TABLE II

CALCULATED HEATS OF FORMATION

Compd.	ΔH, kcal. mole^{-1}
exo	23 ± 4
endo	23
Tricyclo	15
C_7H_{10}	31

$C_5H_6^+$ ions formed are identical with the $C_5H_6^+$ species produced by ionization of cyclopentadiene, presumably having the cyclopentadienide structure. Such an assumption is reasonable for norbornene and the chloronorbornenes. In the case of chloronortricyclene, however, formation of the cyclopentadienide cation would require cleavage of three carbon–carbon bonds and one hydrogen shift. Although this complex process is clearly less probable than the retro-Diels–Alder fragmentation of the three norbornenyl compounds, the energy required for formation of the $C_5H_6^+$ ion from the parent ion (reactions 3 and 6) is equal within experimental error for all four compounds (Table I).

Little thermochemical information is available for other ions whose appearance potentials are here reported. It is possible, however, to use the calculated heats of formation of the parent compounds together with the observed appearance potentials to estimate heats of formation of the ions. Several interesting results emerge. The sum of the ionization potential and the heat of formation of the compound yields a value (Table III) for the heat of formation of the parent ion which is the same within experimental error for all three chloro compounds. This agreement may result from an identity of the three parent ions or it may be only coincidental. The latter alternative would normally seem more reasonable in view of the large differences in mass spectra and energetics between the bicyclic and tricyclic chloro compounds.

TABLE III

HEATS OF FORMATION[a] OF IONS

Ion	*exo*	*endo*	Tricyclo	C_7H_{10}
$C_5H_6^+$	(239)	(239)	(239)	(239)[b]
$C_6H_7^+$	243	245	222	257
$C_7H_9^+$	250	248	236	243
$C_7H_{10}^+$	...	...	...	238
$C_7H_9Cl^+$	234	233	234	...

[a] Given in kilocalories per mole. [b] See ref. 17.

The heat of formation of $C_6H_7^+$ produced according to reaction 2 or 5 can be calculated using the known heat of formation of CH_2Cl (29 kcal. mole^{-1})[21] or CH_3 (32 kcal. mole^{-1}),[18] respectively. The results show considerable scatter although that obtained from chloronortricyclene agrees well with the value given by Lifschitz and Bauer.[16] Results for $C_7H_9^+$ agree within experimental error for the three bicyclic compounds but the result for the tricyclic compound is somewhat lower.

The close similarity in both mass spectra and energetics of the ionization–dissociation processes for *exo-* and *endo*-5-chloro-2-norbornene indicates that these compounds dissociate under electron impact *via* common paths involving common ionic intermediates. This result is not surprising in view of the similar behavior of other sets of isomers such as those studied by Meyerson and co-workers.[22] 3-Chloronortricyclene, on the other hand, exhibits different behavior and, therefore, does not decompose solely through ionic intermediates common to the *exo–endo* pair.

Acknowledgment.—B. H. J. wishes to thank the Petroleum Research Fund of the American Chemical Society for financial support which helped make this work possible.

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[21] A. G. Harrison and T. W. Shannon, *Can. J. Chem.*, **40**, 1730 (1962).

[22] See, for example, H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

Friedel–Crafts Reaction with Silicon-Containing Acid Chlorides as a Synthetic Route to Compounds and Polymers

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In the presence of aluminum chloride, β-trimethylsilylpropionyl chloride was found to undergo a facile elimination reaction yielding trimethylchlorosilane, ethylene, and carbon monoxide, or to acylate effectively an aromatic substrate, depending on reaction conditions. A detailed study of the elimination reaction was made. With ferrocene serving as a prototype aromatic and using trimethylsilyl-, dimethylchlorosilyl-, and methyldichlorosilyl-substituted organic acid chlorides with aluminum chloride catalyst, twenty-one new compounds and polymers were prepared and their structures corroborated by independent syntheses. In connection therewith, other new materials were formed as intermediates. The results with ferrocene indicate that the usefulness of these acid chlorides with aluminum chloride in Friedel–Crafts reactions extends to aromatics with reactivities in the toluene–benzene range, thus opening up a generally useful synthetic route for silylorgano aryl ketone intermediates. Qualitative correlations between acid chloride structures and their stability–reactivity under the Friedel–Crafts conditions used were made.

The literature on aluminum chloride catalyzed Friedel–Crafts reactions with silicon-containing organic acid chlorides appears to consist of one paper by Benkeser and Krysiak who reported the acylation of toluene with *m*- and *p*-trimethylsilylbenzoyl chlorides.[2] Their attempts with the *ortho* isomer were reported as unsuccessful, apparently owing to cleavage of the trimethylsilyl group. Moreover, one would ex-

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[1] To whom inquiries should be addressed.

[2] R. A. Benkeser and H. R. Krysiak, *J. Am. Chem. Soc.*, **76**, 599 (1954).

pect that the susceptibility of the trimethylsilyl–aryl bond to cleavage by acidic reagents would tend to rather limit the synthetic utility of materials containing this bond. No reports were found of such work with trimethylsilylalkanoyl chlorides or with halosilyl-substituted organic acid chlorides, and it was of interest to explore this area as a useful synthetic route for silylorgano aryl ketone intermediates leading to a variety of compounds and polymers.

There appeared to be a similar paucity of literature concerned with the synthesis of materials in which silicon and a metallocene are linked through organic groupings. Trimethylsilylmethylferrocene, prepared by Nesmeyanov and co-workers[3] from ferrocenyllithium and trimethylchlorosilane, was the only instance found of a siliconmetallocene material wherein silicon was not directly linked to the metallocene nucleus.[4] Further, with regard to activity toward aluminum chloride catalyzed acetylation, unsubstituted ferrocene is reported to be about six orders of magnitude more reactive than benzene,[5] while acetylferrocene is only about two orders more reactive, and thus comparable with toluene[5,6] in this respect. Hence, the data from mono- and diacylating ferrocene with a given silicon-containing acid chloride are prototype results providing an indication of what one should expect with other aromatics such as applicable benzenoid substrates as well as other acylable metallocenes.

The homologous pair, β-trimethylsilylpropionyl chloride and γ-trimethylsilylbutyryl chloride, were suitable for the present work. Their lower homologs have not yet been prepared, and the trend of results with this pair would be expected to indicate Friedel–Crafts behavior of their higher homologs, since the inductive effect of the trimethylsilyl group is known to diminish rapidly through the chain.[7] Suitable also were the additional pair, γ-dimethylchlorosilylbutyryl chloride and β-methyldichlorosilylpropionyl chloride,[8] whose utilization afforded a short route to disiloxane and polysiloxane materials as well as information on the effect of halogen linked to silicon.

Results

Attempts to acylate ferrocene with a preformed complex of β-trimethylsilylpropionyl chloride and aluminum chloride failed owing to the immediate decomposition of the acid chloride. This decomposition was found to be an elimination reaction involving silicon as shown by studies which gave the results shown in eq. 1. However, this difficulty was overcome by utilizing reaction conditions which allowed acylation to compete effectively with elimination, namely, by the slow addition of aluminum chloride to a stirred solution containing both the acid chloride and ferrocene. A 76% yield of β-trimethylsilylpropionylferrocene (I) was thus obtained (see Table I). Similarly, an 83% yield of the next homolog (II) was obtained by utilizing γ-trimethylsilylbutyryl chloride.

$$\mathrm{Me_3SiCH_2CH_2COCl} \xrightarrow[\text{(0.32 mole)}]{\mathrm{AlCl_3}} \underset{87\%}{\mathrm{Me_3SiCl}} + \underset{30\%}{\mathrm{CH_2CH_2}} + \underset{85\%}{\mathrm{CO}} \qquad (1)$$

With concentrated sulfuric acid both I and II underwent cleavage of one methyl group[9] from silicon and, upon hydrolysis of the reaction mixture, respectively gave the disiloxane derivatives III and IV-1. The structure of IV-1 was confirmed by an independent synthesis which involved the monoacylation of ferrocene with γ-dimethylchlorosilylbutyryl chloride.

Diacylation of ferrocene with β-trimethylsilylpropionyl chloride gave the heteroannular[10] diketone (V) which, through the sulfuric acid cleavage reaction, was converted into the linear polymer VII. Utilizing γ-trimethylsilylbutyryl chloride, the heteroannular diketone VI was similarly prepared and converted into the linear polymer VIII-1. The structure of polymer VIII-1 was confirmed by an independent synthesis.

After monoacylation of ferrocene with β-methyldichlorosilylpropionyl chloride, the usual hydrolysis step gave directly the silicone polymer IX which contained β-ferrocenylethyl pendant groups. Cohydrolysis of the monoacyl intermediate with dimethyldichlorosilane gave silicone copolymers Xa and Xb.

Further acylation of I with terephthaloyl chloride gave the high molecular weight compound XI.

Most of the ketone-type materials above were reduced, before and after conversion to disiloxane derivatives, to corresponding alkane-type materials. Such alkane-type materials were found to be convertible to disiloxane derivatives, including polymers, by utilizing the sulfuric acid cleavage reaction.

Discussion

Attempts to form separately a complex of β-trimethylsilylpropionyl chloride with aluminum chloride resulted in rapid cleavage of the bond linking the trimethylsilyl group to the organofunctional moiety, even though the carbonyl group in the acid chloride is two carbons removed from the silicon atom, a configuration which generally stabilizes the molecule toward such cleavage.[11] However, under the stated conditions a normal Friedel–Crafts acylation took place. It therefore seems likely that elimination and acylation both proceeded through the same intermediate, $\mathrm{Me_3SiCH_2CH_2COCl{-}AlCl_3}$, whose fate was largely dependent upon the availability of an acylable substrate.

In this connection, eq. 1 strongly resembles eq. 2 below, which was previously reported by Sommer and co-workers, who postulated that the reaction was

$$\mathrm{Me_3SiCH_2CH_2CH_2X} \xrightarrow[\text{(0.02 mole)}]{\mathrm{AlCl_3}} \underset{82\%}{\mathrm{Me_3SiX}} + \underset{92\%}{\underbrace{\mathrm{CH_2CH_2CH_2}}} \qquad (2)$$

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[3] A. N. Nesmeyanov, E. G. Perevalova, and Y. A. Ustynyuk, *Dokl. Akad. Nauk. SSSR*, **133**, 1105 (1960); *Chem. Abstr.*, **54**, 24616*f* (1960).

[4] After the experimental portion of the present work had been completed (private Communications, General Electric Co.), there appeared work by A. D. Petrov, *et al.* [*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk.*, 887 (1962)], who prepared γ-trimethylsilylpropylferrocenylcarbinols from the Grignard of γ-trimethylsilylpropyl chloride and ferrocene carbonyl compounds.

[5] M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Am. Chem. Soc.*, **85**, 1450 (1963).

[6] H. C. Brown, G. Marion, and L. M. Stock, *ibid.*, **81**, 3310 (1959).

[7] (a) L. H. Sommer, J. R. Gold, G. M. Goldberg, and N. S. Marans, *ibid.*, **71**, 1509 (1949); (b) L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

[8] L. H. Sommer, R. E. Van Strien, and F. C. Whitmore, *ibid.*, **71**, 3056 (1949).

[9] (a) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett, and R. P. Pioch, *ibid.*, **73**, 882 (1951); (b) L. H. Sommer, W. P. Barie, and J. R. Gould, *ibid.*, **75**, 3765 (1953).

[10] M. Rosenblum, *Chem. Ind.* (London), 953 (1958); P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954).

[11] L. H. Sommer and R. P. Pioch, *ibid.*, **76**, 1606 (1954).

TABLE I

NEW MATERIALS

Product[a]	Formula[b]	Yield, %[c]	M.p., °C.[d]
I	$\mathrm{Si(CH_3)_3CH_2CH_2COR}$	76	59–60
II	$\mathrm{Si(CH_3)_3CH_2CH_2CH_2COR}$	83	28.5–29.5
III	$\mathrm{O[Si(CH_3)_2CH_2CH_2COR]_2}$	76	136–137
IV-1	$\mathrm{O[Si(CH_3)_2CH_2CH_2CH_2COR]_2}$	77	74–75
V	$\mathrm{Si(CH_3)_3CH_2CH_2COR'COCH_2CH_2Si(CH_3)_3}$	57	115–116
VI	$\mathrm{Si(CH_3)_2CH_2CH_2CH_2COR'COCH_2CH_2CH_2Si(CH_3)_3}$	73	47–48
VII	$\mathrm{[Si(CH_3)_2CH_2CH_2COR'COCH_2CH_2Si(CH_3)_2O]_n}$		
	or[e]		
	$[\mathrm{Si(CH_3)_2}]_n\textit{-alt-}(\mathrm{CH_2CH_2})_n\textit{-alt-}(\mathrm{CO})_n\textit{-alt-}(\mathrm{R'})_n\textit{-alt-}(\mathrm{CO})_n\textit{-alt-}(\mathrm{CH_2CH_2})_n\textit{-alt-}[\mathrm{Si(CH_3)_2O}]_n$	93	...
VIII-1	$[\mathrm{Si(CH_3)_2}]_n\textit{-alt-}(\mathrm{CH_2CH_2CH_2})_n\textit{-alt-}(\mathrm{CO})_n\textit{-alt-}(\mathrm{R'})_n\textit{-alt-}(\mathrm{CO})_n\textit{-alt-}(\mathrm{CH_2CH_2CH_2})_n\textit{-alt-}[\mathrm{Si(CH_3)_2O}]_n$	95	...
IX	$\mathrm{[Si(CH_3)(CH_2CH_2COR)O]_n}$	31	...
Xa	$\overline{81}:\overline{82}\{[\mathrm{Si(CH_3)(CH_2CH_2COR)O}]_n\textit{-co-}[\mathrm{Si(CH_3)_2O}]_n\}^f$	33	
Xb	$\overline{30}:\overline{70}\{[\mathrm{Si(CH_3)(CH_2CH_2COR)O}]_n\textit{-co-}[\mathrm{Si(CH_3)_2O}]_n\}^f$	10	
XI	$\mathrm{Si(CH_3)_3CH_2CH_3COR'COR''COR'COCH_2CH_2Si(CH_3)_3}$	22	147 dec.
XII	$\mathrm{Si(CH_3)_3CH_2CH_2CH_2R}$	78	56–57
XIII	$\mathrm{Si(CH_3)_3(CH_2)_4R}$	91	5
XIV	$\mathrm{O[Si(CH_3)_2(CH_2)_3R]_2}$	82	104–105
XV-I	$\mathrm{O[Si(CH_3)_2(CH_2)_4R]_2}$	67	34–35
XVI	$\mathrm{HOSi(CH_3)_2(CH_2)_4R}$	9	...
XVII	$\mathrm{Si(CH_3)_3(CH_2)_3R'(CH_2)_3Si(CH_3)_3}$	82	20.0–20.5
XVIII	$\mathrm{Si(CH_3)_3(CH_2)_4R'(CH_2)_4Si(CH_3)_3}$	71	−9, −8
XIX	$[\mathrm{Si(CH_3)_3}]_n\textit{-alt-}[\mathrm{(CH_2)_3}]_n\textit{-alt-}(\mathrm{R'})_n\textit{-alt-}[\mathrm{(CH_2)_3}]_n\textit{-alt-}[\mathrm{Si(CH_3)_2O}]_n$	89	...
XX	$\overline{8}:\overline{92}\{[\mathrm{Si(CH_3)_2}]_n\textit{-alt-}[\mathrm{(CH_2)_3}]_n\textit{-alt-}(\mathrm{R'})_n\textit{-alt-}[\mathrm{(CH_2)_3}]_n\textit{-alt-}[\mathrm{Si(CH_3)_2O}]_n\textit{-co-}[\mathrm{Si(CH_3)_2O}]_n\}^f$	52	...
XXI-1	$[\mathrm{Si(CH_3)_2}]_n\textit{-alt-}[\mathrm{(CH_2)_4}]_n\textit{-alt-}(\mathrm{R'})_n\textit{-alt-}[\mathrm{(CH_2)_4}]_n\textit{-alt-}[\mathrm{Si(CH_3)_2O}]_n$	91	...

[a] Corresponding proposed names are given in the Experimental section. [b] In the above formulas, R is $\mathrm{C_5H_4FeC_5H_5}$, R′ is $\mathrm{C_5H_4FeC_5H_4}$, and R″ is p-$\mathrm{C_6H_4}$. [c] Yields are based on starting material indicated in the Experimental section, with no allowances for recoveries. [d] All melting points are corrected, except those falling between −10 and 25°. [e] The first method of representing the polymer formula more clearly relates to prior compound formulas, while the second conforms to the proposed name for the polymer given in the Experimental section and is the method used for the polymers subsequently listed. [f] The ratio of monomers is an estimate. See text.

initiated by aluminum chloride attack at the halide atom.[8] The major differences between these two eliminations were reconciled as follows. The experimental details indicate that part of the ethylene of eq. 1 effectively "poisons" a commensurate amount of the aluminum chloride toward further catalysis of the decomposition. Thus, more aluminum chloride is needed and the yield of ethylene obtained is much lower than the yields of trimethylchlorosilane and carbon monoxide. In agreement, the material balance data showed that a residue remained bound to the aluminum chloride after decomposition of the acid chloride was complete. This residue not only completely solubilized a relatively large amount of aluminum chloride in trimethylchlorosilane, but the weight of residue was equivalent to another 30% yield of ethylene, which in terms of moles closely matches the moles of aluminum chloride required for total decomposition of the acid chloride to occur. Concerning the nature of the decomposition products, it was not considered surprising that eq. 1 gave ethylene and carbon monoxide instead of highly strained cyclopropanone.

As indicated by the simple color test described in the Experimental section, the butyryl analog is much more resistant than β-trimethylsilylpropionyl chloride toward decomposition by aluminum chloride. However, since some gassing was observed when the butyryl analog and aluminum chloride were brought into contact, suggesting partial decomposition, the successful acylation procedure described with β-trimethylsilylpropionyl chloride was also used with the other three silicon-containing acid chlorides, even though the presence of chlorine linked to silicon in two of them would tend to exert a stabilizing[8] influence.

The stability of the ketone linkage in I was demonstrated by the reaction with sulfuric acid which resulted in cleavage of a methyl group from silicon, liberating methane. From earlier works[12,13] with similar structures, most probably a silyl bisulfate was formed, which upon hydrolysis was converted to a silanol that rapidly condensed intermolecularly to give disiloxane III. By the same route, II gave IV-1.

It was logically assumed that the monoacylation of ferrocene with γ-dimethylchlorosilylbutyryl chloride gave the intermediate, γ-dimethylchlorosilylbutyrylferrocene, which upon subsequent contact with moisture was converted into the corresponding silanol whose condensation into disiloxane (IV-2) was catalyzed by the liberated acid. Compound IV-2 was found to be identical with IV-1.

The 56% yield of heteroannular diketone V compared to the 76% yield of monoketone I indicated that I can be acylated by β-trimethylsilylpropionyl chloride about as effectively as unsubstituted ferrocene. On the reasonable premise that I is comparable to acetylferrocene regarding activity toward further acylation,[14] the usefulness of β-trimethylsilylpropionyl chloride with aluminum chloride in Friedel–Crafts reactions thus appears to extend at least to aromatics with the reactivity of toluene. Similarly, the 73% yield of

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(12) L. M. Shorr, H. Freiser, and J. L. Speier, *J. Am. Chem. Soc.*, **77**, 547 (1955).

(13) L. H. Sommer and G. R. Ansul, *ibid.*, **77**, 2482 (1955).

(14) The acetyl and β-trimethylsilylpropionyl groups are comparable inductively,[7] and the latter group is much bulkier.

heteroannular diketone VI indicates that such usefulness of γ-trimethylsilylbutyryl chloride likely extends to aromatics of reactivity in the toluene–benzene range.

By the same route which transformed monoketone I into disiloxane III, heteroannular diketone V was transformed into polymer VII. The evidence described in the Experimental section supports an essentially linear polymeric structure for VII, which would also be anticipated from steric considerations as discussed below.

Schaaf and co-workers[15] reported that the intermediate, $EtOMe_2SiC_5H_4FeC_5H_4SiMe_2OEt$, upon acid hydrolysis gave a high yield of the cyclic compound, $\underbrace{OMe_2SiC_5H_4FeC_5H_4SiMe_2}$. This result is consistent with the reported stability of the disiloxane linkage in a six-atom ring disiloxane-type structure,[16] $\underbrace{OMe_2SiCH_2CH_2CH_2SiMe_2}$, and with other reports[17] which indicate that the bridging of the 1,1′ positions of ferrocene by a trimethylene grouping can be sterically favorable.

Because of the three carbon atoms which separate each silicon atom from the ferrocene nucleus in VII, the chances of its monomer forming a ring would appear to be remote relative to forming a linear polymer.

In passing, it seems reasonable to assume that rotational freedom about the C_5H_4–Fe–C_5H_4 bonds[18] would complement rotational freedom about Si–O–Si bonds[19] in enhancing the flexibility of polymer VII. Similarly, heteroannular diketone VI gave polymer VIII-1, also an essentially linear polymer.

It was logically assumed that the diacylation of ferrocene with γ-dimethylchlorosilylbutyryl chloride gave 1,1′-bis(γ-dimethylchlorosilylbutyryl)ferrocene as an intermediate, as subsequent hydrolysis of the acylation mixture gave polymer VIII-2. Since any monoacylated intermediate present could function as a chain stopper and cause a molecular weight distribution considerably different from that of polymer VIII-1, polymer VIII-2 was fractionated and a middle fraction therefrom was used to confirm the structure of polymer VIII-1. Indirectly, the proposed structure for polymer VII was thus also confirmed. The yields of IV-2 and VIII-2 indicate that γ-dimethylchlorosilylbutyryl chloride with aluminum chloride is useful for acylating aromatics of reactivity in the toluene–benzene range.

By monoacylating ferrocene with β-methyldichlorosilylpropionyl chloride, β-methyldichlorosilylpropionylferrocene was logically assumed to be the intermediate formed. It should be noted that hydrogen chloride was still being evolved 25 hr. after the aluminum chloride addition. Hence, acylation was still progressing, demonstrating the stabilization toward aluminum chloride which was effected by the two chlorines linked to silicon. At this point, perhaps unwisely,[20] 35% more aluminum chloride was added to hasten acylation. After hydrolysis and work-up, before chromatography, the weight of crude polymer IX which was obtained corresponded to a yield of about 70%. This is believed to reflect better the extent of the acylation reaction than does the 31% yield of purified IX obtained from the chromatography column, especially since crude and purified IX gave closely similar infrared spectra. The difficulties inherent in chromatographing crude IX were probably compounded by the formation of a diacylated (tetrafunctional) intermediate through the use of the extra[20] aluminum chloride cited above, likely resulting in some gelation of polymer which contributed to the large holdup which was observed on the column. Considering the demonstrated stability of β-methyldichlorosilylpropionyl chloride toward aluminum chloride and the good yield of crude IX, it is felt that optimization of acylation conditions would render this acid chloride useful for acylating aromatics of reactivity in the toluene–benzene range.

The data from the preparations of I, II, IV-2, and IX qualitatively show an inverse correlation between acid chloride reactivity and degree of chlorine substitution on silicon. This was evident from the subsequent times of hydrogen chloride evolution after combining in the same way ferrocene, the respective acid chloride, and aluminum chloride in molar proportions of 1:1:1.05.

The ratio of monomers shown for silicone copolymers Xa and Xb, obtained by calculating the best fit to the elemental analyses was supported by their infrared spectra in comparison with the spectra of IX and polydimethylsiloxane, which represented the two extremes of composition. In passing, with regard to the effect on low-temperature properties of a silicone polymer, it seems reasonable to expect that the effect of the pendant β-ferrocenoylethyl group would be qualitatively similar to that of the pendant phenyl group.[21]

It is noteworthy that, whereas small yields of ferrocene-containing disiloxane by-products were obtained from the preparations of V, VI, and XI, none was obtained from the preparations of I and II. Most likely, these disiloxane by-products were formed as a result of Me–Si cleavage by the acid, $HAlX_4$.[22] The acylation conditions which gave V, VI, and XI involved relatively higher concentrations of aluminum chloride in combination with longer reaction and stirring times, thus affording greater opportunity for Si–C cleavage by $HAlX_4$ to occur. This may be related to the fact that the rate of Me–Si cleavage by sulfuric acid is greatly influenced by acid concentration.[9b]

Reduction of ketone-type materials to alkane-type materials occurred smoothly with no particular difficulty. The chromatography results indicated that, with molecules containing two carbonyl groups, for instance heteroannular diketones and diketone disiloxanes, it is possible to reduce one carbonyl group to methylene while leaving the other carbonyl group intact.

Disiloxane (XV-2), prepared from XIII through Me–Si cleavage with sulfuric acid, confirmed the structure of

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(15) R. L. Schaaf, P. T. Kan, and C. T. Lenk, *J. Org. Chem.*, **26**, 1790 (1961).

(16) L. H. Sommer, J. H. Masterson, O. W. Steward, and R. H. Leitheiser, *J. Am. Chem. Soc.*, **78**, 2010 (1956).

(17) K. L. Rinehart and R. J. Curby, *ibid.*, **79**, 3290 (1957); P. F. Eiland and R. Pepinsky, *ibid.*, **74**, 4971 (1952).

(18) W. Moffitt, *ibid.*, **76**, 3386 (1954); M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5443 (1958).

(19) E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1951, p. 114.

(20) Excess aluminum chloride over acid chloride promotes diacylation even though the acid chloride is not in excess over ferrocene; see ref. 5 and M. Rosenblum and J. O. Santer, *J. Am. Chem. Soc.*, **81**, 5517 (1959), for an elaboration of this point.

(21) K. E. Polmanteer and M. J. Hunter, *J. Appl. Polymer Sci.*, **1**, 3 (1959).

(22) P. D. George, U. S. Patent 2,802,852 (Aug. 13, 1957).

XV-1, which was first prepared by the reduction of IV-2. An earlier work[13] with analogous alkane-type structures reported that sulfuric acid, in addition to causing Me–Si cleavage, also causes some cleavage of silicon from methylene, and this may have occurred to some degree in the preparation of alkane-type polymers XIX and XXI-1. The structures proposed for these two polymers are considered sound, however, since they were corroborated by the preparation of polymer XXI-2 from polymer VIII-2 through reduction.

Experimental

Ferrocene from the Ethyl Corp. was used as received, since it was found by infrared analysis to be equivalent to ferrocene prepared by the diethylamine method.[23] The infrared spectra were obtained from samples in the form of thin films, as such or in appropriate solvent, between sodium chloride plates with a Perkin–Elmer Model 137 Infracord, and copies thereof may be found elsewhere.[24] The reported elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Acylations were accomplished at 20–25° in flasks wherein stirring was done magnetically and anhydrous conditions were maintained. After the reactants had been combined, the gentle nitrogen flow was stopped and further stirring was done under the solvent blanket. Evolution of hydrogen chloride was followed both by odor and by moist indicator paper. When these tests showed that acylation had stopped, hydrolysis was accomplished by adding the reaction mixture to cold, dilute aqueous acid, followed by an equal volume of methylene chloride and standing for the time indicated. The solvent layer was then separated and thoroughly washed first with water, then dilute alkali, and then again with water. After drying over alumina, the solvent was removed near room temperature at reduced pressure. The results were such that in no case was investigation of the retained water layer considered necessary.

Alcoa F-20 alumina in hexane was the packing used for all chromatography work. All melting points were corrected, excepting those below 25°.

All demethylations with concentrated sulfuric acid were conducted at 20–30° and took place with considerable foaming. Reaction progress was followed through water displacement. The reaction vessel was vigorously shaken to avoid the formation of supersaturated solutions of methane in sulfuric acid.[9b] When gas evolution ceased the reaction mixture was promptly hydrolyzed.

All reductions were performed by the Clemmensen method[25] and were closely monitored for sufficiency of amalgam and acid, with additions made as needed. Since lengthy reflux times were involved, the flask was kept covered with metal foil.

Decomposition of β-Trimethylsilylpropionyl Chloride by Aluminum Chloride.—Known procedures[26,27] were used to convert β-cyanoethyltrichlorosilane, obtained from the General Electric Co., to β-trimethylsilylpropionyl chloride, b.p. 92° (65 mm.), lit.[27] b.p. 92° (65 mm.).

The addition of 4.00 g. (0.0243 mole) of β-trimethylsilylpropionyl chloride to 3.40 g. (0.0255 mole) of anhydrous aluminum chloride in 30 ml. of methylene chloride resulted in rapid dissolution of most of the aluminum chloride. This was immediately followed by a vigorous evolution of gas which soon subsided, concurrent with the copious precipitation of a white solid (presumably previously complexed aluminum chloride). The subsequent addition of this mixture to a solution of 4.52 g. (0.0243 mole) of ferrocene in 25 ml. of methylene chloride gave a dull brown color which remained unchanged upon further stirring for 3 hr. The reaction mixture was then hydrolyzed, worked up, and chromatographed. Hexane elution gave a 50% recovery of ferrocene, identified by its infrared spectrum. Elution with other solvents gave minor amounts of unidentified yellow and orange oils, none of which gave an infrared spectrum corresponding to that of ketone I. These results were confirmed by a second run.

Since preliminary experimentation indicated that methylene chloride did not play a critical role, it was not employed in the characterization of this decomposition.

Without wetting the walls, 5.00 g. (0.0304 mole) of β-trimethylsilylpropionyl chloride was placed in a dry, weighed, 50-ml. test tube which was then fixed in a tilted position. From a small vial 1.30 g. (0.00975 mole) of aluminum chloride powder was carefully deposited onto the upper, inside wall of the tube as a small mound, well removed from the liquid acid chloride. The mouth of the tube was then secured so that the gases subsequently evolved therefrom were routed to a small cold trap set in Dry Ice–acetone, then to a water-filled graduate which was inverted into water. By gentle tapping, very small increments of aluminum chloride powder were displaced downward along the inside wall of the tilted test tube and into contact with the liquid acid chloride. Each increment of powder was solubilized and caused momentary gassing to occur, evident by frothing and by water displacement in the graduate, after which the increment remained in solution. The entire mound of powder was so contacted in small increments over 8 min. with the decomposition taking place close to room temperature. Experimentation with this procedure showed that the amount of aluminum chloride powder used was the minimal required for maximum evolution of gas. More powder was neither solubilized nor caused further gassing to occur.

The cold trap gave 1.00 g. (30%) of trimethylchlorosilane, identified by its infrared spectrum. The weight of the clear, pale yellow solution which remained in the test tube, after allowing for the weight of aluminum chloride used, amounted to 2.55 g. (The theoretical yield of trimethylchlorosilane is 3.30 g.) The test tube was then immersed in a salt–ice bath, and its contents were slowly hydrolyzed with minute pieces of ice, after which an extraction with ether gave 1.40 g. of hexamethyldisiloxane (identified by infrared) which corresponded to an additional 57% yield of trimethylchlorosilane, bringing the total yield thereof to 87%. Further extraction of the hydrolyzed contents of the test tube with methylene chloride gave 0.15 g. of an unidentified brown paste whose infrared spectrum was extremely complex.

Water displacement in the graduate showed that the decomposition also gave 800 cc. (STP) of gas. By infrared analysis, this gas was found to be solely a mixture of carbon monoxide and ethylene, present in a 2.5:1.0 volume ratio and hence in yields of 85 and 30%, respectively. A confirmatory run, made with a small bromine trap inserted after the cold trap, gave 550 cc. (STP) of gas which, by infrared analysis, was found to consist solely of carbon monoxide and hence was an 82% yield thereof. After removal of excess bromine by reduced pressure, the bromine trap gave 1.53 g. (27%) of ethylene bromide, identified by its infrared spectrum, freezing point, and refractive index.

Color Test.—The pronounced difference between the brown color associated with the unsuccessful acylation procedure above and the violet color associated with the successful acylation procedure below was quickly evident on running the rough equivalent of each procedure in miniature. To one small test tube was added solvent, aluminum chloride, and β-trimethylsilylpropionyl chloride. Solid ferrocene was added after the gassing had subsided, and a dull brown color developed on shaking. The same materials in the same amounts were added to another small test tube, except the aluminum chloride was added last, after which shaking of the tube gave a deep violet color.

β-Trimethylsilylpropionylferrocene (I).—To a solution of 4.52 g. (0.0243 mole) of ferrocene and 4.00 g. (0.0243 mole) of β-trimethylsilylpropionyl chloride in 50 ml. of methylene chloride, 3.40 g. (0.0255 mole) of aluminum chloride was uniformly added as small increments of powder over 80 min. so that no foaming occurred during the addition. A deep violet color developed and hydrogen chloride was evolved. After stirring for an additional 30 min., hydrogen chloride evolution was no longer detected. The reaction mixture was then hydrolyzed, followed by standing overnight. After work-up, the product was taken up in hexane and chromatographed. Hexane elution gave a 5% recovery of ferrocene. Elution by a hexane–ether mixture gave 5.80 g. (76% on acid chloride) of I, orange crystals, m.p. 59–60°.

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(23) G. Wilkinson, *Org. Syn.*, **36**, 34 (1956).

(24) E. V. Wilkus, Ph.D. Thesis (Rensselaer Polytechnic Institute), March 1963.

(25) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., Inc., New York, N. Y., 1948, p. 157.

(26) A. D. Petrov, S. I. Sadykh-Zade, and V. M. Vdovin, *Dokl. Akad. Nauk SSSR*, **100**, 711 (1955); *Chem. Abstr.*, **50**, 157*h* (1956).

(27) L. H. Sommer and J. Rockett, *J. Am. Chem. Soc.*, **73**, 5130 (1951).

Anal. Calcd. for $C_{16}H_{22}FeOSi$: C, 61.2; H, 7.1: Fe, 17.8; Si, 8.9. Found: C, 61.1; H, 7.1; Fe, 17.8; Si, 8.7.

Using the method of Shriner and Fuson,[28] I readily formed a 2,4-dinitrophenylhydrazone, m.p. 215° dec.

This preparation of I was repeated, except that the acylation mixture was stirred an additional 19 hr. before hydrolysis, with essentially the same results: 2% recovery of ferrocene and 77% yield of I. After standing 1 month, I gave the same melting point and the same infrared spectrum, which was consistent with the proposed structure.

γ-Trimethylsilylbutyrylferrocene (II).—By known procedures,[26,27] γ-cyanopropyldimethylchlorosilane, obtained from the General Electric Co., was converted to γ-trimethylsilylbutyric acid, b.p. 122.5° (16 mm.), lit.[29] b.p. 123° (16 mm.), which was in turn converted to γ-trimethylsilylbutyryl chloride, b.p. 75° (15 mm.).

To a solution of 4.52 g. (0.0243 mole) of ferrocene and 4.30 g. (0.0243 mole) of γ-trimethylsilylbutyryl chloride in 50 ml. of methylene chloride, 3.40 g. (0.0255 mole) of aluminum chloride was uniformly added as small increments of powder over 30 min. After stirring for an additional 30 min., hydrogen chloride evolution was no longer detected. The violet reaction mixture was then hydrolyzed, followed by standing overnight. After work-up, the oily product was taken up in hexane and chromatographed. Hexane elution gave a 5% recovery of ferrocene. Elution with a hexane–ether mixture gave 6.65 g. (83% on acid chloride) of II as an orange oil. After solidifying over Dry Ice and allowing to warm, II passed to a melt and then to orange crystals, m.p. 28.5–29.5°.

Anal. Calcd. for $C_{17}H_{24}FeOSi$: C, 62.2; H, 7.4; Fe, 17.0; Si, 8.6. Found: C, 62.3; H, 7.4; Fe, 17.2; Si, 8.7.

Compound II readily gave a 2,4-dinitrophenylhydrazone, m.p. 181° dec. The infrared spectra from I and II were closely similar.

1,3-Bis(β-ferrocenoylethyl)tetramethyldisiloxane (III).—To 0.50 g. of I was added 10 ml. of concentrated sulfuric acid. The reaction mixture immediately turned blue-green and within minutes commenced evolving gas. The reaction vessel was then shaken[9b] for 30 min., during which time there was evolved a volume of gas corresponding to more than 80% of the theoretical[9a] amount of methane (the evolved gas being identified as such by mass spectroscopy). Hydrolysis was then promptly accomplished by carefully adding the reaction mixture to 25 ml. of externally cooled water. An orange precipitate rapidly formed which was extracted with an ether–methylene chloride mixture after standing overnight. On removal of solvent, the product was taken up in a hexane–ether mixture and chromatographed. Hexane elution gave no fractionation. Elution with a hexane–ether mixture gave 0.37 g. (76%) of III, orange crystals, m.p. 136–137° (which was again obtained upon cooling and then reheating the once-melted material).

Anal. Calcd. for $C_{30}H_{38}Fe_2O_3Si_2$: C, 58.6; H, 6.2; Fe, 18.2; Si, 9.1. Found: C, 58.4; H, 5.9; Fe, 17.6; Si, 9.4.

Compared with that of I, the infrared spectrum of III showed the following differences: appearance of absorption characteristic for the linear disiloxane linkage[16] and alteration of previous absorption bands characteristic for the trimethylsilyl grouping.

1,3-Bis(γ-ferrocenoylpropyl)tetramethyldisiloxane (IV-1).—Using a procedure closely similar to that preceding, 0.40 g. of II gave 0.30 g. (77%) of IV-1, orange crystals, m.p. 74–75°. The infrared spectra from III and IV-1 were closely similar.

Anal. Calcd. for $C_{32}H_{42}Fe_2O_3Si_2$: C, 59.8; H, 6.6; Si, 8.7. Found: C, 59.6; H, 6.4; Si, 8.4.

Structure Proof of IV-1 by Independent Synthesis (IV-2).—In 50 ml. of methylene chloride there was dissolved 4.52 g. (0.0243 mole) of ferrocene and 4.84 g. (0.0243 mole) of γ-dimethylchlorosilylbutyryl chloride, b.p. 68° (4.5 mm.), which was obtained from the General Electric Co. To this solution, 3.40 g. (0.0255 mole) of aluminum chloride was uniformly added as small increments of powder over 60 min. After stirring for an additional 90 min., checking at 30-min. intervals, hydrogen chloride evolution was no longer detected and the violet reaction mixture was then hydrolyzed and allowed to stand overnight. After work-up, the product was taken up in a hexane–ether mixture and chromatographed. Elution with a hexane–ether mixture first gave a 7% recovery of ferrocene, then a trace amount of unidentified orange paste, and finally 5.88 g. (75% on acid chloride) of IV-2, orange crystals, m.p. 74–75°.

Anal. Calcd. for $C_{32}H_{42}Fe_2O_3Si_2$: C, 59.8; H, 6.6; Fe, 17.4; Si, 8.7. Found: C, 60.1; H, 6.7; Fe, 17.2; Si, 8.7.

Compounds IV-1 and IV-2 gave the same infrared spectrum and a mixture melting point was undepressed.

1,1′-Bis(β-trimethylsilylpropionyl)ferrocene (V).—To a solution of 4.52 g. (0.0243 mole) of ferrocene and 8.00 g. (0.0486 mole) of β-trimethylsilylpropionyl chloride in 60 ml. of methylene chloride, 6.80 g. (0.051 mole) of aluminum chloride was uniformly added as small increments of powder over 110 min. The violet reaction mixture was then stirred overnight, after which hydrogen chloride evolution could not be detected. Hydrolysis was then accomplished, followed by standing overnight. After work-up, the product was taken up in a hexane–ether mixture and chromatographed. Hexane elution gave an orange band very slowly which gave 1.07 g. (14% on ferrocene) of I, identified by infrared. Elution with a hexane–ether mixture gave 6.13 g. (57% on ferrocene) of V, orange crystals, m.p. 115–116°. Consistent with the proposed heteroannular[10] diketone structure, the "9–10" bands[10] of ferrocene were absent in the infrared spectrum of V.

Anal. Calcd. for $C_{22}H_{34}FeO_2Si_2$: C, 59.7; H, 7.8; Fe, 12.6; Si, 12.7. Found: C, 59.8; H, 8.0; Fe, 12.4; Si, 12.7.

Ether elution gave 0.35 g. of orange crystals melting at 99–108°, which infrared analysis indicated were a mixture of disiloxane derivatives of I and V.

1,1′-Bis(γ-trimethylsilylbutyryl)ferrocene (VI).—To a solution of 2.08 g. (0.0112 mole) of ferrocene and 4.00 g. (0.0224 mole) of γ-trimethylsilylbutyryl chloride in 60 ml. of methylene chloride, 3.14 g. (0.0235 mole) of aluminum chloride was uniformly added as small increments of powder over 110 min. The violet reaction mixture was then allowed to stir overnight, after which hydrogen chloride evolution could not be detected. Hydrolysis was then accomplished, followed by standing overnight. Subsequent work-up and chromatography procedures closely resembled those of the preceding preparation. Yields of 0.29 g. (8% on ferrocene) of II and 3.85 g. (73% on ferrocene) of VI, orange crystals, m.p. 47–48°, were obtained.

Anal. Calcd. for $C_{24}H_{38}FeO_2Si_2$: C, 61.3; H, 8.1; Fe, 11.9; Si, 11.9. Found: C, 61.5; H, 8.2; Fe, 11.9; Si, 12.2.

Elution with ether gave 0.17 g. of an orange paste which infrared analysis indicated was a mixture of disiloxane derivatives of II and VI. The infrared spectra from V and VI were closely similar.

Poly[(dimethyl)silamer-*alt*-ethamer-*alt*-carbonylamer-*alt*-ferrocenylenamer-1,1′-*alt*-carbonylamer-*alt*-ethamer-*alt*-(dimethyl)-siloxamer][30] (VII).—The addition of 10 ml. of concentrated sulfuric acid to 0.50 g. of V, followed by shaking[9b] the reaction vessel for 30 min. gave more than 90% of the theoretical[9a] amount of methane. The green reaction mixture was then promptly hydrolyzed by carefully adding it to 25 ml. of externally cooled water, whereupon a viscous orange residue quickly deposited onto the sides of the hydrolysis vessel. After standing overnight, the clear water phase was decanted and the viscous residue was washed five times with water and taken up in methylene chloride. After drying over alumina, the solvent was removed. A viscous orange material, which could be drawn into long wispy filaments, was thus obtained. Its infrared spectrum differed from that of starting compound V only in the following ways: appearance of a very strong band peaking at 9.5 μ for linear[16] disiloxane linkages; alteration of the prior trimethylsilyl absorption pattern in the 11.5–13.5-μ range; and appearance of a slight band at 3.0 μ, which is consistent with the presence of a minor level of terminal silanol. This polymeric material was then extracted several times with boiling water to assure complete removal of sulfuric acid, after which it was stored under vacuum over Drierite for 2 weeks to effect silanol condensation. The material then exhibited rubber-like characteristics which rendered its removal from the glass container extremely difficult. Its infrared spectrum showed the nearly complete disappearance of the absorption band at 3.0 μ, which is consistent with the change in rheology; the yield of VII was 0.45 g. (93%). In this additionally condensed state, VII was submitted for elemental analysis.

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[28] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

[29] L. H. Sommer, F. P. Mackay, O. W. Steward, and P. G. Campbell, *J. Am. Chem. Soc.*, **79**, 2764 (1957).

[30] This proposed name is based upon the rules and examples for polymer nomenclature given by a committee report, *J. Polymer Sci.*, **8**, 274 (1952); M. L. Huggins, G. Natta, V. Desreux, and H. L. Mark, *ibid.*, **56**, 153 (1962).

Anal. Calcd. for $(C_{20}H_{28}FeO_3Si_2)_n$: C, 56.1; H, 6.6; Fe, 13.0; Si, 13.1. Found: C, 55.8; H, 6.8; Fe, 13.0; Si, 13.2.

Poly[(dimethyl)silamer-*alt*-propamer-*alt*-carbonylamer-*alt*-ferrocenylenamer-1,1′-*alt*-carbonylamer-*alt*-propamer-*alt*-(dimethyl)siloxamer][30] **(VIII-1).**—Starting with 0.50 g. of VI and 10 ml. of concentrated sulfuric acid, the steps of the preceding preparation were repeated. At comparable stages the product gave infrared and rheology results closely resembling those of VII. After dry storage, 0.46 g. (96%) of VIII-1 was obtained.

Anal. Calcd. for $(C_{22}H_{32}FeO_3Si_2)_n$: C, 57.9; H, 7.1; Fe, 12.2; Si, 12.3. Found: C, 57.9; H, 7.0; Fe, 12.0; Si, 12.1.

Proof of Structure of VIII-1 by Independent Synthesis (VIII-2).—To a solution of 4.52 g. (0.0243 mole) of ferrocene and 9.68 g. (0.0486 mole) of γ-dimethylchlorosilylbutyryl chloride in 70 ml. of methylene cholride, 6.80 g. (0.0510 mole) of aluminum chloride was uniformly added as small increments of powder over 120 min. and the violet reaction mixture was stirred for 24 hr. Hydrolysis was then accomplished, followed by standing for 2 weeks. After work-up, the product was concentrated in methylene chloride and chromatographed. Hexane elution gave a recovery of a trace of ferrocene. The column was then successively washed with a hexane–ether mixture, ether, an ether–methylene chloride mixture, and, finally, methylene chloride. Each washing gave a waxy, orange material which differed only slightly in its infrared results from one fraction to another. Aside from a minor difference in absorption for silanol at 3.0 μ, the infrared spectrum representing the middle portion of this fractionation was identical with that of polymer VIII-1. The combined weight of these fractions was 6.30 g. (approximately 57% on ferrocene). A middle fraction was submitted for elemental analysis.

Anal. Calcd. for $(C_{22}H_{32}FeO_3Si_2)_n$: C, 57.9; H, 7.1; Fe, 12.2; Si, 12.3. Found: C, 57.5; H, 7.6; Fe, 12.2; Si, 11.8.

Poly(methyl)(β-ferrocenoylethyl)siloxamer[30] **(IX).**—In 100 ml. of methylene chloride there was dissolved 9.04 g. (0.0486 mole) of ferrocene and 9.96 g. (0.0486 mole) of β-methyldichlorosilylpropionyl chloride, b.p. 74–75° (4 mm.), which was obtained from the General Electric Co. Then 6.80 g. (0.0510 mole) of aluminum chloride was uniformly added as small increments over 90 min. After stirring for an additional 25 hr., hydrogen chloride was still being evolved, and an additional 2.40 g. (0.018 mole) of aluminum chloride was added over 20 min. Upon stirring for an additional 15 min., evolution of hydrogen chloride was no longer detected and an additional 1.80 g. (0.0096 mole) of solid ferrocene was added. After stirring for an additional 30 min., one-half of the acylation mixture was withdrawn and hydrolyzed. Upon standing for 1 week, the hydrolysis mixture was worked up and 5.3 g. of an extremely viscous orange residue was obtained. After obtaining an infrared spectrum, this residue was taken up in an ether–methylene chloride mixture and chromatographed. Hexane elution gave a 10% recovery of ferrocene. Ether alone failed to elute the product, but an ether–methylene chloride mixture gave 2.23 g. (31% on acid chloride) of IX as an extremely viscous, transparent deep orange material, which with difficulty could be drawn into short filaments. Crude and purified IX gave closely similar infrared spectra.

Anal. Calcd. for $(C_{14}H_{16}FeO_2Si)_n$: C, 56.0; H, 5.4; Fe, 18.6; Si, 9.4. Found: C, 56.4; H, 5.5; Fe, 17.9; Si, 9.4.

On the column was left a broad orange band which could not be eluted with methanol or with methanol–water mixtures.

Poly-$\overline{18}$:$\overline{82}$[(methyl)(β-ferrocenoylethyl)siloxamer-*co*-(dimethyl)siloxamer][30] **(Xa) and Poly-$\overline{30}$:$\overline{70}$[(methyl)(β-ferrocenoylethyl)siloxamer-*co*-(dimethyl)siloxamer]**[30] **(Xb).**—To the retained half of the acylation mixture which gave IX was added 27.15 g. (0.211 mole) of dimethyldichlorosilane. After stirring for an additional 15 min., the mixture was hydrolyzed and allowed to stand for 2 weeks. Subsequent work-up gave 17.1 g. of an orange fluid which was taken up in hexane and chromatographed. Hexane elution first gave 5.10 g. (33% on dimethyldichlorosilane) of polydimethylsiloxane fluid, identified by infrared, then a 14% recovery of ferrocene, and then another 1% of polydimethylsiloxane. Elution with a hexane–ether mixture gave 5.05 g. (33% on acid chloride) of Xa as a mobile, light orange fluid. Elution with an ether–methylene chloride mixture gave 1.15 g. (10% on acid chloride) of Xb, which was more viscous and of a deeper orange color. The monomer ratios were estimated through the best fit to the elemental analyses.

Anal. Calcd. for Xa, $[(C_{14}H_{16}FeO_2Si)_1(C_2H_6OSi)_{4.5}]_n$: C, 43.6; H, 6.8; Fe, 8.8. Found: C, 44.6; H, 7.2; Fe, 7.8.

Anal. Calcd. for Xb, $[(C_{14}H_{16}FeO_2Si)_1(C_2H_6OSi)_{2.3}]_n$: C, 47.5; H, 6.4; Fe, 11.9. Found: C, 4.76; H, 6.4; Fe, 11.9.

Left on the column was a broad orange band which could not be eluted with methanol or with methanol–water mixtures.

Terephthaloylbis[1′-(β-trimethylsilylpropionyl)ferrocene] (XI).—To 40 ml. of methylene chloride was added 3.00 g. (0.00954 mole) of I and 0.93 g. (0.00456 mole) of terephthaloyl chloride as small hard pieces. After stirring for an additional 30 min., it was noted that many of the pieces had not dissolved. Nevertheless, 2.74 g. (0.0205 mole) of aluminum chloride powder was uniformly added over 15 min. After stirring for an additional 27 hr., hydrogen chloride was still being evolved. An additional 1.00 g. (0.0075 mole) of aluminum chloride was added, followed by stirring for an additional 5 hr., after which time hydrogen chloride evolution was not detected. Following hydrolysis and work-up, the product was taken up in an ether–methylene chloride mixture and chromatographed. Elution by hexane gave a 4% recovery of I; by ether, 0.33 g. (11% on I) of III, identified by infrared; by methylene chloride, 0.75 g. (22% on I) of XI, red-orange crystals, m.p. 147° dec. The infrared spectrum of XI was consistent with the proposed structure, the absence of "9–10" bands[10] showing that each ferrocene nucleus was heteroannularly disubstituted,[10] and a doublet showing that two types of ketone linkages, alkyl–aryl and aryl–aryl, were present.

Anal. Calcd. for $C_{40}H_{46}Fe_2O_4Si_2$: C, 63.3; H, 6.1; Fe, 14.7; Si, 7.4. Found: C, 63.2; H, 6.1; Fe, 14.4; Si, 7.1.

Elution with methanol gave 0.55 g. of an unidentified red solid. Remaining on the column was a dark red band which could not be eluted.

γ-Trimethylsilylpropylferrocene (XII).—The following is a typical Clemmensen[25] reduction procedure used in the present work. Using 1.00 g. of mercuric chloride, 15 ml. of water, 1.0 ml. of concentrated hydrochloric acid, and 10 g. of zinc dust, an amalgam was prepared.[25] To a three-necked flask fitted with a condenser was added the amalgam followed by 20 ml. of concentrated hydrochloric acid and then by 2.00 g. of I dissolved in 20 ml. of hexane. The flask was then heated at reflux for 47 hr., during which time additional acid and/or amalgam was added as needed. Reduction progress was followed by infrared results on samples periodically taken from the solvent layer. Subsequent work-up included a thorough extraction of the amalgam residue. The product was chromatographed as a hexane concentrate. Hexane elution gave 1.50 g. (78%) of XII, yellow crystals, m.p. 56–57°.

Anal. Calcd. for $C_{16}H_{24}FeSi$: C, 64.0; H, 8.1; Fe, 18.6; Si, 9.4. Found: C, 64.0; H, 8.0; Fe, 18.4; Si, 9.5.

δ-Trimethylsilylbutylferrocene (XIII).—Similarly, 2.50 g. of II in hexane was subjected to reduction for 38 hr. followed by work-up and chromatography which gave by hexane elution 2.18 g. (91%) of XIII as a yellow oil. After solidifying over Dry Ice and then allowing to warm, XIII melted sharply at 5°. The infrared spectra from XII and XIII were closely similar.

Anal. Calcd. for $C_{17}H_{26}FeSi$: C, 65.0; H, 8.3; Fe, 17.8; Si, 8.9. Found: C, 64.8; H, 8.2; Fe, 17.7; Si, 8.7.

1,3-Bis(γ-ferrocenylpropyl)tetramethyldisiloxane (XIV).—Similarly, 1.50 g. of III in benzene was subjected to reduction for 43 hr., followed by work-up and chromatography which gave by hexane elution 1.18 g. (83%) of XIV, yellow crystals, m.p. 104–105°.

Anal. Calcd. for $C_{30}H_{42}Fe_2OSi_2$: C, 61.4; H, 7.2; Fe, 19.1; Si, 9.6. Found: C, 61.5; H, 7.4; Fe, 19.1; Si, 9.4.

Ether elution gave 0.20 g. of an orange paste which, by infrared analysis, appeared to be a mixture of III with an intermediate reduction product in which only one carbonyl group was reduced.

1,3-Bis(δ-ferrocenylbutyl)tetramethyldisiloxane (XV-1).—Similarly, 2.50 g. of IV-2 in benzene was subjected to reduction for 76 hr. followed by work-up and chromatography which gave by hexane elution 1.60 g. (67%) of XV-1, a yellow oil which slowly crystallized, m.p. 34–35°. The infrared spectra of XIV and XV-1 were closely similar.

Anal. Calcd. for $C_{32}H_{46}Fe_2OSi_2$: C, 62.5; H, 7.6; Fe, 18.2; Si, 9.1. Found: C, 62.8; H, 7.8; Fe, 18.0; Si, 9.2.

Ether elution gave 0.45 g. of an orange oil which by infrared analysis appeared to be a mixture of IV-2 with intermediate reduction product.

Proof of Structure of XV-1 by Independent Synthesis (XV-2).—The addition of 10 ml. of concentrated sulfuric acid to 0.55 g. of XIII followed by shaking the reaction vessel for an additional 6 min. gave more than a 90% yield[9a] of methane. Without delay, the blue reaction mixture was carefully added to 25 ml. of externally cooled water, resulting in the formation of a blue aqueous solution with some blue oil present. After standing for 10 min. the blue color remained, thus indicating that the product was still protonated.[31] Therefore, aqueous potassium hydroxide was slowly added with external cooling until the aqueous phase turned yellow and was basic to litmus. Meanwhile more blue oil appeared and with shaking also turned yellow. The product was extracted with ether and chromatographed. Hexane elution gave 0.35 g. (65%) of XV-2, a yellow oil whose infrared spectrum was identical with that of XV-1. On standing, XV-2 passed to yellow crystals, m.p. 34–35°. A mixture melting point with XV-1 was undepressed.

Anal. Calcd. for $C_{32}H_{46}Fe_2OSi_2$: C, 62.5; H, 7.6; Fe, 18.2; Si, 9.1. Found: C, 62.8; H, 7.7; Fe, 18.1; Si, 9.1.

On the column there remained a faint yellow band.

δ-Dimethylhydroxysilylbutylferrocene (XVI).—The faint yellow band was eluted with a hexane–ether mixture and gave 0.05 g. (9%) of XVI as a yellow oil whose infrared spectrum differed from that of XIII only in the following ways: appearance of a strong band for silanol at 3.0 μ, and alteration of the prior trimethylsilyl absorption pattern in the 11.5–13.5-μ range.

1,1′-Bis(γ-trimethylsilylpropyl)ferrocene (XVII).—Dissolved in benzene, 2.80 g. of V was subjected to reduction for 35 hr., followed by work-up and chromatography which gave by hexane elution 2.15 g. (82%) of XVII as a yellow oil which melted sharply at 20–20.5° only after prolonged standing at reduced pressure.

Anal. Calcd. for $C_{22}H_{38}FeSi_2$: C, 63.8; H, 9.2; Fe, 13.5; Si, 13.5. Found: C, 63.9; H, 9.4; Fe, 13.2; Si, 13.6.

Ether elution gave 0.20 g. of an orange oil which, by infrared analysis, appeared to be a mixture of V with an intermediate reduction product in which only one carbonyl group was reduced.

1,1′-Bis(δ-trimethylsilylbutyl)ferrocene (XVIII).—Similarly, 2.50 g. of VI in benzene was subjected to reduction for 61 hr., followed by work-up and chromatography which gave by hexane elution 1.68 g. (72%) of XVIII as a yellow oil which melted sharply at −9 to −8° only after prolonged standing at reduced pressure. The infrared spectra from XVII and XVIII were closely similar.

Anal. Calcd. for $C_{24}H_{42}FeSi_2$: C, 65.1; H, 9.6; Fe, 12.6; Si, 12.7. Found: C, 65.1; H, 9.8; Fe, 12.5; Si, 12.9.

Ether elution gave 0.50 g. of an orange oil which, by infrared analysis, appeared to be a mixture of VI with intermediate reduction product.

Poly[(dimethyl)silamer-*alt*-propamer-*alt*-ferrocenylenamer-1,1′-*alt*-propamer-*alt*-(dimethyl)siloxamer][30] (XIX).—The addition of 3 ml. of concentrated sulfuric acid to 0.45 g. of XVII followed by shaking the reaction vessel for 7 min. gave a volume of gas corresponding to more than a 90% yield[9a] of methane. The blue reaction mixture was then promptly hydrolyzed by carefully adding it to 25 ml. of externally cooled water, resulting in a deep blue solution with some blue oil present. Careful treatment with aqueous alkali (cooling) followed by shaking discharged the blue color, and the product, present in the form of yellow curds, was extracted with an ether–methylene chloride mixture. After drying, removal of solvent gave 0.40 g. (89%) of XIX as a viscous yellow material which could be drawn into long wispy filaments and whose infrared spectrum showed the same evidence for polymer formation as in the case of the corresponding ketone-type polymer VII.

Poly-8:92[(dimethyl)silamer-*alt*-propamer-*alt*-ferrocenylenamer-1,1′-*alt*-propamer-*alt*-(dimethyl)siloxamer-*co*-(dimethyl)siloxamer][30] (XX).—To 0.25 g. (0.0006 mole) of XVII was added 3 ml. of concentrated sulfuric acid, and the reaction vessel was shaken for 8 min., at which point gas evolution ceased. Thereafter, 1.50 g. (0.0116 mole) of dimethyldichlorosilane was added and the reaction mixture was shaken for 12 min. until the clear upper chlorosilane layer merged with the blue bottom layer and hydrogen chloride evolution ceased. The reaction mixture was then promptly hydrolyzed by carefully adding it to 25 ml. of ice water, after which the blue color was changed to yellow by the addition (cooling) of aqueous alkali. Extraction with an ether–methylene chloride mixture gave the product as a pale yellow oil. After an infrared spectrum was taken, this oil was taken up in hexane and chromatographed. Elution with hexane first gave 0.08 g. (9% on chlorosilane) of polydimethylsiloxane fluid and then a trace amount of unidentified yellow paste. Successive washings with hexane, then a hexane–ether mixture, then ether served to progressively move, without splitting, the remaining yellow band down the column. Eluted with an ether–methylene chloride mixture, this band gave 0.38 g. (52% on XVII) of XX, a pale yellow oil whose infrared spectrum was indistinguishable from that of the crude product before fractionation. The ratio of monomers in XX was determined by the best fit to the elemental analyses.

Anal. Calcd. for $[(C_{20}H_{32}FeOSi_2)_1(C_2H_6OSi)_{11}]_n$: C, 39.9; H, 8.1; Fe, 4.6. Found: C, 40.4; H, 8.7; Fe, 5.2.

Poly[(dimethyl)silamer-*alt*-butamer-*alt*-ferrocenylenamer-1,1′-*alt*-butamer-*alt*-(dimethyl)siloxamer][30] (XXI-1).—Starting with 0.50 g. of XVIII and 3 ml. of concentrated sulfuric acid, the steps described in the preparation of XIX were repeated to give similar infrared and rheology results. Obtained was 0.45 g. (91%) of yellow polymer XXI-1. The infrared spectra from XIX and XXI-1 were closely similar.

Proof of Structure of XXI-1 by Independent Synthesis (XXI-2).—Dissolved in benzene, 2.40 g. of the ketone-type polymer VIII-2 was subjected to reduction. A reflux time of 85 hr. was required to eliminate the infrared absorption band for carbonyl. After work-up there was obtained 1.40 g. (62%) of XXI-2 as a viscous yellow material. The infrared spectra from XXI-1 and XXI-2 were identical, except that the latter gave less absorption for silanol at 3.0 μ.

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