Silylcarbonium ions from the reaction of silylcarbinols with boron trifluoride

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The behavior of silylcarbonium ions, Si—C⁺, generated from various types of α -silylcarbinol with boron trifluoride under a variety of conditions of temperature and solvent has been examined. Four distinct types of reaction have been observed, depending on the conditions and the structure of the carbinol. These are: 1,2-migration of aryl groups from silicon to carbon, yielding a fluorosilane; Friedel-Crafts substitution of the carbonium ion on an aromatic substrate; elimination of the elements of water to give a vinylsilane; and isomerization to the β -silylcarbonium ion by hydrogen migration, followed by elimination of the silyl group to give a simple fluorosilane and an alkene (*i.e.* a β -elimination). Factors affecting the partitioning between these pathways are discussed.

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The classic work of Sommer *et al.* (1) on the reaction of chloroalkylsilanes with Lewis acids clearly established that silylcarbonium ions \equiv Si- $\stackrel{+}{C}$ -- could be readily generated and that

these tended to exhibit two types of behavior, (a) migration of an alkyl group from silicon and/or (b) migration of hydrogen from the adjacent carbon to give a β -silylcarbonium ion (eq. 1).

Alk₃SiCHCI-CH-
$$\xrightarrow{AICI_3}$$

Alk₂SiCI-CHAlk-CH-
Alk₃SiCH-CH- $\xrightarrow{Alk_3SiCH-CH-}$

[1]

The behavior of these species has been recently reviewed (2). Studies by Kumada *et al.* (3) indicated that silyl groups also migrated readily from silicon to carbon, and studies by Eaborn and Jeffrey (4) showed small amounts of aryl migration from silicon to carbon took place when compounds such as dimethylarylsilylmethyl ethyl ether were treated with aqueous alcoholic hydrogen fluoride. All of these reactions have been described in the literature as analogs of a Wagner-Meerwein rearrangement (eq. 2) although no unambiguous evidence for the formation of a free siliconium ion has been found.

The existence in this laboratory of a wide variety of α -silylcarbinols (α -hydroxysilanes) (5) offered the possibility of providing a wide variety



of silylcarbonium ions which could serve for the further study of these reactions, in particular the migration of aryl groups from silicon to carbon, which at the time our work was initiated was relatively unknown. A preliminary account of part of this work has already appeared (6) and this paper will present and discuss the data obtained in greater detail.

As isomerizing agent for the silylcarbinols, gaseous boron trifluoride was employed, this having proven to be much more effective than boron fluoride etherate (since reactions could be completed in minutes, rather than hours or days) and much milder than aluminum chloride, which is known to lead to cleavage of aromatic groups from silicon (7).

In the course of the study on the various silylphenyl carbinols two reactions were observed, 1,2-migrations from silicon, and Friedel–Crafts substitution reactions. It is convenient to present the results in sections related to the general structure of the carbinols studied.

In virtually all of the reactions of silylcarbinols with boron trifluoride, it appears quite clear, as will be subsequently established, that relatively

free silylcarbonium ions, $Si-\dot{C}$, are generated, and the discussion of data to follow will pre-

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ArX

Ph₂Si-CHPh

Ph₂Si-

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-CHPh₂

 $Ph_{3}Si - CHPh(\bigcirc)X$

[3]

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suppose the formation and existence of these species. However, no direct evidence in support of the isomeric siliconium ions was found during the course of this work.

Ph H

-ĊPh

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Ph2Si-

BF₃

Silylmonophenylcarbinols: R₃SiCHOHAr

When silylmonophenylcarbinols were treated in various solvents with gaseous BF_3 , two distinct kinds of reaction were observed; rearrangement (R), involving migration of an aryl group from silicon to the carbon originally bearing the hydroxyl group (during which process an Si—F bond is formed) and, Friedel–Crafts substitution (S), in which the intermediate silylcarbonium ion reacts with an aromatic solvent, *e.g.* eq. 3.

In all cases where substituted aromatics were used as solvents, only para-substituted derivatives were isolated, and no evidence for other positions of substitution was noted.

Table 1 summarizes the data obtained with silylmonophenylcarbinols. Several trends are evident which appear to have straightforward explanations.

(a) For a given silylcarbinol at a given temperature, the greater the electron-donating ability of the substituent on the aromatic ring of the solvent, the greater is the proportion (given as a percent here and elsewhere) of substitution product obtained: *e.g.* as solvents at 23°; toluene \approx *tert*-butylbenzene \approx anisole, 100 S; benzene, 50 S; fluorobenzene, 0 S. Obviously the more reactive the solvent is toward electrophilic substitution, the more favored the intermolecular Friedel-Crafts reaction would be.

(b) For a given silylcarbinol in a given solvent, the higher the temperature, the greater the proportion of rearrangement; *e.g.* for triphenylsilylphenylcarbinol in benzene; 5° , 10 R; 23° , 50 R; 80° , 100 R. Since the two competing reactions will have different activation energies the reaction with the higher activation energy will experience the greater acceleration in rate with increasing temperature (8). It follows that the activation energy for rearrangement is greater than that for substitution.

(R)

(S)

(c) The more electron-donating the parasubstituent on the phenyl group attached to the carbinol carbon, the greater is the amount of rearrangement product formed: e.g. in benzene at 23°, OMe, 100 R; CMe₃, 78 R; H, 50 R; Cl, 44 R. This infers that stabilization of the proposed benzyl type silylcarbonium ion intermediate

(Ph₃SiCH—C₆H₄X-p) facilitates rearrangement relative to substitution. It has been demonstrated by Nenitzescu (9) that electron-donating substituents on the aromatic ring in benzyl carbonium ions increase the rate of the Friedel– Crafts reactions of the ions by stabilization of the transition state; hence it is clear from our results that such substituents stabilize the transition state of the 1,2-migrations from silicon to an even greater extent.

(d) The more electron-donating the parasubstituents on the aromatic rings attached to silicon, the greater is the proportion of rearrangement: e.g. in benzene at 23°, CMe₃, 100 R; H, 50 R; Cl, 0 R. Since the rearrangement process can be conceived as an intramolecular electrophilic attack by the carbonium ion on the aromatic groups attached to silicon, it follows that the more susceptible these are to electrophilic attack the more readily the rearrangement should take place.

(e) Trimethylsilylphenylcarbinols fail to rearrange, and either undergo Friedel-Crafts substitution with an aromatic solvent exclusively, or, in a non-aromatic solvent, yield polymer. The failure to observe the migration of alkyl groups infers that much greater energy is required for alkyl migration from silicon to carbon than for aryl migration, as would have been expected, and the formation of substitution products indicates that the activation energy for this process is lower than for alkyl migration. The polymer formation observed in the absence of an

TABLE 1

Proportion (%) of rearrangement (R) and Friedel-Crafts substitution (S) for silylmonophenylcarbinols with various solvents and temperatures*

		Temperature (°C)			
Compound	Solvent	5	23	80	Other
Ph ₃ SiCHOHPh	$\begin{array}{c} C_{6}H_{6} \\ C_{6}H_{5}Me \\ C_{6}H_{5}F \\ C_{6}H_{5}OMe \\ C_{5}H_{5}CMe_{3} \\ C_{6}H_{14} \\ \end{array}$	10 R 90 S	50 R 50 S 100 S 100 R 100 S 100 S 100 S 100 R	100 R	30 R 70 S‡ 85 R 15 S§
Ph₃SiCHOHC ₆ H₄OMe-p	C6H6 C6H5CMe3 C6H14	100 R	100 R 100 S 100 R	100 R	
Ph ₃ SiCHOHC ₆ H ₄ CMe ₃ -p	C6H6 C6H5Me C6H14	64 R 36 S	78 R 22 S 100 S 100 R	100 R	
Ph₃SiCHOHC₀H₄Cl-p	C6H6 C6H5Me C6H14	33 R 66 S	44 R 56 S 100 S 100 R	80 R 20 S	
$(p-Me_3CC_6H_4)_3SiCHOHPh$	C ₆ H ₆ C ₆ H₅Me		100 R 100 S		
(p-ClC ₆ H ₄) ₃ SiCHOHPh	C_6H_6 C_6H_{14}		100 S 100 R		
Me ₃ SiCHOHPh	$C_{6}H_{5}X\P$ $C_{6}H_{14}$		100 S Polymer		
*Reaction being studied is:	ArX				
ł	R_3 SiCHOHR' \xrightarrow{AIA}_{BE_1} R_2 FS	$SiCHRR'(R) + R_3SiC$	$CHR'C_6H_4X-p(S).$		
†Proportions of products, accurate to confirmed the proportions given. For d ‡Temperature of run was 110° . §Temperature of run was -40° . $\ C_6H_{14}$ is <i>n</i> -hexanc. $\ X = H$, OMe, CMe ₃ , or F.) about 5%, were estimate etails of the reactions see	d by n.m.r. technique the Experimental sect	s and are given as p ion.	ercentages. Isolated	l yields generally

		1.	ABLE 2				
Products	from	silyldiph	enylcarbind	ls with	BF ₃	at	23°

Compound	Solvent	Product	%
Ph ₃ SiCPh ₂ OH Ph ₂ MeSiCPh ₂ OH PhMe ₂ SiCPh ₂ OH Me ₃ SiCPh ₂ OH 1-NpPhMeSiCPh ₂ OH	C_6H_5Me C_6H_5Me C_6H_5Me C_6H_14 C_6H_6	Ph ₂ FSiCPh ₃ PhMeFSiCPh ₃ Me ₂ FSiCPh ₃ Me ₂ FSiCMePh ₂ 1-NpMeFSiCPh ₃ PhMeFSiCPh ₂ -1-Np	100 R 100 R 100 R 100 R { 90 R 10 R

*Product detected by n.m.r. but not isolated.

aromatic solvent probably arose from attack of the carbonium ion on the aromatic ring of a second molecule.

Silyldiphenylcarbinols

In contrast to the competing reactions observed with silylmonophenylcarbinols, silyldiphenylcarbinols were observed to undergo rearrangement only, as indicated in Table 2.

In view of the sterically hindered nature of the intermediate carbonium ion, it perhaps is not surprising that Friedel-Crafts substitution with an aromatic solvent did not occur. As was inferred earlier, and is now evident, in any competition between alkyl and aryl migration from silicon to carbon, only the latter occurs, since only aryl migration was observed in diphenylmethyl- or phenyldimethylsilyldiphenyl-

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TABLE 3 Results of the reaction of silylmethylphenylcarbinols with BF_3^*

Compound	Solvent	-40	23	32	110
Ph₃SiCOHMeC ₆ H₄OMe	C ₆ H ₅ Me C ₅ H ₁₂	100 E 100 R	100 E	10 R 90 E	100 E
Ph ₃ SiCOHMeC ₆ H ₅	C6H5Me C5H12	70 R 30 E 100 R	100 E	100 R	100 E
$Ph_3SiCOHMeC_6H_4Cl$	C_6H_5Me C_5H_{12}	80 R 20 E 100 R	66 R 33 E	100 R	100 E

* $R = Ph_2FSiCMePh(C_6H_4X_{-p}); E = Ph_3SiC(C_6H_4X_{-p})=CH_2.$

carbinols. However, in contrast to the situation with silylmonophenylcarbinols, trimethylsilyldiphenylcarbinol was observed to undergo alkyl rearrangement rather than polymer formation. When either a phenyl or an α -naphthyl group was capable of undergoing migration, as with 1 - naphthylphenylmethylsilyldiphenylcarbinol, phenyl migration occurred about nine times more frequently than naphthyl migration, the latter possibly being inhibited by the steric requirements of the transition state.

Silylmethylarylcarbinols: R_3 SiCOHMeC₆H₄X-p

When an alkyl group is attached to the carbonium ion generated from a silylcarbinol with boron trifluoride, additional types of reaction other than rearrangement (R) or Friedel-Crafts substitution (S) may occur. Elimination of a proton (E) would constitute an overall dehydration of the parent carbinol. In addition the possibility exists, previously observed in other cases (10), of isomerization (I)

caused by hydrogen migration, converting the original silylcarbonium ion to its β -isomer, which could then react in a variety of ways. Of the four possible reactions outlined in Scheme 1, only rearrangement and proton elimination were observed with the silylmethylarylcarbinols. The results obtained are presented in Table 3. Friedel–Crafts substitution may not occur because of steric considerations, as was proposed to explain the behavior of the silyldiphenyl-carbinols. The failure of the tertiary ion to isomerize to the primary (β) carbonium ion (I) is understandable because of unfavorable differences in stability.

Of the two processes elimination and rearrangement, it is evident from Table 3 that the former is favored by higher temperature. The nature of the solvent also plays an important role in determining the relative importance of the two reactions, pentane (non-solvating) favoring rearrangement but toluene (ion-solvating) favoring elimination. It is also evident that para-sub-

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Products from triphenylsilylphenyl-p-substituted benzylcarbinols treated with BF3 in toluene at various temperatures'

	Products, %Yields					
Carbinol	 R†	E‡	Stilbene (cis-trans)§	Ph₃SiF	Ph₃SiOH	
-40°						
PhaSiCOHPhCH ₂ C ₆ H ₄ CMe ₃ -p	17	0	67(50-50)	36	19	
Ph ₃ SiCOHPhCH ₂ C ₅ H ₅	27	Ō	38(90-10)	20	17	
Ph ₃ SiCOHPhCH ₂ C ₆ H ₄ Cl-p	51	0	38(100-0)	13	25	
110°						
Ph ₃ SiCOHPhCH ₂ C ₆ H ₄ CMe ₃ -p	0	37	53(28-72)	12	19	
Ph ₃ SiCOHPhCH ₂ C ₆ H ₅	0	33	26(90–10)	6	18	
Ph ₃ SiCOHPhCH ₂ C ₆ H ₄ Cl-p	0	28	43(90–10)	5	29	

*Yields reported are of isolated material. The *cis-trans* proportions are based on spectroscopic data. $T = Ph_2FSiCPh_2CH_3C_6H_4X-p.$ $T = Ph_3Si H$

Ph C_6H_4X-p §Stilbene = PhCH=CHC₆H₄X-p(*is*-trans proportions) = IE'.

stituents on the aryl groups attached to carbon play an important role in determining whether rearrangement or elimination is the major reaction occurring, electron-donating substituents (e.g. OMe) favoring elimination, presumably because charge delocalization by the aromatic ring attached to carbon in the transition state is of paramount importance.

Silyl-p-substituted Benzylphenylcarbinols: $Ph_3SiCOHPhCH_2C_6H_4X-p$

The *p*-substituted-benzylphenylcarbinols were

formed by treatment of benzoyltriphenylsilane with the appropriate Grignard reagent (eq. 4).

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Treatment of these carbinols with BF₃ could be expected to yield silylcarbonium ions which could attack the toluene used as solvent (S), rearrange (R), or directly lose a proton to form a silyl-substituted stilbene (E). Additionally, hydrogen migration could occur (I) to give the isomeric β -silylcarbonium ion, a reasonable reaction here since the β -ion would also be benzylic in character and thus of comparable stability. This β -ion could lose a proton to give, by this alternative route, the same silvistilbene, but loss of a proton from a β -silylcarbonium ion

is not commonly observed (11). The alternative process available to the β -silylcarbonium ion, elimination of the silvl group as triphenylfluorosilane, IE', with the formation of an alkene, in this case a stilbene, is well-documented behavior commonly observed in β -elimination reactions (11). These possibilities are outlined in Scheme 2.

The reaction products from the carbinols examined gave evidence that each of the possible reaction pathways except Friedel-Crafts substitution had occurred: again, as in previous situations involving tertiary carbonium ions, steric effects presumably preclude substitution taking place. The reaction mixtures were sufficiently complex that estimation of the proportions of various products could not be carried out from n.m.r. spectral data alone, and the data reported in Table 4 are isolated yields, and thus not very precise in some cases. In the separation of the products by column chromatography some triphenylfluorosilane was hydrolyzed to triphenylsilanol, so that the sum of the yields of these two products constitutes some measure of the overall amount of elimination of silicon (IE') occurring from the β -silylcarbonium ions.

As is evident from the data in Table 4, the reactions are highly temperature sensitive. At -40°, rearrangement of an aryl group from silicon to carbon (R) or isomerization of the α -silylcarbonium ion to the β -ion, followed by loss of silicon (IE'), were the only processes observed, no silylstilbene, the product of simple



elimination (E), being detected. Less rearrangement and more isomerization occurred when the benzyl group had an electron-donating substituent attached, presumably because isomerization would be more favorable when the new β -ion could be stabilized whereas the α -ion would be relatively unaffected by substituents on the benzyl group. A surprising amount of the stilbene resulting from the IE' process was the *cis*isomer.

At the elevated temperature (110°), no rearrangement product was detected. Elimination of a proton from the α -silylcarbonium ion (E) yielding silylstilbene was a major reaction and the silylstilbenes isolated were shown by comparison with authentic samples to be exclusively the isomers where both aryl groups were *cis* to one another, suggesting that less steric interaction occurs between *cis*-aryl groups than when an aryl group and a triphenylsilyl group are *cis* to one another. The other process occurring at 110° was again isomerization–elimination (IE') since significant amounts of fluorosilane and silanol and *cis*- and *trans*-stilbenes were isolated.

It seems probable that the silylstilbenes observed arise solely by loss of a proton from the α -silylcarbonium ion. Loss of a proton from β -silylcarbonium ions is not normally observed, loss of silicon being the usual process (11). In the present work, and as a test of the source of the silylstilbenes, the β -silylcarbinol 1-phenyl-2-triphenylsilylethanol was treated with BF₃ in toluene (eq. 5); triphenylfluorosilane was isolated in high yield. No silylalkene, the product of proton elimination, could be detected. Hence, we believe the silylstilbene arises solely by loss of a proton from the α -silylcarbonium ion, whereas fluorosilane and *cis*- and *trans*-stilbenes are the only products produced by any β -silylcarbonium ion formed.

Since treatment of either the *cis*- or *trans*stilbene with BF_3 under the reaction conditions caused no isomerization, it appears that the proportions of *cis*- and *trans*-stilbenes obtained from the reaction of the silylcarbinols with BF_3 are somehow specifically related to their silylcarbonium ion precursors. While it would be possible to speculate as to a possible explanation for the proportions in which they are formed it seems more prudent to await further information.

Aliphatic Silylcarbinols

Three triphenylsilylcarbinols having only hydrogen or aliphatic groups attached to the carbinol carbon were subjected to treatment with BF_3 in hexane and in toluene.

Triphenylsilylcarbinol was found to resist reaction and was recovered unchanged after

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$\begin{array}{c cccc} Ph_{3}GeCHOHPh & C_{6}H_{6} & 23 & 100 \ S \\ C_{6}H_{6} & 80 & 5 \ R \ 95 \ S \\ C_{c}H_{5}F & -20 & 100 \ S \\ C_{6}H_{14} & 23 & 100 \ R \\ \end{array}$ $\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Compound	Solvent	Temperature (°C)	Products	Results with Si analog
$\frac{Ph_{3}GeCOHPh_{2}}{C_{6}H_{14}}$	GeCHOHPh	$\begin{array}{c} C_6H_6\\ C_6H_6\\ C_6H_5F\\ C_6H_{14}\end{array}$	23 80 -20 23	100 S 5 R 95 S 100 S 100 R	50 R 50 S 100 R 100 R
	GeCOHPh ₂	ArX or C ₆ H ₁₄	23	100 R	100 R
Ph ₃ SiCH ₂ CHOHPh $\xrightarrow{BF_3}$ Ph ₃ SiCH ₂ -CHPh $\xrightarrow{Ph_3SiF}$ +	₃ SiCH ₂ CHOHPh	$\xrightarrow{C_6H_{14}}$ $\xrightarrow{BF_3} \rightarrow$	Ph ₃ SiCH ₂ -CHPh	Ph ₃ SiF +	CH ₂ =CHP

		TABLE 5		
Products	from	germylcarbinols	with	BF ₃

treatment with BF₃ in hexane at 23°, or in toluene at either 40 or 110°. Similarly 1-triphenylsilylethanol failed to react in hexane or toluene at 23°. This inertness may be due to the instability of the anticipated carbonium ions, since it is known that under the reaction conditions employed neither methanol nor ethanol undergoes Friedel–Crafts reactions (12).

2-Triphenylsilyl-2-propanol reacted with BF_3 to give only isopropenyltriphenylsilane, the dehydration product, under a variety of reaction conditions including hexane at 23°, or toluene at -40 or +110 °C.

Germylcarbinols and Carbinols:

[5]

 $Ph_3GeCPhOHR(R = H, Ph),$ $Ph_3CCHOHPh$

The reactions of boron trifluoride with a few germylcarbinols were investigated to compare with the behavior of the analogous silicon compounds. The data are summarized in Table 5.

Both the germylmono- and diphenylcarbinols behaved rather like their silicon analogs, although the germylmonophenyl carbinols showed a greater tendency to undergo substitution rather than rearrangement under similar conditions, compared with their silicon analogs.

When 1,2,2,2-tetraphenylethanol was treated with boron fluoride for comparison purposes in a variety of solvents at various temperatures, under all conditions the only product formed was tetraphenylethylene (eq. 6).

[6]
$$Ph_3C$$
—CHOHPh $\xrightarrow{BF_3}$ Ph_3C —CHPh \rightarrow
+ Ph_2C —CHPh₂ \rightarrow Ph_2C =:CPh₂

Thus the reactions of the carbinols Ph_3 -MCHPhOH (M = C, Si, Ge) with boron fluoride depend noticeably on the nature of the atom M. Each carbinol can be presumed to have

formed the carbonium ion Ph₃MCHPh.

In non-aromatic solvents, each underwent rearrangement involving migration of phenyl from M to the adjacent electron-deficient carbon atom. In aromatic solvents, as the atom M changes from Ge to Si to C, it is observed that the amount of Friedel-Crafts substitution of the original carbonium ion diminishes relative to the amount of 1,2-phenyl migration. One of the reasons for this may be the decreasing size of M, resulting in differing steric effects. In particular, with the smaller size of carbon, there will be an increase in the steric repulsions between the three phenyl groups attached to M, increasing the driving force for migration. Additionally, the smaller the atom M is, the more sterically shielded the carbonium ion is likely to be, making approach of the aromatic solvent necessary for Friedel-Crafts substitution more difficult. Both these effects will tend to increase the amount of 1,2migration and reduce the amount of substitution on changing M from Ge to Si to C.

Carbonium Ions

In the discussion so far it has been assumed that carbonium ion intermediates were created by reaction of the silylcarbinols with BF_3 . Some fairly compelling evidence for these assumptions exists as will be described below.

Attempts to trap silylcarbonium ions as methyl ethers by adding the deep red solution, formed

CANADIAN JOURNAL OF CHEMISTRY. VOL. 48, 1970 Ph₂MeSi-CPh₂OMe $\stackrel{\mathbf{BF}_3}{\longrightarrow}$ MeOH Ph₂MeSi-ČPh₂ [7] Ph2MeSiCPh2OH PhMeSiFCPh₃ (75% yield) LIAIHA Ph2MeSiCHPh2 (60%) Ph₃SiCHC₆H₄OMe ЬМе MeOH Ph₃Si-CHC₆H₄OMe [8] Ph₃SiCHOHC₆H₄OMe Ph₃SiCH(C₆H₄OMe) Toluene C₆H₄Me) Ph₃SiCH₂C₆H₄OMe

by addition of BF_3 to a solution of diphenylmethylsilyldiphenylcarbinol in toluene at -40° . to methanol at -60° failed, since only the normal rearrangement product phenylmethyltritylfluorosilane was obtained (eq. 7). However, when the deep red solution was treated with ethereal lithium aluminum hydride, following the procedure of Brown for trapping carbonium ions as the hydride derivative (13) a 60% yield of diphenylmethylsilylphenylmethane was isolated, strongly suggestive of an intermediate carbonium ion.

Similarly, the deep red solution formed at -40° triphenylsilyl - p - methoxyphenylcarbinol from with BF_3 in toluene when treated with methanol failed to yield the methyl ether, the Friedel-Crafts substitution product with toluene being obtained in greater than 80% yield. However, when treated with ethereal lithium aluminum hydride, a mixture of the hydride and the Friedel-Crafts product was obtained (eq. 8). These results indicate that under conditions where either rearrangement or substitution was normally found to occur exclusively, low temperature quenching led to the formation of compounds logically explicable in terms of an intermediate carbonium ion.

We have sought further evidence for the existence of the carbonium ions by obtaining n.m.r. spectra of various species following the general procedures developed by Olah et al. (14). Thus dissolving the silylcarbinols in a mixture of antimony pentachloride – sulfur dioxide at -60°C gave rise to deeply colored solutions whose n.m.r. spectra were readily interpretable as due to silylcarbonium ions being present in high yield.

Table 6 presents the data for the various silylcarbonium ions observed, together with the data of Olah et al. (14, 15) for related carbonium ions. In general the spectra were not clean and integration always indicated too many aromatic protons. This, coupled to the inability to recover recognizable products after quenching with methanol, suggests that extensive cleavage of the aromatic groups on silicon took place. Aryl-silicon bonds are well known to be susceptible to cleavage under these conditions (16). In view of these observations it is apparent that the n.m.r. spectra obtained for the silvlalkylcarbonium ions are the more useful in illustrating the existence of the silvlcarbonium ions because the alkyl resonances may be compared to those of the related carbonium ions. The phenyl resonances although in general appearing to be in the expected region may contain significant amounts of $C_6H_5^+$ ion or related species thus confusing the spectra in this region.

The preceding data make it possible to explain the reactions of boron trifluoride with the silylcarbinols as involving silylcarbonium ion intermediates which rearrange, or which undergo elimination reactions. Certain details of the over-

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TABLE 6

The n.m.r. spectra of silylcarbonium ions in SbCl₅:SO₂ at -60°

Ions Resonance position δ		
Ph₃SiĆPhMe	3.61 (s) (Si ⁺ _C Me), 7.3–8.4 (Aryl)	
Ph₃Si ⁺ _C MeC ₆ H₄F	3.58 (s) (Si ⁺ _{CMe}), 7.3–8.4 (Aryl)	
Ph ₃ Si ⁺ _C Ph ₂	7.5–8.3 (Aryl)	
PhMe ₂ Si ⁺ _C Ph ₂	0.75 (s, Me), 7.7–8.3 (Aryl)	
Ph ₃ Si ⁺ _C (C ₆ H₄OMe)CH ₂ Ph	4.4 (OMe), 4.6 (s) ($\stackrel{+}{C}$ -CH ₂ Ph), 7.0-8.0 (Aryl)	
Ph ₃ Si ⁺ CPhCH ₂ Ph	5.2 (s) (CH_2 Ph), 7.0–8.5 (Aryl)	
PhEt ⁺ _C Me	3.5 (s) (⁺ CMe)	
Me ₃ Č	3.83 (s)	
Ph ₃ CCPh₂	7.4–8.3 (Aryl)	
Ph ₂ ⁺ CH ₂ Ph	5.1 (s) (CH_2Ph), 7.1 (m) (CH_2Ph), 7.5-8.3 (Aryl)	

all mechanism have not been clearly resolved however. There is no evidence that siliconium ions are intermediate species in the rearrangement reactions. No products were isolated from any reaction whose formation would have involved reaction of a siliconium ion with an aromatic substrate. Further, when triphenylsilanol in toluene was treated with BF₃ in the hope of forming triphenylsiliconium ion, which could then react with the aromatic substrate, only tris(triphenylsiloxy)boron was formed. If siliconium ions are not involved, as seems probable. then the degree to which fluoride ion or some other anion is involved in the migration process, and the timing of the silicon-fluorine bond formation relative to aryl migration from silicon to carbon is not yet clearly established. Recent studies in these laboratories (17) have shown that silyldiazoalkanes, on treatment with acid, a process presumed to give silylcarbonium ions (or ion pairs), give the simpler addition product R₃SiCHXR, with no rearrangement product being formed (eq. 9). However, if the diazo [9] $R_3SiCN_2R' + HX \rightarrow R_3Si-CHR' \rightarrow R_3SiCHXR$

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X-

compound is treated with $BF_3 \cdot Et_2O$ (under conditions where some water may be present) or if the addition product $R_3SiCHXR$ is treated with $BF_3 \cdot Et_2O$, then the expected rearrangement and Friedel-Crafts substitution products are obtained (18) (eq. 10).

$$\begin{array}{c} R_{3}SiCN_{2}R \\ [10] \quad \text{or} \quad & \frac{BF_{3} \cdot Et_{2}O \text{ in}}{toluene} \\ R_{3}SiCHXR \quad & F \\ R_{3}SiCHYR \quad & F \\ R_{3}SiCHPhC_{6}H_{4}Me_{7}F \\ \end{array}$$

It is therefore evident that more than the mere formation of a simple silylcarbonium ion is required for rearrangement to occur, and it is obvious that BF_3 is a particularly good reagent for effecting rearrangements of aryl groups from silicon to carbon. However, a clearer understanding of the processes involved and their timing must await further studies.

Experimental

The silylcarbinols employed in this study were known compounds prepared according to published routes as noted below for each family: silylphenylcarbinols (5), silyldiphenylcarbinols (19, 20), silylphenylbenzylcarbinols (5), silylphenylmethylcarbinols (5), and silylalkylcarbinols (21).

The solvents employed were reagent grade and the boron trifluoride (Matheson) was used direct from the cylinder without purification.

Most reactions were carried out following a standard procedure. The silylcarbinol was dissolved in the desired solvent in a 100 ml round-bottomed flask under nitrogen, and the solution was stirred magnetically. Cooling when desired was effected by Dry Ice – acetone or ice-baths, and reactions at elevated temperatures were usually carried out at reflux.

Boron trifluoride was rapidly bubbled directly into the solution until the effluent gases fumed, which was taken as an indication that excess boron fluoride had been added. This usually required only a few seconds. In many

Reagent		X/'-1 1¥	Melting	Anal	ysis†
solvent	Product	(%)	(°C)		H
(a) Products from	Ph ₃ SiCHOHPh				
C ₆ H ₅ OMe	Ph ₃ SiCHPhC ₆ H ₄ OMe-p	87‡	172–174	84.15 84.46	6.17 6.27
C ₆ H ₅ Me C ₆ H ₁₄	Ph ₃ SiCHPhC ₆ H ₄ Me- <i>p</i> Ph ₂ FSiCHPh ₂	79‡ 94∥	185–186 154–155	81.53 81.61	§ 5.71 5.82
(b) Products from C ₆ H₅Me	<i>Ph</i> ₃ <i>SiCHOH(C</i> ₆ <i>H</i> ₄ <i>Cl-p)</i> Ph ₃ <i>SiCH</i> (C ₆ H ₄ Cl- <i>p</i>)(C ₆ H ₄ Me- <i>p</i>)	66¶	160–161	80.88 80.85	5.73
C ₆ H ₁₄	$Ph_2FSiCHPh(C_6H_4Cl-p)$	75	102–104	74.49 74.47	5.00 4.92
(c) Products from C ₆ H₅Me	$\begin{array}{l} Ph_{3}SiCHOH(C_{6}H_{4}CMe_{3}\text{-}p) \\ Ph_{3}SiCH(C_{6}H_{4}CMe_{3}\text{-}p)(C_{6}H_{4}Me\text{-}p) \end{array}$	65	144-145	87.04 87.01	7.30
C ₆ H ₁₄	$Ph_2FSiCHPh(C_6H_4CMe_3-p)$	86	147–149	82.01 81.42	6.88 6.97
(d) Products from	$(p-XC_6H_4)_3$ SiCHOHPh				
C₅H₅	$(p-C C_6H_4)_3$ SiCHPh ₂	68	194–196	70.23 69.97	4.37 4.42
C ₆ H ₆	$(p-Me_3CC_6H_4)_2FSiCHPh(C_6H_4CMe_3-p)$	70	154–156	82.70 82.50	8.40
C ₆ H₅Me	$(p-Me_3CC_6H_4)_3SiCHPh(C_6H_4Me-p)$	59	206207	86.76 86.03	8.61 8.30
(e) Products from	$Ph_nMe_{3-n}SiCOHPh_2$				
C ₆ H₅Me	Ph ₂ FSiCPh ₃	85‡**	186–187	83.82 83.50	5.67 5.69
C ₆ H₅Me	PhMeFSiCPh ₃	83‡	150-151	81.61 82.12	6.06
C₀H₅Me	Me ₂ FSiCPh ₃	70	134–135	78.68	6.60
C ₆ H₅Me	Me ₂ FSiCMePh ₂	56	††	74.34 74.65	7.41 7.24
(f) Products from C ₆ H ₅ OMe	Me₃SiCHOHPh Me₃SiCHPh(C6H₄OMe-p)	64	57-58‡‡	75.49	8.19
C ₆ H ₅ CMe ₃	$Me_3SiCHPh(C_6H_4CMe_3-p)$	53	\$\$	75.15 81.02	9.38
C ₆ H₅Me	$Me_3SiCHPh(C_6H_4Me-p)$	78	35-36‡	79.92 79.77	8.72
C6H6 C6H5F	Me ₃ SiCHPh ₂ Me ₃ SiCHPh(C ₆ H ₄ F-p)	70 52	74–75∥∥ 49–50‡	74.36 74.23	§ 7.14 7.21

TABLE 7	
Products from the reactions of silylcarbinols with BF	'3

Yields are based on material isolated from 0.5 g runs in 50 ml of solvent at a temperature of either 23° or as otherwise noted. [†]Top line, calculated values; second line, found values. [‡]Recrystallized from methanol. [§]Identified by mixed m.p. with authentic sample. [¶]In C₆H₆F, yield was 85%; in C₆H₆ at 80°, yield was 77% after recrystallization from petroleum ether (b.p. 90–100°). Reduction of product with LiAlH₄ gave Ph₂HSiCHPh₂ m.p. 130–132°. Anal. Calcd, for C₃₁H₂₅Si: C, 85.64; H, 6.33. Found: C, 85.58; H, 6.18. [¶]Recrystallized from petroleum ether (b.p. 90–100°).
*On reduction with LiAlH₄, Ph₂HSiCPh₃ was obtained ,m.p. 152–154°, from petroleum ether. Anal. Calcd, for C₃₁H₂₆Si: C, 87.27; H, 6.14. Found: C, 87.35; H, 6.01. [†]Liquid: b.p. 55%0.02 mm. [‡]Recrystallized from petrate at -70°. [§]SHigh boiling liquid purified by chromatography on alumina. [§][]Recrystallized from ethanol.

Xof			Tomporatura	Viold	Melting	Ana	lysis
reagent	Solvent	Product	(°C)	(%)	(°C) C	Н	
H H	C_6H_5Me C_5H_{12}	Ph ₃ SiCPh=CH ₂ * Ph ₂ FSiCMePh ₂	23 32	82 58	133–135† 88–90§	81.61	‡ 6.06
Cl	C ₆ H₅Me	$Ph_3SiC(C_6H_4Cl-p)=CH_2$	110	81	123–124†	78.64 78.14	5.33
Cl	C_5H_{12}	$Ph_2FSiCMePh(C_6H_4Cl-p)$	32	60	106-108§	74.87	5.32
OMe	C ₆ H₅Me	$Ph_3SiC(C_6H_4OMe-p) = CH_2$	40¶ĭ	90	100–101†	82.59 82.61	6.16
OMe	C5H12	$Ph_2FSiCMePh(C_6H_4OMe-p)$	- 40	64	112-113§	78.54 78.31	6.07 6.01

TABLE 8	
Data from reactions of silvlcarbinols $Ph_3SiCOHMe(C_6H_4X_{-p})$ in various solv	ents

*The u.v. spectrum, λ_{mpx} (EtOH) 249 m μ (8800). †Recrystallized from ethanol. ‡Identified by mixed m.p. with authentic sample. §Recrystallized from methanol. "The u.v. spectrum, λ_{max} (EtOH) 255 m μ (10 800). "The u.v. spectrum, λ_{max} (EtOH) 264 (10 000), 268 (10 300), 272 m μ (s) (9600).

of the reactions highly colored (red-yellow) intermediate solutions were observed. Reactions were worked-up by quenching in water followed by ether extraction. Where mixtures of products were obtained they were identified by comparison with the spectra of authentic samples, and the ratio of the products was determined by n.m.r. integration. Several typical examples are given below, and the results of all reactions will be found in Tables 7 - 10.

Nuclear Magnetic Resonance

Nuclear magnetic resonance was extensively employed in this work to establish the ratio of mixtures of products. While the positions of absorptions associated with particular groups varied very little between the members of a family of compounds (e.g. p-CMe₃, δ 1.20-1.32; *p*-OMe, δ 3.64–3.73; *p*-Me, δ 2.25–2.29; Si–CH– δ 4.08–4.3 p.p.m., etc.) absorptions associated with many frequently encountered combinations of compounds were readily identified. Thus, for example, from the reaction of triphenylsilylphenylcarbinol with BF_3 in toluene (eq. 11), the products formed, benzhydryldiphenylfluorosilane and p-methylbenzhydryltriphenylsilane were easily distinguished, and the proportions readily established by integration. In the fluorosilane, the benzylic

[11] $Ph_3SiCHOHPh \rightarrow$

 $Ph_2FSiCHPh_2 + Ph_3SiCHPhC_6H_4Me-p$

proton occurred as a doublet, at δ 4.1 p.p.m., J = 7 Hz, being split by the adjacent fluorine whereas the p-tolyl compound could be estimated quantitatively both by the benzylic proton which occurred as a singlet at δ 4.36 p.p.m., and by the intensity of the methyl signal at 2.25 p.p.m.

In the compounds containing methoxyphenyl groups the four aromatic protons usually were observed as an AB quartet at about 6.7-6.9 p.p.m., separate from the other aromatic proton signals, indicating unambiguously that substitution had occurred in the para position, but p-tolyl- or p-t-butylphenyl- signals usually overlapped other aromatic protons.

The ¹⁹F spectra of a variety of compounds, e.g. Ph2FSiCHPh2, Ph2FSiCPh3, etc. were consistent with the structures assigned. Details of some typical spectra are given in Table 11.

Reaction of Triphenylsilylphenylcarbinol in Hexane at 23 °C

Boron trifluoride was bubbled into a solution of 0.5 g (1.37 mmole) of triphenylsilylphenylcarbinol in 50 ml of hexane for a few seconds until the effluent gases fumed. The reaction mixture was guenched in water, and the ether extracts, after drying with magnesium sulfate, were evaporated to dryness to give a colorless oil which was crystallized from petroleum ether (b.p. 90-100°) to give 0.47 g (94%) of benzhydryldiphenylfluorosilane, Ph₂FSiCHPh₂, m.p. 154-155°; n.m.r. (CCl₄); δ 4.1 (1H, d, J = 7, SiCH), 7.1-7.2 p.p.m. (20H, m, Ar).

Reaction of Triphenyl-p-chlorophenylcarbinol in Toluene at 23°

Boron trifluoride was bubbled into a solution of 0.5 g (1.25 mmole) of triphenylsilyl-p-chlorophenylcarbinol in 50 ml of toluene at 23°. After quenching with water and extraction with ether, the dried ether layer was evaporated under reduced pressure to give a colorless oil which was crystallized from petroleum ether (b.p. 90-100°) to give 0.35 g (66%) of triphenyl-p-chloro-p'-methylbenzhydrylsilane, $Ph_3SiCH(C_6H_4Cl-p)$ (C_6H_4Me-p), m.p. 160-161°; n.m.r. (CCl₄); δ 2.26 (3H, s, Me), 4.36 (1H, s, SiCH), 6.85-7.3 p.p.m. (23H, m, Ar).

Reaction of Phenyldimethylsilyldiphenylcarbinol in Toluene at -40°

Boron trifluoride was bubbled into a solution of 2.0 g (6.4 mmole) of the above carbinol in 50 ml of toluene at -40 °C for 30 s. An immediate red coloration appeared and persisted over 30 min, at which time the mixture was removed from the cold bath and allowed to warm to

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Temperature of x of reaction reagent (°C)			Viald	Melting	Analysis	
		Product	(%)	(°C)	C	Н
Cl	- 40	$Ph_2FSiCPh_2(CH_2C_6H_4Cl-p)$	51	134-135.5	77.93	5.3
		cis-PhCH≕CHC6H₄Cl-p* Ph₃SiF Ph₃SiOH	38 13 25	6264 153-154		† †
Cl	110	Ph ₃ SiCPh=CHC ₆ H ₄ Cl-p‡	28	151-152.5	81.23	5.3
		trans-PhCH=CHC ₆ H ₄ Cl-p* cis-PhCH=CHC ₆ H ₄ Cl-p*	4 40	131-132.5	01.50	†
		Ph₃SiF Ph₃SiOH	5 29	62–64 153–154		† †
CMe ₃	- 40	$Ph_2FSiCPh_2(CH_2C_6H_4CMe_3-p)$	17	167	83.98 84 12	6.8
	trans-PhCH=CHC ₆ H ₄ CMe ₃ -p§ cis-PhCH=CHC ₆ H ₄ CMe ₃ -p	35 32	95–97	04.12	†	
		Ph₃SiF Ph₃SiOH	36 19	63–64 153–154		† †
CMe ₃	110	$Ph_3SiCPh=CHC_6H_4CMe_3-p\P$	37	209–211	87.75	6.93
		trans-PhCH=CHC6H4CMe3-p§	37	96–97	91.49 91.06	8.5
		cis-PhCH==CHC ₆ H₄CMe₃-p∥ Ph₃SiF Ph₃SiOH	15 12 17	63-64 152-154		† †
н	- 40	$Ph_2FSiCPh_2(CH_2Ph)$	27	135–136	83.78 83.70	5.93
		trans-PhCH=CHPh* cis-PhCH=CHPh*	3 38	124-125	05.70	†
		Ph₃SiF Ph₃SiOH	20 16	63–64 153–154		† †
Н	110	Ph ₃ SiCPh=CHPh**	35	110–112	87.61 87.30	5.9
		trans-PhCH==CHPh* cis-PhCH==CHPh*	3 26	124-125	07.50	† +
		Ph3SiOH	4 14	63–64 153–154		T t

TABLE 9

Products from reactions of Ph_SiCOHPh(CH_C, H, X-n) in toluene at various temperatures

*The u.v. spectrum was in accord with data of ref. 24. †Identified by mixed melting point with an authentic sample. λ_{max} (EtOH) 298 mµ (18 800). λ_{max} (EtOH) 298 (27 600), 311 mµ (27 600). $\|\lambda_{max}$ (EtOH) 263 mµ (14 000). $\|\lambda_{max}$ (EtOH) 265 mµ (20 800).

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room temperature. As warming occurred, the red color began to fade, and when gone, the mixture was quenched in water and extracted with ether. After drying the extracts over magnesium sulfate, the ether was removed yielding a white solid, which after recrystallization from cyclohexane gave 1.42 g (70%) of triphenylmethyldimethylfluorosilane, Me₂FSiCPh₃, m.p. 134–135°; n.m.r. (CCl₄); δ 0.23 (6H, d, J = 7.5, Me₂SiF), 7.25 p.p.m. (15H, s, Ar).

Generation and Trapping of Diphenylmethylsilyldiphenylcarbonium Ion

A solution of 0.3 g (0.79 mmole) of diphenylmethylsilyldiphenylcarbinol in 50 ml of toluene at -40° was treated with BF3 for a few seconds. A deep red suspension was formed and persisted as long as the temperature was kept cold. Addition of the suspension with vigorous stirring to an ether solution of excess lithium aluminum hydride at -40° led to immediate loss of the red color. After warming to room temperature and aqueous acid work-up, the dried ether extracts gave an oil which on recrystallization from methanol gave 0.17 g (59%) of diphenylmethylbenzhydrylsilane, m.p. 104-105°, identified by mixed m.p. with an authentic sample.

Trapping of Triphenylsilyl-p-methoxyphenylcarbonium Ion

Boron fluoride was bubbled into a solution of 1.6 g (4.0 mmole) of triphenylsilyl-p-methoxyphenylcarbinol in 50 ml of toluene at -40 °C. A pale red solution was formed which was slowly added to a solution of excess

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Data for products of reactions of triphenylgermylcarbinols with BF₃ in various solvents at 23°

Solvent				Melting	Analysis	
	Reagent	Product	(%)	(°C)	С	Н
C ₆ H ₆	Ph ₃ GeCHOHPh	Ph ₃ GeCHPh ₂	81	158-160*		t
C ₆ H₅Me	Ph₃GeCHOHPh	Ph ₃ GeCHPhC ₆ H ₄ Me-p	84	176–178	79.20 79.84	5.82 6.06
C ₆ H₅F	Ph ₃ GeCHOHPh	$Ph_3GeCHPh(C_6H_4F-p)$	74	156-157*	76.10 75.58	5.15 5.25
C ₆ H ₁₄	Ph₃GeCHOHPh	$Ph_2FGeCHPh_2$	77	147-148‡	72.69 72.67	5.13 5.27
C ₆ H ₁₄	$Ph_3GeCOHPh_2$	$Ph_2FGeCPh_3$ §	78	202–204	76.14 76.35	5.12 5.18

*Recrystallized from methanol. †Identified by mixed m.p. with an authentic sample. ‡Recrystallized from petroleum ether (b.p. 90-100°). §When solvent was toluene, yield of Ph₂FGeCPh₃ was 70%. On reduction with LiAIH₄, Ph₂HGeCPh₃ was obtained, m.p. 164-166° from based ethanol. Anal. Caled. for C₃₁H₂₆Ge: C, 79.03; H, 5.56. Found: C, 79.37; H, 5.54.

		TABLE 1	1	
The n.m.r.	data	of typical	reaction	products

Compound	δ(CCl ₄) p.p.m.
Ph ₂ FSiCHPh ₂	7.1–7.2 (m, Ar); 4.1 (d, $J = 7$ Hz, CH)
Ph ₂ FSiCHPhC ₆ H ₄ CMe ₃ -p	7.1–7.3 (m, Ar); 4.08 (d, $J = 7$ Hz, CH); 1.28 (s, CMe ₃)
Me ₂ FSiCHPh ₂ Me	7.2 (s, Ph); 1.73 (s, broad, C-Me); 0.14 (d, $J = 7.5$ Hz, Me ₂ Si)
Ph₃SiCHPhC ₆ H₄OMe- <i>p</i>	7.0-7.2 (m, Ph); 6.71 (AB q, $J = 8$ Hz, v ₀ $\delta_2 = 15.5$ Hz, C ₆ H ₄ OMe); 3.68 (s, OMe); 4.3 (s, CH)
$(p-Me_3CC_6H_4)_3SiCHPhC_6H_4Me-p$	6.9–7.3 (m, Ar); 4.31 (s, CH); 2.28 (s, ArMe); 1.30 (s, CMe ₃)
Ph ₂ FGeCHPh ₂	7.2 (m, Ph); 4.45 (d, $J = 4$ Hz, CH)
$Me_3SiCHPhC_6H_4F$ -p	7.0-7.5 (m, Ar); 3.42 (s, CH); 0.02 (s, Me ₃ Si)

lithium aluminum hydride in ether at -40° . The red color disappeared. After warming to room temperature, and aqueous work-up, the dried ether extracts gave an oil on removal of the solvent. Recrystallization from 1:1 ethanol-hexane gave 0.03 g (16%) of *p*-methoxy-*p'*-methylbenzhydryltriphenylsilane, m.p. 164°, identified by mixture m.p. Concentration of the mother liquors gave 0.48 g (30%) of p-methoxybenzyltriphenylsilane, m.p. 103-105°, identified by spectra and mixed m.p.

Reaction of Triphenylsilylphenylbenzylcarbinol with BF₃ in Toluene at -40°

Boron trifluoride was bubbled through a solution of 1.0 g (2.20 mmole) of the carbinol in 50 ml of toluene. A red color was formed immediately which soon faded. When colorless, water was added and the mixture was extracted with ether, the extracts being dried over anhydrous magnesium sulfate. Removal of the ether gave a viscous oil whose i.r. spectrum showed no absorption in the

2.7-2.8 µ (SiO-H) region. The oil was chromatographed on a $1 \times 5^{\prime\prime}$ silica gel column. Elution with hexane (250 ml) gave 0.15 g (38%) of an oil shown to be cisstilbene by comparison of its spectral properties with published data (10-12). Further elution with 250 ml hexane gave an oil containing both trans-stilbene and triphenylfluorosilane, from which was isolated 0.007 g (3%) of *trans*-stilbene, m.p. 123–124°, identified by mixed m.p. On further elution with 400 ml of hexane, an oil was isolated which crystallized from methanol to yield 0.12 g (20%) of triphenylfluorosilane, m.p. 62-64°, identified by mixed m.p. Elution with 500 ml of carbon tetrachloride yielded a white solid which was recrystallized from methanol to yield 0.27 g (27%) of 1,1,2-triphenylethyldiphenylfluorosilane, m.p. 135-136°. Finally, elution with 125 ml of benzene gave material which, after crystallization from carbon tetrachloride, afforded 0.10 g (16%) of triphenylsilanol, m.p. 153-154°. Chromatography of authentic triphenylfluorosilane on a similar

column under similar conditions led to conversion of part of the fluorosilane to silanol.

Reaction of Triphenylsilylphenylbenzylcarbinol with BF_3 in Toluene at 110°

Boron trifluoride was bubbled into a solution of 0.9 g (1.98 mmole) of carbinol in 50 ml of refluxing toluene for a few seconds. No colored species were formed. Work-up in the usual manner gave an oil which was crystallized from boiling methanol to give 0.30 g (35%) of α -triphenylsilyl-*cis*-stilbene, m.p. 110–112°, shown to be identical to a material produced by an alternate route (22).

Solvent was removed from the mother liquors under reduced pressure and the oil was chromatographed on a $1 \times 3''$ silica gel column. Elution with 500 ml of hexane gave 0.095 g (26%) of *cis*-stilbene, identified by its spectral properties. From the next 150 ml of hexane was isolated 0.005 g (3%) of *trans*-stilbene, mp. 122-124°, identified by mixed m.p. From the next 300 ml of hexane was isolated 0.023 g (4%) of triphenylfluorosilane, m.p. 62-64°, identified by mixed m.p. Elution with 150 ml of carbon tetrachloride yielded an additional 0.05 g (total 0.30 g, 34%) of triphenylsilyl-*cis*-stilbene. Finally, elution with 150 ml of benzene yielded, after recrystallization from carbon tetrachloride, 0.077 g (14%) of triphenylsilanol, m.p. 152-154°, identified by mixed m.p.

Reaction of Triphenylsilylmethylphenylcarbinol with BF_3 in Toluene at -40 °C

Boron trifluoride was bubbled into a solution of 0.5 g (1.32 mmole) of the carbinol in 50 ml of toluene at -40° for a few seconds. Aqueous work-up as usual gave a solid, shown by n.m.r. spectrum to consist of α -triphenylsilyl-styrene and 1,1-diphenylethyldiphenylfluorosilane in the ratio of 3:2. The solid was dissolved in hexane and chromatographed on a 1 × 3" column of neutral Woelm alumina. Elution with 150 ml of hexane gave 0.11 g (23%) of α -triphenylsilylstyrene, which after recrystallization from petroleum ether (b.p. 60–70°) had m.p. 132–134°. A mixed m.p. with an authentic sample was not depressed. Further elution with 200 ml of hexane gave 0.21 g (41%) of the fluorosilane, m.p. 88–90° after recrystallization from methanol.

Treatment of Triphenylsilylpropanol in Toluene at 23 °C

Boron fluoride was bubbled into a solution of 0.5 g (1.53 mmole) of 2-triphenylsilyl-2-propanol in 50 ml of toluene. No coloration was observed and the reaction was worked-up in the normal manner. Removal of the solvents left a white solid that was recrystallized from ethanol to yield 0.42 g (89%) of isopropenyltriphenylsilane, m.p. 94–95 °C. A mixed m.p. with an authentic sample was not depressed. When the reaction was repeated in pentane 0.35 g (72%) of isopropenyltriphenylsilane was obtained.

Treatment of 2-Triphenylsilyl-1-phenylethanol in Toluene at 23 °C

Boron fluoride was bubbled into a solution of 0.5 g (1.35 mmole) of 2-triphenylsilyl-1-phenylethanol in 50 ml toluene. The reaction mixture was worked-up in the normal manner to leave a solid that was recrystallized from methanol to yield 0.21 g (56%) of triphenylfluorosilane, m.p. 62–63 °C, identified by mixed m.p. with an authentic sample.

Synthesis of cis- and trans-p-t-Butylstilbene

A mixture of 5.0 g (0.0276 mole) of *p-t*-butylbenzyl chloride and 7.24 g (0.0276 mole) of triphenylphosphine was heated for 13 h in 5 ml of benzene. Filtration gave 5.2 g (46%) of *p-t*-butylbenzyltriphenylphosphonium chloride, m.p. 206–209° with decomposition.

To 5.2 g (0.013 mole) of the phosphonium salt in ether was added slowly 2.0 ml (0.013 mole) of phenyllithium in ether. After stirring for 3 h, a solution of 1.35 g (0.012 mole) of benzaldehyde in 10 ml of ether was added slowly. After stirring for 16 h, the reaction was worked-up with aqueous acid, and the dried ether extracts afforded a sticky solid, which was crystallized from methanol. This yielded 0.53 g of *trans-p-t*-butylstilbene, m.p. 96–97° which on recrystallization had m.p. 99–100°.

Anal. Calcd. for $C_{18}H_{20}$: C, 91.53; H, 8.47. Found: C, 91.10; H, 8.65.

The n.m.r.: (CCl₄), δ 7.2–7.5 (complex, aryl), 7.0 (s, vinyl), 1.32 p.p.m. (s, CMe₃); u.v.: λ_{max} (MeOH), 298 (ε, 27 600), 311 mµ (ε, 27 600).

Solvent from the mother liquor from the above was removed under reduced pressure and the residual material was treated with 1–2 ml of carbon tetrachloride, some insoluble material being filtered off. The solution was transferred to a $1/2 \times 10^{\prime\prime}$ alumina column, and was eluted with hexane. Virtually no material was eluted in the first 350 ml of solvent, but the next 200 ml yielded 0.40 g (14%) of *cis-p-t*-butylstilbene as a viscous oil, characterized by its spectra. The n.m.r.: (CCl₄), δ 7.2 (s, Ar) 7.1 (s, Ar), 6.5 (s, =CH), 1.28 p.p.m. (s, CMe₃); u.v.: λ_{max} (MeOH), 263 mµ (ϵ , 14 000).

Further elution of the column with 100 ml of carbon tetrachloride yielded 0.22 g of the *trans*-isomer (total 0.75 g, 27%).

Treatment of Triphenylgermylphenylcarbinol in Benzene at 23 °C

Boron fluoride was bubbled into a solution of 0.3 g (7.3 mmole) of triphenylgermylphenylcarbinol in 50 ml of benzene. No coloration was observed and the reaction mixture was quenched in water, extracted with ether, and dried with magnesium sulfate. Removal of the solvents under reduced pressure left a white solid. The solid was recrystallized from methanol to yield 0.28 g (81%) of benzhydryltriphenylgermane, m.p. 158–160 °C. A mixed m.p. with an authentic sample was not depressed.

Treatment of 1,2,2,2-Tetraphenylethanol in Anisole at -40 °C

Boron fluoride was bubbled into a solution of 0.35 g (1.0 mmole) of 1,2,2,2-tetraphenylethanol in 50 ml of anisole. A red coloration was observed but this faded very quickly and the reaction was quenched in water and extracted with ether. After drying with magnesium sulfate the solvents were removed under reduced pressure to leave a white solid that was recrystallized from benzene to yield 0.21 g (63%) of tetraphenylethylene, m.p. 227 °C. A mixed m.p. with an authentic sample was not depressed. A repeat of the reaction with 0.2 g (5.7 mmole) of the carbinol in 50 ml of hexane at 23° produced 0.11 g (58%) of tetraphenylethylene as the only product detected.

Treatment of Triphenylsilanol with BF₃ in Toluene

Boron fluoride was bubbled into a solution of 0.5 g

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(1.83 mmole) of triphenylsilanol in 50 ml of toluene at 23 °C. No coloration was observed and the reaction was quenched in water after about 30 s. The reaction mixture was extracted with ether and dried with magnesium sulfate. The solvents were removed under reduced pressure leaving a white solid that was recrystallized from methanol yielding 0.37 g (83%) of tris(triphenylsiloxy)boron, (Ph₃SiO)₃B, (23) m.p. 153-154 °C.

Anal. Calcd. for C54H45O3Si3B: C, 77.58; H, 5.56. Found: C, 77.41; H, 5.42.

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