[Contribution from the Department of Chemistry of the University of Buffalo]

STUDIES IN SILICO-ORGANIC COMPOUNDS. X. THE CHEMICAL PROPERTIES OF TRISUBSTITUTED SILANES[1,2]

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INTRODUCTION

The properties of trisubstituted silanes, containing one hydrogen atom connected to silicon, have already been studied from both the chemical (1) and the physical (2) point of view. It seems to be the concensus of opinion that silane hydrogen shows considerable evidence of being electronegative in character and this work was undertaken with the purpose of further exploring the field to obtain more evidence on this point.

Five halogenations were carried out with good yields. Thus tribenzylchlorosilane, and triethylchlorosilane were prepared by the action of chlorine on the proper silane and in a similar manner bromination resulted in the formation of tribenzylbromosilane, tricyclohexylbromosilane, and triethylbromosilane. An analogous reaction, the bromination of triphenylsilane, was carried out by Kipping and Murray in 1929 (12). Hydrolytic reactions were successfully carried out on all of these products except tribenzylchlorosilane.

Halogenation, in itself, is no evidence of the positive, negative, or non-polar character of the silane hydrogen. It might be assumed however that a polar nature is favored by the ease with which these halogenations were carried out.

It was desired to find some reagent with a reactive halogen which could quite definitely be considered negative halogen and which would effect interchange between that halogen and silane hydrogen. Such compounds were found in the benzoyl halides and certain of their derivatives.

The following reactions were carried out with moderate success:

I. $C_6H_5COCl + HSi(CH_2C_6H_5)_3 \rightarrow C_6H_5CHO + (C_6H_5CH_2)_3SiCl$
II. $C_6H_5COBr + HSi(C_2H_5)_3 \rightarrow C_6H_5CHO + (C_2H_5)_3SiBr$
III. $C_6H_5COBr + HSi(CH_2C_6H_5)_3 \rightarrow C_6H_5CHO + (C_6H_5CH_2)_3SiBr$
IV. $p\text{-}C_2H_5OC_6H_4COCl + HSi(C_2H_5)_3 \rightarrow p\text{-}C_2H_5OC_6H_4CHO + (C_2H_5)_3SiCl$
V. $p\text{-}C_2H_5OC_6H_4COCl + HSi(CH_2C_6H_5)_3 \rightarrow p\text{-}C_2H_5OC_6H_4CHO + (C_6H_5CH_2)_3SiCl$
VI. $p\text{-}C_2H_5OC_6H_4COBr + HSi(CH_2C_6H_5)_3 \rightarrow p\text{-}C_2H_5OC_6H_4CHO + (C_6H_5CH_2)_3SiBr$

o-Chlorobenzoyl chloride did not react with triethylsilane save in the presence of aluminum chloride. The reaction of benzoyl chloride with triethylsilane was also carried out in the presence of aluminum chloride.

These results in general seem to bear out the assumption that the silane hydrogen is electronegative in character.

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[1] This paper represents a portion of the thesis presented by the first author in partial fulfillment of the requirements of the degree of Doctor of Philosophy at the University of Buffalo.

[2] The work on which this paper is based comprises a portion of the program of research being carried out under contract with the Office of Naval Research.

Physical data relative to products and derivatives will be found in Table I. Certain other combinations were attempted without success, namely with tribenzylsilane: acetic anhydride, propionic anhydride, benzyl bromide, *p*-nitrobenzoyl chloride, *p*-chlorobenzoyl chloride, and *o*-chlorobenzoyl chloride, and with triethylsilane: triphenylchlorosilane and benzoyl chloride.

EXPERIMENTAL PART

Chlorination reactions. Chlorine gas was passed into a solution of 15.5 cc. (0.1 mole) of triethylsilane in 50 cc. of carbon tetrachloride for one hour at room temperature, under anhydrous conditions. The product, *triethylchlorosilane,* was isolated in 60% yield, b.p. 143–144° (760 mm.); literature, m.p. 144–145° (760 mm.) (3); n_D^{20} 1.4320; literature, n_D^{20} 1.4321 (3). In similar manner, 15.1 g. (0.05 mole) of tribenzylsilane in 125 cc. of anhydrous carbon tetrachloride was converted to *tribenzylchlorosilane* in lower yield, m.p. 141–142°; literature, m.p. 141° (4). Triethylsilane and tribenzylsilane were prepared in accordance with procedures already in the literature (5).

TABLE I

PHYSICAL CONSTANTS

	B.P., °C.	M.P, °C.	n_D^{20}
$(C_2H_5)_3SiCl$[a]	143–144		1.4320
$(C_2H_5)_3SiBr$[b]	162–163		
$(C_2H_5)_3SiOH$[c]	153–154		
$[(C_2H_5)_3Si]_2O$[d]	231		
$(C_6H_{11})_3SiBr$[e]		114–115	
$[(C_6H_{11})_3Si]_2O$[e]		176–178	
$(C_6H_5CH_2)_3SiCl$[f]		141–142	
$(C_6H_5CH_2)_3SiOH$[g]		105–106	
$(C_6H_5CH_2)_3SiBr$[e]		144–145	

[a] B.p. 144–145° (729 mm.), n_D^{20} 1.4311 (3). [b] B.p. 162–163° (760 mm.) (6). [c] B.p. 154° (760 mm.) (9). [d] B.p. 231° (760 mm.) (9). [e] New compound. [f] M.p. 141° (4). [g] M.p. 106° (7).

Bromination reactions. Bromine (5.13 cc., 0.1 mole) in 200 cc. of anhydrous carbon tetrachloride was added dropwise to 15.45 cc. (0.1 mole) of triethylsilane in 35 cc. of the same solvent. The reaction was slightly exothermic. The mixture was refluxed for 90 minutes. The product was *triethylbromosilane* in 30% yield, b.p. 162–163° (760 mm.); literature, b.p. 162–163° (760 mm.) (6). In similar manner, *tricyclohexylbromosilane* was also prepared though in lower yields, m.p. 114–115° (recrystallized).

Anal. Calc'd for $C_{18}H_{33}BrSi$: Br, 22.39. Found: Br, 22.09.

Tricyclohexylbromosilane was dissolved in aqueous ethanol and boiled for 15 minutes with water. Crystals separated, probably *hexacyclohexyldisiloxane,* m.p. 176–178°.

Anal. Calc'd for $C_{36}H_{66}OSi_2$: C, 75.73; H, 11.58.
Found: C, 73.52; H, 11.33.

By the same procedure, *tribenzylbromosilane* was also prepared from 0.5 mole of tribenzylsilane, m.p. 144–145°.

Anal. Calc'd for $C_{21}H_{21}BrSi$: Br, 20.98. Found: Br, 20.60.

Hydrolysis with heated 50% ethanol resulted in the formation of tribenzylhydroxysilane, m.p. 105–106°; literature, m.p. 106° (7). Mixture melting point with tribenzylchlorosilane, 135–138°; reddish purple in carbon tetrachloride with chlorine water.

Reactions with benzoyl chloride. Benzoyl chloride (5.33 cc., 0.05 mole) in 20 cc. of anhydrous ether was added to 13 g. (0.043 mole) of tribenzylsilane in 80 cc. of anhydrous ether with stirring. The mixture was refluxed for 5 hours. Benzaldehyde (2 cc.) was isolated, b.p. 175–179°, positive test with Tollens reagent. A smaller amount of tribenzylchlorosilane was isolated, m.p. 141–142°. Benzoyl chloride, alone, did not react with triethylsilane. However, when 23 cc. of triethylsilane (0.15 mole) in 60 cc. of anhydrous ether was mixed with 17.98 cc. (0.15 mole) of benzoyl chloride and aluminum chloride (0.2 g.) was added, reaction took place during a 6-hour reflux period. Triethylchlorosilane (7 cc.) was isolated, b.p. 141–144°, n_D^{20} 1.4312; approximately 30% yield. Benzaldehyde was identified as the 2,4-dinitrophenylhydrazone, m.p. 237°; literature, m.p. 235° (8).

Reactions with benzoyl bromide. Benzoyl bromide (23.6 cc., 0.2 mole) was added to 31.0 cc. (0.2 mole) of triethylsilane in 100 cc. of dry ether with stirring. The mixture was refluxed for 19 hours. Triethylsilane (17 cc.) was recovered. Triethylbromosilane (6 cc.) was isolated, b.p. 165–167° (760 mm.), in approximately 15% yield. Triethylbromosilane was refluxed with 50% ethanol for 30 minutes, forming hexaethyldisiloxane, b.p. 231° (760 mm.); literature, b.p. 231° (9). As before, benzaldehyde was identified by precipitation as the 2,4-dinitrophenylhydrazone, m.p. 238–239°. In a similar manner, 0.1 mole of benzoyl bromide was allowed to react with 0.1 mole of tribenzylsilane in 200 cc. of anhydrous ether. The mixture was refluxed for four hours. Tribenzylbromosilane was isolated, m.p. 141–143°. Tribenzylbromosilane was refluxed for 15 minutes with 50% ethanol with the formation of tribenzylhydroxysilane, m.p. 103°; literature, m.p. 106° (7). Benzaldehyde was identified by its boiling point, 175–185° and by its positive test with Tollens reagent.

Reaction with o-chlorobenzoyl chloride. o-Chlorobenzoyl chloride did not react with tribenzylsilane, nor did the *para*-isomer. *o*-Chlorobenzoyl chloride reacted with triethylsilane only in the presence of aluminum chloride. Triethylsilane (23 cc., 0.15 mole), *o*-chlorobenzoyl chloride (15 cc., 0.15 mole), and 0.4 g. of aluminum chloride were heated gently to initiate reaction, then cooled in an ice-bath. At the end of five minutes the reaction had subsided and the system was refluxed for four hours. Triethylchlorosilane (6 cc.) was isolated; 3 cc. had b.p. 140–142° (760 mm.), n_D^{20} 1.4311 and 3 cc. had b.p. 142–143° (760 mm.), n_D^{20} 1.4314. *o*-Chlorobenzaldehyde, 5 cc., was also isolated, b.p. 210–215° (760 mm.); literature, b.p. 208° (760 mm.) (10).

Reactions with p-ethoxybenzoyl chloride. p-Ethoxybenzoyl chloride (18.45 g., 0.1 mole) was added to 15.5 cc. (0.1 mole) of triethylsilane in 75 cc. of anhydrous ether and refluxed for 19 hours. Triethylchlorosilane, 3 cc., was isolated, b.p. 144–146° (760 mm.), n_D^{20} 1.4311. When triethylchlorosilane was refluxed with 50% ethanol, triethylhydroxysilane was formed, b.p. 153–154° (760 mm.); literature, b.p. 154° (760 mm.) (9). The residue from the original reaction yielded a small amount of *p*-ethoxybenzaldehyde, b.p. 141–143° (20 mm.); literature, b.p. 140° (20 mm.) (11). *p*-Ethoxybenzoyl chloride was prepared by the action of phosphorus trichloride on *p*-ethoxybenzoic acid (11), b.p. 130–139° (16 mm.). In similar manner, *p*-ethoxybenzoyl chloride reacted with tribenzylsilane in 0.1-molar quantities yielding tribenzylchlorosilane, m.p. 139–140°, identified by mixture melting point. *p*-Ethoxybenzaldehyde, 6 cc., was also identified, b.p. 135–141° (19.5 mm.).

Reaction with p-ethoxybenzoyl bromide. p-Ethoxybenzoyl bromide did not react with triethylsilane. However, reaction occurred when 28 g. (0.122 mole) of *p*-ethoxybenzoyl bromide was added to 23.7 g. (0.0785 mole) of tribenzylsilane in 75 cc. of anhydrous ether; the mixture was refluxed eight hours. Tribenzylbromosilane, m.p. 144°, and 10 cc. of *p*-ethoxybenzaldehyde, b.p. 139–145° (20 mm.) were isolated. Tribenzylsilane was further identified by conversion to tribenzylhydroxysilane as before, m.p. 104–106°.

SUMMARY

1. By direct halogenation in carbon tetrachloride, the following have been prepared: triethylchlorosilane, tribenzylchlorosilane, triethylbromosilane, tricyclohexylbromosilane, and tribenzylbromosilane.

2. Benzoyl chloride has been found to react with tribenzylsilane to form benzaldehyde and tribenzylchlorosilane. With triethylsilane a comparable reaction

was brought about but only with the catalytic aid of aluminum chloride. Benzoyl bromide reacted with triethylsilane to form triethylbromosilane, identified by conversion to hexaethyldisiloxane. Similarly tribenzylbromosilane was prepared and converted to tribenzylhydroxysilane.

3. *o*-Chlorobenzoyl chloride did not react with tribenzylsilane nor did the *para*-isomer. However, the *ortho* compound reacted with triethylsilane in the presence of aluminum chloride to form triethylchlorosilane and *o*-chlorobenzaldehyde.

4. *p*-Ethoxybenzoyl chloride reacted with triethylsilane to form triethylchlorosilane and with tribenzylsilane to form tribenzylchlorosilane. Triethylchlorosilane was identified by conversion to triethylhydroxysilane. *p*-Ethoxybenzaldehyde was also formed in each case.

5. *p*-Ethoxybenzoyl bromide did not react with triethylsilane, but with tribenzylsilane it gave tribenzylbromosilane and *p*-ethoxybenzaldehyde. Tribenzylbromosilane was identified by conversion to tribenzylhydroxysilane.

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