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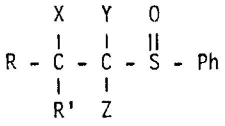
ELIMINATIVE DEOXYGENATION OF SUBSTITUTED-α-HALOSULFOXIDES

Vichai Reutrakul* and Patcharin Poochaivatananon
Department of Chemistry, Faculty of Science, Mahidol University,
Rama VI Road, Bangkok 10400, Thailand

ABSTRACT: The reaction of substituted-α-halosulfoxides with $TiCl_4$–Zn in ether gave the corresponding phenyl vinyl sulfides in good yields.

Substituted α-halosulfoxides of the structural type 1 are very useful synthetic intermediates. Syntheses of α,β-unsaturated aldehydes[1], epoxysulfoxides[1], halomethyl ketones[2], vinyl chlorides[3], and thioesters[4] from such intermediates 1 have been reported. We have been interested in the possibility of deoxygenating[5] and generating thionium[6] species from compounds of the type 1. In this letter, we wish to report our preliminary results in this area. We have found that $TiCl_4$-Zn in ether[7] could effect the eliminative deoxygenation of α-mono-, di-chlorosulfoxides and α-mono-, di-chloro-β-hydroxysulfoxides to give the corresponding phenyl vinyl sulfides[8] and phenyl chlorovinyl sulfides[9] in good yields.



$$R-\underset{R'}{\overset{X}{C}}-\underset{Z}{\overset{Y}{C}}-\overset{O}{\overset{\|}{S}}-Ph$$

1

R, R' = alkyl, aryl, H
X = H, OH
Y = H, Cl, Br
Z = H, Cl

The following procedure is illustrative: zinc (6 equiv.) was mixed with titatnium (IV) chloride (3 equiv.) in ether at room temperature. The solution was stirred for 2 minutes before the addition (dropwise) of the α-chloro sulfoxide solution in methylene chloride. After the addition was completed, the solution was refluxed with stirring for additional 10 minutes. Water was added to the cooled reaction mixture and the aqueous solution was extracted with chloroform to give the phenyl vinyl sulfides. The results are summarized in Table I.

Table I

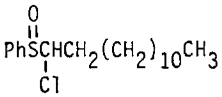
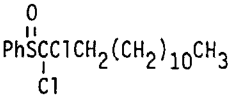
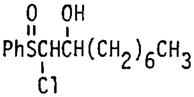
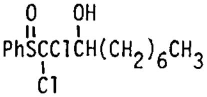
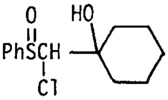
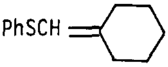
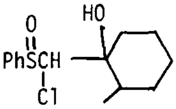
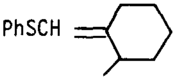
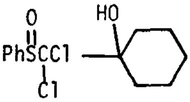
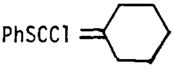
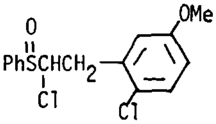
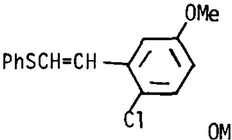
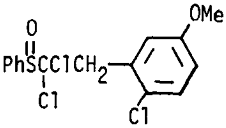
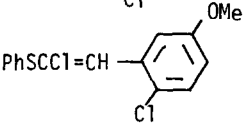
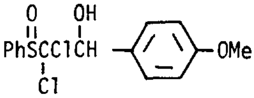
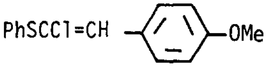
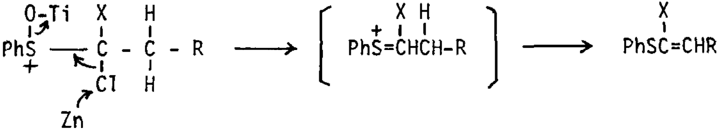
Entry	Compounds	Products (%)
1	 $\mathrm{Ph\overset{O}{\overset{\|}{S}}\underset{Cl}{C}HCH_2(CH_2)_{10}CH_3}$	$\mathrm{PhSCH{=}CH(CH_2)_{10}CH_3}$ (31)

Table I (cont.)

Entry	Compounds	Products (%)	
2	 $Ph\overset{O}{S}\underset{Cl}{C}ClCH_2(CH_2)_{10}CH_3$	$PhSCCl{=}CH(CH_2)_{10}CH_3$	(85)
3	 $Ph\overset{O}{S}\underset{Cl}{C}H\overset{OH}{C}H(CH_2)_6CH_3$	$PhSCH{=}CH(CH_2)_6CH_3$	(49)
4	 $Ph\overset{O}{S}\underset{Cl}{C}Cl\overset{OH}{C}H(CH_2)_6CH_3$	$PhSCCl{=}CH(CH_2)_6CH_3$	(57)
5			(84)
6			(60)
7			(87)
8			(57)
9			(73)
10			(78)

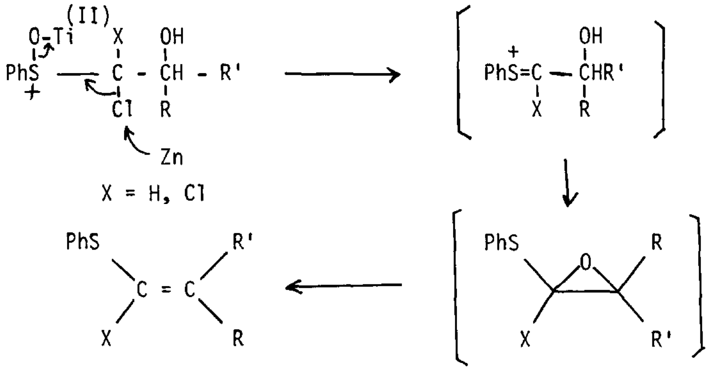
The reaction poses quite an interesting question from the mechanistic point of view. The possible mechanisms for the eliminative deoxygenation are proposed in equations (1) and (2)

(II)



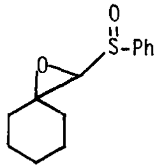
(1)

X = H, Cl

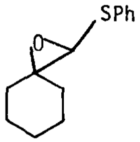


(2)

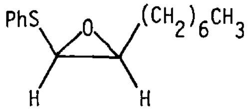
Our postulate seems to be substantiated by two factors. In the first instance, when the epoxysulfoxide[1] 2 was subjected to the same eliminative deoxygenation conditions, the vinyl sulfide (entry 5) could be isolated in 60% yield. Furthermore, when the ratio of compound 2: zinc: titanium (IV) chloride was varied from 1:6:3 to 1:2:1, the labile epoxysulfide[10] 3 could be isolated in a small yield (8%).



2



3



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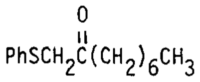

$PhSCH_2\overset{\overset{O}{\|}}{C}(CH_2)_6CH_3$

5

The second piece of evidence seems to substantiate the formation of the epoxysulfide by the intramolecular trapping of the thionium ion by the hydroxyl group derived from the eliminative deoxygenation of the sulfoxide in entry 3. When the ratio of the sulfoxide: zinc: $TiCl_4$ was varied from 1:6:3 to 1:4:2, the vinyl sulfide was isolated in 31% yield together with 26% yield of the α-phenylthioketone 5. Presumably, compound 5 was derived from the rearrangement of the epoxysulfide[10] 4. It is also known that the titanium (II) species can deoxygenate epoxides to the corresponding olefins[11].

Our results represent a novel chemistry of compounds of the type 1. It also provides a convenient method for the generation of thionium ion and a facile entry to phenyl vinyl and phenyl chlorovinyl sulfides. Further exploratory work is in progress.

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