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THE USE OF LANTHANIDE SHIFT REAGENTS IN STRUCTURAL STUDIES OF PHOSPHINE OXIDES

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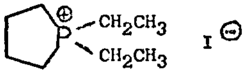
During a recent investigation[1] it was important to identify the phosphine oxides formed in the alkaline hydrolysis of the cyclic salts (1) and (2). The use of nmr Shift reagents appeared to offer a facile solution to this problem[2]. At the time that this work was carried out these reagents had not been used to study phosphine oxides and so initial investigations involved the known triethyl- and tri-n-butyl phosphine oxides. However, recently a number of publications[3] have appeared dealing with specific uses of Shift reagents in ^{1}H [3] and ^{31}P [3b] nmr spectra of compounds containing P=O bonds.

(1)



(2)

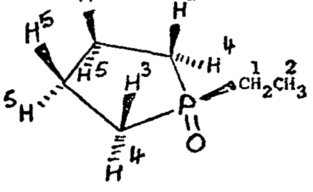
The results obtained from spectra run in $CDCl_3$ in the presence of various concentrations of shift complex are given in the table. $Pr(dpm)_3$ is less satisfactory for phosphine oxides than the europium complex since with the former reagent the shifts are positive (upfield). This requires a 'crossover' of absorptions at lower field before good resolution is obtained and hence much higher concentrations of $Pr(dpm)_3$. Δ M values (table) (which are generally larger for $Pr(dpm)_3$ than $Eu(dpm)_3$ [4]) are similar in magnitude to those obtained for sulphoxides (Δ Eu = 8·9 for CH_3SOCH_3 [5]).

$(\overset{2}{C}H_3\overset{1}{C}H_2)_3\ P{=}O$

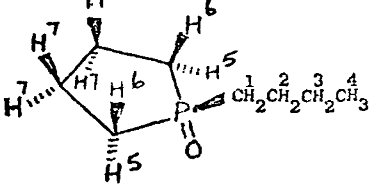
(3)

$(\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2)_3\ P{=}O$

(4)



(5)



(6)

Nmr spectra of triethyl-(3) and tri-*n*-butyl-(4) phosphine oxides in the presence of $Eu(dpm)_3$ were readily interpreted with molar ratios of complex to oxide of 0·4–0·5, although a distinct deviation from proportionality was observed with molar ratios $> 0{\cdot}6$.[6] In the triethyl case J_{PCH} (11 Hz) and J_{PCCH} (15.5 Hz) were obtained; these couplings cannot be measured in the absence of shift reagent without decoupling facilities. Phosphorus-hydrogen coupling constants could not be obtained for tri-*n*-butylphosphine oxide due to broadening of the α and β hydrogen absorptions, although $J_{H_\gamma - H_\delta}$ (7·5 Hz) could be measured.

The magnitude of the shift due to $M(dpm)_3$ reagents is inversely proportional to the cube of the distance from the metal atom[7] and in most cases (but not all[8]) angular effects can be ignored. Correlations in conformationally mobile systems [e.g. (4)] are generally difficult[5]; however the cyclic oxides (5) and (6) contain a fairly rigid ring system which appears to allow resolution of absorptions due to H^6 and H^5 in (6) and H^3 and H^4 in (5). These results indicate that $Eu(dpm)_3$ could be used to identify *cis* and *trans* isomers of 5-membered cyclic phosphine oxides[3a]. Measurements obtained from molecular models[9] substantiate the inverse cube relationship in these cases.

TABLE

Oxide	(a) ΔEu_1	ΔEu_2	ΔEu_3	ΔEu_4	ΔEu_5	ΔEu_6	ΔEu_7	ΔPr_1	ΔPr_2	ΔPr_3	ΔPr_4
3	7.1	4.8	-	-	-	-	-	10.7	7.2	-	-
4	7.8	6.8	2.0	0.5	-	-	-	10.5	8.5	3.2	1.4
5	6.6	4.3	5.5	6.6	3.0	-	-				
6	6.2	4.6	1.8	1.1	6.2	4.6	2.5				

(a) $\Delta M = \delta\,(CDCl_3) - \delta\,[CDCl_3 + \text{equimolar amount of } M(dpm)_n]$ [10]

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