# β-Hydroxy Ketones from the Iodine-catalysed Reaction of α-Bromo Ketone with Aldehydes Mediated by Trialkylstibine†

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β-Hydroxy ketones can be synthesized in excellent yield by the iodine-catalysed reaction of α-bromo ketones with various aldehydes mediated by trialkylstibine.

Aldol condensation is one of the most important methods of carbon–carbon bond formation but usually results in mixtures of products arising from self condensation, mixed condensation, and retro-aldol reaction.[1] Numerous efforts have been made to improve the procedure of which the transition metal-catalysed reaction of silyl enol ethers with carbonyl compounds seems to be the most promising.[2] Based on a Reformatsky-type reaction, the regiospecific aldol condensation with couple attack of $Et_2AlCl$–Zn[3] or $Et_2AlCl$–$Bu_3SnLi$[4] has been reported. The recent report of the reaction of α-halogeno ketones with carbonyl compounds promoted by $CeI_3$–NaI[5] prompted us to report here a new regioselective, simple, and efficient method for the synthesis of β-hydroxy ketones under mild conditions.

## Results and Discussion

In our studies on the application of organoantimony compounds in organic synthesis, we found a reaction of α-bromo ketones with aldehydes mediated by tributylstibine to form α,β-unsaturated ketones.[6] However, when 3-bromobutan-2-one was heated with 2-furaldehyde in the presence of tributylstibine at 90 °C for 6 h, 4-(2-furyl)-3-methylbuten-2-one was obtained (47%), accompanied by 4-(2-furyl)-4-hydroxy-2-methylbutan-2-one (39%). At room temperature, no reaction between these compounds took place, suggesting that a catalyst was necessary if the β-hydroxy ketone was to be obtained as the main product.

It is well known that iodo ketones are more reactive than the corresponding bromo-ketones, and halogen exchange readily takes place between sodium iodide and bromo ketones.[7] Iodine readily oxidizes trialkylstibine[8] to form di-iodotrialkylstiborane. If pentavalent organoiodoantimony has some extent of polarity,[9] halogen exchange with α-bromo ketone would occur. Based on these considerations, a catalytic amount of iodine (2—4 mol%) was added to a mixture of equivalent amounts of 3-bromobutan-2-one, aldehyde (**1**), and trialkylstibine (**2**) and the mixture stirred at room temperature; the aldehyde completely disappeared as monitored by $^1H$ n.m.r. spectroscopy. After treatment with a protic solvent such as ethanol, the reaction mixture was chromatographed on an alumina–silica gel (1 : 1) column to give the hydroxy ketones (**3**) in excellent yield.

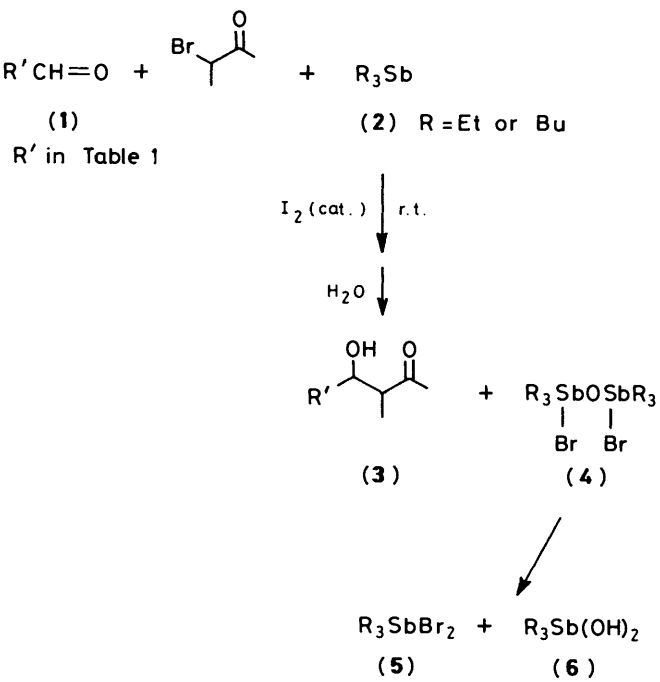
When tributylstibine (**2**; R = Bu) was used, after the reaction mixture was treated with light petroleum and left, a white solid, characterized as bis(bromotributylantimony) oxide (**4**; R = Bu), was deposited (Scheme 1). Tributylstibine dibromide (**5**; R = Bu) and dihydroxide (**6**; R = Bu) were obtained when the mixture was subjected to chromatography on a silica gel column, eluting with ethyl acetate and then with methanol; they arise from the hydrolysis[10] and the disproportionation[11] of the oxide on silica gel. Reaction conditions, yields, and diastereoisomeric ratios for the product are given in Table 1.

In contrast with the above result, no reaction occurred when a mixture of benzaldehyde, 3-bromobutan-2-one, and triethyl-

**Table 1.** β-Hydroxy ketone from 3-bromobutanone and aldehydes

| Compound (1) | R′ | R in $R_3Sb$ | Condition (5—15 °C/ h) | Yield[a] (%) | Ratio[b] (*erythro*/ *threo*) |
|---|---|---|---|---|---|
| (a) | i-$C_4H_9$– | Bu | 24 | 60 | 57:43 |
| (b) | $C_8H_{17}$– | Et | 25 | 84 | 50:50 |
| (c) | MeCH=CH– | Bu | 50 | 87 | 50:50 |
| (d) | PhCH=CH– | Et | 22 | 94 | 54:46 |
| (e) | Furyl | Bu | 30 | 86 | 58:42 |
| (f) | 2-Pyridyl | Bu | 40 | 80 | 42:58 |
| (g) | 3-Pyridyl | Et | 16 | 81 | 40:60 |
| (h) | Ph | Et | 16 | 98 | 60:40 |
| | | Bu | 16 | 60[c] | |
| (i) | *p*-$ClC_6H_4$– | Bu | 48 | 94 | 58:42 |
| (j) | *p*-$BrC_6H_4$– | Et | 20 | 90 | 58:42 |
| (k) | 6-$MeC_6H_6$– | Bu | 54 | 81 | 44:56 |
| (l)[d] | *p*-$NO_2C_6H_4$– | Bu | 1.5 | 95 | 61:39 |

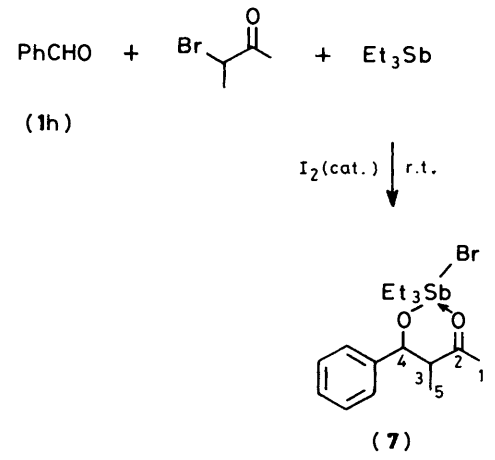
[a] Isolated yield by chromatography. [b] The ratio of diastereoisomers was estimated by $^1H$ n.m.r. [c] Estimated by $^1H$ n.m.r. [d] From 3-iodobutan-2-one.




Scheme 1.

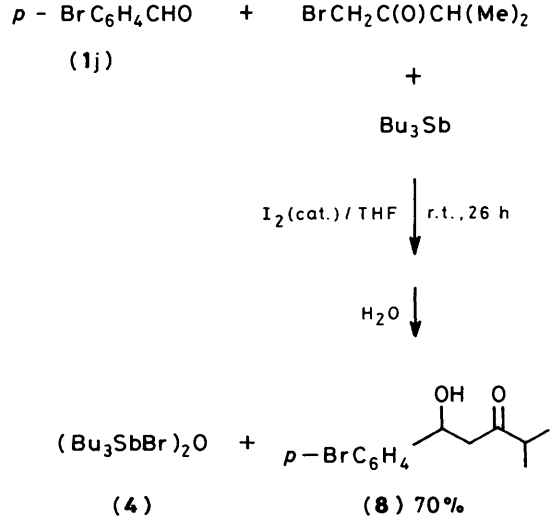
† This paper is the 60th report on the studies of the application of elemento-organic compounds of the fifteenth and sixteenth groups in organic synthesis.

stibine was stirred at room temperature for 16 h in the absence of iodine. However when iodine was added, $^1$H n.m.r. showed that the aldehyde completely disappeared after 16 h, and two sets of doublet peaks appeared at δ 4.55 and 4.83 with *J* values 10 and 6 Hz, respectively. The peak intensity ratio was 41:59. Simultaneously, aromatic protons appeared in the form of two singlet peaks with chemical shifts of 7.27 and 7.24. These two sets of peaks can be assigned to the *threo*- and *erythro*-intermediate (**7**) (Scheme 2).




**Scheme 2.**

In compound (**7**), the characteristic carbonyl absorption appeared lower than usual at 1 640 cm$^{-1}$. This could be due to the carbonyl group co-ordinating to antimony; pentavalent antimony has six-band co-ordination characteristics.[13] $^1$H N.m.r. spectrum showed that the chemical shifts of the C-5 methyl were 0.68 (d, *J* 6.5 Hz) and 1.08 (d, *J* 6.5 Hz), which may correspond to *threo*- and *erythro*-forms of compound (**7**), respectively. The difference between these two values is larger than that of the corresponding final product, 4-hydroxy-3-methyl-4-phenylbutan-2-one [δ 0.77 (d, *J* 6.5 Hz) and 0.98 (d, *J* 6.5 Hz)]. The difference in chemical environment between the C-5 methyls of the *threo*- and *erythro*-forms is due to the rigidity of the co-ordinated six-membered ring of (**7**). Attempts to purify the antimony complex failed due to its moisture sensitivity. This reaction was also performed in the absence of solvent or by refluxing in tetrahydrofuran. When ketones were used as substrates under similar conditions, they were recovered unchanged. Triethylstibine is a more active mediator than tributylstibine [see (**1h**) in Table 1].




**Scheme 3.**

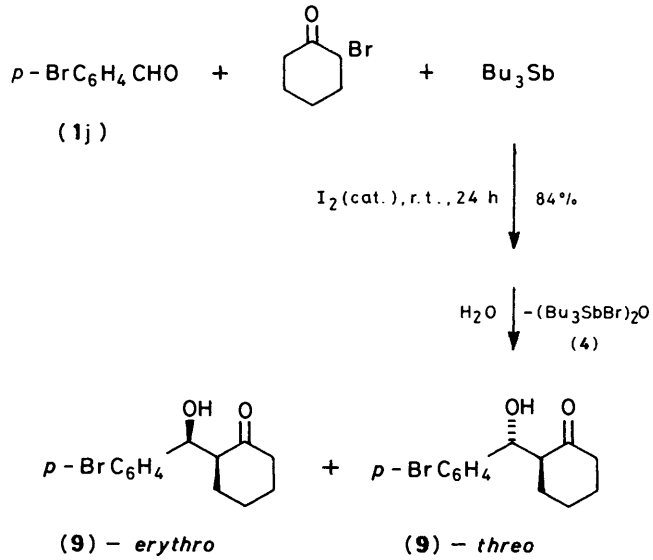
**Table 2.** The catalytic effect of some iodides

| R (in $R_3Sb$) | Catalyst | Amount of catalyst (mol%) | Time (h) | Yield* (%) |
|---|---|---|---|---|
| Et | $I_2$ | 4 | 16 | 100 |
| Et | $Et_3SbI_2$ | 6.5 | 17 | 95 |
| Bu | NaI | 27 | 48 | 82 |
| Bu | $CH_2$=$CHCH_2I$ | 10 | 48 | 100 |

* Estimated by $^1$H n.m.r.

Bromoethyl isopropyl ketone underwent a similar reaction to form compound (**8**), and was more active than 3-bromobutan-2-one as shown in Scheme 3.

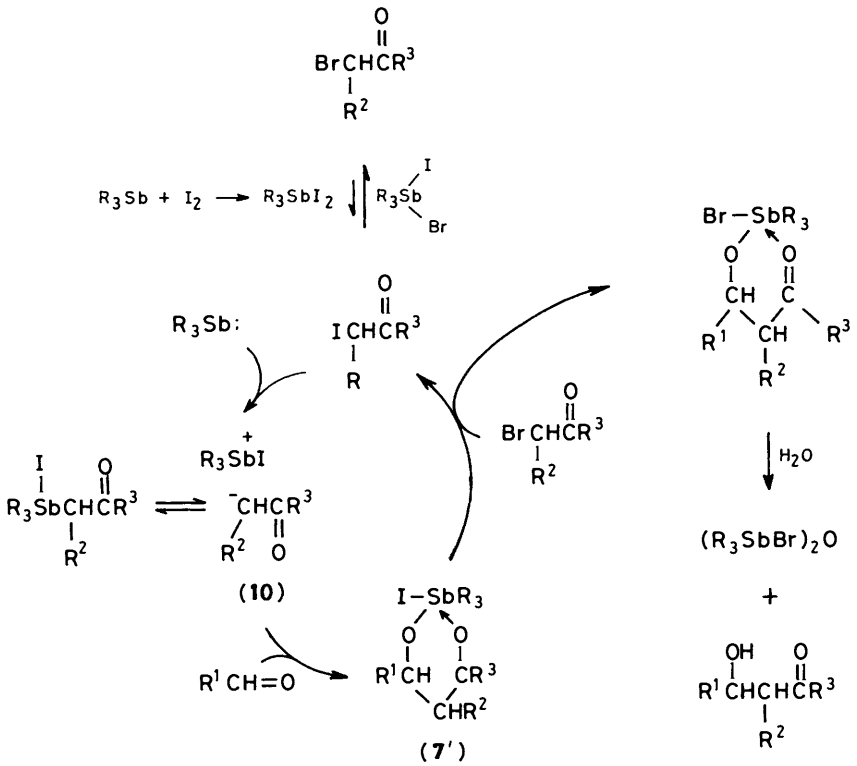
The mixture of diastereoisomers (**9**) was obtained with α-bromocyclohexanone under similar conditions (Scheme 4).



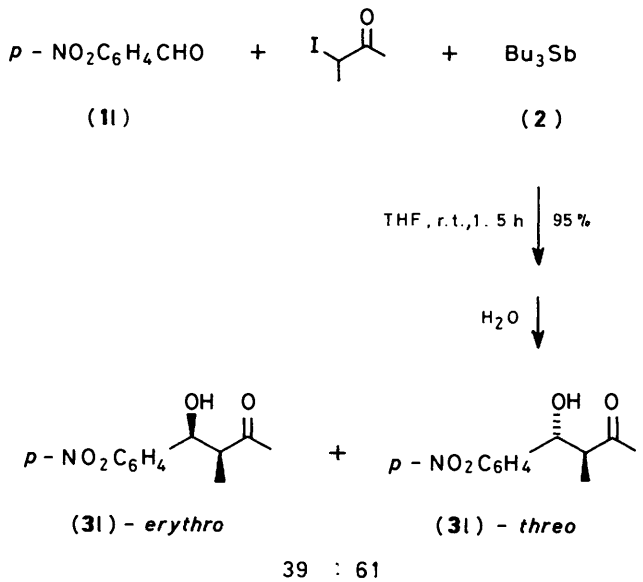

**Scheme 4.**

According to the $^1$H n.m.r. spectrum of the iodine-catalysed reaction mixture, trialkylstibine and α-bromo ketone disappeared slowly as the reaction time was prolonged. The iodine was, therefore, not acting as a radical initiator—in fact, triethylstibine di-iodide, allyl iodide, and sodium iodide had the same catalytic properties. Table 2 depicts the catalytic effect of iodide compounds on the reaction of 3-bromobutan-2-one with benzaldehyde mediated by trialkylstibine.

On the basis of these experimental results, we postulate that the reaction undergoes a process such as that shown in Scheme 5. Trialkylstibine di-iodide may function as a source for halogen exchange with α-bromo ketone but this step may be slow because the corresponding iodo compound was not detected by $^1$H n.m.r. In fact, the reaction could be accomplished faster with 3-iodobutan-2-one instead of the bromide, *e.g.*, the reaction shown in Scheme 6 was complete in 1.5 h, even when the less active tributylstibine was used.



Scheme 5.



Scheme 6.

The iodine in 3-iodobutan-2-one is easily attacked by trialkylstibine due to its lower electronegativity. The carbanion (**10**) can be formed in this manner. The addition product of the carbanion to carbonyl compound, intermediate (**7'**) is not readily deoxygenated at the lower reaction temperature adopted. The β-hydroxy ketone was obtained after hydrolysis.[14]

## Experimental

3-Bromobutan-2-one,[15] bromomethyl isopropyl ketone,[15] and α-bromocyclohexanone[17] were prepared by literature methods. Triethyl-[18] and tributyl-stibine[19] were synthesized by the reaction of an alkyl Grignard reagent with antimony trichloride. 3-Iodobutan-2-one was derived from the halogen exchange of α-bromobutanone and sodium iodide.[20] N.m.r. spectra were recorded on a Varian EM360-A instrument in $CCl_4$ with tetramethylsilane (TMS) as internal standard and are reported in δ units. I.r. spectra (neat, unless otherwise stated) were measured on an IR-440 i.r. spectrophotometer. M.s. were obtained on a Finnigan 4021 spectrometer.

Triethylstibine di-iodide was prepared from the reaction of iodine with triethylstibine in dichloromethane, as a yellow solid, (quantitative), m.p. 260 °C; δ 1.00 (t, 9 H, *J* 8.0 Hz) and 3.12 (q, 6 H, *J* 8.0 Hz); $\nu_{max.}$(KCl) 1 180s, 970s, and 720s (Found: C, 15.55; H, 3.25. Calc. for $C_6H_{15}I_2Sb$: C, 15.63; H, 3.20%).

*Typical Procedure for the Synthesis of* β-*Hydroxy Ketones.*—4-*Hydroxy*-3-*methyl*-4-*phenylbutan*-2-*one* (**3h**). Benzaldehyde (318 mg, 3.0 mmol), 3-bromobutan-2-one (480 mg, 3.2 mmol), tributylstibine (880 mg, 3.0 mmol), and iodine (20 mg, 0.08 mmol) were stirred at 5—15 °C for 54 h. After addition of light petroleum (0.5 ml) and ethanol (*ca.* 0.2 ml), the solution was stirred at room temperature for a further 0.5 h, cooled at −78 °C for 3 h, then allowed to stand at room temperature for 12 h. The white solid obtained (380 mg, 34%) was collected, dried, and characterized as bis(bromotributylantimony)oxide (**4**; R = Bu), m.p. 61—63 °C; δ 1.01 (t, 9 H, *J* 5.0 Hz), 1.22—1.68 (m, 6 H), 1.68—2.06 (m, 6 H), and 2.06—2.51 (m, 6 H); $\nu_{max.}$(KCl) 2 900s, 1 460s, 780s, and 750vs; *m/z* (rel. intensity) 373 ($Bu_3SbBr$, 100%), 179 (20), and 57 (66) [Found: C, 37.95; H, 7.15; Br, 20.9. Calc. for $C_{24}H_{54}Br_2OSb_2$ (762.004): C, 37.83; H, 7.14; Br, 20.97%]. The mother liquor after concentration was poured into a 1:1 alumina–silica gel column and eluted with ethyl acetate, whereupon compound (**3h**) (505 mg, 93%) was obtained as a colourless oil, b.p. 103 °C/1.0 mmHg (lit.,[21] 102 °C/0.7 mmHg; ratio of *erythro*- and *threo*-isomers is given in Table 1; δ(*threo*) 0.77 (d, 3 H, *J* 6.5 Hz), 2.08 (s, 3 H), 2.70 (m, 1

H), 3.40 (d, 1 H, *J* 4.0 Hz), 4.55 (dd, 1 H, *J* 9.5 and 4.0 Hz), and 7.20 (s, 5 H); δ(*erythro*) 0.98 (d, 3 H, *J* 6.5 Hz), 1.97 (s, 3 H), 2.70 (m, 1 H), 3.50 (d, 1 H, *J* 4.0 Hz), 4.86 (dd, 1 H, *J* 4.0 and 4.0 Hz), and 7.20 (s, 5 H); $\nu_{max.}$ 3 400s, 1 700vs, 1 060m, and 1 000m.

4-Hydroxy-3,6-dimethylheptan-2-one (**3a**). Yield 60%, b.p. 68 °C/1.5 mmHg; δ(*threo*) 0.92 (d, 6 H, *J* 6.5 Hz), 1.04 (d, 3 H, *J* 7.0 Hz), 1.14—1.40 (m, 1 H), 1.40—1.80 (m, 2 H), 2.10 (s, 3 H), 2.10—2.60 (m, 1 H), 2.50 (br s, 1 H), and 3.35—3.66 (m, 1 H); δ(*erythro*) 0.94 (d, 6 H, *J* 6.5 Hz), 1.07 (d, 3 H, *J* 7.0 Hz), 1.14—1.40 (m, 1 H), 1.40—1.80 (m, 2 H), 2.10 (s, 3 H), 2.10—2.60 (m, 1 H), 2.50 (br s, 1 H), and 3.83 (dt, 1 H, *J* 8.5 and 3.5 Hz); $\nu_{max.}$ 3 450s, 1 700s, 1 172m, and 1 030m; *m/z* (rel. intensity) 159 ($M^+$ + 1, 100%), 141 (98), 123 (76), and 72 (11) [Found: C, 68.2; H, 11.7. Calc. for $C_9H_{18}O_2$ (158.243): C, 68.31; H, 11.47%].

4-Hydroxy-3-methyldodecan-2-one (**3b**). Yield 86%, b.p. 116 °C/1 mmHg; δ 0.88 (t, 3 H, *J* 5.0 Hz), 1.06 (d, 3 H, *J* 7.0 Hz), 1.30 (br s, 14 H), 2.10 (s, 3 H), 2.36 (m, 1 H), 2.78 (br s, 1 H), 3.72 (m, 0.5 H, *threo*), and 3.90 (m, 0.5 H, *erythro*); $\nu_{max.}$ 3 400s, 1 700s, and 1 170m; *m/z* (rel. intensity) 215 ($M^+$ + 1, 65%), 197 (100), 72 (42), and 43 (87) [Found: C, 73.1; H, 12.4. Calc. for $C_{13}H_{26}O_2$ (214.351): C, 72.85; H, 12.23].

(*E*)-4-*Hydroxy*-3-*methylhept*-5-*en*-2-*one* (**3c**). Yield 87%, b.p. 92 °C/2.0 mmHg; δ(*threo*) 0.93 (d, 3 H, *J* 6.5 Hz), 1.68 (d, 3 H, *J* 5.8 Hz), 2.10 (s, 3 H), 2.40 (m, 1 H), 2.76 (br s, 1 H), 4.19 (m, 1 H), and 5.46 (m, 2 H); δ(*erythro*) 1.04 (d, 3 H, *J* 6.5 Hz), 1.68 (d, 3 H, *J* 5.8 Hz), 2.10 (s, 3 H), 2.40 (m, 1 H), 2.76 (br s, 1 H), 3.90 (m, 1 H), and 5.46 (m, 2 H); $\nu_{max.}$ 3 400s, 1 700vs, and 960s; *m/z* (rel. intensity) 143 ($M^+$ + 1, 4%), 142 ($M^+$, 2%), 125 (17), 71 (47), and 43 (100) [Found: C, 67.15; H, 9.55. Calc. for $C_8H_{14}O_2$ (142.200): C, 67.57; H, 9.92%].

(*E*)-4-Hydroxy-3-methyl-6-phenylhex-5-en-2-one (**3d**). Yield 94%, colourless oil; δ(*threo*) 1.00 (d, 3 H, *J* 6.0 Hz), 2.12 (s, 3 H), 2.72 (m, 1 H), 2.96 (br s, 1 H), 4.19 (dd, 1 H, *J* 6.0 and 9.0 Hz), 6.02 (dd, 1 H, 15.0 and 6.0 Hz), 6.48 (dd, 1 H, *J* 15.0 and 2.0 Hz), and 7.20 (s, 5 H); δ(*erythro*) 1.10 (d, 3 H, *J* 6.0 Hz), 2.12 (s, 3 H), 2.72 (m, 1 H), 2.96 (br s, 1 H), 4.48 (dd, 1 H, *J* 6.0 and 4.5 Hz), 6.02 (dd, 1 H, *J* 15.0 and 6.0 Hz), 6.48 (dd, 1 H, *J* 15.0 and 2.0 Hz), and 7.20 (s, 5 H); $\nu_{max.}$ 3 400s, 1 700vs, and 965s; *m/z* (rel. intensity) 204 ($M^+$, 16%), 189 (16), 187 (14), and 133 (100) [Found: C, 76.23; H, 7.88. Calc. for $C_{13}H_{16}O_2$ (204.271): C, 76.44; H, 7.90%].

4-Hydroxy-3-methyl-4-(2-furyl)butan-2-one (**3e**). Yield 86%, colourless oil, b.p. 102 °C/1.0 mmHg (lit.,[22] 117—118 °C/10 mmHg); δ(*threo*) 0.88 (d, 3 H, *J* 7.0 Hz), 2.10 (s, 3 H), 2.73—3.16 (m, 1 H), 3.53 (d, 1 H, *J* 7.0 Hz), 4.59 (dd, 1 H, *J* 7.0 and 4.5 Hz), 6.24 (m, 2 H), and 7.23 (s, 1 H); δ(*erythro*) 1.03 (d, *J* 7.0 Hz), 2.03 (s, 3 H), 2.73—3.16 (m, 1 H), 3.40 (d, 1 H, *J* 4.5 Hz), 4.88 (dd, 1 H, *J* 4.5 and 4.5 Hz), 6.24 (m, 2 H), and 7.23 (s, 1 H); $\nu_{max.}$ 3 380s, 1 700s, and 1 000s.

4-Hydroxy-3-methyl-4-(2-pyridyl)butan-2-one (**3f**). Yield 80%, colourless oil (lit.,[23] m.p. 72—74 °C); δ(*threo*) 0.89 (d, 3 H, *J* 7.0 Hz), 2.13 (s, 3 H), 3.02 (m, 1 H), 4.19 (br s, 1 H), 4.63 (d, 1 H, *J* 6.0 Hz), 6.92—7.78 (m, 3 H), and 8.87 (d, 1 H, *J* 5.0 Hz); δ(*erythro*) 1.00 (d, 3 H, *J* 7.0 Hz), 2.06 (s, 3 H), 3.02 (m, 1 H), 4.19 (br s, 1 H), 5.01 (d, 1 H, *J* 3.0 Hz), 6.92—7.78 (m, 3 H), and 8.87 (d, *J* 5.0 Hz, 1 H); $\nu_{max.}$ 3 350s, 1 700vs, and 1 040m.

4-Hydroxy-3-methyl-4-(3-pyridyl)butan-2-one (**3g**). Yield 81%, colourless oil (lit.,[23] oil); δ(*threo*) 0.86 (d, 3 H, *J* 7.0 Hz), 2.24 (s, 3 H), 2.87 (m, 1 H), 4.00 (br s, 1 H), 4.76 (d, 1 H, *J* 8.5 Hz), 7.32 (m, 1 H), 7.73 (m, 2 H), and 8.45 (br s, 1 H); δ(*erythro*) 1.08 (d, 3 H, *J* 7.0 Hz), 2.13 (s, 3 H), 2.87 (m, 1 H), 4.00 (br s, 1 H), 5.12 (d, 1 H, *J* 4.0 Hz), 7.32 (m, 1 H), 7.73 (m, 2 H), and 8.45 (br s, 1 H); $\nu_{max.}$ 3 300s, 1 700s, and 1 020m.

4-(4-Chlorophenyl)-4-hydroxy-3-methylbutan-2-one (**3i**). Yield 94%, colourless oil; δ(*threo*) 0.84 (d, 3 H, *J* 7.0 Hz), 2.10 (s, 3 H), 2.48—2.88 (m, 1 H), 3.15 (s, 1 H), 4.54 (dd, 1 H, *J* 7.0 and 4.0 Hz), 7.20 (s, 4 H); δ(*erythro*) 0.96 (d, 3 H, *J* 7.0 Hz), 2.06 (s, 3 H), 2.48—2.88 (m, 1 H), 3.19 (s, 1 H), 4.95 (dd, 1 H, *J* 3.0 and 3.0 Hz), and 7.20 (s, 4 H); $\nu_{max.}$ 3 400vs, 1 700vs, and 1 090s; *m/z* (rel. intensity) 212 ($M^+$, 7%), 197 (26), 195 (63), 141 (75), and 43 (100) [Found: C, 62.35; H, 6.2; Cl, 16.86. Calc. for $C_{11}H_{13}ClO_2$ (212.678): C, 62.12; H, 6.16; Cl, 16.67%].

4-(4-Bromophenyl)-4-hydroxy-3-methylbutan-2-one (**3j**). Yield 84%; δ(*threo*) 0.88 (d, 3 H, *J* 7.0 Hz), 2.11 (s, 3 H), 2.30—2.96 (m, 1 H), 3.61 (d, 1 H, *J* 4.0 Hz), 4.49 (dd, 1 H, *J* 4.0 and 9.0 Hz), 7.09 (d, 2 H, *J* 9.0 Hz), and 7.39 (d, 2 H, *J* 9.0 Hz); δ(*erythro*) 0.98 (d, 3 H, *J* 7.0 Hz), 2.05 (s, 3 H), 2.30—2.96 (m, 1 H), 3.50 (d, 1 H, *J* 3.0 Hz), 4.90 (dd, 1 H, *J* 3.0 and 3.0 Hz), 7.09 (d, 2 H, *J* 9.0 Hz), and 7.39 (d, 2 H, *J* 9.0 Hz). The pure *threo*-isomer was obtained by recrystallizing the mixture from ethyl acetate–light petroleum, as a white solid, m.p. 98—99 °C; $\nu_{max.}$ 3 360s, 1 705vs, and 1 005s; *m/z* (rel. intensity) 257 ($M^+$ + 1, 9%), 256 ($M^+$, 3%), 241 (100), 239 (96), and 159 (18) [Found: C, 51.25; H, 5.15; Br, 30.95. Calc. for $C_{11}H_{13}BrO_2$ (257.129); C, 51.38; H, 5.10; Br, 31.08%].

4-Hydroxy-3-methyl-4-(6-methylcyclohexa-1,3-dienyl)-butan-2-one (**3k**). Yield 81%, colourless oil; δ 0.93 (m, 6 H), 2.10 (m, 5 H), 2.34—2.84 (m, 2 H), 3.02 (br s, 1 H), 3.97 (m, 0.56 H, *threo*), 4.31 (m, 0.44 H, *erythro*), and 5.62 (m, 3 H); $\nu_{max.}$ 3 420s, 1 705vs, 1 175m, 1 000m, and 700s; *m/z* (rel. intensity) 195 ($M^+$ + 1, 1%), 194 ($M^+$, 1%), 177 (1), 123 (12), 77 (35), and 43 (100) [Found: C, 74.4; H, 9.05. Calc. for $C_{12}H_{18}O_2$ (194.276): C, 74.19; H, 9.34%].

5-(4-Bromophenyl)-5-hydroxy-2-methylpentan-3-one (**8**). Yield 70%, white crystals, m.p. 71—74 °C; δ 1.06 (d, 6 H, *J* 6.0 Hz), 2.46 (hept., 1 H), 2.65 (d, 2 H, *J* 6.0 Hz), 3.40 (d, 1 H, *J* 3.0 Hz), 5.00 (m, 1 H), 7.13 (d, 2 H, *J* 8.5 Hz), and 7.41 (d, 2 H, *J* 8.5 Hz); $\nu_{max.}$(KCl) 3 450s, 1 705s, and 1 050s; *m/z* (rel. intensity) 270 ($M^+$, 18%), 255 (84), 253 (81), 227 (26), 185 (22), and 71 (100); [Found: C, 52.85; H, 5.55; Br, 29.75. Calc. for $C_{12}H_{15}BrO_2$ (271.156): C, 53.15; H, 5.58; Br, 29.46%].

2-(4-Bromo-α-hydroxybenzyl)cyclohexanone (**9**). Yield 84%, m.p. 84—85 °C; *erythro*/*threo* ratio 29:71; δ(*threo*) 1.10—2.60 (m, 9 H), 3.64 (d, 1 H, *J* 3.0 Hz), 4.58 (dd, 1 H, *J* 3.0 and 8.5 Hz), 7.07 (d, 2 H, *J* 8.5 Hz), and 7.36 (d, 2 H, *J* 8.5 Hz); δ(*erythro*) 1.10—2.60 (m, 9 H), 2.90 (d, 1 H, *J* 3.5 Hz), 5.16 (m, 1 H), 7.07 (d, 2 H, *J* 8.5 Hz), and 7.36 (d, 2 H, *J* 8.5 Hz); $\nu_{max.}$(KCl) 3 500s, 3 440s, 1 695s, and 1 685s; *m/z* (rel. intensity) 282 ($M^+$, 8%), 265 (26), 185 (66), and 98 (100); [Found: C, 55.3; H, 5.15; Br, 27.9. Calc. for $C_{13}H_{15}BrO_2$ (283.154): C, 55.14; H, 5.34; Br, 28.22%].

4-Hydroxy-3-methyl-4-(4-nitrophenyl)butan-2-one (**3l**). Yield 95%, yellow solid, m.p. 59 °C (lit.,[22] 62 °C); *erythro*/*threo* ratio 61:39; δ 0.91 (d, 1.17 H, *J* 6.5 Hz, *threo*), 0.98 (d, 1.83 H, *J* 6.5 Hz, *erythro*), 2.16 (s, 3 H), 2.73 (m, 1 H), 3.49 (br s, 1 H), 4.73 (m, 0.39 H, *threo*), 5.15 (m, 0.61 H, *erythro*), 7.46 (d, 2 H, *J* 8.0 Hz), and 8.14 (d, 2 H, *J* 8.0 Hz); $\nu_{max.}$ 3 450s, 1 705s, 1 520s, and 1 345s.

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