Research (Grant No. AFOSR-75-2748) and the National Science Foundation (Grant No. CHE77-22639).

References and Notes

(1) Double strand of 30-mil type 3D-218 tungsten wire from General Electric, coated with zirconium powder available from Pfaltz and Bauer Inc.
(2) R. J. Remick, J. E. Dobson, B. E. Wilburn, and P. S. Skell, *Inorg. Synth.*, **19** (1978).
(3) G. A. Ozin, W. E. Klotzbucher, and S. A. Mitchell, *Inorg. Chem.*, **16**, 3063 (1977).
(4) S. C. Davis and K. J. Klabunde, *J. Am. Chem. Soc.*, **100**, 5973 (1978), have reported small amounts of hydrolysis hydrocarbons from cocondensation of nickel atoms with pentane; they suggest that this is not a reaction of nickel atoms, but one that occurs after clustering. Ozin et al.[3] have direct spectroscopic evidence for vanadium atom clustering in the presence of alkanes, without any indication of reactions with the hydrocarbon.
(5) Department of Chemistry, University of Jyväskylä, Finland.

Robert J. Remick, Tuula A. Asunta,[5] Philip S. Skell*
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802
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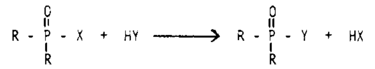
Pentacoordinate Intermediates in Displacement at Sterically Hindered Phosphorus. A Correction

Sir:

A central problem in the fundamental understanding of reactions at phosphorus is the question of whether pentacoordinate intermediates exist along the reaction pathway. As part of a series of investigations on displacement at phosphorus,[1] we have utilized phosphinates as substrates in order to have a single functional group (eq 1). A preference for associative pathways in displacement at phosphorus was clearly demonstrated by studies of the rate of solvolysis of phosphinyl chlorides, $R_2P(O)Cl$, and the behavior of phosphinic acids, R_2PO_2H, in strong acid.[2,3] Since there are a large number of stable pentacoordinate phosphorus compounds, it seems reasonable that the lowest energy associative pathway for displacement at phosphorus will involve an addition-elimination mechanism through a pentacoordinate intermediate. With cyclic phosphates, rate phenomena indicate that conformationally mobile pentacoordinate species are intermediates in displacement reactions,[4] and a large number of cyclic, pentacoordinate adducts have been isolated and investigated,[5] but, with acyclic phosphorus substrates, it has been difficult to gain clear evidence for pentacoordinate intermediates.



$$R-\underset{R}{\overset{O}{\overset{\|}{P}}}-X + HY \longrightarrow R-\underset{R}{\overset{O}{\overset{\|}{P}}}-Y + HX \qquad (1)$$

1 **2**

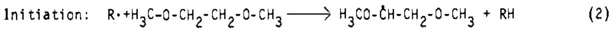
Some time ago, we called attention to an induction period in the rate of alkaline hydrolysis (at 75 °C in 60:40 dimethoxyethane-water) of methyl diisopropylphosphinate (**1a**, R = $CH(CH_3)_2$, X = OCH_3), and we suggested that this might be explained by slow development of a steady-state concentration of a pentacoordinate intermediate with this sterically hindered ester.[1,6] However, when we tried to fit the experimental observations by numerical integration and analogue computation[7] to the expected kinetic scheme, $\mathbf{1} + HO^- \rightleftharpoons \mathrm{I} \rightarrow$ products, we could not find an adequate fit. This led us to additional experiments which we now report.

NMR spectroscopic observation of **1a** and the reaction products was utilized because of the highly diagnostic features: **1a** has an OCH_3 doublet and a CCH_3 octet (nonequivalent CH_3's and PCCH and HCCH couplings). At 75 °C in alkaline 60:40 dimethoxyethane-d_{10}:D_2O (or in basic D_2O) over periods during which HO^- had been consumed in the earlier reported experiments,[1,6] little decrease in the OCH_3 doublet was observed. At 100 °C in alkaline D_2O, the OCH_3 doublet did disappear and the CCH_3 octet became a quartet consistent with hydrolysis giving $R_2PO_2^-$.[8] These results demonstrated that the consumption of HO^- observed earlier at 75 °C in dimethoxyethane-water must be due to some other reaction than hydrolysis of the phosphinate ester.

When the same reaction in dimethoxyethane-water was followed titrimetrically at 75 °C, but with ratios of ester:base being 1:2 and 1:4, both experiments gave induction periods though of varying duration. There was an exponential increase in the rate of consumption of base toward the end of the reaction and more than 1 equiv of HO^- was consumed; this observation is consistent with oxidation of the solvent by a free-radical, chain process. This hypothesis was supported by the fact that, when the reactions were done under a nitrogen atmosphere, there was no consumption of base. Furthermore, the reaction mixtures containing dimethoxyethane gave positive tests for the presence of peroxides using catechol. In contrast to the induction periods observed in dimethoxyethane-water, in water the reaction of methyl diisopropylphosphinate (**1a**) with base at 100.1 and 120.1 °C followed clean second-order kinetics with no induction period. The reaction was followed titrimetrically and NMR was used to identify the reaction as hydrolysis. The rate constants were $2.8 \times 10^{-4}\ M^{-1}\ s^{-1}$ and $5.3 \times 10^{-5}\ M^{-1}\ s^{-1}$ at 120.1 and 100.1 °C, respectively. The corresponding activation parameters are $\Delta H^{\ddagger} = 23.6$ kcal/mol, $\Delta G^{\ddagger} = 29.3$ kcal/mol, and $\Delta S^{\ddagger} = -15$ eu.

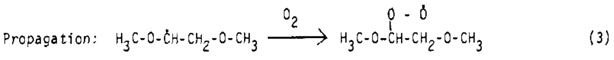
Because the reactions in dimethoxyethane-water were carried out in volumetric flasks which were opened to remove aliquots, the solution was exposed to oxygen leading to the formation of peroxides and consequent autoxidation[9,10] of dimethoxyethane.

A reasonable explanation involves a chain mechanism for oxidation (eq 2-4) in which the observed initiation period involves the generation of the radical **3** which is stabilized by both α- and β-oxy substituents.[9] The product hydroperoxide **4** would be expected to be reactive with base,[10,11] resulting in formation of the ester **5** (eq 5) which would consume base through hydrolysis.



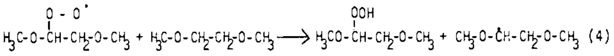
$$\text{Initiation:}\quad R\cdot + H_3C-O-CH_2-CH_2-O-CH_3 \longrightarrow H_3CO-\dot{C}H-CH_2-O-CH_3 + RH \qquad (2)$$

3



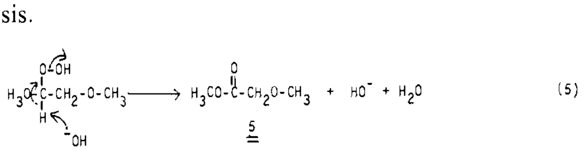
$$\text{Propagation:}\quad H_3C-O-\dot{C}H-CH_2-O-CH_3 \xrightarrow{O_2} H_3C-O-\overset{O-\dot{O}}{CH}-CH_2-O-CH_3 \qquad (3)$$

3



$$H_3C-O-\overset{O-O^{\cdot}}{CH}-CH_2-O-CH_3 + H_3C-O-CH_2-CH_2-O-CH_3 \longrightarrow H_3CO-\overset{OOH}{CH}-CH_2-O-CH_3 + CH_3-O-\dot{C}H-CH_2-O-CH_3 \qquad (4)$$

4 **3**



$$H_3CO-\underset{H}{\overset{O-OH}{C}}-CH_2-O-CH_3 \longrightarrow H_3CO-\overset{O}{\overset{\|}{C}}-CH_2O-CH_3 + HO^- + H_2O \qquad (5)$$

5

Therefore, our previously reported observations are, regrettably, in error; the alkaline hydrolysis of **1a** in H_2O shows no induction period and no kinetic evidence for a pentacoordinate intermediate. The apparent induction period in hydroxide consumption appears to be due to oxidation of the solvent, dimethoxyethane.

Acknowledgments. This research was supported in part by Grant AM-12743 from the National Institute of Health and in part by Wesleyan University.

References and Notes

(1) See R. D. Cook, C. E. Diebert, W. Schwarz, P. C. Turley, and P. Haake, *J. Am. Chem. Soc.*, **95**, 8088 (1973).

(2) P. Haake and P. S. Ossip, *J. Am. Chem. Soc.*, **93**, 6919, 6924 (1971).
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(4) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968).
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(6) R. D. Cook, P. C. Turley, C. E. Diebert, A. H. Fierman, and P. Haake, *J. Am. Chem. Soc.*, **94**, 9260 (1972).
(7) There was an error in the analogue circuit used for the data reported in ref 1 and 6.
(8) This experiment was suggested by the observations in W. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968).
(9) C. Walling, "Free Radicals in Solution", Wiley, New York, 1957.
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(11) E. Rieche and E. Schmitz, *Chem. Ber.*, **90**, 1082 (1957).
(12) Department of Chemistry, American University of Beirut, Beirut, Lebanon.

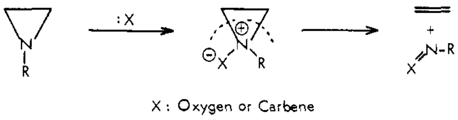
Jubrail Rahil, Robert D. Cook,[12] Paul Haake*
Department of Chemistry, Wesleyan University
Middletown, Connecticut 06457

Received October 30, 1978

Fragmentation Reaction of Ylide. 6. A New Type of Fragmentation Reaction of Aziridinones

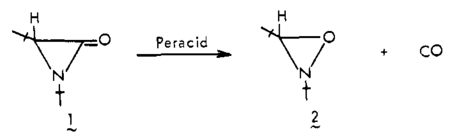
Sir:

Reaction of a number of sustituted aziridines with carbene causes fragmentation of both C–N bonds of the aziridine ring in a single step forming a olefin and imine derivatives.[1] Aziridine *N*-oxide which is considered to be an intermediate in the oxidation reaction of aziridine by peroxy acid also reacts in a manner resembling that of aziridinium ylide because of similar electronic circumstances.[2,3] Here, we report a new type of fragmentation reaction observed in the oxidation of α-lactams by peroxide in various solvent systems.



X : Oxygen or Carbene

1,3-Di-*tert*-butylaziridinone is one of the most stable α-lactams known; several days of refluxing is necessary to solvolyze it with methanol.[4] In acid-catalyzed methanolysis, 2-methoxy-3,3-dimethyl-*N*-*tert*-butylbutyramide has been reported as the sole reaction product.[4] In our experiment, however, 1,3-di-*tert*-butylaziridinone disappeared immediately upon addition of *m*-chloroperbenzoic acid in methanol at 0 °C with vigorous gas generation and was converted into 2,3-di-*tert*-butyloxaziridine in quantitative yield. The structure of the oxaziridine (**2**) was determined by comparison with an authentic sample which was prepared according to literature.[5]

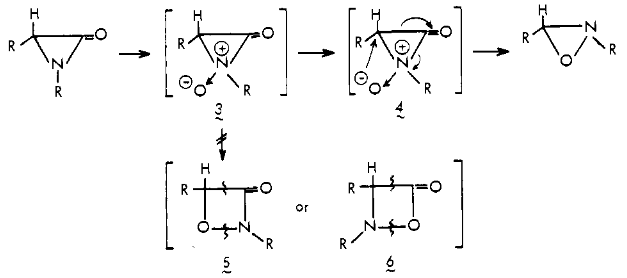


The generated gas, collected in a gas trap and analyzed by VPC, using a Porapak QP column (50–80 mesh) at room temperature, contained 90% carbon monoxide, 10% oxygen, and 0.5% carbon dioxide. The observed yield of carbon monoxide to the starting α-lactam was 80%. Although this value was not quantitative, the yield was not so high as expected, perhaps because of the difficulty in collecting the gas.

Methanol was a suitable solvent for a smooth reaction. However, aprotic solvents, for example, dichloromethane, benzene, ether and hexane, also gave a good yield of oxaziridine. *m*-Chloroperbenzoic acid and peracetic acid were used as oxidation reagents for the new fragmentation of α-lactams and we found that 1 mol equiv of peracid was enough to cause the reaction. Hydrogen peroxide in water was also tried and gave oxaziridine in good yield accompanied by formation of a small amount of unidentified byproduct which may have been due to hydrolysis of the starting material or a reaction intermediate.

1-*tert*-Butyl-3-phenylaziridinone[6] also underwent the same reaction as 1,3-di-*tert*-butylaziridinone with peracid. Here, the α-lactam ring was very sensitive to the acid in *m*-chloroperbenzoic acid or peracetic acid and the yield of 2-*tert*-butyl-3-phenyloxaziridine was very low. However, addition of lithium carbonate to the reaction system to prevent the reaction of free carboxylic acid with lactam improved the yield of 2-*tert*-butyl-3-phenyloxaziridine to 60–70% in methanol solution.

This new fragmentation reaction of α-lactam probably proceeds by the formation of aziridinone *N*-oxide in the first step, although weak nucleophilicity is expected at the lone pair of nitrogen of the aziridinone ring.[7,8] After the formation of aziridinone *N*-oxide (**3**), two possibilities remain: (a) direct fragmentation of the *N*-oxide as shown in **4** or (b) decarbonylation of the four-membered intermediate **5** or **6** which is formed by ring expansion of the *N*-oxide.



Analogous four-membered compounds of **5** and **6** have already been described as a cycloaddition product between ketenes and nitroso derivatives. The **5** analogue is generally stable thermally under usual reaction conditions and reportedly undergoes a dissociation reaction to isocyanate and carbonyl compounds with strong heating. The four-membered analogue of intermediate **6** is usually unstable and decomposes to imine and carbon dioxide.[9] These characteristic properties of the four-membered-ring analogues **5** and **6** are very different from those found in our oxidation reaction of α-lactams. Therefore, **5** and **6** probably are not found in our reaction and aziridinone *N*-oxide may be converted in a single step to oxaziridine as shown in **4**.[10]

In the oxidation reaction of 1,2-di-*tert*-butylaziridine with *m*-chloroperbenzoic acid in methanol solution at 0 °C, we also observed a 6–7% yield of 2,3-di-*tert*-butyloxaziridine within the main reaction product, 2-methyl-2-nitrosopropane.[11] The reaction seemed to proceed via formation of aziridine *N*-oxide and aziridinone *N*-oxide as shown. We believe that this is the first example of oxidation of the carbon atom in an aziridine structure by organic peroxide.[12]