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4-SILYLTETRACHLOROPYRIDINES

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SUMMARY

The reactions of (2,3,5,6-tetrachloropyridyl)magnesium chloride with various organochlorosilanes are described together with details of the IR, NMR and UV spectra of the products.

INTRODUCTION

A prior report[1] dealt with the preparation of (2,3,5,6-tetrachloropyridyl)-magnesium chloride from pentachloropyridine and magnesium in THF and its reactions with some chlorosilanes to give 4-silylsubstituted tetrachloropyridines in satisfactory yields. Among other relevant studies[2,3] are those by Wakefield and co-workers[3]. We now report the preparation of several new 4-silyltetrachloropyridines by the reaction of the Grignard reagent with various organochlorosilanes. IR, NMR and UV spectral data are given.

RESULTS AND DISCUSSION

From our studies on the stability of the Grignard reagent in THF*, it was found that (2,3,5,6-tetrachloropyridyl)magnesium chloride is quite stable, under nitrogen, for several hours at room temperature, but not at reflux temperature**.

Many silanes, containing one, two, or three tetrachloropyridyl groups were prepared by addition of a chloro-, dichloro-, or trichlorosilane to the Grignard reagent in THF at 0°. The IR spectra of these compounds in nujol showed characteristic absorption bands at 1282 ± 2, 1075 ± 1 and 658 ± 10 cm^{-1}, associated with the tetrachloropyridyl group. The intensities of the above three absorptions are directly related to the number of 2,3,5,6-tetrachloropyridyl groups attached to silicon.

The NMR spectra of the 4-silyltetrachloropyridines in carbon tetrachloride are recorded in Table 1. Successive introduction of 2,3,5,6-tetrachloropyridyl groups in place of methyl or phenyl causes a shift of the silicon–methyl absorption to lower field, probably due to the electron withdrawing effect of the 2,3,5,6-tetrachloropyridyl group. As the chemical shifts of the SiMe$_3$ group in $C_5Cl_4NSiMe_3$ and $C_6Cl_5SiMe_3$

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* For the preparation of this Grignard reagent in ether see refs. 3 and 4.

** Unpublished studies to appear later, on the relative stabilities (and the sensitivities of Color Test I) of perhaloarylmetallic compounds have shown that the yield decreases by 20% in a 24 h period at room temperature.

TABLE 1

UV AND NMR SPECTRA OF 4-SUBSTITUTED TETRACHLOROPYRIDINES

Compound[a]	Ultraviolet[b]		NMR[c]
	λ_{max}(mμ)	ε_{max}	τ(ppm)
$RSiMe_3$	301	5,100	9.45 (s), Si–Me
$RSiMe_2H$	301	3,400	9.45 (d), Si–Me[d] 5.05 (septet), Si–H
$RSiMe_2Ph$	302	6,000	9.26 (s), Si–Me 2.70 (m), Si–Ph
$RSiMePh_2$	303	5,060	8.97 (s), Si–Me 2.60 (m), Si–Ph
RSiMePhH	302	4,300	9.18 (d), Si–Me[d] 4.37 (q), Si–H 2.67 (m), Si–Ph
$RSiPh_2H$	303	5,350	4.01 (s), Si–H 2.58 (m), Si–Ph
R_2SiMe_2	303	9,970	9.01 (s), Si–Me
R_2SiPh_2	305	10,450	2.50 (m), Si–Ph
$R_2SiMePh$	304	9,600	8.69 (s), Si–Me 2.50 (m), Si–Ph
R_3SiMe	311	19,750	8.61 (s), Si–Me
$RSiPh_2(C_6Cl_5)$	306	5,650	
$RSiPh_3$	306	5,560	
$RSi(CH{=}CH_2)Ph_2$	305	6,000	
RH	300,295,290, 285,281 (sh)	3,875, 4,000, 5,230, 4,380, 3,360	
RCl	296,290, ca. 300 (inf)	5,120, 5,010	
RBr[7]	301,292	4,520, 4,370	
RI[7]	302,294	4,340, 4,220	
REt[8]	290,285,233	4,000, 4,080, 8,660	
RPh[9]	296,235	3,920, 16,000	
RCOOH[7]	292	5,550	

[a] $R = 2,3,5,6\text{-}C_5Cl_4N$. [b] Solvent, cyclohexane; sh = shoulder; inf = inflexion. [c] Solvent, carbon tetrachloride with TMS as internal standard. [d] $J = 7$ Hz.

[ref. 5: τ 9.45] are at the same position, the Hammett substituent constant for the tetrachloropyridyl group may be similar to that of the pentachlorophenyl group[6].

The UV spectra of some 4-substituted tetrachloropyridines in cyclohexane are shown in Table 1. For all 4-silyl-substituted tetrachloropyridines, an inflexion was observed on the band between 301–311 mμ at longer wavelengths (7–9 mμ higher). Introduction of electronegative atoms or groups has a dramatic effect on the spectral properties. There is a bathochromic shift of ca. 40 mμ when all the hydrogens in pyridine are replaced by chlorine atoms (pyridine, λ_{max} 252 mμ; pentachloropyridine, λ_{max} 296 mμ). The same differential behavior is noticed in the spectra of 4-substituted tetrachloropyridines and their hydrogen analogs. For example, 2,3,5,6-tetrachloroisonicotinic acid, 4-ethyl-, 4-phenyl-, and 4-(triphenylsilyl)tetrachloropyridine absorb at 292, 290, 296 and 306 mμ, respectively, whereas the absorption maxima for the corresponding hydrogen analogs are: 272, 255, 250, 271 mμ. This is in agreement with the general observation that electronegative groups or atoms bring about a red shift.

The UV spectra of pyridine and its derivatives are sensitive to the polarity of the solvent and hyperchromic effects have been noticed in changing from cyclohexane to ethanol/acid mixtures[10,11]. No such behavior has been observed in 4-substituted tetrachloropyridines. Pentachloropyridine, 4-bromo-, 4-iodo-, 4-ethyl-, 4-phenyl-, and 4-hydrogentetrachloropyridines showed no bathochromic or hyperchromic shifts when the solvent was changed from cyclohexane to 95% ethanol or ethanol/hydrochloric acid (4/1) mixture. It seems that due to strongly electron withdrawing chlorine atoms, the basicity of nitrogen is much reduced and, therefore, may be unable to sustain solvent–solute interactions, presumably through hydrogen bonding. A similar observation was made in the case of 2,3,5,6-tetrachloroisonicotinic acid It is felt that due to the decreased basicity of nitrogen, even in strongly polar solvents like ethanol/acid mixtures, the acid exists as normal molecules, unlike isonicotinic acid in which case a zwitterion structure has been proposed which will be favored in a more polar medium[11].

A further red shift has been observed in the spectra of 4-silyltetrachloropyridines. Since the increase in the number of electronegative groups markedly affects the

TABLE 2

PREPARATION OF 4-SILYLTETRACHLOROPYRIDINES

Compound[a]	Yield[b] (%)	M.p. (°C)	Solvent of crystallization	Grignard reagent (moles)	Chlorosilane (moles)	Analysis found (calcd.)(%)		
						C	H	Si
$RSiMe_3$	80	62–63	MeOH	0.04	Me_3SiCl (0.05)	33.75 (33.22)	3.38 (3.12)	
$RSiMe_2H$	75	115–116	Me_2CO	0.04	HMe_2SiCl (0.05)	30.57 (30.57)	2.50 (2.57)[d]	
$RSiMe_2Ph$	65	88–89	MeOH	0.04	$Me_2PhSiCl$ (0.05)	44.84 (44.45)	3.26 (3.13)[e]	
$RSiMePh_2$	52	131–132	Pet. ether (b.p. 60–70°)	0.04	$MePh_2SiCl$ (0.04)	52.25 (52.30)	3.29 (3.14)	
RSiMePhH	55	81–82	Pet. ether (b.p. 40–60°)	0.04	HMePhSiCl (0.04)			8.23 (8.34)
$RSiPh_3$	50	247–249	Pet. ether (b.p. 60–70°)	0.04	Ph_3SiCl (0.03)	58.50 (58.10)	3.48 (3.16)	
$RSiPh_2H$	61	106–107	Pet. ether (b.p. 60–70°)	0.04	HPh_2SiCl (0.035)	51.42 (51.13)	2.53 (2.76)	
$R(C_6Cl_5)SiPh_2$	48	232–233	CCl_4	0.04	$(C_6Cl_5)Ph_2SiCl$ (0.032)			4.41 (4.33)
$RSiPh_2(CH{=}CH_2)$	35	102–103	Pet ether (b.p. 60–70°)	0.04	$Ph_2(CH{=}CH_2)SiCl$ (0.04)			6.01 (6.60)
R_2SiMe_2	68	168–169	CCl_4	0.04	Me_2SiCl_2 (0.018)	29.10 (29.39)	1.36 (1.23)	
R_2SiPh_2	43	256–258	CCl_4	0.04	Ph_2SiCl_2 (0.018)			4.49 (4.56)
$R_2SiMePh$	40	234–235	CCl_4	0.10	$MePhSiCl_2$ (0.041)			5.05 (5.09)
R_3SiMe	43	286–288	CCl_4	0.08	$MeSiCl_3$ (0.021)			4.12 (4.05)

[a] R = 2,3,5,6-tetrachloropyridyl. [b] Yields based on crystallized products. [c] Quantity based on pentachloropyridine. [d] Found: N, 5.1. Calcd.: N, 5.09%. [e] Found: N, 3.99. Calcd.: N, 4.20%.

spectra, bathochromic shifts are observed on increasing the number of such groups. The position of the absorption maxima undergoes a red shift on replacing methyl groups in (2,3,5,6-tetrachloropyridyl)trimethylsilane by 2,3,5,6-tetrachloropyridyl groups, and the molar absorptivities increase in a fairly additive manner.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry oxygen-free nitrogen. Ethereal solvents were dried over sodium, and THF was further purified by distillation from sodium–benzophenone ketyl. Organochlorosilanes were obtained from the Dow-Corning Corporation and the Union Carbide Corporation and used without further purification. n-Butyllithium in hexane was from the Foote Mineral Company.

IR spectra were determined as nujol mulls on a Perkin–Elmer model 21 spectrophotometer. NMR spectra were recorded in carbon tetrachloride, using a Varian A60 spectrometer. UV spectra were obtained on a Cary Model 14R recording spectrophotometer.

General procedure for the preparation of (2,3,5,6-*tetrachloropyridyl*)*silanes*

To the Grignard reagent at 0° was added the chlorosilane in a small volume of THF and the mixture stirred at the ambient temperature overnight (ca. 16 h). The mixture was hydrolyzed with dilute hydrochloric acid, extracted with ether, and the extract dried ($MgSO_4$). Evaporation of the solvent left a dark brown oil which was chromatographed on a column of silica gel in petroleum ether (b.p. 60–70°) and further eluted with CCl_4. The eluate was then evaporated and the tetrachloropyridylsilane crystallized from the appropriate solvent. All data are recorded in Table 2. Every compound had the correct molecular weight as determined by mass spectrometry.

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