

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 $\nu(\text{N—O})$ in 4-substituted pyridine *N*-oxides is sensitive to the nature of the substituent¹. The absorption shifts to higher 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 $\nu(\text{N—O})$ 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 $\nu(\text{N—O})$ (measured in Nujol) with $\sigma(\text{PyNO})$, a substituent constant defined by them and based upon the difference between the conjugate acid $\text{p}K_a$ values for the unsubstituted and substituted pyridine *N*-oxides. On the basis of this correlation, an approximate $\sigma(\text{PyNO})$ value of 0.6 can be estimated for the $(\text{CH}_3)_3\text{Si}$ and $(\text{CH}_3)_3\text{Ge}$ substituents, with a somewhat lower value for the $(\text{CH}_3)_3\text{Sn}$ group. By way of comparison with some common electron-withdrawing substituents on the 4-position, $\sigma(\text{PyNO})$ values of 0.61 and 0.57 have been tabulated for the COOH and COOCH_3 groups². A value of 0.21 is given for the 4-chloro substituent, and 4-chloropyridine *N*-oxide has a $\nu(\text{N—O})$ 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) ₃ C	1259	—	1240	1251
(CH ₃) ₃ Si	1275	1250	1260	1248
(C ₂ H ₅) ₃ Si	1275	1234 ^d	1256	1240 ^e
(CH ₃) ₃ Ge	1270	1239	1259	1238
(CH ₃) ₃ Sn	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 CS₂ solutions (ref. 12). ^c Attributed to the R₃M group (ref. 13). This absorption generally shows an intensity 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.

documented⁵. 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 potential⁶ and ESR⁷ 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*-oxide⁸. With the exception of the tin compound, they were prepared by the oxidation of the corresponding substituted pyridine with hydrogen peroxide in glacial acetic acid⁹. Because of the sensitivity of aryltin compounds to glacial acetic acid at elevated temperatures, 4-trimethylstannylpyridine was oxidized (in only 10% yield) with permaleic acid¹⁰ in chloroform at room temperature. 4-Triethylsilylpyridine as well as the germlyl- and stannyl-pyridines were prepared from 4-pyridyllithium and the appropriate trialkylmetal halide by the method previously used in the preparation of 4-trimethylsilylpyridine¹¹. 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 $\pm 0.3\%$ 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		
			$\tau(\text{CH}_3)$ or $\tau(\text{C}_2\text{H}_5)$	$\tau(\text{H}_\alpha)^b$	$\tau(\text{H}_\beta)$
4-Et ₃ SiC ₅ H ₄ N	67/0.3	1.5002	9.12	1.44	2.68
4-Me ₃ GeC ₅ H ₄ N	59/2.5	1.5060	9.63	1.42	2.66
4-Me ₃ SnC ₅ H ₄ N	59/0.3	1.5383	9.70	1.50	2.67
4-Me ₃ SiC ₅ H ₄ NO	111–113		9.70	1.76	2.58
4-Et ₃ SiC ₅ H ₄ NO	49–51		9.10	1.76	2.61
4-Me ₃ GeC ₅ H ₄ NO	116–118		9.56	1.77	2.62
4-Me ₃ SnC ₅ H ₄ NO	131–133		9.65	1.81	2.61

^aLiquids measured without solvent; TMS used as internal standard. Solids measured in CDCl₃ solution containing TMS. CH₃–M absorptions are singlets, all others are multiplets. ^bRefers to ring position adjacent to nitrogen; lower field ring absorption generally assigned to H_α (ref. 14).

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