in the indicated linear manner. Large fractionation factors for hydrogen bonds are observed only for quite strong bases such as hydroxide and methoxide anions. At a pK for the conjugate acid of about 9-10, unit factors are already observed.[34] This suggests a very quick fall-off of the isotope effect for solvation as basicity decreases. The estimate $B_{OC} = 0.69$ is thus a maximum estimate, and many reasonable transition-state structures with $B_{OC} < 0.69$ are consistent with the findings.

(c) Nucleophilic attack at methyl by one of the molecules of solvation, rather than by the methoxide anion itself:

$$CH_3O\sim\sim H\sim\sim O(CH_3)\cdots CH_3\cdots S<$$

By the argument given above (probable nonlinear dependence on ln ϕ on pK for solvating molecules), ϕ_T could well be about unity for two of the initial molecules of solvation. The third hydrogen bond might well remain intact, however, serving in effect as a connecting link for transfer of negative charge to the nucleophilic oxygen. Such a model produces $\phi_T = 0.82$. Isotope effects substantially larger than this (1/0.82 = 1.21) are commonly observed for bridging protons in general acid-base catalyzed reactions[25,26] (note that this model corresponds to general base catalysis by methoxide ion of methanol attack at the methyl carbon). For this reason, we consider this model also to be relatively improbable.

Conclusions

The C-13 isotope effect of 1.07-1.08 shows that substantial C-S bond fission has occurred at the transition state. The absence or near absence of an α-3D secondary isotope effect shows that substantial C-O bond formation has occurred. The solvent isotope effect k_{CH_3OD}/k_{CH_3OH} of about 2 is large enough to show that very considerable desolvation of methoxide anion has been completed at the transition state, but the effect is short of the expected equilibrium effect of 2.47 for complete desolvation. Therefore solvent reorganization has proceeded to a large, but still quite incomplete, extent.

Models that can be excluded on the basis of these findings include (i) models in which solvent reorganization is the major activation step, with no C-O bond formation or C-S bond fission at the transition state, (ii) models in which C-S bond fission precedes C-O bond formation, in a separate reaction step, with either step rate determining, and (iii) models in which the initial-state solvation of the methoxide anion is maintained intact at the transition state.

Experimental Section

Materials. Methanol (Mallinckrodt analytical reagent grade) and methanol-O-d (Stohler Isotope Chemicals, 99% D) were dried with magnesium and distilled. Basic materials in these solvents, titratable by sulfuric acid, were present at ca. 10^{-4} M. These solvents were stored in sealed glass containers and kept in desiccators over calcium sulfate. The deuterium contents of the deuterated methanol solutions were determined by an NMR method. Sodium methoxide solutions were prepared by dissolution of clean sodium in cold methanol under nitrogen. These stock solutions were standardized with potassium hydrogen phthalate (Mallinckrodt analytical grade, dried at 120 °C). Lithium perchlorate (G. Frederic Smith, anhydrous reagent grade) was dried under vacuum and kept in a desiccator. S-Methyldibenzothiophenium tetrafluoroborate and its isotopic isomers were prepared as described originally by Acheson and Harrison[35] and later by Gray et al.[17] (treatment of CH_3I or its isotopic isomers with dibenzothiophene and silver tetrafluoroborate). Isotopic mixtures of methanol solvents were prepared gravimetrically. Sodium methoxide-lithium perchlorate reaction solutions were prepared by mixing appropriate weights of lithium perchlorate with known volumes of sodium methoxide stock solution in 50-mL volumetric flasks, followed by dilution. Total salt concentration was maintained at 0.100_0 M.

Kinetics. The data acquisition system, consisting of a Cary-118 spectrophotometer interfaced to a microcomputer, has been described elsewhere.[16-18,29] Stock solutions of substrate ($7.5-7.8 \times 10^{-2}$ M) were prepared fresh and kept cold on ice. Cuvettes containing 3.50 mL of the reaction solution were allowed to reach thermal equilibrium in the thermostated cell holder of the Cary-118. The reaction was initiated by injection of 20 μL of the substrate solution into the cuvette, and the increase in absorbance at 322 nm was monitored. First-order rate constants were obtained by a weighted, nonlinear least-squares fit of the data to an exponential function.

Registry No. Methoxide, 3315-60-4; S-methyldibenzothiophenium tetrafluoroborate, 29829-22-9; carbon-13, 14762-74-4; deuterium, 7782-39-0.

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Competition between Modes of Solvolytic Participation in Cyclopent-3-enyl Tosylate

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Abstract: Cyclopent-3-enyl tosylate has been prepared with a stereochemical proton label in order to distinguish the solvolytic pathways of double bond participation (substitution with retention) and solvent displacement (inversion). The product in either case has the same carbon skeleton as starting material. The modes may be distinguished by examination of the single 5-proton resonance in cyclopent-3-enyl-*1,2,2,3,4,(cis-5)*-d_6 tosylate. The reaction was found to proceed with inversion (solvent displacement) in acetic acid and in 70% 1,4-dioxane/water. In formic acid, however, the reaction occurs entirely with retention (double bond participation). The low nucleophilicity and high ionizing power of this solvent promote the retention pathway, previously thought not to occur in this structure. Participation by the double bond in this five-membered ring is slightly stronger than that in the analogous six-membered ring in formolysis.

The most spectacular example of intramolecular participation by double bonds[2] in solvolysis may be the 10^{11} acceleration found in the *anti*-7-norborn-2-enyl system **1**, which produces a bishomocyclopropenyl ion through symmetrical interaction of both

1 2

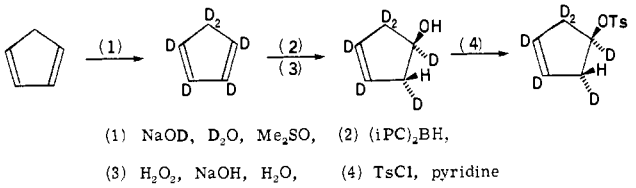
ends of the double bond with the developing positive charge.[3] In contrast, the *exo*-2-norborn-5-enyl system **2** shows a slight rate

(1) This work was supported by the National Science Foundation, Grant CHE80-25601.

(2) Hanack, M.; Schneider, H.-J. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 666-667.

0002-7863/83/1505-1954$01.50/0

Scheme I



(1) NaOD, D_2O, Me_2SO, (2) $(iPC)_2BH$,
(3) H_2O_2, NaOH, H_2O, (4) TsCl, pyridine

deceleration. Nonetheless, participation does occur, though weakly, as has been shown by a number of methods.[4] This substrate (**2**) proceeds to a homoallylic intermediate, in which one end of the double bond interacts with the developing positive charge much more strongly than does the other end. Monocyclic analogous of **1** and **2** provide an interesting comparison (**3** and **4**). The six-membered ring proceeds to an unsymmetrical ion

3 4

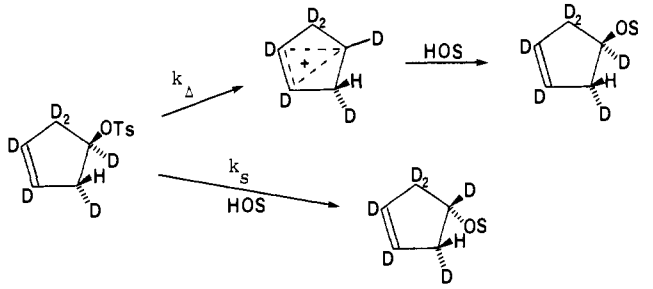
and has been a model for homoallylic participation for many years.[2,5] Like most unsymmetrical systems, **4** in fact exhibits rather weak double bond participation that is extremely solvent dependent.[5] The five-membered ring can proceed to a symmetrical bishomocyclopropenyl ion, but until recently[6] it was thought not to exhibit any amount of participation. Rate retardations and the absence of bicyclic products were considered to be definitive.[7] It was suggested that the monocyclic substrate **3** is nearly planar, whereas the additional bridge in the bicyclic case **1** brings the double bond into a more favorable orientation with respect to the leaving group.

We recently demonstrated that the formolysis of **3** takes place entirely by double bond participation.[6] Whereas the previous investigations used rates and product studies,[7] we used a stereochemical approach. We suggested that differences between our observations[6] and the earlier work[7] may be the result of differences in solvent. We now report a study of the solvolysis of cyclopent-3-enyl tosylate (**3**) in three solvents, with a range of nucleophilicities and ionizing powers. These results demonstrate that the mechanism of solvolysis of **3** can be either double bond participation or solvent participation, the choice being determined by solvent properties.

Results

Stereochemistry was introduced into the achiral system **3** without the use of perturbing substituents through the use of deuterium labeling (Scheme I). All of the protons in cyclopentadiene were removed by exhaustive deuteration. Hydroboration with diisopinocamphenylborane[8] gave the homoallylic alcohol, containing a single proton cis to the hydroxyl. Tosylation then produced the desired compound **3**-d_5-cis(H/OTs). This material provides a handle on the stereochemistry of the pathways leading to homoallylic substitution product. Solvolysis with participation by the double bond would lead via the bishomocyclopropenium ion intermediate to a substitution product with retention (Scheme II) (**3**-d_5-cis(H/OS). Direct solvent participation at the 1-position would lead to a product with inversion (**3**-d_5-trans(H/OS)).

Scheme II



Solvolysis was carried out in formic acid, acetic acid, and 70% 1,4-dioxane water, whose ionizing powers and nucleophilicities (Y, N) respectively are (3.04, −2.35), (−0.61, −2.35), and (~0.0, ~0.0).[9] Thus, the aqueous solvent is highly ionizing and strongly nucleophilic, whereas acetic acid is lower in both properties. Formic acid is highly ionizing (much more so than the aqueous solvent) but poorly nucleophilic. In each case, the solvent was buffered, and the reaction was carried out for seven half-lives. The product alcohol or ester was isolated by gas or liquid chromatography, and the amount of retention or inversion was measured by examination of the ^1H NMR spectrum.

Hydrolysis provided mostly elimination. The substitution product was isolated and analyzed. The resonance of the 5-proton in the deuterated product was compared to that of unlabeled alcohol and to that of starting material (a model for retention). The resonances of the cis and trans 5-protons in the unlabeled material are separated even at 80 MHz. In the starting (retained) alcohol, only the high-field resonance remains. In the product alcohol, only the low-field resonance remains, corresponding to inverted material. We concluded that hydrolysis of cyclopent-3-enyl tosylate occurs with at least 95% inversion.

Acetolysis results were very similar. These could be analyzed at 60 MHz and compared to unlabeled acetate and retained acetate prepared from the starting alcohol. The order of resonances was the same as in the alcohol. The resonance for the 5-proton again indicated that the reaction takes place essentially entirely with inversion (>95%).

Overlap of the 5-protons in the formate required that the product be analyzed at 360 MHz. At this field, there was good separation of the cis and trans 5-proton resonances. The resonance from the solvolysis product corresponded to the high-field peak, as did the retained material obtained by treatment of the alcohol with formyl fluoride.[10] There was no observable material at the position of the trans (inversion) proton resonance. Thus formolysis occurs with at least 95% retention.[11] In each case (OH, OAc, OCHO), the high-field resonance was due to the 5-proton cis to OR. Only in formolysis was the product resonance at the high-field position.

Because double bond participation in cyclopent-3-enyl tosylate is a borderline phenomenon, we thought that it would be interesting to apply the Raber–Harris approach to test for molecularity.[12] This method has proved to be helpful in distinguishing bimolecular (k_s) from unimolecular (k_c or k_Δ) pathways in pseudo-first-order solvolysis reactions. It takes advantage of the fact that aqueous ethanol solutions of variable water content have nearly constant nucleophilicity and variable ionizing power, whereas aqueous trifluoroethanol solutions have large changes in nucleophilicity and a relatively unchanging ionizing power. The differing responses are examined in log–log plots of the rates of a given

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(4) Lambert, J. B.; Holcomb, A. G. *J. Am. Chem. Soc.* **1971**, *93*, 2994–3001. The rate ratio for cyclohex-3-enyl tosylate to cyclohexyl tosylate is 0.70 in 70% aqueous 1,4-dioxane, 0.67 in acetic acid, and 1.2 in formic acid.
(5) Lambert, J. B.; Featherman, S. I. *J. Am. Chem. Soc.* **1977**, *99*, 1542–1546.
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(8) Hess, H. M.; Brown, H. C. *J. Org. Chem.* **1967**, *32*, 4138–4139.
(9) Schadt, F. L.; Schleyer, P. v. R. *Tetrahedron Lett.* 1974, 2335–2338.
(10) Olah, G. A.; Kuhn, S. J. *J. Am. Chem. Soc.* **1960**, *82*, 2380–2382.
(11) Our original communication[6] claimed 99% inversion. Our present figure represents higher conservatism rather than any change in the data.
(12) Raber, D. J.; Neal, W. C., Jr.; Dukes, M. D.; Harris, J. M.; Mount, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 8137–8146. Harris, J. M.; Mount, D. L.; Smith, M. R.; Neal, W. C., Jr.; Dukes, M. D.; Raber, D. J. *Ibid.* **1978**, *100*, 8147–8156.

Table I. Solvolysis Rates at 60 °C

compd	solvent	k, s^{-1}
cyclopent-3-enyl tosylate	EtOH	$(2.98 \pm 0.01) \times 10^{-5}$
	90% EtOH	$(8.10 \pm 0.02) \times 10^{-5}$
	80% EtOH	$(1.80 \pm 0.01) \times 10^{-4}$
	70% EtOH	$(3.36 \pm 0.01) \times 10^{-4}$
	60% EtOH	$(5.73 \pm 0.01) \times 10^{-4}$
	50% EtOH	$(1.00 \pm 0.01) \times 10^{-3}$
	97% TFE[a]	$(1.94 \pm 0.01) \times 10^{-4}$
	80% TFE[a]	$(4.10 \pm 0.02) \times 10^{-4}$
	60% TFE[a]	$(9.26 \pm 0.06) \times 10^{-4}$
cyclohex-3-enyl tosylate	80% EtOH	$(5.94 \pm 0.01) \times 10^{-5}$
	70% EtOH	$(1.14 \pm 0.02) \times 10^{-4}$
	60% EtOH	$(2.22 \pm 0.01) \times 10^{-4}$
	50% EtOH	$(4.29 \pm 0.01) \times 10^{-4}$
	97% TFE[a]	$(9.08 \pm 0.03) \times 10^{-5}$
	80% TFE[a]	$(2.18 \pm 0.01) \times 10^{-4}$
	60% TFE[a]	$(4.59 \pm 0.01) \times 10^{-4}$

[a] Trifluorethanol/H_2O, w/w percent.

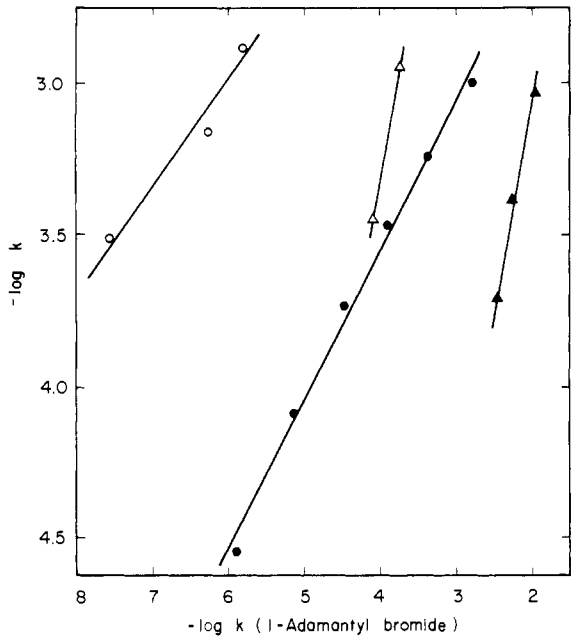

Figure 1. Log–log plot of the rates of solvolysis of 1-adamantyl bromide vs. those of cyclopentyl brosylate[12] at 25 °C (open symbols) or cyclopent-3-enyl tosylate at 61 °C (closed symbols). Circles represent data for aqueous ethanol, triangles for aqueous trifluoroethanol.

substrate vs. that of 1-adamantyl bromide (unimolecular) for aqueous mixtures of both ethanol and trifluoroethanol. In a unimolecular reaction, solvent nucleophilicity is not important and the points for both solvents will fall on the same line, i.e., the data will correlate with the data for 1-adamantyl bromide. In a bimolecular reaction, the solvent mixtures will exhibit different responses, and separate lines will be obtained for the two solvents.

Solvolysis rates for cyclopent-3-enyl tosylate (**3**) were measured in the appropriate solvent mixtures (Table I). For comparison, rates were also measured for the six-membered analogue, cyclohex-3-enyl tosylate (**4**) (Table I). Data for the corresponding saturated systems, cyclopentyl and cyclohexyl, were available from the literature.[12] The Raber–Harris plots are given in Figures 1 and 2 for the five- and six-membered rings. Translations of the points for the saturated systems result from difference in temperature.

Discussion

Hydrolysis and acetolysis of cyclopent-3-enyl tosylate proceed by inversion of configuration to the alcohol and acetate, respectively. These results are in accord with the earlier interpretations by Hanack and by Bartlett[7] that this molecule solvolyzes by a solvent displacement mechanism in water and acetic acid. In contrast, formolysis takes place entirely with retention of configuration. In this solvent, double bond participation occurs to produce the bishomocyclopropenyl cation, which is opened by solvent to give the observed stereochemistry. The low nucleophilicity of this solvent, combined with its high ionizing power, promotes intramolecular stabilization of charge through double bond participation. This system had not previously been examined in this solvent or in one of the highly fluorinated solvents that has been found to enhance internal participation.

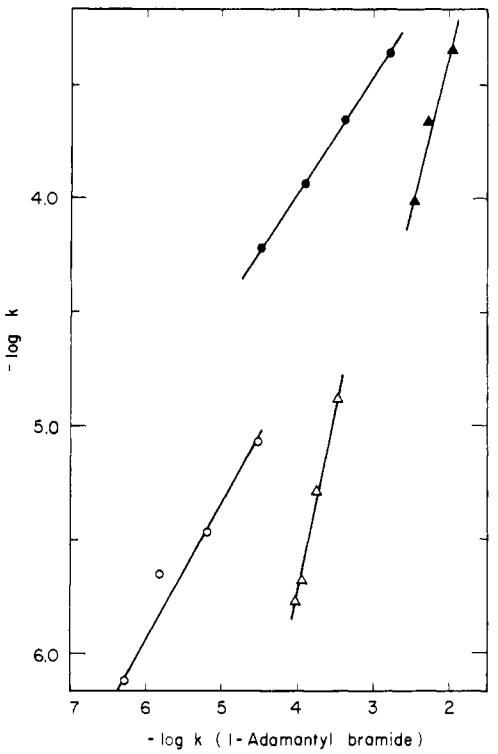

Figure 2. Log–log plot of the rates of solvolysis of 1-adamantyl bromide vs. those of cyclohexyl tosylate[12] at 25 °C (open symbols) or cyclohex-3-enyl tosylate at 61 °C (closed symbols). Circles represent data for aqueous ethanol, triangles for aqueous trifluoroethanol.

These observations with cyclopent-3-enyl tosylate (**3**) are similar to our earlier results with cyclohex-3-enyl tosylate (**4**).[5] In the six-membered ring, we found inversion for water, nearly all inversion for acetic acid, and 60% retention for formic acid. The five-membered ring exhibits a higher proportion of double bond participation in formic acid (>95% vs. 60%), which may be attributed to the more symmetrical nature of bishomocyclopropenyl cation of **3**, compared with the homoallylic cation of **4**.

Even though we now find these two systems to be very similar, the earlier literature viewed them in divergent terms, with the five-membered ring almost a paradigm for a nonparticipating system and the six-membered ring a model for homoallylic participation. Although no earlier results were incorrectly interpreted, generalizations derived therefrom were unwarranted. The situation resulted from lack of a full range of solvents and from overemphasis on kinetic results in the absence of stereochemical results.

Application of the Raber–Harris method to both the five- and the six-membered unsaturated rings produced two distinct lines for the mixed ethanol and trifluoroethanol solvents. The results for the respective unsaturated rings are very similar to those for the saturated rings, which have been demonstrated to occur by solvent displacement even in formic acid.[13,14] The data shown in Figures 1 and 2 for the unsaturated rings were examined by the three suggested statistical criteria,[12] the slope, the intercept, and the correlation coefficient, and were found by each to correspond to a bimolecular mechanism for both ring systems. Raber and Harris, however, point out that this approach is not unam-

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biguous when k_s is mixed with other, unimolecular mechanisms, unless the bimolecular and unimolecular components can be factored apart, as they did for 2-phenyl-1-propyl tosylate. Thus, two interpretations are consistent with the present data. A mixed mechanism for cyclohex-3-enyl and cyclopent-3-enyl tosylates in aqueous trifluoroethanol could give the two-line plots of Figures 1 and 2. Alternatively, the two-line plots might result from a fully bimolecular reaction for both substrates, as the ionizing power of the aqueous trifluoroethanols is much less than that of formic acid ($\Delta Y = 1.2$ for 97% trifluoroethanol[9]). One can conclude from the plots only that a purely unimolecular mechanism is not present. In view of the lower ionizing power of aqueous ethanol and trifluoroethanol compared with that of formic acid, these results are not in contradiction with the stereochemical results. The very small amount of substitution product, compared with elimination, precluded application of the stereochemical approach to 97% trifluoroethanol.

Conclusions

Double bond participation is the predominant form of substitution for the solvolysis of cyclopent-3-enyl tosylate in formic acid, a solvent of very low nucleophilicity and high ionizing power. In solvents with higher nucleophilicity or lower ionizing power, such as acetic acid and water, nucleophilic displacement takes over as the major pathway. These conclusions were reached by examination of the stereochemistry of the substitution reaction through deuterium labeling. They are qualitatively similar to those reached for the six-membered analogue, cyclohex-3-enyl tosylate. In formic acid, double bond participation is slightly stronger for the five-membered ring, possibly reflecting the higher stability of the more symmetrical bishomocyclopropenyl cation formed in this system. Application of the Raber–Harris method for the determination of molecularity in solvolysis reactions in aqueous ethanol and trifluoroethanol led to the conclusion that the reaction takes place in these solvents either by solvent displacement or by competitive first- and second-order processes.

Experimental Section

Proton NMR spectra were taken at 60 MHz on a Perkin-Elmer R20B, at 80 MHz on a Varian CFT-20, and at 360 MHz on a Nicolet NT-360.[15]

Cyclopentadiene-d_6. To 80 mL of D_2O, cooled to 0 °C, was added 8.4 g of Na at a slow enough rate to keep the temperature below 10 °C. After addition was complete, 40 mL of this $NaOD/D_2O$ solution was syringed into a flask containing 36 mL of freshly cracked cyclopentadiene (Aldrich) and 40 mL of Me_2SO at 0 °C. The mixture was stirred vigorously for 1 h. The resulting layers were separated, and the top layer (cyclopentadiene) was syringed into another flask containing 40 mL of the $NaOD/D_2O$ solution and 40 mL of Me_2SO at 0 °C. The mixture was again stirred for 1 h, and the layers were separated. This entire procedure was repeated 3 times for a total of six exchanges, at which time the diene was determined by ^1H NMR spectroscopy to be >99% deuterated. Approximately 24 mL (67%) of cyclopentadiene-d_6 was recovered.

Cyclopent-3-enol-*1,2,2,3,4,(cis-5)*-d_6. To 59.4 mL of dry α-pinene (Aldrich) cooled to 0 °C was added 170 mL of a 1 M BH_3/THF solution (Aldrich) at a slow enough rate to keep the temperature below 5 °C. Stirring was continued at 0 °C for 2 h, and 28 mL of cyclopentadiene-d_6 was added dropwise. The mixture was warmed to room temperature and stirred overnight. Water (6 mL) was slowly added, and evolution of H_2 was observed. Next, 55 mL of a 3 N NaOH solution was added dropwise, and the resulting solution was stirred for 1.5 h. The solution was cooled to 0 °C, and 55 mL of 30% H_2O_2 was added dropwise. Stirring was continued for 3 h. The solution was decanted from the crystalline $B(OH)_3$, the solid was washed with H_2O and diethyl ether, and all the liquids were combined. The solution was saturated with NaCl, and the organic and aqueous layers were separated. The organic layer was evaporated under vacuum to a volume of 100 mL. To this solution was added 60 mL of diethyl ether and 170 mL of 1 M $AgNO_3$. The resulting solution was stirred vigorously for 30 min. The black precipitate was filtered off, and the layers were separated. The organic layer was washed with 2 × 20 mL of 12 M $AgNO_3$, and the aqueous layer was washed with 2 × 60 mL of ether. All aqueous fractions were combined, and excess saturated NaCl solution was added to precipitate the Ag^+ as AgCl. The AgCl was filtered off, and the precipitate was washed with both ether and H_2O. The solution was then extracted with 5 × 60 mL of ether, and the organic layer was dried ($MgSO_4$). Evaporation of the ether left approximately 5 mL of a light yellow liquid. Distillation yielded 3 g (~10%) of a clear, colorless liquid: bp 47–60 °C (20 mmHg); NMR ($CDCl_3$) δ 2.25 (t (J_{HD} = 3 Hz), 1, CH), 3.05 (s, 1, OH).

Cyclopent-3-enyl-*1,2,2,3,4,(cis-5)*-d_6 Tosylate. A solution of 1.26 g (0.015 mol) of cyclopent-3-enyl-d_6 in 25 mL of dry pyridine was cooled to 0 °C in an ice bath and treated with 5.70 g (0.03 mol) of *p*-toluenesulfonyl chloride (Eastman). The mixture was refrigerated for 24 h, after which time long needles of pyridine hydrochloride were observed. The mixture was poured onto 150 g of ice/water and stirred for 15 min. The resulting clear, colorless oil was extracted out with 3 × 50 mL of ether and washed with 3 × 50 mL of saturated $CuSO_4$ to remove the excess pyridine. The ethereal solution was dried (Na_2SO_4) and evaporated under a stream of N_2 to give a yellow oil, which crystallized on cooling (2.82 g, 79%). Recrystallization 3 times from pentane gave a sharply melting solid: mp 53–54 °C; NMR ($CDCl_3$) δ 2.36 (t (J_{HD} = 3 Hz), 1, CH), 2.43 (s, 3, CH_3), 7.32–7.78 (AB q, 4, CH–CH).

Cyclopent-3-enyl-*1,2,2,3,4,(cis-5)*-d_6 Formate. Cyclopent-3-enol-d_6 (2.1 g, 0.025 mol) and 2.5 g (0.025 mol) of triethylamine were dissolved in 50 mL of dry diethyl ether and cooled to 0 °C in an ice bath. Formyl fluoride[10] (2.4 g, 0.05 mol) (freshly distilled) was bubbled into the reaction mixture by warming the liquid slowly with a CCl_4/dry ice slush. The reaction temperature was maintained below 5 °C throughout the addition (about 1 h). The mixture was then stirred for an additional hour at 0 °C. The salt was filtered off, and the ethereal solution was washed with $NaHCO_3$. After the solution was dried over $MgSO_4$ and K_2CO_3, the ether was removed by careful fractional distillation to yield the desired formate: NMR ($CDCl_3$) δ 2.40 (t (J_{HD} = 3 Hz), 1, CH), 8.00 (s, 1, CHO).

Cyclopent-3-enyl-*1,2,2,3,4,(cis-5)*-d_6 Acetate. To 0.25 g (0.0025 mol) of cyclopent-3-enyl-d_6 was added 0.25 g (0.0025 mol, 0.23 mL) of acetic anhydride. After the addition of a small drop of concentrated H_2SO_4, the solution became very hot. The solution was allowed to cool for 10 min and then was neutralized with K_2CO_3. The mixture was diluted with $CDCl_3$, filtered, and dried over $MgSO_4$ and K_2CO_3: NMR ($CDCl_3$) δ 1.88 (s, 3, $COCH_3$), 2.15 (t (J_{HD} = 3 Hz), 1, CH).

Purification of Solvents. Formic Acid. Crude formic acid (Eastman, 97%) was stirred with an excess of boric anhydride for several days under N_2 and distilled through a 10-in., vacuum-jacketed column, packed with glass helixes, bp 100.5–101.0 °C.

Acetic Acid. Glacial acetic acid (400 mL) was refluxed with 1 mL of acetic anhydride for 24 h, after which time 1 g of CrO_3 was added. The dry acetic acid was refluxed for 2 h and distilled under N_2 through a 10-in., vacuum-jacketed column, packed with glass helixes, bp 117–118 °C. Enough acetic anhydride was then added to make the final solution 1% acetic anhydride/acetic acid.

1,4-Dioxane was purified by the method of Fieser.[16] The purified solvent was stored over Na and distilled shortly before use.

Kinetic Methods. Rates in the aqueous solvents were determined conductometrically with an Industrial Instruments Model RC 16B2 conductivity bridge. The conductivity cell (Industrial Instruments) had black Pt electrodes, cell constant 0.42 cm^{-1}, and a volume of approximately 35 mL. In a typical experiment, enough substrate to make a solution approximately 10^{-3} M was added to the cell, which contained 20 mL of solvent. The cell was then stoppered and equilibrated in a constant-temperature bath (Haake Model NB22) for at least 5 min with stirring. Solvolyses were followed by taking 10 or more readings approximately equally spaced in conductance over 2–3 half-lives. An infinity point was taken after 10 half-lives. The raw conductance data were then fitted to a first-order rate equation by means of a least-squares computer program. The precision of the fit to first-order kinetics was satisfactory over at least 3 half-lives in the aqueous ethanol and aqueous trifluoroethanol solvents.

Acetolysis of Cyclopent-3-enyl-d_6 Tosylate. Cyclopent-3-enyl-*1,2,2,3,4,(cis-5)*-d_6 tosylate (0.244 g, 0.001 mol) and potassium acetate (0.018 g, 0.0011 mol) were dissolved in enough acetic acid/1% acetic anhydride to make 10 mL (0.1 M in tosylate). The solution was placed in a glass tube and sealed under N_2. The temperature was held at 70 °C for 72 h by means of a constant-temperature bath. The solution was cooled, washed with brine, and extracted with 5 × 20 mL of diethyl ether. The organic portions were washed with saturated $NaHCO_3$ solution and dried over $MgSO_4$. The ether was removed by careful fractional distillation, and the acetate was purified by preparative VPC.

(15) We are indebted to Dr. Stephen M. Wharry for recording the 360-MHz spectra at the Purdue University Biochemical Magnetic Resonance Laboratory, which is supported by the National Institutes of Health, Division of Research Resources (Grant RR01077).

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Formolysis of Cyclopent-3-enyl-d_6 Tosylate. Cyclopent-3-enyl-*1,2,2,3,4,*(cis-*5*)-d_6 tosylate (0.119 g, 0.005 mol) and sodium formate (0.0371 g, 0.00056 mol) were dissilved in 5 mL of formic acid (solution 0.1 M in tosylate). The solution was placed in a glass tube and sealed under N_2. The temperature was held at 35 °C for 12 h by means of a constant-temperature bath. The solution was cooled, washed with brine, and extracted with 5 × 10 mL of diethyl ether. The organic portions were washed with saturated $NaHCO_3$ solutions and dried ($MgSO_4$). The ether was removed by careful fractional distillation.

Hydrolysis of Cyclopent-3-enyl-d_6 Tosylate. Cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 tosylate (0.244 g, 0.001 mol) and 2,6-lutidine (0.214 g, 0.002 mol) were dissolved in enough 70% 1,4-dioxane/water to make 10 mL (0.1 M in tosylate). The solution was placed in glass tube and sealed under N_2. The temperature was held at 70 °C for 24 h by means of a constant-temperature bath. The reaction mixture was cooled, poured into H_2O, and extracted with diethyl ether. The organic portions were washed with ice-cold 10% HCl, saturated aqueous $NaHCO_3$, and saturated NaCl. The ether was dried (K_2CO_3) and removed by careful distillation through a Vigreux column.

Registry No. Cyclopentadiene, 542-92-7; cyclopentadiene-d_6, 2102-16-1; cyclopent-3-enol-*1,2,2,3,4,*(*cis-5*)-d_6, 84752-75-0; cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 tosylate, 74260-25-6; cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 formate, 74260-26-7; cyclopent-3-enyl-*1,2,2,3,4,*(*cis-5*)-d_6 acetate, 84774-92-5; cyclopentyl brosylate, 4596-40-1; cyclopent-3-enyl tosylate, 36367-85-8; cyclohexyl tosylate, 953-91-3; cyclohex-3-enyl tosylate, 26431-20-9.

Photochemical Reactions of α-Oxo Amides. Norrish Type II Reactions via Zwitterionic Intermediates

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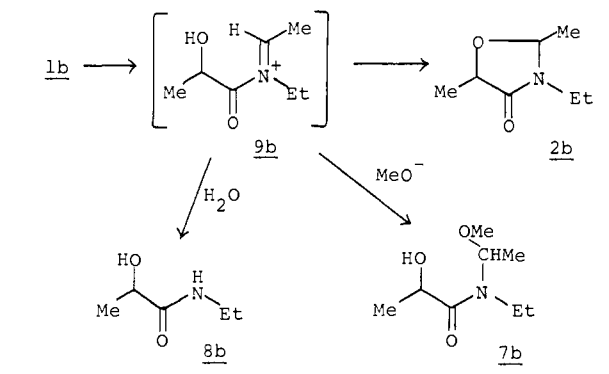
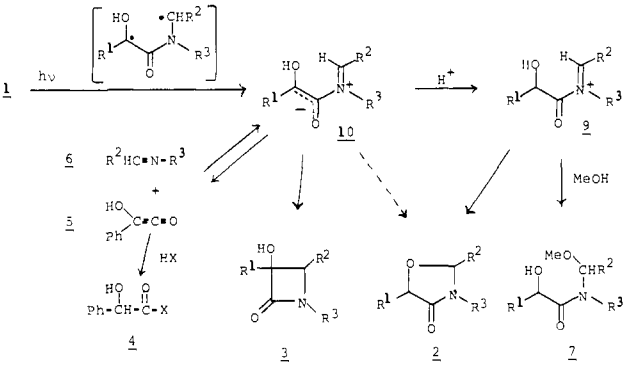
Abstract: The mechanism of the photochemical reactions of α-oxo amides was studied. Establishment of the intermediacy of zwitterions was accomplished by the detection of iminium ions formed by protonation of the zwitterions and by the independent generation of the zwitterions by the reaction of hydroxyphenylketene with imines. The remarkable substituent and solvent effects in the photoreactions were rationalized on the basis of the mechanism.

The photochemistry of α-oxo amides has received much attention because of the synthetic utilities,[1-6] and is of interest also mechanistically since α-dicarbonyl compounds show considerably different photochemical behavior from that of monoketones.[7] Photolysis of N,N-disubstituted α-oxo amides gives three types of products, oxazolidin-4-ones (**2**), β-lactams (**3**), and hydroxyketene-derived products, mandelic acid derivatives (**4**).[1,3a] The formation of these products has been explained in terms of 1,4-diradical intermediates formed by γ-hydrogen abstraction (type II photoprocesses).[1-6] However, the photoreactions show remarkable solvent and substituent effects which are not easily explained by the diradical mechanism.[3a] We have investigated the mechanism of the photoreactions and clarified that the intermediates are zwitterions. Intermediacy of 1,4-diradicals in usual type II reactions is well established.[8] The photochemical reactions of α-oxo amides provide the first example of type II reactions which involve zwitterionic intermediates. The solvent and substituent effects are also discussed in this paper.

Scheme I



Scheme II



Results and Discussions

α-Oxo amides chosen in this mechanistic study are shown in Figure 1. Since photoreactions of some α-oxo amides in aprotic solvents are sensitive to moisture and the reproducibilities of these reactions are not always good, the present study is mainly con-

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