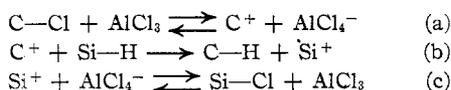


num chloride,<sup>8</sup> with aqueous and alcoholic bases,<sup>7</sup> and with lithium amide in ammonia,<sup>8</sup> offer evidence that the silicon-hydrogen bond readily undergoes fission to give a hydride ion (H<sup>-</sup>)<sup>10</sup>. These data indicate that hydrogen-halogen exchange of Type I proceeds by the following mechanism



In (a) the electrophilic aluminum chloride, which is known to ionize the carbon-halogen bond catalytically,<sup>9</sup> gives a carbonium ion. This electronically deficient fragment must stabilize itself by attracting an electron pair. While this ordinarily occurs intramolecularly,<sup>11</sup> or by union with an anion such as Cl<sup>-</sup>, in this case the carbonium ion first formed or a rearranged carbonium ion stabilizes itself by attack on the Si-H bond, taking the electron pair with the attached H as in (b). Probably simultaneously, step (c) occurs with formation of the silicon-chlorine bond and regeneration of the catalyst. In the present study, the *n*-hexane obtained from *n*-hexyl chloride may have been formed by step (b) from a *n*-hexyl or *s*-hexyl carbonium ion. The isopentane and 2,3-dimethylbutane obtained from neopentyl chloride and 1-chloro-3,3-dimethylbutane, respectively, resulted from rearranged carbonium ions formed in the usual way.<sup>11</sup>

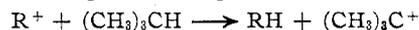
A similar mechanism is involved in the hydrogen-halogen exchange of alkyl halides and isoparaffins in the presence of aluminum halides.<sup>12</sup> The

(10) Cf. Meals, *THIS JOURNAL*, **68**, 1880 (1946).

(11) Cf. Whitmore, (a) *ibid.*, **54**, 3274 (1932); (b) *Ind. Eng. Chem.*, **26**, 94 (1934).

(12) (a) Barlett, Condon and Schneider, *THIS JOURNAL*, **66**, 1531 (1944); (b) Schmerling, *ibid.*, **67**, 1778 (1945).

same type of transfer of an electron pair with the attached H occurs in ordinary alkylation reactions,<sup>13</sup> involving such a step as



Other cases of the formation of a saturated hydrocarbon by rearrangement reported in the literature are the occurrence of small amounts of neopentane in the hydrogenation of trimethylethylene in a silent electric discharge<sup>14</sup> and of 2,3-dimethylbutane in the action of neopentylcarbinyl chloride with a large excess of isobutane and aluminum chloride under thirty atmospheres pressure.<sup>12b</sup>

**Acknowledgment.**—We thank Dr. T. J. Brice for the fractional distillation of the isopentane.

### Summary

1. Hydrogen-halogen exchange reactions of triethylsilane with three aliphatic chlorides in the presence of aluminum chloride are reported.

2. *n*-Hexyl chloride gave *n*-hexane; neopentyl chloride and neopentylcarbinyl chloride gave the rearrangement products, isopentane and 2,3-dimethylbutane, respectively.

3. A mechanism for exchange of silicon-hydrogen with carbon-chlorine in the presence of aluminum chloride is proposed.

4. Reaction of triethylsilane with diethyldichlorosilane in the presence of aluminum chloride gave two new compounds, diethylsilane and diethylchlorosilane. This apparently provides a good preparation for compounds of the type R<sub>2</sub>SiH<sub>2</sub> and R<sub>2</sub>SiHCl, in which R is an organic group.

(13) Ciapetta, *Ind. Eng. Chem.*, **37**, 1210 (1945).

(14) Meneghini and Sargato, *Gazz. chim. ital.*, **62**, 621 (1932).

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RECEIVED MARCH 18, 1947

[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY<sup>1</sup>]

## Preparation of Substituted Acetoxy Silanes

BY H. A. SCHUYTEN, J. W. WEAVER AND J. DAVID REID

### Introduction

The use of alkyl chlorosilanes, such as dimethyldichlorosilane, to impart water repellency to cotton textiles has been patented.<sup>1a</sup> Unfortunately, the hydrogen chloride produced during the reaction of the silane with adsorbed moisture or cellulosic hydroxyls may seriously weaken the cloth unless elaborate and efficient equipment is employed to avoid this difficulty.

With the object of preventing acid degradation, the writers prepared a number of short chain substituted acetoxy silanes for application to cloth in

place of the chlorosilanes. The present paper describes the preparation and properties of a number of these acetoxy silanes.

During the preparation of this paper, a patent was issued to Barry,<sup>2</sup> describing the use of alkyl and alkoxy acetoxy silanes with aliphatic chains containing at least eight carbon atoms as good water-repellent agents.

Silicon tetraacetate was first prepared in 1867 by Friedel and Ladenburg<sup>3</sup> by the reaction of silicon tetrachloride with acetic anhydride. More recently the same compound was obtained in low yields by Volnov<sup>4</sup> through the action of organic

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(1a) W. I. Patnode, U. S. Patent 2,306,222, December 22, 1942.

(2) A. J. Barry, U. S. Patent 2,405,988, August 20, 1946.

(3) C. Friedel and A. Ladenburg, *Ann.*, **145**, 174 (1867).

(4) J. N. Volnov, *J. Gen. Chem. U. S. S. R.*, **9**, 2269 (1939).

TABLE I  
 SUBSTITUTED ACETOXY SILANES

Compound	Diluent	Yield, %	B. p., °C.		$d_{25}^4$	Formula	Silicon, %		Neut. equiv.	
			Mm.				Calcd.	Found	Calcd.	Found
Silicon tetraacetate	Benzene	51.0	...	...	...	$C_8H_{12}O_8Si$	...	...	66.06	66.66
Methyltriacetoxysilane <sup>b</sup>	Ether	.. <sup>c</sup>	94-95	9	1.1677	$C_7H_{10}O_6Si$	12.74	12.34	73.41	73.02
Methylacetoxysilane <sup>b</sup>	30-60° pet. ether	58.6	83-84	45	1.0761	$C_6H_{10}O_4Si$	17.30	...	81.10	81.10
Dimethyldiacetoxysilane <sup>b</sup>	Ether	40.5	44-45	3	1.0485	$C_6H_{12}O_4Si$	15.74	15.78	89.11	89.73
Trimethylacetoxysilane	Ether	64.3	30-31	35	0.8961	$C_6H_{12}O_4Si$	21.22	19.93	132.2	134.1
Ethyltriacetoxysilane <sup>b</sup>	30-60° pet. ether	57.0	97-99	4	1.1426	$C_8H_{14}O_6Si$	11.98	11.79	78.08	77.64
Diethyldiacetoxysilane <sup>b</sup>	70-110° pet. ether	37.0	70-72	4	1.0190	$C_8H_{16}O_4Si$	13.74	13.47	102.1	103.7
Isopropyltriacetoxysilane <sup>b</sup>	30-60° pet. ether	35.8	91-92	3	1.1104	$C_9H_{16}O_6Si$	11.30	11.73	82.76	84.21
Tri-(isoamyloxy)-acetoxysilane <sup>b</sup>	Ether	40.5	124-127	1	0.9252	$C_{17}H_{36}O_4Si$	8.05	7.31	348.5	362.0

<sup>a</sup> Melting point 110° (uncor.). <sup>b</sup> New compounds. <sup>c</sup> Prepared from mixed methylchlorosilanes. <sup>d</sup> Decomposed on standing.

acetates on silicon tetrachloride. Triethylacetoxysilane has been prepared through the action of acetic anhydride on triethylethoxysilane<sup>5</sup> and trimethylacetoxysilane<sup>6</sup> by a similar reaction on trimethyl-2-chloroethoxysilane. This reaction with ethyl orthosilicate resulted in the formation of triethoxyacetoxysilane.<sup>7</sup> The latter reaction has also been studied in some detail by Post and Hofrichter<sup>8</sup> in their studies of the acetylation of silico orthoesters. These workers obtained mixtures of various ethoxyacetoxysilanes. Rauter<sup>9</sup> obtained acetyl chloride by the reaction of potassium acetate with silicon tetrachloride at 180°, while Montonna<sup>10</sup> obtained acetic anhydride in 50% yields in a similar reaction. Barry<sup>2</sup> describes the formation of various long chain acetoxysilanes by the reaction of substituted chlorosilanes with sodium acetate at temperatures of 60 to 120° and times up to twenty hours. Yields are not given.

Since silicon tetraacetate may be considered a mixed anhydride of acetic and orthosilicic acids, the use of the classical method for the preparation of mixed anhydrides appears logical. This method involves the reaction of a chloride of one acid with an anhydrous salt of another in a suitable solvent. Alkyl chlorosilanes and alkoxychlorosilanes may be considered acid chlorides, and the same method should apply.

This is verified by the reaction of silicon tetrachloride and anhydrous sodium acetate in anhydrous medium to produce the expected mixed anhydride, and by the reaction of the alkyl and alkoxy chlorosilanes to form the corresponding alkyl and alkoxy acetoxy silanes. The sodium chloride by-product remains insoluble in the anhydrous solvent.

Although yields are in the neighborhood of only 50%, which nevertheless compares favorably with yields of Volnov and Post and Hofrichter by other methods, the sodium acetate method has the advantage of being direct and easy of manipu-

lation, and the products obtained have a fair degree of purity. The decomposition of silicon tetraacetate with heat into silicon dioxide and acetic anhydride<sup>3</sup> very probably accounts in major part for the low yields in the preparation of acetoxysilanes, and explains the formation of acetic anhydride by Montonna.<sup>10</sup> Excess silicon tetrachloride and the high temperature of reaction (180°) would yield acetyl chloride as obtained by Rauter.<sup>9</sup>

### Experimental

**Apparatus.**—A 500-ml. gas washing bottle fitted with a 60-mm. coarse fritted glass disk near the bottom and a side arm connected below the disk (Pyrex 31750) was used as a reaction vessel. This was fitted with a mercury sealed stirrer and a reflux condenser equipped with a dropping funnel and an outlet protected with calcium chloride tubes. Thus it was possible to carry out the reaction and to filter the product without contact with moist atmosphere.

**Materials.**—Mixed methylchlorosilanes were prepared by the method of Rochow and Gilliam.<sup>11</sup> No separation was made on the starting material. The final products, the mixed acetoxysilanes, were separated by distillation under reduced pressure. Dimethyldichlorosilane and trimethylchlorosilane were obtained from General Electric Corporation, Schenectady, New York. Tri-(isoamyloxy)-chlorosilane was prepared by the method of Kalinin.<sup>12</sup> Ethyltrichlorosilane and diethyldichlorosilane were obtained from Eastman Kodak Company. Isopropyltrichlorosilane was prepared by the reaction of isopropylmagnesium iodide on silicon tetrachloride.

**Analyses.**—Silicon was determined<sup>13</sup> by decomposition of the sample in a Parr peroxide bomb, followed by the usual gravimetric procedure.

Neutral equivalents were determined by hydrolysis in standard base and back titration with standard acid. The time of hydrolysis depended on substitution. Silicon tetraacetate, the longest, required half an hour at 60°.

**Procedure.**—In each case approximately one-fourth mole of the silane, dissolved in 50 ml. of the diluent, was added dropwise to a slurry of twice the calculated amount of anhydrous sodium acetate in 200 ml. of diluent, contained in the reaction vessel. The rate of addition was so controlled that gentle refluxing was maintained. The reaction proceeded smoothly and exothermically. Stirring was continued for one hour after addition was complete. The solution was removed by suction and the sodium chloride-sodium acetate residue was washed twice with fresh diluent. The combined solution and washings were stripped and the residue was distilled through a 12-

(5) A. Ladenburg, *Ber.*, **5**, 319 (1872); *Ann.*, **164**, 300 (1872).

(6) R. O. Sauer and W. Patnode, *THIS JOURNAL*, **67**, 1548 (1945).

(7) C. Friedel and J. M. Crafts, *Am. J. Sci. Arts*, [2] **43**, 331 (1867).

(8) H. W. Post and C. H. Hofrichter, Jr., *J. Org. Chem.*, **5**, 443 (1940).

(9) G. Rauter, *Ann.*, **270**, 235 (1892).

(10) R. E. Montonna, *THIS JOURNAL*, **49**, 2114 (1927).

(11) E. G. Rochow and W. F. Gilliam, U. S. Patent 2,383,818, August 28, 1945.

(12) M. N. Kalinin, *Compt. rend. acad. sci. U. R. S. S.*, **26**, 365 (1940).

(13) We are indebted to Mr. Julian F. Jurgens of the Analytical Section for silicon determinations.

inch Vigreux column. Since distillation at normal pressure gave decomposition in some cases, reduced pressure was used. Results are summarized in Table I.

### Summary

1. Silicon tetraacetate and substituted acetoxysilanes have been prepared from the corre-

sponding chlorides and anhydrous sodium acetate in an anhydrous solvent.

2. The physical properties of some substituted acetoxysilanes are recorded.

3. Seven of the compounds reported are new.

NEW ORLEANS, LA.

RECEIVED APRIL 7, 1947

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

## The Synthesis of Amino-substituted Phosphonic Acids. I

BY GENNADY M. KOSOLAPOFF

The purpose of this paper is to present the general synthetic schemes which have been used in this Laboratory over the course of several years for the syntheses of typical representatives of amino-substituted phosphonic acids.

The amino-aromatic phosphonic acids have been prepared either by reduction of the corresponding nitro derivatives by means of tin and hydrochloric acid<sup>1</sup> in poor yields or by the ammonolysis of the corresponding chloro derivatives in satisfactory yields.<sup>2</sup> Since the nitro derivatives are more readily available in some cases than are the chloro derivatives, we investigated the former reaction scheme and found that good yields of the amino-acids can be obtained when the reduction is effected by sodium sulfide solutions.

In the case of aliphatic or aralkyl acids having the amino-group on the aliphatic portion of the molecule, there are several general synthetic methods which have to be selected according to the type of amino-phosphonic acid desired. In the case of an  $\omega$ -amino derivative there is the choice between the ammonolysis of the  $\omega$ -halo derivative or the coupling of the  $\omega$ -halo derivative with potassium phthalimide, following by the removal of the phthalic acid portion by hydrolysis. The latter reaction is the more desirable one because of the lack of side-reactions. Furthermore, in a number of instances, the reaction may be advantageously inverted, *i. e.*,  $N$ - $\omega$ -haloalkylphthalimides may be reacted with trialkyl phosphites and the products hydrolyzed to the desired  $\omega$ -aminoalkanephosphonic acids.

If the amino group is desired on the same carbon atom as the phosphono group, the choice lies between: (a) the ammonolysis of an  $\alpha$ -halophosphonic acid, obtainable either by the addition of phosphorus trichloride to the appropriate aldehyde or ketone or by reduction of an appropriate  $\alpha$ -keto derivative to the hydroxy derivative, followed by conversion of the hydroxy group to a halo-substituent, and (b) the reduction of a variety of nitrogen derivatives of  $\alpha$ -keto-phosphonic acids. The choice between the various possibilities is conditioned primarily by the availability of the necessary intermediates.

There are two additional preparatory methods for amino-phosphonic acids which, however, appear to be rather limited in scope. The conversion of dichlorosphosphites of methylolamides into the corresponding dichlorides of acylated aminomethanephosphonic acid<sup>3</sup> is limited to the aminomethane acid. The other is the Hofmann degradation of the C-amide of the appropriate phosphonocarboxylic acid, which method was used by Finkelstein<sup>4</sup> to prepare  $\beta$ -aminoethanephosphonic acid. This procedure gives satisfactory results with the simpler members of the class but may be limited in the application to derivatives sensitive under the conditions of the Hofmann reaction.

The typical procedures are presented in the experimental part.

### Experimental

#### I. Amino-aromatic Phosphonic Acids

**A. Phosphanilic Acid.**—The method used by Bauer<sup>2</sup> needs only the comment that for the preparation of larger amounts of the product, the use of a hydrogenation apparatus of 2-3 liter capacity is to be preferred over the use of sealed tubes.

**B. *p*-Aminobenzylphosphonic Acid.**—*p*-Nitrobenzylphosphonic acid<sup>5</sup> (20 g.) was suspended in 75 cc. of water and was brought into solution by the addition of dilute sodium hydroxide solution to pH 9. This solution was treated with 42 g. of sodium sulfide nonahydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) in 100 cc. of water and was heated for one hour to 90-95°. The cooled solution was carefully acidified by hydrochloric acid, evaporated to dryness and the precipitate extracted with 50 cc. of concentrated hydrochloric acid. The acid filtrate was diluted to 80 cc. and treated with 25% sodium hydroxide until just acid to congo red. The *p*-aminobenzylphosphonic acid was filtered off upon cooling; yield was 65%. The acid is a pale yellow powder, which melts with decomposition at 323-325°, and is amphoterically soluble.

*Anal.* Calcd.: N, 7.4. Found: N, 7.29, 7.56.

#### II. Aminoaliphatic Phosphonic Acids

**A. 2-Aminoethane Phosphonic Acid.**— $\beta$ -Bromoethylphthalimide (39 g.) and triethyl phosphite (26 g.) were heated to 160° for four and one-half hours in an apparatus described earlier<sup>6</sup>; approximately 80% of the theoretical amount of ethyl bromide was collected in the receiver. The residual oil was shaken out with 25 cc. of hexane and was treated with 150 cc. of 48% hydrobromic acid. The mixture was refluxed for five hours and cooled. The

(3) J. Fikl, U. S. Patents 2,304,156 and 2,328,358.

(4) Finkelstein, *THIS JOURNAL*, **68**, 2397 (1946).

(5) Litthauer, *Ber.*, **22**, 2144 (1889).

(6) Kosolapoff, *THIS JOURNAL*, **66**, 109 (1944).

(1) Michaelis and Benzinger, *Ann.*, **188**, 275 (1877).

(2) Bauer, *THIS JOURNAL*, **63**, 2137 (1941).