Table 4. Absorption bands in infra-red spectra of MOOH.

MOOH	Absorption cm^{-1}	Ref.
Y	3610	16
Eu	3585	8
Dy	3600	
Ho	3610	
Er	3610	
Yb	3610	
Free OH^-	3580–3670	14
	3590–3650	15

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Alkaline Decomposition of Some Unsaturated Cyclic Phosphonium Compounds

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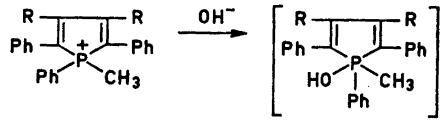
The alkaline decomposition of quaternary phosphonium compounds has been studied by several workers.[1-7] It has been found that the reaction of hydroxyl ions with alkyl- as well as aryl-substituted phosphonium compounds gives phosphine oxides and hydrocarbons as chief products. Depending on the stability of the leaving negatively charged organic group, the decomposition is known to obey third order [1-7] or second order kinetics.[5] The order of readiness with which the hydrocarbon group is displaced by hydroxyl ions is: *p*-nitrobenzyl > benzyl > phenyl > methyl > phenethyl > ethyl higher alkyl groups.

This paper reports the hydrolysis of the five-membered unsaturated cyclic phosphonium compounds, 1,2,5-triphenyl-1-methyl phospholium iodide (III) and 1,2,3,4,5-pentaphenyl-1-methyl phospholium iodide (IV). Similar to the observation of Aksnes and Songstad [5] for the decomposition of *p*-nitrobenzyl-substituted phosphonium compounds, the present compounds show second order kinetics: first order dependence on the concentration of phosphonium ion and first order on hydroxyl ion (Table 1). The hydrolysis results in cleavage of the five-membered ring at the P—C bond with formation of phosphine oxide; methyl phenyl (1,4-diphenyl-



III: R = H
IV: R = Ph

V: R = H
VI: R = Ph

Table 1. Second order rate constants and calculated activation data for the reaction between hydroxyl ions and 1,2,5-triphenyl-1-methyl phospholium iodide (III) and 1,2,3,4,5-pentaphenyl-1-methyl phospholium iodide (IV), respectively. The reactions were performed in 50 % volume of water-ethanol.

Compound as iodide	Conc. of phosphonium salt mole/l	Conc. of OH^- mole/l	Rate constant l mole^{-1} min^{-1} 0°	10°	20°	Activation energy kcal/mole	Frequency factor log A (l mole^{-1}min^{-1})
III	0.0164	0.0164	44.70	92.04		11.1	10.4
	0.0164	0.0273	51.42	105.18		11.0	10.5
IV	0.0076	0.0076		7.32	15.36	12.2	10.3

1,3-butadienyl) phosphine oxide (V) from (III), and methyl phenyl (1,2,3,4-tetraphenyl-1,3-butadienyl) phosphine oxide (VI) from (IV).

In agreement with the ring cleavage, the infrared spectra of the products (V) and (VI) show strong bands at 1210, 1300, and 1452 cm^{-1} which are assigned to the vibration of the P=O, P=CH_3, and P—Ph bonds, respectively.

The conjugation between the five-membered ring and the phenyl groups attached to it will give rise to an electronically much more stabilized anion during the decomposition than does the phenyl group linked directly to phosphorus. No ring preserved product is therefore found. This conclusion is confirmed also by the very low activation energies calculated for the alkaline decomposition of the cyclic compounds (11—12 kcal) as compared with the approx. 35 kcal calculated for the cleavage of phosphonium compounds where the phenyl group is the leaving group.[4]

Experimental. 1,2,5-Triphenyl phosphole (I) and *1,2,3,4,5-pentaphenyl phosphole (II)* were synthesized according to the method of Cambell and Braye;[1,2] m.p. (I): 187.5°C (reported:[1] 187.5°C), m.p. (II): 254°C (reported:[2] 254°C).

The corresponding methyl substituted phosphonium iodides were made by adding methyl iodide to a 0.3 M solution of the phosphole in benzene. The compounds were recrystallized from ethanol-ether mixture until pure products were obtained as shown by iodide analysis.

1,2,5-Triphenyl-1-methyl phospholium iodide (III) m.p. 230°C. (Found: I 27.70, 27.74. Calc. for $C_{23}H_{20}PI$: 27.94).

1,2,3,4,5-Pentaphenyl-1-methyl phospholium iodide (IV) m.p. 330°C. (Found: I 20.83, 20.84. Calc. for $C_{35}H_{28}PI$: 20.92). The hydrolysis products from (III) and (IV) were recrystallized four times from ethanol-water.

Methyl phenyl (1,4-diphenyl-1,3-butadienyl) phosphine oxide (V) m.p. 169—170°C. (Found: C 80.20; H 5.81; P 8.97. Calc. for $C_{23}H_{21}OP$: C 80.23; H 6.1; P 9.01).

Methyl phenyl (1,2,3,4-tetraphenyl-1,3-butadienyl) phosphine oxide (VI) m.p. 204°C. (Found: C 85.14; H 5.94. Calc. for $C_{35}H_{29}OP$: C 85.00; H 5.90).

Kinetic measurements. The reaction between the phosphonium salts and sodium hydroxide was performed with equivalent as well as different amounts of both reagents. The course of the reaction was followed by titration of unreacted hydroxyl ions after fixed time intervals. The reaction was followed until approximately 70 % hydrolysis.

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