A Convenient Method for the Hydrolysis of Vinyl Sulfides to Ketones

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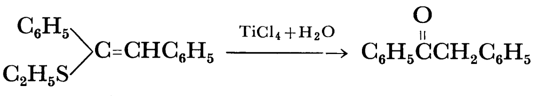
In this communication, a convenient method for the hydrolysis of vinyl sulfides to ketones by the use of $TiCl_4$ is reported. In the previous paper,[1] it was shown that $AgClO_4$ is effective for the hydrolysis of thioketals or thioacetals. However, it was found that the $AgClO_4$-promoted hydrolysis of vinyl sulfide gave the hydrolyzed product in a low yield. Hydrolysis of vinyl sulfides has been generally performed under rather drastic acidic conditions[2] except the Hg(II)-promoted hydrolysis[3] reported by Corey *et al.*

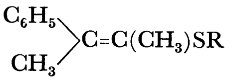
Based on the consideration that there are two possible ways of activation of vinyl sulfides towards hydrolysis, namely the activation of carbon-carbon double bond and carbon-sulfur bond, we examined the hydrolysis using various metal salts which might have strong affinity toward either double bond or sulfur atom. Finally, it was established that vinyl sulfides were easily hydrolyzed in the presence of 2 molar amounts of $TiCl_4$. For example, when α-ethylthiostilbene, **1**, was added to 2 molar amounts of $TiCl_4$ in acetonitrile at room temperature, the color of the solution changed from yellow to deep red. After stirring for about 20 min, 4 molar amounts of water was added and the reaction mixture was stirred at room temperature for an additional 4 hr. Then usual work-up afforded desoxybenzoin, **2**, in 78% yield and 21% of **1** was recovered. Further, it was found that, when 2 molar amounts of $Pb_2O(OH)_2$ was added in the above reaction in order to remove ethanethiol formed at the same time, the increase of the yield was achieved and **2** was obtained in 92% yield and 8% of **1** was recovered. On the other hand, in the case of phenyl vinyl sulfide, there was no remarkable effect in the yield by the addition of $Pb_2O(OH)_2$.



$$(C_6H_5)(C_2H_5S)C{=}CHC_6H_5 \xrightarrow{TiCl_4+H_2O} C_6H_5\overset{O}{\overset{\|}{C}}CH_2C_6H_5$$

1 **2**

In a similar manner, various vinyl sulfides were hydrolyzed to the corresponding ketones in high yields. For example, β-aryl substituted vinyl sulfide[4], **3**, was hydrolyzed quantitatively to 3-phenyl-2-butanone by the use of $TiCl_4$ in acetic acid. The results are shown in Table 1.



$$(C_6H_5)(CH_3)C{=}C(CH_3)SR$$

3 $R=C_2H_5$ or C_6H_5

In conclusion, it is noted that vinyl sulfides are easily hydrolyzed to the corresponding ketones in high yields without accompanying by-product under mild conditions by the action of $TiCl_4$. Further works are now in progress and will be reported at a later date.

Table 1. $R^1R^2C{=}CR^3(SR^4) \xrightarrow{2TiCl_4\,+\,4H_2O\,+\,n\ Pb_2O(OH)_2} R^1R^2CH\overset{O}{\overset{\|}{C}}R^3$

Vinyl sulfide				Solvent	n	Time (hr)	Isolated yield (%) [recovered vinyl sulfide (%)]
R^1	R^2	R^3	R_4				
C_6H_5	H	C_6H_5	C_2H_5	C_6H_6	2	4	94
				CH_3CN	0	4	78[21]
				CH_3CN	2	4	92[8]
				CH_3CO_2H	0	4	97
C_6H_5	n-C_4H_9	C_6H_5	C_2H_5	C_6H_6	2.2	12	91[a]
				CH_3CO_2H	0	4	quant
CH_3	H	C_6H_5	C_6H_5	CH_3CN	0	6	88
				CH_3CO_2H	0	6	90
				CH_2Cl_2	0	6	95
C_6H_5	H	C_6H_5	C_6H_5	CH_3CO_2H	0	7	96
C_6H_5	n-C_4H_9	C_6H_5	C_6H_5	CH_2Cl_2	0	14	62[b]
C_6H_5	CH_3	CH_3	C_2H_5	CH_3CO_2H	0	4	quant
C_6H_5	CH_3	CH_3	C_6H_5	CH_3CO_2H	0	7	97

a) 2.2 molar amounts of $TiCl_4$ was used. b) 5 molar amounts of H_2O was added.

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1) T. Mukaiyama, S. Kobayashi, K. Kamio, and H. Takei, *Chem. Lett.*, **1972**, 273.

2) J. H. S. Weiland and J. F. Arens, *Rec. Trav. Chim. Pays-Bas*, **79**, 1293 (1960). B. S. Kupin and A. A. PeTrov, *Zh. Org. Khim.*, **3**, 975 (1967). T. Mukaiyama, S. Fukuyama, and T. Kumamoto, *Tetrahedron Lett.*, **1968**, 3787.

3) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970).

4) E. J. Corey and J. I. Shulman reported[3] that the Hg(II)-promoted hydrolysis of β-aryl substituted vinyl sulfide required an elevated temperature.