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A tandem Finkelstein-rearrangement–elimination reaction: a straightforward synthetic route to allyl esters

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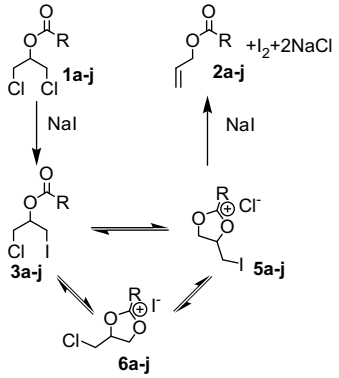
ABSTRACT

Allyl esters can be obtained by a Finkelstein-rearrangement–elimination reaction of 2-chloro-1-(chloromethyl)ethyl esters induced by NaI. Sodium iodide can be used below equivalence using a reductive agent as sodium thiosulfate. High yields are obtained with most of the diverse esters studied. The method described avoids the use of allyl alcohol as a reagent. 2-Chloro-1-(chloromethyl)ethyl esters are prepared from glycerol, the main by-product of biodiesel industry. The effectiveness of iodine as reagent to hydrolyze allyl esters is also confirmed.

1. Introduction

Agricultural raw materials have become a matter of interest in the 21st century in the search for new sources of chemicals to help sustainable development. Oils and fats of vegetable and animal origin make up the greatest proportion of the current consumption of renewable raw materials in the chemical industry because they offer a large number of possibilities for application.[1] Recently, the industrial interest in vegetable oils has increased because they constitute the raw material for the biodiesel industry. One of the by-products of this industry is glycerol, which already has many applications.[2] However, the expected increase in biodiesel production is stimulating research to find new industrial applications for glycerol.[3] Glycerol can be easily transformed into several 2-chloro-1-(chloromethyl)ethyl esters directly[4–6] or through its transformation to different derivatives as 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (solketal) and a subsequent one-pot esterification–chlorination.[7] These esters are putative precursors of 2-chloro-1-(iodomethyl)ethyl esters (**3a**–**j** in Scheme 1), which are versatile starting materials with a chiral center.

While trying to induce desymmetrisztion in the 2-chloro-1-(chloromethyl)ethyl esters, we found that NaI was able to induce the formation of the corresponding allyl esters starting from **1a**.[8] Herein we report different parameters having an effect on the allyl esters formation by the Finkelstein-rearrangement–elimination reaction of 2-chloro-1-(chloromethyl)ethyl esters induced by NaI. To the best of our knowledge, this type of combined reaction in the presence of NaI is unprecedented.



Scheme 1. Proposed mechanism for allyl ester formation (R=entries **a**–**j**, Table 1).

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2. Results and discussion

First, we studied the treatment of **1a** with NaI (2.0 equiv) in acetone at 80 °C for 48 h. Ester **2a** was obtained in moderate yield. Nevertheless, considering that allyl esters have many applications in such wide-ranging fields as cosmetics,[9] flavorings,[10] resins,[11] energy storage,[12] olefin metathesis,[13] and precursors in allylation reactions[14–16] a set of experiments were carried out trying to improve the yield of this new reaction.

When the same reaction was carried out at 115 °C using butanone as solvent, the yield increased up to 93%.

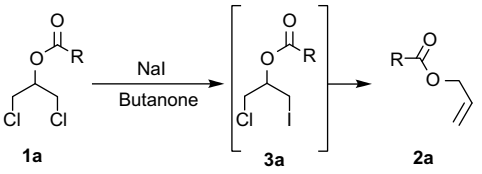
To study the scope of this reaction, the same process was studied with several alkyl and aryl acids (Table 1). Yields varied from 61% (entry **h**) to 98% (entry **d**). Finally, the process was scaled up to 30 times using 2-chloro-1-(chloromethyl)ethyl esters **1a** and **1j**. The yields were 91% and 82% of purified allyl esters **2a** and **2j**, respectively.

Our approach differs from most of the methods described so far in that the use of allyl alcohol, undesired residue on some allylic ester preparations,[17] is avoided. These methods use catalysts such as hydrogen chloride,[18,19] sulfuric acid,[20,21] and titanium sulfate,[22] or enzymes such as lipases.[23] Allyl acetate can also be prepared by acetoxylation of propylene[18] and pyrolysis of 1,3-diacetoxypropane[24] and 1,2-diacetoxypropane.[25]

To study some aspects of the mechanism of this transformation, two different approaches were followed. First, the progress of the reaction between **1a** and sodium iodide in butanone at 115 °C was studied for 48 h. Besides the starting compound **1a** and the final allyl palmitate (**2a**), the formation of about 48% 2-chloro-1-(iodomethyl)ethyl palmitate (**3a**) as an intermediate compound was observed (chromatographic peak at t_R=34.7 min presenting ions $[M]^+$: 458; $[M-Cl]^+$: 423; $[M-I]^+$: 331; $[M-C_3H_5ICl]^+$: 255; and $[C_3H_5ICl]^+$: 203) after 6 h of reaction (see Supplementary data).

Figure 1 shows the progress of the reaction. Whereas the starting ester **1a** had almost disappeared after 6 h, **3a** reached its maximum concentration between 3 and 6 h, and then a gradual decline was observed. Allyl palmitate (**2a**) and a dark color, considered to be due to free iodine, appeared as the reaction time increased. A dynamic NMR experiment carried out for 28 h using CD_3COCD_3 (see Supplementary data) only permitted the detection of the compounds indicated in Figure 1.

Second, the same reaction was studied using different ratios of **1a** to NaI. Figure 2 shows that when amounts of NaI are used under equivalence, the reaction is not complete and the formation of small amounts of **4a** is observed. When 1:1 molar ratio was used, only **4a** was recovered after 48 h of reaction. When using the 1:2 and 1:4 molar ratios, the reaction progressed to **2a** without detecting the formation of **4a**.



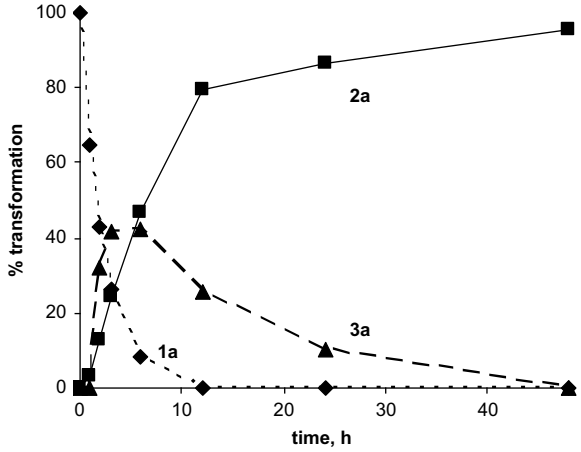
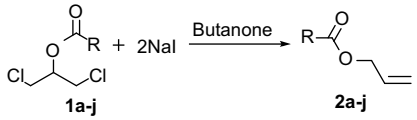


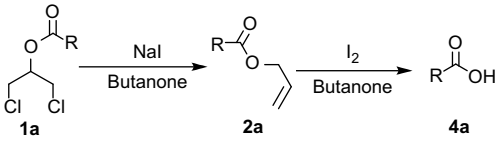
Figure 1. Evolution of the starting material (**1a**), the final product (**2a**), and an intermediate (**3a**) in presence of NaI at 115 °C (R=$CH_3(CH_2)_{14}$).

Based on these results, the mechanism of the present reaction is proposed as shown in Scheme 1. Substitution of chlorine by iodine forms the compounds **3a–j**. Nucleophilic attack of the sp^2 oxygen present in the carboxylic group could form the 1,3-dioxolane cations **5a–j** and **6a–j**, similar to the intermediates proposed by several authors.[4,26] Intermediates **6a–j** could be transformed to **5a–j** by a new chlorine–iodine exchange. Compounds **5a–j** could also be formed from 2-iodo-1-(iodomethyl)ethyl esters (not shown in Scheme 1). However, these esters were not detected in the NMR experiment indicated above. Finally, **5a–j** could be transformed into the stable **2a–j** through the corresponding ring opening. This last step is very similar to that proposed by several authors for some dehalogenation reactions occurring in polar solvents. Barluenga et al.[27] proposed the formation of an allyl alcohol through an

Table 1
2-Chloro-1-(chloromethyl)ethyl ester (**1a–j**) dechlorination with sodium iodide in butanone



Entry (**1**)	R	Isolate yield (%) **2**
a	$CH_3(CH_2)_{14}$	93
b	$CH_3(CH_2)_8$	91
c	$(CH_3)_3C$	84
d	C_6H_5–CH=CH	98
e	C_6H_5	97
f	*o*-Cl–C_6H_4	81
g	*p*-NO_2–C_6H_4	96
h	*o*-HO–C_6H_4	61
i	1-Naphthyl	96
j	2-Naphthyl	83



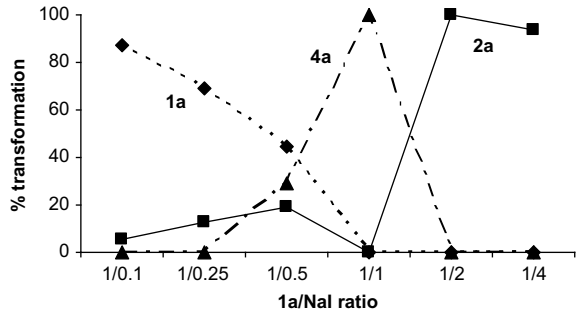


Figure 2. Effect of **1a**/NaI ratio in the products obtained from the transformation of **1a** after 48 h of reaction at 115 °C (R=$CH_3(CH_2)_{14}$).

iodide-induced β-elimination of an epiiodohydrin. Similar iodide-induced β-elimination mechanism was proposed for the sodium iodide dehalogenation of *vic*-bromochlorides and *vic*-dichlorides.[28] Moreover, ionic mechanisms were proposed for some abnormal Finkelstein reactions[29] and the decomposition of ethylene diiodide in polar solvents.[30] Compounds **2a–j** could also be formed from **6a–j** through the corresponding ring opening (not shown in Scheme 1). In this case ClI will be formed.

When NaI was not in molar excess, the amount of iodide anion was not sufficient to bring the reaction to full completion. Moreover, the presence of some free iodine could cause the hydrolysis of a certain amount of **2a**.

Taksande et al.[31] have recently described iodine as a useful catalyst for hydrolyzing allyl esters in DMSO. As the amount of NaI increases, the amount of **4a** can also increase, as can the iodine present. This could explain why only **4a** is obtained when the 1:1 **1a**/NaI molar ratio was used. An extra increase in NaI could help the formation of I_3^-, which could stop the hydrolysis.

To confirm this hypothesis, **2a** was heated in the presence of different amounts of I_2/NaI mixture for 24 h. Figure 3 shows that when NaI was not present compound **2a** was fully hydrolyzed. This confirms that iodine is a suitable reagent for the hydrolysis of allyl esters even in butanone.[31] When the NaI amount increased, hydrolysis decreased. Finally, from an I_2/NaI ratio of 70:30 onward **2a** was not hydrolyzed.

Considering these results a final set of experiments was planned using esters **1a** and **1j** again. They consisted on the introduction of sodium thiosulfate as an I_2 reducing agent in the reaction media. Using this approach, we tried to maintain the I_2 concentration below that, which causes allyl esters hydrolysis while trying to diminish the amount of NaI, an expensive reagent. Moreover, iodide anion should always be present to catalyze the rearrangement–elimination reaction.

Table 2 shows that reaction can be carried out using amounts of NaI below the equivalence. Thus, 89% crude yield of **2a** is reached after 48 h using 0.5 mol of this salt. Yields are poorest for **2j**. However, 94% crude yield of **2j** could be obtained using 1 mmol NaI, half of the stochiometric equivalents needed. This confirms that iodine concentration is maintained below the amount needed to cause the hydrolysis of allyl esters. No free acid was detected in any of these experiments. Nevertheless, the reaction time needed to reach similar yields depends on the amount of initial NaI used. This confirms that iodide anion should be present in the rate-determining step of this reaction. An increase of the amount of sodium thiosulfate does not cause an increase of the reaction rate nor the yield (results not shown). These results could be explained considering the low solubility of sodium thiosulfate in butanone.

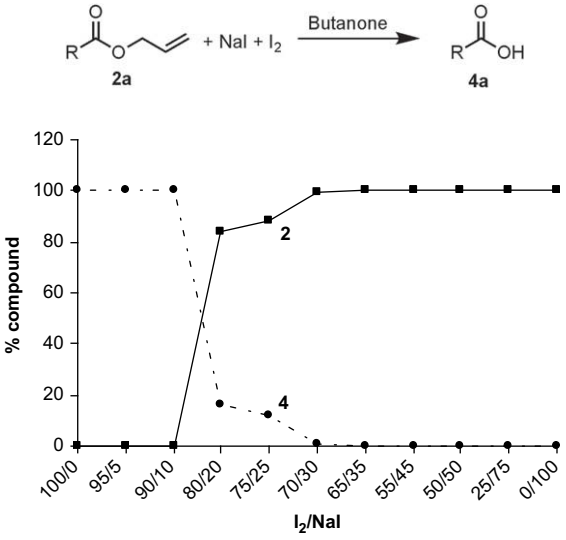


Figure 3. Evolution of the hydrolysis of **2a** in presence of different relative amounts of I_2 and NaI. The reaction was carried out at 110 °C for 24 h (R=$CH_3(CH_2)_{14}$).

3. Summary

2-Chloro-1-(chloromethyl)ethyl alkyl or aryl esters prepared from glycerol can be transformed to the corresponding allyl ester when 2 equiv of NaI is used. Shorter reaction times yield noteworthy amounts (almost 50%) of 2-chloro-1-(iodomethyl)ethyl esters, a potentially valuable compound to be obtained. Using less NaI leads to the formation of carboxylic acid unless a reducing agent like sodium thiosulfate is present in the reaction media. In this case, the reaction can be carried out to completion using 0.5 mmol (0.25 equiv) of NaI during 48 h. Iodine in butanone is a suitable reagent to hydrolyze some allyl esters.

The application of this methodology to the synthesis of chiral halohydrin esters to be used as building blocks is under study, as is the utilization of butanone/iodine mixture as hydrolyzing system for other allyl esters. Both studies will be reported in due course.

4. Experimental section

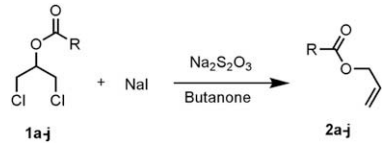
4.1. Material and methods

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a VARIAN 400 spectrometer. All chemical shifts are reported in delta units (δ), parts per million (ppm) relative to the singlet at 7.26 ppm of $CDCl_3$ for ^{1}H and centre line of a triplet at 77.00 ppm for ^{13}C NMR. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quin: quintet, m: multiplet.

GC-FID analyses were performed in an Agilent Technologies 6890N equipped with a DB5-MS column (J&W) (30 m×0.25 μm×0.25 mm) and He as carrier gas. The following chromatographic conditions were used: constant flow 2 mL/min, split injection ratio 20:1 at 300 °C. Oven started at 50 °C for 5 min, temperature was increased at 5 °C/min to 110 °C, then increased at 10 °C/min until final temperature of 260 °C for 15 min. Tridecane from Aldrich was used as internal standard to carry out GC quantification.

GC–MS analyses were performed in an Agilent Technologies 6890N equipped with a DB5-MS column (J&W) (30 m×0.25 μm×0.25 mm) coupled to an Agilent Technologies 5973 Network detector and He as

Table 2
2-Chloro-1-(chloromethyl)ethyl ester (**1a–j**) dechlorination with sodium iodide/sodium thiosulfate in butanone



Entry (**1**)	NaI (equiv)	Crude yield (%) **2**	
		24 h	48 h
a	0.50	98	99
a	0.38	95	98
a	0.25	72	89
a	0.13	43	66
a	0.05	12	18
j	0.50	87	94
j	0.38	52	71
j	0.25	40	50
j	0.13	18	38
j	0.05	6	11

carrier gas. The following chromatographic conditions were used: constant flow 2 mL/min, split injection ratio 20:1 at 280 °C. Oven started at 50 °C for 5 min, temperature was increased at 5 °C/min to 110 °C, then increased at 10 °C/min until final temperature of 260 °C for 15 min.

IR spectra were recorded on a Magna IR 560 NicoleT FTIR spectrophotometer in the range 4000–600 cm^{-1} with KBr pellets or with diamond HATR from SpectraTech as specified. Spectra are reported in reciprocal centimeters (cm^{-1}).

High-resolution mass spectral (HRMS) data were obtained by direct infusion on LC-TOF-MS Waters LCT Premier XE using ESI or APCI or on Waters GCT Premier using EI as specified.

4.2. General procedure for the preparation of 2-chloro-1-(chloromethyl)ethyl esters (2a–j)

A carboxylic acid (1 mmol), glycerol (184 mg, 2 mmol), and CTMS (540 mg, 5 mmol) were added to a reaction vial fitted with a PTFE-lined cap. The mixture was heated at 80 °C for 48 h. After cooling, an organic solvent was added, and the mixture was washed three times with water. The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated under vacuum. The crude product was purified by crystallization, distillation, or SiO_2 column chromatography. Spectroscopic data are in accordance with the literature.[6,7]

4.3. General procedure for the preparation of allyl esters (2a–j)

A solution of 2-chloro-1-(chloromethyl)ethyl ester (0.5 mmol) and sodium iodide (300 mg, 2 mmol) in dried butanone (1 mL) was heated for 48 h at 115 °C in a reaction vial. After cooling, *tert*-butyl methyl ether was added; the mixture was washed with saturated solution of $Na_2S_2O_3$ and water. The upper layer was recovered and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum to give the allyl derivate. The crude was purified by SiO_2 column chromatography to give the corresponding allyl ester.

4.4. General procedure for the preparation of allyl esters using $Na_2S_2O_3$ (2a–j)

A solution of 2-chloro-1-(chloromethyl)ethyl ester (0.5 mmol), sodium iodide (150–15 mg, 1–0.1 mmol) and (158 mg, 1 mmol) in dried butanone (1 mL) was heated for 24–48 h at 115 °C in a reaction vial. After cooling, *tert*-butyl methyl ether was added; the mixture was washed with water. The upper layer was recovered and dried over anhydrous $MgSO_4$. The solvent was evaporated under vacuum to give the allyl derivate. The crude was analyzed by GC to determine the yield of the corresponding allyl ester.

4.5. Scaled up preparation of allyl palmitate (2a)

Prepared following the general procedure in a 125 mL reaction vial fitted with PFE-lined cap. A solution of 2-chloro-1-(chloromethyl)ethyl palmitate **3a** (6.6 g, 18 mmol) and sodium iodide (10 g, 67 mmol) in dried butanone (25 mL) yielded the allyl palmitate **12a** (4.9 g, 91%).

4.6. Scaled up preparation of allyl 2-naphthoate (2j)

Prepared as described above. A solution of 2-chloro-1-(chloromethyl)ethyl naphthoate **3j** (7.1 g, 27 mmol) and sodium iodide (16.2 g, 108 mmol) in dried butanone (30 mL) yielded the allyl 2-naphthoate (**12j**) (4.3 g, 82%).

4.7. Study of the evolution of 1,3-dichloro-2-propyl palmitate (1a), 1-chloro-3-iodo-2-propyl palmitate (3a), and allyl palmitate using dynamic ^{1}H NMR spectra

In a screw cap NMR tube were added 2-chloro-1-(chloromethyl)ethyl palmitate (**1a**) (25,5 mg, 0.07 mmol), sodium iodide (42 mg, 0.28 mmol), and 1.5 mL acetone-d_6. The mixture was introduced in NMR spectrometer at 80 °C for 30 h recording one spectrum every 2 h until the end of the experiment.

4.8. Reaction progress study (Fig. 1 main text)

2-Chloro-1-(chloromethyl)ethyl palmitate (**1a**, 366 mg; 1 mmol) and sodium iodide (600 mg, 4 mmol) in dried butanone (1.5 mL) were heated at 115 °C in a reaction vial. Samples were collected in triplicate at 2, 4, 8, 16, 24, 48 h and analyzed by GC and GC–MS in duplicate.

4.9. Influence of sodium iodide ratio (Fig. 2 main text)

2-Chloro-1-(chloromethyl)ethyl palmitate[5] (**1a**, 366 mg; 1 mmol), dried butanone (1.5 mL) and the amounts of sodium iodide as indicated in the following table:

NaI (mg)	**1a**/NaI molar ratio
15	1:0.1
37.5	1:0.25
75	1:0.5
150	1:1
300	1:2
600	1:4

were heated at 115 °C for 48 h in a reaction vial. Samples were collected and analyzed by GC and GC–MS in duplicate.

4.10. Stability in front NaI/I_2 ratio (Fig. 3 main text)

Allyl palmitate (**2a**, 50 mg; 0,17 mmol) was heated in presence of different I_2,NaI molar ratios (100:0; 95:5; 90:10; 80:20; 75:25; 70:30; 65:35; 55:45; 50:50; 25:75; 0:100) for 24 h at 110 °C in a reaction vial. The samples were collected and analyzed by GC–MS in duplicate.

4.11. Analytical data

*4.11.1. Allyl palmitate (**2a**)*

CAS: 43211-62-7: ^{1}H NMR ($CDCl_3$) δ: 5.92 (m, 1H, CH_2–CH=CH_2), 5.31 (dq, J_{trans}=17.2 Hz, J_{gem}=1.6 Hz, 1H, CH=CH_2), 5.23 (dq, J_{cis}=10.2 Hz, J_{gem}=1.2 Hz, 1H, CH=CH_2), 4.57 (dt, J_1=5.5 Hz, J_2=1.5 Hz, 2H, CH_2–CH=CH_2), 2.33 (t, J=7 Hz, 2H, $CH_{2(\alpha)(C=O)}$), 1.63 (quin, J=7.5 Hz, 2H, $CH_{2(\beta)(C=O)}$), 1.25 (m, 24H, CH_2), 0.88 (t, J=7 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 173.7 (C=O), 132.6 (CH=), 118.3 (=CH_2), 65.1 (O–CH_2), 34.5 ($CH_{2(\alpha)(C=O)}$), 32.2 (CH_2–CH_2–CH_3), 29.9, 29.8, 29.7, 29.6, 29.5, 29.4 (CH_2), 25.2 ($CH_{2(\beta)(C=O)}$), 22.9 (CH_2–CH_3), 14.3 (CH_3). GC–MS m/z: 296 $[M]^+$, 267 $[M-C_2H_3]^+$, 253 $[M-C_3H_5]^+$, 239 $[M-OC_3H_5]^+$. IR ATR ν_{max}: 3075, 2924, 2853, 1740, 1592, 1437, 1245, 1115, 1051, 747 cm^{-1}.

*4.11.2. Allyl caprate (**2b**)*

CAS: 57856-81-2: ^{1}H NMR ($CDCl_3$) δ: 5.91 (m, 1H, CH_2–CH=CH_2), 5.26 (m, 2H, CH=CH_2), 4.56 (dd, J_1=5.6 Hz, J_2=1.2 Hz, 2H, CH_2–CH=CH_2), 2.33 (t, J=8 Hz, 2H, $CH_{2(\alpha)(C=O)}$), 1.62 (m, 2H, $CH_{2(\beta)(C=O)}$), 1.25 (m, 12H, CH_2), 0.87 (t, J=6.8 Hz, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 173.7 (C=O), 132.5 (CH=), 118.2 (=CH_2), 65.1 (O–CH_2),

34.5 ($CH_{2(\alpha)(C=O)}$), 32.1 (CH_2–CH_2–CH_3), 29.6, 29.5, 29.4 (CH_2), 25.2 ($CH_{2(\beta)(C=O)}$), 22.9 (CH_2–CH_3), 14.3 (CH_3). GC–MS *m*/*z*: 212 $[M]^+$, 183 $[M-C_2H_3]^+$, 169 $[M-C_3H_5]^+$, 155 $[M-OC_3H_5]^+$. IR KBr film ν_{max}: 3074, 2924, 2854, 1737, 1460, 1159, 989, 723 cm^{-1}.

*4.11.3. Allyl pivaloate (**2c**)*

CAS: 15784-26-6. Spectroscopic data are in accordance with the literature.[32]

*4.11.4. Allyl cinnamate (**2d**)*

CAS: 1866-31-5. Spectroscopic data are in accordance with the literature.[33]

*4.11.5. Allyl benzoate (**2e**)*

CAS: 583-04-0. Spectroscopic data are in accordance with the literature.[34]

*4.11.6. Allyl 2-chlorobenzoate (**2f**)*

CAS: 15721-27-4. Spectroscopic data are in accordance with the literature.[34]

*4.11.7. Allyl 4-nitrobenzoate (**2g**)*

CAS: 15757-80-7: ^1H NMR ($CDCl_3$) δ: 8.28 (m, 4H, CH_{ar}), 6.05 (m, 1H, CH_2–CH=CH_2), 5.43 (dq, J_{trans}=17.2 Hz, J_{gem}=1.6 Hz, 1H, CH=CH_2), 5.34 (dq, J_{cis}=10 Hz, J_{gem}=1.2 Hz, 1H, CH=CH_2), 4.87 (dt, J_1=6 Hz, J_2=1.6 Hz, 2H, CH_2–CH=CH_2). ^{13}C NMR ($CDCl_3$) δ: 164.6 (*C*=O), 150.8 (CH_{ar}–NO_2), 135.8 (*C*H=), 131.7, 131.1, 131.0, 123.9, 123.8 (CH_{ar}),119.4 (=CH_2), 66.7 (O–CH_2). GC–MS *m*/*z*: 207 $[M]^+$, 150 $[M-CO_2C_3H_5]^+$, 134 $[M-NO_2C_2H_3]^+$, 120 $[M-NO_2C_3H_5]^+$, 104 $[M-CO_2C_3H_5]^+$, 76 $[M-C_2H_2CO_2C_3H_5]^+$. IR KBr film ν_{max}: 3112, 3080, 2962, 1727, 1528, 1351, 1260, 1099, 1016, 872, 799, 719 cm^{-1}.

*4.11.8. Allyl salicylate (**2h**)*

CAS: 10484-09-0. Spectroscopic data are in accordance with the literature.[35]

*4.11.9. Allyl 1-naphthoate (**2i**)*

CAS: 53548-26-8. Spectroscopic data are in accordance with the literature.[36]

*4.11.10. Allyl 2-naphthoate (**2j**)*

CAS: 53409-01-1: ^1H NMR ($CDCl_3$) δ: 8.64 (s, 1H, CH_{ar}), 8.08 (dd, J_1=8.4 Hz, J_2=1.2 Hz, 1H, CH_{ar}), 7.96 (d, J=8 Hz, 1H, CH_{ar}), 7.89 (d, J=8.8 Hz, 2H, 2CH_{ar}), 7.57 (m, 2H, 2CH_{ar}), 6.10 (m, 1H, CH_2–C*H*=CH_2), 5.46 (dq, J_{trans}=16.8 Hz, J_{gem}=1.6 Hz, 1H, CH=CH_2), 5.34 (dq, J_{cis}=10.4 Hz, J_{gem}=1.2 Hz, 1H, CH=CH_2), 4.89 (dt, J_1=5.6 Hz, J_2=1.2 Hz, 2H, CH_2–CH=CH_2). ^{13}C NMR ($CDCl_3$) δ: 166.6 (*C*=O), 135.8, 132.7 (CH_{ar}), 132.5 (*C*H=CH_2), 131.4, 129.6, 128.5, 128.4, 128.0, 127.6, 126.8, 125.4 (CH_{ar}), 118.6 (CH=CH_2), 65.9 (O–CH_2). GC–MS *m*/*z*: 212 $[M]^+$, 155 $[M-OC_3H_5]^+$, 127 $[M-CO_2C_3H_5]^+$. IR ATR ν_{max}: 3060, 3022, 2942, 1719, 1631, 1469, 1355, 1281, 1227, 1196, 1130, 1093, 980, 778, 762 cm^{-1}.

4.12. Determination of 2-chloro-1-(iodomethyl)ethyl palmitate (3a)

During the GC–MS analysis of the samples obtained in the reaction of **1a** with NaI, a chromatographic peak at t_R=34.7 min was detected. Its MS presented characteristic ions of **3a** ($[M]^+$: 458; $[M-Cl]^+$: 423; $[M-I]^+$: 331; $[M-C_3H_5ICl]^+$: 255; and $[C_3H_5ICl]^+$: 203). To confirm the presence of this intermediate compound, these samples were analyzed by ^1H NMR. The formation of **3a** was evidenced by the presence of a characteristic quintuplet at 4.93 and a multiplet at 3.42 ppm of the O–C*H* and CH_2–I groups, respectively.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.042.

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