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THE SOLVOLYSIS OF 2-(TRIMETHYLSILYL)-*x*-METHYLPYRIDINES (*x*=3–6) BY METHANOL AND BY WATER

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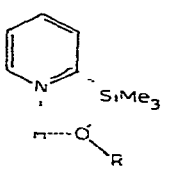
SUMMARY

The methanolysis and hydrolysis of 2-Me_3Si-*x*-MeC_5H_3N (*x*=3–6) have been studied. The relative reactivities are (*x*=)3 < 5 < H < 6 < 4 for methanolysis, and 5 < *H* < 3 < 6 < 4 for hydrolysis (H=2-$Me_3SiC_5H_4N$); they are the result of an interplay of activation enthalpy and activation entropy changes. These activation parameters are consistent with the mechanism proposed earlier.

INTRODUCTION

We have recently reported that 2-(trimethylsilyl)-, 2-(trimethylgermyl)-, and 2-(trimethylstannyl)pyridine are solvolysed by water and alcohols, as are 2-silylpyridines containing groups other than methyl on the silicon[1–4]. A reaction mechanism involving rate-determining nucleophilic attack by the oxygen of the solvent on silicon (or germanium or tin) with electrophilic assistance by the hydrogen of the



(I)

solvent on nitrogen through a 5-centred cyclic activated complex (I) has been proposed. This paper reports the solvolysis of the four isomeric 2-(trimethylsilyl)-*x*-methylpyridines (*x*=3–6) by water and by methanol.

DISCUSSION

Second-order rate constants [calculated from the observed first-order rate constants (see ref. 1)] for these reactions are given in Table 1, and activation parameters calculated from these results are given in Table 2. The results in Table 1 (which also includes the rate constants for the solvolysis of 2-(trimethylsilyl)pyridine[1]) give relative rates for the methanolysis (at 60.40°) of 2-Me_3Si(R)C_5H_3N of (R=)H 1, 3-Me 0.64, 4-Me 2.14, 5-Me 0.93, 6-Me 1.47, and relative rates for the hydrolysis (at 30.2°)

TABLE 1

RATE CONSTANTS FOR THE SOLVOLYSIS OF 2-$Me_3Si(R)C_5H_3N$ BY MeOH AND H_2O

R	MeOH		H_2O[a]	
	Temp. (±0.02°)	10^6k_2[b] (l mole^{-1} sec^{-1})	Temp. (±0.02°)	10^6k_2[b] (l·mole^{-1}·sec^{-1})
3-Me	60.40°	8.37	46.80°	45.5
	55.26	6.29	40.36	29.6
	50.50	4.70	30.38	12.8
	45.24	3.64		
4-Me	60.40	28.1	46.80	56.8
	55.26	20.5	40.36	33.6
	50.50	15.4	30.20	13.8
	45.24	10.3		
5-Me	60.40	12.2	46.80	24.0
	55.26	8.73	40.36	14.1
	49.96	6.13	30.20	5.76
	45.24	4.37		
6-Me	60.40	19.3	46.80	51.3
	55.26	14.0	40.36	31.4
	50.12	9.97	30.38	12.9
	45.24	7.50		
H[c]	60.40	13.1	30.20	8.09

[a] 2×10^{-3} *M* NaOH (see ref. 1) [b] k_2's obtained from the observed first-order rate constants (k_1) by dividing k_1 by the appropriate molarity of the solvent. [c] From ref. 1.

of (R=)H 1, 3-Me 1.58, 4-Me 1.70, 5-Me 0.71, 6-Me 1.59; *i.e.*, for the methanolysis and the hydrolysis the reactivity increases as (R=)5-Me < H < 6-Me < 4-Me. 2-(Trimethylsilyl)-3-methylpyridine is relatively more reactive in the hydrolysis (of the same reactivity as the 6-methyl isomer) than in the methanolysis (the least reactive). The relative rates of methanolysis and hydrolysis of 2-(trimethylsilyl)-3-methylpyridine (at 45°) are 1 : 12.5. For the other four compounds this ratio is 1 : 6.2(±0.6).

This is an unusual reactivity sequence with a methyl group activating the reaction when in the 4- or 6-position, and retarding the reaction when in the 5-position,

TABLE 2

ACTIVATION PARAMETERS AT 50° FOR THE SOLVOLYSIS OF 2-$Me_3Si(R)C_5H_3N$ BY MeOH AND H_2O

R	$\Delta H^{\neq}$ (kcal mole^{-1})[a]		$\Delta S^{\neq}$ (cal·mole^{-1}·deg^{-1})[a]		$\Delta G^{\neq}$ (kcal·mole^{-1})	
	MeOH	H_2O	MeOH	H_2O	MeOH	H_2O
3-Me	11.1	14.4	−49	−34	26.9	25.4
4-Me	13.2	15.8	−40	−29	26.1	25.2
5-Me	13.6	16.0	−40	−30	26.5	25.7
6-Me	12.6	15.6	−43	−29	26.5	25.0
H[b]	12.9	16.1	−42	−29	26.5	25.5

[a] The standard deviation of $\Delta H^{\neq}$ is < 0.5 kcal·mole^{-1}, and that of $\Delta S^{\neq}$ is < 1 cal·mole^{-1}·deg^{-1}. [b] From ref. 1.

and it is tempting to rationalise it in terms of electron donation by the methyl groups affecting the energy of the activated complex via the nitrogen or via the 2-carbon of the pyridine ring. However care must be taken in interpreting the results in terms of enthalpy changes alone. A change in the free energy of activation ($\Delta G^{\neq}$), (*i.e.*, a change in rate) is the result of opposing changes in the enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation, sometimes the enthalpy change is dominant and sometimes the entropy change.

The relatively low enthalpies and large negative entropies of activation (Table 2) are consistent with the proposed reaction mechanism[1]. For the solvolyses of the 3-isomer the activation enthalpies are significantly smaller and the activation entropies are significantly more negative than for the other compounds, in support of a proximity effect in the activated complex being important for this compound.

In view of the complex interplay of enthalpy and entropy changes it is not possible to analyse these results further. Certainly any explanation in terms of inductive electron release (mentioned above), which assumes entropy effects to be constant, will be incorrect.

This effect of a methyl substituent in the pyridine ring on the solvolysis of the Si–C bond of a 2-silylpyridine is quite small, the most is more reactive than the least by a factor of only three. It would be of interest to study the solvolysis of some 2-silylpyridines with more highly activating or deactivating substituents in the pyridine ring*. Unfortunately our attempts so far to prepare such compounds have been unsuccessful.

EXPERIMENTAL

Preparation of compounds

2-(*Trimethylsilyl*)-3-*methylpyridine*. 2-Bromo-3-methylpyridine (30 g, 0.175 mole), prepared by the method of Craig[5], in ether, (50 cm^3) was added to a solution of butyllithium (0.175 mole) in ether (100 cm^3) at −50°, followed by trimethylchlorosilane (19 g, 0.176 mole) in ether (50 cm^3). The mixture was allowed to warm to room temperature and was then heated under reflux for 1 h. The lithium bromide was filtered off and the ether solution fractionated giving 2-(trimethylsilyl)-3-methylpyridine (5 g, 16%), b.p. 199°/753 mm, n_D^{25} 1.4970. (Found: C, 65.1, H, 9.4, N, 8.0. $C_9H_{15}NSi$ calcd.: C, 65.4, H, 9.2, N, 8.5%.)

2-(*Trimethylsilyl*)-4-*methylpyridine*. Prepared as above (32%), b.p. 72.5/10 mm, n_D^{14} 1.4952. (Found: C, 66.0, H, 9.7, N, 8.4. $C_9H_{15}NSi$ calcd.: C, 65.4, H, 9.2, N. 8.5%.)

2-(*Trimethylsilyl*)-5-*methylpyridine*. Prepared as above (19%), b.p. 74.5°/8 mm, n_D^{25} 1.4880. (Found: C, 64.9, H, 9.2, N, 8.1. $C_9H_{15}NSi$ calcd.: C, 65.4, H, 9.2, N, 8.5%.)

2-(*Trimethylsilyl*)-6-*methylpyridine*. Prepared as above (32%), b.p. 178°/756 mm, $n_D^{25.2}$ 1.4868. (Found: C, 65.1, H, 9.1, N, 8.3. $C_9H_{15}NSi$ calcd.: C, 65.4, H, 9.2, H, 8.5%.)

All four compounds were further purified by preparative gas-liquid chromatography before use in kinetic studies. NMR spectra confirmed the structures.

* We have observed the methanolysis of one other ring-substituted pyridine, namely 2-(trimethylsilyl)-quinoline. The ultra-violet spectrum of a solution of this compound in methanol changed to that of quinoline in 24 h at room temperature.

Kinetic method

This was as described previously[1].

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