

heptane, *n*-hexane and carbon disulfide. Combined with the figures of Horiuti for the same gases in carbon tetrachloride and benzene, they

are seen to increase strongly with decreasing internal pressures of the solvents.

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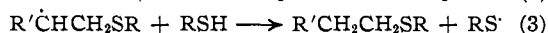
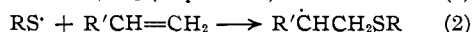
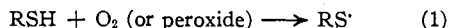
[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

The Reaction of Mercaptans with Alkenyl Silanes

By CHARLES A. BURKHARD

In a previous paper the peroxide catalyzed addition of trichlorosilane to vinyl- and allyl-trichlorosilanes to form α,ω -bis-trichlorosilylalkanes was discussed.¹ A continuation of the study of peroxide catalyzed addition reactions involving alkenyl silanes has shown that mercaptans react with alkenyl silanes to form thio ethers.

Kharasch, *et al.*,² have proposed that the addition of the mercapto group to an olefin proceeds by a free-radical chain-transfer type reaction.



The addition of the mercapto group to an alkenyl silane appears to proceed by the same reaction mechanism as that proposed by Kharasch for the addition of mercaptans to olefins,³ since the reaction is catalyzed by peroxide and proceeds

The presence of a silicon atom in the olefin does not appear to inhibit the addition reaction. Furthermore, it has been shown that the addition reaction proceeds normally when one or more of the following groups is also attached to the silicon atom to which the alkenyl group is attached: (1) alkyl group, (2) alkoxy group, (3) siloxane linkages and (4) a second alkenyl group.

The carbon-silicon bond is not weakened by the presence of the sulfur atom in the delta position (with respect to the silicon atom) as evidenced by the stability of these compounds when they are used in the presence of acids or alcoholic caustic. On the other hand, a halogen atom attached to either the beta or gamma carbon atom in an ethyl- or *n*-propylsilane causes a weakening of the carbon-silicon bond and in the presence of an alkali cleavage of this bond occurs.⁴

The types of compounds that can be prepared will depend on the type of mercaptan

TABLE I
NEW ALKENYL SILANES AND MERCAPTO ADDUCTS

Compound	Formula	Reagents used olefin ^d thiol	B. p., °C.	Mm.
I Allyltriethoxysilane ^a	$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$		100	50
II Allyltrimethylsilane ^b	$\text{CH}_2=\text{CHCH}_2\text{Si}(\text{CH}_3)_3$		85-86	
III Diallyldimethylsilane	$(\text{CH}_2=\text{CHCH}_2)_2\text{Si}(\text{CH}_3)_2$		68	50
IV Allylpentamethylidisiloxane	$(\text{CH}_2=\text{CHCH}_2)_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$		141.5-142	
V 1,3-Diallyltetramethylidisiloxane	$[(\text{CH}_2=\text{CHCH}_2)_2\text{Si}(\text{CH}_3)_2]_2\text{O}$		179-180	758.3
VI 3-Thia-6-sila-6,6-dimethylheptanoic acid	$(\text{CH}_3)_2\text{Si}(\text{CH}_2\text{CH}_2\text{SCH}_2\text{CO}_2\text{H})_2$	<i>o</i> <i>f</i>	143-144	7
VII 3-Thia-7-sila-7,7-dimethyloctanoic acid	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$	II <i>f</i>	164-166	9
VIII 3-Thia-7,7-dimethyl-7-trimethylsiloxy-7-silaheptanoic acid	$(\text{CH}_3)_2\text{SiOSi}(\text{CH}_3)_3(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{H}$	IV <i>f</i>	149-150.2	2
IX Ethyl 3-thia-7-sila-7,7-triethoxyheptanoate	$(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_3)_2\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$	I <i>o</i>	200-201.5	50
X Ethyl 3-thia-7,7-dimethyl-7-silaoctanoate	$(\text{CH}_3)_2\text{Si}(\text{CH}_2)_2\text{SCH}_2\text{CO}_2\text{C}_2\text{H}_5$	II <i>o</i>	148-149 262-264	24
XI 1-(<i>p</i> -Tolylthio)-3-trimethylsilylpropane	$\text{CH}_3\text{C}_6\text{H}_4\text{S}(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$	II <i>h</i>	206-209	46
XII <i>p</i> -Tolyl-3-thia-7,7-dimethyl-7-silaoctanamide	$\text{CH}_3\text{C}_6\text{H}_4\text{NHCOCH}_2\text{S}(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2$		M. p. 72.5-73	
XIII	$[-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2(\text{CH}_2)_2\text{SCH}_2\text{CO}_2(\text{CH}_2)_2\text{O}_2\text{CCH}_2\text{S}-]_2$	III		
XIV	$[-(\text{CH}_2)_2\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3(\text{CH}_2)_2\text{SCH}_2\text{CO}_2(\text{CH}_2)_2\text{O}_2\text{CCH}_2\text{S}-]_2$	V		

exclusively by addition of the sulfur-hydrogen bond to the olefinic linkage forming a thio ether. The formation of the thioether is evidenced by the following facts: (1) elemental analyses indicate that no loss of sulfur has occurred during the reaction and (2) no mercapto group is detectable in the purified reaction products (reaction with I_2/KI solution).

(1) Burkhard and Krieble, *THIS JOURNAL*, **69**, 2687 (1947).

(2) Kharasch, Read and Mayo, *Chem. & Ind.*, **57**, 752 (1938).

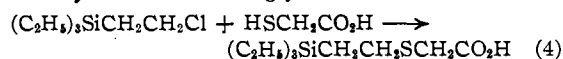
(3) For a review of the addition reaction of the mercapto group to olefins see Mayo and Walling, *Chem. Revs.*, **27**, 387 (1940).

and alkenyl silane that are used, *e. g.*, thiols, thioglycolic acid and its esters have been used to prepare thio ethers, thia acids and thia esters. When dimercaptans and dialkenylsilanes are allowed to react, viscous oils result. These viscous oils are similar to those reported by Marvel and Chambers⁵ in which dithiols and dienes were allowed to react to form polyalkylene sulfides.

(4) Sommer, Dorfman, Goldberg and Whitmore, *THIS JOURNAL*, **68**, 488 (1946).

(5) Marvel and Chambers, *ibid.*, **70**, 993 (1948).

Larsson⁶ recently reported thia acids of the type described in this paper. These compounds were prepared by reaction of a (halogenoalkyl)-trialkylsilane and thioglycolic acid.



These acids were used to confirm the identity of the (α - and β -halogenoalkyl)-silanes.

During this investigation, several new silanes were prepared, diallyldimethylsilane, allylpentamethylsiloxane and 1,3-diallyltetramethylsiloxane. Allyltrimethylsilane and diallyldimethylsilane were prepared by the reaction of methylmagnesium bromide with the corresponding allylchlorosilane. Allylpentamethyl- and 1,3-diallyltetramethylsiloxane were prepared by co-hydrolysis of allyldimethylchlorosilane⁷ and trimethylchlorosilane in a mixture of ether and water. Attempts to equilibrate 1,3-diallyltetramethylsiloxane with hexamethylsiloxane using an acidic catalyst failed to give allylpentamethylsiloxane.⁸ In fact, the allyl group was cleaved yielding propylene. The allyl-silicon bond is also cleaved by alkali.⁹

Experimental

Preparation of Allylsilanes.—Allyltriethoxysilane¹⁰ was prepared by the reaction of allyltrichlorosilane with absolute ethanol using quinoline as a hydrogen chloride acceptor. Allyltrimethylsilane and diallyldimethylsilane were prepared by reaction of methyl magnesium bromide with allyltrichlorosilane and diallyldichlorosilane, respectively.

Allylpentamethylsiloxane and 1,3-diallyltetramethylsiloxane were prepared by co-hydrolysis of allyldimethylchlorosilane⁷ and trimethylchlorosilane in a 1:3 molar ratio using an ether-water mixture. The physical properties of these new compounds are given in Table I.

Cleavage of the Allyl-Silicon Bond.—Attempts to equilibrate hexamethylsiloxane and 1,3-diallyltetramethylsiloxane at room temperature using concentrated sulfuric acid as the catalyst⁸ resulted in the formation of propylene. No allylpentamethylsiloxane was isolated.

Attempts to form the sodium salt of allyl siliconic acid by the reaction of aqueous sodium hydroxide and allyltrichlorosilane (molar ratio of 4:1) at room temperature resulted in the formation of propylene⁹ (identified by its mass spectrum).

Addition Reaction of Mercaptans and Olefinic Silanes.—The addition products are prepared by shaking the desired olefin and excess mercaptan together until the solution becomes warm. This reaction is exothermic. Generally, the olefin and mercaptan are insoluble, but as the reaction proceeds the solution becomes homogeneous. When necessary, a small amount of benzoyl peroxide may be added to initiate the reaction. The products are recovered by distillation. The new compounds and their physical properties are given in Table I. In those cases where thioglycolic acid is used, it is possible to use either 75% aqueous thioglycolic acid or freshly distilled 100% thioglycolic acid.

As a typical example, the preparation of 3-thia-7,7-dimethyl-7-silaoctanoic acid is given. A mixture of 10 g. of allyltrimethylsilane and 15 g. of 98% thioglycolic acid¹¹ is placed in a bottle and shaken until a one-phase system results, which generally requires five to ten minutes. The reaction is exothermic. The reaction product is washed with water to remove the excess thioglycolic acid, and upon distillation 9.8 g. of 3-thia-7,7-dimethyl-7-silaoctanoic acid is obtained. Analytical and physical data for this compound are shown in Table I.

Compound XII was prepared by saponification of X

TABLE I (Continued)

n_D^{20}	d_4^{20}	M_{RD}^c		Calcd.			Analyses, %						Neut. or sapon. eq.		Yield, %				
		Calcd.	Found	C	H	S	Found			Calcd.	Found								
1.4073	0.9030	55.03	55.7	52.90	9.87		51.9	51.9	52.4	9.2	9.6	9.2			..				
1.4069	.7125	39.06	39.5	63.08	12.35		62.5	62.3		12.6	12.3				..				
1.4409	.7651	47.71	48.4	68.50	11.50		68.4	67.7	68.1	11.6	11.5	11.3			58				
1.4061	.7948	57.79	58.2	51.01	10.69		51.0	50.6	51.0	10.4	10.6				..				
1.4280	.8208	66.52	67.3	56.02	10.35		56.4	56.3		10.3	10.4				..				
1.4811	1.0139	53.45	53.9			16.67							16.60	16.69	N, 192.3	193	193	25	
1.4790	1.0009	59.33	58.5			15.54							15.59	15.62	N, 206	200		54	
1.4588	0.9902	77.79	77.4			11.43							11.28	11.32	N, 280.5	282		46	
1.4479	1.0301	83.60	84.3			9.88							9.81	9.86	S, 324.5	308	306	48	
1.4630	0.9493	67.62	68.0	51.24	9.46	13.66	51.3	51.1		9.3	9.5		13.57	13.61	S, 234.4	230	229	63	
1.5267	0.9408	76.34	77.8			13.45							13.46	13.40				18	
				60.97	8.53		61.4	60.7	60.8	8.3	8.2	7.8							..
						18.29							18.7	18.6					..
						15.10							16.2	16.3					..

^a Allyltriethoxysilane was previously reported by Andrianov, see ref. 10, however the above values for n_D^{20} and d_4^{20} differ somewhat from those previously reported. ^b Allyltrimethylsilane was reported recently, ref. 9. ^c M_{RD} values calculated by the method of Sauer, THIS JOURNAL, 68, 954 (1946). ^d The olefin is noted by compound number. ^e Trimethylvinylsilane. ^f Thioglycolic acid. ^g Ethyl thioglycolate. ^h *p*-Thiocresol. ⁱ Ethylene bis-thioglycolate

(6) Larsson, *Trans. Chalmers Univ. Technol.*, Gothenberg, Sweden, No. 79, 13 (1948); *ibid.*, No. 79, 17 (1948); *Svensk Kem. Tid.*, 60, 178 (1948).

(7) Hurd, THIS JOURNAL, 67, 1813 (1945).

(8) Patnode and Wilcock, *ibid.*, 68, 361 (1946).

(9) Sommer, Tyler and Whitmore [*ibid.*, 70, 2872 (1948)] recently reported the acid and alkali cleavage of the allyl-silicon bond in allyltrimethylsilane.

(10) Allyltriethoxysilane was previously reported by Andrianov, *et al.*, *J. Gen. Chem. (U. S. S. R.)*, 3, 558 (1938); *Elektrichestvo*, [4] 39 (1946).

followed by the customary reaction with thionyl chloride and *p*-toluidine.¹²

A sulfuric acid equilibration of VIII with a polydimethylsiloxane⁸ oil gave sulfur-containing acids.

Anal. Calcd.: S (from original mixture), 1.04. Found: S, 1.05, 1.00.

(11) The 98% thioglycolic acid is prepared by a vacuum distillation of the commercially available 75% aqueous solution.

(12) Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1940, p. 132.

Reaction of Diallylsilanes and Polymercaptans.—Compounds XIII and XIV, which are viscous oils, were prepared by reaction of ethylene bis-thioglycolate with diallyldimethylsilane and 1,3-diallyltetramethyldisiloxane, respectively.

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Summary

1. The addition reaction of mercaptans to alkenyl silanes has been studied.

2. Thio ethers, thia acids and thia esters have been prepared by the reaction of mercaptans, thioglycolic acid and its esters with alkenyl silanes.

3. Dimercaptans and dialkenylsilanes react to form viscous oils.

4. The presence of sulfur in the delta position with respect to the silicon does not appear to affect the stability of the carbon-silicon bond toward acids or bases.

5. Diallyldimethylsilane, allylpentamethyldisiloxane and 1,3-diallyltetramethyldisiloxane have been prepared and characterized.

SCHENECTADY 5, N. Y.

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[FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Gaseous Detonations. I. Stationary Waves in Hydrogen-Oxygen Mixtures¹

BY DONALD J. BERETS, EDWARD F. GREENE AND G. B. KISTIAKOWSKY

The existence of gaseous detonation waves was recognized nearly seventy years ago and since then a great deal of experimental and theoretical work has been done on this subject. The phenomena involved in their initiation appear to be extremely complicated according to experimental evidence and they have not received much theoretical attention. On the other hand, a successful theory of stationary detonation waves does exist, which treats them from a hydrothermodynamic point of view, disregarding finer kinetic and chemical details. This so-called Chapman-Jouguet^{1a} theory interprets detonation waves as shock waves in which the continuing degradation of shock energy into heat is balanced by the release of energy by the spontaneous chemical reactions of the explosive substance. Detonation waves, therefore, can possess stationary character. Specifically, the theory assumes that the chemical reactions reach the state of chemical equilibrium. The energy set free in the spontaneous reaction is quantitatively utilized for the propagation of the shock wave in accordance with the Rankine-Hugoniot equations.²

Analyzing the implications of this theory from the point of view of finite chemical reaction rates, v. Neumann³ showed that the front of a detonation wave must be a mechanical shock in the unreacted material. Chemical reactions are initiated by the compression and heating due to the shock. There follows in the wave a layer of incompletely reacted material in which, normally, pressure drops and temperature rises. This layer

has a stationary pressure profile even though energy is constantly drained from it, because of the energy evolution in the chemical reaction. With the completion of the reaction the stationary profile of the wave ends because the supply of useful energy is exhausted. What follows is a rarefaction wave, whose pressure profile changes with time as the wave progresses through the medium. To maintain a stationary character of the detonation wave, the rarefaction must not be able to overtake it. This defines the value of the detonation velocity as the sum of the acoustic and material ("particle") velocities in the plane in which the reaction is completed. This plane will be called the Chapman-Jouguet plane. The theory does not forbid further chemical changes to take place in the rarefaction wave, following pressure and temperature changes, but their occurrence has no effect on the detonation wave because, looked at from this region, the detonation front propagates with supersonic velocity.

A critical experimental test of the quantitative applicability of the Chapman-Jouguet theory was carried out by Lewis and Friauf.⁴ They compared its predictions with the experimentally determined detonation velocities in hydrogen-oxygen mixtures, to some of which nitrogen, helium or argon were added. The theory agreed quite well with experiments for mixtures in which hydrogen and oxygen concentrations were not too low provided it was assumed that in the Chapman-Jouguet plane the reaction reached the state of thermodynamic equilibrium, rather than completion. The "complete reaction" of v. Neumann must therefore be interpreted as equilibrium. This is not surprising because no net work can be gained from subsequent chemical changes, accompanying pressure and tempera-

(1) The research reported in this document was made possible by funds extended Harvard University under O. N. R. Contract N5ori-76 T. O. XIX NR-053-094.

(1a) Chapman, *Phil. Mag.*, **47**, 90 (1899); Jouguet, *J. de math.*, **347** (1905); **6**, (1906).

(2) Rankine, *Phil. Trans.*, **180**, 277 (1870); Hugoniot, *J. l'ecole polytech.*, **57**, 3 (1887); **58**, 1 (1889).

(3) v. Neumann, O. S. R. D. Report No. 549 (1942).

(4) Lewis and Friauf, *THIS JOURNAL*, **52**, 3905 (1930); references there to earlier calculations.