

PHOTODEHYDRATION OF SULFOXIDES

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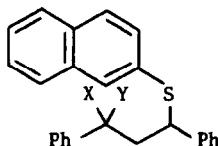
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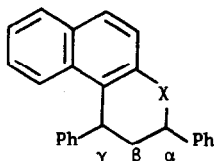
Photorearrangement of 2,2-dimethylthiachroman-1-oxide has been reported to give 2-isopropyl benzothiophene as the major reaction product.<sup>1</sup> Although a mechanism was suggested to account for this transformation, to our knowledge, no detailed investigation of this reaction has been described. We wish to report the related photodehydration of sulfoxides 4 to thiophene 1 (Scheme I), and present experimental evidence in support of a mechanism for these interesting conversions.

Triton-B catalyzed addition of 2-naphthalenethiol to benzalacetophenone in ethanol gave  $\beta$ -ketosulfide 1 in 98% yield, mp 129-130°. Reduction of 1 with lithium aluminum hydride in benzene-ether gave two epimeric alcohols 2a (55% yield, mp 115-118°) and 2b (40%, mp 78-88°).



1, X = Y = O

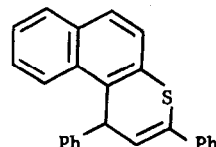
2, X = H; Y = OH



3, X = S

4, X = SO

5, X = SO<sub>2</sub>



6

Reaction of 2a with stannic chloride in methylene chloride (1 hr at 25°) produced a single cyclized product 3a in 91% yield, mp 150-151°, m/e 352. Controlled oxidation of 3a with *m*-chloroperbenzoic acid in chloroform afforded two sulfoxides 4a (48% yield, mp 261-263°, m/e

368), and 4b (30%, mp 214-217°, m/e 368). That 4a and 4b were sulfoxide pyramidal isomers was demonstrated by peracid oxidation of both 4a and 4b to a single sulfone 5 (mp 270°, m/e 384). In a similar manner, alcohol 2b was converted to an epimeric sulfide 3b (mp 190-193°), and thence to sulfoxide pyramidal isomers 4c (mp 226-228°) and 4d (mp 187°).

Pyrex-filtered irradiation of  $10^{-2}$  M degassed<sup>3</sup> benzene solutions of any isomer 4a - 4d resulted in the formation of 2-benzyl-3-phenylnaphtho[2,1-b]thiophene 11 (74% isolated yield, mp 115-116°), trace amounts of 3 and 5<sup>1</sup> (tlc analysis), and water.<sup>4</sup> Thiophene 11 has been unambiguously prepared by polyphosphoric acid cyclodehydration<sup>5</sup> of naphthyl- $\beta$ -ketosulfide 14.

The mechanism considered for transformation 4  $\rightarrow$  11 is shown in Scheme I. In order to demonstrate that an ionic intermediate such as 9 could be involved, sulfoxide 4 was irradiated in the presence of a nucleophilic solvent. Photolysis of a  $10^{-2}$  M degassed solution of any isomer 4a - 4b in benzene-methanol (equal volumes) resulted in the formation of a single methanol incorporated product 12 (85% isolated yield, m/e 382, mp sulfone derivative 13, 188-189°)<sup>6</sup>, sulfide 3 (5%), sulfone 5 (9%), and no thiophene 11. Thiophene 11 was photostable to these reaction conditions.

Dehydration of an intermediate such as 7 or 8 could give vinyl sulfide 6, which in a second photochemical step might produce either 11 or 12. Accordingly, vinyl sulfide 6 was prepared<sup>6</sup> but produced neither thiophene 11 when irradiated in benzene, nor  $\beta$ -methoxysulfide 12 when irradiated in methanolic solution.<sup>7</sup> These results rule out the intermediacy of 6 in the observed photo-reactions of sulfoxide 4.

If the mechanism depicted in Scheme I were correct, then only the proton on the  $\beta$ -carbon atom in 4 would be lost in the process 4  $\rightarrow$  12. To probe this question, analogs of 4 with deuterium labels on the  $\alpha$ - and  $\gamma$ -carbon atoms were required. We have selected a route to deuterated 4, which labeled both the  $\alpha$ - and  $\gamma$ - positions, but not the  $\beta$ -carbon atom.

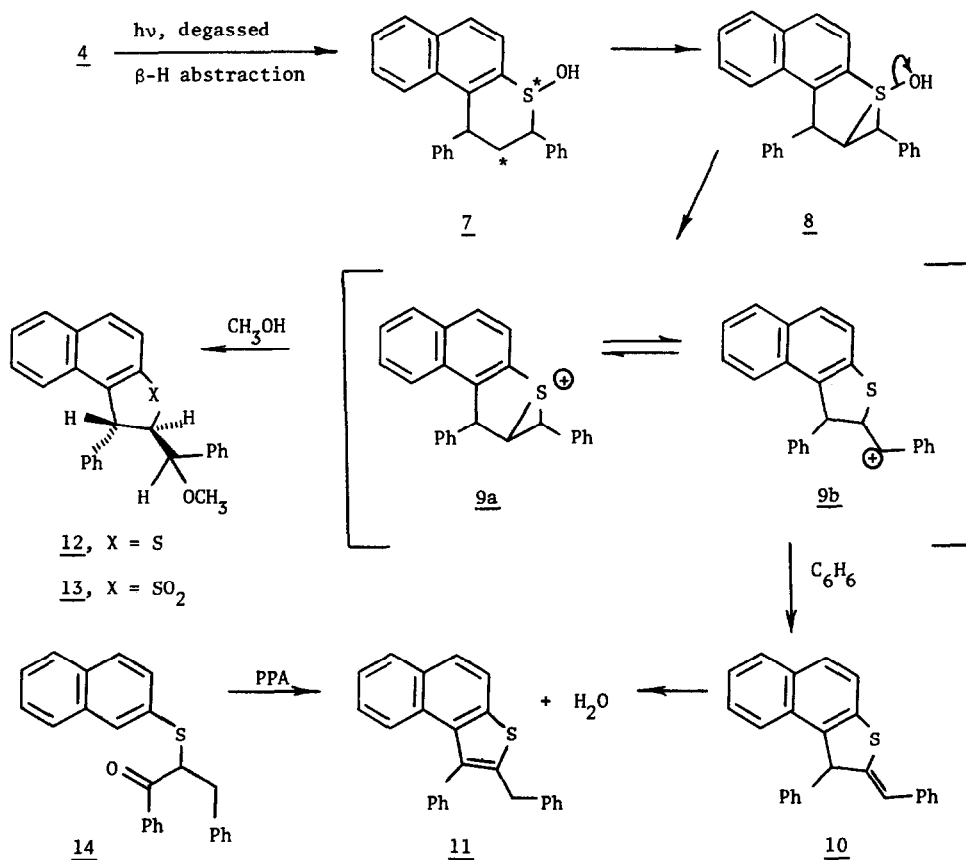
Monodeutero-2a (56% yield, mp 101-106°) was obtained from the reduction of 1 with lithium aluminum deuteride. Reaction of 2a-d<sub>1</sub> with stannic chloride in methylene chloride gave monodeuterio-3 (97% deuterium incorporation by mass spectral analysis). Inspection of nmr resonance as well as electron impact fragmentation of 3-d<sub>1</sub> demonstrated that 35% of the available deuterium label was at the  $\alpha$ -carbon atom, 65% resided at the  $\gamma$ -position, and none could be detected at the  $\beta$ -carbon. These results are consistent with partial equivalency of the  $\alpha$ - and  $\beta$ -carbon atoms during the conversion 2a  $\rightarrow$  3.<sup>8</sup> Peracid oxidation of 3-d<sub>1</sub> gave monodeutero-4. Spectral data

confirmed that deuterium incorporation in 3 and 4 was identical.

Irradiation of 4-d<sub>1</sub> in benzene methanol solution gave monodeutero-12 (98% deuterium retention), the label of which was distributed at the diaryl-methine carbon (67%) and the methyl-ether-methine carbon (31%). Clearly then, only the proton on the β-carbon atom in 4 has been lost in the process 4 → 12.

All these data lend support to the mechanism considered in Scheme I. Thus, initial photo-excitation of 4 followed by sulfoxide abstraction of a β-hydrogen atom could give 7, which, after

SCHEME I



closure to 8, would suffer loss of hydroxide ion to give the sulfur-stabilized cation 9. In the absence of a suitable nucleophile, proton-loss followed by rearrangement to thiophene 11 is the reaction course. In the presence of methanol, intermediate 9 undergoes solvolysis to give 12

stereospecifically.<sup>9</sup> This remarkable result clearly demonstrates the potential synthetic utility of this phototransformation. Furthermore, sulfoxides 4a - 4d all give 12 irregardless of the relative stereochemistry at sulfur or the  $\alpha$ - and  $\gamma$ -carbon atoms in 4. Racemization might be possible via 9b, however, prior epimerization of the  $\alpha$ -carbon atom in sulfoxides 4a - 4d cannot be ruled out.<sup>10</sup>

The abstraction of a  $\beta$ -hydrogen atom by the excited sulfoxide is intriguing from a synthetic as well as mechanistic point of view. It is anticipated that this reaction may be of use in generating new and interesting sulfur heterocycles. In the following communication, we compare this process to the photomethanolysis of a related vinyl sulfide.

#### Acknowledgment

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#### References

1. R. A. Archer and B. S. Kitchell, J. Amer. Chem. Soc., 88, 3462 (1966).
2. Satisfactory elemental analyses and spectra compatible with structural assignments were obtained for all new compounds. All melting points are uncorrected.
3. Reaction solutions were irradiated in sealed Pyrex tubes degassed by four freeze-pump-thaw cycles with a mercury-diffusion-pump vacuum.
4. The presence of water was determined by nmr and vpc analysis (Poropak-Q Column, 50°).
5. O. Dann and M. Kokorudz, Chem. Ber., 91, 172 (1958).
6. The detailed assignment of structure in 13 together with the preparation and photochemistry of vinyl sulfide 6 is discussed in the accompanying communication.
7. It is interesting to compare the chemically induced dehydration of sulfoxide 4 to give vinyl sulfide 6 with the photodehydration accompanied by rearrangement of 4 to give thiophene 11.
8. The mechanism of deuterium scrambling in the conversion 2 + 3 is currently under investigation.
9. Irradiation of 4 in the presence of acetic acid resulted in formation of the acetate analog of 12 (75% isolated yield).
10. A. G. Schultz and R. H. Schlessinger, Chem. Commun., 1294 (1970).