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COMPLEXING OF PHOSPHORYL-CONTAINING COMPOUNDS BY TRIS(DIPIVALOMETHANO)EUROPIUM (III)

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Abstract—The addition of $Eu(DPM)_3$ to phosphoryl-bearing molecules produces striking spectral simplification by virtue of strong and almost complete complexing of the P=O group. The chemical shift induced by this complexing is dependent on the distance between the particular hydrogen shifted, by the complex, and the complexed site. In various molecules containing both P=O and other lone pair electron sites, complexing was found to be greater at the P=O, and only once this site was fully complexed, the other moieties underwent considerable complexing.

THE METAL EXTRACTING ability of compounds such as phosphine oxides, phosphinates, phosphonates, and organic phosphates, due to complexing, is well known.[1] Particularly interesting are the very strong complexes formed with uranyl nitrate.[2,3] This kind of complexing was found to induce considerable shifts in the NMR signals belonging to protons adjacent to the complexed phosphoryl group. In a previous report[4] we have shown that these shifts, induced by the uranyl nitrate complexing are not only a bonding effect but also a spatial effect and this latter fact has proved to be a useful tool in the elucidation of the stereochemistry of some phosphabicyclic compounds.

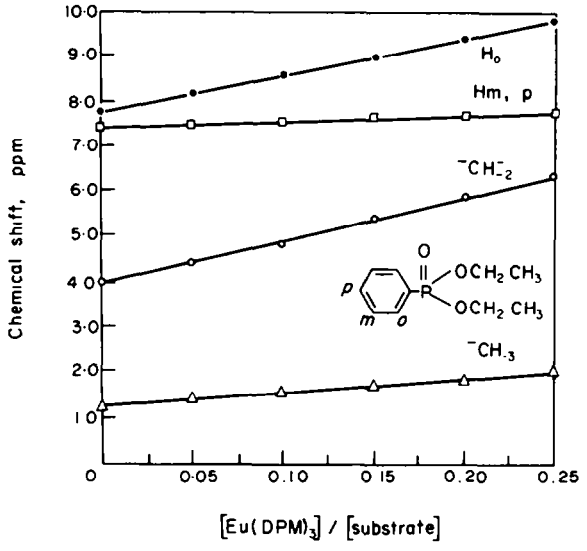
Recently, several reports dealing with the use of the NMR shift reagent $Eu(DPM)_3$ have been published.[5] In all of these, the simplification of the NMR spectra was achieved due to complexing of the lone electron pair on oxygen or nitrogen at various functional sites, with the europium reagent. Recognizing the power of this shift reagent, and presupposing that a phosphoryl group, by nature of its strong dipolar character[6] would form strong complexes with $Eu(DPM)_3$, the NMR spectra of complexed phosphonate, phospholene oxides, phosphole oxide and 8-phosphabicyclo-[3.2.1]octanic system derivatives were studied.

From the NMR spectrum of complexed diethyl phenylphosphonate (1), the first spectrum recorded (Graph 1) it was clear that $Eu(DPM)_3$ caused quite considerable shifts, even at low molar ratios.

Comparison of the shifts of the *o*-Ph protons in the phosphonate, with the corresponding protons of the 1-Ph group in 1,2-diphenyl ethanol[5a] showed that the shift in the case of the phosphonate was 70% of that in the substituted ethanol. The graph also clearly demonstrates the linear relationship between the chemical shift of each particular hydrogen atom and the molar ratio of the $Eu(DPM)_3$ and the substrate, as is well known in other cases.[5] As expected[2,3] signals attributed to protons α to the P=O group, are shifted more than those β or γ to this site.

Most fascinating results were obtained from the complexing of 1,2,5-triphenylphosphole oxide (2) (Fig. 1). When uncomplexed, this substance shows a very com-

GRAPH 1



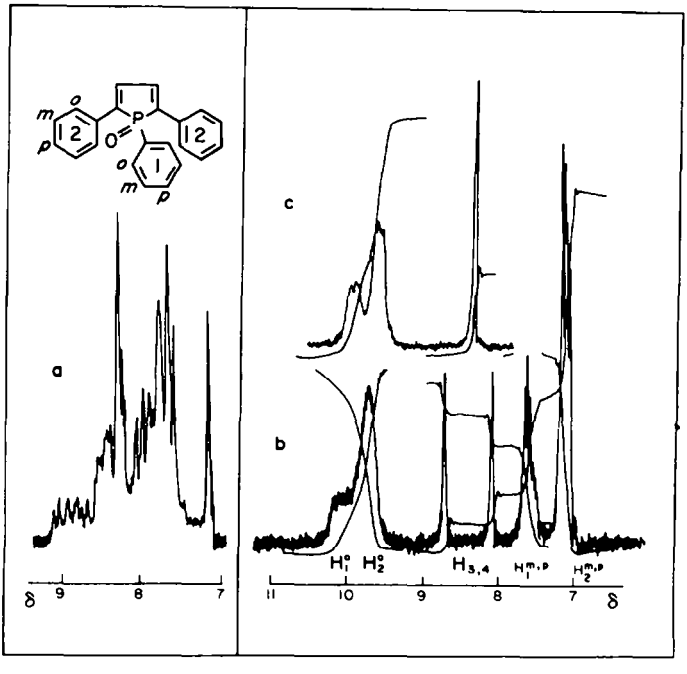


FIG 1. NMR spectrum of 1,2,5-triphenylphosphole oxide (2) a. Uncomplexed b. Complexed with Eu(DPM)$_3$ (0·47 equivalents) c. P-irradiated.

(The symbols Ho, Hm and Hp here and in other figures and tables stand for the *ortho*, *meta* and *para* positions on the aromatic rings.)

plicated proton NMR spectrum,[7] (Fig. 1a) from which very little data can be obtained. Addition of $Eu(DPM)_3$ to this compound in $CDCl_3$, at a molar ratio of 0·47 gave rise to five well separated multiplets (Fig. 1b). Decoupling experiments, including P-decoupling (Fig. 1c) and integration ratio, enabled us to assign the different signals to the various protons of the molecule.

The influence of $Eu(DPM)_3$ is variously attributed to; (a) an effect through bonds, and (b) a direct effect through space. The relative importance of these effects has not yet been decided, whereas from the NMR spectra of compounds **1** and **2** it is not possible to distinguish between the two effects, the spectra of 1-phenyl-phospholene-oxide (**3**) and 1-phenyl-3,4-dimethyl-phospholene-oxide (**4**) show that the second effect definitely exists, whereas the first is still arguable.

In compounds **3** and **4**, the C_2, as well as the C_5, geminal proton pair, which in the uncomplexed material exhibited almost the same chemical shift, divided into two groups upon complexing with $Eu(DPM)_3$, giving rise to an ABP spectrum in the case of **4** and ABXP in the case of **3** (Table 1).* Thus showing the dependence of the induced shift of each one of the geminal protons on its direct distance from the complexed site.

In all the above examples, the only site which could give rise to complexing was the P═O group. It was reasonable to assume, as indeed we later proved, that even if additional lone pair electron bearing functional moieties were present in the same molecule, the P═O would be most strongly complexed due to its great polarity, while the additional sites would give rise to only weak, undetectable complexes. The isomeric 8-phenyl-8-oxo-8-phosphabicyclo[3.2.1]octan-3-ones (**5** and **6**) which

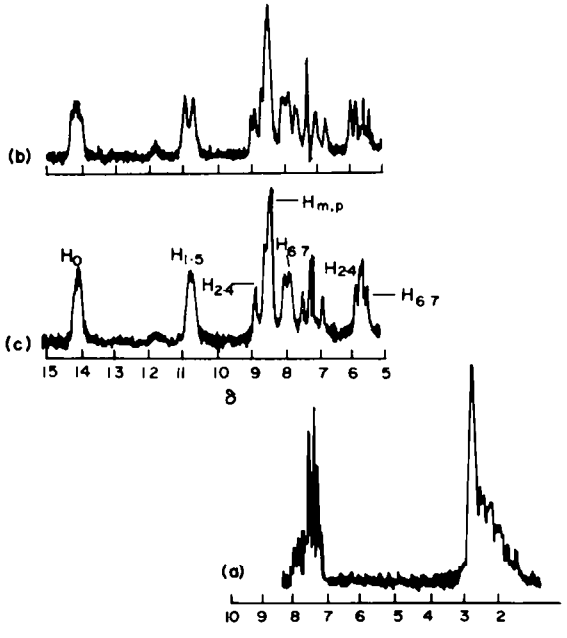
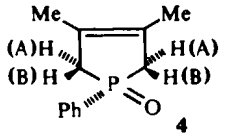
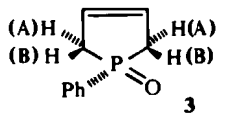


FIG 2. NMR spectrum of compound **6**, a. Uncomplexed b. Complexed with $Eu(DPM)_3$ (1·56 equivalents) c. P-decoupled.

* The solvent dependence of the chemical shift was found to be the same as reported[5] for other complexes of $Eu(DPM)_3$, i.e. $CCl_4 > CDCl_3 \geqslant CD_3CN$.

TABLE 1

Compound	$H_2(A)(H_5(A))$		$H_2(B)(H_5(B))$		$=C-C\underline{H}_3$		$=C-\underline{H}$		H_o		$H_{m,p}$	
	δo^a	δc^b	δo	δc	δo	δc	δo	δc	δo	δc	δo	δc
	$\Delta\delta^c$		$\Delta\delta$		$\Delta\delta$		$\Delta\delta$		$\Delta\delta$		$\Delta\delta$	
 4	2·73	4·08	2·73	4·50	1·78	2·08	—		7·80	9·44	7·50	7·80
	1·35		1·77		0·30				1·64		0·30	
 3	2·80	4·31	2·80	4·74	—		6·02	6·63	7·76	9·76	7·50	7·83
	1·51		1·94				0·61		2·00		0·33	

All chemical shifts are given in PPM ($CDCl_3$)

[a] Uncomplexed.

[b] Complexed ([Eu(DPM)]/[Substrate] = 0·25).

[c] $\Delta\delta = \delta c - \delta o$.

normally produce very complicated spectra, were good models for checking this assumption. As is shown in Fig. 2 for compound **6**, the $Eu(DPM)_3$ complexation considerably simplified the spectra to the point where every class of protons appeared separately.

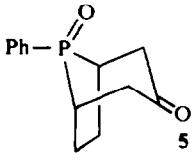
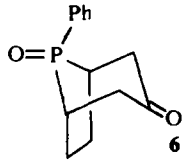
From the NMR data of compounds **5** and **6** (Fig. 2, Table 2, Graph 2 and Graph 3) the following facts could be clearly seen:

a. Protons α to the P=O are shifted much more than those α to the C=O group.*

b. The phenylic protons α to the P=O are considerably shifted, a shift which is approximately the same as in the former compounds containing the Ph-P=O group only.

c. Inversion of P-configuration especially influenced those protons which are directed towards the phosphoryl group.

TABLE 2

Compound	Δδ 0·25 (ppm)						
	$H_6(H_7)$	$H_6(H_7)$	$H_2(H_4)$	$H_2(H_4)$	$H_1(H_5)$	H_o	$H_{m,p}$
 **5**	1·00	1·00	0·60 (eq)	1·51 (ax)	2·08	1·90	0·43
 **6**	0·60	1·3 ± 0·1	1·1 ± 0·1[a]	0·7 ± 0·1[b]	1·90	1·40	0·24

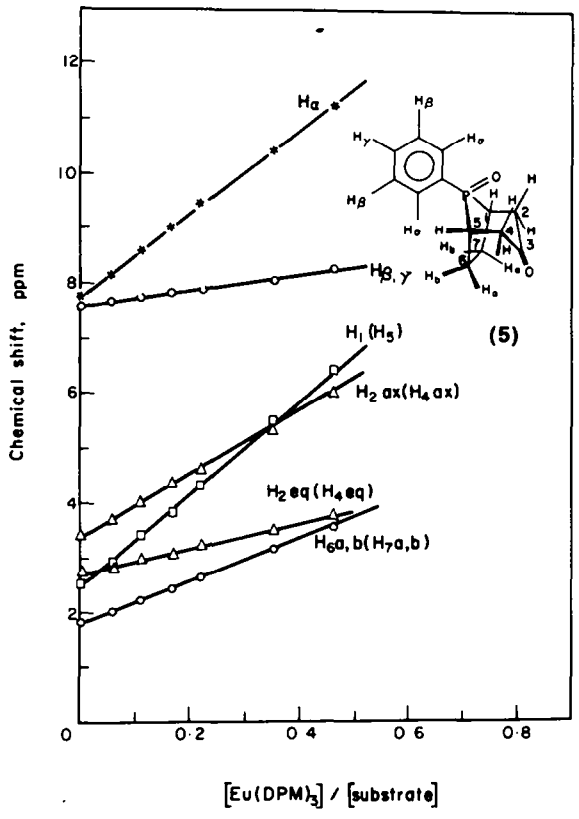
[a] $^3J_{P-H}$ = 7·5 cps. [b] $^3J_{P-H}$ = 27 cps. If a Karplus-like equation holds in this case, then *a* are the axial and *b* are the equatorial protons.

Most interesting were the slopes of the chemical shift *vs.* $Eu(DPM)_3$ concentration. It is clearly seen (Graph 3) that up to a molar concentration of one, the protons most effected are those near the P=O group, while above this value the direction of the lines changed in a manner clearly showing that the complexation of the C=O group was dominant. Moreover, the fact that the changes are at a molar ratio of *ca.* 1, suggests that the equilibrium between the substrate and the P=O complexed form, lies almost completely to the side of the complex.

From all the above results, obtained for the two P-epimers (**5** and **6**), it could be learned that in addition to linearity of δ *vs* molar ratio (Graph 2 and 3) and the selectivity in spatial influence on the proper protons (Table 2), the P=O group is indeed the major site of complexing rather than the C=O group. The superiority of P=O group over alcoholic group in complexing was also shown in the case

* It must be mentioned that the corresponding phosphines were also examined and as mentioned before,[5a] it was found that $\Delta\delta_{0.45}$ for the C_1 and C_5 protons was near to zero.

GRAPH 2



of 3α-hydroxy-8-oxo-8-phenyl-8-phosphabicyclo[3.2.1]octane (7) where $\Delta\delta_{0.25}$ H_1 (H_5) = 1·90 ± 0·2 and $\Delta\delta_{0.25}$ (C-3β—H) = 0·22 ± 0·05 ppm only.*

The results for some other derivatives of the phosphabicyclic system are given in Table 3. Among these compounds, of particular interest was the ketal **10**, in which the two pairs of ketalic protons which are seven bonds away from the P=O but have a different distance from the complexed site, were differently shifted, once more proving the spatial effect.

The complexation of compound **4**, was also carried out with the use of the diamagnetic shift reagent $Pr(DPM)_3$. From Table 4 it can be seen that $Pr(DPM)_3$ is a more powerful shift reagent than $Eu(DPM)_3$. However, in most cases, because of its diamagnetic shift, we have found $Eu(DPM)_3$ to be more suitable.

In conclusion, we have found that the P=O group is strongly complexed in the various phosphoryl-bearing compounds, complexing is almost complete and has a spatial effect. Complexing of P=O very greatly simplifies the spectra of P=O bearing compounds, even in the presence of other lone pair electron moieties which undergo complexing at much lower strength.

* $\Delta\delta_{0.25}$ for H_1 in *cis*-4-t-butylcyclohexanol is 4·5 ppm.[5c]

GRAPH 3

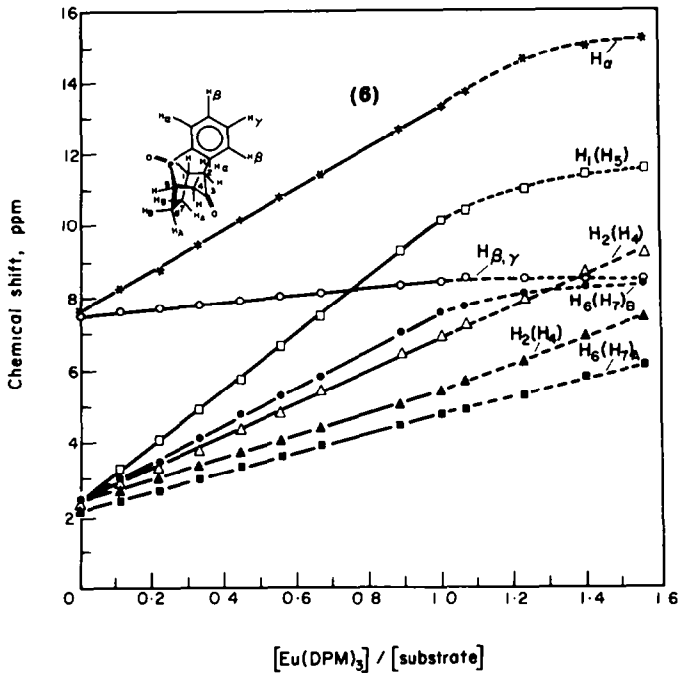
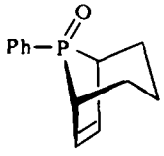
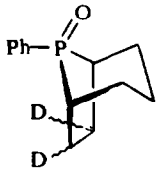
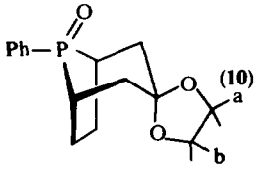
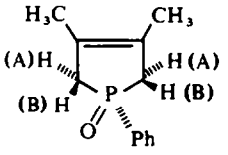


TABLE 3

Compound*		Δδ 0·25 (ppm)			
		$H_1(H_5)$	H_o	$H_{m,p}$	Other protons
	(8)	1·94	1·76	0·19	$H_6(H_7)$ 0·95
	(9)	1·96	1·32	0·17	—
	(10)	2·08	1·22	0·10	Ha 0·25 Hb 0·00

* in $CDCl_3$.

TABLE 4



	Δδ 0·3 (ppm)*	
	$Eu(DPM)_3$	$Pr(DPM)_3$
$-CH_3$	−0·45	+0·85
H_2A (H_5A)	−1·75	+3·81
H_2B (H_5B)	−2·47	+4·58
H_o	−2·18	+0·73
$H_{m,p}$	−0·42	+3·67

* In CCl_4.

EXPERIMENTAL

NMR spectra measured on a Jeol JNM-C-60HL spectrometer operated at 60 MHz at normal probe temperatures. Chemical shifts are in δ units (ppm) from internal TMS.

Substrates for study were obtained as follows: diethylphenylphosphonate (**1**), was synthesized according to Kosolapoff.[8] 1,2,5-triphenylphosphole-1-oxide (**2**), was obtained according to the method reported by Campbell *et al.*.[7] The preparation of 1-phenyl-3-phospholene-1-oxide and 1-phenyl-3,4-dimethyl-3-phospholene-1-oxide (**3** and **4** respectively) was carried out according to Quin *et al.*[9] The synthesis of the two P-epimers of 8-phenyl-8-phosphabicyclo[3.2.1]octan-3-one, their oxides (**5** and **6**) and the ketalic

Compounds **7**, **8** and **9** showed correct elemental analysis, and their proposed structures were well supported by spectral data. Full description of the synthesis and characterization of these new compounds will be published later.

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