Highly Regio- and Stereoselective Allylation of α-Diketones via the Fluorosilicate Route

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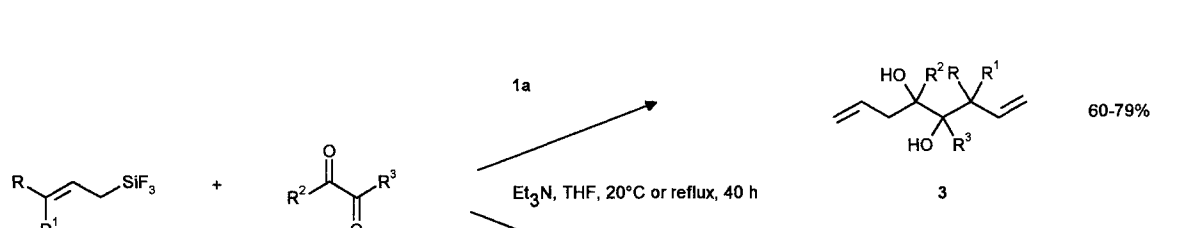
Allylation of enolizable α-diketones with allyltrifluorosilanes in the presence of triethylamine gave the corresponding tertiary homoallyl alcohols in good yield in a highly regio- and stereospecific manner. The reaction proceeds as diallylation with allyltrifluorosilanes yielding the 1,2-diols with high diastereoselectivity. The more sterically demanding crotyl- and prenyltrifluorosilanes lead exclusively to monoallylated products with the allyl group being added γ-regioselectively. In addition, highly diastereoselective crotylation was observed in the formation of the monoallylated α-hydroxy ketones. Asymmetric α-diketones were generally allylated at the less enolized ketone group except when both diketone and allylsilane were sterically hindered.

The addition of allylic organometallics to carbonyl compounds is an important synthetic reaction for the preparation of homoallylic alcohols.[2] Recently, reactions of hypercoordinate allylsilanes with various carbonyl compounds have been investigated as a unique allylation method.[3-5] In the presence of Lewis acids allyltrialkylsilanes react with aldehydes and ketones very smoothly in a γ-regioselective fashion. The stereochemistry of this reaction is rather simple with both (*E*)- and (*Z*)-but-2-enylsilanes giving *syn* products. By contrast, the stereochemistry of allylation with hypercoordinated allylic silicates, which can be prepared in situ from tetracoordinated species, is completely different and highly diastereoselective. These compounds only react with aldehydes, but in certain cases (α-hydroxy ketones, α-oxo carboxylic acids) other carbonyl compounds, capable of coordinating to silicon and leading to a cyclic transition state, can be allylated.[4]

Now we wish to report the allylation of α-diketones.[6] To our knowledge, the addition of allylmetal compounds to α-diketones has been scarcely studied so far.[7-11] In our investigations we found that allyltrifluorosilanes react in the presence of triethylamine with enolizable α-diketones under mild conditions in very good yield with high carbonyl and allyl regioselectivity and diastereoselectivity. Steric factors in the allylsilanes control whether the reaction leads to mono- or diallylated products (Scheme 1). While allyltrifluorosilane yielded exclusively α-diols, the crotyl- and prenyltrifluorosilanes reacted γ-regioselectively to give α-hydroxy ketones.

When allylsilane **1a** was used, even at decreased reaction temperatures and with an equimolar ratio of starting materials, the formation of diallylated products clearly dominated. In contrast, at elevated temperatures and using a 3-fold excess of the silane no more than 5–10% of α-diols were formed in the reactions of crotylsilanes **1b** and **1c**. Under the same reaction conditions prenyltrifluorosilane **1d** still gave exclusively the monoallylated



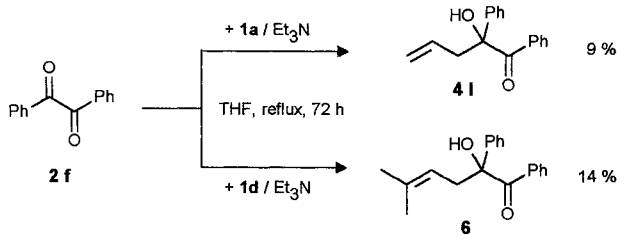
1a R = R[1] = H
1b R = Me; R[1] = H
1c R = H; R[1] = Me
1d R = R[1] = Me

2a R[2] = R[3] = Me
2b R[2] = Me; R[3] = Ph
2c R[2],R[3] = $(CH_2)_4$
2d R[2],R[3] = $(CH_2)_2CHCH_3$
2e R[2] = Me; R[3] = Et

3	R	R[1]	R[2]	R[3]	4	R	R[1]	R[2]	R[3]	4,5	R	R[1]	R[2]	R[3]
a	H	H	Me	Me	a	H	H	Me	Me	g	Me	H	Me	Ph
b	H	H	Me	Ph	b	H	H	$(CH_2)_4$		h	Me	Me	Me	Ph
c	H	H	$(CH_2)_4$		c	Me	Me	Me	Me	i	Me	H	$(CH_2)_2CHCH_3$	
d	H	H	$(CH_2)_2CHCH_3$		d	Me	Me	$(CH_2)_4$		j	Me	Me	Me	Et
e	Me	Me	Me	Me	e	Me	H	Me	Me	k	Me	Me	Me	Et
f	Me	Me	$(CH_2)_4$		f	Me	H	$(CH_2)_4$		l	H	H	Ph	Ph

Scheme 1

α-hydroxy ketones. Benzil **2f**, a nonenolizable α-diketone, was allylated by allyltrifluorosilanes only under drastic reaction conditions and in very low yield (Scheme 2). The loss of γ-allyl regioselectivity suggests a reaction mechanism different from that of enolizable diketones involving a noncyclic transition state (radical or anionic).



Scheme 2

Enolizable α-diketones reacted with allyltrifluorosilane to give diallylated products with high diastereoselectivity (Table 1). A similar high *syn/anti* selectivity, but with inferior yields, was reported for the allylation of α-diketones by allyl alcohol and $SnCl_2$ in the presence of Pd catalyst.[8] A remarkable three-center stereocontrol was observed in the diallylation of the asymmetric cyclic diketone **2d** with only one out of four possible configurational isomers of **3d** being formed.

Table 1. Diallylation of α-Diketones **2a–d** with Allyltrifluorosilane **1a** at 20 °C

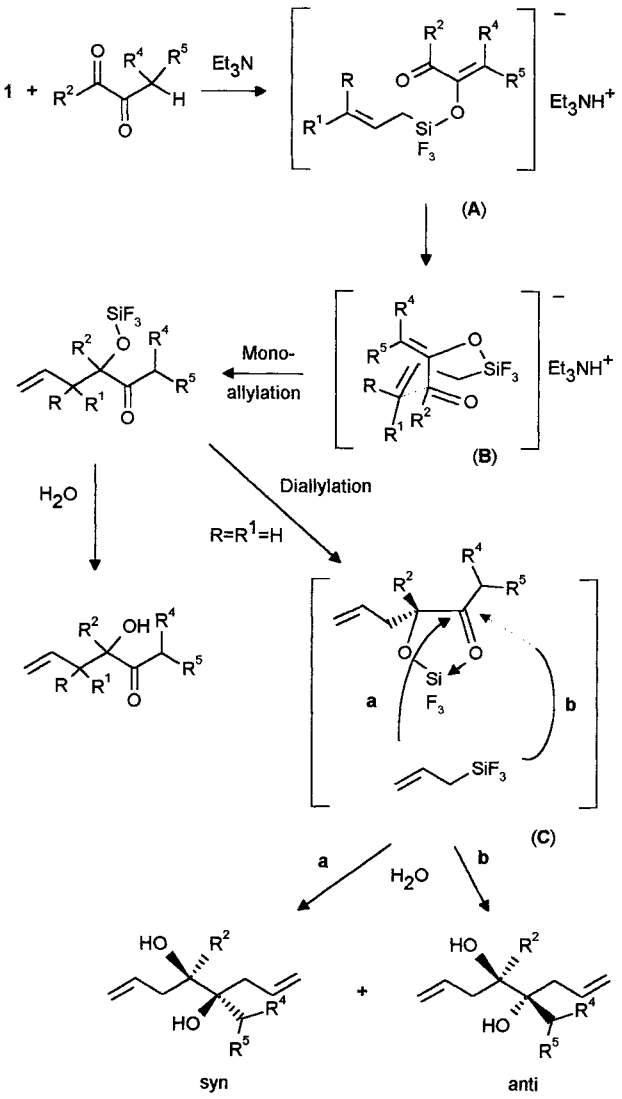
α-Diketone	Product	Yield (%)	Diastereomeric Ratio *syn/anti*
2a	**3a**	72	70 : 30[a]
2b	**3b**	60	5 : 95[a]
2c	**3c**	79	100 : 0[a]
2d	**3d**	63	100 : 0[b]

[a] Stereochemistry determined by ketal formation with 2,2-dimethoxypropane.

[b] Only one out of four possible configurational isomers was obtained. A Me–OH–*cis* structure is supported by ^{1}H NMR NOE difference experiments.

A mechanism involving a bicyclic transition state **(B)** and leading to a silyl ether in which the trifluorosilyl group can activate the adjacent carbonyl group as an intramolecular Lewis acid is proposed (Scheme 3). A second attack of the less sterically demanding allyltrifluorosilane results in stereoselective diallylation (**C**). This is supported by the observation that the second allylation proceeds faster than the initial attack.

In order to investigate whether a stepwise diallylation results in a different diastereoselectivity, monoallylated α-hydroxy ketones were also used in the reaction with allyltrifluorosilane (Table 2). However, both chemical yield and *syn/anti* selectivity did not differ significantly from the results obtained in the diallylation reactions. Thus, an alternative mechanism involving fluoride-catalyzed exchange of the trifluorosilyl by an allyldifluorosilyl group cannot be totally excluded. By addition of allyltrifluorosilane to the monoallylated products from the reactions of α-diketones with prenyltrifluorosilane, novel asymmetrically allylated α-diols **3e** and **3f** were accessible in a *syn* specific manner (Table 2).



Scheme 3

Crotyl- and prenyltrifluorosilanes led exclusively to monoallylated products with the allyl group added γ-regioselectively and, thus, complementing the recently report-

Table 2. Allylation of Monoallylated α-Hydroxy Ketones **4a–d** with Allyltrifluorosilane **1a** at Reflux Temperature

α-Hydroxy Ketone	Product	Yield (%)	Diastereomeric Ratio *syn/anti*
4a[a]	**3a**	78	69 : 31
4b[b]	**3c**	68	100 : 0
4c	**3e**	71	100 : 0
4d	**3f**	34	100 : 0

[a] Prepared by reaction of α-diketone **2a** with allylmagnesium bromide.

[b] Prepared by reaction of α-diketone **2c** with allylmagnesium bromide.

ed α-regioselective photochemical allylation of α-diketones by allylstannanes.[9,10] In addition, the reactions of **1b** and **1c** proceeded in a highly diastereoselective manner representing the first example of γ-regioselective and diastereoselective monoallylation of α-diketones (Table 3). A known procedure using allyl bromide–zinc complexes for the addition to α-diketones showed no diastereoselectivity.[7]

Table 3. Monoallylation of Symmetric α-Diketones **2a, c** with Allyltrifluorosilanes **1b, c** at 20°C and **1d** at Reflux Temperature

α-Diketone	Silane	Product	Yield (%)	Diastereomeric Ratio (A)/(B)[a]
2a	**1b** (*E*/*Z* 88 : 12)	**4e**	67	88 : 12
2a	**1c** (*E*/*Z* 3 : 97)	**4e**	69	4 : 96
2a	**1d**	**4c**	58	–
2c	**1b**	**4f**	74	88 : 12
2c	**1c**	**4f**	75	4 : 96
2c	**1d**	**4d**	81	–

[a] Stereochemistry not determined.

Moreover, in the reactions of asymmetric α-diketones (Table 4) the diastereoselectivity was coupled with a very high carbonyl regioselectivity which has so far not yet been achieved by other allylation methods and differs strongly from the sterically controlled regioselectivity in the Lewis acid catalyzed addition of allyltrialkylsilanes.[9] In agreement with the proposed mechanism asymmetric α-diketones were generally allylated at the less enolized ketone group. However, increased steric requirements for both the diketone and the allyltrifluorosilane led to a change in the regioselectivity. As in **2b** only the acetyl group can be enolized it must be assumed that in the hypercoordinated bicyclic transition state the allyltrifluorosilane cannot only be activated by a hydroxy but also by a second ketone group.

Table 4. Monoallylation of Asymmetric α-Diketones **2b, d, e** with Allyltrifluorosilanes **1b, c** at 20°C and **1d** at Reflux Temperature

α-Diketone	Silane	Products	Yield (%)	Regiomeric Ratio **4/5**	Diastereomeric Ratio of the Main Regiomer (A)/(B)[a]
2b	**1b** (*E*/*Z* 88 : 12)	**4/5g**	69	3 : 97	89 : 11
2b	**1c** (*E*/*Z* 3 : 97)	**4/6g**	65	2 : 98	3 : 97
2b	**1d**	**4/5h**	75	71 : 29	–
2d	**1d**	**4/5i**	68	100 : 0[b]	–
2e	**1b**	**4/5j**	65	100 : 0	90 : 10
2e	**1c**	**4/5j**	67	100 : 0	4 : 96
2e	**1d**	**4/5k**	68	100 : 0	–

[a] Stereochemistry not determined.
[b] The ratio of configurational isomers is 74 : 26.

In summary, the scope of the highly chemo-, regio- and diastereoselective allylation of carbonyl compounds via the fluorosilicate route has been successfully extended to α-diketones.

Diketones **2a–f** are commercially available. Hydroxy ketones **4a** and **4b** were prepared by the reaction of allylmagnesium chloride with diketones **2a** and **2d** in 21 and 34% yield, respectively. Allyltrifluorosilanes **1a–d** were prepared as previously described.[12] The *E*/*Z* ratios of crotylfluorosilanes **2b** and **2c** were determined by GC (Shimadzu 15A, CPB-1, 50 m). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer ($CDCl_3$). Chemical shifts are based on the residual solvent resonances. Mass spectra were obtained on a Shimadzu QP-100 spectrometer. Melting points are uncorrected. The diastereomeric ratios of the products were determined by GC (Shimadzu 15A, CBP-20, 25 m). All new compounds gave satisfactory microanalyses: C ± 0.28, H ± 0.30.

General Procedure A (Table 1):
A THF solution (5 mL) of allyltrifluorosilane **1a** (5 mmol), α-diketone **2a–d** (2 mmol) and Et_3N (5 mmol) was stirred for 40 h under N_2 at 20°C. The reaction was quenched by adding 1 M HCl/Et_2O, the organic layer separated, washed with 1 M NaOH, water, brine and dried ($MgSO_4$). Evaporation of the ether and chromatography through a short column (silica gel, hexane/Et_2O, 4:1) gave the product.

General Procedure B (Table 2):
A THF solution (5 mL) of allyltrifluorosilane **1a** (3 mmol), α-hydroxy ketone **4a–d** (2 mmol) and Et_3N (3 mmol) was refluxed for 40 h under N_2. The reaction was quenched by adding 1 M HCl/Et_2O, the organic layer separated, washed with 1 M NaOH, water, brine and dried ($MgSO_4$). Evaporation of the ether and chromatography through a short column (silica gel, hexane/Et_2O 4:1) gave the product.

General Procedure C (Tables 3 and 4):
A THF solution (5 mL) of allyltrifluorosilane **1b–d** (3 mmol), α-diketone **2a–e** (2 mmol) and Et_3N (3 mmol) was stirred for 40 h under N_2 at the given temperature. The reaction was quenched by adding 1 M HCl/Et_2O, the organic layer separated, washed with 1 M NaOH, water, brine and dried ($MgSO_4$). Evaporation of the ether and chromatography through a short column (silica gel, hexane/Et_2O 4:1) gave the product.

Preparation of Acetonides (for Table 1):
A mixture of α-diol **3a–c** (1 mmol), 2,2-dimethoxypropane (3 mL) and $TsOH \cdot H_2O$ (10 mg) was allowed to stand for 20 h at r.t. The mixture was diluted with Et_2O (10 mL), washed with 10% aq $NaHCO_3$ (10 mL) and the organic layer dried, solvent evaporated, chromatographed through a short column (silica gel, hexane/Et_2O 8:1) gave 92% (**3a'**), 76% (**3b'**) and 70% (**3c'**) yield of acetonide.

4,5-Dimethylocta-1,7-diene-4,5-diol (**3a**):[13] (no assignment of *syn* and *anti* isomers) mixture *syn*/*anti* 70:30; colorless crystals; mp 53–55°C.

^{1}H NMR: δ = 1.08 (*syn*) and 1.10 (*anti*) (s, 6H), 2.06–2.15 (m, 2H), 2.35–2.46 (m, 4H, incl. 2 OH), 5.01–5.10 (m, 4H), 5.82–5.94 (m, 2H).

^{13}C NMR: *syn*: δ = 21.6, 41.3, 76.5, 118.8, 135.0.
anti: δ = 22.0, 41.1, 76.6, 118.7, 134.8.

MS (EI): *m*/*z* (%) = 129 [(M^+ − 41), 11], 111 (10), 85 (25), 43 (100), 41 (83).

4,5-Di-O-isopropylidene-4,5-dimethylocta-1,7-diene (**3a'**):[8] mixture of *trans*/*cis* 70:30; colorless oil.

^{1}H NMR: δ = 1.13 (*trans*) and 1.14 (*cis*) (s, 6H), 1.39 (*cis*) and 1.40 (*trans*) and 1.42 (*cis*) (s, 6H), 1.96–2.03 (m, 2H), 2.50–2.56 (m, 2H), 5.00–5.10 (m, 4H), 5.79–5.90 (m, 2H).

^{13}C NMR: *trans*: δ = 20.3, 29.8, 41.6, 84.5, 107.0, 118.4, 134.6.
cis: δ = 21.8, 29.8, 29.9, 40.9, 84.4, 106.9, 118.4, 134.4.

MS (EI): m/z (%) = 195 [($M^+ - 15$), 26], 135 (10), 111 (21), 73 (47), 43 (100), 41 (40).

anti-4-Methyl-5-phenylocta-1,7-diene-4,5-diol (**3b**): colorless oil.

^{1}H NMR: δ = 1.19 (s, 3H), 1.67–1.74 (m, 1H), 2.43–2.49 (m, 1H), 2.46 (s, 1H, OH), 2.67 (s, 1H, OH), 2.73–2.81 (m, 1H), 3.04–3.10 (m, 1H), 4.92–5.19 (m, 4H), 5.39–5.47 (m, 1H), 5.76–5.85 (m, 1H), 7.21–7.50 (m, 5H).

^{13}C NMR: δ = 21.3, 40.1, 41.4, 76.4, 80.1, 118.5, 120.4, 127.3, 127.4, 128.1, 134.4, 134.9, 142.4.

MS (EI): m/z (%) = 215 [($M^+ - 17$), 0.5], 191 (1), 173 (4), 148 (18), 105 (49), 77 (15), 43 (100).

cis-4,5-Di-O-isopropylidene-4-methyl-5-phenylocta-1,7-diene (**3b'**): colorless oil.

^{1}H NMR: δ = 1.40 (s, 3H), 1.56 (s, 6H), 1.82–1.87 (m, 1H), 2.15–2.21 (m, 1H), 2.72 (dd, J = 6.4 and 14.2 Hz, 1H), 2.90 (dd, J = 7.3 and 14.2 Hz, 1H), 4.82–5.02 (m, 4H), 5.42–5.52 (m, 1H), 5.67–5.78 (m, 1H), 7.21–7.40 (m, 5H).

^{13}C NMR: δ = 20.4, 29.8, 30.2, 41.6, 42.8, 85.5, 89.0, 107.8, 118.1, 118.3, 125.8, 127.2, 128.4, 133.9, 134.5, 141.0.

MS (EI): m/z (%) = 257 [($M^+ - 15$), 2], 231 (14), 173 (32), 105 (65), 43 (100).

cis-1,2-Diallylcyclohexane-1,2-diol (**3c**):[14] (only ^{1}H NMR data given) colorless oil.

^{13}C NMR: δ = 21.7, 32.9, 39.4, 75.5, 118.3, 134.4.

MS (EI): m/z (%) = 155 [($M^+ - 41$), 10], 137 (16), 119 (12), 41 (100).

cis-1,2-Diallyl-1,2-di-O-isopropylidenecyclohexane (**3c'**):[8] colorless oil.

^{1}H NMR: δ = 1.24–1.31 (m, 2H), 1.38–1.57 (m, 4H), 1.45 (s, 3H), 1.51 (s, 3H), 1.89–1.95 (m, 2H), 2.08 (dd, J = 8.6 and 14.0 Hz, 2H), 2.57 (dd, J = 5.4 and 14.0 Hz, 2H), 5.02–5.12 (m, 4H), 5.82–5.96 (m, 2H).

^{13}C NMR: δ = 21.9, 30.1, 30.5, 33.0, 40.3, 83.2, 107.1, 118.0, 134.6.

MS (EI): m/z (%) = 221 [($M^+ - 15$), 7], 195 (26), 161 (4), 137 (100), 119 (20), 41 (83).

(1α,2α,3α)-1,2-Diallyl-3-methylcyclopentane-1,2-diol (**3d**): colorless oil.

^{1}H NMR: δ = 0.89 (d, J = 6.9 Hz, 3H), 1.29–1.41 (m, 1H), 1.53–1.95 (m, 4H), 2.06 (dd, J = 7.9 and 13.6 Hz, 1H), 2.16–2.21 (m, 2H), 2.30 (dd, J = 6.2 and 13.6 Hz, 1H), 2.50 (s, 1H, OH), 2.61 (s, 1H, OH), 4.98–5.08 (m, 4H), 5.81–5.99 (m, 2H).

^{1}H-NOE experiments: 3-CH_3 irradiated: no effect on 2-CH_2 (allyl).
3-CH irradiated: positive effect on 2-CH_2 (allyl).

^{13}C NMR: δ = 15.4, 28.6, 33.9, 39.9, 40.2, 40.9, 81.3, 83.6, 118.4, 118.5, 134.4, 134.5.

MS (EI): m/z (%) = 155 [($M^+ - 41$), 9], 137 (18), 109 (21), 41 (100).

syn-3,3,4,5-Tetramethylocta-1,7-diene-4,5-diol (**3e**): colorless oil.

^{1}H NMR: δ = 1.15 (s, 3H), 1.16 (s, 3H), 1.18 (s, 3H), 1.24 (s, 3H), 2.14 (dd, J = 7.9 and 13.8 Hz, 1H), 2.23 (s, 1H, OH), 2.54 (dd, J = 7.2 and 13.8 Hz, 1H), 2.82 (s, 1H, OH), 4.97–5.14 (m, 4H), 5.81–5.93 (m, 1H), 6.24 (dd, J = 10.9 and 17.6 Hz, 1H).

^{13}C NMR: δ = 20.1, 24.1, 24.9, 25.6, 43.1, 45.9, 79.0, 79.8, 111.8, 119.0, 135.0, 147.4.

MS (EI): m/z (%) = 157 [($M^+ - 41$), 7], 139 (9), 129 (34), 121 (9), 111 (34), 69 (100).

cis-2-Allyl-1-(1,1-dimethylallyl)cyclohexane-1,2-diol (**3f**): colorless oil.

^{1}H NMR: δ = 1.13 (s, 3H), 1.16 (s, 3H), 1.40–1.56 (m, 8H), 2.05 (s, 1H, OH), 2.46–2.52 (m, 2H), 2.74 (s, 1H, OH), 5.01–5.07 (m, 4H), 5.75–5.88 (m, 1H), 6.21–6.31 (m, 1H).

^{13}C NMR: δ = 21.2, 22.8, 24.4, 26.0, 29.9, 34.2, 40.3, 46.1, 78.8, 79.7, 112.2, 117.9, 134.2, 147.6.

MS (EI): m/z (%) = 165 [($M^+ - 59$), 2], 155 (6), 147 (2), 137 (7), 69 (45) 41 (100).

3-Hydroxy-3-methylhex-5-en-2-one (**4a**):[7] (no ^{13}C NMR data given) colorless liquid.

^{13}C NMR: δ = 24.2, 25.0, 44.0, 78.9, 119.0, 132.4, 212.0.

2-Allyl-2-hydroxycyclohexanone (**4b**):[14] (no ^{13}C NMR data given) colorless liquid.

^{13}C NMR: δ = 22.7, 28.0, 38.5, 40.5, 42.0, 79.0, 118.9, 131.9, 213.6.

2-Hydroxy-3,4,4-trimethylhex-5-en-2-one (**4c**):[7] (only ^{1}H NMR data given) colorless liquid.

^{13}C NMR: δ = 20.6, 21.5, 22.6, 27.2, 43.3, 82.5, 113.2, 144.4, 213.0.

MS (EI): m/z (%) = 123 [($M^+ - 33$), 1], 113 (13), 88 (29), 87 (3), 69 (28), 43 (100).

2-(1,1-Dimethylallyl)-2-hydroxycyclohexanone (**4d**): colorless liquid.

^{1}H NMR: δ = 0.93 (s, 3H), 1.05 (s, 3H), 1.62–1.69 (m, 4H), 1.88–1.94 (m, 1H), 2.20–2.28 (m, 1H), 3.60 (s, 1H, OH), 4.97 (dd, J = 1.1 and 17.6 Hz, 1H), 5.04 (dd, J = 1.1 and 10.8 Hz, 1H), 5.98 (dd, J = 10.8 and 17.6 Hz, 1H).

^{13}C NMR: δ = 21.8, 22.0, 23.2, 26.6, 35.9, 40.1, 44.0, 81.8, 113.8, 145.2, 215.6.

MS (EI): m/z (%) = 149 [($M^+ - 33$), 2], 139 (3), 114 (100), 69 (39).

3-Hydroxy-3,4-dimethylhex-5-en-2-one (**4e**):[7] diastereomeric mixtures (A)/(B), colorless liquid.

^{1}H NMR: δ = (A): 0.82 (d, J = 7.1 Hz, 3H), 1.26 (s, 3H), 2.19 (s, 3H), 2.36–2.48 (m, 1H), 3.75 (s, 1H, OH), 5.05–5.12 (m, 2H), 5.72–5.84 (m, 1H).
(B): 1.10 (d, J = 7.1 Hz, 3H), 1.30 (s, 3H), 2.16 (s, 3H), 2.45–2.52 (m, 1H), 3.85 (s, 1H, OH), 4.93–5.05 (m, 2H), 5.60–5.73 (m, 1H).

^{13}C NMR: δ = (A): 15.2, 24.1, 24.3, 45.6, 80.5, 117.0, 138.9, 212.4.
(B): 13.7, 22.6, 24.0, 45.0, 80.4, 115.4, 138.9, 211.7.

MS (EI): m/z (%) = 125 [($M^+ - 17$), 15], 99 (100), 88 (43), 87 (42), 55 (68), 43 (99).

2-Hydroxy-2-(1-methylallyl)cyclohexanone (**4f**):[15] diastereomeric mixtures (A)/(B), colorless liquid.

^{1}H NMR: δ = (A): 1.00 (d, J = 6.7 Hz, 3H), 1.30–1.63 (m, 4H), 1.97–2.04 (m, 1H), 2.21–2.41 (m, 3H), 2.61–2.65 (m, 1H), 3.77 (s, 1H, OH), 4.79–4.91 (m, 2H), 5.43–5.55 (m, 1H).
(B): 0.69 (d, J = 6.7 Hz, 3H), 1.30–1.65 (m, 4H), 1.97–2.04 (m, 1H), 2.21–2.44 (m, 3H), 2.60–2.65 (m, 1H), 3.85 (s, 1H, OH), 4.98–5.04 (m, 2H), 5.61–5.73 (m, 1H).

^{13}C NMR: δ = (A): 13.6, 22.3, 28.3, 38.3, 38.6, 42.0, 80.8, 116.7, 138.4, 214.0.
(B): 14.5, 21.9, 28.2, 38.2, 39.4, 42.4, 80.6, 115.5, 138.8, 214.6.

MS (EI): m/z (%) = 168 (M^+, 1), 151 (2), 135 (3), 114 (47), 55 (100).

2-Hydroxy-2,3-dimethyl-1-phenylpent-4-en-1-one (**4g**): major diastereomer from reaction of **1b**, colorless liquid.

^{1}H NMR: δ = 1.17 (d, J = 6.7 Hz, 3H), 1.57 (s, 3H), 3.39–3.43 (m, 1H), 4.08 (s, 1H, OH), 4.71–4.90 (m, 2H), 5.63–5.75 (m, 1H), 7.20–8.01 (m, 5H).

^{13}C NMR: δ = 14.2, 24.8, 46.4, 81.0, 116.4, 129.9, 130.0, 135.6, 138.6, 140.4, 204.7.

2-Hydroxy-2,3,3-trimethyl-1-phenylpent-4-en-1-one (**4h**): colorless liquid.

^{1}H NMR: δ = 1.03 (s, 3H), 1.05 (s, 3H), 1.56 (s, 3H), 3.58 (s, 1H, OH), 4.91–4.99 (m, 2H), 5.84–5.93 (m, 1H), 7.24–7.86 (m, 5H).

^{13}C NMR: δ = 22.8, 22.9, 23.0, 44.6, 84.2, 114.2, 128.2, 130.0, 130.0, 132.2, 139.8, 144.4, 206.9.

MS (EI): m/z (%) = 201 [($M^+ - 17$), 8], 185 (1), 175 (20), 150 (15), 113 (29), 105 (100), 77 (69), 69 (13).

2-(1,1-Dimethylallyl)-2-hydroxy-5-methylcyclopentanone (**4i**): isomeric mixture (A)/(B) 74:26; colorless oil.

^{1}H NMR: δ = (A)/(B): 1.02–1.08 (m, 9H), 1.41–1.52 (m, 2H), 1.64 (bs, 1H, OH), 1.74–1.81 (m, 2H), 2.14–2.23 (m, 1H), 5.02–5.14 (m, 2H), 5.93–6.10 (m, 1H).

^{13}C NMR: δ = (A): 13.9, 20.8, 22.3, 27.5, 30.6, 42.6, 45.4, 81.2, 114.8, 143.5, 220.5.

(B): 15.0, 21.2, 22.8, 27.0, 31.4, 42.0, 42.6, 81.5, 114.6, 143.8, 222.1.

MS (EI): *m/z* (%) = 182 (M^+, 0.5%), 114 (100), 99 (97), 97 (92), 70 (98).

4-Hydroxy-4,5-dimethylhept-6-en-3-one **(4j)**: diastereomeric mixtures (A)/(B); colorless liquid.

^{1}H NMR: δ = (A): 0.72 (d, J = 6.8 Hz, 3H), 1.02 (t, J = 7.1 Hz, 3H), 1.18 (s, 3H), 2.33–2.50 (m, 3H), 3.74 (s, 1H, OH), 4.97–5.04 (m, 2H), 5.65–5.78 (m, 1H).

(B): 0.96 (t, J = 7.1 Hz, 3H), 1.02 (d, J = 6.8 Hz, 3H), 1.23 (s, 3H), 2.38–2.54 (m, 1H), 2.44 (q, J = 7.1 Hz, 2H), 3.79 (s, 1H, OH), 4.84–4.93 (m, 2H), 5.51–5.63 (m, 1H).

^{13}C NMR: δ = (A): 7.9, 15.3, 24.4, 29.4, 45.9, 80.3, 116.7, 139.9, 215.2.

(B): 7.4, 13.8, 22.9, 29.5, 45.4, 80.4, 115.3, 139.2, 214.4.

MS (EI): *m/z* (%) = 13 [(M^+ − 17), 8], 102 (6), 99 (45), 57 (82), 43 (100).

4-Hydroxy-4,5,5-trimethylhept-6-en-3-one **(4k)**: colorless liquid.

^{1}H NMR: δ = 0.88 (s, 3H), 0.93 (t, J = 7.3 Hz, 3H), 0.97 (s, 3H), 1.23 (s, 3H), 2.35–2.53 (m, 2H), 3.65 (s, 1H, OH), 4.91–5.00 (m, 2H), 5.90 (dd, J = 10.6 and 17.5 Hz, 1H).

^{13}C NMR: δ = 8.0, 20.7, 21.6, 23.0, 32.4, 43.6, 82.6, 113.7, 144.5, 215.7.

MS (EI): *m/z* (%) = 153 [(M^+ − 17), 1], 137 (1), 113 (87), 102 (100), 87 (44), 69 (98), 57 (99).

2-Hydroxy-1,2-diphenylpent-4-en-1-one **(4l)**:[7]

MS (EI): *m/z* (%) = 235 [(M^+ − 17), 0.5], 211 (0.5), 183 (2), 147 (17), 105 (100), 77 (49), 41 (11).

3-Hydroxy-4-methyl-3-phenylhex-5-en-2-one **(5g)**: diastereomeric mixtures (A)/(B), colorless liquid.

^{1}H NMR: δ = (A): 1.02 (d, J = 6.5 Hz, 3H), 2.12 (s, 3H), 3.38–3.44 (m, 1H), 4.28 (s, 1H, OH), 4.97–5.11 (m, 2H), 5.65–5.76 (m, 1H), 7.19–7.55 (m, 5H).

(B): 1.00 (d, J = 6.5 Hz, 3H), 2.08 (s, 3H), 3.31–3.38 (m, 1H), 4.52 (s, 1H, OH), 5.05–5.22 (m, 2H), 5.75–5.88 (m, 1H), 7.22–7.58 (m, 5H).

^{13}C NMR: δ = (A): 14.6, 24.4, 42.6, 85.1, 117.0, 127.0, 127.9, 128.7, 138.5, 140.4, 209.3.

(B): 14.7, 24.1, 43.6, 85.5, 116.8, 127.1, 128.0, 128.9, 138.8, 139.7, 209.2.

MS (EI): *m/z* (%) = 187 [(M^+ − 17), 12], 161 (29), 149 (3), 105 (90), 43 (100).

3-Hydroxy-4,4-dimethyl-3-phenylhex-5-en-2-one **(5h)**: colorless liquid.

^{1}H NMR: δ = 1.01 (s, 3H), 1.16 (s, 3H), 2.10 (s, 3H), 3.25 (s, 1H, OH), 5.07–5.16 (m, 2H), 5.88–5.99 (m, 1H), 7.22–7.52 (m, 5H).

^{13}C NMR: δ = 22.9, 23.0, 28.6, 45.7, 85.2, 115.5, 127.5, 127.8, 127.9, 137.8, 144.6, 210.8.

2-Hydroxy-5-methyl-1,2-diphenylhex-4-en-1-one **(6)**:[16] colorless oil.

^{13}C NMR: δ = 18.1, 26.3, 38.3, 82.3, 117.6, 125.9, 128.3, 128.4, 129.1, 130.3, 132.8, 135.0, 137.7, 142.4, 201.7.

MS (EI): *m/z* (%) = 211 [(M^+ − 69), 1], 175 (33), 105 (100), 77 (51).

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