The Solvolysis of 2-Pyridyltrimethyl-silane, -germane, and -stannane by Alcohols and by Water

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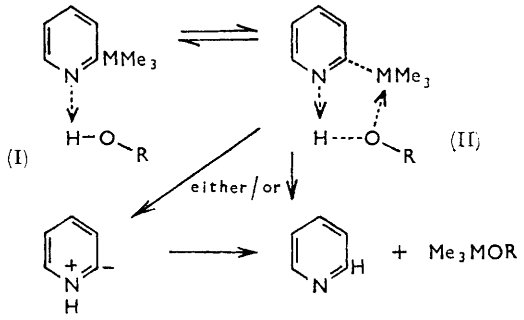
2-Pyridyltrimethyl-stannane and -germane, like the silane, react with water or methanol to give pyridine and trimethyltin(germanium) hydroxide or trimethyltin(germanium) methoxide. The relative rates of hydrolysis of 2-$Me_3MC_5H_4N$ (M = Si 1, Ge ~ 10^{-4}, Sn 22) are consistent with a reaction mechanism involving rate-determining nucleophilic substitution by the oxygen of the solvent on the metal through a 5-centred cyclic activated complex. Small activation enthalpies, high negative activation entropies, and the absence of a solvent isotope effect support this mechanism.

We recently reported[1] that, in water, methanol, or ethanol, 2-trimethylsilylpyridine reacts with the solvent to give pyridine and trimethylsilanol or the trimethylalkoxysilane. The mechanism proposed for the reaction (Scheme with M = Si, R = H, Me, or Et) 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 of structure close to the intermediate (II).



2-Trimethylstannylpyridine is also solvolysed, as is, at a much slower rate, 2-trimethylgermylpyridine.[2] A kinetic study of the solvolyses of these latter two compounds indicates that they react by a similar mechanism.

RESULTS AND DISCUSSION

The solvolysis of 2-trimethylstannylpyridine with water or alcohols gives pyridine and trimethyltin hydroxide or alkoxide. The reaction products have been identified by gas–liquid chromatography, and mass, n.m.r., and ultraviolet spectroscopy. The reactions with water, heavy water, methanol, or ethanol have been studied over a range of temperatures. Second-order rate constants, calculated from the observed first-order rate constants by dividing by the concentration of the solvent,[†] and activation parameters calculated from these rate constants, are given in the Table, which also contains selected rate constants and activation parameters for solvolyses of 2-trimethylsilylpyridine.[1]

2-Trimethylgermylpyridine and 4-methyl-2-trimethylgermylpyridine have also been prepared, and we have attempted to study their solvolyses. Unfortunately, the solvolysis rates were slow and a trace amount of an impurity with a high absorption in the ultraviolet was formed. From the small change in optical density measured during the early part of the reaction, we have estimated a value of the second-order rate constant for the hydrolysis of 2-trimethylgermylpyridine, and this is in the Table.[‡]

Rate constants and activation parameters at 50° for the solvolysis of 2-$Me_3MC_5H_4N$ (M = Si, Ge, or Sn) by H_2O, D_2O, MeOH, or EtOH

M	Solvent	Temp. (±0·02°)	10^6k_2 [a] (l. mole^{-1} sec.$^{-1}$)	$\Delta H^\ddagger$ [b] (kcal. mole^{-1})	$\Delta S^\ddagger$ [b] (cal. mole^{-1} deg.$^{-1}$)
Sn	H_2O	50°	1000 [c]		
,,	,,	39·98	541		
,,	,,	35·00	408		
,,	,,	30·00	293		
,,	,,	25·50	202	12·0	−35
,,	D_2O [d]	39·98	428		
,,	,,	35·00	330		
,,	,,	30·00	230	11·1	−39
,,	MeOH	60·40	15·0		
,,	,,	55·26	10·2		
,,	,,	50·10	7·24		
,,	,,	40·38	3·29	15·1	−36
,,	EtOH	70·06	6·38		
,,	,,	59·97	2·94		
,,	,,	50·10	1·38	16·3	−35
Ge	H_2O	50	*ca.* 0·004		
Si [e]	,,	50·20	45·0	16·1	−29
,, [e]	MeOH	50·04	7·24	14·0	−36
,, [e]	EtOH	50·10	*ca.* 0·07	12·9	−42

[a] k_2 values obtained from the observed first-order rate constants (k_1) by dividing k_1 by the appropriate molarity of the solvent (at each temperature). [b] The standard deviation of $\Delta H^\ddagger$ is <0·5 kcal. mole^{-1}, and that of $\Delta S^\ddagger$ is <1 cal. mole^{-1} deg.$^{-1}$. [c] By extrapolation from the following four rate constants. [d] D_2O is of 99·95 or 99·7% purity. [e] From ref. 1.

The low activation enthalpies and large negative activation entropies for 2-trimethylstannylpyridine (Table) are strong support for a reaction mechanism similar to that for 2-trimethylsilylpyridine, through a cyclic activated complex of structure similar to (II) (Scheme).[3]

[†] This assumes that the reaction is bimolecular, with one reactant (the solvent) in great excess. If the observed first-order rate constants are used, the activation enthalpies are almost the same as those in the Table, and the activation entropies are more positive by 8 and 6 cal. mole^{-1} deg.$^{-1}$ for H_2O (and D_2O) and MeOH respectively.

[‡] Pyridine identified as the reaction product by gas–liquid chromatography.

[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] R. E. Dessy and F. Paulik, *Bull. Soc. chim. France*, 1963, 1373.

The isotope effect (k_{H_2O}/k_{D_2O}) is 1·25 ± 0·02 in the temperature range 30—40°. This value close to 1, like that for 2-trimethylsilylpyridine, indicates that the O–H or O–D bond is not being broken in the rate-determining step of the reaction.

The relative rates of hydrolysis* of 2-$Me_3MC_5H_4N$ (at 50°) are (M =) Ge ~10^{-4}, Si 1, Sn 22. This reactivity sequence is that expected for a nucleophilic substitution at the metal atom,[4,5]† and is as would be expected for the proposed mechanism (Scheme with M = Si, Ge, or Sn; R = H) where the hydrogen-bonded intermediate (I) is formed from the reactants in a fast step and nucleophilic attack by oxygen on the metal gives the intermediate (II), the formation of this intermediate being the slow step of the reaction.

The relative rates of solvolysis of 2-$Me_3SnC_5H_4N$ in H_2O, MeOH, and EtOH are 725, 5, and 1 respectively. This decrease in rate for these solvents is also found for 2-trimethylsilylpyridine.[1] We have pointed out[1] that these relative rates are in the order expected if steric hindrance is important, as it might be for a reaction involving a cyclic activated complex. Also, the acidity of the hydroxy-group hydrogen and the polarity of the solvent decrease in a manner consistent with the observed decrease in reactivity. These relative rates are probably the net result of quite complex effects. The activation parameters would indicate that this decrease in rate for 2-trimethylsilylpyridine is the result of a dominant decrease in the activation entropy, and for 2-trimethylstannylpyridine the result of a dominant increase in the activation enthalpy.

The relative rates of solvolysis of 2-$Me_3MC_5H_4N$ are (M =) Si 1, Sn 22 for H_2O, (M =) Si 1, Sn 1 for MeOH, and (M =) Si 1, Sn 20 for EtOH (Table). The relative rates in water and ethanol are as expected for a nucleophilic substitution. The equal rates in methanol are more difficult to interpret. It is likely that the net result is due to the subtle balancing of enthalpy and entropy effects.

EXPERIMENTAL

2-*Trimethylstannylpyridine*.—A mixture of 2-chloropyridine (50 g., 0·44 mole), trimethyltin chloride (88 g., 0·44 mole), and tetrahydrofuran (200 c.c.) was added during 4 hr. to magnesium turnings (13·5 g., 0·55 g.-atom) in tetrahydrofuran (100 c.c.) cooled in an ice-bath. After addition, the mixture was stirred at room temperature for 18 hr. and for 2 hr. under reflux. Tetrahydrofuran (200 c.c.) was distilled off, and dry benzene (250 c.c.) added. After boiling under reflux for 1 hr. the benzene–tetrahydrofuran mixture was decanted. This procedure of adding dry benzene, refluxing, and decanting was repeated three times. The benzene extracts were combined and fractionated, giving 2-*trimethylstannylpyridine* (10 g., 12%), b.p. 75°/4 mm., $n_D^{23\cdot5}$ 1·5367 (Found: C, 39·6; H, 5·7; N, 5·9. $C_8H_{13}NSn$ requires C, 39·8; H, 5·4; N, 5·8%).

2-*Trimethylgermylpyridine*.—Tetramethylgermane was prepared by the method of Dennis and Hance,[8] and from this, trimethyliodogermane was prepared by the method of Seyferth and Kahlen.[9] This was hydrolysed to hexamethyldigermoxane which with hydrobromic acid gave trimethylbromogermane. 2-Trimethylgermylpyridine was prepared, as 2-trimethylstannylpyridine, from the trimethylbromogermane (15 g., 0·08 mole) and 2-chloropyridine (8·7 g., 0·08 mole). After the addition of one batch of dry benzene, dry triethylamine (150 c.c.) was added and the reaction mixture filtered. Fractionation of the filtrate gave 2-*trimethylgermylpyridine* (4 g., 27%), b.p. 73°/11 mm., $n_D^{24\cdot5}$ 1·5066 (Found: C, 49·8; H, 7·1; N, 7·6. $C_8H_{13}NGe$ requires C, 49·1; H, 6·7; N, 7·2%).

4-*Methyl*-2-*trimethylgermylpyridine*.—A solution of 2-bromo-4-methylpyridine (26 g., 0·15 mole), previously prepared by the method of Craig,[10] in dry ether (50 c.c.), was added slowly to n-butyl-lithium (12 g., 0·15 g.-atom) in dry ether (100 c.c.), cooled in a Dry Ice/acetone bath. After vigorous stirring for 5 min., trimethylbromogermane (29 g., 0·147 mole) in ether (50 c.c.) was added. The mixture was allowed to warm to room temperature, and was then heated under reflux for ½ hr. After hydrolysis, the ether layer was dried and fractionated, giving 4-*methyl*-2-*trimethylgermylpyridine* (10 g., 32%), b.p. 210°/762 mm., n_D^{25} 1·4910.

All samples used for kinetic studies were further purified by preparative gas–liquid chromatography. N.m.r. spectra confirm the structures.

Kinetic Method.—This was as described previously.[1] For fast reactions a modified technique was used; the optical densities were recorded on a tape recorder and timed later. Reactions with a half-life of down to 15 sec. could be followed on a Unicam SP 500 spectrophotometer.

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* All hydrolyses are in 2 × 10^{-3}M-sodium hydroxide (see ref. 1).

† The reasons for these relative reactivities are not fully understood; nuclear shielding from silicon to germanium,[6] and the effects of lower bond strength and greater bond polarisability from germanium to tin[4] have been proposed.

In contrast to this sequence of reactivities for silicon, germanium, and tin compounds for nucleophilic substitution, the relative reactivities for electrophilic cleavage of a C–M bond are (M =) Si < Ge ≪ Sn.[7]

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