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REACTION OF VINYL SULFIDES WITH ALDEHYDES IN THE PRESENCE OF LEWIS ACIDS

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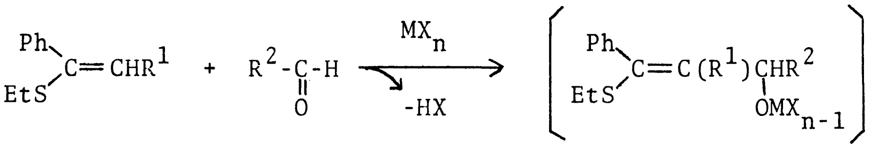
A wide variety of ethyl 3-indenyl sulfides were easily prepared by the reaction of vinyl sulfides with aldehydes in the presence of various Lewis acids such as aluminum chloride.

Recently, it was reported in our laboratory that silyl enol ethers or enol acetates react with various carbonyl compounds in the presence of Lewis acids to afford the addition products in excellent yields.1) Further, it was shown that vinyl sulfides are conveniently prepared by treating ketones and thiols with $TiCl_4$.2)

In the present experiment, the reaction of vinyl sulfides with aldehydes in the presence of various Lewis acids was tried with the expectation that the addition product [III] would be formed by the nucleophilic attack of vinyl sulfides to carbonyl compounds as shown in the following equation.

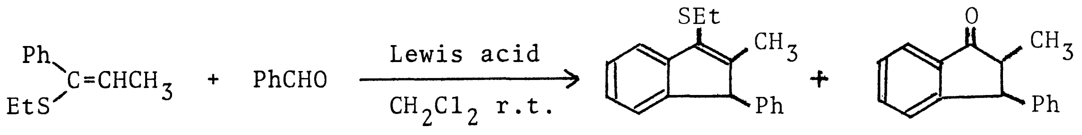


[I] [II] [III]

When vinyl sulfide (I: $R^1=CH_3$) is allowed to react with benzaldehyde [II] in the presence of $AlCl_3$, ethyl 3-indenyl sulfide was produced in a fairly good yield probably through the intramolecular Friedel-Crafts reaction of [III] initially formed. For example, a CH_2Cl_2 solution of 1-ethylthio-1-phenyl-1-propene [1] was added dropwise into a CH_2Cl_2 solution of equimolar amounts of benzaldehyde and a Lewis acid, such as $AlCl_3$, $TiCl_4$, $SnCl_4$ or $ZnCl_2$, at room temperature under an argon atmosphere and the mixture was stirred for 0.5∿1.0 hr. After being quenched with water, 3-ethylthio-2-methyl-1-phenylindene [2] and 2-methyl-3-phenyl-1-indanone [3]3) were isolated by silica gel column chromatography as shown in Table I.

Among various Lewis acids examined, it was found that $AlCl_3$ is the most suitable for the preparation of indene derivative [2]. Therefore, 1-ethylthio-1-phenyl-1-propene [1] was treated with several aldehydes in the presence of $AlCl_3$, and it was found that the corresponding ethyl 2-methyl-3-indenyl sulfides were prepared in excellent yields.

Table I



[1] [2] [3]

Lewis acid	Time(hr)	Yield of [2](%)	 [3](%)
$AlCl_3$	1.0	84	—
$TiCl_4$*	0.5	65	17
$SnCl_4$	1.0	39	2
$ZnCl_2$	24.0	trace	—

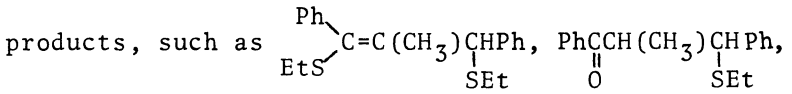
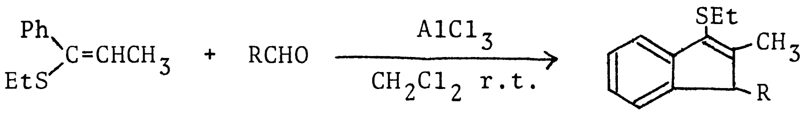
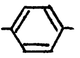
*) When $TiCl_4$ was employed in this reaction, several products, such as  $\mathrm{Ph(EtS)C{=}C(CH_3)\underset{SEt}{CH}Ph}$, $\mathrm{Ph\underset{O}{C}CH(CH_3)\underset{SEt}{CH}Ph}$, $PhCOCH_2CH_3$ and $PhCH(SEt)_2$ were isolated along with [2] and [3].

Table II

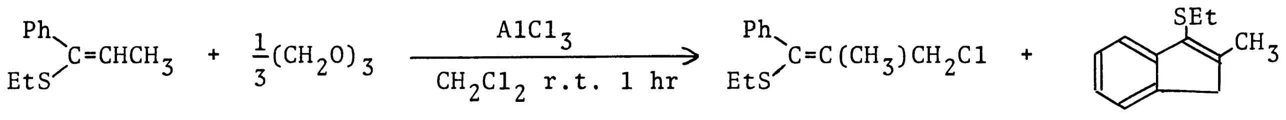


[1] [4]

R	Time(hr)	Yield of [4]* (%)
Ph	1.0	84
$PhCH_2CH_2$-	1.0	65
CH_3CH_2-	3.0	61
$(CH_3)_2CH$-	3.0	46
NO_2- 	3.5	92

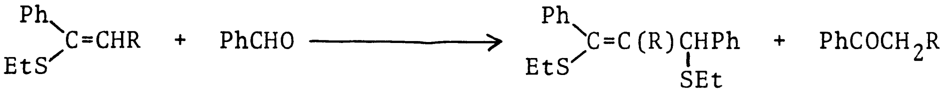
*) The products have ir and nmr spectra and elemental analysis in accord with the assigned structures.

When trioxane was used instead of the aldehydes mentioned above, the mixture of ethyl 3-chloro-2-methyl-1-phenyl-1-propenyl sulfide [5] and ethyl 2-methyl-3-indenyl sulfide [6] were obtained in 43% and 37% yields, respectively.[4)]



[1] [5] [6]

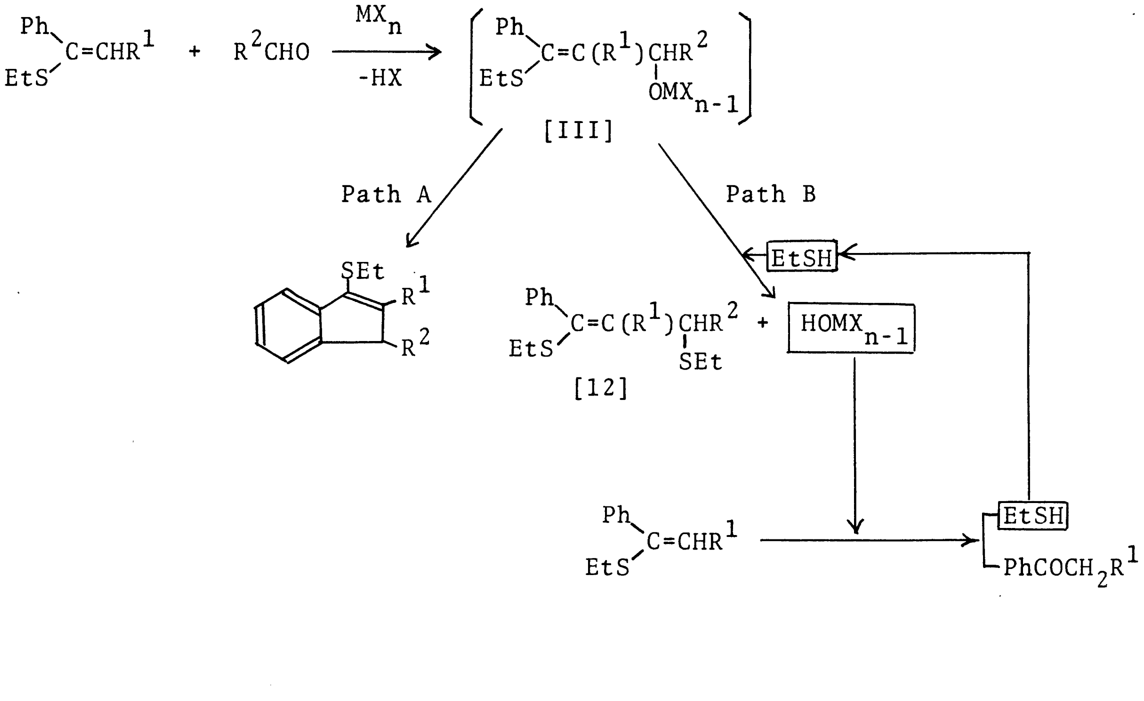
In the case of the reaction of ethyl α-phenylstyryl sulfide [7] with benzaldehyde, the sulfide [7] was recovered almost quantitatively when $BF_3 \cdot OEt_2$ or $AlCl_3$ was used as Lewis acid. 1,3-Bis(ethylthio)-1,2,3-triphenyl-1-propene [8] was isolated in a 41 ∿ 52% yield along with deoxybenzoin only when $TiCl_4$ was employed. On the other hand, in the reaction of α-ethylthiostyrene [9] with benzaldehyde, $BF_3 \cdot OEt_2$ was the most suitable Lewis acid and 1,3-bis(ethylthio)-1,3-diphenyl-1-propene [10] and acetophenone were isolated. When the other Lewis acid such as $TiCl_4$ or $AlCl_3$ was used, the reaction was complicated and many spots were detected by tlc.



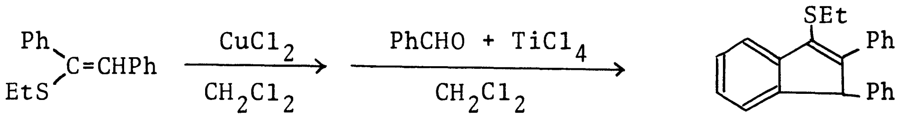
[7]: R=Ph
[9]: R=H

[8]: R=Ph 41～52%
[10]: R=H 36%

A probable mechanism for the addition reaction of vinyl sulfide to aldehyde is shown in the following scheme. The nucleophilic attack of vinyl sulfide toward aldehyde-Lewis acid complex results in the formation of the key intermediate [III] by the loss of HX. On this stage, when $AlCl_3$ was used as Lewis acid, the intramolecular Friedel-Crafts reaction (Path A) takes place rapidly to afford 3-indenyl sulfide. On the other hand, when $BF_3 \cdot OEt_2$ or $TiCl_4$ was employed, the nucleophilic displacement of ethanethiol (Path B) proceeds predominantly giving sulfide [12] over the intramolecular Friedel-Crafts reaction (Path A).



Since vinyl sulfides used in this experiment usually contain a trace amount of ethanethiol after purification by distillation, vinyl sulfide [7] was treated with $CuCl_2$ before use in order to scavenge ethanethiol. For example, a CH_2Cl_2 solution of ethyl α-phenylstyryl sulfide [7] was treated with 2 molar amounts of $CuCl_2$ at room temperature for 15 min and this solution was added to a mixture of $TiCl_4$ and benzaldehyde in CH_2Cl_2. After being stirred at room temperature for 10 min , ethyl 1,2-diphenyl-3-indenyl sulfide [13] was isolated in 36% yield, as expected.



[7] [13]

In summary, it is noted that 3-indenyl sulfide derivatives were prepared conveniently by the reaction of vinyl sulfides with aldehydes in the presence of Lewis acids. Since it is already known that ethyl 3-indenyl sulfides are easily converted into 1-indanone derivatives by the hydrolysis with $TiCl_4$,⁵⁾ a wide variety of 1-indanone derivatives is easily available by this method.

REFERENCES

1) a) T. Mukaiyama, K. Narasaka, and K. Banno, Chem. Lett., 1011 (1973).
   b) T. Mukaiyama, K. Izawa, and K. Saigo, Chem. Lett., (4) (1974) in press.
2) T. Mukaiyama and K. Saigo, Chem. Lett., 479 (1973).
3) 2-Methyl-3-phenyl-1-indanone [3] was assumed to result from the hydrolysis of ethyl 3-indenyl sulfide [2] by the action of $TiCl_4$.5)
4) The amounts of [5] and [6] were determined by the nmr analysis.
5) T. Mukaiyama, K. Kamio, S. Kobayashi, and H. Takei, Bull. Chem. Soc. Japan, **45**, 3723 (1972).

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