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A Simple Route to Acylsilane Enol Esters from Enol Esters

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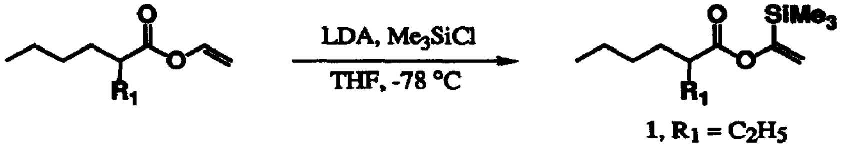
Abstract: *A new methodology is described for the synthesis of enol esters of acylsilanes, from readily available vinyl esters. A solution of LDA is added to a mixture of an enol ester (preferably sterically congested, with only one α - carboxyl proton, eg 2-ethylhexanoate) and a chlorosilane at -78°C to afford the product.*

During the course of some recent work on silyl ketene acetals, we sought to prepare the trimethylsilyl ketene acetal of vinyl 2-ethylhexanoate. To our surprise, the attempted conversion of this compound to the trimethylsilyl ketene acetal under standard conditions (addition of the ester in THF to 1.1 eq of LDA in THF at -78 °C, followed by quenching with 1.2 eq of Me_3SiCl) afforded the product of vinyl metalation (**1**) instead.[1] This result was surprising in light of the substantial difference in pK_a that would be expected between the proton next to the carboxyl group and the vinyl proton. Furthermore, the unusual structure of **1**, an enol ester of an acylsilane, represents a structural class that heretofore has been relatively inaccessible.[2]



1, $R_1 = C_2H_5$

This unexpected result prompted us to extend this methodology to other substrates, and to examine the potential scope of this transformation. Results are summarized in Table 1. It was found that addition of LDA to a premixed solution of the vinyl ester and Me_3SiCl at -78 °C afforded the highest yields (Entry **1a** vs. **1b**). It will be noted that the reaction works very well with Me_3SiCl and Et_3SiCl (Entries **1a**, **2**, **5**, **6**, **7**), less so with $Ph_2MeSiCl$ (Entry **3**), and not at all with t-$BuMe_2SiCl$ (Entry **4**). Reducing the steric demand about the proton α to the carboxyl groups (R_1 = Et ⇒ Me ⇒ H) results in increasing formation of the expected silyl ketene acetal. However, in these cases the desired vinyl silyl products may be obtained in modest yield by the use of 2.2 eq LDA and 2.4 eq Me_3SiCl (Entry **9**).[3] Attempts to intercept the putative vinyl anion responsible for the formation of **1** with other electrophiles, such as benzaldehyde and iodomethane, were unsuccessful. In these cases the starting vinyl ester was not recovered following standard workup. Allowing the vinyl anion to equilibrate for varying lengths of time up to 0.5 h at -78 °C prior quenching with Me_3SiCl did not result in a significant decrease in the yield of **1** beyond that obtained in Entry **1b**.

A representative procedure is as follows: A solution of LDA (8.4 mmol) in 4 mL of THF was added dropwise to a solution of vinyl 2-ethylhexanoate (1.55 mL, 8.0 mmol) and Me_3SiCl (1.12 mL, 8.8 mmol) in 15 mL of THF at -78 °C. After 0.5 h at -78 °C, the mixture was allowed to come to 20 °C and was kept at 20 °C for 15 min. The mixture was then diluted with 60 mL of hexane, washed with 1 M HCl (2 x 20 mL), saturated $NaHCO_3$ (1 x 20 mL), water (3 x 20 mL), brine (1 x 20 mL), dried and evaporated. Kugelrohr distillation gave 1.807 g (93%) of **1**. ^1H NMR ($CDCl_3$): $\delta = 5.40$ (s, 1 H, =CH); 5.16 (s, 1 H, =CH); 2.34 (m, 1 H, 2-CH); 1.73 - 1.55 (m, 4 H, 4- and 5 CH_2); 1.33 - 1.30 (m, 4 H, 3- and 3'-CH_2); 0.94 (t, 3 H, 4'-CH_3); 0.89 (t, 3 H, 6-CH_3); 0.17 (s, 9 H, $SiMe_3$). IR (neat): 3080 (=CH); 1735 (ester C=O); 1685 (C=C) cm^{-1}. MS (CI, NH_3): 243 (M + H^+); 227 (-CH_4). Analysis: Calculated for $C_{13}H_{26}O_2Si$: C 64.41%; H 10.81%. Found: C 64.63%; H 10.94%.

Table 1

Entry	Starting Material	Product	Yield[a]
1a	$CH_3(CH_2)_3CH(C_2H_5)CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_3CH(C_2H_5)CO_2C(SiMe_3){=}CH_2$	93%
1b	$CH_3(CH_2)_3CH(C_2H_5)CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_3CH(C_2H_5)CO_2C(SiMe_3){=}CH_2$	80%[c]
2	$CH_3(CH_2)_3CH(C_2H_5)CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_3CH(C_2H_5)CO_2C(SiEt_3){=}CH_2$	72%
3	$CH_3(CH_2)_3CH(C_2H_5)CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_3CH(C_2H_5)CO_2C(SiMePh_2){=}CH_2$	35%[d]
4	$CH_3(CH_2)_3CH(C_2H_5)CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_3CH(C_2H_5)CO_2C(SiMe_2tBu){=}CH_2$	trace
5	$CH_3(CH_2)_3CH(CH_3)CO_2CH{=}CH_2$[e]	$CH_3(CH_2)_3CH(CH_3)CO_2C(SiMe_3){=}CH_2$	70%
6	$C_6H_5CO_2CH{=}CH_2$[b]	$C_6H_5CO_2C(SiMe_3){=}CH_2$	64%
7	$(CH_3)_3CCO_2CH{=}CH_2$[b]	$(CH_3)_3CCO_2C(SiMe_3){=}CH_2$	86%
8	$CH_3(CH_2)_8CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_8CO_2C(SiMe_3){=}CH_2$	trace[f]
9	$CH_3(CH_2)_8CO_2CH{=}CH_2$[b]	$CH_3(CH_2)_8CO_2C(SiMe_3){=}CH_2$	25%[d,g]

[a] Purified yield. All products gave satisfactory ^1H NMR, IR, MS, and CHN data. [b] Starting vinyl ester obtained from Polysciences, Inc., 400 Valley Road, Warrington, PA 18976. [c] Ester added to LDA/Me_3SiCl premix at -78 °C. [d] Product purified by chromatography. [e] Starting material prepared according to Ref. 4.
[f] With 1.1 eq LDA/1.2 eq Me_3SiCl. [g] With 2.2 eq LDA/2.4 eq Me_3SiCl.

References and Notes

1. The trimethylsilyl group of **1** was unaffected by aqueous 1 M HCl; however, **1** was immediately restored to vinyl 2-ethylhexanoate upon treatment with Bu_4NF in wet THF.
2. See, for example, Ricci, A.; Degl'Innocenti, A. *Synthesis* 1987, 647 - 660.
3. The purified α-trimethylsilyl vinyl ester **1** could be converted to the corresponding trimethylsilyl or t-butyldimethylsilyl ketene acetal upon exposure to LDA/R_3SiCl/HMPA at -78 °C. Attempts to form the trimethylsilyl ketene acetal (R_3 = Me) by a one-flask procedure from vinyl 2-ethylhexanoate were unsuccessful. The silyl ketene acetals of **1** (R_3 = Me_3 or $tBuMe_2$) were readily decomposed by aqueous 1 M HCl to afford **1**.
4. Prepared in 68% yield from the acid (1.0 eq), vinyl acetate (3.5 eq), $Hg(OAc)_2$ (1.5 mol%), $Cu(OAc)_2$ (0.5 mol%), and pTsOH (1.5 mol%, reflux, 2 h), bp 45 °C (1 torr). See Mayne, J. E. O.; Warson, H.; Parsons, R. J. *Brit. Patent 827,718* (20 Feb. 1960).

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