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

STUDIES IN SILICO-ORGANIC COMPOUNDS. XIII. ADDITIONAL CHEMICAL PROPERTIES OF TRIALKOXYSILANES[1, 2]

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INTRODUCTION

This paper is intended to complete the preceding contribution (1) and to carry farther certain phases of the work of Jenkins (2) for the purpose of gathering more evidence concerning the reactivity of silane hydrogen and its possible electronegative character.

The action of organic acid halides on tetraalkoxysilanes was first investigated some time ago (3, 4, 5) but trialkoxysilanes have not hitherto been subjected to this type of reaction.

It has been found that certain organic acid halides react with triethylsilane and tribenzylsilane (2) with replacement of silane hydrogen by chlorine or bromine. The yields are not outstanding, in fact in one case no reaction could be obtained at all save in the presence of aluminum chloride.

The action of benzoyl chloride on triethoxysilane under the experimental conditions outlined here caused interchange between chlorine and ethoxyl:

1. $HSi(OC_2H_5)_3 + C_6H_5COCl \rightarrow C_6H_5COOC_2H_5 + (C_2H_5O)_2SiHCl$

These results were obtained under three sets of conditions, in 1:1 molar ratio with aluminum chloride, in 1:1 ratio without aluminum chloride, and in molar ratio of one silicon compound to two of halide, also without aluminum chloride. When tri-*n*-propoxysilane was used however, there was disproportionation in the presence of aluminum chloride. Consequently, one run was carried out to test the effect of aluminum chloride alone on tri-*n*-propoxysilane. Tetra-*n*-propoxysilane was the major product.

The action of acetic anhydride on tetraethoxysilane was reported by Friede and Crafts (6) in 1866:

2. $Si(OC_2H_5)_4 + (CH_3CO)_2O \rightarrow CH_3COOSi(OC_2H_5)_3 + CH_3COOC_2H_5$

Acetic anhydride also reacts with trimethyl-β-chloroethoxysilane (7) and with triethylethoxysilane (5). Ethyltriethoxysilane has, more recently, been found to react as well (8).

This work has shown that acetic anhydride reacts with triethoxysilane in equimolar quantities with interchange of acetate and ethoxyl:

3. $HSi(OC_2H_5)_3 + (CH_3CO)_2O \rightarrow CH_3COOSiH(OC_2H_5)_2 + CH_3COOC_2H_5$

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[1] The work on which this report is based comprises part of a program of research carried out under contract with the Office of Naval Research.

[2] Submitted by the first author to the Graduate School of Arts and Sciences of the University of Buffalo in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

but that an excess of anhydride reacts in a different manner:

4. $CH_3COOSiH(OC_2H_5)_2 + (CH_3CO)_2O \rightarrow (CH_3COO)_2Si(OC_2H_5)_2 + CH_3CHO$

Tri-*n*-propoxysilane reacted in analogous fashion but isolation of the products using 1:1 molar ratio proved difficult and an exact statement of the course of this reaction is therefore avoided.

EXPERIMENTAL

Triethoxysilane and benzoyl chloride. Triethoxysilane (32 g., 0.23 mole) was mixed with 32.4 g. (0.23 mole) of benzoyl chloride. To this was added 0.1 g. of anhydrous aluminum chloride. After several hours of refluxing, the solution turned yellow, darkening with time to a dull orange. Refluxing continued for 24 hours. Fractionation yielded 9.8 g. of diethoxychlorosilane, b.p. 107–110° (743 mm.), n_D^{25} 1.3845, d_4^{25} 0.9806; yield, 24%.

TABLE I

DATA SUPPLEMENTARY TO EXPERIMENTAL PART

REACTANTS	FINAL VOL., CC.	TOTAL VOL. PRODUCTS, CC.	ISOLATED VOL. UNREACTED, CC.
$HSi(OC_2H_5)_3$, C_6H_5COCl, $AlCl_3$	50	21	10
$HSi(OC_2H_5)_3$, C_6H_5COCl	50	21	10
$HSi(OC_2H_5)_3$, $2C_6H_5COCl$	77	14	14
$HSi(OC_3H_7)_3$, C_6H_5COCl, $AlCl_3$	37	9	10
$HSi(OC_3H_7)_3$, C_6H_5COCl	45	26	?
$HSi(OC_3H_7)_3$, $2C_6H_5COCl$	69	37	20
$HSi(OC_2H_5)_3$, $(CH_3CO)_2O$	63	35	12
$HSi(OC_2H_5)_3$, $(CH_3CO)_2O$	116	51	40
$HSi(OC_3H_7)_3$, $(CH_3CO)_2O$	45	12	11
$HSi(OC_3H_7)_3$, $4(CH_3CO)_2O$	158	42	98

The difference between the sum of the 2nd and 3rd columns and the 1st column could easily have been explained by the existence of siliceous residues after distillation. Yields listed under EXPERIMENTAL were calculated on smaller volumes of purified products.

Anal. Calc'd for $C_4H_{11}ClO_2Si$: Si, 18.1; Cl, 23.00; Silane H, 0.648; M. R., 36.32 (12).
Found: Si, 18.0; Cl, 23.40; Silane H, 0.616; M.R., 36.33.

Ethyl benzoate was also isolated, 10 g., b.p. 207–209° (743 mm.), n_D^{25} 1.4880, yield, 29%. When the two reactants were mixed in the same amounts but without aluminum chloride, refluxed and distilled as above, 4 g. of diethoxychlorosilane was obtained and 8g. of ethyl benzoate; yields of 10% and 23% respectively. Using double molar quantities of benzoyl chloride, without aluminum chloride, and proceeding as previously described, the yields were 4 g. of diethoxychlorosilane and 5 g. of ethyl benzoate, 10% and 14.5% respectively.

Tri-n-propoxysilane and benzoyl chloride. Tri-*n*-propoxysilane, (33 g., 0.11 mole) was slowly treated with 15.6 g. (0.11 mole) of dry benzoyl chloride and 0.1 g. of aluminum chloride. The system was refluxed for 20 hours. After the first few hours, a pale yellow color developed, gradually deepening. Fractionation yielded 3 cc. of di-*n*-propoxychlorosilane, b.p. 26–28° (7 mm.), n_D^{25} 1.3978, d_4^{25} 0.9587, 14% yield.

Anal. Calc'd for $C_6H_{15}ClO_2Si$: Si, 15.3; Cl, 19.4; Silane H, 0.548; M.R., 45.58.
Found: Si, 15.1; Cl, 19.8; Silane H, 0.540; M.R., 46.06.

There was also 6 cc. of tri-*n*-propoxychlorosilane, b.p. 56–57° (5 mm.), n_D^{25} 1.4068, d_4^{25} 0.9826; yield, 20%.

Anal. Calc'd for $C_9H_{21}ClO_3Si$: Si, 11.6; Cl, 14.76; Silane H, 0.00; M.R., 59.97 (12).
Found: Si, 11.5; Cl, 14.30; Silane H, 0.00; M.R., 60.26 (12).

No aldehyde was found.

Without aluminum chloride, equimolar amounts of the two reactants (0.204 mole) gave 6 g. of di-*n*-propoxychlorosilane, b.p. 150–155° (743 mm.), n_D^{25} 1.4008, d_4^{25} 0.9562; yield, 18%.

Anal. Calc'd for $C_6H_{15}ClO_3Si$: M.R., 45.58 (12). Found: M.R., 46.23.

There was also isolated 12 g. of *n*-propyl benzoate, b.p. (found) 225–229° (760 mm.), literature (9) 229.5° (760 mm.); n_D^{20} 1.5000, d_4^{20} 1.024.

Anal. Calc'd for $C_{10}H_{12}O_2$: M.R., 46.83 (12). Found: M.R., 47.11.

Using double quantities of benzoyl chloride there was isolated 6.7 g. of di-*n*-propoxychlorosilane, b.p. 48–49° (8 mm.), n_D^{25} 1.4004, 30% yield. Impure benzaldehyde was also isolated, b.p. 76–84° (4 mm.), yielding a positive test with sodium bisulfite and 2,4-dinitrophenylhydrazine. Purification of the 2,4-dinitrophenylhydrazone was not possible. *n*-Propyl benzoate was also isolated in nearly quantitative yield.

Tri-n-propoxysilane and aluminum chloride. To test the effect of aluminum chloride alone on one of these trialkoxysilanes, 35 g. (0.17 mole) of tri-*n*-propoxysilane was refluxed with 0.1 g. of aluminum chloride for 20 hours. There was isolated 9.1 g. of tetra-*n*-propoxysilane, b.p. found 223–226° (741 mm.), literature (10) 225–227° (760 mm.), n_D^{25} 1.3991; yield, 20%.

Triethoxysilane and acetic anhydride. Triethoxysilane, 30 g. (0.183 mole) was added to 18.7 g. (0.183 mole) of pure acetic anhydride and the system refluxed for six hours. Distillation produced 20 g. of ethyl acetate, b.p. 65–73° (742 mm.). Acetoxydiethoxysilane was also isolated, 9.8 g., b.p. 52–53° (11 mm.), n_D^{25} 1.3824, d_4^{25} 0.9836; yield, 35%.

Anal. Calc'd for $C_6H_{14}O_4Si$: Si, 15.7; Silane H, 0.562; M.R., 42.08 (12).
Found: Si, 15.3; Silane H, 0.536; M.R., 42.00.

When refluxed for 24 hours, the major product was $(CH_3COO)_2Si(OC_2H_5)_2$, b.p. 92–95° (4 mm.). Using excess acetic anhydride, 4 times molar proportions, 29 g. of ethyl acetate was isolated and 9 g. of diacetoxydiethoxysilane, b.p. 92–93° (11 mm.), n_D^{25} 1.3947, d_4^{25} 1.086; yield, 16%.

Anal. Calc'd for $C_8H_{16}O_6Si$: Si, 11.9; Silane H, 0.0; M.R., 51.84 (12).
Found: Si, 11.8; Silane H, 0.0; M.R., 51.97.

In the Dry Ice-trap there was found a solid whose 2,4-dinitrophenylhydrazone was prepared; m.p. found 169°, literature (11) 168°, corresponding to the value for the 2,4-dinitrophenylhydrazone of acetaldehyde.

Tri-n-propoxysilane and acetic anhydride. With reactants in 1:1 molar ratio, 0.2 mole of each in 50 cc. of anhydrous benzene, there was an odor of acetaldehyde about the lower fractions but no further evidence of its presence could be obtained. *n*-Propyl acetate was isolated, 11 g., b.p. 94–96° (740 mm.), n_D^{25} 1.3995; yield, 33%. No pure silicon compound could be isolated. Using 0.22 mole of tri-*n*-propoxysilane and 0.88 mole of acetic anhydride, impure precipitates were obtained by the action of sodium bisulfite and 2,4-dinitrophenylhydrazine on certain fractions of the reaction mixture. Diacetoxydi-*n*-propoxysilane was isolated in 9 g. yield, b.p. 153–154° (37 mm.), n_D^{25} 1.4025, d_4^{25} 1.045; yield, 15%.

Anal. Calc'd for $C_{10}H_{20}O_6Si$: Si, 10.6; M.R., 61.10 (12).
Found: Si, 10.3; M.R., 61.44.

Approximately 20 cc. of n-propyl acetate was also obtained.

CONCLUSIONS

The results of this work make still more logical the assumption that silane hydrogen is electronegative. The work of Jenkins (2) has touched upon the action of benzoyl chloride on trialkylsilanes or similar derivatives of aromatic radicals. It was thought that if the substituents were themselves electronegative, the electronegativity of silane hydrogen might thereby be decreased. The evidence favors this assumption. Benzoyl chloride and acetic anhydride may react with any one of three alkoxyl groups or with silane hydrogen in the two compounds herein investigated. One alkoxy group is removed first, as was shown by the reaction with tri-*n*-propoxysilane, then the hydrogen. This would indicate that the reactivity of the silane hydrogen is less than that of any *n*-propoxyl group in $HSi(OC_3H_7\text{-}n)_3$ but that once a chlorine atom or an acetate group has appeared to form $(n\text{-}C_3H_7O)_2SiHCl$ or $CH_3COOSiH(OC_3H_7\text{-}n)_2$, the hydrogen is the most reactive of the remaining three.

SUMMARY

1. Data are presented on the reaction between benzoyl chloride and triethoxysilane, also tri-*n*-propoxysilane. The normal reaction involves interchange between chlorine and alkoxyl. Aluminum chloride, however, catalyzes disproportionation with formation of tetra-*n*-propoxysilane. Isolable disproportionation products were not identified in the case of the triethyoxysilane.

2. The action of acetic anhydride on the two trialkoxysilanes was also studied. The normal reaction was again that of interchange between acetate and alkoxyl. An excess of anhydride, however, caused interchange between silane hydrogen and acetate.

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