

## Nucleophilic Displacement on Phosphorus in Phosphonium Compounds where Phosphorus is Part of Five- and Six-Membered Heterocycles

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The rates of the alkaline decomposition of cyclotetramethylene and cyclopentamethylene methyl phenyl phosphonium iodides have been measured at different temperatures.

The phosphonium compound containing the phosphorus atom in the five-membered ring is decomposed more than 1300 times as rapidly as the corresponding six-membered ring compound and the open chain analogue. The rings are preserved during the reactions.

From the temperature dependence of the decomposition it is found that, within experimental errors, the rate increase is due to a higher frequency factor.

The experimental data are discussed in relation to the "*I*-strain" concept.

The rate of solvolysis of cycloalkyl halides and arenesulphonates are known to be strongly dependent on the ring size.<sup>1-4</sup> Brown *et al.*<sup>1</sup> have attempted to rationalize the results for both uni- and bimolecular substitution in terms of "*I*-strain" defined as the change in internal strain resulting from change in the coordination number of the carbon ring atom involved in the substitution. Thus, formation of a carbonium ion from a cyclopentyl halide should result in a decrease of strain through release of the eclipsing of the hydrogen atoms on adjacent carbon atoms, whereas formation of a planar carbonium ion from a cyclohexyl compound in the chair form, should increase the strain through eclipsing of originally staggered hydrogen atoms. In  $S_N2$  substitution the carbon atom would be forced into a more or less planar configuration producing an effect in the same direction as for  $S_N1$  reactions. Steric hindrance to the approach of the nucleophile seems, however, to reduce the rate of  $S_N2$  displacement in cycloalkyl halides relative to the open chain analogues.<sup>5</sup>

Displacement on the heteroatom in heterocyclic compounds, where a change in hybridization of the heteroatom accompanies the substitution, should also show dependence on the ring size. Thus, West<sup>6</sup> observed the following order of decreasing rates for the alkaline hydrolysis of cycloalkyl silanes:

five-membered ring > seven-membered ring > open chain > six-membered ring. Nucleophilic displacement on phosphorus in phosphonium compounds involves a change in hybridization from tetrahedral  $sp^3$  to bipyramidal  $sp^3d$  hybridization, and the ring size of cyclic phosphonium compounds might therefore be expected to affect the rate. This paper reports studies of the alkaline decomposition of cyclotetramethylene and cyclopentamethylene methyl phenyl phosphonium iodides, where the phosphorus atom is part of a five- respectively six-membered ring.

### EXPERIMENTAL

*Cyclotetramethylene phenyl phosphine* (I) and *cyclopentamethylene phenyl phosphine* (II) were synthesized according to the method of Grüttner and Krause.<sup>7,8</sup> Physical data for (I) were: b.p.<sub>10</sub> 123°,  $n_D^{20}$  1.5909,  $d^{20}$  1.033, (reported:<sup>9</sup> b.p.<sub>10</sub> 133°,  $n_D^{20}$  1.5894,  $d^{20}$  1.0354), and for (II): b.p.<sub>9</sub> 128°,  $n_D^{20}$  1.5882,  $d^{20}$  1.029, (reported:<sup>9</sup> b.p.<sub>16</sub> 143°,  $n_D^{20}$  1.5886,  $d^{21,6}$  1.0306).

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

*Cyclotetramethylene methyl phenyl phosphonium iodide*, m.p. 129.5°C, reported:<sup>9</sup> 130°C. (Found I 41.19, 41.11. Calc. for  $C_{11}H_{16}PI$ : I 41.39).

*Cyclopentamethylene methyl phenyl phosphonium iodide*, m.p. 175°C, reported:<sup>9</sup> 176°C. (Found I 39.42; 39.48. Calc. for  $C_{12}H_{18}PI$ : I 39.68).

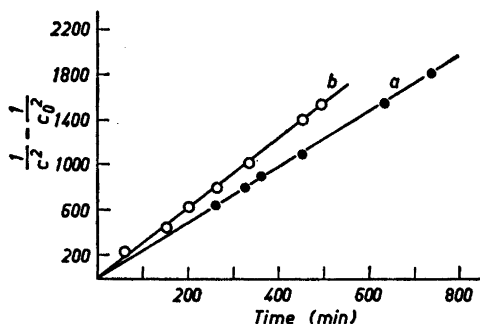
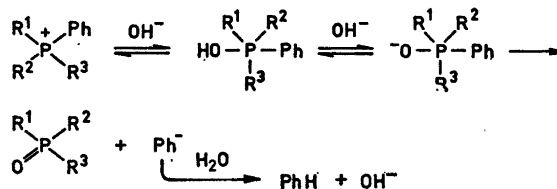


Fig. 1. Third order plots of the alkaline decomposition of phosphonium iodides in 93.4 wt. % ethanol-water mixture containing 0.04279 M NaOH. a) 0.04279 M cyclotetramethylene methyl phenyl phosphonium iodide at 40°C. b) 0.04279 M cyclopentamethylene methyl phenyl phosphonium iodide at 75°C.

*Kinetic measurements* were performed as previously described.<sup>9</sup> Both of the cyclic phosphonium iodides followed third order kinetics as shown in Fig. 1. The calculated rate constants together with activation energies and frequency factors are recorded in Table 1.



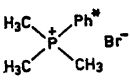
### DISCUSSION

Kinetic data for the alkaline decomposition of phosphonium salts are consistent with the view that the reaction between the hydroxyl ion and the phosphonium cation proceeds through a pentacovalent intermediate.<sup>10-14</sup> The observed third order rate dependence, second order in hydroxyl ion and first order in phosphonium ion concentration, is in accordance with the following reaction scheme:



In the alkaline decomposition of alkyl and cycloalkyl phenyl phosphonium salts, the phenyl group is always the leaving group. In the cyclic phosphonium compounds studied in this paper, the substituents R<sup>1</sup> and R<sup>2</sup> and the phosphorus atom are part of a five-membered respectively six-membered ring. Atomic models show that rotation of the phenyl and methyl groups in the five-membered phospholan compound is severely restricted due to eclipsing with the ring α-hydrogen atoms, whereas in the phosphorinan compound with chair configuration of the six-membered ring, the eclipsing is much less critical. In the more open structure of the *sp*<sup>3</sup>*d*-hybridized pentacovalent intermediate of the alkaline decomposition, all of the eclipsing strain in both compounds will be relieved, and since the release of strain is greater for the phospholan compound than for the phosphorinan compound, a higher rate of alkaline decomposition of the former should be expected. The experimental data in Table 1 are in accordance with this view. When the rate constant of alkaline decomposition of the five-membered phospholan derivative is extrapolated to 75°C the compound is found to react more than 1300 times as fast as the corresponding six-membered phosphorinan compound (Table 1). The rate of decomposition of the latter is nearly equal to that of trimethyl phenyl phosphonium bromide (Table 1), in contrast to S<sub>N</sub>1 displacement on carbon where a strong reduction is observed on passing from alkyl halides to cyclo-

Table 1. Rate data for the alkaline decomposition of phosphonium salts in ethanol-water mixtures.

Phosphonium compound	Medium wt. % ethanol	Rate constant, l <sup>2</sup> mole <sup>-2</sup> min <sup>-1</sup>					Activation energy, kcal/mole c	Frequency factor, log A
		35°C	40°C	70°C	75°C	80°C		
	93.4	1.563	4.167	—	1862 (calc.)	—	37.6	26.9
	93.4	—	—	0.5517	1.227	—	38	23.7
	74.8	—	—	—	0.0828	0.1740	36	21.7
	83.9	—	—	—	0.3105	0.6704	37	23.1
	93.4	—	—	—	1.673	3.388	34.5	21.9

\* Data from previous work.<sup>10</sup>

hexyl halides. This reduction is generally believed to be due to steric hindrance to the approach of the nucleophile in the  $S_N2$  transition state.<sup>5</sup> Due to the greater atomic radius of phosphorus as compared to carbon, steric hindrance to the approach of the hydroxyl ion may be less critical in the alkaline decomposition of phosphonium salts.

The data in Table 1 show the somewhat unexpected result that, within experimental errors, the high rate of decomposition of the five-membered phosphonium compounds as compared with the six-membered one and the open chain analog, is due to a greater frequency factor. The same was found by West<sup>6</sup> for the alkaline hydrolysis of cycloalkyl silanes. The steric strain concept predicts a decrease in activation energy due to the assumed release of strain energy in the transition state.<sup>1</sup> The favourable frequency factor for the alkaline decomposition of the five-membered phosphonium compound may possibly be due to a statistical effect: The almost planar configuration of the phospholan ring together with the strongly hindered rotation of its substituents (phenyl and methyl) leave the phosphorus atom at any time very exposed to attack from the hydroxyl ion; this may be expected to increase the number of effective collisions between the two ions.

Work on displacement reactions on phosphorus in other five-membered ring systems<sup>15</sup> is of interest in this context. Thus 2-hydroxy-2-oxy-1,3,2-dioxaphospholan hydrolysis at a rate approximately  $10^7$  times as fast as 2-hydroxy-2-oxy-1,3,2-dioxaphosphorinan. It was assumed that the rate increase is due chiefly to release of strain energy in the transition state.<sup>16</sup> In analogy with the present findings it may, however, be expected that a considerable part of the rate increase will be found in the frequency factor. Measurements of hydrolysis at different temperatures, of heterocycles containing phosphorus in five- and six-membered rings, are in progress in this laboratory.

#### REFERENCES

1. Brown, H. C., Fletcher, R. S. and Johannesen, R. B. *J. Am. Chem. Soc.* **73** (1951) 212.
2. Roberts, J. D. and Chambers, V. C. *J. Am. Chem. Soc.* **73** (1951) 5034.
3. Brown, H. C. and Borkowski, M. *J. Am. Chem. Soc.* **74** (1952) 1894.
4. Roberts, J. D. *J. Am. Chem. Soc.* **71** (1949) 1880.
5. Hine, J. *Physical Organic Chemistry*, McGraw-Hill Book Company, New York 1962, p. 178.
6. West, R. *J. Am. Chem. Soc.* **76** (1954) 6015.
7. Grüttner, G. and Krause, E. *Ber.* **49** (1916) 437.
8. Grüttner, G. and Wiernik, M. *Ber.* **48** (1915) 1476.
9. Issleib, K. and Häusler, S. *Chem. Ber.* **94** (1961) 113.
10. Aksnes, G. and Brudvik, L. J. *Acta Chem. Scand.* **17** (1963) 1616.
11. Fenton, G. W. and Ingold, C. K. *J. Chem. Soc.* **1929** 2342.
12. McEwen, W. E., Vander Werf, C. A. and Zander, M. J. *J. Am. Chem. Soc.* **81** (1959) 3806.
13. Hoffmann, H. *Ann.* **634** (1960) 1.
14. Aksnes, G. and Songstad, J. *Acta Chem. Scand.* **16** (1962) 1426.
15. Cox, Jr., J. R. and Ramsay, O. B. *Chem. Rev.* **64** (1964) 332.
16. Haake, P. C. and Westheimer, F. H. *J. Am. Chem. Soc.* **83** (1961) 1102.

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