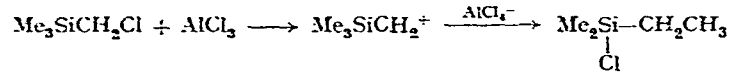
Preliminary Notes

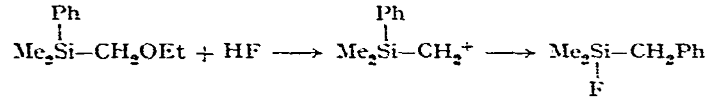
Rearrangements and electrophilic substitutions of α-silylcarbonium ions

Lewis acid-catalyzed rearrangements of alkyl groups from a silicon atom to an adjacent carbon atom are well described in the literature[1], a typical example being the following reaction[2]:



$$\mathrm{Me_3SiCH_2Cl + AlCl_3 \longrightarrow Me_3SiCH_2^+ \xrightarrow{AlCl_4^-} Me_2\underset{\displaystyle Cl}{\underset{|}{Si}}{-}CH_2CH_3}$$

Surprisingly, aryl migrations under comparable conditions are relatively unknown, the sole example reported in Eaborn's excellent book[1] being the following[3], which occurs in low yield:



$$\mathrm{Me_2\overset{\displaystyle Ph}{\overset{|}{Si}}{-}CH_2OEt + HF \longrightarrow Me_2\overset{\displaystyle Ph}{\overset{|}{Si}}{-}CH_2^+ \longrightarrow Me_2\underset{\displaystyle F}{\underset{|}{Si}}{-}CH_2Ph}$$

We have recently found conditions whereby α-silylcarbonium ions can be readily generated and where, depending on the structure and/or conditions, they may be caused to cleanly rearrange with phenyl migration from silicon to carbon, or alternatively, to cleanly effect electrophilic substitution of an aromatic compound.

Table 1 summarizes briefly our findings to date. α-Silyldiphenylcarbinols, preferentially in a relatively non-basic solvent, are smoothly converted by boron fluoride to carbonium ions which rearrange, fluorine becoming attached to silicon in place of the migrating group. Phenylmethylcarbinols appear to dehydrate only, no rearrangement product or substitution product being formed in either ether or toluene solvents. Monophenylcarbinols undergo rearrangement cleanly when boron fluoride and an inert solvent is used, boron fluoride etherate giving only low yields after prolonged reaction times, but boron fluoride in hexane giving essentially quantitative yields of rearrangement product in a matter of minutes at room temperature. However, in solvents susceptible to electrophilic substitution, particularly where these are more reactive than benzene, rearrangement does not occur, the α-silylcarbonium ion instead attacking the aromatic solvent (*e.g* toluene, anisole, or *tert*-butylbenzene) giving *para*-substitution products in high yield. While an exhaustive search for possible *ortho*-substitution products has not been completed, to date only *para*-substitution has been found from α-silylcarbonium ions. This appears consistent with the bulk of the electrophilic reagent. In benzene itself, at room temperature, approximately equal amounts of substitution and rearrangement occur, and with solvents less susceptible than benzene to electrophilic substitution, rearrangement again is the predominant course of the reaction. To date we have found no reaction, either rearrangement or substitution, with simple silylcarbinols such as triphenylsilylmethanol or 1-triphenylsilylethanol.

To the extent that the reactions have been studied, similar results are obtained from α-germylcarbinols. Carbinols themselves such as 1,1,1,2-tetraphenylethanol, rearrange under the conditions of the reaction, but then lose a proton to form alkenes such as tetraphenylethylene.

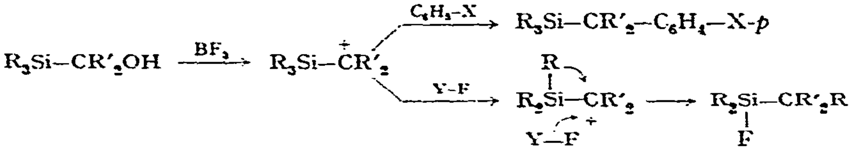
TABLE I

REACTIONS OF CARBINOLS WITH BF_3

Carbinol	*Conditions*[a]		*Products*	*Yield* (%)
Ph_3SiCPh_2OH	BF_3–Et_2O	12 h	$Ph_2FSiCPh_3$	81
	BF_3–toluene		$Ph_2FSiCPh_3$	94
$Ph_3SiCMePhOH$	BF_3–Et_2O	48 h	$Ph_3SiCPh{=}CH_2$	87
	BF_3–toluene		$Ph_3SiCPh{=}CH_2$	92
$Ph_3SiCHPhOH$	BF_3–Et_2O	48 h	$Ph_2FSiCHPh_2$	50
	BF_3–hexane		$Ph_2FSiCHPh_2$	94
	BF_3–toluene		$Ph_3SiCHPh\ C_6H_4Me$-*p*	98
	BF_3–anisole		$Ph_3SiCHPh\ C_6H_4OMe$-*p*	87
	BF_3–$PhCMe_3$	0°, 20 min, 7%	$Ph_3SiCHPh\ C_6H_4CMe_3$-*p*	54
	BF_3–benzene		$Ph_3SiCHPh_2$	50[b]
			$Ph_2FSiCHPh_2$	50[b]
	BF_3–PhBr		$Ph_2FSiCHPh_2$	89
	BF_3–PhF		$Ph_2FSiCHPh_2$	85
Ph_3Si-CHOH(*p*-ClC_6H_4)	BF_3–benzene,	5°, 10 min	$Ph_3SiCHPh\ C_6H_4Cl$-*p*	61[b]
			$Ph_2FSiCHPh\ C_6H_4Cl$-*p*	39[b]
$Ph_3SiCHOH$(*p*-FC_6H_4)	BF_3–benzene	5°, 10 min	$Ph_3SiCHPh\ C_6H_4F$-*p*	60[b]
			$Ph_2FSiCHPh\ C_6H_4F$-*p*	40[b]
Ph_3GeCPh_2OH	BF_3–Et_2O	12 h	$Ph_2FGeCPh_3$	52
	BF_3–hexane		$Ph_2FGeCPh_3$	81
$Ph_3GeCHPhOH$	BF_3–hexane		$Ph_2FGeCHPh_2$	95
	BF_3–toluene		$Ph_3GeCHPh\ C_6H_4Me$-*p*	85
$Ph_3CCHPhOH$	BF_3–hexane		$Ph_2C{=}CPh_2$	60
	BF_3–toluene		$Ph_2C{=}CPh_2$	75
Ph_3SiOH	BF_3–toluene		$(Ph_3SiO)_3B$	90

[a] All reactions, unless noted, were run at room temperature (approximately 21°) with reaction times of 1–4 min as approximately 1% solutions. [b] Proportions estimated by NMR techniques. Yields of isolated products were lower.

Although these reactions could be written as typical Wagner-Meerwein rearrangements which would involve intermediate siliconium ions, no evidence has been found so far suggesting the intermediacy of these species in the sense that no products resulting from attack of siliconium ion on aromatic substrate has been detected by NMR techniques. Under the conditions of the reaction triphenylsilanol itself in toluene forms no triphenyl-*p*-tolylsilane, the only product of the reaction being tris(triphenylsilyl) borate[4], in contrast to the reported behaviour of triethylsilanol with boron fluoride etherate[5]. On this evidence we suggest, following the initial formation of α-silylcarbonium ions, that if these do not attack the solvent giving electrophilic substitution, then a concerted attack by some fluoride ion containing species (*e.g.* HF, $HOBF_2$, HBF_4, or fluoride ion) on silicon accompanies and facilitates the migration of phenyl from silicon to carbon.



The reactions were carried out by bubbling BF_3 into stirred solutions of the carbinols in appropriate solvents. Structures assigned have been confirmed by analysis, infrared and NMR spectra, and in some cases mixed melting points with authentic samples prepared by different unambiguous routes. We are continuing our investigations on these reactions from both the mechanistic and synthetic point of view. To date it has provided an excellent route to certain substituted diphenyl- and triphenylmethylsilanes, obtainable only with difficulty by other routes.

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The effect of copper(I) chloride on the addition of Grignard reagents to ester carbonyl groups

As part of a study of the conjugate addition of Grignard reagents to α,β-unsaturated esters[1] (for leading references see ref. 1) we have recently investigated the reaction of butylmagnesium bromide with *sec*-butyl cyclopropanecarboxylate and di-*sec*-butyl cyclopropane-1,1-dicarboxylate[2]. We found that for both these esters the Grignard reagent attacks the ester molecule at the carbonyl group only, the sole reaction product being a tertiary alcohol. When the reactions were carried out in the presence of copper(I) chloride the direction of the attack was still the same, but the ratios produced of tertiary alcohol to unreacted ester were considerably smaller than when the reactions were uncatalyzed. This effect of copper(I) chloride was particularly pronounced in the case of the cyclopropanemonocarboxylic ester.

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