Anal. Calcd. for $C_{16}H_{24}Si$: C, 78.6; H, 9.90. Found: C, 78.8; H, 9.96.

Di-*t*-butylphenylsilane.—The procedure described above was repeated using the *t*-butylmagnesium bromide prepared from 279 g. (1.53 moles) of *t*-butyl bromide and 25 g. (0.118 mole) of phenyltrichlorosilane. The volatile material produced by heating the reaction mixture to 160–170° was passed into an ice-cooled chloroform solution of bromine. The chloroform solution was washed with an aqueous saturated solution of sodium sulfite to remove the excess bromine. The chloroform layer was dried over Drierite and the chloroform removed by distillation. The residual isobutylene bromide distilled at 149° (747 mm.), yield 27 g. (0.128 mole). This compound was identified by its boiling point and infrared spectrum.

The di-*t*-butylphenylsilane, which was obtained upon working up the residue in the distillation flask, distilled at 46° (0.4 mm.), yield 5.5 g. (10%), $n^{25}D$ 1.489.

Anal. Calcd. for $C_{14}H_{24}Si$: C, 76.4; H, 10.96. Found: C, 76.6; H, 10.90.

Attempted Preparation of Di-*o*-tolylphenylsilane.—The procedure described above was repeated using the Grignard reagent prepared from 190 g. (1.1 moles) of *o*-tolyl bromide and 11 g. (0.077 mole) of phenyltrichlorosilane. Ether was the only volatile compound recovered when the reaction mixture was heated to 160–170°. Upon working up the residue in the distillation flask and distilling the organic layer, toluene and a high-boiling, semi-crystalline material were obtained. An infrared spectrum of this material did not show the Si–H bond. This material was dissolved in a hot solution of alcoholic sodium hydroxide, from which 4 g. of a white crystalline solid precipitated upon cooling. Recrystallization from absolute alcohol gave a product which melted at 87–89°. Infrared spectral analysis showed the solid to contain the following groups: C_6H_5–Si, *o*-$CH_3C_6H_4$–Si–OH and Si–O. This compound may be di-*o*-tolylphenylsilanol, (*o*-$CH_3C_6H_4)_2C_6H_5SiOH$.

Anal. Calcd. for $C_{20}H_{20}OSi$: C, 78.9; H, 6.60. Found: C. 79.0; H, 7.2.

Another experiment was conducted in which the above procedure was modified by holding the reaction mixture at the reflux temperature for 4 hr. Upon hydrolysis of the reaction mixture a white solid was precipitated. This solid was recrystallized from hot toluene, giving 1.6 g. (0.07 mole) of product, m.p. 103°; identified as being *o*-tolylphenylsilanediol, (*o*-$CH_3C_6H_4)C_6H_5Si(OH)_2$.

Anal. Calcd. for $C_{13}H_{14}O_2Si$: C, 67.8; H, 6.10. Found: C, 67.8; H, 6.3.

Acknowledgments.—Analyses were by Miss J. Dickey of the Indiana University Microanalytical Laboratory. This paper is based upon work performed under contract Nonr-90802-Task NR 356-321 (Office of Naval Research).

BLOOMINGTON, IND.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Aliphatic Organo-functional Siloxanes. V. Synthesis of Monomers by Platinum-catalyzed Addition of Methyldichlorosilane to Unsaturated Esters and Nitriles[1]

BY L. H. SOMMER, F. P. MACKAY, O. W. STEWARD AND P. G. CAMPBELL

RECEIVED NOVEMBER 23, 1956

Extension of an important synthesis discovered by G. H. Wagner, which involves platinum-catalyzed addition of silicon hydrides to olefins, has resulted in simple synthetic routes to nine monomers for organo-functional siloxanes. The nitriles and esters being reported have a functionality of 2 at the silicon atom. Reaction of methyldichlorosilane with acrylate esters results in addition of the silyl group to the non-terminal olefinic carbon and thus gives products in which the ester group is readily cleaved from silicon. In important contrast, methacrylate esters give addition of the silyl group to the terminal olefinic carbon and yield adducts which are stable toward cleavage of the ester group from silicon. Olefins in which the functional group is not conjugated with the double bond give products resulting from addition of the silyl group to the terminal olefinic carbon.

Introduction.—If organosilicon chemistry is to progress appreciably beyond the point represented in organic chemistry by monomers and polymers in which the basic chain of atoms (C–C–C bonds in organic chemistry and Si–O–Si groupings in organosilicon chemistry) bears unsubstituted hydrocarbon substituents, it seems essential that simple synthetic procedures be developed for the preparation of monomers which can easily be converted to aliphatic organo-functional siloxanes.

Previous publications from this Laboratory have reported synthetic approaches to aliphatic organo-functional siloxanes involving selective cleavage of one methyl group from trimethylsilyl, Me_3Si, in a variety of organo-functional silanes through reaction with concd. sulfuric acid.[2a,b,c]

More recently, the direct synthesis of organosiloxane esters and acids from halomethylsiloxanes and halomethylethoxysilanes has been reported. These latter syntheses represented a definite improvement over the former method and involved reaction, in suitable solvents, of the halomethylsilanes with anions derived from ethyl malonate and ethyl cyanoacetate. Organofunctional monomers in which the silicon is mono- as well as difunctional can be made by this synthesis.[2d]

However, an even simpler and more direct synthetic route obviously was desirable. In the present paper we wish to record such a synthesis which leads easily to aliphatic organo-functional monomers in which the functionality at the silicon atom is 2.

The addition of trichlorosilane to simple olefins proceeds smoothly and in excellent yield in the presence of diacetyl peroxide or ultraviolet light.[3] Addition of compounds containing the Si–H bond

$$R—CH=CH_2 + HSiCl_3 \xrightarrow[\text{or u.v. light}]{(CH_3COO)_2} RCH_2CH_2SiCl_3$$

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[1] Paper 52 in a series on organosilicon chemistry. For Paper 51, see L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1008 (1957).

[2] (a) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, THIS JOURNAL, **75**, 2932 (1953); (b) L. H. Sommer, W. D. English, G. R. Ansul and D. N. Vivona, *ibid.*, **77**, 2485 (1955); (c) L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., *ibid.*, **76**, 1609 (1954); (d) L. H. Sommer, J. M. Masterson, O. W. Steward and R. H. Leitheiser, *ibid.*, **78**, 2010 (1956).

[3] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **69**, 188 (1947); **70**, 484 (1948); C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947).

to olefins also takes place in the absence of a catalyst at elevated temperatures (about 300°).[4]

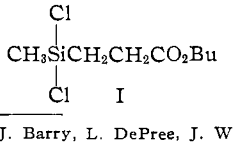
More recently, the addition of phenylsilane, diphenylsilane, phenylmethylsilane, amylsilane and tribromosilane to olefins in the presence of *t*-butyl perbenzoate has been reported.[5] However, attempts to extend this procedure to readily available olefins such as methyl acrylate or acrylonitrile resulted in rapid polymerization of the olefin. Thus, peroxide-catalyzed additions of silanes to olefins containing functional groups suffer from the limitations placed on this procedure by the polymerization of the readily available "vinyl monomers." A further limitation is provided by the greatly decreased reactivity of the Si–H bond in alkyldichlorosilanes as compared to trichlorosilane when a peroxide catalyst is used.[3]

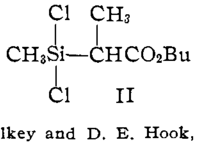
In 1953, G. H. Wagner reported the use of platinum supported on finely divided charcoal as a catalyst for the addition of silicon hydrides to a number of olefins and to acetylene.[6] The addition reactions were performed at pressures of 45 to 115 p.s.i. and reaction temperatures of 100 to 300°. The olefins used were ethylene, allyl chloride, trichloroethylene, vinylidene fluoride and butadiene. Trichlorosilane was the silicon hydride most generally used. However, examples of addition reactions of triethoxysilane, ethyldichlorosilane and dichlorosilane also were reported.

In another publication Wagner and co-workers[7] reported the preparation of β-phenylethyltrichlorosilane by addition of trichlorosilane to styrene at 200° (20 hr. in a stainless steel pressure reactor) in the presence of *t*-butylcatechol (inhibitor) using 5% platinum on powdered charcoal. The yield of product was excellent.

In view of the above good results obtained with platinized charcoal catalyst using an easily polymerizable olefin such as styrene, it seemed that this catalyst might also be effective for the addition of silicon hydrides to other readily available "vinyl monomers." Application of this procedure to olefinic esters would provide a simple and direct route to the intermediates for organopolysiloxane ester systems.

Platinum-catalyzed Addition of Methyldichlorosilane to Acrylates and Methacrylates.—In the present work reaction of *n*-butyl acrylate with methyldichlorosilane (2% Pt–C catalyst) in an all-glass apparatus at atmospheric pressure proceeded slowly. During 16 hr. the boiling point of the reaction mixture increased from 67 to 145°. Fractionation gave a 42% yield of adduct which analyzed correctly for *n*-butyl methyldichlorosilylpropionate. Addition of Si–H to the olefinic linkage can lead to two adduct structures.

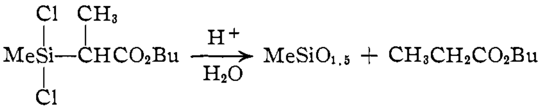

$CH_3\overset{Cl}{\underset{Cl}{Si}}CH_2CH_2CO_2Bu$ I


$CH_3\overset{Cl}{\underset{Cl}{Si}}-\overset{CH_3}{C}HCO_2Bu$ II

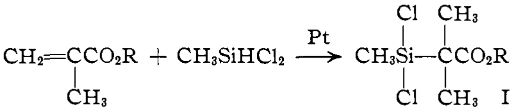
Structure II contains the Si—C—C=O grouping which is known to give carbon–silicon cleavage with acids and bases. For example, ethyl trimethylsilylacetate gives ethyl acetate when treated with dilute acid.[8] In contrast, structure I contains the

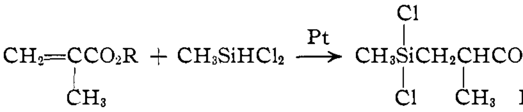
$$2Me_3SiCH_2CO_2Et \xrightarrow[H_2O]{H^+} Me_3SiOSiMe_3 + 2CH_3CO_2Et$$

Si—C—C—C=O system which is stable toward cleavage of its C–Si bond with most reagents. When the adduct obtained from *n*-butyl acrylate was treated with water, a resinous solid separated and an oily upper layer formed. The organic layer upon distillation gave a 75% yield of *n*-butyl propionate. This result indicates structure II for the adduct.[9]


$$Me\overset{Cl}{\underset{Cl}{Si}}-\overset{CH_3}{C}HCO_2Bu \xrightarrow[H_2O]{H^+} MeSiO_{1.5} + CH_3CH_2CO_2Bu$$

As another possible means of synthesizing the Si—C—C—C=O system through the platinum-catalyzed addition of silicon hydrides to olefins, the use of methacrylate esters was investigated next. The basis for this study was the possibility that the α-methyl group in methacrylate esters would lead to the desired mode of addition because of the steric requirements of that methyl group and/or its hyperconjugation with the olefinic double bond.


$$CH_2{=}\underset{CH_3}{C}CO_2R + CH_3SiHCl_2 \xrightarrow{Pt} CH_3\overset{Cl}{\underset{Cl}{Si}}-\overset{CH_3}{\underset{CH_3}{C}}CO_2R$$ III


$$CH_2{=}\underset{CH_3}{C}CO_2R + CH_3SiHCl_2 \xrightarrow{Pt} CH_3\overset{Cl}{\underset{Cl}{Si}}CH_2\underset{CH_3}{C}HCO_2R$$ IV

The latter reaction was in fact realized with *n*-butyl methacrylate and compound IV (R = *n*-Bu) was obtained.

When methyldichlorosilane and *n*-butyl methacrylate were heated in the presence of 2% Pt–C, the boiling point of the reaction mixture increased to a maximum of 120° after 3 hr. Fractionation gave a 32% yield of *n*-butyl α-methyl-β-methyldichlorosilylpropionate, IV (R = *n*-Bu). This product when poured into water gave an oil but no solid. Treatment of this oil with hot acetic–hydrochloric acid mixture gave a stiff, acidic, silicon-containing polymer. If addition had given a product containing the silicon atom linked to the α-carbon of the methacrylate ester, the expected hydrolysis products would be methylpolysiloxane and *n*-butyl iso-

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(4) A. J. Barry, L. DePree, J. W. Gilkey and D. E. Hook, THIS JOURNAL, **69**, 2916 (1947).

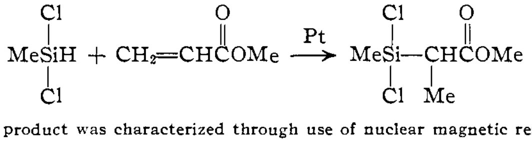
(5) J. L. Speier, R. Zimmerman and J. Webster, *ibid.*, **78**, 2278 (1956).

(6) G. H. Wagner, U. S. Patent 2,637,738, May 5 (1953).

(7) G. H. Wagner, D. L. Bailey, A. N. Pines, M. L. Dunham and D. B. McIntire, *Ind. Eng. Chem.*, **45**, 367 (1953).

(8) J. R. Gold, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **70**, 2874 (1948).

(9) Subsequent to the completion of our work, L. Goodman, R. M. Silverstein and J. N. Shoolery, *ibid.*, **78**, 4493 (1956), reported that methyldichlorosilane adds to methyl acrylate in the presence of platinum as


$$Me\overset{Cl}{\underset{Cl}{Si}}H + CH_2{=}CH\overset{O}{\overset{\|}{C}}OMe \xrightarrow{Pt} Me\overset{Cl}{\underset{Cl}{Si}}-\underset{Me}{C}H\overset{O}{\overset{\|}{C}}OMe$$

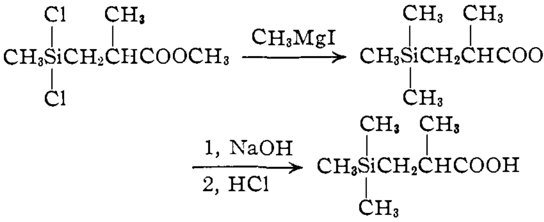
The product was characterized through use of nuclear magnetic resonance.

butyrate. Neither of these substances was formed on treatment of the adduct with water. (A definitive proof of the structures of the adducts obtained from methyl and ethyl methacrylates with methyldichlorosilane is given below.)

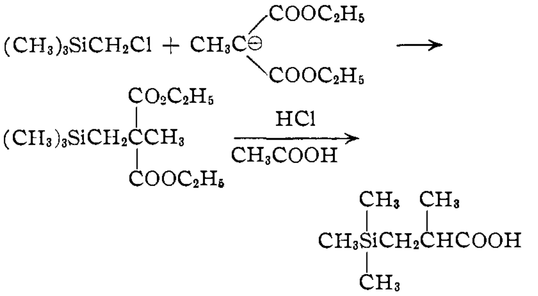
The addition of silicon hydrides to *methyl* methacrylate would provide an exceedingly convenient method for the preparation of silicon-containing esters since methyl methacrylate is more readily available than other methacrylate esters. Methyl methacrylate and methyldichlorosilane were heated together in the presence of 2% Pt–C. Within 3 hr. the boiling point of the reaction mixture increased from 54 to 142°. Fractionation gave a 58% yield of methyl α-methyl-β-methyldichlorosilylpropionate, IV (R = Me). There remained a large residue from the distillation which was believed to be polymerized methyl methacrylate. This corresponded to 24.5% of the starting quantity of ester. In subsequent experiments the yield of adduct was increased to 86% by the use of hexane as a solvent. An excess of methyldichlorosilane (100%) also increased the yield to 70%. Both of these procedures lowered the reaction temperature and greatly decreased the amount of polymerization of the methyl methacrylate. Similar results were obtained with ethyl methacrylate giving ethyl α-methyl-β-methyldichlorosilylpropionate, IV (R = Et) in 74% yield.

The structures of the methylacrylate methyldichlorosilane adducts were strongly indicated by their stability to acid. In contrast to ethyl trimethylsilylacetate, carbon–silicon cleavage did not occur when the adduct of methyl methacrylate and methyldichlorosilane was heated for 12 hr. with a mixture of concentrated hydrochloric and acetic acids. This indicates that the methyldichlorosilyl group is attached to the carbon atom which is beta to the carbonyl group as in structure IV.

A more definitive proof of structure for the methyldichlorosilane–methacrylate adducts was provided by the syntheses



$$\mathrm{CH_3\underset{Cl}{\overset{Cl}{Si}}CH_2\overset{CH_3}{C}HCOOCH_3} \xrightarrow{\mathrm{CH_3MgI}} \mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}CH_2\overset{CH_3}{C}HCOOCH_3} \xrightarrow[\text{2, HCl}]{\text{1, NaOH}} \mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}CH_2\overset{CH_3}{C}HCOOH} \quad (1)$$



$$\mathrm{(CH_3)_3SiCH_2Cl + CH_3C^{\ominus}\begin{matrix}\diagup COOC_2H_5\\ \diagdown COOC_2H_5\end{matrix}} \longrightarrow \mathrm{(CH_3)_3SiCH_2\underset{COOC_2H_5}{\overset{CO_2C_2H_5}{C}}CH_3} \xrightarrow[\mathrm{CH_3COOH}]{\mathrm{HCl}} \mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}CH_2\overset{CH_3}{C}HCOOH} \quad (2)$$

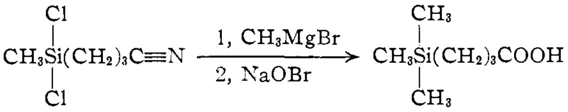
The carboxylic acid obtained from the methyldichlorosilane–methyl methacrylate adduct in sequence 1 was identical in physical properties with the acid obtained from the independent synthesis in sequence 2. The p-bromoanilide derivatives had the same m.p. and mixed m.p. Thus structure IV is shown to be the correct one.

Platinum-catalyzed Addition of Methyldichlorosilane to Unconjugated Olefinic Esters and Nitriles.—Table I gives data on the addition of methyldichlorosilane to nine olefinic esters and nitriles. Methyldichlorosilane reacts very readily with all of the unconjugated olefinic esters and nitriles in Table I. For the addition reactions of these olefins with methyldichlorosilane, it is usually advisable to add the silane slowly to the olefin and catalyst maintained at a temperature of 70–100°. The reaction is generally quite exothermic and may become very vigorous if all of the reactants are mixed and then heated. Platinum-on-charcoal catalyst (2% Pt) in the amount of 1 g. per mole of olefin is usually sufficient.

The methacrylates are far less reactive than the other olefins listed in Table I and hence can be mixed with catalyst and methyldichlorosilane and then heated.

Evidence for addition of the silyl group to the terminal carbon of the unconjugated olefinic esters and nitriles of Table I was obtained by means of proofs of structure for three of the adducts.

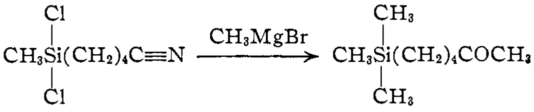
The adduct from allyl cyanide was treated with methylmagnesium bromide to give 5-trimethylsilyl-2-pentanone and the ketone was then converted to the corresponding known[2a] carboxylic acid.



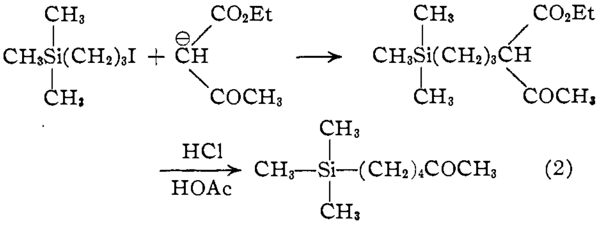
$$\mathrm{CH_3\underset{Cl}{\overset{Cl}{Si}}(CH_2)_3C{\equiv}N} \xrightarrow[\text{2, NaOBr}]{\text{1, CH}_3\text{MgBr}} \mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}(CH_2)_3COOH}$$

The authentic γ-trimethylsilylbutyric acid[2a] and the acid derived from the adduct had the same physical properties and gave derivatives with p-bromophenacyl bromide having the same melting point. A mixed m.p. showed no depression.

The adduct from 4-pentenonitrile was treated with methylmagnesium bromide to give 6-trimethylsilyl-2-hexanone. The same ketone was obtained from an acetoacetic ester synthesis using 3-iodopropyltrimethylsilane.



$$\mathrm{CH_3\underset{Cl}{\overset{Cl}{Si}}(CH_2)_4C{\equiv}N} \xrightarrow{\mathrm{CH_3MgBr}} \mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}(CH_2)_4COCH_3} \quad (1)$$



$$\mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}(CH_2)_3I + \overset{\ominus}{C}H\begin{matrix}\diagup CO_2Et\\ \diagdown COCH_3\end{matrix}} \longrightarrow \mathrm{CH_3\underset{CH_3}{\overset{CH_3}{Si}}(CH_2)_3CH\begin{matrix}\diagup CO_2Et\\ \diagdown COCH_3\end{matrix}} \xrightarrow[\mathrm{HOAc}]{\mathrm{HCl}} \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}(CH_2)_4COCH_3} \quad (2)$$

The authentic ketone from sequence 2 and the ketone obtained from the adduct had the same physical properties and gave derivatives with 2,4-dinitrophenylhydrazine having the same melting points. A mixed m.p. showed no depression.

The adduct from ethyl 4-pentenoate was treated with methylmagnesium bromide to give 6-trimethylsilyl-2-methylhexan-2-ol. The same alcohol, as

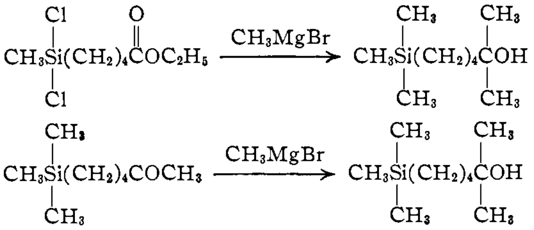
TABLE I

ADDITION OF METHYLDICHLOROSILANE TO UNSATURATED ESTERS AND NITRILES

Olefin	Product	Yield,[b] %	B.p. °C.	B.p. Mm.	Silicon, % Calcd.	Silicon, % Found	Chlorine, % Calcd.	Chlorine, % Found
$CH_2{=}C(CH_3)CO_2CH_3$	$CH_3(Cl_2)SiCH_2CH(CH_3)CO_2CH_3$	86	79	10	13.1	12.8	33.0	32.7
$CH_2{=}C(CH_3)CO_2C_2H_5$	$CH_3(Cl_2)SiCH_2CH(CH_3)CO_2C_2H_5$	74	105	17	12.2	12.0	30.9	31.0
$CH_2{=}C(CH_3)CO_2$-$n$$C_4H_9$	$CH_3(Cl_2)SiCH_2CH(CH_3)CO_2$-$n$-$C_4H_9$	32	78	3	10.9	10.8	27.6	27.3
$CH_2{=}CHCH_2CO_2C_2H_5$	$CH_3(Cl_2)SiCH_2CH_2CH_2CO_2C_2H_5$[a]	81	108	12	12.2	12.6	30.9	31.2
$CH_2{=}CHCH_2CH_2CO_2C_2H_5$	$CH_3(Cl_2)SiCH_2CH_2CH_2CH_2CO_2C_2H_5$	85	118	8	11.5	11.7	29.2	29.2
$CH_2{=}CHCH_2CH(CO_2C_2H_5)_2$	$CH_3(Cl_2)SiCH_2CH_2CH_2CH(CO_2C_2H_5)_2$[a]	74	154	5	8.9	9.2	22.5	22.4
$CH_2{=}CHCH_2C{\equiv}N$	$CH_3(Cl_2)SiCH_2CH_2CH_2C{\equiv}N$	73	122	17	15.4	15.8	38.9	39.1
$CH_2{=}C(CH_3)CH_2C{\equiv}N$	$CH_3(Cl_2)SiCH_2CH(CH_3)CH_2C{\equiv}N$[a]	43	116	12	14.3	14.4	36.1	36.0
$CH_2{=}CHCH_2CH_2C{\equiv}N$	$CH_3(Cl_2)SiCH_2CH_2CH_2CH_2C{\equiv}N$	66	137	12	14.3	14.3	36.1	36.1

[a] Proposed structure for the adduct but definitive proof not obtained. [b] Yields are based on amount of olefin since an excess (about 10–20%) of methyldichlorosilane generally was used.

shown by physical properties and identical infrared spectrum, was obtained from reaction of 6-trimethylsilyl-2-hexanone with methylmagnesium bromide.



$$CH_3Si(Cl)_2(CH_2)_4C(=O)OC_2H_5 \xrightarrow{CH_3MgBr} CH_3Si(CH_3)_2(CH_2)_4C(CH_3)_2OH$$

$$CH_3Si(CH_3)_2(CH_2)_4COCH_3 \xrightarrow{CH_3MgBr} CH_3Si(CH_3)_2(CH_2)_4C(CH_3)_2OH$$

Experimental

Starting Materials.—Methyldichlorosilane, b.p. 41°, was obtained from Dow Corning Corp. and fractionally distilled before being used. Methyl methacrylate was used directly as obtained from Rohm and Haas Co. Ethyl methacrylate was the commercial grade supplied by Monomer–Polymer Inc. n-Butyl methacrylate was prepared by the reaction of methacrylic acid with n-butyl alcohol in the presence of sulfuric acid and hydroquinone. n-Butyl acrylate was supplied by Union Carbide and Carbon Corp. Ethyl vinylacetate was prepared from vinylacetyl chloride by the method of Jeffery and Vogel.[10] Dehydrochlorination of 4-chlorovaleronitrile, supplied by the du Pont Co., was effected in 50% yield by the use of quinoline, giving 4-pentenonitrile, b.p. 143° (730 mm.), $n^{20}D$ 1.4206.[11] 4-Pentenoic acid[12] was prepared by hydrolysis of 4-pentenonitrile. Ethyl 4-pentenoate was prepared from the acid by the method of Paul.[13]

The 2% Pt–C catalyst was supplied by Baker and Co.

Reaction of n-Butyl Acrylate and Methyldichlorosilane.—In an all-glass apparatus consisting of a 500-cc. flask and a glass-jointed condenser were placed 90 g., 0.7 mole, of n-butyl acrylate, 82 g., 0.71 mole, of methyldichlorosilane and 1 g. of 2% platinum-on-charcoal. After heating at reflux temperature for 16 hr., the temperature of the boiling reaction products was 145° as compared to an initial temperature of 67°. The reaction mixture was cooled, filtered to remove the catalyst and fractionated. There was obtained 71.7 g., 0.29 mole, of n-butyl methyldichlorosilylpropionate, b.p. 76° (3 mm.), 42% yield.

Anal. Calcd. for $C_8H_{16}SiO_2Cl_2$: Si, 11.5; Cl, 29.2. Found: Si, 11.7; Cl, 28.4.

When 20 g., 0.08 mole, of the adduct was poured into water, a solid and two liquid layers were formed. The solid was removed by filtration and the liquid layers were separated. Fractionation of the dried upper layer gave n-butyl propionate, b.p. 145°, 8 g., 0.06 mole, 75% yield, sapn. equiv. 131 (calcd. 130). This experiment clearly shows rapid C–Si cleavage and thus strongly indicates that the adduct is n-butyl α-methyldichlorosilylpropionate (II).

Reaction of n-Butyl Methacrylate and Methyldichlorosilane.—In an all glass apparatus consisting of a 500-cc. flask and a condenser were placed 72 g., 0.5 mole, of methyldichlorosilane, 1 g. of 2% Pt–C and 2 g. of hydroquinone (inhibitor). After heating for 3 hr. at reflux, the temperature of the reaction products in the flask had reached 120°. Heating at reflux was continued for 10 additional hr., but there was no further temperature rise. At this point the reaction mixture was cooled and 27 g., 0.23 mole, of additional methyldichlorosilane and 0.25 g. of Pt–C were added. Heating was then resumed, but the temperature fell to 87° where it remained during 12 more hr. of heating. Fractional distillation of the product gave n-butyl α-methyl-β-methyldichlorosilylpropionate (IV), 42.8 g., 0.16 mole, 32% of theoretical. When the product was treated with water, an oil was formed which contained no n-butyl isobutyrate. Further treatment of the oil with hot concd. hydrochloric–glacial acetic acid mixture gave no C–Si cleavage. A polysiloxane–polycarboxylic acid was obtained as a stiff polymer with considerable affinity for glass surfaces.

Reaction of Methyl Methacrylate and Methyldichlorosilane.—(a) In an all-glass apparatus consisting of a 500-cc. flask and a condenser were placed 110 g., 1.1 moles, of methyl methacrylate; 138 g., 1.2 moles, of methyldichlorosilane; 1.5 g., of 2% Pt–C and 1 g. of hydroquinone. This mixture was heated to the boiling point, 54°. The temperature rose steadily. After 3 hr. of heating, it had reached 142°. There was no additional temperature rise in 24 more hr. of heating. Fractionation gave methyl α-methyl-β-methyldichlorosilylpropionate, compound IV ($R = CH_3$), in 58% yield.

(b) The reaction was carried out in the same apparatus as above with the following quantities of materials: 50 g., 0.5 mole, of methyl methacrylate; 115 g., 1 mole, of methyldichlorosilane; 1 g. of 2% Pt–C; 1 g. of hydroquinone. These materials were heated from 60 to 87° (excess CH_3SiHCl_2 kept the temperature down) for 24 hr. The yield of product was 70% of the theoretical.

(c) The reaction was carried out with the following quantities of materials: 50 g., 0.5 mole, methyl methacrylate; 65 g., 0.56 mole, of methyldichlorosilane; 0.5 g. of 2% Pt–C; 1 g. of hydroquinone; 200 cc. of hexane as a solvent. These materials were heated from 64 to 75° for 16 hr. The yield of product was 86%.

(d) The reaction was attempted with the following materials: 100 g., 1 mole, of methyl methacrylate; 200 g., 1.8 moles, of methyldichlorosilane; 0.5 g. of *rhodium*-on-charcoal (Baker and Co.). When the rhodium catalyst was added to the methyldichlorosilane, there was a small flash of flame which immediately stopped. The reaction mixture was then heated at 56° for three days. No adduct was obtained.

Use of 5% palladium-on-charcoal and of Raney nickel as catalysts also gave *no* Si–H addition.

Additions of Methyldichlorosilane to Unconjugated Olefinic Esters and Nitriles.—A detailed description of the general procedure used in a typical reaction is as follows: Allyl cyanide, 101 g., 1.5 moles, and 0.75 g. of 2% Pt–C catalyst were placed in an all-glass apparatus equipped with a thermometer well, separatory funnel and condenser. (Rubber stoppers were *not* used in these preparations to avoid the possibility of sulfur poisoning of the catalyst.) The apparatus was vented through a concd. sulfuric acid Gilman trap. Allyl cyanide was then heated to reflux temperature

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[10] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 658 (1948).

[11] R. Paul and H. Cottin, *Bull. soc. chim.*, [5] **4**, 933 (1937).

[12] R. Linstead and H. Rydon, *J. Chem. Soc.*, 580 (1933).

[13] R. Paul, *Ann. chim.*, [10] **18**, 332 (1932).

and methyldichlorosilane, 195 g., 1.7 moles, was added dropwise over a period of 2 hr. The reaction mixture was then heated overnight to ensure complete reaction. Fractionation of the filtered reaction product by means of a column packed with glass helices gave the product in 73% yield.

Proof of the Structure of the Methacrylate–Methyldichlorosilane Adducts. A. Reaction of Methylmagnesium Iodide with the Adduct, Methyl α-Methyl-β-methyldichlorosilylpropionate.—Addition of methylmagnesium iodide, 1 mole in 300 cc. of ether, to 108 g., 0.5 mole, of the adduct during 5 hr. was followed by stirring at room temperature for 20 hr. Treatment with water and dilute hydrochloric acid followed by fractionation gave methyl α-methyl-β-trimethylsilylpropionate, 22.4 g., 0.16 mole, b.p. 78° (28 mm.), $n^{20}_{\rm D}$ 1.4202, 32% yield.

Anal. Calcd. for $C_8H_{18}SiO_2$: Si, 16.1; sapn. equiv., 174; $MR_{\rm D}$, 50.57. Found: Si, 15.8; sapn. equiv., 173; $MR_{\rm D}$, 50.50.

B. Saponification of Methyl α-Methyl-β-trimethylsilylpropionate.—A mixture of 19.3 g., 0.11 mole, of methyl α-methyl-β-trimethylsilylpropionate, 5 g., 0.12 mole, of sodium hydroxide, 10 cc. of ethyl alcohol and 10 cc. of water was refluxed on the steam-bath for 14 hr. It was then cooled and acidified with hydrochloric acid. The layers were separated and the water layer was extracted with ether. The ether extracts were combined with the main organic layer and the combined layers were dried over anhydrous magnesium sulfate. Fractional distillation gave 10.9 g., 0.068 mole, 62% yield, of α-methyl-β-trimethylsilylpropionic acid, b.p. 90° (3 mm.), $n^{20}_{\rm D}$ 1.4309.[14]

Anal. Calcd. for $C_7H_{16}SiO_2$: Si, 17.5; neut. equiv., 160. Found: Si, 17.6; neut. equiv., 159.

In a 50-cc. flask were placed 1 g. of α-methyl-β-trimethylsilylpropionic acid, 40 cc. of benzene and 0.5 g. of thionyl chloride. These materials were allowed to react at room temperature with shaking. After 2 hr., 1.2 g. of *p*-bromoaniline was added, and the reaction mixture was heated on the steam-bath for 2 minutes. The reaction mixture was then filtered. The filtrate was extracted with 5% hydrochloric acid and then evaporated to dryness. Recrystallization from hexane gave shiny white plates, m.p. 117.2–117.5°.

Anal. Calcd. for $C_{13}H_{20}O_2SiBrN$: Si, 8.50. Found: Si, 8.70.

C. Preparation of Authentic α-Methyl-β-trimethylsilylpropionic Acid.—This acid was prepared again by reaction in ethanol of sodiomethylmalonic ester with chloromethyltriethylsilane, followed by treatment of the resulting diethyl (trimethylsilylmethyl)-methylmalonate with concd. hydrochloric–glacial acetic acid mixture. Fractionation gave the acid having b.p. 90° (3 mm.), $n^{20}_{\rm D}$ 1.4311.

The *p*-bromoanilide prepared by the procedure described above had m.p. 117–117.5°. A mixed melting point of the derivatives gave no depression.

Proof of the Structure of the Allyl Cyanide–Methyldichlorosilane Adduct.—A solution of the adduct (γ-cyanopropyl)-methyldichlorosilane, 136 g., 0.75 mole, in 200 cc. of ether was added to 2.7 moles of methylmagnesium bromide in 700 cc. of ether. After stirring and refluxing for 12 hr., the reaction mixture was hydrolyzed and treated with hydrochloric acid. Fractionation gave 5-trimethylsilyl-2-pentanone, 33.6 g., 0.21 mole, b.p. 71° (13 mm.), $n^{20}_{\rm D}$ 1.4231, d^{20} 0.8279, 30% yield.

Anal. Calcd. for $C_8H_{18}SiO$: Si, 17.7; $MR_{\rm D}$, 48.80. Found: Si, 17.3; $MR_{\rm D}$, 48.90.

Oxidation of 5-trimethylsilyl-2-pentanone with sodium hypobromite gave γ-trimethylsilylbutyric acid in 41% yield, b.p. 123° (16 mm.), $n^{25}_{\rm D}$ 1.4308.[15]

The *p*-bromophenacyl bromide derivative of the acid obtained from the adduct had m.p. 61–62°. *Anal.* Calcd. for $C_{15}H_{21}O_3SiBr$: Si, 7.85. Found: Si, 7.89.

The *p*-bromophenacyl bromide derivative from authentic acid[16] also had m.p. 61–62° and gave no depression in a mixed melting point determination.

Proof of the Structure of the Adduct from 4-Pentenonitrile and Methyldichlorosilane.—The adduct, 98.1 g., 0.5 mole, dissolved in 200 cc. of ether was stirred with methylmagnesium bromide, 1.75 moles, for 2 days and the reaction mixture was then hydrolyzed with water followed by dilute hydrochloric acid. The water layer was extracted three times with ether and the combined ether layers dried over magnesium sulfate. Fractional distillation gave 6-trimethylsilyl-2-hexanone, b.p. 85° (10 mm.), $n^{20}_{\rm D}$ 1.4289, d^{20} 0.8281.

Anal. Calcd. for $C_9H_{20}OSi$: Si, 16.3; $MR_{\rm D}$, 53.43. Found: Si, 16.6; $MR_{\rm D}$, 53.62.

The 2,4-dinitrophenylhydrazone was prepared and had m.p. 92.4–93°.

Anal. Calcd. for $C_{15}H_{24}O_4SiN_4$: Si, 7.97. Found: Si, 8.14.

The following comprises a description of the synthesis of authentic 6-trimethylsilyl-2-hexanone.

(γ-Chloropropyl)-methyldichlorosilane was prepared by addition of methyldichlorosilane to allyl chloride in the presence of 2% Pt–C. The product had b.p. 80° (18 mm.) and was obtained in 59% yield.

Anal. Calcd. for $C_4H_9ClSiCl_2$: Si, 14.7; Cl (attached to silicon), 37.0. Found: Si, 15.0; Cl (titration with 0.1 *N* alkali), 37.2.

Failure of the C–Cl bond to react with dilute alkali on titration shows that the product is indeed (γ-chloropropyl)-methyldichlorosilane and is not the adduct which would result from addition of the methyldichlorosilyl group to the non-terminal olefinic carbon. The latter would contain a C–Cl bond beta to silicon and should react quantitatively with alkali giving β-elimination.[16]

Treatment of (γ-chloropropyl)-methyldichlorosilane with excess methylmagnesium iodide gave γ-chloropropyltrimethylsilane, b.p. 148° (733 mm.), $n^{20}_{\rm D}$ 1.4310, d^{20} 0.8825, in 80% yield.

Anal. Calcd. for $C_6H_{15}SiCl$: Si, 18.6; $MR_{\rm D}$, 44.38. Found: Si, 18.8; $MR_{\rm D}$, 44.19.

Reaction of γ-chloropropyltrimethylsilane with sodium iodide in dry acetone gave γ-iodopropyltrimethylsilane, b.p. 103° (47 mm.), $n^{20}_{\rm D}$ 1.4910, d^{20} 1.3334, in 63% yield.

Anal. Calcd. for $C_6H_{15}SiI$: Si, 11.6; $MR_{\rm D}$, 52.40. Found: Si, 11.9; $MR_{\rm D}$, 52.59.

A solution of 133 g., 0.55 mole, of γ-iodopropyltrimethylsilane in 100 cc. of absolute alcohol was heated to reflux, and ethyl sodioacetoacetate, 0.55 mole, dissolved in 250 cc. of ethanol, was added *to* the iodide during 2.5 hr. The reaction mixture was then brought to the neutral point with hydrochloric acid. After distillation of the ethanol, removal of sodium iodide by washing with water, and drying, fractionation gave ethyl (γ-trimethylsilylpropyl)-acetoacetate, 92.2 g., 0.38 mole, b.p. 132° (9 mm.), $n^{20}_{\rm D}$ 1.4389, d^{20} 0.9269, a 68% yield.

Anal. Calcd. for $C_{12}H_{24}O_3Si$: Si, 11.5; $MR_{\rm D}$, 69.09. Found: Si, 11.6; $MR_{\rm D}$, 69.30.

The above substituted acetoacetate on heating with concd. hydrochloric acid gave authentic 6-trimethylsilyl-2-hexanone, b.p. 85° (10 mm.), $n^{20}_{\rm D}$ 1.4289, in 82% yield.

The 2,4-dinitrophenylhydrazone derivative of the authentic ketone had m.p. 92.5–93°. A mixed melting point with the derivative obtained above from the ketone derived from the adduct gave no depression.

Proof of the Structure of the Adduct from Ethyl 4-Pentenoate and Methyldichlorosilane.—The adduct, 60.8 g., 0.25 mole, was treated with 1.4 moles of methylmagnesium bromide. Fractionation of the product gave 6-trimethylsilyl-2-methylhexan-2-ol, 35.7 g., 0.19 mole, b.p. 93° (8 mm.), $n^{20}_{\rm D}$ 1.4377, d^{20} 0.8294, a 76% yield.

Anal. Calcd. for $C_{10}H_{24}OSi$: Si, 14.9; $MR_{\rm D}$, 59.61. Found: Si, 15.0; $MR_{\rm D}$, 59.53.

Authentic 6-trimethylsilyl-2-methylhexan-2-ol was pre-

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(14) α-Methyl-β-trimethylsilylpropionic acid was prepared previously by reaction of ethyl α-methyl-α-trimethylsilylmethylacetoacetate with sodium ethylate in ethanol followed by treatment with hydrochloric acid. This gave the carboxylic acid having b.p. 92° (4 mm.), $n^{20}_{\rm D}$ 1.4310; L. H. Sommer and N. S. Marans, THIS JOURNAL, **72**, 1935 (1950).

(15) γ-Trimethylsilylbutyric acid was prepared previously by carbonation of the Grignard reagent derived from γ-bromopropyltrimethylsilane and had b.p. 118° (10 mm.), $n^{20}_{\rm D}$ 1.4324.[2a]

(16) L. H. Sommer, E. Dorfman, G. M. Goldberg and F. C. Whitmore, THIS JOURNAL, **68**, 488 (1946).

pared from 6-trimethylsilyl-2-hexanone by treatment with methylmagnesium bromide in the usual manner. The authentic alcohol had b.p. 93° (8 mm.), n^{20}_{D} 1.4376, d^{20} 0.8290.

Infrared spectra of the authentic alcohol and the alcohol derived from the adduct were identical.

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[CONTRIBUTION NO. 2148 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Chromatographic Separation and Identification of Some Peptides in Partial Hydrolysates of White Turkey Feather Calamus

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Chromatographic investigations of partial acidic hydrolysates of unoxidized and oxidized white turkey feather calamus have resulted in the isolation and identification of 59 peptides. The sequences which have been observed suggest that unusual sequences do not occur in feather keratin. The possible relation of some of the more prominent sequences to the spatial structure of the proteins is discussed. The isolation and identification of cysteic acid peptides by means of ion-exchange chromatography are described.

Many published investigations treat the feather as a more or less homogeneous unit despite its visually apparent and morphologically distinct parts and despite the fact that the parts of a feather are known to develop from specific portions of the papilla.[1] Recent analyses[2,3] have shown that the amino acid composition is not identical in all parts of a feather, so that a distinct and properly characterized part only should be utilized for chemical investigations. The relatively good orientation which is observed in certain feather parts by X-ray diffraction might lead one to conclude that they are composed of a reasonably homogeneous protein, but cell walls and cell debris from the original growing feather certainly are not absent. Purification of the protein without alteration unfortunately is impossible because of its insolubility, so one is forced to use the material as it is obtained. Woodin[4] has obtained soluble keratin from whole feathers in an apparently homogeneous state with a molecular weight of about 10,000. This material is not unaltered protein inasmuch as it has been isolated after either oxidation or reduction. In the present paper, we describe the isolation and identification of peptides from partial hydrolysates of unaltered protein and of oxidized protein from white turkey feather calamus. Although the rachis has usually been used when well-oriented feather protein is desired, we have chosen the calamus for four reasons: (1) rachis and calamus develop from the same portion of the papilla, (2) the amino acid compositions are essentially identical, (3) the X-ray diffraction patterns for most of the calamus and for the rachis are identical,[5] and (4) necessary amounts of calamus are easy to obtain whereas the separation of the rachis from the medulla is laborious.

Experimental

Source of Calamus and Preparation of Oxidized Calamus.—The sample of white turkey feather calamus was prepared in the way previously described.[2]

Oxidized calamus for the investigation of cysteic acid peptides was prepared in the following manner which combines features of the methods of Schram, Moore and Bigwood[6] and of Hirs.[7] Preformed performic acid was prepared by mixing 9 volumes of 90% formic acid and one volume of 30% hydrogen peroxide. After an hour at room temperature, the mixture was cooled to 0° in an ice-bath and 25 ml. was added to 500 mg. of calamus in the form of pieces about 1 mm. square and 0.1 mm. thick. The reaction mixture was maintained at 0° for 16 hr. during which time the pieces of calamus became swollen but did not dissolve to any obvious extent. The reaction mixture was transferred with 50 ml. of ice-cold water to 350 ml. of ice-cold water in a lyophilizing bulb. The solution was then frozen and the solvents were removed by lyophilization. The process was repeated after the addition of 80 ml. of water. The residue contained pieces in the form of original calamus as well as the usual voluminous residue which soluble substances form on lyophilizing and it was evident that considerable solution had occurred during some part of the procedure.

Partial Hydrolysis of Calamus and Oxidized Calamus.—A 300-mg. sample of calamus and 3 ml. of concd. hydrochloric acid (Baker's Analyzed Reagent Grade) were placed in a 5-ml. volumetric flask. The stem of the flask was attached parallel to a shaft which was inclined at 45° and rotated at 25 r.p.m. In this way, the reaction mixture was constantly agitated for 48 hr. at 37°. Within a few minutes after hydrolysis was begun, the pieces of calamus began to swell and continued to do so until the liquid was almost filled. Gradual dissolving took place and was complete in 3 to 3.5 hr. to give a light brown solution which darkened somewhat during the remainder of the hydrolysis. After about 24 hr., a very small amount of dark insoluble material had become attached to the flask at the surface of the liquid; it was somewhat greasy and had a density less than that of water. It may be composed of sterols or fatty acids.

A 240-mg. sample of oxidized calamus in 2.5 ml. of concd. hydrochloric acid was hydrolyzed at 37° for 48 hr. with constant agitation as above. Most of the material dissolved almost immediately and the remainder within an hour to give a light brown solution. The same type of insoluble residue appeared after about 24 hr. At the end of the partial hydrolysis, the reaction mixture was transferred with 100 ml. of water to a lyophilizing bulb, the solution was frozen, and

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(1) F. R. Lillie, *Biol. Rev.*, **17**, 247 (1942).

(2) W. A. Schroeder and L. M. Kay, THIS JOURNAL, **77**, 3901 (1955). A definition of terms relating to feathers is presented in this reference.

(3) W. H. Ward, C. H. Binkley and N. S. Snell, *Textile Res. J.*, **25**, 314 (1955).

(4) A. M. Woodin, *Biochem. J.*, **57**, 99 (1954).

(5) S. Krimm, private communication. Krimm has observed with turkey feathers that the proximal tip of the calamus is unoriented, that good orientation is present but changes in direction within the first 6 mm. from the tip and then is unchanged in direction and character throughout the remainder of the calamus and rachis.

(6) E. Schram, S. Moore and E. J. Bigwood, *Biochem. J.*, **57**, 33 (1954).

(7) C. H. W. Hirs, *J. Biol. Chem.*, **219**, 611 (1956).