known to proceed with little or no isotope effect and with no D loss.[8,9]

The data in this and the previous paper[2] can be analyzed in a more quantitative way. Let P be the ratio of the rate of abstraction of a C-6 *endo* hydrogen to that of a C-6 *exo* hydrogen; let Y_{exo} and Y_{endo}, respectively, represent the positive isotope effects (k_H/k_D) for loss of a C-6 *exo* deuterium and a C-6 *endo* deuterium; and let F be the fraction of nortricyclene produced by an E1 path (therefore $30.6F$ is the deuterium lost by the E1 path).[2]

For the bimolecular path to nortricyclene from 6-*exo*-*d*-**2** at low base concentration eq 1 may be written, and for 6-*endo*-*d*-**2** similar considerations lead to eq 2. The value of F is 0.10 (obtained as described above) and solution of eq 1 and 2 leads to $Y_{exo}Y_{endo} = 7.63$. If Y_{exo} is essentially the same as Y_{endo}, then this isotope effect (Y) is 2.8, and P becomes 2.5. Similar treatment of the entire data[2] leads to Table II.[10] The preference

$$\frac{\%\ endo\text{-H lost}}{\%\ exo\text{-D lost}} = \frac{100 - (15.8 - 30.6F)}{15.8 - 30.6F} = PY_{exo} \quad (1)$$

$$\frac{\%\ endo\text{-D lost}}{\%\ exo\text{-H lost}} = \frac{50.5 - 30.6F}{100 - (50.5 - 30.6F)} = \frac{P}{Y_{endo}} \quad (2)$$

(P) for abstraction of an *endo* hydrogen over that of an *exo* hydrogen represents the net outcome of steric and stereoelectronic factors in the norbornyl systems, and these *endo* preferences could be considerably higher in the absence of a steric disadvantage.[11] Cyclic or quasi-cyclic transition states could be important in the U system.[12]

Table II. Nortricyclene Formation from Norbornyl Tosylates in *t*-BuOH–KO-*t*-Bu

Approx concn of KO-*t*-Bu, *M*	Substrate (temp, °C)	Approx amount of Nortricyclene from E1 and E2 paths	*P*	*Y*
	exo-Tosylate (60)	100% E1	1[a]	2.1[2]
	endo-Tosylate (135)	10% E1	1[a]	2.1[b]
		90% E2	2.5	2.8
0.9	*exo*-Tosylate (60)	13% E1	1[a]	2.1[b]
		87% E2	1.5	1.6
	endo-Tosylate (135)	100% E2	1.7	1.8

[a] In a bridged norbornyl cation the *exo–endo* distinction at C-6 is lost, and so $P = 1$. [b] Value taken to be the same as for *exo*-tosylate at 60° at low base concentration.[2]

(8) A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **88**, 4543 (1966).

(9) (a) A carbene that is protonated to the norbornyl cation should lead to the same consequences as a conventional E1 path. (b) For α eliminations see: W. Kirmse, *Angew. Chem.*, 77, 1 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 1 (1965); G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965); M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, **87**, 2293 (1965).

(10) In this treatment we must assume that a norbornyl cation produced in the E1 component at "high" base concentration behaves quantitatively the same as the norbornyl cation produced in the "low base" solution.

(11) A. F. Thomas and B. Willhalm, *Tetrahedron Letters*, 1309 (1965); J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, 4465 (1975); A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem. Soc.*, **89**, 68 (1967).

(12) *Cf.* 1,2 eliminations [J. Zavada, J. Krupicka, and J. Sicher, *Chem. Commun.*, 66 (1967)].

Alex Nickon, Nick H. Werstiuk
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218
Received February 28, 1967.

Hydrolysis of Esters of Bicycloheptyl- and -heptenylphosphinic Acids[1]

Sir:

The rate of hydrolysis of five-membered cyclic phosphates (such as methyl ethylene phosphate) is accelerated as much as a millionfold not only with ring opening but also with hydrolysis of the ester group external to the ring.[2,3] The rapid hydrolysis external to the ring has been explained[3] by assuming that the ring strain in the five-membered ring is diminished, without ring opening, in a transition state that has a naturally small (*e.g.*, 90°) O–P–O bond angle; the complete mechanism involves a "pseudo-rotation" [3,4] between two trigonal-bipyramidal intermediates. Furthermore, esters of simple five-membered cyclic phosphinic acids do not show enhanced rates of hydrolysis[3,5] relative to their acyclic analogs, presumably because the formation of trigonal-bipyramidal phosphorane intermediates[6] in this case demands that an alkyl group be placed in apical position. This configuration is energetically unfavorable[3,7,8] and could explain a lowered rate. The structure is, however, not forbidden,[8,9] so that one may predict that trigonal bipyramids with alkyl substituents in apical positions may still be favored for those cases where an especially large diminution in ring strain accompanies the formation of the intermediate. Such strained compounds have now been prepared;[10] the predicted rate enhancements have been observed and are reported in Table I. (The structures of II and III are presented in the accompanying communication.[10])

Inspection of Table I shows that, in acid, the first ester group of II is hydrolyzed 100 times faster at 26° than the second ester group at 100°; the rate difference, at a common temperature, is probably of the order of 10^5. The rate of acid hydrolysis of the first ester group of II, extrapolated to a common temperature, is probably about 10^5 times that of an appropriate monocyclic analog, whereas the rate of the hydrolysis of the second ester group is comparable to that of its monocyclic analog. In alkali, the rate of hydrolysis of the first ester group is nearly 10^8 times that of the second, and almost 10^5 times that of its monocyclic analog; the hydrolysis of the second ester group is retarded by a factor of about 30 relative to a comparable monocyclic ester.

(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-31,117-02, F. K. of National Institutes of Health Predoctoral Fellowship 5-F1-GM-28,819-01, and E. A. D. of National Institutes of Health Predoctoral Fellowship 5-F1-GM-20,008-04.

(2) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961); F. Covitz and F. H. Westheimer, *ibid.*, **85**, 1773 (1963).

(3) E. A. Dennis and F. H. Westheimer, *ibid.*, **88**, 3431, 3432 (1966).

(4) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960).

(5) G. Aksnes and K. Bergesen, *Acta Chem. Scand.*, **20**, 2508 (1966).

(6) W. C. Hamilton, S. J. LaPlaca, and F. Ramirez, *J. Am. Chem. Soc.*, 87, 127 (1965); F. Ramirez, *Pure Appl. Chem.*, **9**, 337 (1964); *Bull. Soc. Chim. France*, 2443 (1966).

(7) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); R. Schmutzler, *Angew. Chem. Intern. Ed. Engl.*, 4, 496 (1965).

(8) E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

(9) D. Gorenstein, and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 2762 (1967).

10) R. Kluger, F. Kerst, D. G. Lee, and F. H. Westheimer, *J. Am. Chem. Soc.*, **89**, 3919 (1967).

Table I. Rate Constants[a] for Hydrolyses in D_2O

Compound	Temp, °C	k (acid)	Temp, °C	k (acid)	Temp, °C	k (base)	Temp, °C	k (base)
II	26	3×10^{-3} [b]	100	2×10^{-6} [c]	30	6×10 [b,d]	25	1×10^{-5}
	100	2×10^{-5}			25	1×10^{-2}		
			100	7×10^{-6}			25	3×10^{-4}
III	100	$>3 \times 10^{-4}$ [b]	100	1×10^{-6} [c]	30	2 [b,d]	91	3×10^{-5} [c,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 alkali[11] 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 10^8-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 D_2O 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.

(11) Professor Aksnes has written us that further investigations, subsequent to his publication,[5] 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 D_2O, 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).

Ronald Kluger, Fred Kerst, Donald G. Lee
Edward A. Dennis, F. H. Westheimer
James Bryant Conant Laboratory of the Department of Chemistry
Harvard University, Cambridge, Massachusetts
Received April 24, 1967

Some Substituted 7-Ethoxy-7-phosphabicycloheptene and -heptane 7-Oxides[1]

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 hypothesis[2] 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 position[3] of bicyclic systems. Their hydrolytic behavior is reported in the accompanying communication.[4]

We had previously[3] 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

(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).