Acknowledgment. This research was supported by a grant (No. AI 04769) from the National Institute of Allergy and Infectious Diseases. We thank Dr. M. F. Grostic, Upjohn Co., for assistance in determining the high-resolution mass spectra.

(10) We have recently shown, for example, that the $C_5H_3^+$ ion is derived at least in part from the $C_7H_5^+$ ion (89 → 63; m^* 44.59; Calcd 44.60).

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Stereochemistry at Trivalent Nitrogen. II. Diastereomers Which Differ in Configuration at Nitrogen[1]

Sir:

Although the isolation of stereoisomers which differ in configuration at trisubstituted nitrogen has remained a goal of organic chemists for many years, attempts to isolate such stereoisomers have for the most part been frustrated by the low barriers to pyramidal inversion which obtain in ammonia and most of its derivatives. The recent isolation of *cis* and *trans* diastereomers of 1-chloro-2-methylaziridine[2,2a] prompts us to disclose the isolation of one of a pair of diastereomers which differ in configuration at nitrogen in an acyclic trivalent nitrogen compound, N-trichloromethanesulfenyl-N-(1-phenylethyl)benzenesulfonamide, ($C_6H_5SO_2N(SCCl_3)CH(CH_3)C_6H_5$, **1**), and to report on its configurational stability.

Reaction of *dl*-N-(1-phenylethyl)benzenesulfonamide with *n*-butyllithium followed by trichloromethanesulfenyl chloride affords **1**[3] in high yield[4] (54%). As the nmr spectrum (Figure 1A) clearly indicates, solutions of **1** at room temperature are composed of mixtures of two diastereomers. Thus two methyl doublets almost equal in intensity (1.05:1.00) are observed at δ 1.27 and 1.78. These two diastereomers are interconverted by epimerization at a chiral center which is configurationally labile as indicated by the nmr spectra observed at elevated temperatures. As the temperature is raised above 55°, the two doublets broaden, coalesce (T_c = 68°), and finally sharpen until one doublet is observed at temperatures at which epimerization is rapid on the nmr time scale. Although, strictly speaking, equal population of sites does not apply, the near equality of the mole fractions of the two diastereomers permits a reasonable approximation to the rate constant at T_c to be obtained by application of the Gutowsky–Holm equation.[5] The rate constant was used in the Eyring equation to calculate the approximate free energy of activation ($\Delta\nu_{\max}$ 31 Hz, T_c +68°, $\Delta G^{\ddagger} \approx$ 17.2 kcal/mol at 68°; solvent bromobenzene).

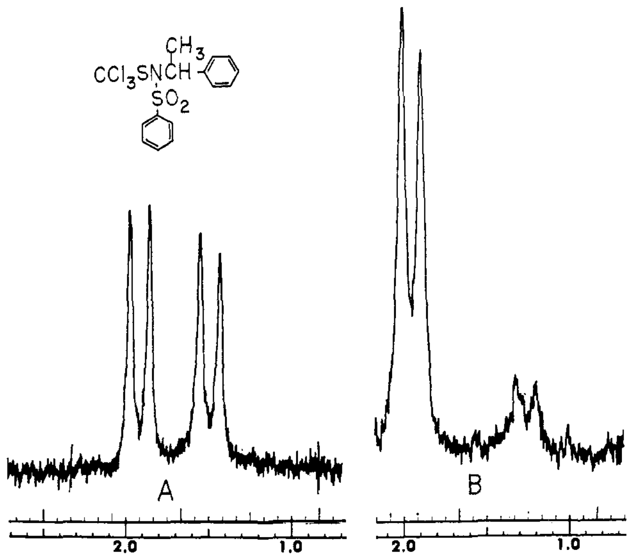

Figure 1. Nmr spectrum of **1**: (A) room temperature, nearly equal mixture of diastereomers; (B) low temperature (−70°), predominantly one diastereomer.

Crystallization of **1** from cyclohexane or methanol proceeds with concomitant second-order asymmetric transformation,[6] resulting in crystals which are diastereomerically homogeneous. This event is manifest not only in the narrow melting range observed, 84–85.5°, but also in the nmr spectra of solutions prepared at low temperatures. When **1** is dissolved in dichloromethane at temperatures below −70°, the nmr spectrum observed (Figure 1B) is not that of a nearly equal mixture of diastereomers but rather indicates the preponderance of a single diastereomer which corresponds to the low-field doublet observed in the room-temperature spectrum.[7] At these temperatures **1** *is configurationally stable at nitrogen on the isolation time scale.* When the temperature is raised to −61° epimerization occurs at a measurable rate and the doublet at higher field begins to grow at the expense of the low-field signal. Although the spectral changes at high temperatures are reversible, those that occur on raising the temperature from −70° to above −60° are irreversible, indicative of a change in the composition of the sample from a nearly pure diastereomer to a nearly equal mixture of diastereomers.

Although the nmr data do not permit a definitive assignment of the rate process which results in epimerization at nitrogen, two alternative rationalizations suggest themselves. The explanation most in agreement with precedent attributes the epimerization to inversion of the nitrogen pyramid. It is now firmly established[2,8]

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(1) Part I: M. Raban, *Chem. Commun.*, 1017 (1967).

(2) S. J. Brois, *J. Am. Chem. Soc.*, **90**, 508 (1968).

(2a) NOTE ADDED IN PROOF. "Invertomers" of 7-chloro-7-azabicyclo[4.1.0]heptane have also been isolated: D. Felix and A. Eschenmoser, *Angew. Chem.*, **80**, 197 (1968).

(3) Satisfactory elemental analyses were obtained for all new compounds. Nmr spectra were measured on a Varian A-60A spectrometer equipped with a variable-temperature accessory. Probe temperatures were obtained by examination of methanol spectra in the usual way.

(4) N-(Trichloromethanesulfenyl)benzenesulfonamide has been prepared in low yield (5%) by reaction of benzenesulfonamide with trichloromethanesulfenyl chloride in dry benzene: A. Senning, *Acta Chem. Scand.*, **21**, 1567 (1967).

(5) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 42.

(7) A small, variable amount of the high-field diastereomer was observed as the result of momentary warming of the sample during its transfer into the spectrometer probe.

(8) (a) S. J. Brois, *J. Am. Chem. Soc.*, **90**, 506 (1968); (b) A. Mannschreck, R. Radeglia, E. Gründemann, and R. Ohme, *Chem. Ber.*, **100**, 1778 (1967); E. Fahr, W. Fischer, A. Jung, L. Sauer, and A. Mannschreck, *Tetrahedron Letters*, 161 (1967); (c) J. E. Anderson and J. M.

that an adjacent heteroatom can decrease the rate of nitrogen inversion in cyclic systems. The increased pyramidal stability has been attributed to increased repulsion between the lone pairs on nitrogen and on the heteroatom in the transition state for inversion and to the electronegativity of the heteroatom.

Alternatively, in acyclic compounds, such as **1**, lone-pair repulsion might also lead to a barrier to rotation around the nitrogen–heteroatom bond like that which obtains in disulfides.[9] This explanation, too, can account for the nmr data presented for **1**, as well as those observed for other sulfenamides,[1] trialkylhydroxylamines,[10] and other acyclic compounds, and has been used to explain the nmr spectral data of N,O-diacyl-N-alkylhydroxylamines[11] as well as substituted hydrazines.[12] The results of further experiments designed to distinguish between these two alternatives will be reported subsequently.

In an effort to determine whether the substantial electronegativity of the trichloromethyl group plays an important role in raising the barrier, the nmr spectra of N-(*p*-toluenesulfenyl)-N-(1-phenylethyl)benzenesulfonamide ($C_6H_5SO_2N(SC_6H_4CH_3)CH(CH_3)C_6H_5$, **2**) have also been examined. In contrast to **1**, the room-temperature spectrum of **2** features a single doublet at δ 1.44 and a single *p*-toluene methyl singlet at δ 2.28. That this is the result of rapid epimerization rather than accidental equivalence or the presence of a single diastereomer is indicated by the low-temperature spectra. As the temperature is lowered the spectrum broadens, and at $-60°$ the spectrum features two doublets at δ 1.22 and 1.57 and two *p*-tolyl methyl singlets at δ 2.23 and 2.39, in both cases of nearly equal intensity. The free energy of activation at the coalescence temperature was calculated using the *p*-toluene signals ($\Delta\nu_{\max}$ 9.4 Hz, T_c $-38°$, $\Delta G \approx 12.3$ kcal/mol; solvent, deuteriochloroform). The large differences in the free energies of activation for the epimerization of **1** and **2** support the suggestion[1] that the trichloromethyl group plays an important role in raising the barrier and serves to bring into clearer perspective the observations that N,N-dimethyltrichloromethanesulfinamides exhibit nonequivalence at low temperatures while other sulfinamides do not.[13,14]

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Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967); (d) J. Lee and K. G. Orrell, *Trans. Faraday Soc.*, **61**, 2342 (1965).

(9) O. Foss in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Ltd., London, 1961, p 75.

(10) (a) D. L. Griffith and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 4089 (1965); (b) R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. McCreath, *J. Chem. Soc.*, 7203 (1965).

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The Role of Chromium(IV) in Oxidations by Chromic Acid. The Oxidative Cleavage of Cyclobutanol

Sir:

Two-thirds of the products formed in a chromic acid oxidation[1] originate not from a direct action of hexavalent chromium but from reactions with tetra- and/or pentavalent chromium compounds.[2] Scheme I

Scheme I

$$\begin{aligned}
\mathrm{Cr(VI)} + \mathrm{S} &\longrightarrow \mathrm{Cr(IV)} + \mathrm{P}_6\\
\mathrm{Cr(IV)} + \mathrm{Cr(VI)} &\longrightarrow 2\mathrm{Cr(V)}\\
2\mathrm{Cr(V)} + 2\mathrm{S} &\longrightarrow 2\mathrm{Cr(III)} + 2\mathrm{P}_5
\end{aligned}$$

represents the simplest and by far more popular reaction mechanism which can be written.

According to this mechanism the substrate can be oxidized in principle to two different products.[3] This mechanism is characterized by the absence of any reaction between chromium(IV) and the organic substrate, implying that such a reaction must be slow compared with the rapid reaction between chromium(IV) and chromium(VI). The mechanism further requires chromium(V) to be an effective oxidant for organic substrates.

A mechanism involving both chromium(IV) and chromium(V) oxidation of the organic compound has been considered by Westheimer[2] (Scheme II), where

Scheme II

$$\begin{aligned}
\mathrm{Cr(VI)} + \mathrm{S} &\longrightarrow \mathrm{Cr(IV)} + \mathrm{P}_6\\
\mathrm{Cr(IV)} + \mathrm{S} &\longrightarrow \mathrm{R}\cdot + \mathrm{Cr(III)}\\
\mathrm{Cr(VI)} + \mathrm{R}\cdot &\longrightarrow \mathrm{Cr(V)} + \mathrm{P}_4\\
\mathrm{Cr(V)} + \mathrm{S} &\longrightarrow \mathrm{Cr(III)} + \mathrm{P}_5
\end{aligned}$$

$\mathrm{R}\cdot$ is an intermediate free radical and P_6, P_5, and P_4 the products originating from reactions of the substrate S with a hexa-, penta-, and tetravalent chromium species, respectively.

Several mechanisms involving only chromium(VI) and chromium(IV) oxidation of the substrate can also be written. One example postulating a disproportionation of chromium(V) is given in Scheme III.

Scheme III

$$\begin{aligned}
\mathrm{Cr(VI)} + \mathrm{S} &\longrightarrow \mathrm{Cr(IV)} + \mathrm{P}_6\\
2\mathrm{Cr(IV)} + 2\mathrm{S} &\longrightarrow 2\mathrm{Cr(III)} + 2\mathrm{R}\cdot\\
2\mathrm{Cr(VI)} + 2\mathrm{R}\cdot &\longrightarrow 2\mathrm{Cr(V)} + 2\mathrm{P}_4\\
2\mathrm{Cr(V)} &\longrightarrow \mathrm{Cr(IV)} + \mathrm{Cr(VI)}
\end{aligned}$$

The question of chromium(IV) reactivity, formulated almost 20 years ago,[2] thus still remains crucial to any further exploration of chromic acid oxidations. In this communication we wish to present evidence for a rapid reaction between chromium(IV) and an organic substrate, cyclobutanol, thus ruling mechanism I out at least for this particular compound.

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[1] For recent excellent reviews of chromic acid oxidations see: K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press Inc., New York, N. Y., 1965; R. Stewart, "Oxidation Mechanisms: Application to Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1964.

[2] W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949).

[3] The formation of chromium(V) and its accumulation in the reaction mixture to a measurable concentration has recently been demonstrated by Wiberg.[4]

[4] K. B. Wiberg and H. Schäfer, *J. Am. Chem. Soc.*, **89**, 455 (1967).