CHEMISTRY LETTERS, pp. 479-482, 1973. Published by the Chemical Society of Japan

A CONVENIENT METHOD FOR THE PREPARATION OF VINYL SULFIDES FROM CARBONYL COMPOUNDS BY USING $TiCl_4$

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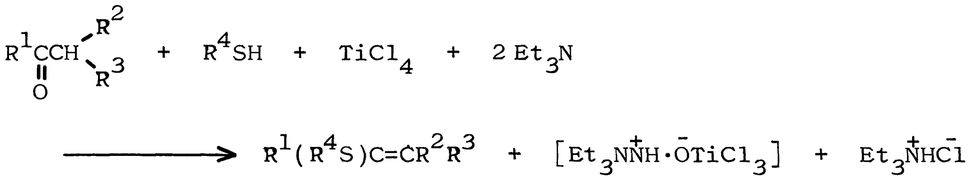
Various ketones, such as deoxybenzoin, propiophenone, phenylacetone, benzylacetone, cyclohexanone and 2-methylcyclohexanone, and aldehyde such as 3-phenylpropionaldehyde were smoothly converted to the corresponding vinyl sulfides in good yields by the treatments with thiols in the presence of $TiCl_4$.

In the previous paper, it was reported that vinyl sulfide is hydrolyzed to give the corresponding carbonyl compound in good yield at room temperature by the use of $TiCl_4$.1) Based on this result, a convenient method for the preparation of vinyl sulfide was investigated with the expectation that the vinyl sulfide would be an unique protecting group of carbonyl compound. Relatively little work has been reported on the direct preparation of vinyl sulfide from carbonyl compound except for the elimination of thiol from thioacetal by the action of acid catalyst2) and for the dehydration from hemithioacetal by the steric hindrance about carbonyl function.3) In this communication, a convenient method for the conversion of carbonyl compound to vinyl sulfide by the treatment with thiol in the presence of $TiCl_4$ and tertiary amine is reported.

In a typical experiment, a mixture of ethanethiol (0.34 g, 5.5 mmol) and triethylamine (1.01 g, 10 mmol) in 20 ml of THF was added drop by drop into a vigorously stirred solution of phenylacetone (0.69 g, 5.1 mmol) and $TiCl_4$ (0.95 g, 5 mmol) in 60 ml of THF under an argon atmosphere at room temperature. The color of the solution changed from orange to deep red and immediately turned to the former orange. After being stirred for additional 5 hr, ethyl 1-methylstyryl sulfide was obtained in 82% yield (0.75 g).

In a similar manner, various ketones such as deoxybenzoin, propiophenone, benzylacetone, cyclohexanone and 2-methylcyclohexanone were smoothly converted to the corresponding vinyl sulfides in good yields. Also, a favorable result was obtained by using benzenethiol in place of ethanethiol in the above mentioned reactions as shown in the table.

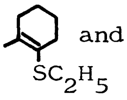
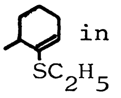


$$R^1C(=O)CHR^2R^3 + R^4SH + TiCl_4 + 2\,Et_3N \longrightarrow R^1(R^4S)C{=}CR^2R^3 + [Et_3\overset{+}{N}H\cdot\overset{-}{O}TiCl_3] + Et_3\overset{+}{N}H\overset{-}{Cl}$$

R^1	R^2	R^3	R^4	Conditions Temp.	Time(hr)	Yield(%)
C_6H_5	C_6H_5	H	C_2H_5	r.t.	6	91[a)]
C_6H_5	C_6H_5	H	C_6H_5	r.t.	14	59[a)]
C_6H_5	CH_3	H	C_2H_5	r.t.	6	87[a)]
C_6H_5	CH_3	H	C_6H_5	r.t.	14	65[a)]
CH_3	C_6H_5	H	C_2H_5	r.t.	6	82[a)]
CH_3	C_6H_5	H	C_6H_5	r.t.	14	72[a)]
CH_3	$C_6H_5CH_2$	H	C_2H_5	r.t.	6	87[a)]
CH_3	$C_6H_5CH_2$	H	C_6H_5	r.t.	14	74[a)]
$-(CH_2)_4-$		H	C_2H_5	r.t.	6	79
$-(CH_2)_4-$		H	C_6H_5	r.t.	14	50
$-(CH_2)_4-$		CH_3	C_2H_5	r.t.	6	79[b)]
H	$C_6H_2CH_2$	H	C_2H_5	r.t.	40	55[a)]

Elemental analysis and spectroscopic properties establish the molecular formula and structure.

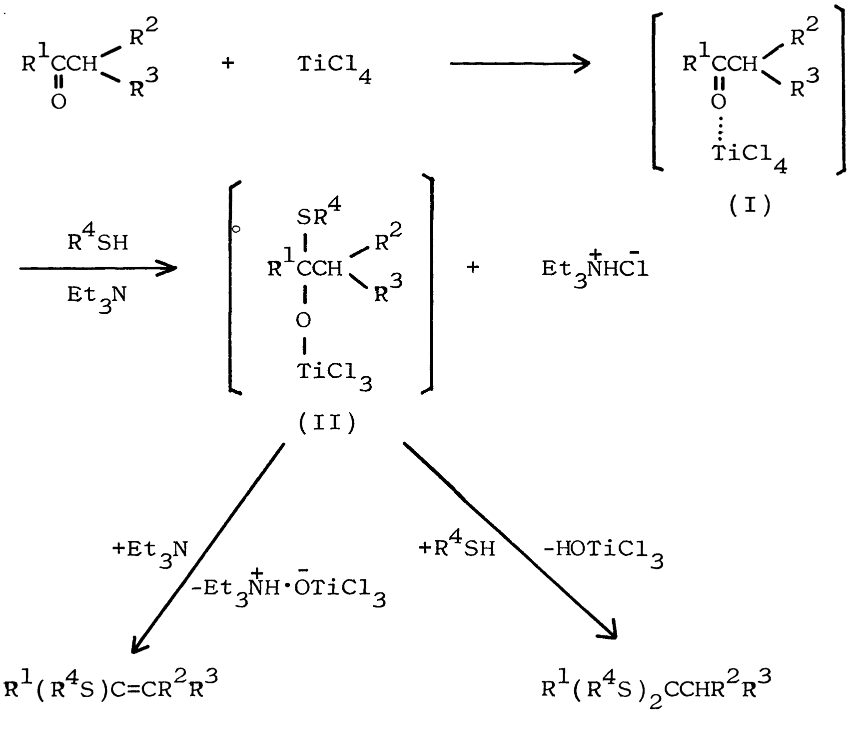
a) Mixture of cis and trans isomers

b) Mixture of  and  in the ratio about 2.0 : 1.0

On the other hand, it was found that 1-phenyl-2,2-bis(ethylthio)propane was obtained in 80% yield (based on ethanethiol used) from phenylacetone in the absence of triethylamine and ethyl 1-methylstyryl sulfide could not be detected. Further, it was found that ethyl 1-methylstyryl sulfide was obtained only in 36% yield by the addition of ethanethiol to the reaction mixture of phenylacetone, $TiCl_4$ and triethylamine.

From these results, it is concluded that the yield of vinyl sulfide markedly depends on the reaction condition, i.e., the order of the addition of the reagents (ketone, thiol and triethylamine) to a THF solution of $TiCl_4$. The most favorable result was obtained when the mixture of thiol and triethylamine was added to the solution of $TiCl_4$ and ketone.

These results indicate that the reaction may proceed through an initial formation of a key intermediate (II) produced from the $TiCl_4$-ketone complex (I), thiol and triethylamine. On this stage, when the elimination of $Et_3\overset{+}{N}H\cdot\overset{-}{O}TiCl_3$ by the action of triethylamine proceeds more rapidly than the nucleophilic displacement of thiol, vinyl sulfide results predominantly. While, in the absence of triethylamine, the nucleophilic displacement of thiol proceeds much faster than the elimination of $HOTiCl_3$ to afford thioacetal as a major product.



Contrary to the cases of ketones, yield of vinyl sulfide from aldehyde was very low even when aldehyde was treated with $TiCl_4$, ethanethiol and triethylamine under the condition similar to the case of ketone. For example, ethyl 3-phenyl-1-propenyl sulfide was obtained only in 10% yield when 3-phenylpropionaldehyde was allowed to react with $TiCl_4$, ethanethiol and triethylamine. This difficulty was overcome by adding the mixture of aldehyde, ethanethiol and triethylamine into $TiCl_4$ according to the following procedure; the mixture of 3-phenylpropionaldehyde (0.69 g, 5.1 mmol), ethanethiol (0.34 g, 5.5 mmol) and triethylamine (0.55 g, 5.5 mmol) in 50 ml of 1,2-dimethoxyethane was added dropwise into a vigorously stirred solution of $TiCl_4$ (1.89 g, 10 mmol) in 40 ml of 1,2-dimethoxyethane under an argon atmosphere at room temperature and precipitates appeared soon. After being stirred for 40 hr, usual work up afforded ethyl 3-phenyl-1-propenyl sulfide in 55% yield.

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

Acknowledgment. The authors wish to express their thanks to Dr. Hisashi Takei for his helpful discussion.

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(Received March 13, 1973)