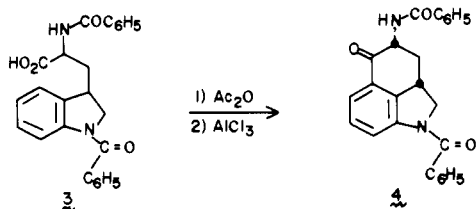


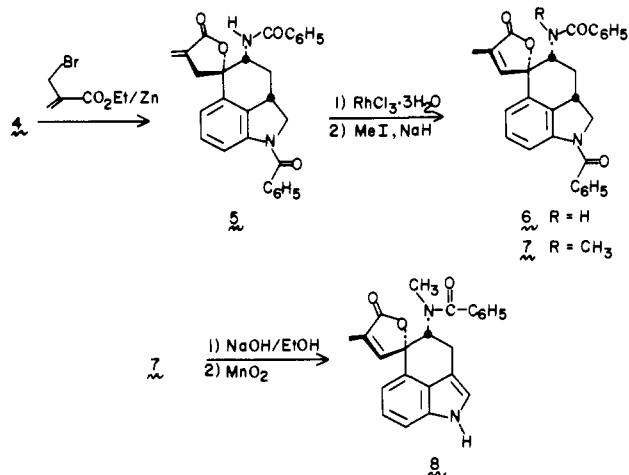
purposes, we have developed procedures which are quite compatible with this goal. Here we record the first total synthesis of the racemic rugulovasines.

As starting material, DL-tryptophan appeared likely, and a suitably blocked form was found in Witkop's<sup>5</sup> dihydro, dibenzoyl derivative **3**. Dehydration (Ac<sub>2</sub>O, 100 °C, 15 min) afforded the



azlactone which cyclized<sup>6</sup> readily under Friedel-Crafts conditions (AlCl<sub>3</sub>, ClCH<sub>2</sub>-CH<sub>2</sub>Cl, reflux, 30 min) to ketone **4**,<sup>7</sup> mp 172-173 °C (from MeOH).

Treatment of **4** with a solution derived from the action of Zn on ethyl α-(bromomethyl)acrylate<sup>8</sup> (THF, 50 °C, 14 h) gave the methylene lactone **5**, mp 218-219 °C, as a single isomer which



cleanly rearranged to the butenolide **6**, mp >275 °C, under the influence of RhCl<sub>3</sub>·3H<sub>2</sub>O<sup>9</sup> (CHCl<sub>3</sub>/EtOH/H<sub>2</sub>O, 90 °C, 14 h). Alkylation (MeI/NaH, DMF, 25 °C, 30 min) gave **7**, mp 251-252 °C, mild hydrolysis (MeOH/HCl, 60 °C, 4 h or NaOH, H<sub>2</sub>O/EtOH, 75 °C, 1 h) selectively exposed the indole function, and oxidation<sup>10</sup> (MnO<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 25 °C, 30 min) regenerated the indole. The monobenzoylrugulovasine **8**, mp 237-238 °C, was thus obtained in 25% overall yield from **3**.

Removal of the benzoyl group of **8** proved troublesome since decomposition was observed under acidic hydrolysis conditions, and only opening of the lactone occurred under the usual basic hydrolysis conditions. However, with a modification of Gassman's<sup>11</sup> procedure (*t*-BuOK, NaOH, THF/Me<sub>2</sub>SO, 80 °C, 4 h)

(5) Daly, J. W.; Mauger, A. N.; Yonemitsu, O.; Antonov, V. K.; Takase, K.; Witkop, B. *Biochemistry* 1967, 6, 648-654.

(6) (a) Intermolecular Friedel-Crafts acylations with azlactones have been reported: Balaban, A. T.; Bally, I.; Frangopol, P. T.; Bacescu, M.; Cioranescu, E.; Birladeanu, L. *Tetrahedron* 1963, 19, 169-176, and earlier work by these authors. (b) For intramolecular acylation of indole derivatives (anhydride): Szmuzkovicz, J. *J. Org. Chem.* 1964, 29, 843-849. (c) (Acid chloride) Kornfeld, E. C.; Fornefeld, E. J.; Kline, G. B.; Mann, M. J.; Morrison, D. E.; Jones, R. G.; Woodward, R. B. *J. Am. Chem. Soc.* 1956, 78, 3087-3114.

(7) All new compounds were characterized by elemental analysis and showed the expected spectroscopic features. Stereochemical assignments were based on NMR spectra obtained at 300 or 600 MHz; in particular, the 1,3-cis relationship of the methine protons of **4** was evident from decoupling experiments at 600 MHz.

(8) Ohler, E.; Reininger, K.; Schmidt, U. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 457-458.

(9) We thank Professor P. A. Grieco for his advice concerning this reagent. See: Grieco, P. A.; Nishizawa, M.; Marinovic, N.; Ehmann, W. J. *J. Am. Chem. Soc.* 1976, 98, 7102-7104. Biellmann, J. F.; Jung, M. J. *Ibid.* 1968, 90, 1673-1674. Andrieux, J.; Barton, D. H. R.; Patin, H. *J. Chem. Soc., Perkin Trans. 1* 1977, 359-363.

(10) Jansen, A. B. A.; Surtees, J. R. *J. Chem. Soc.* 1964, 5573-5577.

followed by neutralization, a single product, identical (physical properties, TLC, and published spectra<sup>12</sup>) to rugulovasine A (hydrate), was obtained. Hence, we assign the relative stereochemistry of **5** and subsequent compounds, as shown, and conclude that lactone opening protects the system from isomerization during the final deblocking step in the synthesis. Dissolution of this substance in MeOH at room temperature for 2 days gave a mixture of rugulovasines A and B from which **2** could be obtained by chromatography as previously described.<sup>1-4</sup>

Starting from L-tryptophan, a diastereomer of **3**<sup>5</sup> was obtained which was converted as described above to optically active **4**, [α]<sub>D</sub><sup>25</sup> +176° (c 0.9, CHCl<sub>3</sub>). Since the intermediate azlactone surely epimerizes at the α carbon, **4** owes its optical activity to the fixed chirality at the γ carbon and the stereospecificity of the Friedel-Crafts reaction. We have converted this substance to **8**, [α]<sub>D</sub><sup>25</sup> -349° (c 0.5, CHCl<sub>3</sub>), whose optical purity is >98% as determined by NMR with optically active shift reagents. We shall report on the racemization and interconversion of the rugulovasines at a later date; in the meantime, we note that **4** incorporates much of the functionality required for the synthesis of other ergot alkaloids.<sup>6c,13</sup>

**Acknowledgments.** We are pleased to acknowledge stimulating discussions and advice from Professor A. P. Kozikowski.

(11) Gassman, P. G.; Hodgson, P. K. G.; Balchunis, R. J. *J. Am. Chem. Soc.* 1976, 98, 1275-1276.

(12) We warmly thank Professor S. M. Weinreb for NMR spectra of these alkaloids.

(13) See, for examples: Floss, H. G. *Tetrahedron* 1976, 32, 873-912; the rugulovasines are, in fact, isomers of lysergic acid.

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## Deuterium and Oxygen-18 Isotope Effects on Nucleophilic Displacement by Monomeric Water in Aprotic Solvents

Sir:

We report that the H<sub>2</sub>O/D<sub>2</sub>O rate-constant ratio for nucleophilic attack by water at a methyl carbon (eq 1) is reduced to very



near unity when the water is a dilute solute in a dipolar aprotic solvent. We have observed this for three leaving groups [CH<sub>3</sub>X equals 1-methylthiophenium ion (MeTh<sup>+</sup>),<sup>1</sup> methyl perchlorate (MeOClO<sub>3</sub>),<sup>2</sup> and methyl trifluoromethanesulfonate (MeOTf)<sup>3</sup>] and for two aprotic solvents [acetonitrile (MeCN),<sup>4</sup> and tetrahydrothiophene 1,1-dioxide (TMSO<sub>2</sub>; sulfolane)<sup>5</sup>]. We have also observed that the corresponding H<sub>2</sub><sup>16</sup>O/H<sub>2</sub><sup>18</sup>O rate-constant ratio is 1.002 ± 0.004 (95% confidence limits) for the reaction of MeTh<sup>+</sup> with dilute H<sub>2</sub>O in TMSO<sub>2</sub> at 35 °C. Although alternative explanations exist (vide infra), these observations are consistent with a mechanism in which no significant positive charge is present on the L<sub>2</sub>O oxygen in the rate-determining transition state and thus in which the rate-determining process does not involve (and

(1) Used as the PF<sub>6</sub><sup>-</sup> salt; prepared as described: Heldeweg, R. F.; Hoogveen, H. *Tetrahedron Lett.* 1974, 75.

(2) Used as a stock solution in MeCN; prepared as described: Radell, J.; Connolly, J. W.; Raymond, A. J. *J. Am. Chem. Soc.* 1961, 83, 3958.

(3) Aldrich 99+% Gold Label, used without purification.

(4) Aldrich 99+% Spectrophotometric Gold Label, used without purification.

(5) Purified as described: Lewis, E. S.; Vanderpool, S. H. *J. Am. Chem. Soc.* 1977, 99, 1946.

Table I. Rate Constants<sup>a</sup> and Isotope Effects<sup>b</sup> for Nucleophilic Displacement by L<sub>2</sub>O

CH <sub>3</sub> X	T, °C <sup>c</sup>	in L <sub>2</sub> O		in MeCN		in TMSO <sub>2</sub>	
		10 <sup>4</sup> k <sub>ψ</sub> <sup>H</sup>	k <sub>ψ</sub> <sup>H</sup> /k <sub>ψ</sub> <sup>D</sup>	10 <sup>4</sup> k <sub>1</sub> <sup>H</sup>	k <sub>1</sub> <sup>H</sup> /k <sub>1</sub> <sup>D</sup>	10 <sup>4</sup> k <sub>1</sub> <sup>H</sup>	k <sub>1</sub> <sup>H</sup> /k <sub>1</sub> <sup>D</sup>
MeTh <sup>+</sup>	25.0	7.4	1.128 ± 0.002 (5)	2.09 <sup>d</sup>	1.015 ± 0.016 (12)		
	30.0					4.4 <sup>d</sup>	1.001 ± 0.006 (9)
MeOCIO <sub>3</sub>	25.0	17.4	1.199 ± 0.012 (5)				
	35.0			1.23 <sup>d</sup>	0.995 ± 0.011 (8)	6.8 <sup>d</sup>	0.996 ± 0.012 (8)
MeOTf	15.0	251	1.239 ± 0.014 (4)				
	25.0			5.6 <sup>e</sup>	0.97 ± 0.02 (11)		

<sup>a</sup> For L<sub>2</sub>O solvent, k<sub>ψ</sub> is in s<sup>-1</sup> and the standard deviation of the listed value (σ) < 0.5%. For MeCN and TMSO<sub>2</sub> solvents, observed k<sub>ψ</sub> values had σ < 2%, derived (eq 2 or 3) k<sub>1</sub> values are in M<sup>-1</sup> s<sup>-1</sup>, σ ≈ 2% for k<sub>1</sub> from eq 2, and σ ≈ 4% for k<sub>1</sub> from eq 3. <sup>b</sup> See text for method of minimizing the uncertainty in k<sub>1</sub><sup>H</sup>/k<sub>1</sub><sup>D</sup> ratios; the uncertainty listed for each ratio is twice the standard deviation of the quoted mean; the number in parentheses is the number of observed ratios used to calculate that mean. <sup>c</sup> Reported temperatures are accurate to ±0.1 °C; the variation in temperature during the determination of any one rate-constant ratio was <0.05 °C. <sup>d</sup> From fit of k<sub>ψ</sub><sup>H</sup> to eq 2 in the range 0 < [H<sub>2</sub>O] < 1 M. <sup>e</sup> From fit of k<sub>ψ</sub><sup>H</sup> to eq 3 in the range 0 < [H<sub>2</sub>O] < 0.5 M.

is not preceded by) any significant covalent-bonding interaction between the nucleophile and the methyl carbon.

All reactions were followed by UV spectroscopy in a Cary 16K spectrophotometer; for reactions of MeTh<sup>+</sup>, the thiophenium to thiophene absorbance change was monitored at 267 nm; for MeOCIO<sub>3</sub> and MeOTf, the solutions contained a slight excess of a nonnucleophilic base, and the absorbance change resulting from protonation of that indicator base was followed [2,4,6-trimethylpyridine in L<sub>2</sub>O at 265 nm; 2,6-bis(1,1-dimethylethyl)pyridine in MeCN and TMSO<sub>2</sub> at 270 nm]. Concentrations of MeTh<sup>+</sup>, MeOCIO<sub>3</sub>, and MeOTf were ≤10<sup>-4</sup> M. Temperature control was within ±0.05 °C (thermistor in cell), and the observed rates were independent of the concentration of the indicator base. In each run, the absorbance change obeyed a first-order rate law; the pseudo-first-order rate constants (k<sub>ψ</sub>) for MeTh<sup>+</sup> and MeOCIO<sub>3</sub> in MeCN and TMSO<sub>2</sub> were linearly related to the water concentration (eq 2) when [L<sub>2</sub>O] < 1 M while for MeOTf in

$$k_{\psi}^L = k_0 + k_1^L[L_2O] \quad (2)$$

MeCN the dependence of k<sub>ψ</sub><sup>L</sup> on [L<sub>2</sub>O] in that range of [L<sub>2</sub>O] contained a significant quadratic term (eq 3, k<sub>2</sub><sup>L</sup>/k<sub>1</sub><sup>L</sup> ≈ 0.6).

$$k_{\psi}^L = k_0 + k_1^L[L_2O] + k_2^L[L_2O]^2 \quad (3)$$

Product identity from MeTh<sup>+</sup> was verified by <sup>1</sup>H NMR with CD<sub>3</sub>CN as solvent: the k<sub>0</sub> term in eq 2 corresponds to production of thiophene and CD<sub>3</sub>CNCH<sub>3</sub><sup>+</sup> (which gives CD<sub>3</sub>CONLCH<sub>3</sub> in the presence of added L<sub>2</sub>O); the k<sub>1</sub><sup>L</sup> term corresponds to production of thiophene and CH<sub>3</sub>OL.

Pairs of reactions with equal concentrations of H<sub>2</sub>O and D<sub>2</sub>O (or natural-abundance H<sub>2</sub>O and 99 atom % H<sub>2</sub><sup>18</sup>O) were run simultaneously in the same thermostated cell holder to facilitate cancellation of errors in the isotopic rate-constant ratio. The values of k<sub>1</sub><sup>H</sup>/k<sub>1</sub><sup>D</sup> and 2σ<sub>m</sub> (approximate 95% confidence limits) listed in Table I were obtained for reactions which obey eq 2 by averaging the observed values of (k<sub>ψ</sub><sup>H</sup> - k<sub>0</sub>)/(k<sub>ψ</sub><sup>D</sup> - k<sub>0</sub>), where k<sub>ψ</sub><sup>H</sup> and k<sub>ψ</sub><sup>D</sup> are from a pair of reactions run simultaneously and k<sub>0</sub> is the common intercept of plots of k<sub>ψ</sub><sup>H</sup> vs. [H<sub>2</sub>O] and k<sub>ψ</sub><sup>D</sup> vs. [D<sub>2</sub>O]; for the one reaction which obeys eq 3, (k<sub>ψ</sub><sup>H</sup> - k<sub>0</sub>)/(k<sub>ψ</sub><sup>D</sup> - k<sub>0</sub>) was extrapolated to [L<sub>2</sub>O] = 0. Each k<sub>1</sub><sup>H</sup>/k<sub>1</sub><sup>D</sup> value thus obtained agreed with the ratio of separately evaluated (via least-squares fits of the same k<sub>ψ</sub> values to eq 2 or 3) k<sub>1</sub><sup>H</sup> and k<sub>1</sub><sup>D</sup>, and had a smaller standard deviation.

Infrared spectra and other evidence<sup>6,7</sup> indicate that water is monomeric in MeCN when [L<sub>2</sub>O] < 1 M, and the available evidence concerning hydration of cations in MeCN suggests that MeTh<sup>+</sup> should be predominantly unhydrated in this range of [L<sub>2</sub>O].<sup>8</sup> Thus, the first-order dependence on [L<sub>2</sub>O] of the k<sub>1</sub><sup>L</sup> terms in eq 2 and 3 implies that a single L<sub>2</sub>O moiety is present in the corresponding rate-determining transition states. The

correspondence between k<sub>1</sub><sup>L</sup>[L<sub>2</sub>O] and the CH<sub>3</sub>OL yield shows that this L<sub>2</sub>O acts as a nucleophile toward carbon and thus that k<sub>1</sub><sup>L</sup> refers to bimolecular nucleophilic displacement by monomeric L<sub>2</sub>O.

The intent of this communication is to compare such reactions of monomeric L<sub>2</sub>O to the corresponding hydrolysis reactions when pure liquid (highly associated) L<sub>2</sub>O is both the nucleophile and the solvent. Note the contrast in Table I between the k<sub>ψ</sub><sup>H</sup>/k<sub>ψ</sub><sup>D</sup> ratios observed when H<sub>2</sub>O and D<sub>2</sub>O are the solvents and the k<sub>1</sub><sup>H</sup>/k<sub>1</sub><sup>D</sup> ratios near unity observed when the water is a dilute solute. For an activated complex with the structure L<sub>2</sub>O<sup>δ+</sup>...CH<sub>3</sub>...X<sup>δ-</sup>, k<sub>1</sub><sup>H</sup>/k<sub>1</sub><sup>D</sup> for reaction in aprotic media is given by the fractionation factor ratio, φ<sub>OL</sub><sup>2</sup>/φ<sub>OL+</sub><sup>2δ</sup>. If φ<sub>OL</sub>/φ<sub>OL+</sub> is not equal to unity in MeCN and TMSO<sub>2</sub> (vide infra; in L<sub>2</sub>O it is about 0.7<sup>-1</sup> and φ<sub>OL</sub><sup>2</sup>/φ<sub>OL+</sub><sup>2δ</sup> ≈ 0.7<sup>-2δ</sup>), then k<sub>1</sub><sup>H</sup>/k<sub>1</sub><sup>D</sup> ≈ 1.00 implies δ ≈ 0.

The H<sub>2</sub><sup>16</sup>O/H<sub>2</sub><sup>18</sup>O ratio cited above for H<sub>2</sub>O + MeTh<sup>+</sup> in TMSO<sub>2</sub> also is consistent with an activated complex structure in which δ = 0. However, it does not rigorously require δ = 0; for 0 < δ < 1, k<sub>1</sub><sup>16</sup>/k<sub>1</sub><sup>18</sup> is a product of two factors: one > 1 and the other < 1.<sup>10</sup> Preliminary calculations<sup>11</sup> applying BEBOVIB<sup>12</sup> to a model for H<sub>2</sub>O + MeTh<sup>+</sup> suggest that k<sub>1</sub><sup>16</sup>/k<sub>1</sub><sup>18</sup> is near 1.03 for small (but nonzero) δ, falls to near 0.95 as δ increases to near unity, and passes through 1.00 near δ = 0.2. This expected range of k<sub>1</sub><sup>16</sup>/k<sub>1</sub><sup>18</sup> is similar to that predicted by Schowen et al.<sup>13</sup> for the addition of OH<sup>-</sup> to CH<sub>3</sub>CHO.

For reactions in liquid L<sub>2</sub>O, the k<sub>ψ</sub><sup>H</sup>/k<sub>ψ</sub><sup>D</sup> ratio could contain contributions from three factors (eq 4). The first is the factor k<sub>ψ</sub><sup>H</sup>/k<sub>ψ</sub><sup>D</sup> = [φ<sub>OL</sub><sup>2</sup>/φ<sub>OL+</sub><sup>2δ</sup>][exp(ΔΔG°<sub>Tr</sub>/RT)][τ<sub>D</sub>/τ<sub>H}] (4)</sub>

of 0.7<sup>-2δ</sup> mentioned above. The second arises from inequality of the values of ΔG° for transferring reactant and activated complex (without exchange) from H<sub>2</sub>O and D<sub>2</sub>O. The third is present only if motion along the reaction coordinate through the transition state is composed wholly or partly of reorganization of solvent structure; its value is expected<sup>15</sup> to be comparable to the D<sub>2</sub>O/H<sub>2</sub>O viscosity ratio or dielectric relaxation time ratio (≈1.2).

If the internal structure of the activated complex in L<sub>2</sub>O has δ ≈ 0, then the first and second factors in eq 4 are near unity and the observed solvent isotope effect arises from the inequality of the rotational relaxation times for liquid D<sub>2</sub>O and H<sub>2</sub>O. Such an origin for the solvent isotope effect on solvolysis in water was first proposed by Robertson and co-workers.<sup>16</sup> Independent

(9) E.g., Schowen, K. B. J. In "Transition States of Biochemical Process"; Gandour, R. D.; Schowen, R. L., Eds.; Plenum Press: New York, 1978; Chapter 6, and references cited therein.

(10) Fry, A. in "Isotope Effects in Chemical Reactions"; Collins, C. J.; Bowman, N. S., Eds.; Van Nostrand-Reinhold; Princeton, 1970; Chapter 6.

(11) Kurz, J. L.; Williams, D. A., unpublished results.

(12) We thank Professor Sims for making this program available to us and for advising us concerning its use. This program has been used by others in published calculations.<sup>13,14</sup>

(13) Hogg, J. L.; Rodgers, J.; Kovach, I.; Schowen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 79.

(14) Burton, G. W.; Sims, L. B.; Wilson, J. C.; Fry, A. *J. Am. Chem. Soc.* **1977**, *99*, 3371.

(15) Kurz, J. L.; Kurz, L. C. *J. Am. Chem. Soc.* **1972**, *94*, 4451.

(6) Muney, W. S.; Coetzee, J. F. *J. Phys. Chem.* **1962**, *66*, 89.

(7) Chantooni, M. K., Jr.; Koltzoff, I. M. *J. Am. Chem. Soc.* **1967**, *89*, 1582.

(8) E.g., MeTh<sup>+</sup> should be less hydrated than K<sup>+</sup> or Cs<sup>+</sup>, and those cations in MeCN have k ≤ 1 M<sup>-1</sup> for M<sup>+</sup> + H<sub>2</sub>O = M·OH<sub>2</sub><sup>+</sup>.

arguments that such activated complexes have reactant-like internal structures and solvent reorganization as their reaction coordinates have been based on  $pK_a(\neq)$  and its temperature dependence.<sup>17</sup> A strikingly analogous conclusion about the reaction coordinate in cation-anion recombinations has been published recently by Ritchie.<sup>18</sup>

As alluded to above, rigorous deduction of the value of  $\delta$  from observed values of  $k_1^H/k_1^D$  in MeCN and TMSO<sub>2</sub> requires knowledge concerning the values of  $\phi_{OL^+}$  and  $\phi_{OL}$  in those solvents. If  $\phi_{OL^+} = \phi_{OL}$ , then  $k_1^H/k_1^D = 1.00$  (as observed) for all possible values of  $\delta$ . Although we regard this alternative origin of  $k_1^H/k_1^D$  as unlikely, experiments designed to measure  $\phi_{OL^+}$  relative to  $\phi_{OL}$  in aprotic media are in progress.

**Acknowledgments.** We gratefully acknowledge support of this work by the National Science Foundation (CHE 76-21052).

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(17) (a) Kurz, J. L.; Harris, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 4117. (b) Kurz, J. L. *Acc. Chem. Res.* **1972**, *5*, 1. (c) Kurz, J. L.; Lee, Y.-N. *J. Am. Chem. Soc.* **1975**, *97*, 3841.

(18) Ritchie, C. D. *Pure Appl. Chem.* **1979**, *51*, 153.

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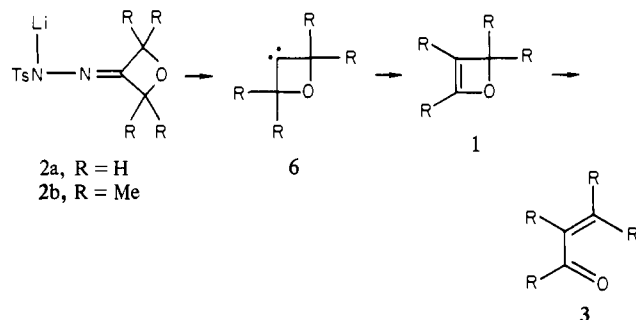
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## Oxetene: Synthesis and Energetics of Electrocyclic Ring Opening

Sir:

Although several substituted oxetenes have been synthesized,<sup>1</sup> the parent compound (**1a**) has not yet been prepared. We now report the synthesis of this unique strained ring compound and an investigation of the kinetics of its electrocyclic ring opening to acrolein.

Hortman and Bhattacharjya<sup>2</sup> reported that pyrolysis of tosylhydrazone lithium salt **2b** leads to 3,4-dimethyl-3-penten-2-one (**3b**). Although tetramethyloxetene **1b** was not isolated in this



reaction, the authors claim it is an intermediate. The rearrangement of **1b** to **3b** has been reported.<sup>3</sup> Accordingly, we have prepared the tosylhydrazone lithium salt **2a**<sup>4</sup> from 3-oxetanone.<sup>5</sup>

(1) (a) Kobayashi, Y.; Hanzawa, Y.; Miyashita, W.; Kumadaki, I. *J. Am. Chem. Soc.* **1979**, *101*, 6445. (b) Koo, Ja-Young; Schuster, G. B. *Ibid.* **1977**, *99*, 5403. (c) Friedrich, L. E.; Bower, J. D. *Ibid.* **1973**, *95*, 6869. (d) Friedrich, L. E.; Schuster, G. B. *Ibid.* **1969**, *91*, 7204. (e) Hollander, J.; Woolf, C. Belgian Patent 671 439, 1966; *Chem. Abstr.* **1966**, *65*, 8875a.

(2) Hortman, A. G.; Bhattacharjya, A. *J. Am. Chem. Soc.* **1976**, *98*, 7081.

(3) Friedrich, L. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1971**, *93*, 4602.

(4) Kaufman, G. M.; Smith, J. A.; Vander-Stouw, G. G.; Schechter, H. *J. Am. Chem. Soc.* **1965**, *87*, 935.

(5) 3-Oxetanone was prepared by the method of Williams<sup>6</sup> and by a modification of the method of Wojtowicz, Polak, and Zaslowsky.<sup>7</sup>

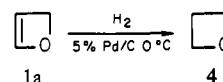
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(7) Wojtowicz, J. A.; Polak, R. J. *J. Org. Chem.* **1973**, *38*, 2061. Wojtowicz, J. A.; Polak, R. J.; Zaslowsky, J. A. *Ibid.* **1971**, *36*, 2232.

Compound **2a** was flash pyrolyzed at 180–190 °C in vacuo, and volatile reaction products were collected at –196 °C. NMR analysis indicated acrolein and a compound thought to be oxetene were present in a 0.2–0.5:1 ratio. Oxetene could be further purified by trap to trap distillation from –110 to –196 °C. This procedure removed the majority of acrolein, leaving oxetene of >90% purity in the –110 °C trap. The only observable impurity was acrolein. The yield of **1a** was 11% on the basis of starting tosylhydrazone.

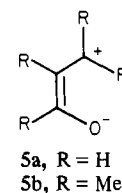
Spectral data are consistent with an assignment of the oxetene structure: NMR (CDCl<sub>3</sub>, –25 °C)  $\delta$  5.27 (br s, 2 H), 5.73 (br s, 1 H), 6.70 (br s, 1 H); IR (gas phase, 25 °C) 3020 (w), 3000 (s), 2970 (m), 1565 (m), 1285 (m), 1025 (s), 920 (s), 880 (s), 665 (s), 425 (s) cm<sup>-1</sup>. The IR band at 1565 cm<sup>-1</sup> is assigned to the C=C stretch in analogy with the C=C stretch in cyclobutene which appears at 1566 cm<sup>-1</sup>.<sup>8,9</sup>

The chemical reactivity of **1a** also provides evidence for its structure. Hydrogenation of **1a** to oxetane **4** was accomplished by reacting a gaseous mixture of **1a** and hydrogen over 5% Pd



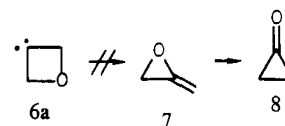
on activated charcoal at 0 °C. The IR spectrum of the product was identical with that of **4**. When a CDCl<sub>3</sub> solution of **1a** was allowed to stand at 25 °C, smooth rearrangement to acrolein (**3a**) occurred. Similarly, the gas-phase rearrangement of **1a** to **3a** at various temperatures was followed by IR spectroscopy. The kinetics of this gas-phase electrocyclic ring opening of **1a** to **3a** were measured at 35, 44.5, 57, and 86.2 °C. From these data, an activation enthalpy of 24.1 ± 1.5 kcal/mol and an activation entropy of 0.0 ± 3.1 eu were calculated. We have previously used the MINDO/3<sup>10,11</sup> molecular-orbital method to calculate a value of 30.7 kcal/mol for the activation enthalpy of this ring opening.

The presence of the electronegative oxygen atom in **1a** raises the possibility of a polar transition state such as **5** for the elec-



trocyclic ring opening. However, the fact that the  $\Delta H^\ddagger$  for the opening of **1a** in the gas phase is similar to that reported for **1b** in various solvents appears to preclude a polar transition state such as **5**. If this transition state was important, electron donation in **1b** would accelerate the rearrangement compared to that of **1a**. Friedrich and Schuster<sup>3</sup> have concluded there is little charge separation in the transition state for the ring opening of **1b**.

Pyrolysis of the tosylhydrazone salt **2a** undoubtedly proceeds via 3-oxacyclobutylidene **6a**. It is of interest that no evidence for ring contraction of **6a** to allene oxide **7** could be obtained. Al-



though allene oxide is unknown, calculations suggest its rearrangement to cyclopropanone **8** is facile.<sup>11</sup> However, careful analysis of the pyrolysis products from **2a** revealed no **8** was

(8) Lord, R. C.; Rea, D. G. *J. Org. Chem.* **1957**, *79*, 2401.

(9) L. E. Friedrich and P. Y.-S. Lam of the University of Rochester have informed us in a private communication that they have prepared **1a**, whose spectral properties are identical with those reported here, by a selenoxide pyrolysis.

(10) Dewar, M. J. S.; Metius, P. J.; Student, P. J.; Brown, A.; Bingham, R. C.; Lo, D. H.; Ramsden, C. A.; Killmar, H.; Weiner, P.; Bischof, P. K. "MINDO/3; Modified Intermediate Neglect of Differential Overlap", Program 279, Quantum Chemistry Program Exchange, Indiana University, 1975. The program was modified to operate on our IBM 370/158 computer.

(11) Figuera, J. M.; Shevlin, P. B.; Worley, S. D. *J. Am. Chem. Soc.* **1976**, *98*, 3820.