




Table I. Rate Constants^a for Hydrolyses in D₂O

Compound	Temp, °C	<i>k</i> (acid)	Temp, °C	<i>k</i> (acid)	Temp, °C	<i>k</i> (base)	Temp, °C	<i>k</i> (base)
II	26	3×10^{-3b}	100	2×10^{-8c}	30	$6 \times 10^{b,d}$	25	1×10^{-5}
	100	2×10^{-5}			25	1×10^{-2}		
			100	7×10^{-6}			25	3×10^{-4}
III	100	$>3 \times 10^{-4b}$	100	1×10^{-8c}	30	$2^{b,d}$	91	$3 \times 10^{-5c,e}$
	100	9×10^{-6}	100	9×10^{-6}	25	2×10^{-4}	25	2×10^{-4}

^a In liters/mole sec; determined by nmr methods unless otherwise noted. ^b First ester group. ^c Second ester group. ^d Determined by use of a pH-Stat. ^e NMR Specialties, Inc., Teflon liner used.

The first ester group of III is nowhere near so labile as that of II. Nevertheless, the rate of its hydrolysis in alkali¹¹ exceeds that of the second ester group (extrapolated to a common temperature) by a factor of about 10^7 and exceeds that of its monocyclic analog by a factor of 10^4 . The large retardation—about 10^3 -fold—in the rate of hydrolysis of the second ester group of III compared to that of its monocyclic analog is reasonable on electrostatic grounds provided that the tricyclic system in II and III has the *exo* configuration. The rate of hydrolysis in acid of the first ester group in III exceeds that of the second by a factor of at least 300, and that of its monocyclic analog by a factor of at least 30. Since it is possible that hydrolysis of the ester group in the tricyclic system occurs with P–O cleavage, while that of the monocyclic analog occurs with C–O cleavage, the actual rate difference at phosphorus may be considerably larger than that for the over-all rates. The ester group that hydrolyses rapidly in II and III is presumably the one at position 7 of the phosphabicycloheptane or -heptene system.

If trigonal-bipyramidal intermediates are indeed involved in these hydrolyses, and if the transition state for the hydrolysis of an ester is reasonably symmetrical, then the hydrolysis must take place with pseudo-rotation between one trigonal-bipyramidal intermediate and another, in accordance with previous theory.³ The large difference in rate between the hydrolyses of II and III may be caused by the larger strain in the former; the type of special interactions noted for 7-halobicycloheptenes seems relatively unlikely,¹² since II and III show the same qualitative behavior.

The rate constants here recorded apply, in all cases, to regions where second-order kinetics are obeyed. Most constants were determined by nmr analysis of reactions mixtures in D₂O and are therefore relatively crude numbers; fortunately for the large differences here discussed, high precision is not essential. For all the compounds except II, the entire quartet for the

methylene group of the ethanol produced during hydrolysis was cleanly separated from the multiplet of the methylene group of the corresponding ethyl ester, so that integration of the areas of these peaks was always possible, and the data are therefore as reliable as the integrator of the Varian A-60. For II, the rates were estimated by comparing the heights of the peak for the methyl protons of ethanol with those for the ester.

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Some Substituted 7-Ethoxy-7-phosphabicycloheptene and -heptane 7-Oxides¹

Sir:

Strain in five-membered cyclic phosphates, but not in previously known phosphonates and phosphinates, greatly enhances the rate of hydrolysis *external* to the ring. To test our hypothesis² concerning the cause of this phenomenon further, we have sought esters with maximum strain in a bond angle at phosphorus. We now report the preparation of three highly strained compounds: phosphinic esters with phosphorus at the bridge position³ of bicyclic systems. Their hydrolytic behavior is reported in the accompanying communication.⁴

We had previously³ prepared 1-ethoxyphosphole 1-oxide (I) and found that, although it does not readily react with dienophiles, it dimerizes with a rate constant of about 0.5 l./mole sec at 25°. The Diels–Alder dimer has now been isolated in crystalline form and assigned structure II, where the stereochemistry of the ring junction and of the substituents on phosphorus is uncertain. On hydrogenation, II yields III, where the stereochemistry is likewise uncertain. The synthesis of 3,4-dimethyl-1-ethoxyphosphole 1-oxide (IV) was attempted, since it was expected on the basis of analogy

(11) Professor Aksnes has written us that further investigations, subsequent to his publication,⁶ have shown that his sample of the ethyl ester of tetramethylenephosphinic acid contains considerable 1,8-dichlorooctane as impurity; this impurity presumably accounts for the incomplete solubility of his material in water. It may also account for most of the discrepancy between his rate and ours. Our rates were measured at 25° in D₂O, Aksnes and Bergesen's at 50° in 50% ethanol. After extrapolation to a common temperature, our rate constant is ten times theirs. Although much of this difference is caused by a solvent effect, a redetermination of the rate of saponification of this ethyl ester at 50° in 50% ethanol gives, in our hands, a rate about 2.5 that reported by the Norwegian investigators.

(12) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).

(1) This research was supported by the National Science Foundation under Grant GP-2098 and by the Petroleum Research Fund of the American Chemical Society. R. K. is the recipient of National Institutes of Health Predoctoral Fellowship 5-F1-GM-21,117-02, and F. K. of National Institutes of Health Predoctoral Fellowship 5-F1-GM-28,819-01.

(2) E. A. Dennis and F. H. Westheimer, *J. Am. Chem. Soc.*, **88**, 3431, 3432 (1966).

(3) D. A. Usher and F. H. Westheimer, *ibid.*, **86**, 4732 (1964).

(4) R. Kluger, F. Kerst, D. G. Lee, E. A. Dennis, and F. H. Westheimer, *ibid.*, **89**, 3918 (1967).

