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ALLYLSILANES AS SYNTHETIC INTERMEDIATES. II. SYNTHESES OF HOMOALLYL ETHERS FROM ALLYLSILANES AND ACETALS PROMOTED BY TITANIUM TETRACHLORIDE[1)]

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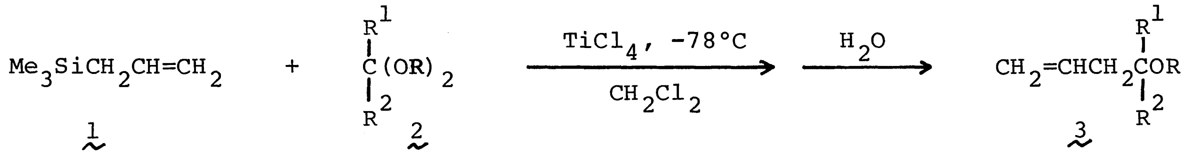
The reaction of allylsilanes with acetals in the presence of titanium tetrachloride afforded homoallyl ethers in good yields. The reaction took place regiospecifically with transposition of the allyl group.

We have recently found that γ,δ-unsaturated alcohols were obtained regiospecifically from allylsilanes and various carbonyl compounds in the presence of titanium tetrachloride in good yields under mild conditions.[2)] In this paper we report that allylsilanes react with various acetals including aliphatic, alicyclic and aromatic acetals or with ethyl orthoformate in the presence of titanium tetrachloride to afford the corresponding homoallyl ethers at low temperature in good yields.[3)]



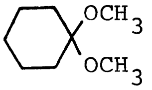
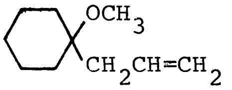
$$\underset{\mathbf{1}}{\mathrm{Me_3SiCH_2CH{=}CH_2}} + \underset{\mathbf{2}}{\overset{\mathrm{R^1}}{\underset{\mathrm{R^2}}{\mathrm{C(OR)_2}}}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{TiCl_4},\ -78\,^\circ\mathrm{C}} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{3}}{\mathrm{CH_2{=}CHCH_2}\overset{\mathrm{R^1}}{\underset{\mathrm{R^2}}{\mathrm{C}}}\mathrm{OR}} \qquad (1)$$

The following experimental procedure is representative of the conversion. To a solution of an acetal (2mmol) in dry dichloromethane (3ml) at -78°C under nitrogen were added titanium tetrachloride (2mmol) dropwise with a syringe. Subsequently an allylsilane (2mmol) in dichloromethane (2ml) was added from a dropping funnel and the mixture was stirred for 3h. Water was added to the mixture which was subsequently extracted twice with ether (10ml). The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated at the reduced pressure. The residue was subjected to silicagel column chromatography, yielding a homoallyl ether (**3**). The products were mostly pure to give correct analyses and were characterized by glc, nmr, and ir spectra. In all cases, transfer of the allylic group from an allylsilane to an acetal carbon occurred very smoothly. The results of the reaction at room temperature were less satisfactory because of the contamination of polymeric products.

It was noticeable that ethyl orthoformate reacts with allylsilanes to give a diallylated product instead of a homoallyl acetal by the same procedure. Apparently, the reaction of allylsilane with the resulting acetal is faster than the monoallylation of the orthoformate. The results are listed in Table 1.

$$\underset{\mathbf{1}}{\mathrm{2Me_3SiCH_2CH{=}CH_2}} + \underset{\mathbf{4}}{\mathrm{CH(OCH_2CH_3)_3}} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{TiCl_4},\ -78\,^\circ\mathrm{C}} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{5}}{\mathrm{(CH_2{=}CHCH_2)_2CHOCH_2CH_3}} \qquad (2)$$

Table 1 Synthesis of Homoallyl Ethers

Run	Allylsilane	Acetal	Reaction time(hr)	Product	(yield, %)
1	**1**	$CH_3(CH_2)_3CH(OCH_3)_2$	3	$CH_3(CH_2)_3CH(OCH_3)CH_2CH{=}CH_2$	(77)
2	**1**	$PhCH_2CH_2CH(OCH_3)_2$	3	$PhCH_2CH_2CH(OCH_3)CH_2CH{=}CH_2$	(93)
3	**1**	$BrCH_2CH(OCH_2CH_3)_2$	3	$BrCH_2CH(OCH_2CH_3)CH_2CH{=}CH_2$	(90)
4	**1**	$CH_3(CH_2)_2CHBrCH(OCH_3)_2$	3	$CH_3(CH_2)_2CHBrCH(OCH_3)CH_2CH{=}CH_2$	(91)
5	**1**	$CH_3(CH_2)_3CH(OCH_2CH_3)_2$	3	$CH_3(CH_2)_3CH(OCH_2CH_3)CH_2CH{=}CH_2$	(76)[a]
6	**1**	$PhCH(OCH_3)_2$	1[b]	$PhCH(OCH_3)CH_2CH{=}CH_2$	(74)[a]
7	**1**		3		(71)[a]
8	**1**	$(CH_3)_2C(OCH_3)_2$	3	$(CH_3)_2C(OCH_3)CH_2CH{=}CH_2$	(98)[a]
9	**1**	$CH(OCH_2CH_3)_3$	3[c]	$CH(OCH_2CH_3)(CH_2CH{=}CH_2)_2$	(24)[a]
10	**6**	$CH_3(CH_2)_3CH(OCH_3)_2$	3	$CH_3(CH_2)_3CH(OCH_3)C(CH_3)_2CH{=}CH_2$	(80)

[a] Determined by glc. [b] $BF_3{\cdot}OEt_2$ was used as a Lewis acid. [c] Room temperature.

The regiospecific transposition in the allyl part was observed in the following example. The related work is in progress.$^{4)}$

$$Me_3SiCH_2CH{=}C(CH_3)_2\ (\mathbf{6}) + R^1R^2C(OR)_2 \xrightarrow[CH_2Cl_2]{TiCl_4} \xrightarrow{H_2O} CH_2{=}CHC(CH_3)_2CR^1R^2OR \qquad (3)$$

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References

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