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Allyltin trihalides: direct synthesis and reactivity†

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Summary – Stable functionalized allyltin trihalides **2** are prepared in excellent yields by direct reaction of stannous halides with allyl bromide precursors **1**. They can be alkylated providing a straightforward route to useful functionalized allyltrialkylstannanes **6**. Compound **2** also react easily with aldehydes and ketones, under very mild conditions, to provide a useful access to various α-methylene-γ-lactones **9**.

allyl bromide / stannous halide / allyltin trihalide / allyltrialkyltin / α-methylene-γ-lactone

Introduction

There is a growing interest in finding new synthetic methodologies to use organostannanes for organic synthesis, without producing organotin by-products such as trialkyltins. The drawbacks are well known : their toxicity coupled with difficulties often encountered in separating reaction products from organotin residues.

At present there are two possible strategies for avoiding these problems. The first lies in fixing the organotin reagent on a polymeric substrate. These "ready-to-use" supported reagents represent a significant step in the field of reduction reactions with organotin hydrides [1]. The other method consists of synthesizing new functionalized reactive organometallic compounds which do not generate any organotin species after work-up. From this point of view, alkyltin trihalides appeared to be one of the most promising families of organotin compounds.

Although they were discovered more than 100 years ago, alkyltin trihalides have received little attention from synthetic chemists. The main limiting factor has been a lack of a convenient preparation, which does not also give undesirable products such as di- or trialkyltin halides as in the Kocheskov's redistributions [2]. Further difficulties lie in the high reactivity of the Sn-X bond which is a source of instability and promotes premature reactions. In this area of chemistry, we focused our attention on the synthesis of functionalized allyltin trihalides. Although the preparation of allylbromodichlorostannane was previously reported by Tagliavini [3], this method is still limited to the unsubstituted allyl group.

Synthesis of the allyltin trihalides

Our methodology is based on the direct reaction between functionalized allyl bromides **1** and stannous halides in the presence of lithium bromide as catalyst (fig 1). As pointed out by Corey [4], stannous chloride and lithium bromide may generate the nucleophile $^-SnCl_2Br$, which we found to be sufficiently reactive to produce allyltin trihalides **2** [5].

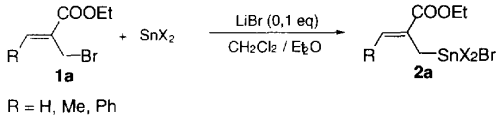


Fig 1

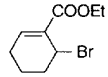
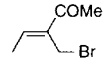
Interestingly, the reaction conditions are particularly mild compared with the approaches used for the synthesis of functionalized monoalkylstannanes, either by the *in situ* generation of trichlorotin hydride [6], or by the reaction of tin tetrachloride with silyl enol ethers [7] or siloxycyclopropanes [8]. Futhermore, all the monoallylstannanes synthesized (table I) can be manipulated in air and are stable for several weeks at room temperature, provided they are protected from moisture.

This exceptional stability compared to that observed for the simple allylbromodichlorostannane may be explained by an intramolecular complexation of the tin atom by the carbonyl group. This five-membered intramolecular Sn-O coordination is clearly shown in the infrared spectrum by the substantial shift of the C=O band, and in the ^{119}Sn NMR spectrum by the displacement of the resonances to higher fields. Although this

† Dedicated, with respect and admiration, to Professor emeritus Raymond Calas, who initiated and developed the discipline of organometallic chemistry at the University of Bordeaux.

* Correspondence and reprints

Table I. Synthesis of allyltin trihalides **2**.

Entry	Allyl bromides		Tin halide	Stannanes	(%) [9]
1		**1a**	$SnCl_2$	**2a**	(74)
2		**1b**	$SnCl_2$	**2b**	(84)
3		**1c**	$SnCl_2$	**2c**	(0)
4		**1d**	$SnCl_2$	**2d**	(61)
5		**1e**	$SnCl_2$	**2e**	(87)
6		**1f**	$SnCl_2$	**2f**	(94)
7		**1a**	$SnBr_2$	**2g**	(61)
8		**1b**	$SnBr_2$	**2h**	(85)

has not been proven, the complexation may occur at an earlier stage of the reaction, and could explain therefore the fact that we have never been able to prepare **4**, from the cyano-substituted allyl bromides **3** (R = Me, *i*Pr, Ph, fig 2). In contrast with previous ideas, it is noteworthy that all the reactions with crotyl bromides (entries 2, 6 and 8) occurred with retention of the double bond stereochemistry giving the corresponding (*Z*) organotin products [5]. Surprisingly, we did not observe the formation of the trihalotin compound starting from the phenyl-substituted allyl bromide **1c**, probably due to the deactivation of the allylic system by the conjugation with the phenyl group (entry 3).

Fig 2

Despite the stabilization of the tin atom, the Sn-X bonds remain reactive and the products made with stannous chloride (table I, entries 1-6) were actually mixtures of the four species $RSnCl_3$, $RSnCl_2Br$, $RSnClBr_2$ and $RSnBr_3$ as a result of rapid halogen exchange. ^1H and ^{13}C NMR gave average values, but the four isomers were clearly distinguished by ^{119}Sn NMR and mass spectroscopy. The proportions calculated by integration of the ^{119}Sn NMR spectra were found to be close to the statistical values [10]. On the other hand, the adducts made with stannous bromide (entries 7 and 8) gave the same ^1H and ^{13}C NMR spectra than **2a** and **2b** but showed a unique resonance in ^{119}Sn NMR.

The Sn-C bond also remains relatively weak and the choice of the solvent was critical. It is well known that intramolecular chelation can be broken by using coordinating solvents leading to hexacoordinated tin species [11]. In order to preserve the selectivity of the reaction, weakly coordinating conditions are necessary (ether/dichloromethane 1:1) since the use of tetrahydrofuran led to a mixture of mono and diallyltin compounds in the ratio of 2.3:1. The diallyltin product probably came from a redistribution reaction between two monoallyltin halides complexed by tetrahydrofuran leading to stannic halide and hexacoordinated diallyldihalotin **5** (fig 3).

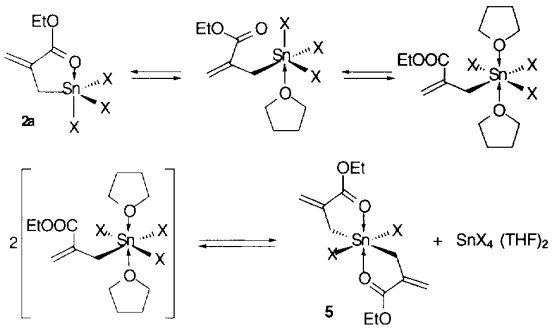


Fig 3

Radical reactivity of allyltin trihalides

Allyltriorganotins are used for radical-induced allylic transfer [12] and, when the allyl chain is substituted by an electron-withdrawing group, they show a greater reactivity than unsubstituted allyltrialkyltins, but their preparation is quite laborious [13]. The direct transfer of the allylic moiety from the allyltin trihalide itself would be more interesting. However, under the same radical conditions with isopropyl iodide, only the dimerization product **8** of the allylic radical was isolated, in 69% yield (fig 4).

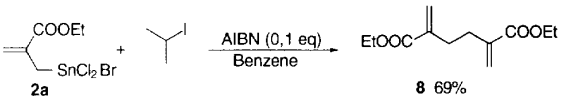


Fig 4

This result confirms the reactivity of the Sn-C bond toward homolytic cleavage, and also demonstrates that under these conditions the tin-centered radical $^{\bullet}SnX_3$ cannot induce an efficient chain radical transfer. Electron spin resonance studies of tin-centered radicals tend to prove that $^{\bullet}SnX_3$ radicals are relatively stable and not prone to fragmentation in contrast to $^{\bullet}SnRX_2$ radicals [14]. Thus, a possible explanation for the formation of compound **8** could be a halogen abstraction by the tin radical directly from the precursor **2a** (fig 5).

Nevertheless, by benefiting from the reactivity of the Sn-X bond, it was possible to alkylate the tin atom without damaging the functionalized allylic moiety even when a ketone was present (table II, entry 3) simply by adding 3 equivalents of Grignard reagent to the crude monoallyltin **2** at −78°C.

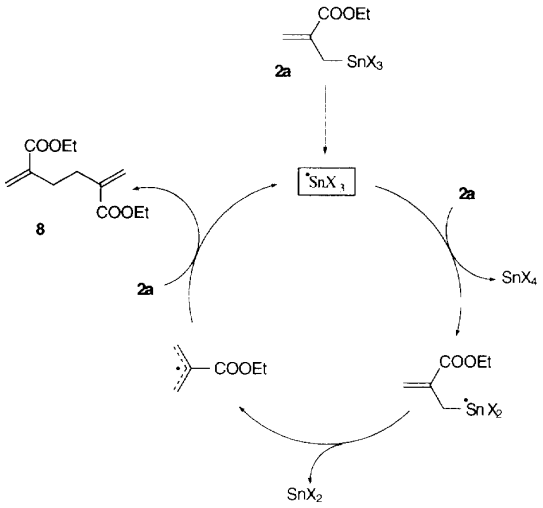
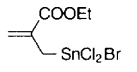
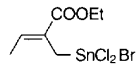
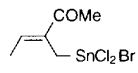
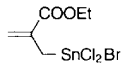


Fig 5

Table II. Alkylation of allyltin trihalides **2**.

Entry	Trihaloallyltins		Grignard reagent	Allyltrialkyltins	
1		**2a**	BuMgBr	**6a**	(67)
2		**2b**	BuMgBr	**6b**	(74)
3		**2f**	BuMgBr	**6c**	(70)
4		**2a**	PhMgBr	**6d**	(65)

Allyltin trihalides now provide a more straightforward route to these useful reagents, which can react as shown in figure 6.

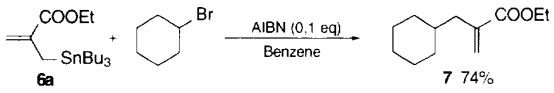


Fig 6

Ionic reactivity of allyltin trihalides

Allyl transfer to various electrophiles using allylic tributyltin reagents is quite well documented [15] and Barbier-type allylation of aldehydes using allylic halides and tin (II) halides is a known reaction [16]. However, most of these methods seem to be limited either by the nature of the allylic tin species used or by the reaction conditions and the nature of the organotin residues. Hence we were interested in observing the direct allylic transfer by an ionic mechanism from allyltin trihalides **2** [17]. Interestingly, in spite of the electron-withdrawing group, **2a** reacted readily as a good allylic carbanion equivalent with benzaldehyde to produce the corresponding α-methylene-γ-lactone **9a** in 83% yield (fig 7).

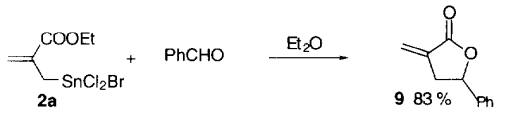


Fig 7

This reaction did not produce the expected homoallylic alcohol **10a**, but led directly to α-methylene-γ-lactone **9a** after cyclization of the transient alkoxytrihalotin A. The reaction probably proceeds primarily by an equilibrium between the intramolecularly complexed form **2a** and an intermediate in which the tin atom is intermolecularly complexed to the carbonyl of the benzaldehyde. Simultaneous enhancement of the nucleophilicity of the allylic moiety and activation of the carbonyl substrate allow the nucleophilic addition to proceed with allylic transposition, implying a cyclic six-centered transition state close to the Zimmerman-Traxler model invoked for many aldol reactions [18]. The alkoxytrihalotin formed, **A**, is reactive enough to promote the lactonization step with elimination of ethoxytrihalostannane (fig 8).

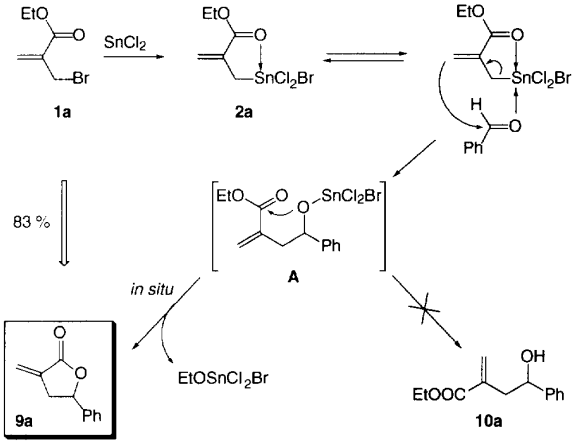
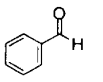
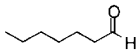
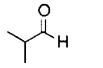
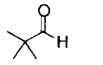
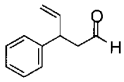
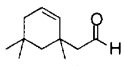
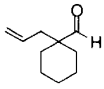
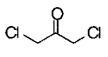
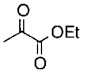
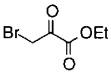
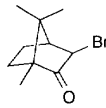
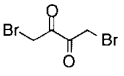


Fig 8

α-Bromomethyl acrylates **1** are widely employed synthons for the preparation of α-methylene-γ-lactones [19]. Zinc is the most commonly used metal in these reactions, and only few examples are reported with tin halides [20]. In none of these cases had an organotin intermediate been characterized or isolated, and the lactonization needed a supplementary step or an acidic medium. In contrast, the non-aqueous neutral conditions used here allowed cyclization under particularly mild conditions. It is noteworthy that a simple aqueous wash of the reaction mixture decomposes the ethoxytrihalostannane furnishing non-toxic tin hydroxide, allowing an easy separation of all the organic products from tin residues.

The reaction appears to be quite general with aldehydes and shows some chemoselectivity (table III). The reactivity differences observed for various aldehydes is mainly due to steric hindrance. Indeed, when the carbonyl group is shielded (entries 3 and 7), the reaction must be performed in refluxing THF (procedure II) instead of ether (procedure I). At first, the scope of this reaction with ketones seemed to be more limited, due to the lower nucleophilicity of the organotin reagent in comparison with more reactive organometallic species such as organozincs [21]. In fact, this lack of reactivity goes together with a fairly good selectivity, according to the nature of the carbonyl compounds, as the reaction did not occur with acyclic ketones (entry 8) but did proceed with cyclic ketones (entries 9 and 10). More interestingly, reaction of **2a** with ketones activated

Table III. Addition of **2a** to carbonyl compounds.

Entry	Carbonyl compounds	Procedure	Methylene lactones (yields %)	
1		I	**9a**	(87)
2		I	**9b**	(89)
3		I	**9c**	(81)
4		II	**9d**	(68)
5		I	**9e**	(62)
6		I	**9f**	(71)
7		II	**9g**	(42)
8		II	**9h**	(0)
9		II	**9i**	(54)
10		II	**9j**	(40)
11		II	**9k**	(66)
12		II	**9l**	(69)
13		II	**9m**	(70)
14		II	**9n**	(0)
15		II	**9o**	(51)

by electron-withdrawing groups (halogen or carbonyl) led to the corresponding functionalized α-methylene-γ-lactones in good yields (entries 11-13). However, the sensitivity of the reaction to the above-mentioned steric effects did not permit the synthesis of the lactone derived from bromocamphor (entry 14). However, for the same reason, this allowed the synthesis of lactone **9o** functionalized by a keto group, simply by starting from the corresponding diketone. The reaction of the second carbonyl group is avoided even though it is activated (entry 15).

Furthermore, the presence of the carbonyl group may stabilize the transient alkoxytrihalotin **B** by a five-membered intramolecular coordination (fig 9). This coordination is strong enough to obtain the homoallylic alcohol **10b,c** (procedure I) or the cyclized methylene lactone **9l,m** (procedure II) simply by varying the experimental procedure.

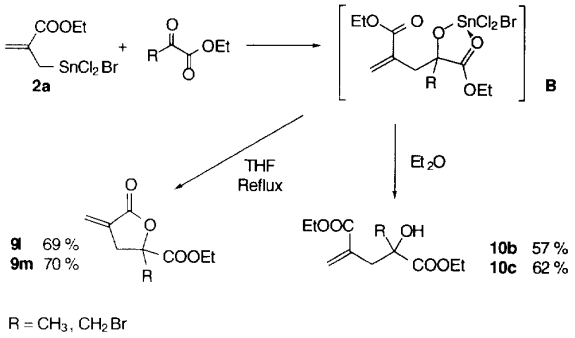
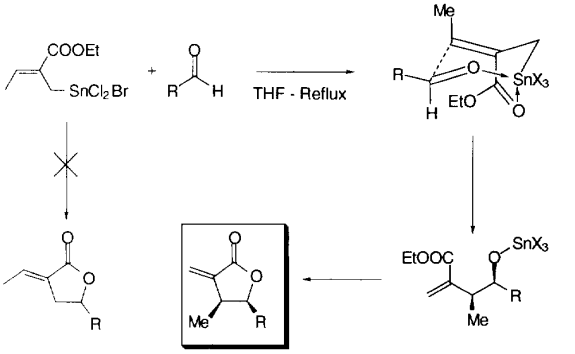


Fig 9

We also investigated the diasteroselectivity of the reaction, since the reaction of crotyltrihalotin **2b** with carbonyl compounds produces two stereogenic centers (fig 10). In all cases, we isolated the α-methylene-β-methyl-γ-lactones confirming that reaction with transposition was the unique pathway when using allylstannanes **2** [21]. It also appeared that the stereoselectivity of the reaction was directed by the six-membered transition state, in which the R group of the aldehyde tended to occupy an equatorial position, avoiding the 1,3-diaxial interaction with the ethoxycarbonyl group. The products were formed preferentially (86:14 for **11a** and 90:10 for **11b**) as the *syn* substituted α-methylene-γ-lactones [22].



11a : R = Ph (78%) ; de (%) = 72
11b : R = iPr (77%) ; de (%) = 80

Fig 10

Steric hindrance is not the only factor influencing the stereoselectivity of the reaction. Indeed, the use of potential bidentate substrates can dramatically affect the stereochemistry of the lactone. A reaction was performed with ethyl pyruvate in which the steric discrimination between the methyl and the ethoxycarbonyl group is not as evident as in the two previous examples. Nevertheless, lactone **11c** was obtained as a single isomer. Correlation between the two methyl groups in NOESY NMR experiment confirmed the *syn* relationship of these two methyls, in agreement with the hexa-coordination of the tin atom, **C**, by the two carbonyl groups of the substrate (fig 11).

Conclusion

Functionalized allyltin trihalides can be prepared by direct synthesis from tin (II) halides. They have been shown to be useful nucleophilic reagents for the transfer of the allyl

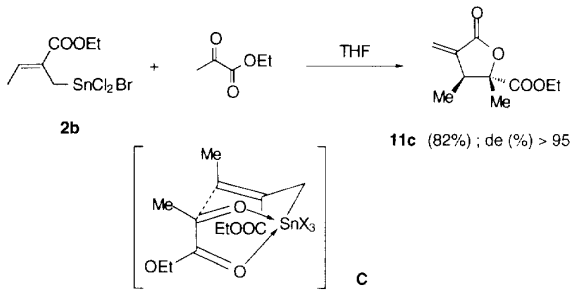


Fig 11

moiety on aldehydes and ketones. The hydrolytic work-up allows an easy recovery of the reaction products. Some control of stereochemistry can be reached and the ability of the tin atom to accept high levels of coordination is thought to be crucial.

Due to the strong difference in reactivity between trihaloorganotin and tetraorganotin reagents, the forthcoming stages of this work will also deal with the design of new reagents in order to study to what extent the nature of the substituent on tin affects the reactivity.

Experimental section

General procedure for the preparation of the allyltin trihalides **2a-h**

In a 50 mL three-necked round-bottomed flask were mixed the allylic bromide **1** (25 mmol) and anhydrous stannous halide (25 mmol) under an inert atmosphere. After addition of dichloromethane (10 mL), anhydrous ether (10 mL) and lithium bromide (216 mg, 2.5 mmol), the mixture was heated at reflux for 2 h. After cooling and concentration under reduced pressure, the residue was dissolved in chloroform (50 mL) and filtered. Removal of the solvent gave the crude monoallylstannane **2** as a yellow oil (up to 97%) or orange solids, which can be stored or used for the lactonization reactions without any further purification. However, the products can be precipitated (**2e**, **2f**), or distilled providing with a minimum of decomposition, **2**, as colorless liquids.

- *Ethyl 2-[(bromodichlorostannyl)methyl]prop-2-enoate* **2a**

IR (film) : 1 640, 1 605, 1 420, 1 380, 1 335, 1 205, 1 005 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.39 (t, J = 7.1 Hz, 3H), 2.96 (bs, 2H, $^2J_{H-Sn}$ = 118.1 Hz), 4.43 (q, J = 7.1 Hz, 2H), 6.04 (bs, 1H, $^4J_{H-Sn}$ = 30.8 Hz), 6.43 (bs, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.0, 31.9 (CH_2-Sn, bs), 65.6, 125.4, 129.4 ($^3J_{C-Sn}$ = 152 Hz), 172.9.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : dδ −322.2 (R-$SnBr_3$) −264.0 (R-$SnClBr_2$), −204.4 (R-$SnCl_2Br$), −144.0 (R-$SnCl_3$).

- *Ethyl (Z)-2-[(bromodichlorostannyl)methyl]but-2-enoate* **2b**

IR (film) : 1 635, 1 605, 1 405, 1 310, 1 150, 1 060, 1 005, 720, 680 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.41 (t, J = 7.1 Hz, 3H), 2.05 (dt, J = 7.1 Hz and 1.4 Hz, 3H, $^5J_{H-Sn}$ = 25.2 Hz), 2.83 (s, 2H, $^2J_{H-Sn}$ = 117.6 Hz), 4.45 (q, J = 7.1 Hz, 2H), 7.31 (qt, J = 7.1 Hz and 2.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.1, 16.7, 27.1 ($^1J_{C-Sn}$ = 837 Hz), 65.5, 123.8 ($^2J_{C-Sn}$ = 68 Hz), 144.9 ($^3J_{C-Sn}$ = 152 Hz), 173.6.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −350.9 (R-$SnBr_3$), −284.8 (R-$SnClBr_2$), −219.1 (R-$SnCl_2Br$), −154.7 (R-$SnCl_3$).

- *Ethyl 6-(Bromodichlorostannyl)cyclohex-1-ene-1-carboxylate* **2d**

IR (film) : 1 635, 1 605, 1 405, 1 310, 1 150, 1 060, 1 005, 720, 680 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.39 (t, J = 7.1 Hz, 3H), 1.56-2.08 (m, 3H), 2.36-2.50 (m, 3H), 3.15 (bs, 1H, $^2J_{H-Sn}$ = 124 Hz), 4.44 (q, J = 7.1 Hz, 2H), 7.30 (m, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.1, 22.4, 25.0, 25.8, 42.6 ($^1J_{C-Sn}$ = 833 Hz), 64.8, 126.9, 145.7 ($^3J_{C-Sn}$ = 114 Hz), 172.8.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −290.2 (R-$SnBr_3$), −244.2 (R-$SnClBr_2$), −199.6 (R-$SnCl_2Br$), −135.4 (R-$SnCl_3$).

- *3-[(Bromodichlorostannyl)methyl]but-3-en-2-one* **2e**

IR (film) : 1 620, 1 590 (C=O), 1 320, 1 050, 740 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 2.61 (s, 3H), 2.68 (bs, 2H), 6.42 (s, 1H), 6.55 (s, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 23.7, 26.1 (CH_2-Sn, bs), 27.5 (CH_2-Sn, bs), 29.0 (CH_2-Sn, bs), 30.4 (CH_2-Sn, bs), 132.4, 140.3, 205.1. **2e** is the only case where the four species can be distinguished by ^{13}C NMR.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −330.8 (R-$SnBr_3$), −264.9 (R-$SnClBr_2$), −199.6 (R-$SnCl_2Br$), −135.4 (R-$SnCl_3$).

- *(Z)-3-[(Bromodichlorostannyl)methyl]pent-3-en-2-one* **2f**

IR (film) : 1 625, 1 585 (C=O), 1 390, 1 290, 1 040, 740, 660 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 2.18 (dt, J = 7.0 Hz and 1.3 Hz, 3H, $^5J_{H-Sn}$ = 13.4 Hz), 2.49 (bs, 2H, $^2J_{H-Sn}$ = 109.1 Hz), 2.60 (s, 3H), 7.46 (q, J = 7.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 17.9, 27.1 (bs), 23.5, 134.2 ($^2J_{C-Sn}$ = 36.1 Hz), 151.5 ($^3J_{C-Sn}$ = 154.4 Hz), 204.0 ($^3J_{C-Sn}$ = 59.2 Hz).

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −347.5 (R-$SnBr_3$), −276.3 (R-$SnClBr_2$), −207.4 (R-$SnCl_2Br$), −141.2 (R-$SnCl_3$).

- *Ethyl 2-[(tribromostannyl)methyl]prop-2-enoate* **2g**

IR (film) : 1 640, 1 605 (C=O), 1 420, 1 380, 1 335, 1 205, 1 005, 930, 740 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.40 (t, J = 7.1 Hz, 3H), 3.14 (bs, 2H, $^2J_{H-Sn}$ = 109.9 Hz), 4.42 (q, J = 7.1 Hz, 2H), 6.05 (bs, 1H, $^4J_{H-Sn}$ = 35.8 Hz), 6.43 (bs, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.0, 35.0 (CH_2-Sn, $^1J_{C-Sn}$ = 720 Hz), 64.8, 128.7, 132.5 ($^3J_{C-Sn}$ = 145 Hz), 171.8.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −322.2.

- *(Z)-Ethyl 2-[(tribromostannyl)methyl]but-2-enoate* **2h**

IR (film) : 1 635, 1 605 (C=O), 1 400, 1 380, 1 305, 1 150, 1 060, 890, 720 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.36 (t, J = 7.1 Hz, 3H), 1.99 (dt, J = 7.2 Hz and 1.4 Hz, 3H, $^5J_{H-Sn}$ = 29.0 Hz), 2.93 (m, 2H, $^2J_{H-Sn}$ = 110.0 Hz), 4.39 (q, J = 7.1 Hz, 2H), 7.22 (qt, J = 7.1 Hz and 1.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.2, 16.6, 29.4 ($^1J_{C-Sn}$ = 755 Hz), 65.1, 124.8 ($^2J_{C-Sn}$ = 73.8 Hz), 143.8 ($^3J_{C-Sn}$ = 144 Hz), 173.6 ($^3J_{C-Sn}$ = 70.6 Hz).

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −350.9.

General procedure for the preparation of the allyltrialkyltins **6a-d**

In a 100 mL round-bottomed flask was dissolved the monoallylstannane **2** (9 mmol) in anhydrous THF (45 mL) under an inert atmosphere. After cooling at −78°C a solution of the Grignard's reagent (2 M in Et_2O) was slowly added (3 equiv, 13.5 mL), the reaction mixture was stirred at −78°C for 1 h, then allowed to warm to room temperature and stirred for 1 h further. The slurry mixture was then hydrolyzed and extracted with ether three times. The combined organic layer was washed with brine and dried over Na_2SO_4. After concentration under reduced pressure the residual oil was purified by flash chromatography on silica gel (petrol/ether 100:0 to 90:10), providing **6a-d** as colorless liquids.

• *Ethyl 2-[(tributylstannyl)methyl]prop-2-enoate* **6a**

IR (film) : 2 950, 2 920, 1 710 (C=O), 1 615, 1 320, 1 295, 1 180, 1 080, 905 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.79-0.88 (m, 15H), 1.22-1.47 (m, 15H), 1.94 (bs, 2H, $^2J_{H-Sn}$ = 75.8 Hz), 4.16 (q, J = 7.2 Hz, 2H), 5.25 (bs, 1H, $^4J_{H-Sn}$ = 24.4 Hz), 5.78 (d, 1H, J = 1.7 Hz, $^4J_{H-Sn}$ = 24.0 Hz).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 9.8 (3C, $^1J_{C-Sn}$ = 323 Hz), 13.8 (3C), 14.4, 15.0 ($^1J_{C-Sn}$ = 244 Hz), 27.5 (3C), 29.1 (3C), 60.7, 118.5 ($^3J_{C-Sn}$ = 37.4 Hz), 141.4, 167.9.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −9.7.

• *Ethyl (Z)-2-[(tributylstannyl)methyl]but-2-enoate* **6b**

IR (film) : 2 960, 2 920, 1 700 (C=O), 1 630, 1 270, 1 155, 1 050, 725 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.79-0.90 (m, 15H), 1.21-1.57 (m, 15H), 1.71 (d, J = 7.2 Hz, 3H, $^5J_{H-Sn}$ = 23.4 Hz), 1.89 (s, 2H, $^2J_{H-Sn}$ = 58.2 Hz), 4.15 (q, J = 7.1 Hz, 2H), 6.54 (q, J = 7.1 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 9.6 ($^1J_{C-Sn}$ = 246 Hz), 10.0 (3C, $^1J_{C-Sn}$ = 318.6 Hz), 13.7 (3C), 14.4 (2C), 27.4 (3C), 29.1 (3C), 60.3, 129.6 ($^3J_{C-Sn}$ = 37.2 Hz), 133.8 ($^2J_{C-Sn}$ = 42.9 Hz), 168.4 ($^3J_{C-Sn}$ = 8.6 Hz).

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −7.5.

• *(Z)-3-[(tributylstannyl)methyl]pent-3-en-2-one* **6c**

IR (film) : 2 975, 2 955, 1 665 (C=O), 1 460, 1 370, 1 620, 1 270, 1 020, 795 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.66-0.88 (m, 15H), 1.14-1.45 (m, 12H), 1.72-1.76 (m, 5H, $^2J_{H-Sn}$ = 60.4 Hz), 2.20 (s, 3H), 6.37 (q, J = 7.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 8.4 ($^1J_{C-Sn}$ = 245.1 Hz), 10.1 (3C, $^1J_{C-Sn}$ = 320.3 Hz), 13.7 (3C), 14.9, 25.1, 27.4 (3C), 29.1 (3C), 131.6 ($^3J_{C-Sn}$ = 35.3 Hz), 144.3 ($^2J_{C-Sn}$ = 41.0 Hz), 199.5.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −7.9.

• *Ethyl 2-[(triphenylstannyl)methyl]prop-2-enoate* **6d**

IR (film) : 3 060, 2 980, 1 700 (C=O), 1 610, 1 430, 1 330, 1 300, 1 180, 1 100, 1 080, 1 020, 895, 720, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.18 (t, J = 7.1 Hz, 3H), 2.82 (s, 2H, $^2J_{H-Sn}$ = 69.0 Hz), 4.06 (q, J = 7.1 Hz, 2H), 5.65 (s, 1H), 6.11 (s, 1H), 7.46-7.58 (m, 9H), 7.71-7.81 (m, 6H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 13.9, 17.3 (CH_2-Sn, $^1J_{C-Sn}$ = 345.2 Hz), 60.7, 121.0, 128.4 (6C), 128.9 (3C, $^3J_{C-Sn}$ = 152 Hz), 137.0 (6C), 138.7 (3C), 139.5, 167.3.

^{119}Sn NMR ($CDCl_3$, 75 MHz) : δ −115.0.

Procedure for the radical reaction

In a 50 mL two-necked round-bottomed flask equipped with a water condenser were mixed under argon bromocyclohexanone (4.34 mmol) and **6a** (1.25 eq, 2.2 g) in degassed benzene (25 mL). After addition of AIBN (0.1 equiv) the reaction mixture was stirred under reflux for 16 h. Removal of the solvent then gave a residual oil which was purified by flash chromatography on silica gel (petrol/ether 100:0 to 90:10), providing **7** as a colorless liquid (74% yield).

• *Ethyl 2-(cyclohexylmethyl)propenoate* **7**

IR (film) : 2 920, 2 840, 1 720, 1 630, 1 445, 1 305, 1 200, 1 180, 1 160, 110, 1 025, 940, 810 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.73-1.64 (m, 14H), 2.11 (d, J = 7.0 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 5.38 (s, 1H), 6.06 (s, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.2, 26.3 (2C), 26.6, 33.1 (2C), 36.7, 40.0, 60.5, 125.4, 139.5, 167.5.

General procedure for the lactonization reaction

Procedure I : Carbonyl compound (5.0 mmol) and crude organotin **2a** (5.0 mmol) were mixed in anhydrous ether (20 mL). After stirring at 25°C the reaction mixture was pourred into water and extracted with ether three times. The combined organic layer was washed with brine, dried over Na_2SO_4. After concentration under reduced pressure the residual oil was purified by flash chromatography on silica gel, providing lactones **9** or homoallylic alcohols **10**.

Procedure II : Carbonyl compound (5.0 mmol) and crude organotin **2a** or **2b** (5.0 mmol) were mixed in anhydrous THF (20 mL). After stirring for 3 h at reflux, the reaction mixture were concentrated, diluted in ether (50 mL), poured into water and extracted with ether three times. The combined organic layer was washed with brine, dried over Na_2SO_4. After concentration under reduced pressure the residual oil was purified by flash chromatography on silica gel, providing lactones **9** and **11**.

• *3-Methylidene-5-phenyl-dihydrofuran-2(3H)-one* **9a**

Procedure I, reaction time : 3 h

IR (film) : 3 050, 1 765, 1 660, 1 270, 1 130, 1 025, 800, 725, 690 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 2.84 (m, J = 17.1 Hz, 1H), 3.36 (dd, J = 17.1, 8.0 Hz, 1H), 5.47 (t, J = 7.4 Hz, 1H), 5.65 (bt, J = 1.4 Hz, 1H), 6.24 (t, J = 2.7 Hz, 1H), 7.21-7.52 (m, 5H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 36.1, 78.0, 122.3, 125.4 (2C), 128.5, 128.7 (2C), 134.3, 139.8, 170.1.

Anal calc for $C_{11}H_{10}O_2$: C, 75.85; H, 5.79. Found : C, 75.62; H, 5.83.

• *5-Hexyl-3-methylidene-dihydrofuran-2(3H)-one* **9b**

Procedure I, reaction time : 6 h

IR (film) : 2 920, 2 840, 1 760, 1 660, 1 270, 1 120, 800 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.81 (t, J = 7.0 Hz, 3H), 1.21-1.67 (m, 10H), 2.52 (ddt, J = 17.1, 6.0, 3.0 Hz, 1H), 3.01 (ddt, J = 17.1, 7.6, 1.4 Hz, 1H), 4.45 (m, 1H), 5.56 (t, J = 2.4 Hz, 1H), 6.13 (t, J = 2.7 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.0, 22.5, 24.8, 28.9, 31.6, 33.5, 36.2, 77.6, 121.8, 134.8, 170.4.

Anal calc for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found : C, 72.17; H, 9.99.

• *5-Isopropyl-3-methylidene-dihydrofuran-2(3H)-one* **9c**

Procedure I, reaction time : 12 h

IR (film) : 3 050, 2 920, 1 765, 1 660, 1 270, 800 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.73 (d, J = 6.8 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H), 1.65 (oct, J = 6.8 Hz, 1H), 2.45 (ddt, J = 17.3, 6.5, 3.0 Hz, 1H), 2.81 (ddt, J = 17.3, 7.7, 2.5 Hz, 1H), 4.05 (bq, J = 6.8 Hz, 1H), 5.43 (t, J = 2.5 Hz, 1H), 5.95 (t, J = 3.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 16.8, 17.2, 30.6, 32.9, 81.7, 121.0, 134.9, 169.8.

Anal calc for $C_8H_{12}O_2$: C, 68.55 ; H, 8.63. Found : C, 68.39 ; H, 8.78.

- *5-*tert*-Butyl-3-methylidene-dihydrofuran-2(3H)-one* **9d**

Procedure II, reaction time : 12 h

IR (film) : 2 960, 1 765, 1 660, 1 280, 1 130, 1 000, 980, 800, 725 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.87 (s, 9H), 2.61 (ddt, J = 17.5, 6.7, 2.9 Hz, 1H), 2.77 (ddt, J = 17.5, 7.9, 2.4 Hz, 1H), 4.12 (dd, J = 7.9, 6.7 Hz, 1H), 5.56 (t, J = 2.4 Hz, 1H), 6.12 (t, J = 2.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 24.6 (3C), 28.7, 34.2, 84.6, 121.6, 135.2, 170.0.

Anal calc for $C_9H_{14}O_2$: C, 70.10 ; H, 9.15 . Found : C, 69.96 ; H, 9.30.

- *3-Methylidene-5-(2-phenylbut-3-enyl)-dihydrofuran-2(3H)-one* **9e**

Procedure I, reaction time : 6 h. Obtained as a 3:2 mixture of diastereomers.

IR (film) : 3 070, 3 020, 1 760, 1 660, 1 630, 1 270, 1 120, 1 000, 980, 900, 800, 720 cm^{-1}.

Major isomer : ^1H NMR ($CDCl_3$, 250 MHz) : δ 1.86-2.16 (m, 2H), 2.59 (ddt, J = 17.1, 6.2, 2.9 Hz, 1H), 3.05 (ddt, J = 17.1, 7.6, 2.4 Hz, 1H), 3.57 (m, 1H), 4.49 (m, 1H), 5.02-5.22 (m, 2H), 5.61 (t, J = 2.4 Hz, 1H), 5.94 (m, 1H), 6.21 (t, J = 2.8 Hz, 1H), 7.16-7.50 (m, 5H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 33.4, 41.8, 45.6, 75.1, 115.6, 122.9, 126.7, 127.3 (2C), 128.8 (2C), 134.4, 140.0, 142.9, 169.9.

Minor isomer : ^1H NMR ($CDCl_3$, 250 MHz) : δ 1.86-2.16 (m, 2H), 2.51 (ddt, J = 17.1, 6.2, 2.9 Hz, 1H), 2.91 (ddt, J = 17.1, 7.6, 2.4 Hz, 1H), 3.57 (m, 1H), 4.23 (m, 1H), 5.02-5.22 (m, 2H), 5.58 (t, J = 2.4 Hz, 1H), 6.01 (m, 1H), 6.19 (t, J = 2.8 Hz, 1H), 7.16-7.50 (m, 5H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 33.3, 41.7, 45.4, 75.0, 114.2, 122.8, 126.8, 128.0 (2C), 128.8 (2C), 134.4, 140.9, 142.0, 169.9.

Anal calc for $C_{15}H_{16}O_2$: C, 78.92 ; H, 7.06. Found : C, 78.91 ; H, 7.24.

- *3-Methylidene-5-[(1,5,5-trimethylcyclohex-2-enyl) methyl]-dihydrofuran-2(3H)-one* **9f**

Procedure I, reaction time : 6 h. Obtained as a 3:2 mixture of diastereomers.

IR (film) : 2 940, 1 760, 1 660, 1 270, 1 120, 800, 720 cm^{-1}.

Major isomer : ^1H NMR ($CDCl_3$, 250 MHz) : δ 0.88 (s, 3H), 0.90 (s, 3H), 1.04 (s, 3H), 1.24-1.83 (m, 6H), 2.48 (ddt, J = 17.0, 6.5, 3.1 Hz, 1H), 2.99 (ddt, J = 17.0, 7.2, 2.3 Hz, 1H), 4.51 (m, 1H), 5.39 (bs, 1H), 5.51-5.58 (m, 2H), 6.11 (t, J = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 28.6, 28.8, 30.0, 31.8, 35.0, 35.8, 38.5, 47.5, 50.7, 75.4, 121.5, 124.6, 134.2, 134.9, 170.4.

Minor isomer : ^1H NMR ($CDCl_3$, 250 MHz) : δ 0.88 (s, 3H), 0.90 (s, 3H), 1.03 (s, 3H), 1.24-1.83 (m, 6H), 2.50 (ddt, J = 17.0, 6.5, 3.1 Hz, 1H), 3.02 (ddt, J = 17.0, 7.2, 2.3 Hz, 1H), 4.55 (m, 1H), 5.35 (bs, 1H), 5.51-5.58 (m, 2H), 6.12 (t, J = 2.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 28.5, 29.5, 29.9, 31.0, 34.7, 35.7, 38.6, 48.4, 50.3, 75.2, 121.4, 124.6, 133.9, 134.9, 170.4.

Anal calc for $C_{15}H_{22}O_2$: C, 76.88 ; H, 9.46. Found : C, 77.06 ; H, 9.44.

- *5-(1-Allylcyclohexyl)-3-methylidene-dihydrofuran-2(3H)-one* **9g**

Procedure II, reaction time : 12 h

IR (film) : 3 040, 2 920, 2 860, 1 760, 1 670, 1 630, 1 450, 1 270, 1 230, 1 030, 1 000, 980, 800, 730 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 0.84-1.70 (m, 10H), 1.81-2.27 (m, 2H), 2.76 (m, 2H), 4.35 (t, J = 7.5 Hz, 1H), 4.96 (bs, 1H), 5.02 (bs, 1H), 5.54 (t, J = 2.5 Hz, 1H), 5.70 (m, 1H), 6.10 (t, J = 3.0 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 20.7, 20.9, 25.8, 27.6, 28.9, 29.6, 35.9, 39.2, 81.9, 117.9, 121.4, 133.6, 135.1, 170.3.

Anal calc for $C_{14}H_{20}O_2$: C, 76.33 ; H, 9.15. Found : C, 76.25 ; H, 9.15.

- *7-Methylidene-5-oxaspiro[3.4]octan-6-one* **9i**

Procedure II, reaction time : 12 h

IR (film) : 2 940, 2 840, 1 760, 1 660, 1 300, 1 270, 1 125, 1 095, 940, 800 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.48-1.86 (m, 2H), 2.05 (m, 2H), 2.42 (m, 2H), 2.94 (t, J = 2.8 Hz, 2H), 5.53 (t, J = 2.4 Hz, 1H), 6.09 (t, J = 2.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 11.9, 35.6 (2C), 39.7, 82.3, 121.8, 135.1, 169.8.

Anal calc for $C_8H_{10}O_2$: C, 69.54 ; H, 7.30. Found : C, 69.39 ; H, 7.57.

- *3-Methylidene-1-oxaspiro[4.5]decan-2-one* **9j**

Procedure II, reaction time : 24 h

IR (film) : 2 920, 2 840, 1 760, 1 660, 1 300, 1 270, 1 190, 1 100, 1 030, 940, 800 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.28-1.92 (m, 10H), 2.87 (t, J = 2.8 Hz, 2H), 5.62 (t, J = 2.5 Hz, 1H), 6.21 (t, J = 2.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 22.4 (2C), 24.7, 37.4 (2C), 39.4, 83.4, 122.1, 135.6, 169.9.

Anal calc for $C_{10}H_{14}O_2$: C, 72.26 ; H, 8.49. Found : C, 72.03 ; H, 8.56.

- *5,5-Di(chloromethyl)-3-methylidene-dihydrofuran-2(3H)-one* **9k**

Procedure II, reaction time : 24 h

IR (film) : 2 960, 1 775, 1 665, 1 435, 1 270, 1 140, 1 040, 1 030, 950, 810 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 2.99 (bt, J = 2.8 Hz, 2H), 3.71 (d, J = 11.9 Hz, 2H), 3.80 (d, J = 11.9 Hz, 2H), 5.75 (t, J = 2.9 Hz, 1H), 6.32 (t, J = 2.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 33.8, 47.4 (2C), 82.0, 124.0, 133.2, 168.3.

Anal calc for $C_7H_8O_2Cl_2$: C, 43.11; H, 4.13. Found : C, 42.82 ; H, 4.18.

- *Ethyl 2-methyl-4-methylidene-5-oxo-tetrahydrofuran-2-carboxylate* **9l**

Procedure II, reaction time : 12 h

IR (film) : 2 960, 1 760, 1 660, 1 230, 1 180, 1 110, 1 030, 800 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz) : δ 1.21 (t, J = 7.1 Hz, 3H), 1.60 (s, 3H), 2.75 (dt, J = 17.4, 2.8 Hz, 1H), 3.13 (dt, J = 17.4,

2.4 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 5.61 (t, J = 2.5 Hz, 1H), 6.18 (t, J = 2.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.0, 24.1, 38.6, 62.2, 80.8, 122.8, 135.5, 169.0, 171.2.

Anal calc for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found : C, 58.61; H, 6.62.

• *Ethyl 2-(bromomethyl)-4-methylidene-5-oxo-tetrahydrofuran-2-carboxylate* **9m**

Procedure II, reaction time : 12 h

IR (film) : 2 960, 1 770, 1 655, 1 260, 1 230, 1 170, 1 105, 1 000, 930, 840, 800 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 1.21 (t, J = 7.1 Hz, 3H), 3.05 (dt, J = 17.9, 2.9 Hz, 1H), 3.19 (dt, J = 17.9, 2.5 Hz, 1H), 3.68 (d, J = 11.2 Hz, 1H), 3.77 (dt, J = 11.2 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 5.66 (t, J = 2.5 Hz, 1H), 6.17 (t, J = 2.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 13.8, 35.2, 35.4, 62.8, 81.2, 123.7, 132.3, 168.0, 168.3.

Anal calc for $C_9H_{11}O_4Br$: C, 41.09; H, 4.21. Found : C, 40.77; H, 4.31.

• *Diethyl 4-hydroxypent-1-ene-2,4-dicarboxylate* **10b**

Procedure I, reaction time : 24 h

IR (film) : 3 460, 2 970, 1 730, 1 710, 1 630, 1 370, 1 260, 1 220, 1 170, 1 110, 1 020, 950 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 1.21 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.37 (s, 3H), 2.60 (d, J = 13.9 Hz, 1H), 2.78 (d, J = 13.9 Hz, 1H), 4.12 (m, 4H), 5.61 (bs, 1H), 6.19 (d, J = 1.5 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.1 (2C), 25.5, 41.8, 61.1, 61.7, 74.2, 128.8, 135.8, 167.7, 175.9.

• *Diethyl 5-bromo-4-hydroxypent-1-ene-2,4-dicarboxylate* **10c**

Procedure I, reaction time : 24 h

IR (film) : 3 420, 2 960, 1 730, 1 650, 1 260, 1 230, 1 170, 1 110, 1 030, 935 cm^{-1}.

^{1}H NMR ($CDCl_3$, 250 MHz) : δ 1.23 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 2.77 (AB syst, J = 13.9 Hz, 1H), 2.82 (AB syst, J = 13.9 Hz, 1H), 3.45 (d, J = 10.3 Hz, 1H), 3.66 (d, J = 10.3 Hz, 1H), 3.86 (bs, 1H), 4.15 (m, 4H), 5.68 (bs, 1H), 6.23 (d, J = 1.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.1 (2C), 38.7, 38.9, 61.2, 62.5, 76.4, 129.6, 134.7, 167.3, 172.5.

• *4-Methyl-2-methylidene-5-phenyl-dihydrofuran-2(3H)-one* **11a**

Procedure II, reaction time : 12 h

IR (film) : 3 040, 2 980, 1 770, 1 660, 1 270, 1 250, 1 150, 1 125, 1 000, 975, 800, 695 cm^{-1}.

Major isomer : ^{1}H NMR ($CDCl_3$, 250 MHz) : δ 0.76 (d, J = 7.1 Hz, 3H), 3.42 (m, 1H), 5.55 (d, J = 2.4 Hz, 1H), 5.60 (d, J = 8.1 Hz, 1H), 6.29 (d, J = 2.8 Hz, 1H), 7.34 (m, 5H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 15.3, 38.8, 82.1, 121.6, 125.9 (2C), 128.3, 128.4 (2C), 136.3, 140.0, 170.0.

Minor isomer : ^{1}H NMR ($CDCl_3$, 250 MHz) : δ 1.28 (d, J = 6.8 Hz, 3H), 2.92 (m, 1H), 4.88 (d, J = 7.6 Hz, 2H), 5.55 (d, J = 2.4 Hz, 1H), 6.29 (d, J = 2.8 Hz, 1H), 7.16 (m, 5H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 15.7, 43.3, 85.9, 120.9, 125.8 (2C), 128.5 (2C), 128.8, 138.2, 140.3, 170.6.

• *5-Isopropyl-4-methyl-2-methylidene-dihydrofuran-2(3H)-one* **11b**

Procedure II, reaction time : 12 h

IR (film) : 2 980, 1 765, 1 660, 1 265, 1 245, 1 160, 1 110, 950, 810 cm^{-1}.

Major isomer : ^{1}H NMR ($CDCl_3$, 250 MHz) : δ 0.94 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 1.14 (d, J = 7.1 Hz, 3H), 1.86 (oct, J = 6.7 Hz, 1H), 3.11 (m, 1H), 4.06 (dd, J = 7.7, 6.6 Hz, 1H), 5.51 (d, J = 2.0 Hz, 1H), 6.11 (d, J = 2.2 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 14.5, 18.6, 19.0, 28.6, 37.4, 86.0, 120.0, 142.2, 170.7.

• *Ethyl 2,3-dimethyl-4-methylidene-5-oxo-tetrahydrofuran-2-carboxylate* **11c**

Procedure II, reaction time : 12 h

IR (film) : 2 960, 1 760, 1 660, 1 270, 1 240, 1 180, 1 110, 1 030, 990, 800 cm^{-1}.

Major isomer : ^{1}H NMR ($CDCl_3$, 250 MHz) : δ 1.20 (d, J = 7.0 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 1.40 (3H, s), 3.16 (qt, J = 7.0, 2.8 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 5.53 (d, J = 2.6 Hz, 1H), 6.18 (d, J = 2.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, 63 MHz) : δ 13.9, 14.0, 18.8, 41.3, 61.9, 83.9, 121.8, 139.3, 168.4, 171.2.

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