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Preliminary communication

N–O stretching frequencies for some organosilicon-, organogermanium-, and organotin-substituted pyridine *N*-oxides

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Studies have shown that the position of the infrared absorption due to ν(N–O) in 4-substituted pyridine *N*-oxides is sensitive to the nature of the substituent[1]. The absorption shifts to higer wavenumbers with the increasing electron-withdrawing behavior of the substituent, apparently because of an increase in the degree of back-donation from the oxygen $2p_\pi$-orbital into the π-system of the ring (*vide infra*). This results in an increase in the N–O double bond character. We have prepared a novel series of pyridine *N*-oxides, substituted in the 4-position with R_3Si, R_3Ge, and R_3Sn groups, and using the N–O stretching frequency as a probe, we have found significant evidence for electron withdrawal by these organometallic substituents

The data listed in Table 1 show in nearly every case a substantial increase in ν(N–O) for the organometallic derivatives when compared with either the unsubstituted pyridine *N*-oxide or the tert-butyl derivative. Nelson *et al.*,[2] have correlated values of ν(N–O) (measured in Nujol) with σ(PyNO), a substituent constant defined by them and based upon the difference between the conjugate acid pK_a values for the unsubstituted and substituted pyridine *N*-oxides. On the basis of this correlation, an approximate σ(PyNO) value of 0.6 can be estimated for the $(CH_3)_3Si$ and $(CH_3)_3Ge$ substituents, with a somewhat lower value for the $(CH_3)_3Sn$ group. By way of comparison with some common electron-withdrawing substituents on the 4-position, σ(PyNO) values of 0.61 and 0.57 have been tabulated for the COOH and $COOCH_3$ groups[2]. A value of 0.21 is given for the 4-chloro substituent, and 4-chloropyridine *N*-oxide has a ν(N–O) of 1248 cm^{-1} (Nujol)[3].

From the increased basicity of organosilicon-, organogermanium-, and organotin-substituted pyridines over the unsubstituted pyridine, Anderson *et al.*[4] have concluded that the organometallic groups act primarily as electron donors when attached to the pyridine nucleus. The greater electronegativity of nitrogen compared to carbon enhances the electron-withdrawing character of the aromatic ring. On the other hand, the inductive electron-withdrawing behavior of the N–O group in pyridine *N*-oxide is opposed by the back-donation from the oxygen $2p_\pi$-orbital into the π-system of the ring, which increases the π-electron density at the 4-(and 2-) positions. This phenomenon appears to be well

TABLE 1

INFRARED DATA[a] ON 4-SUBSTITUTED PYRIDINE *N*-OXIDES (VALUES IN cm^{-1})

Substituent	2% CS_2 solution		Nujol mull	
	N–O Stretching frequency[b]	Accompanying absorption[c]	N–O Stretching frequency	Accompanying absorption[c]
$(CH_3)_3C$	1259	–	1240	1251
$(CH_3)_3Si$	1275	1250	1260	1248
$(C_2H_5)_3Si$	1275	1234[d]	1256	1240[e]
$(CH_3)_3Ge$	1270	1239	1259	1238
$(CH_3)_3Sn$	1268	–	1252	–
H	1265[f]	–	1244	–

[a] Data obtained with a Perkin–Elmer 621 infrared spectrophotometer. Values are accurate to better than ± 1 cm^{-1}. [b] Band assignments made principally on the basis of shifts observed upon addition of methanol to the CS_2 solutions (ref. 12). [c] Attributed to the R_3M group (ref. 13). This absorption generally shows an intensitivity to a change in medium, unlike ν(N–O), and a near coincidence to the same absorption in the corresponding 4-substituted pyridines. [d] Weak absorption compared to ν(N–O). [e] Shoulder. [f] Accompanied by a shoulder at 1272 cm^{-1}.

documented[5]. Therefore, if dative p_π-d_π bonding obtains between the 4-position of the ring (with its enhanced π-electron density) and the silicon, germanium or tin atoms, the organometallic groups can act as electron acceptors when attached to the pyridine *N*-oxide nucleus. The result is an increase in O→ring back-donation compared to pyridine *N*-oxide or its alkyl derivatives, and the observed increase in ν(N–O). In this study, it is difficult to avoid a conclusion based upon dative p_π–d_π bonding involving the silicon, germanium, or tin. This conclusion is supported by recent studies of ionization potential[6] and ESR[7] measurements on aryl-silanes and -germanes. A similar phenomenon in aryltin compounds appears less well substantiated.

All of the organometallic pyridine *N*-oxide derivatives reported here are new compounds. The only previous report on these derivatives concerned 3-trimethylsilylpyridine *N*-oxide[8]. With the exception of the tin compound, they were prepared by the oxidation of the corresponding substituted pyridine with hydrogen peroxide in glacial acetic acid[9]. Because of the sensitivity of aryltin compounds to glacial acetic acid at elevated temperatures, 4-trimethylstannylpyridine was oxidized (in only 10% yield) with permaleic acid[10] in chloroform at room temperature. 4-Triethylsilylpyridine as well as the germyl- and stannyl-pyridines were prepared from 4-pyridyllithium and the appropriate trialkylmetal halide by the method previously used in the preparation of 4-trimethylsilylpyridine[11]. The physical properties and NMR spectral data for the new compounds prepared★ are given in Table 2.

★ Satisfactory analytical data have been obtained for all new compounds (within ± 0.3% of the calculated values).

TABLE 2

PHYSICAL PROPERTIES AND NMR SPECTRAL DATA

Compound	B.p. (°C/mm) or m.p. (°C)	n_D^{25}	Chemical shifts (ppm)[a]		
			$\tau(CH_3)$ or $\tau(C_2H_5)$	$\tau(H_\alpha)$[b]	$\tau(H_\beta)$
4-$Et_3SiC_5H_4N$	67/0.3	1.5002	9.12	1.44	2.68
4-$Me_3GeC_5H_4N$	59/2.5	1.5060	9.63	1.42	2.66
4-$Me_3SnC_5H_4N$	59/0.3	1.5383	9.70	1.50	2.67
4-$Me_3SiC_5H_4NO$	111–113		9.70	1.76	2.58
4-$Et_3SiC_5H_4NO$	49–51		9.10	1.76	2.61
4-$Me_3GeC_5H_4NO$	116–118		9.56	1.77	2.62
4-$Me_3SnC_5H_4NO$	131–133		9.65	1.81	2.61

[a] Liquids measured without solvent; TMS used as internal standard. Solids measured in $CDCl_3$ solution containing TMS. CH_3–M absorptions are singlets, all others are multiplets. [b] Refers to ring position adjacent to nitrogen; lower field ring absorption generally assigned to H_α (ref. 14).

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