Tetrahedron Letters No.46, pp. 4017-4019, 1969. Pergamon Press. Printed in Great Britain.

ANALYSIS OF THE NMR SPECTRA OF β-SUBSTITUTED ETHYLPHOSPHONATES: A REVERSAL IN THE MAGNITUDE OF J_{PCCH} AND J_{PCH}

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(Received in USA 29 July 1969; received in UK for publication 29 August 1969)

For proton-phosphorus coupling constants, one generally observes the relative magnitude of J_{PCCH} to be larger than J_{PCH} (1). For example, in triethylphosphite J_{PCCH} = 13.7 Hz. and J_{PCH} = 0.5 Hz (2). In tetracoordinate phosphorus compounds such as diethyl ethylphosphonate (1), J_{PCCH} = 18.0 Hz and J_{PCH} = 7.5 Hz (3). It has been suggested that this anomalous behavior is due to significant contributions to the Fermi contact interaction by various one-electron terms (2). We wish to report the analysis of the NMR spectra of a series of dimethyl β-substituted ethylphosphonates ($XCH_2CH_2P(O)(OCH_3)_2$) in which the reverse of the above trend is observed: $|J_{PCH}| > |J_{PCCH}|$.

All compounds were prepared by known procedures, or modifications thereof, and will be reported elsewhere. The above phosphonates exhibit proton spectra which are of the AA'BB'X type. Assignment of the chemical shifts and, hence, the coupling constants is based on the following: (a) the upfield proton resonance varies by only 0.48 ppm with all substituents; (b) the downfield proton resonance varies by 0.89 ppm and correlates with the shift expected on the basis of Shoolery's additive constants (4); (c) the phosphorus-proton coupling constant in the upfield resonance is not affected by temperature; and (d) the phosphorus-proton coupling constants in the downfield resonance changes with temperature by as much as 2.0 Hz. Only the assignment of the downfield resonance to the methylene protons adjacent to the substituent (X) and the upfield resonance to the methylene protons adjacent to phosphorus is consistent with the above.

Data obtained from the first-order analysis of the ^1H and ^{31}P spectra (5) are given in Table I. The relative signs of J_{PCH} and J_{PCCH} have been determined to be negative and positive respectively (6). Compared to I, β-substitution in the ethyl group causes a decrease in J_{PCH}. There is a general correlation between J_{PCH} and the electronegativity of the substituent; as the electronegativity increases, J_{PCH} decreases. Part of the decrease in J_{PCH} for the phosphonates reported here, compared to I, may be due to the difference in the alkoxyl groups on phosphorus. However, the difference in J_{PCH} for dimethyl and diethyl β-t-butoxyethylphosphonate has recently been determined to be 0.1 Hz. (7). Therefore, the decrease in J_{PCH} for the phosphonates is due to the β-substituent. It appears that the effect of β-substituents on geminal P-H coupling constants is similar to that observed for geminal H-H coupling constants (8).

Table I

$X\overset{(1)}{CH_2}\overset{(2)}{CH_2}P(O)(OCH_3)_2$

X	V_1^a	V_2	V_{CH_3}	J_{PCH}^b	J_{PCCH}	J_{POCH_3}	ϕP^c
CN	2.14	2.69	3.64	16.9	14.9	10.8	83.4
Cl	2.31	3.74	3.73	18.4	11.0	11.0	84.0
Br	2.42	3.58	3.72	18.6	10.0	10.9	84.2
$CH_3O\overset{O}{C}$	2.02	2.53	3.68	17.4	13.4	10.8	79.9
CH_3O	2.04	3.56	3.67	18.5	14.6	10.8	79.6
$CH_3\overset{O}{\overset{\|\|}{C}}$	1.94	2.70	3.67	17.7	12.1	10.8	78.2

a. In ppm downfield from internal TMS

b. In Hz.

c. In ppm upfield from external P_4O_6.

A similar decrease, compared to I, is observed for the substituent effect on J_{PCCH}. However, there is no correlation of J_{PCCH} with either the electronegativity or Taft's inductive parameter (9) of the substituent. This is not suprising since rotation about the C-C bond will influence this coupling (10). Recent NMR studies on the angular dependence of J_{PCCH} in rigid and freely-rotating systems (10, 11) indicate a gauche coupling constant of 6.0 Hz and a trans coupling constant of 50.0 Hz. Using these values and making the assumption of equal population of the conformers of the phosphonates, yields a value of J_{PCCH} of 21.0 Hz. Thus, the smaller values of J_{PCCH} for the phosphonates indicates that the more stable conformer is the one which has phosphorus and the substituent trans to each other. Griffin and Kundu (7) have recently reported nonequivalence of the methylene protons adjacent to phosphorus in dimethyl β-t-butoxyethylphosphonate. This was attributed to restricted rotation about the carbon-carbon bond since the nonequivalence disappeared upon raising the temperature. Therefore, the reversal in the trend noted above is due to two factors: (a) a decrease in J_{PCH} caused by substituent effects and, (b) a decrease in J_{PCCH} caused by the increase in population of the trans conformer plus possibly some decrease due to the substituent. One must, however, use caution in similar systems since it is possible that the gauche conformers could be lower in energy than the trans conformer resulting in a large increase in J_{PCCH}.

It has generally been assumed that phosphorus chemical shifts are influenced only by varying substituents directly bonded to phosphorus (12). That the effect of the substituents is transmitted to phosphorus and not confined only to the ethyl group is shown by the ^{31}P chemical shifts (Table I). The range of ^{31}P shifts with all substituents is 5.8 ppm. There is a good correlation between the ^{31}P shifts and Taft's inductive parameters indicating that the effect of β-substituents on ^{31}P chemical shifts operates through an inductive electron withdrawl from phosphorus.

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