Study of the Progress of the Reaction at 5°. A solution of the *syn*-benzobicyclooctadienol **2** in chloroform (1 ml, 237.8 mg/ml) was added over 1 min to a stirred mixture of trifluoroacetic acid and 98% sulfuric acid (exactly 1:1, 20 ml, 32.6 g) maintained at 5°. At intervals 1-ml portions were withdrawn, quenched with ice, and extracted with 200 μl of a solution of hexamethylbenzene in chloro-

form (5.343 mg/ml). The extracts were analyzed by vpc (10-ft 15% FFAP on Chromosorb W at 200°); the results are given in Figure 2.

In the absence of a pure sample of the *anti* alcohol **1**, a mixture of 58.7% **1** and 41.5% **2** was examined by the above procedure, with closely similar results.

Carbonium Ion–Silane Hydride Transfer Reactions. I.
Scope and Stereochemistry
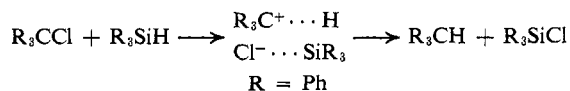
Francis A. Carey and Henry S. Tremper

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22903. Received November 27, 1967

Abstract: Carbonium ions varying in stability over a range of greater than 24 pK units were readily reduced to the corresponding hydrocarbons by hydride transfer from organosilanes. 2,6,2′,6′,2′′,6′′-Hexamethoxytriphenylmethane (**9**) was formed in 95% yield from the alcohol and triethylsilane in acetic acid but fragmented to *m*-dimethoxybenzene and 2,6,2′,6′-tetramethoxydiphenylmethyl cation in methylene chloride–trifluoroacetic acid. Reduction of either *cis-* (**15**) or *trans*-4-*t*-butyl-1-phenylcyclohexanol (**16**) afforded mixtures of *cis-* and *trans*-4-*t*-butyl-1-phenylcyclohexanes in which the *trans/cis* ratio was independent of the isomer used and the nature of the groups bonded to silicon. The *trans/cis* ratio did depend on the number of groups other than hydrogen bonded to silicon, being *ca.* 1.8 for triorganosilanes and *ca.* 4.0 for diorganosilanes and phenylsilane. The relative reactivity of the silanes used was triethyl > trioctyl ∼ diethyl > diphenyl ∼ triphenyl > phenyl. The results are interpreted as requiring carbonium ion intermediates for hydride transfer to occur and the stereoselectivity rationalized on the basis of "product development control." The higher percentage of elimination from equatorial alcohol (axial phenyl) than from axial alcohol (equatorial phenyl) is believed to result from the higher ground-state energy of the former.

Since silicon is more electropositive than carbon, silanes are good donors of hydride to carbonium ions. The reaction

$$(CH_3)_3SiH + (CH_3)_3C^+ \longrightarrow (CH_3)_3Si^+ + (CH_3)_3CH$$
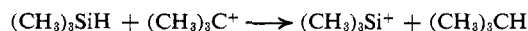
has been calculated to be exothermic by 8 kcal/mol in the gas phase from electron impact measurements of bond energies.[1] Experimental evidence regarding the effectiveness of silanes as hydride donors to carbonium ions can be found in the observation made some time ago that *n*-hexyl chloride is converted to *n*-hexane and neopentyl chloride to isopentane by triethylsilane in the presence of aluminum chloride.[2] More recently the hydrogen–halogen exchange between trityl chloride and triphenylsilane in ionizing solvents has been studied and a mechanism proposed involving a four-center transition state between the carbonium chloride ion pair and the silane.[3]

$$R_3CCl + R_3SiH \longrightarrow \begin{array}{c} R_3C^+ \cdots H \\ Cl^- \cdots SiR_3 \end{array} \longrightarrow R_3CH + R_3SiCl$$
$$R = Ph$$

Consistent with this description is the report that the reaction proceeds with complete retention of configuration at asymmetric silicon.[4]

Intermolecular hydride transfer reactions *between carbons* are generally considered to involve a linear array

of atoms in the transition state and to require a true carbonium ion ("open sextet") in order to occur.[5,6] Deno has discussed this requirement and pointed out that the capacity to abstract hydride from a neutral donor appears to be the unique reaction of carbonium ions not allowed their covalent precursors such as protonated alcohols. Thus, while *t*-butyl alcohol will undergo [18]O exchange with solvent, alkylate olefins and nitriles, and eliminate to olefin in 60% sulfuric acid, a medium in which the alcohol is protonated but negligible carbonium ion formation takes place, it does not abstract hydride from xanthene. Hydride transfer does take place, however, in 96% sulfuric acid where the equilibrium concentration of the *t*-butyl and derived cations is significant.[7]

We were interested in determining if similar restrictions applied to hydride transfers from silanes and investigating these reactions as probes for carbonium ion behavior. This paper reports our study of the scope of carbonium ion–silane hydride transfer reactions and some observations regarding their stereoselectivity and stereospecificity.

Results

The survey of carbonium ions reduced to the corresponding alkanes presented in Table I strikingly demonstrates the efficiency of silanes in donating hydride to carbonium ions. These carbonium ions were chosen to

(1) G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Am. Chem. Soc.*, **87**, 5327 (1965).
(2) F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *ibid.*, **69**, 2108 (1947).
(3) J. Y. Corey and R. West, *ibid.*, **85**, 2430 (1963).
(4) J. D. Austin and C. Eaborn, *J. Chem. Soc.*, 2279 (1964).

(5) N. C. Deno, H. Peterson, and G. Saines, *Chem. Rev.*, **60**, 7 (1960).
(6) N. C. Deno, G. Saines, and M. Spangler, *J. Am. Chem. Soc.*, **84**, 3297 (1962).
(7) N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **86**, 1745 (1964).

Table I. Silane Reductions of Carbonium Ions

Cation	pK_{R^+}	Conditions[a]	Yield,[b] %
2,6,2',6,2'',6''-Hexamethoxytriphenylmethyl (1)	>6.5[c]	A–triethylsilane	95
		B–triethylsilane	0
Triphenylcyclopropenyl (2)	3.18[d]	A–triethylsilane	80
9-p-Anisylxanthyl (3)	1.55[e]	B–triethylsilane	68
		B–triphenylsilane	94
9-Phenylxanthyl (4)	1.1[e]	A–triethylsilane	77
		B–triethylsilane	75
		B–triphenylsilane	80
Tri-p-anisylmethyl (5)	0.82[f]	B–triphenylsilane	87
Triphenylmethyl (6)	−6.63[f]	A–triethylsilane	0
		B–triethylsilane	59
		B–triphenylsilane	74
Diphenylmethyl (7)	−13.3[f]	B–triphenylsilane	70
2,4,6-Trimethylbenzyl (8)	−17.4[f]	B–triphenylsilane	41[g] 89[h]

[a] Conditions: A, pure acetic acid; B, methylene chloride containing 2 equiv of trifluoroacetic acid. [b] Of the corresponding alkane. [c] J. C. Martin and R. G. Smith, J. Am. Chem. Soc., 86, 2252 (1964). [d] R. Breslow, J. Lockhart, and H. W. Chang, ibid., 83, 2375 (1961). [e] R. A. Diffenbach, Ph.D. Thesis, The Pennsylvania State University, 1966, cited in A. E. Young, V. R. Sandel, and H. H. Freedman, J. Am. Chem. Soc., 88, 4532 (1966). [f] N. Deno, J. Jaruzelski, and A. Schriesheim, ibid., 77, 3044 (1955). [g] Isolated yield. [h] Determined by quantitative glpc.

offer a minimum of competing reaction paths and to cover a wide range of pK_{R^+}.[8] In most cases the carbonium ions were generated from the corresponding alcohol either in pure acetic acid (A) or in methylene chloride containing trifluoroacetic acid. Media of high acidity were avoided owing to the known instability of silanes to such conditions.

The two media vary somewhat in their applicability, acetic acid being effective only for the more stable of the carbonium ions. This is illustrated by the observation that while triphenylmethanol is reduced by silanes to triphenylmethane in the presence of trifluoroacetic acid at 25° it is recovered unchanged from acetic acid solutions of silanes. It therefore appears from this experiment that the necessity of significant carbonium ion formation applies also to silane hydride transfers. Further evidence in support of this point is presented later. On the other hand, acetic acid was the medium of choice for the reduction of the 1,2,3-triphenylcyclopropenyl cation, since in this case the carbonium ion is formed with ease from the corresponding t-butyl ether while the product, 1,2,3-triphenylcyclopropene, has been reported to be acid sensitive.[9]

This same condition of an acid-labile reduction product also appears in the case of the reduction of 2,6,2',6',2'',6''-hexamethoxytriphenylmethyl cation (1). When this cation was generated from the corresponding alcohol in acetic acid containing excess triethylsilane a deep purple color characteristic of the cation[10] formed which was discharged within 5 min. Aqueous quenching of the reaction mixture afforded directly a white solid, mp 186–187°, in 95% yield which was identified as

2,6,2',6',2'',6''-hexamethoxytriphenylmethane (9) by a satisfactory microanalysis and comparing its physical properties (ir, nmr, melting point) with those reported for this compound prepared by a different method.[11] When the reduction was attempted using trifluoroacetic acid to generate 1 in methylene chloride solution the course of the reaction apparently proceeded in the same manner; a deep purple color formed which quickly faded, but the product obtained was much different. This material melted at 138.5–139° and showed a relatively simple nmr spectrum consisting of an AB₂ aromatic multiplet and singlets at τ 6.38 and 6.0 (integral ratio 3:6:1). The nmr spectrum and microanalytical data (see Experimental Section) are consistent with this compound being 2,6,2',6'-tetramethoxydiphenylmethane (11), formed in 89% yield presumably by the following sequence of reactions.
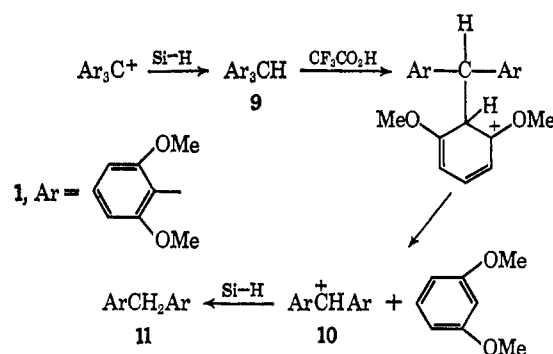
The possible intermediacy of 9 was tested by subjecting it to the same experimental conditions. It was found to be cleaved to 11 in 78% yield within 5 min at 25° using trifluoroacetic acid–triethylsilane–methylene chloride. That this fragmentation reaction occurs so readily is probably the result of three factors all operating together: (1) the ease of protonation of the electron-rich m-dimethoxybenzene ring, (2) the fragmentation step producing a stable carbonium ion,[12] (3) the substantial relief of steric compression upon fragmentation.[13]

Cleavage of carbonium ions to neutral molecules and other cations is a well-known process.[14,15] Recently the related fragmentation of the coumaranone 12 to

(8) The values listed in Table I for 1 and 2 are pK_a values rather than pK_{R^+} since they were calculated using pH as the acidity function rather than H_R. For relatively stable ions such as these pK_{R^+} is more positive than pK_a.

(9) P. Wolf and R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1963, p 257.
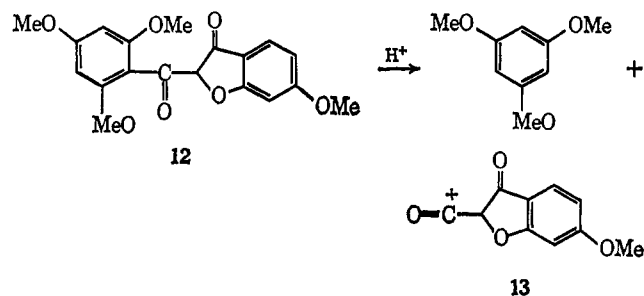
(10) J. C. Martin and R. G. Smith, J. Am. Chem. Soc., 86, 2252 (1964).

(11) Private communication from Professor J. C. Martin. The unusual nmr spectrum of this compound, characterized by a highly deshielded benzylic proton, will be discussed in a publication by Professor Martin.

(12) The pK_{R^+} of ion 10 has not been measured but is probably greater than +1.

(13) This relief of steric strain also manifests itself in the ready cleavage of 2,6,2',6',2'',6''-hexamethoxytriphenylmethanol under basic conditions (unpublished studies of J. C. Martin and R. K. Howe cited in ref 10).

(14) N. C. Deno and E. Sacher, J. Am. Chem. Soc., 87, 5120 (1965).

(15) C. A. Grob and P. W. Schiess, Angew. Chem. Intern. Ed. Engl., 6, 1 (1967).

1,3,5-trimethoxybenzene and **13** has been reported to proceed readily.[16]

Under the conditions used the reducible cations cover a range of stability of at least 24 pK_{R^+} units. The upper limit is not known since the pK_{R^+} of **1** is not known with certainty. The very stable sesquixanthydryl cation **14** was not reduced and so would appear to be past the upper limit of maximum pK_{R^+} to abstract hydride from silanes.

14
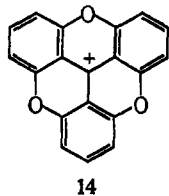
The lower limit for reduction under the mildly acidic conditions used in this experiment appears to be the last carbonium ion for which accurate pK_{R^+} data are known, the 2,4,6-trimethylbenzyl cation (**8**).

8
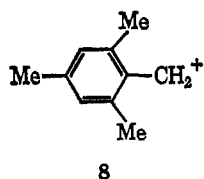
In the case of **8** the progress of the reaction was monitored by gas chromatography to ensure that the reduction product, isodurene, was not being formed by acid-catalyzed disproportionation[5] of mesityl alcohol. It was found that disproportionation of the alcohol did not occur under these conditions but rather that the starting alcohol was rapidly converted to mesityl trifluoroacetate and that this was then reduced to isodurene. Quantitative glpc analysis using tetralin as an internal standard indicated that after 20 min a 75% yield of isodurene was formed with the remainder being mesityl trifluoroacetate. After 1 hr, the yield of isodurene had increased to 89%.

The observation that no reduction of benzyl or cinnamyl alcohol occurred under these conditions serves as evidence that a significant concentration of free carbonium ions must be produced from the protonated alcohol for hydride transfer to occur.

An earlier investigation revealed that the reduction of optically active 2-phenyl-2-butanol with triethylsilane in chloroform containing trifluoroacetic acid proceeded with complete racemization of the asymmetric center to give optically inactive 2-phenylbutane in good yield.[17] This latter fact is also in accord with carbonium ions being the only intermediates capable of abstracting hydride from silanes in these reactions. It contrasts with the observation made in the same study that optically active 2-phenyl-2-butyl chloride when treated with lithium aluminum hydride gave 2-phenylbutane with net inversion of configuration.

To obtain additional evidence bearing on the stereochemistry and steric requirements in the transition state for hydride transfers we examined the reduction of cis-4-t-butyl-1-phenylcyclohexanol (**15**) and trans-4-t-butyl-1-phenylcyclohexanol (**16**) with a variety of

(16) R. Bryant and D. L. Haslam, *J. Chem. Soc.*, C, 1345 (1967).
(17) F. A. Carey, Ph.D. Thesis, The Pennsylvania State University, 1963.

Table II. Reduction of 4-t-Butyl-1-phenylcyclohexanols[a]

Alcohol	Silane	Product composition, %			trans/ cis
		17	18	19	
15	Triethyl	20	39	41	1.8
	Triethyl (5.4 equiv)	17	38	45	2.2
	Trioctyl	15	21	64	1.4
	Triphenyl	10	18	72	1.8
	Diethyl	12	54	34	4.5
	Diethyl (0.6 equiv)	7	29	64	4.1
	Diphenyl	11	42	47	3.8
	Diphenyl (0.6 equiv)	6	24	70	4.0
	Phenyl	3	13	84	4.3
16	Triethyl	28	50	22	1.8
	Triethyl (5.4 equiv)	27	51	22	1.9
	Trioctyl	24	36	40	1.5
	Triphenyl	20	29	51	1.5
	Diethyl	16	54	30	3.4
	Diethyl (0.6 equiv)	11	44	45	4.0
	Diphenyl	13	49	38	3.8
	Diphenyl (0.6 equiv)	10	40	50	4.0
	Phenyl	10	40	50	4.0

[a] Unless otherwise indicated the molar ratio of silane to alcohol was 1.3:1. In all experiments the molar ratio of trifluoroacetic acid to alcohol was 2.2:1.

silanes. From either **15** or **16** the product mixture was composed of cis-4-t-butyl-1-phenylcyclohexane (**17**), trans-4-t-butyl-1-phenycyclohexane (**18**), and 4-t-butyl-1-phenylcyclohexene (**19**). The results of this study are summarized in Table II.
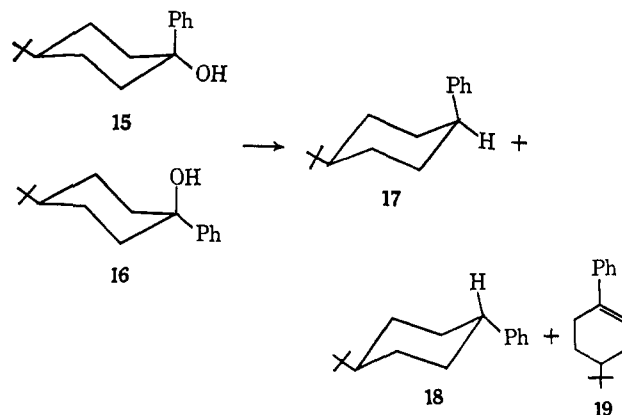
Particular attention should be directed to the fact that while the relative amounts of hydride transfer and elimination vary for **15** and **16** the trans/cis ratio of 4-t-butylphenylcyclohexanes is independent of the configuration of starting alcohol. This is indicative of a common intermediate leading to **17** and **18** which is most likely the free carbonium ion. It is unlikely that a significant fraction of **17** and **18** is formed from **19** since in a control experiment using triethylsilane the conversion of **19** to **17** and **18** amounted to only 10% under the reaction conditions.

The trans/cis ratio depends only on the number of substituents other than hydrogen bonded to silicon and not on their size or electronic characteristics. The trisubstituted silanes gave trans/cis ratios of 1.4–2.2, the disubstituted silanes ratios of 3.4–4.5, and phenylsilane a trans/cis ratio of 4.0–4.3.

It should also be noted that the proportion of elimination to **19** is uniformly greater for **15** than for **16**. The axial alcohol in this instance, in contrast to the usual generalization,[18] gives less elimination than the equato-

rial alcohol. On comparing the relative amount of elimination to **19** with the amount of hydride transfer as given by the sum of **17** plus **18** a qualitative estimate of the efficiency of the various silanes may be derived. On this basis, the relative efficiencies of the silanes are as follows: triethyl > trioctyl ~ diethyl > diphenyl > triphenyl > phenyl.[19] This is contrary to the order found by West who reported trityl halides to be more readily reduced by triphenylsilane than by triethylsilane.[3]

Discussion

The fact that under the mildly acidic conditions used in this study only those alcohols which form relatively stable carbonium ions are reduced to the corresponding alkanes indicates that abstraction of hydride from silicon, like carbon, requires a true carbonium ion intermediate. Protonated alcohols or encumbered carbonium ions do not appear capable of abstracting hydride from silanes. This requirement, coupled with the generally good yields, should make this reaction valuable in certain synthetic problems where it is desired to convert C-O to C-H in the presence of other reducible groups. Also, the efficient and irreversible scavenging of carbonium ions by silanes may provide unique information about the structure of carbonium ions since the attacking species (Si-H) is neither charged nor, in the usual sense of the word, nucleophilic.[20] The reactions may be carried out in a variety of solvents including those of low ionizing power such as methylene chloride and chloroform. These features are an interesting contrast to the irreversible scavenging of carbonium ions by borohydride reported by Bell and Brown.[21] Their technique utilizes a charged nucleophile (BH_4^-) in an ionizing solvent (water–diglyme).

The data in Table II are also consistent with a carbonium ion intermediate as the hydride-abstracting species. The relative amounts of **17** and **18** formed are independent of the configuration of the starting alcohol. The amounts of olefin produced do depend on the nature of the starting material since olefin may be derived from either the carbonium ion or protonated alcohol.[22] In every case the percentage of elimination to olefin was greater from **15** (equatorial OH) than from **16** (axial OH). This is a reversal of the usual tendency of more ready elimination from axial alcohols than from equatorial alcohols but is readily understood if one considers that the generalization has arisen from observations of the behavior of *secondary* alcohols. Part of the driving force for elimination of axial hydroxyl derives from a greater relief of steric strain in the transition state leading to elimination in secondary systems. The epimer in which the hydroxyl group is axial is ordinarily higher in ground-state energy than the epimer in which the hydroxyl group is equatorial. This situation is reversed in the specific case of **15** and **16** since it is the phenyl group which suffers the greater steric com-

pression; the epimer with the equatorial hydroxyl group (**15**) is higher in ground-state energy than the epimer with the axial hydroxyl group (**16**). Therefore, in going to the transition state for elimination more steric strain is relieved from **15** than from **16**.

The other factor responsible for axial alcohols being more susceptible to elimination than equatorial alcohols, the stereoelectronically favorable *anti* arrangement of proton and leaving group being more easily accommodated from axial alcohols, would appear to be less important under the reaction conditions employed here where the mechanism approaches E1.

The dependence of the *trans/cis* ratio on the number of organic groups bonded to silicon reflects steric interactions in the transition state for hydride transfer. Examination of representations of the transition states for axial attack (A) and equatorial attack (B) shows that the relative energies will depend on the interactions between R_1 and the axial hydrogens in each.

A   B
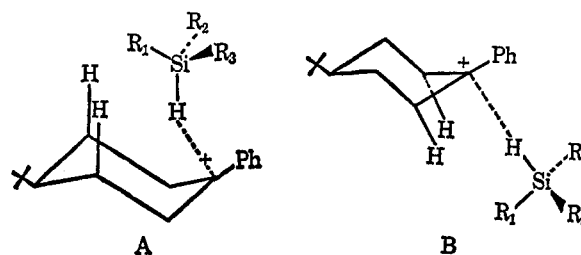
When R_1 is hydrogen these steric repulsions will be a minimum and product development control becomes more important (higher *trans/cis* ratio). When R_1 is alkyl or aryl transition state B suffers less crowding than A and the *trans/cis* ratio is lowered. As expected there is no difference in the *trans/cis* ratio between diphenylsilane and phenylsilane since the group involved (R_2 or R_3) is not subject to steric crowding.

In all cases the major product is the thermodynamically favored **18** while the kinetically favored **17** is the minor one. We believe the most economical explanation for this is product development control.[23] This concept has recently been questioned as being of significance in determining the product distribution obtained in nucleophilic additions to unsaturated centers exocyclic to six-membered rings such as cyclohexanones and alkylidenecyclohexanes.[24] In these reactions it is claimed that the important factor is the distance between the attacking reagent and the unsaturated center in the transition state. From inspection of models it is seen that the axial direction is the less hindered when this distance is less than 1.8–2.0 Å and the equatorial direction is the less hindered when this distance is greater than 1.8–2.0 Å. Variation in stereoselectivity is seen as a consequence of the variation of the nucleophile–substrate distance in the transition state. Certainly this is a factor to consider but the results of our study cannot be adequately explained on this basis. Since there is no correlation whatever between the reactivity of the silane and the *trans/cis* ratio it is not correct to say that this ratio is a function of the Si–H–C distance in the transition state. Some factor other than the closeness of approach of the reagent must be used to

(18) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 92.

(19) This order is in accord with quantitative measures of reaction rates made by Miss Chia-lin Wang which will be reported in due course.

(20) In this regard we have conducted some preliminary work on the reduction of the 2-phenyl-2-norbornyl cation which indicate highly stereoselective (*exo* attack) hydride transfer. Details will be reported when this work is complete.

(21) H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 1473 (1966).

(22) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **84**, 3296 (1962).

(23) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

(24) (a) J-C. Richer, *J. Org. Chem*, **30**, 324 (1965); (b) J. A. Marshall and R. D. Carroll, *ibid.*, **30**, 2748 (1965); (c) R. G. Carlson and N. S. Behn, *ibid.*, **32**, 1363 (1967).

explain the observed distribution of products. For the lack of reasonable alternatives we are content to ascribe the dominance of **18** over **17** to product development control.[25]

As previously noted the order of reactivity of the various silanes does not coincide with the observations of West. Our observed order of reactivity does coincide with that reported by Sommer and Lloyd[26] for the bromination and chlorination of silanes.

$$R_3SiH + X_2 \longrightarrow R_3SiX + HX$$

$$X = Br, Cl$$
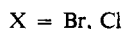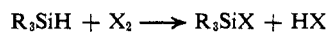
For these reactions which, like the carbonium ion hydride transfer, are an electrophilic attack on the Si–H bond the relative reactivities have been found to be $alkyl_3SiH > aryl_3SiH > aryl_2SiH_2$. The value of ρ^* is -4.2 for both chlorination and bromination, i.e., silicon becomes more positively charged in the transition state. We are currently conducting a kinetic study of carbonium ion–silane hydride transfers with a variety of silanes to clarify this point.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are corrected. Infrared spectra were obtained on a Perkin-Elmer 337 grating spectrophotometer either as KBr disks or as 5% solutions in CCl_4 or $CHCl_3$ and calibrated against the 1601- and 1028-cm^{-1} bands of polystyrene. All nmr spectra were measured on ca. 20% solutions in $CDCl_3$ containing tetramethylsilane as an internal standard using a Varian A-60 spectrometer. The glpc units used were a MicroTek hydrogen flame instrument and a Varian Aerograph 90-P thermal conductivity instrument. Areas were determined by planimeter integration. Microanalyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Mulheim, or Galbraith Laboratories, Inc.

All of the silanes used in the study are commercially available from the Pierce Chemical Company, Rockford, Ill., except for phenylsilane. This compound was prepared by lithium aluminum hydride reduction of phenyltrichlorosilane obtained from Pierce. Trifluoroacetic acid was Eastman White Label grade used without further purification.

Reduction of 2,6,2′,6′,2′′,6′′-Hexamethoxytriphenylmethyl Cation (1). Method A. To 3.0 ml of acetic acid was added 440 mg of 2,6,2′,6′,2′′,6′′-hexamethoxytriphenylmethanol[1] (1 mmol). A deep purple color formed immediately. After standing 24 hr at 25°, 0.5 ml of triethylsilane was added, and the purple color was observed to be discharged within 1 min. Water (40 ml) was added and the solution filtered to yield 400 mg (95%) of a white precipitate, mp 185.5–187°, which was recrystallized from ethanol to give the analytical sample, mp 186–187°.

Anal. Calcd for $C_{25}H_{28}O_6$: C, 70.74; H, 6.65. Found: C, 70.62; H, 6.61.

The nmr spectrum showed a singlet at τ 6.62 (methoxyl protons) and the aromatic protons as the expected AB_2 multiplet from τ 2.8 to 3.6. Within this multiplet was an extra peak at τ 3.52 assigned to the benzylic proton. The integral ratio of the methoxyl proton signal to that of the protons in the low-field region was 18:10. Strong absorptions were found in the infrared spectrum at 1580, 1460, 1250, and 1105 cm^{-1} (KBr disk).

Method B. Trifluoroacetic acid (0.2 ml) was added to a solution of 440 mg (1 mmol) of 2,6,2′,6′,2′′,6′′-hexamethoxytriphenylmethanol in 7 ml of methylene chloride containing 0.5 ml of triethylsilane. A deep purple color formed immediately which disappeared within 5 min. The solution was then neutralized with solid potassium carbonate, filtered, and evaporated to leave a white solid

which was washed with hexane to give 230 mg (80%) of 2,6,2′,6′-tetramethoxydiphenylmethane (11), mp 135–138.5°.

The analytical sample was recrystallized from 95% ethanol, mp 138.5–139°.

Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 71.01; H, 6.98.

The nmr spectrum exhibited singlets at τ 6.38 (methoxyl) and 6.0 (benzylic methylene) and the AB_2 multiplet of aromatic protons at τ 2.8–3.7. The integral ratios were 12:2:6, respectively. The infrared spectrum of **11** had strong absorptions at 1590, 1470, 1250, and 1110 cm^{-1} (CCl_4).

The same product was obtained in 89% yield when the reduction was carried out by addition of triethylsilane to a solution of **1** in methylene chloride–trifluoroacetic acid which had stood for 40 hr at 25°.

Reaction of 2,6,2′,6′,2′′,6′′-Hexamethoxytriphenylmethane (9) with Triethylsilane in Trifluoroacetic Acid–Methylene Chloride. To a solution of 200 mg of **9** (0.47 mmol) in 3.0 ml of methylene chloride was added 0.2 ml of triethylsilane and 0.1 ml of trifluoroacetic acid. A red solution formed. After 5 min, the solution was diluted with 10 ml of methylene chloride, neutralized with solid potassium carbonate, filtered, and evaporated. The residue was recrystallized from 95% ethanol to give 135 mg (78%) of **11**, mp 138.5–139.5°. Analysis of the solution before evaporation by glpc (5-ft 20% SE-30 on Chromosorb P column at 150° and 40 cc of helium/min) confirmed the presence of m-dimethoxybenzene formed in the fragmentation step.

Reduction of 1,2,3-Triphenylcyclopropenyl Cation (2). A solution of triphenylcyclopropenyl t-butyl ether[27] (500 mg, 1.45 mmol) in 3.0 ml of acetic acid containing 0.5 ml of triethylsilane was stirred at 25° for 20 hr. Water (20 ml) was added and the solution extracted twice with 15-ml portions of methylene chloride. The organic layers were washed with two 20-ml portions of saturated sodium bicarbonate solution, dried over potassium carbonate, and evaporated to leave a partially crystalline syrup. Recrystallization from aqueous ethanol afforded 290 mg (80%) of white crystalline product, mp 100–105°, identified as 1,2,3-triphenylcyclopropene by comparison of its ir and nmr spectra with those reported.[28] A further recrystallization from ethanol gave material of mp 109–110° (lit.[28] 112–113°).

Reduction of 9-Phenylxanthyl Cation (4). A. A solution of 274 mg (1 mmol) of 9-phenylxanthydrol[29] in 3.0 ml of acetic acid containing 0.5 ml of triethylsilane was stirred for 48 hr at 25°, then quenched by adding 40 ml of water. The product was filtered and recrystallized from 95% ethanol to yield 197.5 mg (77%) of (9-phenylxanthene, mp 142.5–144.5° (lit.[30] 145°).

B. To 274 mg (1 mmol) of 9-phenylxanthydrol and 260 mg (1 mmol) of triphenylsilane in 5.0 ml of methylene chloride was added 228 mg (2 mmol) of trifluoroacetic acid in 2.0 ml of methylene chloride. After 48 hr, solid sodium carbonate was added, the solution filtered through a short column of 10 g of basic alumina, and the column washed with 100 ml of methylene chloride. Evaporation afforded 260 mg of crude product which was recrystallized from ethanol to give 207 mg (80%) of 9-phenylxanthene, mp 142–144°.

On eluting the column with ether 256 mg of crude triphenylsilanol (93%) was obtained, mp 137–148°. Recrystallization from hexane raised the melting point to 152–153°.

The nmr spectrum of the reduction product confirmed its structure as 9-phenylxanthene: singlet at τ 4.8 (benzylic, 1 proton), aromatic multiplet at τ 2.9 (13.8 protons).

Reduction of Diphenylmethyl Cation (7). Trifluoroacetic acid (2.0 ml) was added to a solution of 1.68 g (10 mmol) of benzhydrol and 2.60 g (10 mmol) of triphenylsilane in 25 ml of methylene chloride. After 2 hr, potassium carbonate was added and the solution analyzed by glpc (5-ft 20% Carbowax 20M on Firebrick at 200°). The only volatile product was diphenylmethane identified by comparison of its retention time with authentic material.

Reduction of Mesityl Cation (8). To a solution of 100 mg (0.67 mmol) of 2,4,6-trimethylbenzyl alcohol[31] and 0.2 ml of triethylsilane in 3.0 ml of methylene chloride was added 0.2 ml of trifluoroacetic acid. After 20 min, solid sodium carbonate was added and the reaction mixture analyzed by glpc (5-ft 20% SE-30 on Chromosorb

(25) The possibility that torsional effects operate to determine product distribution is an open question. A Dreiding model of the carbonium ion has the phenyl group eclipsed with the 2,6-equatorial hydrogens. Movement of the phenyl group either in the axial or equatorial sense will diminish this interaction.

(26) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, p 107; N. C. Lloyd, Ph.D. Thesis, The Pennsylvania State University, 1962.

(27) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1967).

(28) R. Breslow and P. Dowd, *ibid.*, **85**, 2729 (1963).

(29) M. Gomberg and L. H. Cone, *Ann.*, **370**, 142 (1909).

(30) F. Ullman and G. Engi, *Ber.*, **37**, 2367 (1904).

(31) M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3645 (1951).

P column at 150°, 40 cc of helium/min). Two peaks other than those of silane-derived products appeared having retention times of 4.2 and 7.4 min in relative amounts of 79 and 21%, respectively. The major component was identified as isodurene (1,2,3,5-tetramethylbenzene) by comparison with pure material purchased from Aldrich. The yield of isodurene was determined to be 67.6 mg (75%) by addition of 74.1 mg of tetralin to the product and analysis by glpc. Analysis of a known mixture of tetralin and isodurene verified that their molar responses to the thermal conductivity detector were the same.

A similar experiment in which the reaction time was extended to 1.5 hr showed isodurene with only trace amounts of the higher boiling component. The analytical yield was 89%.

The minor component was shown to be mesityl trifluoroacetate by independent synthesis and comparison of retention times.

Mesityl alcohol (36 mg, retention time 9.5 min) was dissolved in 1.0 ml of methylene chloride, and 0.1 ml of trifluoroacetic acid was added. After 20 min the reaction mixture was quenched with sodium carbonate and analyzed by glpc. A single peak with retention time 7.1 min was observed. The solution was filtered and evaporated to leave 43 mg of a clear syrup exhibiting trifluoroacetate ester carbonyl absorption in the ir at 1780 cm⁻¹ and C–O absorption at 1142 cm⁻¹. The nmr spectrum was consistent with the structure showing four singlets at τ 7.70, 7.63 (nine protons), 4.56 (two protons), and 3.09 (two protons).

When the reduction of mesityl alcohol with triphenylsilane was carried out on a 10-mmol scale and the crude product purified by evaporative distillation 556 mg (41%) of isodurene was obtained which was further identified by its ir and nmr spectra. Both the crude and purified materials were void of absorbance in the 1700-cm⁻¹ region which, if present, would be indicative of 2,4,6-trimethylbenzaldehyde formed by disproportionation.

Reduction of cis- and trans-4-t-Butyl-1-phenylcyclohexanols (15 and 16). cis-4-t-Butyl-1-phenylcyclohexanol (15), trans-4-t-butyl-1-phenylcyclohexanol (16), cis-4-t-butyl-1-phenylcyclohexane (17), trans-4-t-butyl-1-phenylcyclohexane (18), and 4-t-butyl-1-phenylcyclohexane (19) were prepared by the methods described by Garbisch and Patterson.[32] A solution of 15 or 19 (0.93 mmol) in 4.0 ml of methylene chloride plus 1.2 mmol of the appropriate silane

(32) (a) E. W. Garbisch, Jr., J. Org. Chem., 26, 4165 (1961); (b) E. W. Garbisch, Jr., and D. B. Patterson, J. Am. Chem. Soc., 85, 3228 (1963).

was treated with 228 mg (2 mol) of trifluoroacetic acid and allowed to stand at 25° for 0.5 hr. Solid potassium carbonate was added and the reaction mixture analyzed by gas chromatography using a 10-ft 15% Carbowax 20M on Chromosorb P column at 190°. Peaks were identified by comparing retention times with those of the standards and areas determined by planimeter integration. Response ratios were taken as unity since Garbisch had previously shown no significant deviations from unity for a wide variety of similar compounds.[33]

In an experiment designed to test the possibility that the products were derived from initial elimination to the olefin followed by protonation of the olefin to the carbonium ion, 19 was subjected to the same reaction conditions and found to be less than 10% converted to 17 and 18.

Attempted Reduction of Benzyl Alcohol. To a solution of 87.3 mg of benzyl alcohol (0.80 mmol) and 148 mg (0.57 mmol) of triphenylsilane in 0.5 ml of deuteriochloroform in an nmr tube was added ten drops of trifluoroacetic acid. After 19 hr at 25°, there was no diminution of the Si–H resonance at τ 4.5 and no formation of toluene. Similar results were obtained with cinnamyl alcohol.

Attempted Reduction of Sesquixanthydryl Cation (14). Sesquixanthydrol[10] (302 mg, 1 mmol) was dissolved in 7.0 ml of methylene chloride and 0.50 ml of triethylsilane, and 0.20 ml of trifluoroacetic acid was added. An orange solution resulted which did not lighten over the course of 24 hr. Potassium carbonate was added and the solution filtered and evaporated to leave 333 mg of orange solid, mp 205–215° dec. This material resisted purification. Sesquixanthene is reported as a white solid, mp 280–300° dec.[10]

In acetic acid containing triethylsilane again the orange color of cation 14 was not discharged.

(33) E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, ibid., 87, 2932 (1965).

Stable Carbonium Ions. LXI.[1] Methylfluorobenzenonium Ions

Geroge A. Olah and Thomas E. Kiovsky[2]

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received October 30, 1967

Abstract: Protonation of fluorotoluenes and fluoromesitylenes in fluorosulfonic acid–antimony pentafluoride solution gives stable methylfluorobenzenonium ions (methylfluorohexadienyl cations). ¹H and ¹⁹F nmr spectra of these ions were obtained and structures assigned. It was found that a fluorine atom takes preference over a methyl group in directing the position of protonation.

As an extension of our previous work on fluorobenzenonium ions[3] we have studied methyl-substituted fluorocyclohexadienyl cations (methylfluorobenzenonium ions). Nuclear magnetic resonance investigations were expected to yield information about the structure as well as further information about nmr coupling constants in these new fluorocarbonium ions.

(1) Part LX: G. A. Olah and M. Calin, J. Am. Chem. Soc., 90, 405 (1968).
(2) Postdoctoral research investigator, 1967.
(3) G. A. Olah and T. E. Kiovsky, J. Am. Chem. Soc., 89, 5692 (1967).

Results and Discussion

Mono-, di-, tri-, and tetrafluorotoluenes as well as mono-, di-, and trifluoromesitylenes were protonated in the extremely strong acid system FSO₃H–SbF₅. All the ions could be observed in neat fluorosulfonic

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