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ASSIGNMENT OF CONFIGURATIONS OF SOME DIMETHYL BICYCLO[2.2.1]HEPTYL PHOSPHONATES BY NMR. W-TYPE $^{31}\underline{P}$-C-C-C-$^{1}\underline{H}$ COUPLINGS*

Claude Benezra

Department of Chemistry, University of Ottawa, Ottawa, Canada.

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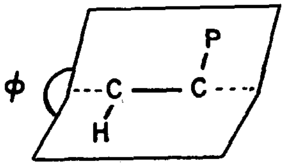
Previous results (1) have shown that the vicinal $^{31}P,^{1}H$ spin-spin coupling is probably a function of dihedral angle Ø. This also appears to be the case for $^{31}\underline{P}$-C-O-$^{1}\underline{H}$ coupling constants in phosphates (2a) and dioxaphosphorinanes (2b) and angular dependence has been shown in $^{2}J_{PH}$ in phosphines (3) (the angle being defined in this latter case by the lone pair of phosphorus and the hydrogen atom).



The results described here establish now the validity of the Karplus-type (4) relationship $J_{\underline{P}CC\underline{H}} = f(\emptyset)$ and provide a quick method for assignment of configuration of bicycloheptylphosphonates. Some particularly large values for long-range P-C-C-C-H due to the favourable geometric arrangement in the bicycloheptane system are also described.

Dimethyl 2,2,5,5-tetramethyltetrahydrofuran-3-ol-3-phosphonate (I) is a relevant example of dihedral angular dependence (1). $\emptyset_a$ and $\emptyset_b$ have been shown by X-Ray studies (5) to be equal to 30 and 90° respectively. The corresponding $^{3}J_{PH_a}$ and $^{3}J_{PH_b}$ are 7

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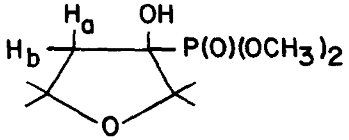
[*] Considered as Part V of NMR of Phosphonates. For Part IV see Bull. soc. chim. France, 3161 (1967)

and < 0.5 Hz. Nevertheless, because of the conformational mobility of (I) in solution, it is not certain that ϕ_b is still equal to ~90°. The bicyclo[2.2.1]heptane system is ideal for dihedral angular dependence studies, since in such system the geometry is being fixed. Attachment of $-P(O)(OCH_3)_2$ moiety to position 2 providesdihedral relationships of 90° (P_{2endo},H_1), 30° (P_{2exo},H_1), 120° (P_{2exo},H_{3endo} and P_{2endo},H_{3exo}) and 0° (P_{2exo},H_{3exo} and P_{2endo},H_{3endo}). Since bridgehead protons are easily recognizable, they may serve as standard to determine whether the dimethylphosphono moiety is endo or exo.

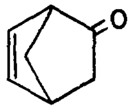
We have synthesized the Abramov adducts (6) of dimethyl hydrogen phosphonate(II) to various bicyclic ketones: norbornen-2-one(III), 2-norbornanone(IV) and 7-syn-bromonorbornan-2-one(V).



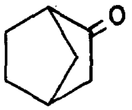
I

$HP(O)(OCH_3)_2$

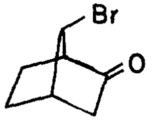
II



III



IV



V

Addition of (II) to norbornenone(III) results in the formation of two epimers to which structure (VI) and (VII) have been assigned on the following basis.[§] The NMR spectrum of compound(VI) is very similar to that of endo-norbornen-2-ol (7) and the NMR of (VII) looks like the NMR of the exo-norbornenol. The NMR spectrum of (VI) is completely interpretable in a first order analysis. The ^{31}P decoupled spectrum shows an AB quartet (with further coupling with bridgehead protons) at 6.15 ppm (2H, CH=CH), a s at 4.88 ppm (1H, OH, exchangeable with D_2O), 2s at 3.76 and 3.73 ppm (6H, non-equivalent $-O-CH_3$), m at 3.16 ppm (1H, H_1), m at

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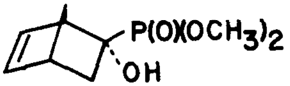
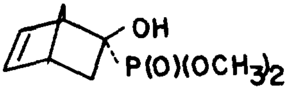
[§] All new compounds described here gave satisfactory analyses and IR spectra, compatible with the assigned structures. NMR spectra were performed in $CDCl_3$ or CCl_4 solutions on a Varian HA-100. Chemical shifts are given in δ values and referred to TMS as internal standard. ^{31}P decoupling experiments have been performed with an NMR specialties heteronuclear spin decoupler.

2.81 ppm, a *d* of *d* at 2.09 ppm (1H, H_{3exo}), an AB quartet centered at 1.52 ppm (2H, H_7) and a *d* of *d* at 1.11 ppm (1H,H_{3endo}). Comparison of normal spectrum and ^{31}P decoupled spectrum shows the following P,H coupling constants: J_{PH_1} ($\emptyset \sim 30^{\circ}$) = 7.5 Hz, $J_{PH_{3exo}}$ ($\emptyset \sim 0^{\circ}$) = 16.5 Hz, $J_{PH_{3endo}}$ ($\emptyset \sim 120^{\circ}$) = 6 Hz, $J_{P-C-O-H}$ = 1 Hz. The large value found for J_{PH} ($\emptyset \sim 0^{\circ}$) is consistent with a Karplus-type relationship between $^3J_{PH}$ and Ø.# One of the interesting features of the spectrum is the large W coupling between ^{31}P and H_6 ($J \sim 3$ Hz). The bicyclo [2.2.1]heptane system is well known to provide many examples of W-type H,H couplings (8).



VI



VII

Although the NMR spectrum of (VII) is less readily interpretable, *there is no ^{31}P,^{1}H* coupling with H_1,which shows that P,H ($\emptyset \sim 90^{\circ}$) < 0.5 Hz.

This last property ($J_{P_{2endo}},H_1$ < 0.5 Hz) can now be used for the assignment of configuration of the three following hydroxyphosphonates.

Dimethyl hydrogen phosphonate(II) adds to norbornanone(V) to give two epimers (9) to which structures (VIII) and (IX) have been assigned on the basis that P couples with H_1 in isomer(VIII) and not in isomer(IX). The *exo*-P(O)$(OCH_3)_2$ configuration has been further confirmed by quantitative catalytic hydrogenation of (VI) to (VIII).

Addition of (II) to 7-*syn*-bromonorbornan-2-one(V) (10) gives only one epimer to which structure(X) has been assigned (no P,H coupling). The formation of only one epimer is not surprising since the presence of a *syn* bromine atom strongly hinders the *exo* side of the molecule, leading mostly to *endo*-addition (10). ^{31}P couples with H_{7anti} with a 5 Hz long-range coupling constant. This is the largest four σ-bonds ^{31}P,^{1}H coupling constant so far described to our knowledge (J_{PCCCH} ranging from 0.8 to 1.5 Hz have been described earlier (11). More

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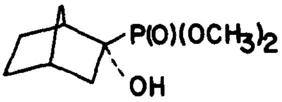
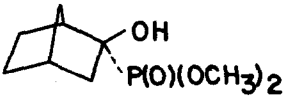
$^3J_{PH}$ ($\emptyset \sim 180^{\circ}$) has been shown in steroidal phosphonates (1) to be equal to 33 - 35 Hz.

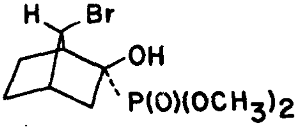
work along those lines is in progress.



VIII



IX



X

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