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A CONVENIENT METHOD FOR THE PREPARATION OF STYRENE DERIVATIVES BY THE USE OF $TiCl_4$ AND Zn

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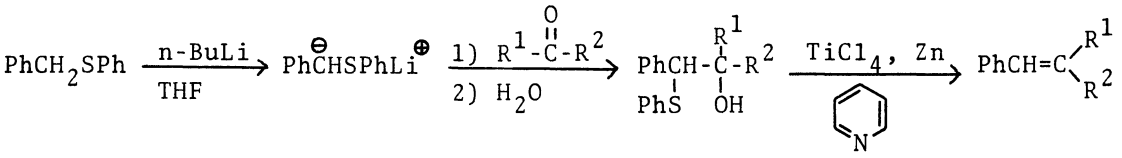
β-Hydroxysulfides, prepared by the reaction of α-lithio benzyl phenyl sulfide with various aldehydes or ketones, gave styrene derivatives in good yields when treated with $TiCl_4$ and Zn.

Recently, many methods have been reported for the preparation of olefins from carbonyl compounds by the use of sulfur containing intermediates with hydroxyl group at the β-position.[2)~5)] In the course of study on the exploration of new synthetic reactions using $TiCl_4$, it was recently found that β-hydroxythioacetals could be converted to vinylsulfides in good yields by the treatment with $TiCl_4$ and Zn.[6)] In this paper we report a convenient method of synthesizing styrene derivatives starting from various aldehydes or ketones by the use of $TiCl_4$ and Zn.



(I) (II) (III) (IV)

β-Hydroxysulfides (III) can be prepared from various aldehydes or ketones and the α-lithio compound (II) derived from benzyl phenyl sulfide (I). The application of $TiCl_4$ and Zn to (III) resulted in the formation of styrene derivatives (IV) as shown in the above equation.

In a typical experiment, a hexane solution of n-butyllithium (10.5 mmol) was added dropwise into a stirred solution of benzyl phenyl sulfide (2.00 g, 10.0 mmol) in 10 ml THF under argon atmosphere at -78°C. The solution changed to faint red and then immediately turned to yellow suspension, which was presumed to be the α-lithio compound. After stirring for 1hr was added a solution of acetophenone (1.20 g, 10.0 mmol) in 15 ml THF, and then the temperature was elevated gradually to -30°C. The yellow color faded gradually showing consumption of the α-lithio compound. At this stage 10 ml water was added to this solution to quench the reaction. Usual experimental work-up gave 1,2-diphenyl-1-phenylthio-2-propanol (III d) (2.72 g) in 85% yield. A solution of (III d) (0.416 g, 1.30 mmol)

dissolved in 4 ml pyridine was added to a stirred suspension of $TiCl_4$ (0.47 g, 2.5 mmol) in 4 ml pyridine. The color change from yellow to red after 3 hrs was presumed to show the formation of the titanium alkoxide. After the addition of 0.6 g of Zn powder to this solution, it was refluxed for 3 hrs, and then quenched by addition of 10 ml of 1.2 N NaOH solution. Usual work-up gave 1,2-diphenylpropene (IV d) (0.252 g) in 91% yield. In a similar manner, various aldehydes or ketones gave the corresponding β-hydroxysulfide (III a~g) in good yields, from which styrene derivatives (IV a~g) were obtained in good yields as shown in the following table.

	R^1	R^2	Yield (%) (III)	(IV)
a	C_5H_{11}	H	73	64*
b	$PhCH_2CH_2$	H	94	79
c	Ph	H	97	87
d	Ph	CH_3	85	91
e	Ph	Ph	93	92
f	$PhCH_2CH_2$	CH_3	75	80
g	$-(CH_2)_5-$		93	87

*In this case (IV a) was obtained by the treatment of (III a) with the low valent titanium compounds prepared from $TiCl_4$ and Zn.

Little work has been done concerning the synthesis of styrene derivatives from aldehydes and ketones. Only work of this type describes the preparation of various styrene derivatives from limited carbonyl compounds, namely aromatic or conjugated.[7] The present process provides a useful and convenient method for the preparation of various kinds of styrene derivatives starting from a variety of carbonyl compounds, not only aromatic or conjugated but also aliphatic ones. Further works on the scope of the reactions are now in progress.

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References and Notes

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