Tetrahedron Letters No. 29, pp. 2775-2778, 1971. Pergamon Press. Printed in Great Britain.

SIX-MEMBERED RING PHOSPHORUS HETEROCYCLES.

USE OF EUROPIUM SHIFT REAGENT IN THE ANALYSIS OF THE P.M.R. SPECTRUM OF TRANS-2-METHYL-5-t-BUTYL-2-OXO-1,3,2-DIOXAPHOSPHORINANE

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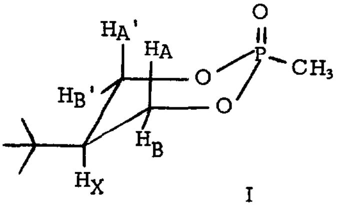
(Received in USA 8 June 1971; received in UK for publication 21 June 1971)

A considerable amount of work has been published[1] in the past few years concerning the conformations of saturated six-membered ring heterocycles containing phosphorus including phosphites, phosphates, phosphonites and phosphonates. The bulk of these investigations has involved analysis of very complex non-first order spectra of the AA'BB'X or AA'BB'XY type using iterative computer analysis procedures.

Recently, the lanthanide complexes have been shown to be powerful shift reagents for the simplification of nmr spectra[2]. We report here the use of tris(dipivalomethanato)europium (III), Eu(dpm)$_3$, to give greatly simplified spectra for trans-2-methyl-5-t-butyl-2-oxo-1,3,2-dioxaphosphorinane, (I). We previously reported[1d] results of analysis of chemical shifts and coupling constants for this compound using an ABXY approximation for the methylene region of the spectrum followed by iterative analysis of the AA'BB'XY system using the LAOCN3 program.[3] The trans stereochemistry and chair-form conformation for I in the solid state had been established by X-ray crystallography.[4]



I

Addition of tris(dipivalomethanato)europium (III), Eu(dpm)$_3$, in incremental amounts to a 0.2 M solution of I in CCl$_4$ gave downfield shifts which were linear in concentration of added Eu(dpm)$_3$

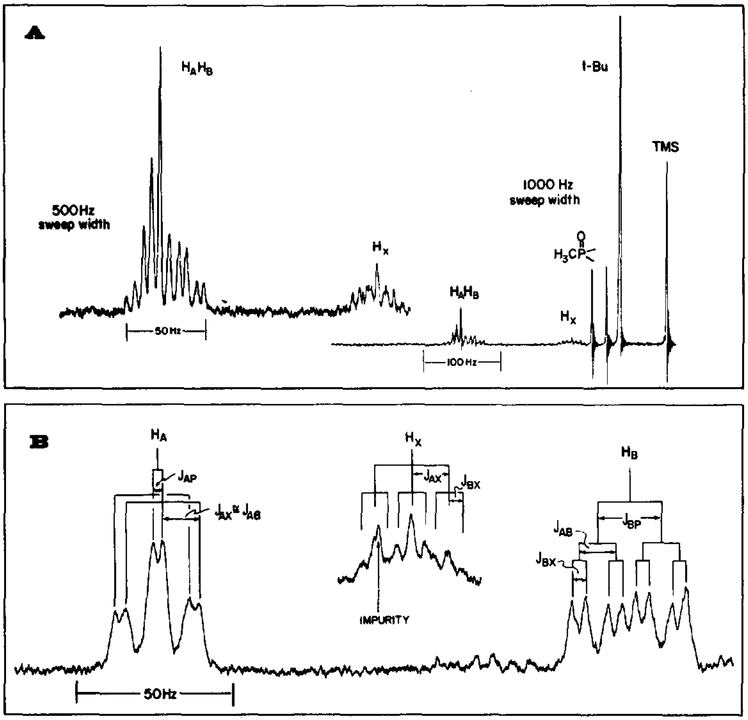


Fig. P.m.r. spectra of I: A, 0.2 M I in CCl_4; B, mole ratio $Eu(dpm)_3/I$, 0.5.

for all proton resonances. The sensitivity of each proton to added $Eu(dpm)_3$, expressed in terms of shift (Hz) vs. mole ratio $[Eu(dpm)_3/I]$, appears in Table I. The methylene hydrogens H_A and H_B, which overlap at 60 MHz ($\Delta\nu$ = 6 Hz), are moved well apart at $Eu(dpm)_3/I$ mole ratio 0.5,

Table I. Influence of Added $Eu(dpm)_3$ on Proton Chemical Shifts of Methylphosphonate I

Proton	H_A	H_B	H_X	2-Me	5-Bu^t
Sensitivity	552	256	288	448	72

($\Delta\nu$ = 142 Hz). This results in a spectrum which appears to be first order (See Fig.). Analysis on a first order A_2M_2XY basis[5] of both the methylene and methine regions leads to the coupling constants reported in Table II where they are compared to those which we obtained[11] with I in $CDCl_3$ by use of LAOCN3. Agreement is seen to be very good considering the reduced resolution accompanying $Eu(dpm)_3$ addition. The chemical shifts (given in parenthesis) for the $Eu(dpm)_3$ experiments were obtained by extrapolation of the chemical shift vs. mole ratio $[Eu(dpm)_3/I]$ plots to zero $[Eu(dpm)_3]$.

Table II. P.m.r. Data for I[a]

$\frac{\text{moles Eu(dpm)}_3}{\text{moles I}}$	J_{AB}[b]	J_{AX}	J_{BX}	J_{AP}	J_{BP}	ν_X[c]	ν_A	ν_B	$\nu_{5\text{-Bu}^t}$	$\nu_{2\text{-CH}_3}$
0.5	-11[d]	11	4	3	20	263	525 (274)[e]	383 (264)[e]	95	306
0[f]	-11.1[d]	10.5	4.47	4.14	20.2	123	264	258	58	90

a. At 60 MHz, 35°, 0.2 M I in CCl_4. b. Coupling constants in Hz. c. Chemical shifts in Hz downfield from TMS as internal standard. d. Assumed negative. Other J's assumed positive. e. By extrapolation to zero $[Eu(dpm)_3]$ of plots of chemical shift vs. mole ratio $[Eu(dpm)_3/I]$. f. J and ν values from computer assisted analysis using LAOCN3, sample in $CDCl_3$.[11]

The coordination of $Eu(dpm)_3$ appears to involve phosphoryl oxygen since similar shifting effects were not observed with the corresponding thiophosphonate or the trivalent methyl phosphite analog. The responses for H_A and H_B are of magnitudes relative to each other expected if H_A is closer to the coordination site than H_B. Models show this to be clearly so for the conformation shown with phosphoryl oxygen axial. It appears likely that this method will prove of value in determining configuration at phosphorus in such systems since in the cis form the sensitivities for H_A and H_B are changed.

The $Eu(dpm)_3$ reagent has given for other trans-1,3,2-dioxaphosphorinanes analogous to I apparent first order spectra essentially identical to those obtained at 220 MHz. The first order assumption was verified by spectral simulations at 60 MHz. The results, and those with the cis isomers, will be reported in a full paper .

Acknowledgement. This work was supported by a grant (CA 11045) from the National Cancer Institute of the Public Health Service.

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5. That this is really an AA'MM'XY case is seen by the fact that the upfield (equatorial) proton (H_B) signals are poorly resolved triplets resulting from cross-ring couplings. In previous studies[1d,k] we found that analyses of the methylene region of cases like I in terms of an ABXY approximation gave the same coupling constants as did the AA'BB'XY refinement.