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PARAMAGNETIC ADDUCTS OF GROUP IVB RADICALS WITH 4-SUBSTITUTED PYRIDINES

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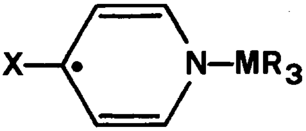
Organosilyl, organogermyl and organotin radicals are known to add easily to carbon-carbon[1)], carbon-oxygen[2)] and nitrogen-oxygen[3)] double bonds, thus giving radical adducts persistent enough to be studied by e.s.r. spectroscopy. Addition occurs in the latter two cases at the oxygen atom. Examples are also reported of the addition of silyl radicals to nitrogen-nitrogen and carbon-nitrogen double bonds; these include the adducts of diphenyldiazomethane[4)] and of several pyridines[5)]. With the latter derivatives the trimethylsilyl radicals were generated from $[(CH_3)_3Si]_2Hg$ and found to add to the heterocyclic nitrogen.

We wish to report here that pyridine adducts with silyl, germyl and, in one case, stannyl radicals may be readily obtained by irradiating solutions of the appropriate silane, germane or tin hydride in di-$\underline{t}$-Butyl peroxide containing the pyridine substrate. By using this method we have been able to produce the radicals reported in the Table and having the following general structure.



The adducts were generated in open quartz tubes by irradiation with a 1 kW mercury lamp under stationary conditions at nearly room temperature. Degassing of the solutions did not result in any improvement of the quality of the e.s.r. spectra.

While silyl and germyl adducts could be observed for all the different 4-substituted pyridines we used, except the 4-aminopyridine, only in one case (i.e. X=CN) we were able to record the spectrum of the tin adduct, this being probably due to the weakness of the nitrogen-tin bond. With the ethyl ester of the isonicotinic acid (3), irradiation in the presence of hexa-$\underline{n}$-Butylditin led to the corresponding 1-hydropyridinyl radical.

The measured hyperfine splitting constants are reported in the Table. The assignment of these splittings to the various positions is straightforward for derivatives (1)-(4) and (6) and parallels that one already reported for the correspondingly substituted 1-methylpyridinyls[6] and 1-hydropyridinyls[7]. The thiophen proton splittings in (7) have been assigned by analogy with other neutral radicals

TABLE - Hyperfine splitting constants (G) for the radical adducts of 4-substituted pyridines.

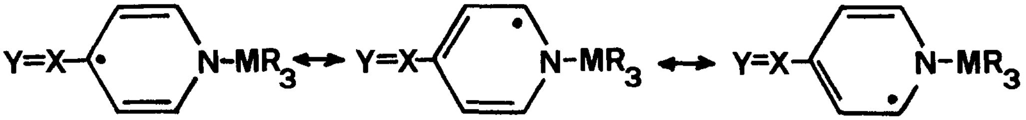
Compound	X	MR_3	$\underline{a}_{2,6}$	$\underline{a}_{3,5}$	$\underline{a}_N$	$\underline{a}_X$	
(1a)	CMe_3	$SiPh_3$	6.42	1.51	3.42	0.25[a]	
(1b)	CMe_3	$GePh_3$	6.07	1.36	4.95	0.23[a]	
(2a)	CN	$SiPh_3$	4.95	0.40	3.98	1.97[b]	
(2b)	CN	$GePh_3$	4.48	0.14	5.07	1.96[b]	
(2c)	CN	$SnBut_3$	4.35	0.0	5.35	2.00[b]	
(2d)*	CN	H	4.39	0.0	5.36	2.00[b]	4.39⌿
(2e)*	CN	CH_3	4.14	0.15	6.32	1.94[b]	5.47⌿⌿
(3a)	COOEt	$SiPh_3$	4.80 4.63	0.16 0.12	3.88	0.75[c]	
(3b)	COOEt	$GePh_3$	4.29 4.21	0.20 0.13	5.00	0.78[c]	
(3d)	COOEt	H	4.01 3.95	0.39 0.35	5.22	0.78[c]	4.48⌿
(4a)	$COCH_3$	$SiPh_3$	4.25 3.65	0.38 0.10≠	3.75	2.05[d]	
(4b)	$COCH_3$	$GePh_3$	3.77 3.57	0.80 0.42	4.37	2.40[d]	
(5a)	NH_2	$SiPh_3$	6.26	1.42	3.40	1.30[b]	
(6a)	Ph	$SiPh_3$	4.80	0.85	3.15	2.68 ($H_{\underline{o}}$), 0.85 ($H_{\underline{m}}$), 3.07 ($H_{\underline{p}}$)	
(6b)	Ph	$GePh_3$	4.35	0.70&	4.35	2.65 ($H_{\underline{o}}$), 0.70 ($H_{\underline{m}}$), 3.15 ($H_{\underline{p}}$)	
(7a)	2-Th	$SiPh_3$	4.46	0.89	2.82	4.00 (H_5), 1.07 (H_4), 4.75 (H_3)	
(7b)	2-Th	$GePh_3$	4.11	0.72	3.90	4.00 (H_5), 1.07 (H_4), 4.80 (H_3)	

$\underline{a}$, 9 protons; $\underline{b}$, 1 nitrogen; $\underline{c}$, 2 protons; *, in toluene; ⌿, $\underline{a}_H^{NH}$; ⌿⌿, $\underline{a}_{Me}^{NMe}$; ≠, splitting not resolved determined from computer simulation; &, tentative assignment.

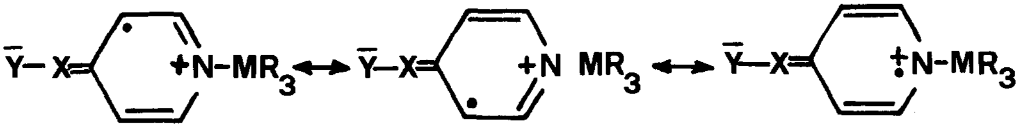
containing the 2-thienyl group[3)].

Some doubts may arise concerning the identification of the 4-amino-1-triphenylsilylpiridinyl (5a), as no splitting from hydrogens of the amino group has been detected. Since, however, this coupling should be strongly temperature dependent because of the effect of the rotation of the NH_2 group out of the molecular plane, a situation already encountered in the similar 4-amino-2,6-di-^{t}Butylphenoxyl radical[8)], it might well be that in our experimental conditions its value is very close to zero. Attempts to record the e.s.r. spectrum at different temperatures were unsuccessfull.

An understanding of the effect exerted on the hyperfine splitting constants of the pyridine ring atoms by the various substituents and entering groups, may be achieved on the basis of the apolar (Ia)-(Ic) and zwitterionic (IIa)-(IIc) resonance structures which may be written for our systems.



(Ia) (Ib) (Ic)



(IIa) (IIb) (IIc)

The polar structures will be favoured by the presence of electron withdrawing substituents in the 4-position and by MR_3 groups attached to the nitrogen atom which can easily delocalize the positive charge, i.e. electron releasing groups. An increasing importance of these polar mesomeric forms would produce a decrease of $a_{2,6}$, an increase of $a_{3,5}$ and of the nitrogen splitting. As far as the effect of the substituent in position 4 is concerned the observed trend of the ring proton couplings in the (1)-(5) adducts is consistent with the above interpretation, mainly if considering that $a_{3,5}$ is almost certainly positive in (1a,b), (2a,b), (3a) and (5a), and negative in the other radicals[9)]. In the case of the adducts of 4-phenylpyridine (6) and 4-(2-thienyl)pyridine (7) the observed splittings reflect the greater delocalizing capability of the 2-thienyl group with respect to phenyl[3)].

The effect of the entering group can be conveniently discussed by examining the results for the 4-cyano pyridine adducts (2), for which a wider set of data are reported, including those for 4-cyano-1-methylpyridinyl (2e)[6)] and 4-cyano-1-hydropyridinyl (2d) measured in a weakly polar solvent as toluene. The decrease of $a_{2,6}$ following the sequence $SiR_3 > GeR_3 > SnR_3 \simeq H > CH_3$ suggests that the contribution of polar structures to the mesomeric system becomes increasingly important along the same series. Also the trend of $\underline{a}_{3,5}$ and $\underline{a}_N$ is in agreement with this explanation. It can be noticed that the relative effect of proton and methyl is consistent with the known electron-donor character of the latter group. Therefore it can be safely concluded that group IVB organometallic substituents behave in these radicals as electron-acceptors, their electron-withdrawing power being very strong with silicon and vanishingly small for tin. Although a less complete set of comparative data could be obtained for the other derivatives, the variations of the reported hyperfine splittings follow the same trend as for radicals (2a)-(2e).

The electron-acceptor ability of silyl and germyl groups could be due either to partecipation of the empty metal $\underline{d}$ orbitals to the π system or to hyperconjugative interactions between the aromatic ring π orbitals and the M-C(Ph) σ bonds. MO calculations are in progress to try to clarify this point.

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References

1) J.R. Kochi, in "Advances in Free Radical Chemistry" vol. V, pp.189, G.F. Williams Ed., Elek Science, London, 1975.

2) A. Hudson and R.A. Jackson, Chem. Comm., 1323, 1969; A.J. Bowles, A. Hudson and R.A. Jackson, J.Chem.Soc.(B), 1947, 1971; A. Alberti and A. Hudson, Chem. Phys.Letters, 48, 331 (1977).

3) C.M. Camaggi, G.F. Pedulli, P. Placucci, and M. Tiecco, J.C.S. Perkin II, 1226, 1974; G.F. Pedulli, P. Zanirato, A. Alberti, and M. Tiecco, J.C.S. Perkin II, 293, 1975.

4) P.P. Gaspar, C.T. Ho, and K.Y. Choo, J.Amer.Chem.Soc., 96, 7819 (1974).

5) B. Schroeder, W.P. Neumann, J. Hollaender, and H.P. Becker, Angew.Chem.Internat Edn., 11, 850 (1972).

6) L. Grossi, F. Minisci, and G.F. Pedulli, J.C.S. Perkin II, 943, 1977.

7) J.K. Dohrmann and R. Becker, J. Magn.Resonance, 27, 371 (1977).

8) A.J. Stone and A. Carrington, Trans. Faraday Soc., 61, 2593 (1965).

9) M. Guerra, F. Bernardi, and G.F. Pedulli, Chem. Phys.Letters, 48, 311 (1977).

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