[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO]

STUDIES IN SILICO-ORGANIC COMPOUNDS. IV.

THE ACTION OF ORGANIC ACID HALIDES AND OF HYDROHALOGEN ACIDS ON SILICO-ORTHOESTERS[1]

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It was the primary purpose of this investigation to study the action of organic acid halides on silico-orthoesters. Interest in this problem was first aroused when it was discovered that most of the fundamental work herein was carried out long ago and in some cases had not been reported as completely as might have been expected. As the work developed it soon became apparent that data should be at hand concerning the action of dry hydrohalogen acids on silico-orthoesters.

Friedel and Crafts (1) in 1866, reported the discovery of a reaction between acetyl chloride and ethyl orthosilicate.

$$\text{I.} \qquad Si(OC_2H_5)_4 + CH_3COCl = ClSi(OC_2H_5)_3 + CH_3COOC_2H_5$$

These investigators prepared the same product, triethoxysilicon chloride, by another method, namely the action of phosphorus pentachloride on ethyl orthosilicate. The work was continued by Friedel and Ladenburg (2, 3), not only making use of ethyl orthosilicate but ethyl ethane orthosiliconate as well. The silicon compound present after the reaction was completed was not isolated in the second case, but its hydrolysis product gave a satisfactory analysis for ethane siliconic acid. The reaction product could have been $C_2H_5Si(OC_2H_5)_3$, $C_2H_5SiCl_3$, or compounds with varying numbers of ethoxyl groups and chlorines. Ethyl acetate was also isolated.

Ladenburg (4) reported two years later on the reaction between benzoyl chloride and ethyl ethane orthosiliconate in which ethyl benzoate and $C_2H_5Si(OC_2H_5)_2Cl$ were formed.

Analogous reactions exist in the chemistry of the carbon series of orthoformates (5).

To date, work carried out on the action of hydrohalogen acids on silico-orthoesters has been confined to reactions in the field of hydrolysis (4, 6). The closest analogies which could be found lie in the field of the carbon orthoformates (7, 8).

$$\text{II.} \qquad HC(OC_2H_5)_3 + HCl = C_2H_5Cl + HCOOC_2H_5 + C_2H_5OH$$

$$\text{III.} \qquad HC(OC_3H_7)_3 + 2HBr = 2C_3H_7Br + HCOOH + C_3H_7OH$$

$$\text{IV.} \qquad HC(OC_2H_5)_3 + 3HI = 3C_2H_5I + HCOOH + HOH$$

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[1] Abstract of a thesis presented by the second author in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

DISCUSSION

Acetyl chloride has been found to react with ethyl orthosilicate in the molar ratio of one to one at 135° with the production of a ninety per cent yield of triethoxysilicon chloride (Equation I). Two moles of acetyl chloride react with one of ethyl orthosilicate in a sealed tube at 185° giving a fair yield of impure diethoxysilicon dichloride. When treated in the same manner, with five moles of chloride to one of orthoester, a slight amount of ethoxysilicon trichloride was formed. Two other runs were made, in a steel bomb, at 200° the molar proportions being two of chloride to one of orthoester in one case and one to one in the other. Only ethyl acetate could be identified from either run. Dry, spongy, siliceous polymers were found after distillation of ethyl acetate. Butyl orthosilicate reacted at 185° in a sealed tube with an equimolar amount of acetyl chloride to form tributoxysilicon chloride.

Equimolar amounts of ethyl orthosilicate and benzoyl chloride were heated together for five hours just at the boiling point of the mixture. Considerable darkening took place and distillation revealed the formation of a seventy per cent yield of triethoxysilicon chloride along with an eighty-eight per cent yield of ethyl benzoate. As a means of identification the product from this run (No. 7, Table I) was treated with butyl alcohol, producing butyl triethyl orthosilicate.

$$\text{V.} \qquad C_4H_9OH + ClSi(OC_2H_5)_3 = HCl + C_4H_9OSi(OC_2H_5)_3$$

Repeating the run, using four molar times the amount of benzoyl chloride did not give a product capable of identification.

Polyalkoxysilicon acylates have already been prepared (9). It seemed of interest to study the reaction of one or two of these compounds with an acyl halide to determine the course of the reaction. It was not known whether the halogen atom of the halide would attach to silicon with the formation of an organic acid anhydride or to the acyl radical forming a different acyl halide. Accordingly, triethoxysilicyl acetate and acetyl chloride were allowed to react, in the molar ratio of one to two, at about 40° for three hours. No reaction took place. Equimolar amounts were then heated in a sealed tube at 185° for five hours. Distillation of this product gave no compounds capable of identification although some reaction had taken place. The same may be said of the attempted reaction between triethoxysilicyl propionate and acetyl chloride, in equimolar amounts at 185° in a sealed tube for ninety minutes.

In all the above described reactions, varying quantities of polymerized siliceous material were formed.

A study of the action of acid bromides on silico-orthoesters developed rather unusual features. Acetyl bromide was found to react with ethyl orthosilicate in equimolar proportions when heated for two hours at 185°, with the production of no homogeneous silicon-containing material. Ethyl bromide was formed in twenty per cent yield and ethyl acetate, eighty per cent. A slowly rising boiling point of the remainder of the material indicated that polymerization had taken place. All of these fractions showed positive tests for bromine but this was not surprising, since hydrogen bromide was given off during distillation. In exactly the same manner, benzoyl bromide reacted with ethyl orthosilicate, giving rise to a twenty-six per cent yield of ethyl bromide and sixty-eight per cent yield of ethyl benzoate. Acetyl bromide was found to react with butyl orthosilicate to produce butyl bromide but butyl acetate could not be separated from the remainder of the material in condition pure enough for accurate determination, although there was evidence for its existence. The run was made under exactly the same conditions as those described above, save that the heating was limited to one hour. A small amount of a compound was isolated, however, which gave the correct bromine analysis for tributoxysilicon bromide. As will be explained under Conclusions, it was thought that an ether might be the intermediate in some of these reactions. Consequently, one run was carried out as was No. 2, save that dibutyl ether was added to the reactants. The results were the same as would have been expected had no ether been present. Analogous results were obtained when a mixture of dibutyl ether, ethyl orthosilicate and benzoyl bromide was heated in a sealed tube. Acetyl chloride did not react with dibutyl ether in the absence of the orthosilicate.

TABLE I

RUN	REACTANTS	CONDITIONS	PRODUCTS
1	$Si(OC_2H_5)_4 + CH_3COCl$	120 min, 135°	$ClSi(OC_2H_5)_3$
2	$Si(OC_2H_5)_4 + 2CH_3COCl$	60 min, 185° (sealed tube)	$Cl_2Si(OC_2H_5)_2$
3	$Si(OC_2H_5)_4 + 5CH_3COCl$	60 min, 185° (sealed tube)	$Cl_3Si(OC_2H_5)$
4	$Si(OC_2H_5)_4 + 2CH_3COCl$	60 min, 200° (bomb)	polymers
5	$Si(OC_2H_5)_4 + CH_3COCl$	60 min, 200° (bomb)	polymers
6	$Si(OC_4H_9)_4 + CH_3COCl$	60 min, 185° (sealed tube)	$ClSi(OC_4H_9)_3$
7	$Si(OC_2H_5)_4 + C_6H_5COCl$	300 min, b.p.	$ClSi(OC_2H_5)_3$
8	$Si(OC_2H_5)_4 + 4C_6H_5COCl$	120 min, b.p.	unidentifiable
9	$CH_3COOSi(OC_2H_5)_3 + 2CH_3COCl$	180 min, 40°	no reaction
10	$CH_3COOSi(OC_2H_5)_3 + CH_3COCl$	300 min, 180° (sealed tube)	unidentifiable
11	$C_2H_5COOSi(OC_2H_5)_3 + CH_3COCl$	90 min, 185° (sealed tube)	unidentifiable

TABLE II

RUN	REACTANTS	CONDITIONS	RESULTS
12	$Si(OC_2H_5)_4 + CH_3COBr$	120 min, 185° (sealed tube)	$C_2H_5Br + CH_3COOC_2H_5$
13	$Si(OC_2H_5)_4 + C_6H_5COBr$	120 min, 185° (sealed tube)	$C_2H_5Br + C_6H_5COOC_2H_5$
14	$Si(OC_4H_9)_4 + CH_3COBr$	60 min, 185° (sealed tube)	$C_4H_9Br + CH_3COOC_4H_9$ $BrSi(OC_4H_9)_3$(?)

Because of the evolution of hydrogen bromide from some of the reaction mixtures on distillation, it was thought desirable to investigate the action of dry hydrohalides on ethyl and butyl orthosilicates.

Thoroughly dried hydrogen chloride was passed through ethyl orthosilicate at room temperature. An ice and salt-bath in series, after the reaction chamber, did not condense anything. At one time the reaction flask warmed up slightly.

An estimated three per cent yield of ethyl alcohol resulted on distillation of the products, two-thirds of the orthoester was recovered and the remainder consisted of polymerized silicon compounds. Repeating the procedure, using a solid carbon dioxide trap instead of ice and salt, gave no different results. In a third run, 25 cc. of a saturated solution of dry hydrogen chloride in ethyl orthosilicate was sealed in a tube and heated to 185° for one hour. On distillation, excess hydrogen chloride was caught in sodium hydroxide, and in addition, about 7 cc. was condensed in the CO_2 trap, probably ethyl chloride.

When dry hydrogen chloride was bubbled through butyl orthosilicate no evidence of a reaction could be detected, nor could any products be isolated even after heating in a sealed tube as before.

There was a much more pronounced heat effect when dry hydrogen bromide was bubbled through ethyl orthosilicate, the temperature rising as high as 50–60° at times, this increase varying as the flow of gas. A small amount of ethyl bromide and of ethyl alcohol was isolated in a trap of ice and salt. When treated in the same manner, butyl orthosilicate yielded less than two per cent of butyl alcohol and about twenty per cent of butyl bromide.

TABLE III

RUN	REACTANTS	CONDITION	RESULTS
15	$Si(OC_2H_5)_4 + xHCl$[a]	room temperature	C_2H_5Cl (?)
16	$Si(OC_2H_5)_4 + xHCl$	room temperature	C_2H_5Cl (?)
17	$Si(OC_2H_5)_4 + xHCl$	60 min, 185° (sealed tube)	C_2H_5Cl (?)
18	$Si(OC_4H_9)_4 + xHCl$	room temperature	?
19	$Si(OC_4H_9)_4 + xHCl$	60 min, 185° (sealed tube)	?
20	$Si(OC_2H_5)_4 + xHBr$	room temperature	C_2H_5Br
21	$Si(OC_4H_9)_4 + xHBr$	room temperature	$C_4H_9Br + C_4H_9OH$
22	$Si(OC_2H_5)_4 + xHI$	room temperature	$C_2H_5I + C_2H_5OH$
23	$Si(OC_4H_9)_4 + xHI$	room temperature	$C_4H_9I + C_4H_9OH$

[a] x denotes undetermined amounts.

Ethyl orthosilicate reacted in the same manner with dry hydrogen iodide to form much ethyl alcohol and ethyl iodide. Accurate determinations of percentage yields were not feasible owing to the difficulty of quantitative separation of alcohol and iodide. Butyl orthosilicate reacted thus, to form butyl alcohol and butyl iodide.

EXPERIMENTAL PART

Ethyl orthosilicate used in this work was obtained from the Carbide and Carbon Chemicals Corporation, freshly distilled. Acetyl chloride, acetyl bromide, benzoyl chloride and benzoyl bromide were purchased from the Eastman Kodak Company, or were of a comparable grade. Butyl orthosilicate was prepared by the action of butyl alcohol on silicon tetrachloride and fractionation of the products. Hydrogen chloride was prepared from concentrated hydrochloric acid and concentrated sulfuric acid, then passed over phosphorus pentoxide before being allowed to enter the reaction chamber. Hydrogen bromide was prepared by the interaction of water, bromine and red phosphorus. It was dried by passage through tubes of calcium chloride and phosphorus pentoxide. Hydrogen iodide was prepared by the action of water on red phosphorus and a large excess of iodine, then dried by passage over phosphorus pentoxide.

Triethoxysilicyl acetate was prepared by the action of acetic anhydride on ethyl orthosilicate (9). Triethoxysilicyl propionate was prepared in like manner, by the action of propionic anhydride on ethyl orthosilicate (9).

Butyl triethyl orthosilicate was prepared in Run 7, Table I, by the action of butyl alcohol on triethoxysilicon chloride, b.p. 88–90° (16 mm.), n_D^{20} 1.3945, literature b.p. 82.5° (15 mm.), n_D^{20} 1.395 (9). These data were checked by another preparation from butyl alcohol and ethyl orthosilicate, b.p. 87° (14 mm.), n_D^{20} 1.3925. In the course of the latter run diethyl dibutyl orthosilicate was formed, b.p. 105–107° (14 mm.), n_D^{20} 1.4010.

Triethoxysilicon chloride was identified, b.p. 156–157° (744 mm.), Run 1, Table I, 154–159°, Run 7, Table I, Cl found 16.6, theory 17.9, Run 1, Table I.

Diethoxysilicon dichloride was identified b.p 135–137° (748 mm.), Cl found 36.2, theory 37.5; Si found 15.6, theory 14.8, Run 2, Table I.

Tributoxysilicon chloride was identified b.p. 84–85° (1 mm.), Cl found 12.50, theory 12.55; Si found 20.0, theory 21.3, Run 6, Table I.

Tributoxysilicon bromide was identified, Br found 23.4, theory 24.9, Run 14, Table II.

Other compounds isolated in the course of the work were identified in the same general manner, by the determination of their simple physical constants.

CONCLUSIONS

It has been shown that the reaction of an organic acid chloride on ethyl or butyl orthosilicate results in the formation of the expected trialkoxysilicon chloride. When the relative amount of acid chloride is increased, the corresponding dialkoxysilicon dichloride is formed. Optimum conditions seem to include heating, preferably in a sealed tube. The formation of alkyl bromide when acetyl or benzoyl bromide is used complicates any concept of reaction mechanism.

With the alkyl bromides it was at first thought possible that the orthosilicate decomposed under the influence of the acid halide to a metasilicate and an ether

$$\text{VI.} \qquad SiO(OC_2H_5)_4 = OSi(OC_2H_5)_2 + C_2H_5OC_2H_5$$

and that the ether then reacted with the acid halide. But separate runs carried out in the presence of dibutyl ether failed to produce any evidence in favor of a reaction of this type. At the present time it seems improbable to suspect a direct splitting off of ethyl from ethyl orthosilicate—no evidence exists which could be accepted as proof of this type of orthoester decomposition. A break between ethyl and oxygen might be slightly more probable if the halogen were already attached to silicon, as for example:

$$\text{VII.} \qquad BrSi(OC_2H_5)_3 = C_2H_5Br + OSi(OC_2H_5)_2,$$

but there is no proof for this mechanism either. The facts are, however, that both alkyl bromide and alkyl acetate, or benzoate, were formed when acid bromide reacted with silico-orthoester.

The action of dry hydrohalogen acids on silico-orthoesters bears out the general concept of the relative reactivities of these acids in organic media, namely that hydriodic acid is the most reactive of the three, hydrobromic second, and hydrochloric acid least. Qualitatively, the relative amounts of halide isolated check with this fact. Although no proof exists, a mechanism might be assumed providing for the formation, first, of alcohol, which then would be expected to react with dry hydrohalogen acid

VIII. $$Si(OC_2H_5)_4 + HI = ISi(OC_2H_5)_3 + C_2H_5OH$$

IX. $$C_2H_5OH + HI = HOH + C_2H_5I$$

X. $$HOH + ISi(OC_2H_5)_3 = HI + C_2H_5OH + OSi(OC_2H_5)_2$$

Polymerized silicon compounds could easily form by silicon-ether formation as soon as hydroxyl groups appear attached to silicon. These polymers were always obtained.

SUMMARY

1. The action of acetyl chloride on ethyl orthosilicate, butyl orthosilicate, triethoxysilicyl acetate, and triethoxysilicyl propionate has been investigated within restricted sets of conditions. Benzoyl chloride has been found to react with ethyl orthosilicate at the boiling point of the mixture.

2. Acetyl bromide has been found to react with ethyl and butyl orthosilicates, and benzoyl bromide with the former orthoester. The results are somewhat different as contrasted with those found in the case noted under '1.'

3. Dry hydrohalogen acids react with ethyl orthosilicates with results which could be explained on the assumption of the alcohol as intermediate. Dry hydrobromic and hydriodic acids were found to react with ethyl orthobutyrate. No definite proof is submitted as to the mechanism, however.

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