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Preliminary communication

Non-equivalent methylene protons in the 220 MHz NMR spectra of Group IVB alkyls

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Considerable interest has been shown recently in chemically indistinguishable but magnetically non-equivalent methylene and methyl protons in alkyl derivatives of the elements of Group I, II[1,2] and V[3,4]. We report here the observation of such an effect for the α-methylene protons of Group IVB alkyls, in the form of their tri-n-propylchloro derivatives. The enhanced chemical shifts obtained with the 220 MHz instrument reduces the complex spectra usually obtained at 60 or 100 MHz for Group IVB alkyls to essentially first order in many cases *e.g.* triethylchlorosilane and tri-n-propylsilane.

However as shown in Fig.1 for the tri-n-propylchloro derivatives of silicon,

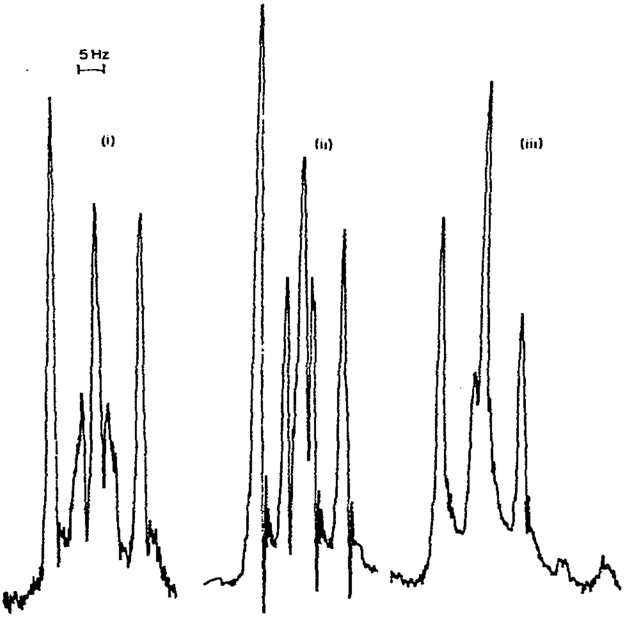
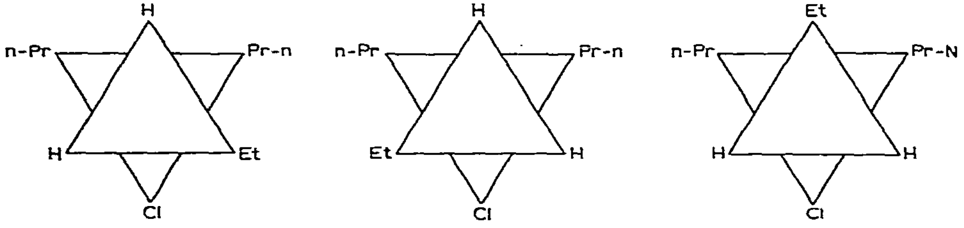


Fig.1. ^{1}H NMR spectra of the α-methylene groups for n-Pr_3MCl, where M = Si (i), Ge (ii) and Sn (iii) at 220 MHz/sec.

germanium and to a much lesser extent tin the anticipated triplet absorption of the α-methylene protons is distorted in a manner consistent with magnetic non-equivalence of the two protons. These absorptions showed a slight temperature dependence, when examined over the range of −30° to +100° with the expected tendency to collapse to a triplet at high temperature.

Three distinct interpretations of magnetic non-equivalence in alkyl–element systems have been proposed: (1) steric hindrance to rotation about the carbon–metal bond, resulting in a superimposition of spectra of different conformers, (2) unequal populations of rotation conformers about the $C\alpha$–$C\beta$ bond, with averaging of proton environments at high temperature due to breaking and reforming of carbon–metal bonds with inversion at the α-carbon, as proposed by Roberts and his coworkers[1] for Group I–III alkyls and (3) due to inherent asymmetry as observed by McFarlane[3] for diisopropylphenylphosphine.

For the n-propylchloro compounds of Group IVB reported here our preliminary results are consistent with case (1) in which we are observing the superimposition of the spectra of the conformers shown in Fig.2 due to restricted rotation about the carbon–metal bond. Both the absence of non-equivalence in the spectrum of tri-n-propylsilane, which is attributable to replacing the bulky chlorine atom by a hydrogen, thus reducing steric interaction with the ethyl groups of the n-propyl, and the relatively small variation with temperature observed, are consistent with this conclusion[5].



(I) (II) (III)

Fig.2. Rotational conformers of n-Pr_3MCl; M is at the rear.

The very slight distortion observed for the tin derivative may be interpreted in two ways. Firstly the increase in size in the sequence Si < Ge < Sn and consequent lengthening of the carbon–metal bond reduces steric hindrance to rotation about the carbon–tin bond relative to the germanium and silicon analogues. However, very recently Peddle and Redl[6] have reported that for asymmetric 1,1-dimethylbenzylchlorotin compounds the ^1H NMR absorption of non-equivalent methyl groups can be coalesced in polar solvents and at high concentrations by facile chloride–chloride exchange with concomitant inversion at the tin centre. Similarly, in the present case, it is possible that the almost first order spectrum for tri-n-propylchlorotin is due to chloride–chloride exchange allowing rapid equilibration of the conformers in Fig.2, which is not possible with the more stable metal–chloride bonds of germanium and silicon. Both of these possibilities and a wider range of Group IVB alkyls are currently under investigation.

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