

A Facile Synthesis of Two Series of Multifunctional Carbon Compounds from α,α -Dihalo Ketones Using Allylsamarium Bromide

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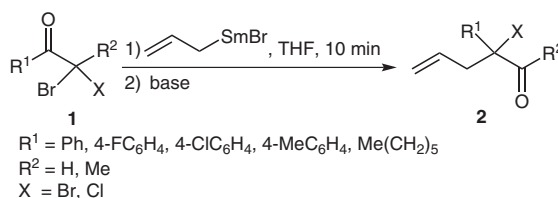
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Abstract: The use of allylsamarium bromide to effect two different reactions on the common starting material, α,α -dihalo ketones, is presented. With DMF, α -halo- α -allyl aldehydes were obtained, while α -hydroxy- α -allyl aldehyde acetals were obtained in the presence of NaOMe/MeOH.

Key words: samarium, aldehydes, acetals, rearrangement, synthesis

The reactions of allylmetals with carbonyl compounds are of interest to synthetic chemists. Homoallyl alcohols are the usual products of these reactions,¹ which may be readily transformed into aldehydes, or can undergo a facile one-carbon homologation to α -lactones via hydroformylation, or be selectively epoxidized to introduce a third chiral center. Compounds containing a carbon atom bearing three or four different labile functional groups are categorized as multifunctional carbon compounds.^{2–4} These compounds should be of considerable significance in theoretical and synthetic organic chemistry. But little attention has been paid to the synthesis of homoallylic alcohols containing other attractive functional groups utilizing these methods via multifunctional carbonyl compounds. Considering the above reports, the development of new and simple synthetic methods for the efficient preparation of multifunctional carbon compounds is therefore an interesting challenge. We report herein the reaction of α,α -dihalo ketones with allylsamarium bromide under different conditions to afford two series of multifunctional carbon compounds, α -halo- α -allyl aldehydes⁴ and α -hydroxy- α -allyl aldehyde acetals, which, to our knowledge, have not been studied so far. It is worth noting that, in the work presented here, allylsamarium(II) bromide reagent, which is well known to have high reducing ability, can add to α,α -dibromo ketones without reducing them. It is also different from other organometallic reagents (such as *n*-BuLi, PhMgBr, Et₂Zn), which often tend to support metal–halogen exchange reaction.⁵

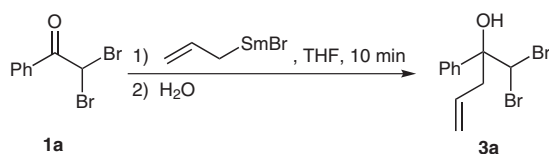
As shown in Scheme 1, α,α -dihalo ketones **1** react with allylsamarium bromide in THF at room temperature, fol-



Scheme 1

lowed by the addition of a base to give α -halo- α -allyl aldehydes **2**.

First, we investigated the effect of the base on the yield of product **2a**. The results are summarized in Table 1. Initially, without base, no desired aldehyde could be detected in the reaction (Table 1, entry 1). Instead of the desired compound, 1,1-dibromo-2-phenylpent-4-en-2-ol (**3a**) was obtained after the reaction was quenched with water (Scheme 2).



Scheme 2

Some bases such as K₂CO₃/MeOH, K₂CO₃/*t*-BuOH, HNEt₂, Et₃N, pyridine, or NaOH had an effect to the reaction, but yields were generally lower (Table 1, entries 3, 5–9). When DMF, DMSO, or HMPA was used, the yield of product was very similar (Table 1, entries 10–13). The effect of these additives can enhance the nucleophilicity of the alkoxide by coordinating to samarium. After screening different bases and additives, DMF appeared to be a good choice and was used in this method. With the optimized reaction conditions, a variety of α,α -dihalo ketones were prepared and subjected to this reaction. The results are shown in Table 2.

When R² = Me (Table 2, entry 7), the reaction gave a lower product yield (36%) and when R² was even larger (R² = Ph, Table 2, entries 11, 12), no desired products were obtained. Instead, α -halo ketones **5k, l** were obtained (Scheme 3), which might have formed by metal–halogen exchange reaction or reductive reaction.⁵ When X = Cl (Table 2, entry 5), the reaction also gave a lower product

Table 1 Comparison of the Effect of Bases in the Reaction of α,α -Dibromo-1-phenylethanone with Allylsamarium Bromide^a

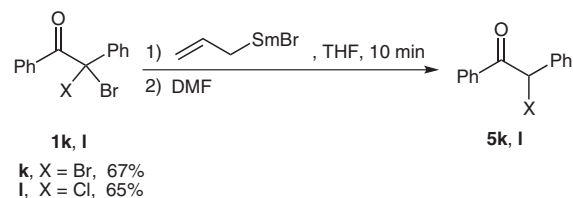
Entry	Base	Amount	Time (h)	Yield (%) ^b
1	none	—	12	0
2	K ₂ CO ₃	10 mmol	24	0
3	K ₂ CO ₃ ^c	10 mmol	1	39
4	K ₂ CO ₃ ^c	10 mmol	10	0
5	K ₂ CO ₃ ^d	10 mmol	12	12
6	HNEt ₂ ^e	10 mL	2	34
7	Et ₃ N ^e	10 mL	1	32
8	pyridine ^e	10 mL	1	7
9	NaOH	10 mL	10	16
10	HMPA ^e	10 mL	0.25	52
11	DMF ^e	10 mL	0.25	54
12	DMSO ^e	10 mL	0.25	52
13	CaH ₂ ^f	10 mmol	12	53

^a All reactions were carried out in THF at r.t.^b Isolated yields based on α,α -dibromo ketones.^c MeOH (10 mL) was added to the reaction mixture.^d *t*-BuOH (10 mL) was added to the reaction mixture.^e Distilled from sodium or CaH₂ under N₂.^f DMSO (10 mL) was added to the reaction mixture.**Table 2** Reactions of α,α -Dihalo Ketones with Allylsamarium Bromide Followed by Addition of DMF

Entry	1	2	Yield (%) ^a
1	1a (R ¹ = Ph, R ² = H, X = Br)	2a	54
2	1b (R ¹ = 4-MeC ₆ H ₄ , R ² = H, X = Br)	2b	41
3	1c (R ¹ = 4-FC ₆ H ₄ , R ² = H, X = Br)	2c	45
4	1d (R ¹ = 4-ClC ₆ H ₄ , R ² = H, X = Br)	2d	52
5	1e (R ¹ = 4-ClC ₆ H ₄ , R ² = H, X = Cl)	2e	34
6	1f (R ¹ = Me(CH ₂) ₅ , R ² = H, X = Br)	2f	49
7	1g (R ¹ = Ph, R ² = Me, X = Br)	2g	36
8	1h (R ¹ = 4-NO ₂ C ₆ H ₄ , R ² = H, X = Br)	—	n.r.
9	1i (R ¹ = 3-NO ₂ C ₆ H ₄ , R ² = H, X = Br)	—	n.r.
10	1j (R ¹ = 2-ClC ₆ H ₄ , R ² = H, X = Br)	—	n.r.
11	1k (R ¹ = Ph, R ² = Ph, X = Br)	—	0 (67) ^b
12	1l (R ¹ = Ph, R ² = Ph, X = Cl)	—	0 (65) ^c

^a Isolated yields based on α,α -dihalo ketones.^b Yield of **5k**.^c Yield of **5l**.

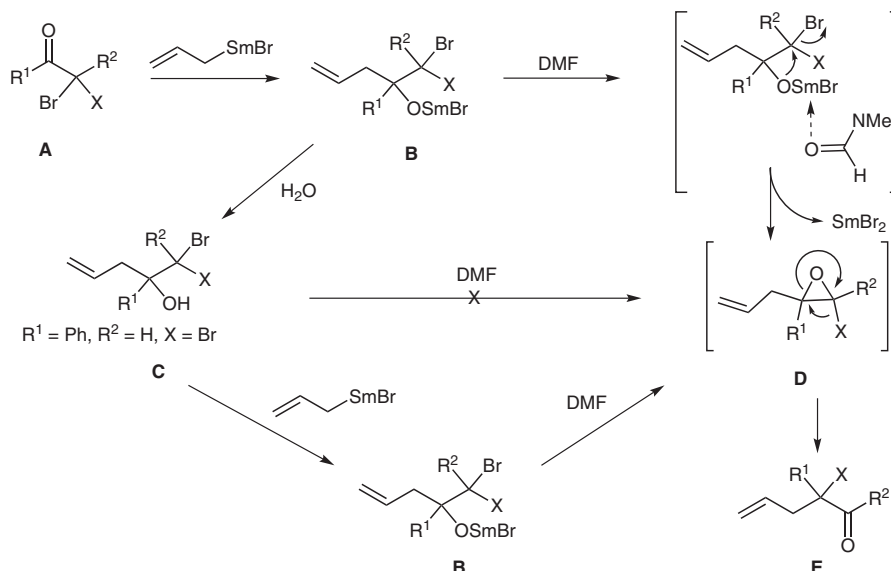
yield (34%); the reason probably is that the Br is more reactive than Cl. However, α,α -dihaloketone bearing a 4-nitro or a 3-nitro group on the aromatic ring (Table 2, entries 8, 9), could not react with allylsamarium bromide. This might be a result of the oxygen atom of substrate coordinating with the Sm atom of allylsamarium bromide, which hinders the reaction of allylsamarium bromide with substrate. Meanwhile, no reaction of 2,2-dibromo-1-(2-chlorophenyl)ethanone (**1j**) was observed under the same conditions (Table 2, entry 10), probably due to the steric hindrance in the substrate.

**Scheme 3**

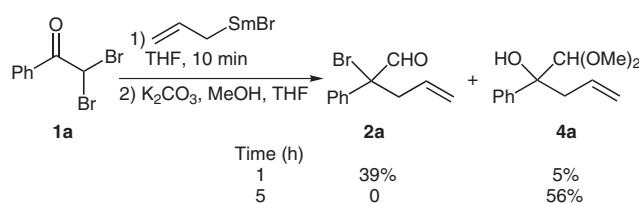
A possible mechanism is proposed in Scheme 4 according to literature.⁶ First, the α,α -dihalo ketone **A** undergoes allylation leading to the intermediate **B**. If the reaction was quenched with water, the product **C** could be obtained. If anhydrous DMF was added to the solution of **B**, the oxygen atom of DMF would coordinate to the Sm atom of **B**. This coordination results in the enhanced nucleophilicity of the oxygen atom. Therefore, the intermediate **B** undergoes intramolecular nucleophilic substitution to provide an α -halo epoxide **D**, which gets converted into the desired product **E**. When DMF was added to the solution of compound **C** (using **3a**, R¹ = Ph, R² = H, X = Br) in THF, and the reaction mixture was stirred for 10 hours, no reaction occurred. However, initial deprotonation of compound **C** using 1.5 equivalents of allylsamarium bromide in THF, followed by the addition of anhydrous DMF, can also lead to the desired aldehyde **E** (**2a**).

It is interesting that when K₂CO₃ together with MeOH or *t*-BuOH were used in the reaction (Table 1, entries 3 and 5), the yield of **2a** depended on the reaction time (Scheme 5). When the reaction time was one hour, the yield of the aldehyde **2a** was 39% and 1,1-dimethoxy-2-phenylpent-4-en-2-ol (**4a**) was also obtained in 5% yield. If the reaction mixture was stirred for five hours, **2a** was not detected and **4a** was obtained in a yield of 56%. Compound **4a** is also one of the multifunctional carbon compounds; we therefore investigated the effect of different bases on the synthesis of **4a** (Scheme 6, Table 3).

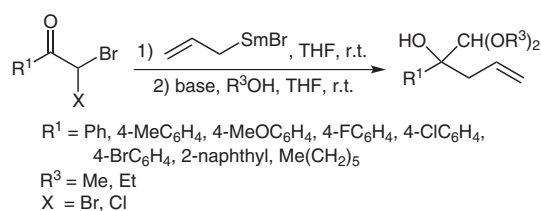
The yield of the product depends on the strength of the base. NaOAc, Et₃N, and pyridine did not have any effect on the reaction (Table 3, entries 1, 10, and 11), while the other bases such as Cs₂CO₃, NaOH, or CaH₂ can promote this reaction with lower yields (Table 3, entries 4–6). When NaH or NaOMe was used, the yields were very similar (Table 3, entries 7–9). After screening different bases, NaOMe appeared to be the best choice for this reaction.



Scheme 4

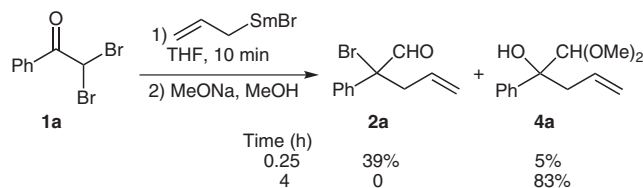


Scheme 5



Scheme 6

As shown in Scheme 7, when 2,2-dibromo-1-phenylethanone (**1a**) was treated with allylsamarium bromide and NaOMe/MeOH, the yield of product **4a** was related to the reaction time. When the reaction was run for 15 minutes, **4a** was obtained in a yield of 5% and 2-bromo-2-phenylpent-4-enal (**2a**) was formed as the main product (39%). When the reaction mixture was stirred for four hours, **2a** could not be detected and **4a** was obtained in a yield of 83%.



Scheme 7

Table 3 Comparison of the Effect of Bases in the Reaction of α,α -Dibromo-1-phenylethanone with Allylsamarium Bromide and MeOH^{a,b}

Entry	Base	Time (h)	Yield (%) ^c
1	NaOAc (10 mmol)	24	0
2	Na ₂ CO ₃ (10 mmol)	12	trace
3	K ₂ CO ₃ (10 mmol)	5	56
4	Cs ₂ CO ₃ (10 mmol)	5	70
5	NaOH (10 mmol)	12	34
6	CaH ₂ (10 mmol)	5	50
7	NaH (10 mmol)	5	82
8	NaOMe (10 mmol)	4	83
9	NaOMe (5 mmol)	4	82
10	pyridine (10 mL) ^d	12	0
11	Et ₃ N (10 mL) ^d	12	0

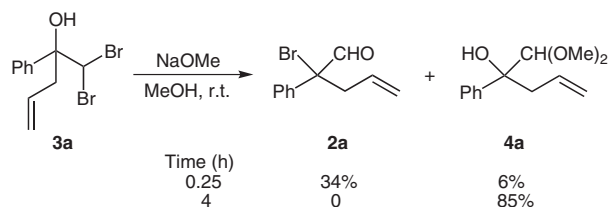
^a All reactions were carried out in THF at r.t.

^b MeOH (10 mL) distilled from Mg was added to the reaction mixture.

^c Isolated yields based on α,α -dibromo ketones.

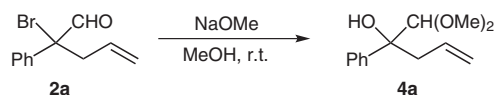
^d Distilled from sodium or CaH₂ under N₂.

The reaction of 1,1-dibromo-2-phenylpent-4-en-2-ol (**3a**) with NaOMe in MeOH at room temperature was also investigated (Scheme 8). When the reaction time was 15 minutes, the yield of the aldehyde, 2-bromo-2-phenylpent-4-enal (**2a**), was 34% and 1,1-dimethoxy-2-phenylpent-4-en-2-ol (**4a**) was obtained simultaneously in a yield of 6%. When the reaction mixture was stirred for four hours, **2a** was not detected and **4a** was obtained in a yield of 85%.



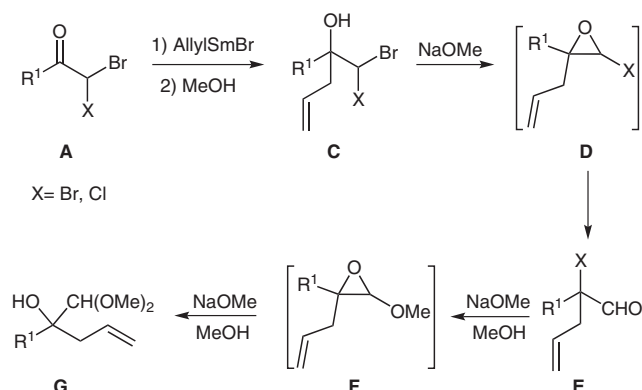
Scheme 8

Under the same reaction condition, **2a** was converted into 1,1-dimethoxy-2-phenylpent-4-en-2-ol (**4a**) in a yield of 88% (Scheme 9).



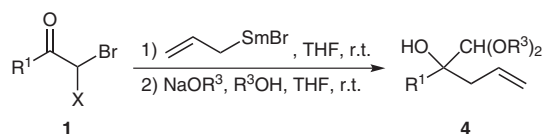
Scheme 9

Based on the experimental results, a plausible pathway for the formation of **4** is illustrated in Scheme 10.⁶ First, the α,α -dihalo ketone **A** undergoes allylation leading to the product **C**. The product **C** undergoes intramolecular nucleophilic substitution providing an α -halo epoxide **D**, which gets converted into the α -halo- α -allyl aldehyde **E**. The α -halo aldehyde **E** was converted into the terminal product **G** by successive nucleophilic attack of methoxide anion on the aldehyde **E** and on the generated α -methoxy-epoxide **F**.



Scheme 10

With these preliminary results in hand, we paid our attention to a wide scope of α,α -dihalo ketones **1** under the optimized reaction condition (Scheme 11). The results are shown in Table 4.



Scheme 11

Table 4 Different α -Hydroxy- α -allyl Aldehyde Acetals **4** from α,α -Dihalo Ketones ^a

Entry	1	R ³	4	Yield (%) ^b
1	1a R ¹ = Ph, X = Br	Me	4a	82
2	1b R ¹ = 4-MeC ₆ H ₄ , X = Br	Me	4b	83
3	1c R ¹ = 4-FC ₆ H ₄ , X = Br	Me	4c	85
4	1d R ¹ = 4-ClC ₆ H ₄ , X = Br	Me	4d	84
5	1e R ¹ = 4-ClC ₆ H ₄ , X = Cl	Me	4d	82
6	1f R ¹ = Me(CH ₂) ₅ , X = Br	Me	4f	81
7	1m R ¹ = 4-BrC ₆ H ₄ , X = Br	Me	4m	83
8	1n R ¹ = 4-MeOC ₆ H ₄ , X = Br	Me	4n	78
9	1o R ¹ = 2-naphthyl, X = Br	Me	4o	82
10	1p R ¹ = Ph, X = Br	Et	4p	56

^a All reactions were carried out at r.t.

^b Isolated yields.

Both electron-donating and electron-withdrawing substituents on the aryl unit were tolerated (Table 4, entries 1–4, 7–9); in addition, when X = Cl (Table 4, entry 5), the reaction gives a similar product yield. The aliphatic substrate (Table 4, entry 6) can also be converted into the corresponding product in satisfactory yield. When EtOH was used instead of MeOH (Table 4, entry 10), a considerable decrease in yield took place (56%).

In addition, some other organometallic reagents were tried in the experiment in the hope of obtaining results with a similar reaction type. We found that when 2,2-dibromo-1-phenylethanone (**1a**) was treated with allylzinc bromide reagent⁷ or allylindium bromide reagent⁸ (Allyl₃In₂Br₃) under the same condition no desired product was detected. And we also found that the Reformatsky reagent⁹ (BrZnCH₂CO₂Et) and Grignard reagent (4-MeC₆H₄MgBr) did not react with 2,2-dibromo-1-phenylethanone (**1a**) in THF at room temperature.

In conclusion, the reaction of allylsamarium bromide with various α,α -dihalo ketones provided a convenient and rapid access to two series of trifunctional carbon compounds, α -halo- α -allyl aldehydes and α -hydroxy- α -allyl aldehyde acetals, under different reaction conditions. The advantages, such as low reaction temperature, fast reaction rate, and one-pot operation make this method an attractive and practical synthesis for multifunctional carbon compounds.

THF and Et₃N were distilled from sodium benzophenone under N₂. HNEt₃ was distilled from Na under N₂. DMF, DMSO, and HMPA were distilled from CaH₂ under N₂. MeOH was distilled from Mg under N₂. All reactions were conducted under a N₂ atmosphere. Metallic samarium and all solvents were purchased from commercial sources, and used without further purification. Flash column chromatography was carried out on Merck silica gel (300–400 mesh). ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 400 MHz

spectrometer as solutions in CDCl_3 . Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the CHCl_3 signal ($\delta = 77.50$). High-resolution mass spectra were obtained with a GCT-TOF instrument. The starting material **1f** was prepared by published methods,¹⁰ others by bromination of respective ketones. Other chemicals were purchased from Aldrich or Acros chemical company and used without further purification.

α,α -Dibromo Ketones; General Procedure

A solution of ketone (10 mmol) in glacial AcOH (10 mL) was heated to 50°C with stirring, and Br_2 (22 mmol) in glacial AcOH (5 mL) was added dropwise. When the decoloration of Br_2 had ceased, NaOAc (7 g) was added in portions. The reaction mixture was stirred for 15 min after the addition of Br_2 , and cooled in a refrigerator for 2 h, and then poured into cold H_2O (100 mL). The crystals formed were collected by filtration and recrystallized from 95% MeOH , if necessary.

1,1-Dibromo-2-phenylpent-4-en-2-ol (**3a**)

Allyl bromide (1.2 mmol) and Sm (1.1 mmol) were mixed in anhyd THF (10 mL) under N_2 at r.t. The mixture was stirred for about 1 h until the Sm powder had disappeared. 2,2-Dibromo-1-phenylethanone (**1a**; 278 mg, 1 mmol) in THF (3 mL) was added dropwise. The mixture was stirred for 10 min, then quenched with MeOH (10 mL) to give **3a**; yield: 293 mg (92%).

^1H NMR (400 MHz, CDCl_3): $\delta = 7.46$ – 7.30 (m, 5 H), 5.98 (s, 1 H), 5.56–5.46 (m, 1 H), 5.15–5.05 (m, 2 H), 2.92 (d, $J = 6.8$ Hz, 2 H), 2.83 (s, 1 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 140.55$, 132.39, 128.59, 128.34, 126.58, 120.55, 78.99, 57.68, 43.89.

HRMS (EI^+): m/z calcd for $\text{C}_8\text{H}_7^{79}\text{Br}^{81}\text{BrO}$ [$\text{M}^+ - \text{C}_3\text{H}_5$]: 278.8843; found: 278.8813.

α -Halo, α -allyl Aldehydes **2**; General Procedure

Allyl bromide (1.2 mmol) and Sm (1.1 mmol) were mixed in anhyd THF (10 mL) under N_2 at r.t. The mixture was stirred for about 5 min, and a purple color was formed. The stirring was continued until the Sm powder had disappeared (1 h). Then a solution of the substrate α,α -dihalo ketone was added dropwise and the reaction was monitored by TLC. The reaction mixture was stirred for 10 min and then anhyd DMF (10 mL) was added. The mixture was stirred for another 15 min (when $\text{X} = \text{Cl}$, the mixture was stirred for 10 h) and then poured into cold H_2O (10 mL) and 5% HCl (10 mL) was added. The resulting mixture was extracted with Et_2O (4×15 mL) and the combined Et_2O layers were dried (MgSO_4). The solvent was removed by evaporation under reduced pressure. Purification of the residue by column chromatography on silica gel [300–400 mesh, eluent: petroleum ether (bp 60 – 90°C)] afforded the product.

2-Bromo-2-phenylpent-4-enal (**2a**)

IR (KBr): 3080, 2901, 2834, 2728, 1732, 1649, 1601, 1488, 1450, 995, 918, 752, 694 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 9.47$ (s, 1 H), 7.44–7.34 (m, 5 H), 5.74–5.60 (m, 1 H), 5.11–5.05 (m, 2 H), 3.11 (d, $J = 9.2$ Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 190.37$, 135.63, 132.61, 129.23, 129.29, 128.58, 120.23, 74.06, 43.39.

HRMS (EI^+): m/z calcd for $\text{C}_{11}\text{H}_{11}^{81}\text{BrO}$ [M^+]: 239.9973; found: 240.0038; m/z calcd for $\text{C}_{11}\text{H}_{11}^{79}\text{BrO}$ [M^+]: 237.9993; found: 238.0006.

2-Bromo-2-p-tolylpent-4-enal (**2b**)

IR (KBr): 3087, 2923, 2834, 2702, 1729, 1639, 1607, 1514, 1431, 992, 925, 816 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 9.44$ (s, 1 H), 7.32–7.17 (m, 4 H), 5.73–5.63 (m, 1 H), 5.10–5.05 (m, 2 H), 3.10 (d, $J = 6.8$ Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 190.41$, 139.27, 132.77, 132.70, 129.92, 128.43, 120.00, 74.06, 43.22, 21.44.

HRMS (EI^+): m/z calcd for $\text{C}_{12}\text{H}_{13}^{81}\text{BrO}$ [M^+]: 254.0129; found: 254.0130; m/z calcd for $\text{C}_{12}\text{H}_{13}^{79}\text{BrO}$ [M^+]: 252.0150; found: 252.0162.

2-Bromo-2-(4-fluorophenyl)pent-4-enal (**2c**)

IR (KBr): 3086, 2924, 2831, 2723, 1728, 1643, 1589, 1489, 1427, 1002, 925, 825 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 9.46$ (s, 1 H), 7.44–7.06 (m, 4 H), 5.72–5.63 (m, 1 H), 5.13–5.06 (m, 2 H), 3.10 (d, $J = 3.2$ Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 190.23$, 163.14 ($^1J_{\text{C,F}} = 248.2$ Hz), 132.36, 131.66, 130.58 ($^3J_{\text{C,F}} = 8.4$ Hz), 120.53, 116.26 ($^2J_{\text{C,F}} = 21.7$ Hz), 73.11, 43.47.

HRMS (EI^+): m/z calcd for $\text{C}_{11}\text{H}_{10}^{81}\text{BrFO}$ [M^+]: 257.9879; found: 257.9884; m/z calcd for $\text{C}_{11}\text{H}_{10}^{79}\text{BrFO}$ [M^+]: 255.9899; found: 255.9874.

2-Bromo-2-(4-chlorophenyl)pent-4-enal (**2d**)

IR (KBr): 3078, 2916, 2831, 2729, 1728, 1643, 1589, 1489, 1427, 1095, 1010, 925, 825 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 9.45$ (s, 1 H), 7.37 (m, 4 H), 5.71–5.61 (m, 1 H), 5.13–5.06 (m, 2 H), 3.09 (d, $J = 3.2$ Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 190.06$, 135.48, 134.33, 132.21, 130.06, 129.44, 120.66, 73.06, 43.36.

HRMS (EI^+): m/z calcd for $\text{C}_{11}\text{H}_{10}^{79}\text{Br}^{35}\text{ClO}$ [M^+]: 271.9604; found: 271.9599; m/z calcd for $\text{C}_{11}\text{H}_{10}^{81}\text{Br}^{35}\text{ClO}$ [M^+]: 273.9583; found: 273.9567.

2-Chloro-2-(4-chlorophenyl)pent-4-enal (**2e**)

IR (KBr): 3093, 2901, 2834, 2715, 1735, 1643, 1597, 1496, 1095, 1010, 925, 825 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 9.39$ (s, 1 H), 7.38 (m, 4 H), 5.70–5.61 (m, 1 H), 5.13–5.08 (m, 2 H), 3.01 (d, $J = 6.8$ Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 191.92$, 135.47, 134.09, 131.26, 129.48, 129.08, 120.83, 77.18, 42.91.

HRMS (EI^+): m/z calcd for $\text{C}_{11}\text{H}_{10}^{35}\text{Cl}_2\text{O}$ [M^+]: 228.0109; found: 228.0112; m/z calcd for $\text{C}_{11}\text{H}_{10}^{35}\text{Cl}^{37}\text{ClO}$ [M^+]: 230.0079; found: 230.0141.

2-Allyl-2-bromooctanal (**2f**)

IR (KBr): 3086, 2931, 2862, 2723, 1728, 1643, 1465, 1381, 995, 925 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 9.39$ (s, 1 H), 5.84–5.74 (m, 1 H), 5.21–5.17 (m, 2 H), 2.77 (t, $J = 6.8$ Hz, 2 H), 2.01–1.91 (m, 2 H), 1.29–1.45 (m, 8 H), 0.88 (t, $J = 6.3$ Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): $\delta = 193.98$, 132.50, 120.29, 73.39, 40.77, 36.72, 31.92, 29.68, 25.61, 22.96, 14.48.

HRMS (EI^+): m/z calcd for $\text{C}_{11}\text{H}_{19}^{81}\text{BrO}$ [M^+]: 248.0599; found: 248.0952; m/z calcd for $\text{C}_{11}\text{H}_{19}^{79}\text{BrO}$ [M^+]: 248.0619; found: 248.0674.

3-Bromo-3-phenylhex-5-en-2-one (**2g**)

IR (KBr): 3087, 2923, 2834, 2702, 1729, 1639, 1607, 1514, 1431, 992, 925, 816 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): $\delta = 7.42$ – 7.29 (m, 5 H), 5.64–5.54 (m, 1 H), 5.03–4.97 (m, 2 H), 3.15–3.01 (m, 2 H), 2.21 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 201.48, 137.83, 133.26, 129.08, 128.72, 127.77, 119.61, 75.79, 46.10, 26.32.

HRMS (EI^+): m/z calcd for $\text{C}_{12}\text{H}_{13}^{79}\text{BrO}$ [M^+]: 252.0150; found: 252.0138; m/z calcd for $\text{C}_{12}\text{H}_{13}^{81}\text{BrO}$ [M^+]: 254.0129; found: 254.0159.

α -Hydroxy- α -allyl Aldehyde Acetals **4**; General Procedure

Allyl bromide (1.2 mmol) and Sm (1.1 mmol) were mixed in anhyd THF (10 mL) under N_2 at r.t. The mixture was stirred for about 10 min, and a purple color was formed. The stirring was continued until the Sm powder had disappeared (1 h). Then a solution of the substrate α,α -dihalo ketone was added dropwise (the reaction was monitored by TLC). The reaction mixture was stirred for 10 min and then MeOH (or EtOH) (10 mL) was added followed by NaOMe (or NaOEt) (5 mmol) in portions. The mixture was stirred for 4 h and filtered. The solvent was removed by evaporation under reduced pressure to give the crude product as an oil, which was purified by column chromatography on silica gel (eluent: PE–EtOAc, 15:1).

1,1-Dimethoxy-2-phenylpent-4-en-2-ol (**4a**)

IR (KBr): 3556, 3070, 2939, 2839, 1643, 1604, 1496, 1450, 1188, 1149, 1072, 979, 918, 763, 702 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.52–7.21 (m, 5 H), 5.68–5.57 (m, 1 H), 5.08–4.98 (m, 2 H), 4.24 (s, 1 H), 3.38 (d, J = 14.8 Hz, 6 H), 2.81–2.65 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 142.57, 133.90, 128.29, 127.37, 126.88, 118.90, 110.85, 78.11, 58.41 (d, J = 10.1 Hz), 41.30.

HRMS (EI^+): m/z calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 204.1150; found: 204.1156.

1,1-Dimethoxy-2-*p*-tolylpent-4-en-2-ol (**4b**)

IR (KBr): 3564, 3078, 2931, 2839, 1643, 1512, 1450, 1188, 1149, 1080, 979, 918, 817 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.40–7.13 (m, 4 H), 5.68–5.57 (m, 1 H), 5.10–5.00 (m, 2 H), 4.23 (s, 1 H), 3.41 (d, J = 14.8 Hz, 6 H), 2.81–2.62 (m, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 139.51, 136.83, 133.96, 129.02, 126.74, 118.83, 110.94, 77.96, 58.42 (d, J = 15.5 Hz), 41.25, 21.47.

HRMS (EI^+): m/z calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$ [M^+]: 236.1412; found: 236.1414.

2-(4-Fluorophenyl)-1,1-dimethoxypent-4-en-2-ol (**4c**)

IR (KBr): 3564, 3078, 2939, 2839, 1643, 1604, 1512, 1450, 1226, 1188, 1072, 979, 918, 840 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.51–6.99 (m, 4 H), 5.66–5.56 (m, 1 H), 5.10–5.02 (m, 2 H), 4.21 (s, 1 H), 3.43 (d, J = 22.8 Hz, 6 H), 2.79–2.63 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 162.28 ($^1J_{\text{C,F}}$ = 243.7 Hz), 138.13 ($^4J_{\text{C,F}}$ = 3.1 Hz), 133.52, 128.64 ($^3J_{\text{C,F}}$ = 7.9 Hz), 119.16, 115.00 ($^2J_{\text{C,F}}$ = 20.9 Hz), 110.86, 77.82, 58.56 (d, J = 18.1 Hz), 41.25.

HRMS (EI^+): m/z calcd for $\text{C}_{13}\text{H}_{15}\text{FO}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 222.1056; found: 222.1060.

2-(4-Chlorophenyl)-1,1-dimethoxypent-4-en-2-ol (**4d**)

IR (KBr): 3556, 3078, 2939, 2839, 1643, 1597, 1496, 1450, 1188, 1080, 979, 918, 833 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.46–7.27 (m, 4 H), 5.63–5.57 (m, 1 H), 5.07–4.99 (m, 2 H), 4.20 (s, 1 H), 3.40 (d, J = 19.6 Hz, 6 H), 2.79–2.65 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 141.02, 133.38, 133.29, 128.45, 128.40, 119.32, 110.72, 77.86, 58.61 (d, J = 13.9 Hz), 41.27.

HRMS (EI^+): m/z calcd for $\text{C}_{13}\text{H}_{15}^{35}\text{ClO}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 238.0761; found: 238.0762.

4-(Dimethoxymethyl)dec-1-en-4-ol (**4f**)

IR (KBr): 3587, 3502, 3078, 2954, 2931, 2862, 1643, 1465, 1080, 979, 918 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 5.94–5.84 (m, 1 H), 5.11–5.06 (m, 2 H), 4.12 (s, 1 H), 3.54 (d, J = 1.2 Hz, 6 H), 2.32–2.29 (m, 2 H), 2.05 (s, 1 H), 1.52–1.48 (m, 2 H), 1.38–1.28 (m, 8 H), 0.88 (t, J = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 134.59, 118.23, 110.04, 76.31, 58.61 (d, J = 4.2 Hz), 39.90, 35.21, 32.26, 30.43, 23.23, 23.08, 14.54.

HRMS (EI^+): m/z calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 212.1776; found: 212.1779.

2-(4-Bromophenyl)-1,1-dimethoxypent-4-en-2-ol (**4m**)

IR (KBr): 3558, 3078, 2937, 2839, 1643, 1604, 1496, 1450, 1188, 1072, 979, 918, 833 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.47–7.38 (m, 4 H), 5.65–5.54 (m, 1 H), 5.10–5.02 (m, 2 H), 4.21 (s, 1 H), 3.43 (d, J = 19.2 Hz, 6 H), 2.77–2.61 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 141.54, 133.33, 131.31, 128.81, 121.53, 119.31, 110.61, 77.87, 58.60 (d, J = 13.8 Hz), 41.21.

HRMS (EI^+): m/z calcd for $\text{C}_{13}\text{H}_{15}^{79}\text{BrO}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 282.0255; found: 282.0245; m/z calcd for $\text{C}_{13}\text{H}_{15}^{81}\text{BrO}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 284.0235; found: 284.0235.

1,1-Dimethoxy-2-(4-methoxyphenyl)pent-4-en-2-ol (**4n**)

IR (KBr): 3556, 3078, 2954, 2839, 1612, 1512, 1465, 1249, 1180, 1080, 979, 918, 833 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.44–6.86 (m, 4 H), 5.69–5.58 (m, 1 H), 5.10–5.01 (m, 2 H), 4.21 (s, 1 H), 3.80 (s, 3 H), 3.41 (d, J = 22.4 Hz, 6 H), 2.81–2.61 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 158.83, 134.49, 133.91, 128.02, 118.86, 113.57, 111.04, 77.82, 58.48 (d, J = 23.5 Hz), 55.54, 41.06.

HRMS (EI^+): m/z calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$ [$\text{M}^+ - \text{H}_2\text{O}$]: 234.1256; found: 234.1262.

1,1-Dimethoxy-2-(naphthalen-2-yl)pent-4-en-2-ol (**4o**)

IR (KBr): 3564, 3062, 2939, 2831, 1643, 1543, 1450, 1072, 972, 910, 748, 694 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 8.03–7.42 (m, 7 H), 5.65–5.59 (m, 1 H), 5.12–4.98 (m, 2 H), 4.33 (s, 1 H), 3.39 (d, J = 13.6 Hz, 6 H), 2.94–2.74 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 140.13, 133.78, 133.59, 132.94, 128.82, 127.91, 127.83, 126.31, 126.27, 125.91, 125.20, 119.11, 110.89, 78.34, 58.49 (d, J = 11.1 Hz), 41.29.

HRMS (EI^+): m/z calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 254.1307; found: 254.1309.

1,1-Diethoxy-2-phenylpent-4-en-2-ol (**4p**)

IR (KBr): 3587, 3078, 2939, 2839, 1643, 1597, 1496, 1450, 1188, 1149, 1080, 979, 918, 752, 694 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 7.53–7.22 (m, 5 H), 5.70–5.59 (m, 1 H), 5.10–4.99 (m, 2 H), 4.36 (s, 1 H), 3.79–3.67 (m, 2 H), 3.46–3.29 (m, 2 H), 2.87–2.68 (m, 3 H), 1.15 (t, J = 6.8 Hz, 6 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 142.55, 134.12, 128.20, 127.29, 127.01, 118.65, 108.38, 77.93, 66.39 (d, J = 5.0 Hz), 40.80, 15.73 (d, J = 12.3 Hz).

HRMS (EI^+): m/z calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$ [$\text{M}^+ - \text{H}_2\text{O}$]: 232.1463; found: 232.1470.

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