

[a]Monitored by GC. [b]Isolated yield based on **I**. All products are 1:1 mixtures of diastereoisomers.

The here reported results are rationalized by a catalytic pathway in which ferrocene works as a halogen atom carrier in a redox process,[1b, 5a, 12] in a similar pathway to that proposed for Fe(II)-chloride promoted Kharasch addition[13] (Scheme 2): ferrocene is oxidized by the haloderivative to the ferricinium salt $(C_5H_5)_2Fe^+Cl^-$,[8b] which then transfers the chlorine atom to the radical adduct.



Scheme 2

EXPERIMENTAL

Alkenes and ferrocene were standard grade commercial products and used without further purification. DMF was dried over three batches of 3Å sieves (5% w/v, 12h) and used without degassing. Methyl 2,2-dichloropropanoate was synthesized starting from the corresponding sodium salt by nucleophilic substitution with CH_3I; the other methyl 2,2-dichloro-carboxylates were prepared according to our previous procedure[14]. Mass spectra were obtained on a combined HP 5890 GC - HP 5989A MS Engine. ^{1}H-NMR and IR spectra were recorded on a Bruker DPX 200 and a Philips PU9700 spectrometers respectively. Carbon and hydrogen were analyzed with a Carlo Erba model 1106 elemental analyzer.

General procedure for the alkyl-halo addition promoted by ferrocene.

Typically, a mixture of ferrocene (0.2 mmol), 1-octene (5 mmol) and methyl 2,2-dichlorocarboxylate (2 mmol) in DMF (2 ml) are stirred at 100°C for 24 h under argon. The mixture is then poured in 5% aqueous HCl (10 ml) and extracted with CH_2Cl_2 (3 x 5 ml). The organic phases are dried over Na_2SO_4 and evaporated. The products (indistillable oils) are isolated and purified by silica-gel chromatography using 1:9 diethyl ether/petroleum ether (40-60°C) as eluant.

Methyl 2-butyl-2,4-dichloro-decanoate

^{1}H-NMR ∂ ($CDCl_3$): 0.85-0.98 (6H, m, 2 x $-C\underline{H}_3$); 1.16-1.54 (12H, m, $-CCl-CH_2-(C\underline{H}_2)_2-CH_3$; $-CHCl-CH_2-(C\underline{H}_2)_4-CH_3$); 1.67-1.90 (2H, m, $-CCl-C\underline{H}_2-(CH_2)_2-CH_3$); 1.97-2.29 (2H, m, $-CHCl-C\underline{H}_2-(CH_2)_4-CH_3$); 2.45-2.70 (2H, m, $-CCl-C\underline{H}_2-CHCl$); 3.80 (3H, s, $-OC\underline{H}_3$); 4.05-4.32 (1H, m, $-CH_2-C\underline{H}Cl-CH_2-$).

MS (EI, 70 eV) m/z: 275 (3%) [M^+-Cl]; 254 (28%) [$M^+-C_4H_8$]; 239 (17%) [$M^+-Cl-HCl$]; 207 (4%) [$M^+-Cl-HCl-CH_3OH$]; 179 (19%) [$M^+-Cl-HCl-CH_3OH-CO$]; 164 (92%) [$M^+-C_{48}H_{15}Cl$]; 121 (68%) [$M^+-C_{48}H_{15}Cl-C_3H_7$]; 41 (100%).

IR (neat) cm^{-1}: 1735 $\nu_{C=O}$

Anal. Calcd. for $C_{15}H_{28}Cl_2O_2$: C, 57.88%; H, 9.07%. Found: C, 58.1%; H, 9.1%.

Methyl 2,4-dichloro-2-isopropyl-decanoate

^{1}H-NMR ∂ ($CDCl_3$): 0.90 (3H, t, $-CH_2-C\underline{H}_3$); 0.95-1.08 (6H, $-CH(C\underline{H}_3)_2$); 1.14-1.81 (10H, m, 5 x $-C\underline{H}_2-$); 2.18-2.63 (3H, m, $-C\underline{H}_2-CCl-C\underline{H}(CH_3)_2$); 3.79 (3H, s, $-OC\underline{H}_3$); 4.09-4.29 (1H, m, $-CH_2-C\underline{H}Cl-CH_2-$).

MS (EI, 70 eV) m/z: 225 (9%) [$M^+-Cl-HCl$]; 193 (3%) [$M^+-Cl-HCl-CH_3OH$]; 165 (14%) [$M^+-Cl-HCl-CH_3OH-CO$]; 150 (63%) [$M^+-C_8H_{15}Cl$]; 121 (90%); 41 (100%).

IR (neat) cm^{-1}: 1740 $\nu_{C=O}$

Anal. Calcd. for $C_{14}H_{26}Cl_2O_2$: C, 56.57%; H, 8.82%. Found: C, 56.7%; H, 9.0%.

Methyl 2,4-dichloro-2-methyl-decanoate

^{1}H-NMR ∂ ($CDCl_3$): 0.88 (3H, t, $-CH_2-C\underline{H}_3$); 1.19-1.60 (8H, m, 4 x $-C\underline{H}_2-$); 1.72 (2H, m, $-CHCl-C\underline{H}_2-CH_2-$); 1.83 (3H, s, $CCl-C\underline{H}_3$); 2.29-2.73 (2H, m, $-CCl-C\underline{H}_2-CHCl-$); 3.78 (3H, s, $-OC\underline{H}_3$); 4.00-4.18 (1H, m, $-CH_2-C\underline{H}Cl-CH_2-$).

MS (EI, 70 eV) m/z: 197 (7%) [M$^+$-Cl-HCl]; 165 (17%) [M$^+$-Cl-HCl-CH$_3$OH]; 137 (10%) [M$^+$-Cl-HCl-CH$_3$OH-CO]; 122 (100%) [M$^+$-C$_8$H$_{15}$Cl].
IR (neat) cm^{-1}: 1740 $\nu_{C=O}$
Anal. Calcd. for $C_{12}H_{22}Cl_2O_2$: C, 53.54%; H, 8.24%. Found: C, 53.7%; H, 8.1%.

Methyl 2,4-dichloro-decanoate
^{1}H-NMR ∂ (CDCl$_3$): 0.91 (3H, t, -CH$_2$-C$\underline{H}_3$); 1.23-1.63 (8H, m, 4 x -C$\underline{H}_2$-); 1.67-1.87 (2H, m, -CHCl-C$\underline{H}_2$-CH$_2$-); 2.16-2.59 (2H, m, -CCl-C$\underline{H}_2$-CHCl-); 3.83 (3H, s, -OC$\underline{H}_3$); 3.90-4.25 (1H, m, -CH$_2$-C$\underline{H}$Cl-CH$_2$-); 4.53-4.71 (1H, m, -C$\underline{H}$Cl-COOCH$_3$).
MS (EI, 70 eV) m/z: 219 (2%) [M$^+$-Cl]; 183 (18%) [M$^+$-Cl-HCl]; 151 (5%) [M$^+$-Cl-HCl-CH$_3$OH]; 123 (16%) [M$^+$-Cl-HCl-CH$_3$OH-CO]; 108 (100%) [M$^+$-C$_8$H$_{15}$Cl].
IR (neat) cm^{-1}: 1745 $\nu_{C=O}$
Anal. Calcd. for $C_{11}H_{20}Cl_2O_2$: C, 51.77%; H, 7.90%. Found: C, 51.7%; H, 8.0%.

Methyl 4-(4-cyclohexenyl)-2,4-dichloro-2-methyl-butanoate
^{1}H-NMR ∂ (CDCl$_3$): 1.40-1.63 (1H, m, -CH$_2$-C$\underline{H}$-CH$_2$-); 1.88 (3H, s, C$\underline{H}_3$CCl-); 1.66-1.98 (2H, m, -CH$_2$-CH-C$\underline{H}_2$-CH$_2$-CH=CH-); 1.98-2.22 (4H, m, -C$\underline{H}_2$-CH=CH-C$\underline{H}_2$-); 2.37-2.75 (2H, m, -CCl-C$\underline{H}_2$-CHCl-); 3.81 (3H, s, -OC$\underline{H}_3$); 4.04-4.20 (1H, m, -CH$_2$-C$\underline{H}$Cl-CH-); 5.70 (2H, s, -C$\underline{H}$=C$\underline{H}$-).
MS (EI, 70 eV) m/z: 229 (7%) [M$^+$-Cl]; 193 (6%) [M$^+$-Cl-HCl]; 161 (12%) [M$^+$-Cl-HCl-CH$_3$OH]; 133 (34%) [M$^+$-Cl-HCl-CH$_3$OH-CO]; 122 (83%) [M$^+$-C$_8$H$_{10}$Cl]; 79 (100%).
IR (neat) cm^{-1}: 1740 $\nu_{C=O}$
Anal. Calcd. for $C_{12}H_{18}Cl_2O_2$: C, 52.36%; H, 10.25%. Found: C, 52.6%; H, 10.1%.

Methyl 2,4-dichloro-2-methyl-5-phenyl-pentanoate
^{1}H-NMR ∂ (CDCl$_3$): 1.82 (3H, s, C$\underline{H}_3$CCl-); 2.37-2.75 (2H, m, -CCl-C$\underline{H}_2$-CHCl-); 3.02-3.16 (2H, m, -CHCl-C$\underline{H}_2$-C$_6$H$_5$); 3.77 (3H, s, -OC$\underline{H}_3$); 4.22-4.43 (1H, m, -CH$_2$-C$\underline{H}$Cl-CH$_2$-); 7.19-7.39 (5H, m, -C$_6\underline{H}_5$).
MS (EI, 70 eV) m/z: 202 (78%) [M$^+$-Cl-HCl]; 171 (11%) [M$^+$-Cl-HCl-CH$_3$OH]; 143 (64%) [M$^+$-Cl-HCl-CH$_3$OH-CO]; 122 (9%) [M$^+$-C$_9$H$_9$Cl]; 91 (100%) [C$_7$H$_7$].
IR (neat) cm^{-1}: 1740 $\nu_{C=O}$
Anal. Calcd. for $C_{13}H_{26}Cl_2O_2$: C, 54.74%; H, 9.19%. Found: C, 54.9%; H, 9.4%.

Methyl 2,4-dichloro-2-methyl-9-decenoate
^{1}H-NMR ∂ (CDCl$_3$): 1.33-1.83 (8H, m, 3 x -C$\underline{H}_2$-); 1.70 (2H, m, -CHCl-C$\underline{H}_2$-CH$_2$-); 1.86 (3H, s, CCl-C$\underline{H}_3$); 2.31-2.76 (2H, m, -CCl-C$\underline{H}_2$-CHCl-); 3.80 (3H, s, -OC$\underline{H}_3$); 4.11 (1H, m, -CH$_2$-C$\underline{H}$Cl-CH$_2$-); 5.00 (2H, m, -CH=C$\underline{H}_2$); 6.00 (1H, m, -C$\underline{H}$=CH$_2$).
MS (EI, 70 eV) m/z: 231 (21%) [M$^+$-Cl]; 195 (21%) [M$^+$-Cl-HCl]; 163 (25%) [M$^+$-Cl-HCl-CH$_3$OH]; 135 (37%) [M$^+$-Cl-HCl-CH$_3$OH-CO]; 122 (100%) [M$^+$-C$_8$H$_{13}$Cl]; 41 (98%) [C$_3$H$_5$].
IR (neat) cm^{-1}: 1740 $\nu_{C=O}$

$C_{12}H_{14}Cl_2O_2$: C, 53.94%; H, 7.54%. Found: C, 54.1%; H, 7.7%.

Methyl 2,4-dichloro-2-methyl-1,13-tridecandioate

^{1}H-NMR ∂ ($CDCl_3$): 1.86 (3H, s, $C\underline{H}_3CCl$-); 1.15-1.83 (14H, m, 7 x -$C\underline{H}_2$-); 2.24-2.78 (4H, m, -$C\underline{H}_2$-CHCl-$C\underline{H}_2$-); 3.68 (3H, s, -CH_2-$COOC\underline{H}_3$); 3.80 (3H, s, -CCl-$COOC\underline{H}_3$); 4.00-4.22 (1H, m, -CH_2-$C\underline{H}Cl$-CH_2-).
MS (EI, 70 eV) m/z: 283 (4%) [M^+-Cl-HCl]; 122 (83%) [M^+-$C_{12}H_{21}ClO_2$]; 98 (100%).
IR (neat) cm^{-1}: 1740 $\nu_{C=O}$
Anal. Calcd. for $C_{16}H_{28}Cl_2O_4$: C, 54.09%; H, 7.94%. Found: C, 54.2%; H, 8.1%.

Methyl 2,4-dichloro-2-methyl-4-phenylbutanoate

^{1}H-NMR ∂ ($CDCl_3$): 1.81 and 1.88 (3H, s, $C\underline{H}_3CCl$-); 2.67-3.14 (2H, m, -CCl-$C\underline{H}_2$-CHCl-); 3.50 and 3.76 (3H, s, -$OC\underline{H}_3$); 5.14-5.27 (1H, m, -CH_2-$C\underline{H}Cl$-C_6H_5); 7.19-7.51 (5H, m, -$C_6\underline{H}_5$).
MS (EI, 70 eV) m/z: 189 (2%) [M^+-Cl-HCl]; 129 (18%) [M^+-Cl-HCl-CH_3OH-CO]; 122 (100%) [M^+-C_8H_7Cl]; 77 (5%) [C_6H_5].
IR (neat) cm^{-1}: 1740 $\nu_{C=O}$
Anal. Calcd. for $C_{12}H_{14}Cl_2O_2$: C, 55.19%; H, 5.40%. Found: C, 55.3%; H, 5.4%.

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