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PHOTOMETHANOLYSIS OF A VINYL SULFIDE

A. G. Schultz*

Department of Chemistry, Cornell University
Ithaca, New York 14850

R. H. Schlessinger

Department of Chemistry, University of Rochester
Rochester, New York 14627

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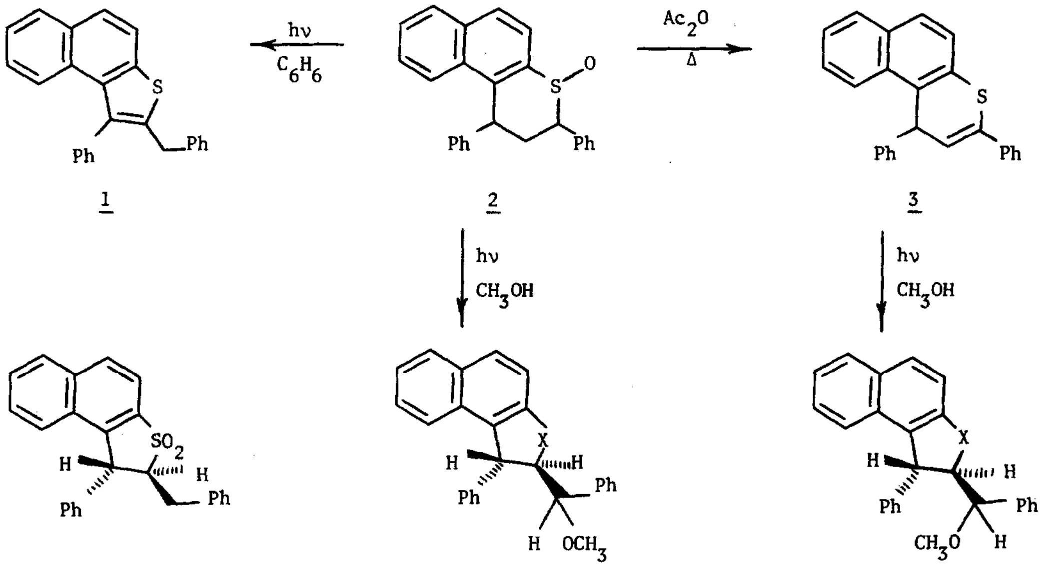
In the preceding communication, we describe the photoconversion of sulfoxide 2 to naphthothiophene 1 in benzene and to β-methoxysulfide 5 in methanolic solution. During the course of that study, the photochemistry of vinyl sulfide 3 was investigated. Herein, we report the results of this investigation, which led to the discovery of a potentially useful vinyl sulfide photomethanolysis reaction.[1]

Pummerer reaction[2] of sulfoxide 2 in freshly distilled acetic anhydride (140°, 6 hr) gave vinyl sulfide 3 (80% yield, mp 178-180°, m/e 350).[3] The nmr spectrum of 3 exhibits resonance centered at δ 5.86 (methine proton, doublet, J = 7.0 Hz), 6.54 (vinyl proton, doublet, J = 7.0 Hz), and a complex multiplet at 7.0 - 8.0 (sixteen aromatic protons).

Pyrex-filtered irradiation of 10^{-2} M degassed solutions of 3 in benzene-methanol (equal volumes) gave a single methanol incorporated product 8 (83% isolated yield, m/e 382, mp sulfone derivative 10, 231-234°). Under identical conditions, vinyl sulfide 3 was found to be indefinitely stable in the dark.

That 8 is diastereomerically related to photoproduct 5, obtained by photolysis of sulfoxide 2 in methanol, was demonstrated by the following observations. Controlled oxidation of 5 and 8 with m-chloroperbenzoic acid gave sulfoxides 6 and 9 respectively; both were converted by refluxing acetic anhydride to a single naphtho [2,1-b]thiophene 11 (mp 108-110°, m/e 380). Bromination of thiophene 1 with N-bromosuccinimide in carbon tetrachloride gave a monobromo-derivative, which when treated with sodium methoxide in methanol also produced only 11.

Assignment of stereochemistry in dihydrothiophenes 5 and 8 is based on nmr and chemical information. Thus, 5 exhibits non-aromatic resonance centered at δ 3.20 (methyl, singlet), 3.89 (methine adjacent to sulfur, doublet of doublets, J = 10 Hz and J = 1.0 Hz), 4.19 (methine adjacent to oxygen, doublet, J = 10 Hz), and 5.65 (diarylmethine, doublet, J = 1.0 Hz) while 8 gives resonance at δ 3.25 (methyl, singlet), 3.88 (methine adjacent to sulfur, doublet of



1

2

3

4

5, X = S

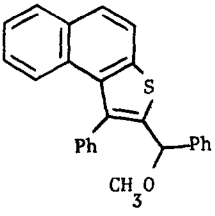
6, X = SO

7, X = SO_2 (mp 189°)

8, X = S

9, X = SO

10, X = SO_2 (mp 234°)



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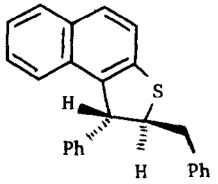

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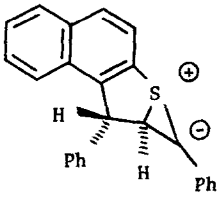

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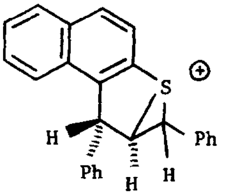

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doublets, J = 9.0 Hz and J = 2.0 Hz), 4.20 (methine adjacent to oxygen, doublet, J = 9.0 Hz) and 4.78 (diarylmethine, doublet, J = 2.0 Hz). The small coupling constant for dihydrothiophene ring protons in both 5 and 8 is generally indicative[4] of *trans*-stereochemistry. Furthermore, the near-identical chemical shift values for the methine proton adjacent to sulfur in 5 and 8 are consistent with the same ring stereochemistry in both these isomers.

Treatment of either sulfone 7 or 10 with 47% hydriodic acid[5] in refluxing acetic acid solution gave molecular iodine and a single sulfone 4 (95% isolated yield, mp 178°, m/e 384). Both 7 and 10 were recovered unchanged when 37% hydrochloric acid was substituted for hydriodic acid, indicating that epimerization was not occurring under these strongly acidic conditions. These data confirm that 5 and 8 are diastereoisomers and are epimeric at the methyl-ether-methine carbon atom.

The site of solvent hydrogen atom incorporation in 8 was determined by irradiation of vinyl sulfide 3 in methanol-d_1. In this case, monodeutero-8 was isolated and gave nmr resonance centered at δ 3.88 (doublet, J = 2.0 Hz) and 4.78 (doublet, J = 2.0 Hz). No resonance occurred at δ 4.20, which indicated that deuterium resided exclusively on the methyl-ether-methine carbon in 8.[6]

We have considered, but do not believe, that carbene 12 might be an intermediate in the formation of 8.[7] The high degree of stereoselectivity in methanolysis and the absence of addition products when 3 was irradiated in the presence of cyclohexene is not indicative of a free carbene. Furthermore, insertion into an adjacent carbon-hydrogen bond has been observed for 2-thioalkylcarbenes.[8] Irradiation of vinyl sulfide 3 in neutral solvents did not produce any thiophene 1, the anticipated product of intramolecular carbene insertion and subsequent aromatization.

A reactive intermediate consistent with all the experimental data is ylide 13.[9] Photoinitiated electrocyclic bonding in vinyl sulfide 3 would generate 13, which could react with methanol to give β-methoxy sulfide 8.[10] If a discrete sulfonium ion 14 is involved in methanolysis, then it must be epimeric at the site of protonation with the hypothetical sulfonium ion generated in the photolysis of sulfoxide 2. The remarkable stereochemical control in these complimentary photoreactions should be synthetically useful. One of us is currently involved in extending this investigation to other systems.*

Acknowledgment

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References

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2. For a comprehensive survey of the Pummerer reaction, see: L. Horner and P. Kaiser, Justus Liebigs Ann. Chem., 626, 19 (1959).
3. Satisfactory elemental analyses and spectra compatible with structural assignments were obtained for all new compounds. All melting points are uncorrected.
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5. Hydriodic acid has been used for the cleavage of methyl ethers [V. Deulofeu and T. J. Guerrero, Org. Syn., Coll. Vol., 3, 586 (1955)] and for the reductive removal of halogens [E. F. M. Stephenson, Org. Syn., Coll. Vol., 3, 475 (1955)].
6. The coupling constant for the ring-hydrogens in monodeutero-10 is J = 5.0 Hz which appears to be typical of trans-2-alkyl-3-phenyl-2,3-dihydronaphtho[2,1-b]thiophene-1,1-dioxides; A. G. Schultz, unpublished results.
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