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**Preliminary communication**

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# PREPARATION OF α, β-UNSATURATED ACYLTRIMETHYLSILANES

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## Summary

α, β-Unsaturated acyltrimethylsilanes were prepared in good yield from the trimethylsilyl enol ethers of the corresponding acylsilanes through phenylsulfenylation and oxidation, followed by thermal decomposition of the resulting α-phenylsulfinylacylsilanes.

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In connection with our studies of the use of organosilicon compounds as reagents in organic synthesis, we required α, β-unsaturated acylsilanes. Although acylsilanes are well known [1], there have been no reports on the synthesis of α, β-unsaturated derivatives. We recently reported an efficient method for the preparation of trimethylsilyl enol ethers of acyltrimethylsilanes, (I) through the oxidation reaction of the corresponding lithium 1,1-bis(trimethylsilyl)alk-1-oxide with benzophenone [2,3] *. We describe here a simple preparative method for α, β-unsaturated acyltrimethylsilanes which is based on the silyl enol ether I. In this process, I was treated with phenylsulfenyl chloride (10% excess) in carbon tetrachloride at —20° C for 5 min. Bulb to bulb distillation or chromatography on silica gel of the reaction mixture afforded the corresponding α-phenylsulfenylacyltrimethylsilane (II) in excellent yield. Substrates possessing a remote C=C bond (e.g., Ic) also gave the mono-sulfenylated product II in satisfactory yield on such treatment at lower temperature ( —78° ) in methylene chloride, although the formation of the bis-sulfenylated product (12%) could not be excluded completely. Oxidation of the resulting sulfide II with *m*-chloroperbenzoic acid proceeded in the expected manner and afforded III in good yield when carried out at 0° C for 5 min in methylene chloride, followed by chromatography on silica gel. The oxidation of II with four equivalents of sodium metaperiodate [4] was quite slow in aqueous methanol at room temperature. Some slight difficulty also was encountered in the isolation of sulfoxide

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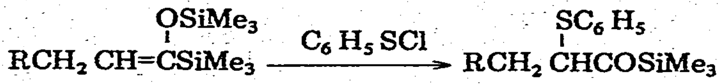
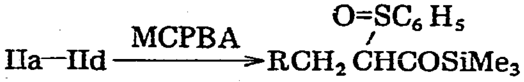
* For the preparation of 1,1-bis(trimethylsilyl)alkan-1-ol see ref. 3.

III in that partial conversion to the corresponding α-phenylsulfinyl aldehyde occurred when it was heated in the presence of water. Thermal decomposition of the sulfoxide III [5] to give the desired α,β-unsaturated acyltrimethylsilane IV could be achieved by heating III in hexane for 5 h. In this decomposition reaction employment of higher temperatures for shorter period does not give IV



$$RCH_2CH{=}\overset{OSiMe_3}{C}SiMe_3 \xrightarrow{C_6H_5SCl} RCH_2\overset{SC_6H_5}{C}HCOSiMe_3$$

| | |
|---|---|
| (Ia) $R = C_3H_7$ | (IIa) 93% (96–98°C/0.07 Torr) |
| (Ib) $R = C_5H_{11}$ | (IIb) 94% (122–125°C/0.07 Torr) |
| (Ic) $R = CH_2{=}CH(CH_2)_6$ | (IIc) 75% (133–135°C/0.07 Torr) |
| (Id) $R = C_6H_5$ | (IId) 96% (132–134°C/0.08 Torr) |



$$\text{IIa–IId} \xrightarrow{MCPBA} RCH_2\overset{O=SC_6H_5}{C}HCOSiMe_3$$

(IIIa) 87%
(IIIb) 85%
(IIIc) 84%
(IIId) 83%

$$\text{IIIa–IIId} \xrightarrow{\Delta} RCH{=}CHCOSiMe_3$$

(IVa) 76% (67–70°C/4.5 Torr)
(IVb) 76% (53–55°C/0.1 Torr)
(IVc) 79% (75–77°C/0.07 Torr)
(IVd) 92% (77–79°C/0.1 Torr)

without formation of by-product. For example, heating IIIa at 135°C for 1 h in xylene resulted in an appreciable decrease of the yield (42% for IVa), accompanied by formation of other unidentified products. Satisfactory analytical data were obtained for II and IV.

The products IIa, IIIa, and IVa exhibited the following spectral data.

IIa: NMR ($CCl_4$, methylene chloride as internal standard); δ (ppm) 0.27 (s, 9H), 0.95 (t, $J$ 5 Hz, 3H), 1.15–2.10 (m, 6H), 3.72 (t, $J$ 6 Hz, 1H), and 7.25 (s, 5H). IR (neat); 1632, 1249, and 843 $cm^{-1}$.

IIIa (a mixture of diastereomers): ($CCl_4$); δ (ppm) − 0.05 (s, 5.4H, $SiMe_3$), 0.23 (s, 3.6H, $SiMe_3$), 0.86 (t, $J$ 5 Hz, 3H), 1.05–1.55 (m, 4H), 1.55–2.10 (m, 2H), 4.00 (t, $J$ 6 Hz, 0.4H, SO—CH—CO), 4.13 (t, $J$ 6 Hz, 0.6H, SO—CH—CO), and 7.50 (s, 5H). IR (neat); 1638, 1250, 1050, and 847 $cm^{-1}$.

IVa: NMR ($CCl_4$); δ (ppm) 0.25 (s, 9H), 0.97 (t, $J$ 7 Hz, 3H), 1.55 (m, 2H), 2.25 (q, $J$ 6 Hz, 2H), 6.12 (d.d, $J$ 1.5 and 15 Hz, 1H), and 6.63 (d.t, $J$ 15 and 6 Hz, 1H). IR (neat); 1635, 1590, 1250, 975, and 845 $cm^{-1}$. UV (cyclohexane); $\lambda_{max}(\epsilon)$, 425 (53), 440 (46), and 445 (34) nm.

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