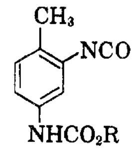
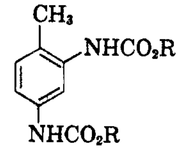
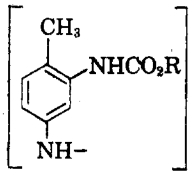
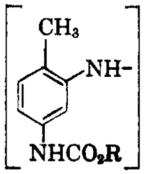
TABLE I

Compound	R	Carbon		Hydrogen		Nitrogen			
		Calcd.	Found	Calcd.	Found	Calcd.	Found	M.P., °C.	Yield, %
II 	Methyl	58.23	57.82	4.88	5.18	13.58	13.65	94–96	79
	Ethyl	60.05	60.28	5.49	5.71	12.75	12.91	51–59	85
	Butyl	62.88	63.78	6.49	6.55	11.28	11.35	144/0.2 mm.	70
	Octyl	67.06	67.38	7.94	7.67	9.20	9.47	40–42	69
	Hexadecyl	72.08	72.87	9.67	9.78	6.72	6.60	70.5–73.5	87
III 	Methyl[5]							170–171	99
	Ethyl[5]							136	97
	Butyl	63.33	63.57	8.12	7.99	8.68	8.81	80	96
	Octyl	69.09	69.13	9 74	8.93	6.44	6.40	69	96
	Hexadecyl	74.72	73.60	11.32	10.60	4.25	4.47	95–96	97
VI 	Methyl	61.46	59.71	5.74	5.91	14.50	14.00	201–204	89
	Ethyl	60.85	61.30	6.32	6.35	13.52	13.60	197–198	68
	Butyl	63.80	63.94	7.28	7.05	11.91	12.16	152–154	82
	Octyl	68.01	67.68	8.65	7.77	9.61	9 26	131–132	75
	Hexadecyl	72.91	71.05	10.24	9.27	6.94	7.24	124–125	62
IV 	Methyl	61.46	61.52	5.74	5.23	14.50	14.81	239–240	91
	Ethyl	60.85	60.87	6.32	6.33	13.52	13.63	206–207	82
	Butyl	63.80	62.74	7.28	7.15	11.91	12.05	186	90
	Octyl	68.01	68.24	8.65	8.50	9.61	10.03	180	85
	Hexadecyl	72.91	72.80	10.24	10.40	6.94	6.77	173.5–174	41

anhydrous petroleum ether–diethyl ether, and dried in a vacuum desiccator.

The product, after drying, was pulverized in a mortar and washed again with diethyl ether, petroleum ether, and dried in a vacuum oven at 50°C. The infrared spectrum was identical with that of a commercial sample prepared by du Pont under the trade name Hylene T. U., melting range[7] 172–178°C. Melting point of the product, 172–175°C.

The reaction of methanol with V to yield the corresponding urea-carbamate was carried out by weighing 0.05 moles Compound V into a 100 ml. three-neck flask followed by the addition of 0.10 mole methanol, 0.5 ml. of pyridine, and 50 ml. of chloroform. The reaction was allowed to reflux for 16 hr. with stirring. The unreacted V was removed by filtration and the desired product obtained by evaporating the filtrate under vacuum. The product was pulverized in a mortar and washed several times with acetone.

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Halogen-Containing Silane Monomers

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The work reported herein covers the synthesis of several new halogen-containing silane monomers. These compounds were prepared in connection with a study of silicon elastomers with potential resistance to hydrocarbon solvents. Three approaches were utilized: additions of silicon halides to Grignard reagents, Diels-Alder additions of halogenated dienes to vinyl and allyl silanes, and additions of perhalogenated methanes to vinyl silanes. Table I summarizes the pertinent information for the five new compounds prepared.

The Diels-Alder reaction of vinyltrichlorosilane and of vinyltriethoxysilane with hexachlorocyclopentadiene has been described by Kleiman.[1] Tarrant[2] has reported the peroxide-catalyzed addition of $CBrCl_3$ to vinyltrichlorosilane and to vinyltrimethylsilane. Lovelace and Rausch[3] have reported

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[7] Hylene, T. U., Pamphlet HR-9, E. I. du Pont de Nemours & Co., Inc., December 1955.

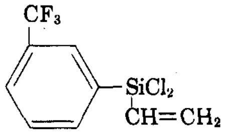
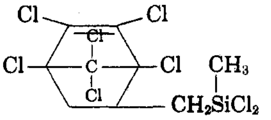
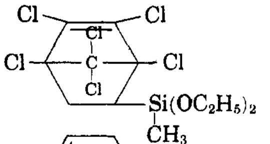
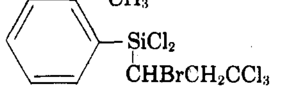
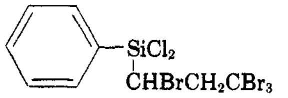
(1) Morton Kleiman, U. S. Patent 2,697,089 (Dec. 14, 1954).

(2) P. Tarrant, WADC Progress Report No. 2 (Aug. 12, 1954), and WADC Progress Report 3 (Oct. 15, 1954). Contract AF 33(600)-26593.

(3) A. M. Lovelace and D. A. Rausch, *Abstracts of 128th Meeting of the American Chemical Society*, Minneapolis, September 1955, p. 40.

TABLE I

HALOGENATED SILANE MONOMERS

Compound	Method[a]	Conversion	B.P. °C. (Mm.)	n_D^{25}	Analysis: % Hydrolyzable Chlorine[b] Calcd.	% Hydrolyzable Chlorine[b] Found	% Silicon Calcd.	% Silicon Found
(A) 	I	57.5	91-92(10)	1.4755	26.2	26.6, 26.7		
(B) 	II	57	135-137(0.7)		16.6	16.0, 16.1		
(C) 	II	79	120-138(2)[c]				6.49	6.43, 6.52[d]
(D) 	III	64	120-126(2)		17.7	18.3, 18.6		
(E) 	III	64	175(1)		13.3	13.3, 13.5		

[a] Method I: Grignard reaction. Method II: Diels-Alder reaction. Method III: Addition of perhalogenated methane. [b] Hydrolyzable chlorine in these compounds refers only to the chlorines attached directly to silicon. [c] This boiling range has been reproduced on careful fractionation through a 50 × 1 cm. glass-helix packed column. We offer the explanation that the product is a mixture of cis-trans isomer resulting from restricted rotation about the ring C—Si bond. The interposition of a CH_2 group as in (B) apparently gave a non-hindered product which distilled reproducibility within a narrow range. [d] These analyses refer to the first and last fractions within the stated boiling range.

the γ-ray induced additions of $CBrCl_3$ to vinyltrichlorosilane.

EXPERIMENTAL[4]

Method I. The Grignard reagent was prepared from 90 g. (0.40 mole) of *m*-bromobenzotrifluoride[5] and 10 g. (0.40 g.-atoms) of magnesium in 200 ml. of ether. This solution was added with stirring to 260 ml. (2.0 mole) of vinyltrichlorosilane over a period of 2 hr. while maintaining the temperature at 10-15°. The mixture was stirred overnight at room temperature and was filtered by suction with exclusion of atmospheric moisture. After distillation of the excess vinyltrichlorosilane (Silicone Division of Union Carbide Corp.) the residue was distilled from a Claisen flask yielding compound (A) with the constants recorded in Table I. There was also collected a fraction, b.p. 124-129° (3 mm.) which constitutes a 5.2% conversion to what is presumably bis(trifluoromethylphenyl)vinylchlorosilane.

Method II. Hexachlorocyclopentadiene, 28 g. (0.10 mole), was heated to reflux and 16.4 g. (0.10 mole) of vinylmethyldiethoxysilane (Peninsular Chemical Inc.) was added dropwise with stirring. After the addition the mixture was heated at 135-150° for an additional 12 hr. The mixture was distilled from a Claisen flask. After a small forerun of hexachlorocyclopentadiene, the product (C) was collected.

When allylmethyldichlorosilane was used as the olefin to prepare compound (B), it was necessary to maintain the silane at 100-120° during the addition of hexachlorocyclopentadiene.[6] Overheating caused extensive polymerization during one preparation.

Method III. Phenylvinyldichlorosilane, 5.0 g. (0.025 mole), was added dropwise, with stirring to 0.05 mole of the halogenated methane, maintained at 90° under a nitrogen atmosphere. Concurrently 0.1 g. of benzoyl peroxide was added in small portions. The addition of the silane required 15 min. and the reaction mixture was held at 90° for an additional 2 hr. The products were distilled from a Claisen flask.

Attempts to add ethyl bromoacetate, ethyl acetoacetate, or perchloromethylmercaptan to phenylvinyldichlorosilane gave back much of the starting materials along with intractable residues.

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The analytical determinations were carried out in the Analytical Section of Stanford Research Institute.

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[4] Boiling points are uncorrected.

[5] J. K. Simons and E. O. Ramler, *J. Am. Chem. Soc.*, **65**, 391 (1943).

[6] D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1813 (1945).