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CONTRIBUTIONS TO GROUP IV ORGANOMETALLIC CHEMISTRY

III *. REACTION OF DIMETHYLAMINOTRIMETHYLSILANE WITH 2-HYDROXYPYRIDINES AND 2-HYDROXYPYRIMIDINES

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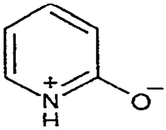
Summary

The reactions of 2-hydroxypyridines and 2-hydroxypyrimidines with diethylaminotrimethylsilane have been studied and ^{1}H and ^{13}C NMR spectra of the resultant organosilanes confirm that the reactions occur at the oxygen atom and not at the nitrogen atom.

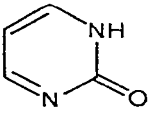
Introduction

The structures of trimethylsilamides have been studied in some detail by ^{1}H NMR which has demonstrated that they can exist in the amide or imidate form or as an equilibrium mixture of both [2,3].

2-Hydroxypyridines are both weak acids and bases and can exist as zwitter ions of type I. Physical measurements in water have shown that for 2-hydroxypyridine only about one part in 10^3 is in the hydroxy form.



(I)



(II)

It is also to be expected that in the case of 2-hydroxypyrimidines the second nitrogen atom would increase the stability of the pyrimidone II. That 2-hydroxypyridine and 2-hydroxypyrimidine exist in the pyridone and pyrimidone forms is supported from infrared spectral studies. Their spectra contain bands

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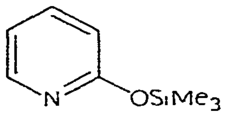
at 3198 m, 3165 cm^{-1} (NH ν(str)), 1650 cm^{-1} (C=O ν(str)) and 3195 cm^{-1} (NH ν(str)), 1733 and 1647 cm^{-1} (C=O ν(str)) respectively [4].

We were therefore interested to determine whether the reaction of diethylaminotrimethylsilane and a 2-hydroxypyridine or pyrimidine resulted in the formation of *O*-substituted (III, IV) or *N*-substituted (V, VI) products.



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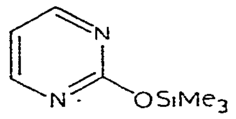

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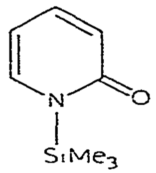

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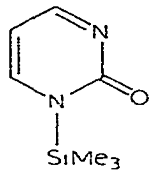
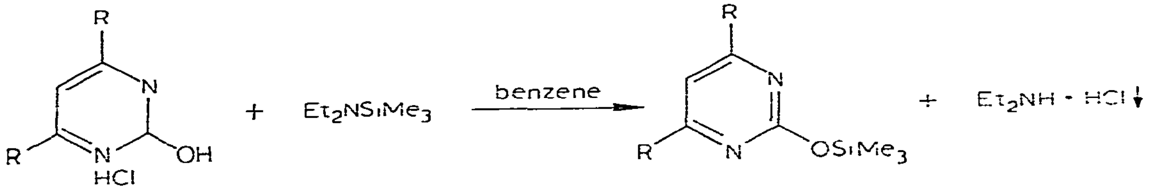


(VI)

Results and discussion

Diethylaminotrimethylsilane was heated under reflux with the hydrochlorides of 2-hydroxypyrimidine and 2-hydroxy-4,6-dimethylpyrimidine for three hours.



R = H (VII) ; R = Me (VIII)

The reaction was facilitated by the formation of diethylamine hydrochloride which precipitated out of solution.

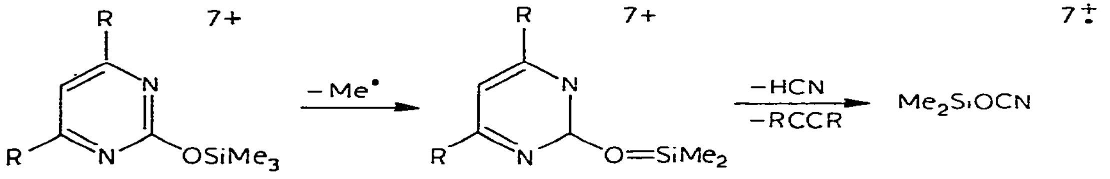
The infrared spectra of (VII) and (VIII) did not contain bands in the region characteristic of a carbonyl stretching frequency which indicates that the reaction had taken place at the oxygen atom and not at the nitrogen atom. This was further substantiated by ^{1}H and ^{13}C NMR studies (see Table 1). The ^{1}H NMR spectrum of (VII) contains a singlet (9H), a doublet (2H) and a triplet (1H) and the ^{13}C NMR spectrum consists of four lines. The ^{1}H NMR spectrum of (VIII) contains three singlets (9H, 6H and 1H respectively) and the ^{13}C NMR spectrum

TABLE 1

^{1}H AND ^{13}C NMR ASSIGNMENTS (WRT TMS) FOR (VII) AND (VIII)

Compound	Chemical shifts								
	C-2	C-4	C-5	C-6	H-4	H-5	H-6	C(SiMe$_3$)	H(SiMe$_3$)
VII	164.43	115.53	159.94	115.53	8.60 (d,J = 5 Hz)	7.01 (t,J = 5 Hz)	8.60	—0.13	0.365
VIII	166.32	113.57	169.03	113.57	—	7.10	—	0.12	0.310
VIII	C-4(Me)	C-6(Me)	H-4(Me)	H-6(Me)					
	23.66	23.66	2.438	2.438					

consists of five lines. These results show that both compounds have a plane of symmetry which can only be achieved if the reaction occurs at the oxygen atom (IV) and not the nitrogen atom (VI). The base peak in the mass spectra arises from the loss of a methyl radical with a peak in each spectrum at *m/e* 100 which we assign to the Me_2SiOCN ion.



(R = H or Me)

In the case of the 2-hydroxypyridines it is more difficult to establish that the products of their reaction with diethylaminotrimethylsilane are *O*- and not *N*-substituted in so far as the reaction product in either case is an unsymmetrical compound. However this difficulty was partly overcome by comparing the results obtained from the hydroxypyridines with those of caprolactam.

Caprolactam and diethylaminotrimethylsilane were heated under reflux, in benzene, for three hours. That the product of the reaction (XI) is the *N*-silylated compound can be inferred from the following results. Firstly by the presence of bands in the infrared spectrum at 1670 and 1640 cm^{-1} (characteristic of a carbonyl-stretching frequency band) and the absence of bands in the 3200 cm^{-1} region, secondly there is very little change in the position of the UV_{max}; 219 $m\mu$ for the silyl compound and 220 $m\mu$ for caprolactam (cyclohexane as solvent) and finally there is very little change between the ^{13}C NMR values obtained for the silyl compound and caprolactam (Table 2).

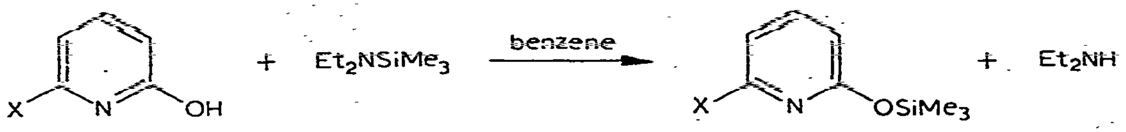
Diethylaminotrimethylsilane and the 2-hydroxypyridines were heated in refluxing benzene for about three hours. Without a detailed X-ray study it is not possible to prove conclusively that the reaction results in the formation of *O*-substituted (III) or *N*-substituted (V) products. However a study of the infrared spectra, UV spectra and ^{13}C NMR spectra of (IX) and (X) very strongly suggests

TABLE 2

^{13}C NMR ASSIGNMENTS (WRT TMS) AND UV λ_{max} FOR (IX)(X) AND (XI)

Compound	Chemical shifts								
	C-2	C-3	C-4	C-5	C-6	C($SiMe_3$)	C-7	C-6(Me)	$\lambda_{max}(m\mu)$ (cyclohexane)
IX	163.19	112.95	138.92	116.72	147.41	0.93	—	—	272
IX[a]	164.8	111.4	138.2	116.9	148.0	—	—	—	—
IX[b]	165.3	106.7	134.8	120.1	141.6	—	—	—	295
X	161.62	108.60	138.45	115.15	155.80	0.00	—	23.29	273
X[a]	164.0	108.9	137.4	115.8	157.3	—	—	—	—
X[b]	166.11	106.05	141.84	116.36	145.97	—	—	18.92	298
XI	182.00	37.84	23.89	30.08	31.05	0.35	44.40	—	219
XI[b]	179.5	36.8	23.2	29.7	30.6	—	42.6	—	220

[a] Calculated values for the 2-alkoxypyridine [5] [b] Values for the 2-pyridone and caprolactam compounds.



X = H = (IX)
X = Me = (X)

that they can be formulated as *O*-substituted compounds.

Firstly in the infrared spectra there was an absence of peaks assignable to the ν(CO) which were present in the starting materials, secondly there was a shift in the λ_{max} (Table 2) between the starting materials and the silyl compounds in contrast to the results obtained for caprolactam and thirdly a study of the ^{13}C NMR spectra (in C_6D_6/CCl_4 or $CDCl_3$) (Table 2) show that in each case the position of all the peaks are changed on silyation and that they are very similar to those calculated for a substituted hydroxypyridine model. The mass spectra of (IX) and (X) contain only two peaks of greater than 5% intensity due to the P^+ and $P - 15^+$ ions with the latter being the base peak.

In conclusion the reaction of diethylaminotrimethylsilane with 2-hydroxypyrimidines results in the formation of *O*-silylated products and IR, UV and ^{13}C NMR studies strongly indicate that the position of substitution in the case of 2-hydroxypyridines is also at the oxygen atom.

Experimental

The infrared spectra were recorded using a PE457 spectrometer and the mass spectra were recorded using an AEI MS902 mass spectrometer at 70 ev and 170°C. ^{1}H NMR spectra were recorded on a Perkin—Elmer R 10 spectrometer and line positions are relative to internal TMS. ^{13}C NMR spectra were recorded on a JEOL PS100 FT spectrometer and line positions are relative to internal TMS.

Reaction of caprolactam with diethylaminotrimethylsilane

Caprolactam (2.83 g, 0.025 mol) and diethylaminotrimethylsilane (3.7 g, 0.025 mol) were heated under reflux in benzene for three hours. After removal of the volatile materials, under reduced pressure, the residue on distillation afforded *N*-trimethylsilylcaprolactam, (2.8 g, 60%), bp 56—58°C/0.4 mmHg. (Found: C, 58.20; H, 10.45; N, 7.6 *M* 185, $C_9H_{19}NOSi$ calcd.: C, 58.32; H, 10.33; N, 7.56% *M* 185.)

Reaction of 2-hydroxypyridine with diethylaminotrimethylsilane

2-Hydroxypyridine (2.38 g, 0.025 mol) and diethylaminotrimethylsilane (3.7 g, 0.025 mol) were heated under reflux in benzene for three hours. After removal of the volatile materials, under reduced pressure, the residue on distillation afforded 2-trimethylsiloxypyridine (3.17 g, 76.0%), bp 34—38°C/1.0 mmHg. (Found: C, 57.21; H, 7.99; N, 8.22, *M* 167, $C_8H_{13}NOSi$ calcd.: C, 57.44; H, 7.83; N, 8.37% *M* 167.)

2-Trimethylsiloxy-6-methylpyridine (62%) bp 44°C/0.2 mmHg. (Found: C, 58.89; H, 9.00; N, 7.51 *M* 181, $C_9H_{15}NOSi$ calcd.: C, 59.62; H, 8.34; N, 7.73% *M* 181) was obtained by the same method.

Reaction of 2-hydroxy-4,6-dimethylpyrimidine with diethylaminotrimethylsilane

Diethylaminotrimethylsilane (3.7 g, 0.025 mol) and 2-hydroxy-4,6-dimethylpyrimidine hydrochloride (4.02 g, 0.025 mol) were heated under reflux in benzene for three hours. The diethylamine hydrochloride formed in the reaction was filtered off and after removal of the solvent, under reduced pressure, the residue on distillation afforded 2-trimethylsiloxy-4,6-dimethylpyrimidine (3.4 g, 68%) bp 60—65°C/0.2 mmHg. (Found: C, 54.35; H, 7.93; N, 13.89% *M* 196, $C_9H_{16}N_2OSi$ calcd.: C, 55.10; H, 8.16; N, 14.28% *M* 196.)

2-Trimethylsiloxypyrimidine (62%) bp 30—32°C/0.1 mmHg. (Found: C, 49.72; H, 7.51; N, 17. 09 *M* 168, $C_7H_{12}N_2OSi$ calcd.: C, 50.00; H, 7.14; N, 16.66% *M* 168) was obtained by the same method.

Ackowledgement

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