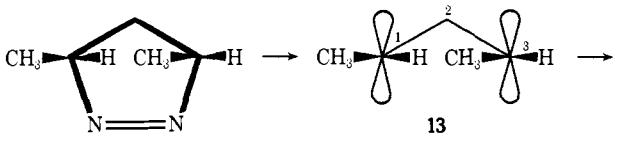
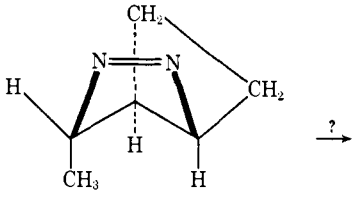
mixture and began converting to 1-methylcyclopentene above 400° but were equilibrated less than 1% at 250°. Thus the **5e**/**5n** ratios observed at low temperatures (less than 5% conversion of pyrazolines to products) are true kinetic ratios and the stereochemistry is *predominantly singly inverted*.[7b]

The ratio of **5e** to **5n** is similar to those obtained from *cis*- and *trans*-3,5-dimethylpyrazolines[2] (**12c** and **12t**) and *endo*- and *exo*-4-methyl-2,3-diazabicyclo[3.3.0]oct-2-enes.[8] The predominant single inversion of stereochemistry observed in the decomposition of **12c** and **12t**

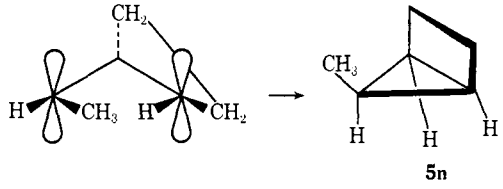


12t **13**

was accounted for[2] by postulating the intermediacy of a π-cyclopropane or 0,0 diradical intermediate (*e.g.*, **13**) which has been predicted on the basis of approximate molecular orbital calculations to undergo ring closure in a conrotatory sense.[1] However, if **13** is responsible for the single-inversion product formed from **12**, its formation must require an energy only slightly lower than that of some other, less stereoselective process because some double retention and double inversion products are also formed.[2b] Raising the energy of **13**—for example, by connecting C_2 and C_3 with a short carbon chain—should allow this secondary process to become predominant. As can be seen from the data reported here, however, connecting C_2 and C_3 by *even a two-carbon bridge* (which inspection of model shows should severely strain the 0,0 intermediate) produces essentially no change in the propensity of these pyrazolines to undergo decomposition with inversion of configuration.



1e



5n

The complete absence of any strain effect on the stereochemistry of pyrazoline decomposition makes it seem very unlikely that the single inverting part of this stereochemistry is controlled by conrotation of a 0,0 intermediate. We once again suggest that Roth's hypothesis,[9] involving sequential C–N cleavage and backside displacement of N_2 in a nitrogen-containing intermediate (**11**, Scheme II), is a viable alternative.[10] Besides accounting well for our observations, this hypothesis is also consistent with recent kinetic data on the decomposition of acyclic azo compounds,[11] with *ab initio* calculations[12] which question on theoretical grounds the existence of a predominantly conrotating trimethylene diradical intermediate, and with earlier experimental work which suggested that 0,0 diradicals were probably not involved in the isomerization of 1,2-dialkylcyclopropanes.[13]

Acknowledgments. We are grateful to Drs. Bruce Hawkins, Geoffrey Hawkes, and John D. Roberts for assistance in obtaining and interpreting ^{13}C nmr spectra, to Dr. L. B. Friedman, Wellesley College, for helpful discussions, and to the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for financial support.

(8) (a) P. B. Condit and R. G. Bergman, *Chem. Commun.*, 4 (1971); (b) see also M. P. Schneider and R. J. Crawford, *Can. J. Chem.*, **48**, 628 (1970).

(9) (a) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, **702**, 1 (1967); see also (b) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **89**, 7133 (1967); (c) the Roth hypothesis[7a,9a] also provides a reasonable alternative to the so-called "recoil" mechanism,[9b] which has recently been questioned on theoretical grounds; *cf.* F. S. Collins, J. K. George, and C. Trindle, *ibid.*, **94**, 3732 (1972).

(10) (a) We believe that R_1R_2C–N cleavage in **1** is concurrent with or followed closely by C_4–C_5 cleavage, leading only to **6**. This mode therefore leads to no methylbicyclopentanes and does not complicate the stereochemistry of formation of these products. However, our mechanism requires that cleavage of the R_1R_2C–N bond be at least competitive with cleavage of the cyclobutyl C–N bond in **1e** and **1n**. Whether this is consistent with observations in acyclic systems is difficult to determine. For example, 1,1′-dicyanoazocyclobutane decomposes in solution 36 times slower than does the corresponding strain-free dicyclohexyl compound.[10b] Because cyano-substituted systems probably decompose by a concerted mechanism in which both C–N bonds break simultaneously,[10c] the six/four ring size effect to be expected in one-bond cleavage would be $(36)^{1/2}$ or 6. However, this rate difference is totally entropy controlled; the activation energy for the four-ring compound is actually *lower* than that for the six.[10b] These considerations, combined with the demonstrably profound effect of chain branching on the rate of azo compound decompositions,[10d] make it seem quite reasonable that both C–N cleavage reactions illustrated in Scheme II take place at similar rates. (b) C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *J. Amer. Chem. Soc.*, **75**, 2078 (1953); (c) S. Seltzer and S. G. Mylonakis, *ibid.*, **89**, 6584 (1967), and earlier papers; (d) C. G. Overberger, W. F. Hale, M. B. Berenbaum, and A. B. Finestone, *ibid.*, **76**, 6185 (1954).

(11) K. Takagi and R. J. Crawford, *ibid.*, **93**, 5910 (1971).

(12) (a) K. Q. Siu, W. M. St. John, and E. F. Hayes, *ibid.*, **92**, 7249 (1970); (b) J. A. Horsley, Y. Hean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *ibid.*, **94**, 282 (1972); (c) P. J. Hay, W. J. Hunt, and W. A. Goddard, *ibid.*, **94**, 638 (1972).

(13) (a) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **90**, 7344 (1968); R. G. Berman and W. L. Carter, *ibid.*, **91**, 7411 (1969).

(14) National Science Foundation Predoctoral Fellow, 1967–1971.

(15) Alfred P. Sloan Foundation Fellow, 1970–1972; Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Awardee, 1970–1975.

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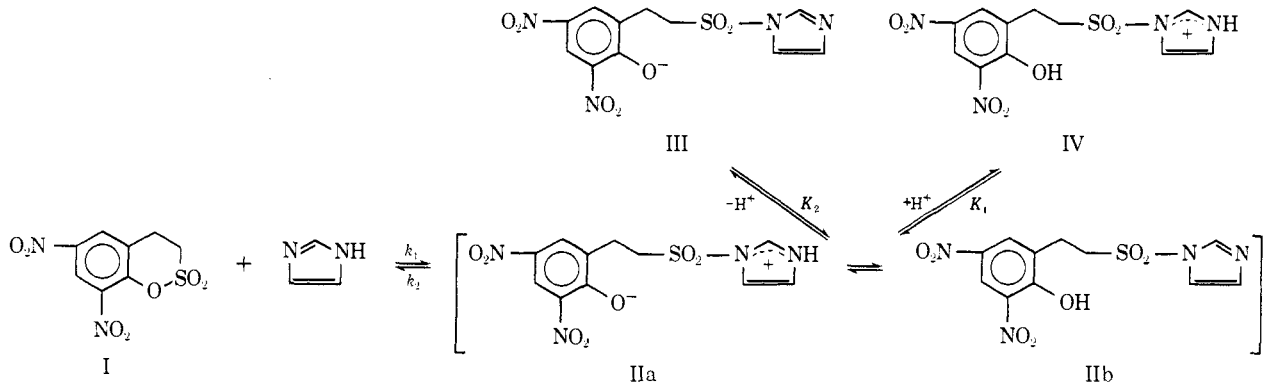
The Readily Reversible Nucleophilic Reaction of Imidazole with β-(2-Hydroxy-3,5-dinitrophenyl)ethanesulfonic Acid Sultone

Sir:

The study of the hydrolytic reactivity of aromatic five-membered cyclic sulfonates has yielded important information concerning not only the influence of ring structure on reactivity, but also the mechanism of action of serine proteases.[1] The sulfonylation of the

(1) E. T. Kaiser, *Accounts Chem. Res.*, **3**, 145 (1970).

Scheme I



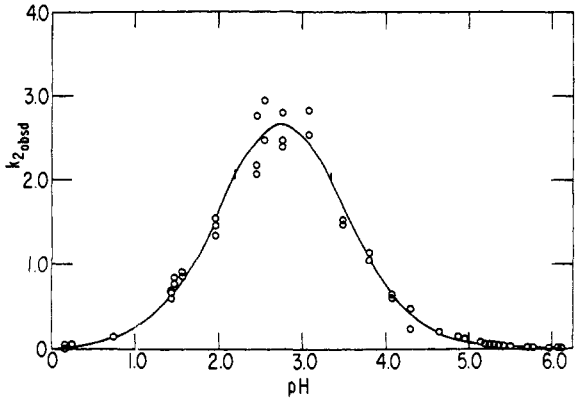


Figure 1. Plot of the observed first-order rate constants for the cyclization of the sulfonylimidazole species.

active-site serine hydroxyl in α-chymotrypsin by the highly strained five-membered cyclic ester 2-hydroxy-5-nitro-α-toluenesulfonic acid sultone involves a ring-opening reaction catalyzed by the enzyme. This reaction is readily reversible, and when kinetic control predominates, the sultone and free enzyme are regenerated from the sulfonyl–enzyme species. Unfortunately, until the present time, a readily reversible ring-opening process has not been observed in a corresponding simple organic model system. In order to determine whether the ready reversibility of the ring-opening nucleophilic reaction is a specific consequence of the enzymatic catalysis or if it is a more general phenomenon, we have been searching for a suitable organic model reaction.

The search has concentrated on the use of imidazole as the appropriate organic catalyst because it is both a good nucleophile and a good leaving group. If the enzymatic phenomenon is primarily due to the intrinsic tendency of the ring-opened systems to cyclize rapidly, then it appears that this process is kinetically more favorable for the production of five- rather than six-membered cyclic sulfonates.[1] For this reason it was not surprising that imidazole acted as a general base catalyst in the hydrolysis of the five-membered cyclic ester 2-hydroxy-5-nitro-α-toluenesulfonic acid sultone because the corresponding nucleophilic reaction was suppressed by its too ready reversibility.[2] Since cyclization of the species resulting from nucleophile-catalyzed ring opening of a six-membered sultone should occur less rapidly, study of such a system would be expected to provide a better opportunity to observe the kinetic behavior of the ring-opened species.

Scheme I describes the species produced by the reaction of β-(2-hydroxy-3,5-dinitrophenyl)ethanesulfonic acid sultone (I)[3] with imidazole (Im) in the pH range 1–8. The equilibria, dependent upon both [Im] and pH, may be approached from either direction. When the starting material is I, it may be shown that the equilibrium absorbance (A) of products is given by eq 1 and the observed first-order rate constant for attainment of equilibrium is given by eq 2.

$$\frac{[\mathrm{I}]_0}{A} = \frac{1 + \left[\frac{k_1K_2}{k_2\mathrm{H}^+} + \frac{k_1}{k_2} + \frac{k_1\mathrm{H}^+}{k_2K_1}\right][\mathrm{Im}]}{\left[\frac{\epsilon_{\mathrm{III}}k_1K_2}{k_2\mathrm{H}^+} + \frac{\epsilon_{\mathrm{II}}k_1}{k_2} + \frac{\epsilon_{\mathrm{IV}}k_1\mathrm{H}^+}{k_2K_1}\right][\mathrm{Im}]} \quad (1)$$

$$k_{\mathrm{obsd}} = k_1[\mathrm{Im}] + \frac{k_2}{\frac{K_2}{\mathrm{H}^+} + 1 + \frac{\mathrm{H}^+}{K_1}} \quad (2)[4]$$

In fact, a linear dependence of $1/A$ on $1/[\mathrm{Im}]$ was observed at any constant pH, and a replot of the x intercepts of these lines yields a value for the complex equilibrium constant connecting species I and III: $k_1K_2/k_2 = (8.4 \pm 0.6) \times 10^{-7}$. This treatment also shows $\epsilon_{\mathrm{III}} = (1.08 \pm 0.07) \times 10^4$ cm^{-1} M^{-1} at 400 nm, consistent with phenoxide formation.

Analysis of the linear plots of k_{obsd} *vs.* [Im] gives $k_1 = (1.39 \pm 0.07) \times 10^{-2}$ M^{-1} sec^{-1}, $k_2/K_2 = (1.45 \pm 0.05) \times 10^4$ M^{-1} sec^{-1}. This provides an independent measurement of the equilibrium constant $k_1K_2/k_2 = (9.6 \pm 0.8) \times 10^{-7}$, agreeing with the measurement from equilibrium data.

Because the equilibria strongly favor the closed form I at H^+ values near K_1 and K_2, it was necessary to determine these constants by using sulfonamide III as starting material.[5] The pH of a solution of III was lowered, and the absorbance decay measured at 400 or 350 nm. A plot of the observed rate constants *vs.* pH (Figure 1) describes a bell-shaped curve which is simply interpreted as indicating a reactive species with two ioniz-

(2) E. T. Kaiser, K.-W. Lo, K. Kudo, and W. Berg, *Bioorg. Chem.*, 1, 32 (1971).

(3) K.-W. Lo, Ph.D. Thesis, University of Chicago, 1968, p 49.

(4) When the pH of the experiment is well above K_2 these equations have the simpler forms $[\mathrm{I}]_0/A = (k_2\mathrm{H}^+/k_1K_2\epsilon_{\mathrm{III}})(1/[\mathrm{Im}]) + (1/\epsilon_{\mathrm{III}})$ and $k_{\mathrm{obsd}} = k_1[\mathrm{Im}] + (k_2\mathrm{H}^+/K_2)$.

(5) The imidazolium salt of III was synthesized by the reaction of I with 2 equiv of imidazole in dry acetonitrile at room temperature for 15 hr. The crystals deposited had mp 105–105.5°, and satisfactory nmr, ir, and analytical data were obtained. An aqueous solution of this compound has uv and visible spectra identical with those produced by the addition of I to imidazole solutions at high pH, and these solutions, upon pH adjustment, recyclized at identical rates.

able groups. Analysis shows $pK_1 = 2.19 \pm 0.06$, $pK_2 = 3.34 \pm 0.06$, and $k_2 = 4.3 \pm 0.3$ sec^{-1}, again agreeing with measurements described above.[6] Although IIa and IIb are kinetically indistinguishable, IIa contains both the better nucleophile and better leaving group for recyclization, and can close to products I and Im without proton transfer. It seems reasonable, therefore, to postulate that this zwitterionic species is the reactive one.

In summary, our data demonstrate that in the absence of an enzyme a readily reversible nucleophilic reaction of a cyclic sulfonate can be observed. Comparison of the behavior of the five-membered cyclic ester 2-hydroxy-5-nitro-α-toluenesulfonic acid sultone when treated with imidazole[2] to that of the six-membered sultone I fully supports our premise that intramolecular nucleophilic attack resulting in recyclization should be less favorable and therefore more easily observable in the case of the six-membered system. Exactly the same reactivity pattern has been seen when the corresponding *o*-hydroxy-substituted phenylmethanesulfonyl- and β-phenylethanesulfonylchymotrypsin species are compared.[1,7] The kinetic and equilibrium behaviors seen in the present study show again that as a model catalyst imidazole is an excellent choice for the simulation of enzymatic reactions.

Acknowledgment. The support of this research by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged as are helpful discussions with Professor F. J. Kézdy.

(6) This measurement, $k_2/K_2 = (0.94 \pm 0.2) \times 10^4$, agrees reasonably well with $(1.45 \pm 0.05) \times 10^4$ obtained above, especially considering the variations in reaction media (different buffer systems, including strong acids).

(7) Unpublished results of W. Berg.

(8) Predoctoral Trainee of the National Institute of General Medical Sciences.

(9) Postdoctoral Fellow of the National Institute of General Medical Sciences.

(10) Fellow of the Alfred P. Sloan Foundation.

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Octahedral Vanadium(IV) Complexes. Synthesis and Stereochemistry of Vanadium(IV) β-Diketonates

Sir:

The chemistry of vanadium(IV) is dominated by the VO^{2+} ion and its metal complexes, a great many of which exhibit square-pyramidal coordination,[1] *e.g.*, $VO(acac)_2$ ($acac^- = CH_3COCHCOCH_3^-$). Octahedral complexes of the simple V^{4+} ion, in which the vanadium is not attached to a doubly bonded oxygen atom, *e.g.*, VCl_6^{2-}, are rare,[2] and, to our knowledge, the recently reported complexes[3] with the dinegative anion of 1,2-dihydroxybenzene and its derivatives, $[V(RC_6H_3O_2)_3]^{2-}$, are the only well-characterized octahedral tris chelates of V^{4+}. No cationic complexes are known, with the possible exception of $[V(en)_3]F_4$.[4] Apart from $V(acac)_2Cl_2$ and $V(bzac)_2Cl_2$ ($bzac^- = C_6H_5COCHCOCH_3^-$)[5] the only neutral octahedral complexes of V^{4+} are adducts of VCl_4.

We now report the synthesis and characterization of the octahedral vanadium(IV) β diketonates $V(acac)_2Cl_2$, $V(dpm)_2X_2$ ($dpm^- = t\text{-}C_4H_9COCHCO\text{-}t\text{-}C_4H_9^-$; X = Cl, Br, NCO, or NCS), and $[V(dik)_3]^+Y^-$ (dik = acac or dpm; $Y^- = FeCl_4^-$ or $SbCl_6^-$). The latter compounds represent the first well-characterized cationic complexes of V^{4+}.

The $V(dik)_2Cl_2$ complexes were prepared in good yield by reaction of the diketone with VCl_4 in anhydrous benzene or dichloromethane–hexane. Metathesis reactions of $V(dpm)_2Cl_2$ with HBr, AgOCN, and NaSCN in benzene or dichloromethane afforded $V(dpm)_2X_2$ (X = Br, NCO, or NCS). Similar reactions were attempted with HI and KSeCN; however, both resulted in apparent reduction of the vanadium(IV) rather than formation of the $V(dpm)_2X_2$ complex. The cationic complexes, $[V(dik)_3]^+[FeCl_4]^-$ and $[V(dik)_3]^+[SbCl_6]^-$, were prepared by reaction of $V(dik)_2Cl_2$ with anhydrous $FeCl_3$ or $SbCl_5$ in dichloromethane. Satisfactory analytical data have been obtained for all of the complexes. All are readily hydrolyzed on contact with the atmosphere.

Molecular weight and conductance data indicate that the $V(dik)_2X_2$ complexes are monomeric and essentially nonelectrolytes in nitrobenzene; $[V(dik)_3]^+Y^-$ are 1:1 electrolytes. Effective magnetic moments (1.66–1.80 BM), measured by nmr in dichloromethane, are approximately equal to the spin-only value (1.73 BM) expected for vanadium(IV). $[V(dpm)_3]^+[SbCl_6]^-$ (in dichloromethane at room temperature) gives a very broad esr signal having a line width of ~600 G and a *g* value of 1.93. Superimposed on this broad, single line is a sharp, eight-line spectrum which is believed to arise from a trace of a hydrolysis product containing the VO^{2+} moiety.

All of the complexes are intensely colored red or violet owing to charge-transfer bands at 15,000–18,000 and ~28,000 cm^{-1} (ϵ 2000–8000) which are assigned to diketonate(π) → metal(d) and metal(d) → diketonate(π^*) transitions, respectively. Additional bands in the visible spectra of the $V(dik)_2X_2$ complexes appear to involve halogen(π) → metal(d) charge transfer. Unfortunately, the d–d transitions are obscured by the charge-transfer bands.

The far-infrared spectrum of $V(dpm)_2Cl_2$ (Figure 1) depends on phase, and the changes in the spectrum on changing the solvent suggest that there is an equilibrium in solution between the cis and trans isomers, with the isomer present in the solid state decreasing in concentration with increasing dielectric constant of the solvent. Most important are changes in the V–Cl stretching region. A band at ~385 cm^{-1} in the solution spectra increases in intensity with increasing solvent dielectric constant at the expense of the strong band at ~362 cm^{-1}; only the latter band is present in the spectrum of the solid. Measurement of the orientation molar polarization in carbon tetrachloride (335 cm^2) and in benzene (498 cm^2) permits the 385-cm^{-1}

(1) J. Selbin, *Chem. Rev.*, 65, 153 (1965); *Coord. Chem. Rev.*, 1, 293 (1966).

(2) D. Nicholls, *ibid.*, 1, 379 (1966).

(3) R. P. Henry, P. C. H. Mitchell, and J. E. Prue, *J. Chem. Soc. A*, 3392 (1971).

(4) R. G. Cavell and H. C. Clark, *J. Inorg. Nucl. Chem.*, 17, 257 (1961).

(5) H. Funk, G. Mohaupt, and A. Paul, *Z. Anorg. Allg. Chem.*, 302, 199 (1959).