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HYDROLYTIC AND THERMAL DECOMPOSITION STUDIES OF SOME 7-SILANORBORNADIENES

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SUMMARY

The reaction of water with 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene was investigated and found to give a benzyldimethylsilanol. The thermal elimination of dimethylsilylene was studied for five different 7-silanorbornadienes and the ease of elimination correlated to the substituents on the basal carbon atoms. In general, stability towards elimination is increased by bulky or electron withdrawing substituents. The reaction of dimethylsilylene with trichloro- and trifluoroborane was investigated and both were found to give dihalodimethylsilane instead of insertion products.

INTRODUCTION

The formation of dimethylsilylene, Me_2Si:, by the thermolysis of 7,7-dimethyl-7-silanorbornadienes has been reported by several investigators[1-4], yet very little information is available which correlates the substitution on the 7-silanorbornadienes with the ease of loss of silylene. The reaction of a compound with dimethylsilylene is most easily carried out by copyrolysis of the compound in question with a 7,7-dimethyl-7-silanorbornadiene[2,3]. Therefore, all reactants and products must be stable at the temperature the 7-silanorbornadiene eliminates silylene. The lowest decomposition temperature reported for dimethylsilylene elimination by a 7,7-dimethyl-7-silanorbornadiene, that is at the same time a good precursor for dimethylsilylene, is 250–300°[2]. This temperature is too high to study the reaction of Me_2Si: with many organic and inorganic compounds. It therefore became necessary to have a better understanding of the factors which influence the stability of the 7-silanorbornadienes so that dimethylsilylene precursors can be prepared which eliminate at lower and synthetically more desirable temperatures.

We wish to report now the results of an investigation which, when coupled with those results already reported[1-5], give a better understanding of the factors that govern the stability of the 7,7-dimethyl-7-silanorbornadienes.

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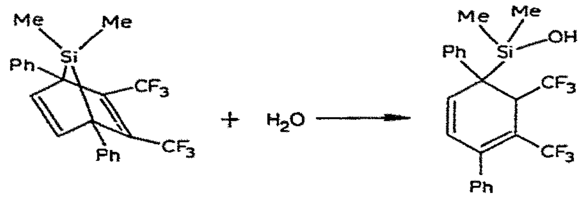
RESULTS AND DISCUSSION

During several investigations by the authors over the last four years, it has been observed that many of the organosilicon compounds used in this and previous investigations decompose on standing in closed but not evacuated containers or on being dissolved in wet solvents. In general the compounds which are colorless turn yellow and oily and the yellow compounds take on a red-brown tint and turn oily. The decomposition of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VI) has been shown to be due to photo-induced oxidation[6]. Except for 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, the organosilicon compounds used in these investigations appear to be water sensitive. This is suggested by the fact that they all decompose more rapidly when dissolved in a wet polar solvent than they do when pure or when dissolved in non-polar solvents. As 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (I) has a shorter shelf-life, 1–3 days, than the other compounds worked with, 3–6 months, the reaction of this compound with water was chosen for a more thorough investigation. The reaction [eqn. (1)] was carried out at 25° in benzene solution and proceeded very readily to give [5,6-bis(trifluoromethyl)-1,4-diphenyl-2,4-cyclohexadienyl]dimethylsilanol (II).



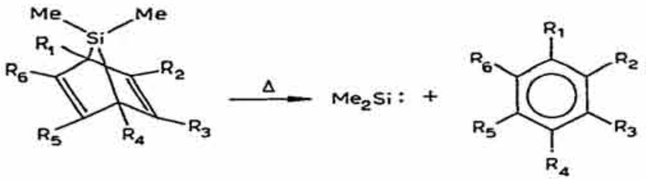
(I) (II)

(1)

The formula of silanol (II) was assigned from the IR, mass spectral and analytical data. The structure was assigned mainly from the NMR spectrum. In particular, the location of the hydrogen atom in the 6 position was necessitated by a quartet in the NMR spectrum at τ 5.97 which is assigned to a lone hydrogen coupling with a CF_3 group. The reaction of 7-silanorbornadienes with nucleophiles under more forcing conditions has been reported by Gilman, Cottis and Atwell[3], however, it now appears that these compounds are attacked by weak nucleophiles and should be handled with some care during preparation and storage.

It is interesting to compare the reaction of bis(trifluoromethyl)-7-silanorbornadiene (I) with water to the nucleophilic decomposition of 2,3-benzo-1,4,5,6,7,7-hexaphenyl-7-silanorbornadiene and 1,4,5,6,7,7-hexaphenyl-7-silanorbornadiene-2,3-dimethylcarboxylate[3]. When the benzohexaphenyl-7-silanorbornadiene is chromatographed on a basic alumina column, it gives dihydronaphthyldiphenylsilanol by a reaction which appears to be analogous to that of silanorbornadiene (I) with water. However, the decomposition of the dicarboxy-7-silanorbornadiene on basic alumina gives dimethyltetraphenylphthalate. It, therefore, appears that the trifluoromethyl groups have little effect on the nucleophilic decomposition of 7-silanorbornadienes other than that expected for a strongly electron-withdrawing group. On the other hand, electron-withdrawing carboxy groups have been postulated to participate directly in the decomposition of the carboxy substituted 7-silanorbornadienes[3] and, thus, give products which are considerably different from that observed for the nucleophilic decomposition of 7-silanorbornadiene (I).

The factors which govern the thermal stability of the 7-silanorbornadienes towards elimination of dimethylsilylene [eqn. (2)] are much more difficult to assess. When using 7-silanorbornadienes as precursors for dimethylsilylene, the elimination reaction is normally carried out in a sealed tube at high temperatures. Although good yields of products have been isolated from the reaction of the dimethylsilylene thus generated with other compounds for some 7-silanorbornadienes[1-3], generally the reactions are very messy and the products difficult to purify. Since these types of reactions do not lend themselves well to kinetic studies, reactions which do must be studied and the results extrapolated back to the system under consideration.



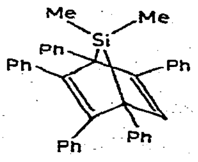
(2)

The method used in this investigation to obtain information on the elimination of dimethylsilylene from 7-silanorbornadienes was to carry out the pyrolyses in the low pressure ($< 10^{-4}$ mmHg) gas phase using the heated reservoir of the mass spectrometer as the reaction chamber. The decrease in the peak intensity of the parent ion for the 7-silanorbornadiene was used to follow the reaction. A stable, inert, standard was employed to correct the intensity of the parent ion for loss of sample through the molecular leak. In practice, the log of the intensity of the parent peak for the 7-silanorbornadiene divided by the intensity of the parent peak for the standard, log (I/I_{std}), was plotted as a function of time using a linear least squares regression technique. In every case the data fit a first order plot with zero or near zero coefficients for the second and third order terms. The slopes of the straight line plots of log (I/I_{std}) *vs.* time thus obtained for 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene (III), 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (IV) and 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (V) are given in Table 1.

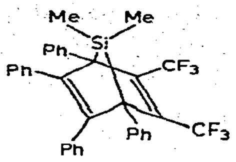
TABLE 1

KINETICS OF THE ELIMINATION OF DIMETHYLSILYLENE BY 7-SILANORBORNADIENES

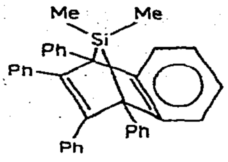
Compound	*Temp.* (°C)	*Slope* (10^{-3} *min*$^{-1}$) *of* $\log(I/I_s)$ *vs. t*	*Rate constant* (10^{-3} *min*$^{-1}$)
(III)	200	-2.5 ± 0.1	5.8 ± 0.2
		-2.7 ± 0.2	6.2 ± 0.5
(IV)	250	-0.29 ± 0.13	0.67 ± 0.30
		-0.31 ± 0.10	0.71 ± 0.23
(V)	250	-0.36 ± 0.02	0.83 ± 0.05
		-0.37 ± 0.02	0.85 ± 0.05



(III)



(IV)

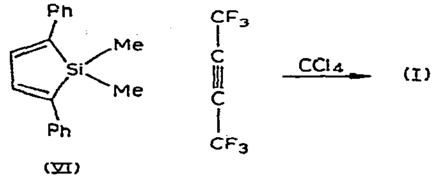


(V)

The first order rate constants, calculated by equating the slopes to $-k \cdot t/2.303$, for compounds (III), (IV), and (V) are also given. Using the mass spectrometer available to us this procedure is applicable only to 7-silanorbornadienes which eliminate dimethylsilylene between 100 and 250° with a half-life for the reaction of at least 1 h.

Of five 7-silanorbornadienes investigated, only three gave results that were meaningful, and in fact, the results for 7-silanorbornadienes (III), (IV), and (V) have rather large statistical errors associated with them. This is particularly true for the 2,3-bis(trifluoromethyl)-1,4,5,6-tetraphenyl derivative (IV) which not only eliminates dimethylsilylene very slowly but also has a parent ion of medium intensity and a low vapor pressure at 250°, the maximum temperature of the apparatus used. The effect of these three factors was to give results that are considerably in error. Nevertheless, when one considers the reactions being investigated, the results have significance concerning the effect of substituents on the ease of elimination of silylene by 7-silanorbornadienes; although very little reliability can be placed on the absolute values of the rate constants.

Information concerning the stability of 7-silanorbornadiene (I) toward elimination of dimethylsilylene is more qualitative but has been obtained in two ways. During attempts to record the mass spectrum of (I) using the direct inlet probe, only the spectrum of 2,3-bis(trifluoromethyl)-1,4-diphenylbenzene was obtained even when the highest temperature the compound was heated to was 70°. This indicates that 7-silanobornadiene (I) eliminates dimethylsilylene very rapidly in the gas phase at 70°. This is substantiated by the study of the preparation and decomposition of (I) using the nuclear magnetic resonance spectrometer. The results of this experiment are that silacyclopentadiene (VI) reacts with hexafluoro-2-butyne [eqn. (3)] very slowly at 25° to give 7-silanorbornadiene (I). The reaction is much more rapid at 50° but at this temperature (I) starts to decompose and at 80° the decomposition of (I) is fairly rapid.



(VI)

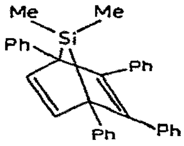
(3)

Although the elimination of dimethylsilylene by 7-silanorbornadienes (I) and (IV) in the low pressure gas phase is strongly supported by the mass spectral work, that they do so in sealed tubes is not so clear. Hota and Willis[4] suggest, from their work, that 7-silanorbornadiene (IV) does not give dimethylsilylene on decomposition.

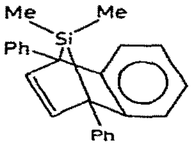
It is our opinion however that it does, but that the dimethylsilylene once eliminated abstracts fluorine atoms from the CF_3 groups on reactant or product molecules to give difluorodimethylsilane as the major product. This is further substantiated by the formation of difluoro- and dichlorodimethylsilane as the major volatile products in the reaction of dimethylsilylene with BF_3 and BCl_3, respectively. That is, the stabilities of the silicon–fluorine and silicon–chlorine bonds are great enough for abstraction of fluorine or chlorine from boron or carbon to be the preferred reaction path for dimethylsilylene under these conditions.

The NMR work reported here on the formation and decomposition of 7,7-dimethyl-1,2,3,4-tetraphenyl-7-silanorbornadiene (VII) further supports the conclusion reached previously about this compound[1]. That is, 7-silanorbornadiene (VII) forms very slowly at temperatures of 150 to 200° by the Diels–Alder reaction of diphenylacetylene with silacyclopentadiene (VI), yet it eliminates dimethylsilylene very rapidly at these temperatures. In fact, the concentration of (VII) does not become large enough to detect by NMR, even when the products of elimination are isolated[1].

Information concerning the stability of another 7-silanorbornadiene has just been published[5]. When 2,3-benzo-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (VIII) is formed at −78° and then allowed to warm up, it apparently eliminates dimethylsilylene before it reaches 0°. This appears to be the least stable of the 7-silanorbornadienes yet worked with.



(VII)



(VIII)

The most stable 7-silanorbornadienes, (IV) and (V), are both fully substituted on the basal carbon atoms with the next most stable, (III), having five substituents around the basal ring. The 7-silanorbornadienes with only four substituents on carbon [(I), (VII), and (VIII)] are all much less stable than the previous three. Thus, the greater the steric strain around the basal plane the more stable the 7-silanorbornadiene towards elimination. This is consistent with a transition state that has the basal carbon taking on a planar arrangement similar to the benzoid product.

The two-7-silanorbornadienes with the strong electron withdrawing trifluoromethyl groups on the basal carbon atoms, (I) and (IV), appear to be the most stable towards elimination of their respective groups. Thus, stability seems to be increased by electron withdrawing groups on the basal carbon atoms. The reason this is so is not clear but it does indicate that fewer electron withdrawing groups on the basal carbon atoms should lead to 7-silanorbornadienes that are both isolable and eliminate dimethylsilylene at synthetically useful temperatures. The problem arises in finding an electron withdrawing substituent that does not react with dimethylsilylene or is not reactive towards coreactants.

One possible solution in many situations might be to prepare a 7-silanorbornadiene using dicyanoacetylene as the dienophile; however, the coreactants of interest to us, mainly boron hydrides, are in general not compatible with cyano groups. Therefore this system was not investigated. A second alternative may be to use 7-silanorbornadiene (VIII) as a precursor for dimethyl silylene[5]. If this compound can be purified at a temperature below its decomposition point it should prove to be a very useful source of dimethylsilylene.

EXPERIMENTAL

Instrumentation

IR spectra were recorded using a Perkin–Elmer model 237b Infracord and were standardized against polyethylene. Melting points were obtained on a Thomas–Hoover melting point apparatus and are reported uncorrected. NMR spectra were recorded on a Jeolco C-60H spectrometer using dichloromethane as the primary reference. The chemical shifts reported are relative to tetramethylsilane and have been corrected for solvent effects to the primary reference signal. The mass spectra were obtained using a Hitachi RMU-6H mass spectrometer. Only the parent peak, base peak and other important peaks are reported here. Elemental analyses of the compounds were done by Galbraith Laboratories, Inc., Knoxville, Tennessee 37921.

Chemicals

The preparation of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (VI), 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene (III), 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (IV), and 2,3-benzo-7,7-dimethyl-1,4,5,6-tetraphenyl-7-silanorbornadiene (V) have been reported previously[1,2,4,6,7]. Samples of all of these compounds were characterized by melting points, IR, mass and NMR spectrometry, and elemental analyses. All physical data agreed with that published or with that expected for the compounds.

Diphenylacetylene (Aldrich Chemicals), boron trichloride (K & K Rare and Fine Chemicals), boron trifluoride (Matheson Chemicals), hexafluoro-2-butyne (PCR Inc.), and all alkane solvents (Matheson Chemicals) were used without further purification. All other solvents (Matheson Chemicals) were dried by refluxing with either lithium aluminum hydride, barium oxide or phosphorus pentoxide and distilled before using.

Preparation of 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (I)

In a typical experiment, a 50 ml pyrex tube, fitted with a break-seal, was charged with 0.36 g (1.4 mmoles) of diphenylsilacyclopentadiene (VI), 5.0 ml of CCl_4 and 1.2 g (7.4 mmoles) of hexafluoro-2-butyne using high vacuum techniques[8]. The tube was sealed and reaction carried out at 25° for a period of not less than two weeks.

After opening the reaction tube and removing the volatile contents the non-volatile residue was dissolved in 5 ml of n-hexane and the product precipitated at $-78°$. Upon filtration and recrystallization from n-hexane, 0.36 g (0.85 mmoles) of pure bis(trifluoromethyl)diphenyl-7-silanorbornadiene (I) was obtained. This material gave the following physical data: m.p. 95–100° decomp., ^1H NMR (60 MHz, CCl_4), τ 2.73 (s, 10H), 3.00 (s, 2H), 9.32 (s, 3H), 9.84 (s, 3H); IR (KBr pellet) 3030 (w), 1605 (w), 1585 (w), 1560 (w), 1540 (w), 1500 (w), 1450 (w), 1405 (m), 1300 (m), 1260 (m), 1240 (m), 1165 (s), 1120 (s), 1040 (w), 1020 (m), 980 (w), 935 (w), 915 (w), 865 (m), 835 (w), 785 (m), 760 (m), 740 (m), 720 (w), 695 (s), 665 (w). (Found: C, 62.16; H, 4.32; F, 26.95; Si, 6.70; mol. wt., 435. $C_{22}H_{18}F_6Si$ calcd.: C, 62.27; H, 4.24; F, 26.87; Si, 6.62%; mol. wt., 424.)

Reaction of 7-silanorbornadiene (I) with water. The preparation of [5,6-bis(trifluoromethyl)-1,4-diphenyl-2,4-cyclohexadienyl]dimethyl(silanol) (II).

A 50 ml pyrex tube was charged with 0.68 g (1.6 mmoles) of 7-silanorbornadiene (I), 0.5 ml water and 5.0 ml benzene and the tube evacuated and sealed. The mixture was then reacted at 25°. Within ½ h, the solution turned from clear to a light yellow. After 5 days at room temperature, the reaction tube was opened and all volatile material removed under high vacuum. The residue was dissolved in benzene/hexane 1/1 and passed through a 15 cm column of anhydrous magnesium sulfate to remove the last traces of excess water. The solvent was removed and the residue taken up in n-hexane. Upon cooling the mixture at 0°, a white precipitate formed and was separated by decantation, washed with cold n-hexane and vacuum dried. A 0.18 g (0.41 mmole) yield of (II) was isolated. Purified samples of silanol (II) gave the following physical data: m.p. 116.0–117.5°; H NMR (60 MHz, CCl_4) τ 2.6 (m, 10H), 3.25 (d, 1H, J 6Hz), 3.92 (d, 1H, J 6 Hz), 5.97 (q, 1H, 8 Hz), 8.09 (s, 1H), 9.68 (s, 6H); mass spectrum (70 eV) m/e (rel. intensity) 442 (< 1) P, 368 (36) $[P-(Ph)_2SiO]$, 259 (100); UV max (cyclohexane) 326 nm (ε 5,300); IR (KBr pellet) 3520 (m), 3430 (m), 3025 (w), 2960 (w), 2940 (w), 1595 (w), 1573 (w), 1500 (m), 1450 (m), 1405 (w), 1363 (m), 1350 (m), 1322 (w), 1260 (s), 1237 (s), 1170 (s), 1130 (s), 1090 (m), 1060 (w), 1037 (m), 1000 (w), 987 (w), 960 (w), 917 (m), 890 (m), 860 (s), 825 (m), 800 (s), 785 (m), 770 (s), 720 (m), 707 (s), 685 (m), 670 (m). (Found: C, 59.66; H, 4.52; F, 25.93. $C_{22}H_{20}F_6OSi$ calcd.: C, 59.72; H, 4.52; F, 25.79%.)

Pyrolysis studies of 2,3-bis(trifluoromethyl)-7,7-dimethyl-1,4-diphenyl-7-silanorbornadiene (I)

A 0.050 g sample of 7-silanorbornadiene (I) was placed in a tube which was evacuated, sealed, and then placed in an oven at 115°. After 24 h, the tube was opened and the contents vacuum fractionated to yield a trace of a volatile compound and a non-volatile residue. The volatile material was shown to be difluorodimethylsilane by comparison of its mass spectrum with that of an authentic sample. Mass spectral analysis of the nonvolatile residue indicated that, at least four compounds were present in significant amounts. These compounds had parent peaks at m/e 307, 328, 348 and 366. The compound with a parent peak of 366 was identified as 2,3-bis(trifluoromethyl)-1,4-diphenylbenzene by comparison of its mass spectral fragmentation pattern with that of an authentic sample.

The pure 2,3-bis(trifluoromethyl)-1,4-diphenylbenzene was obtained by repeated recrystallizations, from 60–90° petroleum ether, of a sample of mixed products obtained from the thermal decomposition of several grams of 7-silanorbornadiene (I). This pure sample gave the following physical data: m.p. 102.5–103°; mass spectrum (70 eV) m/e (rel. intensity) 366 (21), 328 (24), 307 (22), 259 (56), 77 (100), 18 (23). (Found: C, 65.8; H, 3.56; F, 30.8. $C_{20}H_{12}F_6$ calcd.: C, 65.5; H, 3.29; F, 31.3%.)

When 7-silanorbornadiene (I) was pyrolysed at 80° for 14 h in the presence of diphenylacetylene, the products were the same as those observed for the above pyrolysis. In particular, exhaustive mass spectral analysis of the products showed that no 1,1,4,4-tetramethyl-2,3,5,6-tetraphenyl-1,4-disilacyclohexadiene was present[7].

When the samples of 7-silanorbornadiene (I) were introduced into the heated reservoir of the mass spectrometer, which was thermostatted at 200°, or when they were introduced to the mass spectrometer through the direct inlet system, with all components at 70°, only the spectrum of 2,3-bis(trifluoromethyl)-1,4-diphenylbenzene was obtained.

The formation and thermal decomposition of 7-silanorbornadiene (I) were also studied using NMR. A 15 cm pyrex tube, fitted with a vacuum line connection and a sintered glass filter connected to an NMR tube, was charged with 0.10 g silacyclopentadiene (VI), 1.0 g hexafluoro-2-butyne and 10 ml of spectroquality CCl_4. The tube was evacuated and sealed and the reaction mixture allowed to warm to 25°. After shaking the tube constantly at 25° for 5 days, the mixture was filtered into the NMR tube, excess solvent removed under vacuum and the NMR tube sealed from the rest of the system. An NMR taken on the sample at this time indicated that a 2/1 mixture of 7-silanorbornadiene (I) and diphenylsilacyclopentadiene (VI) was present. The NMR tube was then heated at 50° for 24 h and the spectrum taken again. By this time the silicon–methyl resonance for silacyclopentadiene (VI) at τ 9.45 had all but disappeared and a new silicon–methyl resonance appeared at τ 9.22. The silicon–methyl resonances for 7-silanorbornadiene (I) at τ 9.32 and 9.84 had decreased in intensity slightly from the earlier spectrum. After another 24 h at 50° the silicon–methyl resonance of diphenylsilacyclopentadiene (VI) had completely disappeared and those for 7-silanorbornadiene (I) had decreased considerably in intensity. The new resonance at 9.22 was quite large and a general increase in the baseline between 9.22 and 10 was noticeable. The sample was then heated at 80° for 24 h and the NMR run again. By this time the only sharp resonance in the silicon–methyl region was the one at τ 9.22. The baseline from 9.22 to 10 was considerably raised thus indicating that $SiMe_2$ polymer had been formed.

Kinetics studies of the thermal decomposition of 7-silanorbornadienes (III), (IV) and (V)

The procedure used was to place volatilized samples of the 7-silanorbornadiene along with a standard into the heated, constant temperature reservoir of the mass spectrometer and to monitor the elimination of dimethylsilylene by recording spectra every 15 to 30 min through about 2 half-lives of the sample. The reservoir and all other components of the mass spectrometer were kept at the same temperature with a temperature variation of ±10° or less. The standard, tris(pentafluoroethyl)-*s*-triazine or tris(heptafluoropropyl)-*s*-triazine (PCR, Inc.), was selected such that its molecular weight was close to that of the sample under investigation and its fragmentation pattern did not interfere with that of the sample. The weight of standard used was in the order of 20 to 30% of the weight of sample. During each determination the total pressure inside the mass spectrometer was less than 5 microns.

Pyrolysis of 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene (III) in the presence of BCl_3 and BF_3

In typical experiments, 1 mmole of 7-silanorbornadiene (III) was placed in a pyrolysis tube and then 10 mmoles of borane condensed in. The tube was sealed and the reaction carried out in a furnace ca. 220° for 4 h. The tube was then opened and the volatile products separated by trap to trap fractionation. The volatile products were analysed by mass spectrometry.

For the pyrolyses with BCl_3 as a substrate, a 65% yield of dichlorodimethylsilane, Me_2SiCl_2, was received as the only volatile product from the reaction. Likewise, a 32% yield of difluorodimethylsilane, Me_2SiF_2, was the only volatile product isolated from the copyrolysis of BF_3 with 7-silanorbornadiene (III). The nonvolatile residues from all of these pyrolyses were shown to contain pentaphenylbenzene by mass spectrometry [*m/e* (rel. intensity) 459 (41), 458 (100, *P*)] and melting point [244–245.5° (lit.[2] 246–249°)]. No other identifiable compound could be isolated from the residues by recrystallization from several different solvents, sublimation at temperatures to 200° or by column chromatography on neutral alumina or silica gel.

Formation and decomposition of 7,7-dimethyl-1,2,3,4-tetraphenyl-7-silanorbornadiene (II) in the NMR spectrometer

An NMR tube was filled with the 1/1 solid state complex of 1,1-dimethyl-2,5-diphenylsilacyclopentadiene (VI) and diphenylacetylene[1], the tube sealed and the sample placed in the spectrometer. The temperature was raised, over a period of 3 h, from 100 to 200°. At 105° the spectrum recorded was just the sum of those for the reactants. At 150° the peaks had sharpened considerably but still no resonances due to 7-silanorbornadiene (VII) were observed. By the time the temperature had reached 200°, the intensity of the peaks observed at 105 and 150° had decreased considerably and the noise level in the phenyl and methyl-silicon proton regions had increased considerably. Still, no signals expected for the silicon methyl groups of (VII) were observed.

ACKNOWLEDGEMENT

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