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[4+2]-CYCLOADDITIONS OF SILYLATED AND NON SILYLATED THIONES WITH VINYL TRIMETHYLSILYL KETONE: NOVEL SYNTHESIS OF 4H-1,3-OXATHIINS.

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Summary. 4H-1,3-Oxathiins are obtained by an high-yield heterocycloaddition of thiones with vinyltrimethylsilylketone, behaving as heterodiene. 4H-1,3-Oxathiins can be oxidized to the corresponding S-oxides, which are the formal cycloadducts of sulphines.

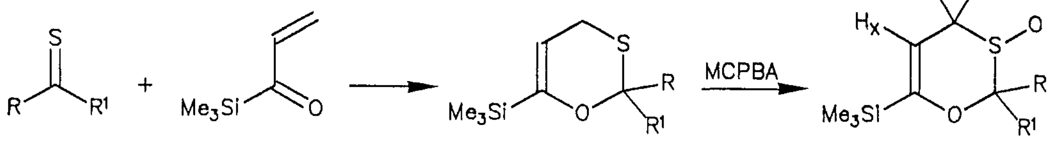
The high reactivity of thiones in [4+2]-cycloaddition with dienes[1] and heterodienes[2], is well documented in the literature. Such cycloaddition reactions serve as an important source of sulphur containing six membered heterocycles.

The Diels-Alder reactivity of vinyl silyl ketones was tested with 2,3-dimethylbutadiene[3], however during this reaction a significant amount of the reverse electron demand adduct (viz.cycloaddition with one of the double carbon-carbon bond of 2,3-dimethylbutadiene) was formed, implying that vinylsilyl ketones can react as dienophiles as well as dienes. The aim of this paper is to demonstrate that the high reactivity of thiones **1** as heterodienophiles[1h] can promote the reaction with vinyl silyl ketone **2** as a heterodiene (Scheme 1). In fact, the reaction of **1a-c** and **2**[4] in diethyl ether at room temperature afforded in good to quantitative yields the 4H-1,3-oxathiins **3a-c** (Table 1). Similar results were obtained with silyl thioketones[5] **1d-e** which have a relatively high dienophilicity. The adducts **3d-e** contain a silyl group attached to a sp^3 carbon atom, which can be replaced by a proton[1h].

The adducts **3** are moderately stable in solution. They show a partial retrocycloaddition reaction and therefore they need to be crystallized at room temperature. The structures of **3** were established by IR, ^1H and ^{13}C NMR[6] as well as with exact mass measurements. Common feature of products **3** are an IR band at 1070-1080 cm^{-1}, which is typical for an ether function.

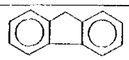
Further structure proof for **3** was provided by their oxidation. Treatment of adducts **3** with one mole of MCPBA in diethyl ether at -20°C gave the corresponding S-oxides **4** (Scheme 1). The presence of the SO band at 1060-1065 cm^{-1} in the IR spectrum confirms the regiochemistry of the cycloaddition reaction. The alternative structure **5** would have given

Scheme 1

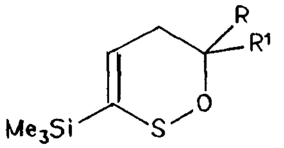


1 a-e   2   3 a-e   4 a-e

Table 1

	R	R^1	3: Yield (%)	M.p. (^{o}C)	4: Yield (%)	M.p. (^{o}C)
a	$C_6H_4CH_3$-p	$C_6H_4CH_3$-p	100	90-2	93	92-4
b	$C_6H_4OCH_3$-p	$C_6H_4OCH_3$-p	98	88-92	100	156-7
c			80	108-112	88	152-154
d	Ph	$SiMe_3$	100	solid -20 ^{o}C	44[a]	88-90
e	Ph	$SiPh_3$	75	104-106	15	[b]

[a] calculated by 1H-NMR on the crude; [b] the product could not be crystallized owing to its instability.



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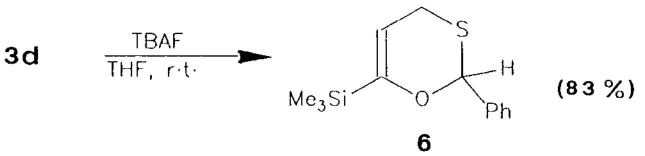
a sulphinic ester by oxidation, for which an IR absorption at 1120–1130 cm^{-1} would have been expected. The sulphoxides 4 are very stable compounds in comparison with sulphides 3. Yields and melting points for 4 are collected in Table 1. Due to the presence of the sulphoxide function the two hydrogens of the adjacent methylene group are diastereotopic, which is a typical feature in the ^{1}H NMR spectrum.[7] Products 4 can formally be considered as the adducts derived from cycloaddition of sulphines (thione S-oxides) and 2. Attempts to obtain adducts 4 by direct cycloaddition of sulphines on 2 met with no success. Yields of the oxidation reaction are good for **3a–c**, but lower for **3d** and **3e**. Only one of the two possible diastereoisomers of **4d** and **4e** could be isolated, presumably the one with the anti-structure. In addition, a complex mixture was obtained which could not be unravelled. The lower yields of the oxidation reaction from **3d** and **3e** can be attributed to a Sila-Pummerer rearrangement of the syn isomer; this rearrangement was previously observed during the oxidation of 6-phenyl-6-trimethylsilyl or 6-triphenylsilyl-5,6-dihydro-2H-thiopyran[1h] and of 3,4-dimethyl-6-t-butyl-6-trimethylsilyl-5,6-dihydro-2H-thiopyran[8].

Adduct **3d** could chemoselectively be protodesilylated with tetrabutylammonium fluoride in THF at room temperature to give product **6**[9] in high yield (Scheme 2).

Scheme 2



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This product formally represents the cycloadduct derived from thiobenzaldehyde[1h,10], in other words compound **1d** has served as a synthetic equivalent for thiobenzaldehyde.

The new cycloaddition described here offers a good method for the synthesis of 4H-1,3-oxathiins. It should be noted that in the literature only very few examples of these heterocycles have been reported[11a,b].

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6. ^{1}H NMR (200 MHz, $CDCl_3$) for selected compounds **3** are given below:
3a: δ 0.23 (9H, s, $SiMe_3$), 2.33 (6H, s, CH_3), 2.93 (2H, d, J = 4 Hz, CH_2), 5.16 (1H, t, vinyl H), 7-7.65 (8H, q, J = 8 Hz, ArH).
3c: δ 0.09 (9H, s, $SiMe_3$), 3.52 (2H, d, J = 4.5 Hz, CH_2), 5.48 (1H, t, vinyl H), 7.3-7.7 (8H, m, ArH).
3d: δ 0.05 (9H, s, $SiMe_3$), 0.2 (9H, s, $SiMe_3$), 2.65 (2H, d, J = 6 Hz, CH_2), 5.1 (1H, t, vinyl H), 7.1-7.5 (5H, m, ArH). ^{13}C NMR (50.3 MHz, $CDCl_3$) of compound **3a** : δ 160.17 (C), 140.67 (C), 137.6 (C), 129.9 (CH), 127.0 (CH), 108.13 (CH), 87.83 (C), 24.36 (CH_2), 20.85 (CH_3), -2.63 (CH_3).
7. ^{1}H NMR (200 MHz, $CDCl_3$) for selected compounds **4** are given below:
4a: δ 0.3 (9H, s, $SiMe_3$), 2.30 (3H, s, CH_3) and 2.33 (3H, s, CH_3), 2.85 (1H, dd, J_{AB}=16.9 Hz, J_{AX}= 2.7 Hz, H_A), 3.25 (1H, dd, J_{AB}=16.9 Hz, J_{BX}= 5.9 Hz, H_B), 4.87 (1H, dd, H_X), 7.1-7.5 (8H, m, ArH).
4c: δ 0.15 (9H, s, $SiMe_3$), 3.57 (1H, dd, J_{AB}=18 Hz, J_{AX}= 5 Hz, H_A), 3.82 (1H, dd, J_{AB}=18 Hz, J_{BX}= 3 Hz, H_B), 5.20 (1H, dd, H_X), 7.2-7.8 (8H, m, ArH).
4d: δ 0.15 (9H, s, $SiMe_3$), 0.27 (9H, s, $SiMe_3$), 2.83 (1H, dd, J_{AB} = 17 Hz, J_{AX}=2 Hz, H_A), 3.03 (1H, dd, J_{AB}= 17 Hz, J_{BX} = 7 Hz, H_B), 4.85 (1H, dd, H_X), 7.1-7.4 (5H, m, ArH). ^{13}C NMR (50.3 MHz, $CDCl_3$) of compound **4a**: δ 160.58 (C), 138.79 (C), 135.83 (C), 130.32 (C), 129.62 (CH), 129.05 (CH), 128.22 (C), 127.22 (CH), 125.89 (CH), 99.27 (CH), 91.93 (C), 41.58 (CH_2), 20.95 (CH_3), -2.62 (CH_3).
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9. **6**; oil; IR (CS_2) ν_{max} 1080 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.15 (9H, s, $SiMe_3$), 3.0 (1H, dd, J_{AB} =17.2 Hz, J_{AX} = 6.2 Hz), 3.65 (1H, dd, J_{AB} = 17.2 Hz, J_{BX} = 2.6 Hz), 5.3 (1H, dd, vinyl H), 5.9 (1H, s, CH), 7.2-7.6 (5H, m, ArH).
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