CHEMISTRY LETTERS, pp. 499-502, 1978. Published by the Chemical Society of Japan

SELECTIVE ALLYLATIONS OF α,β-UNSATURATED ACETALS WITH ALLYLSILANES IN THE PRESENCE OF LEWIS ACID[1)]

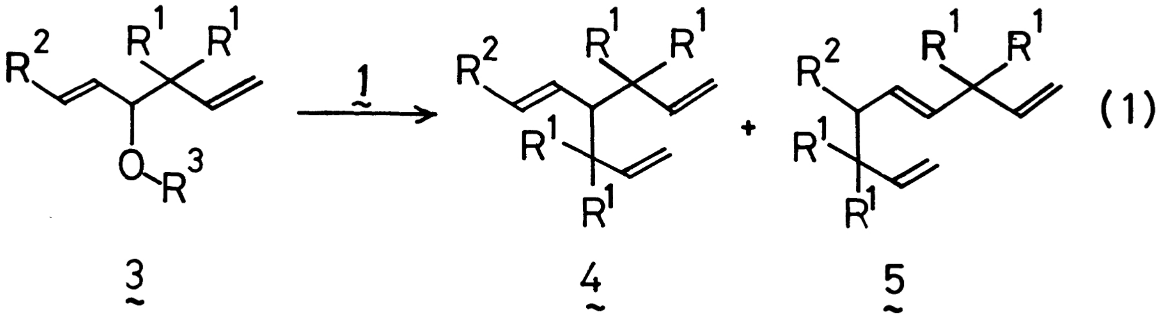
Akira HOSOMI, Masahiko ENDO, and Hideki SAKURAI
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980

The reaction of allylsilanes with α,β-unsaturated acetals in the presence of titanium tetrachloride afforded diallylated compounds, while monoallylated compounds were obtained selectively by the reaction promoted by aluminum trichloride or boron trifluoride-ether complex.

In earlier papers, we have descirbed a variety of reactions of allylsilanes applied to organic syntheses.[2-6)] In the present paper, we wish to report a new allylation reaction of α,β-unsaturated acetals with allylsilanes in the presence of Lewis acids. The mode of the reaction critically depends on the nature of the Lewis acids, reaction temperature, and the structure of the α,β-unsaturated acetals. The overall synthetic transformation is represented by the following equation.

$$Me_3SiCH_2CH{=}CR^1_2 \quad + \quad R^2CH{=}CHCH(OR^3)_2 \longrightarrow$$

1 a : R = H   2
b : R = Me



(1)

With titanium tetrachloride as an activator, diallylated products (4 and/or 5) can be obtained in good yields from α,β-unsaturated acetals, no monoallylated one being detected. The results are listed in Table 1. The regiospecific 1,3-allyl transposition in the allylic part was observed in a similar fashion to previous cases[2-4)] as shown in entries 3 and 8 in Table 1. The β-substituent of α,β-unsaturated acetals has a significant influence on the product ratios of 4 to 5. The former (4) is the allylated compound at the acetal carbon, while in the latter (5)

Table 1. Syntheses of the diallylated compounds (4 and/or 5) via the reaction of allylsilanes (1) with α,β-unsaturated acetals (2) in the presence of $TiCl_4$ at -78°C in CH_2Cl_2[a)]

Entry	Allylsilane	Acetal R^2	Acetal R^3	Reaction Time (h)	% Yield[b,c)] of 4 + 5 (4 : 5)[d)]
1	1a	Ph	Me	3	100 (52 : 48)
2	1a	Ph	Et	3	78 (52 : 48)
3	1b	Ph	Et	16	37 (11 : 89)
4	1a	Me	Me	3	61 (0 : 100)
5	1a	Me	Et	3	33 (0 : 100)
6	1a	H	Et	3	trace
7	1a	*n*-Pr	Et	3	21 (0 : 100)
8	1b	*n*-Pr	Et	12	34 (0 : 100)

a) The reactions were carried out with 1 (2.4 mmol), 2 (1.0 mmol), and $TiCl_4$ (1.0 mmol). See note 7 for further details. b) Yields of isolated and purified materials. c) Yields are not always optimized. d) Determined by glc.

Table 2. Syntheses of the monoallylated compound (3) via the reaction of allylsilanes (1) with α,β-unsaturated acetals (2) at -78°C in CH_2Cl_2[a)]

Entry	Allylsilane	Acetal R^2	Acetal R^3	Lewis acid	Reaction Time (h)	% Yield[b,c)] of 3
1	1a[c)]	Ph	Et[c)]	$AlCl_3$[c)]	6	70
2	1a	Ph	Et	$BF_3 \cdot OEt_2$	3	45
3	1a	*n*-Pr	Et	$AlCl_3$	3	27
4	1b	*n*-Pr	Et	$AlCl_3$	9	26

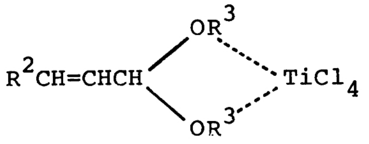
a) The reactions were carried out with 1 (1.2 mmol), 2 (1.0 mmol), and a Lewis acid (1.0 mmol) except for entry 3, where 10 mmole scale of reactants were used with the same ratio. b) Yields are not optimized. c) Yields after isolation.

the second allylation takes place in the manner of conjugate addition. Alkyl substituents such as methyl and n-propyl as R^2 in 2 yielded selectively 1,4,8-trienes. (5) (entries 4-8), while mixtures of 4 and 5 were obtained when R^2 was the phenyl group (entries 1-3).[7]

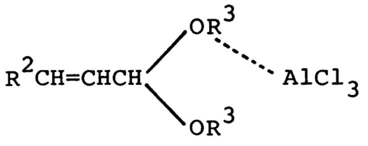
It is noteworthy that the monoallylated product (3) was not formed even at low temperature (-78°C), irrespective of the structure of the starting acetal, when titanium tetrachloride was used as a Lewis acid.[8] Although the reaction of allylsilanes (1) with α,β-unsaturated acetals (2) seems to proceed in the stepwise manner in two stages as shown in the eq. 1, the reaction of the allylsilane with the allyl ether, the product of the first step, occurs efficiently in the second step,[9] and apparently, it is faster than the monoallylation of 2 in the presence of titanium tetrachloride.

However, it was found that the monoallylated proudct (3) was selectively obtained in the same combination of allylsilanes and acetals at -78°C by the use of aluminum chloride or boron trifluoride etherate as an activator of the reaction. Selected examples of the preparation of 3-alkoxy-1,5-dienes (3) are shown in Table 2. It was necessary, in these cases, to avoid both the elevated temperature and the prolonged reaction time, in order to prevent the product from polymerization and further allylation.

The effect of the Lewis acid on this allylation reaction may be explained in terms of the difference in the coordinating ability between the Lewis acids[10] to acetals, as shown in 6 and 7. Thus, titanium tetrachloride can coordinate to both alkoxy groups, while aluminum chloride can activate only one of them. Boron trifluoride etherate activates also only one alkoxy group. As a result, the second allylation takes place rather smoothly with titanium tetrachloride as an activator to give diallylated compounds (4) and/or (5), while with aluminum chloride or boron trifluoride etherate, the second allylation is difficult, since the Lewis acids can no longer activate the products of the first allylation.



6

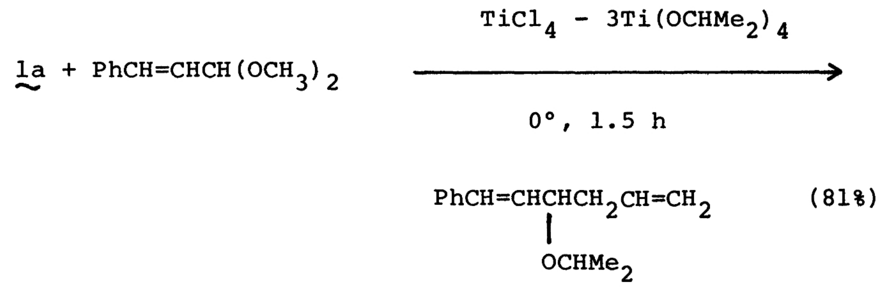


7

Acknowledgment. We thank Toshiba Silicon Co., Ltd., for a gift of chlorosilanes.

References and Notes

1) Chemistry of Organosilicon Compounds 111.
2) A. Hosomi and H. Sakurai, Tetrahedron Lett., 1295 (1976); ibid., 4041 (1977).
3) A. Hosomi, M. Endo, and H. Sakurai, Chem. Lett., 941 (1976).
4) A. Hosomi and H. Sakurai, J. Am. Chem. Soc., **99**, 1673 (1977).
5) A. Hosomi, H. Hashimoto, and H. Sakurai, J. Org. Chem., in press.
6) For the reaction of allylsilanes, see also; J. -P. Pillot, J. Dunogues, and R. Calas, Tetrahedron Lett., 1871 (1976); D. Deleris, J. Dunogues, and R. Calas, ibid., 2449 (1976); I Ojima, Y. Miyazawa, and M. Kumagai, JCS Chem. Commun., 927 (1976); I. Ojima, M. Kumagai, and Y. Miyazawa, Tetrahedron Lett., 1385 (1977).
7) As a typical run, to a solution of **2** (1.0 mmol) in dry dichloromethane (2 mL) at -78°C under nitrogen were added titanium tetrachloride (1.0 mmol) dropwise with a syringe. Subsequently, **1** (2.4 mmol) in dichloromethane (2 mL) was added from a dropping funnel and the mixture was stirred for the period indicated in the Table. A mixture of water and ether was added to the reaction mixture which was subsequently extracted with ether. The organic layer was dried over anhydrous sodium sulfate, and freed of solvent under reduced pressure. The crude products were purified by preparative TLC on silica gel with a mixture of n-hexane and benzene as an eluent or by GLC. Products were fully characterized by NMR, IR and mass spectra, GLC, and elemental analyses.
8) Addition of three equivalents of titanium tetraisopropoxide resulted in the formation of a monoallylated product accompanied with exchange of the alkoxy group in good yield.



$$\mathbf{1a} + \mathrm{PhCH{=}CHCH(OCH_3)_2} \xrightarrow[0°,\ 1.5\ \mathrm{h}]{\mathrm{TiCl_4\ -\ 3Ti(OCHMe_2)_4}} \underset{\mathrm{OCHMe_2}}{\mathrm{PhCH{=}CHCHCH_2CH{=}CH_2}} \quad (81\%)$$

9) In fact, we found that allyl ethers prepared independently undergo allylation with allylsilanes in the presence of a Lewis acid to give 1,5-dienes. Details will be published in a forthcoming paper.
10) F. A. Cotton and G. Willkinson, "Advanced Inorganic Chemistry," 2nd ed., John Wiley & Sons, New York, 1972, p. 255; 434; 799.

(Received January 18, 1978)