Journal of Organometallic Chemistry, 352 (1988) 223–238
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Crossed aldol-type reactions catalyzed by rhodium complexes

Susumu Sato, Isamu Matsuda *, and Yusuke Izumi

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464 (Japan)

(Received February 13th, 1988)

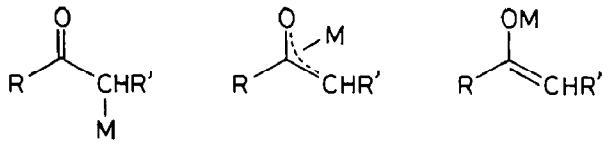
Abstract

Crossed aldol-type reactions of enol trimethylsilyl ethers with aldehydes and ketones are smooth when carried out with a catalytic amount of a rhodium complex, $Rh_4(CO)_{12}$ or [Rh(COD)(DPPB)]X (X = PF_6 and ClO_4; COD = cycloocta-1,5-diene, DPPB = 1,4-bis(diphenylphosphino)butane), under neutral conditions. A suitable catalyst enables the isolation of three different types of aldol reaction product, β-trimethylsiloxy ketones, β-hydroxy ketones, and α,β-unsaturated ketones. $Rh_4(CO)_{12}$ and [Rh(COD)(DPPB)]ClO_4 also catalyze the reaction of enol trimethylsilyl ethers with acetals or ketals, whereas [Rh(COD)(DPPB)]PF_6 does not. When [Rh(COD)(DPPB)]ClO_4 is used as the catalyst, this type of aldol reaction is extended to the one-pot synthesis of trisubstituted furans from enol trimethylsilyl ether and α-trimethylsiloxy acetal.

Introduction

The generation and reactions of organo-transition metal enolates have witnessed burgeoning interest in organic synthesis. Oxygen-bound early transition-metal enolates (type **3**, M = Ti, Zr), in particular, have been generated in situ and have found use in controlling the stereochemistry in aldol reactions with aldehydes [1–3].

On the other hand, there is extremely little fundamental information on



1 2 3

Fig. 1.

0022-328X/88/$03.50 © 1988 Elsevier Sequoia S.A.

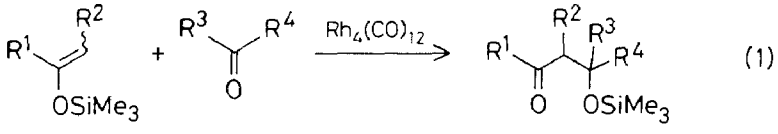
carbon–carbon bond formation reactions mediated by late transition-metal enolates. Although several relatively stable carbon-bound transition-metal (type **1**, M = Co, Rh, Ir, Mo, W, Re) were generated and isolated [4–8], they were unable to induce the subsequent carbon–carbon bond formation, except when the conversion to η^3-enolates (type **2**) was possible [7,9].

Recently, we demonstrated that the rhodium(I) hydride complex $RhH(PPh_3)_4$ is an efficient catalyst in the coupling reaction of vinyl ketones with aldehydes [10]. The reaction proceeds via the intermediacy of rhodium enolates (type **2** or **3**) which are formed by a Michael type interaction of Rh–H with vinyl ketones [10,11]. The promising use of rhodium enolates for carbon–carbon bond formations has encouraged us to look for general enolate sources. With this objective in mind we report here rhodium catalyzed aldol-type reactions of enol trimethylsilyl ethers with aldehydes, ketones, acetals, ketals, and orthoesters under almost neutral conditions.

Results and discussion

Reaction of enol trimethylsilyl ethers with aldehydes

2-(Trimethylsiloxy)propene (**4a**) was treated with hexanal at 100 °C in the presence of 2 mol% of $Rh_4(CO)_{12}$ to give 4-trimethylsiloxy-2-nonanone (**5a**) as the sole product in 71% yield. Neither protodesilylation nor dehydration was observed in **5a** under the reaction conditions. The structure of **5a** was confirmed by the presence of ν(C=O) absorption at 1715 cm^{-1} in the IR spectrum, by the two sharp singlets (δ 0.10, Me_3Si, and 2.16, $COCH_3$) and two multiplets (δ 2.55, $MeCOCH_2$, and 4.15, $SiOCH$) showing an ABX spin coupling pattern in the ^1H NMR spectrum, and by the elemental analysis. Although this reaction is a well-known aldol coupling, it should be noted that the reaction of enol trimethylsilyl ether with aldehyde was catalyzed by $Rh_4(CO)_{12}$ in the absence of acid or base. Other enol trimethylsilyl ethers **4** reacted analogously with several aldehydes and ketones as shown in eq. 1. The results are listed in Table 1.



(1)

4 5

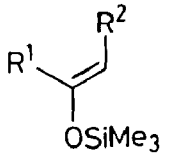
In all cases β-trimethylsiloxyalkanones (**5**) were obtained as the sole product, with concomitant recovery of starting materials. Yields of **5** were not improved by longer reaction times because the catalyst decomposed to form a black precipitate. Shorter reaction times (entry 3, Table 1) or lower reaction temperatures (entry 2, Table 1) decreased the yields of **5**.

The aldol reactions of **4a** with ketones (entries 12, 13, 14, 15, Table 1) gave relatively low yields of **5**. 1-(Trimethylsiloxy)cyclohexene (**4e**) did not react with acetone at all (entry 16, Table 1). These results imply that the steric congestion around both coupling sites becomes a serious inhibiting factor in the rhodium-catalyzed aldol reactions.

Although it has been reported that the reaction of enol silyl ethers with aldehydes proceeded under neutral conditions by use of a high-pressure technique (10 kbar) [12], the reaction of **4a** with hexanal did not give aldol-type product in the absence of $Rh_4(CO)_{12}$ under the usual conditions (100 °C, 25 h, in a sealed tube). An

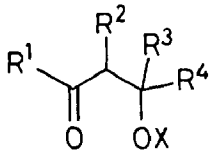
analogous reaction was completely inhibited even in the presence of $Rh_4(CO)_{12}$ when one equivalent of 1,4-bis(diphenylphosphino)butane (DPPB) or triethylamine was added. Several other neutral complexes, $RhH(PPh_3)_4$, $RhH(PPh_3)_3$, $RuHCl(PPh_3)_3$, $RuH_4(PPh_3)_3$, $PdCl_2(CH_3CN)_2$, and $Ru_3(CO)_{12}$ showed no catalytic activity in analogous reactions.

The cationic complex [Rh(COD)(DPPB)]X (X = PF_6, BF_4, and ClO_4) is an alternative choice of catalyst for the aldol reaction between **4** and aldehydes. Thus, a reaction of **4a** (2 mmol) with hexanal (2.2 mmol) was catalyzed by 2 mol% of [Rh(COD)(DPPB)]PF_6 to give a mixture of two aldol-type products, 4-trimethylsiloxy-2-nonanone (**5a**) (45%), and its protodesilylated product, 4-hydroxy-2-nonanone (**6a**), in 27% (eq. 2). The presence of triethylamine (equimolar to Rh) had very



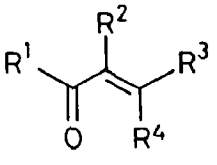
4

4a : R^1 = Me, R^2 = H
4b : R^1 = Ph, R^2 = H
4c : R^1 = Et, R^2 = Me
4d : R^1 = Ph, R^2 = Me
4e : R^1, R^2 = $-(CH_2)_4-$



5 : X = $SiMe_3$
6 : X = H
8 : X = Me

	R^1	R^2	R^3	R^4
a	Me	H	n-C_5H_{11}	H
b	Me	H	n-C_7H_{15}	H
c	Me	H	Cyclohexyl	H
d	Me	H	Ph	H
e	Ph	H	n-C_5H_{11}	H
f	Ph	H	Ph	H
g	Et	Me	Et	H
h	Et	Me	n-C_5H_{11}	H
i	Et	Me	Ph	H
j	Ph	Me	Ph	H
k	$-(CH_2)_4-$		n-C_5H_{11}	H
l	$-(CH_2)_4-$		Cyclohexyl	H
m	$-(CH_2)_4-$		Ph	H
n	Me	H	Me	Me
o	Me	H	n-C_6H_{13}	Me
p	Me	H	$-(CH_2)_5-$	
q	Me	H	Ph	Me
r	Ph	H	Me	Me
s	$-(CH_2)_4-$		Me	Me
t	Me	Me	H	OMe
u	$-(CH_2)_4-$		H	OMe



7

Scheme 1

Table 1

Aldol reactions of **4** with aldehydes and ketones catalyzed by $Rh_4(CO)_{12}$

Entry	Enol silyl ether			Carbonyl compound		Conditions (°C/h)	Product **5**	Yield [a] (%)	*Syn*/*Anti* [b]
	4	R^1	R^2	R^3	R^4				
1	**4a**	Me	H	n-C_5H_{11}	H	100/21	**5a**	71	
2	**4a**	Me	H	n-C_5H_{11}	H	40/23	**5a**	0	
3	**4a**	Me	H	n-C_5H_{11}	H	100/2	**5a**	57	
4	**4a**	Me	H	Cyclohexyl	H	100/20	**5c**	35	
5	**4a**	Me	H	Ph	H	100/16	**5d**	61	
6	**4c** [c]	Et	Me	n-C_5H_{11}	H	100/19	**5h**	71	54/46
7	**4c** [d]	Et	Me	n-C_5H_{11}	H	100/45	**5h**	63	50/50
8	**4c** [e]	Et	Me	Ph	H	100/19	**5i**	54	50/50
9	**4e**	$(CH_2)_4$		n-C_5H_{11}	H	100/21	**5k**	71	56/44
10	**4e**	$(CH_2)_4$		Cyclohexyl	H	100/18	**5l**	52	56/44
11	**4e**	$(CH_2)_4$		Ph	H	100/17	**5m**	83	56/44
12	**4a**	Me	H	Me	Me	100/40	**5n**	43	
13	**4a**	Me	H	n-C_6H_{13}	Me	100/66	**5o**	22	
14	**4a**	Me	H	$(CH_2)_5$	Me	100/94	**5p**	35	
15	**4a**	Me	H	Ph	Me	100/69	**5q**	23	
16	**4e**	$(CH_2)_4$		Me	Me	100/36	**5s**	0	

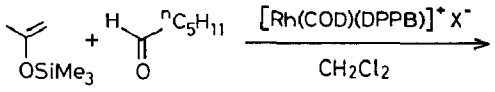
[a] Isolated yield. [b] Determined by GLC analysis. [c] $E/Z = 83/17$. [d] $E/Z = 10/90$. [e] $E/Z = 22/78$.

Table 2

Aldol reactions of 4 with aldehydes catalyzed by [Rh(COD)(DPPB)]X.

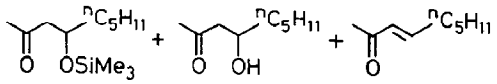
Entry	Enol silyl etheri			Aldehyde R^3	Conditions (°C/h)	Yield (%)			
	4	R^1	R^2			X = PF_6		X = ClO_4	
						6	7	6	7
1	4a	Me	H	n-C_5H_{11}	100/15	66	0	0	77
2	4a	Me	H	n-C_5H_{11}	100/0.25	12	0	74	0
3	4a	Me	H	n-C_5H_{11}	40/20	7	0	70	0
4	4a	Me	H	Cyclohexyl	100/18	20	0	25	0
5	4b	Ph	H	n-C_5H_{11}	100/15	53	0	0	26
6	4b	Ph	H	n-C_5H_{11}	100/0.25	–	–	5	25
7	4c	Et	Me	Et	100/15	0	0	0	22
8	4c	Et	Me	Ph	100/25	–	–	20	0
9	4e	$(CH_2)_4$		n-C_5H_{11}	100/15	19	0	0	0

little effect on the yield and the selectivity of the aldol type products in the reaction of **4a** with hexanal. This point is very different from the case of $Rh_4(CO)_{12}$.



4a

(2)



5a 6a 7a

Pure **6a** was obtained in 66% yield after the crude products were protodesilylated by a mixture of n-Bu_4NF/MeOH/THF. When [Rh(COD)(DPPB)]BF_4 was used as a catalyst **5a** was obtained in 9% yield. In sharp contrast to [Rh(COD)(DPPB)]BF_4, the cationic complex [Rh(COD)(DPPB)]ClO_4 catalyzed the aldol reactions more effectively than [Rh(COD)(DPPB)]PF_6 (entries 2 and 3, Table 2); however, the content of **5a** was considerably decreased because of the protodesilylation which gave **6a** under the reaction conditions. Moreover, dehydration of **6a** was effected under forcing conditions to give 3-nonen-2-one (**7a**) as the sole product (entry 1, Table 2). The results are listed in Table 2.

It is apparent from the above results that the catalytic efficiency in aldol reactions largely depends on the anionic part of [Rh(COD)(DPPB)]X. However, analogous complexes [Rh(COD)(DPPE)]PF_6, [Rh(COD)$(PPh_3)_2$]PF_6, [Ir(COD)-(DPPB)]PF_6, and [Ir(COD)$(PMePh_2)_2$]PF_6 did not catalyze aldol reactions.

Reactions of enol trimethylsilyl ethers with acetals

Although $Rh_4(CO)_{12}$ and [Rh(COD)(DPPB)]X are effective catalysts in aldol-type homologations, the role of rhodium metal was not clear. Use of different electrophiles was suggested to throw light on how the substrates are activated by the catalyst. Thus, a benzene solution of **4a** (1.2 mmol) and dimethoxyphenylmethane (1.0 mmol) was heated at 100 °C for 15 h in a sealed tube containing a catalytic amount of $Rh_4(CO)_{12}$ (2 mol% relative to Rh atom). Purification of the reaction

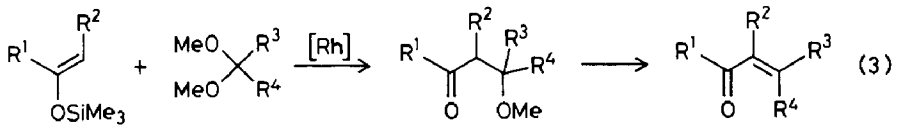
Table 3

Aldol-type reactions of **4** with acetals, ketals, and orthoesters catalyzed by rhodium complexes

Entry	Enol silyl ether			Acetals		Catalyst [a]	Conditions (°C/h)	Yield (%) [b]		*Syn/Anti* [c]
	4	R^1	R^2	R^3	R^4			**8**	**7**	
1	**4a**	Me	H	n-C_7H_{15}	H	A	100/16	46	0	
2	**4a**	Me	H	n-C_7H_{15}	H	B	100/16	0	49	
3	**4a**	Me	H	Ph	H	A	100/15	58	0	
4	**4a**	Me	H	Ph	H	B	100/16	0	58	
5	**4a**	Me	H	Ph	H	A	20/44	0	0	
6	**4a**	Me	H	Ph	H	B	20/42	58	0	
7	**4a**	Me	H	PhCH=CH	H	A	100/19	0	0	
8	**4b**	Ph	H	Ph	H	B	20/39	47	0	
9	**4c**	Et	Me [d]	Ph	H	A	100/17	61	0	51/49
10	**4d**	Ph	Me	Ph	H	A	100/15	80	0	54/46
11	**4e**	$(CH_2)_4$		Ph	H	A	100/9	55	0	65/35
12	**4a**	Me	H	Me	Me	A	100/17	32	0	
13	**4a**	Me	H	n-C_6H_{13}	Me	A	100/19	79	0	
14	**4a**	Me	H	n-C_6H_{13}	Me	B	100/17	0	trace	
15	**4b**	Ph	H	Me	Me	A	100/15	74	14	
16	**4e**	$(CH_2)_4$		Me	Me	A	100/17	15	0	
17	**4a**	Me	H	H	OMe	A	100/18	48	0	
18	**4a**	Me	H	Me	OMe	A	100/15	0	0	
19	**4e**	$(CH_2)_4$		H	OMe	A	100/16	79	0	
20	**4e**	$(CH_2)_4$		Me	OMe	A	100/20	0	0	

[a] A: $Rh_4(CO)_{12}$ (2 mol% based on Rh), B: [Rh(COD)(DPPB)]ClO_4 (2 mol%). [b] Isolated yield. [c] Determined by GLC analysis. [d] $E/Z = 22/78$.

mixture by column chromatography on silica gel gave the aldol adduct, 4-methoxy-4-phenyl-2-butanone (**8d**), in 58% yield as the sole product (eq. 3). Prolonged reaction at 100 °C caused the β-elimination of methanol from **8d** to give a mixture of **8d** and benzylideneacetone (**7d**) (**8d** and **7d** were obtained in 33 and 24% yields, respectively, after reaction for 47 h). Coupling of enol trimethylsilyl ethers with acetals, ketals, or methyl orthoformate was analogously catalyzed by $Rh_4(CO)_{12}$ to give **8** in moderate to good yield within a limited reaction time. In this case steric congestion around the coupling sites affects the product formation as is the case for the reaction of enol silyl ethers with aldehydes. The reaction of 1-(trimethylsiloxy)cyclohexene (**4e**) with 2,2-dimethoxypropane gave **8** in poor yield (entry 16, Table 3). Trimethoxymethane reacts readily with **4** to give β,β-dimethoxyalkanone (entries 17 and 19, Table 3); however, 1,1,1-trimethoxyethane was found to gave no aldol-type products (entries 18 and 20, Table 3).



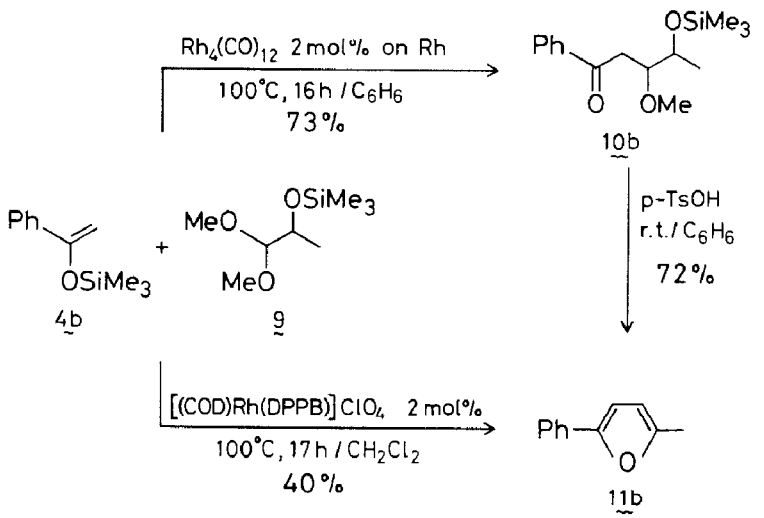
4 8 7

On the other hand, when [Rh(COD)(DPPB)]ClO_4 was used as the catalyst, **7d** was obtained selectively in the reaction of **4a** with dimethoxyphenylmethane. The subsequent β-elimination of MeOH from **8** was suppressed by lowering the reaction temperature to 25 °C. However, the analogous cationic complex [Rh(COD)(DPPB)]-PF_6 showed no catalytic activity in the present homologation, in contrast to the reaction between enol silyl ethers and aldehydes described above. These results are listed in Table 3.

Although satisfactory diastereoselectivity was not observed in the present rhodium catalyzed aldol-type reaction (Tables 1 and 3), rhodium complexes can catalyze this type of carbon–carbon bond formation. It is noteworthy that [Rh(COD)(DPPB)]-ClO_4 catalyzes the reaction of **4a** or **4b** with dimethoxyphenylmethane even at room temperature to give **8d** or **8f** without β-elimination (entries 6 and 8, Table 3). Therefore, a catalytic route to enantioselective aldol addition becomes possible once a chiral rhodium complex is introduced. Unsatisfactory results have been described recently [13].

The trimethylsilyl group of **5** remains intact after the aldol-type homologation catalyzed by $Rh_4(CO)_{12}$. This is in contrast to the reaction in which [Rh(COD)(DPPB)]X is used as catalyst because it is accompanied by protodesilylation and dehydration to give **6** and **7**. This finding suggests that aldol reaction of polyfunctionalized materials can be controlled at the different stages only by use of a selected rhodium catalyst. For example, the reaction of α-trimethylsiloxystyrene (**4b**) with an equivalent of 1,1-dimethoxy-2-trimethylsiloxypropane (**9**) proceeds smoothly with $Rh_4(CO)_{12}$ as catalyst to give **10b** in 73% yield. This method offers a facile route to 1,2,4-trioxygenated compounds bearing differently protected hydroxy groups.

On the other hand, 5-methyl-2-phenylfuran (**11b**) was obtained directly in 40% yield when [Rh(COD)(DPPB)]ClO_4 was used as catalyst in the reaction of **4b** with **9**.

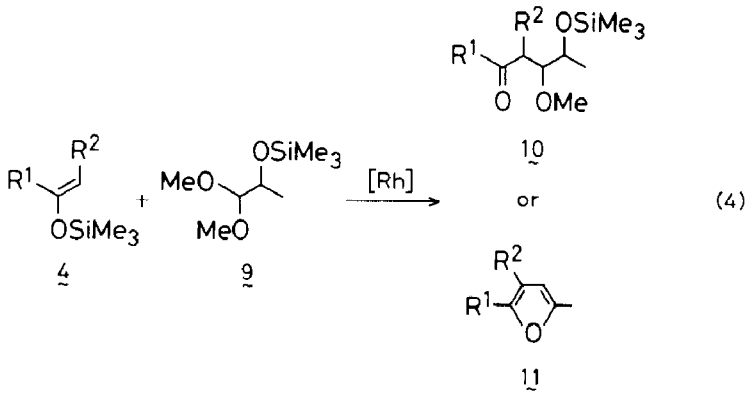


Scheme 2

The formation of **11b** is the result of a multi-step conversion of which one step is an aldol-type reaction [14]. In fact, the isolated aldol adduct **10b** was cyclized to 2,5-disubstituted furan (**11b**) in 72% yield by action of a catalytic amount of *p*-toluenesulfonic acid (Scheme 2).

Although yields are not very high, there is a wide choice of catalysts for use in the present rhodium-catalyzed synthesis of furan derivatives. Some results of the reactions between enol trimethylsilyl ethers and **9** are shown in Table 4.

Since several attempts to isolate the intermediate of the rhodium-catalyzed aldol reaction were fruitless, the precise role of the rhodium complex has become no clearer. However, the catalytic cycle of the present aldol coupling can be explained in terms of the putative intermediacy of rhodium enolates. The intervention of analogous enolates have been postulated in the isomerization of β-trimethylsilyl allyl alcohols to give α-trimethylsilyl ketones [11] and the coupling of vinyl ketones with aldehydes [10]. Further study is now in progress.



(4)

Experimental

All reactions were carried out under argon or nitrogen. Boiling points are the bath temperatures for bulb-to-bulb distillations. IR spectra were recorded on a JASCO IRA-2 spectrometer. Proton NMR spectra were recorded with a HITACHI R-600 instrument using tetramethylsilane as an internal standard. Dry solvents were distilled under dry N_2 and degassed in vacuum just before use: benzene was distilled from sodium metal, and dichloromethane was distilled from phosphorus pentoxide.

Dodecacarbonyltetrarhodium [15], cycloocta-1,5-diene[1,4-bis(diphenylphosphino)butane]rhodium hexafluorophosphate [16], cycloocta-1,5-diene[1,4-bis(diphenylphosphino)butane]rhodium perchlorate [17], and enol trimethylsilyl ethers [18] were prepared by published procedures. Aldehydes, ketones, acetals, ketals and orthoesters were purchased from Tokyo Kasei Chemicals and distilled before use.

Aldol-type reactions catalyzed by rhodium complexes

Procedures for **5a**, **6a**, **7a** and **8d** are described as typical examples. The data of **5**, **6**, **7**, and **8** are summarized in Tables 1, 2, 3, 5, 6, 7, 8, and 11.

4-Trimethylsiloxy-2-nonanone (5a). A solution of 150 mg (0.87 mmol) of **4a** in benzene (1 ml), 87 mg (1.16 mmol) of hexanal, and 2.7 mg (0.0036 mmol) of $Rh_4(CO)_{12}$ was placed in a 10-mm ∅ Pyrex tube, under argon. The tube was sealed and heated at 100 °C in an oil bath for 21 h. The resulting yellow solution was concentrated under reduced pressure, and subsequent bulb-to-bulb distillation gave 142 mg (71%) of **5a** as a colorless oil.

4-Hydroxy-2-nonanone (6a). A solution of 267 mg (2.05 mmol) of **4a** in dichloromethane (1 ml), 159 mg (1.59 mmol) of hexanal, and 30 mg (0.039 mmol) of [Rh(COD)(DPPB)]PF_6 was placed in a 10-mm ∅ Pyrex tube, under argon. The tube was sealed and heated at 100 °C in an oil bath for 15 h. The resulting brown solution was concentrated under reduced pressure and diluted with hexane (15 ml) to give a yellow precipitate. After filtration of the solution, the filtrate was concentrated under reduced pressure to give a crude mixture of **5a** and **6a** (**5a**/**6a** = 64/36, determined by ^1H NMR). This yellow oil was diluted with MeOH (10 ml) and a THF solution of n-Bu_4NF (1 *M*, 0.2 ml) was added to the resulting solution. The reaction mixture was stirred for 45 min at room temperature and concentrated under reduced pressure. The resulting oil was diluted with diethyl ether (10 ml) and

Table 4

Aldol-type reactions of **4** with **9** catalyzed by rhodium complexes

Entry	4	R^1	R^2	Catalyst (°C/h)	Conditions	Product (%)	Yield [a]
1	**4b**	Ph	H	$Rh_4(CO)_{12}$	100/14	**10b**	73
2	**4c** [b]	Et	Me	$Rh_4(CO)_{12}$	100/15	**10c**	86
3	**4e**	$(CH_2)_4$		$Rh_4(CO)_{12}$	100/42	**10e**	18
4	**4b**	Ph	H	[Rh(COD)(DPPB)]ClO_4	100/17	**11b**	40
5	**4c**	Et	Me	[Rh(COD)(DPPB)]ClO_4	100/19	**11c**	32
6	**4d**	Ph	Me	[Rh(COD)(DPPB)]ClO_4	100/16	**11d**	24
7	**4e**	$(CH_2)_4$		[Rh(COD)(DPPB)]ClO_4	100/42	**11e**	2

[a] Isolated yield. [b] $E/Z = 22/78$.

washed with brine (3 × 15 ml). The organic phase was separated, dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and submitted to subsequent bulb-to-bulb distillation to give 166 mg (66%) of **6a** as a colorless oil.

3-Nonen-2-one (7a). A solution of 170 mg (1.31 mmol) of in **4a** dichloromethane (1.5 ml), 151 mg (1.51 mmol) of hexanal, and 10 mg (0.014 mmol) of [Rh(COD)(DPPB)]ClO_4 was placed in a 10-mm ∅ Pyrex tube, under argon. The tube was sealed and heated at 100 °C in an oil bath for 15 h. The resulting brown solution was concentrated under reduced pressure and diluted with hexane (15 ml) to give a yellow precipitate. After filtration of the solution, the filtrate was concentrated under reduced pressure, and subsequent bulb-to-bulb distillation gave 141 mg (77%) of **7a** as a colorless oil.

4-Methoxy-4-phenyl-2-butanone (8d). (a) A solution of 164 mg (1.25 mmol) of **4a** in benzene (1.5 ml), 133 mg (0.87 mmol) of dimethoxyphenylmethane, and 2.4 mg (0.0032 mmol) of $Rh_4(CO)_{12}$ was placed in a 10-mm ∅ Pyrex tube, under argon. The tube was sealed and heated at 100 °C in an oil bath for 15 h. The resulting yellow solution was concentrated under reduced pressure and the unchanged acetal was removed by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate, 90/10) as an eluent. Subsequent bulb-to-bulb distillation gave 89 mg (58%) of **8d** as a colorless oil.

(b) A solution of 213 mg (1.64 mmol) of **4a** in dichloromethane (6 ml), 197 mg (1.30 mmol) of dimethoxyphenylmethane, and 28 mg (0.038 mmol) of [Rh(COD)(DPPB)]ClO_4 was stirred for 42 h under nitrogen at room temperature. The resulting yellow solution was diluted with hexane (30 ml) and the precipitated yellow solid was removed by filtration. The filtrate was concentrated under reduced pressure and submitted to subsequent bulb-to-bulb distillation to give 134 mg (0.75 mmol) of **8d** as a colorless oil.

Table 5

Spectral data of **5**

Entry	5	B.p. (°C/Torr)	IR (CCl_4)		^{1}H NMR ($CDCl_3$) [a]		
			ν(C=O) (cm^{-1})	$\delta(SiMe_3)$	$SiMe_3$	(C=O)C*H*	SiOC*H*
1	**5a**	100/0.6	1715	1238	0.10(s, 9H)	2.55(m, 2H)	4.15(m, 1H)
2	**5c**	117/0.6	1715	1240	0.08(s, 9H)	2.55(m, 2H)	3.96(m, 1H)
3	**5d**	115/0.6	1710	1238	0.00(s, 9H)	2.80(m, 2H)	5.16(m, 1H)
4	**5h**	130/0.6	1719	1242	0.06(s, 4.5H) 0.11(s, 4.5H)	2.2–3.0(m, 1H)	3.7–4.1(m, 1H)
5	**5i**	133/0.6	1712	1240	0.00(s, 4.5H) 0.10(s, 4.5H)	2.5–3.3(m, 1H)	4.73(d, *J* 9.5 Hz, 0.5H) 4.88(d, *J* 7.1 Hz, 0.5H)
6	**5k**	145/2	1705	1243	0.10(s, 9H)	[b]	4.15(m, 1H)
7	**5l**	148/0.6	1710	1241	0.08(s, 9H)	[b]	3.95(m, 1H)
8	**5m**	137/0.6	1700	1240	0.00(s, 4.5H) 0.06(s, 4.5H)	[b]	5.10(d, *J* 8.2 Hz, 0.5H) 5.37(d, *J* 4.7 Hz, 0.5H)
9	**5n**	100/4	1702	1242	0.11(s, 9H)	2.53(s, 3H)	
10	**5o**	125/0.6	1705	1242	0.12(s, 9H)	2.54(d, *J* 4.2 Hz, 2H)	
11	**5p**	107/0.6	1709	1243	0.12(s, 9H)	2.60(s, 2H)	–
12	**5q**	150/0.6	1704	1245	0.09(s, 9H)	2.83(d, *J* 5.8 Hz, 2H)	

[a] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25 °C. [b] Indistinguishable.

Preparation of 1,1-dimethoxy-2-trimethylsiloxypropane (9). To a solution of 23.7 g (200 mmol) of 1,1-dimethoxy-2-propanone in MeOH (40 ml) was added slowly 2.6 g (68.8 mmol) of sodium borohydride at 0 °C. After the mixture had been quenched with water (10 ml), the resulting mixture was extracted with CH_2Cl_2 (5 × 40 ml), and the organic portion was dried over anhydrous $MgSO_4$. Concentration of the solution under reduced pressure gave 17 g (71%) of crude 1,1-dimethoxy-2-propanol as a colorless oil. IR (CCl_4): 3620 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): 1.18 (d, *J* 6.6 Hz, 3H, CC*H*$_3$), 2.72 (broad s, 1H, O*H*), 3.40 (s, 3H, OC*H*$_3$), 3.44 (s, 3H, OCH$_3$), 3.83 (q, *J* 6.6 Hz, 1H, OC*H*C), 4.07 (d, *J* 6.6 Hz, 1H, OC*H*O).

A diethyl ether (100 ml) solution of 10.1 g (100 mmol) of triethylamine, 8.7 g (80 mmol) of chlorotrimethylsilane, and 9.6 g (80 mmol) of the crude alcohol obtained, 1,1-dimethoxy-2-propanol, was stirred for 12 h at room temperature. The resulting mixture was poured into aqueous $NaHCO_3$ (200 ml) containing crushed ice and washed with cold aqueous $NaHCO_3$ (5 × 100 ml). The organic portion was dried over anhydrous $MgSO_4$ and distilled under reduced pressure to give 11.7 g (76%) of **9** as a colorless oil. B.p.: 84 °C/52 Torr. IR(CCl_4): 1242 (SiC) cm^{-1}. ^1H NMR($CDCl_3$): 0.11 (s, 9H, *H*$_3$CSi), 1.15 (d, *J* 6.2 Hz, 3H, CC*H*$_3$), 3.42 (s, 3H, OC*H*$_3$), 3.85 (q, *J* = 6.2 Hz, 1H, OC*H*C), 4.04 (d, *J* 6.2 Hz, 1H, OC*H*O).

Table 6

Spectral data of **6**

Entry	**6**	B.p. (°C/Torr)	IR (CCl_4)		^1H NMR ($CDCl_3$) [a]	
			ν(O–H) (cm^{-1})	ν(C=O)	(C=O)C*H*	C*H*–OH
1	**6a**	120/2	3570	1708	2.45(m, 2H)	4.00(m, 1H)
2	**6c**	102/0.6	3580	1711	2.61(m, 2H)	3.78(m, 1H)
3	**6e**	142/0.6	3600	1680	3.02(m, 2H)	4.25(m, 1H)
4	**6i**	115/0.6	3610	1712	2.8–3.4(m, 1H)	4.66(d, *J* 8.0 Hz, 0.5H) 5.01(d, *J* 4.4 Hz, 0.5H)
5	**6k**	110/0.6	3570	1700	[b]	3.9–4.3(m, 1H)

[a] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25 °C. [b] Indistinguishable.

Table 7

Spectral data of **7**

Entry	**7**	B.p. (°C/Torr)	IR (CCl_4)		^1H NMR ($CDCl_3$) [a]	
			ν(C=O) (cm^{-1})	ν(C=C) (cm^{-1})	(C=O)C*H*=	(C=O)CH=C*H*–
1	**7a**	92/2	1680	1630	6.01(d, *J* 16.0 Hz, 1H)	6.68(d of t, *J* 16.4, 7.0 Hz, 1H)
2	**7b**	98/2	1680	1630	6.09(d, *J* 16.4 Hz, 1H)	6.87(d of t, *J* 16.4, 7.0 Hz, 1H)
3	**7d**	80/2	1678	1590	7.27(d, *J* 17.1 Hz, 1H)	7.91(d, *J* 17.1 Hz, 1H)
4	**7e**	122/0.6	1680	1600	6.6–7.4(m, 2H) [b]	
5	**7g**	77/20	1692	1640	–	6.50(6, *J* 7.4 Hz, 0.5 H) 6.61(t, *J* 7.4 Hz, 0.5H)
6	**7r**	102/06	1675	1600	6.78(broad m, 1H)	–

[a] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25 °C. [b] Indistinguishable.

Aldol reaction of ***4*** *with* ***9***

Procedures for **10b** and **11b** are described as typical examples. The data of **10** and **11** are listed in Tables 4, 9, 10, and 11.

*3-Methoxy-1-phenyl-4-trimethylsiloxy-1-pentanone (**10b**).* A solution of 126 mg (0.66 mmol) of **4b** in benzene (1.5 ml), 108 mg (0.56 mmol) of **9**, and 4.0 mg (0.0054

Table 8

Spectral data of **8**

Entry	8	B.p. (°C/Torr)	IR (CCl_4)	^{1}H NMR ($CDCl_3$) [a]		
			ν(C=O) (cm^{-1})	(C=O)C*H*	OCH_3	MeOC*H*
1	**8b**	90/0.6	1715	2.58(m, 2H)	3.33(s, 3H)	3.70(m, 1H)
2	**8d**	115/0.6	1712	2.75(m, 2H)	3.19(s, 3H)	4.64(m, 1H)
3	**8f**	154/0.6	1689	3.50(m, 2H)	3.26(s, 3H)	4.93(m, 1H)
4	**8i**	122/0.6	1715	[b]	3.11(s, 1.5H)	4.23(d, *J* 10.3 Hz, 0.5H)
					3.23(s, 1.5H)	4.32(d, *J* 7.9 Hz, 0.5H)
5	**8j**	165/0.6	1682	3.6–4.1(m, 1H)	3.11(s, 1.5H)	4.49(d, *J* 8.5 Hz, 0.5H)
					3.23(s, 1.5H)	4.51(d, *J* 11.0 Hz, 0.5H)
6	**8m**	140/0.6	1696			
			(*anti*) [c]	[b]	3.19(s, 3H)	4.53(d, *J* 8.6 Hz, 1H)
			(*syn*)	[b]	3.24(s, 3H)	4.76(d, *J* 4.7 Hz, 1H)
7	**8n**	95/22	1705	2.59(s, 2H)	3.25(s, 3H)	–
8	**8o**	111/0.6	1700	2.57(s, 2H)	3.19(s, 3H)	–
9	**8r**	118/0.6	1685	3.16(s, 2H)	3.25(s, 3H)	–
10	**8s**	100/0.6	1700	[b]	3.14(s, 3H)	–
11	**8t**	85/25	1710	2.76(d, *J* 5.9 Hz, 2H)	3.38(s, 6H)	4.81(t, *J* 5.9 Hz, 1H)
12	**8u**	106/2	1701	[b]	3.41(s, 6H)	4.68(d, *J* 6.3 Hz, 1H)

[a] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25 °C. [b] Indistinguishable. [c] Diastereomers were separated by column chromatography on silica gel.

Table 9

Spectral data of **10** [a]

Entry	10	B.p. (°C/Torr)	IR (CCl_4) (cm^{-1})	^{1}H NMR ($CDCl_3$) [b] (ppm)
1	**10b**	153/0.6	1242($SiCH_3$)	0.10(s, 4.5H, $SiCH_3$)
			1710(C=O)	0.11(s, 4.5H, $SiCH_3$)
				1.19(d, J 6.4 Hz, 3H, CH_3)
				3.0–3.3(m, 2H, (C=O)CH_2)
				3.41(s, 3H, OCH_3)
				3.6–4.2(m, 2H, 2×O–C*H*)
2	**10c**	110/6	1242($SiCH_3$)	0.08-0.12(9H, $SiCH_3$) [c]
			1707(C=O)	2.54(q, *J* 7.2 Hz, 2H, (C=O)CH_2)
				3.36–3.46(3H, OCH_3) [c]
3	**10e**	123/0.6	1240($SiCH_3$)	0.14(s, 4H, $SiCH_3$)
			1700(C=O)	0.18(s, 5H, $SiCH_3$)
				1.22(d, *J* 6.4 Hz, 3H, CH_3)
				3.52(s, 3H, OCH_3)

[a] Diastereomers are not identified. [b] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25 °C. [c] Indistinguishable.

Table 10

Spectral data of **11**

Entry	**11**	B.p. (°C/Torr)	IR (CCl_4) (cm^{-1})	^1H NMR ($CDCl_3$) [a] (ppm)
1	**11b**	120/0.6	1595(C=C)	2.38(d, *J* 0.7 Hz, 3H, CH_3) 6.08(d of d, *J* 3.4, 0.7 Hz, 1H, O-CMe=C*H*) 6.57(d, *J* 3.4 Hz, 1H, O-CPh=C*H*)
2	**11c**	52/80	1600(C=C)	1.17(t, *J* 7.6 Hz, 3H, CH_2CH_3) 1.90(s, 3H, =CCH_3) 2.22(s, 3H, =CCH_3) 2.54(q, *J* 7.6 Hz, 2H, CH_2CH_3) 5.75(s, 1H, =C*H*)
3	**11d**	126/0.6	1596(C=C)	2.22(s, 3H, =CCH_3) 2.32(s, 3H, =CCH_3) 5.94(s, 1H, =C*H*)
4	**11e**	140/20	1602(C=C)	2.26(s, 3H, =CCH_3) 5.79(s, 1H, =C*H*)

[a] Shifts are in ppm, relative to $SiMe_4$ at 60 MHz and 25 °C.

mmol) of $Rh_4(CO)_{12}$ was placed in a 10-mm ∅ Pyrex tube, under argon. The tube was sealed and heated at 100 °C in an oil bath for 14 h, and the resulting yellow solution was concentrated under reduced pressure. The crude product obtained was purified by column chromatography on silica gel using a mixed solvent (hexane/ethyl acetate, 90/10) as an eluent. Subsequent bulb-to-bulb distillation gave 114 mg (73%) of **10b** as a colorless oil.

*5-Methyl-2-phenylfuran (**11b**).* (a) To a solution of 97 mg (0.35 mmol) of **10b** in benzene (5 ml), 14 mg (0.076 mmol) of *p*-toluenesulfonic acid was added at room temperature. The resulting mixture was refluxed for 10 min, diluted with Et_2O (20 ml), and washed with aqueous $NaHCO_3$ (2 × 20 ml) and brine (2 × 20 ml). The organic portion was dried over anhydrous $MgSO_4$ and submitted to bulb-to-bulb distillation to give 37 mg (72%) of **11b** as an orange oil.

(b) A solution of 98 mg (0.51 mmol) of **4b** in dichloromethane (1.5 ml), 94 mg (0.49 mmol) of **9**, and 17 mg (0.024 mmol) of [Rh(COD)(DPPB)]ClO_4 was placed in a 10-mm ∅ Pyrex tube, under argon. The tube was sealed and heated at 100 °C in an oil bath for 17 h. The resulting brown solution was concentrated under reduced pressure and purified by column chromatography on silica gel using hexane as an eluent. Subsequent bulb-to-bulb distillation gave 29 mg (40%) of **11b** as an orange oil.

Table 11

Analytical data

Entry	Compound	Analysis (Found(calcd.)(%))		Formula
		C	H	
1	**5a**	62.39 (62.26)	11.46 (11.37)	$C_{12}H_{26}O_2Si$
2	**5c**	64.53 (64.41)	10.75 (10.81)	$C_{13}H_{26}O_2Si$
3	**5d**	65.95 (66.05)	8.43 (8.53)	$C_{13}H_{20}O_2Si$
4	**5h**	65.22 (65.06)	11.63 (11.70)	$C_{14}H_{30}O_2Si$
5	**5i**	ref. 19		
6	**5k**	66.53 (66.61)	11.26 (11.18)	$C_{15}H_{30}O_2Si$
7	**5l**	68.20 (68.03)	10.93 (10.70)	$C_{16}H_{30}O_2Si$
8	**5m**	ref. 20		
9	**5n**	ref. 21		
10	**5o**	65.20 (65.06)	11.59 (11.70)	$C_{14}H_{30}O_2Si$
11	**5p**	63.03 (63.10)	10.59 (10.59)	$C_{12}H_{24}O_2Si$
12	**5q**	67.22 (67.15)	8.75 (8.86)	$C_{14}H_{22}O_2Si$
13	**6a**	ref. 22		
14	**6c**	70.72 (70.55)	10.61 (10.66)	$C_{10}H_{18}O_2$
15	**6e**	76.45 (76.33)	9.21 (9.15)	$C_{14}H_{20}O_2$
16	**6i**	ref. 23		
17	**6k**	72.55 (72.68)	11.30 (11.18)	$C_{12}H_{22}O_2$
18	**7a**	ref. 23		
19	**7b**	ref. 24		
20	**7e**	73.26 (83.12)	8.99 (8.97)	$C_{14}H_{18}O$
21	**7g**	76.02 (76.14)	11.19 (11.18)	$C_8H_{14}O$
22	**7r**	82.33 (82.46)	7.52 (7.55)	$C_{11}H_{12}O$
23	**8b**	71.88 (71.95)	12.10 (12.08)	$C_{12}H_{24}O_2$
24	**8d**	73.86 (74.13)	8.02 (7.92)	$C_{11}H_{14}O_2$
25	**8f**	79.79 (79.97)	6.68 (6.71)	$C_{16}H_{16}O_2$
26	**8i**	75.58 (75.69)	8.82 (8.80)	$C_{13}H_{18}O_2$
27	**8j**	80.12 (80.28)	7.08 (7.13)	$C_{17}H_{18}O_2$
28	**8m**	77.20 (77.03)	8.33 (8.31)	$C_{14}H_{18}O_2$
29	**8n**	ref. 25		
30	**8o**	72.23 (71.95)	12.30 (12.08)	$C_{12}H_{24}O_2$

Table 11 (continued)

Entry	Compound	Analysis (Found(calcd.)(%))		Formula
		C	H	
31	**8r**	75.11	8.45	$C_{12}H_{16}O_2$
		(74.97)	(8.39)	
32	**8s**	70.43	10.48	$C_{10}H_{18}O_2$
		(70.55)	(10.66)	
33	**8t**	ref. 26		
34	**8u**	ref. 27		
35	**10b**	64.02	8.66	$C_{15}H_{24}O_3Si$
		(64.24)	(8.63)	
36	**10c**	58.31	10.43	$C_{12}H_{26}O_3Si$
		(58.49)	(10.63)	
37	**10e**	60.37	10.23	$C_{13}H_{26}O_3Si$
		(60.42)	(10.14)	
38	**11b**	ref. 28		
39	**11c**	77.54	9.77	$C_8H_{12}O$
		(77.38)	(9.74)	
40	**11d**	83.58	6.97	$C_{12}H_{12}O$
		(83.69)	(7.02)	
41	**11e**	79.16	8.80	$C_9H_{12}O$
		(79.37)	(8.88)	

Acknowledgment

One of us (I. M.) thanks the Ishida Foundation for financial support of part of this work and the Shin-etsu Chemical Co. Ltd. for a gift of chlorotrimethylsilane.

References

1 D.A. Evans and L.A. McGee, Tetrahedron Lett., 21 (1980) 3975.
2 Y. Yamamoto and K. Maruyama, Tetrahedron Lett., 21 (1980) 4607.
3 J.R. Stille and R.H. Grubbs, J. Am. Chem. Soc., 105 (1983) 1664.
4 R.B. Silverman and D. Dolphin, J. Am. Chem. Soc., 98 (1976) 4633.
5 D. Milstein and J.C. Calabrese, J. Am. Chem. Soc., 104 (1982) 3773.
6 D. Milstein, J. Am. Chem. Soc., 104 (1982) 5227.
7 J.J. Doney, R.G. Bergman, and C.H. Heathcock, J. Am. Chem. Soc., 107 (1985) 3724.
8 (a) Y. Aoyama, T. Yoshida, and H. Ogoshi, Tetrahedron Lett., 26 (1985) 6107;
(b) Y. Aoyama, Y. Tanaka, T. Yoshida, H. Toi, and H. Ogoshi, J. Organomet. Chem., 329 (1987) 251.
9 Y. Ito, H. Aoyama, T. Hirao, A. Mochizuki, and T. Saegusa, J. Am. Chem. Soc., 101 (1979) 494.
10 S. Sato, I. Matsuda, and Y. Izumi, Chem. Lett., (1985) 1875.
11 (a) S. Sato, I. Matsuda, and Y. Izumi, Tetrahedron Lett., 24 (1983) 2787.
(b) S. Sato, I. Matsuda, and Y. Izumi, Tetrahedron Lett., 24 (1983) 3855.
(c) S. Sato, I. Matsuda, and Y. Izumi, J. Organomet. Chem., 344 (1988) 71.
12 Y. Yamamoto, K. Maruyama, and K. Katsumoto, J. Am. Chem. Soc., 105 (1983) 6963.
13 M.T. Reetz and A.E. Vougioukas, Tetrahedron Lett., 28 (1987) 793.
14 T. Mukaiyama, H. Ishihara, and K. Inomata, Chem. Lett., (1975) 527.
15 S. Martinengo, P. Chini, and G. Giordano, J. Organomet. Chem., 27 (1971) 389.
16 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 2397.
17 (a) H.O. House, L.J. Czuba, M. Gall, and H.D. Olmstead, J. Org. Chem., 34 (1969) 2324; (b) R.E. Ireland, R.H. Mueller, and A.K. Willard, J. Am. Chem. Soc., 98 (1976) 2868; (c) C.H. Heathcock, S.K. Davidson, K.T. Hug, and L.A. Flippin, J. Org. Chem., 51 (1986) 3027; (d) E. Nakamura, K. Hashimoto, and I. Kuwajima, Tetrahedron Lett., (1978) 2079; (e) I. Matsuda, S. Sato, M. Hattori, and Y. Izumi, ibid., 26 (1985) 3215.

18 E. Nakamura, M. Shimizu, I. Kuwajima, J. Sakata, K. Yokoyama, and R. Noyori, J. Org. Chem., 48 (1983) 932.
19 T. Mukaiyama, K. Banno, and K. Narasaka, J. Am. Chem. Soc., 96 (1974) 7503.
20 D.J. Costa, N.E. Boutin, and J.G. Riess, Tetrahedron, 30 (1974) 3793.
21 E.J. Corey and D. Enders, Chem. Ber., 111 (1978) 1362.
22 C.H. Heathcock, C.T. Buse, W.A. Kleschick, M.C. Pirrung, J.E. Sohn, and J. Lampe, J. Org. Chem., 45 (1980) 1066.
23 A.A. Jaxa-Chamiec, P.G. Sammes, and P.D. Kennewell, J. Chem. Soc., Perkin Trans. 1, (1980) 170.
24 A. Focella, S. Teitel, and A. Brossi, J. Org. Chem., 42 (1977) 3456.
25 T. Sato, G. Izumi, and T. Imamura, J. Chem. Soc., Perkin Trans. 1, (1976) 788.
26 F. Bohlmann and D. Kornig, Chem. Ber., 107 (1974) 1780.
27 W.L. Mock and H-R. Tsou, J. Org. Chem., 46 (1981) 2557.
28 T. Nishio and Y. Omote, J. Chem. Soc., Perkin Trans. 1, (1979) 1703.