

have $a_\alpha \sim 18$, $a_\beta \sim 33$, $a_\gamma < 0.3$ G,¹⁰ and $g = 2.0043$ – 2.0050 , are homologs of the acetyl radical previously studied by several workers^{4,11,12} and found to have $a_\alpha = 19.7$ and $a_\gamma = 0.27$ G and $g = 2.0044$. Comparison of these parameters with those of the isoelectronic allyl radicals¹³ appears to confirm recent conclusions¹⁴ that β -carbonyl radicals are essentially alkyl-like with very little resonance stabilization of the type observed for allylic systems. Further experimental results bearing on this interesting question will be reported in due course.

Acknowledgments. This work was supported in part by AEC Contract No. AT(11-1)-3435 and by NSF Science Development Grant No. GU-3184. D. W. P. thanks the Merck Foundation for a Faculty Development Award, Dr. T. Cohen for valuable discussions, and Mr. M. O. Luke of Merck, Sharp & Dohme of Canada, Ltd., for the gift of adamantane- d_{16} .

(10) Determined from a comparison of the epr spectra of the cyclohexanonyl and cyclohexanonyl-2,6,6- d_3 radicals in adamantane- d_{16} .

(11) W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 3625 (1964).

(12) G. Golde, K. Möbius, and W. Kaminski, *Z. Naturforsch., A*, 24, 1214 (1969).

(13) See, for example, J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 90, 7157 (1968); D. W. Pratt, D. M. Camaioni, and D. E. Wood, unpublished results.

(14) G. A. Russell and J. Lokensgard, *J. Amer. Chem. Soc.*, 89, 5059 (1967); K. D. King, D. M. Golden, and S. W. Benson, *ibid.*, 92, 5541 (1970).

(15) Undergraduate Research Participant.

Donald M. Camaioni,¹⁵ David W. Pratt*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15213

Received July 20, 1972

Pentacoordinate Intermediates and the Rate-Determining Step in Displacement at Phosphorus

Sir:

There has been great interest recently in pentacoordinate intermediates in nucleophilic displacement reactions at tetracoordinate phosphorus.¹ Although stable pentacoordinate phosphorus compounds are known,² there has been little experimental evidence for pentacoordinate intermediates along reaction pathways.³ Although we previously found⁴ that the effects of ring strain indicate an intermediate **2** in the alkaline hydrolysis of phosphinate esters (eq 1), we can now present direct kinetic evidence for a pentacoordinate intermediate **2** and for rate-determining breakdown of the intermediate to products.

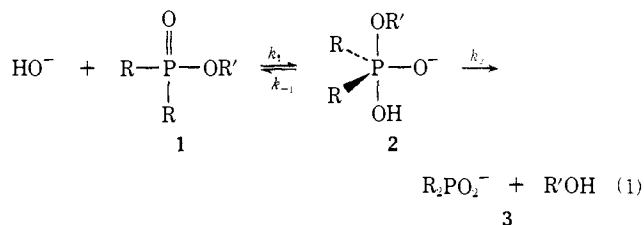
The rates of hydrolysis of a series of phosphinates **1** were evaluated titrimetrically by quenching an aliquot with acid and back-titrating with base. The reactions followed second-order kinetics, $v = k[\text{HO}^-]$.

(1) (a) F. H. Westheimer, *Accounts Chem. Res.*, 1, 70 (1968); (b) K. Mislow, *ibid.*, 3, 321 (1970); (c) I. Ugi, D. Marquarding, H. Klusacek, P. Gillespie, and F. Ramirez, *ibid.*, 4, 288 (1971).

(2) (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, 20, 245 (1966); (b) F. Ramirez, *Accounts Chem. Res.*, 1, 168 (1968).

(3) Available evidence includes: (a) the kinetics of alkaline hydrolysis of phosphonium ions (M. Zanger, C. A. VanderWerf, and W. E. McEwen, *J. Amer. Chem. Soc.*, 81, 3806 (1959)); (b) ring strain effects on rates of hydrolysis and ¹⁸O exchange (P. Haake and F. H. Westheimer, *ibid.*, 83, 1102 (1961)); (c) certain data (ref 1) indicate pseudorotation of a pentacoordinate species.

(4) P. Haake, R. D. Cook, T. Koizumi, P. S. Ossip, W. Schwartz, and D. A. Tyssee, *J. Amer. Chem. Soc.*, 92, 3828 (1970).



[ester]. The rate constants were highly dependent on the substituents at phosphorus and oxygen (Tables I and II). Experiments in oxygen-18 enriched water

Table I. Rate Constants for the Alkaline Hydrolysis of $(\text{C}_6\text{H}_5)_2\text{PO}_2\text{R}$ at 50°

R	$10^3k, M^{-1} \text{sec}^{-1}$ ^a		Rel k
	33% dioxane-water	50% dioxane-water	
CH ₃	14.7		320
CH ₂ CH ₃	1.21		27
CH ₂ CH ₂ CH ₃		0.494	12
CH(CH ₃) ₂	0.0457	0.0428	1
CH ₂ CH(CH ₃) ₂		0.226	5
CH ₂ C(CH ₃) ₃		0.0397	0.9

^a Most k values are the average of two-three separately determined constants.

Table II. Rate Constants for the Alkaline Hydrolysis of $\text{R}_2\text{PO}_2\text{CH}_3$ in 60% Dimethoxyethane-Water at 75°

R	$10^3k, M^{-1} \text{sec}^{-1}$ ^a	Rel k
CH ₃	500 ^b	160
CH ₂ CH ₃	10.9	4
(CH ₂) ₂ CH ₃	3.08	1
CH ₂ C ₆ H ₅	11.5	4
CH(CH ₃) ₂	0.3 ^c	0.1
C ₆ H ₅	43	14

^a Ionic strength constant at 0.1 M . ^b Extrapolated from data at 30 and 50° by $\log k$ vs. $1/T$. ^c An induction period preceded this rate.

have demonstrated that these esters hydrolyze by cleavage of the P–O bond.⁵

The hydrolysis of methyl diisopropylphosphinate (**1**, R = $i\text{-C}_3\text{H}_7$; R' = CH₃) was unusual in that an induction period preceded second-order kinetics (Table II). The hydrolysis curve was analyzed by an analog computer with a circuit corresponding to eq 1. An excellent fit was observed corresponding to: $k_1 = 2.4 \times 10^{-3} M^{-1} \text{sec}^{-1}$, $k_{-1} = 1.6 \times 10^{-2} \text{sec}^{-1}$, $k_2 = 0.20 \times 10^{-2} \text{sec}^{-1}$. Therefore, it appears that the induction period corresponds to initial accumulation of the pentacoordinate intermediate, **2**, and rate-determining breakdown of **2** to products (k_2 is an order of magnitude less than k_{-1}). Kinetic observation of an intermediate in this case probably can be attributed to the steric effect of the two isopropyl substituents.

Analysis of the relative rates in Tables I and II indicates generality of these hypotheses of an intermediate and rate-determining breakdown of **2** to products. The large rate effects in Table I contrast with the rates of alkaline hydrolysis of acetates where the rate ratio for R groups in CH₃CO₂R was isopropyl:ethyl:methyl

(5) P. Haake, C. E. Diebert, and R. S. Marmor, *Tetrahedron Lett.*, 5247 (1968). However, the *tert*-butyl ester reacts very rapidly, probably by a pathway involving C–O cleavage; see P. Haake and C. E. Diebert, *J. Amer. Chem. Soc.*, 93, 6931 (1971).

= 1:4:6;⁶ therefore, an initial hypothesis⁵ was that the rates in Table I are largely due to steric effects. However, the data do not correlate with E_s but do correlate reasonably well with σ^* . Treatment⁷ of the data by eq 2 yields $\rho^* = 11$ and δ (the steric reac-

$$\log(k/k_{\text{CH}_3}) = \rho^* \sigma^* + \delta E_s \quad (2)$$

tion constant) = 0.6. A smaller number of rates give $\rho^* = 8$ for the alkaline hydrolysis of $(\text{C}_2\text{H}_5)_2\text{-PO}_2\text{R}$. These ρ^* values are too large to be explained by rate-determining attack of HO^- to form the pentacoordinate intermediate 2. Rather, the breakdown of the intermediate 2 to products must be rate determining.⁸ The large ρ^* values can then be understood as a primary effect of the R' substituents on the value of k_2 since the transition state for k_2 has a partial negative charge on the oxygen atom of the developing alkoxide anion, $\text{R}'\text{O}^-$. There will also be a secondary effect on the concentration of 2 which will be destabilized by electron donation from R' relative to the ground state, 1. Since our hypothesis results in the rate law, $v = k_2[2]$, these two effects will both contribute.

The hypothesis of rate-determining breakdown of 2 to products is also supported by the following. (1) The relative rates of alkaline hydrolysis of $\text{R}_2\text{PO}_2\text{CH}_3$ (Table II) indicate that both steric and electronic effects are important as expected for substituents at phosphorus. (2) It is useful to examine this system in terms of the chemical dynamics of the intermediate 2 and evaluate the relative energies for loss of RO^- and loss of HO^- . Since alkoxide ions are more basic than hydroxide ion, a higher barrier would be expected for k_2 than k_{-1} .⁸ (3) When R' is an aryl group, then $\text{C}_6\text{H}_5\text{O}^-$ will be a better leaving group than HO^- and the barrier for k_1 and k_{-1} should be the highest point on the energy profile. This change in rate-determining step is in agreement with (a) the much faster rate⁹ for $(\text{C}_6\text{H}_5)_2\text{PO}_2\text{C}_6\text{H}_5$ than for the isopropyl ester (Table I), and (b) $\rho = 2.2$ for $(\text{C}_6\text{H}_5)_2\text{PO}_2\text{C}_6\text{H}_4\text{X}$.⁹

We have not been able to observe any ^{18}O exchange during the alkaline hydrolysis of either $(\text{C}_6\text{H}_5)_2\text{PO}_2\text{R}$ or $(\text{C}_2\text{H}_5)_2\text{PO}_2\text{R}$ in $^{18}\text{OH}_2$ enriched solvents.⁵ This indicates that a high-energy pseudorotation of the pentacoordinate intermediate 2 is necessary to put the HO and O^- groups in positions which would allow proton exchange and equivalence. Polarity arguments support 2 as the most likely geometry for the intermediate if trigonal-bipyramidal geometry holds.^{1,2}

To summarize, in the alkaline hydrolysis of phosphinates (eq 1) there is evidence for a pentacoordinate intermediate which breaks down to products in the rate-determining step, and the geometry and charge of the pentacoordinate intermediate do not allow ^{18}O exchange between $^{18}\text{OH}_2$ and ester.

Acknowledgment. This research was supported by grants from the National Institute of Arthritis and

(6) E. J. Salmi and R. Leimu, *Suom. Kemistilehti B*, **20**, 43 (1947).

(7) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13. We used a modification of eq 2 for analysis of the data: dividing through by σ^* permits a simple graphical analysis of the equation $[\log(k/k_{\text{CH}_3})]/\sigma^* = \delta E_s/\sigma^* + \rho^*$.

(8) These questions applied to carboxylate derivatives are discussed by W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, Chapter 10.

(9) P. Haake, D. R. McCoy, W. Okamura, S. R. Alpha, S. Y. Wong, D. A. Tyssee, J. P. McNeal, and R. D. Cook, *Tetrahedron Lett.*, 5243 (1968).

Metabolic Diseases, the National Science Foundation, and the Alfred P. Sloan Foundation. A. H. F. was supported by a summer grant from the Du Pont Co.

Robert D. Cook

Department of Chemistry, American University of Beirut
Beirut, Lebanon

Patricia C. Turley, Curtis E. Diebert
Arthur H. Fierman, Paul Haake*

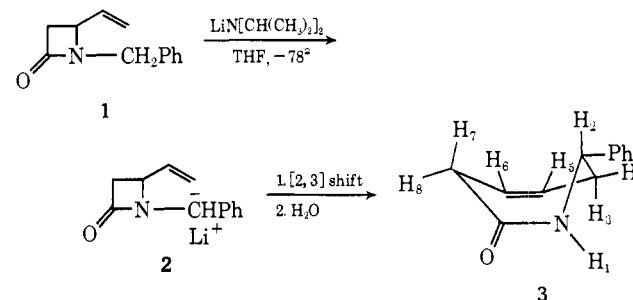
Department of Chemistry, Wesleyan University
Middletown, Connecticut 06457

Received August 4, 1972

Base-Induced Ring Enlargements of 1-Benzyl- and 1-Allyl-2-azetidiones

Sir:

As part of a study of the metallation of 1-alkyl- and 1-aryl-2-azetidiones in the 3 position,¹ we attempted the preparation of the 3-lithio derivatives of 1-benzyl-4-vinyl-2-azetidione (1)² by reaction of 1 with lithium diisopropylamide in tetrahydrofuran solution at -78° . Instead of the desired result, we obtained in virtually quantitative yield the seven-membered ring unsaturated lactam 3. The structure of 3 is based on its elemental



analysis² and spectroscopic properties. The infrared spectrum showed bands at 3420 (N-H) and 1655 cm^{-1} (C=O) while the nmr had peaks at δ 2.4–3.0 (m, $\text{H}_3\text{H}_4\text{H}_8$), 3.5–3.8 (m, H_7), 4.8–5.1 (m, H_2), 4.6–4.75 (m, H_5H_6), 4.8–5.0 (br, H_1), and 7.37 (s, aromatic H).

The transformation $1 \rightarrow 3$ is interpretable in terms of a [2,3] sigmatropic rearrangement of the intermediate benzylic carbanion 2. A number of such rearrangements involving sulfonium ylides,³ ammonium ylides,⁴ anions α to oxygen,⁵ and fluorenyl carbanions⁶ have recently been described in considerable detail. The ease with which the above rearrangement occurred is undoubtedly due to relief of ring strain in going from a four- to a seven-membered ring. In agreement with this is the observation that the carbanion from *N*-allyl-*N*-benzylbenzamide did not undergo a [2,3] sigmatropic

(1) T. Durst and M. J. LeBelle, *Can. J. Chem.*, **50**, 3196 (1972).

(2) All 1-alkylated azetidiones were prepared by reaction of the corresponding *N*-H azetidione with the appropriate alkyl halide in the presence of powdered KOH (M. J. LeBelle, M.Sc. Thesis, University of Ottawa, 1972). All new compounds reported herein had correct elemental analyses and/or exact molecular weight determinations.

(3) For example: (a) J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969); (b) J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *ibid.*, **90**, 4758 (1968); (c) B. M. Trost and R. LaRochelle, *Tetrahedron Lett.*, 3327 (1968); (d) G. M. Blackburn, W. D. Ollis, C. Smith, and I. O. Sutherland, *Chem. Commun.*, 99 (1969).

(4) (a) R. W. Jemison and W. D. Ollis, *ibid.*, 294 (1969); (b) G. V. Kaiser, C. W. Ashbrook, and J. E. Baldwin, *J. Amer. Chem. Soc.*, **93**, 2342 (1971).

(5) (a) J. E. Baldwin and J. E. Patrick, *ibid.*, **93**, 3558 (1971); (b) V. Rautenstrauch, *Chem. Commun.*, 4 (1970).

(6) J. E. Baldwin and F. J. Urban, *ibid.*, 165 (1970).