The physical properties of these salts have been investigated and microphotographs taken which depict a wholly different crystalline form for each one. The fact that the salts crystallized easily from hot alcohol enabled us to prepare them in very pure condition.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

ALKYL ORTHOSILICATES[1]

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Though ethyl orthosilicate was discovered as long ago as 1846 by Ebelmen,[3] it has not been extensively studied. Khotinsky and Seregenkoff[4] found that one and only one of its ethoxy groups is exchanged for the radical of the Grignard reagent. It seemed desirable to learn more about the preparation and reactions of alkyl orthosilicates.

Results

The method of preparing ethyl orthosilicate has been improved, the yield being brought up to 70%. New esters were made from *n*-butyl, *n*-amyl, *n*-heptyl, *n*-octyl and *β*-chloro-ethyl alcohols, though the last two were impossible to purify as they are liquids which could not be distilled Attempts to obtain orthosilicates from secondary alcohols proved unsuccessful, the reaction taking another course. With mercaptan silicon tetrachloride reacts only partially, even when heated to 200° for twenty hours.

It has long been known that ethyl orthosilicate ethylates water and acetic acid. It has been found to yield diethyl phthalate with phthalic anhydride, according to this equation:

$$C_6H_4(CO)_2O + (C_2H_5O)_4Si \longrightarrow C_6H_4(CO_2C_2H_5)_2 + (C_2H_5O)_2SiO$$

Similarly ethyl acetate is obtained with acetanhydride. With sulfuric acid, diethyl sulfate is formed. Benzoic acid reacts with it very sluggishly but ethyl benzoate is formed. *p*-Nitrobenzoic acid could not be made to react. It could not be made to react with phenol, *β*-naphthol or thiophenyl. In the presence of aluminum chloride benzene is ethylated by it even up to hexa-ethylbenzene.

When ethyl, or methyl, orthosilicate reacts with water or acetic acid under the proper conditions, the silicic acid produced separates as a gel. This is of interest since it does not contain electrolytes which are so difficult

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[1] In memory of Ira Remsen.

[2] From the Ph.D. dissertation of A. W. Dearing, 1927.

[3] Ebelmen, *Ann.*, **57**, 334 (1846).

[4] Khotinsky and Seregenkoff, *Ber.*, **41**, 2948 (1908).

to wash out of the gel from sodium silicate. The silica obtained from methyl orthosilicate is 50% of the weight of the ester. The shrinkage of the gel prepared from this or the ethyl ester is only a fraction of that of the gel precipitated in the usual way from sodium silicate. This suggested the possibility of obtaining disks of silica gel which might be used for osmotic pressure measurements. Disks were obtained, best by the action of moist air on the ester, but none perfect enough for the desired purpose. In parallel experiments in which a mixture of the vapors of acetic acid and ethyl alcohol was passed over silica gel at 180°, the gel from ethyl orthosilicate proved to be decidedly more active than a carefully prepared specimen of the gel from sodium silicate. More recently, gel purified by Patrick by boiling with nitric acid has appeared to be about as active as our gel. As the gel from the alkyl orthosilicates can be made in benzene solution by the action of the calculated amount of water or acetic acid, a product is obtained the surface of which has never been wet by water. It was thought that such a gel might show different absorptive power from that precipitated in water solution. This did not prove to be the case.

Experimental

The difficulty in the preparation of alkyl orthosilicates is that four molecules of hydrogen chloride are eliminated for each molecule of silicon tetrachloride that reacts. The large evolution of gas causes a considerable loss of the volatile reactants. The method which proved to be best is to add the silicon tetrachloride, which must be free from higher boiling compounds, dropwise to the alcohol cooled in a freezing mixture. The alcohol must be perfectly anhydrous and is used in about 10% excess to insure the reaction of all of the chlorine. The escaping hydrogen chloride is led through a small amount of cold alcohol to recover the silicon tetrachloride that is carried off. After the reaction is judged to be complete, dry air is drawn through the product for several hours to rid it of hydrogen chloride. The ester is then fractionated in a vacuum with the careful exclusion of moisture. To avoid decomposition the esters of the higher alcohols must be distilled at very low pressures.

Ethyl orthosilicate was obtained in 70% yield. It boils at 165–167° at 760 mm. The properties of the new esters are given in tabular form.

TABLE I

ESTERS OF ORTHOSILICIC ACID

Alkyl	B. p., °C.	Press., mm.	Density 0°/4°	Density 25°/4°	Silicon, % Calcd.	Silicon, % Found	
n-Butyl	160–5	20	0.9353	0.9194	8.82	8.75	8.63
n-Amyl	145–50	3	.9117	.8933	7.53	7.45	7.49
n-Heptyl	200–15	3	.9097	.8958	5.79	5.99	6.03
n-Octyl	240	3	...	...	5.19	5.23	5.09

Phenylethyl alcohol reacted as was expected but the product could not be purified, as it decomposed when distillation was attempted even with a good vacuum. It was heated at 90° in a vacuum for some hours, which eliminated most of the excess of the alcohol but even then it was only about 88% pure, as analysis for silicon showed 4.88 and 4.84% instead of the calculated 5.53. Its density is about 1.09.

Silicon tetrachloride was added to four equivalents of anhydrous ethylene chlorohydrin. Reaction took place as usual. As the products could not be distilled, it was purified by heating in a vacuum for some hours, which gave a product which analysis showed to be 94% pure.

This product was refluxed for several hours with an excess of aniline hydrochloride and a white amorphous material was obtained. This resembled silicic acid in appearance but is soluble in alcohol and ether. It could not be recrystallized and hence little weight can be attached to the analysis for silicon, which corresponded to the formula $(C_6H_5NHC_2H_4)_4Si$. Very similar products were obtained with dimethylaniline and pyridine.

Silicon tetrachloride reacts vigorously with *iso*propyl alcohol but converts it to propylene and *iso*propyl chloride. With mercaptan it gave no reaction under the usual conditions. A mixture of mercaptan and silicon tetrachloride was heated at 200° in a sealed tube for twenty hours. The evaporation of the reactants left a small amount of liquid boiling at 125° but this still contained chlorine, which shows that the replacement takes place very slowly.

Ethyl orthosilicate was heated with one molecule of phthalic anhydride for eight hours at 160°. The ethyl phthalate formed was separated by fractionation *in vacuo* and identified by boiling point, density and saponification number. A similar experiment was tried with acetanhydride and ethyl acetate identified.

To a mixture of benzene and ethyl orthosilicate, aluminum chloride was added. A reaction took place at once. The mixture was heated for several hours, poured onto ice and extracted with ether. Hexa-ethylbenzene was identified by its melting point. The intermediate ethylated benzenes were present but not in sufficient amounts for separation.

Silica Gel from Ethyl Orthosilicate.—A shallow layer of the ester reacts with water vapor and finally sets to a gel, but more uniform results are obtained by adding the calculated amount of water to the ester diluted with 1.5 times its volume of alcohol. If too much alcohol is used the gel does not set properly.

A non-aqueous gel was prepared by refluxing a mixture of four parts of acetic acid to one of the ester for an hour and allowing it to stand overnight. The excess of acetic acid was gotten rid of by soaking the gel in dry benzene, which was poured off and replaced by fresh benzene every day for four days. The gel was then dried in a vacuum and the soaking and drying repeated every three or four days for three weeks. The gel prepared in this manner was excellent in appearance and proved to be an excellent catalyst for vapor phase esterification, but its absorption from water solution was practically identical with that of the regular gel.

A variation of this method was to dissolve the ester and the required amount of acetic acid in dry benzene and boil until gel formation took place on cooling. Usually about eight hours' boiling was required. The gel formation seems to take place rather suddenly after long heating. In one experiment the mixture was boiled for seven and three-fourths hours and gave no appearance of gel formation on cooling. Further heating for fifteen minutes caused it to become viscous and to set to a stiff gel on cooling. This gel was purified as described above and had the same properties.

Acids higher up in the acetic acid series were used for preparing the gel but these acids did not give as good a product. In one case paraffin wax was dissolved in the benzene with the idea that it might coat the gel and diminish its affinity for water.

In whatever way the gel was prepared it acted the same when put into water and showed the same absorption as the regular silica gel.

Esterification experiments similar to those of Milligan and Reid[5] were run to compare the special gel obtained as described above with the regular silica gel. The whole aim was to get comparative results. The sample of gel was contained in a tube surrounded by the vapor of boiling cyclohexanol. A mixture of equivalent amounts of absolute ethyl alcohol and acetic acid was dropped at the desired rate from a calibrated capillary tip into a bulb which served as a vaporizing chamber from which it passed into the catalyst tube. The products were condensed, weighed and titrated immediately. The results are given in the table below.

TABLE II

PERCENTAGE ESTERIFICATION OVER REGULAR AND SPECIAL SILICA GEL

Time of contact, sec.	Regular gel	Special gel	Time of contact, sec.	Regular gel	Special gel
11.3	20.5	29	26.4	34	46.5
11.3	28	29.5	26.4	35	49
11.3	29	29	123	49.5	82.5
11.3	29	30	123	50	78.5
26.4	43	47	123	53	89
26.4	33	46.5			

There are considerable irregularities in the results but the special gel shows decidedly greater activity at the slower rates.

Summary

The preparation of ethyl orthosilicate has been improved and a number of new orthosilicate esters have been prepared. The reactions of ethyl

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[5] Milligan, Chappell and Reid, *J. Phys. Chem.*, **38**, 872 (1924).

orthosilicate have been investigated. It has been used to prepare silica gel free from strong electrolytes and some of the properties of such gel have been studied.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME 1,2-DIALKYL CYCLOPENTANE DERIVATIVES[1,2]

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As cyclic hydrocarbons are found in some petroleums it is important to know more of the chemistry of this class. The derivatives of cyclopentane have not been extensively studied; it seemed desirable to synthesize more of them so as to extend our knowledge of the properties of the members of this group. The particular line chosen was the 1,2-dialkyl cyclopentanes. The reaction chosen for the preparation of these hydrocarbons led quite unexpectedly to the formation of the corresponding unsaturated hydrocarbons. Due to the expiration of the grant, time was not available for the reduction of the latter to the saturated derivatives, and it was deemed best to publish the results obtained.

The necessary intermediate for the study was α-ethyl-cyclopentanone. This compound is supposed to have been obtained by Best and Thorpe[5] by the hydrolysis of 2-cyano-2-methyl-cyclopentane-one-1. They described it as boiling at 149° at 756 mm. and gave the melting point of its semicarbazone as 177°. This compound prepared by our method boils at 160–161° (755 mm.) corr. and its semicarbazone melts at 189° corr. We started with ethyl adipate (I), which was made to undergo an internal acetoacetic ester condensation to form the ethyl ester of α-carbethoxy-cyclopentanone (II). The sodium compound of this[6] reacted with ethyl iodide to give the ethyl derivative (III), which by the ketone splitting left α-ethyl-cyclopentanone (IV). By the Grignard reaction this ketone was converted to the tertiary alcohol (V). This was transformed into the iodide. It was intended to remove the iodine by reduction to obtain the 1,2-alkyl-ethyl-cyclo-pentane (VI). When this was attempted an unsaturated hydrocarbon was obtained.

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[1] In memory of Ira Remsen.

[2] This paper presents the results of an investigation of cyclopentane derivatives listed as Project 15 of the American Petroleum Institute. Financial assistance has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Co. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[3] American Petroleum Institute Research Fellow.

[4] Director, American Petroleum Institute Research Project 15.

[5] Best and Thorpe, *J. Chem. Soc.*, **95**, 713 (1909).

[6] Rysselberge, *Bull. sci. acad. roy. Belg.*, [5] **12**, 171 (1926).