CHEMISTRY LETTERS, pp. 1219 - 1220, 1984.

TITANIUM TETRACHLORIDE PROMOTED REDUCTION OF ALKENYL SULFIDES USING TRIETHYLSILANE AS A REDUCING AGENT

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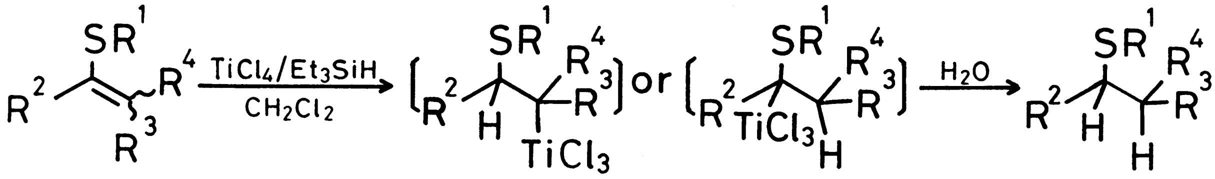
Alkenyl sulfides were reduced to the corresponding alkyl sulfides with triethylsilane in the presence of titanium tetrachloride in good yields. The reduction proceeds via -phenylthioalkyltitanium intermediate.

Although the reduction of alkenes with organosilane in the presence of trifluoroacetic acid or noble metal catalysts[1)] has been extensively investigated, Titanium tetrachloride promoted reduction of alkenes has not been reported with exception of the reduction of α,β-unsaturated ketones.[2)]

In the course of our study on the synthesis and reactions of alkenyl sulfides, we found that alkenyl sulfide (1) was reduced to the corresponding alkyl sulfide (2) by treatment with triethylsilane in the presence of an equimolar amount of titanium tetrachloride or boron trifluoride etherate.



1 3 4 2

The typical procedure is described for the reduction of 1-phenylthiocyclohexene: To a CH_2Cl_2 (3 ml) solution of 1-phenylthiocyclohexene (190 mg, 1 mmol) and triethylsilane (128 mg, 1.1 mmol) was added a CH_2Cl_2 solution of titanium tetrachloride (0.65 mol/dm^3, 1.68 ml) at -78 °C. After stirring for 30 min, the reaction was quenched by addition of water, extracted with CH_2Cl_2, and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed on silica gel (hexane) and cyclohexyl phenyl sulfide (182 mg) was isolated in 95% yield.

In a similar manner, various alkenyl sulfides (1) were reduced to the corresponding alkyl sulfides (2) (Table 1). The results listed in the table indicated that the yield of alkyl sulfide depended on the structure of alkenyl sulfide. When monosubstituted alkenyl sulfides were allowed to react with the silane in the presence of titanium tetrachloride, the reactions were complicated and alkyl sulfides were produced only in moderate yields. On the other hand, the reduction of di or trisubstituted alkenyl sulfides gave reduced products in good to high yields.

Table 1. Reduction of alkenyl sulfides (**1**)

R^1	R^2	R^3	R^4	Temp °C	Time h	Yield %
CH_3	$CH_3(CH_2)_7$	H	H	r.t.	overnight	37
				-78-r.t.	overnight	55
Ph	H	$Ph(CH_2)_2$	H	r.t.	overnight	—
				-78-r.t.	6	43
Ph	H	CH_3CH_2	H	-78-r.t.	overnight	58
Ph	H	$CH_3(CH_2)_4$	H	-78	0.75	26
Ph	Ph	H	H	-78	2	53
				0-r.t.	overnight	55[a)]
CH_3CH_2	Ph	Ph	H	r.t.	overnight	73
				r.t.	overnight	80[a)]
CH_3CH_2	Ph	$CH_3(CH_2)_5$	H	r.t.	overnight	46
				-78	1.5	76
CH_3CH_2	$-(CH_2)_4-$		H	-78	1.5	61
Ph	Ph	Ph	H	-78-r.t.	overnight	77
Ph	$-(CH_2)_4-$		H	-78	0.5	95
Ph	CH_3	CH_3	H	-78	0.5	95
Ph	CH_3	CH_3	CH_3	-78	0.5	90
Ph	Ph	CH_3	H	-78-r.t.	overnight	80

a) Boron trifluoride etherate was used as a Lewis acid.

It is reasonable to assume that the present reduction proceeds through the formation of an alkyltitanium intermediate (**3** or **4**) as depicted in the above equation. In order to determine the structure of the intermediate, the reaction was quenched with D_2O which in effect monitors the production of the hydrometallated intermediate. Since the quenching with D_2O of the reductions of 2-methyl-3-phenylthio-2-butene and 2-phenylthio-2-butene gave 2-deuterio-2-methyl-3-phenylthiobutane and 2-deuterio-3-phenylthiobutane in 85% and 84% yields, respectively, the intermediate of the present hydrotitanation was found to be β-phenylthioalkyltitanium (**3**).

The reactions of the titanium compounds (**3**) are now under investigation and will be reported soon.

References

1) A. Hajós, "Complex Hydrides," Elsevier, Amsterdam (1979), p. 196; E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), p. 325.

2) E. Yoshii and T. Kozumi, I. Hayashi, and Y. Hiroi, Chem. Pharm. Bull. (Tokyo), **25**, 1468 (1979).

(Received April 20, 1984)