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A CONVENIENT METHOD FOR THE PREPARATION OF VINYL SULFIDES AND OLEFINS BY THE USE OF $TiCl_4$ AND Zn

Teruaki MUKAIYAMA, Manzo SHIONO, and Toshio SATO
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

β-Hydroxythioacetals or β-hydroxysulfides, prepared by the reactions of α-lithio thioacetals or α-lithio sulfides with aldehydes or ketones, were converted into vinyl sulfides or olefins in good yields by the treatment with $TiCl_4$ and Zn.

Recently, it was found that aldehydes and ketones were reduced by the low valent titanium compound, produced from $TiCl_4$ and Zn, to give the corresponding pinacols or olefins in high yields.[1] The olefin formation in this reaction was explained by assuming the initial formation of intermediates, titanium vicinal dialkoxides, which were deoxygenated by application of heat.

In the present experiment, we examined the reduction of alkoxides with arylthio groups in the β-position instead of the vicinal dialkoxides with the consideration that titanium compounds similarly had affinities for sulfur atom.[2)3)] Consequently, it was found that olefins and vinyl sulfides were also obtained in good yields from β-hydroxysulfides and β-hydroxythioacetals by the treatment with $TiCl_4$ and Zn under similar conditions. For example, 1,1-bis(phenylthio)-2-heptanol, prepared by the reaction of bis(phenylthio)methyllithium with hexanal, was converted into its titanium alkoxide by treating with $TiCl_4$ and Et_3N. Then, the reduction of the alkoxides resulted in the formation of 1-phenylthio-1-heptene in 60% yield. After various examinations by varying the solvents and bases, it was found that 1-phenylthio-1-heptene was produced in good yields when the solvent and the base were dioxane-ammonia or pyridine. Various β-hydroxythioacetals were also converted into the corresponding vinyl sulfides in good yields (See Table I).

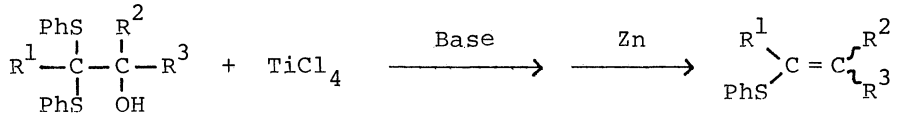
Similarly, β-hydroxysulfides, prepared by the reactions of α-lithio alkyl 2-pyridyl sulfides[4] with aldehydes or ketones, were converted into olefins in good yields as shown below.

$$\underset{\substack{\text{PyS}\ \ \text{OH}}}{\text{PhCH=CHCHCHC}_5\text{H}_{11}} + TiCl_4 \xrightarrow[\text{[O]}]{NH_3} \xrightarrow[\text{r.t., 10hr}]{\text{Zn}} \underset{71\%}{\text{PhCH=CHCH=CHC}_5\text{H}_{11}}$$

$$\underset{\substack{\text{Ph}\\ \text{OH}}}{\text{PySCH}_2\text{C}-\text{Ph}} + TiCl_4 \xrightarrow[\text{[O]}]{NH_3} \xrightarrow[\text{refl. 2hr}]{\text{Zn}} \underset{86\%}{\text{CH}_2=\text{C}(\text{Ph})_2}$$

In a typical experiment, 1,1-bis(phenylthio)-2-heptanol (345 mg, 1.04 mmol) in 4 ml of dry pyridine was added to the yellow suspension of $TiCl_4$ (367 mg, 1.93 mmol) in 4 ml of pyridine. After being stirred for 4 hr, the solution turned clear red.

Table I.



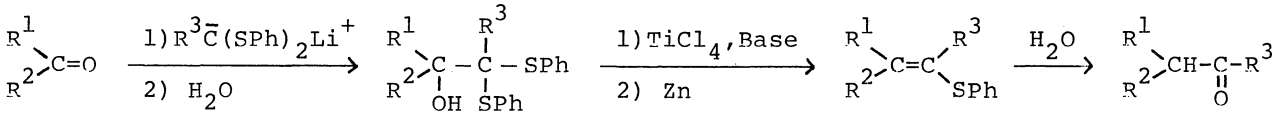
(I) (II)

(I) R^1	R^2	R^3	Reaction Conditions Base	Solvent	Temp.	Time(hr)	(II) Yield(%)
H	C_5H_{11}	H	NH_3		refl.	5	80
H	C_5H_{11}	H			"	3	84
H	Ph	H	"	"	"	4	84
H	Ph	CH_3	"	"	"	6	91 a)
H	Ph	Ph	"	"	"	4	79
H	$-(CH_2)_5-$		"	"	"	2	90
C_4H_9	C_5H_{11}	H	"	"	"	2	82 b)
CH_3	$-(CH_2)_4-$		"	"	"	1	71

a) When Et_3N was used as base in dioxane, (II) was obtained in 45% yield.
b) The reaction mixture was poured to an aq. $NaHCO_3$ solution. When 1 N NaOH was added to the reaction mixture, (II) and 5-undecanone were obtained in 15% and 65% yields, respectively. The latter was produced by the hydrolysis of (II).

Zn powder (400 mg, 6.1 mmol) was added and then the reaction mixture was refluxed for 3 hr. Usual work-up afforded 1-phenylthio-1-heptene in 84% yield.

The convenient olefin synthesis from β-hydroxysulfides or β-hydroxythioacetals was already reported by Kuwajima[5] and Coates.[6] The present reaction also affords a convenient method for the preparation of vinyl sulfides and olefins in high yields by using readily available $TiCl_4$ and Zn. Moreover, it is already shown that vinyl sulfides obtained are easily hydrolyzed to ketones by the use of $TiCl_4$.[2] Therefore, this reaction provides a convenient route for the possible introduction of acyl group to carbonyl carbon under reductive conditions.



Further works on the scope and utility of the reactions are now in progress.

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