glycine, which displays resonances at 88.0 and 90.15 ppm. On the basis of these observations, the major resonance at 84.5 ppm in unfolded hemoglobins is assigned to glycyl residues, whose conformations and modes of solvation have been randomized.

The effect of primary structure on the ^{15}N chemical shifts of polypeptide residues is a subject of current controversy. Nearest neighbor residue effects on ^{15}N chemical shifts have been reported for some glycyl peptides[10e] and not for others.[16] the side-chain groups of nearest neighbor residues are probably too distant to alter significantly, via through-bond electronic effects, the degree of polarization of the peptide bond or charge density on nitrogen. The reported nearest neighbor effects on the ^{15}N chemical shifts are most likely due to conformation and solvation effects which would be averaged out in a true random coil.

We conclude that the ^{15}N resonances in denatured hemoglobin that do not have glycyl random coil chemical shifts represent glycyl residues, whose conformations or hydrogen bonding modes have not been completely averaged in the unfolded polypeptide. These residues could be part of residual structures that may constitute nucleation sites for protein folding.

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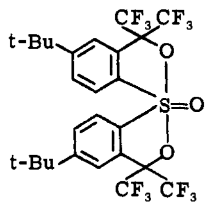
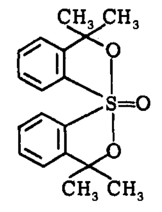
An Alkylaryldialkoxysulfurane Oxide with Labile α Protons. A New Kind of Pentacoordinated Sulfur Ylide[1]

Sir:

Although a number of sulfurane oxides, including **1** and **2**, have been prepared,[2] none of them contains hydrogens α to sulfur. Compound **1** was found to be inert toward aqueous base or acid.[2i,j] In contrast, **2** rapidly fragments to give a sulfone enol upon addition of acid.[21]

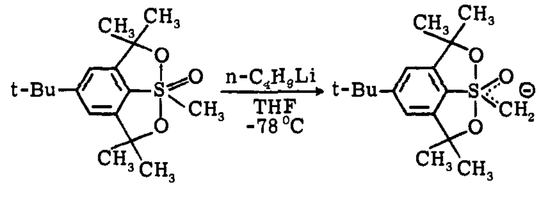


1



2

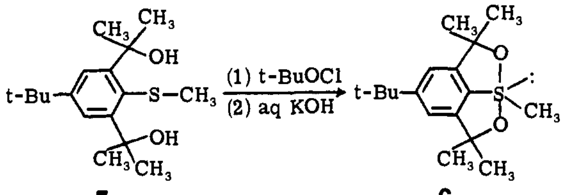
We now report the synthesis of the first alkylaryldialkoxysulfurane oxide (**3**) and evidence for a remarkable lability of its α protons via a pentacoordinated sulfur ylide (**4**) formed by loss of a methyl proton to base.



3 **4**

The target molecule **3**,[3] mp 195-197 °C, was prepared in 57% yield from diol **5**[4] using phase-transfer oxidation,[5] as shown in Scheme I, in the final step. Sulfurane **6** is a stable white crystalline solid, mp 155-156 °C.[6] Slow deuterium exchange of the *S*-methyl protons was observed by NMR when a sample of **6** was dissolved in 0.3 mL of pyridine-d_5 containing 4 drops of 20% NaOD-D_2O.[7]

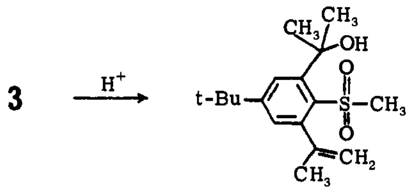
Scheme I



5 **6**

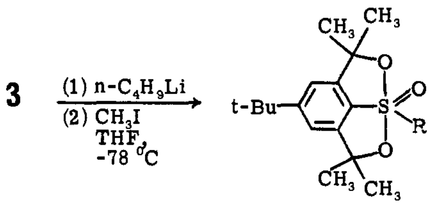
$$\mathbf{6} \xrightarrow[\substack{(\text{n-C}_4\text{H}_9)_4\text{NBr} \\ \text{C}_6\text{H}_6/\text{H}_2\text{O}\ (1:1)}]{\text{KMnO}_4} \mathbf{3}$$

As expected,[21] sulfurane oxide **3** is acid sensitive, quickly giving sulfone enol **7**[8] (mp 172-173 °C) in $CHCl_3$ containing a trace of HCl. Compound **3**, unlike **2**, is stable in pyridine solution for at least 3 months without any change. Deuterium exchange of the methyl protons is complete within minutes at room temperature, even in the absence of base, when excess D_2O is added to an acetone-d_6 solution of sulfurane oxide **3**. In pyridine-d_5 solution with D_2O, methyl proton exchange is complete within seconds for **3** under conditions which show negligible exchange of the methanesulfonyl protons of **7**.



7

When 1 equiv of *n*-butyllithium is added to a THF solution of **3** at −78 °C, a pale yellowish solution of **4** is obtained. Sulfur



8a, R = CH_2CH_3
b, R = $CH(CH_3)_2$

ylide **4** is trapped by the addition of a large excess of CH_3I to the solution to give the monoalkylated product **8a**, mp 151–152 °C.[9] A mixture of **8a** and **8b**[10] was observed by NMR when a slight excess of CH_3I was added under similar conditions. These findings clearly indicate **4** to be an intermediate in these methylation reactions.

Further work on the structure of **4** and its reactions with other electrophiles is underway in our laboratory.

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(3) Anal. ($C_{17}H_{26}O_3S$) C, H, S. ^1H NMR ($CDCl_3$–pyridine-d_5): δ 7.36 (s, 2, ArH), 3.68 (s, 3, SCH_3), 1.58 (s, 6, $OCCH_3$), 1.54 (s, 6, $OCCH_3$), 1.42 (s, 9, t-C_4H_9). IR ($CHCl_3$): 1182 cm^{-1} (s, S=O stretch).
(4) Diol **5** was prepared from the corresponding diacid by successive treatment with thionyl chloride, ethanol and pyridine, and methylmagnesium bromide in ether. The diacid was synthesized from 2,6-dimethyl-4-*tert*-butylbromobenzene as follows: Dimethylbromobenzene was oxidized to the dicarboxylic acid with $KMnO_4$, which in turn was treated with sodium hydrosulfide to convert the bromo substituent to thiol. The diacid thiophenol was methylated at sulfur with dimethyl sulfate in aqueous NaOH.
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(6) Anal. ($C_{17}H_{26}O_2S$) C, H, S. ^1H NMR ($CDCl_3$, 220 MHz): δ 7.25 (s, 2, ArH), 3.33 (s, 3, SCH_3), 1.51 (s, 6, $OCCH_3$), 1.49 (s, 6, $OCCH_3$), 1.41 (s, 9, t-C_4H_9).
(7) All exchange experiments observed by NMR were followed by observing the disappearance of the *S*-methyl proton peak. No other changes in the spectra were noted.
(8) Anal. ($C_{17}H_{26}O_3S$) C, H, S. ^1H NMR ($CDCl_3$): δ 7.30 and 7.04 (AB pattern, 2, J_{AB} = 1.7 Hz, ArH), 5.37 (br s, 1, OH), 5.04 (br m, 1, olefinic CH), 4.65 (br m, 1, olefinic CH), 3.41 (s, 3, SO_2CH_3), 2.23 (br s, 3, CH_3 at olefinic carbon), 1.71 (s, 6, $OCCH_3$), 1.30 (s, 9, t-C_4H_9).
(9) Anal. ($C_{18}H_{28}O_3S$) C, H, S. ^1H NMR ($CDCl_3$–pyridine-d_5, 220 MHz): δ 7.35 (s, 2, ArH), 3.89 (q, 2, J = 7 Hz, $SC\mathbf{H}_2CH_3$), 1.57 (s, 12, $OCCH_3$), 1.41 (s, 9, t-C_4H_9), 1.31 (t, 3, J = 7 Hz, $SCH_2C\mathbf{H}_3$). IR ($CHCl_3$): 1176 cm^{-1} (s, S=O stretch).
(10) Compound **8b** was observed by ^1H NMR but not isolated.

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Frequency Dependence of Laser-Initiated Reaction Rates of CF_2ClCF_2Cl

Sir:

In an earlier communication,[1] we reported on a large difference in the reaction rates of CF_2ClCF_2Cl induced by continuous (CW) laser radiation for two frequencies (921 and 1051 cm^{-1}) corresponding to the centers of different absorption bands of the compound. Since the two absorption peaks have nearly the same strength, with the slightly stronger 1051-cm^{-1} band actually giving the smaller reaction rate, the implication drawn was that significant compartmentalization of energy in vibrational modes was taking place, despite V-V transfer.

We wish to correct this interpretation as a result of further studies of the compound. In the earlier work, the optical absorptions used for band comparison were obtained with a standard spectrophotometer, where the incident intensity is low and the sample is at room temperature. Under laser radiation, the conditions are quite different, and band profiles are strongly altered. We have now measured reaction rates and optical absorptions under the same conditions as rate measurements for a *series* of frequencies covering the 921- and 1051-cm^{-1} bands of CF_2ClCF_2Cl.

The results show that the basis of comparison used in our earlier work is not the proper one. Reaction rates maximize at frequencies considerably below the absorption peaks of 921 and 1051 cm^{-1}, an effect termed "red shift". If we compare *maximal* rates for the two bands, they differ by only a factor of three, indicating little, if any, mode energy compartmentalization. Moreover, the 1051-cm^{-1} band is now the one with the higher maximal rate.

However, there *is* strong evidence that the reaction is vibrationally enhanced, i.e., nonthermal. This comes from a comparison of reaction rate and laser-induced optical absorption as a function of frequency, with corroborating evidence from experiments using a "temperature probe" gas.

All measurements were made on 200 Torr of CF_2ClCF_2Cl in a glass cell with KCl windows. The cell is 9.6 cm between windows along the laser path and has an inner diameter of 2.2 cm. There is also a cross arm 4.9 cm long for infrared diagnostics during laser irradiation. The laser beam for all measurements had a diameter of 0.1 cm, which was essentially constant over cell path, and an incident power of 4 W that was virtually all absorbed within the cell. Optical absorptions were measured in a shorter cell over a 1.3-cm path, providing ~30% transmission. In the latter case, a comparison of the diameters of incident and transmitted beams showed little evidence of self-focussing effects.[2] Reaction rates of CF_2ClCF_2Cl were measured by monitoring the growth of absorption of the 1331-cm^{-1} band of the product C_2F_4, which appears to be a primary product in all our experiments to date. Maximum rates did not exceed ~10^{-1} Torr/s (measured over cell volume). Only initial rates are reported, corresponding to small percentage product concentrations.

As shown by the curves R in Figure 1, the reaction rate of CF_2ClCF_2Cl maximizes at frequencies ~30 cm^{-1} *below* ground-state absorption peaks. This "red shift" effect has been observed[3] in the laser-driven reaction of BCl_3 with $B(CH_3)_3$, where a shift of 15 cm^{-1} was noted, and has been ascribed to vibrational anharmonicity, with laser excitation taking place between states that are considerably above ground vibrational state. The maximum rate associated with the 1051-cm^{-1} band is approximately three times as large as that of the 921-cm^{-1} band. This factor is quite different from that obtained by comparing rates at the band-center frequencies, as done in our earlier report.[4]

The standard absorption band profiles are shown by the dashed curves α_0 in Figure 1. Laser-induced absorption is indicated by the curves α, measured for the same conditions as reaction rates, namely, a 4-W beam incident on 200 Torr of CF_2ClCF_2Cl. Both α and α_0 are given in the same normalized units (cm^{-1} $Torr^{-1}$) for comparison, but the laser-induced α is actually an average over the path length, since it is intensity dependent and, to a lesser degree, pressure dependent. Our