Assignment of Configuration to 2,2,3,4,4-Pentamethylphosphetan Oxides Using Tris(dipivalomethanato)europium(III)

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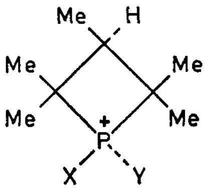
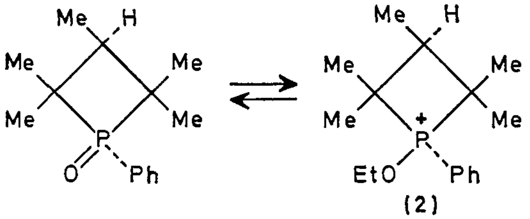
Summary *cis*- and *trans*-isomers of 2,2,3,4,4-pentamethylphosphetan oxides can be distinguished by the paramagnetic shifts of the respective 3-protons in their n.m.r. spectra in the presence of tris(dipivalomethanato)europium(III), Eu(DPM)$_3$.

NUCLEOPHILIC substitutions of good leaving groups at the phosphorus of the phosphetans (**1**) are usually held to proceed with retention of configuration at phosphorus[1,2] although definitive proof has been produced in few cases. Mislow[3] showed that in hydrolysis of the ethoxyphosphonium salt (**2**) nucleophilic attack at phosphorus gave the oxide from which the salt was prepared by *O*-alkylation; the hydrolysis must therefore involve retention of configuration. Cremer[4] showed that the methyl esters (**3**; R = OCD_3) and (**4**; R = OCD_3) in methanolic sodium methoxide exchange their trideuteriomethoxy-groups for methoxy without equilibration of the two isomers. In other cases the assumption of retention at phosphorus leads to a consistent picture, but in view of the importance of the stereochemical course of these substitutions in their mechanistic interpretation[2] a method of assigning the configuration of the phosphetans (**3**) and (**4**) by physical means was sought. We now report that this assignment can be made with the europium shift reagent, tris(dipivalomethanato)europium(III).[5]



(1)



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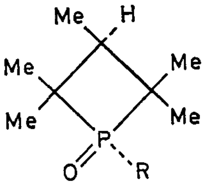

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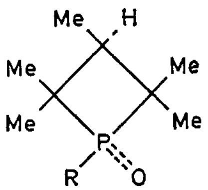

(4)

Chemical shifts were recorded in deuteriochloroform containing 0·48 molar equivalent of Eu(DPM)$_3$ and the results are given in the Table. Those isomers which are known (**3**; R = Ph[6]) or have been assumed to be *trans* (**3**; R = OEt,[1] SEt,[7] Me,[8] CH_2Ph,[9] and $NH{\cdot}CH_2Ph$[10]) show a shift in the position of the 3-proton of 135—160 Hz while in those isomers which are known (**4**; R = Ph[11]) or have been assumed to be *cis* (**4**; R = OEt,[7] SEt,[7] Me,[7] and $NH{\cdot}CH_2Ph$[10]) the shift of these protons is 187—262 Hz. This difference would allow assignment of configuration to a 2,2,3,4,4-pentamethylphosphetan oxide of unknown geometry. Other shifts, *e.g.* of one pair of α-methyl groups, are less definitive but show a consistent difference in the two series. The greater shift of the 3-proton in the *cis*-isomers implies that the europium co-ordinates with the phosphoryl oxygen in all cases.

TABLE[a]

N.m.r. spectra of phosphetan oxides (3) *and* (4) *in* $CDCl_3$ *in the presence of* 0·48 *molar equivalent of* $Eu(DPM)_3$

R	Isomer	3-Me	3-H	2,4-Me_2	2,4-Me_2	Others			
Ph	(3)	7·58 82	5·25 160	6·92 118	5·73 166				
Ph	(4)	7·58 83	3·33 224	6·78 119	5·68 174				
Me	(3)	7·80 78	6·25 140	7·35 89	6·1 158	P.Me	5·83 158		
Me	(4)	7·73 81	4·80 187	7·22 100	5·85 169		5·97 150		
OEt	(3)	7·68 86	6·0 145	6·92 114	6·20 155	O.CH_2	2·57 194	O.C.Me	7·58 65
OEt	(4)	7·50 97	4·55 224	6·70 131	5·80 174		2·68 196		7·47 76
NH.CH_2Ph	(3)	7·70 84	6·17 135	7·17 99	6·03 162	N.CH_2	3·52 133		
NH.CH_2Ph	(4)	7·73 84	4·33 234	7·10 112	5·90 171		3·87 117		
SEt	(3)	7·63 87	5·73 154	6·82 115	5·83 171	S.CH_2	4·08 177	S.C.Me	7·70 51
SEt	(4)	7·27 108	3·58 262	6·43 145	5·50 191		4·13 180		7·33 81
CH_2Ph	(3)	7·63 88	5·83 144	7·23 96	5·83 176	P.CH_2	3·83 173		

[a] The chemical shift (τ) is followed by the shift (Hz) from the normal position in $CDCl_3$.

The complexes formed with the europium reagent and phosphetan sulphides were insoluble in deuteriochloroform.

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