Tetrahedron Letters,Vol.25,No.51,pp 5947-5948,1984
Printed in Great Britain 0040-4039/84 $3.00 + .00

A FACILE ENTREE TO α-OXO SULFINES BY REACTION OF THIONYL CHLORIDE WITH SILYL ENOL ETHERS

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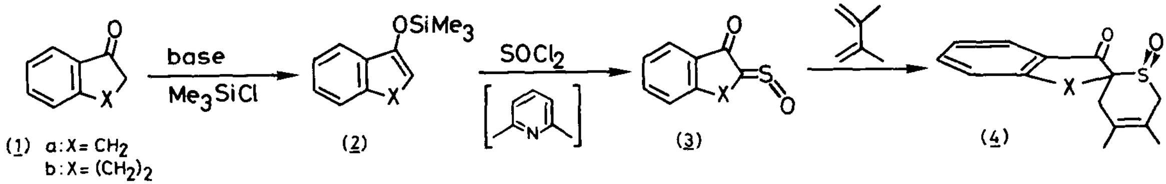
Abstract: Silyl enol ethers derived from 1-indanone, 2-indanone,α-tetralone and 4-chromanone react with thionyl chloride to give α-oxo sulfines (3) which can be either isolated or trapped by a cycloaddition reaction with a diene.

In a recent report[1] we described the preparation of some α-oxo sulfines (S-oxides of monothio-1,2-diones) by the reaction of thionyl chloride with α-methylene ketones. However, this method seemed to be limited to those ketones in which the methylene group is sufficiently active[2]. This observation suggest that the enol content of the ketone plays an essential role in this reaction leading to an α-oxo sulfine. Therefore, we decided to rivet the ketone in its enol form by converting it into the corresponding silyl enol ether and reacting that with thionyl chloride.

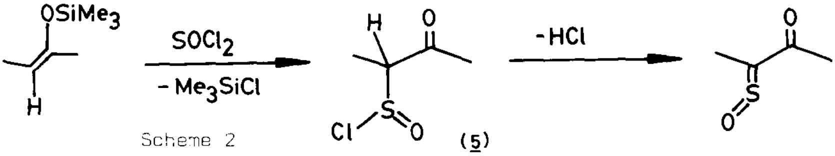
Accordingly, 1-trimethylsilyloxy-1-indene (2a), derived from 1-indanone (1a) was treated with thionyl chloride (light petroleum, 25 °C). A surprisingly fast reaction took place: in 5 min time α-oxo sulfine 3a crystallized out from the reaction mixture in 48% yield (scheme 1). [m.p. 130° (decomp.); IR (KBr): 1675, 1090 ^{1}H-NMR ($CDCl_3$): δ4.17 (s, 2H, CH_2), 7.36-7.80 (m, 4H, aromat.)].



Scheme 1

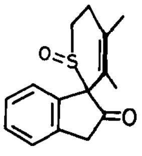
In the same facile manner 1-trimethylsilyloxy-3,4-dihydro-1-naphthalene (2b) derived from α-tetralone (1b) gave sulfine 3b. Both sulfines (3a,b) smoothly react with 2,3-dimethyl-1,3-butadiene (CH_2Cl_2, 25 °C, 0.5 h) in a Diels-Alder fashion to form the dihydrothiapyran-1-oxides 4a and 4b, respectively. These cycloadducts also can be obtained in a one-pot procedure, *i.e.* by adding thionyl chloride to a mixture of the silyl enol ether 2a or 2b, 2,6-lutidine (1 equiv.) and an excess of 2,3-dimethyl-1,3-butadiene (CH_2Cl_2, 0 °C, 2 h) (scheme 1). 2,6-Lutidine turned out to be an effective HCl-trapping agent in these reactions, with pyridine the results were unsatisfactory.

We suggest that the sulfines are formed as depicted in scheme 2. Thus, first formation of β-oxo sulfinyl chloride 5[3,4] which then eliminates hydrogen chloride to give the α-oxo sulfines. Probably, part of the silyl enol ether functions as hydrogen chloride trapping agent.



Scheme 2

Attemps to convert 4-trimethylsilyloxy-1,2-benzopyran **2c** derived from 4-chromanone **1c** into the sulfine **3c** failed because the product did not crystallize out. However, by using the described one-pot procedure the cycloadduct **4c** was obtained in good yield. Analogously, the silyl enol ether derived from 2-indanone **6**, *i.e.* 2-trimethylsilyloxy-1-indene **7**, was converted into the cycloadduct **9** in high yield. Yields, physical and spectral data are compiled in the table.



(9)

TABLE. Synthesis of α-oxo sulfines and/or their cycloadducts with 2,3-dimethyl-1,3-butadiene[+]

Starting material	sulfine	yield (%)	m.p. (°C)	cycloadduct	yield[a] (%)	m.p. (°C)
2a	3a	48	130 (decomp.)	4a[b]	75	154-156
2b	3a[c]	28	98-99	4b[d]:	66	138-142
2c	3c	e		4c[f]	70	159
7	8	e		9[g]	89	131

(a) One pot procedure was used; all compounds were isolated by flash chromatography on silica gel (petroleum 60-80 °C - ethyl acetate). (b) IR (KBr): 1705, 1040; ^{1}H NMR ($CDCl_3$): δ1.63, 1.72 (2xs, 6H, CH_3), 2.04-3.94 (m, 6H, CH_2), 7.2-7.7 (m, 4H, aromat.). (c) IR (KBr): 1635, 1100; ^{1}H-NMR ($CDCl_3$) δ3.0 (m, 2H, CH_2), 3.33 (m, 2H, CH_2), 7.14-7.46 (m, 3H, aromat.), 7.97 (d, J 6.6 Hz, aromat.). (d) IR (KBr): 1650, 1040; ^{1}H-NMR ($CDCl_3$): δ1.73 (s, 6H, CH_3), 2.2-3.5 (m, 8H, CH_2), 7.15-7.5 (m, 3H, aromat.), 8.0 (m, 1H, aromat.). (e) Sulfine could not be isolated. (f) IR (KBr): 1670, 1040; ^{1}H-NMR ($CDCl_3$): δ1.93 (s, 6H, CH_3, 2.30 (s, 2H, CH_2), 3.27 (s, 2H, CH_2SO), 4.37+4.81 (ABq, 2H, J 12.0 Hz, CH_2O), 6.9-7.9 (m, 4H, aromat.). (g) IR (KBr): 1740, 1050; ^{1}H-NMR ($CDCl_3$): δ1.75, 1.80 (2xs, 6H, CH_3), 2.34-3.44 (m, 4H, $CH_2C{=}CCH_2$), 3.38+3.72 (ABq, 2H, J 21.6 Hz, CH_2CO), 7.34 (s, 4H, aromat.).

We want to emphasize that the α-oxo sulfines **3c** and **8** cannot be isolated due to rapid hydrolysis furnishing the starting ketones **1** and **6**, respectively. This sensitivity of α-oxo sulfines to water may be the reason that this new reaction of silyl enol ethers with thionyl chloride has been overlooked in the past. α-Oxo sulfines are new members of the sulfine family. As silyl enol ethers can be obtained from several types of carbonyl compounds the new reaction presented here constitutes an attractive and facile access to a variety of functionalized sulfines which opens new prospects with these sulfur heterocumulenes.

REFERENCES and NOTES

[+] All compounds gave satisfactory analytical data.

1. B.G. Lenz, R.C. Haltiwanger and B. Zwanenburg. J. Chem. Soc. Chem. Comm. **1984**, 502.
2. The reaction of ketones with thionyl chloride can lead to a variety of products, for a recent review, see K. Oka, Synthesis **1981**, 661.
3. Cf the formation of β-oxo sulfoxides from sulfinyl chlorides and silyl enol ethers, N.A. Meanwell and C.R. Johnson, Synthesis **1982**, 283.
4. V.N. Sergeev, G.S. Zaitseva and Y.I. Baukov, Zh. Obshch. Khim. **1980**, 699; Chem. Abstr. **93**, 132020m (1980).

(Received in UK 27 September 1984)