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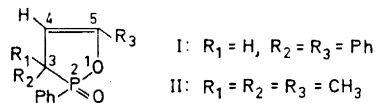
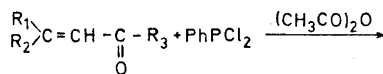
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NMR and Kinetic Studies of Some Oxaphospholene Derivatives

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Some years ago the syntheses of 2-oxo-2,3,5-triphenyl-1,2-oxaphospholene (I) and 2-oxo-2-phenyl-3,3,5-trimethyl-1,2-oxaphospholene (II) were reported.¹ The compounds were prepared from phenylphosphine dichloride, acetic anhydride, and the unsaturated ketones benzalacetophenone and mesityloxide, respectively.



The NMR spectrum of the olefinic proton in position 4 in compound I occurs as two doublets ($\delta = 4.72$) due to the coupling to the phosphorus atom and the proton in position 3 (Table 1). The same magnitude of the phosphorus coupling is also found in compound II, but the doublet is further splitted into two quartets (Fig. 1), due to

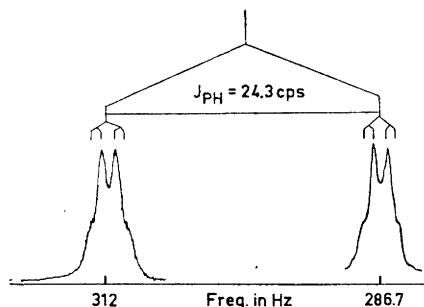


Fig. 1. Spectrum at 60 Mc of the olefinic proton in II in CDCl_3 with TMS as internal standard.

the coupling of the olefinic proton to the protons of the methyl group in position 5. This was confirmed by irradiation of the

5-methyl group which resulted in a transformation of the two quartets to a doublet. The NMR spectrum of the methyl groups in II consists of well separated signals, one quartet at low field ($\delta=1.94$) and two doublets at higher field ($\delta=1.41$ and $\delta=0.89$) (Fig. 2). Both doublets are

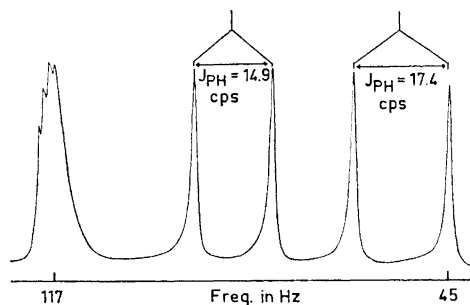


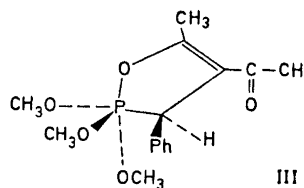
Fig. 2. Spectrum at 60 Mc of the methyl groups in II in CDCl_3 with TMS as internal standard.

believed to arise from the methyl groups in position 3 which are coupled to the phosphorus atom, the doublet at $\delta=1.41$ is ascribed to the methyl group which lies nearest to the deshielding phosphoryl group.

The alkaline hydrolysis of the oxaphospholene derivatives is very rapid. In analogy with cyclic phosphinates, phosphonates, and phosphates,^{2,3} the present compounds show second order kinetics, first order in phosphinate ester conc., and first order in hydroxyl ion conc. The enol formed during hydrolytic cleavage of the P—O bond of the phospholene ring rearranges immediately to the corresponding keto-phosphinic acid.¹

Esters of oxaphospholane and dioxaphospholane are known to hydrolyse 10^5 – 10^8 times more rapidly than open chain analogs.^{2,4,5} The reason for the rapid reaction of the cyclic compounds has been explained as due to ring strain,^{6,7} but later²⁻⁵ it was assumed that the high rate was also due to an easy formation of a trigonal bipyramidal intermediate or transition state. The X-ray analysis of 1,3,2-dioxaphospholanes^{8,9} has shown that the phosphorus atom lies at the centre of a nearly perfect trigonal bipyramid with one of the ring oxygen atom in apical position. The apical P—O bonds were found to be 0.16 Å longer than the equatorial ones. A similar configuration seems reasonable for the transition state formed in the hydrolysis of dioxaphospholane esters.^{2,5}

When the phospholane ring contains one α -oxygen atom, this more electronegative atom probably will occupy the apical position in the transition state during hydrolysis, and the ring α -carbon atom the equatorial position.² The latter assumption has been strongly supported by low-temperature NMR measurements of the cyclic tetraalkoxyalkylphosphorane, 2,2,2-trimethoxy-3-phenyl-4-acetyl-5-methyl-4-oxaphospholane (III).¹⁰



At room temperature the NMR spectrum of (III) showed only one kind of methoxyl

Table I. Chemical shifts and coupling constants for I and II.

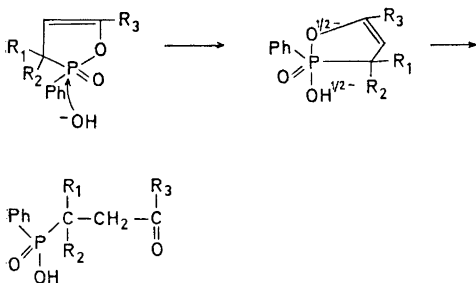
Compound		Chemical shifts ppm from TMS	Coupling constants cps
I	4-Proton	4.72	$J_{\text{PH}} = 24.1$
II	4-Proton	4.99	$J_{\text{PH}} = 24.3$
	3,3-Dimethyl	1.41	$J_{\text{PH}} = 14.9$
		0.89	$J_{\text{PH}} = 17.4$
	5-Methyl	1.95	$J_{\text{PH}} = 1.3$
			$J_{\text{H-C=C-CH}_3} = 1.2$

Table 2. Second order rate constants and calculated activation parameters for the alkaline hydrolysis of I and II. The reactions were performed in water.

Compound	pH	Rate constant l mole ⁻¹ sec ⁻¹				E kcal/mole	log A	ΔS*
		30°	35°	40°	50°			
I	7.50	1030		1922		11.7 ± 0.6	11.5	-8.0
	8.00	1028	1306	1950	3337			
II	9.00	98		186	350	12.5 ± 0.6	11.1	-10.4
	9.50	97		184				

group. At -65°C, however, the signals from the methoxyl groups appeared as two separate doublets with integrated intensities of 1:2, corresponding to one apical and two equatorial methoxyl groups.¹⁰ Since the pseudo-rotation is restricted at such low temperatures, it was concluded that alkyl groups preferentially occupy equatorial positions and oxygen atoms apical positions.

The rates of the alkaline hydrolysis of the oxaphospholene esters I and II (Table 1) are of the same magnitude as the rates of oxa- and dioxaphospholane esters.^{2,4,5} A similar configuration of the transition state during the hydrolysis is therefore reasonable.



Experimental. The syntheses and physical data of 2-oxo-2,3,5-triphenyl-1,2-oxaphospholene (I) and 2-oxo-2-phenyl-3,3,5-trimethyl-1,2-oxaphospholene (II) have been reported.¹ The NMR spectra were measured at 60 Mc (JEOL C-60 H) in 20% solution of the compound in CDCl₃.

Kinetic measurements were performed on a recording pH-stat, Radiometer TTT 1c, at various pH-values. The hydrolysis was studied as a pseudo first-order reaction, and the method of Guggenheim¹² was used for evaluation of the rate constants (Table 2). Measurements were made at three or four separate temperatures, each of which was kept constant within ±0.01°C. The average error of the calculated rate constants is estimated to ±2%.

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