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RICHMOND, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

γ-Ray Initiated Reactions. II. The Addition of Silicon Hydrides to Alkenes[1]

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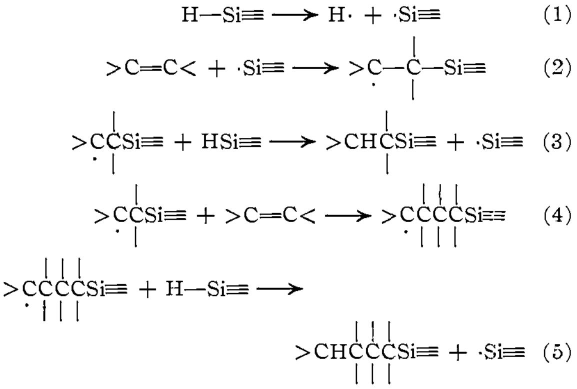
Trichlorosilane and methyldichlorosilane add to the double bond of certain alkenes in the presence of γ-rays as initiator. These compounds include octene-1, isobutylene, butene-2, 2-methyl-2-butene, cyclopentene, cyclohexene, 1-methylcyclohexene, allyl chloride, allyl acetate, allyl cyanide, *cis*-1,2-dichloroethylene, 3,3,4,4,4-pentafluoro-1-butene, 2-methyl-3,3,-4,4,4-pentafluoro-1-butene, 3,3,4,4,5,5,5-heptafluoro-1-pentene and 2-methyl-3,3,4,4,5,5,5-heptafluoro-1-pentene. Ethyl cinnamate, diethyl fumarate, indene and *trans*-stilbene were unreactive. Styrene and α-methylstyrene gave high-boiling silicon polymers. In addition to the isolation of the saturated monomeric adducts, some high-boiling alkylsilyl substituted derivatives were also obtained. Some of the adducts obtained in this way were converted to their tetraalkylsilyl derivatives or hydrolyzed to form polysiloxanes. On hydrolysis 3,3,4,4,5,5,5-heptafluoro-1-pentyltrichlorosilane gave unexpectedly a liquid siloxane.

Several publications have disclosed the addition of silicon hydrides to a number of alkenes under the activation of peroxides and ultraviolet light.[3] Recently two reports have appeared on such type of addition to fluorine-containing alkenes.[4] These involve the addition of silicon hydrides to tetrafluoroethylene photochemically and to chlorotrifluoroethylene, trifluoropropene, 1,1,2-trichloro-3,-3,3-trifluoropropene and 2,3,3,4,4,4-hexafluorobutene using peroxides and ultraviolet light. The yields of the products varied appreciably and were dependent both on the experimental conditions and on the nature of the reactants.

The present investigation differs primarily from the above work in that the reaction was carried out using γ-rays from a 3.0 kilocurie Co^{60} source as initiator at room temperature and also since additional alkenes were used. Trichlorosilane and methyldichlorosilane were added to some simple alkenes. The reaction was clean and went almost quantitatively, giving the expected adducts (Table I). Similarly the reaction was carried out on a number of alkenes which have functional groups and fluorine atoms (Tables II and III).

Other investigators have postulated that the addition of silicon hydrides to alkenes is a free-radical chain reaction. Their proposed mechanism for this reaction[5,3a] includes the steps



$$\mathrm{H{-}Si{\equiv}} \longrightarrow \mathrm{H\cdot} + \mathrm{\cdot Si{\equiv}} \qquad (1)$$

$$\mathrm{{>}C{=}C{<}} + \mathrm{\cdot Si{\equiv}} \longrightarrow \mathrm{{>}\underset{\cdot}{C}{-}\overset{|}{\underset{|}{C}}{-}Si{\equiv}} \qquad (2)$$

$$\mathrm{{>}\underset{\cdot}{C}\overset{|}{\underset{|}{C}}Si{\equiv}} + \mathrm{HSi{\equiv}} \longrightarrow \mathrm{{>}CH\overset{|}{\underset{|}{C}}Si{\equiv}} + \mathrm{\cdot Si{\equiv}} \qquad (3)$$

$$\mathrm{{>}\underset{\cdot}{C}\overset{|}{\underset{|}{C}}Si{\equiv}} + \mathrm{{>}C{=}C{<}} \longrightarrow \mathrm{{>}\underset{\cdot}{C}\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}Si{\equiv}} \qquad (4)$$

$$\mathrm{{>}\underset{\cdot}{C}\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}Si{\equiv}} + \mathrm{H{-}Si{\equiv}} \longrightarrow \mathrm{{>}CH\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}Si{\equiv}} + \mathrm{\cdot Si{\equiv}} \qquad (5)$$

In the work being reported in this paper, the rate of the reaction of simple alkenes to form the monomeric products (equation 3) was predominant. But in case of other alkenes as allyl chloride, allyl acetate and *cis*-1,2-dichloroethylene it was found that the second reaction, which is responsible for the formation of high-boiling materials (equation 4), was a strong competitor. Styrene and α-methylstyrene formed high-boiling products to the exclusion of monomeric products. The lesser reactivity of methyldichlorosilane toward alkenes (Table III) was not unexpected because of the difference in the electrophilic character of the methyl derivative. Although the addition of silicon hydrides to 1-alkenes has been shown by other investigators to yield the 1-isomer exclusively,[3a] the addition compound of trichlorosilane to allyl cyanide could be either $\mathrm{CNCH_2CH_2CH_2SiCl_3}$ (I) or $\mathrm{CNCH_2CH(CH_3)\text{-}SiCl_3}$ (II) or a mixture of them.[6] In order to distinguish between the two structures, the product prepared in this work was converted to the trimethyl acid amide derivative which was found to have properties identical with those of γ-trimethylsilylbutyric acid amide which is described in the literature.[7] By analogy, the addition com-

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[2] On leave from the Department of Chemistry, University College for Girls, A'in Shams University, Cairo, Egypt, under a travel grant as a Fulbright Visiting Scholar.

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TABLE I

SILANE ADDUCTS PREVIOUSLY DESCRIBED IN THE LITERATURE

Alkenes	Wt. used, g.	Adducts	γ-Radiation time, hr.	Yield,[a] %	B.p. °C.	B.p. Mm.	n^{25}D
		With trichlorosilane					
Octene-1	15	$CH_3(CH_2)_7SiCl_3$	40	99	112	15	1.4453
Isobutylene	20.5	$(CH_3)_2CHCH_2SiCl_3$	70	95	141	760	1.4346
Butene-2	12.7	$CH_3CH_2CH(CH_3)SiCl_3$	65	95	57–58	34	1.4403
2-Methyl-2-butene	14	$C_5H_{11}SiCl_3$	63	94	44–45	8	1.4489
Cyclohexene	30	$C_6H_{11}SiCl_3$	57	98	81	10	1.4773
Styrene	30	Visc. glassy material (6 g.)[b]	20		.....	..	....
		With methyldichlorosilane					
Octene-1	11.2	$CH_3(CH_2)_7Si(CH_3)Cl_2$ Visc. res. (1.5 g.)[c]	62	55	117–118	21	1.4422
Cyclohexene	12.3	$C_6H_{11}Si(CH_3)Cl_2$	62	45	83	15	1.4711
Allyl acetate	20	$AcO(CH_2)_3Si(CH_3)Cl_2$ Visc. res. (14 g.)[d]	85	47	121	30	1.4437

[a] Yield based on total alkene used. [b] Chlorine content, 4.4%. [c] Chlorine content, found 17.4%; theory for adducts: 1:1, 31.3%; 2:1, 19.1%; 3:1, 14.4%. [d] Chlorine content, 21.2%; calculated for $H[AcOCH_2CHCH_2]_2Si(Cl_2)CH_3$, 22.4%.

TABLE II

TRICHLOROSILANE ADDUCTS

Alkenes	Wt. used, g.	Adducts	γ-Radiation time, hr.	Yield,[a] %	B.p. °C.	B.p. Mm.	n^{25}D	Analyses, %[g] Silicon Calcd.	Silicon Found	Chlorine (hydrol.) Calcd.	Chlorine (hydrol.) Found
Cyclopentene	13.6	$C_5H_9SiCl_3$	39	96	70–71	19	1.4688	13.8	13.86	52.3	52.6
1-Methylcyclohexene	6.7	$C_6H_{10}(CH_3)SiCl_3$	61	92	82–83	8	1.4805	12.13	12.14	45.98	46.03
Allyl chloride	15.3	$ClCH_2(CH_2)_2SiCl_3$[b]	62	40	58–60	8	1.4646	13.24	13.41	50.21	50.25[e]
										Cl, 66.95	66.42
		$H[CH_2ClCHCH_2]_2SiCl_3$		34	80–110	1.4	1.4871	9.73	11.55	36.90	36.60[e]
										Cl, 61.5	59.6
		Residue (3.5 g.)		..	.....	..	....	...	...	[f]	18.6[e]
Allyl acetate	20	$AcO(CH_2)_3SiCl_3$	61	22	101–102	34	1.4380	11.92	12.18	45.15	45.41[e]
		$H[AcOCH_2CHCH_2]_2SiCl_3$		71	120	24	1.4474	8.36	8.34	31.68	31.67[e]
		Residue (8 g.)		..	.....	..	....	...	...	[f]	35.15[e]
Allyl cyanide	16	$CN(CH_2)_3SiCl_3$[c]	61	8	93–94	8	1.4654	13.87	13.81	52.51	52.31[e]
										N, 6.92	6.91
		Residue (13 g.)		..	.....	..	....	...	...	[f]	37.8[e]
cis-1,2-Dichloroethylene	19.4	$CH_2ClCHClSiCl_3$[d]	68	27	63–64	13	1.4762	12.07	11.96	45.76	45.58[e]
										Cl, 76.33	76.54
		$CH_2Cl(CHCl)_3SiCl_3$		12	103–105	13	1.4996	...	...	53.82	54.68[e]
										Cl, 75.42	75.72
α-Methylstyrene	17.7	Visc. oil (0.9 g.)	39	..	115–120	0.4	....	...[h]	6.19	[f]	6.96
3,3,4,4,4-Pentafluoro-1-butene	10.2	$C_2F_5(CH_2)_2SiCl_3$	66	40	120	..	1.3705	9.98	9.19	37.78	37.31
		Residue (1.4 g.)		..	.....	..	....	...	...	[f]	20.7
2-Methyl-3,3,4,4,4-pentafluoro-1-butene	19	$C_2F_5CH(CH_3)CH_2SiCl_3$	65	9	64–65	28	1.3812	9.50	9.37	35.99	36.04
										F, 32.14	31.96
3,3,4,4,5,5,5-Heptafluoro-1-pentene	16	$C_3F_7(CH_2)_2SiCl_3$	61	52	62–64	49	1.3626	8.47	8.33	32.08	31.94
										F, 40.11	40.16
		Residue (0.9 g.)		..	.....	..	....	...	...	[f]	26.0
2-Methyl-3,3,4,4,5,5,5-heptafluoro-1-pentene	28	$C_3F_7CH(CH_3)CH_2SiCl_3$	65	11	53–54	24	1.3722	8.13	8.22	30.78	30.63
										F, 38.49	38.52

[a] Yield based on total alkene used. [b] Ref. 3b reported the analysis for chlorine only. [c] To prove its structure, it was methylated with CH_3MgI to give $CN(CH_2)_3Si(CH_3)_3$,[6] b.p. 91–92° (25 mm.), n^{25}D 1.4254, yield 62.5%. *Anal.* Calcd. for $C_7H_{15}SiN$: C, 59.50; H, 10.70; Si, 19.88; N, 9.91. Found: C, 59.62; H, 10.63; Si, 19.81; N, 9.92. This was hydrolyzed to its acid amide $(CH_3)_3Si(CH_2)_3CONH_2$, colorless flakes from a mixture of light petroleum (b.p. 30–40° and 90–100°); m.p. 65–67° (ref. 7 gives m.p. 66.5–66.7°). [d] Ref. 7a reported the preparation of this compound by another method. [e] Volhard method (very slightly acidic $AgNO_3$ solution) was used. [f] Amount of polymerization is unknown; therefore analysis cannot be calculated. [g] C and H analyses were also made of nearly all compounds for which formulas are given and these agreed very closely with calculated data.

pounds of trichlorosilane with allyl acetate and with allyl chloride are presumed to be $AcO(CH_2)_3SiCl_3$ and $Cl(CH_2)_3SiCl_3$. The free radical addition of trichlorosilane and methyldichlorosilane to the fluoro-1-alkene should give mainly the 1-isomer analogous to the addition in the case of 3,3,3-trifluoropropene.[4b,8] Some 1,2-disubstituted alkenes were found to be remarkably unreactive[9] toward the trichlorosilane, *e.g.*, ethyl cinnamate,[10] diethyl fumarate, indene and *trans*-stilbene.

A few of the alkylchlorosilanes were converted to their more stable derivatives as, for example, to tetraalkylsilanes through the Grignard reaction and to siloxanes by hydrolysis (Table IV). Dialkyldichlorosilanes, on hydrolysis, yield the corresponding silanediols which easily condense to linear siloxanes which are usually liquids, and alkyltrichlorosilanes gave highly cross-linked siloxanes as white silica-like solids. Surprisingly, heptafluoropentyltrichlorosilane on hydrolysis has been found to yield a liquid (Table IV). Further work is being carried on to determine the nature of this prod-

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TABLE III

METHYLDICHLOROSILANE ADDUCTS

Alkenes	Wt. used, g.	Adducts	γ-Radiation time, hr.	Yield,[a] %	B.p. °C.	B.p. Mm.	$n^{25}D$	Composition %[c] Silicon Calcd.	Silicon Found	Chlorine (hydrol.) Calcd.	Chlorine (hydrol.) Found
Butene-2	12.7	$CH_3CH_2CH(CH_3)Si(CH_3)Cl_2$	65	57	45	20	1.4343	16.37	16.33	41.49	41.02
2-Methyl-2-butene	14	$C_5H_{11}Si(CH_3)Cl_2$	63	30	49–50	11	1.4433	15.14	15.22	38.32	37.96
Cyclopentene	13.6	$C_5H_9Si(CH_3)Cl_2$	62	20	75	23	1.4627	15.35	14.84	38.7	37.80
		Residue (0.9 g.)		..	.....	..	....	...	...	...	21.34
Allyl chloride	15.3	$Cl(CH_2)_3Si(CH_3)Cl_2$	65	4	68–70	15	1.4585	14.67	14.52	37.07	36.40[b]
										Cl, 55.61	55.57
		$H[CH_2ClCHCH_2]_2Si(CH_3)Cl_3$		11	105–110	2	1.4820	10.48	10.11	26.45	25.74[b]
										Cl, 52.90	51.61
		Residue (3.9 g.)			.....	..	....	...	...	...	13.1[b]
2-Methyl-3,3,4,4,4-pentafluoro-1-butene	20	$C_2F_5CH(CH_3)CH_2Si(CH_3)Cl_2$	87	1.7	65	52	1.3884	10.21	9.73	25.77	25.09
										F, 34.52	34.41
		Residue (1.2 g.)			.....	..	....	...	...	...	22.13
3,3,4,4,5,5,5-Heptafluoro-1-pentene	13.5	$C_3F_7(CH_2)_2Si(CH_3)Cl_2$	111	23	54–55	33	1.3707	9.03	9.07	22.79	22.75
										F, 42.75	42.77
		Residue (2.1 g.)			.....	..	....	...	...	...	19.12
2-Methyl-3,3,4,4,5,5,5-heptafluoro-1-pentene	15	$C_3F_7CH(CH_3)CH_2Si(CH_3)Cl_2$	85	6.4	65	26	1.3748	8.64	8.71	21.81	21.56
										F, 40.90	40.71

[a] Yield based on total alkene used. [b] Volhard method was used. [c] C and H analyses also were made for all compounds for which formulas are given except those from allyl chloride. The analyses agreed closely with calculated values.

TABLE IV

TETRAALKYLSILANES[b] AND SILOXANES

Compound	B.p. °C.	B.p. Mm.	$n^{25}D$	Yield,[a] %	Silicon, % Calcd.	Silicon, % Found	Fluorine, % Calcd.	Fluorine, % Found
$C_5H_{11}Si(CH_3)_3$	50	37	1.4191	61	19.46	19.08	...	...
$[C_5H_{11}Si(CH_3)O]_x$	..	..	1.4478	..	21.56	19.99	...	...
$[C_5H_9Si(CH_3)O]_x$	..	..	1.4747	..	21.90	21.4	...	...
$C_6H_{10}(CH_3)Si(CH_3)_3$	85	40	1.4519	54	16.48	16.56	...	...
$C_2F_5(CH_2)_2Si(CH_3)_3$	100–101	..	1.3000	56	12.75	12.56	43.13	43.12
$C_3F_7(CH_2)_2Si(CH_3)_3$	36	30	1.3390	50	10.39	10.44	49.21	49.14
$[C_3F_7(CH_2)_2Si(CH_3)O]_x$	110–140	1	1.3592	71.5	10.96	11.55	...	...
$[C_3F_7(CH_2)SiO_{1.5}]_x$	.....	..	1.3530	98	11.27	11.12	53.38	53.60

[a] Yield based on total alkylhalosilane used. [b] C and H analyses were also made of the tetraalkylsilanes and the data agreed closely with calculated values.

uct and to find out how general this type of reaction may be.

Experimental[11]

γ-Radiation was obtained from a 3.0 kilocurie Co^{60} source.

Reagents.—Trichlorosilane, methyldichlorosilane and most of the alkenes were redistilled commercial products (pure grade). The fluoroalkenes were synthesized by published procedures.[12]

The Addition Reaction.—A Pyrex tube was charged with the alkene (1 equiv.) and the silicon hydride (3 equiv.); in the case of the fluoroalkenes, the ratio was 1:4. Dry nitrogen was passed through the mixture for 15 minutes while cooling prior to sealing the tubes. The sealed tube was exposed to irradiation at room temperature for the time shown in the tables at a rate of 810,000 r.e.p. per hour. The tube was opened, the unreacted silicon hydride and alkene were removed by distillation and the residual products were separated by repeated fractionation.

Grignard Reaction.—Methylmagnesium iodide was prepared in slight excess in the usual manner from magnesium and methyl iodide. The chlorosilane compound, in ether, was added dropwise with stirring while the reaction mixture was cooled with an ice-bath. The mixture was refluxed for about 17 hr., the ether distilled off and the residue heated on a steam-bath for 5 hr. The ether that had been distilled off was then added and the mixture was hydrolyzed with water. The precipitate was dissolved with 10% sulfuric acid. The ether layer was separated from the aqueous layer and the latter was extracted twice with ether. The combined ether extracts were then washed successively with water, sodium bisulfite solution, and water and then dried over magnesium sulfate. After filtration and removal of ether, the residue was distilled.

Method of Hydrolysis.—The alkylchlorosilane compound (about 3 to 4 g.) was dissolved in cold ether. Ice-water (100 ml.) was added dropwise with stirring, the mixture was shaken for five minutes and the ether layer was separated from the aqueous layer. The latter was extracted twice with ether and the combined ether extracts were washed with dilute ammonia solution and then water. The solvent was removed by distillation and the residue was dried under vacuum at 100°.

Hydrolyzable chlorine was determined by the Volhard method or by dissolving the material in aqueous alcohol and titrating the solutions with standard alkali using phenolphthalein as indicator.[13] Melting and boiling points are uncorrected.

Unreactive Alkenes.—Ethyl cinnamate, diethyl fumarate, indene and *trans*-stilbene were found to be unreactive toward trichlorosilane even when they were irradiated for more than 60 hr.

ANN ARBOR, MICHIGAN

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[11] Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Schwarzkoff Microanalytical Laboratory, Woodside, N. Y.

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