

COMMUNICATIONS TO THE EDITOR

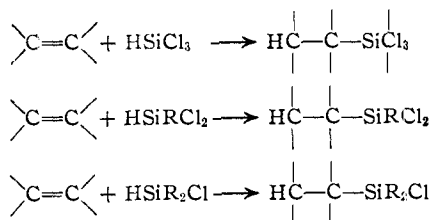
THE REACTION OF OLEFINS AND CHLORO-HYDROSILANES

Sir:

The preparation of octyltrichlorosilane from octene and trichlorosilane using diacetyl peroxide or ultraviolet light as catalyst was reported by Sommer, *et al.*¹

While a good yield of product was obtained, certain disadvantages are resident in the use of peroxides to facilitate this reaction.

In an extensive program considerably prior to the above publication, we synthesized many organosilicon derivatives by reactions of the following types, employing a wide variety of hydrocarbons containing olefinic double bonds



These reactions were accomplished without addition of catalyst or other reagent, by merely heating the reaction mixtures under pressure. The times and temperatures were chosen by a consideration of reaction kinetics determined at several temperatures. Temperatures employed varied from 160°, where the reactions are slow, to 400°, where the reactions are rapid but where some decomposition may occur. The method is illustrated by the following experiments.

Octadecyltrichlorosilane was prepared by heating in a 2.4-liter bomb a mixture of 406 g. of trichlorosilane and 756 g. of octadecene. The temperature was raised to 300° over a two and one-half-hour period. The pressure increased regularly to 276 p. s. i. maximum at 276°, then dropped to 180 p. s. i. when 300° was reached; when it leveled at 65 p. s. i. after eighteen hours at 300°, the run was discontinued. The yield was 94% of the theoretical.

n-Propylmethyl-dichlorosilane was prepared by similarly bombing 345 g. of methyl-dichlorosilane with 128 g. of propylene overnight at 300° (1120 p. s. i. max.) On distillation, propylmethyl-dichlorosilane was isolated at 123–124° (747 mm.). The yield was 72% of the theoretical; some hexylmethyl-dichlorosilane was formed.

A wide variety of compounds were similarly prepared by treating 1-alkenes from ethylene through octadecene, 2-butene, isobutene, cyclohexene, diisobutylene, 1,3-butadiene and 1,5-

(1) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *THIS JOURNAL*, **69**, 188 (1947).

hexadiene with trichlorosilane, tribromosilane, methyl-dichlorosilane, ethyl-dichlorosilane, phenyl-dichlorosilane, diethylchlorosilane, diphenylchlorosilane and methylphenylchlorosilane.

The 1-alkenes yielded *n*-alkyl derivatives almost exclusively. With trichlorosilane, 2-butene yielded *s*-butyltrichlorosilane while isobutene gave only isobutyltrichlorosilane. Thus it is evident that the electron-rich carbon of the olefin becomes linked to the electron-accepting silicon in trichlorosilane, the HSi nucleus of which may be regarded as a pseudo-aluminum; a chlorine likely becomes bonded, at least in a transition state, to the adjacent electropositive carbon whereafter its exchange with the labile H on the silicon generates the normal alkyltrichlorosilane. Silicon tetrachloride does not react similarly.

Of the various compounds prepared by this method, the following are new to the literature:

Compound	Boiling point	
	°C.	Mm.
<i>s</i> -Butyltrichlorosilane	145–146	736
2-Methylpentyltrichlorosilane	98	50
3-(2,2,4-Trimethylpentyl)-trichlorosilane	94–96	20
<i>n</i> -Hexadecyltrichlorosilane	194–196	7.5
<i>n</i> -Octadecyltrichlorosilane	185–199	2–3
<i>n</i> -Butenyltrichlorosilane	64	40
Trichlorosilyl-(trichlorosilylethyl)-cyclohexane	161	6
<i>n</i> -Hexenyltrichlorosilane	103–140	50
bis-(Trichlorosilyl)-hexane	148–153	10
<i>n</i> -Propyltribromosilane	183	756
Ethylmethyl-dichlorosilane	100	744
Methylpropyl-dichlorosilane	123–124	747
<i>n</i> -Butylmethyl-dichlorosilane	147.5–148	744
<i>n</i> -Hexylmethyl-dichlorosilane	192	743
Methyloctyl-dichlorosilane	100–116	20
Methyloctadecyl-dichlorosilane	200–210	6
Cyclohexylmethyl-dichlorosilane	204	745
Phenylpropyl-dichlorosilane	140–144	44–47
Diethylpropylchlorosilane	164–166	742
Methylphenylpropylchlorosilane	124–126	30
Diphenylpropylchlorosilane	174–176	10

A series of papers on this subject will be forthcoming.

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RECEIVED OCTOBER 20, 1947

FREE RADICAL REACTIONS OF ALDEHYDES

Sir:

Some recent work of ours on free radical reactions of aldehydes in the liquid phase has re-