

307. Correlation between Reactivity of the 1-Carbon Atom in Alcohols, and Certain Properties of Alkoxysilanes.

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The rate at which the entity ROH_2Cl forms alkyl chloride or hinders replacement of chlorine attached to silicon is important in chlorosilane systems. Alcohols with a phenyl group attached to the 1-carbon atom give alkyl chloride quickly, thus hindering formation of alkoxysilanes, and hydrogen chloride reacts with the silanes to give alkyl chloride directly or *via* the alcohol. Alcohols with a more remote phenyl group behave as does butan-1-ol, taken as an arbitrary standard of ordinary reactivity. Interaction between an alkoxytrimethylsilane and silicon tetrachloride gave chlorosilanes from 1-phenylethanol and diphenylmethanol, the first reported examples of chloro-esters of reactive alcohols in inorganic non-metal halide systems.

THE reactivity of the 1-carbon atom in an alcohol is governed by the kind as well as the number of substituents attached to it.^{1,2} In silane chemistry alcohols containing a phenyl group remote from the 1-carbon atom (excluding examples in which a double bond is interposed) behave as *n*-butanol, considered as an arbitrary standard of *ordinary* reactivity, and afford the tetra-alkoxysilane with silicon tetrachloride alone,³ whereas those with a phenyl group attached to the 1-carbon atom (except benzyl alcohol which is somewhat peculiar) give alkyl chloride and silica, accompanied in some cases by other products. Thus 1-phenylethanol gives alkyl chloride and hydrated silica,⁴ as *tert.*-butyl alcohol does; diphenylmethanol gives chlorodiphenylmethane and bisdiphenylmethyl ether;³ yet benzyl alcohol gives the alkoxysilane. Probably owing to an electromeric effect the silane could not be obtained from cinnamyl alcohol in absence of base. In the presence of pyridine the tetra-alkoxysilanes were prepared in good yield from primary and secondary alcohols, whereas reaction with 2-phenylbutan-2-ol gives only the dialkoxy-compound, as has previously been shown for *tert.*-butyl alcohol.^{4,5}

With trimethylchlorosilane the reactive alcohols gave alkyl chloride, and the others did not give good yields of alkoxytrimethylsilane, presumably because of intervention by hydrogen chloride, and attempts to remove the gas at low pressure removed also the volatile chlorosilane. In the presence of pyridine, good yields of alkoxysilanes were obtained (see Table).

¹ Gerrard and Shepherd, *J.*, 1953, 2069; Gerrard, Green, and Phillips, *J.*, 1954, 1148; Gerrard and Howe, *J.*, 1955, 505.

² Gerrard, Madden, and Tolcher, *J. Appl. Chem.*, 1955, 5, 28.

³ Gerrard and Kilburn, *Research*, 1954, 7, 57 s.

⁴ Gerrard and Woodhead, *J.*, 1951, 519.

⁵ Miner, Brian, Holysz, and Pedlow, *Ind. Eng. Chem.*, 1947, 39, 1368.

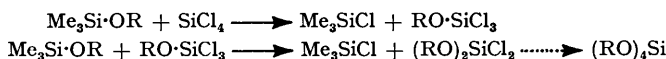
Preparation of alkoxytrimethylsilanes.

Alcohol	Yield (%)	B. p./mm.	n_D^{20}	n_D^{20}	Found		(CH ₃) ₃ Si·OR requires	
					C (%)	H (%)	C (%)	H (%)
Bu ^t OH	78	101°/754	—	1.3913	57.6	12.1	57.6	12.3
Benzyl alcohol	84	92°/19	0.9205	1.4773	67.4	8.9	66.7	8.9
2-Phenylethanol	85	102°/18	0.9086	1.4739	68.2	9.3	68.1	9.3
3-Phenylpropanol	88	118°/19	0.9073	1.4744	69.7	9.8	69.3	9.6
1-Phenylethanol	85	91°/14	0.9059	1.4702	68.1	9.1	68.1	9.3
1-Phenylpropan-2-ol	79	102°/18	0.8974	1.4690	69.5	9.6	69.3	9.6
Cinnamyl alcohol	79	128°/15	0.9375	1.5105	69.8	8.8	69.8	8.7
2-Phenylbutan-2-ol	72	108°/16	0.9153	1.4805	71.1	9.8	70.4	9.9
Diphenylmethanol	89	111°/0.6	0.9903	1.5290	75.5	7.5	74.9	7.8
1 : 2-Diphenylethanol	85	90°/0.005	0.9733	1.5198	76.1	8.2	75.6	8.15
1 : 3-Diphenylpropan-2-ol...	70	99°/0.02	0.9864	1.5281	76.4	8.15	76.0	8.45

(m. p. 35°)

Analogously with the interaction of hydrogen chloride and the tetra-alkoxysilanes,³ the alkoxytrimethylsilanes, afforded trimethylchlorosilane and either the alcohol from esters with a remotely attached phenyl group (except cinnamyl derivative), or the alkyl chloride from esters with a 1-phenyl group (but also the cinnamyl compound), and in the latter cases it is conceivable that alcohol is first formed and then quickly converted into alkyl chloride.

The interaction of a tetra-alkoxysilane and silicon tetrachloride has long been formulated as a means of preparing alkoxychlorosilanes, but the reaction is slow even at 150° for the *n*-butyl ester,⁶ and we now show that with the (phenylalkoxy)silanes reaction occurs slowly at 60° (7 days), those with a 1-phenyl group giving alkyl chloride, those with a more remote group giving chlorosilanes. Of more interest is the quicker interaction of silicon tetrachloride (1 mol.) and the alkoxytrimethylsilanes (4 mols.) :



Silanes with a remote phenyl group give the tetra-esters. The tetra-ester was obtained from the benzyl ester, but from the 1-phenylethyl ester chlorotri-(1-phenylethoxy)silane was obtained. This is the first recorded example of such a chloro-ester in the 1-phenylethanol-inorganic non-metal halide systems. We attribute success in this instance to the complete absence of hydrogen chloride. Similar remarks apply to chlorotri(diphenylmethoxy)silane which was likewise obtained. Even the 2-phenylbutan-2-ol ester afforded trimethylchlorosilane and a product which did not decompose until heated to 130°, whereupon it gave 2-phenylbut-2-ene. The cinnamyl ester gave the tetra-ester, and the 1 : 3-diphenylpropan-2-ol ester gave the dichlorosilane.

The alkoxytriphenylsilane system was examined, but gave no additional information of relevance.

EXPERIMENTAL

Tetra-alkoxysilanes.—The silanes used were those already described ; ³ *tetracinnamyloxysilane* (crude, 95% ; pure, 81%), m. p. 84° (from *n*-hexane) (Found : C, 76.5 ; H, 6.5 ; Si, 5.0. C₃₆H₃₆O₄Si requires C, 77.2 ; H, 6.4 ; Si, 5.0%), was obtained from the alcohol (4 mols.), pyridine (4 mols.) and silicon tetrachloride (1 mol.). 2-Phenylbutan-2-ol gave slowly a precipitate of pyridine hydrochloride in only 50% yield ; violent decomposition occurred at 125°/0.2 mm. Tetrabenzoyloxysilane had m. p. 31.5° (from *n*-hexane at -60°).

Passage of hydrogen chloride into a suspension of tetracinnamyloxysilane in *n*-hexane at 20° gave cinnamyl chloride (53%), b. p. 42°/0.02 mm. (Found : Cl, 22.8. Calc. for C₉H₉Cl : Cl, 23.2%). The silane could not be obtained by the interaction of cinnamyl alcohol and silicon tetrachloride in ether at 20°.

Silicon tetrachloride (1 mol. ; in ether, 10 mols.) was added dropwise to 2-phenylbutan-2-ol (23.6 g., 1 mol. ; in ether, 50 mols.) at 20°. Volatile matter was immediately withdrawn at 20°/15 mm., hydrogen chloride (83%) being evolved, and the residue was extracted with *n*-hexane. The final residue, on ignition, gave silica (94%). The solution afforded 2-phenylbut-2-ene (96%), b. p. 77°/15 mm., n_D^{20} 1.4345 (Found : C, 90.6 ; H, 9.3. Calc. for C₁₀H₁₂ :

⁶ Gerrard and Jones, *J.*, 1952, 1690.

C, 90.9; H, 9.1%), oxidised by potassium permanganate to acetophenone (3:5-dinitrophenylhydrazone, m. p. 237—238°).

Interaction of Silicon Tetrachloride and Tetra-alkoxysilanes.—The tetrachloride (1 mol.) and tetrabenzoyloxysilane (1 mol.) were mixed; the container was sealed and kept at 60° for 7 days. Soluble matter was extracted by *n*-hexane in a Soxhlet apparatus, and on ignition the residue afforded silica (82%). Benzyl chloride (88%), b. p. 64°/12 mm. (Found: Cl, 27.8. Calc. for C_7H_7Cl : Cl, 28.0%), was obtained from the solution.

Tetra-(1-phenylethoxy)silane (7.86 g. 1 mol.) gave silica (92%), 1-chloro-1-phenylethane (1.32 g.), b. p. 64°/10 mm. (Found: Cl, 25.0. Calc. for C_8H_9Cl : Cl, 25.3%), and polystyrene (3.73 g.). (Extraction was by chloroform.)

Tetracinnamyloxysilane (4.52 g., 1 mol.) gave silica (98%), cinnamyl chloride (0.95 g.), b. p. 60°/0.07 mm., n_D^{20} 1.5642 (Found: Cl, 23.4. Calc. for C_9H_9Cl : Cl, 23.3%), and other products. (Extraction was by chloroform.)

Tetra(diphenylmethoxy)silane (4.02 g., 1 mol.) gave silica (68%), diphenylmethyl chloride (2.58 g.), b. p. 106°/0.4 mm., n_D^{20} 1.5960 (Found: Cl, 17.3. Calc. for $C_{13}H_{11}Cl$: Cl, 17.5%), and a residue (1.0 g.). (Extraction was by ether.)

Tetra-(1:2-diphenylethoxy)silane (3.40 g.) gave hydrogen chloride at considerable pressure in the tube. Silica (99%), 1:2-diphenylethyl chloride (0.21 g.), which could not be purified, and *sym*-hexaphenylcyclohexane (1.12 g.), b. p. 229°/0.03 mm. (Found: C, 92.6; H, 7.1. Calc. for $C_{42}H_{36}$: C, 93.4; H, 6.6%) (Found: *M*, 527. Calc.: *M*, 540), were obtained. (Extraction was by *n*-pentane, then chloroform.)

Tetra-(2-phenylethoxy)silane (6.65 g.) gave a mixture from which unchanged silicon tetrachloride (1.21 g.) was removed at 20°/0.07 mm., and then *trichloro-2-phenylethoxysilane* (1.39 g.), b. p. 74—80°/0.07 mm., n_D^{20} 1.4950 (Found: Cl, 40.6; Si, 10.7. $C_9H_9OCl_3Si$ requires Cl, 41.7; Si, 10.9%), mixtures of the lower chlorosilanes containing diminishing amounts of chlorine and silicon, unchanged alkoxyxilane (3.0 g.), and a residue (1.26 g.) were obtained.

Tetra-3-phenylpropoxysilane (7.10 g.) gave *trichloro-3-phenylpropoxysilane* (0.34 g.), b. p. 40°/0.02 mm. (Found: Cl, 38.9. $C_9H_{11}OCl_3Si$ requires Cl, 39.5%), *dichlorodi-(3-phenylpropoxy)silane* (0.28 g.), b. p. 140°/4 × 10⁻³ mm., n_D^{20} 1.5224 (Found: Cl, 19.3; Si, 7.5. $C_{18}H_{22}O_2Cl_2Si$ requires Cl, 19.3; Si, 7.6%), and mixtures (total, 4.5 g.) of the latter with the monochlorosilane.

Tetra-(1-methyl-2-phenylethoxy)silane (7.16 g.) gave *trichloro-1-methyl-2-phenylethoxysilane* (0.54 g.), b. p. 56°/0.03 mm. (Found: Cl, 38.6. $C_9H_{11}OCl_3Si$ requires Cl, 39.5%), *dichlorodi-(1-methyl-2-phenylethoxy)silane* (5.9 g.), b. p. 111°/0.01 mm., n_D^{20} 1.5144, d_4^{20} 1.1340 (Found: C, 59.3; H, 6.0; Cl, 19.4; Si, 7.6. $C_{18}H_{26}O_2Cl_2Si$ requires C, 58.7; H, 6.0; Cl, 19.3; Si, 7.6), a mixture (1.52 g.) of this silane with monochlorosilane, and a residue (1.24 g.) (Found: Si, 9.7%).

Tetra-1-benzyl-2-phenylethoxysilane (4.55 g.) gave mixtures of chlorosilanes which were difficult to fractionate. The impure *trichlorosilane* (1.16 g.), b. p. 114—116°/0.01 mm., *di-(1-benzyl-2-phenylethoxy)dichlorosilane* (1.32 g.), b. p. 210°/0.01 mm., n_D^{20} 1.5645, d_4^{20} 1.445 (Found: Cl, 13.7; Si, 5.2. $C_{30}H_{30}O_2Cl_2Si$ requires Cl, 13.6; Si, 5.4%), *tri-(1-benzyl-2-phenylethoxy)chlorosilane* (0.42 g.), b. p. 240—250°/0.01 mm. (Found: Si, 4.0. Calc. for $C_{45}H_{45}O_3ClSi$: Si, 4.0%), and a residue (1.58 g.) were obtained.

Preparation of Alkoxytrimethylsilanes.—Trimethylchlorosilane (1 mol.) in ether (4 mols.) was added dropwise to the alcohol (1 mol.) and pyridine (1 mol.) in ether (30 mols.) at 15°. Only 80—85% (or less in some cases) of the calculated amount of pyridine hydrochloride was immediately precipitated, and even after the mixture had been set aside for 12 hr., the yield was nearly always less than 95%. This corresponded with the presence of about 5% of alcohol, and owing to the formation of an azeotrope a considerable amount of the silane had to be rejected during distillation. Consequently the yields given in the Table are less than the amounts of silanes actually formed. Alcohol in the crude product was also removed by heating the liquid with pyridine and chlorosilane for 2 hr. at 60°. The product was decanted from the base hydrochloride, and distilled.

Interaction of Hydrogen Chloride and Alkoxytrimethylsilane.—Dry hydrogen chloride was passed into the ester for 90 min. at -10°; trimethylchlorosilane (77—90% yield) was trapped at -80°. There were mainly two types of result: formation of alcohol, Bu^a , $Ph\cdot CH_2\cdot CH_2$, $Ph\cdot CH_2\cdot CH_2\cdot CH_2$, $(Ph\cdot CH_2)_2CH$, $Ph\cdot CH_2\cdot CHPh$; or formation of alkyl chloride, $Ph\cdot CH_2$, $Ph\cdot CHMe$, $Ph\cdot CH_2\cdot CHMe$, $Ph\cdot CH\cdot CH\cdot CH_2$, $Ph\cdot CEtMe$, Ph_2CH .

Interaction of Silicon Tetrachloride and Alkoxytrimethylsilane.—The tetrachloride (1 mol.) and alkoxyxilane (4 mols.) were mixed at room temperature. After the stated time interval, trimethylchlorosilane was withdrawn at 0.3 mm. and trapped at -80° (Found: Cl, 32.4 ± 0.4%), and the residue was distilled.

The benzyl ester (9.00 g.) (24 hr.) gave tetrabenzoyloxysilane (4.38 g.), b. p. 210—212°/0.1 mm., n_D^{20} 1.5599 (Found: Si, 6.2. Calc. for $C_{28}H_{28}O_4Si$: Si, 6.1%); the 2-phenylethyl ester (9.70 g.) (2.5 hr.) gave tetra-(2-phenylethoxy)silane (5.46 g.), b. p. 226°/10⁻³ mm., n_D^{20} 1.5480 (Found: Si, 5.7. Calc. for $C_{32}H_{36}O_4Si$: Si, 5.5%); the 3-phenylpropyl ester (10.4 g.) (16 hr.) gave tetra-3-phenylpropoxysilane (5.88 g.), b. p. 186—195°/10⁻⁵ mm., n_D^{19} 1.5402 (Found: C, 76.8; H, 7.8; Si, 5.1. Calc. for $C_{36}H_{44}O_4Si$: C, 76.2; H, 7.75; Si, 4.9%); the 1-phenylethyl ester (3.59 g.) (14 hr.) gave *chlorotri-(1-phenylethoxy)silane* (1.80 g.), b. p. 185°/0.07 mm., n_D^{20} 1.5347 (Found: Cl, 8.0; Si, 6.5. $C_{24}H_{27}O_3ClSi$ requires Cl, 8.3; Si, 6.6%); and the 1-methyl-2-phenylethyl ester (10.4 g.) gave a very slowly separable mixture (1.23 g.), b. p. 180—210°/5 × 10⁻³ mm., of chlorosilane and tetra-ester (Found: Cl, 6.1%), and tetra-(1-methyl-2-phenylethoxy)silane (5.02 g.), b. p. 210—212°/5 × 10⁻³ mm., n_D^{20} 1.5312 (Found: Si, 5.0. Calc. for $C_{36}H_{44}O_4Si$: Si, 4.9%). The cinnamyl ester (9.5 g.) (16 hr.) evolved heat on mixing, and eventually gave a white solid which after being crushed gave trimethylchlorosilane (2.31 g.) and tetracinnamyloxysilane (5.47 g.), m. p. 84—85° (from *n*-hexane) (Found: C, 76.5; H, 6.4; Si, 5.1. Calc. for $C_{36}H_{36}O_4Si$: C, 77.2; H, 6.4; Si, 5.0%). The diphenylmethyl ester (13.6 g.) (14 hr.) gave *chlorotri(diphenylmethoxy)silane* (5.71 g.), m. p. 99—100° (from *n*-heptane) (Found: C, 76.4; H, 5.8; Cl, 5.7; Si, 4.5. $C_{30}H_{33}O_3ClSi$ requires C, 76.4; H, 5.4; Cl, 5.8; Si, 4.6%).

The 1-methyl-2-phenylethyl ester (5.23 g.) (3 hr.) gave unchanged ester (1.57 g.), and dichloro-di-(1-methyl-2-phenylethoxy)silane (2.34 g.) b. p. 240—250°/0.03 mm., n_D^{20} 1.5755 (Found: Cl, 12.5; Si, 5.2. Calc. for $C_{30}H_{30}O_2Cl_2Si$: Cl, 13.6; Si, 5.4%). The 1:2-diphenylethyl ester (1.92 g.) (16 hr.) gave decomposition products, comprising alkyl chloride and stilbene, m. p. 123—125° (from *n*-hexane). The 1-methyl-1-phenylpropyl ester (11.1 g.) (5 days) gave trimethylchlorosilane (1.45 g.), and at 130° violent effervescence occurred, silica (ignited, 0.70 g., 95%) was precipitated, and trimethylchlorosilane (3.02 g.), 2-phenylbut-2-ene (4.0 g.), b. p. 78°/14 mm., n_D^{20} 1.5290 [oxidised by chromium trioxide in acetic acid to acetophenone (2:4-dinitrophenylhydrazone, m. p. 238°)], and a mixture (2.92 g.) of 2-phenylbut-2-ene and 2-chloro-2-phenylbutane, b. p. 78—82°/14 mm. (Found: Cl, 6.8%), were obtained.

tert.-Butoxysilanes.—Hydrogen chloride was passed into *tert.*-butoxytrichlorosilane b. p. 132—134°, n_D^{20} 1.4145 (Found: Cl, 51.1. Calc. for $C_4H_9OCl_3Si$: Cl, 51.4%) (7.76 g.), for 6 hr. at 21°, and *tert.*-butyl chloride (35%), b. p. 50—51° (Found: Cl, 37.8. Calc. for C_4H_9Cl : Cl, 38.4%), was trapped at -80°, leaving a viscous gel (6.0 g.).

Hydrogen chloride was passed into di-*tert.*-butoxydichlorosilane, b. p. 62°/10 mm. (Found: Cl, 28.7. Calc. for $C_8H_{18}O_2Cl_2Si$: Cl, 28.9%) (13.7 g.), for 2 hr. at 6°, and *tert.*-butyl chloride (81%), b. p. 50—51° (Found: Cl, 37.7%), was condensed at -80°.

The dichlorosilane (7.3 g., 1 mol.) and *tert.*-butyl alcohol (4.4 g., 2 mols.), heated under reflux at 80° for 1 hr., gave *tert.*-butyl chloride (4.25 g.), b. p. 50—51° (Found: Cl, 37.8%), and silica gel (2.2 g.) (ignited to silica, 1.40 g., 78%).

Alkoxytriphenylsilanes.—These were prepared from the alcohol (1 mol.), pyridine (1 mol.), and triphenylchlorosilane (1 mol.) in ether (30 mols.) at 0°, base hydrochloride being precipitated much more slowly than with trimethylchlorosilane.

Hydrogen chloride was passed into *triphenyl-2-phenylethoxysilane*, b. p. 185°/0.01 mm., m. p. 56—57° (after recrystallisation from *n*-heptane at -60°) (Found: C, 82.2; H, 6.2; Si, 7.4. $C_{26}H_{24}OSi$ requires C, 82.2; H, 6.3; Si, 7.4%) (3.72 g.) in *n*-heptane (15 c.c.) at 16° for 1 hr. Chlorotriphenylsilane (38%) was filtered off and 2-phenylethanol (36%), b. p. 45°/0.05 mm., and unchanged silane (60%) were obtained from the filtrate. From the silane (5.07 g., 4 mols.) and tetrachloride (1 mol.) (sealed tube at 60° for 7 days), the chlorotriphenylsilane (80%), m. p. 104°, and tetra-2-phenylethoxysilane (1.93 g.), b. p. 250°/0.03 mm. (Found: Si, 5.6. Calc. for $C_{32}H_{36}O_4Si$: Si, 5.5%), were obtained. Similarly benzyloxytriphenylsilane (3.3 g.) gave chlorotriphenylsilane (83%), m. p. 104—105° (Found: Cl, 11.9; Si, 9.55. Calc. for $C_{18}H_{15}ClSi$: Cl, 12.0; Si, 9.5%), unchanged silane (0.6 g.) (Found: Si, 7.7%), and tetrabenzoyloxysilane (0.6 g.), b. p. 210°/0.01 mm. (Found: Si, 6.3. Calc. for $C_{28}H_{28}O_4Si$: Si, 6.1%). *Diphenylmethoxytriphenylsilane* (64%), b. p. 210—212°/0.01 mm., n_D^{20} 1.6252, d_4^{20} 1.085 (Found: C, 84.4; H, 5.8. $C_{31}H_{26}OSi$ requires C, 84.2; H, 5.9%) (2.20 g.), afforded hexaphenyldisiloxane (0.62 g.), m. p. 230° (from *n*-heptane) (Found: C, 81.5; H, 5.8. Calc. for $C_{36}H_{30}O_2Si$: C, 80.9; H, 5.6%), diphenylmethyl chloride (49%), b. p. 99—100°/0.2 mm., n_D^{20} 1.5978 (Found: Cl, 17.0. Calc. for $C_{13}H_{11}Cl$: Cl, 17.5%), and unchanged silane (0.39 g.), b. p. 200—220°/0.2 mm.

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