The Solvolysis of Silicon Substituted 2-Silylpyridines by Alcohols and by Water

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2-Dimethyl-, 2-triethyl-, and 2-triphenyl-silylpyridine react with hydroxylic solvents in a similar manner to 2-trimethylsilylpyridine. The rates of methanolysis are in the order dimethyl- > trimethyl- > triphenyl- > triethyl-silylpyridine. For the alkyl substituents, steric or electronic effects could be the dominant factor. The triphenyl compound is less reactive in this than in other nucleophilic substitutions, probably because the cyclic activated complex for this reaction will involve crowding of the phenyl groups. Formation of a cyclic activated complex is supported by the enthalpies and entropies of activation.

2-TRIMETHYLSILYLPYRIDINE and the germanium and tin analogues react with water, methanol, and ethanol to give pyridine and the corresponding organometallic hydroxide or alkoxide.[1-4] The experimental features, reported in detail elsewhere,[1,4] are that (i) only the 2-substituted pyridines react, (ii) the reaction is inhibited by added acid, (iii) added base has no effect, (iv) the reaction is first order in silane, (v) the activation entropy is large and negative, (vi) there is no primary isotope effect, (viii) there is a marked decrease in the reaction rate from water to methanol to ethanol to higher alcohols, and (viii) retention of configuration at silicon occurs if an optically active silane is used. These features are readily accounted for by a mechanism which involves nucleophilic substitution by oxygen of the solvent on silicon, with electrophilic assistance by hydrogen of the solvent on nitrogen, through a 5-centred cyclic activated complex A. We have examined the effect of silicon substituents other than methyl on the kinetics of these reactions.

RESULTS AND DISCUSSION

The Solvolyses of 2-Dimethylsilylpyridine.—For this compound there exists the possibility of an alternative reaction, the solvolysis of the silicon–hydrogen bond:

$$2\text{-}C_5H_4N{\cdot}SiMe_2H + R^2OH \longrightarrow 2\text{-}C_5H_4N{\cdot}SiMe_2OR^2 + H_2$$

This reaction did not occur; the n.m.r. spectrum of the product of the methanolysis was that of dimethylmethoxysilane. Also no gas bubbles were formed in the solution during any of these studies.

The hydrolysis was much too rapid to be studied by our technique. Second-order rate constants for the ethanolysis and the methanolysis calculated from the observed first-order rate constants (see ref. 1), and activation parameters are given in the Table. The proposed mechanism of this reaction[1] is consistent with these results. Note the very low activation enthalpy and very large negative activation entropy for the ethanolysis.

The solvolyses of 2-Triethylsilyl- and 2-Triphenylsilylpyridine.—2-Triethylsilylpyridine has a very low solubility in water; for the hydrolysis a solution in ethanol (a drop) was added to water (*ca.* 2 c.c.) in the reaction cell. Second-order rate constants for the hydrolysis and activation parameters calculated from them are given in the Table. The low activation enthalpy and high negative activation entropy again support the proposed reaction mechanism. The methanolysis of 2-triethylsilylpyridine was too slow to be studied by our technique.

Rate constants and activation parameters at 50° for the solvolysis of 2-($R^1R^2{}_2Si$)C_5H_4N

R^1	R^2	Solvent	Temp. (±0·02°)	10^6k_2 [a] (l. mole^{-1} sec.$^{-1}$)	$\Delta H^‡$ [b] (kcal. mole^{-1})	$\Delta S^‡$ [b] (cal. mole^{-1} deg.$^{-1}$)
H	Me	MeOH	49·84°	745		
H	Me	MeOH	39·98	342		
H	Me	MeOH	30·16	159	14·6	−28
H	Me	EtOH	49·90	27·4		
H	Me	EtOH	40·28	17·8		
H	Me	EtOH	30·38	10·9	8·6	−53
Et	Et	H_2O [c]	69·97	5·29		
Et	Et	H_2O [c]	60·04	2·80		
Et	Et	H_2O [c]	50·10	1·57	12·8	−46
Ph	Ph	MeOH	50·00	0·503		
Me	Me	H_2O [c]	50·20	45·0 [d]	16·1	−29
Me	Me	MeOH	50·04	7·24 [d]	12·9	−42
Me	Me	EtOH	50·10	*ca.* 0·07 [d]		

[a] Obtained from the observed first-order rate constants (k_1) by dividing k_1 by the appropriate molarity of the solvent. [b] The standard deviation of $\Delta H^‡$ is <0·5 kcal. mole^{-1}, and that of $\Delta S^‡$ is <1 cal. mole^{-1} deg.$^{-1}$. [c] 2×10^{-3}M-Sodium hydroxide solution (see ref. 1). [d] From ref. 1.

2-Triphenylsilylpyridine is insoluble in water and has a very low solubility in methanol; a *ca.* 10^{-4}M-solution could not be obtained for an accurate kinetic study, but methanolysis did occur and a rate-constant is given in the Table. This rate constant is at least ten times that for 2-triethylsilylpyridine.

Relative Reactivities.—The ratio of the rate of methanolysis to that of ethanolysis of 2-dimethylsilylpyridine is 21(±6) : 1 over a 20° temperature range (Table). The enthalpy of activation becomes much smaller and the entropy of activation becomes much more negative when the solvent is changed from methanol to ethanol (Table). The dominant feature in determining the relative rates is the decrease in the activation entropy, as was found for the solvolysis of 2-trimethylsilylpyridine,[1] and contrary to that found for 2-trimethylstannylpyridine.[3]

The Table also contains selected data for the solvolysis of 2-trimethylsilylpyridine.[1] The relative rates of solvolysis of 2-(substituted silyl)pyridines (at 50°) are triethyl 1, trimethyl 29, in water; triphenyl 0·07,

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[1] D. G. Anderson, M. A. M. Bradney, and D. E. Webster, *J. Chem. Soc.* (*B*), 1968, 450.

[2] D. G. Anderson, M. A. M. Bradney, B. A. Loveland, and D. E. Webster, *Chem. and Ind.*, 1964, 505.

[3] D. G. Anderson and D. E. Webster, *J. Chem. Soc.* (*B*), 1968, 765.

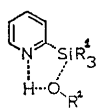
[4] D. G. Anderson and D. E. Webster, *J. Chem. Soc.* (*B*), in the press.

trimethyl 1, dimethyl 103 in methanol; and trimethyl 1, dimethyl 390 in ethanol. Hence for the methanolysis the reactivities are in the order triethyl < triphenyl < trimethyl < dimethyl. This reactivity sequence is also likely for hydrolysis and ethanolysis; only the position of 2-triphenylsilylpyridine is in doubt.

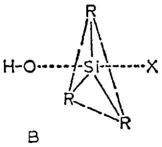
The sequence triethyl < trimethyl < dimethyl is consistent with that expected for facilitation of reaction by the decrease in the inductive electron release of the alkyl groups. It is also the sequence expected if steric hindrance to attack at silicon is important. Steric effects appear to be dominant for other nucleophilic substitutions at silicon,[5,6]* and they may be responsible for the relative reactivities reported here, as it can be seen from the Table that the increase in rate is due to a dominant decrease in the activation entropy (in water for the triethyl and trimethyl compounds, and in methanol for the trimethyl and dimethyl compounds).

In a number of nucleophilic substitutions at silicon the triphenylsilyl compound is more reactive than the corresponding trialkylsilyl compounds.[8-11] For this reaction 2-triphenylsilylpyridine is more reactive than 2-triethylsilylpyridine but less reactive than 2-trimethylsilylpyridine [the ratio of the reactivity of 2-trimethyl- to that of 2-triphenyl-silylpyridine is 15 : 1 (Table)]. A quantitative comparison of the trimethyl- and triphenylsilyl groups for another nucleophilic substitution, alkaline solvolysis of trimethyl- and triphenyl-silane, is possible by combining the results of Schott and Harzdorf[10] (who report relative rates for the alkaline solvolysis of trisubstituted silanes in 7·8 wt.% aqueous ethanol at 20°: triethyl 1, triphenyl *ca.* 310) with that of Steward and Pierce,[12] (who report relative rates for the alkaline solvolysis of trisubstituted silanes in 6·3 wt.% aqueous ethanol at 0°: triethyl 1, trimethyl 20). The relative rates trimethyl 1, triphenyl 15 are obtained. This is the opposite of what is found for our solvolysis.

This difference can perhaps be explained by the structure of the activated complex in our reactions compared with that in others. We have proposed that our complex is cyclic as shown in A;† the complex for other nucleophilic substitutions is as shown in B. In B the non-reacting groups (R) have moved further apart than in the tetrahedral reactant molecule, whereas in A the non-reacting groups (R^1) have moved closer together. Steric crowding in the activated complex will probably be greater for the triphenylsilyl than for the trimethylsilyl compound, and this will probably invert the relative rates from the order expected from consideration of the electronic effects of phenyl and methyl substituents.



A



B

EXPERIMENTAL

2-*Triethylsilylpyridine.*—Triethylchlorosilane was prepared from silicon tetrachloride by way of tetraethoxysilane and hexaethyldisiloxane by a published method.[13] 2-Bromopyridine (33 g., 0·21 mole) in dry ether (25 c.c.) was added during 5 min. to n-butyl-lithium (0·21 mole) in dry ether (40 c.c.) at −50°. Triethylchlorosilane (30 g., 0·20 mole) was then added and the mixture was allowed to warm to room temperature and then heated under reflux for 1 hr. The lithium bromide was filtered off and the ether solution was fractionated to give 2-*triethylsilylpyridine* (4 g., 10%), b.p. 98°/6 mm., $n_D^{24\cdot8}$ 1·4957 (Found: C, 69·0; H, 10·0. $C_{11}H_{19}NSi$ requires C, 68·3; H, 9·9%).

2-*Triphenylsilylpyridine.*—Triphenylchlorosilane was prepared from diphenyldichlorosilane (1 mol.) and phenylmagnesium bromide (1 mol.). The triphenylchlorosilane is extracted by replacing the diethyl ether solvent with dry toluene, filtering off the magnesium halides, and concentrating the toluene solution; triphenylchlorosilane is then precipitated.[14] 2-*Triphenylsilylpyridine* was prepared like 2-triethylsilylpyridine by reaction of triphenylchlorosilane with 2-lithiopyridine. The mixture was allowed to warm to room temperature and heated at 40° for 1 hr.; the Gilman colour test A[15] was then negative. The mixture was hydrolysed and the brown precipitate was filtered off; it gave white crystals of 2-*triphenylsilylpyridine* (15%), m.p. 181° [from light petroleum (b.p. 80—100°)] (Found: C, 82·7; H, 6·1. $C_{23}H_{19}NSi$ requires C, 81·9; H, 5·7%).

2-*Dimethylsilylpyridine.*—This compound was prepared like 2-trimethylsilylpyridine,[1] by use of the same molar quantities. Fractional distillation of the product gave 2-*dimethylsilylpyridine* (30 g., 50%), b.p. 179°/762 mm., $n_D^{24\cdot8}$ 1·5000 (Found: C, 59·8; H, 8·2. $C_7H_{11}NSi$ requires C, 61·3; H, 8·1%).

The two liquids were further purified by preparative g.l.c. before use in kinetic studies. The n.m.r. spectra of the three compounds confirm the structures.

Kinetic Method.—This was as described previously.[1] For the fast reactions the reported modified technique was used.[3]

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* Steric effects are reported to be responsible for the decrease in reactivity of triethyl- compared with trimethyl-silyl compounds in electrophilic cleavage of the Si–C bond.[7]

† The hybridisation of the silicon will presumably approximate to sp^3d, and the complex may be trigonal bipyramidal ($sp^3d_{z^2}$) or square pyramidal ($sp^3d_{x^2-y^2}$).

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