was fractionated in a packed column to give 1017 g. (84% yield) of $CF_3(CF_2)_3H$ boiling at 14° at 740 mm. The molecular weight of this product was 220 (theoretical for C_4F_9H, 220). The infrared spectrum of this compound indicated the presence of C–H absorption at 3015 cm.$^{-1}$.

Anal. Calcd. for C_4F_9H: C, 21.8; F, 77.7. Found: C, 21.7; F, 77.4.

Acknowledgments.—The authors would like to thank Minnesota Mining and Manufacturing Company for permission to publish these data. The assistance of Mr. R. J. Koshar, Mr. W. A. Severson, Dr. P. W. Trott and others participating in the experimental work is appreciated. Thanks is also extended to Dr. H. E. Freier, Dr. W. E. Keiser and Mr. D. G. Weiblen of the Analytical Section, Central Research Department, for the analytical determinations and the infrared spectrograms.

ST. PAUL, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Hydrogen Chloride Cleavage of Some Trimethylarylsilanes

BY ROBERT A. BENKESER AND HENRY R. KRYSIAK

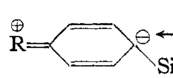
RECEIVED MARCH 20, 1953

A series of *m*- and *p*-substituted aryltrimethylsilanes has been cleaved with hydrogen chloride in glacial acetic acid, and the following order of decrease in ease of cleavage has been noted: *p*-methoxyphenyl and *p*-dimethylaminophenyl > *p*-tolyl > *m*-methoxyphenyl > *m*-tolyl > phenyl > *p*-chlorophenyl > *m*-chlorophenyl > *m*-dimethylaminophenyl. A differential method of analysis of the cleavage product which involves total titration and a gasometric procedure is described. An attempted empirical correlation between the ease of cleavage of the aryltrimethylsilanes and Hammett substituent constants indicates that the *m*-dimethylamino group does not follow the trend of the other groups and that a dimethylammonium ion is undoubtedly the important species present rather than the dimethylamino group. This correlation also appears to indicate that it may be possible to carry out side-chain reactions involving electrophilic reagents with a minimum of cleavage of the trimethylsilyl group if a substituent is present on the aromatic nucleus whose σ-value is more positive than +0.4. Some evidence is cited for this prediction.

A considerable interest has been shown recently in the cleavage of arylalkylsilanes by acidic reagents.[1a,b,c,d,e]

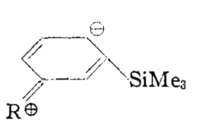
Gilman and Marshall[1a] have shown that, under the influence of hydrogen chloride in a glacial acetic acid solvent, the lability of the trimethylsilyl group in *p*-substituted trimethylarylsilanes decreases in the following order: *p*-anisyl and *p*-dimethylaminophenyl > *p*-tolyl > phenyl > *p*-chlorophenyl.

The ease of cleavage by an acidic reagent thus appears to be facilitated when the trimethylarylsilane contains substituents capable of furnishing a high electron density at the aryl C–Si bond. This behavior would be predicted if one visualizes the mechanism to involve a proton attack on the carbon atom holding the silicon (I).



R = ortho-para-director

I



II

One would expect that the ease of cleavage of trimethylarylsilanes with ortho–para-directors substituted meta would be less than if these groups were substituted para, since the electron density at the aryl C–Si bond would be less in the former case than in the latter, making electrophilic attack less likely on the carbon atom holding the silicon (II). Also, one might expect that the relative difference in ease of cleavage between meta- and para-compounds containing strong ortho–para-directors would be less than in the cleavage of weaker ortho–para-directors under the same conditions, because the aromatic ring as a whole would be much richer in electrons in the former case, and thus more susceptible to attack by electrophilic reagents. For example, one might expect a difference in ease of cleavage of only a few per cent. between *m*- and *p*-trimethylsilylphenol, whereas under comparable conditions the difference in ease of cleavage between *m*- and *p*-tolyltrimethylsilane could amount to perhaps 10–20%.

It became of interest, therefore, to prepare a series of these *m*- and *p*-substituted aryltrimethylsilanes, and to cleave them under comparable conditions with hydrogen chloride in glacial acetic acid solvent.

Since it was suspected that the difference in ease of cleavage between some of the isomers containing powerful ortho–para-directing substituents would probably not be too great, an attempt was made to achieve reaction conditions as nearly reproducible as possible.

Experimental

General Cleavage Procedure.—The cleavage apparatus consisted of a 250-ml. 3-neck flask fitted with a thermometer well, gas dispersion tube, and a 300-mm. Allihn condenser to which was connected an efficient trap fitted with stopcocks and a drying tube. To the gas dispersion tube was connected a safety trap, flowmeter, mercury safety valve and a three-way stopcock through which could be introduced either hydrogen chloride or nitrogen.

Dry hydrogen chloride flowing at a rate of 5 millimoles per minute was dispersed through a solution of 0.02 mole of the trimethylarylsilane in 100 ml. of glacial acetic acid[1a] maintained at 112–114°. Ice-water was circulated through the condenser, and the trimethylchlorosilane trap was maintained at −40° by means of a Dry Ice–trichloroethylene-bath. All runs were one hour long. At the conclusion of each run, dry nitrogen was passed through the apparatus for five minutes at the same differential pressure as the hydrogen chloride in order to sweep out any remaining trimethylchlorosilane. The trap was then removed from the

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[1] (a) H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949); (b) H. Gilman and J. F. Nobis, *ibid.*, **72**, 2629 (1950); (c) S. V. Sunthankar and H. Gilman, *ibid.*, **72**, 4884 (1950); (d) H. H. Szmant, O. M. Devlin and G. A. Brost, *ibid.*, **73**, 3059 (1951); (e) G. Illuminati, J. F. Nobis and H. Gilman, *ibid.*, **73**, 5887 (1951).

system and allowed to warm up to *ca.* 25°. During this warming up period, the stopcocks on the trap were periodically opened to release the pressure developed as a consequence of the hydrogen chloride escaping from solution. The trap was finally swept out with dry nitrogen for three seconds and weighed.

The aromatic cleavage product remaining in the acetic acid was worked up as described by Gilman and Marshall.[1a]

Analysis of Trimethylchlorosilane.—Samples of trimethylchlorosilane from all the cleavage runs were tested for the presence of aromatic fragments by means of the Friedel–Crafts reaction[2]; only the tolyltrimethylsilanes and phenyltrimethylsilane gave a positive test. Thus the volatile products resulting from the cleavage of these three compounds consisted of a mixture of trimethylchlorosilane, benzene or toluene, a small amount of dissolved hydrogen chloride, and possibly a small amount of acetic acid.

In order to determine the number of moles of trimethylchlorosilane present in the mixtures, a differential type of analysis was performed. First, a sample of the trimethylchlorosilane was hydrolyzed and titrated against sodium hydroxide to obtain total acidity. Then, a second sample of trimethylchlorosilane was analyzed for the amount of dissolved hydrogen chloride and acetic acid by means of a modified "Grignard machine." The difference between the two values obtained in this manner gave the number of equivalents of trimethylchlorosilane per unit weight of sample and, from this value, the number of moles of trimethylchlorosilane could be determined readily.

The modified portion of the reaction vessel of the active hydrogen apparatus consisted of a tubular vessel about 12 by 3 cm. to which was sealed a cold finger 10 by 2 cm. Near the top was sealed a tube which could be fitted with a serum stopple, and at the opposite side was sealed a stopcock.

The remaining portion of the apparatus to which this reaction flask was connected consisted of the usual gas buret assembly.[3]

After a sample of the trimethylchlorosilane had been transferred, without exposure to the atmosphere, from the trap to the previously weighed reaction flask, the flask was reweighed and connected to the gas buret assembly. The cold finger of the flask was filled with a slush of ice, and about 15 minutes were allowed to elapse in order for the system to come to equilibrium. The system was then balanced to atmospheric pressure. Ethylmagnesium iodide in *n*-butyl ether was introduced into the reaction flask through the rubber serum stopple[4] by means of a hypodermic syringe and needle.[5] From the amount of evolved ethane, the number of equivalents of hydrogen chloride and acetic acid was determined.

The trimethylchlorosilane samples resulting from the cleavage of the trimethylarylsilanes containing relatively non-volatile aromatic cleavage products were analyzed by the above gasometric method only. This was done in order to determine whether a significant amount of acetic acid and hydrogen chloride contributed to the weight of trimethylchlorosilane obtained. The results indicated that the amount of hydrogen chloride and acetic acid present did not change the values of percentages of cleavages by more than 1.5–2.5%, which was within the limits of reproducibility of the cleavage runs.

The gas apparatus was standardized by using a pure sample of benzoic acid dissolved in benzene which had previously been dried over sodium. When the analysis had been carried out, a 94% yield of gas was obtained.

Trimethyl-*p*-methoxyphenylsilane.—To 0.25 mole of *p*-methoxyphenyllithium[6] was added 27 g. (0.25 mole) of trimethylchlorosilane in 100 ml. of ether. From this point, the reaction was carried out and the product worked up essentially in accordance with the directions of Gilman and Nobis.[1b] Upon distillation through a Todd column, there was obtained 25 g. (55%) of a product boiling at 220.5° (747 mm.), n^{20}_{D} 1.5033, d^{20}_{4} 0.9398; MR_{D} calcd. 56.47, MR_{D} found 56.77.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.55. Found: Si, 15.72.

Trimethyl-*m*-dimethylaminophenylsilane.—Trimethyl-*m*-dimethylaminophenylsilane was prepared according to the directions of Ranck[7,8]; yield 84%, b.p. 109–110° (8 mm.). n^{20}_{D} 1.5265.

Trimethyl-*m*-tolylsilane.—To 0.5 mole of *m*-tolyllithium[9] was added a solution of 54 g. (0.5 mole) of trimethylchlorosilane in 100 ml. of ether over a 90-minute period. Upon completion of this addition, stirring and refluxing were continued for an additional two hours, which resulted in a negative Color Test I.[10] After hydrolysis, the reaction mixture was worked up in the usual manner. Distillation yielded 70 g. (84%) of a product,[11a] which boiled at 188.0° (747 mm.), n^{20}_{D} 1.4930.

Trimethyl-*m*-methoxyphenylsilane.—Attempted preparation of trimethyl-*m*-methoxyphenylsilane through the lithium intermediate resulted in negligible amounts of the desired product.

To 6.6 g. (0.27 g.-atom) of magnesium turnings suspended in 100 ml. of ether was added a solution of 51.0 g. (0.27 mole) of *m*-bromoanisole and 100 ml. of ether over a two-hour period. A small amount of ethyl iodide–magnesium mixture was added in order to start the reaction. After all the *m*-bromoanisole had been added, stirring and refluxing were continued for three hours, whereupon 29.5 g. (0.27 mole) of trimethylchlorosilane in 75 ml. of ether was added over a half-hour period. Stirring and refluxing were continued for several hours, after which time the major part of the ether was distilled off. Heating of the reaction mixture on a steam-bath was continued for 24 hours. It was then hydrolyzed with saturated ammonium chloride solution; the resulting layers were separated, and the aqueous layer was extracted with ether. After the combined ether extracts and main reaction product had been dried over Drierite and the ether stripped off, fractional distillation yielded 17.7 g (36%) of a product which boiled at 216° (751 mm.), n^{20}_{D} 1.5020, d^{20}_{4} 0.9383; MR_{D} calcd. 56.47, MR_{D} found 56.57.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.55. Found: Si, 15.59.

Trimethyl-*m*-chlorophenylsilane.[11b,12]—*m*-Chlorophenyllithium was prepared according to the directions of Gilman, *et al.*[13]

To a solution of 0.46 mole of *n*-butyllithium,[14] cooled in an ice-bath and vigorously stirred, was added 88 g. (0.46 mole) of *m*-bromochlorobenzene in 100 ml. of ether over a ten-minute period. The resulting mixture was stirred an additional ten minutes and then 50 g. (0.46 mole) of trimethylchlorosilane in 75 ml. of ether was added over a period of a half-hour. A fairly rapid precipitation of lithium chloride was noted during this time. When all the trimethylchlorosilane had been added, the ice-bath was removed, and stirring was continued for an additional three hours. After hydrolysis, the reaction product was worked up as usual. Fractional distillation yielded 56.5 g. (62%) of a product which boiled at 100.5° (22 mm.), n^{20}_{D} 1.5099, n^{25}_{D} 1.5070.

Trimethyl-*p*-tolylsilane.—This compound[11b] was prepared in accordance with the directions of Gilman and Marshall.[1a] To 0.5 mole of *p*-tolyllithium was added 54.3 g. (0.5 mole)

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(2) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 88.

(3) J. B. Niederl and V. Niederl, "Micromethods of Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 263–265.

(4) Serum stopples size #711 were kindly furnished by Mr. L. F. Woelfling, Faultless Rubber Company, Ashland, Ohio.

(5) H. E. Zaugg and W. M. Lauer, *Anal. Chem.*, **20**, 1022 (1948).

(6) *p*-Methoxyphenyllithium was prepared by the method of J. T. Edward, in H. Gilman and R. A. Benkeser, THIS JOURNAL, **69**, 123 (1947).

(7) R. O. Ranck, M.S. Thesis, Purdue University, 1951.

(8) R. A. Benkeser and H. R. Krysiak, THIS JOURNAL, **75**, 2421 (1953).

(9) H. Gilman, E. A. Zoellner and W. M. Selby, *ibid.*, **54**, 1957 (1932).

(10) H. Gilman and F. Schultz, *ibid.*, **47**, 2002 (1925).

(11) (a) Trimethyl-*m*-tolylsilane has also been prepared satisfactorily through the use of sodium as the coupling agent (H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, *ibid.*, **73**, 3798 (1951); (b) prepared also through the Grignard reagent, ref. 10.

(12) Trimethyl-*m*-chlorophenylsilane has been prepared through the Grignard reagent (J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2924 (1949)).

(13) H. Gilman, R. V. Christian and S. M. Spatz, *ibid.*, **68**, 979 (1946).

(14) R. G. Jones and H. Gilman in Roger Adams, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 352.

of trimethylchlorosilane in 100 ml. of ether over a period of one hour. The reaction mixture was allowed to reflux and stir overnight, after which time it was hydrolyzed and worked up as usual. Fractional distillation yielded 59 g. (72%) of a product boiling at 192° (745 mm.), n^{20}D 1.4915.

Trimethyl-*p*-dimethylaminophenylsilane.—This compound was prepared as described by Gilman and Marshall.[1a] From 0.37 mole of *p*-dimethylaminophenyllithium and 0.37 mole of trimethylchlorosilane was obtained 53.7 g. (76%) of a material which boiled at 136° (20 mm.), n^{20}D 1.5344.

Results and Discussion

Table I lists the results of the cleavage runs.

TABLE I

HYDROGEN CHLORIDE CLEAVAGE OF TRIMETHYLARYLSILANES[a]

ArSiMe₃, Ar–	Yield, % Me_3SiCl	ArH
Phenyl[b]	78	
m-Tolyl	81	[c]
p-Tolyl	93	
m-Dimethylaminophenyl	8	[d]
p-Dimethylaminophenyl	94	
m-Chlorophenyl	11	[c]
p-Chlorophenyl[e]	40	
m-Methoxyphenyl	82	[c]
p-Methoxyphenyl	94	

[a] All cleavage runs were carried out over a one-hour period with 0.02 mole of the trimethylarylsilane. [b] Kindly supplied by Mr. D. S. Holton. [c] Identified as the 2,4-dinitro derivative. [d] No dimethylaniline could be isolated for identification purposes; however, the uncleaved arylsilane was isolated and presumed to be trimethyl-*m*-dimethylaminophenylsilane from the refractive index and m.p. of its methiodide (195°, uncor.). [e] Kindly supplied by Mr. D. J. Foster.

The results thus obtained cannot be employed in an absolute sense, but must be used merely as comparative values characteristic of the apparatus that was used. Such factors as variable flow rates of hydrogen chloride and insufficient sweeping out of the system with dry nitrogen at the conclusion of a run affect the yield of trimethylchlorosilane obtained. For example, when the rate of hydrogen chloride was approximately doubled, the yield of trimethylchlorosilane obtained from phenyltrimethylsilane as analyzed by the differential method was increased about 10%. Also, when trimethyl-*m*-tolylsilane was cleaved with hydrogen chloride under our standardized conditions, and at the conclusion of the run, dry nitrogen was passed through the system for one minute instead of five, the yield of cleavage product dropped 12%. With conditions as nearly reproducible as possible, results could be duplicated within 2–3%.

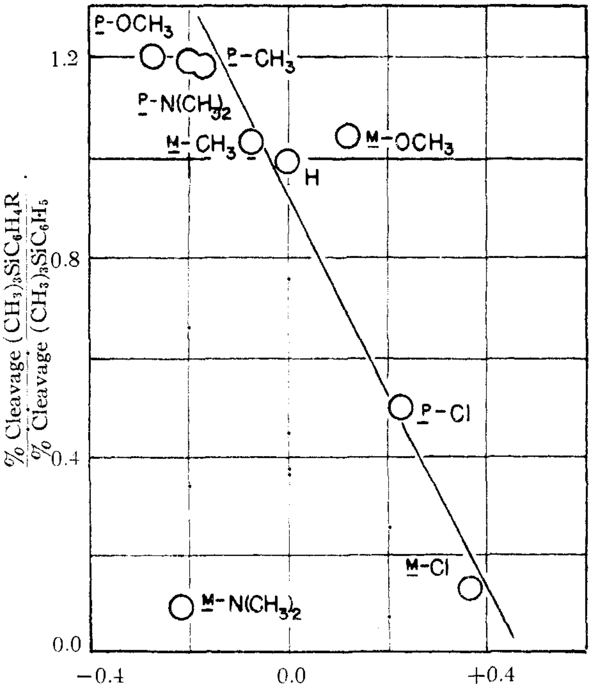


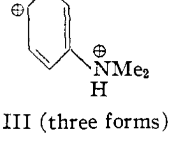
Fig. 1.—Empirical relationship between ease of cleavage of substituted-phenyltrimethylsilanes by hydrogen chloride in refluxing glacial acetic acid in one hour, and Hammett substituent constants.

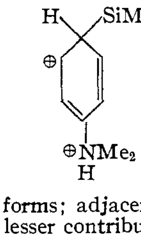
The ease of cleavage as shown by Table I follows the expected order, which agrees with that obtained by Gilman and Marshall.[1a] The ease of cleavage of the two trimethylchlorophenylsilane isomers also bears out nicely the deactivating influence of the chlorine atom.

An apparent anomaly is the great difference in ease of cleavage of the two trimethyl-dimethylaminophenylsilanes. The substituent group undoubtedly is *not* *m*-dimethylamino, but a rather stable dimethylammonium ion at the temperature in question by virtue of which its strong *I*-inductive influence might thereby diminish the ease of cleavage of the trimethylsilyl group.

It might be argued that the *p*-dimethylamino isomer should also exist to a large extent in the protonated or salt form and consequently be more resistant to cleavage than was actually found to be the case. It has been shown that the σ_p-value for the trimethylsilyl group in dimethylanilines is positive, whereas σ_m is negative.[8] Thus the *p*-amine is a somewhat weaker base than the *m*-amine. Under the vigorous cleavage conditions it is not unlikely that these effects are somewhat augmented. As a consequence the salt of the *p*-amine would be more highly dissociated than that of the *m*-amine.

If *both* amines existed largely in the salt form, considerations of transition states such as III and IV for the cleavages analogous to those proposed for nitration of phenyltrimethylammonium salts[15] would lead to a conclusion contrary to that found experimentally, *i.e.*, the meta isomer would be cleaved more readily than the para. On the other hand, if both isomers existed largely as the free amines, one might expect the difference in ease of cleavage to amount to perhaps 10–20%, and thus


III (three forms)


IV (three forms; adjacent charge form, lesser contribution)

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(15) J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, **73**, 2181 (1951).

be comparable to that observed in the case of the methoxyphenyltrimethylsilanes. To account for the large difference in cleavage of the amines, therefore, one has to assume that the equilibrium between the free *m*-amine and its salt lies largely in the direction of the salt form, while that of the *p*-amine lies principally in the direction of the free base.

In Fig. 1, we have attempted to correlate the ease of cleavage of the aryltrimethylsilanes in an *empirical* manner with a convenient standard of reference, namely, the substituent constants of Hammett.[16,17] Two important deductions can be made from this plot. First, it is obvious that the *m*-dimethylamino group is not in line with the trend of the other groups as has already been discussed. Secondly, if the slope of the line be continued to zero cleavage, it is seen to intersect the abscissa at a σ value slightly greater than +0.4. One might thus predict that it would be possible to carry out side-chain reactions involving electrophilic reagents or in acid media with a minimum of cleavage of the trimethylsilyl group if a substituent is present on the aromatic nucleus the σ-value of which is more positive than +0.4. Some substantiation of this prediction was obtained when we were able to prepare the acid chlorides of both the *m*- and *p*-trimethylsilylbenzoic acids using thionyl chloride with no observable cleavage of the trimethylsilyl group.[8,18,19,20]

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(16) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

(17) S. V. Sunthankar and H. Gilman, *J. Org. Chem.*, **15**, 1200 (1950), pointed out the interesting relationship between the acid cleavage of the aryl C–Si bond and the σ constants of substituents in a benzene ring.

(18) From *p*-trimethylsilylbenzoic acid was obtained *via* the acid chloride, a quantitative yield of *p*-trimethylsilylbenzamide, m.p. 155°. *Anal.* Calcd. for $C_{10}H_{15}NOSi$: N, 7.25; Si, 14.52. Found: N, 7.29; Si, 14.32. R. A. Benkeser and R. E. Robinson, unpublished results.

(19) Work now in progress in this Laboratory involving the successful Friedel–Crafts acylation of aromatic systems with silicon-containing aroyl halides offers further support of the stability of the aryl-C-Si linkage in these cases.

(20) K. C. Frisch and P. D. Schroff, THIS JOURNAL, **75**, 1249 (1953), prepared *p*-trimethylsilylbenzoyl chloride using thionyl chloride in the presence of pyridine as a hydrogen chloride acceptor because they feared that the trimethylsilyl group would be cleaved off; however, we have prepared both the *m*- and *p*-trimethylsilylbenzoyl chlorides in essentially quantitative yields by simply refluxing the silicon-containing acids in excess thionyl chloride for about a 90-minute period. *p*-Trimethylsilylbenzoyl chloride, b.p. 75–76° (1 mm.), n^{20}_{D} 1.5315. *Anal.* Calcd. for $C_{10}H_{13}ClOSi$: Si, 13.19. Found: Si, 13.09.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Alkaline Cleavage of Tetrasubstituted Silanes

BY HENRY GILMAN, A. G. BROOK AND LEWIS S. MILLER

RECEIVED APRIL 17, 1953

A qualitative study of the rate of cleavage of a number of tetrasubstituted silanes by potassium hydroxide in various solvents has been made. The results indicate a relationship between the ease of cleavage of a hydrocarbon radical from silicon and the electron-attracting properties of the radical. The results are consistent with a cleavage mechanism involving a pentacovalent silicon atom in the transition state. (Trichloromethyl)-triphenylsilane has been found to be cleaved by both *n*-butyl- and phenyllithium.

Many investigations have been reported whose ultimate purpose has been to establish a general series by which the relative ease of cleavage of an organic radical from a metal could be predicted. While silicon is not generally considered to be a metal, it has been found to behave in a manner qualitatively analogous to metals in cleavage reactions. Although a comprehensive survey of the cleavage reactions of organosilicon compounds has never been made, numerous isolated examples by both acidic and alkaline reagents have been reported, particularly of the various halogen- and oxygen-substituted alkylsilanes. The purpose of the present study was to extend the realm of these investigations to the field of alkaline cleavage of tetrasubstituted aryl- and mixed arylalkylsilanes, and to attempt to correlate the ease with which a hydrocarbon fragment, as a carbanion, was cleaved from silicon by the nucleophilic reagent with the acid strength of the parent hydrocarbon.

To summarize briefly the work previously reported, it has been found that silicon–halogen bonds are readily cleaved by nucleophilic reagents,[1,2] silicon–hydrogen,[2] silicon–oxygen,[1a,2] and silicon–silicon bonds[2] are less readily cleaved and silicon–carbon bonds are least readily cleaved by these reagents. In particular, it has been observed that alkylsilanes are quite stable in the presence of alkali,[3] but substitution by halogen leads to less stable compounds more easily cleaved by base, particularly when highly substituted.[4] Unsaturated alkylsilanes such as allyltrimethylsilane appear to be less stable than the saturated analogs.[5]

When unsaturation in the form of phenyl groups is introduced, the tetrasubstituted silanes become quite susceptible to cleavage by nucleophilic reagents. Thus benzyl-, benzhydryl- and triphenylmethyltrimethylsilane are smoothly cleaved by potassium or sodium amide, or by the alkali alkoxides,[6] and both trimethyl- and triethyl-1-indenylsilane are cleaved by alkali, although the related trimethyl-1-indanylsilane is quite stable.[7] The

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(1) (a) F. S. Kipping, *Proc. Roy. Soc.* (*London*), **159**, 139 (1937); S. R. Robinson, *Sci. J. Roy. Coll. Sci.*, **15**, 24 (1945); (b) C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

(2) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951.

(3) C. Pape, *Ann.*, **222**, 354 (1884).

(4) R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945); R. H. Krieble and J. R. Elliott, *ibid.*, **68**, 2291 (1946); F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 485 (1946); E. Larsson and L. O. Knopp, *Acta Chem. Scand.*, **1**, 268 (1947) [*C. A.*, **42**, 5416 (1948)].

(5) Yu. N. Vol'nov and A. Reutt, *J. Gen. Chem. U.S.S.R.*, **10**, 1600 (1940) [*C. A.*, **35**, 2853 (1941)]; L. H. Sommer, L. J. Tyler and F. C. Whitmore, THIS JOURNAL, **70**, 2872 (1948).

(6) C. R. Hauser and C. R. Hance, THIS JOURNAL, **73**, 5846 (1951); see also, L. S. Miller, Doctoral Dissertation, Iowa State College, 1950.

(7) L. H. Sommer and N. S. Marans, THIS JOURNAL, **73**, 5135 (1951).