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ALKYLATION OF SILYL ENOL ETHERS WITH PUMMERER GENERATED VINYL THIONIUM IONS

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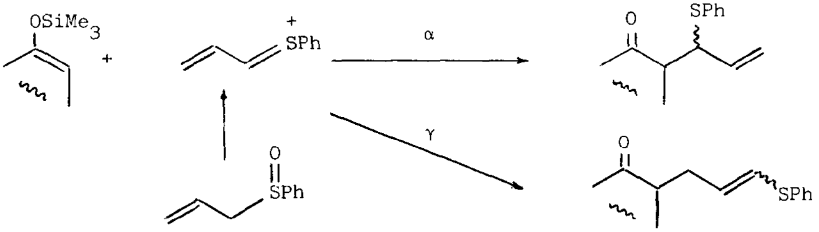
Abstract: Silyl enol ethers (1,2) are γ-alkylated in moderate yields by a series of vinyl thionium ions generated from the corresponding allylic sulphoxides (3-6) with TMSOTf and diisopropylethylamine in CH_2Cl_2 at -78°C.

In recent years alkylation of Pummerer intermediates has been put to good synthetic use both inter- and intramolecularly[1-2]. Although silyl enol ethers have been successfully thioalkylated under mild Lewis acid conditions using a variety of substituted α-chlorosulphides[3], to date no report has appeared on alkylation of silyl enol ethers by vinyl thionium ions generated from allylic sulphoxides under Pummerer conditions. In this communication we report on studies directed towards the latter end. Scheme 1 summarises the two possible products (α or γ) for alkylation of a silyl enol ether by phenyl allyl sulphoxide.

Scheme 1



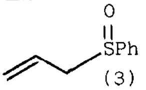
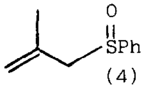
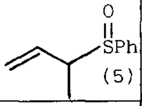
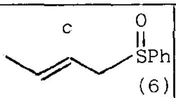
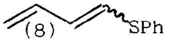
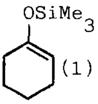
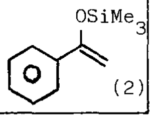
In developing Pummerer generation conditions compatible with silyl enol ethers we have found that the most favourable reaction conditions constitute inverse addition of allyl sulphoxide to a mixture of excess silyl enol ether (1.5eq), TMSOTf (1.3eq) and diisopropylethylamine (Hünigs base), (1.3eq) in CH_2Cl_2 at -78°C for 1 hr. The presence of base at -78°C was essential and larger amounts of Lewis acid only marginally improved yields. Other (Lewis acid)/base combinations or higher temperatures gave inferior results while phenyl sulphoxides gave better results than n-butyl or t-butyl derivatives[4]. Yields compare favourably with those for alkylation of aromatic compounds with unactivated sulphoxides using an "activator" in conjunction with a Lewis acid.[2]

Table 1 summarises the regiochemical outcomes for a series of alkylations of the silyl enol ethers of cyclohexanone and acetophenone (1,2) with a range of substituted allyl phenyl sulphoxides. The highest yields were obtained with unsubstituted and β-methylallyl sulphoxides (3,4) with exclusive γ-substitution, while α-methyl sulphoxide (5) gave a poorer yield on account of the higher temperature needed (-20°C). Consistent with recent work reported by Miller[5a] the γ-methyl substituted sulphoxide (6) gave the diene sulphide (8) (see Table 1) as the major product suggesting that deprotonation of the vinyl thionium ion in this case is faster than attack by the silyl enol ether. Interestingly, the alkylated product was that of α-attack presumably as a result of steric hindrance to the soft end of the alkylating agent.

Finally the vinyl sulphoxide (7) was investigated and as expected gave the same product as that from allylic sulphoxide (3) albeit in lower yield (-40°C/4hrs was required).

Since vinyl sulphides can be hydrolysed to carbonyl compounds this new method compliments existing methodology based on Michael additions of silyl enol ethers to enones[6] and alkylation of lithium enolates using γ-chloro vinyl sulphides[5b].

Table 1

 (3)	 (4)	 (5)	c  (6)	 E:Z:50:50 (7)		Silyl enol ether
63[b] γ	64 γ	24 γ	36 23  (8) α	34 γ	Yield Product[a]	 (1)
62 γ	72 γ	-	-	-	Yield Product	 (2)

a: all reactions were carried out on a 1 mmole scale unless otherwise stated. γ-alkylations gave one major geometrical isomer while diastereomers were obtained for the α-product from (6). New compounds were characterised by their 500 MHz ^{1}H-nmr and mass spectra.

b: 2 mmole of silyl enol ether used to 1 mmole of sulphoxide.

c: On a 4 mmole scale.

NOTES AND REFERENCES

1. P. Magnus, T. Gallagher, P. Brown and P. Pappalardo, Acc. Res., 17, 35, 1984.
2. Ioannis Stamos, Tetrahedron Letters., 477, and 2787, 1985.
3. I. Fleming and J. Iqbal, Tetrahedron Letters., 24, 327, 1983.
4. n-Butyl allyl sulphoxide gave a yield of only 30% (warmed to -20°C before quenching), while t-butyl allyl sulphoxide didn't react at -78°C.

5(a)R.D. Miller and D.R. McKean, Tetrahedron Letters., 24, 2619, 1983. (b) A.J. Mura, D.A. Bennett and T. Cohen, ibid., 50, 4433, 1975.

6. K. Narasaka, K. Soai, and T. Mukaiyama, Chem. Lett., 1223, 1974.

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