ALDOL-TYPE REACTIONS BETWEEN TRIMETHYLSILYL ENOL ETHERS AND ACETALS WITH THE AID OF RHODIUM COMPLEX

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Summary: Aldol-type reactions of trimethylsilyl enol ethers with acetals, ketals, and orthoesters are successfully performed with the aid of a catalytic amount of rhodium complex, $Rh_4(CO)_{12}$ or $[Rh(COD)(DPPB)]^+ClO_4^-$, under neutral conditions.

Despite the current widespread upsurge of interest in the selective reactions catalyzed by rhodium complexes,¹ relatively limited patterns of carbon-carbon bond formation have been reported.^{1,2} Especially there are extremely few rudimentary informations in aldol type coupling mediated by rhodium complexes, though the generation and reactions of early transitionmetal enolates have witnessed the burgeoning interest in the stereocontrolled aldol reactions.³ Recently we have demonstrated that rhodium complexes, Rh₄(CO)₁₂ and [Rh(COD)(DPPB)]⁺X⁻ (X=PF₆ or ClO₄), are efficient catalysts in the aldol-type reaction between silyl enol ethers and aldehydes.⁴ The intermediacy of rhodium enolate is quite important in these reactions. The behavior of rhodium resembles the coupling reaction of vinyl ketone with aldehvde reported previously.⁵ The feasible generation of rhodium enolate from silyl enol ethers, prompts us to reveal the scope of its nucleophilicity from the view-point of rhodium catalyzed carbon-carbon bond formation. In the course of our investigations, we report here the rhodium catalyzed aldoltype reaction of trimethylsilyl enol ethers with acetals, ketals, and orthoesters under neutral conditions.

Thus, a benzene solution of 2-trimethylsiloxypropene (1a) (1.2 mmol) and dimethoxyphenylmethane (2a) (1.0 mmol) was heated at 100° C for 15 h in a sealed tube contained a catalytic amount of $\text{Rh}_4(\text{CO})_{12}$ (2 mol% on Rh atom). After purification of the reaction mixture by a column chromatography on



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silica gel, the aldol-type adduct **3a** was obtained as a sole product in 58 % yield. However, the longer reaction time caused partly the subsequent β -elimination of MeOH from **3a** to give a mixture of **3a** and α,β -unsaturated ketone **4a** (**3a** and **4a** were obtained in 33% and 24% yield, respectively, after the reaction for 47 h). Analogously, Rh₄(CO)₁₂ was an effective catalyst uniformly in a coupling of trimethylsilyl enol ethers with acetals, ketals, or methyl orthoformate to give **3** within the described time in the Tables.

When a cationic complex, $[Rh(COD)(DPPB)]^+ClO_4^ [COD=1,5-cyclooctadiene, DPPB=bis(1,4-diphenylphosphino)butane], was used as a catalyst in <math>CH_2Cl_2$ solution, α,β -unsaturated ketone **4a** was isolated as a sole product under the

Entry	Acetals		Catalyst	Conditions	Yield _% a)	
	R ³	R ⁴		°C/h	3	4
1	ⁿ C7 ^H 15	н	$Rh_4(CO)_{12}$	100/16	46	0
2	ⁿ C ₇ H ₁₅	Н	[Rh(COD)(DPPB)] Clo_4	100/16	0	49
3	Ph	н	$Rh_4(CO)_{12}$	100/15	58	0
4	Ph	Н	[Rh(COD)(DPPB)] Clo_4	100/16	0	58
5	Ph	Н	$[Rh(COD)(DPPB)]ClO_4$	20/42	58	0
6	PhCH=CH	Н	$Rh_4(CO)_{12}$	100/19	0	0
7	Me	Me	$Rh_4(CO)_{12}$	100/17	32	0
8	ⁿ C6 ^H 13	Me	$Rh_4(CO)_{12}$	100/19	79	0
9	ⁿ C ₆ ^H 13	Me	$[Rh(COD)(DPPB)]ClO_4$	100/17	0	2
10	H	OMe	Rh ₄ (CO) ₁₂	100/18	48	0
11	Me	OMe	$Rh_4(CO)_{12}$	100/16	0	0

Table 1. Aldol-type reactions between 1a (R^1 =Me, R^2 =H) and acetals with the aid of rhodium complexes.

a) Isolated yield.

Table 2. Aldol-type reactions between trimethylsilyl enol ethers and 2a (R^3 =Ph, R^4 =H) with the aid of $Rh_4(CO)_{12}$.

Entry	Silyl enol R ¹	ether R ²	Conditions ^O C/h	Yield of 3 ^{a)} %	Syn:Anti
1	Me	Н	100/15	58	
2	Et	Me ^{b)}	100/17	61	51:49
3	-(CH ₂)4	-	100/ 9	55	65 : 35
4	Ph	Me	100/15	80	54:46

a) Isolated yield. b) E:Z = 22:78.

analogous conditions to the case of $Rh_4(CO)_{12}$ catalyst. On the contrary, exchange of the anion part from ClO_4^- to PF_6^- prohibited completely the catalytic efficiency of $[Rh(COD)(DPPB)]^+X^-$ in the present homologation. This point is remarkably different from the reaction between silyl enol ethers and aldehydes.⁴ The results are summarized in Table 1 and Table 2.

It is noteworthy that the reaction catalyzed by $[Rh(COD)(DPPB)]^+ClO_4^$ proceeded even at room temperature to give β -methoxyketone 3 without β elimination (entry 5, Table 1). The fact shows a feasibility to the enantioselective aldol additions using chiral rhodium catalyst.⁶

The trimethylsiloxy group of α -trimethylsiloxy acetal remains intact during aldol type homologation catalyzed by $Rh_4(CO)_{12}$. For example, a reaction of α -trimethylsiloxystyrene (1b) (1.0 mmol) and 1,1-dimethoxy-2-trimethylsiloxypropane (5) (1.0 mmol) in benzene proceeded smoothly in the presence of $Rh_4(CO)_{12}$ (0.005 mmol) to give 6^7 in 73% yield after separation by a column chromatography on silica gel. Thus, the present method offers a facile route to 1,2,4-trioxycompounds bearing differently protected hydroxy groups.

On the other hand, an analogous reaction between **1b** and **5** catalyzed by 2 mol% of $[Rh(COD)(DPPB)]^+ClO_4^-$ in CH_2Cl_2 resulted to give **7** directly in 40 % yield.⁸ The aldol adduct **6** cyclized subsequently to 2,5-disubstituted furan **7** in 72 % yield by the assist of a catalytic amount of *p*-toluenesulfonic acid (Scheme 1). In spite of the moderate yield, the present rhodium catalyzed



Scheme 1.

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route to furan has enough room to choose catalyst corresponding to the required situations.

In contrast to the successful intermolecular carbon-carbon bond formation, the stereoselectivity is not satisfied in the rhodium catalyzed aldol-type reaction (Table 2). However, it should be stressed that aldoltype reactions between trimethylsilyl enol ethers and acetals as well as aldehydes could be performed with the aid of rhodium complexes under neutral conditions. Although the mechanistic aspect of the reaction is not clear in the present time, the intermediacy of rhodium enolate in the catalytic cycle is a plausible elucidation like as the examples reported previously.^{5,9,10} Further studies are now in progress.

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