Pergamon

Tetrahedron, Vol. 53, No. 52, pp. 17761-17768, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10241-1

Halogen Atom Transfer Radical Addition of α-Polychloroesters to Olefins Promoted by Fe^0 Filings

Luca Forti,* Franco Ghelfi, Emanuela Libertini, Ugo M. Pagnoni and Ercole Soragni

Dipartimento di Chimica, Università di Modena, Via Campi 183, I-41100, Modena (Italy)

Abstract: The Kharasch addition of methyl 2,2-dichlorocarboxylates or trichloro acetic acid derivatives to alkenes, affording the corresponding 1:1 adducts, is promoted by the iron filings/N,N-dimethylformamide system. © 1997 Elsevier Science Ltd.

INTRODUCTION

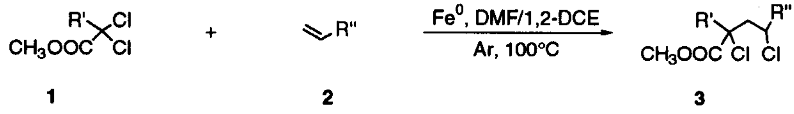
The halogen atom transfer radical additions (HATRA) of α-haloesters to alkenes have been widely investigated, since these reactions lead to γ-haloesters, useful intermediates for the synthesis of butyrolactones,[1] which are, in turn, precursors of a number of biologically active compounds.[1a,2]

In 1948 Kharasch demonstrated the functionalization of alkenes by HATRA of simple α-Br-esters initiated by diacetyl peroxide.[1b] After this work, much attention has been paid on the use of alkyl trihaloacetate in these reactions,[3] while dihalogenated esters have been essentially restricted to some dichloroacetates[4] or α,α-dichloro olefinic esters.[5] The best approaches devised to carry out these alkyl-halo-additions utilise transition metal salts or their complexes as promoters.[4,5] These routes, however, generally require rather vigorous conditions, such as prolonged heating to 100-160°C, very likely to facilitate the C-halogen bond cleavage.

Nowadays there is an increasing interest towards the use of environmentally friendly reagents. Iron, a cheap and safe metal, which has recently found satisfactory applications in water decontamination from polyhalocompounds,[6] appears promising as a promoter for radical addition; the first step in its action is indeed the generation of radicals. As an element it has been little used as a radical promoter;[7] however, its carbonyl complexes,[8] in spite of their hazard, have found many applications in radical alkyl-halo-additions. We have recently described some applications of iron-promoted Kharasch reactions[9] and now we report that the HATRA of methyl 2,2-dichlorocarboxylates or trichloro acetic acid derivatives to alkenes can be efficiently promoted by iron filings at 50°-100°C in N,N-dimethylformamide (DMF)/1,2-dichloroethane (DCE).

RESULTS AND DISCUSSION

In a previous study, we reported that the addition of methyl 2-Br-2-Cl-carboxylates to alkenes was effectively carried out by iron in DMF/DCE.[9] Although the reaction proceeded with satisfactory yields by using iron powder at 25°C, the better results were obtained at 80°C with iron filings; at this temperature, however, because of the weakness of the C-Br bond, relatively high amounts of trans-halogenated and cyclic by-products were obtained, which complicate the separation and the purification of the Kharasch adducts. To overcome these problems we tried the corresponding 2,2-dichloro adducts, and found that methyl 2,2-dichlorocarboxylates add to 1-alkenes in good yields by using Fe^0 filings (10 mol%) in DMF/DCE at 100°C (scheme 1).[10]



1a: R' = CH_3
1b: R' = n-C_4H_9
1c: R' = i-C_3H_7
1d: R' = $C_6H_5CH_2$
1e: R' = C_6H_5
1f: R' = H

2a: R" = n-C_6H_{13}
2b: R" = $(CH_3)_3C$
2c: R" = CH_3COOCH_2
2d: R" = C_6H_5
2e: R" = $C_6H_5CH_2$
2f: R" = $CH_3OCO(CH_2)_8$
2g: R" = 3-cyclohexenyl
2h: R" CH_3OCO
2i: R" = $(CH_3)_3SiOCH_2$
2j: R" = $(CH_3)_3SiCH_2$

3a: R' = CH_3; R" = n-C_6H_{13}
3b: R' = CH_3; R" = $(CH_3)_3C$
3c: R' = CH_3; R" = CH_3COOCH_2
3d: R' = CH_3; R" = C_6H_5
3e: R' = CH_3; R" = $C_6H_5CH_2$
3f: R' = CH_3; R" = $CH_3OCO(CH_2)_8$
3g: R' = CH_3; R" = 3-cyclohexenyl
3h: R' = CH_3; R" CH_3OCO
3i: R' = CH_3; R" = $(CH_3)_3SiOCH_2$
3j: R' = CH_3; R" = $(CH_3)_3SiCH_2$
3k: R' = n-C_4H_9; R" = n-C_6H_{13}
3l: R' = i-C_3H_7; R" = n-C_6H_{13}
3m: R' = $C_6H_5CH_2$; R" = n-C_6H_{13}
3n: R' = C_6H_5; R" = n-C_6H_{13}
3o: R' = H; R" = n-C_6H_{13}

scheme 1

Temperature and solvent are important parameters for obtaining satisfactory results. At 80°C in DMF, owing to the stronger C-Cl bond, the halo-alkyl-addition, even with 20 mol% of Fe^0 filings, does not proceed; at higher temperature, e.g. 120°C, the reaction becomes faster, but yields of the 1:1 adduct are reduced by the formation of telomeric by-products. Only in DMF, especially when diluted with a co-solvent such as DCE or propyl ether (PE), halo-alkyl-addition occur easily.[11] Other solvents structurally correlated to DMF, i.e. formamide (FA), N,N-diethylformamide (DEF), N-methylformamide (MFA), N,N-dimethylacetamide (DMA) have also been tested, but exclusively DMA and DEF gave positive results. We think that DMF not only acts as a cleaner of the metal surface, dissolving the ferrous salts formed in the course of the reaction, but also as an iron activator, as shown by the inactivity of the less basic solvents MFA and FA.[12]

Unlike 2-bromo-2-chloro-esters, 2,2-dichloroesters allow workers to use a more favourable alkene/ester ratio (3:2 against 5:2 mol/mol). In fact, owing to the higher strength of the C-Cl bond, the initiation step is slower and therefore, less alkene is required to prevent the formation of succinates. The yields of these by-products are also affected by the iron particle size; owing to the high number of active centres, iron powder produces indeed an exceeding amount of radicals, which increases the radical homocoupling termination probability.

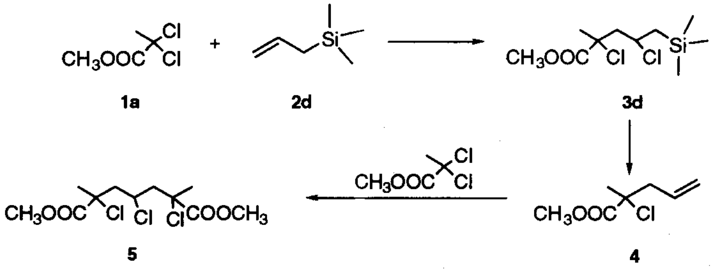
The procedure is satisfactory only with terminal alkenes, as can be seen in table 1; steric effects heavily hinder intermolecular radical addition[13] when internal or cyclic alkenes are involved. Some functional groups can be present on the olefinic receptors without interfering with the HATRA process; hydroxyl group, however, needs protection as acetate.

Table 1. Addition of methyl 2,2-dichlorocarboxylates (**1a-f**) to various alkenes (**2a-j**) promoted by Fe^0.[a]

esters	alkenes	t(h)	conversion (mol%)[b]	3 (mol%)[c]
1a	2a	16	98	80
1a	2b	24	66	39
1a	2c	16	99	60
1a	2d	16	99	60
1a	2e	16	95	64
1a	2f	24	97	70
1a	2g	16	100	65
1a	2h	16	25	6
1a	2i	16	90	50
1a	2j	16	98	37
1b	2a	16	99	81
1c	2a	16	98	79
1d	2a	16	100	52
1e	2a	16	25	-
1f	2a	24	92	76

[a] Reaction performed on 24 mmol of ester under Ar at 100°C in 6ml of 1:1 DMF/DCE mixture; ester:alkene:iron = 10:15:1. [b] Conversion monitored by GC. [c] Isolated yields based on 1; the products are 1:1 mixture of diastereoisomers.

Allylation of the ester, affording product **4**, is observed with allyltrimethylsilane **2d**, as a result of the easy dehydrochlorination of the product **3d** (scheme 2); **4** may undergo a further addition of carbalkoxy chloromethyl radical, which may be prevented by a larger amount of allylsilane (2:4 instead of 2:3).

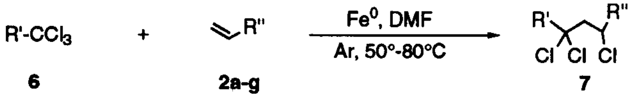


scheme 2

Easy polymerizable alkenes have also been tested; while methylacrylate gives extensive telomerization, styrene affords the 1:1 adduct in fair yield. The addition of **1a** to methyl 10-undecenoate **2g**, an alkene of considerable interest as a renewable material,[14] affords **3g** in good yield; however methyl 10-undecenoate:dichloroester telomers (2:1 and 3:1) are always present, also working under more dilute conditions and even with a stoichiometric ratio between **1a** and **2g**.[15]

The HATRA of a number of dichloroesters with 1-octene **2a** (table 1) affords generally satisfactory yields. Only methyl 2,2-dichloro-2-phenyl-acetate **1e** fails the addition, likely due to the phenyl stabilised radical intermediate,[16] in this case the succinate derivative is, in fact, the main product. The low yield obtained with methyl 2,2-dichloro-3-phenyl-propanoate **1d** is due to the easy dehydrochlorination of the Kharasch product.

The reported procedure has been applied, with little modification, to the addition of trichloroacetic acid derivatives to alkenes. With these haloderivatives, the best results were obtained with alkyl trichloroacetates and CCl_3CN by using DMF alone and working with an halo-derivative:alkene:iron ratio of 3:2:1 at 50°-100°C (scheme 3 and table 2).



6a: $R' = COOCH_3$
6b: $R' = COOC_2H_5$
6c: $R' = CONHCH_3$
6d: $R' = CONH_2$
6e: $R' = CN$

scheme 3

Table 2. Addition of trichloroderivatives (**6a-e**) to alkenes (**2**) promoted by Fe^0.[a]

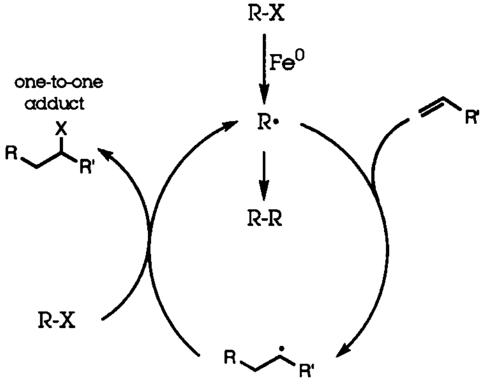
haloderivative	alkene	T(°C)	t(h)	conversion (mol%)[b]	7 (mol%)[c]
6a	2a	60	48	99	89
6a	2b	80	48	90	65
6a	2c	60	48	75	55
6a	2d	60	24	100	82
6a	2e	50	48	80	76
6a	2f	60	48	98	88
6a	2g	60	48	87	50
6b	2a	60	48	95	78
6c	2a	60	48	89	60
6d	2a	60	48	20	18
6e	2a	60	48	96	83

[a]Reaction performed on 45 mmol of haloderivative under Ar in 5 ml of DMF; halocompound:alkene:iron = 3:2:1. [b]Conversion monitored by GC. [c]Isolated yields based on 2.

Monohalogenated esters, i.e. ethyl 2-Br-propanoate and dimethyl chloromalonate afforded poor conversions, likely to be due to the LUMO is not being low enough for an easy interaction between the haloderivative and the metal.[17]

Inhibition of the reaction by both an electron scavenger and a radical inhibitor is consistent with a single electron transfer (SET) initiated radical chain mechanism. When 2,2-dichloropropanoate, indeed, is treated in DMF/DCE at 100°C for 16h with 1-octene and 10 mol% of Fe^0 and 10 mol% of p-dinitrobenzene as SET scavenger,[18] no reaction is observed. Furthermore, the reaction is completely inhibited by air or by hydroquinone.

We propose a free radical chain mechanism initiated by Single Electron Transfer from iron to the halocompound LUMO with concomitant expulsion of a halide anion.[19] However, the intervention of Fe(II), formed during the course of the reaction, cannot be excluded.



scheme 4

In order to examine the morphology of the attack undergone by the iron during the haloester activation reaction (initiation of the radical process), four little plates (about 0.5 x 0.5 cm, 0.1 cm thick) of pure iron were put in the reaction vessel and extracted after 5, 15, 30 and 60 minutes. The plates showed an upper rough, porous surface and a lower smooth one on microscopic observation. From the microphotographs (1500x) one can see that the main corrosion type is a pitting corrosion like that of passivated metals in aqueous solution, but free from solid corrosion products. Independently of the exposure time, the pits seem to have about the same size and the same depth; only their surface density increases. This pits shape agree with a fast activation of reaction sites followed by an equally fast inhibition, due to some corrosion product; however, the microscopic observation of the cross section of the plates has shown that the pits grow "under skin", parallel to the surface. This is an anomalous pitting corrosion, even if, owing to the relatively high temperature and stirring speed of the reaction mixture, the relative motion between solid metallic iron and solution may give rise to erosion or cavitation processes. However, the corrosion phenomena related to haloester activation reactions needs further investigation to explain the dissolution mechanism of iron in the presence of halogenated compounds.

EXPERIMENTAL SECTION

Alkenes, trihaloderivatives and iron filings were standard grade commercial products and used without purification. Dimethylformamide and 1,2-dichloroethane were dried over three batches of 3Å sieves (5% w/v, 12h) and used without degassing. Methyl 2,2-dichloropropanoate was synthesised 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 reported procedure.[20] The electron impact mass spectra were obtained at 70 eV. All IR spectra were measured as neat and the proton chemical shifts were recorded in $CDCl_3$ at 200 MHz.

General Procedure for Alkyl-Halo-Addition Promoted by Fe^0.

Addition of dichloroesters 1a-f to alkenes 2a-j: typically, iron filings (2.4 mmol) were weighted in a Schlenk tube and then DMF (1.5 ml), DCE (1.5 ml)[21] and alkene (36 mmol) were added under argon. The mixture was thermostatted at 100°C and the dichlorocarboxylate (24 mmol) was added by syringe. After stirring for 17h, the mixture was diluted with 50 ml of HCl 5% and extracted with CH_2Cl_2 (3 x 20 ml). The organic layer was dried over Na_2CO_3 and evaporated. The Kharasch adducts were isolated by silica gel chromatography, using petroleum ether (b.p. 40-60°C)/diethyl ether gradient, and their ^{1}H-NMR spectra compared with those of authentic samples.[22]

Addition of trichloderivatives 6a-g to alkenes: typically, iron filings (15 mmol) were weighted in a Schlenk tube and then DMF (5 ml) and alkene (30 mmol) were added under argon. The mixture was thermostatted at 100°C and the trichloroderivative (45 mmol) was added by syringe. After stirring for 24-48h, the mixture was diluted with 50 ml of HCl 5% and extracted with CH_2Cl_2 (3 x 20 ml). The organic layer was dried over Na_2CO_3 and evaporated. The Kharasch adducts were isolated by silica gel chromatography, using petroleum ether (b.p. 40-60°C)/diethyl ether gradient.

Methyl 2,2,4-trichlorodecanoate 7a

^{1}H-NMR $\partial(CDCl_3)$: 0.91 (3H, bt, $-CH_3$); 1.31 (6H, bs, $-CH_2-$); 1.5 (2H, m, $-CH_2-$); 1.78 (2H, m, CH_3CH_2-); 2.83 (1H, dd, J_{AB}=15.2 Hz, J_{AX}=3.3 Hz, $-CCl_2CH_2-$); 3.12 (1H, dd, J_{AB}=15.2 Hz, J_{BX}=8.7 Hz, $-CCl_2CH_2-$); 3.90 (3H, s, $-OCH_3$); 4.21 (1H, m, -CHCl-). MS (EI, 70 eV) m/z: 289 (0.18%); 217 (10%) [M^+-HCl-Cl]; 142 (100%) [$Cl_2CCOOCH_3$]; 121 (28%) [$ClCH(CH_2)COOCH_3$]; 55 (73%) [$C_4H_7^+$].

Anal. Calcd. for $C_{11}H_{19}Cl_3O_2$: C, 45.62%; H, 6.61%. Found: C, 45.54%; H, 6.76%.

Methyl 2,2,4-trichloro-5,5-dimethylhexanoate 7b

^{1}H-NMR $\partial(CDCl_3)$: 1.06 (9H, s, $-CH_3$); 2.88 (1H, dd, J_{AB}=15.2 Hz, J_{AX}=2.4 Hz, $-CCl_2CH_2-$); 3.02 (1H, dd, J_{AB}=15.2 Hz, J_{BX}=9.2 Hz, $-CCl_2CH_2-$); 3.88 (3H, s, $-OCH_3$); 3.98 (1H, dd, J_{AX}=2.4 Hz, J_{BX}=9.2 Hz, -CHCl-). MS (EI, 70 eV) m/z: 260 (0.02%) [M^+]; 142 (2%) [$Cl_2CCOOCH_3$]; 70 (13%) [$C_5H_{10}^+$]; 57 (100%) [$C_4H_9^+$]; 41 (24%) [$C_3H_5^+$].

Anal. Calcd. for $C_9H_{15}Cl_3O_2$: C, 41.33%; H, 5.78%. Found: C, 41.47%; H, 5.72%.

Methyl 2,2,4-trichloro-5-acetylpentanoate 7c

^{1}H-NMR $\partial(CDCl_3)$: 2.13 (3H, s, $-CH_3$); 2.97 (1H, dd, J_{AB}=15.4 Hz, J_{AX}=4.0 Hz, $-CCl_2CH_2-$); 3.09 (1H, dd, J_{AB}=15.4 Hz, J_{BX}=7.2 Hz, $-CCl_2CH_2-$); 3.92 (3H, s, $-OCH_3$); 4.29 (2H, m, $-OCH_2-$); 4.4 (1H, m, -CHCl-). MS (EI, 70 eV) m/z: 278 (0.01%) [M^+]; 181 (5%) [M^+-HCl-CH_3COO]; 145 (4%); 75 (9%); 59 (10%) [CH_3COO^+]; 43 (100%) [CH_3CO^+].

Anal. Calcd. for $C_8H_{11}Cl_3O_4$: C, 34.62%; H, 3,99%. Found: C, 34,50%; H, 4,14%.

Methyl 2,2,4-trichloro-4-phenylbutanoate 7d

^{1}H-NMR $\partial(CDCl_3)$: 3.25 (1H, dd, J_{AB}=14.9 Hz, J_{AX}=6.1 Hz, $-CCl_2CH_2-$); 3.48 (1H, dd, J_{AB}=14.9 Hz, J_{BX}=7.4 Hz, $-CCl_2CH_2-$); 3.71 (3H, s, $-OCH_3$); 5.26 (1H, dd, J_{AX}=6.1 Hz, J_{BX}=7.4 Hz, -CHCl-); 7.41 (5H, m,

ArH). MS (EI, 70 eV) m/z: 281 (1.4%) [M$^+$]; 142 (100%) [$Cl_2CCOOCH_3$]; 125 (62%) [C_6H_5CHCl]; 115 (28%).
Anal. Calcd. for $C_{11}H_{11}Cl_3O_2$: C, 46,92%; H, 3,94%. Found: C, 46,81%; H, 3,96%.

Methyl 2,2,4-trichloro-5-phenylpentanoate 7e
^{1}H-NMR ∂($CDCl_3$): 2.90 (1H, dd, J_{AB}=15.2 Hz, J_{AX}=3.2 Hz, -CCl_2CH_2-); 3.14 (1H, dd, J_{AB}=15.2 Hz, J_{BX}=8.8 Hz, -CCl_2CH_2-); 3.16 (2H, d, J=7 Hz, ArCH2-); 3.91 (3H, s, -OCH_3); 4.46 (1H, m, -CHCl-); 7.34 (5H, m, ArH). MS (EI, 70 eV) m/z: 222 (11%); 187 (7%); 117 (31%); 91 (100%) [$C_7H_7^+$].
Anal. Calcd. for $C_{12}H_{13}Cl_3O_2$: C, 48,76%; H, 4,43%. Found: C, 48,61%; H, 4,53%.

Methyl, ethyl 2,2,4-trichlorotridecandioate 7f
^{1}H-NMR ∂($CDCl_3$): 1.27 (3H, t, J=7.1 Hz, CH_3CH_2-); 1.32 (10H, m, -CH_2-); 1.64 (2H, m, -CH_2-); 1.81 (2H, m, -CH_2-); 2.31 (2H, bt, -$COCH_2$-); 2.82 (1H, dd, J_{AB}=15.2 Hz, J_{AX}=3.3 Hz, -CCl_2CH_2-); 3.13 (1H, dd, J_{AB}=15.2 Hz, J_{BX}=8.8 Hz, -CCl_2CH_2-); 3.91 (3H, s, -OCH_3); 4.15 (2H, q, J=7.1, -$COCH_2CH_3$); 4.18 (1H, m, -CHCl-). MS (EI, 70 eV) m/z: 136 (12%); 121 (11%) [$ClC(CH_2)COOCH_3$]; 95 (18%); 81 (65%); 69 (100%) [$C_5H_9^+$].
Anal. Calcd. for $C_{16}H_{27}Cl_3O_4$: C, 49,31%; H, 6,98%. Found: C, 49,26%; H, 6,93%.

Methyl 2,2,4-trichloro-4-(cyclohexen-3-yl)-butanoate 7g
^{1}H-NMR ∂($CDCl_3$): 1.8-2.2 (7H, m, -CH_2-CH-CH_2-CH_2-); 2.82-2.93 (1H, m, -CCl_2CH_2-); 3.07-3.23 (1H, m, -CCl_2CH_2-); 3.92 (3H, s, -OCH_3); 4.24 (1H, m, -CHCl-); 5.71 (2H, m, -CH=CH-). MS (EI, 70 eV) m/z: 248 (19%) [M+-HCl]; 181 (25%); 138 (100%); 121 (76%); 91 (69%); 77 (62%); 53 (43%).
Anal. Calcd. for $C_{11}H_{15}Cl_3O_2$: C, 46,26%; H, 5,29%. Found: C, 46,14%; H, 5.41%.

Acknowledgements. We thank the C.N.R. (Rome) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) for financial assistance.

REFERENCES AND NOTES

1. (a) Brown, S.P.; Balkrishna, S.B. *Tetrahedron Lett.*, **1981**, 22, 4891; (b) Kharasch, M.S.; Skell, P.S.; Fisher, P.; *J. Am. Chem. Soc.*, **1948**, 70, 1055.
2. Nakano, T.; Kayama, M.; Nagai, Y. *Bull. Soc. Chim. Jpn.*, **1987**, 60, 1049 end references therein.
3. (a) Iqbal, J.; Bhatia, B.; Nayyar, N.K. *Chem. Rev.*, **1994**, 94, 519; (b) Nagashima, H.; Seki, K.; Ozaki, N.; Wakamatsu, H.; Itoh, K.; Tomo, Y.; Tsuji, J. *J. Org. Chem.* **1990**, 55, 985, and references therein; (c) Giese, B.; Ghosez, A.; Zipse, H. in *Houben-Weil*, Georg Thieme Verlag: Stuttgart, **1989**, vol. E19a/2, 876 ff.
4. (a) Pirrung, F.O.H.; Hiemstra, H.; Speckamp, W.N. *Tetrahedron* **1994**, 50, 12415-12442. b) Martin, P.; Steiner, E.; Bellus, D. *Helv. Chim. Acta* **1980**, 1947-1957. c) Matsumoto, H.; Ohkawa, K.; Ikemori, S.; Nakano, T.; Nagai, Y. *Chem. Lett.* **1979**, 1011-1014. d) Matsumoto, H.; Nakano, T.; Ohkawa, K.; Nagai, Y. *ibid.* **1978**, 363-366.
5. (a) Phelps, J.C.; Bergbreiter, D.E.*Tetrahedron Lett.*, **1989**, 3915-3918. b) Hayes, T.K.; Villani, R.; Weinreb, S.M. *J. Am. Chem. Soc.* **1988**, 110, 5533-5543. c) Hayes, T.K.; Parvez, M.; Weinreb, S.M. *J. Org. Chem.* **1986**, 51, 5503-5505.
6. (a) Helland, B.R.; Alvarez, P.J.J.; Schnoor, J.L. *J. Hazard. Mater.*, **1995**, 41, 205; (b) Warren, C.K.; Arnold, R.G.; Bishop, T.L.; Lindholm, L.C.; Betterton, E.A. *J. Hazard. Mater.*, **1995**, 41, 217; (c) Matheson, L.J.; Tratnyek, P.G. *Environ. Sci. Technol.*, **1994**, 28, 2045.
7. (a) Quizen, G.; Weitho, P. *Huaxue Shiji*, **1991**, 13, 231; (b) Chang, C.C.; Yang, C.T.; Chang, C.T. *J. Chin. Chem. Soc.* (Taipei), **1988**, 35, 321; (c) Chen, Q.-Y.; He, Y.-B.; Yang, Z.-Y. *J. Fluorine Chem.*,

1986, 34, 255; (d) Davis, R.; Khazaal, N.M.; Maistry, V. *J. Chem. Soc., Chem. Commun.*, **1986**, 1387; (e) Yusuke, I.; Masato, O. *Japan Kokai* 77,133,908 (C. A. **1978**, 88, 152013m); (f) Karapet'yan, Sh. A.; Belyavskii, A.B.; Kuz'mina, N.A. *Izv. Akad. Nauk SSSr, Ser. Khim.*, **1973**, 6, 1272 (C.A. 1973, 79, 91497n); (g) Santford, W.S.; *Eur. Pat. Appl. Ep.* 131, 561 (C. A. **1973**, 103, 53693a); (h) Hoechst, *Brit.* 803, 463 (C. A. **1959**, 53, 11222b).

8. (a) Freidlina, R.Kh.; Chukovskaya, E.C. *Synthesis*, **1974**, 477; (b) Freidlina, R.Kh.; Velichko, F.K. *Synthesis*, **1977**, 145.
9. (a) Forti, L.; Ghelfi, F.; Pagnoni, U.M. *Tetrahedron Lett.*, **1996**, 37, 2077; (b) Forti, L.; Ghelfi, F.; Lodi Lancellotti, M.; Pagnoni, U.M. *Synthetic Commun.*, **1996**, 26, 1699; (c) Forti, L.; Ghelfi, F.; Pagnoni, U.M. *Tetrahedron Lett.*, **1995**, 36, 2509.
10. Other metals have been tested, but with very poor results.
11. Both in DCE or PE alone the reaction does not proceed.
12. The addition into the reaction mixture of ligands like dipyridyl, pyridine, triphenylphosphine does not produce any sort of improvment; furthermore, when these ligands are used in solvents other than DMF, no reaction was observed.
13. (a) Wu, J.Q.; Beranek, I.; Fischer, H. *Helv. Chim. Acta*, **1995**, 78, 194; (b) Yang, Z.-Yu; Burton, D.J. *J. Org. Chem.*, **1992**, 57, 5144; (c) Ghodoussi, V.; Gleicher, G.J.; Kravetz, M. *J. Org. Chem.*, **1986**, 51, 5007; (d) Walling, C. *Tetrahedron*, **1985**, 41, 3887; (e) Giese, B. *Angew. Chem. Int. Ed. Engl.*, **1983**, 22, 753; (f) Tedder, J.M. *Angew. Chem. Int. Ed. Engl.*, **1982**, 21, 401.
14. Baumann, H.; Buhler, M.; Fochem, H.; Hirsinger, F.; Zoebelein, H.; Falbe, J. *Angew. Chem. Int. Ed. Engl.*, **1988**, 27, 42.
15. The C-C triple bond was completely unreactive; furthermore, the observed low ester conversion suggest a some sort of inhibiting action.
16. Perkins, M.J. *Radical Chemistry*, Ellis Horwood, London, **1994**.
17. Giese, B. *Angew. Chem. Int. Ed. Engl.*, **1983**, 22, 753.
18. Chen, Q.-Y.; Yang, Z.-Y. *J. Chem. Soc., Chem. Commun.*, **1986**, 498.
19. Timokhin, B.V. *Russ. Chem. Rev.*, **1990**, 59, 193.
20. (a) Bellesia, F.; Boni, M.; Ghelfi, F.; Pagnoni, U.M. *Tetrahedron Lett.*, **1994**, 2961; (b) Boni, M.; Ghelfi, F.; Pagnoni, U.M.; Zucchi, C. *Bull. Chem. Soc. Jpn.*, **1994**, 67, 1622.
21. The volume of the reaction mixture greatly affects the yields of the reactions. In fact, high headspace negatively affect the reaction, owing to the partition of olefin and dichloroester between liquid and vapour phase; the best yields are obtained on working with Schlenk capacity little higher than the reaction volume. In this condition the amount of solvent can be drastically reduced.
22. Forti, L.; Ghelfi, F.; Pagnoni, U.M. *Tetrahedron*, **1997**, 53, 4419.

(*Received in UK* 16 *September* 1997; *revised* 21 *October* 1997; *accepted* 23 *October* 1997)