Physical Organosilicon Chemistry. II. The Mass Spectral Cracking Patterns of Phenylsilane and Ortho-, Meta-, and Para-Substituted Benzyl- and Phenyltrimethylsilanes

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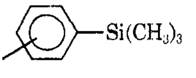
Received June 16, 1970

The mass spectral cracking patterns of 29 organosilicon compounds ($PhSiH_3$, $XC_6H_4CH_2SiMe_3$, $XC_6H_4SiMe_3$) were investigated. They are similar to the analogous carbon compounds except (a) no cracking which would require a carbon–silicon double bond in either the ion or the neutral is observed, and (b) extensive rearrangements occur in the $XC_6H_4SiMe_3$ series which result in the formation of $C_7H_7^+$ and SiX^+ species. Anomalies also appear when a particularly stable ion (as from o-$PhC_6H_4SiMe_3$) may be formed.

The mass spectra of organosilicon compounds (*e.g.*, those containing only carbon bonded to silicon) have received little attention, in spite of the growing accumulation of information concerning organosilicon reactions and reaction mechanisms. Studies of compounds containing silicon–oxygen,[1-5] silicon–nitrogen,[1,2,5] and silicon–sulfur[1] bonds have been conducted as an offspring of the utility of the trimethylsilyl group, $SiMe_3$, in derivativization of functional groups (alcohols, thiols, acids, amines). A "silyl McLafferty rearrangement" been observed in two organosilicon compounds, methyl 4-trimethylsilylbutyrate[6] and 4-trimethylsilylbutyronitrile, but other information on the mass spectra of organosilicon compounds is rare, other than an occasional reference in mass spectral tables.

The interest of this laboratory in physical organosilicon chemistry led to the investigation of the mass spectral cracking patterns of a series of substituted phenyltrimethylsilanes (**1**), benzyltrimethylsilanes (**2**), and phenylsilane (**3**). It was expected that information



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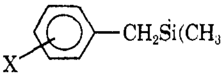

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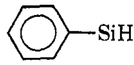

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concerning the facility and nature of rearrangements, if any, could be obtained by varying the electronic character of the substituent. In several of the cases, the analogous *tert*-butylbenzenes were available for comparison, and the rearrangement aptitudes of silicon relative to carbon could be determined.

Experimental Section

Mass Spectra.—All mass spectra were obtained on a CEC 21-491 double-focusing mass spectrometer equipped with variable collector slits. While the maximum resolution of the instrument was $m/\Delta m$ = 3000 with a 10% valley, all spectra recorded were determined with a resolution of *ca.* $m/\Delta m$ = 300. Samples were separated from trace impurities on a 20 ft × $^3/_8$ in. gas chromatography column packed with 20% SE-30 on Chromosorb W, and the effluent was introduced directly into the mass spectrometer's ionization chamber. All spectra were obtained at a source temperature of 190° and an electron energy of 70 eV.

The mass of all significant fragments was determined by the introduction of appropriate mass standards. When there was more than one logically possible structure for a nominal mass number, the exact mass number was determined to permit precise determination of the molecular species. Thus, in the tables of ion intensities, molecular formulas are listed rather than mass/charge ratio. Although all ions were counted when determining the per cent of total ionization, only those of intensity greater than 1% are listed in the tables.

Substituted Phenyltrimethylsilanes.—The preparation and purification of *o*-, *m*-, and *p*-$XC_6H_4SiMe_3$ (X = F, Cl, Me, MeO, Ph, CF_3, NO_2, H) and *m*- and *p*-bis(trimethylsilyl)benzene are reported elsewhere.[7] All compounds gave correct carbon, hydrogen, and silicon analyses.

Benzyltrimethylsilane (8).—To a stirred solution of 1.2 g (0.05 g-atom) of magnesium metal, 5.4 g (0.05 mol) of chlorotrimethylsilane and 100 ml of tetrahydrofuran (THF) was added 6.1 g (0.05 mol) of benzyl chloride at a rate which maintained the solution at its reflux temperature. After addition was complete, heat was applied to maintain the condition of reflux for 12 hr. The solution was treated with 50 ml of a saturated aqueous ammonium chloride solution, the salts were removed by filtration, and the organic layer was separated. After drying with magnesium sulfate, the center cut of the proper distillate was further purified by preparative gas chromatography (20 ft × $^3/_8$ in. 20% SE-30 on Chromosorb W, Varian Aerograph Model 1868). The yield of **8** was 3.3 g (40%). *Anal.* Calcd for $C_{10}H_{16}Si$: C, 73.09; H, 9.81; Si, 17.92. Found: C, 73.25; H, 9.94; Si, 17.65.

***o*-Fluorobenzyltrimethylsilane.**—This compound was prepared as **8** above but from *o*-fluorobenzyl chloride in 42% yield. *Anal.* Calcd for $C_{10}H_{15}SiF$: C, 65.88; H, 8.28; Si, 15.40. Found: C, 65.70; H, 8.30; Si, 15.26.

***m*-Fluorobenzyltrimethylsilane.**—A yield of 33% was achieved as **8** above but starting with *m*-fluorobenzyl chloride. *Anal.* Calcd for $C_{10}H_{15}SiF$: C, 65.88; H, 8.28; Si, 15.40. Found: C, 65.72; H, 8.24; Si, 15.79.

***p*-Fluorobenzyltrimethylsilane.**—From *p*-fluorobenzyl chloride, this compound was prepared as **8** above in 44% yield. *Anal.* Calcd for $C_{10}H_{15}SiF$: C, 65.88; H, 8.28; Si, 15.40. Found: C, 66.06; H, 8.30; Si, 15.56.

Phenylsilane (3).—A solution of 21.1 g (0.10 mol) of phenyltrichlorosilane in 50 ml of THF was added dropwise to a slurry of 3.8 g (0.10 mol) of lithium aluminum hydride in 100 ml of THF. After the addition was complete, the mixture was heated at the reflux temperature for 12 hr. Following decomposition of excess $LiAlH_4$ with 50 ml of dilute hydrochloric acid, the organic layer was separated, dried with magnesium sulfate, and distilled. The yield of **3**, bp 118–120° (760 mm) (reported[8] bp 120°), was 2.5 g (23%). *Anal.* Calcd for C_6H_8Si: C, 66.59; H, 7.45; Si, 25.96. Found: C, 66.78; H, 7.65; Si, 26.19.

Results and Discussion

A. Phenylsilane.—The mass spectral cracking pattern of phenylsilane (**3**) and toluene (**4**) are compared in Table I. The pattern of toluene is quite simple, exhibiting predominantly the parent ion M^+ and $(M-1)^+$. The large $(M-1)^+$ ion has been identified as the

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[1] J. Diekman, J. B. Thomson, and C. Djerassi, *J. Org. Chem.*, **32**, 3904 (1967).

[2] J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **33**, 2271 (1968).

[3] J. Diekman, J. B. Thomson, and C. Djerassi, *ibid.*, **34**, 3147 (1969).

[4] W. J. Richter and A. L. Burlingame, *Chem. Commun.*, 1158 (1968).

[5] K. M. Baker, M. A. Shaw, and D. H. Williams, *ibid.*, 1108 (1969).

[6] W. P. Weber, R. A. Felix, and A. K. Willard, *J. Amer. Chem. Soc.*, **92**, 1420 (1970).

[7] M. E. Freeburger and L. Spialter, *J. Amer. Chem. Soc.*, in press.

[8] A. E. Finholt, A. C. Bond, K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, **69**, 2692 (1947).

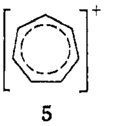
TABLE I

PROMINENT IONS IN THE MASS SPECTRA OF PHENYLSILANE (3), TOLUENE (4), BENZYLTRIMETHYLSILANE (8), AND NEOPENTYLBENZENE (9)

Ion	% of total ionization 3	% of total ionization 4[a]	Ion	% of total ionization 8	% of total ionization 9[b]
M^+	17.4	24.1	M^+	8.4	2.8
$(M-1)^+$	16.8	34.4	$(M-15)^+$	6.1	2.2
$(M-2)^+$	15.6	2.6	$C_7H_8^+$	1.0	18.4
$(M-3)^+$	12.7	1.8	$C_7H_7^+$	9.2	10.0
$C_6H_7^+$	2.8	1.0	$C(CH_3)_3^+$		25.2
$C_6H_6^+$	2.1	1.0	$Si(CH_3)_3^+$	49.7	
$C_6H_5^+$	1.8	1.0	$C_3H_5^+$		7.0
$C_5H_5^+$	2.8	1.0	$C_2H_5^+$		5.8
$C_5H_4^+$	2.3	1.0	$SiCH_3^+$	4.7	
$C_5H_3^+$	2.2	3.3			
SiH^+	2.3				

[a] "Atlas of Mass Spectral Data," Vol. I, E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Ed., Interscience, New York, N.Y., 1969, p 189. [b] Reference a, Vol. II, 1969, p 862.

tropylium ion 5[9] and is common to almost all alkylbenzenes. If an analogous ion were produced from 3, the formal resonance structures would include a carbon-silicon double bond, a system which is extremely unstable.[10] The silicon-containing ions from 3, M^+, $(M - 1)^+$, $(M - 2^+)$, and $(M - 3)^+$ are of approximately equal intensity, suggesting that no resonance stabilization of the $(M - 1)^+$ ion occurs. The structure of the $SiC_6H_7^+$ ion is probably best described as being analogous to the benzyl ion 6, rather than to the tropylium ion 7.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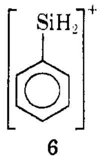
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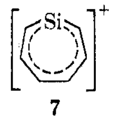
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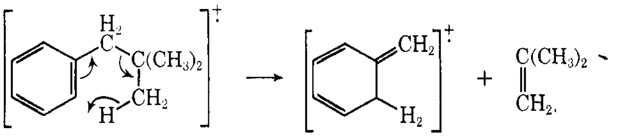
B. Benzylsilanes.—In comparing the data of benzyltrimethylsilane (8) with that of neopentylbenzene (9) (Table I), a striking difference is observed. There is a large amount of $C_7H_8^+$ formed from 9 while only a trace of this ion is produced from 8. The mechanism of $C_7H_8^+$ formation is presented in Scheme I.[9] The generation of this ion from 8 would require the formation of a carbon-silicon double bond in the neutral compound, a process which is not favorable (Scheme II). An essentially equivalent amount of tropylium ion is formed from both 8 and 9; the larger amount of $SiMe_3^+$ from 8, relative to the CMe_3^+ from 9, may reflect either the greater stability of $SiMe_3^+$ or the fact that 8 cannot form the $C_7H_8^+$ ion [note that for 8 ($C_7H_8^+ + C_7H_7^+ + SiMe_3^+$) is 60% of the ion current, for 9 ($C_7H_8^+ + C_7H_7^+ + CMe_3^+$) is 54% of the ion current].

SCHEME I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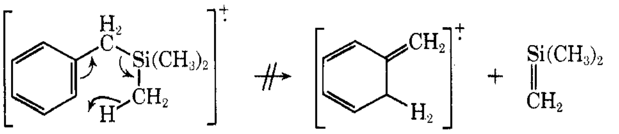
SCHEME II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The $(M - 15)^+$ fragment is larger in 8 than in 9, but this is to be expected. Loss of CH_3 from silicon is common in the cracking patterns of trimethylsilyl ethers,[1,2,4,5] esters,[3] and amines[5]; indeed, the following discussion will provide evidence that it is also a predominant fragmentation mode in phenyltrimethylsilanes.

The ion $C_3H_5^+$, the allylic cation 10, present in aromatic systems possessing a *tert*-butyl group, is absent in all of the trimethylsilyl systems; the analogous silicon-containing ion, $SiC_2H_5^+$, is also absent. Again, for 8 to generate such an ion (11) would require the formation of a carbon-silicon double bond, which appears not to occur.

$$\overset{+}{C}H_2CH{=}CH_2 \longleftrightarrow CH_2{=}CH\overset{+}{C}H_2$$

10

$$\overset{+}{C}H_2SiH{=}CH_2 \longleftrightarrow CH_2{=}SiH\overset{+}{C}H_2$$

11

Substitution of a fluoro group in the ortho, meta, or para position of 8 causes a substantial change in their cracking patterns (Table II). The ion $C_7H_6F^+$, presumably a fluorotropylium ion, is formed, as well as $C_7H_6^+$, which is the second most abundant ion. The appearance of the ion $SiMe_2F^+$ suggests that the substituent is able to migrate to the silicon atom. (This will be seen to be very common in the cracking of substituted phenyltrimethylsilanes.) As might be expected, this ion is most common for the ortho isomer which has the more favorable group juxtaposition. Concomitantly, the $C_7H_6F^+$ species is most abundant in the para case.

TABLE II

PROMINENT IONS IN THE MASS SPECTRA OF *o*-, *m*-, AND *p*-FLUOROBENZYLTRIMETHYLSILANE

Ion	% of total ionization Ortho	% of total ionization Meta	% of total ionization Para
M^+	4.0	3.1	3.7
$(M-15)^+$	0.5	3.6	3.8
$Si(CH_3)_3^+$	27.2	30.7	30.1
$SiCH_3^+$	3.7	4.2	4.7
$C_7H_6F^+$	5.1	5.7	9.6
$C_7H_6^+$	23.0	22.5	23.0
$Si(CH_3)_2F^+$	6.6	3.1	1.9

These data lead to the conclusions that for the benzyltrimethylsilanes (a) fragmentation is similar to that of the carbon analogs except when the fragmentation would produce a carbon-silicon double bond in either the neutral or ionic product species, and (b) if the aromatic ring is substituted, the substituent may migrate to the silicon atom.

C. Substituted Phenyltrimethylsilanes.—The cracking patterns of phenyltrimethylsilane (12), *m*- and *p*-bis(trimethylsilyl)benzene (13 and 14), and *p*-bis(*tert*-butyl)benzene (16) are compared in Table III. They are quite similar, M^+ and $(M - 15)^+$ appearing

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[9] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, New York, N. Y., 1967, p 76.

[10] W. J. Bailey and M. S. Kaufman, Abstracts, 157th National Meeting of the American Chemical Society, April 1969, ORGN 57.

TABLE III

PROMINENT IONS IN THE MASS SPECTRA OF PHENYLTRIMETHYLSILANE (**12**), *m*- AND *p*-BIS(TRIMETHYLSILYL)BENZENE (**13** AND **14**), *tert*-BUTYLBENZENE (**15**), AND *p*-BIS(*tert*-BUTYL)BENZENE (**16**)

Ion	% of total ionization				
	12	**13**	**14**	**15**[a]	**16**[b]
M^+	9.3	11.9	11.3	10.3	4.4
$(M - 15)^+$	62.5	72.0	71.9	36.9	32.9
$C_7H_7^+$	1.0	1.0	1.0	16.8	2.1
$C_4H_9^+$	1.0	1.0	1.0	1.0	6.4
$Si(CH_3)_3^+$	1.0	6.3	5.4		
$C_3H_5^+$	1.0	1.0	1.0	5.8	6.4
$SiCH_3^+$	5.1	1.0	1.0		
$(M - 30)^{2+}$		4.9	3.2		1.6

[a] "Atlas of Mass Spectral Data," Vol. I, E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Ed., Interscience, New York, N. Y., 1969, p 670. [b] Reference *a*, Vol. II, 1969, p 1331.

as the predominant ionic species. The loss of methyl from the silane [affording the $(M - 15)^+$ ion] is the most common fragmentation in all of the substituted species with the exception of some ortho compounds. The $C_3H_5^+$ appears only for the *tert*-butyl species; $SiC_2H_5^+$ is not observed for the silicon species (*vide supra*).

It is interesting to note that virtually no tropylium ion is formed from **12**, **13**, or **14**. Although the formation of $C_7H_7^+$ would require the migration of a methyl fragment into the ring, preceding or concurrent with the loss of a silicon fragment, this ion is observed only when the phenyl ring is substituted (see following discussion). The necessary requirement for this migration appears to be the substituent on the ring. Both bis(trimethylsilyl) compounds afford unusually large doubly charged ions, $(M - 30)^{2+}$, as does *p*-bis(*tert*-butyl)benzene.

Upon comparison of *o*-, *m*-, and *p*-methylphenyltrimethylsilane (**17**, **18**, and **19**) with *m*-methyl-*tert*-butylbenzene (**20**) (Table IV), similarities are again observed.

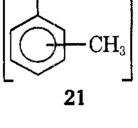
TABLE IV

PROMINENT IONS IN THE MASS SPECTRA OF *o*-, *m*-, AND *p*-METHYLPHENYLTRIMETHYLSILANE (**17**, **18**, AND **19**) AND *m*-METHYL-*tert*-BUTYLBENZENE (**20**)

Ion	% of total ionization			
	17	**18**	**19**	**20**[a]
M^+	5.2	4.8	4.2	7.9
$(M - 15)^+$	21.3	26.1	28.9	32.1
$C_7H_9^+$	1.5	1.6	1.4	4.3
$C_7H_7^+$	3.4	4.4	5.5	4.1
$C_7H_6CH_3^+$	1.9	1.8	1.1	10.4
$SiC_6H_6CH_3^+$	7.9	3.2	2.4	
$Si(CH_3)_3^+$	6.1	3.4	1.5	
$C_3H_5^+$	1.0	1.0	1.0	5.6
$C_3H_3^+$	2.2	3.0	3.0	4.0

[a] "Atlas of Mass Spectral Data," Vol. II, E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Ed., Interscience, New York, N. Y., 1969, p 864.

The ion $SiC_6H_6CH_3^+$, analogous to $C_7H_6CH_3^+$, is much larger for the ortho isomer than for the meta or para isomer. The most probable structure(s) for this ion are **21** and/or **22**, if one excludes the silicon analog of the tropylium ion, *vide supra*. No choice is possible on the basis of the present investigation.



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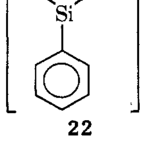

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The chlorophenyltrimethylsilanes show interesting effects (Table V) of substituent position. The tropylium ion is formed in all cases, but in the highest percentage from the ortho isomer. This requires both the migration of methyl from silicon to the ring and removal of chlorine from the ring. The ortho isomer also affords appreciable amounts of $SiC_6H_6Cl^+$ and $SiC_8H_9^+$, the former being the chlorine analog of **21** or **22** and the latter involving loss of CH_3 and Cl (possibly as CH_3Cl) from the parent. Unlike the *tert*-butyl case, no chlorotropylium ion, $C_7H_6Cl^+$, is formed from the silanes. All of the chloro isomers produce some $SiCl^+$, indicating a migration of chlorine to silicon.

TABLE V

PROMINENT IONS IN THE MASS SPECTRA OF *o*-, *m*-, AND *p*-CHLOROPHENYLTRIMETHYLSILANE (**23**, **24**, AND **25**) AND CHLORO-*tert*-BUTYLBENZENE (**26**)

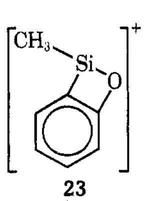
Ion	% of total ionization			
	23	**24**	**25**	**26**[a]
M^+	8.7	12.2	11.2	10.0
$(M - 15)^+$	44.0	76.0	76.9	37.0
$C_7H_7^+$	14.2	3.4	2.5	0.9
$C_7H_6Cl^+$	1.0	1.0	1.0	15.8
$SiC_6H_6Cl^+$	14.0	1.0	1.0	
$SiC_8H_9^+$	8.4	1.0	1.0	
$C_3H_5^+$	1.0	1.0	1.0	6.5
$SiCl^+$	3.3	2.6	2.5	

[a] "Atlas of Mass Spectral Data," Vol. II, E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Ed., Interscience, New York, N. Y., 1969, p 1099. The position of the chloro group is not specified.

Data for the substituents fluoro, methoxy, phenyl, and trifluoromethyl are presented in Table VI. Corresponding data for the *tert*-butyl compounds are not available.

The fluoro case parallels the chloro case. Tropylium ion is formed from all isomers but in the highest percentage from the ortho; $SiC_6H_6F^+$ (fluoro **21** or **22**) is also large for the ortho. A constant, and unexpectedly large, amount of SiF^+ is formed from all the isomers.

The methoxy series shows the same trend, $C_7H_7^+$ being largest for the ortho; however, the methoxy analog of **21** or **22** is not detected. The ortho isomer has a prominent ion of the formula $SiC_6H_4OCH_3^+$, a very strange product requiring loss of three methyl groups which may be formulated as **23** or **24**. Other possibilities exist, but these two appear the most reasonable in light of data from trimethylsilyl ethers.[1,2] Strangely, no $SiOMe^+$ was observed.



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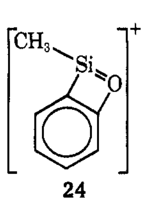

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The biphenyl series (*i.e.*, with phenyl as the substituent) afford very simple patterns, possibly due to the strength of the phenyl–phenyl bond. The ortho isomer produces a large fragment corresponding to $C_{12}H_8$-$SiCH_3^+$ which is presumed to have the fluorene-type

TABLE VI

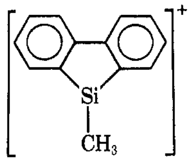
PROMINENT IONS IN THE MASS SPECTRA OF SUBSTITUTED PHENYLTRIMETHYLSILANES

	% of total ionization					
	Fluorophenyltrimethylsilane			Methoxyphenyltrimethylsilane		
Ion	Ortho[a]	Meta[b]	Para[c]	Ortho[d]	Meta[e]	Para[f]
M^+	3.8	3.8	3.6	8.0	18.8	10.2
$(M - 15)^+$	8.9	21.9	27.1	21.5	49.7	64.1
$C_7H_7^+$	17.0	6.6	5.2	6.4	2.8	2.5
$Si(CH_3)_3^+$	1.4	2.3	1.7	1.5	4.0	2.0
$SiCH_3^+$	2.6	6.0	5.9	3.1	2.9	3.5
SiF^+	14.4	14.0	14.9			
$SiC_6H_6F^+$	9.5	0.8	1.3			
$SiC_6H_4OCH_3^+$				39.6	5.6	2.8

	Phenylphenyltrimethylsilane			Trifluoromethylphenyltrimethylsilane		
Ion	Ortho[g]	Meta[h]	Para[i]	Ortho[j]	Meta[k]	Para[l]
M^+	12.9	20.6	14.5	1.9	3.5	5.6
$(M - 15)^+$	43.8	48.7	47.5	9.1	56.1	54.6
$C_7H_7^+$	1.0	1.0	1.0	5.6	1.0	0.7
$Si(CH_3)_3^+$	1.0	1.9	2.5	1.9	1.2	1.2
$SiCH_3^+$	1.0	3.1	4.2	0.9	1.2	1.5
$C_{12}H_8SiCH_3^+$	25.9	3.5	4.0			
SiF^+				2.1	1.1	0.9
$SiF(CH_3)_2^+$				10.0	2.50	2.40
$C_3F_2SiCH_3^+$				8.0	1.0	1.0
$C_3F_2SiH^+$				11.9	1.0	1.0

Registry No.: [a] 1842-26-8; [b] 7217-41-6; [c] 455-17-4; [d] 704-43-8; [e] 17876-90-3; [f] 877-68-9; [g] 17049-39-7; [h] 17938-21-5; [i] 1625-88-3; [j] 312-92-5; [k] 4405-40-7; [l] 312-75-4.

structure **25**. The closely related compound, bis(*o*-biphenyl)silane (**28**), has been reported to afford[11] only



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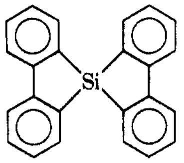

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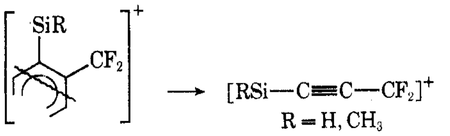
the parent ion under electron impact, an observation confirmed by this laboratory.

The trifluoromethyl compounds show the typical fragments M, $(M - 15)^+$, and $C_7H_7^+$, but the fragments $C_7H_6CF_3^+$ and $SiC_6H_6CF_3^+$, analogous to those formed in the halogen substituted compounds, are absent. A fragment in which fluorine has migrated to the silicon, $SiFMe_2^+$, is present in all three isomers although in largest amount for the ortho. Two additional fragments, $C_3F_2SiCH_3^+$ and $C_3F_2SiH^+$, are formed from the ortho, presumably the result of scission of the aromatic ring (Scheme III).

SCHEME III

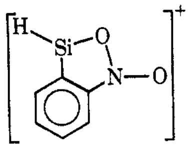


The three nitrophenyltrimethylsilane isomers produce fragments dissimilar to the other compounds (Table VII). Tropylium ion is still present, but the parent ion is substantially reduced, particularly in the ortho case. This ortho compound produces fragments corresponding to $SiC_6H_5NO_2^+$ and $SiC_6H_5NO^+$ which can be depicted by structures **26** and **27**, respectively. When the nitro group is meta or para, fragments which have lost the NO_2 group are produced, *e.g.*, $SiC_6H_9^+$, $SiC_6H_{10}^+$ (because of the large H/C ratio of these ions, they probably contain methyl groups and represent scission of the aromatic ring), and $SiC_7H_7^+$.

TABLE VII

PROMINENT IONS IN THE MASS SPECTRA OF
o-, *m*-, AND *p*-NITROPHENYLTRIMETHYLSILANE

	% of total ionization		
Ion	Ortho	Meta	Para
M^+	1.0	1.0	1.7
$(M - 15)^+$	17.9	20.4	22.4
$C_7H_7^+$	4.6	1.2	1.0
$Si(CH_3)_3^+$	4.0	9.1	8.7
$SiCH_3$	6.3	5.5	8.6
$SiC_6H_5NO_2^+$	8.1	0.5	0.9
$SiC_6H_9^+$	1.0	7.3	1.8
$SiC_6H_{10}^+$	1.0	3.0	8.1
$SiC_6H_5NO^+$	9.9	1.2	2.2
$C_7H_6NO_2^+$	1.8	1.0	1.0
$C_4H_5^+$	0.3	4.3	3.7
$C_7H_7Si^+$	0.6	10.0	8.1
$C_7H_8Si^+$	0.7	1.3	2.1



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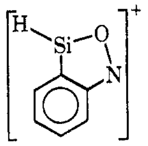

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In summary, the cracking patterns of all the substituted phenyltrimethylsilanes appear similar to the *tert*-butylbenzene analogs with the following exceptions. First, a methyl group may migrate from silicon into the ring producing the tropylium ion. This happens only if the ring is substituted, is most prevalent for halogen substitution, and, for any given substituent, is greatest for the ortho isomer. A direct corollary of this observation is the fact that in the case of halogen substituents, the substituent may migrate to the silicon atom. The degree of this migration, insofar as is measured by the

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[11] R. Coutant and M. Levy, Aerospace Research Laboratories, Technical Report 69-0213, 1969.

amount of SiX^+ produced, is independent of the position of the substituent. Second, no ion corresponding to allyl (*e.g.*, $SiC_2H_5^+$) is formed in any of the cases. This would require a carbon–silicon double bond, the resulting fragments of which are never observed. Third, ions of the general formula $SiC_6H_6X^+$ are observed when methyl or halogen is the substituent corresponding to the structures **21** or **22**. A distinction between which of these is present (ineeed, both may be) is not possible at this time. Fourth, anomalies appear in the ortho cases when a particularly stable ion may be formed, for example, **23**, **24**, or **25**. The nitro and the trifluoromethyl derivatives appear to undergo a fragmentation of the aromatic ring which does not occur in the other compounds.

Registry No.—**3,** 69-45-31; **4,** 108-88-3; **8,** 770-09-2; **9,** 1007-26-7; **12,** 768-32-1; **13,** 2060-89-1; **14,** 13183-70-5; **15,** 98-06-6; **16,** 1012-72-2; **17,** 7450-03-5; **18,** 3728-44-7; **19,** 3728-43-6; **20,** 1075-38-3; **23,** 15842-76-9; **24,** 4405-42-9; **25,** 10557-71-8; **26,** 27378-66-1; *o*-fluorobenzyltrimethylsilane, 1833-40-5; *m*-fluorobenzyltrimethylsilane, 772-48-5; *p*-fluorobenzyltrimethylsilane, 706-25-2; *o*-nitrophenyltrimethylsilane, 15290-22-9; *m*-nitrophenyltrimethylsilane, 15290-24-1; *p*-nitrophenyltrimethylsilane, 4405-33-8.

Studies in Boron Hydrides. IV. Stable Hydride Meisenheimer Adducts[1]

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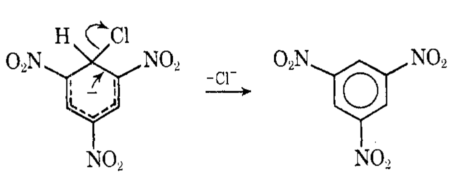
Received September 4, 1970

The addition of hydride from the octahydrotriborate ion to 1-substituted 2,4,6-trinitrobenzenes affords a stable C_3-hydride Meisenheimer adduct. Concurrent with this addition reaction is hydride displacement of the C_1 substituent to form 1,3,5-trinitrobenzene. Under the reaction conditions, 1,3,5-trinitrobenzene is reduced to a monohydride Meisenheimer adduct. Displacement of the C_1 substituent by hydride is favored by substituents which can coordinate with the developing B_3H_7 moiety in the transition state.

Severin[2-4] demonstrated that the reduction of nitroaromatic compounds with sodium tetrahydroborate under alkaline conditions produced the dihydro or polyhydro product. Thus, 1,3,5-trinitrobenzene (**1**), and 1-X-2,4-dinitrobenzene (X = Cl, CH_3, H, etc.) afforded 1,3,5-trinitrocyclohexane and 2-X-3,5-dinitrocyclohex-1-ene, respectively. Kaplan[5] has shown that the reduction of 1-X- or 1,3-X,Y-2,4,6-trinitrobenzenes (X,Y = Br, Cl, OCH_3) under identical conditions yields 1,3,5-trinitrocyclohexane as the sole product. This transformation was formulated[5] for 1-chloro-2,4,6-trinitrobenzene as occurring by attack of hydride at C_1 to produce the anion **2** which rearomatizes by loss of chloride to form **1**. Subsequent reduction of **1** affords 1,3,5-trinitrocyclohexane.

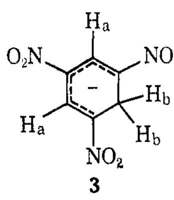


2 **1**

To test this suggested mechanism for the conversion of **1** and mono- and disubstituted trinitrobenzenes to 1,3,5-trinitrocyclohexane, the reaction of these substrates with some hydropolyborate ions which would be weaker hydride donors than tetrahydroborate ion was investigated. By decreasing the formal reduction potential of the hydride donor, it might be possible to interrupt the reduction at an intermediate stage, thereby permitting the isolation of cyclohexadienyl-type products.

Results and Discussion

The reaction of **1** with the *nido*hydropolyborate ions $B_3H_8^-$, $B_9H_{14}^-$, $B_{10}H_{13}^-$, $B_{10}H_{14}^{2-}$, and $B_{10}H_{15}^-$ [6] in such solvents as acetone, acetonitrile, dimethyl sulfoxide, and nitromethane resulted in the formation of dark purple solutions which had absorption maxima at 478 and 582 nm. The position of these absorption maxima are similar to those displayed by 1:1 Meisenheimer adducts of **1** with cyanide,[7] thiophenoxide,[8] and sulfite[9] ions, and piperidine.[10] For preparative work, tetramethylammonium octahydrotriborate proved to be the most convenient reducing agent. On mixing chilled acetonitrile solutions of the reactants, glistening, purple-black crystals separated which analyzed for the tetramethylammonium salt of the hydride Meisenheimer adduct **3**.



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Confirmation of this structural assignment was obtained from the nmr spectrum in dimethyl sulfoxide. This spectrum exhibited lines at $\delta_{Me_4N^+}$ 3.12 (6),[11] δ_{H_b} 3.87 (1.1), and δ_{H_a} 8.24 (1). The line position found for H_a is almost identical with those reported for H_a in the Meisenheimer adducts of **1** with hydroxide

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[1] Part III: A. R. Siedle and T. R. Hill, *J. Inorg. Nucl. Chem.*, **31**, 3874 (1969).

[2] T. Severin and R. Schmitz, *Chem. Ber.*, **95**, 1417 (1962).

[3] T. Severin and M. Adam, *ibid.*, **96**, 448 (1963).

[4] T. Severin, R. Schmitz, and M. Adam, *ibid.*, **96**, 3076 (1963).

[5] L. A. Kaplan, *J. Amer. Chem. Soc.*, **86**, 740 (1964).

[6] The ions $B_6H_6^{2-}$, $B_9H_{10}^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{20}H_{18}^{2-}$ were found to be unreactive.

[7] A. R. Norris, *Can. J. Chem.*, **45**, 2703 (1967).

[8] M. R. Crampton, *J. Chem. Soc. B*, 1208 (1968).

[9] M. R. Crampton, *ibid.*, 1341 (1967).

[10] M. R. Crampton and V. Gold, *ibid.*, 23 (1967).

[11] Chemical shifts are in parts per million downfield from internal tetramethylsilane. Relative intensities are in parentheses; H_a is used as reference.