110. *Interaction of Alcohols with Silicon Tetrachloride.*

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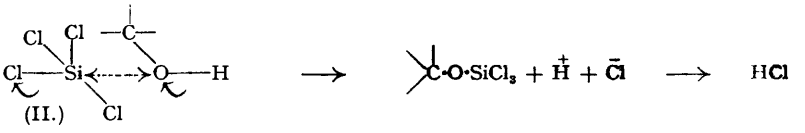
(+)-Octan-2-ol and silicon tetrachloride formed chlorosilanes and tetra-2-octyloxysilane in proportions depending on the proportion of silicon tetrachloride, but none of the chloride, RCl. (+)-1-Phenylethanol formed considerably racemised chloride, RCl, under similar conditions. Whereas hydrogen chloride had no action on tetra-2-octyloxysilane, it rapidly dealkylated the corresponding (+)-1-phenylethyl compound, the chloride formed being considerably racemised. In the presence of pyridine a number of tetra-alkyloxysilanes have been obtained in excellent yield. These and other data are now available for comparison with those from a study of phosphorus trichloride–alcohol systems, and provide a contribution to the eventual elucidation of mechanism.

THE chlorosilanes $RO{\cdot}SiCl_3$, $(RO)_2SiCl_2$, $(RO)_3SiCl$, and the tetra-alkyloxysilane $(RO)_4Si$, were obtained from silicon tetrachloride and (+)-octan-2-ol in proportions depending on the relative amounts of the reagents, whereas formation of 2-chloro-octane was not observed. On the other hand, (+)-1-phenylethanol and the tetrachloride afforded hydrated silica and almost completely racemised 1-chloro-1-phenylethane in large yield.

Tertiary alcohols such as *tert.*-butyl alcohol and 2-methylbutan-2-ol behaved similarly to 1-phenylethanol, except that when mixed with silicon tetrachloride they showed a remarkable reluctance to react. When the mixture was warmed a reaction became vigorous, and hydrated silica (91% yield) was rapidly formed, the other product isolated being the corresponding chloride, RCl.

Formation of the silicon esters may be depicted as due to four-centre, broadside approach of the molecules as in (I), there being but one transition state.

We prefer this picture to an end-on three-centre process shown in (II).



Addition of silicon tetrachloride to a pentane solution of pyridine and the appropriate alcohol readily afforded pyridine hydrochloride and the tetra-alkyloxysilane in excellent yield, thus demonstrating facilitation of broadside approach (I), presumably by hydrogen bond-formation, $ROH{\cdot}{\cdot}{\cdot}NC_5H_5$ (Gerrard, *J.*, 1939, 99). In this system 1-phenylethanol behaved similarly. In the examples of the two tertiary alcohols mentioned, replacement of the third and the fourth chlorine atom could not be effected at room temperature, although the third was replaced when the system was heated. Miner, Bryan, Holysz, and Pedlow (*Ind. Eng. Chem.*, 1947, **39**, 1368) introduced the use of pyridine to effect the formation of dichlorodi-(2-methyl-2-butyloxy)silane and dichlorodi-(*tert.*-butyloxy)silane for the immediate purpose of replacing the chlorine atoms by amino-groups. We extended observations to emphasise the existence of a pronounced

example of what we believe to be steric hindrance to the broadside approach of a third molecule of a tertiary alcohol in the stepwise replacement of chlorine by alkoxyl, in the presence of pyridine, although ethanol is well able to continue the precipitation of pyridine hydrochloride. Models show possible hindrance to the approach of a third tertiary alcohol molecule by the four-centre, broadside mechanism (I), although certain other modes of approach are not so restricted. A very similar effect was noticed by Gerrard and Wyvill (*Research*, 1949, **2**, 536) with respect to trichloro-*tert.*-butyl alcohol and phosphorus trichloride. There was no evidence of hindrance in the example of 1:3-dimethylbutyl alcohol (see table, p. 521) in the silicon tetrachloride system, thus showing the inadequacy in this respect of a slightly more remote branching.

Hydrogen chloride readily effected dealkylation of (+)-tetra-(1-phenylethoxy)silane at −10°, hydrated silica being precipitated, and much-racemised (−)-1-chloro-1-phenylethane being formed in 94% yield. Under similar conditions, (+)-tetra-(2-octyloxy)silane was unaffected by hydrogen chloride.

So far as 1-phenylethanol is concerned, the alcohol–silicon tetrachloride system bears strong analogy with the alcohol–phosphorus trichloride system (Gerrard, *J.*, 1944, 85), presumably because the directing feature is the activity of the alcoholic carbon atom. In the example of octan-2-ol, the systems differ, because the lone pair of electrons on the phosphorus atom of the phosphite $(RO)_3P$ facilitates removal of *one* alkyl group by hydrogen chloride thus : $(RO)_3P + HCl \longrightarrow (RO)_2\overset{\overset{O}{\parallel}}{P}—H + RCl$. The lone pair not being available in the silicon series, it is not surprising that dealkylation is very slow.

Tetra-esters containing branched alkyl groups showed a reluctance to disproportionation with silicon tetrachloride attributed to the screening effect of the branches which form a network round the tetrahedron of which the silicon atom is the centre.

The (+)-2-octyloxychlorosilanes have been described by Gerrard and Woodhead (*Research*, 1949, **2**, 48).

Experimental.

It is stated when reaction mixtures were washed with water, and an aqueous solution of sodium carbonate was also employed, the organic liquids being dried with potassium carbonate and sodium sulphate. Pyridine hydrochloride was separated and analysed without further purification (Calc. : Cl, 30·7; C_5H_5N, 68·4%).

Rotatory powers are stated for $l = 1$, and are expressed always in terms of the (+)-alcohols, although (−)-alcohols were also employed.

Interaction of Silicon Tetrachloride and Alcohols in the Presence of Pyridine.—Silicon tetrachloride (8·5 g., 0·25 mol.) in pentane (10 c.c.) was added dropwise to a solution of (+)-octan-2-ol (26 g., 1 mol.; α_D^{18} +7·28°) and pyridine (15·8 g., 1 mol.) in pentane (125 c.c.) at −10°. Pyridine hydrochloride (Found : Cl, 30·6; C_5H_5N, 68·2%) was quantitatively precipitated, and from the pentane solution (+)-tetra-2-octyloxysilane, b. p. 190°/0·3 mm., α_D^{18} +16·32° (see table), was obtained.

The silane (5 g.) was heated under reflux for 8 hours with an alcoholic solution of potassium hydroxide (10%). The liquid was then diluted with water and, from the washed and dried pentane extract, (+)-octan-2-ol (4·0 g.), b. p. 81°/18 mm., α_D^{20} +7·32°, was obtained.

Dry hydrogen chloride was passed for 2 hours into a pentane solution of (+)-tetra-2-octyloxysilane at −10°. No reaction occurred.

Passage of dry hydrogen bromide into (+)-tetra-2-octyloxysilane [8 g.; α_D^{18} +17·08°; from (+)-alcohol, α_D^{18} +7·76°] in pentane (15 c.c.) for 3 hours at −10° gave small amounts of silica and a mixture (0·5 g.) of alcohol and bromide, b. p. 80°/15 mm., α_D^{18} +4·6° (Found : Br, 11·3%); the tetra-ester (5·1 g.), b. p. 185°/0·5 mm., containing probably a little bromosilane, $(RO)_3SiBr$ (Found : Br, 4·6%), was in the main recovered. There was a residue (2·0 g.) which gelled on being cooled.

Passage of hydrogen iodide through (+)-tetra-2-octyloxysilane (5·44 g.; α_D^{18} +17·08°) for 2 hours at −10° caused the precipitation of hydrated silica (0·75 g. Calc. as SiO_2,H_2O, 0·78 g.) (Found : SiO_2, 77·4. Calc. for SiO_2,H_2O : SiO_2, 76·9%). From the washed and dried pentane filtrate, a mixture of alcohol and iodide (2·5 g.), b. p. 84—90°/17 mm., α_D^{18} −27·36° (Found : I, 30·7%), and the iodide (3·5 g.), b. p. 90—94°/17 mm., α_D^{18} −35·4° (Found : I, 51·4. Calc. for $C_8H_{17}I$: I, 52·9%), were obtained. Some loss of material is attributable to adsorption on the silica, the leaching solvents not being incorporated with the primary pentane filtrate.

Silicon tetrachloride (8·5 g., 0·25 mol.) in *n*-pentane (10 c.c.) was added dropwise to a pentane (50 c.c.) solution of (+)-1-phenylethanol (24·4 g., 1 mol.; α_D^{18} +24·0°) and pyridine (15·8 g., 1 mol.) at −10°, with vigorous stirring. Precipitation of pyridine hydrochloride occurred immediately, and after 1 hour it (20·9 g.) (Found : Cl, 30·7. C_5H_5N, 68·1%) was separated by filtration.

From the filtrate, (+)-alcohol (2·0 g.), b. p. 95°/12 mm., α_D^{18} +22·12°, and (+)-*tetra*-1-*phenylethoxysilane* (20 g.) (see table), b. p. 220°/0·2 mm., α_D^{18} +59·0°, were obtained. Formation of chloride was not detected.

This silane (5 g.) was heated with alcoholic potassium hydroxide as described for the 2-octyl analogue, but hydrolysis was much slower, 24 hours being required. The (+)-alcohol (96%), b. p. 93°/12 mm., α_D^{20} +23·6°, was obtained.

The silane (5 g.), when heated under reflux for 12 hours with an alcoholic solution of hydrochloric acid (5% of concentrated acid in alcohol), afforded (−)-1-chloro-1-phenylethane (4·0 g.), b. p. 80°/25—20 mm., α_D^{18} −2·32° (Found : Cl, 25·1. Calc. : Cl, 25·3%).

(+)-Tetra-1-phenylethoxysilane (5·12 g.; α_D^{18} +57·2°) in pentane (25 c.c.) afforded a steady precipitation of hydrated silica (0·74 g. Calc. : 0·78 g.) and (−)-1-chloro-1-phenylethane (4·5 g.), b. p. 80°/25 mm., α_D^{18} −3·92° (Found : Cl, 24·9. Calc. for C_8H_9Cl : Cl, 25·3%), whilst hydrogen chloride was passed through the mixture for 3 hours at −10°. The loss of material by adsorption on the silica (see previous statement) being considered, the yield of chloride, based on the weight of hydrated silica, was about 94%.

Passage of hydrogen bromide into (+)-tetra-1-phenylethyloxysilane (8·0 g.; α_D^{18} +59·0°; from alcohol, α_D^{18} +24·0°) at −10° afforded (−)-1-bromo-1-phenylethane (8·5 g.), b. p. 88°/14 mm., α_D^{18} −1·0° (Found : Br, 43·4. Calc. for C_8H_9Br : Br, 43·2%), and hydrated silica (0·95 g.).

(+)-Tetra-1-phenylethoxysilane (5·12 g.; α_D^{18} +59·0°) and hydrogen iodide afforded hydrated silica (0·75 g. Calc. : 0·78 g.) and what appeared to be the iodide, α_D^{18} 0° but, immediately after each washing and drying, iodine was liberated, and distillation was not successfully performed.

In the table are recorded results obtained when silicon tetrachloride (8·5 g., 0·25 mol.), the appropriate alcohol (1 mol.), and pyridine (15·8 g., 1 mol.) were mixed in pentane solution (50 c.c.) at −10°. The calculated amount of pyridine hydrochloride is 23·1 g.

Alcohol.	B. p./0·5 mm.	$(RO)_4Si$, yield, %.	Found, %. C.	Found, %. H.	Calc., %. C.	Calc., %. H.	C_5H_5N,HCl, g.
n-Butyl	106—108°	88	60·0	11·05	60·0	11·25	22·5
sec.-Butyl	86—88	94	60·0	11·23	60·0	11·25	22·3
*iso*Butyl	90—91	92	59·7	11·2	60·0	11·25	22·5
1-Octyl	205—210	96	70·7	12·5	70·6	12·5	22·8
2-Octyl	193	85	70·8	12·5	70·6	12·5	23·0
1 : 3-Dimethylbutyl	122	92	67·3	12·2	66·6	12·0	22·6
1-Carbethoxyethyl	178—179	92	48·6	7·1	48·4	7·25	22·8
1-Phenylethyl	220	77	74·8	7·2	75·0	7·1	20·9

Silicon tetrachloride (8·5 g., 0·25 mol.) in *n*-pentane (10 c.c.), added dropwise to a solution of 2-methylbutan-2-ol (17·6 g., 1 mol.) and pyridine (15·8 g., 1 mol.) in *n*-pentane (40 c.c.) at −10°, caused immediate precipitation of pyridine hydrochloride, but the amount (12·6 g.) (Found : Cl, 30·55. C_5H_5N, 68·2%), even after the mixture had been set aside at 15° for 12 hours, was only a half of that expected (23·1 g.). The filtered solution was distilled, and a mixture of pyridine and alcohol (14 g.), b. p. 100—118°, was first obtained, followed by dichlorodi-(2-methyl-2-butoxy)silane (10·5 g.), b. p. 112—115°/25 mm. (Found : Cl, 26·2; Si, 10·1. Calc. for $C_{10}H_{22}O_2Cl_2Si$: Cl, 26·0; Si, 10·25%). Miner, Bryan, Holysz, and Pedlow (*loc. cit.*) obtained their compound from reactants in the molecular ratios $SiCl_4$: ROH : C_5H_5N = 0·5 : 1 : 1, thereby effecting a complete removal of alcohol and pyridine. Our purpose was to give the reagents every opportunity to form the tetra-ester. We repeated the experiment with the proportions used by these workers and obtained pyridine hydrochloride (11·25 g. Calc. : 11·55 g.) and the chlorosilane, b. p. 112—115°/25 mm. (Found : Cl, 26·1%). The mixture obtained from silicon tetrachloride (4·25 g., 0·25 mol.), pyridine (7·9 g., 1 mol.), and the alcohol (20 g., 2·3 mols. excess) was heated under reflux for 4 hours in absence of solvent. Pentane was added and the precipitate (10·4 g.) (Found : Cl, 28·7; SiO_2, 4·1; C_5H_5N, 64·5%) was not pure hydrochloride. From the filtered solution, unchanged alcohol and pyridine, b. p. 100—117°, and chlorotri-(2-methyl-2-butoxy)silane (4·5 g.) b. p. 87—89°/0·5 mm. (Found : Cl, 11·1; Si, 8·4. Calc. : Cl, 10·94; Si, 8·6%), were obtained. There was a considerable amount of solid siliceous residue. Miner *et al.* (*loc. cit.*) obtained this chlorosilane by using pyridine and alcohol in proportions equivalent to three of the four atoms of chlorine in the tetrachloride. Our purpose was to eliminate the fourth atom as well.

It has been shown above that at room temperature only half the chlorine in silicon tetrachloride (0·25 mol.) is precipitated as pyridine hydrochloride in the interaction with the alcohol (1 mol.) in the presence of pyridine (1 mol.). When ethanol (0·5 mol.) was added to this mixture the remainder of the chlorine was readily precipitated as the hydrochloride (total weight, 11·3 g. Calc. : 11·55 g.).

Analogous results were obtained with *tert.*-butyl alcohol. This (1 mol.) with silicon tetrachloride (0·25 mol.) in the presence of pyridine (1 mol.) in pentane solution precipitated as pyridine hydrochloride only half of the chlorine present. Dichlorodi-*tert.*-butoxysilane can be obtained in good yield by the distillation of the filtered solution, b. p. 74°/18 mm. (cf. Miner *et al.*, who obtained this chlorosilane, b. p. 70°/15 mm., by using 0·5 mol. of tetrachloride for each mol. of alcohol and of pyridine). If, however, butan-2-ol (0·5 mol.) or 1-phenylethanol (0·5 mol.) is added to the undistilled mixture, precipitation of pyridine hydrochloride continues (21·3 g. Calc. : 23·1 g.) and accounts for nearly all the chlorine present.

Interaction of Silicon Tetrachloride and Alcohols in Absence of Pyridine.—(+)-Octan-2-ol (13·0 g., 1 mol.; α_D^{18} +8·0°) in *n*-pentane (20 c.c.) was added dropwise (1 hour) to a pentane (25 c.c.) solution of silicon tetrachloride (17 g., 1 mol.) at 0°. After an hour volatile matter was removed in a vacuum at 15°, and from the residue (+)-trichloro-2-octyloxysilane (15·5 g.), b. p. 100°/16 mm., α_D^{18} +14·0° (Found : Cl, 41·0; Si, 10·3. Calc. for $C_8H_{17}OCl_3Si$: Cl, 40·4; Si, 10·6%), and (+)-dichlorodi-2-octyloxysilane (5·0 g.), b. p. 118—120°/0·3 mm., α_D^{18} +17·6° [Found : Cl, 20·5; Si, 7·9. Calc. for $(C_8H_{17}O)_2SiCl_2$: Cl, 19·9; Si, 7·84%], were obtained. Formation of 2-chloro-octane was not observed.

(+)-Octan-2-ol (1·95 g., 1 mol.; α_D^{18} +8·0°) in *n*-pentane (5 c.c.) was added to dichloro-(+)-di-2-octyloxysilane (5·36 g., 1 mol.; α_D^{18} +17·6°) in pentane (10 c.c.) at −10°. The solution was allowed to warm to room temperature (1 hour) and dry air was gently aspirated through the liquid, the effluent gas being passed through an absorption tube. After an hour the liquid was distilled, (+)-chlorotri-2-

octyloxysilane (6·0 g., 89%), b. p. 148°/0·2 mm., α_D^{18} +18·32° [Found: Cl, 8·1; Si, 6·1. Calc. for $(C_8H_{17}O)_3SiCl$: Cl, 7·9; Si, 6·2%], being obtained. During the reaction 0·503 g. (Calc.: 0·548 g.) of hydrogen chloride was evolved. There was no indication of the formation of 2-chloro-octane. The trichlorosilane (6·36 g., 1 mol.), pyridine (5·22 g., 3 mol.), and octan-2-ol (8·6 g., 3 mols.) in pentane (35 c.c.) at −10° afforded pyridine hydrochloride (7·0 g. Calc.: 6·98 g.) (Found: Cl, 30·5; C_5H_5N, 68·2%) and the tetra-ester (12·0 g.), b. p. 190°/0·3 mm.

Whilst silicon tetrachloride (4·25 g., 0·25 mol.) in *n*-pentane (10 c.c.) was added dropwise to (+)-octan-2-ol (13·0 g., 1 mol.; α_D^{18} +7·8°) in *n*-pentane (30 c.c.) at −5°, hydrogen chloride was steadily evolved into an absorption tube. After the gentle aspiration of air for 1 hour at 15°, distillation afforded the tetra-ester (12·0 g.), b. p. 190°/0·3 mm., α_D^{18} +17·20° (Found: C, 70·7; H, 12·6%), which was the only distillate after the removal of pentane at 15°/15 mm. The absorption tube contained Cl, 3·02 g. (Calc.: Cl, 3·55 g.). 2-Chloro-octane was not formed.

(+)-1-Phenylethanol (18·3 g., 1 mol.; α_D^{18} +8·84°) dissolved in *n*-pentane (20 c.c.) was added with stirring to silicon tetrachloride (25·5 g., 1 mol.) in pentane (20 c.c.) at −10°. There was a copious evolution of hydrogen chloride, and gelatinous hydrated silica was formed. At the end of the addition, the latter was separated, washed with ethyl alcohol and ether, and dried in air; it then weighed 3·8 g., and corresponded to SiO_2,H_2O. From the primary filtrate, 1-chloro-1-phenylethane (13·5 g.), b. p. 73—74°/11 mm., α_D^{18} 0° (Found: Cl, 25·2. Calc. for C_8H_9Cl: Cl, 25·3%), fractions, b. p. 79—89°/11 mm. (2·2 g.), α_D^{18} +1·4° (rapidly gelled in contact with air), and b. p. 98—104°/11 mm. (2·4 g.), α_D^{18} +10·0° (believed to be the trichlorosilane, $RO{\cdot}SiCl_3$), and a residue (1·2 g.) which gelled on cooling, were obtained. The intermediate fractions gelled when kept in sealed tubes. The fraction, b. p. 98—104°/11 mm., after being kept sealed for a year, had separated into two layers, the upper being the racemised chloride, b. p. 73°/12 mm.

When the tetrachloride (2·83 g., 0·25 mol.) in pentane (5 c.c.) was added dropwise with stirring to the (+)-alcohol (8·14 g., 1 mol.; α_D^{18} +8·84°) in pentane (20 c.c.) at −10°, a gelatinous precipitate of hydrated silica was formed at each addition. After a further 30 minutes the mixture was filtered, and from the filtrate, by direct distillation, (−)-1-chloro-1-phenylethane (7·5 g.), b. p. 73°/12 mm., α_D^{18} −3·72° (Found: Cl, 25·1. Calc. for C_8H_9Cl: Cl, 25·3%), was obtained, but no silicon compounds were detected. The actual formation of chloride was much greater than recorded above (80%); the precipitated silica adsorbs the product, and considerable volumes of ethyl alcohol and ether were required to free the silica from adsorbed material. The leaching liquids were not incorporated with the primary filtrate. From the weight of hydrated silica (SiO_2,H_2O) (1·20 g. Calc.: 1·30 g.) the amount of chloride formed was 92%.

Silicon tetrachloride (8·5 g., 0·25 mol.) in pentane (10 c.c.) was added dropwise to *tert.*-amyl alcohol (17·6 g., 1 mol.) in pentane (30 c.c.) at −10°. Apparently, there was no reaction, not even at 0°; but at room temperature a reaction became vigorous and was difficult to control. Hydrated silica (3·57 g. Calc.: SiO_2,H_2O, 3·90 g.) separated and was treated as described above. The filtrate afforded *tert.*-amyl chloride (15 g.), b. p. 85° (Found: Cl, 33·3. Calc. for $C_5H_{11}Cl$: Cl, 33·3%), but there was loss of product during fractionation. Based on weight of the hydrated silica the formation of the chloride was 91·5%.

Silicon tetrachloride (4·25 g., 0·25 mol.) in xylene (10 c.c.) was added with stirring to *tert.*-butyl alcohol (7·4 g., 1 mol.) in xylene (20 c.c.). Again reaction was slow in commencing even at 18°, and only at 40° did the reaction show obvious signs of occurrence; then it rapidly became vigorous. Analogously with the foregoing, hydrated silica (1·87 g. Calc.: 1·95 g.) and *tert.*-butyl chloride (6·7 g.), b. p. 51° (Found: Cl, 38·1. Calc. for C_4H_9Cl: Cl, 38·4%), were obtained.

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