Tetrahedron Letters No.51, pp. 5365-5368, 1968. Pergamon Press. Printed in Great Britain.

NMR AND CONFORMATIONS OF SOME 5-t-BUTYL-2-METHOXY- AND 2-CHLORO-1,3,2-DIOXAPHOSPHORINANES

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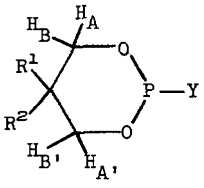
(Received in USA 15 June 1968; received in UK for publication 17 September 1968)

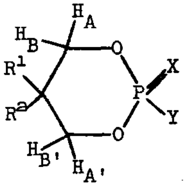
A great deal of effort has been expended in the past decade in nmr studies of the conformation of six-membered rings (1), but six-membered-ring phosphorus heterocycles have received little attention. NMR studies of 5,5-disubstituted-1,3,2-dioxaphosphorinanes, Id and II (2,3), and the synthesis of isomers, presumably cis and trans, of 4- and 5-substituted six-membered ring phosphites (4,5) have recently been reported, however the conformations of these compounds have not been considered in detail. We wish to report the synthesis of the phosphorochloridite, Ia, and a pair of isomeric phosphites, Ib and Ic, and complete analysis of their nmr spectra. Conformational implications of the data are discussed.



Ia: $R^1 = H_M$, R^2 = t-butyl, Y = Cl

Ib, Ic: $R^1 = H_M$, R^2 = t-butyl, Y = OCH_3

Id $R^1 = R^2 = CH_3$ Y = OCH_3



II: $R^1 = R^2$ = alkyl

Y = -OR, Alkyl, phenyl

X = O or S

Table I

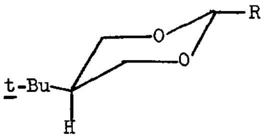
Chemical Shifts[5,6] and Coupling Constants[3,5] for Ia-c.[7]

Compound	$J_{AB}=J_{A'B'}$	$J_{AM}=J_{A'M}$	$J_{BM}=J_{B'M}$	$J_{AX}=J^{3}_{A'X}$	$J_{BX}=J_{B'X}$	ν_A	ν_B	ν_M	$\nu_{\underline{t}\text{-butyl}}$
Ia[1]	-10.90[8]	11.14	3.91	5.24	11.28	4.57	4.25	2.17	0.93
Ib[1]	-10.58	11.87	3.71	2.89	10.98	4.24	3.87	2.00	0.85
Ic[1]	-11.56	4.65	4.90	5.03	8.40	4.39	3.92	1.50	1.02
Ic[2]	-11.50	4.10	3.10	3.90	9.40	4.38	3.82	1.33	1.04

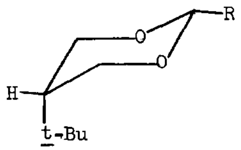
1. Approximately 20% solutions in $CDCl_3$ at 35°. 2. Approximately 20% solution in CS_2 at -62°. 3. in Hz; the cross-ring couplings are <2.0 Hz. 4. Phosphorus = X nucleus. 5. Probable errors of parameters <1.0 Hz. 6. Chemical shifts in ppm from TMS. 7. Compounds Ia-c are representative of an AA'BB'MX spin system and were analysed using the iterative computer program LAOCN3, developed by Bothner-By and Castellano (6). Inspection of the AA'BB' portion of the spectra enabled manual calculation of the simplified ABMX theoretical spectra (7). The parameters derived in this manner were utilized in the calculation of the theoretical AA'BB'MX spectra. 8. Calculated spectra unaffected by sign of J_{AB}; negative geminal coupling assumed (11).

Reaction of 2-*t*-butyl-1,3-propanediol with phosphorus trichloride in ether in the presence of triethyl amine yielded only one isomer of the phosphorochloridite, Ia. Treatment of a solution of Ia in ether with methanol and triethyl amine afforded the isomeric phosphites, Ib and Ic, in a ratio of 1:9 as determined from the intensities of the *t*-butyl signals (Table I) in the nmr spectrum. At temperatures of above 100° or on treatment with traces of acid, this ratio is rapidly changed to an equilibrium value of 9:1. The nmr chemical shifts and coupling constants of these compounds are reported in Table I. Good fits between the observed and calculated spectra of these compounds were obtained, and the excellent fit of the M proton attests to the validity of the line assignments used in computing the AA'BB' portion of the spectra.

Cis-*trans* isomerism has been noted in the 2-alkyl-5-*t*-butyl-1,3-dioxanes for which the conformations IIIa and IIIb seem well established (8). The above data can be interpreted as

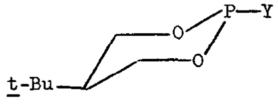


IIIa

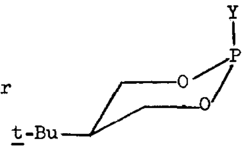


IIIb

the formation of analogous *cis*-*trans* isomers which are interconverted by inversion about the phosphorus center, which is capable of retaining configuration in phosphines (9). The coupling constants J_{AM} and J_{BM} for Ia and Ib are consistent with axial-axial and axial-equatorial relationships for the A, B, and M protons, and correspond to the ranges (10.6-12.1 and 4.4-5.6 Hz) reported for the dioxane series IIIa (8). Thus the *t*-butyl group can be assigned the equatorial position, and rapidly interconverting skew boat forms with the *t*-butyl pseudo-equatorial, which would give $J_{AM} \approx J_{BM}$ (*vide infra*), can be ruled out. The difference in magnitude of J_{AX} and J_{BX} would be predicted for a chair conformation, since the $POCH_A$ and $POCH_B$ dihedral angles, which influence the coupling (10), will be greatly different ($\Delta POCH_A \approx 60°$, $\Delta POCH_B \approx 180°$) and rules out a rigid boat conformation for which $\Delta POCH_A \approx \Delta POCH_B$. These ambient temperature data thus suggest for Ia (Y = Cl) and Ib (Y = OCH_3) the non-interconverting structures shown below.

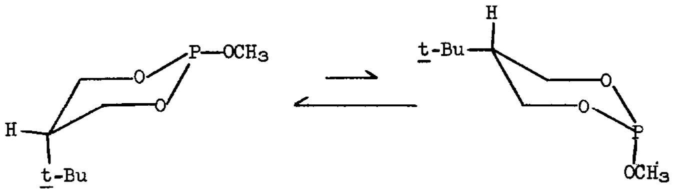


or



On the basis of 1,3-steric interactions, the *trans* structures would seem probable; however, anomeric effects cause 2-methoxy-substituents in 1,3-dioxanes to assume axial rather than equatorial positions (8), hence, the *cis* structures must be considered.[‡]

The nmr data for the less stable phosphite, Ic, are not so readily interpreted. The values J_{AM} (4.65 Hz) and J_{BM} (4.90 Hz) rule out the equatorial *t*-butyl group in a fixed chair conformation such as is proposed for Ia and Ib. If Ic is a chair structure with the *t*-butyl axial, the apparent equatorial-equatorial coupling, J_{BM}, is abnormally large. [J_{ee} in IIIb = 1.1-1.3 Hz (8)]. However, if it is assumed that the observed coupling is a time-averaged one resulting from an equilibrium between Va and Vb in which Va is the predominant conformation, then J_{BM} (J_{ee}) would be increased by the inclusion of a slight amount of axial-axial coupling while J_{AM} would not be appreciably changed since $J_{ea} \approx J_{ae}$.[‡‡]



Va Vb

An alternative possibility is that J_{AM} and J_{BM} for Ic are time averaged values resulting from rapid interconversion of skew boat forms. Examination of Drieding models in which the 5-*t*-butyl is placed psuedo-equatorially indicates that such an equilibrium would serve to decrease the average angle between the methine hydrogen and the psuedo-axial methylene hydrogens below the 180° expected of a rigid true boat, and therefore would reduce the observed coupling, J_{AM}. The average dihedral angle between the methine hydrogen and the psuedo-equatorial methylene hydrogens would be decreased from 60°, thereby increasing the observed coupling, J_{BM}. Both the chair and the boat equilibria discussed above should lead to a reduction in the difference between J_{AX} and J_{BX} as is observed. The low temperature data (Table I) for Ic are indicative of the former interpretation since the observed couplings J_{AM} and J_{BM} are changed to values more compatible with the expected (8) axial-equatorial and equatorial-equatorial couplings for conformer Va. Also, the couplings J_{AX} and J_{BX} are shifted toward normal values of $J_{H\text{-}C\text{-}O\text{-}P}$ for

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[‡] The accompanying communication by White, McEwen, and Verkade presents evidence for axial methoxy-substituents in similar systems.

[‡‡] As mentioned previously in the discussion of Ib the *trans* structures might also be considered in view of possible anomeric effects.

axial and equatorial protons in a fixed chair (see couplings in Ib). The chemical shift of the t-butyl group in compound Ic in CS_2 shifts from 1.01 ppm at 29° to 1.06 ppm at -85° which is in the direction that would be predicted for a larger contribution of conformer Va. The above data, together with the correspondence of the chemical shift values of the t-butyl group in the isomeric phosphites Ib and Ic with those of the isomeric dioxanes IIIa and IIIb (8), and the similarity of the 30 Hz upfield shift of the methine hydrogen in going from Ib to Ic to the 37 Hz upfield shift observed (8) for this hydrogen in going from IIIa to IIIb (R = t-butyl), cause us to strongly favor the chair equilibrium interpretation.

Acknowledgements. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 2439-A4, and by a National Aeronautics and Space Administration Training Grant (J.H.H.). We wish to thank Dr. R. O. Hutchins of Notre Dame University as well as Drs. D. M. Grant and A. J. Jones of the University of Utah for most helpful discussions, Mr. Allen MacKnight for assistance in the ABMX calculations and in the use of the computer, Dr. A. Bothner-By for making the LAOCN3 program available to us, and Dr. J. C. Martin and R. Thrift of the University of Illinois for obtaining the low temperature spectra.

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