Addition Reaction of Vinylic Reagents, Derived from α-Chloroenones, to Carbonyl Compounds Promoted by Samarium Diiodide

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Abstract: A new samarium diiodide-promoted addition reaction of vinylsamarium reagents, derived from (*Z*)-α-chloro-α,β-unsaturated phenones **1**, to both ketones (in THF) and aldehydes (in acetonitrile) led to (*Z*)-2-(1-hydroxyalkyl)-2,3-unsaturated ketones in good yield. These transformations took place with total or very high inversion of the stereochemistry of the C=C double bond of the starting chloroenone, producing the *Z* diastereoisomer. A new methodology to prepare SmI_2 in acetonitrile by sonic treatment of 1,2-diiodoethane with Sm powder is also described. A mechanism to explain this transformation is proposed.

Keywords: Baylis–Hillman reaction · diastereoselectivity · nucleophilic addition · samarium · vinyl reagents

Introduction

Samarium diiodide has become a useful reagent for organic synthesis.[1] It can be used to create C–C bonds through radical or anionic mechanisms. Although deuteration of the anionic intermediate with CH_3OD demonstrated the formation of a vinylsamarium reagent stabilized by a silyl group,[2] to the best of our knowledge, only one example of the addition reaction of vinylic reagents (from acrylamides)[3] to carbonyl compounds, promoted by SmI_2, has been described.[4]

On the other hand, treatment of vinyl organometallic compounds with aldehydes or ketones can afford multifunctionalized natural or unnatural molecules,[5] these products being the same as those prepared by the Baylis–Hillman reaction.[6] However, one of the most serious limitations of the Baylis–Hillman reaction is the impossibility of preparing β-branched Baylis–Hillman adducts,[7] and this is the reason for the limited application of β-branched adducts in organic and medicinal chemistry. Thus, alternative methods need to be developed for synthesizing β-branched Baylis–Hillman adducts. Moreover, the Baylis–Hillman reaction is difficult to carry out with ketones (high pressure is necessary),[8] and the reaction times are long.[9]

Previously, we have reported different C–C bond-formation reactions promoted by SmI_2[10] and a new synthesis of (*Z*)-α-chloro-α,β-unsaturated ketones.[11]

In the present contribution, we report a new methodology for the addition of vinylsamarium reagents, derived from (*Z*)-α-chloro-α,β-unsaturated phenones **1**, to aldehydes or ketones to produce (*Z*)-α-alkylidene-β-hydroxyketones **3**. These transformations are highly stereoselective, and a total or very high inversion[12] of the stereochemistry of the C=C double bond takes place, isolating the *Z* diastereoisomer.

Results and Discussion

Samarium-mediated addition reactions of vinylic reagents to ketones: Initially, we studied the reaction of two (*Z*)-α-chloro-α,β-unsaturated phenones[11] **1** (as the sole starting compound) with samarium diiodide[13] in THF at room temperature. By using these reaction conditions, a vinylic reagent was generated from **1** and added to a second equivalent of **1**. After hydrolysis, the corresponding (*Z*,*Z*)-α-alkylidene-β-hydroxy-γ-chloro-γ,δ-unsaturated ketone **2** was isolated (Scheme 1). Only one diastereoisomer was detected (^1H and ^{13}C NMR spectroscopy), and *Z* stereochemistry of the C=C double bond of the alkylidene group was assumed based on NOESY experiments of compounds **3** (see below). The yields and *Z*/*E* ratio of compounds **2** are given in Table 1.

With these precedents, we studied the reaction of chloroenones **1** with different ketones. Thus, treatment of different α-chloro-α,β-unsaturated phenones **1** with several ketones in

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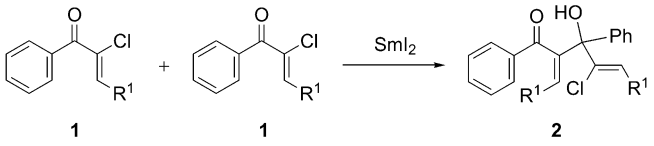


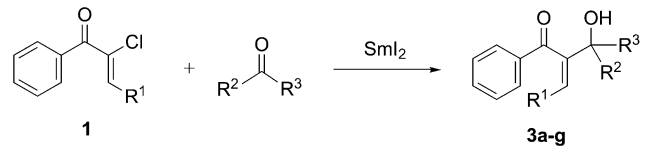
Scheme 1. Synthesis of dimers **2**.

Table 1. Synthesis of dimers **2**.

	R^1	Yield[a] [%]	*Z*/*E*[b] [%]
1	n-C_4H_9	65	> 98/ < 2
2	cyclohexyl	89	> 98/ < 2

[a] Isolated yield after column chromatography based on compound **1**. [b] Determined on the crude reaction by ^{1}H NMR spectroscopy.

the presence of a solution of 2.5 equiv of SmI_2 in THF at room temperature afforded (*Z*)-α-alkylidene-β-hydroxyketones (Scheme 2). The yields and *Z*/*E* ratio of compounds **3a–g** are given in Table 2.



Scheme 2. Reaction between compounds **1** and ketones.

Table 2. Synthesis of compounds **3**.

	Product	R^1	R^2	R^3	Yield[a]	*Z*/*E*[b]
1	**3a**	n-C_4H_9	C_2H_5	CH_3	55	97/3
2	**3b**	n-C_4H_9	Ph	Ph	87	> 99/ < 1
3	**3c**	cyclohexyl	C_2H_5	CH_3	80	95/5
4	**3d**	cyclohexyl	$(CH_2)_5$		61	97/3
5	**3e**	cyclohexyl	CH_2Ph	CH_3	69	98.5/1.5
6	**3f**	Ph	Ph	n-C_3H_7	80	> 99/ < 1
7	**3g**	$PhCH(CH_3)$	$(CH_2)_4$		65	97.5/2.5
8	**3h**	n-C_4H_9	cyclohexyl	H	75	89/11
9	**3i**	cyclohexyl	cyclohexyl	H	52	96.5/3.5
10	**3j**	cyclohexyl	Ph	H	60	96.5/3.5
11	**3k**	cyclohexyl	n-C_7H_{15}	H	72	96/4

[a] Isolated yield after column chromatography based on compound **1**. [b] *Z*/*E* ratio determined by ^{1}H NMR and GC-MS analysis.

Abstract in Spanish: *El diyoduro de samario produce la reacción de adición de aniones vinílicos derivados de fenonas (Z)-α-cloro-α,β-insaturadas **1** a cetonas (en THF) o a aldehídos (en CH_3CN), obteniéndose cetonas (Z)-2-(1-hidroxialquil)-2,3-insaturadas con buen rendimiento. Estas transformaciones tienen lugar con total o muy alta inversión de la estereoquímica del doble enlace de la cloroenona de partida, obteniéndose el diastereoisómero Z. También se describe una nueva metodología para la preparación de SmI_2 en acetonitrilo, por tratamiento de 1,2-diyodoetano y Sm en polvo en un baño de ultrasonidos. Se propone un mecanismo para explicar este proceso.*

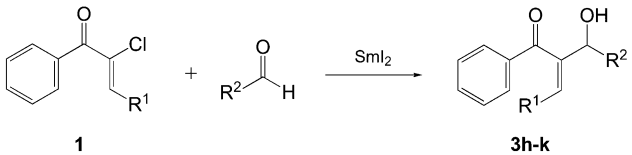
The reaction seems to be general and α-chloro-α,β-unsaturated phenones react with both aromatic and aliphatic ketones, and R^1 on the starting chloroenone can be aliphatic (linear, branched or cyclic) or aromatic.[14]

The *Z*/*E* ratio of the C=C bond of compounds **3** was determined on the crude reaction products by ^{1}H NMR spectroscopy (300 MHz) and GC/MS. The relative *Z* configuration in the C=C double bond was established by NOE experiments in compounds **3d** and **3e**, and the configuration of the other compounds **3** was assigned by analogy.

Addition reactions of chloroenones to aldehydes promoted by samarium diiodide: Significant differences were detected when the same reaction conditions were used to react with aldehydes instead of ketones, and compounds **3** were obtained in a very unpurified form.

Taking into account descriptions of the enhancement of the selectivity of samarium reactions by using acetonitrile as solvent,[15] we carried out the reaction of **1** with aldehydes in acetonitrile. In order to do this, it was necessary to generate SmI_2 in acetonitrile, a process that has been previously described in two methodologies. Kagan et al[15] prepared a solution of SmI_2 in acetonitrile by treatment of Sm with diiodomethane for 8 hours, a long reaction time. The other protocol[16] described the synthesis of SmI_2 in acetonitrile, however some doubt has been cast on this methodology.[1g, 15] We have previously described a rapid and easy methodology for obtaining SmI_2 in THF by sonic treatment of different iodated compounds and Sm.[13] By generalizing this methodology we prepared SmI_2 in acetonitrile. Thus, SmI_2 was easily and rapidly prepared in acetonitrile by reaction of 1,2-diiodoethane and samarium powder in the presence of ultrasonic waves.

Treatment of a mixture of chloroenones **1** and different aldehydes with a solution of 2.5 equiv of SmI_2 in acetonitrile at room temperature over 16 hours gave the corresponding (*Z*)-α-alkylidene-β-hydroxyketones **3h–k**, in good yields, the *Z*/*E* ratio being high or very high (Scheme 3 and Table 2). In general, slight decreases of the *Z*/*E* ratio (except compound **3h**) were obtained with aldehydes in comparison with ketones.



Scheme 3. Reaction between compounds **1** and aldehydes.

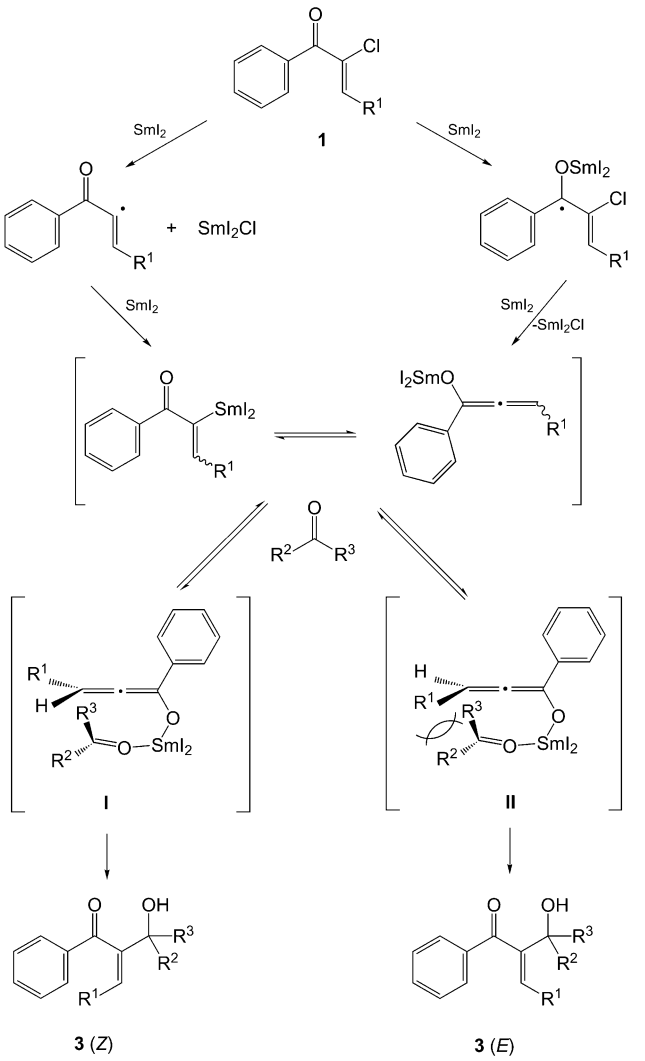
As is shown in Table 2, the reaction also seems to be general, and α-chloro-α,β-unsaturated phenones can react with aromatic and aliphatic aldehydes. When benzaldehyde was used, the pinacol coupling product was observed in the crude reaction mixture (30%, ^{13}C NMR). To the best of our knowledge, this addition reaction of vinylsamarium reagents to an aromatic aldehyde is the first example described in the bibliography. The addition of the previously described vinylsamarium reagents (from acrylamides)[3] to benzaldehyde afforded the benzyl alcohol instead of the corresponding addition product.

As with the compounds derived from ketones, the Z/E ratio of compounds **3h–k** was determined on the crude reaction products by ^{1}H NMR spectroscopy (300 MHz) and GC/MS. In this case, their structure and, consequently, the relative Z configuration in their C=C double bonds, was established by single-crystal X-ray analysis of **3i**.[17]

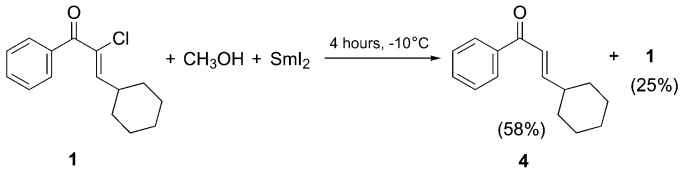
Mechanism: This transformation and the observed stereochemistry of the C=C of products **3** may be explained by assuming that anionic species are involved in the reaction. Initially an equivalent of SmI_2 reduces the C–Cl bond, affording a radical, which can suffer further reduction with a second equivalent of SmI_2 giving the corresponding vinylsamarium reagent. Alternatively, this reagent could also be obtained by a SmI_2-promoted reduction of the starting phenone to a ketyl radical, then reduction to the anion, and, finally, elimination of chloride to the same vinylsamarium reagent (Scheme 4). The addition reaction of the vinylsamarium reagent to the carbonyl compounds might proceed through an allenolate intermediate to give (Z)-α-alkylidene-β-hydroxyketones **3**. Two transition states **I** and **II** are possible, but transition state **I** is preferred, due to the steric repulsions between R^1 and R^2 in **II**.

The lower Z/E ratio obtained in the case of aldehydes can be explained by the minor steric repulsion in transition state **II** between R^1 and R^3 or R^2 (R^3 or $R^2 = H$).

Support for the anionic mechanism is provided by the synthesis of (E)-enone **4**, from treatment of 2-chloro-3-cyclohexyl-1-phenylprop-2-en-1-one with SmI_2 in the presence of MeOH (Scheme 5). In addition, when the same reaction was performed with MeOD instead MeOH, a complex mixture of product was obtained: other side reactions of the vinylsamarium reagent should be faster than deuterium abstraction from MeOD (isotopic effect).



Scheme 4. Proposed mechanism for the addition reaction.



Scheme 5. Reduction with SmI_2/MeOH.

Conclusion

We have described a new nucleophilic addition of vinylic reagents, derived from (Z)-α-chloro-α,β-unsaturated ketones, to ketones or aldehydes that is promoted by samarium diiodide. A total or very high inversion of the stereochemistry of the C=C double bond takes place, and (Z)-α-alkylidene-β-hydroxyketones **3** were isolated as the only or very much the major product. The reaction between chloroenones and aldehydes was carried out in acetonitrile, and a new methodology to synthesize SmI_2 in this solvent has been described. A mechanism to explain the described addition reaction is proposed.

Experimental Section

General: Reactions requiring an inert atmosphere were conducted under dry nitrogen in oven-dried (120 °C) glassware. THF was distilled over sodium/benzophenone immediately prior to use. All reagents were purchased from Aldrich or Merck and were used without further purification. Samarium diiodide in THF was prepared by the sonication of HCI_3 or CH_2I_2 and samarium powder.[13] (Z)-α-chloroenones were prepared by the dehydration of α-chloro-β-hydroxyketones with acetic anhydride/4-dimethylaminopyridine/pyridine at 0 °C.[11] Activated aluminium oxide (neutral) for column chromatography was purchased from Scharlau (AL0835); compounds were visualized on analytical thin-layer

chromatograms (TLC) by exposure to UV light (254 nm) and by cerium molybdate developer.

Synthesis of dimers 2: A solution of the corresponding α-chloroketone **1** (0.4 mmol) in dry THF (2 mL) was added in one go to a solution of SmI_2 (0.4 mmol) in THF (5 mL), and the mixture was stirred at room temperature for thirty minutes. The reaction was quenched with HCl (0.1M), and the crude product was extracted with dichloromethane and purified by column chromatography over alumina (hexane/ethyl acetate 20:1).

(*Z*,*Z*)-4-Chloro-3-hydroxy-2-pentylidene-1,3-diphenylnon-4-en-1-one (2a): $R_f = 0.3$ (hexane/AcOEt, 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.03–7.36 (m, 10H), 6.08 (t, $J = 7.04$ Hz, 1H), 5.83 (t, $J = 7.82$ Hz, 1H), 3.94 (brs, 1H), 2.30 (q, $J = 7.00$ Hz, 2H), 1.88 (q, $J = 7.35$ Hz, 2H), 1.45–1.39 (m, 8H), 0.92 (t, $J = 6.92$ Hz, 3H), 0.78 (t, $J = 6.92$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 198.9$ (C), 141.8 (C), 140.2 (C), 137.9 (C), 137.7 (CH), 136.6 (C), 133.2 (CH), 131.0 (CH), 129.4 (CH), 128.4 (CH), 127.9 (CH), 127.7 (CH), 127.3 (CH), 83.2 (C), 30.9 (CH_2), 30.3 (CH_2), 29.7 (CH_2), 28.4 (CH_2), 22.2 (CH_2), 22.0 (CH_2), 13.8 (CH_3), 13.6 (CH_3); IR (neat): $\tilde{\nu} = 3486$, 3084, 3059, 3027, 2956, 2930, 2857, 1667, 1595, 1579, 1447, 1377, 1258, 1233, 1175, 1033; MS (70 eV): *m*/*z* (%): 410 (<1) [M^+], 392 (7), 375 (5), 357 (30), 317 (24), 301 (14), 105 (100), 77 (25).

(*Z*,*Z*)-4-Chloro-5-cyclohexyl-2-cyclohexylmethylene-3-hydroxy-1,3-diphenylpent-4-en-1-one (2b): $R_f = 0.4$ (hexane/AcOEt 5:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.02$–7.33 (m, 10H), 5.91 (d, $J = 8.70$ Hz, 1H), 5.59 (d, $J = 10.76$ Hz, 1H), 3.67 (brs, 1H), 1.87–0.91 (m, 22H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 198.6$ (C), 141.9 (CH), 141.8 (C), 138.4 (C), 138.1 (C), 136.2 (CH), 134.8 (C), 133.1 (CH), 129.3 (CH), 128.2 (CH), 127.8 (CH), 127.7 (CH), 127.4 (CH), 82.8 (C), 38.6 (CH), 37.9 (CH), 32.0 (CH_2), 31.6 (CH_2), 25.8 (CH_2), 25.4 (CH_2), 25.0 (CH_2); IR (neat): $\tilde{\nu} = 3477$, 3084, 3003, 2925, 2851, 1673, 1595, 1447, 1371, 1266, 1222, 1072; MS (70 eV): *m*/*z* (%): 463 (1) [M^+], 462 (3) [$M^+ - H$], 444 (4), 427 (92), 426 (35), 409 (35), 379 (16), 343 (91), 327 (36), 261 (9), 105 (100), 77 (18).

Synthesis of compounds 3a–g: A solution of the corresponding α-chloroenone **1** and ketone (0.8 mmol) in THF (2 mL) was added in one go to a solution of SmI_2 (1 mmol) in THF (12 mL). The reagents turned yellow in a few seconds. The resulting reaction mixture was stirred at room temperature for two hours, quenched with aqueous HCl (0.1M) and extracted with dichloromethane. Purification by flash column chromatography over alumina (hexane/ethyl acetate 20:1 or 40:1) yielded the corresponding pure compound **3a–g**.

(*Z*)-3-Hydroxy-3-methyl-2-pentylidene-1-phenylpentan-1-one (3a): ^{1}H NMR (300 MHz, $CDCl_3$): $R_f = 0.2$ (hexane/AcOEt 5:1); $\delta = 7.96$–7.42 (m, 5H), 5.90 (t, $J = 7.70$ Hz, 1H), 2.41 (brs, 1H), 1.82–1.64 (m, 4H), 1.36 (s, 3H), 1.30–1.15 (m, 4H), 0.94 (t, $J = 7.40$ Hz, 3H), 0.75 (t, $J = 7.26$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.7$ (C), 144.2 (C), 137.8 (C), 133.3 (CH), 129.3 (CH), 128.5 (CH), 74.8 (C), 34.4 (CH_2), 31.3 (CH_2), 29.4 (CH_2), 27.1 (CH_3), 22.0 (CH_2), 13.7 (CH_3), 8.2 (CH_3); IR (neat): $\tilde{\nu} = 3464$, 3062, 3026, 2960, 2930, 2858, 1660, 1595, 1449, 1231, 1131, 918; MS (70 eV): *m*/*z* (%): 245 (5) [$M^+ - C_2H_5$], 231 (84), 175 (15), 145 (15), 105 (100), 97 (18), 91 (17), 77 (65), 55 (26).

(*Z*)-3-Hydroxy-2-pentylidene-1,3,3-triphenylpropan-1-one (3b): $R_f = 0.3$ (hexane/AcOEt 5:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.01$–7.23 (m, 15H), 5.79 (t, $J = 7.82$ Hz, 1H), 4.56 (brs, 1H), 1.90 (q, $J = 7.16$ Hz, 2H), 1.35–1.10 (m, 4H), 0.78 (t, $J = 6.92$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 200.5$ (C), 145.0 (C), 143.1 (C), 139.1 (CH), 138.1 (C), 133.2 (CH), 129.4 (CH), 128.4 (CH), 127.8 (CH), 127.4 (CH), 127.1 (CH), 82.6 (C), 31.0 (CH_2), 30.1 (CH_2), 22.0 (CH_2), 13.6 (CH_3); IR (neat): $\tilde{\nu} = 3564$, 3054, 2985, 2960, 2929, 2860, 1634, 1595, 1446, 1265, 1025; MS (70 eV): *m*/*z* (%): 182 (42) [$C_{13}H_{11}O^+$], 181 (6), 105 (98), 77 (100), 51 (52).

(*Z*)-2-Cyclohexylmethylene-3-hydroxy-3-methyl-1-phenylpentan-1-one (3c): $R_f = 0.2$ (hexane/AcOEt 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.00–7.41 (m, H), 5.68 (d, $J = 10.53$ Hz, 1H), 2.34 (brs, 1H), 1.80–1.52 (m, 8H), 1.32 (s, 3H), 1.04–0.98 (m, 6H), 0.92 (t, $J = 7.38$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.4$ (C), 142.3 (C), 137.9 (C), 135.0 (CH), 133.2 (CH), 129.2 (CH), 128.3 (CH), 74.5 (CH), 38.5 (CH), 34.4 (CH_2), 32.6 (CH_2), 32.4 (CH_2), 27.2 (CH_3), 25.5 (CH_2), 25.2 (CH_2), 25.1 (CH_2), 8.1 (CH_3); IR (neat): $\tilde{\nu} = 3476$, 3062, 2926, 2853, 1655, 1585, 1580, 1449, 1374, 1312, 1248, 1221, 1174, 1063, 1041, 999; MS (70 eV): *m*/*z* (%): 257 (69) [$M^+ - C_2H_5$], 175 (20), 105 (100), 97 (24), 91 (12), 77 (53), 55 (22).

(*Z*)-3-Cyclohexyl-2-(1-hydroxycyclohexyl)-1-phenylpropenone (3d): $R_f =$ 0.3 (hexane/AcOEt 5:1); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.96$–7.40 (m, 5H), 6.00 (d, $J = 3.72$ Hz, 1H), 2.60 (brs, 1H), 1.85–0.96 (m, 21H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 201.1$ (C), 144.2 (C), 137.9 (C), 134.3 (CH), 133.3 (CH), 129.3 (CH), 128.3 (CH), 72.7 (C), 38.3 (CH), 37.1 (CH_2), 32.4 (CH_2), 25.5 (CH_2), 25.2 (CH_2), 25.1 (CH_2), 21.6 (CH_2); IR (neat): $\tilde{\nu} = 3484$, 3053, 2984, 2930, 2853, 1659, 1579, 1448, 1265; MS (70 eV): *m*/*z* (%): 312 (5) [M^+], 294 (8), 269 (13), 237 (11), 229 (9), 196 (17), 105 (100), 99 (11), 91 (13), 77 (51), 55 (34).

(*Z*)-2-Cyclohexylmethylidene-3-hydroxy-3-methyl-1,4-diphenylbutan-1-one (3e): $R_f = 0.3$ (hexane/AcOEt 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.00–7.30 (m, 10H), 5.40 (d, $J = 10.71$ Hz, 1H), 3.09 (AB, $J = 13.17$ Hz, 2H), 2.09 (brs, 1H), 1.37 (s, 3H), 1.20–0.93 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.2$ (C), 141.5 (C), 138.0 (C), 136.4 (C), 135.3 (CH), 133.2 (CH), 131.1 (CH), 129.3 (CH), 128.4 (CH), 127.8 (CH), 126.5 (CH), 74.0 (C), 47.7 (CH_2), 38.4 (CH), 32.4 (CH_2), 32.2 (CH_2), 27.9 (CH_3), 25.5 (CH_2), 25.2 (CH_2), 25.1 (CH_2); IR (neat): $\tilde{\nu} = 3494$, 3061, 3028, 2923, 2850, 1660, 1595, 1494, 1447, 1372, 1116; MS (70 eV): *m*/*z* (%): 257 (95) [$M^+ - C_7H_7$], 175 (26), 105 (82), 97 (34), 91 (100), 77 (38), 65 (16), 55 (10).

(*Z*)-3-Hydroxy-1,3-diphenyl-2-phenylmethylidenehexan-1-one (3f): $R_f =$ 0.3 (hexane/AcOEt 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.71$–7.05 (m, 16H), 4.14 (brs, 1H), 2.27 (t, $J = 8.28$ Hz, 3H), 1.61–1.25 (m, 2H), 0.97 (t, 7.28 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 201.7$ (C), 144.5 (C), 143.5 (C), 136.2 (C), 135.1 (C), 132.9 (CH), 131.0 (CH), 129.4 (CH), 128.9 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 126.7 (CH), 126.0 (CH), 79.1 (C), 42.5 (CH_2), 16.7 (CH_2), 14.3 (CH_3); IR (neat): $\tilde{\nu} = 3476$, 3061, 3028, 2957, 2871, 1955, 1888, 1809, 1729, 1643, 1494, 1446; MS (70 eV): *m*/*z* (%): 148 (23) [$C_{11}H_{14}O^+$], 130 (5), 120 (19), 106 (14), 105 (100), 78 (12), 77 (84), 51 (46).

(*Z*)-2-(1-Hydroxycyclopentyl)-1,4-diphenylpent-2-en-1-one (3g): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.99$–6.99 (m, 10H), 6.15 (d, $J = 10.76$ Hz, 1H), 3.26 (dq, $J = 6.92$ Hz, $J = 10.76$ Hz, 1H), 2.56 (brs, 1H), 1.88–1.68 (m, 8H), 1.28 (d, $J = 6.92$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 200.6$ (C), 144.3 (C), 142.3 (C), 137.4 (C), 133.6 (CH), 129.5 (CH), 128.5 (CH), 128.4 (CH), 126.7 (CH), 126.2 (CH), 82.6 (C), 39.4 (CH), 39.2 (CH_2), 39.1 (CH_2), 22.8 (CH_2), 21.7 (CH_3); MS (70 eV): *m*/*z* (%): 319 (<1) [$M^+ - 1$], 302 (3), 215 (42), 197 (6), 184 (8), 169 (3), 155 (8), 137 (9), 129 (11), 115 (12), 105 (100), 91 (18), 77 (70); IR (neat): $\tilde{\nu} = 3429$, 3082, 3028, 2955, 2871, 1727, 1667, 1594, 1493, 1454, 1372, 1225, 1042; $R_f = 0.2$ (hexane/AcOEt 5:1).

Synthesis of SmI_2 in acetonitrile: Samarium powder (0.172 g) was placed in a Schlenk tube and heated under vacuum to 150 °C. When it had cooled down again, the Schlenk tube was filled with nitrogen and submerged in an ultrasonic bath. Then a solution of 1,2-diiodoethane (0.282 g) in dry acetonitrile (12 mL) was added to the samarium powder. Sonication of the mixture for two hours gave a deep green solution of samarium diiodide that was used immediately after preparation.

Synthesis of compounds 3h–k: A mixture of the starting α-chloroenone **1** (0.4 mmol) and the corresponding aldehyde (0.5 mmol) in dry acetonitrile (2 mL) was added in one go to a solution of samarium diiodide (1 mmol) in acetonitrile. The solution changed immediately from green to yellow. The reaction mixture was stirred at room temperature overnight and quenched with aqueous HCl (0.1M). Usual workup gave the crude products **3h–k**, which were purified by flash column chromatography over alumina (hexane/ethyl acetate 20:1).

(*Z*)-3-Cyclohexyl-3-hydroxy-2-pentylidene-1-phenylpropan-1-one (3h): $R_f = 0.3$ (hexane/AcOEt 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.96$–7.46 (m, 5H), 5.97 (t, $J = 7.76$ Hz, 1H), 4.04 (d, $J = 6.69$ Hz, 1H), 2.67–0.85 (m, 18H), 0.78 (t, $J = 7.20$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.0$ (C), 140.0 (C), 137.8 (C), 135.7 (CH), 133.3 (CH), 129.2 (CH), 128.5 (CH), 80.3 (CH), 42.2 (CH), 31.2 (CH_2), 30.0 (CH_2), 29.5 (CH_2), 28.2 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 22.1 (CH_2), 13.7 (CH_3); IR (neat): $\tilde{\nu} = 3448$, 3062, 3026, 2959, 2852, 1734, 1661, 1448, 1259, 1232, 1175, 1001; MS (70 eV): *m*/*z* (%): 300 (2) [M^+], 217 (100), 161 (18), 105 (92), 91 (13), 83 (56), 77 (51), 55 (84).

(*Z*)-3-Cyclohexyl-2-cyclohexylmethylidene-3-hydroxy-1-phenylpropan-1-one (3i): $R_f = 0.3$ (hexane/AcOEt 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 8.00–7.44 (m, 5H), 5.73 (d, $J = 10.52$ Hz), 1H, 4.00 (t, $J = 6.16$ Hz, $J =$ 5.64 Hz, 1H), 2.44 (d, $J = 5.64$ Hz, 1H), 1.98–0.92 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 199.9$ (C), 140.0 (CH), 138.3 (C), 137.9 (C), 133.2 (CH), 129.2 (CH), 128.4 (CH), 79.7 (CH), 42.2 (CH), 38.4 (CH), 32.6 (CH_2), 32.5 (CH_2), 29.9 (CH_2), 28.0 (CH_2), 26.3 (CH_2), 25.9 (CH_2), 25.8 (CH_2), 25.6 (CH_2), 25.1 (CH_2); IR (neat): $\tilde{\nu} = 3449$, 3061, 2925, 2862, 2667,

1720, 1655, 1596, 1579, 1450, 1377; MS (70 eV): *m/z* (%): 326 (<1) [M^+], 243 (64), 161 (22), 105 (94), 91 (14), 83 (58), 77 (52), 55 (100).

(*Z*)-2-Cyclohexylmethylidene-3-hydroxy-1,3-diphenylpropan-1-one (3j): $R_f = 0.2$ (hexane/AcOEt 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.73-7.20$ (m, 10H), 5.73 (d, $J = 10.6$ Hz, 1H), 5.51 (s, 1H), 3.29 (br s, 1H), 1.80–0.90 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.1$ (C), 141.4 (C), 139.5 (CH), 139.4 (C), 137.7 (C), 133.2 (CH), 129.0 (CH), 128.2 (CH), 127.5 (CH), 126.3 (CH), 76.4 (CH), 38.3 (CH), 32.4 (CH_2), 32.1 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 25.0 (CH_2); IR (neat): $\tilde{\nu} = 3452$, 3062, 3029, 2929, 2850, 1737, 1660, 1596, 1493, 1449, 1372, 1251, 1094, 1024; MS (70 eV): *m/z* (%): 320 (9) [M^+], 319 (3) [$M^+ - H$], 302 (6), 237 (21), 197 (8), 105 (88), 91 (14), 79 (39), 77 (100), 55 (16).

(*Z*)-2-Cyclohexylmethylidene-3-hydroxy-1-phenyldecan-1-one (3k): ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.95-7.42$ (m, 5H), 5.75 (d, $J = 10.50$ Hz, 1H), 4.29 (t, $J = 6.02$ Hz, 1H), 2.61 (br s, 1H), 1.59–0.82 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 200.1$ (C), 139.9 (C), 138.0 (CH), 137.8 (C), 133.3 (CH), 129.2 (CH), 128.4 (CH), 74.4 (CH), 38.2 (CH), 36.3 (CH_2), 32.5 (CH_2), 32.4 (CH_2), 31.6 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 25.7 (CH_2), 25.5 (CH_2), 25.1 (CH_2), 22.5 (CH_2), 13.9 (CH_3); IR (neat): $\tilde{\nu} = 3271$, 3082, 3062, 3028, 2971, 2924, 2851, 1729, 1655, 1596, 1580, 1312, 1267, 1221, 1174, 1072, 956; $R_f = 0.3$ (hexane/AcOEt 5:1); MS (70 eV): *m/z* (%): 342 (6) [M^+], 324 (22), 259 (21), 243 (90), 225 (26), 197 (7), 161 (35), 155 (14), 105 (100), 91 (28), 83 (33), 77 (80), 67 (23), 57 (39).

Synthesis of compound 4: (*Z*)-2-Chloro-3-cyclohexyl-1-phenylpropenone (0.4 mmol) and MeOH (1.2 mmol) in dry THF (2 mL) were added in one go to a solution of SmI_2 (1 mmol) in THF at $-10\,^\circ$C. The reaction mixture was stirred for 4 hours at the same temperature, quenched with HCl (0.1M), extracted with dichloromethane and filtered through an alumina column. Compound **4** was identified by comparison of the ^{1}H and ^{13}C NMR spectra with the previously isolated pure compound spectra.

(*E*)-3-Cyclohexyl-1-phenylpropenone 4: $R_f = 0.4$ (hexane/AcOEt 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.93-7.26$ (m, 5H), 7.01 (dd, $J = 15.38$, 6.68 Hz, 1H), 6.82 (dd, $J = 15.38$, 1.14 Hz, 1H), 2.26–2.22 (m, 1H), 1.85–1.70 (m, 5H), 1.36–1.19 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 191.3$ (C), 154.9 (CH), 138.0 (C), 132.5 (CH), 128.4 (CH), 123.2 (CH), 41.0 (CH), 31.7 (CH_2), 25.8 (CH_2), 25.7 (CH_2); IR (neat): $\tilde{\nu} = 3084$, 3057, 3025, 2996, 2925, 2851, 1725, 1665, 1614, 1578, 1446, 1336, 1016; MS (70 eV): *m/z* (%): 214(13) [M^+], 157 (6), 120(9), 115 (9), 105 (100), 91 (9), 79 (12), 77 (60), 67 (14), 55 (21), 51 (20).

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