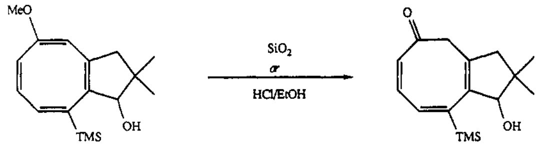
silica gel to ketone **14**, a transformation that is also accomplished in ethanolic HCl. The photoproduct derived from **7** undergoes elimination on concentration and warming, giving the interesting furan derivative **12** (UV $\lambda_{max}$ 232, log $\epsilon$ 2.98; $\lambda_{max}$ 276, log $\epsilon$ 2.34). Optically active products are also easily obtained. Alpine-borane reduction[9] of **1d** provides **2d** in 86% yield ($\alpha^{20}_{D}$ -22.3°, $c$ 0.60, hexane), and photocyclization gives **3d** ($\alpha^{20}_{D}$ -170.3°, $c$ 0.40, hexane). It should also be emphasized that seemingly trivial extensions of Morrison's work fail. For example, an attempt to prepare the asteriscane skeleton[10] by using an analogue of **9** ($Me_3Si$ replaced by $CH_2OSiR_3$ or $CO_2Me$) provides no cyclooctatetraene product.



10 14

While silyl substitution is known to lower the ionization potential of acetylene,[11] the effect is not great enough to satisfy the mnemonic mentioned above, so the 1,2-photoaddition is predicted. In order to compare these results to the intermolecular reactions where energy transfer from the aromatic to the electron-poor acetylene is observed, the fluorescence lifetime of **2d** was measured. It is 4 ns, compared to 37 ns for toluene. This lifetime is consistent with that obtained from the quenching data above. To provide an alternate, nonaromatic trap for any excited acetylene, the allyl ether of **2d** was prepared. On irradiation, it provides only the allyl ether of **3d**. This suggests that if energy transfer occurs, no free excited acetylene is produced. These results challenge current theories of aromatic photoaddition, since ortho additions with $S_1$ benzene are thought to be disfavored. The intramolecular arene/alkynylsilane photoaddition has obvious potential in synthesis of bicyclo[6.3.0]undecane natural products, an area of considerable recent interest.[12] The transformations available to vinylsilanes should also make these photoproducts versatile intermediates in synthesis.[13]

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**Supplementary Material Available:** Short experimental descriptions and spectra for new compounds (2 pages). Ordering information is given on any current masthead page.

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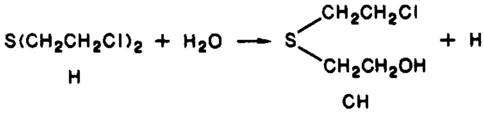
## Direct NMR Measurements of Sulfonium Chlorides Produced from the Hydrolyses of 2-Chloroethyl Sulfides

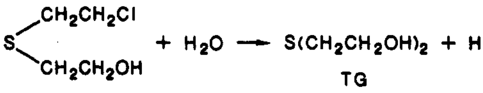
*Summary:* Sulfonium chlorides have been directly identified for the first time with NMR as additional products in the hydrolysis of 2-chloroethyl sulfides.

*Sir:* In our previous kinetic studies[1,2] on the hydrolyses of 2-chloroethyl sulfide derivatives ($10^{-4}$ to $10^{-3}$ M) we occasionally measured lower HCl concentrations in the final reaction mixtures than predicted from stoichiometry, particularly when insufficient organic solvent was used to dissolve the sulfide before mixing with water. (These results were obviously discarded for rate coefficient determinations.) The same problem was also reported by Blandamer and his co-workers during the hydrolysis of $10^{-3}$ M 2-chloroethyl methyl sulfide (CEMS).[3] These authors noted that the proton concentration was lower than the chloride ion concentration in the final reaction mixture, but offered no explanation.

We suspected that this might be caused by the formation of dimeric sulfonium chlorides and that the 2-hydroxyethyl sulfides and HCl (as shown in eq 1 and 2 for



$$\underset{\text{H}}{S(CH_2CH_2Cl)_2} + H_2O \longrightarrow \underset{\text{CH}}{S\begin{matrix} CH_2CH_2Cl \\ CH_2CH_2OH \end{matrix}} + HCl \quad (1)$$



$$S\begin{matrix} CH_2CH_2Cl \\ CH_2CH_2OH \end{matrix} + H_2O \longrightarrow \underset{\text{TG}}{S(CH_2CH_2OH)_2} + HCl \quad (2)$$

2,2′-dichlorodiethyl sulfide (H)) were not the only hydrolysis products. However, according to Bergman and his co-workers,[4] these salts should have been negligible in solutions of less than $10^{-3}$ M sulfide. The authors, though, could only identify and measure these salts indirectly. We have attempted to use NMR to detect the presence of these salts in both the H-water and 2-chloroethyl ethyl sulfide (CEES)-water systems and to follow their formation as a function of time and initial concentration with CEES, since only one sulfonium chloride is expected to form. A Varian XL-200 Superconducting FT-NMR system was used for $^{1}H$ analyses at 200 MHz and for $^{13}C$ at 50 MHz. The $^{1}H$ spectra were obtained by using a $D_2O$ lock and referenced to internal TSP (sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$), while the $^{13}C$ spectra were referenced to external TSP in $D_2O$. All samples were

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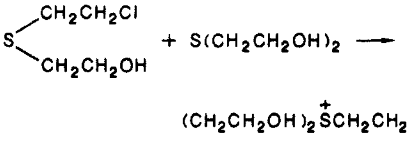
made of distilled reagents, stored, and analyzed at room temperatures. (***WARNING***: 2-Chloroethyl sulfides are potent vesicants and must be handled in a closed system or in a hood with minimum velocity of 100 ft/min). Spectral identifications and peak assignments of the sulfonium cations were based on published data,[5] COSY, and heteronuclear correlated two-dimensional NMR experiments.

Both the H-2TG and the CH-TG salts shown in eq 3 and 4 were identified in the H-water mixtures. The EHT

$$S(CH_2CH_2Cl)_2 + 2S(CH_2CH_2OH)_2 \longrightarrow \underset{\text{H-2TG}}{S[CH_2CH_2\overset{+}{S}(CH_2CH_2OH)_2]_2} + 2Cl^- \quad (3)$$



$$S(CH_2CH_2Cl)(CH_2CH_2OH) + S(CH_2CH_2OH)_2 \longrightarrow \underset{\text{CH-TG}}{(CH_2CH_2OH)_2\overset{+}{S}CH_2CH_2SCH_2CH_2OH} + Cl^- \quad (4)$$

sulfonium chloride shown in eq 5 and 2-hydroxyethyl ethyl sulfide (HEES) were the only compounds found by $^{13}C$ NMR immediately after the CEES–water samples (ranging from 2% to 50% by volume) became one phase. The other possible sulfonium cation, $CH_3CH_2\overset{+}{S}(CH_2CH_2Cl)$-$CH_2CH_2SCH_2CH_3$ (ECT) was not detected in any of the samples. Presumably CEES was converted to HEES and EHT in the aqueous phase as soon as it was dissolved, and chemical reactions at the interface were the driving force for dissolution. In the 2% mixture, about 83 mol % of EHT and 17 mol % of HEES were found after the solution became one phase, but the EHT subsequently hydrolyzed to form HEES and HCl (eq 6) with a pseudo-first-order

$$\underset{\text{CEES}}{CH_3CH_2SCH_2CH_2Cl} + \underset{\text{HEES}}{CH_3CH_2SCH_2CH_2OH} \rightarrow \underset{\text{EHT}}{CH_3CH_2\overset{+}{S}(CH_2CH_2OH)(CH_2CH_2SCH_2CH_3)} + Cl^- \quad (5)$$

$$EHT + H_2O \rightleftharpoons 2CH_3CH_2SCH_2CH_2OH + H^+ \quad (6)$$

rate coefficient[6] of about $6 \times 10^{-7}\ s^{-1}$. Approximately 12 mol % of EHT was still present after 120 days. The hydrolysis rate apparently depended on the HCl contents in water, since 78 mol % of EHT was still present in the 50% sample after more than 2 years. Equation 6 is reversible since an aqueous mixture of 4 M HCl and 3 M HEES reacted to form 93 mol % of EHT sulfonium salt and 7 mol % of HEES, according to $^{13}C$ NMR analysis. NMR measured higher concentrations of EHT in samples of the same concentration of CEES which initially contained excess HEES. Although NMR is limited in detecting concentrations less than 1 mol %, conductivity measurements showed that the $H^+$ production from $2 \times 10^{-4}$ M CEES was also lower in solutions of $6 \times 10^{-4}$ M HEES than in pure water. Therefore, contrary to earlier observations, we believe that these sulfonium chlorides are significant initial products in dilute solutions and stable final products in concentrated aqueous solutions of 2-chloroethyl sulfides. We are currently attempting to isolate these sulfonium chlorides for further study.

The following are the NMR shifts of the salts identified in the reaction mixtures.

**H-2TG**: $^{13}C$ NMR ($H_2O$) δ 28.6 (2 C, $SCH_2$), 43.8 (2 C, $SCH_2CH_2S^+$), 46.4 (4 C, $^+SCH_2CH_2OH$), and 59.0 (4 C, $CH_2OH$); $^1H$ NMR ($H_2O$/TSP) δ 3.21 (t, 4 H, $SCH_2CH_2S^+$), 3.73 (t, 8 H, $^+SCH_2CH_2OH$), 3.85 (t, 4 H, $SCH_2CH_2S^+$), and 4.11 (t, 8 H, $CH_2OH$).

**CH-TG**: $^{13}C$ NMR ($H_2O$) δ 28.6 ($SCH_2CH_2S^+$), 36.3 ($SCH_2CH_2OH$), 44.2 ($^+SCH_2CH_2S$), 46.4 (2 C, $^+SCH_2CH_2OH$), 59.0 (2 C, $^+SCH_2CH_2OH$), and 63.2 ($SCH_2CH_2OH$); most of the $^1H$ signals were buried under the large peaks of H-2TG and TG.

**EHT**: $^{13}C$ NMR ($H_2O$) δ 11.3 ($CH_3CH_2S^+$), 16.9 ($CH_3CH_2S$), 27.9, 28.0 (2 C, $CH_2SCH_2$), 37.4 ($CH_3CH_2S^+$), 42.6 ($SCH_2CH_2S^+$), 45.0 ($HOCH_2CH_2S^+$), 59.0 ($CH_2OH$); $^1H$ NMR ($H_2O/D_2O$/TSP) δ 1.24 (t, 3 H, $CH_3CH_2S$, $J = 7.4$ Hz), 1.47 (t, 3 H, $CH_3CH_2S^+$, $J = 7.4$ Hz), 2.66 (q, 2 H, $CH_3CH_2S$, $J = 7.4$ Hz), 3.05 (t, 2 H, $SCH_2CH_2$, $J = 7.4$ Hz), 3.47 (q, 2 H, $CH_3CH_2S^+$, $J = 7.4$ Hz), 3.58 (t, 2 H, $^+SCH_2CH_2OH$, $J = 5.7$ Hz), 3.68 (t, 2 H, $SCH_2CH_2S^+$, $J = 5.7$ Hz), 4.06 (t, 2 H, $CH_2OH$, $J = 5.7$ Hz).

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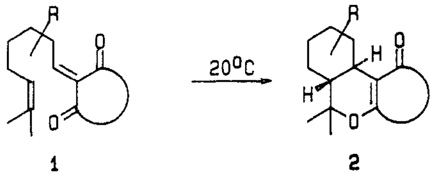
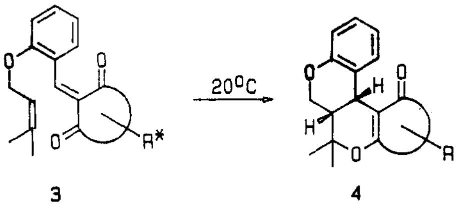
## Stereospecificity in Intramolecular Hetero-Diels-Alder Reactions of 2-Benzylidene-1,3-dicarbonyl Compounds[†1]

*Summary*: The intramolecular hetero-Diels-Alder reaction of 2-benzylidene-1,3-dicarbonyl compounds proceeds via a concerted pathway; this has been shown by using $^{13}C$-labeled dienophiles.

*Sir*: The intramolecular hetero-Diels-Alder reactions[2] of alkylidene- and 2-benzylidene-1,3-dicarbonyls **1** and **3**, which are easily obtainable by condensation of 1,3-dicarbonyls and aldehydes, proceed with high diastereoselectivity.[3] Thus, **1** leads exclusively to the trans-fused dihydropyrans **2** (ni-de[4] > 98%),[5,6] whereas **3** gives the cis-fused cycloadducts **4** (ni-de > 98%).[7] In addition, chirality centers in the chain as well as in the 1,3-dicarbonyls allow a high asymmetric induction (i-de[4] > 95%).[1,5,6,8,9]



**1** **2**



**3** **4**

However, nothing is known so far about the degree of the concertedness[10,11] of these cycloadditions. Since the

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(6) The hydrolyses of sulfonium cations are biomolecular: e.g., Swain, C. G.; Kaiser, L. E. *J. Am. Chem. Soc.* **1958**, *80*, 4089–4094.

[†] Dedicated to Professor George Büchi on the occasion of his 65th birthday.