CHEMISTRY LETTERS, pp. 409-412, 1983. © The Chemical Society of Japan 1983

REACTIONS OF ALLYLSILANES WITH α-CHLORO ETHERS CATALYZED BY IODOTRIMETHYLSILANE OR TRIMETHYLSILYL TRIFLUOROMETHANESULFONATE. SYNTHESIS OF HOMOALLYL ETHERS1)

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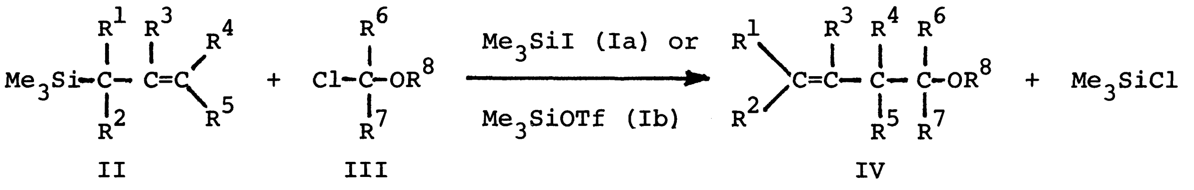
Iodotrimethylsilane and trimethylsilyl triflate activate selectively the C-Cl bond rather than the C-O bond of α-chloro ethers and catalyze the allylation with allylsilanes to give the corresponding homoallyl ethers effectively in good yield.

Iodotrimethylsilane (Ia)2) and trimethylsilyl trifluoromethanesulfonate (Ib)3) can strongly interact especially with an oxygen atom among various heteroatoms in organic compounds to form a silyl oxonium ion and a variety of applications to organic synthesis using a stoichiometric and catalytic amount of these reagents have been recently developed. In this paper, we report that these reagents activate selectively a carbon-chlorine bond of α-chloroalkyl ethers (III), in which two kinds of heteroatom are involved in a molecule, and efficiently catalyze the reaction of III with allylsilanes (II)4,5) to give the substitution product of the allylsilane with an α-alkoxyalkyl, instead of an α-chloroalkyl group, at the γ-position in good yield. (eq. 1)



$$\mathrm{Me_3Si{-}\underset{R^2}{\overset{R^1}{C}}{-}\overset{R^3}{C}{=}C\!<^{R^4}_{R^5}} + \mathrm{Cl{-}\underset{R^7}{\overset{R^6}{C}}{-}OR^8} \xrightarrow[\mathrm{Me_3SiOTf\ (Ib)}]{\mathrm{Me_3SiI\ (Ia)\ or}} {}^{R^1}_{R^2}\!>\!\mathrm{C{=}\overset{R^3}{C}{-}\underset{R^5}{\overset{R^4}{C}}{-}\underset{R^7}{\overset{R^6}{C}}{-}OR^8} + \mathrm{Me_3SiCl} \qquad (1)$$

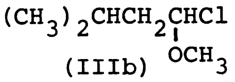
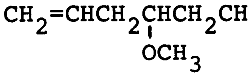
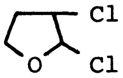
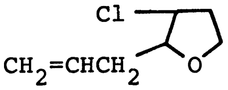
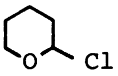
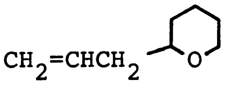
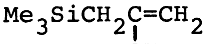
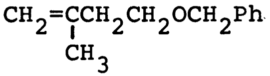
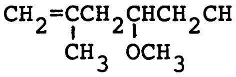
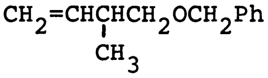
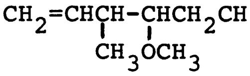
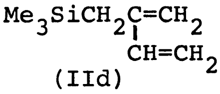
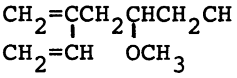
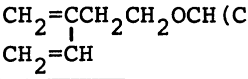
II III IV

This paper reports, to our knowledge, the first example of a catalytic use of I for the activation of a carbon-chlorine bond.6) Although the silyl triflate (Ib) has been known as an activator of mostly oxygen-containing molecules, it is noteworthy that, in these cases, the activation occurred only at the carbon-chlorine bond rather than the carbon-oxygen bond of III. The results are listed in Table 1.

The reaction of II with III proceeds very smoothly in the presence of a catalytic amount of Ia or Ib at temperature lower than room temperature to give the corresponding homoallyl ethers (IV) regiospecifically in good yields. We have found that less than 5 mol% of I is enough to catalyze the reaction. Acetonitrile and dichloromethane were the most suitable solvent among examined.

Among a variety of α-chloro ethers (IIIa-e), IIIb, IIIc and IIId are more reactive than IIIa and IIIe, and, in particular, 1-chloro-3-methylbutyl methyl ether (IIIb) reacts with isoprenylsilane (IId) very smoothly with an aid of Ia or Ib to afford ipsenol methyl ether (IVi) in 80 or 86% yield, respectively.

Table 1. Reactions of allylsilanes (II) with α-chloro ethers (III) catalyzed by iodotrimethylsilane (Ia) or trimethylsilyl triflate (Ib)[a]

Entry	Allylsilane	α-Chloro ether	Conditions	Product (% Yield)[b]	
1	$Me_3SiCH_2CH=CH_2$ (IIa)	$PhCH_2OCH_2Cl$ (IIIa)	Me_3SiI (Ia) rt, 2.5 h	$CH_2=CHCH_2CH_2OCH_2Ph$ (IVa)	(78)
2	IIa	 $(CH_3)_2CHCH_2\underset{OCH_3}{C}HCl$ (IIIb)	Ia, -40°, 10 min then 0°, 20 min	 $CH_2=CHCH_2\underset{OCH_3}{C}HCH_2CH(CH_3)_2$ (IVb)	(72)
3	IIa	IIIb	Ia[c], -20°, 30 min	IVb	(70)
4	IIa	IIIb	Me_3SiOTf (Ib) -20°, 20 min	IVb	(73)
5	IIa	 (IIIc)	Ia[d], -20°, 40 min	 (IVc)	(90)
6	IIa	 (IIId)	Ia[d], -78°∿-20°, 20 min	 (IVd)	(78)
7	 $Me_3SiCH_2\underset{CH_3}{C}=CH_2$ (IIb)	IIIa	Ia, rt, 4.5 h	 $CH_2=\underset{CH_3}{C}CH_2CH_2OCH_2Ph$ (IVe)	(76)
8	IIb	IIIb	Ia, -40°, 15 min then 0°, 1 h	 $CH_2=\underset{CH_3}{C}CH_2\underset{OCH_3}{C}HCH_2CH(CH_3)_2$ (IVf)	(71)
9	IIb	IIIb	Ib, -20°, 25 min	IVf	(68)
10	$Me_3SiCH_2CH=CHCH_3$ (IIc)	IIIa	Ia, rt, 3 h	 $CH_2=CH\underset{CH_3}{C}HCH_2OCH_2Ph$ (IVg)	(72)
11	IIc	IIIb	Ib, -20°, 15 min	 $CH_2=CH\underset{CH_3}{C}H-\underset{OCH_3}{C}HCH_2CH(CH_3)_2$ (IVh)	(80)
12	 $Me_3SiCH_2\underset{CH=CH_2}{C}=CH_2$ (IId)	IIIb	Ia, -40°, 10 min then 0°, 30 min	 $CH_2=\underset{CH_2=CH}{C}CH_2\underset{OCH_3}{C}HCH_2CH(CH_3)_2$ (IVi)	(80)
13	IId	IIIb	Ib, -20°, 10 min	IVi	(86)
14	IId	$(CH_3)_2CHOCH_2Cl$ (IIIe)	Ib, -20°, 1 h	 $CH_2=\underset{CH_2=CH}{C}CH_2CH_2OCH(CH_3)_2$ (IVj)	(74)

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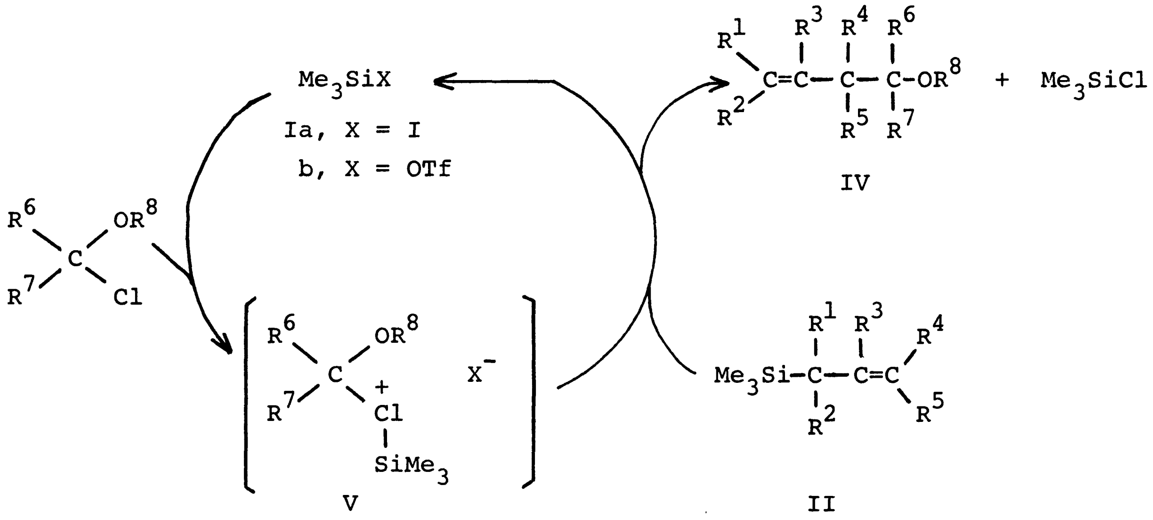
[a] All reactions were carried out in CH_3CN unless otherwise noted. [b] Yields after isolation by TLC. [c] The in situ generated Ia from IIa and iodine was used. See ref. 14. [d] The reaction was carried out in CH_2Cl_2.

It is impressive that cyclic α-chloro ethers such as 2,3-dichlorotetrahydrofuran (IIIc) and 2-chlorotetrahydropyran (IIId) can also be readily allylated only at the α site of the ethers selectively with allyltrimethylsilane with concurrent activation of the carbon-chlorine bond to give the corresponding 2-allyl-3-chlorotetrahydrofuran (IVc) and 2-allyltetrahydropyran (IVd) in 90 and 78 % yield (entries 5 and 6, respectively).[7)]

The regiospecific allyl transfer and the ability of Ia and Ib to govern the site of activation of α-chloro ethers represent the most fascinating facets of this α-alkoxyalkylation. The selectivity of the activation site by I depends mostly upon the stabilizing ability of the adjacent heteroatom toward an incipiently formed carbocation,[8)] and in addition, the driving force of the cleavage of the carbon-chlorine bond may be reasonably attributed to the strong silicon-chlorine bond.[9)]

Although the mechanism of the present reaction should be elucidated by further experiments, the results can be rationalized by Scheme 1, in which the initial formation of an silylhalonium ion (V), stabilized by an adjacent alkoxyalkyl group, takes place selectively at low temperature. An silyloxonium ion that is considered rather frequently as an active intermediate in the reactions of oxygen-containing substrates with I,[2,3,10)] should not be involved in the present case. The facts found in the reaction suggest that the intermediate (V) may undergo the bimolecular nucleophilic displacement by the allylsilane (II).



Scheme 1. A catalytic cycle of the reaction of allylsilane with α-chloro ethers.

A general procedure is as follows.[11)] In a two-necked flask an allylsilane (II) (1.2 mmol) and an α-chloro ether (III) (1.0 mmol) were placed in acetonitrile (2 ml). Two drops of Ia or Ib (ca. 5-10 mol %), which had been prepared from hexamethyldisilane and iodine,[12)] or from chlorotrimethylsilane and trifluoromethanesulfonic acid,[13)] respectively, were added and the resulting mixture was subsequently stirred for a given time indicated in the Table. After hydrolysis with saturated sodium bicarbonate involving pyridine, the resulting solution was extracted with ether and the extract was worked up as usual. A homoallyl ether (IV) was isolated by TLC.

Acknowledgement: We thank Toshiba Silicone Co., Ltd. for a gift of chlorosilanes. The work was supported by the Ministry of Education, Science, and Culture (Grant-in-Aid for Special Project Research, No. 57118002).

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8) It is well-known that the stabilizing effect of the MeO group to the cationic center is larger than that of the Cl group. Thus, the Brown-Okamoto's substituent constants σ^+ in the Hammett correlation are -0.78 for p-MeO and 0.11 for p-Cl. See H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).

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(Received January 14, 1983)