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Tetrahedron Letters 45 (2004) 2367–2370
Tetrahedron Letters

Rhodium(I)-catalyzed regioselective additions of chloroformates to 1,2-dienes

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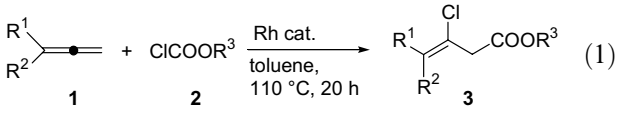
Received 24 December 2003; revised 13 January 2004; accepted 16 January 2004

Abstract—Rhodium phosphine complexes catalyze addition of chloroformates to terminal allenes to afford β-chloro-β,γ-unsaturated esters.

Catalytic addition of heteroatom–carbon bonds to unsaturated carbon linkages is an active area of research these days.[1] We reported previously that chloroformates add across the triple bonds of terminal alkynes in the presence of rhodium complexes, affording β-chloro-α,β-unsaturated esters in good yields with high stereo- and regioselectivity.[1q] Since the products having chlorine and olefinic functionalities are envisioned to be useful in synthetic applications,[2] we have explored the extension of the chloroformate addition to other unsaturated carbon linkages. In this paper we wish to disclose addition reactions of chloroformates to allenes, which furnish a novel synthetic route to β-chloro-β,γ-unsaturated esters with high regioselectivity (Eq. 1).



(1)

In a typical experiment, a mixture of 1,2-nonadiene **1a** (0.5 mmol), ethyl chloroformate **2a** (2.5 mmol) and $RhCl(CO)(PPh_3)_2$ (0.025 mmol; 5 mol% relative to **1a**) in toluene (1.0 mL) was heated at 110 °C for 20 h. Analysis of the resulting mixture by gas chromatography revealed that ethyl (*Z*)-3-chloro-3-decenoate **3a** was formed in 64% yield (Table 1, entry 1).[3,4] GCMS analysis suggested that three other isomeric adducts had also been formed, the ratio being 2:3:91 (**3a**):4, although the structure of these minor isomers was not further characterized. The regiochemistry of product **3a** agreed with

Table 1. Catalytic activity of rhodium complexes in the addition of **2a** to **1a** affording ethyl (*Z*)-3-chloro-3-decenoate **3a**[a]

Entry	Catalyst	Yield of **3a** (%)[b]
1	$RhCl(CO)(PPh_3)_2$	64 (91)
2[c]	$RhCl(CO)(PPh_3)_2$	73 (91)
3	$[RhCl(CO)_2]_2+2PPh_3$	46 (91)
4	$RhCl(CO)(PPh_3)_2+1PPh_3$	Trace
5	$RhCl(PPh_3)_3$	0
6	$[RhCl(CO)_2]_2$	0
7	$RhCl(CO)[P(p\text{-}FC_6H_4)_3]_2$	43 (91)
8	$RhCl(CO)[P(p\text{-}CH_3C_6H_4)_3]_2$	43 (91)
9[c]	$RhCl(CO)[P(p\text{-}CH_3C_6H_4)_3]_2$	69 (91)
10	$Rh(CN)(CO)(PPh_3)_2$	61 (94)
11	$RhCl(CO)(P^iPr_3)_2$	60 (77)
12	$RhCl(CO)(PCy_3)_2$	50 (74)
13	$RhCl(CO)(PPh_2Me)_2$	31 (91)
14	$RhCl(CO)(P^tBu_3)_2$	5 (nd)[e]
15	RhCl(CO)(dppe)[d]	12 (92)
16	RhCl(CO)(dppp)[d]	24 (92)
17	RhCl(CO)(dppb)[d]	28 (91)
18	RhCl(CO)(dppf)[d]	14 (91)

[a] Reactions were carried out at 110 °C for 20 h by using 0.5 mmol of **1a**, 2.5 mmol of **2a** and 0.025 mmol (with respect to Rh metal) of catalyst in 1.0 mL toluene.
[b] GC yields based on the amount of **1a** used. Values in parentheses are selectivities.
[c] 10 mol% of catalyst was used.
[d] dppe: 1,2-bis(diphenylphosphino)ethane. dppp: 1,3-bis(diphenylphosphino)propane. dppb: 1,4-bis(diphenylphosphino)butane. dppf: 1,1′-bis(diphenylphosphino)ferrocene.
[e] Not determined.

Keywords: Rhodium; Addition; Chloroformate; Allene.
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doi:10.1016/j.tetlet.2004.01.102

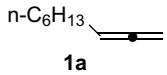
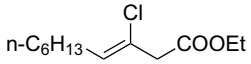
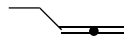
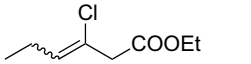
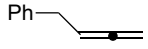
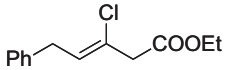
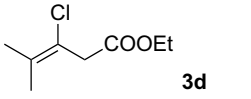
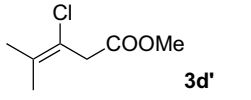
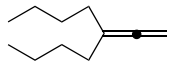
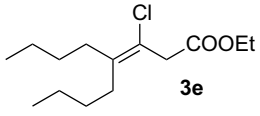
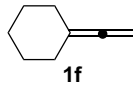
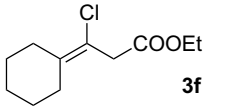
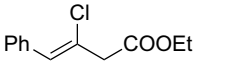
its NMR spectra and was further confirmed by its reduction with $LiAlH_4$ to the corresponding alcohol **4a**, which displayed two triplets at 3.78 and 2.54 ppm ($J = 5.9$ Hz) in ^1H NMR spectroscopy.[5] The *Z* configuration of the olefinic bond was confirmed by an NOE measurement of **3a**, in which a 6% enhancement of the vinylic proton signal was observed upon irradiation at the α-methylene proton of the CH_2COOEt substituent.

To achieve an acceptable yield of **3a**, the use of **2a** in excess of **1** is a prerequisite condition; when the reactions were carried out at a 2:1 or 1:1 ratio of **1a** to **2a**, adduct **3a** was formed only in 22% or 24% yield, respectively. However, the yield was significantly boosted to 64% by using a 1:5 ratio of **1a** to **2a**. The selectivity for **3a** did not change substantially.

Table 1 summarizes the results of the addition reactions of 1,2-nonadiene **1a** with ethyl chloroformate in the presence of various rhodium complexes. Unlike the addition to alkynes,[1q] the present reaction appears rather insensitive to the nature of phosphines. Thus, the use of complexes with PPh_3, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}CH_3C_6H_4)_3$, P^iPr_3, PCy_3, and PPh_2Me as the ligand results in the formation of **3a** in yields ranging from 31% to 64%, although the electronic and/or steric nature of the ligand is very much different. The exceptional case is the reaction with the P^tBu_3 complex, which gave only 5% yield. However, the phosphine/rhodium ratio affects the catalytic performance significantly; the catalyst systems of PPh_3/rhodium being 3 did not promote the reaction as seen in entries 4 and 5. A phosphine-free rhodium complex did not show activity either (entry 6). However, the system generated by $[RhCl(CO)_2]_2$ and 2 equiv of PPh_3 (i.e., the ratio being 1) catalyzed the reaction albeit somewhat slowly (entry 3). On the other hand, rhodium complexes ligated by bidentate phosphines such as dppe, dppp, dppb, and dppf appears to be less efficient than the foregoing bis(monodentate phosphine)rhodium complexes, resulting in 12–28% yields.

The results of $RhCl(CO)(PPh_3)_2$-catalyzed addition reactions of chloroformates to various allenes are summarized in Table 2. Additions of **2a** to alkyl and aralkyl mono-substituted allenes furnish adducts **3** in acceptable yields with high regio- and stereoselectivities (entries 1–3). The reactivity of *gem*-dialkyl-substituted allenes is

Table 2. Rhodium-catalyzed chloroesterification of allenes[a]

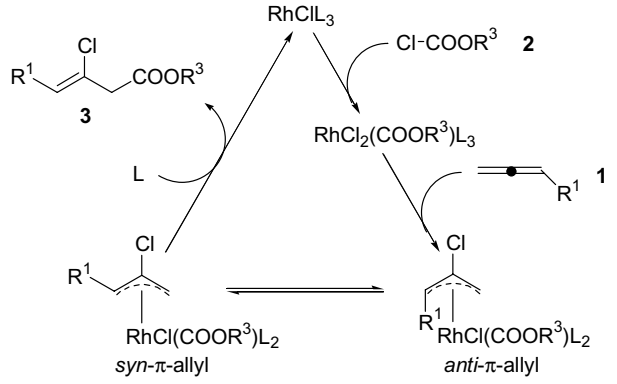
Entry	Allene	Adduct **3**	Yield of **3** (%)[b]
1	 **1a**	 **3a**	64 (91)
2	 **1b**	 **3b**[c]	58 (94)
3	 **1c**	 **3c**	42 (94)
4	 **1d**	 **3d**	75 (98)
5[d]	 **1d**	 **3d'**	71 (98)
6	 **1e**	 **3e**	56 (98)
7	 **1f**	 **3f**	40 (97)
8	 **1g**	 **3g**	10 (61)

[a] Reactions were carried out at 110 °C for 20 h by using 0.5 mmol of allene, 2.5 mmol of **2** and 0.025 mmol of $RhCl(CO)(PPh_3)_2$ in 1.0 mL toluene.
[b] GC yield based on the amount of allene used. Value in parentheses is regioselectivity, which is the value of 100 × **3**/total amount of products having the same molecular weight as **3**.
[c] $Z/E = 89/11$ as determined by GC.
[d] Reaction with methyl chloroformate.

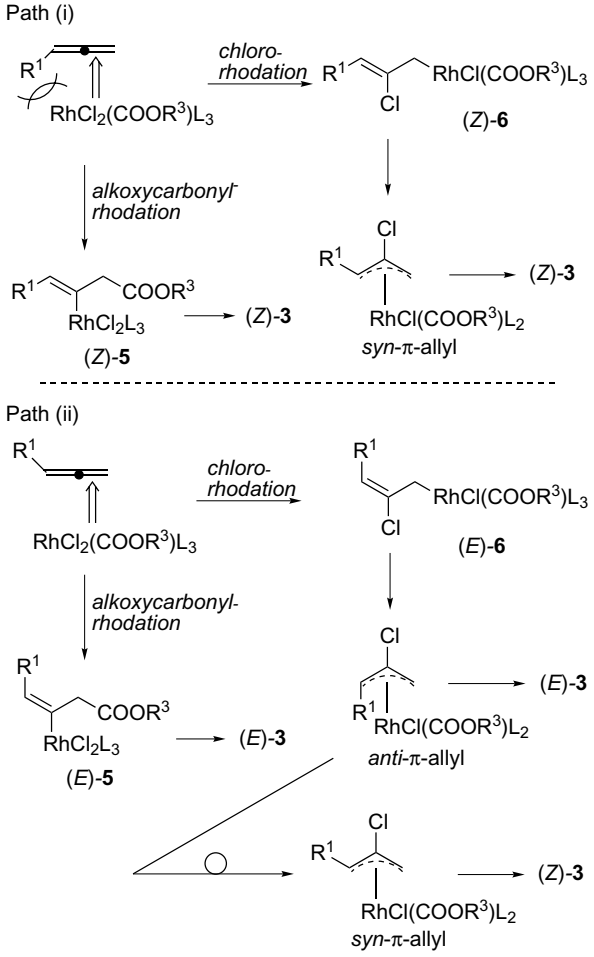
not seriously low as compared with the mono-substituted allenes as entries 4–7 show. However, arylallenes displayed very low reactivity: Phenylallene afforded only 10% yield with a low **3g** selectivity (61%, entry 8)[6] and 1,1-diphenylallene did not give the corresponding adduct at all. Under the same reaction conditions, 1,3-disubstituted, trisubstituted, and tetrasubstituted allenes such as cyclonona-1,2-diene, 5-(2,5-dimethylphenyl)-3,4-octadiene, and tetramethylallene did not conform to the present addition reaction.

Although the mechanistic detail remains to be elucidated, the catalytic cycle illustrated in Scheme 1, similar to that proposed for the addition reaction of **2** with alkynes, is envisioned to operate. The oxidative addition of chloroformates with Vaska-type rhodium complexes has been confirmed to form $RhCl_2(COOR^3)(CO)(PR_3)_2$.[1q] Monitoring the reaction of $RhCl_2(CO)(PPh_2Me)_2(COOMe)$ with **1d** (5 equiv) in toluene-d_8 by ^1H and ^{31}P NMR spectroscopies revealed that the rhodium complex was almost completely consumed upon heating at 110 °C for 4 h, and that **3d′** was formed in 32% yield along with 63% of $RhCl(CO)(PPh_2Me)_2$, ($J_{Rh-P} = 123$ Hz), 15% of $RhCl_3(CO)(PPh_2Me)_2$, ($J_{Rh-P} = 76$ Hz) and 22% of an unidentified complex ($J_{Rh-P} = 134$ Hz).

In the alkyne reaction, insertion into the Cl–Rh bond (chlororhodation), rather than R^3OOC–Rh (alkoxycarbonylrhodation), was proposed to be involved in the catalysis in view of the difficulty of Cl–C reductive elimination reported in precedent papers,[1p,7] although we were unable to provide convincing evidence. We presume that the present reaction of allenes also proceeds through chlororhodation. As for the pre-coordination of the rhodium species to the terminal double bond of the mono-substituted allenes, prior to the insertion of the allene molecule, two possibilities can be considered (paths (i) and (ii), Scheme 2). In path (i), the insertion product complex (*Z*)-**5** or (*Z*)-**6**, formed through either alkoxycarbonylrhodation or chlororhodation, leads eventually to the formation of (*Z*)-**3**, the major product of the catalytic reaction, via Cl–C or C–C reductive elimination, respectively. Although we are unable to rigorously exclude this possibility, path (i) requires the pre-coordination to the more sterically congested olefinic face and hence may not be the major



Scheme 1.



Scheme 2.

pathway. In path (ii), pre-coordination takes place at the less congested olefinic face. In the catalytic reactions of mono-substituted allenes, (*E*)-**3** was only a minor product or not formed at all. Accordingly generation of (*E*)-**5** is safely concluded to be less favored. On the other hand, (*E*)-**6**, generated via chlororhodation, is transformed to *anti* π-allylic species, which, however, can isomerize to the thermodynamically more stable *syn*-isomer. The C–C reductive elimination thereof leads to (*Z*)-**3**. When R^1 is sterically less demanding, direct reductive elimination from *anti* π-allyl intermediate may proceed to some extent, as suggested by the formation of both (*Z*)- and (*E*)-**3b** isomers having an ethyl group as R^1 ($Z/E = 89/11$).

In conclusion, we have developed rhodium-catalyzed addition of chloroformate esters to 1,2-dienes to afford 3-chloro-3-alkenoates **3** with high regioselectivity. Further investigations on the synthetic application of adducts **3** are in progress.

Acknowledgements

We thank the Japan Science and Technology Corporation (JST) for financial support through the CREST

(Core Research for Evolutional Science and Technology) program.

References and notes

1. Review: (a) Kuniyasu, H.; Kurosawa, H. *Chem. Euro. J.* **2002**, *8*, 2661; Si–C: (b) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891; (c) Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hatafusa, T. *J. Org. Chem.* **1988**, *53*, 3539; (d) Takeyama, Y.; Nozaki, K.; Matsumoto, K.; Oshima, K.; Utimoto, K. *Bull Chem. Soc. Jpn.* **1991**, *64*, 1461; Sn–C: (e) Shirakawa, E.; Yoshida, H.; Kurahashi, T.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1998**, *120*, 2975; (f) Shirakawa, E.; Yoshida, H.; Nakao, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 4290; (g) Shirakawa, E.; Yamasaki, K.; Yoshida, H.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121*, 10221; (h) Hua, R.; Onozawa, S.-y.; Tanaka, M. *Organometallics* **2000**, *19*, 3269; (i) Obora, Y.; Baleta, A. S.; Tokunaga, M.; Tsuji, Y. *J. Organomet. Chem.* **2002**, *660*, 173; S–C: (j) Hua, R.; Takeda, H.; Onozawa, S.-y.; Abe, Y.; Tanaka, M. *J. Am. Chem. Soc.* **2001**, *123*, 2899; (k) Sugoh, K.; Kuniyasu, H.; Sugae, T.; Ohtaka, A.; Takai, Y.; Tanaka, A.; Machino, C.; Kambe, N.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, *123*, 5108; Se–C: (l) Zhao, C.-Q.; Huang, X.; Meng, J.-B. *Tetrahedron Lett.* **1998**, *39*, 1933; (m) Hirai, T.; Kuniyasu, H.; Kato, T.; Kurata, Y.; Kambe, N. *Org. Lett.* **2003**, *5*, 3871; C–Cl: (n) Kaneda, K.; Uchiyama, T.; Fujiwara, Y.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1979**, *44*, 55; (o) Yamaguchi, R.; Kawasaki, H.; Yoshitome, T.; Kawanisi, M. *Chem. Lett.* **1982**, 1485; (p) Kokubo, K.; Matsumasa, K.; Miura, M.; Nomura, M. *J. Org. Chem.* **1996**, *61*, 6941; (q) Hua, R.; Shimada, S.; Tanaka, M. *J. Am. Chem. Soc.* **1998**, *120*, 12365; (r) Sugihara, T.; Satoh, T.; Miura, M.; Nomura, M. *Angew. Chem. Int. Ed.* **2003**, *42*, 4672; B–C (intramolecular): (s) Suginome, M.; Yamamoto, A.; Murakmi, M. *J. Am. Chem. Soc.* **2003**, *125*, 6385.
2. Hua, R.; Tanaka, M. *New J. Chem.* **2001**, *25*, 179.
3. General procedure for rhodium-catalyzed additions of chloroformate esters to allenes. In a thick-walled Pyrex tube was placed a mixture of an allene (0.5 mmol), compound **2** (2.5 mmol), rhodium catalyst (0.025 mmol) and toluene (1.0 mL) under nitrogen. The tube was then flame-sealed and the mixture was heated at 110 °C for 20 h with stirring. After cooling, the reaction mixture was diluted with toluene to 2.0 mL and was analyzed by gas chromatography after addition of an appropriate amount of eicosane as internal standard. Volatiles were removed in vacuo and the residue was purified by column chromatograph (silica gel, eluted with hexane) and further by preparative TLC (silica gel, eluted with a 6:1 hexane–diethyl ether mixture) to afford **3** as colorless oil.
4. All products **3** were isolated and gave satisfactory spectral and/or analytical data reported below.
   For ethyl (*Z*)-3-chloro-3-decenoate **3a**: Isolated yield 52%; ^{1}H NMR (300 MHz, C_6D_6) δ 5.33 (t, 1H, $J = 7.0$ Hz), 3.93 (q, 2H, $J = 7.1$ Hz), 3.06 (s, 2H), 2.13 (m, 2H), 1.35–1.10 (m, 8H), 0.92 (t, 3H, $J = 7.1$ Hz), 0.86 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (75.4 MHz, C_6D_6) δ 168.7, 130.0, 126.9, 60.8, 45.1, 31.9, 29.1, 29.0, 28.6, 22.9, 14.2, 14.1; IR (neat): 1744 cm^{-1} (C=O). Anal. calcd for $C_{12}H_{21}ClO_2$: C, 61.94; H, 9.03. Found: C, 62.25; H, 9.27.
   For ethyl 3-chloro-3-hexenoate **3b**: Isolated yield 43%, $Z/E = 86/14$. Anal (Z/E mixture). Calcd for $C_8H_{13}ClO_2$: C, 54.39; H, 7.36. Found: C, 54.35; H, 7.43. (*Z*)-**3b**: ^{1}H NMR (300 MHz, C_6D_6) δ 5.24 (t, 1H, $J = 6.8$ Hz), 3.91 (q, 2H, $J = 7.1$ Hz), 3.03 (s, 2H), 2.04 (m, 2H), 0.91 (t, 3H, $J = 7.1$ Hz), 0.77 (t, 3H, $J = 7.5$ Hz); ^{13}C NMR (75.4 MHz, C_6D_6) δ 168.7, 131.7, 126.4, 60.8, 45.0, 22.3, 14.0, 12.8. (*E*)-**3b**: ^{1}H NMR (300 MHz, C_6D_6) δ 5.62 (t, 1H, $J = 7.6$ Hz), 4.02 (q, 2H, $J = 7.1$ Hz), 3.08 (s, 2H), 0.68 (t, 3H, $J = 7.5$ Hz). Other signals overlap with those of (*Z*)-**3b**. IR (Z/E mixture, neat): 1744 cm^{-1} (C=O).
   For ethyl (*Z*)-3-chloro-5-phenyl-3-pentenoate **3c**: Isolated yield 34%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.14 (m, 5H), 5.84 (t, 1H, $J = 7.1$ Hz), 4.20 (q, 2H, $J = 7.1$ Hz), 3.58 (d, 2H, $J = 7.1$ Hz), 3.37 (s, 2H), 1.29 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 169.3, 139.0, 129.0, 128.5, 128.4, 127.2, 126.3, 61.2, 45.0, 35.0, 14.1; IR (neat): 1742 cm^{-1} (C=O). Anal. calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.29. Found: C, 65.81; H, 5.98.
   For ethyl 3-chloro-4-methyl-3-pentenoate **3d**: Isolated yield 62%; ^{1}H NMR (300 MHz, C_6D_6) δ 3.92 (q, 2H, $J = 7.1$ Hz), 3.18 (s, 2H), 1.65 (s, 3H), 1.37 (s, 3H), 0.92 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (75.4 MHz, C_6D_6) δ 169.0, 131.5, 120.4, 60.8, 41.4, 21.7, 20.2, 14.1; IR (neat): 1744 cm^{-1} (C=O). Anal. calcd for $C_8H_{13}ClO_2$: C, 54.39; H, 7.37. Found: C, 54.19; H, 7.40.
   For methyl 3-chloro-4-methyl-3-pentenoate **3d′**: Isolated yield 58%; ^{1}H NMR (300 MHz, C_6D_6) δ 3.28 (s, 3H), 3.15 (s, 2H), 1.64 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 169.4, 131.6, 120.0, 51.5, 41.2, 21.6, 20.2; IR (neat): 1746 cm^{-1} (C=O); HRMS calcd for $C_7H_{11}ClO_2$ 162.0447, found 162.0429.
   For ethyl 3-chloro-4-butyl-3-octenoate **3e**: Isolated yield 47%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.17 (q, 2H, $J = 7.1$ Hz), 3.39 (s, 2H), 2.23 (t, 2H, $J = 7.6$ Hz), 2.08 (t, 2H, $J = 7.6$ Hz), 1.40–1.23 (m, 11H), 0.93–0.87 (m, 6H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 169.4, 140.4, 120.5, 61.0, 41.2, 33.0, 32.3, 30.5, 29.5, 22.7(2C), 14.1, 14.0, 13.9; IR (neat): 1743 cm^{-1} (C=O); HRMS calcd for $C_{14}H_{25}ClO_2$ 260.1542, found 260.1541.
   For ethyl 3-chloro-3-cyclohexylidenepropionate **3f**: Isolated yield 33%; ^{1}H NMR (300 MHz, C_6D_6) δ 3.92 (q, 2H, $J = 7.1$ Hz), 3.25 (s, 2H), 2.34 (t, 2H, $J = 6.0$ Hz), 1.92 (t, 2H, $J = 6.0$ Hz), 1.41–1.23 (m, 6H), 0.92 (t, 3H, $J = 7.1$ Hz), 0.86 (t, 3H, $J = 7.0$ Hz); ^{13}C NMR (75.4 MHz, C_6D_6) δ 169.1, 139.0, 117.6, 60.7, 41.1, 31.8, 31.2, 27.6, 27.1, 26.3, 14.1; IR (neat): 1744 cm^{-1} (C=O). Anal. calcd for $C_{11}H_{17}ClO_2$: C, 60.97; H, 7.85. Found: C, 60.89; H, 7.97.
   For ethyl (*Z*)-3-chloro-4-phenyl-3-butenoate **3g**: Isolated yield 5%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63–7.60 (m, 2H), 7.39–7.21 (m, 3H), 6.62 (s, 1H), 4.25 (q, 2H, $J = 7.1$ Hz), 3.52 (s, 2H), 1.30 (t, 3H, $J = 7.1$ Hz); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 169.2, 134.0, 129.1, 128.6, 128.2, 128.0, 126.1, 61.3, 46.6, 14.1; IR (neat): 1742 cm^{-1} (C=O). Anal. calcd for $C_{12}H_{13}ClO_2$: C, 64.14; H, 5.79. Found: C, 64.65; H, 5.37.
5. (*Z*)-3-Chloro-3-decen-1-ol **4a**: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (t, 1H, $J = 7.0$ Hz), 3.78 (t, 2H, $J = 5.9$ Hz), 2.54 (t, 2H, $J = 5.9$ Hz), 2.17 (m, 2H), 1.62 ($s_{br.}$, 1H), 1.42–1.27 (m, 8H), 0.87 (t, 3H, $J = 7.0$ Hz). Product **3d** was also reduced to the corresponding alcohol **4d** to confirm the regioselectivity. (*Z*)-3-Chloro-4-methyl-3-penten-1-ol **4d**: Colorless oil; ^{1}H NMR (300 MHz, C_6D_6) δ 3.55 (t, 2H, $J = 6.3$ Hz), 2.38 (t, 2H, $J = 6.3$ Hz), 1.69 (s, 3H), 1.42 (s, 3H), 1.10 ($s_{br.}$, 1H).
6. GC–MS analysis of the reaction mixture disclosed that the reaction produced three adducts in a ratio of 12:61 (**3g**):27. The structures of the two minor isomers have not been characterized yet.
7. (a) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99; (b) Blum, J.; Scharf, G. *J. Org. Chem.* **1970**, *35*, 1895; (c) Kampmeier, J. A.; Hariis, S. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 1478.