Silicon–Fluorine Chemistry. IV. The Reaction of Silicon Difluoride with Aromatic Compounds

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Abstract: A study has been made of the reactions of silicon difluoride with some fluorinated and nonfluorinated aromatic compounds at low temperatures. Perfluorobenzene gives the substitution products $C_6F_5SiF_3$ and $C_6F_4(SiF_3)_2$. Benzene and toluene give a group of compounds of type $ArH(SiF_2)_n$, where $n = 2$ to 8. The compounds $C_6H_6Si_3F_6$ and $C_6H_5CH_3Si_3F_6$ are 1,4-cyclohexadiene derivatives with $-SiF_2-SiF_2-SiF_2-$ bridges across the 3,6-positions. These reactions of silicon difluoride have been contrasted with those of carbenes.

Many examples are known of the reactions of carbenes with unsaturated and aromatic compounds generating three-membered rings or causing substitution or ring enlargement.[1] Such reactivity toward unsaturated systems is not confined to true carbenes as some divalent silicon and germanium compounds also will add to multiple bonds.[2,3] The products, are however, more complex than with the carbenes, and in many cases they have not been well characterized.

The purpose of this study has been to explore the reactions of silicon difluoride, an apparently "carbene-like" molecule, with both fluorinated and nonfluorinated aromatic compounds, and to find in what ways these reactions differ from those of the carbenes. It has already been reported[4] that silicon difluoride shows little reactivity in the gas phase; hence all reactions of the compound with aromatics have been carried out at low temperatures in the condensed phase.

Experimental Section

Silicon difluoride was prepared as described elsewhere[4] from silicon and silicon tetrafluoride at a rate of 5–20 g/hr. The aromatic compounds were vaporized into the stream of silicon difluoride emerging from the furnace at the rate of 1–5 ml of liquid per hour. The mixture of silicon difluoride and aromatic compound was pumped through a trap cooled by liquid nitrogen. The pressure in the system between the furnace and the trap was maintained below 0.2 mm. Higher pressures caused heavy deposits of scaly polymers to build up on the walls of the system with resulting loss of product and also of pumping efficiency.

The condensates were dark brown or red colored at low temperatures, but they became plastic yellow solids on warming to above about −50°. At least 70% of the added aromatic compound could be recovered unchanged by pumping on the solid at room temperature. The best conversion of the aromatics to new compounds was obtained if great care was taken to condense the silicon difluoride and the aromatic at identical levels in the trap. In some cases volatile silicon-containing products could be pumped out of the solid polymers at room temperature in addition to the excess aromatic compound, but generally it was necessary to heat the polymer to 100–140° to liberate appreciable amounts of volatiles.

Purification of the compounds distilled out of the polymers was achieved by a combination of conventional vacuum techniques and gas chromatography. Short columns packed with 25% Kel-F 10 on silicone-treated Chromosorb W were found most satisfactory for both the high-boiling benzene and toluene reaction products and the much more volatile perfluorobenzene products.

Initial analysis of products was carried out using a Bendix time-of-flight mass spectrometer. The reaction products of aromatics and silicon difluoride were found to give well-defined parent ions, facilitating interpretation.

Infrared spectra were taken on a Beckmann IR-9 instrument, ultraviolet spectra on a Bausch and Lomb Spectronic 505 spectrophotometer, and proton and fluorine nmr spectra on Varian A-60 and HR-60 machines, respectively.

Perfluorobenzene and Silicon Difluoride. Cocondensation of silicon difluoride and perfluorobenzene at −196° gave a brown solid. Intermittent blue light flashes were observed during condensation and when the condensate was subsequently allowed to warm to about −150°. Distillation of the final yellow-brown polymer at +120° gave a colorless liquid which was separated into three main fractions.

The lowest-boiling fraction, after gas chromatographic separation, was found to be the compound $C_6H_5SiF_3$. The molecular formula was established from its mass spectrum, which was analogous to that of perfluorotoluene.[5] At low electron voltages large ion peaks were observed at *m/e* 186 and 252, corresponding to $C_6F_6^+$ and $C_6F_8Si^+$, the parent ion, respectively. The infrared spectrum contained the strong ring vibration and C–F stretch at 1491 and 1000 cm^{-1}, respectively, typical of the perfluorophenyl group (see Table I). The fluorine nmr spectrum showed four resonances (Table I) which could be assigned on the basis of position and area to the *ortho*, *meta*, *para*, and SiF_3 fluorine atoms, respectively.

Table I. Infrared and Fluorine Nmr Spectra of $C_6F_5SiF_3$

Infrared Spectrum

Wave number, cm^{-1} (intensity): 448 (m), 481 (w), 520 (m), 737 (m), 816 (s), 913 (s), 987 (s), 1001 (vs), 1112 (vs), 1270 (w), 1317 (m), 1407 (w), 1490 (vs), 1655 (m)

Fluorine Nmr Spectrum[a]

Shift	Description	Assignment	Coupling constants, Hz
125.3	Complex multiplet	*o*-F atoms	. . .
134.8	Triplet	SiF_3-F atoms	$J_{o\text{-}SiF_3}$ 10.3
143.8	Triplet of triplets	*p*-F atom	J_{m-p} 17.7 J_{o-p} 6.6 $J_{SiF_3\text{-}p}$ 250
159.8	Complex multiplet	*m*-F atoms	. . .

[a] Reference, $CCl_3F = 0$ ppm.

Perfluorophenyltrifluorosilane boils at 105°. It is thermally stable to at least 300°, but it is readily hydrolyzed by trace amounts of water to polymeric materials. Dilute hydrofluoric acid converts it almost quantitatively to pentafluorobenzene, which is additional evidence for its structure.

The next fraction in the distillation of the C_6F_6–SiF_2 reaction product was shown by mass spectrometry, nmr spectroscopy, and

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(1) See, for example, E. Chinoporos, *Chem. Rev.*, **63**, 239 (1963).

(2) F. Johnson, R. S. Gohlke, and W. A. Nasutavicus, *J. Organometal. Chem.* (Amsterdam), **3**, 233 (1965).

(3) D. C. Pease, U. S. Patent 2,840,588, assigned to the Du Pont Co., Wilmington, Del., June 24, 1958.

(4) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Am. Chem. Soc.*, **87**, 2824 (1965).

(5) J. R. Majer, *Advan. Fluorine Chem.*, **2**, 255 (1961).

by hydrolysis with hydrofluoric acid to be mainly a mixture of the three position isomers of $C_6H_4(SiF_3)_2$, the *ortho*:*para*:*meta* ratio being roughly 1:6:9. The mass spectrum showed principal ions at *m/e* 186 ($C_6F_6^+$) and 318 ($C_6F_{10}Si_2$) while the fluorine nmr spectrum showed a very strong multiplet at 135 ppm (due to SiF_3 groups) plus several weaker multiplets mostly in the region of the resonances in $C_6F_5SiF_3$. Hydrolysis with 10% HF gave a little C_6F_5H (probably from small amounts of $C_6F_5SiF_3$ or possibly $C_6F_5Si_2F_5$), together with *o*-, *m*-, and *p*-$C_6F_4H_2$ and traces of *sym*-$C_6F_3H_3$. Conversion to these compounds seemed almost quantitative. Thus the relative amounts of the different $C_6F_4(SiF_3)_2$ isomers in the initial product were estimated from the relative peak area ratios of the tetrafluorobenzenes when these were separated by gas chromatography, using a thermal conductivity detector. Attempts to separate the isomers of $C_6F_4(SiF_3)_2$ directly by gas chromatography were unsuccessful because the compounds so readily decomposed on the column or on the surface of the glass or metal handling systems that were used.

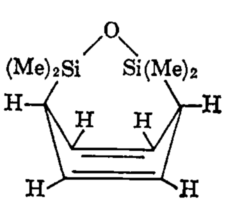
The least volatile fraction was shown mass spectrometrically to contain compounds of molecular formula $C_6F_{12}Si_3$ and $C_6F_{14}Si_4$. The evolution of hydrogen on hydrolysis with 10% HF suggested the presence of Si–Si bonds, so the fraction was probably a mixture of poly-SiF_3-substituted perfluorobenzenes and related compounds containing Si_2F_5 and perhaps Si_3F_7 side chains.

Over-all, about 60% of the perfluorobenzene that underwent reaction with the silicon difluoride was recovered as volatile perfluorobenzene derivatives. Nothing is known of the way in which remaining 40% was bound into the SiF_2–C_6F_6 polymer.

Benzene and Silicon Difluoride. A brown polymer was formed when benzene and silicon difluoride were cocondensed at −196°, but no light was emitted. On warming the product to room temperature, a bright yellow, sticky, polymer was obtained which liberated excess benzene, appreciable amounts of perfluorotetrasilane, and trace amounts of a crystalline compound with molecular formula $C_6H_6Si_2F_4$. Distillation of the polymer at 140° under vacuum gave a mixture of white or yellow liquids and solids.

Mass spectrometric studies of this distillate showed it contained a series of compounds of type $C_6H_6(SiF_2)_n$ where $n = 2$ to at least 8. The spectrum contained only ions of *m/e* values corresponding to $C_6H_6^+$ and $C_6H_6(SiF_2)_n^+$ at very low electron voltages. By far the most abundant compound in the series was $C_6H_6Si_3F_6$. This was obtained as colorless crystals melting at 72.5° by separating it from its homologs on a short gas-chromatographic column. About 20% of the benzene which reacted with the silicon difluoride was recovered as this product. The empirical formula for $C_6H_6Si_3F_6$ was confirmed by elemental analysis. *Anal.* Calcd: C, 26.1; F, 41.3; Si, 30.5; H, 2.19. Found: C, 26.30; F, 41.45; Si, 30.77; H, 2.40.

Hydrolysis of $C_6H_6Si_3F_6$ with 2 *N* KOH or dilute hydrofluoric acid gives very high yields of 1,4-cyclohexadiene. Both its infrared and ultraviolet spectra show conclusively that $C_6H_6Si_3F_6$ does not contain a conjugated carbon–carbon double-bond system. The infrared spectrum is dominated by the very strong Si–F stretch absorptions from 800 to 1000 cm^{-1}. The proton nmr spectrum is closely comparable with that observed by Weyenberg[6] for the compound 2,2,4,4-tetramethyl-3-oxa-2,4-disilabicyclo[3.2.2]nona-6,8-diene[7] (I). Two resonances are observed, a triplet at 2.15 ppm and a broad singlet at 4.74 ppm on the high-field side of the solvent benzene. Their area ratio is very close to 2:1, as required by II. Similarly the fluorine nmr spectrum shows two main resonances at 130 and 134 ppm on the high-field side of CCl_3F with an area ratio of nearly 2:1. All of these facts lead one to postulate a silicon bridge as in II, and thus the compound $C_6H_6(SiF_2)_3$ is more clearly described by the name 2,2,3,3,4,4-hexafluoro-2,3,4-trisilabicyclo-[3.2.2]nona-6,8-diene.



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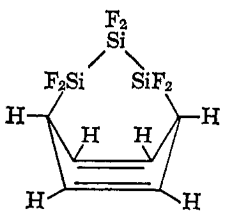
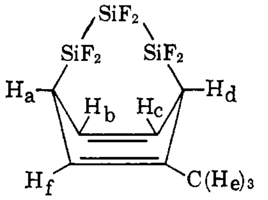


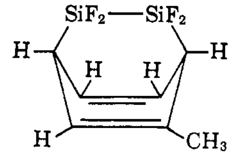
II

Little is yet known about the structure of other compounds in the $C_6H_6(SiF_2)_n$ series. Hydrolysis of $C_6H_6Si_2F_4$ gives 1,4-cyclohexadiene, while hydrolysis of a mixture of all the homologs gives mainly 1,4-cyclohexadiene with some cyclohexene (perhaps formed by hydrogen or silane reduction of a carbon–carbon double bond) together with a trace of 1,3-cyclohexadiene. The last suggests that some 1,2-addition may also have occurred.

Toluene and Silicon Difluoride. The reaction of toluene with silicon difluoride is closely comparable to the benzene reaction. A range of products of type $C_6H_5CH_3\cdot(SiF_2)_n$, where $n = 2$ to at least 4, is obtained. The main product appears to be $C_6H_5CH_3Si_3F_6$. One isomer of this compound was isolated by distilling the SiF_2–$C_6H_5CH_3$ reaction product under high vacuum at 100°, and separating the homologs on a short gas chromatographic column at 80°. It is a solid melting at 37°. Hydrolysis with 2 *N* KOH or dilute hydrofluoric acid gives 2-methyl 1,4-cyclohexadiene. This suggests, by analogy with the benzene compound, that its structure is III.



III



IV

The proton nmr spectrum of the substance dissolved in toluene shows four resonances at 5.66, 5.33, 2.90, and 1.80 ppm (Me_4Si = 0) assigned to the protons $H_b + H_c$, H_f, $H_a + H_d$, and H_e, respectively, with area ratios of 2:1:2:3. The fluorine nmr is quite complicated, with three doublets and a fourth multiplet, which is probably a quartet, but is not inconsistent with the proposed structure III.

Another isomer of compound III was also isolated in small yield from the distillate. The structure of this is still uncertain; it does, however, spontaneously convert to III on standing. Hydrolysis of the small amount of $C_6H_5CH_3Si_2F_4$ which has been isolated gave 3-methyl-1,4-cyclohexadiene, suggesting that it may be IV.

Other Aromatics and Silicon Difluoride. Monofluorobenzene and *p*-difluorobenzene have been shown to behave in part like both benzene and perfluorobenzene in their reactions with silicon difluoride. Phenyltrifluorosilane has been isolated in very small yield from $C_6H_5F + SiF_2$, but in addition some less volatile compounds in the series $FC_6H_5(SiF_2)_n$, where $n = 2$ to 4, have been shown to be present mass spectrometrically. These must be, in part, bridged, unsaturated compounds, because on hydrolysis a monofluoro-1,4-cyclohexadiene is formed in addition to benzene.

p-Difluorobenzene reacts similarly, a very small amount of 4-fluorophenyltrifluorosilane being obtained, together with compounds of the type $F_2C_6H_4(SiF_2)_n$. On hydrolysis with 10% HF, these last give difluoro-1,4-cyclohexadienes, in addition to monofluorobenzene.

Very infrequent light flashes were observed during the cocondensation of both mono- and difluorobenzene with silicon difluoride at −196°.

Discussion

The reactions of benzene and perfluorobenzene with silicon difluoride represent two extremes of behavior for which there is no exact parallel in carbene chemistry.

With benzene the reaction is extremely complex, and the volatiles obtained from the polymer may reveal only part of the way in which benzene is attacked by silicon difluoride. The observed 1,4-addition is unknown for carbenes and this difference probably arises from the different modes of polymerization of carbenes and silicon difluoride. If a carbene dimerizes there is a considerable energy gain when a species containing a carbon–carbon double bond is formed rather than a diradical, *e.g.*

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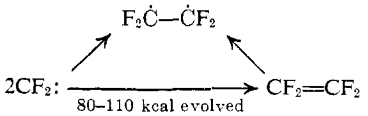
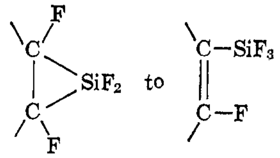
(6) D. R. Weyenberg, private communication.

(7) D. R. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962).



This large energy evolution is unlikely with silicon difluoride, and diradical dimers, trimers, and higher polymers may be formed which would be able to add to aromatics like benzene to form either bridged 1,4-diene derivatives, or, more simply, involatile polymers. Such a mechanism has already been proposed to account for the reactions between silicon difluoride and boron trifluoride.[8] It is clear that 1,2-addition of SiF_2 to nonfluorinated aromatics is not favored at low temperatures, and the only evidence for its occurrence is the small amount of 1,3-cyclohexadiene found in the hydrolysis of the C_6H_6–SiF_2 polymer.

The reaction with perfluorobenzene is simpler. The formation of trifluorosilyl groups is easily explained by the difference between the C–F and the Si–F bond energy, which makes the conversion of



highly exothermic. Monomeric silicon difluoride is probably the attacking species, as there seems to be no way in which diradicals could cause the observed *ortho*:*meta*:*para* isomer ratio in the disubstituted compounds. The rearrangement seems always to be accompanied by blue flashes of light, and these never occur in reactions where the bridged compounds are formed.

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(8) P. L. Timms, T. C. Ehlert, J. L. Margrave, F. Brinckman, T. C. Farrar, and T. P. Coyle *J. Am. Chem. Soc.*, **87**, 3819 (1965).