Study of the Progress of the Reaction at 5°C. 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acid and 98% sulfuric acid (exactly 1:1, 20 ml, 32.6 g) maintained at 5°C. At intervals 1-ml portions were withdrawn, quenched with ice, and extracted with 200 μl of a solution of hexamethylbenzene in chloro-form (5.343 mg/ml).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°C); 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. Tamper

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''-Hexamethoxytriphenylmethane (9) was formed in 95% yield from the alcohol and triethylsilane in acetic acid but fragmented to m-di-methoxybenzene and 1,2,6,2',6',2''-tetramethoxydiphenylmethyl cation in methylene chloride–trifluoroacetic acid. Reduction of either cis- (15) or trans-4-t-buty1-1-phenylcyclohexanol (16) afforded mixtures of cis- and trans-4-t-buty1-1-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

(CH₃)₃SiH + (CH₃)₃C⁺ → (CH₃)₃Si⁺ + (CH₃)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 ionizing solvents has been studied and a mechanism proposed involving a four-center transition state between the carbonium chloride ion pair and the silane.²

R₃CCl + R₃SiH → R₃C⁺...HCl⁻...SiR₃ → R₃CH + R₃SiCl
R = Ph

Consistent with this description is the report that the reaction proceeds with complete retention of configuration at asymmetric silicon.³

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.⁴ 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 ¹⁸O 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-buty1 and derived cations is significant.⁵

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

(3) J. Y. Corey and R. West, ibid., 85, 2430 (1963).
Table I. Silane Reductions of Carbonium Ions

<table>
<thead>
<tr>
<th>Cation</th>
<th>pH</th>
<th>Conditions</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6',2&quot;,6&quot;,6'-Hexamethyl-oxytriphenylmethyl (1)</td>
<td>&gt;6.5</td>
<td>A-triethylsilane</td>
<td>95</td>
</tr>
<tr>
<td>Triphenylcyclopropenyl (2)</td>
<td>3.18</td>
<td>A-triethylsilane</td>
<td>80</td>
</tr>
<tr>
<td>9-p-Anisyloxanthyl (3)</td>
<td>1.55</td>
<td>A-triethylsilane</td>
<td>68</td>
</tr>
<tr>
<td>9-Phenylxanthyl (4)</td>
<td>1.1</td>
<td>A-triethylsilane</td>
<td>77</td>
</tr>
<tr>
<td>Triphenylmethyl (5)</td>
<td>0.82</td>
<td>A-triethylsilane</td>
<td>87</td>
</tr>
<tr>
<td>Triphenylmethanol (7)</td>
<td>-6.63</td>
<td>A-triethylsilane</td>
<td>0</td>
</tr>
<tr>
<td>2,4,6-Trimethylbenzyl (8)</td>
<td>-13.3</td>
<td>B-triethylsilane</td>
<td>70</td>
</tr>
<tr>
<td>2,6,2',6',2&quot;,6&quot;'-hexamethoxytriphenylmethane (9)</td>
<td>-17.4</td>
<td>B-triethylsilane</td>
<td>41</td>
</tr>
<tr>
<td>2,6',2&quot;,6&quot;,6'-hexamethoxytriphenylmethane (9)</td>
<td>-17.4</td>
<td>B-triethylsilane</td>
<td>41</td>
</tr>
</tbody>
</table>

*Conditions: A, pure acetic acid; B, methylene chloride containing 2 equiv of trifluoroacetic acid. Of the corresponding alkane. * Cited in ref 10.

(8) The values listed in Table I for 1 and 2 are pK<sub>R+</sub> values rather than pK<sub>R</sub> since they were calculated using pH as the acidity function rather than H<sub>R</sub>. For relatively stable ions such as these pK<sub>R+</sub> is more positive than pK<sub>R</sub>.


2,6',2",6",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. 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 AB<sub>2</sub> aromatic multiplet and singlets at 6 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, (3) the substantial relief of steric compression upon fragmentation. Recently the related fragmentation of the coumarane 12 to

(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<sub>R+</sub> 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",6'-hexamethoxytriphenylmethane under basic conditions (unpublished studies of J. C. Martin and R. K. Howe cited in ref 10).


1,3,5-trimethoxybenzene and 13 has been reported to proceed readily. 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).

\[
\text{Me} - \begin{align*}
\text{Me} & \quad \text{CH}_3^+ \\
\end{align*}
\]

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. This latter fact is also in accord with carbonium ions being the only intermediates capable of abstracting hydride from silanes.

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 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. 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 silanes. From either 15 or 16 the product mixture was composed of cis-4-t-butyl-1-phenylcyclohexane (17), trans-4-t-butyl-1-phenylcyclohexane (18), and 4-t-butyl-1-phenylcyclohexene (19). The results of this study are summarized in Table II.

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

*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.*

![Diagram](https://via.placeholder.com/150)

Table II. Reduction of 4-t-Butyl-1-phenylcyclohexanol

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, 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 > triocetyl ~ diethyl > diphenyl > triphenyl > phenyl.\textsuperscript{19} This is contrary to the order found by West who reported trietyl halides to be more readily reduced by triphenylsilane than by triethylsilane.\textsuperscript{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.\textsuperscript{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.\textsuperscript{21}

Their technique utilizes a charged nucleophile (BH\textsubscript{3}) 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.\textsuperscript{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 compression; 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 the 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\textsubscript{1} and the axial hydrogens in each.

When R\textsubscript{1} is hydrogen these steric repulsions will be a minimum and product development control becomes more important (higher trans/cis ratio). When R\textsubscript{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\textsubscript{2} or R\textsubscript{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.\textsuperscript{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.\textsuperscript{24} In these reactions it is claimed that the important factor is the distance between the reacting 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


\textsuperscript{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.

\textsuperscript{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.


\textsuperscript{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, 1263 (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 Lloyd26 for the bromination and chlorination of silanes.

\[
\text{R}_{3} \text{SiH} + \text{X} \rightarrow \text{R}_{3} \text{SiX} + \text{HX}
\]

\[X = \text{Br, Cl} \]

For these reactions which, like the carboxonium ion hydride transfer, are an electrophilic attack on the Si-H bond the relative reactivities have been found to be alkylSiH > arylSiH > arylalkylSiH. The value of \( \rho \) 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 carboxonium-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 CCl₄ or CHCl₃ and calibrated against the 1601- and 1028-cm⁻¹ bands of polystyrene. All nmr spectra were measured on ca. 20% solutions in CDC₁₃ containing tetramethylsilane as an internal standard using a Varian A-60 spectrometer. The glpc units used were a MicroTek hydrogen flame ionization 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''-Hexamethoxytriphenylsilyl Cat ion (1). Method A. To 3.0 ml of acetic acid was added 440 mg of 2,6,2',6',2'',6''-hexamethoxytriphenylmethanol (1 mmol). A deep purple color formed immediately. After standing 24 hr at 25°C, 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°C, which was recrystallized from ethanol to give the analytical sample, mp 186-187°C.


The nmr spectrum showed a singlet at \( \tau = 6.62 \) (methylxyl protons) and a broad aromatic multiplet at \( \tau = 2.9 \) to 3.6. Within this multiplet was an extra peak at \( \tau = 3.52 \) assigned to the benzyl proton. The integral ratio of the methoxy 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 200 mg (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 mp 138.5-139.5°C. Analysis of the solution before evaporation by glpc (5-ft 20% SE-30 on Chromosorb P column at 150°C) and 40 cc of helium/min confirmed the presence of \( m \)-dimethoxybenzene formed in the fragmentation step.

Reduction of 1,2,3-Trimethylcyclopropenyl Cation (2). A solution of trimethylcyclopropenyl-4-butyne15 (500 mg, 1.43 mmol) in 10 ml of acetic acid containing 0.5 ml of triethylsilane was stirred at 25°C 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°C, identified as 1,2,3-trimethylcyclopropene by comparison of its ir and nmr spectra with those reported.16 A further recrystallization from ethanol gave material of mp 109-110°C.

Reduction of 9-Phenylxanthylene Cation (3). A. A solution of 274 mg (1 mmol) of 9-phenylxanthydrate17 in 3.0 ml of acetic acid containing 0.5 ml of triethylsilane was stirred for 48 hr at 25°C, 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°C (lit.18 145°C).

B. To 274 mg (1 mmol) of 9-phenylxanthydrol and 260 mg (1 mmol) of triphenylsilanol 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 columns 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°C. On eluting the column with ether 256 mg of crude triphenylsilanol (93%) was obtained, mp 137-148°C. Recrystallization from hexane raised the melting point to 152-153°C. The nmr spectrum of the reduction product confirmed its structure as 9-phenylxanthene: singlet at \( \tau = 4.8 \) (benzyl, 1 proton), aromatic multiplet at \( \tau = 2.9 \) (13.8 protons).

Reduction of Diphenylmethyl Cation (6). Trifluoroacetic acid (2.0 ml) was added to a solution of 1.68 g (10 mmol) of benzyltrimethylsilane in 30 ml of methylene chloride in 20 ml of methylene chloride. After 2 hr, potassium carbonate was added and the solution analyzed by glpc (5-ft 20% Carbosax 20M on Firebrick at 200°C). 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 alcohol19 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 carboneum ion has the phenyl group eclipsed with the 2,6-equatorial hydrogens. Movement of the phenyl group either in the axial or equatorial position does an electrophilic attack on the Si-H bond. Strong absorptions were found at 1580, 1460, 1250, and 1105 cm⁻¹ (KBr disk).

of 4.2 and 7.4 min in relative amounts of 79 and 21%.

The major component was identified as isodurene (1,2,3,5-tetra-
(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 boil-
ing 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 so-
dium carbonate and analyzed by glpc. A single peak with retention
time 7.1 min was observed. The solution was filtered and evap-
orated 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 \(\tau\) 7.70, 7.63 (nine protons), 4.56 (two
protons), and 3.09 (two protons).

When the reduction of mesityl alcohol with triphenylsilane was
carry out on a 10-mmol scale and the crude product purified by
evaporative distillation 556 mg (41%)

Reduction of cis- and trans-4-buty1-1-phenylcyclohexanols (15
and 16). cis-4-buty1-1-phenylcyclohexanol (15), trans-4-buty1-
1-phenylcyclohexanol (16), cis-4-buty1-1-phenylcyclohexane (17),
trans-4-buty1-1-phenylcyclohexane (18), and 4-buty1-1-phenylcyclo-
hexane (19) were prepared by the methods described by Garbisch and Patterson.\(^{13}\) A solution of 15 or 19 (0.93 mmol) in
4.0 ml of methylene chloride plus 1.2 mmol of the appropriate silane
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. Re-
response ratios were taken as unity since Garbisch had previously
shown no significant deviations from unity for a wide variety of
similar compounds.\(^{14}\)

In an experiment designed to test the possibility that the products
were derived from initial elimination to the olefin followed by pro-
tonation 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 deuterochloroform 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 \(\tau\) 4.5 and no for-
tmation of toluene. Similar results were obtained with cinnamyl
alcohol.

Attempted Reduction of Sesquixanthydryl Cation (14). Ses-
quixanthydrolyclic\(^{14}\) (302 mg, 1 mmol) was dissolved in 7.0 ml of methyl-
ene chloride and 0.50 ml of triethylsilane, and 0.20 ml of trifluoro-
acetic 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. Ses-
quixanthene is reported as a white solid, mp 280–300° dec.\(^{15}\)

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

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Stable Carbonium Ions. LXI.\(^{1}\) Methylfluorobenzononium Ions

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Abstract: Protonation of fluorotoluenes and fluoromesitylenes in fluorosulfonic acid–antimony pentfluoride
solution gives stable methylfluorobenzonium ions (methylfluorohexadienyl cations). \(^1\)H and \(^19\)F 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 fluoro-
benzonium ions\(^1\) we have studied methyl-sub-
stituted fluorocyclohexadienyl cations (methylfluoro-
benzonium ions). Nuclear magnetic resonance in-
vestigations were expected to yield information about the
structure as well as further information about nmr cou-
pling constants in these new fluorocarbonium ions.

Results and Discussion

Mono-, di-, tri-, and tetrafluorotoluenes as well as mono-, di-,
and trifluoromesitylenes were protonated in the extremely strong acid system FSO\(_3\)H–SbF\(_5\).
All the ions could be observed in neat fluorosulfonic

\[ \text{HSO}_3\text{F}–\text{SbF}_5 \]

\[ \text{C}_6\text{H}_5\text{F} \]

\[ \text{CH}_3 \]

\[ \text{F} \]

\[ \text{H} \]

\[ \text{H} \]

\[ \text{CH}_3 \]

\[ \text{F} \]

\[ \text{CH}_3 \]

\[ \text{F} \]

\[ \text{I} \]

\[ \text{F} \]