

α, β -Unsaturated Carboxylic Acids from Carbonyl Compounds and 1,1-Bis(trimethylsiloxy)-2-(trimethylsilyl)ethene

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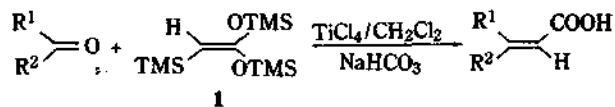
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The reaction of carbonyl compounds with *tert*-butyl trimethylsilyl- α -chloroacetate has been reported to give the corresponding *tert*-butyl esters of α -chloro- α, β -unsaturated carboxylic acids¹. Recently, it was also reported that 4,5-dihydro-5-methyl-2-(trimethylsiloxy)-3-(trimethylsilyl)furan reacts with aldehydes to produce α -ethylidene- γ -butyrolactones². As far as we are aware of, however, the reaction of 1,1-bis(trimethylsiloxy)-2-(trimethylsilyl)ethene (**1**)³ with carbonyl compounds has not been demonstrated to be applicable to the synthesis of α, β -unsaturated carboxylic acids.

Because of our interest in the use of the ketene acetals of certain carboxylic acids and esters for the olefination^{4,5} of carbonyl compounds, we have first examined the reaction of the ketene acetal of trimethylsilylacetic acid, 1,1-bis(trimethylsiloxy)-2-(trimethylsilyl)ethene (**1**), with aldehydes and ketones in the presence of titanium tetrachloride.



The representative experimental procedure is as follows: Under the nitrogen atmosphere at -78°C , to a stirred solution of 3 mmol of benzaldehyde in 10 ml of dry CH_2Cl_2 was added dropwise 10 ml of 1.0 M solution of TiCl_4 in CH_2Cl_2 followed by a solution of 3.3 mmol of 1,1-bis(trimethylsiloxy)-2-(trimethylsilyl)ethene in 5 ml of CH_2Cl_2 . After stirred for 5 hr, the mixture was treated with 0.1 ml of 5% aqueous NaHCO_3 solution and allowed to warm to room temperature. Acidification with 0.1 M aqueous HCl solution, usual work-up and column chromatography on silica gel afforded *trans*-cinnamic acid in 73% yield.

The reaction of the ketene acetal **1** with all the carbonyl compounds tested in this experiment afforded *trans*- α, β -unsaturated carboxylic acids in moderate to good yields (see Table). The *trans* configuration of the double bond generated was verified by the ^1H -nmr spectral data; the large coupling constants (16-17 Hz) between the vinylic protons of the products obtained from aldehydes and no significant change in intensities of the vinylic protons by nuclear Overhauser effect experiment of those obtained from ketones.

On the basis of above spectral data, the formation of the *trans*- α, β -unsaturated carboxylic acids could be best explained by the following mechanism; generation of the β -hydroxy- α -silylcarboxylic acid derivatives via a six-membered transition state⁶ followed by stereospecific *syn* elimina-

Table. Synthesis of α, β -Unsaturated Carboxylic Acids

Entry	R ¹	R ²	Yield*
1	C ₆ H ₅	H	73
2	CH ₂ CH ₂ CH ₃	H	76
3	CH ₂ CH (CH ₃) ₂	H	78
4	CH ₂ CH (C ₂ H ₅) ₂	H	76
5	CH ₂ CH ₃	CH ₃	75
6	CH ₂ CH (CH ₃) ₂	CH ₃	74
7	CH ₂ CH ₂ CH (CH ₃) ₂	CH ₃	76
8	C ₆ H ₅	CH ₃	76
9	C ₆ H ₅	C ₆ H ₅	82
10	C ₆ H ₅	CH ₂ C ₆ H ₅	86

* Isolated yield in %.

tion⁷ during the basic work-up. Extension of the present study to include other α -trimethylsilylated carboxylic acids and esters for the olefination of carbonyl compounds is in progress.

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