

esters of highly reactive allylic terpene alcohols. Preliminary results indicate that the displacement method is also successful for the less reactive homoallylic isopentenyl system. Experiments are now underway to explore the scope of the reaction with other primary alcohols and phosphorus-containing nucleophiles.²¹

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Registry No. 1-OH, 556-82-1; 1-Br, 870-63-3; 1-OPP, 358-72-5; 2-OH, 76985-83-6; 2-Br, 76946-99-1; 2-OPP, 76947-00-7; 3-OH, 106-24-1; 3-Br, 6138-90-5; 3-OPP, 763-10-0; 4-OH, 2284-91-5; 4-Br, 76947-01-8; 4-OPP, 76963-02-5; 5-OH, 4602-84-0; 5-Br, 6874-67-5; 5-OPP, 13058-04-3; tris(tetrabutylammonium) hydrogen pyrophosphate, 76947-02-9.

(21) Recently Zwierzak and Kluba²² reported the syntheses of a variety of monophosphates from the corresponding bromides using tetra-*n*-butyl di-*tert*-butyl phosphate in a displacement reaction, followed by treatment with trifluoroacetic acid to remove the *tert*-butyl groups. Although the procedure can be used to prepare allyl phosphate, it is not applicable to the more acid-sensitive terpene phosphates.

(22) Zwierzak, A.; Kluba, M. *Synthesis* 1978, 770-771.

(23) National Institutes of Health Postdoctoral Fellow, GM 06775.

(24) Research Career Development Awardee, 1975-1980, HL 00084.

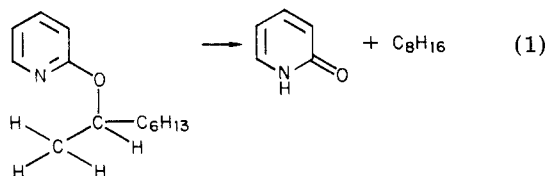
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Pyrolysis of Alkyl Pyridyl Ethers¹

Summary: A study of the mechanism of the pyrolysis of a series of alkyl pyridyl ethers has revealed the absence of any 1,3 alkyl shift and a linear correlation between olefin regiochemistry and pyridine leaving group ability in a thermal elimination reaction.

Sir: The pyrolysis of 2-octyl 2-pyridyl ether (eq 1) affords



a mixture of isomeric octenes and 2-pyridone.² If understood as a cyclic pyrolytic elimination, this is a rare example of such an elimination involving the formal disruption of an aromatic system.³ Moreover, it involves a substrate wherein the electronic and steric features of the leaving group can be varied in a systematic and uncoupled fashion by appropriate substitution on the pyridine ring.

(1) Portions of this work were reported at the ACS Central Regional Meeting, May 7-10, 1979, Columbus, OH.

(2) All pyrolyses were done in an atmospheric pressure flow system, using N₂ carrier gas at 400-500 °C. Products were analyzed by calibrated GLC analysis.

(3) The discovery of the pyrolytic conversion of 2-ethoxypyridine to ethylene and pyridone and its kinetics were reported by Taylor while this work was in progress: Taylor, R. *J. Chem. Soc., Chem. Commun.* 1978, 732.

Table I. Product Distributions and Basicities for 2-Octyl Pyridyl Ethers^{2,6}

	% 1-octene ^a	% <i>trans</i> -2-octene ^a	% <i>cis</i> -2-octene ^a	basicity, ^b kcal/mol
1, X = Y = Br	40	42	18	205.0
2, X = H; Y = Br	45	41	14	207.8
3, X = Y = H	50	36	13	212.6
4, X = Y = CH ₃	57	33	11	219.1
5, X = H; Y = SiMe ₃	61	31	8	219.7
6, X = H; Y = <i>t</i> -Bu	64	29	7	218.6

^a Product distributions are $\pm 1\%$. ^b Basicity values are ± 1 kcal/mol.

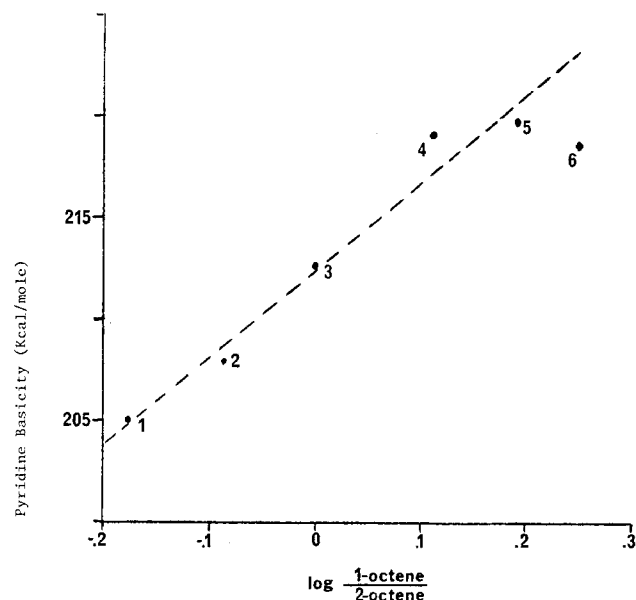
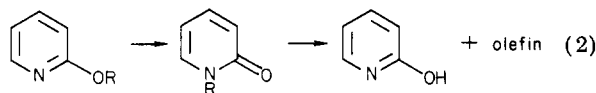


Figure 1.

The studies we report herein have yielded both a description of the transition state of this reaction and an interesting relationship between pyridyl leaving group ability and product regiochemistry.

We considered two general mechanisms. The obvious possibility suggested by eq 1 is a cyclic process using the pyridine lone pair as an internal base.⁴ Alternatively, initial rearrangement of the pyridine ether to an *N*-alkylpyridone followed by elimination, as shown in eq 2,



would yield the same result.⁵ Independent synthesis of *N*-(2-octyl)pyridone and its pyrolysis revealed that under conditions where the pyridine ether gave a 6-8% yield of olefin, the *N*-alkylpyridone yielded little or no (<1%) olefin products. Moreover, no conversion of pyridine ether

(4) The analogous conversion of imidates to olefin and amide has been reported: Marullo, N. P.; Smith, C. D.; Terapan, J. F. *Tetrahedron Lett.* 1966, 6279.

(5) The thermal conversions of 2-methoxypyridine to *N*-methylpyridone and of imidates to amides are known: (a) Wiberg, K. B.; Shryne, T. M.; Kintner, R. R. *J. Am. Chem. Soc.* 1957, 79, 3160; (b) Wislicenus, W.; Goldschmidt, M. *Chem. Ber.* 1900, 33, 1470. Also see: Newkome, G. R.; Kohli, D. K.; Kawato, T.; *J. Org. Chem.* 1980, 45, 4508 and references therein.

to *N*-alkylpyridone could be detected under our pyrolysis conditions. These results categorically exclude the intermediacy of the pyridone in our elimination reaction.

We then investigated the relationship between substituents on the pyridine ring and the competition between Hoffman and Saytzeff elimination. The product distributions for a series of 2-octyl pyridyl ethers are listed in Table I. For analysis purposes, we have also included values for the basicity of the pyridine corresponding to that portion of the ether substrate.⁶ In order to consider our results in terms that would more directly correspond to a linear free-energy relationship, a plot of the log of the ratio of 1-octene to 2-octene vs. pyridine basicity is shown in Figure 1. The correlation suggested by this plot ($r = 0.984$) is also shown. The deviation observed for **6** (6-*tert*-butyl substituent) suggests the onset of a steric effect that promotes production of anomalously large amounts of terminal olefin.⁷ Interestingly, little or no steric effect is observed with a 6-trimethylsilyl substituent.⁸

This kind of correlation has superficial analogy in the work of Bartsch et al. on bimolecular eliminations in solution, where the production of 1-butene in eliminations from 2-iodobutane was correlated with base strength.⁹ They found that stronger bases gave more terminal olefin and that steric effects were only important in extremely hindered bases. We must, however, note that there is an important difference between our reaction and those results. In our systems there is a simultaneous change of both base and leaving group. Since increased basicity corresponds to reduced nucleofugality (leaving-group ability), the observation of increased 1-octene with increased base strength could equally well be correlated with decreased nucleofugality.¹⁰

To decide whether our product selectivity correlated to basicity or nucleofugality we sought a set of substrates that would allow the separation of these two effects. We reasoned that an amine substituent at either the 4 or 6 position of the pyridine ring would greatly increase pyridine basicity while having little or no destabilizing effect on the aryloxy leaving group.¹¹ Thus, a correlation based on basicity would predict substantially increased terminal olefin production, while leaving-group considerations would suggest little or no effect on product distribution. We therefore synthesized and pyrolyzed compounds **2a**, **3a**, and **5a** where X = N(CH₃)₂ instead of H.

We found that the product distributions from **2a**, **3a**, and **5a** were identical ($\pm 1\%$) with those for **2**, **3**, and **5** respectively; i.e., the 4-N(CH₃)₂ group has no effect on the distribution of pyrolysis products. We interpret this to indicate a transition state involving very little N-H bond formation but a great deal of C-O bond cleavage. Clearly, increased partial positive charge on the carbon skeleton as the leaving group improves provides an explanation for

the trend in olefin regiochemistry. We have also observed somewhat enhanced rates of pyrolysis with the electron-poor pyridines (e.g., 6-Br) and with increased alkyl substitution in the alkyl fragment,¹² both of which are consistent with this model.

Further experiments are underway to assess the scope and limits of product control in this reaction and to identify candidates for synthetically useful regiochemical control in such an elimination.

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Registry No. 1, 76999-02-5; 2, 76999-03-6; **2a**, 76999-04-7; 3, 76999-05-8; **3a**, 76999-06-9; 4, 76999-07-0; 5, 76999-08-1; **5a**, 76999-09-2; 6, 76999-10-5; 1-octene, 111-66-0; *trans*-2-octene, 13389-42-9; *cis*-2-octene, 7642-04-8; 2-pyridone, 142-08-5.

(12) Specifically, we compared the reactivity of the *n*-octyl, 2-octyl, and *tert*-butyl ethers under a standard set of reaction conditions.

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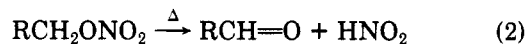
The Transition State in the Carbonyl-Forming Elimination Reaction of Alkyl Nitrates

Summary: The title reaction, now found to involve proton tunneling with base catalysis and a cyclic, nonlinear proton transfer in the uncatalyzed gas-phase process, cannot have (as previously formulated) an E_{CO2} mechanism.

Sir: The base-catalyzed elimination reaction of alkyl nitrates, expressed by eq 1, had been the subject of a con-



siderable number of studies¹⁻⁴ which have led to its formulation as a concerted E_{CO2} process. The postulated mechanism has been based on the results of measurements (with benzyl nitrates) of the primary hydrogen-deuterium isotope effects ($k_{\text{H}}/k_{\text{D}}$) as a function of base, solvent composition, and para substitution, the nitrogen isotope effect (k_{14}/k_{15}) as a function of base strength and parasubstitution, and the occurrence of a minute degree of deuterium exchange in unreacted substrate. In all cases each of the isotope effects were determined at a single temperature in the range of 20-30 °C. Moreover, the reactivity parameters of the uncatalyzed decomposition reaction which takes place in the absence of solvent according to eq 2 have neither been measured nor taken into consideration.



- (1) Buncel, E.; Bourns, A. N. *Can. J. Chem.* 1960, 38, 2457.
 (2) Baker, J. W.; Heggs, T. G. *J. Chem. Soc.* 1955, 616.
 (3) Smith, P. J.; Pollack, C. A.; Bourns, A. N. *Can. J. Chem.* 1975, 53, 1319.
 (4) Pollack, C. A.; Smith, P. J. *Can. J. Chem.* 1971, 49, 3856.

(6) Basicity values are for the gas-phase basicity of each compound's pyridine fragment (H instead of alkoxy) and are (except for **5**) from: Aue, D. H.; Webb, H. M.; Bowers, M. T.; Liotta, C. L.; Alexander, C. J.; Hopkins, H. P. *J. Am. Chem. Soc.* 1976, 98, 854. The basicity of **5** was measured by Ms. Naomi Lev using standard ICR techniques.

(7) For a discussion of hindered pyridine bases in bimolecular eliminations see: Brown, H. C.; Nakagawa, M. *J. Am. Chem. Soc.* 1956, 78, 2197.

(8) Compare to: Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* 1980, 102, 5618.

(9) Bartsch, R. A.; Read, R. A.; Larsen, D. T.; Roberts, D. K.; Scott, K. J.; Cho, B. R. *J. Am. Chem. Soc.* 1979, 101, 1176 and references therein.

(10) This observation has been made for bimolecular eliminations in solution; cf.: Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* 1969, 91, 1376.

(11) 4-N(CH₃)₂ increases pyridine basicity by ca. 15 kcal/mol⁶ while amine substitution at the 3 position of a phenol does little to affect its basicity (Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* 1980, 45, 818).