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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(4) Although the solutions used in the present study of the kinetics of the hydrolysis of 1 contained 9.1% CH_3CN while those employed in the investigation of catechol cyclic sulfite[2] did not, the absence of sizable solvent effects on the value of k_{OH^-} found for 1 makes this comparison a reasonable one.
(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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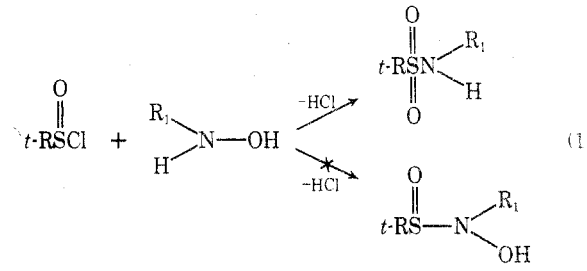
In 1972 Hovius and Engberts[1] reported that the reaction of *tert*-alkylsulfinyl chlorides with hydroxylamines led to formation of *tert*-alkylsulfonamides whereas the expected *N*-hydroxy-*tert*-alkylsulfinamides were not observed (eq 1). Although the mechanism of this oxygen transfer reaction has 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)

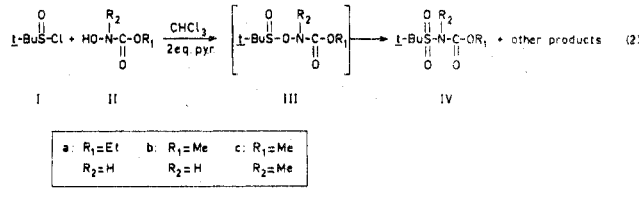
The present investigation was undertaken to determine whether *N*-hydroxycarbamates instead of the hydroxylamines undergo an analogous rearrangement reaction and, if so, whether NMR spectroscopic analysis of the reaction mixture before complete conversion could provide an understanding of the mechanism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



(2)

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-

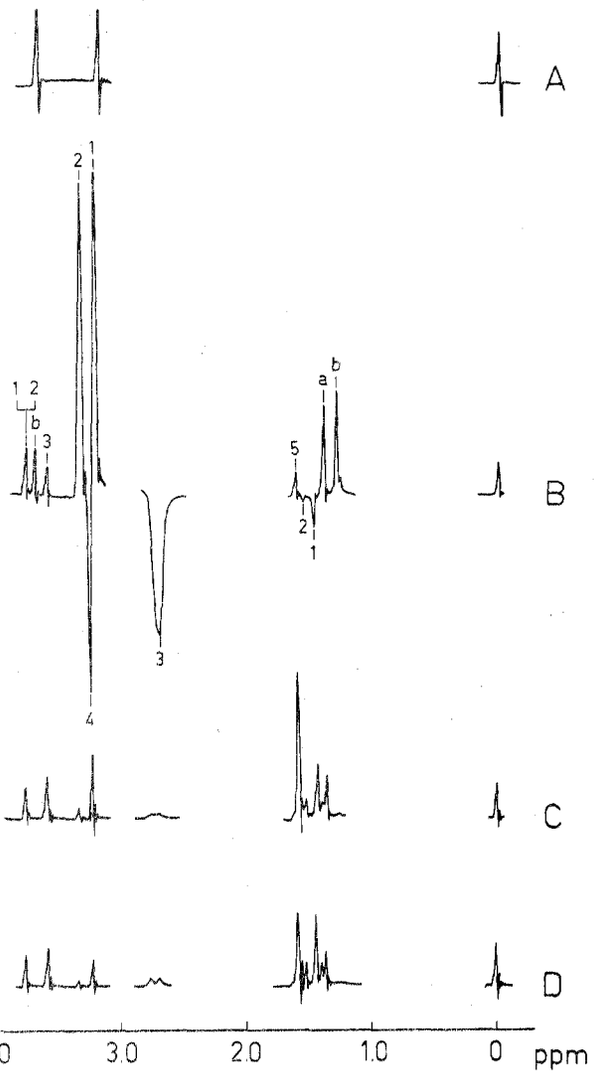


Figure 1. A, IIc in chloroform-d_1; B, CIDNP, 15 sec after addition of I to IIc (signal a is due to excess I, signals b are assigned to IIIc); C, CIDNP, 80 sec after addition of I to IIc; D, spectrum after complete reaction. For the assignment of the transitions 1–5, see Table I.

life of IIIb at probe temperature (ca. 30°) being 75 min. A similar experiment using IIc instead of IIb revealed two important differences. First, the rearrangement of the intermediate IIIc is much faster ($t_{1/2}$ ca. 0.4 min) than that of IIIb. Second, we observe pronounced proton CIDNP (chemically induced dynamic nuclear polarization) effects[5] during conversion of IIIc to the various products in the probe of an NMR spectrometer. We suggest that these results are best accommodated by assuming a thermally induced homolytic cleavage of the nitrogen–oxygen bond of IIIc, resulting in the formation of a radical pair. Apparently, the radical pair from IIIc is sufficiently long lived to allow significant nuclear spin dependent singlet–triplet mixing to occur. Spin selective recombination of this radical pair and diffusion followed by subsequent reaction leads to several products which possess polarized NMR signals (Figure 1). The assignment of transitions 1–5 (Figure 1) to the various reaction products derived from IIc and a description of the CIDNP net effects in the usual nomenclature[5] (A = enhanced absorption, E = emission, N = no polarization) are shown in Table I. The mechanism depicted in Scheme I is proposed to explain the experimental data.[6] The signs (Γ_{ne}) of the CIDNP polarizations are consistent with those predicted by Kaptein's rule[7] for a singlet precursor radical pair. For example, for the NCH_3 peak of

Table I
CIDNP Transitions and Chemical Shifts of Reaction Products Obtained from the Reaction of I with IIc

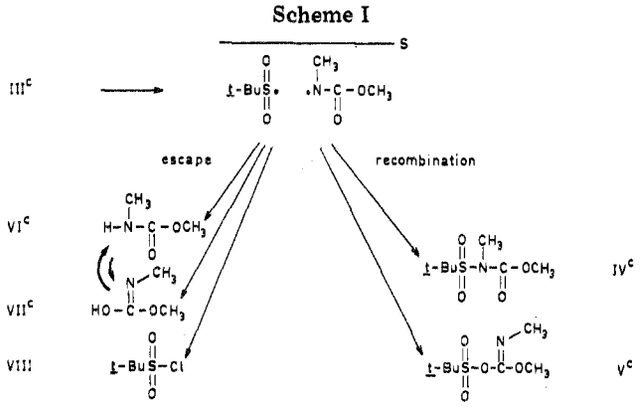
Transition[a]	δ[b] ppm	Proton assignment	CIDNP	Product
1	1.47 (s)	$(CH_3)_3C$	E	IVc
	3.26 (s)	CH_3N	A	IVc
	3.79 (s)	CH_3O	N	IVc
2	1.54 (s)	$(CH_3)_3C$	E	Vc
	3.38 (s)	CH_3N	A	Vc
	3.79 (s)	CH_3O	N	Vc
3	2.74 (s or d)[c]	CH_3N	E	VIc
	3.61 (s)	CH_3O	N	VIc
4	3.32 (s)	CH_3N	E	VII
5	1.60 (s)	$(CH_3)_3C$	A	VIII

[a] See Figure 1. [b] s = singlet, d = doublet. [c] Depending on the concentration of pyridine.

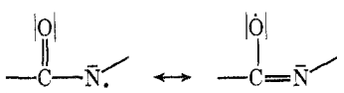
IVc, $\Gamma_{ne} = -+-+ = +$ (A, as observed experimentally) since $g_{\cdot N(CH_3)CO_2CH_3} < g_{t\text{-}BuSO_2\cdot}$[8,9] and $A_{H(NCH_3)}$ is positive. In addition, from the emission found for the *tert*-butyl peak of IVc it may be concluded that $A_{H(t\text{-}BuSO_2)}$ is positive, as expected.

A second recombination product (Vc, yield 11%, Scheme I), which exhibits similar net polarization effects as IVc, is

Scheme I



envisioned to arise as a result of coupling at the carbamoyl oxygen atom. The assignment of structure Vc is based upon NMR and ir spectroscopic data (see Experimental Section) and the formation of this product is reasonable in view of the known resonance interaction in free radicals of the amidyl type.[10]



As expected, the two major escape products, methyl *N*-methylcarbamate (VIc) and *tert*-butylsulfonyl chloride (VIII), showed NMR signals with polarizations opposite to those of the corresponding recombination products.

Finally, it is interesting to note that an emission peak was observed at 3.32 ppm which gradually disappeared until no peak was found after completion of the reaction. We suggest that the emission peak is due to the *N*-methyl group of the imidol VIIc. This product probably originates from escape of the amidyl radical from the initial radical pair followed by hydrogen abstraction by the oxygen atom. Unstable tautomers have been previously detected by CIDNP.[11] Further studies of the behavior of *N*-hydroxy compounds upon treatment with sulfinyl halides are in progress in order to further determine the generality of this type of reaction.

Experimental Section

Elemental analyses were carried out in the Analytical Department of this laboratory under the supervision of Mr. A. F. Hamminga. Melting points were determined using a Reichert melting point apparatus with a microscope attachment. A Varian A-60D spectrometer, using chloroform-d_1 as solvent and Me_4Si as internal standard, was used for the NMR spectra and ir spectra were measured with a Unicam SP 200 instrument.

The starting materials I[12] and IIa–c[13] were prepared according to literature procedures.

Reaction of I with IIa–c. To a stirred solution of 4 mmol of II and 8 mmol of pyridine in 50 ml of chloroform was added 4 mmol of I over a period of 15 min at room temperature. After stirring for an additional 4–6 hr, the chloroform solution was extracted twice with 20 ml of water. The chloroform layer was dried over Na_2SO_4 and the solvent was evaporated. The reaction products were separated by preparative TLC, using silica gel 60 PF and dichloromethane as eluent.

The new compounds IVa–c and Vc are described below; the other reaction products were all identified by comparison (ir and NMR spectral data and, for solids, mixture melting points) with authentic samples. *tert*-Butylsulfonyl chloride (mp 91–93°, lit.[14] 95°) was prepared according to a literature procedure.[14]

Ethyl *N*-*tert*-Butylsulfonylcarbamate (IVa) was obtained in a yield of 35% after crystallization from benzene–petroleum ether (bp 60–80°) as a white solid: mp 84.5–86°; NMR δ 1.27 (t, J = 7 Hz, 2 H, CH_2), 1.47 [s, 9 H, $(CH_3)_3C$], 4.13 ppm (q, J = 7 Hz, ester CH_3); ir (Nujol) 3280 (NH), 1740 (CO), 1325, 1135 (SO_2), 1285 cm^{-1}.

Anal. Calcd for $C_7H_{15}NO_4S$: C, 40.18; H 7.22; N, 6.69; S, 15.32. Found: C, 39.76; H, 7.37; N, 7.17; S, 15.84.

Carbamate IVa was prepared independently in a yield of 35% by using a procedure analogous to that given by Cassidy et al.[15] and starting from 1.3 mmol of *tert*-butanesulfonamide. Ir and NMR spectral data were identical with those given above.

Methyl *N*-*tert*-Butylsulfonylcarbamate (IVb). This carbamate was obtained as described for IVa, yield 59%: white solid: mp 98–101°; NMR δ 1.48 [s, 9 H, $(CH_3)_3C$], 3.79 ppm (s, 3 H, CH_3); ir (CH_2Cl_2) 3280 (NH), 1740 (CO), 1330 and 1130 cm^{-1} (SO_2).

Methyl *N*-Methyl-*N*-*tert*-butylsulfonylcarbamate (IVc). Following the above procedure, this carbamate was isolated as a colorless oil: NMR δ 1.47 [s, 9 H, $(CH_3)_3C$], 3.26 (s, 3 H, NCH_3), 3.79 ppm (s, 3 H, OCH_3); ir (CH_2Cl_2) 1730 (CO), 1345, 1130 (SO_2), 1285, 990, 940, 890 cm^{-1}.

Conversion of IVb into IVc. A freshly prepared solution of diazomethane in ether (ca. 0.2 mmol ml^{-1}) was added at 0° to a solution of 0.092 g (0.47 mmol) of IVb in 10 ml of methanol until the yellow color remained. After stirring for an additional 1 hr at room temperature, the ether and surplus of diazomethane were evaporated to yield IVc in a yield of 90%.

Methyl *N*-methyl-*tert*-butylsulfonyloxycarboximidate (Vc) was a colorless oil, obtained in a yield of 11%: NMR δ 1.54 [s, 9 H, $(CH_3)_3C$], 3.38 (s, 3 H, NCH_3), 3.79 ppm (s, 3 H, OCH_3); ir (CH_2Cl_2) 1720 (C=N), 1345, 1145 (SO_2), 945, 840 cm^{-1}.

CIDNP Experiments. A quartz NMR tube containing 0.030 (0.3 mmol) of IIc and 0.050 g (0.6 mmol) of pyridine in 0.6 ml of chloroform-d_1 was placed in the NMR probe and the spectrum was recorded. Then a slight excess (ca. 0.33 mmol) of I was added and the tube was shaken once. The transitions shown in Figure 1 were obtained by recording the spectrum 15 sec after mixing. After 5 min all signals had obtained normal porportions and no further changes in the NMR spectrum were observed.

Acknowledgment. Stimulating discussions with Dr. R. Kaptein are gratefully acknowledged.

Registry No.—I, 31562-43-3; IIa, 589-41-3; IIb, 584-07-6; IIc, 6092-56-4; IVa, 56908-56-6; IVb, 56908-57-7; IVc, 56908-58-8; Vc, 56908-59-9; VIc, 6642-30-4; VIII, 10490-22-9; diazomethane, 334-88-3.

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Synthesis of $\Delta^{2,2'}$-Bis(1,3-benzodithiolidine) Derivatives and Complex Salts Therefrom with 7,7,8,8-Tetracyanoquinodimethane

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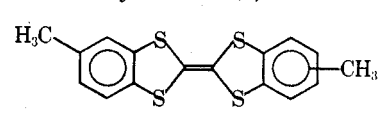
Sharp interest has recently been shown in the design and synthesis of some suitable organic metals[1] and prompts us to report our synthetic results. Several series of the charge-transfer salts including 1,3-dithiolidenes and related selenium analogues have been reported[2–5] and examined for their electrical properties.[2–7] Such charge-transfer salts of appropriate structure can afford organic solids with potential electrical conductivity.[1]

We have found that $\Delta^{2,2'}$-bis(5-methyl-1,3-benzodithiolidene) (1) and 5-methyl-$\Delta^{2,2'}$-bis(1,3-benzodithiolidine) (2)



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