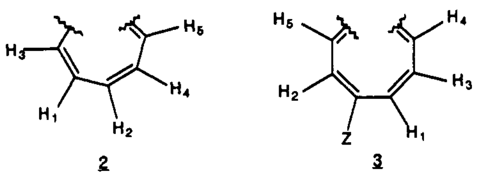

Figure 3. Proton sequences for 2 and 3 determined from $^3J_{HH}$ coupling constants.

constants and one $^3J_{HH}$ value for every proton; these data are consistent with [1,4] addition (Table III) to give structure **7b.**

For **2**, distinguishing between structures **5a** and **5b** and assignement of the final structure was done by using standard NMR correlation logic. From Table II, one can see that protons 1 and 3 and protons 2 and 4 are vicinally coupled through a double bond, whereas protons 1 and 2 and protons 4 and 5 display vicinal coupling through a single bond. These couplings yield the sequence shown in Figure 3. Final assignment of structure **2** between the four remaining possibilities depends on determining a relationship between proton H$_3$ or H$_5$ and one of the substituents on the cyclooctatetraene ring. In the proton NMR spectrum of **2**, the signal of H$_3$ is broadened while all the other protons give sharp lines. This broadening may be due to residual coupling between H$_3$ and the aromatic protons, implying that the aromatic ring and H$_3$ are on adjacent carbons.[9] Hence, the probable structure for **2** is **2a.**

For **3**, correlating the coupling as above, one can see that pairs of protons H$_1$ and H$_3$ are vicinally coupled through a double bond, while protons H$_2$ and H$_5$ and also protons H$_3$ and H$_4$ display vicinal coupling through a single bond. For **3**, proton H$_5$ is broadened compared to H$_4$, and from this we infer residual coupling between H$_5$ and the aromatic ring. The most likely structure for **3** is therefore **3a.**[10]

The photolytic reaction described here is apparently the first example of an intermolecular arene–alkyne dimerization. The predominance of [1,2] addition in our reactions is not without precedent. Cycloaddition of cyanobenzene and internal symmetrical acetylenes takes place to form [1,2]-addition products,[1] and products from [1,2] addition to the aromatic moiety are also found in intramolecular arene–alkyne photocycloadditions.[5]

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Registry No. 1, 2170-06-1; 2, 135865-57-5; 3, 135865-58-6.

Supplementary Material Available: Figures showing expansions of the individual regions of Figures 1 and 2 (3 pages). Ordering information is given on any current masthead page.

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[9] NOE differentiation was attempted, but in this highly coupled system, no clear enhancement was seen.

[10] Other less likely substitution patterns (1,3,5 and 1,3,6) and 2 and 3 can be excluded from the coupling constants given in Tables II and III.

Mechanism of Pyrolysis of 2,2-Diethylhexamethyltrisilane

Musahid Ahmed, Iain M. T. Davidson,* Geraint H. Morgan, and Terry Simpson
Department of Chemistry, The University, Leicester LE1 7RH, Great Britain

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Summary: The main silicon-containing product besides trimethylsilane in the pyrolysis of the title compound is vinyltrimethylsilane, whereas cyclic carbosilanes are formed in the pyrolysis of permethylated oligosilanes. A mechanistic explanation, of relevance to the breakdown of polysilanes, is suggested.

We are undertaking studies of the thermal[1] and photochemical[2] breakdown of oligosilanes as simple models for polysilanes; the latter are of topical interest in view of their potential as photoresists[3] and as precursors to new polymers. We now report on the gas-phase pyrolysis of 2,2-diethylhexamethyltrisilane; the course of this pyrolysis proved to be different from that of octamethyltrisilane, where the major silicon-containing products other than Me$_3$SiH were cyclic carbosilanes, formed in part by a novel elimination of Me$_3$SiH.[1]

Experimental Section

2,2-Diethylhexamethyltrisilane, (Me$_3$Si)$_2$SiEt$_2$ (I), was a gift from Dr. R. G. Taylor of Dow Corning Ltd., who synthesized it by standard methods. Its purity was checked at Leicester by GC/mass spectrometry (HP5995C) and by ^{1}H NMR spectroscopy (AM300).

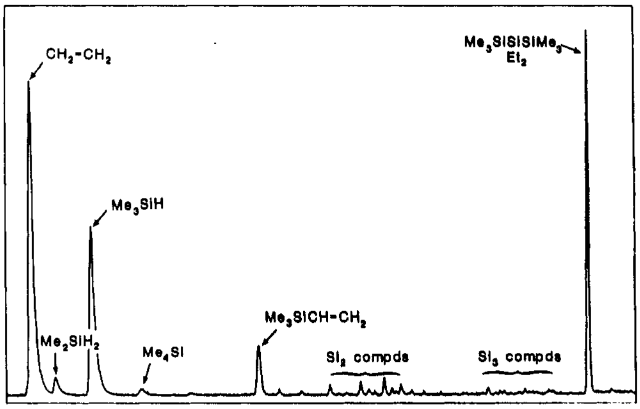

Figure 1.

Pyrolysis of compound I was carried out by our stirred-flow (SFR) technique[4] in a carrier gas of dried deoxygenated helium or nitrogen, with analysis by GC/mass spectrometry or packed-

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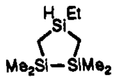
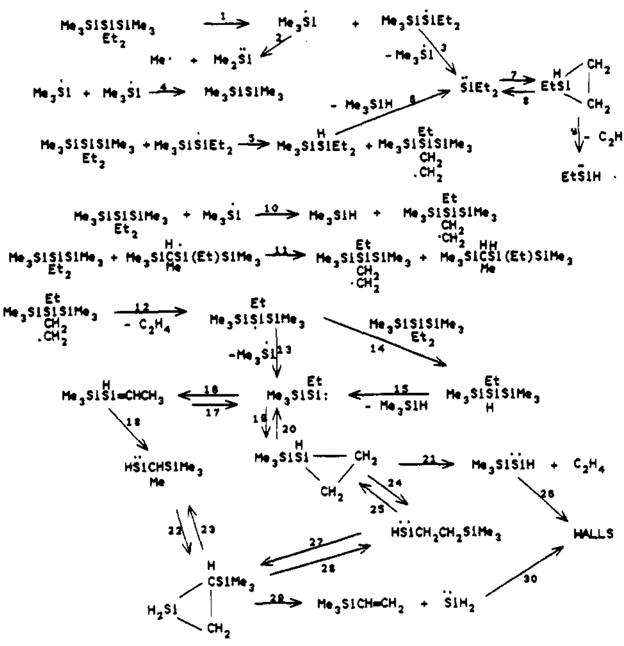
Table I. Minor Products in the Pyrolysis of I

Me_2SiH_2	Me_4Si	Me_3SiEt
$Me_3Si\overset{H}{\underset{Me}{Si}}Et$	$Me_3SiSiMe_3$	$Me_3Si\overset{Me}{Si}Et_2$
$Me_3SiCH_2\overset{H}{Si}Me_2$	$Me_3Si\overset{H}{\underset{Et}{Si}}SiMe_3$	
		

Scheme I



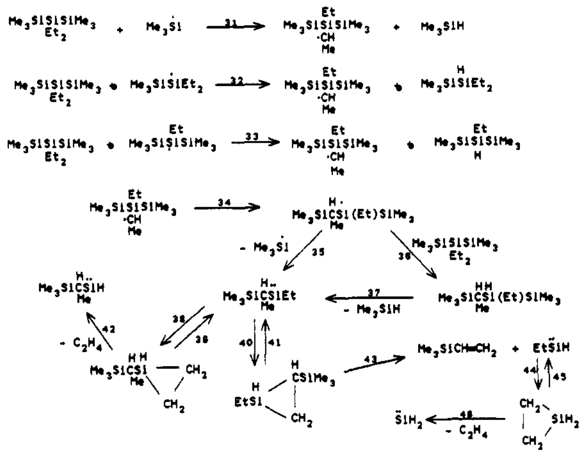
column GC. All major products, and many of the minor ones, were identified by comparison of retention time and GC/mass spectra with those of authentic samples, the remaining minor products being identified by comparison of retention times and mass spectra with those of similar compounds.

Results and Discussion

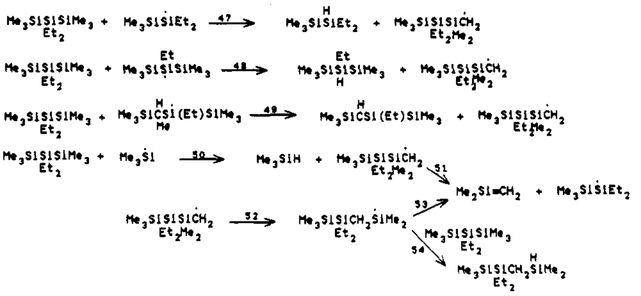
In pyrolyses between 580 and 630 °C, the major products were C_2H_4, Me_3SiH, and vinyltrimethylsilane, $Me_3SiCH{=}CH_2$. At 580 °C, yields of these were 46%, 36%, and 9%, respectively, while at 630 °C the yields were 56%, 30%, and 5%. There were numerous minor products containing one to three silicon atoms, all <3%, but cyclic carbosilanes analogous to those formed in the pyrolysis of octamethyltrisilane were not prominent. The relative importance of the products may be seen from the GC trace of a pyrolysis at 616 °C in Figure 1, while the principal minor products identified are shown in Table I. The reactions resulting from radical attack on the ethyl groups of I, leading to the cyclic products that would have been expected by analogy with octamethyltrisilane[1] are in Schemes I (β-hydrogen abstraction) and II (α-hydrogen abstraction). These schemes also show reasonable routes to the prominent product $Me_3SiCH{=}CH_2$ based on analogies in the organosilicon literature.[5,6] Likewise, H abstraction from a terminal methyl group would lead to the sequence of reactions in Scheme III.

The preferential formation of products envisaged as resulting from silacyclopropane intermediates echoes the work of Barton and Burns on the reactions of *n*-butylmethylsilylene; although several cyclization pathways seem feasible, as shown in Scheme IV, FVP experiments at 680 °C gave a high yield of 1-butene, with no ethene, propene, or any silacycloalkane.[5]

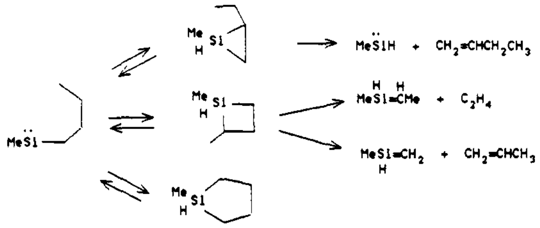
Scheme II



Scheme III



Scheme IV



Further mechanistic information was sought in trapping and kinetic experiments, complemented by computer modeling by numerical integration using the KINAL and ACUCHEM packages.[7] Pyrolysis of I in the presence of toluene did not profoundly affect the kinetics of product composition but gave some $PhCH_2CH_3$ and $PhCH_2SiMe_3$, indicating the presence of $Me_3Si^•$ and $Me^•$ radicals. Likewise, pyrolysis with 2,3-dimethylbuta-1,3-diene had little effect on the kinetics and product composition but gave small quantities of cyclic adducts of the silylenes :SiH_2, :SiMeH, and :$SiMe_2$ or :SiEtH. Kinetic measurements with initial concentrations of I between 10^{-5} and 10^{-6} mol dm^{-3} without trapping agents revealed kinetic complexity; the average order for the formation of C_2H_4, Me_3SiH, and $Me_3SiCH{=}CH_2$ was ca. 1.6. Similar kinetic behavior was observed in the "trapping" experiments; rate reductions caused by added $PhCH_3$ or dimethylbutadiene did not exceed a factor of 2. The small effect of "trapping" agents is understandable; at the low pressures of these

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Table II. Kinetics of Formation of Products and Arrhenius Parameters[a] for 1.6-Order Rate Constants

	C_2H_4		Me_3SiH		$Me_3SiCH{=}CH_2$	
	log *A*	*E*/kJ mol^{-1}	log *A*	*E*/kJ mol^{-1}	log *A*	*E*/kJ mol^{-1}
expt	20.8 ± 0.5	308 ± 9	20.8 ± 0.6	310 ± 9	18.0 ± 0.6	274 ± 10
calcd	20.7 ± 1.6	318 ± 27	19.5 ± 1.4	303 ± 23	19.6 ± 1.4	312 ± 23

[a] *A* factors calculated with moles per cubic decimeter as the unit of concentration.

Table III

reaction	log *A*	*E*/kJ mol^{-1}	source
1	17.3	320	analogy with $Me_3SiSiMe_3$, ref 10
2	14.5	255	ref 11
3	16.0	235	estimated from thermochemistry in ref 12
4	9.0	0	adapted from ref 13
5	10.4	75	ref 13
6	13.3	203	ref 14
7	12.3	44	ref 8
8	14	62	ref 8
9	16.9	108	ref 8
10	10.4	65	adapted from ref 13
11	10.4	80	adapted from ref 13
12	16	154	estimated from thermochemistry
13	16	235	ref 12
14	10.4	80	adapted from ref 13
15	13.3	203	ref 14
16	13.3	182	adapted from ref 15
17	13.9	179	adapted from ref 15
18	14.2	110	adapted from ref 15
19	12.3	44	ref 8
20	14	62	ref 8
21	16.9	108	ref 8
22	12.3	44	ref 8
23	14	62	ref 8
24	14	62	ref 8
25	12.3	44	ref 8
26	4.0	0	arbitrary estimate[a]
27	12.3	44	ref 8
28	14	62	ref 8
29	16.9	108	ref 8
30	4.0	0	arbitrary estimate[a]
31	10.4	65	adapted from ref 13
32	10.4	75	ref 13
33	10.4	80	adapted from ref 13
34	12.3	90	ref 13
35	16	235	ref 12
36	10.4	80	adapted from ref 13
37	13.3	203	ref 14
38	12.3	44	ref 8
39	14	62	ref 8
40	12.3	44	ref 8
41	14	62	ref 8
42	16.9	108	ref 8
43	16.9	108	ref 8
44	12.3	44	ref 8
45	14	62	ref 8
46	16.9	108	ref 8
47	10.4	80	adapted from ref 13
48	10.4	80	adapted from ref 13
49	10.4	80	adapted from ref 13
50	10.4	75	ref 13
51	15	191	ref 13
52	12.3	90	ref 13
53	15	191	ref 13
54	10.4	80	adapted from ref 13

[a] Model shown by sensitivity analysis to be insensitive to chosen value.

experiments bimolecular reactions of radicals with $PhCH_3$, for example, cannot compete with the important unimolecular radical reactions 5 and 32.

The reactions in Schemes I–III were modeled by numerical integration; reaction 4 was the only radical combination reaction to be included because the modeling revealed that [$Me_3Si^•$] was substantially the highest radical concentration. Arrhenius parameters used or estimated for individual reactions are given in Table III; these calculations would not have been possible without access to the recent estimates of rate constants for reactions involving silacyclopropane intermediates, generously provided by Professor H. E. O'Neal.[8] The modeling gave variable reaction orders over a wide range of concentration, but the orders were ca. 1.6 over the range of concentration used experimentally; likewise, curved Arrhenius plots were obtained over an extended temperature range. Experimental and calculated kinetic results based on an order of 1.6 for the formation of all three major products are compared in Table II. Reaction orders close to 1.5 are not unexpected; in Scheme I, for example, reaction 10 (a major route to C_2H_4) would have an order of exactly 1.5 if reaction 4 is the main route for the loss of $Me_3Si^•$ radicals. In view of the evident kinetic complexity, we consider that the agreement between experiment and modeling is sufficiently good for Schemes I–III to be credible.

As already noted, our modeling depends heavily on the Arrhenius parameters for reactions involving silacyclopropane intermediates derived by Ring, O'Neal, and coworkers from their studies of butyl- and pentylsilylenes.[8] We hope that our results will increase confidence in the general applicability of their ideas and kinetic estimates, as well as providing further evidence for the predominance of reaction pathways involving silacyclopropane intermediates.[5,6,8]

The new reaction routes opened up by the presence of an ethyl group on silicon are of interest in relation to the mechanism of breakdown of polysilanes. In their studies of the photoablation of polysilanes, Michl and co-workers[9] have shown that a prominent photothermal process is the elimination of 1-alkenes from alkyl side chains with concomitant Si–H bond formation; they cited the same precedent as we do[5] for suggesting the formation of silacyclopropanes by *β*-C–H insertion, analogous to the reactions leading to $Me_3SiCH{=}CH_2$ in Schemes I and II. Our results may therefore be taken to support their suggestion.

Acknowledgment. We thank the SERC, Dow Corning Ltd., and BP Research International for financial support and are particularly grateful to Dr. Richard G. Taylor of Dow Corning for a gift of trisilane I. We are also indebted to Professor H. E. O'Neal of San Diego State University for access to results in press.

Registry No. $(Me_3Si)_2SiEt_2$, 132884-45-8; toluene, 108-88-3; 2,3-dimethylbuta-1,3-diene, 513-81-5.

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