Efficient Electrosynthesis of α-Chloro-α,β-Unsaturated Carboxylic and Phosphonic Esters Using Magnesium Electrochemical Activation

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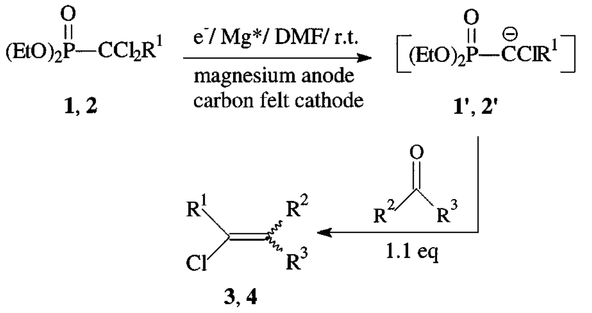
Abstract: Various α-chloro-α,β-unsaturated carboxylic or phosphonic esters were easily and rapidly prepared under mild conditions in DMF, by electrolysing respectively triethyl dichloromethylphosphonoacetate and tetraethyl dichloromethyl-*bis*-phosphonate, then treating the resulting carbanions with a carbonyl compound. The use of an electrochemical activated magnesium anode improved the rate of the reaction.

Key words: α-chloro-α,β-unsaturated carboxylic esters, α-chloro-α,β-unsaturated phosphonic esters, electrosynthesis, Horner–Wadsworth–Emmons olefination,magnesium electrochemical activation

Besides their increasing interest in biochemistry,[1] phosphonates remain essential tools for the synthesis of polyfunctional olefins via the popular Horner–Wadsworth–Emmons (HWE) reaction.[2] Many technical refinements to the original process have been regularly proposed in order to improve the conditions and/or the selectivity of the reaction.[3] Among these techniques, the electrochemical methodology proved to be a very mild way for generating intermediate phosphonate carbanions.[4] Within this context, we have shown recently the advantages of using a magnesium sacrificial anode, which significantly increase the rate and the yield of alkylation,[5a] cycloalkylation[5b] and Michael addition[5c] reactions of such electrogenerated carbanions. Pursuing the study on the applicability of this methodology, we report now our results relating to the electrochemical HWE synthesis of α-chloro-α,β-unsaturated carboxylic esters **3** and α-chloro α,β-unsaturated phosphonic esters **4**, from the readily available[6] phosphonates **1** and **2**, respectively (Scheme).



1, 1', 3 : $R^1 = CO_2Et$; **2, 2', 4** : $R^1 = P(O)(OEt)_2$

Scheme

Electroreductions of **1** or **2** were performed in a water-cooled one compartment-cell and continued until the complete formation of the corresponding carbanion **1'** or **2'** as proved by ^{31}P NMR spectroscopy.[7] In our experiments, the reduction was achieved after 2.5 hours for **1** and after 2 hours for **2**. In comparison with the calculated

Table 1 Electrosynthesis of esters **3** and **4**

Entry	Product **3** or **4**	R^2	R^3	Yield (%)[a] of **3**	(*E*)% : (*Z*)% Ratio[b] of **3**	Yield (%)[a] of **4**	(*E*)% : (*Z*)% Ratio[b] of **4**
1	**a**	Ph	H	74	65 : 35	60	9 : 91
2	**b**	$4\text{-}MeOC_6H_4$	H	61	59 : 41	79	8 : 92
3	**c**	$4\text{-}NO_2C_6H_4$	H	55	60 : 40	78	9 : 91
4	**d**	PhCH=CH	H	50	67 : 33	77	10 : 90
5	**e**	C_5H_{11}	H	40	71 : 29	57	0 : 100
6	**f**	$4\text{-}CF_3\text{-}C_6H_4$	H	75	54 : 46	27[c]	12 : 88
7	**g**	Ph	CF_3	70	11 : 89[d]	50	0 : 100[e]
8	**h**	$(CH_2)_4$		0	–	50	–

[a] Yield of purified product, whose analytical data (microanalysis or HRMS, NMR and MS data) are in good agreement with the expected structures and with previous reports.

[b] Determined on the crude product by gas chromatography ; (*E*)- and (*Z*)-isomer ratio was determined by ^{1}H NMR spectroscopy (entries 1–6).[13]

[c] An important decomposition was observed during the purification.

[d] (*E*)- and (*Z*)-isomer ratio was determined by ^{19}F NMR spectroscopy.[14]

[e] The stereochemistry of the product was determined by ^{13}C NMR spectroscopy.[15]

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Table 2 ^{1}H and ^{13}C NMR and MS Data of Compounds **3**[a]

Product	^{1}H NMR (CDCl$_3$/TMS) δ, *J* (Hz)	^{13}C{^{1}H} NMR (CDCl$_3$/TMS) δ, *J* (Hz)	MS (70 eV) *m/z* (%)
(*E*)-**3c**	1.3 (t, *J* = 7.1, 3H, C*H*$_3$CH$_2$O), 4.3 (q, *J* = 7.1, 2H, CH$_3$C*H*$_2$O), 7.85 (s, 1H, HC=CCl), 7.9 (d, *J* = 8.9, 2H, H$_{o\text{-arom.}}$), 8.2 (d, *J* = 8.9, 2H, H$_{m\text{-arom.}}$)	13.1 (*C*H$_3$CH$_2$O), 62.1 (CH$_3$*C*H$_2$O), 122.6 (C$_{m\text{-arom.}}$), 125.1 (C$_{\text{i-arom.}}$), 130.1 (C$_{o\text{-arom.}}$), 133.2 (H*C*=CCl), 138.1 (HC=*C*Cl), 146.9 (CNO$_2$), 161.5 (C=O)	257 (M$^+$, 30), 255 (M$^+$, 90), 220 (63), 210 (26), 192 (100), 164 (21), 147 (10), 136 (10), 101 (33), 89 (29), 75 (31), 51 (16), 38 (5)
(*Z*)-**3c**	1.1 (t, *J* = 7.1, 3H, C*H*$_3$CH$_2$O), 4.15 (q, *J* = 7.1, 2H, CH$_3$C*H*$_2$O), 7.2 (s, 1H, HC=CCl), 7.4 (d, *J* = 8.8, 2H, H$_{o\text{-arom.}}$), 8.1 (d, *J* = 8.8, 2H, H$_{m\text{-arom.}}$)	12.7 (*C*H$_3$CH$_2$O), 61.6 (CH$_3$*C*H$_2$O), 122.5 (C$_{m\text{-arom.}}$), 125.6 (C$_{i\text{-arom.}}$), 128.3 (C$_{o\text{-arom.}}$), 133.1 (H*C*=CCl), 139.4 (HC=*C*Cl), 146.5 (CNO$_2$), 161.5 (C=O)	257 (M$^+$, 33), 255 (M$^+$, 100), 220 (56), 192 (97), 164 (17), 147 (10), 136 (9), 101 (31), 89 (25), 75 (29), 51 (15), 36 (4)
(*E*)-**3d**[b]	1.35 (t, *J* = 7.1, 6H, C*H*$_3$CH$_2$O), 4.3 (m, 4H, CH$_3$C*H*$_2$O), 7 (d, *J* = 14.9, 1H, H$_\delta$), 7.2 (dd, *J* = 14.9, 8.4, 1H, H$_\gamma$), 7.4 (m, 3 H, H$_{\text{arom}}$), 7.5 (m, 2 H, H$_{\text{arom}}$). , 7.6 (d, *J* = 8.4, 1H, H$_\beta$)	12.7 (*C*H$_3$CH$_2$O), 60.7 (CH$_3$*C*H$_2$O), 121.1 (C$_\alpha$), 121.5 (C$_\gamma$), 126 (C$_{o\text{-arom}}$), 127.3 (C$_{m\text{-arom}}$), 128 (C$_{p\text{-arom}}$), 134.4 (C$_{i\text{-arom}}$), 136.2 (C$_\beta$), 140.5 (C$_\delta$), 161.5 (C= O)	238 (M$^+$, 17), 236(M$^+$, 51), 209 (6), 207 (18), 193 (6), 191 (18), 155 (47), 129 (100), 128 (91), 127 (82), 115 (20), 91 (5), 77 (24), 51 (23), 50(11), 34 (8)
(*Z*)-**3d**[b]	1.35 (t, *J* = 7.1, 6H, C*H*$_3$CH$_2$O), 4.3 (m, 4H, CH$_3$C*H*$_2$O), 6.8 (d, *J* = 15.9, 1H, H$_\delta$), 7 (d, *J* = 11.2, 1H, H$_\beta$), 7.4 (m, 3 H, H$_{\text{arom}}$), 7.5 (m, 2 H, H$_{\text{arom}}$). , 7.9 (dd, *J* = 15.9, 11.2, 1H, H$_\gamma$)	12.6 (*C*H$_3$CH$_2$O), 60.5 (CH$_3$*C*H$_2$O), 119.7 (C$_\alpha$), 122.6 (C$_\gamma$), 125.9 (C$_{o\text{-arom}}$), 127.2 (C$_{m\text{-arom}}$), 127.7 (C$_{p\text{-arom}}$), 134.6 (C$_{i\text{-arom}}$), 139.6 (C$_\beta$), 140.6 (C$_\delta$), 161.2 (C=O)	238 (M$^+$, 20), 236 (M$^+$, 60), 209 (9), 207 (27), 193 (7), 191 (21), 155 (52), 129 (100), 128 (90), 127 (80), 115 (20), 91 (5), 77 (23), 51 (21), 50(9), 34 (8)
(*E*)-**3e**	0.85 (m, 3H, C*H*$_3$), 1.25 (m, 7H, CH$_2$ and OCH$_2$C*H*$_3$), 1.4 (m, 2H, CH$_2$), 2.3 (q, *J* = 7.5, 2H, C*H*$_2$-CH=CCl), 4.2 (q, *J* = 6.65, 2H, OC*H*$_2$CH$_3$), 7.0 (t, *J* = 7.25, 1H, CH$_2$C*H*=CCl)	14.6 (CH$_3$CH$_2$O), 22.8 (*C*H$_3$CH$_2$), 27.8 (CH$_2$), 29.8 (CH$_2$), 31.9 (CH$_2$), 62.5 (CH$_3$*C*H$_2$O), 123.6 (H*C*=ccl), 141.5 (HC=*C*Cl), 161.6 (C=O)	206 (M$^+$, 1), 204 (M$^+$, 3), 180 (2), 178 (6), 169 (14), 159 (13), 141 (6), 135 (76), 122 (42), 107 (100), 95 (42), 83 (20), 70 (40), 55(59), 41 (83), 36 (1)
(*Z*)-**3e**	0.85 (m, 3H, CH$_3$), 1.25 (m, 7H, CH$_2$ and OCH$_2$C*H*$_3$), 1.4 (m, 2H, CH$_2$), 2.5 (q, *J* = 7.5, 2H, C*H*$_2$CH=CCl), 4.2 (q, *J* = 6.65, 2H, OC*H*$_2$CH$_3$), 6.4 (t, *J* = 7.25, 1H, CH$_2$C*H*=CCl)	14.3 (*C*H$_3$CH$_2$O), 22.8 (*C*H$_3$CH$_2$), 29.0 (CH$_2$), 30.3 (CH$_2$), 31.8 (CH$_2$), 62.3 (CH$_3$*C*H$_2$O), 121.0 (H*C*=CCl), 141.1 (HC=*C*Cl), 161.8 (C=O)	206 (M$^+$, 17), 204 (M$^+$, 51), 180 (33), 178 (11), 161 (27), 158 (15), 133 (100), 120 (34), 107 (76), 95 (32), 70 (67), 55(62), 41 (83), 36 (2)
(*E*)-**3f**[c]	1.3 (t, *J* = 7.1, 3H, C*H*$_3$CH$_2$O), 4.3 (q, *J* = 7.1, 2H, CH$_3$C*H*$_2$O), 7.6 (d, *J* = 8.4, 2H, H$_{o\text{-arom.}}$), 7.8 (d, *J* = 8.1, 2H, H$_{m\text{-arom.}}$), 7.85 (s, 1H, HC=CCl)	14.3 (*C*H$_3$CH$_2$O), 62.3 (CH$_3$*C*H$_2$O), 125.1 (C$_{i\text{-arom.}}$), 125.8 (q, *J* = 3.8, C$_{m\text{-arom.}}$), 131 (C$_{o\text{-arom.}}$), 131.4 (q, *J* = 36.1, *C*CF$_3$),135.6 (H*C*=CCl), 136.7 (HC=*C*Cl), 163.3 (C=O), C^{d}F$_3$	280 (M$^+$, 26), 278 (M$^+$, 78), 261 (6), 259 (18), 243 (41), 233 (29), 215 (100), 185 (35), 170 (55), 151 (40), 136 (19), 120 (18), 101 (14), 95 (9), 75 (34), 45 (17), 39 (4)
(*Z*)-**3f**[c]	1.1 (t, *J* = 7.1, 3H, C*H*$_3$CH$_2$O), 4.1 (q, *J* = 7.1, 2H, CH$_3$C*H*$_2$O), 7.1 (s, 1H, HC=CCl),7.3 (d, *J* = 8.2, 2H, H$_{o\text{-arom.}}$), 7.5 (d, *J* = 8.2, 2H, H$_{m\text{-arom.}}$)	14 (*C*H$_3$CH$_2$O), 62.8 (CH$_3$*C*H$_2$O), 125.5 (C$_{i\text{-arom.}}$), 125.6 (q, *J* = 3.8, C$_{m\text{-arom.}}$), 129.1 (C$_{o\text{-arom.}}$), 132.3 (q, *J* = 36.1, *C*CF$_3$), 137.9 (HC=*C*Cl), 163.3 (*C*=O), C^{d}F$_3$	280 (M$^+$, 32), 278 (M$^+$, 96), 261 (6), 259 (18), 243 (50), 215 (100), 205 (34), 185 (33), 170 (54), 151 (36), 120 (16), 101 (12), 95 (8), 75 (29), 50 (12), 38 (4)
(*E*)-**3g**	1.4 (t, *J* = 7, 3H, C*H*$_3$CH$_2$O), 4.4 (q, *J* = 7, 2H, CH$_3$C*H*$_2$O), 7.2 (m, 2H, H$_{\text{arom.}}$), 7.4 (m, 3H, H$_{\text{arom.}}$)	13.7 (*C*H$_3$CH$_2$O), 63.2 (CH$_3$*C*H$_2$O), 128.5 (C$_{o\text{-arom.}}$), 129.2 (C$_{m\text{-arom.}}$), 129.5 (C$_{p\text{-arom}}$), 162.7 (C=O), C^{d}F$_3$, C$^d_{i\text{-arom.}}$, C^d(CF$_3$), C^d(Cl)	280 (M$^+$, 33), 278 (M$^+$, 100), 251 (27), 249 (81), 235 (21), 233 (63), 205 (16), 185 (42), 169 (18), 151 (24), 129 (12), 101 (12), 99 (6), 75 (15), 51 (14), 39 (4)
(*Z*)-**3g**	0.9 (t, *J* = 7, 3H, C*H*$_3$CH$_2$O), 4 (q, *J* = 7, 2H, CH$_3$C*H*$_2$O), 7.2 (m, 2H, H$_{\text{arom.}}$), 7.4 (m, 3H, H$_{\text{arom.}}$)	14.3 (*C*H$_3$CH$_2$O), 62.6 (CH$_3$*C*H$_2$O), 121.9 (q, *J* = 275.8, CF$_3$), 128.3 (C$_{o\text{-arom.}}$), 129 (C$_{m\text{-arom.}}$), 129.4 (C$_{p\text{-arom}}$), 131.4 (q, *J* = 1.7, C$_{i\text{-arom.}}$), 133.8 (q, *J* = 32.4, *C*(CF$_3$)), 162.6 (C=O), C^d(Cl)	280 (M$^+$, 33), 278 (M$^+$, 100), 251 (24), 249 (72), 235 (13), 233 (39), 215 (14), 205 (12), 185 (44), 169 (21), 151 (27), 136 (13), 129 (8), 101 (17), 75 (21), 51 (22), 39 (7)

[a] The following products showed spectroscopic data in full agreement with previous reports refered in brackets: **3a (**Ref. 4 and 11); **3b**(Ref. 11).

[b] The subcript letters (α, β, ...) refer to the position relative to the ester group R^1, namely : R^1(Cl)C$_\alpha$= C$_\beta$H$_\beta$-C$_\gamma$H$_\gamma$= C$_\delta$H$_\delta$-C$_6$H$_5$.

[c] ^{19}F NMR (CDCl$_3$), δ = - 64.2 [(E)-**3f**] ; - 63.9 [(Z)-**3f**].

[d] Signal of very low intensity, not clearly detected.

Table 3 ^{31}P, ^{1}H and ^{13}C NMR and MS Data of Compounds **4**[a]

Product	$^{31}P\{^{1}H\}$ NMR ($CDCl_3$); δ	^{1}H NMR ($CDCl_3$/TMS) δ, J (Hz)	$^{13}C\{^{1}H\}$ NMR ($CDCl_3$/TMS) δ, J (Hz)	MS (70 eV) *m/z* (%)
(*Z*)-**4d**[b]	11.8	1.3 (t, J = 7.1, 6H, CH_3CH_2O), 4.1 (m, 4H, CH_3CH_2O), 6.9 (d, J = 15.4, 1H, H_δ), 7.1 (ddd, J = 15.4, 10.55, 1.9, 1H, H_γ), 7.3 (m, 3 H, H_{arom}) , 7.35 (d, J = 10.55, 1H, H_β), 7.45 (m, 2 H, H_{arom})	16.6 (d, J = 6.5, CH_3CH_2O), 63.5 (d, J = 5.2, CH_3CH_2O), 120.4 (d, J = 210.7, C_α), 122.2 (d, J = 15.8, C_γ), 127.8 ($C_{o\text{-arom}}$), 129.3 ($C_{m\text{-arom}}$), 129.8 ($C_{p\text{-arom}}$), 136.2 ($C_{i\text{-arom}}$), 141.8 (C_δ), 142.7 (d, J = 18.3, C_β)	302 (M^+, 17), 300 (M^+, 51), 265 (96), 237 (34), 209 (100), 191 (17), 173 (16), 162 (16), 128 (59), 115 (29), 102 (18), 77 (18), 51 (12), 39 (5)
(*Z*)-**4e**	11.1	0.9 (t, J = 7.1, 3H, CH_3CH_2), 1.3 (m, 10H, CH_3CH_2O and CH_2), 1.4 (m, 2H, CH_2), 2.27 (tdd, J = 7.1, 7.1, 2.8, 2H, $H_2CCH{=}C$), 4.1 (m, 4H, CH_3CH_2O), 6.9 (dt, J = 14.2, 7.1, 1H, HC=CCl)	14.3 (CH_3), 16.6 (d, J = 6.4, CH_3CH_2O), 22.7 (CH_2), 27.7 (CH_2), 29.4 (d, J = 12.2, $H_2CCH{=}C$), 31.7 (CH_2), 63.3 (d, J = 5.4, CH_3CH_2O), 122.1 (d, J = 214.8, HC=CCl), 147.8 (d, J = 16.7, HC=CCl)	270 (M^+, 4), 268 (M^+, 12), 233 (100), 212 (5), 199 (50), 186 (47), 169 (37), 143 (49), 121 (9), 109 (15), 81 (31), 65 (37), 55 (34), 41 (50)
(*Z*)-**4f**[c]	10.9[d]	1.4 (t, J = 6.8, 6H, CH_3CH_2O), 4.2 (m, 4H, CH_3CH_2O), 7.6 (d, J = 7.6, 2H, H_{arom}), 7.7 (d, J = 15.2, 1H, HC=CCl), 7.9 (d, J = 7.6, 2H, H_{arom})	16.8 (d, J = 6.4, CH_3CH_2O), 64.1 (d, J = 5.4, CH_3CH_2O), 123.8 (d, J = 212.5, HC=CCl), 126.1 (q, J = 3.6, $C_{m\text{-arom}}$), 130.9 ($C_{o\text{-arom}}$), 132.1 (q, J = 32.9, CCF_3), 136.9 (d, J = 16.7, $C_{i\text{- arom}}$), 140.3 (d, J = 18.8, HC=CCl), C^eF_3	344 (M^+, 3), 342 (M^+, 9), 307 (92), 279 (28), 251 (100), 233 (12), 204 (3), 185 (4), 171 (7), 151 (12), 120 (3), 99 (2), 81 (7), 65 (6), 45 (1)
(*Z*)-**4g**[c]	6.6	1.1 (t, J = 7.1, 6H, CH_3CH_2O), 3.8 (m, 2H, CH_3CH_2O), 3.9 (m, 2H, CH_3CH_2O), 7.2 (m, 2H, H_{arom}), 7.4 (m, 3H, H_{arom}),	16.4 (d, J = 6.4, CH_3CH_2O), 64.1 (d, J = 5.4, CH_3CH_2O), 121.9 (qd, J = 279.4, 37.4, CF_3), 128.5 ($C_{o\text{-arom}}$), 129.9 ($C_{m\text{-arom}}$), 130 ($C_{p\text{-arom}}$), 131.6 (dq, J = 211,2.5, HC=CCl), 132.6 (q, J = 3.2, $C_{i\text{-arom}}$), 142.5 (qd, J = 31.5, 18.5, HC=CCl)	344 (M^+, 29), 342 (M^+, 86), 316 (5), 314 (15), 307 (40), 279 (40), 251 (100), 231 (14), 211 (11), 185 (31), 177 (33), 151 (59), 119 (13), 109 (25), 81 (53), 65 (55), 45 (9)

[a] The following products showed spectroscopic data in full agreement with previous reports refered in brackets: **4a (**Refs. 12b, 12d and 16); **4b** and **4c** (Ref. 12d); **4h** (Refs 12b and 12d).

[b] See footnote b, Table 2.

[c] ^{19}F NMR ($CDCl_3$), δ: - 63.6 [(E)-**4f**]; - 63.4 [(Z)-**4f**]; - 60.8 (d, J = 1.4) [(Z)-**4g**].

[d] $\delta_{(E)\text{-isomer}}$ = 11.3.

theoretical duration of a bielectronic electrochemical reduction (2 F.mol^{-1}), namely 4 hours 40 minutes for the quantity of substrate employed (13 mmol), the observed times of electrolysis clearly indicate the occurence of a concomitant chemical reduction at the magnesium anode (noted Mg* in the Scheme) and confirm the previously called «magnesium electrochemical activation» phenomenon.[8] After complete formation of the carbanion,[9] the external power was cut off, then the carbonyl compound was introduced in the cell under inert gas and allowed to react with **1’** or **2’** at room temperature, the reaction being monitored by ^{31}P NMR spectroscopy. With aldehydes (Table 1, Entries 1 to 6) and with an activated ketone (Entry 7), the expected olefination reaction leading to **3** or **4** was nearly quantitative (crude yield > 95%); however, as previously reported,[10] such α-chloro-α,β-unsaturated esters are relatively unstable compounds, which undergo some decomposition during purification. In the case of cyclopentanone (entry 8), the reaction was very slow with **2’**, but nevertheless it was complete after 24 hours; in contrast, no reaction could be detected with **1’**, under our conditions. The stereoselectivity of these electrochemically induced HWE olefination reactions was comparable to the one observed earlier under the usual chemical procedure (lithiated bases/low temperature), with the same substitution pattern of the phosphorus atom, giving predominantly (*E*)-**3**[11] or (*Z*)-**4**[12] isomers, respectively. In contrast to **3**, the remarkable high stereoselectivity of the formation of **4**, could be likely justified by steric interactions, which favoured the less constrained conformational intermediate adducts of the HWE reaction, as recently suggested.[12d]

In conclusion, this electrochemical version of the HWE synthesis of α-chloro-α,β-unsaturated carboxylic and phosphonic esters **3** and **4** appears to be very attractive. The magnesium activation process allows a rapid generation of anions under very mild conditions, in comparison to the usual metallation requirements. The subsequent olefination reaction takes place smoothly at room temperature, leading to the expected products with yield and stereoselectivity similar to the ones obtained by the chemical procedure.

Reagents and solvents were purchased from commercial suppliers. DMF was purified by distillation on CaH_2 under reduced pressure and kept over 4Å molecular sieves under N_2. Tetraethylammonium bromide was purified by recrystallization (EtOH/Et_2O) and dried at 120°C under vaccum during 5 h. Cathodes, purchased from Le Carbone Lorraine, are carbon felt plates (45 mm × 35 mm, depth: 5 mm, specific area: 0.3 $m^2.g^{-1}$). Magnesium anodes, purchased from Prolabo, are rods (diameter: 10 mm). TLC was performed on Merck 60 F-254 silica gel plates and flash chromatography over silica gel (230–400 mesh). Elemental microanalyses were carried out on a Carlo Erba EA 1110 analyser. Mass spectra under electronic impact at 70 eV (m/z and relative abundance in % are given) were obtained with a GC/MS Hewlett Packard 5970 mass selective detector. HRMS measurements under chemical ionisation were performed on a Jeol AX 500 spectrometer. NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300 MHz for proton, 75.4 MHz for carbon, 121.5 MHz for phosphorus and 282.4 MHz for fluorine; chemical shifts (δ) are expressed in ppm relative to TMS for ^1H and ^{13}C nuclei, to H_3PO_4 for ^{31}P nucleus and to $CFCl_3$ for ^{19}F nucleus; coupling constants (J) are given in Hertz; coupling multiplicities are reported using conventional abbreviations. Starting phosphonates **1** and **2** were prepared according to Ref. 6.

α-Chloro-α,β-Uunsaturated Esters 3 and 4; General Procedure

In a purged and water-cooled one-compartment cell, equipped with a carbon felt cathode, a magnesium rod as anode and a magnetic stirrer, a solution of **1** or **2** (13 mmol) in DMF (35 mL) containing Et_4NBr (0.02 $mol.L^{-1}$) was introduced and stirred under a light argon stream. A 150 mA constant current was applied. After the complete formation of the carbanion, the carbonyl compound (14.3 mmol) was introduced. At the end of the reaction, the mixture was poured into THF (100 mL), then made acidic by 1 N HCl (100 mL) and extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with 1N HCl (2 × 50 mL) and dried. The solvents were evaporated in vacuo to give crude **3** or **4**, which were purified by flash chromatography over silica gel (eluent: cyclohexane/Et_2O, 90:10), for **3b–3d**,**4c–4g**, or by bulb-to-bulb distillation, for **3a**, **3e–3g**, **4a**,**4b**,**4h**, leading to pure carboxylic ester **3** or phosphonic ester **4**, whose structures were established by NMR and mass spectroscopy (Tables 2 and 3).

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(7) The $^{31}P\{^1H\}$ NMR signals of the carbanions appeared at δ(DMF, C_6D_6) = 43.5 and 43.15 for **1’** and at 47.75 and 47.5 for **2’**. The presence of two peaks in each case is in agreement with the existence of such stabilized carbanions as slowly interconverting species, see for example:
a) Bottin-Strzalko, T.; Corset, J.; Froment, F.; Pouet, M.-J.; Seyden-Penne, J.; Simonin, M.-P. *J. Org. Chem.* **1980**, *45*, 1270.
b) Bottin-Strzalko, T.; Corset, J.; Froment, F.; Pouet, M.-J.; Seyden-Penne, J.; Simonin, M.-P. *Phosphorus and Sulfur*, **1985**, *22*, 217.

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(9) Carbanions **1’** and **2’** thus electrogenerated are very stable anionic species, which can be kept for 24 h at r.t., under an inert atmosphere, without any loss of their reactivity.

(10) Patois, C.; Savignac, P. *Synlett* **1991**, 517.

(11) Villieras, J.; Perriot, P.; Normant, J. F. *Synthesis* **1978**, 31.
It sould be noted that using more sophisticated substitution pattern of the phosphorus atom led to sustantial increase in (E)-stereoselectivity of **3**: see Ref. 10.

(12) a) Seyferth, D.; Marmor, R. S. *J. Organometal. Chem.* **1973**, *59*, 237.
b) Teulade, M. P.; Savignac, P.; Elia Aboujaoude, E.; Lietgé, S.; Collignon, N. *J. Organometal. Chem.* **1986**, *304*, 283.
c) Lowen, G. T.; Almond, M. R. *J. Org. Chem.* 1994, *59*, 4548.
d) Perlikowska, W.; Mphahele, M. J.; Modro, T. A. *J. Chem. Soc., Perkin Trans. 2*, **1997**, 967.

(13) The chemical shift of the olefinic proton [upfield for the (E)-isomer, downfield for the (Z)-isomer] was the criterion of choice in the case of compounds **3**, see for example Ref. 11. For compounds **4**, the choice was based on the value of the $^3J_{HP}$ coupling constant of the olefinic proton [~ 40 Hz for (Z)-**4** and ~ 13 Hz for (E)-**4**]. See for example Refs 12b and 12d.

(14) By analogy with the corresponding t-butyl ester, the ^{19}F chemical shift of the trifluoromethyl group [upfield for the (E)-isomer, downfield for the (Z)-isomer] was the criterion of choice in this case, see:
Shen, Y.; Gao, S. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2531 and ref. cited therein.
In our case: δ($CDCl_3$) = - 60.8 [(Z)-isomer]; - 61.5 [(E)-isomer].

(15) A value of 4.4 Hz for the $^3J_{P,C\mathit{ipso}\text{-aromatic}}$ coupling constant in the $^{13}C\{^1H\}$ NMR spectrum of **4g** was in agreement with a *cis* P–C=C–C arrangement [(Z)-isomer]; see for example:
Quin, L. D. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G.; Quin, L. D. Eds.; VCH: Deerfield Beach, 1987; p 401.

(16) Teulade, M.-P.; Savignac, P. *J. Organometal. Chem.* **1988**, *338*, 295.

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