

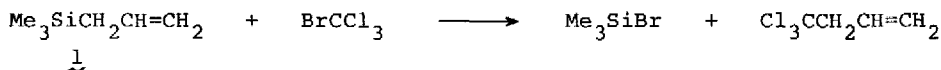
SYNTHESES OF γ,δ -UNSATURATED ALCOHOLS FROM ALLYLSILANES AND CARBONYL COMPOUNDS
IN THE PRESENCE OF TITANIUM TETRACHLORIDE¹

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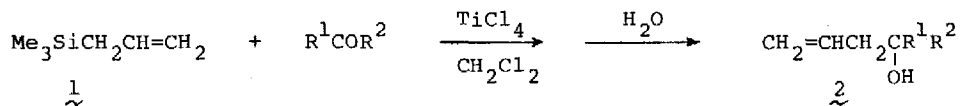
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We have previously reported that trimethylallylsilane (1) is quite reactive toward attack of the electrophilic trichloromethyl radicals derived from bromotrichloromethane, and that the allyl transfer reaction took place effectively to give 4,4,4-trichlorobut-1-ene in reasonable yield.² The high reactivity of 1 toward electrophiles has been explained by $\sigma(\text{Si-C})-\pi$ conjugation.^{3,4}



From a synthetic point of view, 1 may be useful as an intermediate of organic syntheses in the reaction with electrophiles or chemical species with electrophilic nature.⁵ We have explored the possible application of the high reactivity of allylsilanes to synthetic reactions and now found that allyl transfer accompanied with transposition of the allyl group took place very smoothly from allylsilanes to carbonyl compounds activated by a Lewis acid such as TiCl_4 to give γ,δ -unsaturated alcohol in good yield.

When our work is in progress, Calas et al. have reported the addition of organosilicon compounds having an activated Si-C bond such as allylsilanes to α -chloroacetone or chloral in the presence of a Lewis acid such as AlCl_3 , GaCl_3 , and InCl_3 .⁶ Abel and Rowley also reported the reaction of allylic derivatives of both silicon and tin with perhalogenoacetones.⁷ These reactions gave 1-halogenopent-4-en-2-ol derivatives after hydrolysis. However, our present work is new and synthetically more useful than the previous works in that (1) a wide variety of aliphatic, alicyclic and aromatic carbonyl compounds can enter the reaction very smoothly provided these are activated by TiCl_4 ⁸ and (2) a regiospecific transposition occurs in the allylic part.

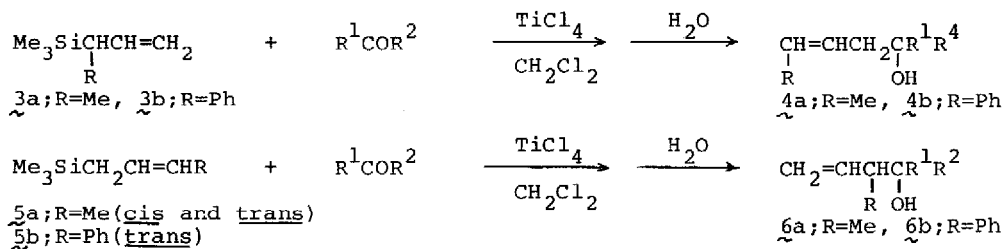


The following experimental procedure is typical. To a solution of a carbonyl compound (2 mmol) and dichloromethane (3 ml) at room temperature under nitrogen was added titanium tetrachloride (1 mmol) dropwise with a syringe. After

stirring for an additional 5 min., an allylsilane (2 mmol) was added rapidly at an ambient temperature, and the mixture was stirred for 1 min. Water was added to the mixture which was subsequently extracted with ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated at reduced pressure. The residue was subjected to silica gel column chromatography, yielding a γ,δ -unsaturated alcohol (2). The products were mostly pure enough to give correct analyses and were characterized by glpc, nmr, ir, and mass spectra. The results are listed in Table 1. The yields listed in the Table are those after isolation and are based on the starting carbonyl compounds.

In all cases, transfer of the allylic group from an allylsilane to a carbonyl group occurred very rapidly. Prolonged stirring after the addition of allylsilanes brings less satisfactory results due to polymerization and other side reactions. Although other Lewis-acid catalysts such as AlCl_3 , SnCl_4 , and $\text{BF}_3\text{-OEt}_2$ are also effective as a substitute for TiCl_4 , yield of the product is usually less satisfactory.

The synthetic utility of this reaction is displayed by the regiospecific transformation of the allylic group to a carbonyl function, in which the carbon-carbon bond formation occurred exclusively at a γ -carbon of allylsilanes. Thus, allylsilane, 3a and 3b, and an equimolar amount of a carbonyl compound in the




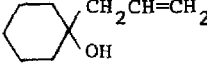

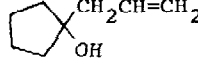
presence of TiCl_4 afforded a trans predominant mixture of two stereoisomers, cis- and trans-4a, and trans-4b, respectively. On the other hand, cis- and trans-5a, and trans-5b reacted with aldehydes or ketones to give exclusively 6a and 6b, respectively.⁹

The reaction mechanism through a cyclic process which involves a nucleophilic attack of the allylsilane to the carbonyl carbon polarized partially by TiCl_4 would be most favorable for explaining the whole results, because the regiospecificity and the trans preference in the stereochemistry of the products are observed actually.

The reaction described in this paper is of advantage to other allylation reactions with allylic reagents of alkali or alkaline-earth metals since addition of these reagents to carbonyl compounds resulted in the formation of products without regiospecificity.¹² Related works are in progress.

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Table 1 Synthesis of γ,δ -unsaturated alcohols

Run	Allylsilane	Ketone or Aldehyde	Reaction time (min)	Product (% yield)
1	<u>1</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_3$ (87)
2	<u>1</u>	$(\text{CH}_3)_2\text{CHCHO}$	10	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{HCH}(\text{CH}_3)_2$ (54)
3	<u>1</u>	$\text{CH}_3(\text{CH}_2)_5\text{CHO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_5\text{CH}_3$ (91)
4	<u>1</u>	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_6\text{CH}_3$ (86)
5	<u>1</u>	$\text{Ph}(\text{CH}_2)_2\text{CHO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{Ph}$ (96)
6	<u>1</u>	PhCHO	1 ^a	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{HPh}$ (58)
7	<u>1</u>	$(\text{CH}_3)_2\text{CO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)_3$ (83)
8	<u>1</u>	$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$ (44)
9	<u>1</u>		3	 (70)
10	<u>1</u>		3	 (44)
11	<u>3a</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	1	$\text{CH}_3\text{CH}=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$ ^b (89)
12	<u>3a</u>	$(\text{CH}_3)_2\text{CO}$	1	$\text{CH}_3\text{CH}=\text{CHCH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$ (72) (<i>cis:trans</i> =37:63)
13	<u>3b</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{PhCH}=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$ ^c (54)
14	<u>trans-5a</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$ (83)
15	<u>trans-5a</u>	$(\text{CH}_3)_2\text{CO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$ (45)
16	<u>cis-5a</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$ (71)
17	<u>cis-5a</u>	$(\text{CH}_3)_2\text{CO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$ (51)
18	<u>5b</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{Ph})\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$ (87)

^a $\text{BF}_3 \cdot \text{OEt}_2$ was used as a Lewis acid. ^b A *cis* and *trans* mixture. ^c A *trans* isomer

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