Reaction of α-Halogeno Ketones with Carbonyl Compounds Promoted by CeI_3, $CeCl_3$–NaI, or $CeCl_3$–$SnCl_2$

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Reaction of α-halogeno ketones with aldehydes in the presence of CeI_3 in tetrahydrofuran is found to give α,β-unsaturated ketones in excellent yields under mild conditions. In contrast, treatment of α-halogeno ketones and carbonyl compounds with $CeCl_3$–NaI or $CeCl_3$–$SnCl_2$ affords β-hydroxy ketones in good yields. It is assumed that these reactions proceed *via* cerium enolates. The combined reagents, however, cannot be applied to a Reformatsky-type reaction. Regiospecific and aldehyde chemoselective aldol synthesis are also described.

Although use of lanthanoid salts in organic synthesis is of current interest,[1] such compounds as ceric ammonium nitrate have been long recognized as strong one-electron transfer oxidizing agents.[2] Recently, divalent samarium was found to be effective for carbon–carbon bond formation between carbonyl compounds and organic halides[3] or electron deficient alkenes.[4] Organic synthesis using trivalent lanthanoid salts has also been studied intensively,[5] lanthanoid trichlorides ($LnCl_3$) appearing to be one of several attractive reagents since they effectively activate carbonyl or halogen groups. Such salts are sometimes employed in combination with other reagents such as $NaBH_4$,[5] $LiAlH_4$,[6] or Grignard reagents[7] for selective reduction or alkylation.

In our preliminary report, we showed that CeI_3 was an effective reagent for carbon–carbon bond formation between α-halogeno ketones and aldehydes to afford α,β-unsaturated ketones.[8] In further work we have found a novel reagent by combining $CeCl_3$ with NaI or $SnCl_2$; either of these reagents is effective for the regioselective formation of cerium enolates from α-halogeno ketones to give β-hydroxy ketones in good yields. In the absence of $CeCl_3$ no reaction occurs. Selective activation of the carbonyl group in an α-halogeno ketone by $CeCl_3$ is responsible for the reaction. The combined reagent system provides a simple and convenient method for aldol synthesis.

Results and Discussion

CeI_3-Mediated C–C Bond Formation between α-Halogeno Ketones and Aldehydes.—Treatment of an equimolar mixture of phenacyl bromide and propionaldehyde with CeI_3 (1 equiv.) in tetrahydrofuran (THF) at room temperature for 1 h, gave 1-phenylpent-2-en-1-one quantitatively. Similar treatment of phenacyl bromide with other aldehydes, gave the corresponding α,β-unsaturated ketones in over 90% yields.

With ketones, however, the desired C–C bond formation did not occur, acetophenone being produced predominantly as a result of reduction. The results are summarized in Table 1. With α,β-unsaturated aldehydes such as cinnamaldehyde and crotonaldehyde, the carbonyl carbon was attacked exclusively to give buta-1,3-dienyl ketones in excellent yields. Other α-halogeno ketones such as 1-chloroacetone, 2-chlorocyclohexanone, and 2-bromocyclohexanone reacted similarly with aldehydes. These results are also shown in Table 1. However, 2-bromopropiophenone and 3-chlorobutan-2-one are exceptions, since their reaction with benzaldehyde did not give the desired α,β-unsaturated ketones, several unidentified compounds being formed instead.

When the reaction was quenched with deuterium oxide, deuteriated acetophenone ($PhCOCH_2D$) was isolated from the reaction with phenacyl bromide. This indicates that the first step of the reaction is dehalogenation by the iodide anion and the reacting species is the cerium enolate.[9] Treatment of a β-hydroxy ketone prepared separately with CeI_3 in THF gave the corresponding α,β-unsaturated ketone quantitatively. This suggests that the cerium enolate reacts with an aldehyde to form the β-hydroxy ketone, which is then subjected to dehydration by CeI_3.

Reaction with $CeCl_3$–NaI.—In the dehalogenation process described above, the iodide anion and cerium atom attack the halogen group and carbonyl oxygen of an α-halogeno ketone, respectively. A similar coupled attack was thus expected when

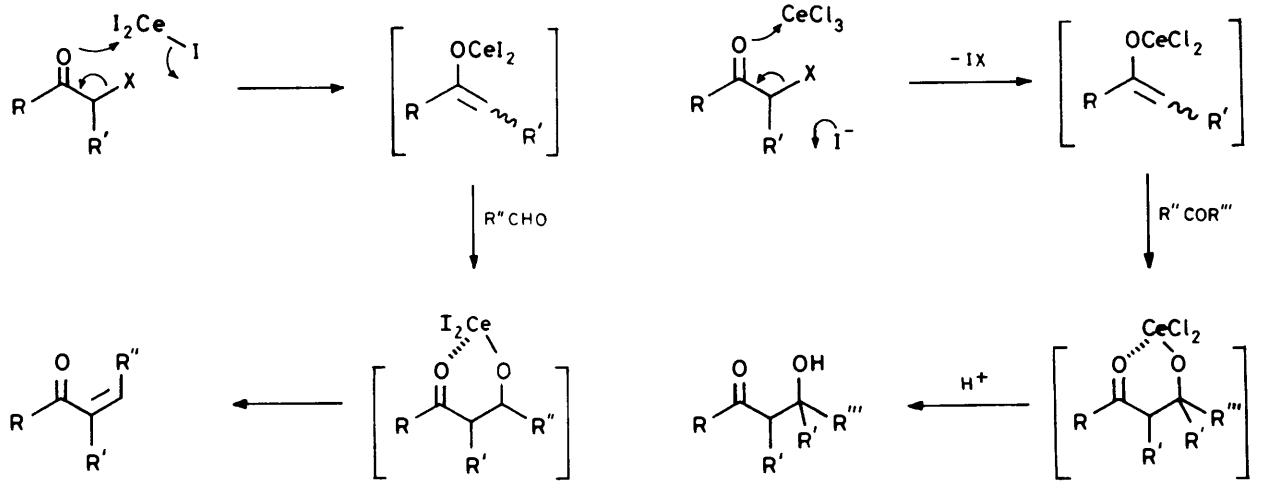


Table 1. The reaction of α-halogeno ketones and aldehydes in the presence of CeI_3[a]

α-Halogeno ketone	Aldehyde	Product	Yield (%)[b]
$PhCOCH_2Br$	MeCHO[c]	PhCOCH–CHMe[d]	95
	EtCHO[c]	PHCOCH=CHEt[d]	95
	PhCHO	PhCOCH=CHPh[d]	98
	OCH=CHCH=CCHO	PhCOCH=CHC=CHCH=CHO	98
	MeCH=CHCHO	PhCOCH=CHCH=CHMe	95
	PhCH=CHCHO	PhCOCH=CHCH=CHPh	95
	MeCH=CHCH=CHCHO	PhCOCH=CHCH=CHCH=CHMe	91
	Me_2C=CHCH$_2$C(Me)=CHCHO	PhCOCH=CHCH=C(Me)CH_2CH_2–CH=CMe_2	90
$MeCOCH_2Cl$	PhCHO	MeCOCH=CHPh	80
$CO(CH_2)_4CHCl$	PHCHO	$CO(CH_2)_4C$=CHPh	70
$CO(CH_2)_4CHBr$	PhCHO	$CO(CH_2)_4C$=CHPh	90

[a] α-Halogeno ketone (2 mmol), aldehyde (2 mmol), CeI_3 (2 mmol), and THF (5 ml); room temperature, 1 h. [b] Isolated yield. [c] Aldehyde (4 mmol). [d] Predominantly *trans*.

Table 2. The reaction of α-halogen ketones with carbonyl compounds in the presence of $CeCl_3$–NaI or $CeCl_3$–$SnCl_2$[a]

α-Halogeno ketone	Carbonyl compound	Reducing agent	Product	Yield (%)[b]
$PhCOCH_2Br$	MeCHO[c]	$SnCl_2$	$PhCOCH_2CH(OH)Me$	87
	EtCHO	NaI	$PhCOCH_2CH(OH)Et$	80
	EtCHO	$SnCl_2$	$PhCOCH_2CH(OH)Et$	76
	2-Furyl CHO	NaI	$PhCOCH_2CH(OH)$(fur-2-yl)	85
	MeCH=CHCHO	$SnCl_2$	$PhCOCH_2CH(OH)CH$=CHMe	79
	Me_2CHCHO	$SnCl_2$	$PhCOCH_2CH(OH)CHMe_2$	95
	MeCOMe[d]	NaI	$PhCOCH_2C(OH)Me_2$	50
	MeCOMe[d]	$SnCl_2$	$PhCOCH_2C(OH)Me_2$	42
	Cyclohexanone	NaI	$PhCOCH_2C(OH)(CH_2)_4CH_2$	50
	Cyclohexanone	$SnCl_2$	$PhCOCH_2C(OH)(CH_2)_4CH_2$	30
	$MeCO(CH_2)_4CHO$	$SnCl_2$	$PhCOCH_2CH(OH)(CH_2)_4COMe$	78
PhCOCH(Br)Me	PhCHO	NaI	PhCOCH(Me)CH(OH)Ph[e]	97
	PhCHO	$SnCl_2$	PhCOCH(Me)CH(OH)Ph[e]	74
	MeCOMe	NaI	$PhCOCH(Me)C(OH)Me_2$	50
	Cyclohexanone	NaI	$PhCOCH(Me)C(OH)(CH_2)_4CH_2$	50
$MeCOCH_2Cl$	PhCHO	NaI	$MeCOCH_2CH(OH)Ph$	85
	PhCHO	$SnCl_2$	—	0
	PhCH=CHCHO	NaI	$MeCOCH_2CH(OH)CH$=CHPh	85
$MeCOCH_2Br$	PhCHO	$SnCl_2$	$MeCOCH_2CH(OH)Ph$	74
	PhCH=CHCHO	$SnCl_2$	$MeCOCH_2CH(OH)CH$=CHPh	74
MeCOCH(Cl)Me	PhCHO	NaI	MeCOCH(Me)CH(OH)Ph[e]	94
	PhCHO	$SnCl_2$	—	0
MeCOCH(Br)CH	PhCHO	$SnCl_2$	MeCOCH(Me)CH(OH)Ph[e]	92
2-Chlorocyclohexanone	PhCHO	NaI	$CO(CH_2)_4CHCH(OH)Ph$[e]	82
	PhCHO	$SnCl_2$	—	0
2-Bromocyclohexanone	PhCHO	NaI	$CO(CH_2)_4CHCH(OH)Ph$[e]	91
	PhCHO	$SnCl_2$	$CO(CH_2)_4CHCH(OH)Ph$[f]	75
	PhCHO	$PbCl_2$	—	0
	MeCOMe	NaI	$CO(CH_2)_4CHC(OH)Me_2$	
2-Bromo-2-methylcyclohexanone	PhCHO	NaI	$CO(CH_2)_4C(Me)CH(OH)Ph$[e]	82
	PhCHO	$SnCl_2$	$CO(CH_2)_4C(Me)CH(OH)Ph$[e]	78
2-Bromo-6-methylcyclohexanone	PhCHO	NaI	$COCH(Me)(CH_2)_3CHCH(OH)Ph$[e]	90
	PhCHO	$SnCl_2$	$COCH(Me)(CH_2)_3CHCH(OH)Ph$[e]	75

[a] α-Halogeno ketone (4 mmol), carbonyl compound (4 mmol), $CeCl_3$ (4 mmol), NaI or $SnCl_2$ (12 mmol), and THF (10 ml); room temperature, 1—2 h. [b] Isolated yield. [c] Aldehyde (8 mmol). [d] Acetone (20 mmol). [e] *threo*:*erythro* 1:1 ~ 3:2. [f] *threo*:*erythro* 17:3.

using $CeCl_3$ and NaI instead of CeI_3. In fact, treatment of an α-halogeno ketone and carbonyl compound with this combined reagent afforded β-hydroxy ketones in good yields. A cerium enolate is again assumed to be a reaction intermediate.

In this reaction, subsequent dehydration hardly occurred. The use of either $CeCl_3$ or NaI alone resulted in the recovery of the starting compounds. Results of the reaction of some α-halogeno ketones with carbonyl compounds are summarized in Table 2.

One equivalent of NaI to the starting compounds was sufficient for the reaction, but a three-fold excess of NaI was usually employed to obtain satisfactory yields of the products. The reaction of 2-bromocyclohexanone, 2-bromopropiophenone, or 3-chlorobutan-2-one with benzaldehyde afforded a mixture of *threo* and *erythro* isomers of the β-hydroxy ketones. The isomer ratios were determined by the relative intensities of the benzylic proton absorptions.[10] The reactions did not proceed stereoselectively, the ratios of *threo* to *erythro* being

Table 3. Stereoselectivity in the reaction of 2-bromocyclohexanone with benzaldehyde in the presence of $LnCl_3$–$SnCl_2$ [a]

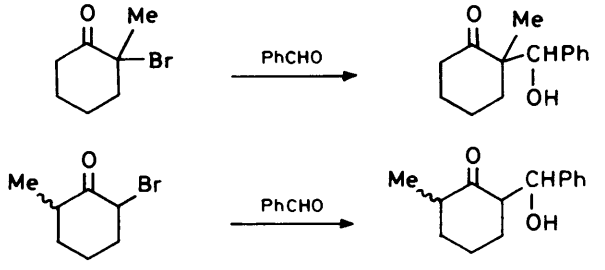
Ln in $LnCl_3$	Product yield (%) [b]	Isomer ratio [c] *threo*:*erythro*
La	98	83:17
Ce	88	83:17
Nd	84	85:15
Sm	80	70:30
Er	76	89:11

[a] 2-Bromocyclohexanone (4 mmol), benzaldehyde (4 mmol), $CeCl_3$ (4 mmol), $SnCl_2$ (12 mmol), and THF (10 ml); room temperature, 2 h. [b] Isolated yield. [c] Determined by ^1H n.m.r.

1:1 ~ 3:2. The mode of addition of the cerium enolate to the α,β-unsaturated aldehyde was 1,2- as observed in the reaction using CeI_3. With ketones, the yields of β-hydroxy ketones were not so satisfactory as with aldehydes (30 ~ 50%), and the reaction was accompanied by a simple reduction of the halogen group of the starting α-halogeno ketone. The elongation of the reaction time and/or the use of an excess of ketone did not improve the yields.

Treatment of ethyl bromoacetate and benzaldehyde with $CeCl_3$–NaI gave no Reformatsky-type product, starting compounds being recovered.

The regiospecificity of the reaction was examined by the reaction of 2-bromo-2-methylcyclohexanone or 2-bromo-6-methylcyclohexanone with benzaldehyde. Each isomer afforded the corresponding β-hydroxy ketone without any contamination of the regioisomer.



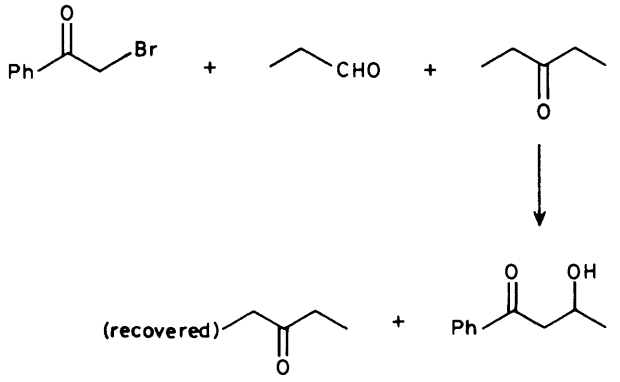
The success of this facile method for the preparation of cerium enolate may be explained as follows. The cerium atom behaves as a Lewis acid which co-ordinates the carbonyl oxygen and promotes the reduction of the halogen group by the iodide anion. Furthermore, the metal enolate enhances the stability of the metal chelate in the synthesis of the β-hydroxy ketone.

Reaction with $LnCl_3$–$SnCl_2$.—The reaction above was also possible when NaI was replaced by $SnCl_2$. No reaction took place in the absence of $CeCl_3$. The combination of $CeCl_3$ with $SnCl_2$, however, could not be applied to α-chloro ketones or Reformatsky-type reactions, starting compounds being recovered (see Table 2). Similarly, $PbCl_2$, gave no reaction: lead and tin are both 4B elements.

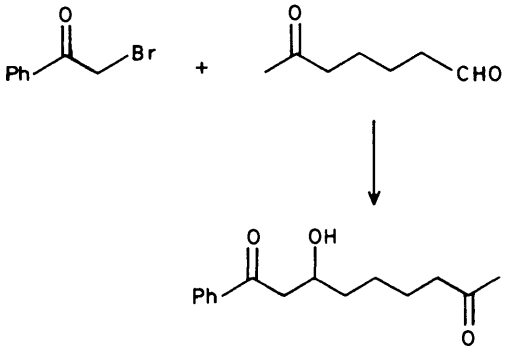
It is interesting that the stereoselectivity of the β-hydroxy ketone from 2-bromocyclohexanone and benzaldehyde is more *threo* selective (*threo*:*erythro* 85:15) than that prepared by $CeCl_3$–NaI and by the reported aldol reaction *via* cerium enolate.[11] The reason for this improved stereochemistry is unclear. To improve the *threo* selectivity in the reaction several other lanthanoid chlorides were tested, but the results were unsuccessful (Table 3). The isomer ratios of *threo* to *erythro* remained virtually the same, *i.e.*, 4:1, despite variation of the lanthanoid metal.

In contrast, tin enolate generated from 2-bromocyclohexanone and low-valent tin is known to react with benzaldehyde to afford the *erythro* isomer predominantly.[12] As described previously, the use of $SnCl_2$ alone gave no product. Considering these facts, it is reasonable to assume that the reaction proceeds *via* a lanthanoid enolate and that tin enolate is not a likely intermediate.

With ketones, the yields of the desired products were again reduced when compared with those of aldehydes. The difference in reactivity between aldehydes and ketones was successfully utilized for the chemoselective aldol synthesis from aldehydes in the presence of ketones. An equimolar mixture of proprionaldehyde and diethyl ketone treated with phenacyl bromide in the presence of $CeCl_3$–$SnCl_2$ gave only an aldol product derived from the proprionaldehyde and recovery of unchanged diethyl ketone.



Chemoselectivity of the aldol synthesis was also observed with the oxo aldehyde 6-oxoheptanal.



Examples of other combined reagents include the organoaluminium system Et_2AlCl–$SnCl_2$.[13] This combination sometimes requires a Pd^0 complex to obtain satisfactory results. Whereas our combined system ($LnCl_3$–$SnCl_2$) functions effectively without further reagents and is insensitive to air and moisture contamination unlike organoaluminium compounds. When $AlCl_3$ or $TiCl_4$ was employed instead of $LnCl_3$, the products were complex and the desired aldol was formed only in poor yield.

Experimental

^1H N.m.r. spectra were recorded with Hitachi R-24 (60 MHz) and Hitachi R-600 (60 MHz) instruments on solutions with Me_4Si as an internal standard. I.r. spectra were taken in CCl_4 solutions with a JASCO-A1. G.l.c. analyses were carried out by using a Shimadzu 6AM apparatus on EGSS-X (3%)-Chromosorb-W (1 and 3 m) and Silicon DC QF-1 (5%)-Chromosorb-W (1 m) columns (N_2 as carrier gas).

Flash column chromatography was performed by EYELA EF-10 apparatus by using Merck Kieselgel 60 (230—400 mesh) or Wako C-300. Preparative t.l.c. separation was conducted using 20 × 20 cm glass plates coated with a 2.0 mm thick layer of Merck Kieselgel PF_{254} gipshaltig.

Cerium chips purchased from Santoku Metal Industry (99.9% purity), were scraped by a rasp and then used as powders (*ca.* 30—40 mesh). Tetrahydrofuran (THF) was distilled from sodium diphenylketyl under nitrogen. Anhydrous $LaCl_3$, $CeCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$, and $ErCl_3$ were obtained by drying the corresponding commercial hydrates with $SOCl_2$.[14] Anhydrous stannous chloride was purchased from Wako Pure Chemicals Co., and further dried at 200 °C *in vacuo* before use. Sodium iodide and zinc were obtained from Nakarai Chemicals Ltd. Phenacyl bromide, 2-chlorocyclohexanone, chloroacetone, 2-bromopropiophenone, and 3-chlorobutan-2-one were commercially available. 2-Bromocyclohexanone, bromoacetone, 3-bromobutan-2-one, and 2-bromo-2-methylcyclohexanone were obtained by bromination of the starting ketones with bromine in ether at −40 to −20 °C.[15] 2-Bromo-6-methylcyclohexanone was prepared according to the literature.[16] 6-Oxoheptanal was prepared by ozonolysis of 1-methylcyclohex-1-ene.[17] Other simple chemicals were commercially available and used without further purification.

Preparation of CeI_3 *and the Reaction of α-Halogeno Ketones with Aldehydes in the Presence of* CeI_3.—*General procedure.* Cerium powder (0.28 g, 2 mmol) and iodine (0.76 g, 3 mmol) were placed in a two-necked round-bottomed flask containing a magnetic stirrer bar, and dry THF (5 ml) was introduced with magnetic stirring. A mild exothermal reaction started and the mixture was stirred at room temperature for 0.5 h during which time a pale orange solid formed. To the resulting pale orange suspension was added simultaneously with stirring at room temperature an α-halogeno ketone (2 mmol) and an aldehyde (2 mmol). The solution became dark red and homogeneous and there was a slight rise of temperature. After being stirred for 1 h, the solution was quenched with aqueous sodium thiosulphate and extracted with chloroform (20 ml × 3), dried ($MgSO_4$) and evaporated under reduced pressure and the crude product was purified by column chromatography on silica gel (hexane–ethyl acetate, 5:1 as eluant) to give the α,β-unsaturated carbonyl compound.

1-*Phenylpent*-2-*en*-1-*one*. δ_H (60 MHz, CCl_4) 1.14 (3 H, t, *J* 7 Hz, Me), 2.1—2.5 (2 H, m, C*H*$_2$Me), 6.8—7.0 (1 H, m, C*H*CH$_2$), 7.3—7.5 (4 H, m, COCH= and Ph), and 7.7—8.0 (2 H, m, Ph); $\nu_{max.}$(neat) 1 601 and 1 660.

1-*Phenylhex*-2-*en*-1-*one*. δ_H (60 MHz, CCl_4), 1.81 (3 H, d, *J* 6 Hz, Me), 6.7—6.8 (1 H, m, =C*H*Me), 7.3—7.5 (4 H, m, COCH= and Ph), and 7.7—8.0 (2 H, m, Ph); $\nu_{max.}$(neat) 1 601 and 1 660.

1-*Phenylocta*-2,4,6-*trien*-1-*one*. δ_H (60 MHz, CCl_4) 1.81 (3 H, d, *J* 7 Hz, Me), 6.0—7.0 (5 H, m, olefinic CH), 7.3—7.5 (4 H, m, COCH= and Ph), and 7.8—8.0 (2 H, m, Ph).

1,5-*Diphenylpenta*-2,4-*dien*-1-*one*. δ_H (60 MHz, CCl_4) 6.8—7.3 (3 H, m, olefinic CH), 7.3—7.6 (11 H, m, COCH= and Ph), and 7.8—8.0 (2 H, m, Ph).

1-*Phenylhexa*-2,4-*dien*-1-*one*. δ_H (60 MHz, CCl_4) 1.81 (3 H, d, *J* 6 Hz, Me), 6.1—6.4 (2 H, m, C*H*=C*H*Me), 6.7—7.0 (1 H, m, COCH=), 7.1—7.5 (4 H, m, COCH= and Ph), and 7.8—8.0 (2 H, m, Ph).

5,9-*Dimethyl*-1-*phenyldeca*-2,4,8-*trien*-1-*one*. δ_H (60 MHz, CCl_4) 1.59 (3 H, s, Me), 1.62 (3 H, s, Me), 1.89 (3 H, s, =C–Me), 2.0—2.2 (4 H, m, CH_2CH_2), 5.0 (1 H, br s, CH_2CH=C), 5.90 (1 H, dd, *J* 8, 17 Hz, CCH–C*H*=), 6.81 (1 H, d, *J* 6 Hz, =CH–C*H*=), 7.3—7.5 (4 H, m, COCH= and Ph), and 7.8—8.0 (2 H, m, Ph).

3(2-*Furyl*)-1-*phenylprop*-2-*en*-1-*one*. δ_H (60 MHz, CCl_4), 6.8—7.2 (2 H, m, furyl CH), 7.4 (3 H + 3 H, br s, furyl and Ph), and 7.8—8.0 (2 H, m, Ph); $\nu_{max.}$(neat) 1 600 and 1 601.

2-*Benzylidenecyclohexanone*. δ_H (60 MHz, CCl_4), 1.5—2.3 (6 H, m, aliphatic CH), 2.90 (2 H, t, CH_2CO), 7.2—7.4 (5 H, m, Ph), 7.63 (1 H, s, CH=); $\nu_{max.}$(neat) 1 600 and 1 705.

Reaction of α-Halogeno Ketones with Carbonyl Compounds in the Presence of $CeCl_3$–NaI.—*General procedure.* Anhydrous $CeCl_3$ (1.00 g, 4 mmol) and NaI (1.80 g, 12 mmol) were placed in a 20 ml two-necked round-bottomed flask containing a magnetic stirrer bar. Dry THF (7 ml) was added with magnetic stirring. To the white suspension was added simultaneously at room temperature a THF (3 ml) solution of an α-halogeno ketone (4 mmol) and a carbonyl compound (4 mmol). The solution became dark red and after 1 h was treated in a similar manner to that described above; the product was isolated by flash chromatography on silica gel (hexane–EtOAc, 3:1).

Reaction of α-Bromo Ketones with Carbonyl Compounds in the Presence of $CeCl_3$–$SnCl_2$.—*General procedure.* To a suspension of $CeCl_3$ (1.00 g, 4 mmol) and $SnCl_2$ (2.27 g, 12 mmol) in dry THF (7 ml) at room temperature was added a THF solution (3 ml) of an α-bromo ketone (4 mmol) and a carbonyl compound. The homogeneous mixture was stirred at room temperature for 2 h, and then poured into dilute HCl. The product was extracted with $CHCl_3$ (30 ml × 3) and the extract dried ($MgSO_4$) and evaporated under reduced pressure. The residue was subjected to preparative t.l.c. to give the pure product.

3-*Hydroxy*-1-*phenylbutan*-1-*one*. δ_H (60 MHz, CCl_4) 1.25 (3 H, d, *J* 6 Hz, Me), 3.10 (2 H, d, *J* 6 Hz, CH_2), 4.36 (1 H, sext, *J* 6 Hz, CHO), 5.58 (1 H, br s, OH), and 7.2—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 414 and 1 650.

3-*Hydroxy*-1-*phenylpentan*-1-*one*. δ_H (60 MHz, CCl_4) 0.99 (3 H, t, *J* 6 Hz, Me), 1.45 (2 H, quint, *J* 6 Hz, CH_2), 2.99 (2 H, d, *J* 6 Hz, COMe), 3.10 (1 H, br s, OH), 4.04 (1 H, quint, *J* 6 Hz, CHO), and 7.3—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 410 and 1 655.

3-*Hydroxy*-4-*methyl*-1-*phenylpentan*-1-*one*. δ_H (60 MHz, CCl_4) 0.99 (6 H, d, *J* 7 Hz, Me), 1.62 (1 H, m, CH), 2.92 (2 H, d, *J* 6 Hz, $COCH_2$), 3.14 (1 H, br s, OH), 3.89 (1 H, q, *J* 6 Hz, CHO), and 7.1—7.8 (5 H, m, Ph); $\nu_{max.}$(neat) 3 387 and 1 690.

3-*Hydroxy*-1-*phenylhex*-4-*en*-1-*one*. δ_H (60 MHz, CCl_4) 1.63 (3 H, d, *J* 7 Hz, Me), 3.05 (2 H, d, *J* 6 Hz, $COCH_2$), 3.20 (1 H, br s, OH), 3.56 (1 H, m, CHO), 5.2—5.7 (1 H, m, =C*H*Me), 6.0—6.3 (1 H, m, CH=), and 7.2—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 393 and 1 721.

3-*Hydroxy*-3-*methyl*-1-*phenylbutan*-1-*one*. δ_H (60 MHz, CCl_4) 1.20 (6 H, s, Me), 2.98 (2 H, s, CH_2), 3.50 (1 H, br s, OH), and 7.2—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 570 and 1 650.

α-(1-*Hydroxycyclohexyl*)*acetophenone*. δ_H (60 MHz, CCl_4) 1.1—2.4 (10 H, m, cyclohexane), 3.05 (2 H, s, CH_2), 3.90 (1 H, br s, OH), and 7.3—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 480 and 1 670.

3-(2-*Furyl*)-3-*hydroxy*-1-*phenylpropan*-1-*one*. δ_H (60 MHz, CCl_4) 3.50 (2 H, d, *J* 7 Hz, Me), 3.49 (1 H, br s, OH), 5.21 (1 H, t, *J* 7 Hz, CHO), 6.2 (2 H, m, furyl), and 7.0—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 450 and 1 660.

3-*Hydroxy*-1-*phenylnonane*-1,8-*dione*. δ_H (60 MHz, CCl_4) 0.8—1.8 (6 H, m, $(CH_2)_3$), 1.80 (3 H, s, Me), 2.3—2.8 (2 H, m, C*H*$_2$COMe), 3.10 (2 H, d, *J* 8 Hz, PhCOC*H*$_2$), 3.33 (1 H, br s, OH), 4.30 (1 H, quint, *J* 8 Hz, CHO), and 7.4—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 440, 1 700, and 1 660.

3-*Hydroxy*-2-*methyl*-1,3-*diphenylpropan*-1-*one*. The ratio of the *erythro* and *threo* isomers was determined by the relative intensities of the methyl group. δ_H (60 MHz, CCl_4) 0.90 (d, *J* 8 Hz, *threo*, Me) and 1.10 (d, *J* 8 Hz, *erythro*, Me) (3 H), 3.62 (1 H, m, C*H*Me), 3.5 (1 H, br s, OH), 4.80 (d, *J* 8 Hz, *threo*, CHO) and 5.09 (d, *J* 3 Hz, *erythro*, CHO) (1H), and 7.0—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 480 and 1 670.

3-*Hydroxy*-2,3-*dimethyl*-1-*phenylbutan*-1-*one*. δ_H (60 MHz, CCl_4) 1.21 (6 H, s, Me), 3.49 (1 H, q, *J* 7 Hz, C*H*Me), 3.60 (1 H, br s, OH), and 7.2—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 400 and 1 670.

α-(1-*Hydroxycyclohexyl*)*propiophenone*. δ_H (60 MHz, CCl_4) 1.17 (3 H, d, *J* 8 Hz, Me), 1.2—2.2 (10 H, m, cyclohexane), 3.28 (1 H, br s, OH), 3.38 (1 H, q, *J* 8 Hz, C*H*Me), and 7.2—8.0 (5 H, m, Ph); $\nu_{max.}$(neat) 3 480 and 1 670.

4-*Hydroxy*-4-*phenylbutan*-2-*one*. δ_H (60 MHz, CCl_4) 2.11 (3 H, s, Me), 2.78 (2 H, dd, *J* 7.5, 4.5 Hz, $COCH_2$), 5.08 (1 H, dd, *J* 7.5, 4.5 Hz, CHO), 5.30 (1 H, br s, OH), and 7.0—7.5 (5 H, m, Ph); $\nu_{max.}$(neat) 3 458 and 1 730.

4-*Hydroxy*-3-*methyl*-4-*phenylbutan*-2-*one*. The isomer ratio of *threo* to *erythro* was determined by the methyl proton absorptions at 0.75 and 0.95; δ_H (60 MHz, CCl_4) 0.75 (d, *J* 8 Hz, *threo* 3-Me) and 0.96 (d, *J* 8 Hz, *erythro* 3-Me) (3 H), 1.93 (s, *erythro* MeCO) and 2.04 (s, *threo* Me*C*O) (3 H), 2.5—2.8 (1 H, m, C*H*Me), 3.21 (1 H, br s, OH), 4.50 (d, *J* 10 Hz, *threo* CHO) and 4.71 (d, *J* 5 Hz, *erythro* CHO) (1 H); $\nu_{max.}$(neat) 3 600 and 1 690.

4-*Hydroxy*-6-*phenylhex*-5-*en*-2-*one*. δ_H (60 MHz, CCl_4) 2.09 (3 H, s, Me), 2.64 (2 H, dd, *J* 8, 3 Hz, $COCH_2$), 3.60 (1 H, br s, OH), 4.65 (1 H, q, *J* 6 Hz, CHO), 6.11 (1 H, dd, *J* 16, 6 Hz, CH=), 6.70 (1 H, d, *J* 16 Hz, =CHPh), and 7.20 (5 H, br s, Ph); $\nu_{max.}$(neat) 3 415 and 1 707.

2-(α-*Hydroxybenzyl*)*cyclohexanone*. The isomer ratio of *erythro* to *threo* was determined by the relative intensities of the benzylic proton absorptions; δ_H (60 MHz, CCl_4) 0.88—2.4 (9 H, m, cyclohexane), 4.0 (1 H, br s, OH), 4.80 (d, *J* 8 Hz, *threo* CHO) and 5.45 (d, *J* 3 Hz, *erythro* CHO) (1 H), and 7.4 (5 H, br s, Ph); $\nu_{max.}$(neat) 3 480 and 1 690.

2-(α-*Hydroxybenzyl*)-2-*methylcyclohexanone*. δ_H (60 MHz, CCl_4) 0.99 and 1.09 (3 H, s, Me), 3.40 (1 H, br s, OH), 4.92 (s, *erythro* CHO) and 5.00 (s, *threo* CHO) (1 H), and 7.20 (5 H, br s, Ph); $\nu_{max.}$(neat) 3 405 and 1 680.

2-(α-*Hydroxybenzyl*)-6-*methylcyclohexanone*. δ_H (60 MHz, CCl_4) 1.10 (d, *J* 4 Hz, Me) and 1.14 (d, *J* 6 Hz, Me) (3 H), 1.0—1.8 (6 H, m, cyclohexane), 2.4—2.9 (2 H, m, CHCOCH), 4.80 (d, *J* 8 Hz) and 4.89 (d, *J* 8 Hz) (*threo*, *cis*, and *trans* CHO), 5.31 (d, *J* 4 Hz, *erythro* CHO) (1 H), and 7.31 (5 H, br s, Ph); $\nu_{max.}$(neat) 3 263 and 1 702.

2-(1′-*Hydroxy*-1-*methylethyl*)*cyclohexanone*. δ_H (60 MHz, CCl_4) 1.0 (6 H, s, Me), 1.2—2.4 (9 H, m, cyclohexane), and 3.0 (1 H, br s, OH); $\nu_{max.}$(neat) 3 480 and 1 700.

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