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THE REACTION OF TRIMETHYLSILYL SULFIDES WITH α,β-UNSATURATED ACETALS. A CONVENIENT METHOD FOR THE PREPARATION OF γ-ALKOXYALLYL SULFIDES

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In the presence of $AlCl_3$, trimethylsilyl sulfides react with α,β-unsaturated acetals to give γ-alkoxyallyl sulfides in good yields.

In the course of our continuing study on the reaction of trimethylsilyl sulfides with carbonyl compounds in the presence of various Lewis acids, it was found that trimethylsilyl sulfides react with carboxylic esters in the presence of $AlCl_3$ to afford the corresponding thiolesters in high yields.[1)] This result indicates that the use of trimethylsilyl sulfide combined with $AlCl_3$ facilitates the nucleophilic attack of RS group of the sulfide on carboxylic ester.[2)]

In this communication, we report a method for the preparation of γ-alkoxyallyl sulfides by the reaction of trimethylsilyl sulfides with α,β-unsaturated acetals in the presence of $AlCl_3$. When α,β-unsaturated dimethyl acetals were allowed to react with phenyl trimethylsilyl sulfide in the presence of an equimolar amount of $AlCl_3$, γ-methoxyallyl sulfides, 1, were preferentially produced under mild conditions in good yields. For example, to an ice cooled THF(4 ml) solution of phenyl trimethylsilyl sulfide (2.2 mmol) and $AlCl_3$(2.2 mmol) was added a THF(2 ml) solution of 2-propenal diethyl acetal (2.0 mmol) under an argon atmosphere. After stirring for 20 min, the reaction mixture was poured into a phosphate buffer solution(pH 7). An organic layer was extracted with ether and the extract was condensed under reduced pressure. The residue was chromatographed on silica gel and 1-ethoxy-3-phenylthio-1-propene was isolated in 77% yield. Contrary to this result, in the case of the acetals containing phenyl group or two alkyl groups at the β-position, γ-methoxyallyl sulfide was not isolated, but α,β-unsaturated thioacetals, 3, were obtained.

Further, it was found that when ethyl trimethylsilyl sulfide was used, α,β-unsaturated thioacetals, 3, were obtained as major products. These thioacetals were formed by direct replacement of RO group by RS group of trimethylsilyl sulfide as shown in eq. (2). The results are summarized in the Table.

1 4 eq.(1)

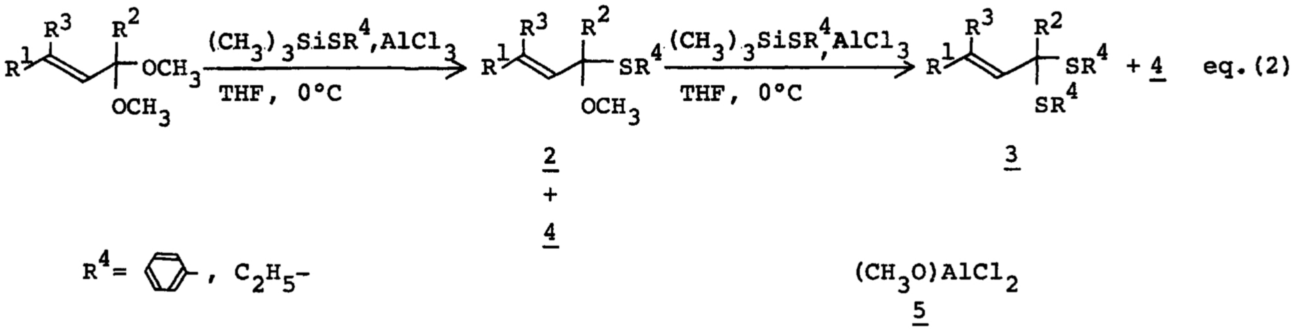
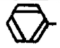
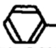


Table. The reaction of trimethysilyl sulfides with α,β-unsaturated dimethyl acetals.

	R^1	R^2	R^3	Yield (%) 1	2	3 c)	Ratio of isomers (E)	: (Z) d)
R^4 = 	H	H	H a)	77			4	3
	CH_3	H	H	83			3	1
	n-C_3H_7	H	H	82			2	1
	H	$-(CH_2)_3-$		79				
		H	H		28	60	2: e) 3: 3	 1
	 $-(CH_2)_2-$	H	CH_3 b)			84	b)	
R^4=C_2H_5-	n-C_3H_7	H	H			86	e)	
	H	$-(CH_2)_3-$		40				
		H	H			86	e)	

a) Diethyl acetal. b) The mixture of (E) and (Z) isomers. c) The yield was based on that 2 molar equivalents of the trimethylsilyl sulfide affords one mole equivalent of the thioacetal. d) Determined by nmr spectra. e) No (Z) isomer was observed by nmr spectra.

It was also found that when 2-hexenal dimethyl acetal was allowed to react with phenyl trimethylsilyl sulfide in the presence of 0.1 molar amount of $AlCl_3$, the γ-methoxyallyl sulfide was obtained in 62% yield and the unreacted acetal was observed on TLC. This result suggests that the α,β-unsaturated acetal activated by $AlCl_3$ reacts with trimethylsilyl sulfide to afford the γ-methoxyallyl sulfide and methyl trimethylsilyl ether, 4. The decrease in the yield of the sulfide in the reaction carried out with a catalytic amount of $AlCl_3$ would be due to the consumption of $AlCl_3$ to produce aluminum alkoxide, 5, by the interaction with methyl trimethylsilyl ether.

REFERENCES

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