Tetrahedron Letters Vol. 21, pp 71 - 74
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0040-4039/80/0101-0071$02.00/0

TRIMETHYLSILYL TRIFLUOROMETHANESULFONATE AS A CATALYST OF THE REACTION OF ALLYLTRIMETHYLSILANE AND ACETALS[1]

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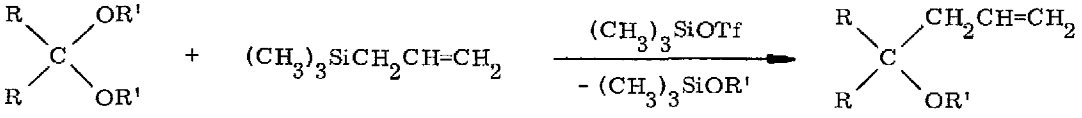
Summary: In the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate, allyltrimethylsilane reacts with acetals to give the corresponding homoallyl ethers in high yields.

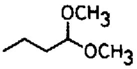
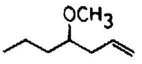
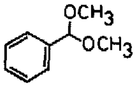
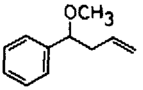
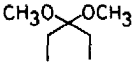
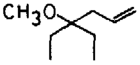
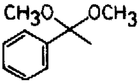
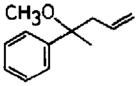
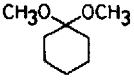
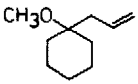
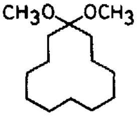
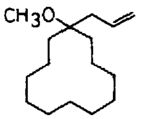
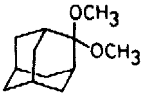
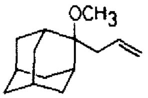
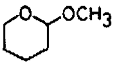
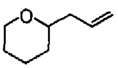
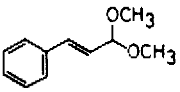
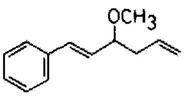
Sakurai and coworkers elaborated an efficient procedure for obtaining homoallyl ethers by reaction of acetals and trialkylallylsilanes with the aid of a stoichiometric amount of Lewis acids such as $TiCl_4$, BF_3, or $AlCl_3$.[2,3] We have found that use of trimethylsilyl trifluoromethanesulfonate (I)[4] as the promoter makes the allylation process catalytic. The catalytic cycle is attained under very mild (aprotic and only feebly nucleophilic) conditions at low temperatures (-78 to -40 °C).



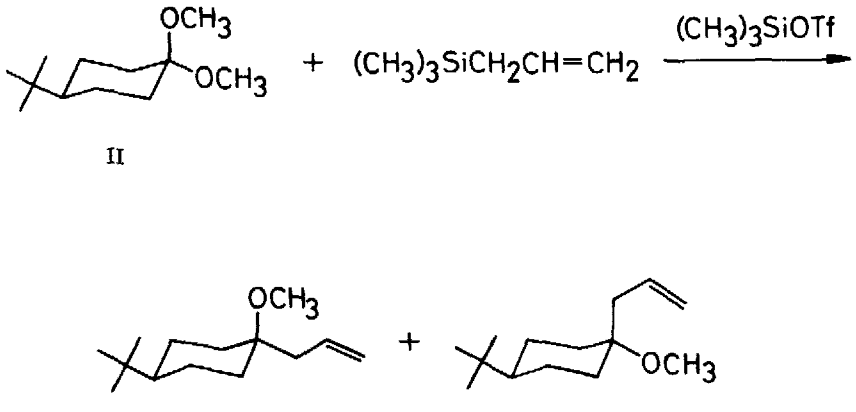
A typical experimental procedure follows. A mixture of I (22 mg, 0.1 mmol, 1 mol %), allyltrimethylsilane (1.31 g, 11.5 mmol), and dry CH_2Cl_2 (1 ml) placed under argon atmosphere was cooled at -78 °C, and to this was added dropwise a solution of benzaldehyde dimethyl acetal (1.60 g, 10.5 mmol) in CH_2Cl_2 (4 ml) by a syringe. The resulting mixture was kept at the same temperature for 6 h with stirring, poured into saturated $NaHCO_3$ solution (10 ml), and extracted by ether (20 ml x 3). The organic layer was washed with brine (10 ml), dried over Na_2SO_4, and concentrated. Chromatography of the residual oil on a silica gel column (35 g, 1:20 ether—hexane as eluent) afforded 4-phenyl-4-methoxy-1-butene (1.51 g, 88% yield) as a colorless oil. Some examples of the reaction are given in Table I.[5]

Notable is the marked stereoselectivity of the catalyzed reaction. Thus reaction of allyltrimethylsilane and 4-t-butylcyclohexanone dimethyl acetal (II) at -40 °C produced a mixture of III and IV (89% yield) with the former, equatorial-allyl stereoisomer III predominating (III/IV = 93:7).[6] Attempted reaction of benzaldehyde, benzophenone, acetophenone, or 4-t-

Table I. Reaction of Acetals with Allyltrimethylsilane in the Presence of $(CH_3)_3SiOTf$[a]

entry	acetal	conditions		product (% yield[b])	
		$(CH_3)_3SiOTf$, mol %	temp, °C (time, h)		
1 2		1 10	-60--45 (15) -78 (1)		(87)[c] (95)[c]
3 4		1 10	-78 (6) -78 (2)		(88) (90)
5		10	-78 (0.2), -50 (1), and -30 (1)		(89)[c]
6		10	-78 (0.2) and -50 (2)		(79)
7		1	-60--45 (18)		(81)
8		10	-78 (0.2) and -40 (1)		(83)
9		10	-78 (0.2) and -40 (1)		(98)[d,e]
10		10	-50 (0.2), -40 (2), and 0 (0.5)		(87)[c,d,f]
11		10	-78~-70 (3)		(78)

[a] Reaction was carried out in dichloromethane under argon atmosphere. Structures of the products were determined by NMR and IR spectra. All new compounds gave correct elemental analysis and/or exact mass spectral data. [b] Isolated yield. [c] Determined by GLC analysis. [d] Based on the converted acetal. [e] Conversion was 59%. [f] Conversion was 78%.



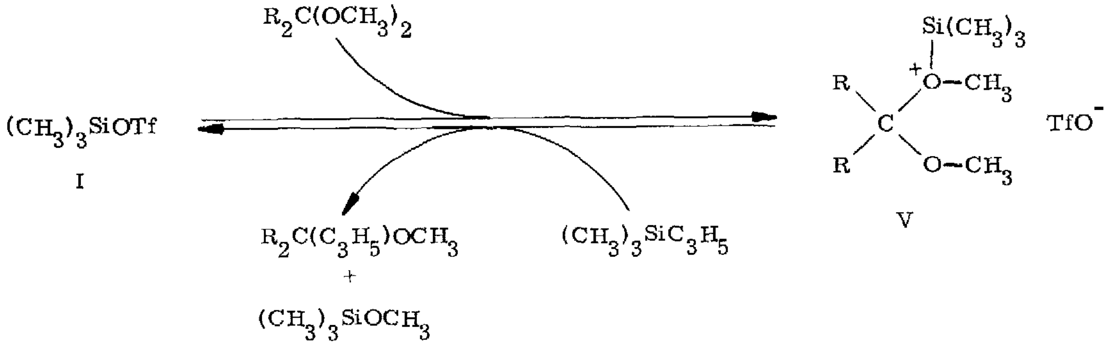
II

III

IV

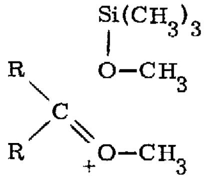
butylcyclohexanone with the allylsilane under the comparable catalytic conditions resulted in recovery of the starting carbonyl compounds. Under forcing conditions (with certain substrates), some complicated condensation products were formed but no or very little allylation products were obtained.

Apparently the trimethylsilyl moiety that has strong affinity to oxygen atom serves as the chain carrier. We consider that the allylation reaction is proceeding by a bimolecular mechanism involving the allylsilane and the oxonium intermediates of type V. The oxonium ion may be envisaged as resonating with the carboxonium ion/methyl trimethylsilyl ether contact pair, VI. In view of the lack of reactivity of carbonyl compound, the free carboxonium ion VII would not be the reactive species, however.[7]

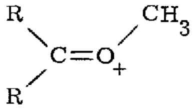


I

V



VI



VII

Acknowledgment. This work was supported in part by a grant from the Ministry of Education, Japanese Government (Grant-in-aid, No. 403022).

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5. Reaction of cyclopentanone dimethyl acetal (10 mol % of $(CH_3)_3SiOTf$, -50 °C, 2 h) followed by the standard workup gave a mixture of the allylation product (17%) and cyclopentanone (83%).
6. Stereoselectivities in the reaction of 4-*t*-butylcyclohexanone and allylmetal reagents are usually only moderate. See, M. Chérest and H. Felkin, *Tetrahedron Lett.*, 2205 (1968); D. Abenhaim, *C. R. Acad. Sci., Ser. C*, **267**, 1426 (1968); D. Abenhaim, E. Henry-Basch, and P. Freon, *Bull. Soc. Chim. Fr.*, 4038 (1969); E. C. Ashby and J. T. Laemmle, *Chem. Rev.*, **75**, 521 (1975); M. Gaudemar, *Tetrahedron*, **32**, 1689 (1976). For the stereoselective allylation with trialkylallyltins and boron trifluoride etherate, see Y. Naruta, S. Ushida, and K. Maruyama, *Chem. Lett.*, 919 (1979).
7. The reagent I interacts strongly with ketone carbonyl group. See, G. Simchen and W. Kober, *Synthesis*, 259 (1976); H. Emde and G. Simchen, *Synthesis*, 867 (1977).

(Received in Japan 27 September 1979)