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The Addition of Silicon Hydrides to Olefinic Double Bonds. Part II. The Use of Group VIII Metal Catalysts

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Some silicon hydrides add to the double bond of olefinic compounds in the presence of platonic chloride, platinized carbon, platinum black, ruthenium chloride and iridium. The addition reaction is exothermic and in many cases very rapid at temperatures from below room temperature to about 100°. Pentene-1 and pentene-2 both form *n*-pentylsilanes under these conditions. Only in the presence of a very active catalyst would cyclohexene react. Silicon hydrides useful in this reaction include trichlorosilane, methyldichlorosilane, dimethylchlorosilane, phenyldichlorosilane, 1,1,3,3-tetramethyldisiloxane, diethoxymethylsilane and others. A wide variety of olefinic compounds are reactive. In some cases allyl acetate and other allyl compounds as well as isopropenyl acetate form propylene.

Many organosilicon compounds have been prepared in recent years with functional groups in the organic portion of the molecules. In general, the syntheses of these have been relatively difficult and unattractive for the manufacture of products of broad usefulness. In this Laboratory we have sought methods of synthesis which require only commercially available intermediates.

A discussion of the addition of silicon hydrides to olefinic double bonds (equation I) along with references is given in recent papers.²



This process brought about by the decomposition of peroxides can be an attractive one leading to many new compounds containing certain functional groups. It has limitations, however, not yet overcome. For example, high yields of adducts are produced with only one abundant silane, trichlorosilane. Also polymers are formed when easily polymerized olefinic compounds such as the acrylates and styrene are used.

During our search for more versatile processes for production of organofunctional silicon compounds, we investigated the use of catalysts to assist the reaction of equation I. A very active catalyst was desired to enable the reaction to proceed smoothly at temperatures low enough to minimize side reactions with certain functional substituents on the olefinic reagent.

The use of platinum, other metals and salts as catalysts has been mentioned in several patents. First among these is a French patent.³ It says that effective "catalysts may be chosen from the compounds and salts of the elements of groups IIIA, IVA, IB and IIB in the periodic table. Metals of group VIII and certain of their salts may also be used successfully." No examples are shown for the use of such catalysts, however.

More explicit information concerning catalysis is given by Wagner⁴ and Strother⁴ who show the use of platinum black, platinized asbestos and platinized silica with olefins and trichlorosilane. They state that palladium is effective.

(1) Dow Corning Corporation, Midland, Mich.

(2) (a) J. L. Speier, Ruth Zimmerman and J. A. Webster, *THIS JOURNAL*, **78**, 2278 (1956); (b) J. L. Speier and J. A. Webster, *J. Org. Chem.*, **21**, 1044 (1956).

(3) C. A. MacKenzie, L. Spialter and M. Schoffman, French Patent 961,876; Nov. 28, 1949.

(4) G. H. Wagner and C. O. Strother, U. S. Patent 2,632,013; Mar. 17, 1953.

Wagner⁵ later showed that platinum deposited on charcoal was an unusually active catalyst with trichlorosilane and acetylene, ethylene, butadiene, allyl chloride or vinylidene fluoride. Temperatures as low as 130° were employed in some examples, but apparently higher temperatures were frequently needed.

Recently Wagner's catalyst⁴ has been used to form polymers of the type $[-\text{SiR}_2\text{CH}_2\text{CH}_2-]_n$, from vinylsilanes $\text{R}_2\text{HSiCH}=\text{CH}_2$.⁶

We have investigated the use of certain catalysts from the group VIII metals and have found several active ones. Chloroplatinic acid has proved to be an extremely active catalyst. Platinum black, platinum-on-carbon and potassium chloroplatinate are also very effective.

In order to screen various catalysts qualitatively for activity at moderate temperatures with common types of olefinic structures, a series of experiments was carried out. Pentene-1, pentene-2 and cyclohexene were chosen as representative olefins to be used with methyldichlorosilane. The combination of these reactants yielded products previously characterized and easily isolated by distillation. Samples containing equivalent amounts to 20% excess methyldichlorosilane were prepared and sealed into 25-mm. Pyrex tubes, along with known amounts of catalysts, and heated in a boiling water-bath. A few tubes were fitted with thermocouple wells. The temperature inside these tubes was measured with a recording potentiometer. The data gathered in this way are in Table I.

In the presence of the more active catalysts the exothermic nature of the reaction was easily observed. The heat of reaction calculated from the bond energy values of Pitzer⁷ is 38 kcal./mole. An estimate of the relative speeds of reactions catalyzed by different catalysts or differing amounts of a given catalyst was obtained in several cases by recording reaction temperatures. Tubes previously described containing thermocouple wells were charged with 39.5 g. of an equimolar solution of olefin and silane. Solutions of chloroplatinic acid in isopropyl alcohol were prepared so that 0.1 ml. gave the desired concentration of catalyst in each tube. The tubes were chilled in Dry Ice, sealed and warmed to about 0° before they were placed in a safety shield of preheated pipe containing mineral

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

(6) J. W. Curry, *THIS JOURNAL*, **78**, 1686 (1956).

(7) K. Pitzer, *ibid.*, **70**, 2140 (1948).

TABLE I
ADDITION OF MeHSiCl₂ TO OLEFINS AT 100°

Hr. ^a	Catalyst Using pentene-1	Moles catalyst Moles olefin × 10 ⁴	Adduct, ^b %
17	None	...	0
17	OsO ₄	1.6	0
17	PdCl ₂ ·2H ₂ O	25	0
8	3% Pd/C	6	4 ^c
17	IrCl ₃	25	50
17	RuCl ₃	25	77
6	RuCl ₃	12.5	63
17	K ₂ PtCl ₄	0.1	65
17	K ₂ PtCl ₄	25	100
6	Pt-black	12.5	92
0.5	H ₂ PtCl ₆ ·6H ₂ O	0.005	93 ^d
1.25	0.06% Pt/C	0.02	84
Using pentene-2			
0.5	H ₂ PtCl ₆ ·6H ₂ O	0.5	89
7	0.06% Pt/C	0.01	0
20	1% Pt/C	10	56
20	K ₂ PtCl ₄	6.25	65
20	RuCl ₃	12.5	55
Using cyclohexene			
16	0.06% Pt/C	0.03	0
17	1% Pt/C	10	Trace
17	Pt-black	12.5	20
17	PdCl ₂ ·2H ₂ O	25	0
6	IrCl ₃	25	0
20	H ₂ PtCl ₆ ·6H ₂ O	0.3	100

^a Samples were heated for the times shown, but in many cases the reaction may have been complete in less time or may have not yet reached completion. ^b Adduct % is taken as the yield of material on the plateau during distillation. Precuts and residue are not included. Distillation was carried out in claisen flasks. ^c This sample was heated at 150–170°. ^d The heat of reaction in this case caused the temperature inside the tube to rise to 210° while the tube was in a boiling water-bath. Certain other mixtures may also have risen above the bath temperature without notice.

oil as a heat transfer medium. The temperature in the sample was recorded for the first 30 minutes with the aid of a millivolt recorder. Figure 1 shows the time-temperature curves from which an indication of the relative rates of reaction with varying catalyst concentration, a comparison of relative reactivities of methylchlorosilane and trichlorosilane and the effectiveness of the catalysts, may be inferred. The time required for a sample to reach its maximum temperature was a function of the reaction rate. Thus the rates decreased from A to C as the catalyst concentration was decreased. The rates of trichlorosilane additions were also slower than methylchlorosilane additions at comparable catalyst concentrations.

The increase in the maximum temperature from A to C can be explained by the higher temperatures of the reaction mixtures at the onset of rapid exothermic reaction. If the differences (ΔT 's) between the maximum temperature and the temperature at the start of rapid exothermic reaction are compared for curves A, B and C, the values are found to decrease.

The products obtained using pentene-2 in Table I appeared to be the same as those obtained using pentene-1. More careful examination proved that only *n*-pentylsilanes were produced from pentene-2,

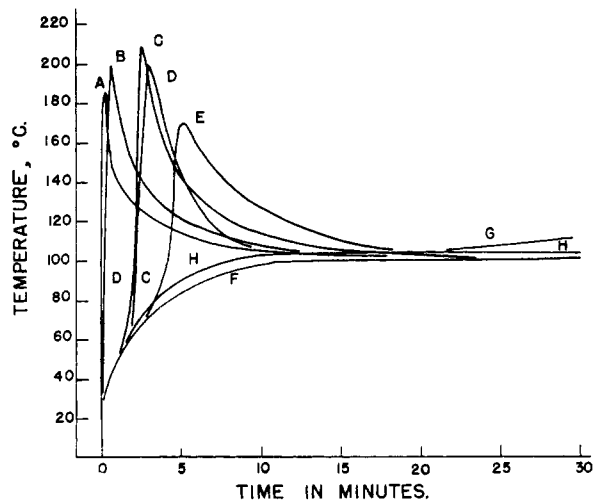


Fig. 1.—Time-temperature curves for reacting mixtures with pentene-1.

Curve	Silane	Catalyst	Moles catalyst mole pentene-1	Adduct, %
A	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁶	94
B	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁶	93
C	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁷	93
D	HSiCl ₃	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁶	95
E	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁸	82
F	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁹	0
G	MeHSiCl ₂	0.06% Pt-C	2 × 10 ⁻⁸	84 ^a
H	HSiCl ₃	H ₂ PtCl ₆ ·6H ₂ O	5 × 10 ⁻⁸	21

^a This sample was heated 1.25 hr. before distillation.

unlikely though this appeared. A comparison of the products obtained in eight experiments indicate that with H₂PtCl₆·6H₂O, platinum-on-carbon or ruthenium chloride as the catalyst pentene-2 yielded *n*-pentylsilanes. Each product had the same infrared absorption spectrum and within the limits of error the same physical properties.

The most effective catalysts were employed to prepare a variety of new compounds listed with their properties in Table III.

Experimental

Reagents.—Trichlorosilane, phenyldichlorosilane, methylchlorosilane, dimethylchlorosilane and diethoxymethylsilane were redistilled commercial products. The phenyldichlorosilane contained approximately 25–30% of close boiling impurities which did not hinder its usefulness. The dimethylchlorosilane contained a small amount of trichlorosilane which was not removed. Hydrolysis of the dimethylchlorosilane yielded the 1,1,3,3-tetramethyldisiloxane used in these experiments along with a small amount of 1,1,5,5-tetramethyl-3-trimethylsilyloxytrisiloxane. These two compounds had the following properties: (HSiMe₂)₂O, b.p. 70.5–71° at 731 mm., n_{25}^D 1.3669, d_{25}^4 0.7494; *R*_D found 0.2995, *R*_D calcd. 0.2992; SiH found 1.46, SiH calcd. 1.50. (HMe₂O)₂SiH, b.p. 154.5–155° at 733 mm., n_{25}^D 1.3791, d_{25}^4 0.8563; *R*_D found 0.2699, *R*_D calcd. 0.2705; SiH found 1.57, SiH calcd. 1.58.

The olefinic compounds were either commercial products or were synthesized by published procedures. The pentene-1 and pentene-2 were from the Phillips Petroleum Co. and were said to be at least 95 mole % pure.

Methylcyclohexyldichlorosilane (XII).—This experimental procedure is typical of those used to gather the data of Tables I and II. A 25-mm. Pyrex tube was charged with cyclohexene (16.4 g., 0.2 mole), methylchlorosilane (34.5 g., 0.3 mole) and 0.2 g. of 0.06% platinum-on-carbon. The tube was sealed and heated 16 hr. in boiling water.

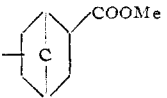

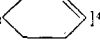
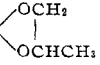
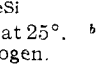
TABLE II
 ADDUCTS OF PENTENE-1 AND PENTENE-2

	From	B.p., °C.	n_D^{25}	d_4^{25}	B.p. ^c	MesSiC ₅ H ₁₁ derivative ^{a,b} n_D^{25}	d_4^{25}
MeCl ₂ SiC ₅ H ₁₁	Pentene-1 ^d	169-170	1.4328	1.013	138.9	1.4069	0.728
MeCl ₂ SiC ₅ H ₁₁	Pentene-2 ^d	170-170.5	1.4323	0.999	138.9	1.4069	.727
MeCl ₂ SiC ₅ H ₁₁	Pentene-2 ^e	169-171	1.4324	.999			
MeCl ₂ SiC ₅ H ₁₁	Pentene-2 ^f	169-170.5	1.4333	1.007			
Cl ₃ SiC ₅ H ₁₁	Pentene-1 ^d	167-168	1.4372	1.130	138.9	1.4069	.727
Cl ₃ SiC ₅ H ₁₁	Pentene-2 ^d	171	1.4376	1.129	138.8	1.4069	.727
Cl ₃ SiC ₅ H ₁₁	Pentene-1 ^g	171	1.4379	1.128	138.8	1.4069	.727
Cl ₃ SiC ₅ H ₁₁	Pentene-2 ^{g,h}	166-167	1.4457	1.151	136.9	1.4150	.743

^a Authentic *n*-pentyltrimethylsilane has^b b.p. 138.9-139.1° at 740 mm., n_D^{25} 1.4069, d_4^{25} 0.7267. ^b These samples were prepared from the chlorosilanes with methylmagnesium bromide in ether in yields of approximately 80% and distilled through a two-foot column packed with 1/8" glass helices. ^c The b.p. at 740 mm. was determined using a thermometer calibrated by the National Bureau of Standards. ^d H₂PtCl₆·6H₂O at 100° as catalyst. ^e 1% platinum-on-charcoal catalyst at 100°. ^f RuCl₃ as catalyst at 100°. ^g These samples are described²⁵ as prepared with *t*-butyl perbenzoate. ^h This sample was found²⁵ to be a mixture of two isomers in the ratio of 70/30.

TABLE III

COMPOUNDS PREPARED FROM SILICON HYDRIDES AND OLEFINS WITH PLATINUM CATALYSTS AND DERIVATIVES OF THESE COMPOUNDS

	Structure	B.p.		n_D^{25}	d_4^{25}	R _D		Neut. equiv.		Sapon. equiv.	
		°C.	Mm.			Found	Calcd.	Found	Calcd.	Found	Calcd.
I	C ₄ H ₉ Cl ₂ Si(CH ₂) ₂ OAc	153	4	1.5107	1.188	0.2517	0.2513	139	142	94.3	92.4
II	[OC ₁ H ₈ Si(CH ₂) ₂ OAc] _x	^a		1.5243	1.159	.2641	.2646	12.9 ^g	12.6 ^g	230	222
III	MeCl ₂ Si(CH ₂) ₂ OAc	142	73	1.4434	1.151	.231	.232	107	107.5	71	71.7
IV	[OMe ₂ Si(CH ₂) ₂ OAc] _x	^b		1.4471	1.104	.242	.243			158 ^e	160 ^e
V	[OMeSi(CH ₂) ₂ OH] _x	Rubbery gel						23.5 ^g	23.7 ^g		
VI	(EtO) ₂ MeSiC ₄ H ₉ OAc	145	49	1.4163	.9622	.2610	.2616			232	234
VII	Me ₂ AcOSiOSiMe ₂ (CH ₂) ₂ OAc	149	25	1.4180	.9906	.2544	.2551	293	296	146	148
VIII	O[SiMe ₂ (CH ₂) ₂ OAc] ₂	179	15	1.4322	.9732	.2666	.2675			166	167
IX	Me ₂ ClSi(CH ₂) ₂ OAc	108-109	25	1.4342	1.018	.2559	.2578	195.1	194.8	97.2	97.4
X	MeCl ₂ SiCH ₂ CH ₂ OAc	117	62	1.4390	1.177	.2248	.2233	100.3	100.5	67.0	67.5
XI	Me ₂ SiCH ₂ CH ₂ OH 3,5-dinitrobenzoate	95 M.p. 66	100	1.4220	.8254	.3079	.3086			9.00 ^h	8.97 ^h
XII	MeCl ₂ Si(cyc-C ₆ H ₁₁)	201-202	Atm.	1.4696	1.09	.256	.256	100.4	99.1		
XIII	MeCl ₂ SiCH ₂ CH ₂ C ₆ H ₅	125-126	20	1.5129	1.125	.2671	.2672	110	110		
XIV	MeCl ₂ Si- 	139	6	1.4912	1.210	.2395	.2398	135	134		
XV	MeCl ₂ SiCHMeCO ₂ Me	80-80.5	25	1.4382	1.173	.2238	.2248	100.9	100.6	69.0	67.0
XVI	MeCl ₂ SiCH ₂ CH ₂ CO ₂ Me	98.5	25	1.4439	1.187	.2239	.2248	101.1	100.6	67.5	67.0
XVII	(Me ₂ SiO) ₂ SiMeCHMeCO ₂ Me	113-118	20	1.4062	0.9158	.2683	.2697	26.4 ^g	27.3 ^g	306	308
XVIII	(Me ₂ SiO) ₂ SiMeCH ₂ CH ₂ CO ₂ Me	122-123	20	1.4081	.9177	.2689	.2697	26.9 ^g	27.3 ^g	304	308
XIX	MeCl ₂ SiCH ₂ CHMeCO ₂ Me	101	25	1.4435	1.151	.2306	.2315	112.2	107.6	73.2	71.7
XX	[OMeSiCH ₂ CHMeCO ₂ Me] ₂	ca. 217 ^c	7	1.4443	1.103	.2410	.2414	491 ^f	480 ^f	165.1	160
XXI	[OMeSiCH ₂ CHMeCO ₂ Me] ₄	ca. 256 ^d	7	1.4482	1.114	.2404	.2414	647 ^f	640 ^f	164.7	160
XXII	MeCl ₂ SiC ₆ H ₄ CH ₂ CN	132	25	1.4551	1.145	.2370	.2366	92.8	91.0		
XXIII	MeCl ₂ Si(CH ₂) ₂ O(CH ₂) ₂ CN	158-164	11-13	1.4571	1.137	.2396	.2402	113.0	113.1		
XXIV	[OMeSi(CH ₂) ₂ O(CH ₂) ₂ CN] _x			1.4620				16.3 ^g	16.4 ^g		
XXV	MeCl ₂ SiCH ₂ CH ₂ - 	110	10	1.4806	1.073	.2651	.2659	112.7	111.6		
XXVI	[OMeSiCH ₂ CH ₂ - ] ₄			1.4902	1.016	.2846	.2876	16.9 ^g	16.7 ^g	680 ^f	672 ^f
XXVII	R = RCH ₂ CH- 	134-139	ca. 2	1.4400-	.980-	.269	.2703	15.5 ^g	15.5 ^g		
XXVIII	R = (EtO) ₂ MeSi- 	126	15	1.4241	.9697	.2632	.2642	11.2 ^g	11.3 ^g		

Viscosity: ^a 1558 cs. at 25°. ^b 61 cs. at 25°. ^c 19.6 cs. at 23.5°. ^d 30.8 cs. at 23.5°. ^e Mol. wt. in benzene 760. ^f Mol. wt. ^g Silicon. ^h Nitrogen.

Distillation showed no product boiling above 83°. The experiment was repeated using 4 g. of 1% Pt/C catalyst, 1 × 10⁻³ mole Pt/mole olefin. Less than 1% boiled above cyclohexene after 17 hr. in the water-bath.

The experiment was repeated using cyclohexene (16.4 g., 0.2 mole) methylchlorosilane (23 g., 0.2 mole) and 0.05 ml. of 0.1 M H₂PtCl₆·6H₂O in isopropyl alcohol (2.5 × 10⁻³ mole/mole cyclohexene). After 20 hr. in boiling water, distillation showed that the entire charge was essentially pure methylcyclohexyldichlorosilane,⁸ b.p. 201-202°, n_D^{25} 1.4696, d_4^{25} 1.09; R_D found 0.256, R_D calcd. 0.256.

(8) A. J. Barry, L. De Pree and J. W. Gilkey, THIS JOURNAL, 69, 2916 (1947), report b.p. 204° at 745 mm.

Phenyldichlorosilylpropyl Acetate (I).—The experimental procedure employed in this example is typical of those used to make the compounds of Table III. Allyl acetate (100 g., 1 mole) was mixed with 1.5 g. of 0.06% platinum-carbon catalyst in a round-bottom flask equipped with a reflux condenser. A mixture containing about 70% by weight of phenyldichlorosilane (about 2.1 moles) was added from a dropping funnel through the top of the condenser. The mixture was warmed gently, and suddenly the temperature rose to 125° from the heat of reaction. An excess of allyl acetate (200 g., 2 moles) was then added slowly during 20 minutes starting at this time so as to maintain a temperature between 125-140°. Soon after the addition was complete the temperature fell and external heat was needed to

maintain about 120° for 1 hr. before the mixture was distilled. Product boiling from 140 to 195° at 4 mm., 516 g., 90% yield, was obtained. This was redistilled to give 356 g., 61%, having constant properties given in Table III.

Hydrolysis of I in benzene solution formed a viscous polymer, II, of Table III.

Methyldichlorosilylpropyl Acetate (III).—Allyl acetate (2120 g., 21.2 moles) mixed with 9 g. of 0.06% platinum-on-carbon was heated to reflux. The heater was removed as methyldichlorosilane was added (2700 g., 23.5 moles) over a period of 5 hr. The heat of reaction kept the mixture above 95° during this time. The product was filtered free of the carbon and devolatilized to yield 4432 g., 97%, n_D^{25} 1.4409. Distillation showed the material to be essentially pure with the properties given in Table III. Hydrolysis in toluene gave a liquid polysiloxane IV. Saponification of this hydrolyzate in ethanolic alkali led to the formation of a product that was not precipitated by the addition of water. The saponification mixture was evaporated to dryness on a steam-table. The residue was extracted with acetone. Evaporation of the acetone extract left a clear amber rubbery gel (V in Table III).

Diethoxymethylsilylpropyl Acetate (VI).—Allyl acetate (50 g., 0.5 mole) containing 0.5 g. of 0.06% platinum-on-carbon was heated to reflux. Diethoxymethylsilane was added during 1 hr. at a temperature of about 120°. Distillation gave VI of Table III in 59% yield.

1-Acetoxypropyl-3-acetoxytetramethyldisiloxane (VII) and 1,3-Bis-acetoxypropyltetramethyldisiloxane (VIII).—*sym*-Tetramethyldisiloxane (100 g., 0.75 mole) was added over a period of 6 hr. to allyl acetate (170 g., 1.7 moles) at 90° containing 1 g. of 0.06% platinum-on-carbon. Heating was continued overnight at 75–80° and at reflux the next day until the reflux temperature rose to 125°. The mixture was filtered and distilled to yield VII, 61 g., 0.207 mole, 28%, and VIII, 72 g., 0.215 mole, 29%, of Table III.

Dimethylchlorosilylpropyl Acetate (IX).—Allyl acetate (1000 g., 10 moles) with 4 g. of 1% platinum-on-carbon was heated to reflux as dimethylchlorosilane (1041 g., 11 moles) was added at a rate to keep the mixture boiling from the heat of reaction. The addition required about 5.5 hr. The product was filtered and distilled. Dimethylchlorosilane was recovered, followed by 77 ml. of dimethyldichlorosilane, b.p. 68–72°, n_D^{25} 1.4021; neut. equiv. found 67, calcd. 64.5. Other volatile products were present but in insufficient amounts to be isolated. A residue of 82 and 1675 g., 86% yield of IX, dimethylchlorosilylpropyl acetate, were obtained.

Hydrolysis of 487 g. of IX with crushed ice yielded 386 g., 91%, of the disiloxane VIII, n_D^{25} 1.4320. Distillation indicated that the hydrolyzate was essentially pure with properties given in Table III.

2-Methyldichlorosilylethyl Acetate (X).—Vinyl acetate (860 g., 10 moles) containing 2.8 ml. of 0.12 *M* H₂PtCl₆·6H₂O in alcohol was heated to reflux. Methyldichlorosilane (1265 g., 11 moles) was added during 6.5 hr. as the reflux temperature rose to 140°. Distillation yielded X, 1443 g., 7.1 moles, 71% yield.

2-Trimethylsilylethanol (XI).—In order to establish the structure of X, 1 mole, 201 g., was added dropwise to 5 moles of MeMgBr in ether. The mixture was stirred for 0.5 hr. and permitted to stand overnight at room temperature. In the morning, the mixture was heated to reflux for 0.5 hr. before it was washed with ammonium chloride solution. Distillation of the washed ethereal solution yielded 79 g., 0.68 mole, 68% yield, of 2-trimethylsilylethanol (XI). The 3,5-dinitrobenzoate was prepared, m.p. 66°, recrystallized from alcohol.

An authentic sample⁹ of 2-trimethylsilylethanol yielded a 3,5-dinitrobenzoate having the same m.p. No depression of m.p. occurred in a mixture of the derivatives, and the infrared spectra of the samples were identical.

(2-Phenylethyl)-methyldichlorosilane (XIII).—Styrene (73 g., 0.7 mole) stabilized with *t*-butylcatechol was heated to 90° in the presence of 0.3 g. of 0.06% Pt/C catalyst as methyldichlorosilane (90 g., 0.78 mole) was added during 3

hr. The mixture was heated an additional 2 hr. and distilled to give XIII, 127 g., 83% yield.

The above chlorosilane was treated with excess methylmagnesium bromide in ether to form (2-phenylethyl)-trimethylsilane in 90% yield, b.p. 102° at 20 mm., n_D^{25} 1.4879, d_4^{25} , 0.8643; *R*_D found 0.3333, *R*_D calcd. 0.3326.

Essentially the same product was prepared from 2-phenylethylmagnesium bromide and trimethylchlorosilane in ether¹⁰; b.p. 101° at 20 mm., n_D^{25} 1.4842, d_4^{25} , 0.8591, *R*_D 0.3331.

The infrared spectra of the two samples were similar in all essential details with the curve of the sample made by addition to styrene having somewhat more distinct absorption maxima. It appears that the adduct is essentially the 2-phenylethylsilane derivative, but a small amount of impurity was present in either one or both of the samples.

Methyl Methyldichlorosilylbicyclo[2.2.1]heptylcarboxylate (XIV).—A mixture of methyldichlorosilane (28.8 g., 0.25 mole) and methyl *cis*-bicyclo[2.2.1]hept-5-ene-2-carboxylate (28.4 g., 0.2 mole) were sealed into a Pyrex tube with 5 × 10⁻⁶ mole of chloroplatinic acid and heated 3.5 hr. in a boiling water-bath. Distillation gave XIV (15.1 g., 28% yield) with a high boiling residue weighing 14.7 g.

XV, XVI: Methyldichlorosilane with Methyl Acrylate.—A nickel plated steel autoclave was charged with methyl acrylate (500 g., 5.81 moles), methyldichlorosilane (1150 g., 10 moles) and 10 g. of 0.06% Pt/C catalyst. The autoclave was heated for 16 hr. above 100°, mostly at 120–125°. The contents were then filtered and distilled. A distillate boiling at 83–102° at 25 mm. (607 g., 52% yield) was obtained leaving a residue of 164 g.

A portion (504 g.) of the distillate was redistilled through a three-foot column packed with Helipak stainless steel. Two isomers were obtained. The lower boiling of these was taken to be XV, methyl 2-(methyldichlorosilyl)-propionate (259 g.).

The higher boiling product XVI (190 g.) was taken to be methyl 3-(methyldichlorosilyl)-propionate.

A mixture of XVI (61 g., 0.3 mole) and trimethylchlorosilane (220 g., 2.04 moles) was added slowly to a slurry of ice in toluene and ether to cause hydrolysis and copolymerization. The organic layer was washed free of acid and distilled. The trisiloxane, (Me₃SiO)₂SiMeCH₂CH₂COOMe (XVIII) was obtained in 25% yield with higher boiling siloxanes which were not separated.

By the same procedure XV formed a trisiloxane XVII in 27% yield.

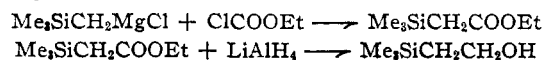
Methyl 3-(Methyldichlorosilyl)-2-methylpropionate (XIX).—Methyl methacrylate (100 g., 1 mole), methyldichlorosilane (158 g., 1.37 moles) and 1 g. of 0.06% Pt/C were sealed into a bottle and heated 8 hr. at 100°. Distillation showed that no adduct had formed. In a second experiment methyl methacrylate (250 g., 2.5 moles) and 2 ml. of 0.1 *M* chloroplatinic acid in isopropyl alcohol were mixed and warmed to 80°. Methyldichlorosilane was added slowly. Without external heat, the temperature rose to about 110° during 1.75 hr. The product was distilled to give 65% yield of XIX. A polymeric residue weighing 63 g. also formed.

Hydrolysis of XIX with crushed ice in benzene yielded a fluid polymer, n_D^{25} 1.4515, d_4^{25} , 1.122; visc. 100 cs. at 25°. To 86 g. of this hydrolyzate about 0.5 g. of finely divided potassium hydroxide was added, and the mixture was distilled completely at reduced pressure at a temperature below 300°. Redistillation of 73 g. of the distillate yielded about 3 g. of a very viscous precur followed by 30.5 g. of the cyclic trisiloxane XX and 29 g. of the cyclic tetrasiloxane XXI of Table III. A very high boiling residue remained.

Methyldichlorosilylbutyronitrile (XXII).—Allyl cyanide (166.4 g., 2.48 moles) and sufficient methyldichlorosilane were mixed so that the reflux temperature was 80°. To the refluxing mixture a few drops of chloroplatinic acid in isopropyl alcohol solution were added. Approximately 10⁻⁶ to 10⁻⁸ mole of catalyst was used. The mixture began to reflux vigorously as the temperature soon rose to 120°. More methyldichlorosilane was added to keep the temperature near 100°. In a short time the reaction subsided and the mixture was distilled. The product XXII was obtained in 70% yield.

Hydrolysis of XXII in benzene with a slurry of ice and water yielded a viscous colorless fluid which was only mod-

(9) L. H. Sommer of the Pennsylvania State University kindly gave us a sample of 2-trimethylsilylethanol which had been prepared according to the scheme



(10) H. Gilman and F. J. Marshall, *THIS JOURNAL*, **71**, 2066 (1949), reported b.p. 211°, n_D^{20} 1.4869, d_4^{20} , 0.8657.

erately soluble in benzene. This fluid appears to be largely hydroxyl end-blocked polysiloxanes of the formula $H[OMe-SiC_2H_4CH_2CN]_xOH$, n_D^{25} 1.4580, d_4^{25} 1.078; R_D found 0.2531, R_D calcd. for $[OMeSiC_2H_4CH_2CN]_x$ 0.2549.

Anal. Calcd. for $[OMeSiC_2H_4CH_2CN]_x$: Si, 22.1; N, 11.0. Found: Si, 21.8; N, 10.7.

[3-(2-Cyanoethoxy)-propyl]-methylchlorosilane (XXIII).—Methylchlorosilane (69 g., 0.6 mole) was added slowly to allyloxypropionitrile (b.p. 114° at 50 mm., n_D^{25} 1.4306, d_4^{25} 0.927, 56 g., 0.5 mole) containing 0.2 ml. of 0.1 *M* chloroplatinic acid. The temperature was maintained at 100–120° without external heating for about 2 hr. Distillation gave 78% yield of XXIII.

Hydrolysis of a portion of this product gave a fluid polysiloxane, XXIV.

In contrast to the relatively smooth addition reactions of the preceding two examples, acrylonitrile formed no adduct during repeated experiments with either chloroplatinic acid or platinum-carbon catalysts.

[2-(Cyclohex-4-enyl)-ethyl]-methylchlorosilane (XXV).—4-Vinylcyclohexene (324 g., 3 moles) with 1.5 g. of 0.06% platinum-carbon was warmed to 100° as methylchlorosilane (433 g., 3.77 moles) was added during 23 hr. Distillation yielded the adduct XXV, 541 g., 81% yield.

The structure of this compound is based upon the known low level of reactivity of the cyclohexene ring (see Table I) in the presence of the catalyst used and the high level of reactivity of terminal olefins. The infrared absorption spectra of the compound essentially confirmed the structure given. The absorption maximum characteristic of the $CH=CH_2$ group was present to only a small extent.

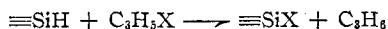
Hydrolysis of XXV in benzene yielded a polysiloxane, n_D^{25} 1.4928, d_4^{25} 1.023, R_D 0.2840; Si found 16.8%, Si calcd. 16.7.

The hydrolyzate distilled completely from potassium hydroxide at approximately 285–291° at about 0.01 mm. to form XXVI.

Tetramethyldisiloxane-1,3-bis-(2-ethyl-4-methyl-1,3-dioxolane) (XXVII).—Tetramethyldisiloxane (74 g., 0.55 mole) was added to 2-vinyl-4-methyl-1,3-dioxolane (114 g., 1.0 mole) using chloroplatinic acid as the catalyst (3×10^{-5} mole). Occasional cooling in an ice-bath was necessary to keep the temperature at about 115° during 0.5 hr. The product was then distilled to produce XXVII in 64% yield.

2-[2-(Diethoxymethylsilyl)-ethyl]-4-methyl-1,3-dioxolane (XXVIII).—A mixture of 2-vinyl-4-methyl-1,3-dioxolane, 0.5 mole, and 0.5 g. of 0.06% Pt/C was heated to 95°. Over a period of 1 hr., diethoxymethylsilane (75 g., 0.56 mole) was added. During addition the temperature was maintained at 110–120° followed by 120–140° for an additional 0.5 hr. Distillation gave a 66% yield of XXVIII.

Formation of Propylene.—In certain experiments a gas formed and unexpected products formed. In these experiments allyl compounds or isopropenyl acetate were used. In no other case was a gas formed in considerable quantities. The gas was identified as propylene which appeared to be formed according to an equation



Compound VII is one example of this in which X was the acetoxy group.

A series of experiments was carried out in which silicon hydrides and olefinic compounds were heated together in the presence of catalyst and any gas produced was caught so that an estimate of the amount could be made. The gas was then passed through bromine in carbon tetrachloride and converted to 1,2-dibromopropane, b.p. 140°, n_D^{25} 1.5176. The results of these experiments are summarized in Table IV.

Discussion

The mechanism by which the catalysts of Table I cause addition of silicon hydrides to olefinic compounds is not clear. It seems likely that these catalysts are essentially similar in their mode of operation even though they differ greatly in activity.

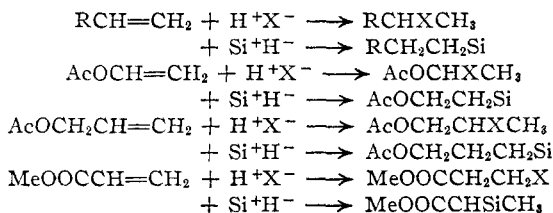
If the silicon hydride is thought of as polarized in the sense Si^+H^- , the additions bear a striking qualitative resemblance to electrophilic additions

TABLE IV

Olefin	Silicon hydride	Catalyst	Propylene, %
Allyl acetate	(MeHSiO) ₄	0.06% Pt/C	35
Allyl acetate	(MeHSiO) ₆	0.06% Pt/C	35
Allyl acetate	MeHSiCl ₂	0.06% Pt/C	0 ^a
Allyl acetate	(MeHSiO) ₄	H ₂ PtCl ₆ ·6H ₂ O	35
Allyl benzoate	O[SiMe ₂ H] ₂	H ₂ PtCl ₆ ·6H ₂ O	36.5
Diallyl phthalate	O[SiMe ₂ H] ₂	H ₂ PtCl ₆ ·6H ₂ O	41
Triallyl cyanurate	O[SiMe ₂ H] ₂	H ₂ PtCl ₆ ·6H ₂ O	46
Isopropenyl acetate	(MeHSiO) ₄	H ₂ PtCl ₆ ·6H ₂ O	61
Isopropenyl acetate	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	30
Vinyl acetate	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	0
Allyl bromide	MeHSiCl ₂	H ₂ PtCl ₆ ·6H ₂ O	25 ^b
Allyl bromide	(MeHSiO) ₄	H ₂ PtCl ₆ ·6H ₂ O	63.5

^a From 1–3% of a gas was obtained but not identified certainly as propylene. ^b MeSiCl₂Br was isolated, b.p. 85–89°, n_D^{25} 1.4395, d_4^{25} 1.557; R_D found 0.1690, R_D calcd. 0.1658; neut. equiv. found 63.1, neut. equiv. calcd. 64.7.

of strong acids H^+X^- , the atoms having the same sign being taken as analogs.¹¹



R = phenyl or alkyl

mostly

Without knowledge of the detailed mechanism the reactions may take, it appears that the silicon group is introduced as an electrophilic fragment Si^+ and the hydrogen atom is introduced as the nucleophilic fragment H^- . In certain cases, the great rate of reaction in the presence of extremely low catalyst concentrations leads one to suspect that the fragments may sometimes add to olefins by means of a chain mechanism.

The unexpected formation of *n*-pentylsilanes from pentene-2 seems most difficult to explain. It does not seem to be caused by rearrangement of the expected 2 or 3 pentylsilanes. A mixture of the pentyltrichlorosilanes formed with a peroxide initiator from pentene-2 and trichlorosilane^{2b} were heated in a sealed glass tube many hours mixed with trichlorosilane and chloroplatinic acid. No rearrangement was detectable. Pentene-2 and chloroplatinic acid were similarly heated but formed no pentene-1. Therefore, it seems likely that the apparent rearrangement occurs during the addition reaction.

The formation of propylene from allyl compounds and from isopropenyl acetate requires additional investigation before a reliable explanation is possible. The propylene is unlikely to form from electrophilic attack of the silicon hydride upon the ester group. Ethyl acetate, butyl acetate, phenyl acetate and benzyl acetate were each unchanged by long heating with tetramethyldisiloxane and chloroplatinic acid. Possibly the propylene results from addition to the double bond to form

(11) See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, for an excellent review and discussion of electrophilic additions to olefinic compounds.

β -acetoxyalkylsilanes which eliminate propylene by β -elimination. The amount of propylene formed would in each case depend upon the tendency of the silicon hydride to add beta to the acetoxy group and upon the ease of β -elimination in the adduct.

Acknowledgments.—The authors wish to express their appreciation to Joan Hickey, Mary Pat David, Gerald Schweitzer and Norman Daugengebaur for their invaluable aid in carrying out many of the experiments.

MIDLAND, MICHIGAN

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

A Study of the Mechanism of the Conversion of Aroyl Peroxides to Anhydrides by Tertiary Phosphines

BY DONALD B. DENNEY AND MICHAEL A. GREENBAUM¹

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Three unsymmetrically substituted aroyl peroxides, which were specifically labeled with oxygen-18, were reduced with tributylphosphine to the corresponding unsymmetrical anhydrides. Systematic degradation of the anhydrides elucidated the distribution of oxygen-18 in these molecules. These data show that the peroxide oxygen attacked by the phosphine, either the α - or β -oxygen (see flow sheet), is governed to a very marked degree by the electron density at the attacked atom. It also has been shown that the ion pairs A and B do not undergo exchange with each other but collapse directly to the products.

It has been demonstrated recently that the reaction of aroyl peroxides with tertiary phosphines proceeds by attack on the peroxidic oxygens to give ion pairs such as A or B.^{2,3} The purpose of the research reported here was to delineate more thoroughly the factors which control the formation of the ion pairs A and B. The three unsymmetrical peroxides *p*-nitrobenzoyl *p*-methoxybenzoyl peroxide-*p*-nitrobenzoyl carbonyl-¹⁸O (IV), *p*-nitrobenzoyl benzoyl peroxide-*p*-nitrobenzoyl carbonyl-¹⁸O (VII) and *p*-phenylbenzoyl benzoyl peroxide-*p*-phenylbenzoyl carbonyl-¹⁸O (XIII) were prepared and allowed to react with tri-*n*-butylphosphine. The labeled anhydrides, *p*-nitrobenzoic *p*-methoxybenzoic (V), *p*-nitrobenzoic benzoic (VIII) and *p*-phenylbenzoic benzoic (XIV) obtained from these reactions were treated with liquid ammonia to give the amides *p*-nitrobenzamide (VI and IX) and *p*-phenylbenzamide (XV). Analysis of the amides gave the oxygen-18 content of the carbonyl and therefore that of the parent carbonyl in the anhydride.⁴ Inspection of the flow sheet demonstrates that attack at the α -oxygen, which gives rise to ion pair A, will ultimately afford an amide with the same excess oxygen-18 content in the carbonyl as was in the original anhydride.

Attack at the β -oxygen leads to an amide which contains only one-half of the original excess oxygen-18. Table I contains the percentage α -attack. Table II contains the analytical data which were used in making these calculations.

It is immediately evident that a *p*-nitro substituent markedly controls the position of attack by

the phosphine. The mechanism of this control is undoubtedly due to the ability of the nitro group to lower the electron density at the α -oxygen both by resonance and induction.⁵ The creation of a

TABLE I

Peroxide	α -Attack ^a , %
<i>p</i> -Nitro- <i>p</i> '-methoxybenzoyl peroxide (IV)	100
<i>p</i> -Nitrobenzoyl benzoyl peroxide (VII)	95
<i>p</i> -Phenylbenzoyl benzoyl peroxide (XIII)	50

^a The % attack at a given position was calculated using the oxygen-18 values of the starting acid and amide and those obtained from the product amides.

partial positive charge in this region enhances the rate of attack of the phosphine relative to a neutral center. The *p*-methoxy group in IV tends to increase the electron density at the β -oxygen, and one finds a diminution in rate of attack at this position as compared to VII. It is important to note that in the reaction of IV and VII the ion pair A, which is formed practically exclusively, appears to be the least stable thermodynamically. The reasons for suggesting this are that in A the anion is derived from the weakest acid and the cation is destabilized by the nitro group. The fact that the least stable ion pair is formed indicates that this is a kinetically controlled process. Such control can arise easily if the transition state for ion pair formation resembles the starting materials rather than the products. A postulation of this kind is in complete harmony with the very marked directive powers of the *p*-nitro group. The fact that very little of the stable ion pair is formed indicates that the reaction is irreversible, or much less likely that collapse to products is much faster than ion pair return, and therefore equilibrium between A and B *via* the starting materials is never set up.

(5) Considerable evidence is available concerning the effect of substituents on the reactions of aroyl peroxides. A good discussion of these effects can be found in A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 79-81.

(1) Alfred P. Sloan Post-doctoral Fellow in Chemistry.

(2) M. A. Greenbaum, D. B. Denney and A. K. Hoffmann, THIS JOURNAL, **78**, 2563 (1956).

(3) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

(4) The above is only true if in the reaction of the anhydrides with ammonia there is no equilibration of the three oxygens. Such is the case if the reaction is carried out in refluxing ammonia; however, at Dry Ice temperatures equilibration can occur. This has been demonstrated by allowing monolabeled benzoic anhydride to react with refluxing ammonia; under these conditions no equilibration occurs; at Dry Ice temperatures the benzamide isolated contains completely equilibrated oxygen. This most interesting observation will be the subject of an article now in preparation.