Nuclear Magnetic Resonance Spectra of Organophosphorus Compounds. I. Long-range Coupling between Phosphorus and Proton through Four Bonds

By Kensuke TAKAHASHI,* Taro YAMASAKI and Goh MIYAZIMA

The Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira-cho, Sendai
The Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Naga-machi, Sendai
Naka Works, Hitachi, Ltd., Ichige-cho 882, *Katsuta, Ibaragi*

(Received September 28, 1966)

In this communication, we will compare the results of the coupling constants observed in some organophosphorus compounds of the type of $(EtO)_nPCl_{3-n}$ with those of $(EtO)_nPXCl_{3-n}$ (X=O or S, and n=3, 2 or 1). Some data were given in Table I and a typical proton spectrum of $EtOPOCl_2$ was shown in Fig. 1. The doubling of the usual 3—4 pattern of the ethyl group is clearly observed in Fig. 1. This is ascribed to the coupling between phosphorus and protons in methyl and methylene groups. As has been shown in Table I, the long-range coupling between phosphorus and proton through four bonds was observed in six pentavalent compounds but unresolved one in three trivalent compounds. The magnitude of the long-range coupling, $^4J_{PH}$, seems to increase in the order of P, PS and PO, while that of the $^3J_{PH}$ increases in the order of P, PO and PS; the effect of the substitution of oxygen by sulfur in the $^4J_{PH}$ is opposite to that in the $^3J_{PH}$. The substitution of an ethoxy group by chlorine causes the increase of the coupling constants both between phosphorus and methyl protons and between phosphorus and methylene protons. This kind of effect caused by some electronegative groups has been discussed by Hendrickson et al.,[1] but the long-range coupling between phosphorus and proton through four bonds has not yet been reported except some acetylenic compounds.[2] The coupling constants between protons in these compounds are almost constant. Another point of interest is that we can determine the relative sign of the coupling constants in this system using the double resonance technique. Preliminary results show $^3J_{PH}$ and $^4J_{PH}$ in $EtOPOCl_2$ (No. 4 in Table I) have the same relative sign. This was determined by partial irradiation of the methylene protons. Spectra were examined on the liquid containing a small amount of TMS as an internal reference. The proton and phosphorus resonances were observed at 60 and 24.288 Mc. p. s. respectively, using a Hitachi H-60 type spectrometer system.

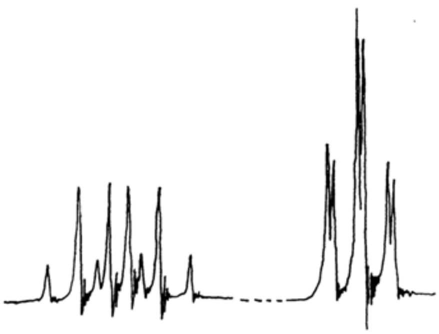

Fig. 1. The proton magnetic resonance spectrum of $EtOPOCl_2$ at 60Mc p. s. Applied magnetic field increases from left to right.

TABLE I. NMR DATA OF SOME ORGANOPHOSPHORUS COMPOUNDS

No.	Compound	Coupling constant, c.p.s.			Chemical shift, p.p.m.*	
		$^3J_{PH}$**	$^4J_{PH}$	$^3J_{HH}$	δ_{CH_3}	δ_{CH_2}
1	$EtOPCl_2$	$8._5$	<0.5	7	1.35	4.27
2	$(EtO)_2PCl$	8	<0.5	7	1.29	4.05_5
3	$(EtO)_3P$	8	<0.5	7	1.21	3.81
4	$EtOPOCl_2$	$11._5$	1.2	7	1.44	4.42_5
5	$(EtO)_2POCl$	10	1.0	7	1.36_5	4.25_5
6	$(EtO)_3PO$	$8._5$	0.7	7	1.28_5	4.04
7	$EtOPSCl_2$	13	1.0	7	1.46	4.43
8	$(EtO)_2PSCl$	11	0.8_5	7	1.37	4.26_5
9	$(EtO)_3PS$	10	0.7	7	1.27_5	4.06

* Referred to TMS
** The notation $^nJ_{ij}$ denotes the coupling constant between nuclei i and j through n bonds.

* Present address: Department of Industrial Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya.

1) J. B. Hendrickson, M. L. Maddox, J. J. Sims and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).
2) C. Charrier, M.-P. Simmonnin, W. Chodkiewicz and P. Cadiot *Compt. rend*, **258**, 1537 (1964).