$J_1 = J_2 = 7.5$ Hz, 2 H), 1.83 (br s, 3 H), 2.06 (m, 2 H), 2.61 (t, $J =$ 7.5 Hz, 2 H), 4.89–5.03 (m, 2 H), 5.65–5.83 (m, 1 H), 5.68 (m, 1 H), 5.85 (m, 1 H); mass spectrum *m/e* 138.1072 (M^+, calcd for $C_9H_{14}O$, 138.1044). Characterization data for **12:** ir 3080, 2980, 2940, 1685 (s), 1645, 1630, 1445, 1415, 1375, 1110, 985, 920, 905 cm^{-1}; mass spectrum *m/e* 138.1056 (M^+, calcd for $C_9H_{14}O$, 138.1044).[16]

Methyl *trans*-5-Propyl-2-cyclopenten-1-yl Ketone (13). A solution of 43 mg of the allyl-substituted ketone **14**[4] was hydrogenated (7 ml of hydrogen) at 1 atm in 2 ml of methanol containing a few milligrams of $Pd/BaSO_4$. Usual work-up and separation on column E afforded **13** as the major product: ir 1710 cm^{-1}; NMR δ 0.92 (t, $J = 6$ Hz, 3 H), 1.66 (m, 4 H), 1.68 (m, 1 H), 1.77 (m, 1 H), 2.05 (m, 4 H), 2.52 (m, 1 H), and 5.51 (m, 2 H); mass spectrum *m/e* 152.1201 (M^+, calcd for $C_{10}H_{16}O$, 152.1201).

Acknowledgment. This investigation was supported in part by National Institutes of Health research grant RR-862 from the Division of Research Facilities and Resources and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No.—7, 110-43-0; **8;** 21889-88-3; **8d,** 56960-41-9; **9,** 106-68-3; **10,** 39256-98-9; **10d,** 56960-42-0; **11,** 56960-43-1; **12,** 56960-44-2; **13,** 56960-45-3; **14,** 52358-90-4; **15,** 52502-24-6; **16,** 103-78-6; **17,** 24476-16-2; **18,** 52358-85-7; **19,** 932-66-1; **20,** 7353-76-6; **21,** 110-12-3; **22,** 3240-09-3; **23,** 928-68-7; **24,** 110-93-0; **25,** 109-49-9; **26,** 1187-87-7; **27,** 30079-93-7; **28,** 123-19-3; **29,** 108-94-1; **30,** 583-60-8; **31,** 4694-17-1; **32,** 29843-84-3; **33,** 141-79-7; **34,** 504-20-1; **35,** 10458-14-7; **36,** 17882-43-8; **37,** 23733-70-2; **38,** 57029-74-0; **39,** 111-13-7; **40,** 3664-60-6; **41,** 821-55-6; **42,** 5009-32-5; **43,** 6175-49-1; **44,** 5009-33-6; levulinic acid, 123-76-2; acetyl chloride, 75-36-5; methyl levulinate dimethyl ketal, 52128-61-7; lithium aluminum hydride, 16853-85-3; 4,4-dimethoxy-1-pentanol, 56960-46-4; tosyl chloride, 98-59-9; 4,4-dimethoxy-1-pentyl tosylate, 56960-47-5; lithium aluminum deuteride, 14128-54-2; EtOD; 925-93-9.

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(16) We thank Dr. R. A. Cormier for preparation of **10–12.**

Notes

The α Effect and Ring-Induced Acceleration of Hydrolysis at a Sulfinyl Center. Buffer and Nucleophile Effects in the Hydrolysis of Diphenyl Sulfite

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Although considerable work on the hydroxide ion and hydronium ion catalyzed hydrolyses of diaryl sulfites, including diphenyl sulfite (**1**), has been described,[1] to date there is a dearth of quantitative information on the susceptibility of the sulfinyl centers in these compounds to reaction with nucleophiles in general. Knowledge of the transition-state properties in the reactions of **1** with nucleophiles is fundamental to an understanding of the large enhancement seen in the value of k_{HO^-} (but not k_{H^+}) when the hydrolysis of catechol cyclic sulfite is compared to that of **1**. In addition, the mechanistic aspects of the sulfitase activity of pepsin attend clarification. In connection with the latter, some studies of the reactions of a series of carboxylate ion with **1** have been made but only over a limited p*K* range of catalysts. We now wish to report a study of the reactivity of **1** in water containing 9.1% (v/v) of CH_3CN at 25°C over a wide pH span and for a broad range of buffer species. The observed rate constants, k_{obsd}, for the hydrolysis of **1** catalyzed by the more basic buffers (e.g., carbonate) show contributions from first-order terms in hydroxide ion and the free base form of the buffer, but no catalysis by acidic buffer species. Thus, k_B (the second-order rate constant for attack by the free base form of the buffer) is obtained readily as the slope of a plot of the values of k_{obsd} vs. the concentration of buffer present as the free base. The intercept of this plot is the solvolytic rate constant (k_{solv}) for that pH. Less basic buffers (e.g., formate) show contributions to k_{obsd} not only from k_{solv} and k_B but also from catalysis by the acidic forms of the buffer (k_A). In these cases, the values of k_{solv} were obtained as the intercepts at zero buffer concentration of plots of k_{obsd} vs. total buffer concentration. The slopes of such graphs were replotted at a constant total buffer concentration against the mole fraction of buffer present in the free base state to give k_A and k_B, as illustrated in Figure 1 for formate buffer. Similar plots for more basic species such as carbonate showed k_A negligible compared to k_B. Values of k_A and k_B for the nucleophiles studied, along with additional data from the literature, are collected in Table I.

By plotting the values of k_{solv} calculated at zero buffer concentration vs. pH, the pH profile of Figure 2 was constructed for the hydrolysis of **1**. From a comparison with

Table I
Second-Order Catalytic Rate Constants for Basic and Acidic Buffer Catalysis of the Hydrolysis of 1 at 25° in 9.1% (v/v) CH_3CN Solutions[a]

Base	pK_a	k_A, M^{-1} sec^{-1}	k_B, M^{-1} sec^{-1}	Ref
OH^-	15.7[b]		7.93×10^4	This work
anti-α-Morphilino-acetophenone oxime	11.32[d]		$(1.62 \pm 0.13) \times 10^4$	This work
CO_3^{2-}	10.33[b]		51.7 ± 8.3	This work
Maleate	6.15[c]		9.5×10^{-3}	7
Hydroxylamine	6.0[c]		1.68	7
Acetate	4.77[c]		6.2×10^{-3}	7
Formate	3.77[b]	$(1.26 \pm 0.92) \times 10^{-5}$	$(5.74 \pm 0.15) \times 10^{-4}$	This work
Methoxyacetate	3.50[c]		6.35×10^{-4}	7
Chloroacetate	2.86[c]	3.3×10^{-5}	1.4×10^{-4}	7
H_2O	−1.7[b]		2.3×10^{-8}	This work[e]

[a] $\mu = 0.1$ except for morphilinoacetophenone oxime results where $\mu = 0.09$. [b] Taken from C. Long, Ed., "Biochemist's Handbook", Van Nostrand, Princeton, N.J., 1961. [c] Reference 7. [d] J. H. Smith, personal communication. [e] Computed from apparent k_{H_2O} of 1.3×10^{-6} sec^{-1}.

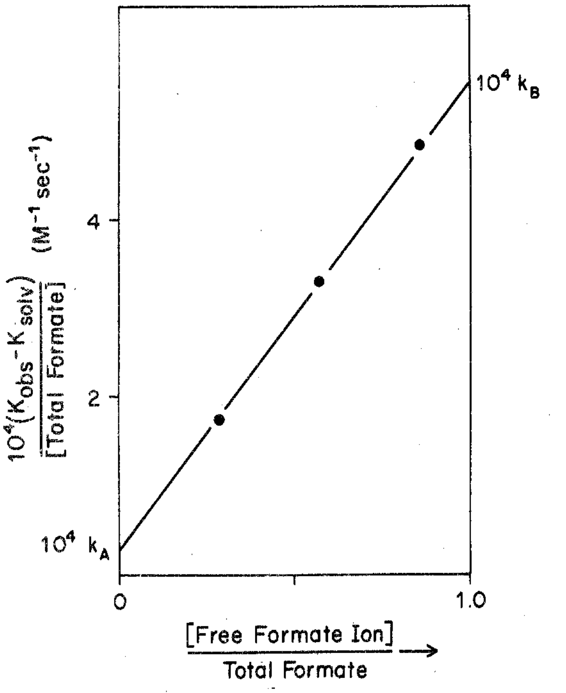

Figure 1. Separation of acidic and base catalytic rate constants in formic buffers for the hydrolysis of 1 at 25°, $\mu = 0.1$, 9.1% (v/v) CH_3CN.

published data[2] it can be calculated that changing the medium from 9.1% CH_3CN (present study) to 1% dioxane[2] increases the magnitude of k_{OH^-} by only 2.8-fold. There is a small plateau between pH 3 and 4 seen in Figure 2 which gives the rate constant for the uncatalyzed attack of water on 1, $k_{H_2O} = 1.31 \times 10^{-6}$ sec^{-1} (Table I). In contrast, significant k_{H_2O} terms were not found for the hydrolysis of the alkyl sulfites ethylene sulfite and dimethyl sulfite,[3] an observation explained by the relative leaving tendencies of alcohols and phenols. From the reported value of k_{H_2O} (2.5×10^{-2} sec^{-1} at 25°) for catechol cyclic sulfite[2,4] the rate acceleration for the uncatalyzed hydrolysis of an aromatic five-membered cyclic sulfite as compared to its open-chain analogue[5,6] is computed as greater than 10^4.

Using the data in Table I, a Bronsted plot has been constructed for the k_B constants in the hydrolysis of 1. As can be seen from Figure 3, a line corresponding to eq 1 has been drawn through the points for all the oxygen nucleophiles, only hydroxylamine and *anti*-α-morpholinoacetophenone oximate ion being omitted from the correlation. The carboxylate ions have been shown to react nucleophilically with 1 in a previous study,[7] and based on the common Bronsted correlation it seems likely, though not certain, that a similar mechanism is involved in the reactions of the other oxygen buffers with 1.[8] Hydroxylamine and *anti*-α-morpholinoacetophenone oximate ion[9] react 86 and 133 times as rapidly as predicted on the basis of the Bronsted dependence. This behavior is typical of α nucleophiles but, as far as we are aware, the α effect has not been shown previously to operate at sulfinyl sulfur. Indeed, relatively little information is available in the literature concerning the α effect at sulfur–oxygen centers and that which does exist is solely for sulfonyl derivatives.[10,11]

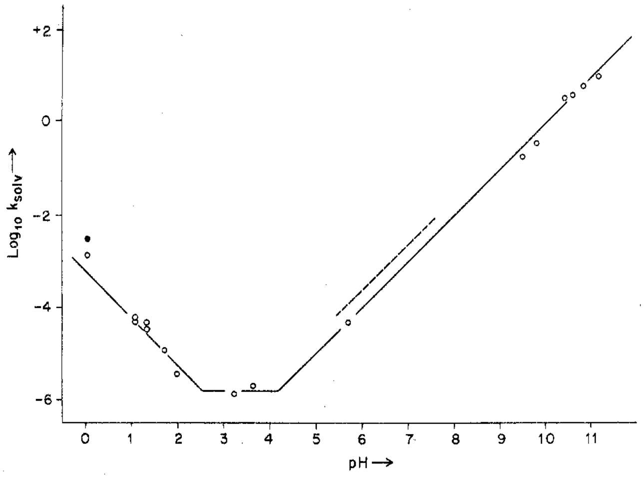

Figure 2. pH dependency of k_{solv} for the hydrolysis of 1 [25°, 9.1% (v/v) CH_3CN, solid line]. For comparison the results of de la Mare et al.[2] are included [25°, 1% (v/v) dioxane, dashed line].

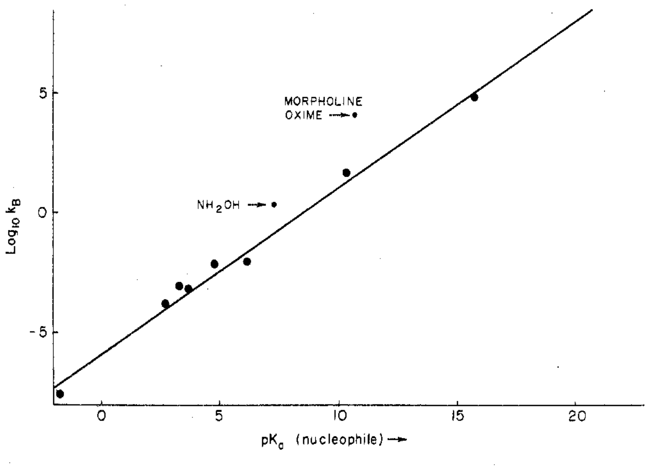

Figure 3. Bronsted plot for nucleophilic catalysis of the hydrolysis of 1. Data from Table I.

In summary, the sulfinyl center is highly electrophilic in diaryl sulfites even without the participation of ring effects. The reactivity of 1 is strongly affected by the nature of the attacking nucleophile and very marked α effects have been observed. Constraint of the sulfite ester group by its incorporation in a five-membered ring causes an even larger acceleration of the uncatalyzed hydrolysis reaction than of the hydroxide ion catalyzed one,[2] as evidenced by a comparison of the reactivity of catechol cyclic sulfite with 1.

Experimental Section

anti-α-Morpholinoacetophenone oxime[9] and freshly distilled diphenyl sulfite[12] were prepared as described in the literature. Morpholine was dried over KOH and distilled through a glass helix packed column (bp 129°). Acetonitrile was fractionally distilled from P_2O_5. All water used was deionized by passage through a Continental mixed-bed ion-exchange column. Water used in stopped-flow experiments was degassed by boiling for several minutes. Inorganic acids and buffer salts were analytical grade.

The reactions of 1 were followed either at 269 nm (pH <10) or at 287 nm (pH >10). The slower reactions were investigated using either Cary 15 or Gilford Model 222 recording spectrophotometers. Fast reactions were followed on a Durrum-Gibson stopped-flow spectrophotometer. Rate data were collected under pseudo-first-order conditions with the concentration of buffer species in large excess over that of the ester. Usually, data were analyzed using plots of log $(A_\infty - A_t)$ vs. time. However, for slower reactions the method of initial rates was adopted.

Acknowledgment. The support of this research by a grant from the National Science Foundation is gratefully acknowledged.

Registry No.—1, 4773-12-0; OH^-, 14280-30-9; CO_3^{2-}, 3812-32-6; H_2O, 7732-18-5; formate, 71-47-6; *anti*-α-morpholinoacetophenone oximate, 57031-42-2.

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(5) While a much higher value of k_{H_2O} (3×10^{-3} sec^{-1}) has been reported previously for 1,[6] the pH of the system studied was not stated, making this measurement questionable, as, even at pH 6, the k_{OH^-} contribution dominates the observed rate (see Figure 2).

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N-tert-Butylsulfonylcarbamates from *tert*-Butylsulfinyl Chloride and *N*-Hydroxycarbamates. Reaction Mechanism and Observation of CIDNP

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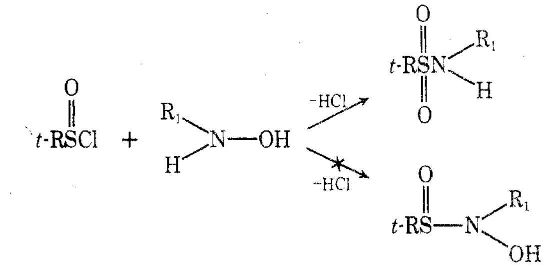
In 1972 Hovius and Engberts[1] reported that the reaction of *tert*-alkylsulfinyl chlorides with hydroxylamines led to formation of *tert*-alkylsulfonamides whereas the expected *N*-hydroxy-*tert*-alkylsulfinamides were not observed (eq 1). Although the mechanism of this oxygen transfer reaction has not been studied, among various possibilities, two mechanisms seem most reasonable: (a) nucleophilic attack of nitrogen on sulfur followed by rearrangement of the *N-tert*-alkylsulfinylhydroxylamine to the observed product via a nitrenium ion intermediate[2] and (b) nucleophilic attack of oxygen on sulfur to give an *O-tert*-alkylsulfinylhydroxylamine followed by rearrangement to the observed product via nitrogen–oxygen bond cleavage,[3] either heterolytically or homolytically.



(1)

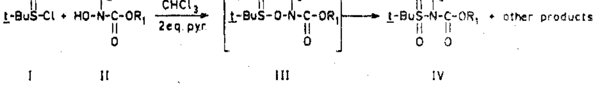
The present investigation was undertaken to determine whether *N*-hydroxycarbamates instead of the hydroxylamines undergo an analogous rearrangement reaction and, if so, whether NMR spectroscopic analysis of the reaction mixture before complete conversion could provide an understanding of the mechanism of the oxygen transfer from nitrogen to sulfur.

Results and Discussion

When *tert*-butylsulfinyl chloride (I) was allowed to react with ethyl *N*-hydroxycarbamate (IIa) in chloroform in the presence of 2 equiv of pyridine,[4] a smooth reaction occurred and ethyl *N-tert*-butylsulfonylcarbamate (IVa) was isolated in a yield of 35% after purification by thin layer chromatography. Similarly, reaction of methyl *N*-hydroxycarbamate (IIb) and methyl *N*-hydroxy-*N*-methylcarbamate (IIc) led to the corresponding *N-tert*-butylsulfonylcarbamates IVb and IVc in yields of 59 and 33%, respectively, as determined by NMR analysis of the final reaction mixtures. Major side products were characterized as methyl carbamate (VIb, 41%, from IIb), methyl *N*-methylcarbamate (VIc, 56%, from IIc), and *tert*-butylsulfonyl chloride (VIII, 23% from IIb and 41% from IIc).

In view of the smooth reactions of the *N*-hydroxycarbamates, an intermediate nitrenium ion, as implied by mechanism a, is highly improbable because of the destabilizing effect of the electron-attracting ester function attached to nitrogen. In addition, the fast reaction of IIc is difficult to reconcile with nucleophilic attack of nitrogen on sulfinyl sulfur.

In order to test for the occurrence of mechanism b (see eq 2) several NMR experiments were conducted in the hope of directly observing intermediate III. Indeed, upon addition of I to a solution of IIb in chloroform-d_1 containing 2 equiv of pyridine, an almost instantaneous shift of the ester *O*-methyl signal from 3.73 to 3.78 ppm was observed together with the appearance of a new *tert*-butyl absorption at 1.29 ppm. This primary product, for which we propose structure IIIb, then slowly rearranges to IVb, the half-


$$\underline{t}\text{-Bu}\overset{\overset{\displaystyle O}{\|}}{S}\text{-Cl} + \text{HO-}\overset{\overset{\displaystyle R_2}{|}}{N}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-OR}_1 \xrightarrow[\text{2eq. pyr}]{\text{CHCl}_3} \left[\underline{t}\text{-Bu}\overset{\overset{\displaystyle O}{\|}}{S}\text{-O-}\overset{\overset{\displaystyle R_2}{|}}{N}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-OR}_1\right] \longrightarrow \underline{t}\text{-Bu}\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}\text{-}\overset{\overset{\displaystyle R_2}{|}}{N}\text{-}\underset{\underset{\displaystyle O}{\|}}{C}\text{-OR}_1 + \text{other products} \quad (2)$$

I II III IV

a: R_1=Et, R_2=H b: R_1=Me, R_2=H c: R_1=Me, R_2=Me