Chloromethyl Trimethylsilylmethyl Sulphide as a Parent Thiocarbonyl Ylide Synthon. A Simple Synthesis of Dihydro- and Tetrahydro-thiophenes

Akira Hosomi, Yumiko Matsuyama, and Hideki Sakurai*

Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Chloromethyl trimethylsilylmethyl sulphide acts as a parent thiocarbonyl ylide synthon and reacts stereospecifically with activated alkenes and alkynes, catalysed by caesium fluoride, in acetonitrile at room temperature to give tetrahydro- and dihydro-thiophene derivatives in good yields.

We have previously reported that the parent azomethine ylide can be generated by the 1,3-elimination reaction of *N*-trimethylsilylmethylaminomethyl ether promoted by an acid and/or a fluoride ion and noted that this methodology can be applied to the generation of other 1,3-dipoles such as thiocarbonyl and carbonyl ylides.[1] During the course of studies to obtain such parent 1,3-dipolar reagents, it has been observed that chloromethyl trimethylsilylmethyl sulphide (**1**) is a useful precursor to the parent thiocarbonyl ylide (**2**).[2] We now describe the preparation and reactions of (**1**). Recently, Achiwa *et al.* have reported independently the formation of a silyl-substituted thiocarbonyl ylide by the thermal 1,3-elimination of an organosilicon compound.[3]

The requisite sulphide (**1**)† was readily prepared by introducing dry hydrochloric acid into a mixture of trimethyl-

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† Compound (**1**) was prepared using a similar method to the synthesis of alkyl chloromethyl sulphide, see L. A. Walter, L. H. Goodson, and R. J. Fosbinder, *J. Am. Chem. Soc.*, 1945, **67**, 655. B.p. 75 °C/20 mmHg; ^{1}H n.m.r. (CCl_4) δ 0.04 (s, 9H), 1.94 (s, 2H), 4.64 (s, 2H).

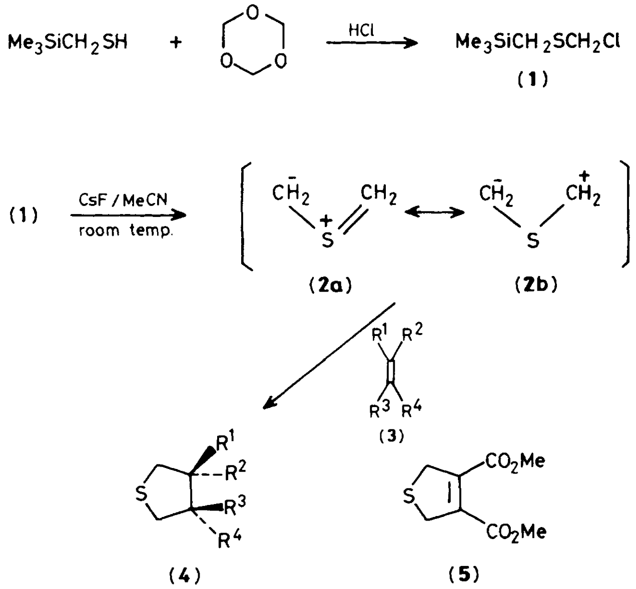
Table 1. Reactions of (**1**) with activated alkenes and alkynes.[a,b]

Dipolarophile (**3**)	% Yield	Product (**4**)
Methyl acrylate	86	$R^1 = CO_2Me, R^2 = R^3 = R^4 = H$
t-Butyldimethylsilyl acrylate	78	$R^1 = CO_2SiMe_2CMe_3, R^2 = R^3 = R^4 = H$
Menth-3-yl acrylate	78[c]	$R^1 = CO_2$menth-3-yl, $R^2 = R^3 = R^4 = H$
Born-2-yl acrylate	65[c]	$R^1 = CO_2$born-2-yl, $R^2 = R^3 = R^4 = H$
Methyl vinyl ketone	82	$R^1 = COMe, R^2 = R^3 = R^4 = H$
Dimethyl fumarate	83	$R^1 = CO_2Me, R^2 = R^3 = H, R^4 = CO_2Me$
Dimethyl maleate	84	$R^1 = CO_2Me, R^2 = H, R^3 = CO_2Me, R^4 = H$
Methyl cinnamate	81	$R^1 = CO_2Me, R^2 = R^3 = H, R^4 = Ph$
Benzylideneacetone	58	$R^1 = COMe, R^2 = R^3 = H, R^4 = Ph$
Dimethyl acetylene-dicarboxylate	56	(**5**)

[a] All reactions were conducted in acetonitrile at room temperature for 15—48 h. [b] Products were isolated by Kugelrohr distillation and all new compounds obtained gave satisfactory spectral data and elemental analysis. [c] A mixture of diastereoisomers.

silylmethanethiol and *s*-trioxane at temperatures below 0 °C in 69% yield.

The reaction of (**1**) with mono-substituted alkenes bearing electron-withdrawing substituents such as various acrylates and methyl vinyl ketone proceeded smoothly in the presence of caesium fluoride in acetonitrile at room temperature to afford the corresponding tetrahydrothiophenes (**4**) in good yield. Disubstituted alkenes such as fumarate, maleate, cinnamate, and benzylideneacetone gave the corresponding tetrahydrothiophenes stereospecifically. Dimethyl acetylenedicarboxylate reacts to give a dihydrothiophene (**5**). The results are listed in Table 1. Cyclic alkenes such as *N*-phenylmaleimide and maleic anhydride did not react with (**1**). Caesium fluoride and acetonitrile are the most suitable activator and solvent, respectively, among those examined. 1,3-Elimination of (**1**) was not observed under thermal conditions.



This reaction of (**1**) provides an unprecedented and convenient route to the parent thiocarbonyl ylide (**2**) under mild conditions. The synthetic utility of the reaction is demonstrated by one step synthesis of five-membered ring compounds containing a sulphur atom *via* [3 + 2] cycloaddition. The ready accessibility of the starting material and simplicity of the conversion under mild reaction conditions should make (**1**) a useful synthetic reagent.

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References

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2 For a review, see R. M. Kellogg, *Tetrahedron*, 1976, **32**, 2165.
3 Y. Terao, M. Tanaka, N. Imai, and K. Achiwa, *Tetrahedron Lett.*, 1985, **26**, 3011.