Allylation of Aldehydes by Allyl- and Crotyltributyltin in the Presence of Catalytic Amounts of Bu_2SnCl_2 Complex

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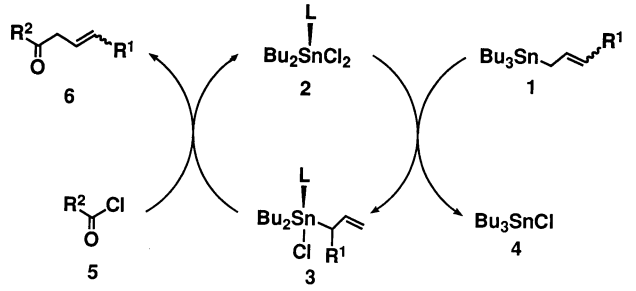
In nearly neutral media, the reaction of allylic tributyltin with aldehydes is effectively catalyzed by Bu_2SnCl_2 complexes. The addition of coordinative reagents and benzoyl chloride as a quencher is required of the catalytic allylation, furnishing homoallyl benzoates in good to excellent yields, where a regioreversed coupling to conventional methods using crotyltributyltin is exclusively observed.

We recently reported that the addition of hexamethylphosphoric triamide (HMPA) or tetraalkylammonium halides effectively promoted the redistribution reaction of allyltributyltin and dibutyltin dichloride to give allyldibutyltin chloride, and that this finding was applied to the addition of acid chlorides to allyltributyltin in the presence of catalytic amounts of a Bu_2SnCl_2 complex, in which the redistribution and a coupling reaction successively occurred (Scheme 1).[1] The reactions of allyltributyltin with carbonyl compounds such as acid chlorides and aldehydes were generally promoted by Pd catalysts[2] and oxophilic Lewis acids,[3-5] respectively, where allylic inversion (S_E2') reactions exclusively occur to give the corresponding allylic inversion products. Contrary to these methods, the reaction with allylic retention remains less explored despite its synthetic importance.[6] Yamamoto et al. reported that a stoichiometric amount of $AlCl_3$–Pr^iOH effects the regioreversed addition, but hindered aldehydes were not adaptable.[7] On the other hand, because the redistribution[8] and the coupling of allyldibutyltin chloride[9] with carbonyl compounds are both indicated to be S_E2' process, a regioreversed coupling to conventional methods is expected to take place in the catalyzed allylation including the redistribution, yielding adducts with retention of crotyl moiety as shown in Scheme 1, while it has been reported that the regioselectivity is apt to be lost in an allylation using catalysts.[10]

We report here the allylation of acid chlorides and aldehydes, where dibutyltin dichloride plays as an effective catalyst together with coordinative compounds such as onium halides. Especially, Selective allylation of aldehydes with retention of an allylic system could be disclosed, and this method is compensatory for the allylations promoted by oxophilic Lewis acids in which the allylic inversion has been generally observed.



Scheme 1.

Results and Discussion

As quite recently reported[1] the reaction of allylic tributyltins **1** with acid chlorides **5** was remarkably catalyzed by dibutyltin dichloride (**2**) together with coordinative compounds (additives) such as phosphine

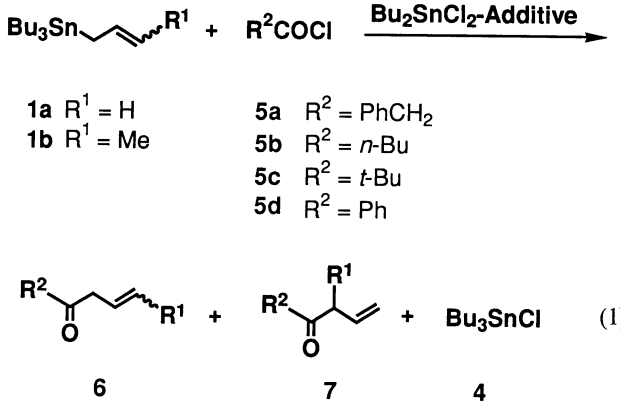
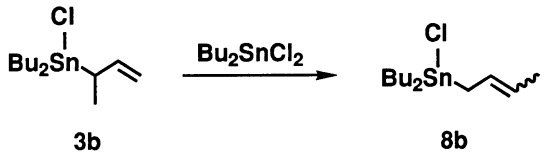


Table 1. Reaction of Allyltributyltin (**1**) with Acid Chlorides (**5**)[a]

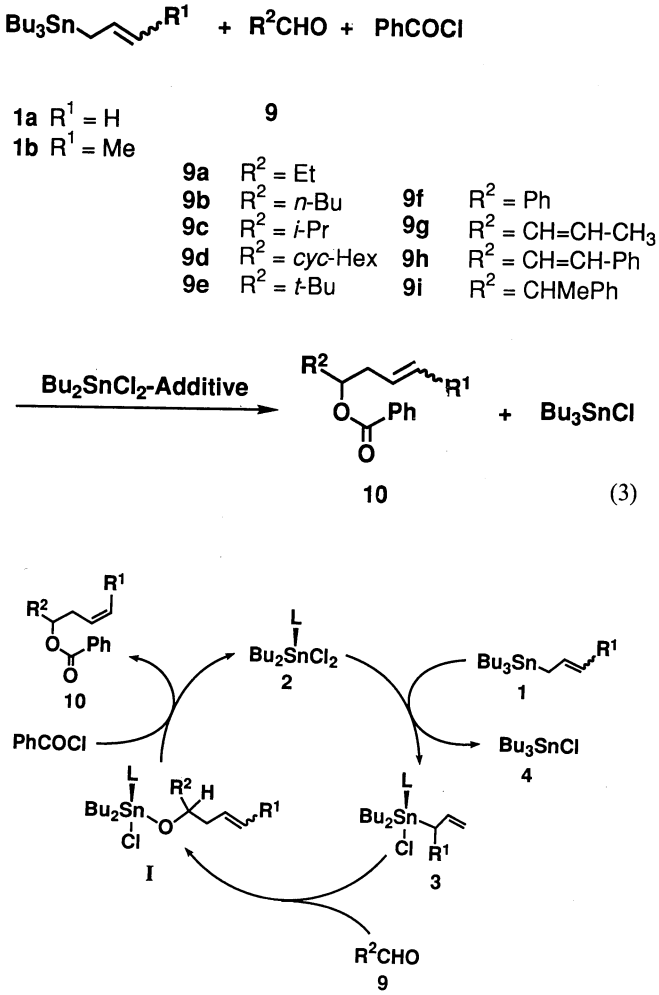
Entry	1	5	Additive	Time/h	Product/%[b]
1	**1a**	**5a**	Et_4NCl	0.5	**6aa** 82
2[c]	**1a**	**5a**	Et_4NCl	5	**6aa** 0
3	**1a**	**5a**	—	3.5	**6aa** 35
4	**1a**	**5a**	$Bu_3P{=}O$	3.5	**6aa** 53
5	**1a**	**5a**	HMPA	3	**6aa** 75
6	**1a**	**5b**	Et_4NCl	3.5	**6ab** 52
7	**1a**	**5c**	Et_4NCl	21	**6ac** 61
8	**1a**	**5d**	Et_4NCl	20	**6ad** 0
9	**1b**	**5a**	Et_4NCl	2	**6ba** 31 (**7ba** 44)
10	**1b**	**5a**	Bu_4NI	1.5	**6ba** 19 (**7ba** 49)
11	**1b**	**5b**	Et_4NCl	4	**6bb** 13 (**7bb** 41)

a) **1**/**5**/Bu_2SnCl_2/Additive=2.2/2/0.2/0.3 mmol, 60°C. b) Determined by GC. c) Without Bu_2SnCl_2.

oxides and tetraalkylammonium halides which are well-known to form complexes with dialkyltin dihalides.[11,12] Tetraethylammonium chloride was the most effective additive investigated to give allyl benzyl ketone (**6aa**) in a 82% yield within 30 min (Entry 1). The results are summarized in Table 1. Here, the low reactivity of benzoyl chloride is noteworthy, and most of the chloride leaved unchanged even after 20 h at 60 °C (Entry 8). A plausible catalytic cycle is shown in Scheme 1. At first the redistribution of **1** with **2** is promoted by an additive.[1] Then the resulting allyldibutyltin chloride (**3**) couples with an acid chloride, and **2** is regenerated. This regeneration is also accelerated by the coordination of an additive.[13-16] Because the both steps are presumed to proceed by S_E2' reaction,[8,9] the selective formation of a **6b** type of crotyl ketone was expected in the coupling of crotyltributyltin with phenylacetyl chloride. However the addition resulted in giving the mixture of **6ba** and **7ba** (41:59) (Entry 9). This result seems to accord with the report that an allylation using catalysts generally lacks regioselectivity with respect to an allylic system.[17] However, we thought that the low reactivity of **5** was responsible for this non-selectivity since the rearrangement of **3b** to **8b** was reported to be caused by a stronger Lewis acid **2** (Eq. 2),[4,8] and so in the next stage the alllylation of aldehydes was attempted.



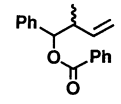
3b **8b** (2)



Scheme 2.

Table 2. Reaction of Allyltributyltin with Aldehydes (**9**)[a]

Entry	1	9	Temp/°C	Additive	Time/h	Product/%
1	**1a**	**9a**	40	Et_4NCl	1.5	**10aa** 84
2	**1a**	**9a**	40	—	4	**10aa** 28
3	**1a**	**9a**	40	HMPA	4	**10aa** 80
4	**1a**	**9b**	40	Et_4NCl	2	**10ab** 70
5	**1a**	**9c**	40	Et_4NCl	2	**10ac** 51
6	**1a**	**9d**	40	Et_4NCl	3	**10ad** 73
7	**1a**	**9e**	40	Et_4NCl	6	**10ae** 43
8	**1a**	**9f**	40	Et_4NCl	0.5	**10af** 86
9	**1a**	**9g**	40	Et_4NCl	1.5	**10ag** 93
10	**1a**	**9h**	40	Et_4NCl	1.5	**10ah** 65
11	**1a**	**9i**	40	Et_4NCl	1.5	**10ai** 71[b]
12	**1b**	**9f**	60	Et_4NCl	6	**10bf** 47 (9)[c]
13	**1b**	**9f**	60	HMPA	5	**10bf** 68
14	**1b**	**9f**	60	Bu_4Nl	3	**10bf** 74
15	**1b**	**9f**	60	Ph_4Pl	3	**10bf** 81
16	**1b**	**9a**	60	Ph_4Pl	5	**10ba** 72
17	**1b**	**9e**	60	Ph_4Pl	8	**10be** 47
18	**1b**	**9g**	60	Ph_4Pl	3	**10bg** 60
19	**1b**	**9i**	60	Ph_4Pl	6	**10bi** 65[d]

a) **1**/**9**/PhCOCl/Bu_2SnCl_2/Additive=2.2/2/2/0.2/0.3 mmol. b) *Threo*/*erythro*=72/28. c) Yield(%) of  (**11bf**). d) *Threo*/*erythro*=66/34.

For the allylation of aldehydes, a presumable catalytic cycle was proposed as shown in Scheme 2 on the basis of the reaction of **5**. To complete this cycle, effective quench of the adduct **I** by an appropriate organic chloride is essential. Neither benzyl, cinnamyl nor allyl chloride effected the catalyzed allylation. Benzoyl chloride, only one acid chloride tolerated for allyldibutyltin chloride as examined above, was the choice of the chloride investigated. Moreover the use of additives strikingly promoted the allylation, for example, Et_4NCl raised the yield of **10aa** from 28% to 84% (Entries 1 and 2 in Table 2). No reaction, of course, took place in the absence of **2**. Thus, the allylation of aldehydes by allyltributyltin could be well constructed under mild conditions (40 °C) by the addition of catalytic amounts of **2** and additives. Table 2 demonstrates the effective allylation of various aldehydes **9a**—**9i**, producing the corresponding homoallyl benzoates in good to high yields.

As can be seen in Table 2 (Entries 12—19), in contrast to acid chlorides the coupling with retention of an allylic system was selectively promoted by the addition of catalytic amounts of Bu_2SnCl_2–Ph_4PI complex, producing linear homoallyl benzoates **10**. Interestingly, Et_4NCl which was an effective catalyst for the allylation of acid chlorides gave the mixture of **10** and branched homoallylic benzoate **11**. The products with retention of an allylic system were selectively obtained at 60 °C within several hours in the range of 47 to 81% yields. Of particular interest is the fact that 2,2-dimethylpropionaldehyde (**9e**) was adaptable to this method since this hindered aldehyde has not been allylated by a reported method.[7] In addition, hindered aldehydes such **9c**, **9d**, and **9i**, were also adaptable to give **10c**, **10d**, and **10i** in good yields.

In conclusion, the allylation of aldehydes by allyltributyltin could be achieved by the use of catalytic amounts of Bu_2SnCl_2 complexes, and the reaction conditions are nearly neutral due to the sufficient use of small amounts of **2** and onium halides. In addition the Lewis acidity of **2** is thought to be weakened by the complexation. All reagents including catalysts are not moisture-sensitive and can be treated without specific caution. The coupling of aldehydes and crotyltributyltin with retention of an allylic system is the most noteworthy feature of this convenient procedure, and compensatory for the conventional Lewis acid-promoted allylation.

Experimental

Apparatus and Materials. IR spectra were recorded on a Hitachi 260-30 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were performed on a Hitachi R-90H or a JEOL JNM-GSX-400 spectrometer. Mass spectra were obtained with a JEOL JMS-DX303 spectrometer (HRMS data software processing, JMS-DA 5000). Analytical GLC was performed on a Shimadzu GC-8A using a 2 m×3 mm glass column packed with Silicone SE-52 on uniport HP (15%, 60—80 mesh). Short-path distillations of products were carried out in a Kugelrohr apparatus.

All acid chlorides, aldehydes, and Bu_2SnCl_2 were commertial ones and were purified by distillation before use. All onium halides were commercial ones and were used without further purification. HMPA was freshly distilled from CaH_2. Allyl- and crotyltributyltin were prepared according to the described methods.[18]

Allylation of Acid Chloride Catalyzed by Bu_2SnCl_2 Complex: Allyltributyltin (**1**) (2.2 mmol) was added to a mixture of Bu_2SnCl_2 (0.2 mmol), Et_4NCl (0.3 mmol) and phenylacetyl chloride (**5a**) (2 mmol) under a dry nitrogen. The mixture was stirred at 60 °C for 0.5 h. Then 50 ml of ether was added and the solution was treated with aqueous ammonium fluoride (10 %, 50 ml) for removal of Bu_3SnCl. The yield of **6aa** (82%) was determined by GLC. After drying over Mg_2SO_4, **6aa** (246 mg, 77%) was isolated by distillation, and identified as follows:

1-Phenyl-4-penten-2-one (6aa): Bp 60 °C/0.1 mmHg (1 mmHg=133.322 Pa); IR 1720 (C=O), 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.24(2H, d, J=7.5 Hz), 3.77 (2H, s), 5.16 (1H, d, J=17.0 Hz), 5.22 (1H, d, J=9.8 Hz), 5.73—6.11 (1H, m), and 7.20—7.40 (5H, m); ^{13}C NMR ($CDCl_3$) δ=46.75 (t), 49.50 (t), 118.83 (t), 126.94 (d), 128.6.1 (d), 129.35 (d), 130.29 (d), 133.89 (s), and 205.63 (s); MS m/z 160 (M^+). Found: C, 82.62; H, 7.53%. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%.

1-Octen-4-one (6ab): Bp 100 °C/23 mmHg; IR 1720 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.90 (3H, t, J=6.4 Hz), 1.06—1.76 (4H, m), 2.44 (2H, t, J=7.3 Hz), 3.16 (2H, d, J=6.8 Hz), 5.12 (1H, d, J=17.1 Hz), 5.15 (1H, d, J=11.0 Hz), and 5.71—6.08 (1H, m); ^{13}C NMR ($CDCl_3$) δ=13.84 (q), 22.44 (t), 26.46 (t), 42.08 (t), 47.72 (t), 118.51 (t), 130.68 (d), and 208.64 (s); MS m/z 126 (M^+). Found: C, 76.31; H, 11.11%. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18%.

2,2-Dimethyl-5-hexen-3-one (6ac):[9] Bp 50 °C/26 mmHg; IR 1720 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.10 (9H, s), 3.23 (2H, d, J=6.8 Hz), 5.02 (1H, d, J=16.3 Hz), 5.04 (1H, d, J=9.8 Hz), and 5.68—6.07 (1H, m).

1-Phenyl-4-hexan-2-one (6ba): Bp 65 °C/0.1 mmHg; IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.57 (3H, d, J=5.3 Hz), 3.20 (2H, d, J=5.9 Hz), 3.71 (2H, s), 5.46—5.79 (2H, m), and 7.16—7.37 (5H, m); ^{13}C NMR ($CDCl_3$) δ=13.05 (q), 40.52 (t), 49.52 (t), 121.59 (d), 126.90 (d), 127.84 (d), 128.61 (d), 129.31 (d), 131.29 (s), and 205.96 (s); MS m/z 174 (M^+). Found: C, 82.98; H, 8.06%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

3-Methyl-1-phenyl-4-penten-2-one (7ba): Bp 60 °C/0.1 mmHg; IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.18 (3H, d, J=5.7 Hz), 3.27—3.50 (1 H, m), 3.76 (2H, s), 5.14 (1H, d, J=15.8 Hz), 5.21 (1H, d, J=10.0 Hz), 5.63—6.04 (1H, m), and 7.14—7.35 (5H, m); ^{13}C NMR ($CDCl_3$) δ=15.95 (q), 47.79 (d), 50.56 (t), 117.12 (t), 126.82 (d), 128.52 (d), 129.47 (d), 134.10 (s), 137.27 (d), and 208.22 (s); MS m/z 174 (M^+). Found: C, 82.89; H, 8.08%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%

2-Nonen-5-one (6bb): Bp 120 °C/25 mmHg; IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.92 (3H, t, J=6.2 Hz), 1.06—1.92 (7H, m, $(CH_2)_2$ of n-Bu group and CH_3), 2.36 (2 H, t, J=7.9 Hz), 3.17 (2 H, d, J=7.0 Hz), and 5.47—5.83 (2H, m); MS m/z 140 (M^+).

3-Methyl-1-octen-4-one (7bb): Bp 100 °C/23 mmHg; IR 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.92 (3H, t, J=5.9 Hz), 1.06—1.82 (7H, m, $(CH_2)_2$ of n-Bu group and CH_3), 2.36 (2H, t,

J=7.7 Hz), 3.04—3.28 (1 H, m), 5.11 (1H, d, J=11.2 Hz), 5.14 (1H, d, J=16.3 Hz), and 5.56—6.02 (1H, m); MS m/z 140 (M^+).

Allylation of Aldehyde by Allyl- and Crotyltributyltin: Benzoyl chloride (2 mmol) and **1** (2.2 mmol) were added to the mixture of Bu_2SnCl_2 (0.2 mmol), Et_4NCl (0.3 mmol), and propionaldehyde (**9a**) (2 mmol) under dry nitrogen. The mixture was stirred at 40 °C for 1.5 h. Then 50 ml of ether was added, and the solution was treated with aqueous ammonium fluoride (10 %, 50 ml) for removal of Bu_3SnCl. The yield of **10aa** (84%) was determined by GLC. After drying over Mg_2SO_4, **10aa** (310 mg, 76%) was isolated by distillation, and identified as follows:

1-Ethyl-3-butenyl Benzoate (10aa): Bp 56 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, J=7.0 Hz), 1.69 (2H, q, J=7.0 Hz), 2.45 (2H, t, J=6.5 Hz), 5.00—5.18 (3H, m), 5.62—6.08 (1H, m), 7.33—7.63 (3H, m), and 7.92—8.09 (2H, m); ^{13}C NMR ($CDCl_3$) δ=9.46 (q), 26.44 (t), 38.03 (t), 74.86 (d), 117.39 (t), 127.97 (d), 129.22 (d), 130.51 (s), 132.40 (d), 133.40 (d), and 165.75 (s); MS m/z 204 (M^+). HRMS. Found: m/z 204.1144. Calcd for $C_{13}H_{16}O_2$: M, 204.1150.

1-Butyl-3-butenyl Benzoate (10ab): Bp 100 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.89 (3H, t, J=5.9 Hz), 1.33—1.73 (6H, m), 2.44 (2H, t, J=6.5 Hz), 4.99—5.24 (3H, m, OCH and =CH_2), 5.62—6.07 (1H, m), 7.31—7.56 (3H, m), and 8.03—8.13(2 H, m); ^{13}C NMR ($CDCl_3$) δ=13.64 (q), 22.27 (t), 27.21 (t), 33.09 (t), 38.40 (t), 73.49 (d), 117.21 (t), 127.82 (d), 129.10 (d), 130.41 (s), 132.21 (d), 133.28 (d), and 165.42 (s); MS m/z 232 (M^+). HRMS. Found: m/z 232.1473. Calcd for $C_{15}H_{20}O_2$: M, 232.1463.

1-Isopropyl-3-butenyl Benzoate (10ac): Bp 80 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.99 (6H, d, J=5.9 Hz), 1.83—2.12 (1H, m), 2.44 (2H, t, J=6.5 Hz), 4.97—5.16 (3H, m, OCH and =CH_2), 5.60—6.06 (1H, m), 7.31—7.55 (3H, m), and 7.99—8.08 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.42 (q), 18.61 (q), 31.02 (d), 35.93 (t), 77.85 (d), 117.18 (t), 128.04 (d), 129.26 (d), 130.51 (s), 132.43 (d), 133.74 (d), and 165.78 (s); MS m/z 177 ($M^+-CH_2-CH=CH_2$). Found: C, 76.90; H, 8.36%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

1-Cyclohexyl-3-butenyl Benzoate (10ad): Bp 130 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.14—1.88 (11H, m), 2.45 (2H, t, J=6.6 Hz), 4.96—5.15 (3H, m, OCH and =CH_2), 5.60—5.98 (1H, m), 7.35—7.56 (3H, m), and 7.99—8.10 (2H, m); ^{13}C NMR ($CDCl_3$) δ=25.80 (t), 26.11 (t), 27.81 (t), 35.71 (t), 40.65 (d), 77.03 (d), 116.97 (t), 127.82 (d), 129.10 (d), 130.38 (s), 132.18 (d), 133.65 (d), and 165.45 (s); MS m/z 258(M^+). HRMS. Found: m/z 258.1625. Calcd for $C_{17}H_{22}O_2$: M, 258.1620.

1-*t*-Butyl-3-butenyl Benzoate (10ae): Bp 85 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.00 (9H, s), 2.38—2.48 (2H, m), 4.88—5.11 (3H, m), 5.57—5.84 (1H, m), 7.41—7.56 (3H, m), and 7.99—8.10 (2 H, m); ^{13}C NMR ($CDCl_3$) δ=25.83 (q), 34.55 (t), 38.61 (s), 79.92 (d), 116.75 (t), 127.94 (d), 129.19 (d), 130.38 (s), 132.30 (d), 134.68 (d), and 165.63 (s); MS m/z 232 (M^+). HRMS. Found: m/z 232.1443. Calcd for $C_{15}H_{20}O_2$: M, 232.1463.

1-Phenyl-3-butenyl Benzoate (10af): Bp 120 °C/0.1 mmHg; IR 1715 (C=O), 1635 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.65—2.85 (2H, m), 5.06 (1H, d, J=10.6 Hz), 5.10 (1H, d, J=16.7 Hz), 5.57—5.84 (1H, m), 6.05 (1H, t, J=6.7 Hz), 7.25—7.56 (8H, m), and 8.03—8.13 (2H, m); ^{13}C NMR ($CDCl_3$) δ=40.74 (t), 75.47 (d), 117.88 (t), 126.18 (d), 127.67 (d), 128.06 (d), 128.16 (d), 129.32 (d), 130.17 (s), 132.61 (d), 132.94 (d), 139.90 (s), and 165.23 (s); MS m/z 252(M^+). HRMS. Found: m/z 252.1150. Calcd for $C_{17}H_{16}O_2$: M, 252.1146.

(*E*)-1-Allyl-2-butenyl Benzoate (10ag): Bp 85 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.71 (3H, d, J=5.7 Hz), 2.51 (2H, t, J=5.7 Hz), 5.07 (1H, d, J=11.2 Hz), 5.10 (1H, d, J=16.9 Hz), 5.46—5.98 (4H, m, -CH=CH-, OCH and -CH=), 7.34—7.55 (3H, m), and 7.99—8.09 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.72 (q), 39.16 (t), 74.37 (d), 117.67 (t), 128.16 (d), 128.92 (d), 129.41 (d), 130.63 (s), 132.61 (d), 133.28 (d), and 165.57 (s); MS m/z 216 (M^+). HRMS. Found: m/z 216.1163. Calcd for $C_{14}H_{16}O_2$: M, 216.1150.

1-[(*E*)-Styryl]-3-butenyl Benzoate (10ah): Bp 163 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.62 (2H, t, J=6.6 Hz), 5.11 (1H, d, J=10.6 Hz), 5.15 (1H, d, J=17.4 Hz), 5.62—5.92 (2H, m, OCH and -CH=), 6.71 (1H, d, J=15.8 Hz), 6.24 (1H, dd, J=15.8 and 6.7 Hz), 7.21—7.55 (8H, m), and 8.02—8.12 (2H, m); ^{13}C NMR ($CDCl_3$) δ=39.04 (t), 74.04 (d), 117.97 (t), 126.36 (d), 126.82 (d), 127.67 (d), 128.07 (d), 128.25 (d), 129.32 (d), 130.29 (s), 132.55 (d), 132.71 (d), 135.99 (s), and 165.26 (s); MS m/z 278 (M^+). HRMS. Found: m/z 278.1320. Calcd for $C_{19}H_{18}O_2$: M, 278.1307.

(1*R*)-1-[(1*S*)-1-Phenylethyl]-3-butenyl Benzoate (10ai *threo*-Form): Bp 136 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.34 (3H, d, J=6.8 Hz), 2.27—2.47 (2H, m), 3.02—3.19 (1H, m, J=6.8 and 7.3 Hz), 4.97 (1H, d, J=15.6 Hz), 4.99 (1H, d, J=11.4 Hz), 5.24—5.55 (1H, m), 5.64—5.93 (1H, m), 7.27 (5H, s), 7.44—7.58 (8H, m), and 8.02—8.11 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.75 (q), 36.69 (t), 43.40 (d), 77.45 (d), 117.64 (t), 126.57 (d), 127.73 (d), 128.10 (d), 128.40 (d), 129.41 (d), 130.41 (s), 132.64 (d), 133.46 (d), 143.04 (s), and 165.90 (s); MS (CI) m/z 281 (M^++1). Found: C, 81.62; H, 7.15%. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%.

(1*R*)-1-[(1*R*)-1-Phenylethyl]-3-butenyl Benzoate (10ai *erythro*-Form): Bp 135 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=1.34 (3H, d, J=6.8 Hz), 2.27—2.47 (2H, m), 3.02—3.19 (1H, m, J=5.9 and 6.8 Hz), 4.97 (1H, d, J=15.6 Hz), 4.99 (1H, d, J=11.4 Hz), 5.24—5.55 (1H, m), 5.64—5.93 (1H, m), 7.27 (5H, s), 7.44—7.58 (8H, m), and 8.02—8.11 (2H, m); ^{13}C NMR ($CDCl_3$) δ=17.24 (q), 36.24 (t), 42.79 (d), 77.12 (d), 117.64 (t), 126.45 (d), 127.73 (d), 128.10 (d), 128.40 (d), 129.41 (d), 130.41 (s), 132.55 (d), 133.58 (d), 142.27 (s), and 165.81 (s); MS (CI) m/z 281 (M^++1).

(*Z*)-1-Phenyl-3-pentenyl Benzoate (10bf): Bp 130 °C/0.1 mmHg; IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.56 (3H, d, J=6.4 Hz), 2.64—2.86 (2H, m), 5.23—5.69 (2H, m, -CH=CH-, $J_{CH=CH}$=11.0 Hz), 6.01 (1H, t, J=6.8 Hz, OCH), 7.27—7.56 (8H, m), and 8.03—8.13 (2H, m); ^{13}C NMR ($CDCl_3$) δ=12.94 (q), 34.13 (t), 76.05 (d), 124.56 (d), 126.39 (d), 127.12 (d), 127.76 (d), 128.25 (d), 129.53 (d), 130.41 (s), 132.76 (d), 140.26 (s), and 165.57 (s); MS m/z 211 ($M^+-CH_2-CH=CH-CH_3$). Found: C, 80.98; H, 6.85. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81.

(1*R*, 2*R*)- and (1*S*, 2*R*)-2-Methyl-1-phenyl-3-butenyl Benzoate (11bf), as a Mixture of *erythro*- and *threo*-Form: Bp 115 °C/0.1 mmHg; IR 1715 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=[0.99 (d, J=7.0 Hz), 1.14 (d, J=6.8 Hz) (3H)], 2.71—2.95 (1H, m), 4.93—5.17 (2H, m), 5.43—5.93 (2 H, m, -CH= and OCH), 7.25—7.66 (8H, m), and 8.04—8.12 (2H, m); ^{13}C NMR ($CDCl_3$) δ=[15.40 (q), 16.46 (q)], [43.17 (d), 43.72 (d)], [79.43 (d), 79.61 (d)], 115.68 (t), 126.99 (d), 127.81 (d),

128.27 (d), 129.55 (d), 130.47 (s), 132.81 (d), [139.06 (s), 139.49 (s)], and 165.50 (s); MS m/z 211 ($M^+-CHCH_3-CH=CH_2$).

(*Z*)-1-Ethyl-3-pentenyl Benzoate (10ba): Bp 75 °C/0.1 mmHg; IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.85 (3H, t, J=7.3 Hz), 1.44—1.90 (5H, m, allylic CH_3 and CH_2 of Et group), 2.51 (2H, t, J=6.5 Hz), 5.09 (1H, t, J=6.2 Hz), 5.36—5.75 (2H, m), 7.31—7.55 (3H, m), and 7.99—8.10 (2H, m); ^{13}C NMR ($CDCl_3$) δ=9.73 (q), 12.94 (q), 26.66 (t), 31.23 (t), 75.65 (d), 126.02 (d), 126.54 (d), 128.13 (d), 129.41 (d), 130.72 (s), 132.52 (d), and 166.06 (s); MS(CI) m/z 219 (M^++1), MS (EI) m/z 163 ($M^+-CH_2-CH=CH-CH_3$). Found: C, 76.86; H, 8.36. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31.

(*Z*)-1-*t*-Butyl-3-pentenyl Benzoate (10be): Bp 75 °C/0.1 mmHg; IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.02 (9 H, s), 1.57 (3H, d, J=3.1 Hz), 2.41 (2H, t, J=5.9 Hz), 5.03 (1H, dd, J=5.6 and 7.6 Hz), 7.31—7.55 (3H, m), and 7.99—8.10 (2H, m); ^{13}C NMR ($CDCl_3$) δ=12.77 (q), 26.10 (q), 27.56 (t), 34.94 (s), 80.80 (d), 125.86 (d), 126.38 (d), 128.12 (d), 129.43 (d), 130.59 (s), 132.48 (d), and 165.99 (s); MS m/z 191 ($M^+-CH_2-CH=CH-CH_3$). Found: C, 78.21; H, 8.98. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%.

(*E*)-1-[(*Z*)-1-Propenyl]-5-pentenyl Benzoate (10bg): Bp 73 °C/0.1 mmHg; IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.64 (3H, d, J=6.4 Hz), 1.71 (3H, d, J=5.9 Hz), 2.42—2.55 (2H, m), 5.36—5.86 (5H, m, two -CH=CH- and OCH), 7.31—7.55 (3 H, m), and 7.99—8.09 (2H, m); ^{13}C NMR ($CDCl_3$) δ=12.81 (q), 17.56 (q), 32.14 (t), 74.61 (d), 124.61 (d), 126.41 (d), 127.97 (d), 128.79 (d), 129.24 (d), 130.56 (s), 132.39 (d), and 165.35 (s); MS m/z 175 ($M^+-CH_2-CH=CH-CH_3$). Found: C, 78.34; H, 7.86. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88.

(1*R*, 3*Z*)-1-[(*S*)-1-Phenylethyl]-3-pentenyl Benzoate (10bi *threo*-Form): Bp 140 °C/0.1 mmHg; IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.35 (3H, d, J=7.3 Hz), 1.51 (3H, d, J=5.3 Hz), 2.30 (2H, t, J=5.7 Hz), 2.94—3.24 (1H, m, J=7.3 Hz), 5.26—5.49 (3 H, m, -CH=CH- and OCH), 7.26 (5H, s), 7.36—7.57 (3H, m), and 7.91—8.12 (2H, m); ^{13}C NMR ($CDCl_3$) δ=12.90 (q), 17.84 (q), 29.79 (t), 43.48 (d), 78.15 (d), 124.98 (d), 126.53 (d), 127.75 (d), 128.18 (d), 129.46 (d), 130.53 (d), 132.60 (d), 143.30 (s), and 165.99 (s).

(1*R*, 3*Z*)-1-[(*R*)-1-Phenylethyl]-3-pentenyl Benzoate (10bi *erythro*-Form): Bp 140 °C/0.1 mmHg; IR 1715 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.35 (3H, d, J=6.8 Hz), 1.51 (3H, d, J=5.3 Hz), 2.30 (2H, t, J=5.7 Hz), 2.94—3.24 (1H, m, J=5.9 and 6.8 Hz), 5.26—5.49 (3H, m, -CH=CH- and OCH), 7.26 (5H, s), 7.36—7.57 (3H, m), and 7.91—8.12 (2H, m); ^{13}C NMR ($CDCl_3$) δ=12.90 (q), 17.44 (q), 29.33 (t), 42.84 (d), 77.78 (d), 124.98 (d), 126.53 (d), 127.75 (d), 128.18 (d), 129.46 (d), 130.53 (d), 132.60 (d), 142.45 (s), and 165.99 (s).

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