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VINYLSILANES AS SUBSTRATES FOR THE SYNTHESIS OF SULFINES

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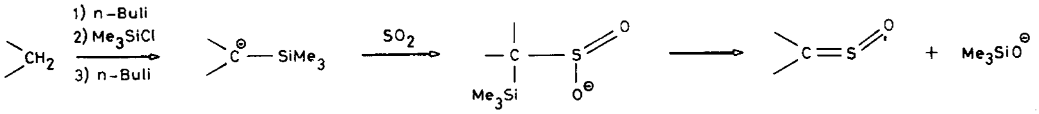
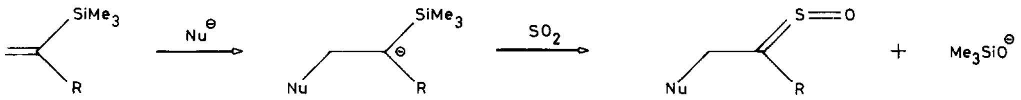
In a recent paper[1] we showed that alkylidenation of sulfur dioxide using α-silyl carbanions represents an attractive new synthetic route to sulfines (thione *S*-oxides). The required α-silyl carbanions were obtained from active methylene compounds by deprotonation, subsequent trimethylsilylation and again deprotonation with base, as outlined in Scheme 1.

Scheme 1



An alternative approach to the preparation of such carbanions is that involving the β-addition of appropriate nucleophilic reagents to vinylsilanes[2-5] Consequently, the synthesis of sulfines should also be possible as depicted in Scheme 2. If successful, this route will lead to sulfines bearing a hydrogen atom at the α-carbon atom, which are not preparable *via* oxidation of the parent thiocarbonyl compounds because of the interfering enethiolisation[6].

Scheme 2



The nucleophilic β-addition to substituted vinylsilanes has received little attention[7]. Factors that govern this addition are the nature of the nucleophile and the relative stability of the resulting α-silyl carbanion[2]. The substituents in the four vinylsilanes 1-4 (see Table) were chosen such that a considerable range in stability of the α-silyl carbanions is achieved. As nucleophilic reagents organolithium compounds of varying reactivity were taken, *viz.* *t*-BuLi, *n*-BuLi, MeLi and PhLi.

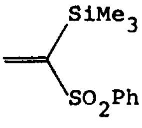
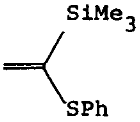
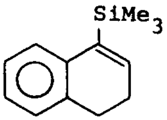
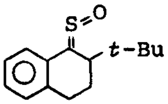
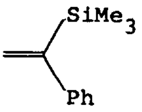
Peterson olefination of the readily available bis-silyl compound $PhSCH(SiMe_3)_2$ with formaldehyde afforded the desired vinylsilane[8] 2. Oxidation of 2 with two equivalents of *m*-chloroperbenzoic acid smoothly gave the new sulfonyl substituted vinylsilane 1 in good yield.

Substrate 1 was treated in THF at -78° with a slight excess of *t*-BuLi in pentane in the presence of two equivalents of tetramethylethylenediamine (TMEDA). Raising the temperature to about -40° for 15 min. ensured the completion of the β-addition reaction. An excess of gaseous sulfur dioxide was then passed through the red solution of the carbanion at -78°. A discharge of colour was observed. The reaction mixture was then poured into a saturated aqueous solution of ammonium chloride. Subsequent work-up gave the almost pure sulfine 5a. Further purification, which was accompanied by a considerable loss of material, was performed by fast column chromatography on silica gel (CH_2Cl_2) employing a pressure of 8 atm. The structure of this new sulfine was established on the basis of spectral data [ν(SO): 1075, 1105; $\nu(SO_2)$: 1142, 1300, 1320 cm^{-1}; NMR ($CDCl_3$): δ 1.02 (*t*-Bu, s), 2.67 (CH_2, s), 7.33-8.10 (arom. prot.) ppm]. The same procedure was used for the reaction of 1 with *n*-BuLi to yield sulfine 5b. In the case of PhLi the use of two equivalents of nucleophile turned out to be essential. The resulting sulfine 5d was crystallized from CH_2Cl_2/pentane/ether at -78°. When less PhLi, *e.g.* one equivalent, was used, the sulfine 5d was contaminated with $PhCH_2CH(SiMe_3)SO_2Ph$ (33%) which was formed by protonation of the intermediate carbanion. The reaction of 1 with MeLi was performed in ether at 20°. Subsequent treatment with sulfur dioxide at -78° afforded sulfine 5c. In all four cases only one isomer of the sulfonylsulfines 5a-d was isolated, most likely the *E*-isomer as deduced from the $\delta(CH_2)$ in the NMR spectrum.

Using essentially the same procedure as described for the preparation of 5a, substrate 2 was brought into reaction with *t*-BuLi. Sulfine 6a was obtained as a mixture of *Z*- and *E*-isomers which could easily be separated by preparative thin layer chromatography (silica gel, CH_2Cl_2). With *n*-BuLi (hexane, -78°) vinylsilane 2 gave sulfine 6b in a rather low yield, together with the thioloester *n*-$BuCH_2C(=O)SPh$, some thiophenol and *n*-$BuCH_2CH(SiMe_3)SPh$. In order to diminish possible scrambling of protons, hexamethylphosphoramide[9] was used instead of TMEDA. However, the results did not improve. MeLi and PhLi gave with vinylsilane 2 a complex reaction mixture from which neither sulfine nor starting material could be isolated.

The substrates 3 and 4 were prepared from the respective ketones by treatment of the corresponding phenylsulfonylhydrazones with an excess of *n*-BuLi and trimethylsilyl chloride[10]. Both substrates were treated with *t*-BuLi (1.6-2 equivalents in pentane/hexane, 20°, 2 equivalents of TMEDA) and SO_2 (-78° → 20°). The sulfines 7a and 9a, respectively, were isolated as single isomers. In addition considerable quantities of the ketones 8a and 10a, corresponding structurally with these sulfines, were obtained. Using the same conditions the vinylsilane 3 gave with *n*-BuLi in hexane the ketone 8b only and substrate 4 ketone 10b only. No sulfines were detected. Reactions of 3 and 4 with the

TABLE

VINYLSILANE	NUCLEOPHILE	PRODUCT	YIELD* (%)
 1	a. *t*-BuLi	5a. *t*-BuCH$_2$C(=SO)SO$_2$Ph [m.p. 25-28°, δ(CH$_2$) 2.67, s]	51
	b. *n*-BuLi	5b. *n*-BuCH$_2$C(=SO)SO$_2$Ph [oil, δ(CH$_2$) 2.73, t]	50
	c. MeLi	5c. MeCH$_2$C(=SO)SO$_2$Ph [oil, δ(CH$_2$) 2.78, q]	74**
	d. PhLi	5d. PhCH$_2$C(=SO)SO$_2$Ph [m.p. 90-92°, δ(CH$_2$) 4.13, s]	72
 2	a. *t*-BuLi	6a. *t*-BuCH$_2$C(=SO)SPh [oil, δ(CH$_2$) 2.78, *E*-isomer; δ(CH$_2$) 2.42, *Z*-isomer; *Z/E*: 15/58]	73
	b. *n*-BuLi	6b. *n*-BuCH$_2$C(=SO)SPh [oil, δ(CH$_2$) 2.84, t, *E*-isomer; δ(CH$_2$) 2.33, t, *Z*-isomer; *Z/E*: 1/1]	15
 3	a. *t*-BuLi	7a.  [oil, δ(CH) 3.92, t]	33
		8a. 3,4-dihydro-2-*t*-butyl-1(2H) naphthalenone	25
	b. *n*-BuLi	8b. 3,4-dihydro-2-*n*-butyl-1(2H) naphthalenone	30
 4	a. *t*-BuLi	9a. *t*-BuCH$_2$C(=SO)Ph [oil, δ(CH$_2$) 3.18, s]	29
		10a. *t*-BuCH$_2$C(=O)Ph	17
	b. *n*-BuLi	10b. *n*-BuCH$_2$C(=O)Ph	42

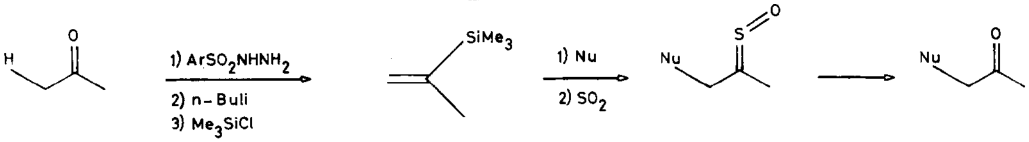
*: Isolated product; **: determined from NMR

nucleophiles MeLi and PhLi were unsuccessful, only starting material was recovered.

The structures of the ketones 8a,b and 10a,b reveal that these carbonyl compounds arise from the corresponding sulfines. It was found that the conversion of these sulfines into ketones takes place under the conditions of the reaction and only to a minor extent during the work-up procedure.

The ultimate reaction sequence as depicted in Scheme 3 formally represents a nucleophilic α-alkylation of a ketone, which is an "Umpolung" of the common electrophilic introduction of an alkyl group into a ketone. By converting the ketone into a vinylsilane the α-carbon atom becomes susceptible to a nucleophilic addition. Restoring the carbonyl function is achieved *via* the intermediacy of a sulfine.

Scheme 3



The conversion[11] of sulfines into ketones also can be accomplished photochemically. Accordingly, irradiation of the crude reaction mixture, containing 7a + 8a, in benzene for 2.5 hr, gave ketone 8a as the major product. Similarly, the mixture of 9a + 10a afforded ketone 10a.

REFERENCES

1. M. van der Leij, P.A.T.W. Porskamp, B.H.M. Lammerink and B. Zwanenburg, Tetrahedron Lett. 1978, 811.
2. L.F. Cason and H.G. Brooks, J. Amer. Chem. Soc. 74, 4582 (1952); J. Org. Chem. 19, 1278 (1954).
3. T.H. Chan, E. Chang and E. Vinokur, Tetrahedron Lett. 1970, 1137; T.H. Chan and E. Chang, J. Org. Chem. 39, 3264 (1974).
4. R.F. Cunico, J. Organomet. Chem. 60, 219 (1973).
5. a. D. Seebach, R. Bürstinghaus, B.T. Gröbel and M. Kolb, Liebigs Ann. Chem. 1977, 830.
   b. G. Stork and B. Ganem, J. Amer. Chem. Soc. 95, 6152 (1973).
   c. S.L. Hartzell and M.W. Rathke, Tetrahedron Lett. 1976, 2737.
6. L. Carlsen and F. Duus, Synthesis 1977, 256 and references cited therein.
7. Most studies deal with the parent vinylsilane (R=H), Cf. ref. 2-4. α-Substituted vinylsilanes are described in ref. 5: R = $SiMe_3$ (a), SMe (a), MeCO (b), *t*-BuCOO (c).
8. B.T. Gröbel and D. Seebach, Chem. Ber. 110, 852 (1977).
9. T.M. Dolak and T.A. Bryson, Tetrahedron Lett. 1977, 1961.
10. T.H. Chan, A. Baldasarre and D. Massuda, Synthesis 1976, 801.
11. B. Zwanenburg and J. Strating, Quart. Rep. Sulfur Chem. 5, 79 (1970).

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