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Reformatsky-type reaction of α-haloketones promoted by titanium tetraiodide

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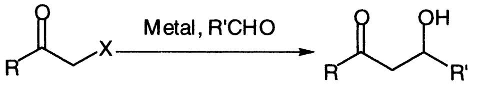
Abstract—Titanium(IV) tetraiodide induces a Reformatsky-type reaction of α-iodoketones with carbonyl compounds to give β-hydroxy ketones in good to high yields. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

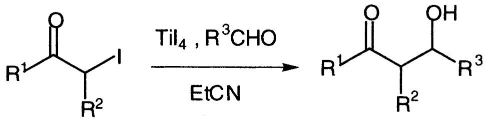
First discovered by Reformatsky in 1887, the reaction of α-halocarbonyl compounds and aldehydes in the presence of zinc is the first example of a large member of now commonly used carbon–carbon bond forming reactions.[1] Reductive formation of enolate species (or their equivalents) makes the reaction proceed under essentially neutral conditions (Eq. (1)). However, the yields of this type of reaction are not always satisfactory. This arises from the low reactivity of zinc metal and of the resulting organometallic reagent: the reaction usually has to be carried out at a high temperature, which causes concurrent undesirable side reactions and/or competitive reactions through several alternate transition states. Recently, several improvements have been made using activated Zn,[2a] Al,[2b] Sn,[2c] Co,[2d] Cr,[2e] Sm,[2f] Ti(II)[2g] and so on. However, most of them use low valent metals, which sometimes causes undesirable side reactions involving dehydration and reduction of unsaturation. It was reported that α,β-unsaturated ketones were produced via aldol and successive dehydration reactions of α-bromacetophenone with various aldehydes using $TiCl_4$ and KI,[3a] and also some improvements made possible the isolation of aldols before dehydration.[3b] Very recently, a combined use of $TiCl_4$ and R_4NI was reported to be a good tool for aldol reaction of α-haloketones.[4]

2. Results and discussion

We have recently found that TiI_4 is an excellent reagent for the reduction of α-diketones and/or sulfoxides, and that it also induces ring-opening-aldol reaction of methoxyallene oxide and pinacol coupling of aldehyhdes.[5] In these reactions, Ti(IV) was thought to be responsible for such facile reductions. In particular, the ability of the iodide ion to displace the iodine α to the carbonyl appears to be responsible for the facile aldol type reaction of methoxyallene oxide recently published,[5c] and therefore, we focus on the applicability of titanium iodide to the formation of enolates from α-iodoketones and subsequent aldol type reactions. In this paper, we describe titanium tetraiodide promoted reaction of α-haloketones with aldehydes to give β-hydroxy ketones in good yields (Eq. (2)). Table 1 summarizes the results of the addition reaction of α-iodoacetophenone to benzaldehyde in the presence of titanium tetraiodide under a variety of reaction conditions.



(1)



(2)

As shown in Table 1, when the reaction was carried out with a slight excess of TiI_4, the desired aldol adduct **2** was obtained in good yield (entry 4). In terms of product yield and the amounts of reagents, the reaction conditions used in entry 6 were employed to compare the effects of halogen in Ti and α-haloacetophenone **1**. When the iodine ligand in TiX_4 was replaced with chlorine or bromine, the reaction did not give the desired product **2** or gave it in low yield, respectively (entries 7 and 8). Replacement of the halogen in **1** also did not give the adduct **2** in satisfactory yields (entries 9 and 10). Thus, for the reductive formation of Ti enolate, the use of TiI_4 with α-iodocarbonyl compounds proved to be necessary. Under the optimum conditions, the addition reaction of a variety of α-haloketones with aldehydes in the presence of titanium tetraiodide are summarized in Table 2.

Keywords: Reformatsky-type reaction; titanium tetraiodide; α-haloketones.

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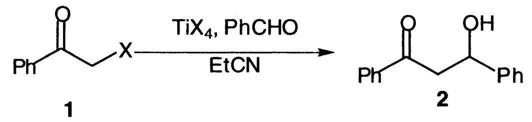
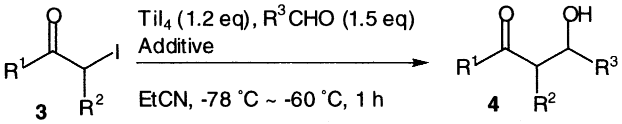
Table 1. Reaction of α-haloacetophenone **1** with benzaldehyde



Entry	X	TiX_4 (equiv.)	PhCHO (equiv.)	Temperature (°C)	Time (h)	Yield (%)[a]
1	I	TiI_4 (1.2)	1.1	−95 to −10	5.5	76
2	I	TiI_4 (1.5)	1.1	−95 to −10	5.0	65
3	I	TiI_4 (2.0)	1.1	−95 to −10	5.0	56
4	I	TiI_4 (1.2)	1.5	−78 to −20	3.0	85
5	I	TiI_4 (1.2)	2.0	−78 to −20	3.0	84
6	I	TiI_4 (1.2)	1.5	−78 to −60	1.0	83
7	I	$TiCl_4$ (1.5)	1.5	−78 to −60	1.0	0
8	I	$TiBr_4$ (1.5)	1.5	−78 to −60	1.0	13
9	Cl	TiI_4 (1.5)	1.5	−78 to −60	1.0	0
10	Br	TiI_4 (1.5)	1.5	−78 to −60	1.0	38

[a] Isolated yield.

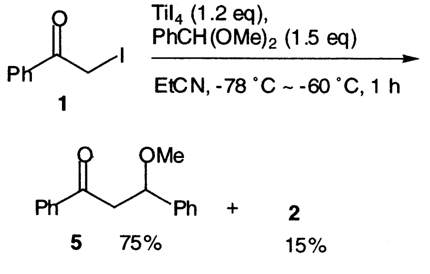
Table 2. Reaction of α-iodoketone with aldehyde in the presence of TiI_4



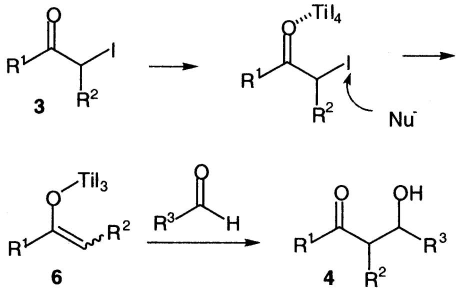
Entry	R^1	R^2	R^3	Additive (equiv.)	Yield (%)[a]	*anti*/*syn*[b]
1	Ph	H	*p*-ClC_6H_4	None	94	–
2	Ph	H	*p*-$MeOC_6H_4$	None	90	–
3	Ph	H	*p*-HOC_6H_4	None	77	–
4	Ph	H	$PhCH_2CH_2$	None	69	–
5	Ph	H	*trans*-$CH_3CH{=}CH$	None	56	–
6	Ph	H	*n*-Bu	None	64	–
7	Ph	H	*c*-Hex	None	73	–
8	Ph	H	*i*-Pr	None	49	–
9	Ph	H	*t*-Bu	None	34	–
10	Et	H	Ph	None	58	–
11	Et	H	$PhCH_2CH_2$	None	57	–
12	*t*-Bu	H	Ph	None	52	–
13	*t*-Bu	H	$PhCH_2CH_2$	None	50	–
14	Ph	Me	Ph	None	87	53:47
15	Ph	Me	Ph	$Ti(O^iPr)_4$ (1.1)	91	47:53
16	Ph	Me	Ph	$BF_3{\cdot}Et_2O$ (1.1)	76	73:27
17	Ph	Me	Ph	$^iPr_2EtN$ (0.6)	90	71:29
18[c]	Ph	Me	Ph	2-Methyl-2-butene (3.0)	88	9:91
19	$-(CH_2)_4-$		Ph	None	81	48:52
20	$-(CH_2)_4-$		Ph	$BF_3{\cdot}Et_2O$ (1.5)	80	75:25

[a] Isolated yield.
[b] Determined by ^1H NMR.
[c] Carried our in 1,4-dioxane at room temperarture.

As shown in Table 2, α-iodoacetophenone smoothly reacted with aromatic, aliphatic, and α,β-unsaturated aldehydes to give aldol products in good to excellent yields (entries 1–9). Hydroxy group on the aromatic ring did not affect addition reaction, and the aldol adduct was obtained in good yield (entry 3). The present reaction is sensitive to the steric congestion around the aldehyde carbon, and as the bulkiness of the α-substituent increased, the product yield became low (entries 6–9). Aliphatic iodomethyl ketones also participated in the present reaction, and the β-hydroxy ketones were obtained in moderated yield (entries 10–13). Diastereoselectivity was examined using α-iodopropiophenone and α-iodocyclohexanone. While in the absence of additives no selectivity was observed (entries 14 and 19), addition of $BF_3{\cdot}Et_2O$ and/or $^iPr_2NEt$ promoted the formation of *anti* adducts (entries 16, 17, and 20). Interestingly, the reaction in the presence of 2-methyl-2-butene in 1,4-dioxane which is known to form a complex with halogen completely altered the diastereoselectivity, and the *syn*-adduct was obtained as a major product (entry 18). This may be due



Scheme 1.



Scheme 2.

to the ability of 2-methyl-2-butene to trap the iodine and/or hydrogen iodide formed concomitantly, and to suppress the isomerization of the initially formed (*Z*)-enolate and/or *syn*-aldol.[6] Furtheremore, acetals also participated in the present reaction to give the β-alkoxy ketone **5** in good yield (Scheme 1).

The present reaction most probably proceeds as follows: TiI_4 reduces α-iodoketone to form Ti-enolate **6** via the attack of some nucleophile involving iodide anion to the iodine. The formation of the metal enolate via attack of iodide anion has been well precedented.[7] Subsequent reaction with aldehyde gives the aldol adduct (Scheme 2).

3. Conclusion

In conclusion, TiI_4 promotes the reaction of α-iodoketones with aldehydes to give aldol products in good to excellent yields, where the reductive formation of Ti enolate without the use of low valent metal species is noteworthy.

4. Experimental

4.1. General

Infrared spectra were determined on a JASCO IR-810 spectrometer. ^{1}H NMR spectra were recorded with JNM EX-270 spectrometers using tetramethylsilane as an internal standard. Exact mass spectra were taken on a Waters micromass ZQ. Propionitrile and 1,4-dioxane were distilled from calcium hydride. Purification of products was performed by column chromatography on silica gel Merck Silica Gel-60, and/or preparative TLC on silica gel Merck Kisel Gel PF254.

4.1.1. 3-Hydroxy-1,3-diphenylpropan-1-one. General procedure for the Reformatsky-type reaction. To a solution of titanium tetraiodide (135.5 mg, 0.244 mmol) in propionitrile (1.0 mL) was added a solution of benzaldehyde (32.4 mg, 0.305 mmol) in propionitrile (1.0 mL) at rt under an argon atmosphere. To the reaction mixture was added a solution of iodoacetophenone (50.0 mg, 0.203 mmol) in propionitrile (1.0 mL) at −78°C. After being stirred at −78 to −60°C, the reaction was quenched with sat. aqueous $NaHCO_3$, and 10% $NaHSO_3$. The mixture was filtered through a Celite pad and extracted with ethyl acetate (10 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by preparative TLC on silica gel (*n*-hexane/ethyl acetate=8:1) gave the title compound (38.3 mg, 83%).

^{1}H NMR ($CDCl_3$) δ 3.37 (d, *J*=6.1 Hz, 2H), 3.59 (brs, 1H), 5.34 (t, *J*=6.1 Hz, 1H), 7.26–7.61 (m, 8H), 7.93–7.97 (m, 2H). IR (neat) 3440, 3050, 1690, 1460, 1220, 755, 705, 690 cm^{-1}. The spectral data are in accordance with those in the literature.[8]

4.1.2. 3-(4-Chlorophenyl)-3-hydroxy-1-phenylpropanan-1-one. ^{1}H NMR ($CDCl_3$) δ 3.32 (d, *J*=1.3 Hz, 1H), 3.34 (s, 1H), 3.67 (d, *J*=3.0 Hz, 1H), 5.29–5.34 (m, 1H), 7.31–7.50 (m, 7H), 7.92–7.96 (m, 2H). IR (neat) 3440, 3070, 1685, 1500, 1460, 1225, 1025, 840, 760, 690 cm^{-1}. The spectral data are in accordance with those in the literature.[3b]

4.1.3. 3-Hydroxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one. ^{1}H NMR ($CDCl_3$) δ 3.34 (s, 1H), 3.36 (d, *J*=3.3 Hz, 1H), 3.53 (br, 1H), 3.80 (s, 3H), 5.36–5.31 (m, 1H), 6.88–6.92 (m, 2H), 7.34–7.37 (m, 2H), 7.42–7.48 (m, 2H), 7.54–7.60 (m, 1H), 7.93–7.96 (m, 2H). IR (neat) 3440, 1690, 1525, 1260, 1185, 1040, 840, 765, 695 cm^{-1}. MS *m*/*z* 241.20 [M−CH_3], 213.24 [M−CH_3−CO].

4.1.4. 3-Hydroxy-3-(4-hydroxyphenyl)-1-phenylpropan-1-one. ^{1}H NMR ($CDCl_3$) δ 3.35 (d, *J*=4.3 Hz, 1H), 3.37 (d, *J*=7.9 Hz, 1H), 3.81 (brs, 1H), 5.26 (dd, *J*=4.3, 7.9 Hz, 1H), 6.31 (brs, 1H), 6.73–6.78 (m, 2H). 7.22–7.26 (m, 2H), 7.42–7.61 (m, 3H), 7.92–7.95 (m, 2H). IR ($CHCl_3$) 3320, 1680, 1605, 1520, 1460, 1220, 840, 760, 695 cm^{-1}. MS *m*/*z* 225.27 [M−H_2O].

4.1.5. 3-Hydroxy-1,5-diphenylpentan-1-one. ^{1}H NMR ($CDCl_3$) δ 1.74–2.02 (m, 2H), 2.70–2.94 (m, 2H), 3.01–3.20 (m, 2H), 3.38 (d, *J*=2.6 Hz, 1H), 4.19–4.29 (m, 1H), 7.15–7.61 (m, 8H), 7.91–7.95 (m, 2H). IR (neat) 3450, 3000, 1690, 1605, 1590, 1505, 1460, 1300, 1220, 750, 700, 595 cm^{-1}. The spectral data are in accordance with those in the literature.[3b]

4.1.6. 3-Hydroxy-1-phenyl-4-hexen-1-one. ^{1}H NMR ($CDCl_3$) δ 1.72 (d, *J*=6.4 Hz, 3H), 3.13 (brs, 1H), 3.17 (d, *J*=2.3 Hz, 1H), 3.19 (s, 1H), 4.70 (dd, *J*=6.3, 12.2 Hz, 1H), 5.55–5.64 (m, 1H), 5.73–5.86 (m, 1H), 7.44–7.62 (m, 3H), 7.94–7.97 (m, 2H). IR (neat) 3440, 1690, 1605, 1455, 1270, 1025, 1010, 975, 770, 750, 700 cm^{-1}. The spectral data are in accordance with those in the literature.[9]

4.1.7. 3-Hydroxy-1-phenylheptan-1-one. ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J*=7.1 Hz, 3H), 1.31–1.68 (m, 6H), 2.99 (brs, 1H), 3.04 (dd, *J*=8.8, 17.5 Hz, 1H), 3.18 (dd, *J*=2.8, 17.5 Hz, 1H), 4.18–4.26 (m, 1H), 7.44–7.62 (m, 3H), 7.94–7.98 (m, 2H). IR (neat) 3440, 1690, 1605, 1460, 1220, 760, 695 cm^{-1}. MS [M$^+$]: 206.13, found: 206.00.

4.1.8. 3-Cyclohexyl-3-hydroxy-1-phenylpropan-1-one. ^{1}H NMR ($CDCl_3$) δ 1.01–1.36 (m, 5H), 1.41–1.55 (m, 1H), 1.61–1.82 (m, 4H), 1.93 (brd, *J*=12.9 Hz, 1H), 3.05 (dd, *J*=9.1, 17.4 Hz, 1H), 3.16 (s, 1H), 3.19 (dd, *J*=2.6, 17.4 Hz, 1H), 3.96–4.03 (m, 1H), 7.44–7.50 (m, 2H), 7.55–7.62 (m, 1H), 7.95–7.99 (m, 2H). IR (neat) 3470, 1690, 1605, 1590, 1460, 1220, 755, 690, 590 cm^{-1}. MS [M$^+$]: 232.15, found: 232.00.

4.1.9. 3-Hydroxy-4-methyl-1-phenylpentan-1-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 0.99 (d, J=6.6 Hz, 3H), 1.02 (d, J=6.3 Hz, 3H), 1.72–1.90 (m, 1H), 3.03 (dd, J=9.4, 17.2 Hz, 1H), 3.18 (dd, J=2.5, 17.2 Hz, 1H), 3.18 (d, J=3.0 Hz, 1H), 3.97–4.03 (m, 1H), 7.45–7.61 (m, 3H), 7.95–7.98 (m, 2H). IR (neat) 3475, 1690, 1610, 1220, 1010, 695 cm^{-1}. The spectral data are in accordance with those in the literature.[10]

4.1.10. 4,4-Dimethyl-3-hydroxy-1-phenylpentan-1-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.00 (s, 9H), 2.98 (dd, J=10.1, 17.2 Hz, 1H), 3.13 (brs, 1H), 3.21 (dd, J=1.8, 17.2 Hz, 1H), 3.90 (brd, J=8.6 Hz, 1H), 7.45–7.48 (m, 2H), 7.56–7.62 (m, 1H), 7.95–7.99 (m, 2H). IR (neat) 3480, 1690, 1605, 1590, 1370, 1310, 1220, 1080, 1020, 760, 690, 605 cm^{-1}. MS [M$^+$]: 206.13, found: 206.00.

4.1.11. 3-Hydroxy-3-methyl-1-phenylbutan-1-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.35 (s, 6H), 3.16 (s, 2H), 4.13 (brs, 1H), 7.45–7.51 (m, 2H), 7.57–7.62 (m, 1H), 7.95 (d, J=7.3 Hz, 2H). IR (neat) 3470, 3410, 1680, 1605, 1460, 1390, 1230, 760, 690 cm^{-1}. The spectral data are in accordance with those in the literature.[10]

4.1.12. 3-Methoxy-1,3-diphenylpropan-1-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 3.08 (dd, J=4.5, 16.5 Hz, 1H), 3.23 (s, 3H), 3.59 (dd, J=8.3, 16.5 Hz, 1H), 4.88 (dd, J=4.5, 8.3 Hz, 1H), 7.29–7.57 (m, 8H), 7.92–7.96 (m, 2H). IR (neat) 3040, 1700, 1610, 1590, 1500, 1460, 1365, 1280, 1220, 1120, 1000, 760, 700, 580 cm^{-1}. MS [M$^+$]: 240.12, found: 240.00.

4.1.13. 1-Hydroxy-1-phenylpentan-3-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.06 (t, J=7.3 Hz, 3H), 2.45 (q, J=7.3 Hz, 2H), 2.78 (dd, J=4.0, 17.5 Hz, 1H), 2.88 (d, J=17.5 Hz, 1H), 3.39 (s, 1H), 5.15 (dd, J=4.0, 8.6 Hz, 1H), 7.25–7.37 (m, 5H). IR (neat) 3400, 1710, 1465, 1420, 1040, 765, 710, 555 cm^{-1}. The spectral data are in accordance with those in the literature.[11]

4.1.14. 3-Hydroxy-1-phenylheptan-5-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.05 (t, J=7.3 Hz, 3H), 1.65–1.89 (m, 2H), 2.44 (q, J=7.3 Hz, 2H), 2.51–2.87 (m, 4H), 3.18 (d, J=3.3 Hz, 1H), 4.02–4.09 (m, 1H), 7.15–7.31 (m, 5H). IR (neat) 3400, 1720, 1510, 1460, 1420, 1040, 750, 710 cm^{-1}.

4.1.15. 1-Hydroxy-4,4-dimethyl-1-phenylpentan-3-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.13 (s, 9H), 2.88 (d, J=5.9 Hz, 2H), 3.58 (brs, 1H), 5.13 (t, J=5.9 Hz, 1H), 7.27–7.37 (m, 5H). IR (neat) 3435, 1715, 1490, 1380, 1085, 765, 710, 580, 560 cm^{-1}. The spectral data are in accordance with those in the literature.[8]

4.1.16. 2,2-Dimethyl-5-hydroxy-7-phenylheptan-3-one. ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.13 (s, 9H), 1.67–1.88 (m, 2H), 2.56 (dd, J=8.9, 17.8 Hz, 1H), 2.69 (dd, J=3.0, 17.8 Hz, 1H), 2.75–2.89 (m, 2H), 3.36 (brs, 1H), 4.02 (br, 1H), 7.15–7.31 (m, 5H). IR (neat) 3450, 1710, 1480, 1460, 1380, 1080, 750, 700 cm^{-1}.

4.1.17. 3-Hydroxy-1,3-diphenyl-2-methylpropan-1-one. To a solution of titanium tetraiodide (135.5 mg, 0.244 mmol) and 2-methyl-2-butene (0.06 mL, 0.609 mmol) in 1,4-dioxane (1.0 mL) was added a solution of benzaldehyde (32.4 mg, 0.305 mmol) in 1,4-dioxane (1.0 mL) at rt under an argon atmosphere. To the reaction mixture was added a solution of 2-iodopropiophenone (52.8 mg, 0.203 mmol) in 1,4-dioxane (1.0 mL) at rt. After being stirred at rt for 1 h, the reaction was quenched with sat. aqueous $\mathrm{NaHCO_3}$, and 10% $\mathrm{NaHSO_3}$. The mixture was filtered through a Celite pad and extracted with ethyl acetate (10 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by preparative TLC on silica gel (*n*-hexane/ethyl acetate=10:1) gave the title compound (43.9 mg, 90%).

syn Isomer; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.19 (d, J=7.3 Hz, 3H), 3.66 (brs, 1H), 3.70 (dq, J=3.0, 7.3 Hz, 1H), 5.25 (d, J=3.0 Hz, 1H), 7.23–7.63 (m, 8H), 7.92–7.96 (m, 2H). IR (neat) 3440, 3035, 1690, 1605, 1585, 1505, 1460, 1225, 980, 755, 710 cm^{-1}. The spectral data are in accordance with those in the literature.[12]

anti Isomer; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.07 (d, J=6.9 Hz, 3H), 2.96 (brs, 1H), 3.81–3.89 (m, 1H), 4.99 (d, J=8.3 Hz, 1H), 7.25–7.60 (m, 8H), 7.92–7.99 (m, 2H). IR (neat) 3440, 3035, 1690, 1605, 1585, 1505, 1460, 1225, 980, 755, 710 cm^{-1}. The spectral data are in accordance with those in the literature.[12]

4.1.18. 2-(1-Hydroxybenzyl)cyclohexanone. To a solution of titanium tetraiodide (135.5 mg, 0.244 mmol) in propionitrile (1.0 mL) was added a solution (1.0 M in $\mathrm{CH_2Cl_2}$) of borontrifluoride etherate (0.31 mL, 0.31 mmol) at −78°C under argon atmosphere. To the mixture was added a solution of benzaldehyde (32.4 mg, 0.305 mmol) in propionitrile (1.0 mL). To the reaction mixture was added a solution of iodoacetophenone (50.0 mg, 0.203 mmol) in propionitrile (1.0 mL) at −78°C. After being stirred at −78 to −60°C, the reaction was quenched with sat. aqueous $\mathrm{NaHCO_3}$, and 10% $\mathrm{NaHSO_3}$. The mixture was filtered through a Celite pad and extracted with ethyl acetate (10 mL×3). The combined organic extracts were dried over anhydrous sodium sulfate and concentrated in vacuo. Purification by preparative TLC on silica gel (*n*-hexane/ethyl acetate=10:1) gave the title compound (33.0 mg, 80%).

anti Isomer; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.22–1.81 (m, 5H), 2.05–2.13 (m, 1H), 2.30–2.67 (m, 3H), 3.96 (d, J=3.0 Hz, 1H), 4.78 (dd, J=2.6, 8.9 Hz, 1H), 7.27–7.39 (m, 5H). IR (neat) 3470, 1700, 1460, 1135, 700 cm^{-1}. The spectral data are in accordance with those in the literature.[10]

syn Isomer; ^{1}H NMR ($\mathrm{CDCl_3}$) δ 1.46–1.88 (m,5H), 2.05–2.12 (m, 1H), 2.31–2.64 (m, 3H), 3.03 (d, J=3.3 Hz, 1H), 5.38–5.40 (m, 1H), 7.22–7.38 (m, 5H). IR (neat) 3470, 1700, 1460, 1135, 700 cm^{-1}. The spectral data are in accordance with those in the literature.[10]

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References

1. Fürstner, A. *Synthesis* **1989**, 571 and references cited therein.
2. (a) Rathke, M. W.; Weipert, P. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp. 277–299 and references cited therein. (b) Kim, B. M.; Williams, S. F.; Masamune, S. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 2, pp. 268–275 and references cited therein. (c) Harada, T.; Mukaiyama, T. *Chem. Lett.* **1982**, *161*, 467. (d) Orsini, F. *J. Org. Chem.* **1997**, *62*, 1159. (e) Dubois, J.-E.; Axiotis, G.; Bertounesque, E. *Tetrahedron Lett.* **1985**, *26*, 4371. (f) Krief, A.; Laval, A.-M. *Chem. Rev.* **1999**, *99*, 745 and references cited therein.
3. (a) Lin, R.; Chen, L.; Zhang, Y. *Youji Huaxue* **1990**, *10*, 454. (b) Zhang, S. *Youji Huaxue* **1997**, *17*, 319.
4. (a) Tsuritani, T.; Ito, S.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1997**, *65*, 5066. (b) Maeda, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1998**, *63*, 4558.
5. (a) Hayakawa, R.; Shimizu, M. *Chem. Lett.* **2000**, 724. (b) Hayakawa, R.; Sahara, T.; Shimizu, M. *Tetrahedron Lett.* **2000**, *41*, 7939. (c) Hayakawa, R.; Shimizu, M. *Org. Lett.* **2000**, *2*, 4079. (d) Shimizu, M.; Shibuya, K.; Hayakawa, R. *Synlett* **2000**, 1437.
6. (a) Frtas, M.; Seebach, D. *Helv. Chim. Acta* **1985**, *68*, 961. (b) Jeffery, E. A.; Meisters, A.; Mole, T. *J. Organomet. Chem.* **1974**, *74*, 365 see also p 373.
7. Borah, H. N.; Boruah, R. C.; Sandhu, J. S. *J. Chem. Soc., Chem. Commun.* **1991**, 154.
8. House, H. O.; Crumrine, D. S.; Teranishi, A. Y.; Olmstead, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 3310.
9. Matsubara, S.; Tsuboniwa, N.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Bull. Chem. Soc. Jpn* **1984**, *57*, 3242.
10. Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *103*, 7503.
11. Gaudemar-Bardone, F.; Gaudemar, M. *J. Organomet. Chem.* **1976**, *104*, 281.
12. Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099.