Hydrosilylation of Long Chain Unsaturated Fatty Acid Esters

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ABSTRACT

The addition of a series of silicon hydrides: trichlorosilane, methyldichlorosilane, dimethylchlorosilane, phenyl dichlorosilane, and methyl phenyl chlorosilane to esters of long chain unsaturated fatty acids, such as oleic, linoleic acids, and 10-undecenoic acid, was studied with respect to catalysts, temperature, and solvents. Higher yields were obtained on carrying out the hydrosilylation reactions in the presence of chloroplatinic acid or Pt on C catalysts in bulk without solvent, as compared with peroxide catalysts. The addition reaction with methyl 10-undecenoate, which has a terminal double bond, gave a higher yield than that with methyl oleate. NMR data of the products from methyl 10-undecenoate and methyl oleate, as well as their reduction products with lithium aluminum hydride, have shown that, with the former ester, the silyl moiety added exclusively to the terminal carbon atom, while, with the latter, no migration of the silyl moiety to the terminal carbon atom was observed.

INTRODUCTION

With the aim of finding some new applications and uses for unsaturated fatty acids, such as oleic and linoleic acids, which are constituents of various oils, we investigated the hydrosilylation reaction of these acids.

Silicon hydrides, such as trichlorosilane, methyldichlorosilane, etc., are known to add to olefinic double bonds under the influence of UV light (1), peroxide catalysts (2), azo catalysts (3), platinum or chloroplatinic acid (4, 5) and on heating at elevated temperature (6), as follows:

$$>C=C< \quad + \quad H\text{-}Si\equiv \xrightarrow{\text{cat.}} H\text{-}\overset{|}{\underset{|}{C}}\text{—}\overset{|}{\underset{|}{C}}\text{-}Si\equiv$$

Very little is known about the addition of silicon hydrides to unsaturated fatty acids (7-9). We studied the addition of a series of silicon hydrides, namely: Cl_3SiH, $MeCl_2SiH$, Me_2ClSiH, $PhCl_2SiH$, PhMeClSiH to oleic, linoleic, and undecenoic acids.

Since silicon hydrides react with free carboxylic groups, the methyl esters of the long chain unsaturated fatty acids were used in the hydrosilylation reactions.

The influence of catalysts, temperature, and solvents upon the hydrosilylation reactions also was studied.

Derivatives of these new long chain fatty acids containing silicon may find uses as lubricants, plasticizers, water repellents, and as starting materials for silicon containing condensation polymers.

EXPERIMENTAL PROCEDURES

Materials

Methyl oleate (Fluka AG, Buchs, Switzerland), methyl linoleate (Aldrich Chemical Co., Milwaukee, Wisc.), methyl linolenate (Fluka), 10-undecenoic acid methyl ester (Pfaltz & Bauer, Flushing, N.Y.), 1-undecen-11-yl-acetate (Fluka), trichlorosilane (Fluka), methyl dichlorosilane, dimethylchlorosilane, phenyldichlorosilane, phenylmethylchlorosilane (P.C.R., Gainesville, Fla.), chloroplatinic acid (B.D.H.), platinum on activated carbon (5% Pt) (Fluka), benzoyl peroxide, and di-tert-butyl peroxide (Fluka) were used.

The addition of the silicon hydrides to the unsaturated fatty acids was carried out according to the following typical procedures.

Procedure A

A mixture of methyl oleate (17.8 g, 0.06 mole), trichlorosilane (16.3 g, 0.12 mole), and 0.1M isopropanolic chloroplatinic acid (1 ml) was heated in a pressure type ampule at 90 C for 5 hr. Excess of trichlorosilane was distilled off; the pure addition product distilled at 180-182/0.1 mm ($n_D^{20}=1.4612$). The yield was 73% based upon methyl oleate. Analysis calculated for $C_{19}H_{37}SiO_2Cl_3$: C, 52.90; H, 8.58; Cl, 24.74. Found: C, 52.82; H, 8.51; Cl, 23.85.

Procedure B

A mixture of methyl oleate (118.4 g, 0.4 mole), methyldichlorosilane (92 g, 0.8 mole), and 0.1M isopropanolic chloroplatinic acid (4 ml) was boiled for 5 hr in an apparatus fitted with an acetone-dry ice reflux condenser. Excess of methyldichlorosilane was distilled off; the addition product boiled at 170-172 C/0.05 mm and solidified on cooling to 18 C; yield 75%, $n_D^{20}=1.4615$. The compound showed the typical IR absorption at 1740 cm^{-1} (ester group) and 1260 cm^{-1} ($Si\text{-}CH_3$ group). Analysis calculated for $C_{20}H_{40}SiO_2Cl_2$: C, 58.39, H, 9.75; Cl, 17.27. Found: C, 58.26; H, 9.70; Cl, 16.92.

Effect of Solvent

A solution of methyl oleate (17.8 g, 0.06 mole), trichlorosilane (16.3 g, 0.12 mole), and 0.1M isopropanolic chloroplatinic acid (1 ml) in dry hexane (100 ml) was refluxed for 5 hr in an apparatus fitted with an acetone-dry ice condenser. The reaction mixture was worked up as in procedure A, the yield was 43% based upon methyl oleate.

Reduction of Chlorosilyl Derivatives

A solution of methyl 10-(chlorodimethylsilyl) undecanoate (2.925 g, 0.01 mole) in dry ether (50 ml) was added dropwise, with stirring, to a suspension of lithium aluminum hydride (0.76 g, 0.02 mole) in dry ether (100 ml). The reaction mixture was stirred and heated under reflux for 4 hr and then cooled to 0 C. Cold water was added dropwise, followed by cold 10% sulfuric acid, until two clear layers formed. The ethereal layer was separated and the aqueous layer extracted with ether. The combined ethereal solutions were washed with water and dried over magnesium sulphate. The ether was evaporated to yield 90% of the product ($n_D^{18}=1.4525$). The compound showed the typical IR absorption at 3300 cm^{-1} (hydroxyl group), 2100 cm^{-1} (Si-H), and 1260 cm^{-1} ($Si\text{-}CH_3$ group). Analysis caluculated for $C_{13}H_{30}SiO$: C, 67.82; H, 13.04. Found: C, 67.78; H, 13.02.

In a similar manner some other chlorosilyl derivatives of methyl oleate and undecanoate were reduced.

RESULTS AND DISCUSSION

The addition reactions to methyl oleate and 1-undecenoic acid methyl ester using chloroplatinic acid ($H_2PtCl_6,6H_2O$), Pt on C, or organic peroxides as catalysts

TABLE I

Addition of Silicon Hydrides to Methyl Oleate[a]

Silicon hydride	Addition product	Yield (%)			$n_D^{20°}$	Boiling point, C (pressure in torr)	Carbon (%)		Hydrogen (%)		Chlorine (%)	
		H_2PtCl_6	Pt on C	Peroxides			Calculated	Found	Calculated	Found	Calculated	Found
Cl_3SiH	$Cl_3SiC_{17}H_{34}COOCH_3$	73	70	32[c]	1.4612	180/0.1	52.90	52.82	8.58	8.51	24.74	23.85
CH_3Cl_2SiH	$CH_3Cl_2SiC_{17}H_{34}COOCH_3$[b]	75	73	23[c]	1.4615	172/0.05	58.39	58.26	9.75	9.70	17.27	16.92
$(CH_3)_2ClSiH$	$(CH_3)_2ClSiC_{17}H_{34}COOCH_3$[b]	47-57	40	traces[c]	1.4590	168/0.05	64.53	63.38	11.01	10.82	9.09	9.00
$PhCl_2SiH$	$PhCl_2SiC_{17}H_{34}COOCH_3$	70	69	38[d]	1.4985	190/0.1	63.42	62.17	8.88	7.79	15.01	15.99
PhMeClSiH	$PhMeClSiC_{17}H_{34}COOCH_3$	65	64	35[d]	1.4851	186/0.1	68.95	68.20	9.94	9.41	7.85	6.57

[a] Experimental conditions: methyl oleate was heated under reflux with excess of silicon hydride in the presence of catalysts. H_2PtCl_6 or Pt/C/methyl oleate = $3x10^{-3}$, peroxide/methyl oleate = $1x10^{-2}$.

[b] Solidified at 17-18 C.

[c] Benzoyl peroxide.

[d] Di-tert-butyl peroxide.

TABLE II

Addition of Silicone Hydrides to 10-Undecenoic Acid Methyl Ester[a]

Silicon hydride	Addition product	Yield %	$n_D^{25°}$	Boiling point, C (pressure in torr)	Carbon (%)		Hydrogen (%)		Chlorine (%)	
					Calculated	Found	Calculated	Found	Calculated	Found
Cl_3SiH	$Cl_3Si(CH_2)_{10}$-$COOCH_3$	95	1.4571	172/2	43.24	43.51	6.91	7.05	31.98	30.85
CH_3Cl_2SiH	$CH_3Cl_2Si(CH_2)_{10}$-$COOCH_3$	97	1.4561	124/0.05	49.84	49.73	8.30	7.68	22.68	21.90
$(CH_3)_2ClSiH$	$(CH_3)_2ClSi(CH_2)_{10}$-$COOCH_3$	90	1.4483	133/0.3	57.43	57.47	9.92	9.83	12.13	12.07
$PhCl_2SiH$	$PhCl_2Si(CH_2)_{10}$-$COOCH_3$	82	1.4992	142/0.05	57.33	57.87	7.46	7.31	18.93	18.21
PhMeClSiH	$PhMeClSi(CH_2)_{10}$-$COOCH_3$	72	1.4965	144/0.05	64.40	64.16	8.76	8.55	10.00	9.45
$CH_3(OC_2H_5)_2SiH$	$CH_3(OC_2H_5)_2Si(CH_2)_{10}$-$COOCH_3$	85	1.4350	138/0.2	61.44	61.44	10.84	10.66	---	---

[a] Experimental conditions: 10-undecenoic acid methyl ester was heated with excess of silicon hydride in the presence of chloroplatinic acid, H_2PtCl_6/10-undecenoic acid methyl ester = $3x10^{-4}$.

were studied.

It was found (Tables I,II) that the highest yields were obtained using chloroplatinic acid or Pt/C as catalysts. The optimum reaction temperatures were between 70-90 C (Table III).

Higher yields were obtained on carrying out the hydrosilylation reactions in bulk without solvents.

We investigated quantitatively the influence of the amount of chloroplatinic acid catalyst on the addition of methyldichlorosilane to methyl oleate and 10-undecenoic acid methyl ester. The results (Table IV) indicate that the terminal C=C double bond of 10-undecenoic acid methyl ester is much more reactive toward hydrosilylation reaction than the internal double bond of methyl oleate. It was reported (10,11) that, in the presence of chloroplatinic acid, trichlorosilane adds to the terminal position of pentene-2 and heptene-3 to yield n-pentyltrichlorosilane and n-heptyltrichlorosilane, respectively. The formation of these products was ascribed to the isomerization of the carbanion initially formed by the addition of a hydride ion to the double bond into a more stable primary carbanion on the terminal carbon atom. It was, therefore, important to determine whether such isomerizations occurred in the present hydrosilylation reactions. Evidence regarding the structure of the addition products of the silicon hydrides to methyl 10-undecenoate and to methyl oleate was obtained from NMR spectra. In all the hydrosilylations of methyl 10-undecenoate (Table II), the silyl moiety was found to be attached to the terminal carbon-atom, as seen from the NMR spectra of each of the addition products, where no terminal methyl group was found, and from integration of the peak areas for the hydrogens attached to the carbon of the newly formed ($-Si-CH_2$), which was equivalent to two hydrogens, and not to one as would have been the case had the addition occurred in the other sense. For example, the NMR spectrum of methyl 10-(chlorodimethylsilyl)undecanoate showed the following peaks (in δ values relative to tetramethylsilane): 0.342 (s,6, $-CH_3$), 0.758 (2, $-\underline{CH_2}-Si\equiv$), 1.258 (16, $-CH_2-$), 2.186 (t,2, $-CH_2-CO_2-$), and

TABLE III

Effect of Temperature upon Yield of Hydrosilylation of Methyl Oleate by Chlorosilanes[a]

Chlorosilane	Yield (%) 20 C	50 C	80-90 C	120-140 C[b]
Cl_3SiH	5	50	73	60
$MeCl_2SiH$	12	60	75	65
Me_2ClSiH	7	40	47-57	43

[a]Experimental conditions: methyl oleate was heated with excess of silicon hydride (2 equiv.) in the presence of chloroplatinic acid. H_2PtCl_6/methyl oleate = $3x10^{-3}$.

[b]Temperature of the outside bath.

TABLE IV

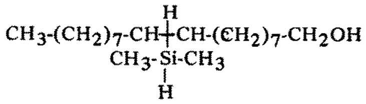
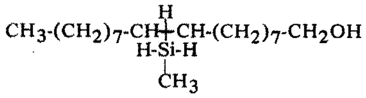
Effect of Amount of Chloroplatinic Acid Catalyst upon Yield of Additon Product of Methyldichlorosilane to Methyl Oleate and 10-Undecenoic Acid Methyl Ester[a]

Catalyzer/fatty acid methyl ester	Yield (%) $CH_3Cl_2SiC_{17}H_{34}COOCH_3$	$CH_3Cl_2Si(CH_2)_{10}COOCH_3$
$6.66x10^{-3}$	75	97
$3.33x10^{-3}$	75	97
$1.66x10^{-3}$	70	97
$0.84x10^{-3}$	70	97
$3.33x10^{-4}$	30	97
$1.66x10^{-4}$	13	94
$3.33x10^{-5}$	traces	86
$1.66x10^{-5}$	0	86
$3.33x10^{-6}$	0	54
$3.33x10^{-7}$	0	8
$3.33x10^{-8}$	0	0

[a]Experimental conditions: fatty acid methyl esters were heated with excess of methyldichlorosilane in the presence of chloroplatinic acid.

TABLE V

Hydrosilyl Derivatives of Undecenoyl and Oleyl Alcohols[a]

	Compounds	Yield (%)	$n_D^{18°}$	Carbon (%) Calculated	Carbon (%) Found	Hydrogen (%) Calculated	Hydrogen (%) Found
I	$(CH_3)_2HSi\text{-}(CH_2)_{10}\text{-}CH_2OH$	90	1.4525	67.82	67.78	13.04	13.02
II	$CH_3H_2Si(CH_2)_{10}\text{-}CH_2OH$	95	1.4565	66.67	66.61	12.96	12.82
III	$SiH_3\text{-}(CH_2)_{10}\text{-}CH_2OH$	92	1.4575	65.35	65.62	12.87	12.59
IV	 $CH_3\text{-}(CH_2)_7\text{-}CH\overset{H}{\underset{\underset{H}{CH_3\text{-}Si\text{-}CH_3}}{-}}CH\text{-}(CH_2)_7\text{-}CH_2OH$	85	1.4672	73.17	73.12	13.42	13.17
V	 $CH_3\text{-}(CH_2)_7\text{-}CH\overset{H}{\underset{\underset{CH_3}{H\text{-}Si\text{-}H}}{-}}CH\text{-}(CH_2)_7\text{-}CH_2OH$	88	1.4678	72.61	72.32	13.38	13.14

[a]Compounds were prepared by reduction of the respective methyl chlorosilyl undecanoate and oleate, with lithium aluminum hydride in ether.

TABLE VI

Addition of Silicon Hydrides to Methyl Linoleate[a]

Silicon hydride	Adduct (1:1)	Yield (%)	$n_D^{22°}$	Boiling point, C (pressure in torr)	Carbon (%)		Hydrogen (%)		Chlorine (%)	
					Calculated	Found	Calculated	Found	Calculated	Found
Cl_3SiH	$Cl_3SiC_{17}H_{32}COOCH_3$	65	1.4680	165/0.05	53.09	54.81	8.14	8.39	24.80	23.50
CH_3Cl_2SiH	$CH_3Cl_2SiC_{17}H_{32}COOCH_3$	70	1.4659	170/175/0.1	56.67	57.57	9.29	8.62	17.35	16.83
$(CH_3)_2ClSiH$	$(CH_3)_2ClSiC_{17}H_{32}COOCH_3$	50	1.4645	160/0.05	64.86	65.86	10.55	10.64	9.13	8.92

[a] Experimental conditions: equimolar amounts of silicon hydride and methyl linoleate were refluxed in the presence of a solution of chloroplatinic acid catalyst. catalyzer /methyl linoleate = $3x10^{-3}$.

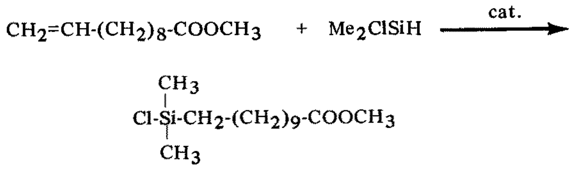
TABLE VII

Addition of Silicon Hydrides to 1-Undecen-11-yl-Acetate[a]

Silicon hydride	Addition product	Yield (%)	$n_D^{25°}$	Boiling point, C (pressure in torr)	Carbon (%)		Hydrogen (%)		Chlorine (%)	
					Calculated	Found	Calculated	Found	Calculated	Found
Cl_3SiH	$Cl_3Si\text{-}(CH_2)_{11}\text{-}OCOCH_3$	93	1.4580	134/0.1	44.95	45.05	7.19	7.30	30.65	30.35
CH_3Cl_2SiH	$CH_3Cl_2Si\text{-}(CH_2)_{11}\text{-}OCOCH_3$	96	1.4540	133-135/0.1	51.37	51.26	8.56	8.53	21.71	21.07
$(CH_3)_2ClSiH$	$(CH_3)_2ClSi\text{-}(CH_2)_{11}\text{-}OCOCH_3$	95	1.4500	126-128/0.1	58.93	58.61	9.69	10.11	11.58	11.10
PhMeClSiH	$PhMeClSi\text{-}(CH_2)_{11}\text{-}OCOCH_3$	93	1.4930	170/0.1	65.13	64.86	8.95	8.91	9.63	9.45

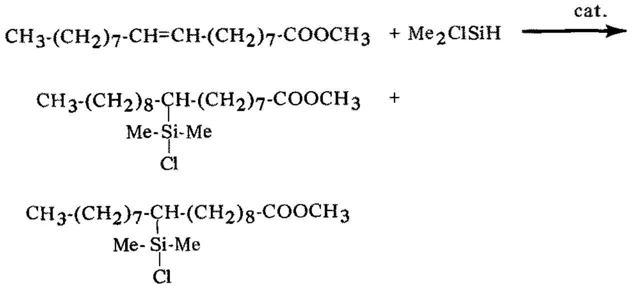
[a] Experimental conditions: 1-undecen-11-yl-acetate was heated with excess of silicon hydride (2 equivalent) in the presence of chloroplatinic acid, H_2PtCl_6/1-undecen-11-yl-acetate = $3x10^{-4}$.

3.553 (s,3,-$COOCH_3$). Hence, the hydrosilylation proceeded as follows:



$$CH_2{=}CH\text{-}(CH_2)_8\text{-}COOCH_3 + Me_2ClSiH \xrightarrow{cat.} Cl\text{-}\overset{CH_3}{\underset{CH_3}{Si}}\text{-}CH_2\text{-}(CH_2)_9\text{-}COOCH_3$$

In the case of methyl oleate which contains an internal 9:10-double bond, we examined the addition products of the hydrosilylation reactions by NMR spectroscopy. In all spectra we found the terminal methyl group in the main fatty acid chain, as well as a (-CH-Si≡) bond (and not a -CH_2-Si, bond), indicating that no migration to the terminal position occurred under the conditions studied. For example:



$$CH_3\text{-}(CH_2)_7\text{-}CH{=}CH\text{-}(CH_2)_7\text{-}COOCH_3 + Me_2ClSiH \xrightarrow{cat.}$$
$$CH_3\text{-}(CH_2)_8\text{-}\underset{\underset{Cl}{Me\text{-}Si\text{-}Me}}{CH}\text{-}(CH_2)_7\text{-}COOCH_3 +$$
$$CH_3\text{-}(CH_2)_7\text{-}\underset{\underset{Cl}{Me\text{-}Si\text{-}Me}}{CH}\text{-}(CH_2)_8\text{-}COOCH_3$$

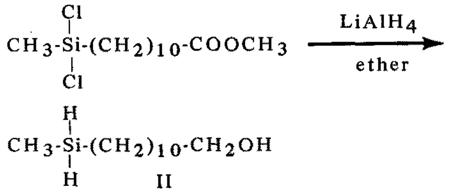
Besides the hydrosilylation, some isomerization of the methyl oleate to the *trans*-isomer occurred, apparently catalyzed by chloroplatinic acid (12), as seen from the IR spectra absorption at 960 cm^{-1}, in unreacted methyl oleate.

The resulting purified adduct, which is a mixture of these two isomers, was used in our further investigations.

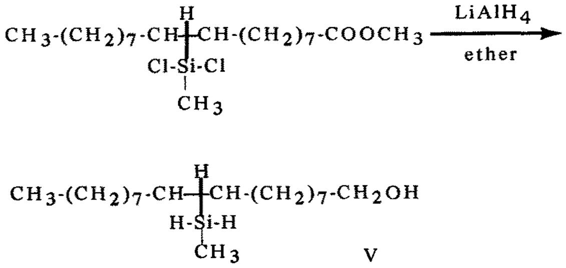
The NMR spectrum of this mixture, methyl 9(10)-(chlorodimethylsilyl)stearate showed the following bands:

0.026(d,6; -CH_3), 0.464(1, -$\underline{CH}$-Si≡), 0.872 (3, $\underline{\text{terminal } CH_3}$), 1.225 (28, -$CH_2$-), 2.202(t,2, -$CH_2$-$CO_2$-), and 3.382 (s,3, -$COOCH_3$).

Further evidence concerning the structure of the addition products of the chlorosilanes to methyl 10-undecenoate and methyl oleate was obtained from the NMR spectra of the compounds obtained by reduction of these products with lithium aluminum hydride (Table V):



$$CH_3\text{-}\overset{Cl}{\underset{Cl}{Si}}\text{-}(CH_2)_{10}\text{-}COOCH_3 \xrightarrow[ether]{LiAlH_4} CH_3\text{-}\overset{H}{\underset{H}{Si}}\text{-}(CH_2)_{10}\text{-}CH_2OH \quad \text{II}$$



$$CH_3\text{-}(CH_2)_7\text{-}CH\overset{H}{\underset{\underset{CH_3}{Cl\text{-}Si\text{-}Cl}}{|}}CH\text{-}(CH_2)_7\text{-}COOCH_3 \xrightarrow[ether]{LiAlH_4}$$
$$CH_3\text{-}(CH_2)_7\text{-}CH\overset{H}{\underset{\underset{CH_3}{H\text{-}Si\text{-}H}}{|}}CH\text{-}(CH_2)_7\text{-}CH_2OH \quad \text{V}$$

Conversion of the Cl-Si bonds to H-Si, leads to the appearance of a new type of hydrogen; to the splitting of the hydrogens of the Si-CH_3 into a doublet or triplet, depending upon the number of hydrogens linked to the silicone; and also to shifting of the peaks of the Si-CH_2 bonds that separates them nicely from adjacent peaks.

The NMR spectra of the reduction products showed that, in the case of methyl 10-undecenoate, all the additions occurred at the terminal position, while in that of methyl oleate, no evidence for addition to the terminal position was found. For example, the NMR spectra of compounds II and V (Table V) showed the following peaks: II: 0.085 (t,3, -CH_3), 0.645 (2, -$\underline{CH_2}$-Si≡), 1.258 (18, -CH_2-), 3.474 (t,2, -CH_2-hydroxyl), and 3.658 (2, H-Si≡). V: 0.103 (t,3, -CH_3), 0.668 (1, -$\underline{CH}$-Si≡), 0.869 (3, terminal CH_3), 1.240 (30, -CH_2-), 3.508 (t,2, -CH_2-hydroxyl), and 3.682 (2, H-Si≡).

Addition reactions of silicon hydrides to methyl linoleate are more complicated than those to methyl oleate, as methyl linoleate contains two double bonds in two different positions; namely, 9:10 and 12:13 of the fatty acid chain. To minimize these complications equimolar amounts of the reactants were used to increase the possibility of addition to one double bond and obtaining the 1:1 adducts.

These adducts, due to the presence of two double bonds in methyl linoleate with similar reactivity toward addition reactions, will be mixtures of 9(10) and 12(13) silyl derivatives, provided that no migration to the double bonds occurred. The results are given in Table VI.

On carrying out the addition reaction of methyl linoleate with excess of silicon hydrides, crude products were obtained, which, according to the elemental analysis, seem to be disilyl substituted linoleates (1:2-adducts), but these could not be isolated by vacuum distillation.

Methyl linolenate which contains three double bonds was reacted with methyl dichlorosilane in the presence of chloroplatinic acid giving the 1:1 adduct.

The addition of silicon hydrides to 1-undecen-11-yl-acetate in the presence of chloroplatinic acid is given in Table VII.

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