to be favorable circumstances may reflect the requirement that the transition state in the formation of the salt be solvated to reduce its energy to an accessible value. The solvation weakens the electrostatic interactions which provide chemical inertia to the formation of the salt. And though the reverse reaction, the decomposition of the salt, derives a driving-force from the electrostatic interactions under discussion, this is diminished because the ions must be solvated to remain in solution, a condition which applies to the transition state though to a lesser extent. In this way the electrostatic effect is so weakened as to leave the nonelectrostatic factors dominant.

Acknowledgment.—This work was supported in part by a grant from the Research Corporation, for which we wish to express our sincere appreciation.

CHICAGO, ILLINOIS

[CONTRIBUTION NO. 64 FROM THE CENTRAL RESEARCH DEPARTMENT OF MINNESOTA MINING AND MANUFACTURING COMPANY]

Pyrolyses of the Salts of the Perfluoro Carboxylic Acids[1]

BY J. D. LAZERTE, L. J. HALS, T. S. REID AND G. H. SMITH

RECEIVED JANUARY 14, 1953

The thermal decomposition of a number of salts of the straight chain perfluoro acids has been investigated. From the sodium salts, terminally unsaturated perfluoro olefins were prepared in yields ranging from 65 to 100%. The reaction is represented by the equation $C_nF_{2n+1}CF_2CF_2CO_2Na \rightarrow C_nF_{2n+1}CF{=}CF_2 + CO_2 + NaF$. Salts of other metals occurring in groups I, II and III of the periodic table, gave varying yields of olefins. Silver perfluorobutyrate and silver perfluorocaprylate decomposed to give C_6F_{14} and $C_{14}F_{30}$, respectively. Tetrafluoroethylene was formed when a mixture of CF_3CO_2Na and NaOH was heated. A series of fluorocarbon hydrides, $C_nF_{2n+1}H$ was prepared by heating salts of the perfluoro acids in ethylene glycol.

While the literature contains references to the decomposition of salts of trifluoroacetic acid, no data had been reported on the pyrolyses of salts of the longer chain perfluoro acids until recently.[2] Experimentation with other salts and other reaction conditions warrant further discussion of these pyrolytic reactions at this time.

The formation of an olefin by the decomposition of a salt was first reported by Pagenstecher[3] who found that when an aqueous solution of sodium α-methyl-β-iodobutyrate was warmed, butene-2 was formed. Wislicenus[4] observed that a hot aqueous solution of sodium 2,3-dichlorobutyrate decomposed to give 1-chloropropene. Later Boeseken[5] found that sodium perchloropropionate underwent a similar type of reaction at 25° to give tetrachloroethylene.

While the salts of the straight chain perfluoro acids do not decompose under such mild conditions to give perfluoro olefins, it has been observed in this Laboratory that when certain of the dry salts containing three or more carbon atoms were heated, the following reaction takes place

$$R_fCF_2CF_2CO_2M \longrightarrow R_fCF{=}CF_2 + CO_2 + MF$$

By means of this reaction, excellent yields of perfluoro olefins were obtained. Since many of the perfluoro acids are now available from the electrochemical fluorination[6] of the parent hydrocarbon acids, a simple synthesis of these olefinic compounds is now available.

The yields of perfluoro olefin resulting from the pyrolytic reaction varied widely with the cation present in the salt. The sodium salts consistently gave the highest yields of terminally unsaturated olefins. The thermal decomposition of the sodium salts of the straight chain acids began at about 230° with the rate of decomposition increasing rapidly as the temperature was raised. At 250–260° a rapid, yet controllable, evolution of perfluoro olefin and CO_2 was obtained. The products from many of the reactions were pure enough after treatment with aqueous base to make fractionation unnecessary. The yields, some of the physical properties, and the analytical data obtained for the terminally unsaturated perfluoro olefins prepared from the sodium salts are shown in Table I. Identification of these unsaturates was based on molecular data, oxidation to perfluoro acids,[7] elemental analyses and infrared absorption spectra of the compounds. Each member of the series having three or more carbon atoms had an infrared absorption peak at 1795 cm.$^{-1}$, which is characteristic of the double bond in $C_nF_{2n+1}CF{=}CF_2$.[7,8]

The products resulting from the decomposition of other salts of perfluoro acids are shown in Table II.

Pyrolyses of potassium salts gave good yields of perfluoro olefins. Potassium perfluorobutyrate decomposed to give a 98% yield of perfluoropropene. Potassium perfluorovalerate, not shown in the table, gave both perfluorobutene-1 and perfluorobutene-2 in a ratio of about 1:4. To form the internally unsaturated olefin, a shift of fluorine in the molecule had to occur. With the perfluorobutyric acid salts of the alkaline earth metals it was

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(1) Presented before the Section on Industrial and Engineering Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, 1952.

(2) L. J. Hals, T. S. Reid and G. H. Smith, THIS JOURNAL, **73**, 4054 (1951).

(3) A. Pagenstecher, *Ann.*, **195**, 115 (1879).

(4) J. Wislicenus, *Ann.*, **248**, 297 (1888).

(5) J. Boeseken, *Rec. trav. chim.*, **46**, 841 (1927).

(6) E. A. Kauck and A. R. Diesslin, *Ind. Eng. Chem.*, **43**, 2332 (1951).

(7) T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearlson, THIS JOURNAL, **75**, 2698 (1953).

(8) Infrared curves on the olefins and hydrides have been filed with Dr. E. C. Creitz of the National Bureau of Standards.

Table I

Terminally Unsaturated Perfluoro Olefins

Olefin	Yield, %	B.p., °C.[a]	$n^{25}D$	Mol. weight Calcd.	Mol. weight Found	Analyses Carbon Calcd.	Analyses Carbon Found	Analyses Fluorine Calcd.	Analyses Fluorine Found
$CF_2=CF_2$	90	−74	...	100	99	...	...	...	...
$CF_3CF=CF_3$	97	−29	...	150	150	...	...	...	...
$C_2F_5CF=CF_2$	91	+1	...	200	201	24.0	24.2	76.0	75.9
$C_3F_7CF=CF_2$	90	29	1.2571	250	250	24.0	24.1	76.0	75.9
$C_5F_{11}CF=CF_2$	86	81	1.2782	350	350	24.0	24.1	76.0	75.9
$C_7F_{15}CF=CF_2$	65	123	1.2868	450	...	24.0	24.0	76.0	75.5

[a] At 730–745 mm.

Table II

Pyrolyses of the Salts of Perfluorobutyric Acid

Salt	Dec. temp., °C.	Yield C_3F_6, %	Other fluorinated products
$C_3F_7CO_2Li$	240–250	20	C_3F_7COF, $(C_3F_7CO)_2O$, $C_3F_7CO_2H$
$C_3F_7CO_2K$	215–235	98	.....
$(C_3F_7CO_2)_2Mg$	275–300	< 5	High boiling liquid
$(C_3F_7CO_2)_2Ca$	275–300	<10	C_3F_7COF, $(C_3F_7CO)_2O$, $C_3F_7CO_2H$
$(C_3F_7CO_2)_2Sr$	275–285	25	C_3F_7COF, $C_3F_7CO_2H$
$(C_3F_7CO_2)_2Ba$	265–275	78	.....
$(C_3F_7CO_2)_2Pb$	300–305	<10	C_3F_7COF, $(C_3F_7CO)_2O$, some $C_3F_7CO_2H$
$(C_3F_7CO_2)_2Cu$	290–300	trace	C_3F_7COF, unidentified
$(C_3F_7CO_2)_3Al$	250	< 5	C_3F_7COF, $C_3F_7CO_2H$, C_2F_6
$C_3F_7CO_2NH_4$	180–200	0	$CF_3CF_2CF_2H$
$C_3F_7CO_2Ag$	300–320	45	C_6H_{14}

noted that as the atomic weight of the metal cation increased so did the yield of the perfluoro olefin. Ammonium perfluorobutyrate was the only perfluorobutyric acid salt which did not yield either perfluoropropene or carbonyl-containing compounds, or both. Instead, an almost quantitative yield of $CF_3CF_2CF_2H$ was obtained. Silver perfluorobutyrate decomposed to give C_3F_6 and C_6F_{14}. Silver perfluorocaprylate underwent the same type of reaction to give $C_{14}F_{30}$ in 77% yield. The coupling reaction obtained with the silver salts of the perfluoro acids has interesting possibilities in the synthesis of fluorocarbons.

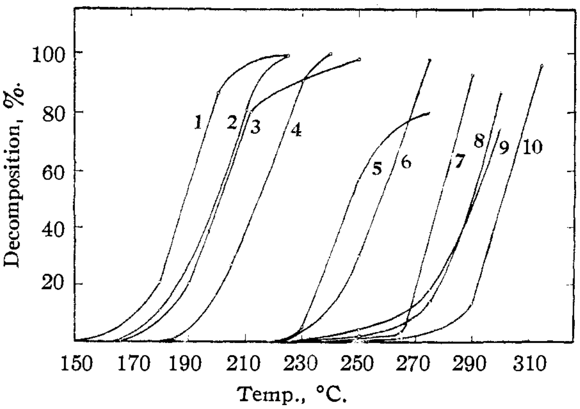

Fig. 1.—Thermal decomposition of some salts of the perfluoro carboxylic acids: samples heated for 30 minutes at 20–25° intervals; 1, n-$C_4F_9CO_2K$; 2, n-$C_3F_7CO_2NH_4$; 3, i-$C_3F_7CO_2Na$; 4, n-$C_3F_7CO_2K$; 5, n-$C_3F_7CO_2Na$; 6, n-$C_5F_{11}CO_2Na$; 7, n-$C_7F_{15}CO_2Ag$; 8, $(n\text{-}C_3F_7CO_2)_2Ba$; 9, $(n\text{-}C_3F_7CO_2)_2Sr$; 10, n-$C_3F_7CO_2Ag$.

Wide differences in the thermal stabilities of some of the salts were noted. To obtain an accurate measure of these differences, small samples were weighed on an analytical balance, then heated for 30 minutes at 20–25° intervals until almost complete decomposition had resulted. The temperature at which 20% decomposition was obtained, was used to make stability comparisons. These values are listed below for a number of salts of perfluorobutyric acid: $C_3F_7CO_2NH_4$, 185°; i-$C_3F_7CO_2Na$, 185°; $C_3F_7CO_2K$, 200°; n-$C_3F_7CO_2Na$, 235°; $(C_3F_7CO_2)_2Ba$, 275°; $(C_3F_7CO_2)_2Sr$, 275°; $C_3F_7CO_2Ag$, 295°. Sodium salts of higher molecular weight straight chain perfluoro acids underwent 20% decomposition at 240–250°. Potassium perfluorovalerate gave 20% decomposition at 20–25° lower than did n-$C_3F_7CO_2K$. Figure 1 is a plot of temperature *vs.* per cent. decomposition from which these values were taken.

Salts of trifluoroacetic acid cannot pyrolyze to form perfluoro olefins in a manner analogous to some of the salts of the higher molecular weight perfluoro acids. Other investigators[9,10] observed that both sodium trifluoroacetate and barium trifluoroacetate gave trifluoroacetyl fluoride and trifluoroacetic anhydride as the predominant decomposition products. No hexafluoroacetone was detected. In the present investigation it was found that lithium and calcium trifluoroacetate decomposed to give these same products. However, when the decomposition of CF_3CO_2Na was carried out in the presence of solid NaOH, a different reaction took place.[11] When the mixture was heated to about 270° a very rapid exothermic reaction occurred to give tetrafluoroethylene along with some trifluoroacetyl fluoride and fluoroform. The minimum yield of tetrafluoroethylene was 32%. As was indicated earlier, the reaction of $C_3F_7CO_2Na$ and solid NaOH gave only perfluoropropene and $CF_3CF_2CF_2H$.

Fluorocarbon hydrides could be prepared in high yield by the addition of water or glycol to the salt. When an aqueous solution of $C_3F_7CO_2Na$ was sealed in a suitable autocalve and heated to 180–200°, a high yield of $CF_3CF_2CF_2H$ resulted. Henne[12] reported the preparation of CF_3H by heating a mixture of CF_3CO_2Na and ethylene glycol

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[9] F. Swarts, *Bull. Sci. Acad. Roy. Belg.*, **8**, 343 (1922).

[10] J. H. Simons, R. L. Bond and R. E. McArthur, This Journal, **62**, 3477 (1940).

[11] U. S. Patent No. 2,601,536 (June 24, 1952); J. D. LaZerte to Minnesota Mining and Manufacturing Company.

[12] A. L. Henne, This Journal, **72**, 299 (1950).

TABLE III

FLUOROCARBON MONOHYDRIDES PREPARED FROM THE SODIUM SALTS OF THE PERFLUORO ACIDS IN ETHYLENE GLYCOL

Hydride	Yield, %	B.p., °C.[a]	$n^{25}\mathrm{D}$	Mol. weight Calcd.	Mol. weight Found	Analyses Carbon Calcd.	Analyses Carbon Found	Analyses Fluorine Calcd.	Analyses Fluorine Found
CF_3CF_2H	98	−50[b]	. . .	120	119	. . .	. . .	. . .	. . .
$CF_3(CF_2)_2H$	97	−16[c]	. . .	170	171	21.2	21.1	78.2	78.0
$CF_3(CF_2)_3H$	84	14[d]	. . .	220	220	21.8	21.7	77.7	77.4
$CF_3(CF_2)_4H$	80	46[e]	. . .	270	271	22.2	22.4	77.5	77.4
$CF_3(CF_2)_6H$	60	94[f]	1.2690	370	. . .	22.7	22.6	77.0	76.7

[a] Approximately 740 mm. [b] Reference (14), b.p. −48.5°. [c] Reference (15), b.p. −17 to −18°. [d] Reference (15), b.p. 14 to 15°. [e] Reference (15), b.p. 45°. [f] Reference (15), b.p. 96 to 97°.

to the reflux temperature of the alcohol. In this Laboratory this method has been found to give excellent yields of the longer chain perfluoro monohydrides. The bulk of the preparations were carried out with the sodium salts. However, an 88% yield of $CF_3CF_2CF_2H$ was obtained from $(C_3F_7CO_2)_2Ba$. Potassium perfluorovalerate in refluxing ethylene glycol gave an 83% yield of $CF_3CF_2CF_2CF_2H$. Table III indicates the fluorocarbon hydrides, along with their yields and properties, obtained from the sodium salts of the perfluoro acids. The infrared absorption spectra of $CF_3(CF_2)_2H$, $CF_3(CF_2)_3H$, $CF_3(CF_2)_4H$, and $CF_3(CF_2)_6H$ all showed absorption due to the C–H band at 2940–2990 cm.$^{-1}$.[13]

Experimental

Preparation of Salts.—The ammonium, lithium, sodium, potassium, calcium, strontium and barium salts of the perfluoro acids were all prepared by neutralizing an aqueous solution of fractionated perfluoro acid with a solution of the hydroxide. Magnesium and lead perfluorobutyrate were made by treating the metal oxides with aqueous perfluorobutyric acid at slightly above 25°. Both salts were very hygroscopic. The $(C_3F_7CO_2)_2Pb$ after vacuum drying was placed in a flask with CCl_4 and further dried by azeotropic distillation. Silver perfluorobutyrate and silver perfluorocaprylate were prepared by treating freshly precipitated Ag_2O with a dilute solution of the perfluoro acid. When dry air was passed into a mixture of finely divided copper powder and excess $C_3F_7CO_2H$ at the reflux temperature of the acid (120°), $(C_3F_7CO_2)_2Cu$ was formed slowly. The procedure reported by Hood and Ihde[16] for the preparation of aluminum salts of the hydrocarbon acids was used to prepare $(C_3F_7CO_2)_3Al$. The reaction between the $AlCl_3$ and the excess $C_3F_7CO_2H$ in the presence of $(C_3F_7CO)_2O$ took place smoothly at 100°. When no more HCl was evolved, the anhydride and excess $C_3F_7CO_2H$ were removed by evaporation and the resulting salt vacuum dried.

The purity of the salts had a great influence on the decomposition reaction. It is suspected that the presence of small quantities of hydrogen-containing salts greatly reduced the yields of the olefin. An inorganic base in the salt undergoing pyrolysis gave a product contaminated with the fluorocarbon monohydride, $C_nF_{2n+1}H$. To avoid this, the *p*H of the salt solution was adjusted to a value between five and seven. Water vapor in the pyrolysis zone also led to the formation of hydrogen-containing compounds.

Pyrolyses Apparatus and Procedures.—The bulk of the experiments were carried out in a Pyrex flask but the reaction went equally well when a stainless steel vessel was used. The rate of decomposition was controlled by varying the amount of current supplied to a Glas-Col mantle. The volatile products were passed through two scrubbers connected in series containing 15% aqueous KOH to remove CO_2 and acidic products. The reaction train was always equipped with a mercury seal to prevent excessive pressure in case of a plug. The scrubbed perfluoro olefin, after passage over P_2O_5, was then condensed in a trap cooled by a mixture of Dry Ice and acetone. When tetrafluoroethylene and perfluoropropene were prepared, a second trap cooled by liquid air was also used. When the total products from the reaction were needed for examination, the scrubbers were omitted from the gas train.

When an olefin which boiled above room temperature was prepared, the total products were collected in a Dry Ice-cooled trap connected directly to the pyrolysis flask. After the reaction was completed, the product was slowly warmed to 0° to vaporize the bulk of the CO_2 and was then washed with cold aqueous base to remove acidic components. Difficulty was sometimes experienced in obtaining complete conversion of the salt in large scale reactions. It was necessary to cool the reactor, purge the system with N_2, and break up the hard solid residue. Continued heating then gave almost complete conversion of the salt. Using these procedures, laboratory preparations of up to ten pounds of olefin were accomplished. No difficulty was experienced in stopping or starting the reaction at will. This, however, was not the case with the reaction between CF_3CO_2Na and NaOH since this particular reaction is very exothermic.

Tetrafluoroethylene and perfluoropropene could be prepared in better than 98% purity without fractionation. The impurities were fluorocarbons and fluorocarbon hydrides which could be tolerated in the reaction products for most uses. The higher molecular weight olefins were usually fractionated in packed columns to remove trace amounts of other unsaturated compounds. One per cent. by weight of $(C_3H_7)_3N$ was always added to tetrafluoroethylene to prevent the explosive polymerization of this monomer.

The preparation of the fluorocarbon hydrides was carried out in equipment very similar to that used for the pyrolysis of the dry salt. The only difference was the use of a large distillation flask to contain the salt and excess glycol. This allowed the glycol to reflux in the flask and resulted in easier removal of the hydrides.

Preparation of Perfluoropentene-1.—The preparation of perfluoropentene-1 can be used as an example of the preparation of a perfluoro olefin by the pyrolysis of a salt of a perfluoro acid.

$C_5F_{11}CO_2Na$ was prepared in 93% yield by neutralizing $C_5F_{11}CO_2H$ with aqueous NaOH.

Anal. Calcd. for $C_6F_{11}O_2Na$: Na, 6.95; F, 62.2. Found: Na, 6.87; F, 61.1; H_2O, 0.06.

When 210 g. (0.625 mole) of this salt was pyrolyzed, decomposition was first noticed at 210°. The reaction became rapid yet controllable at about 250°. Fraction of the scrubbed and dried product in a packed column gave 141 g. (90% yield) of perfluoropentene-1, b.p. 28.0–29.0°, molecular weight 250. Infrared spectral analysis showed strong absorption at 1795 cm.$^{-1}$, the characteristic absorption frequency for straight chain terminally unsaturated perfluoro olefins.

Preparation of 1-Hydroperfluorobutane.—A total of 1681 g. (5.58 moles) of $C_4F_9CO_2K$ and 907 g. (14.6 moles) of $HOCH_2CH_2OH$ was charged to a large Pyrex flask equipped with a heating mantle and a condenser. The condenser was connected to two scrubbers containing 15% aqueous KOH solution. This was in turn followed by a P_2O_5 tube and a large liquid air cooled condensing trap. The reaction began when the flask contents had reached 170°. Over a period of five hours, the temperature was raised to 190°. A total of 1169 g. of product was recovered. This material

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(13) Infrared curves on the olefins and hydrides have been filed with Dr. E. C. Creitz of the National Bureau of Standards.

(14) D. S. Young, N. Fukuhara and L. A. Bigelow, THIS JOURNAL, **62**, 1171 (1940).

(15) A. F. Benning and J. D. Park, U. S. Patent No. 2,490,764 (December 13, 1949).

(16) G. C. Hood and A. J. Ihde, THIS JOURNAL, **72**, 2094 (1950).

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.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Hydrogen Chloride Cleavage of Some Trimethylarylsilanes

BY ROBERT A. BENKESER AND HENRY R. KRYSIAK

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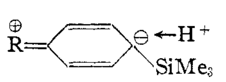
A series of *m*- and *p*-substituted aryltrimethylsilanes has been cleaved with hydrogen chloride in glacial acetic acid, and the following order of decrease in ease of cleavage has been noted: *p*-methoxyphenyl and *p*-dimethylaminophenyl > *p*-tolyl > *m*-methoxyphenyl > *m*-tolyl > phenyl > *p*-chlorophenyl > *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]

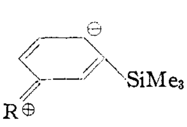
Gilman and Marshall[1a] have shown that, under the influence of hydrogen chloride in a glacial acetic acid solvent, the lability of the trimethylsilyl group in *p*-substituted trimethylarylsilanes decreases in the following order: *p*-anisyl and *p*-dimethylaminophenyl > *p*-tolyl > phenyl > *p*-chlorophenyl.

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).