Journal of Organometallic Chemistry, 70 (1974) 383—385

METAL-SUBSTITUTED OXIRANES
A ^{1}H NMR STUDY OF TIN AND LEAD DERIVATIVES

GIORGIO BARBIERI and FERDINANDO TADDEI
Istituto di Chimica Organica, Università, Via Campi 183, 41100 Modena (Italy)
(Received October 5th, 1973)

Summary

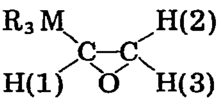
The analysis of the main and the satellite ^{1}H NMR spectra of oxirane tin and lead derivatives is reported. Chemical shifts and coupling constants are discussed in terms of possible electronic interactions between the metal atom and the oxirane ring.

Introduction

Cyclopropyl derivatives of tin and lead are known and their NMR spectra have been completely analyzed for both proton—proton and proton—metal nuclear interactions [1]. Oxirane compounds containing silicon [2] as well as several differently substituted oxiranes have been widely investigated in proton magnetic resonance; both chemical shifts and proton—proton coupling constants have been derived and discussed [2—4], but silicon—proton coupling constants have not been reported.

We have recently synthesized some tin and lead derivatives of oxirane with the purpose of analysing their main and satellite spectra and obtaining the corresponding parameters.

The oxirane ring is said [5] to be able to some extent to transmit conjugation, and since *d* orbitals of tin and lead seem to be available for $(d—p)\pi$ interactions with unsaturated organic groups [6], we shall discuss the proton chemical shifts of compounds(I) and (II) in the light of this. The proton signals of ethylene oxide in carbon tetrachloride are found at δ 2.56 ppm, and are only slightly solvent dependent [7]. When substituting one proton by an $SnMe_3$ or



[(Ia) M = Sn, R = Me; (Ib) M = Sn, R = Ph; (IIa) M = Pb, R = Ph.]

CMe_3 group, almost the same small low-field shift is produced (for tert-butyl oxirane [7] δ_1 is found at 2.60 ppm), thus effects other than conjugation must surely be involved. When the $SnPh_3$ group is substituted for the $SnMe_3$ group, almost the same low-field shift is observed for δ_1 in oxirane derivatives and for the protons of a methyl group in $MeSnMe_3$ (δ 0.07 ppm) and $MeSnPh_3$ (δ 0.71 ppm). The low-field shift observed should thus involve a global effect of the $SnPh_3$ group and not a conjugative interaction between tin and the oxirane ring. The lower electronegativity of tin with respect to carbon should cause some electron shift from M to the phenyl ring, and thus make the metal atom even more positive; this effect must be the origin of the low-field shift of oxirane protons in compound(Ib) with respect to compound(Ia). A somewhat different effect is produced by the substituent on the H(2) and H(3) protons even if their low-field shift is parallel in compounds (Ia) and (Ib). The different behaviour of these two protons is most probably due to a mutual polarization of the C—H bonds in these systems [4], which leads to different degrees of sensitivity to substituent effects for the two protons.

The $PbPh_3$ group causes considerable deshielding at H(1), while the deshielding effect on H(2) and H(3) is only slightly higher than that of the $SnPh_3$ group. This must involve a higher electron-withdrawing effect of the $PbPh_3$ group accompanied by a larger magnetic anisotropy of the neighbouring lead atom [8].

The proton—proton coupling constants are in the same range as those normally found in monosubstituted epoxides [3]: these values increase [2] slightly with the electronegativity of the first atom in the substituent. In this context $PbPh_3$ behaves as a more electronegative group than $SnPh_3$.

Finally, long-range metal—proton coupling constants deserve some mention. Previously, it was reported [9] that in mercury, lead and tin derivatives of furan and thiophene, long-range M—H coupling constants are linearly correlated to the corresponding J(HH) values of the unsubstituted heterocycles. This does not hold for oxirane derivatives (I) and (II), since, clearly, $J(M\text{—}H_{gem})$ is very large compared with the other J(M—H) couplings, while in oxirane the three J(HH) couplings have very similar values [10]. It has not been possible to establish correlations with the corresponding constants in vinyl and ethyl derivatives such as those found in the case of cyclopropyl derivatives [1]. Theoretical calculations may perhaps show whether this behaviour is due to peculiarities of the bonds in these systems or to a contribution of terms other than the Fermi contact mechanism in this particular case.

Experimental

The compounds were prepared by oxidation of the corresponding vinyl derivatives using the method reported by Emmons and Pagano [11]. Separation from the unreacted vinyl derivative was carried out by column chromatography, eluant n-pentane/ether 10/1 on Florisil. After crystallization from n-pentane, the following m.p. (and conversion yield) were found: (Ia), m.p. 80-81° (41%); (Ib), m.p. 90-91° (50%); (IIa), m.p. 85-86° (31%). All the derivatives gave satisfactory elemental analysis.

The spectra were recorded at 60 MHz with a JEOL-JNM C-60HL spectro-

TABLE 1

CHEMICAL SHIFTS (δ ppm) AND COUPLING CONSTANTS (Hz) FOR OXIRANE DERIVATIVES OF TIN AND LEAD

Compound	δ_1	δ_2	δ_3	δ_{CH_3}	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{M,1}{}^a$	$J_{M,2}{}^a$	$J_{M,3}{}^a$	$J_{M,CH_3}{}^a$
(Ia)	2.663	2.588	2.989	0.154	4.26	5.47	5.69	108.65/113.79	19.96/20.72	16.29/16.41	53.20/55.59
(Ib)	3.192	2.750	3.056		3.98	5.20	5.65	122.13/127.81	21.07/22.07	19.21/19.49	
(IIa)	4.084	3.056	3.148		3.79	4.84	5.48	267.45	27.97	23.70	

[a] In the case of tin derivatives these coupling constants refer to the isotopes $^{117}Sn/^{119}Sn$ and for lead derivatives to the isotope ^{207}Pb.

meter in chloroform-d_1 solution. Spectra analysis was performed with the LAOOCN 3 program [12]. Chemical shifts (δ values) and coupling constants determined from main and satellite spectra are given in Table 1 and show differences within 0.1 Hz.

References

1 P.A. Scherr and J.P. Oliver, J. Amer. Chem. Soc., 94 (1972) 8026.
2 K.L. Williamson, C.A. Landford and C.R. Nicholson, J. Amer. Chem. Soc., 86 (1964) 762.
3 C.A. Reilly and J.D. Swalen, J. Chem. Phys., 32 (1960) 1378; ibid. 34 (1961) 980;
C. Walling and P.S. Fredricks, J. Amer. Chem. Soc., 84 (1962) 3326;
B.P. Dailey, A. Gawer and W.C. Neikam, Discuss. Faraday Soc., 34 (1962) 18;
G. Allen, D.J. Blears and K.H. Webb, J. Chem. Soc., (1965) 810.
4 G. Ceccarelli, G. Berti, G. Lippi and B. Macchia, Org. Magn. Resonance, 2 (1970) 379.
5 R.G. Pews and N.D. Ojha, Chem. Comm., (1970) 1033.
6 E.A.V. Ebsworth, Organometallic Compounds of the Group IV Elements, Edited by A.G. McDiarmid, Vol. I, Part. I, New York (1968).
7 P. Lazzeretti, I. Moretti, F. Taddei and G. Torre, Org. Magn. Resonance, 5 (1973) 385.
8 P.N. Preston, L.H. Sutcliffe and B. Taylor, Spectrochim. Acta, Part A, 28 (1972) 197.
9 L. Lunazzi, M. Tiecco, C.A. Boicelli and F. Taddei, J. Mol. Spectrosc., 35 (1970) 190;
G. Barbieri and F. Taddei, J. Chem. Soc. B, (1971) 1903; ibid. (1972) 262.
10 F.S. Mortimer, J. Mol. Spectrosc, 5 (1960) 199.
11 W.D. Emmons and A.S. Pagano, J. Amer. Chem. Soc., 77 (1955) 89.
12 S. Castellano and A.A. Bothner-By, J. Chem. Phys., 41 (1964) 3863.