GEMINAL INTERPROTON COUPLING CONSTANTS IN 2,2,3,3-TETRAMETHYLBUTANE AND TETRAMETHYLSILANE*

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In spite of considerable interest in geminal interproton coupling[1,2] no data are available for methane derivatives of type CH_3X where X is electropositive. Using previously described methods,[3] we were able to obtain the results summarized in Table 1. It can be seen that the geminal coupling in tetramethylsilane (Table 1)

Table 1

N.M.R. DATA ON PARTIALLY DEUTERATED COMPOUNDS

Compound	$J_{H,H}$ (c/s)	H,D Isotope Effects from Differences between	
		$-CH_3$ and $-CH_2D$	$-CH_3$ and $-CHD_2$
$(CH_3)_4Si$	$14\cdot15\pm0\cdot08$	$1\cdot09\pm0\cdot03$	—
$(CH_3)_3C-C(CH_3)_3$	$12\cdot50\pm0\cdot07$	—	$3\cdot14\pm0\cdot01$

Table 2

EXPERIMENTAL CONDITIONS FOR DEUTERIUM EXCHANGE

Substrate	Substrate Quantity	D_2O (ml)	Catalyst (g)	Reaction Time (days)	Av. Deuterium Content (D atom/molecule)
$(CH_3)_4Si$	0·23 ml	4	0·2	36	3·9
$(CH_3)_3C-C(CH_3)_3$	0·4 g	12	0·6	33	17·0

has a significantly higher absolute magnitude§ than that in methane ($12\cdot4\pm0\cdot6$ c/s)[1,2] in agreement with the prediction made by Pople and Bothner-By.[1] Geminal coupling in 2,2,3,3-tetramethylbutane (Table 1) also appears to be higher than that in methane, but the difference is within the uncertainty of the measurements.

In view of the high value of J_{gem} in tetramethylsilane, it may be possible that the magnitudes of J_{gem} in compounds of structure $(CH_3)_4X$, where X = C, Ge, Sn, and

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§ The signs of the geminal coupling constants considered here can be safely assumed to be negative.[1]

[1] Pople, J. A., and Bothner-By, A. A., *J. chem. Phys.*, 1965, **42**, 1339, and references therein.

[2] Niedrich, R. A., Grant, D. M., and Barfield, M., *J. chem. Phys.*, 1965, **42**, 3733.

[3] Macdonald, C. G., Shannon, J. S., and Sternhell, S., *Aust. J. Chem.*, 1964, **17**, 38.

Pb, could throw some light on the currently controversial[4] problem of electronegativities of Group IV elements.

The magnitudes of the deuterium isotope effects (Table 1), are unexceptional.[3]

Experimental

(*a*) *Preparation of Deuterated Compounds*

Using the apparatus previously described[5] reaction tubes of capacity 30 ml containing 10% palladium on charcoal (Light's) were subjected to two cycles of evacuation to 0·1 torr followed by admission of hydrogen to atmospheric pressure. A stream of hydrogen (100 ml/min) was then passed over the catalyst for 30 min at room temperature. Degassed deuterium oxide and the substrate were added, the tubes were cooled in liquid nitrogen, evacuated to 0·1 torr, sealed, and agitated for a period at 110–120°. The exchanged tetramethylbutane was recovered as previously described[5] while the exchanged tetramethylsilane was recovered by distillation into a trap at −80°. Average deuterium contents of the products were determined from the M−15 peaks in their 70-eV mass spectra. Details of the experimental condition are given in Table 2.

(*b*) *Proton Magnetic Resonance Spectroscopy*

The spectra of the deuterated compounds (as approximately 10% solutions in carbon tetrachloride) were recorded on a Varian A60 spectrometer. The geminal interproton coupling constants were obtained by multiplying the experimentally obtained[3] protium–deuterium coupling constants by 6·55;[3] the results quoted in Table 1 represent averages of at least 14 scans and the standard deviation refers only to the accuracy of measurement of the spectra.

[4] Drago, R. S., *Rec. chem. Progr.*, 1965, **26**, 157.

[5] Macdonald, C. G., and Shannon, J. S., *Aust. J. Chem.*, 1965, **18**, 1009.