Tetrahedron Letters Vol. 21, pp 3903 - 3906
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/1001-3903$02.00/0

STEREOSPECIFIC PHOTOCYCLIZATION OF α-BISULFENYLATED KETO COMPOUNDS.[1] CIS-DIHYDROBENZOTHIOPHENES.

Tadashi Sasaki*, Kenji Hayakawa, and Sumio Nishida

Institute of Applied Organic Chemistry, Faculty of Engineering
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

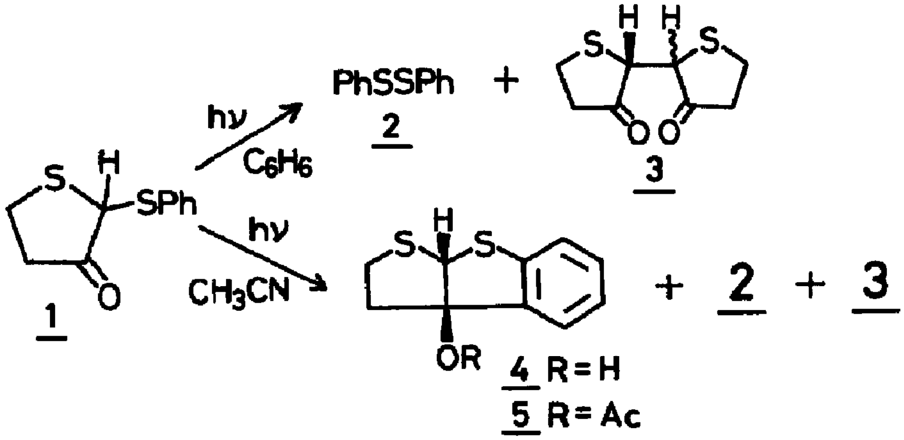
Summary: Irradiation of α-bisulfenylated keto compounds in acetonitrile affords the cis-fused dihydrobenzothiophenes which are dehydrated to benzothiophenes in high yields.

Introduction of a sulfur substituent to α position of a carbonyl group enhances the thermodynamic acidity of an adjacent proton by $\sim 10^3$ over a simple ketone and stabilizes an anion (enolate) at the carbon bearing sulfur.[2] Such a fact allows sulfur to be widely used in organic synthesis as a chemical control element.[3] However, the effect of sulfur substituents in photochemical reaction has received little atention because of the easiness of photochemical homolytic C,S-bond cleavage.[4] We have examined the photochemical behavior of α-bisulfenylated keto compounds as part of our studies on organic photochemistry.[1]

A number of α-bisulfenylated keto compounds (1 and 7-13) were prepared in high yield from the corresponding β-keto sulfides by successive treatment with NCS/CCl_4 and thiophenol/triethylamine/CH_2Cl_2.[5] Irradiation of an argon-degassed benzene solution (5×10^{-3} M) of keto sulfide 1 with a 100-W high pressure mercury lamp through a Pyrex filter resulted in a rapid disappearance of 1, and afforded diphenyl disulfide (2) (63%) and a 3:4 diastereomeric mixture of 3[6] (49%) (eq 1). These products were considered to be formed by the radical mechanism.[4]

A remarkable solvent effect was observed. The similar irradiation (30 min) of 1 in acetonitrile gave dihydrothiophene 4 as the major product (43%) together with 2 (25%) and 3 (21%) (eq 2). Compound 4 was also obtained (20%) when methanol was used as the solvent. The structural assignment of 4 (oil) was based on its spectroscopic data: m/e 210 (M^+), 192 (M^+-H_2O); IR (neat) 3380 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45-3.40 (m, 4H, methylene), 3.10 (s, 1H, exchangeable, OH), 4.77 (s, 1H, methine), 7.08-7.25 (m, 4H, aromatic), and the chemical conversions. The alcohol 4 was converted (Ac_2O/4-dimethylaniopyridine/pyridine) to the acetate 5, mp 135-137 °C; m/e 252 (M^+); δ 2.08 (s, 3H), 2.6-3.7 (m, 4H), 7.26-7.14 (m,4H). Tretment of 4 with $BF_3 \cdot Et_2O/CH_2Cl_2$ gave a quantitative yield of benzothiophene 6, mp 58-60 °C; δ

3.13-4.02 (A_2B_2-signal, 4H), 7.1-7.9 (m, 4H). The cis configuration of 4 was determined on the basis of (a) the abnormally low chemical shift of the sulfur methine proton (the van der Waals effect)[7] (b) the strongest shift (shift slope 1.03) next to the hydroxyl signal (5.02) in the Eu(fod)$_3$ study and (c) the low field shift of this signal ($\Delta\delta$=-0.35 ppm) in acetate 5.



(1)

(2)

The generality of this stereospecific photocyclization in acetonitrile was explored with substrates 7-13 (Table 1). In most cases, cis-dihydrothiophenes were obtained as the virtually sole product and the photoproducts were easily dehydrated to the corresponding benzothiophenes by treating with $BF_3 \cdot Et_2O$. Photolysis of α-deuterated 11b gave 2 (46%) and 18b (45%) with complete deuteration at the sulfur methine position (Table 1).

From these results, two mechanistic paths a and b (eq 3) may be postulated to account for the formation of cis-dihydrothiophenes. Since S-aryl vinyl sulfides are well known to photocyclize in a conrotatory fashion,[8,9] the above results can be explained by the prior enolization to 1a which photocyclizes to the thiocarbonyl ylide A (path a).[10,11] The intramolecular protonation by the bridgehead hydroxyl group would lead to the cis dihydrothiophene.[12] Alternatively, the reaction occurs by the direct cyclization mechanism via the intermediate B (path b). The cis ring closure would be favored here by the steric reasons.

The presence of two sulfur substituents is essential for the above reactions and the simple S-phenyl β-keto sulfides are photoinert under the same conditions. Furthermore, the decreased yield of 18b compared with 18a indicates the involvement of deuterium-migration in the reaction. From these observations, path a seems to be much preferable. The detailed mechanistic studies of this novel photocyclization are in progress.

Table 1. Photolyses of β-Keto Sulfides and Dehydration of the Photoproducts[a,b]

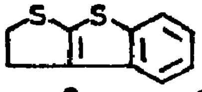
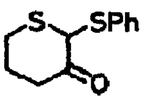
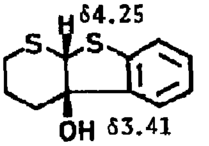
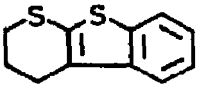
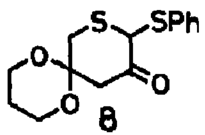
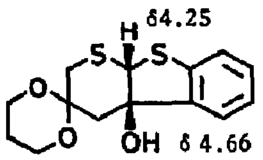
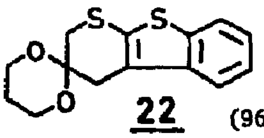
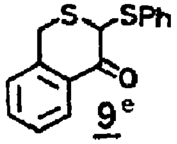
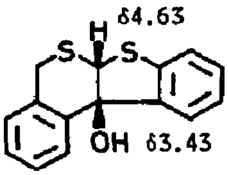
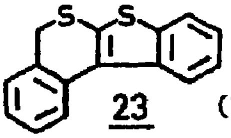
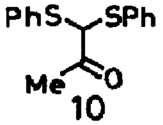
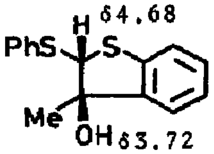
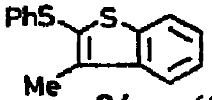
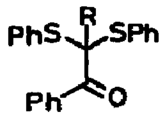
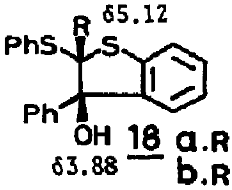
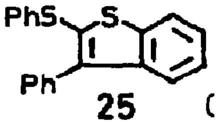
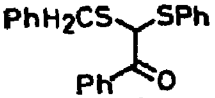
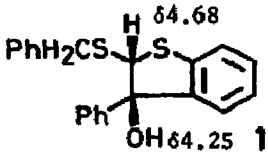
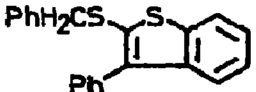
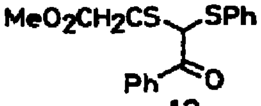
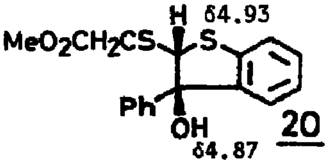
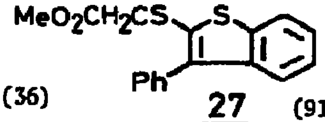
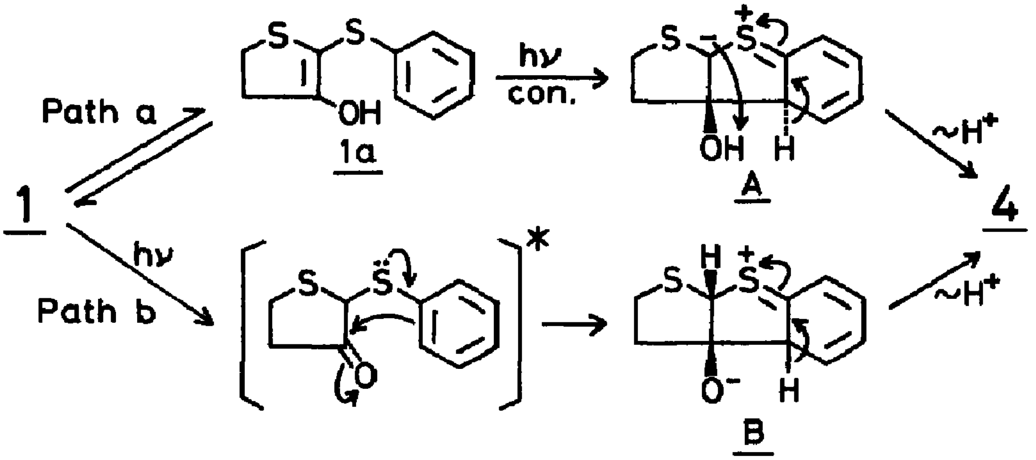
starting materials	photoproducts[c] (yield %)	dehydration products (yield %)[d]
1	4 (43)	 6 (100)
 7	 14 (43)	 21 (97)
 8	 15 (53)	 22 (96)
 9[e]	 16 (-)[f]	 23 (30)[g]
 10	 17 (19)[h]	 24 (99)
 11 a. R=H b. R=D	 18 a.R=H (71) b.R=D (45)	 25 (95)
 12	 19 (46)	 26 (92)
 13	 20 (36)	 27 (91)

Table 1. (continued) [a] All photolyses were carried out in acetonitrile (5×10^{-3} M, Pyrex). [b] Dehydration was effected by treating with $BF_3 \cdot Et_2O$ in CH_2Cl_2 at room temperature. [c] All products were purely isolated by column chromatography using hexane/ether and the yields are based on the starting materials consumed (~80% conversion). [d] Isolated yields. [e] A quartz filter was used. [f] 16 was found to be easily dehydrated to 23 during work-up. [g] Overall yield from 9. [h] The major product was 1-phenylthio-propan-2-one (38%).



(3)

References

1. Photochemistry of Organosulfur Compounds. Part 2. For part 1, see T. Sasaki, K. Hayakawa Tetrahedron Lett., 21, 1525 (1980).
2. R.M. Coates, H.D. Pigott, J. Ollinger, Tetrahedron Lett., 3955 (1974).
3. For a review, see B.M. Trost, Chem. Rev., 78, 363 (1978).
4. A. Schönberg, A.K. Fateen, S. Omran, J. Am. Chem. Soc., 78, 1224.
5. Satisfactory elemental analyses and spectra compatible with the structural assignments were obtained for all new compounds.
6. Spectral data of 3 are as follows. IR (neat) 1720 cm^{-1}; MS m/e 202 (parent), 101 (base); ^1H NMR ($CDCl_3$) δ 4.19 (s, 0.86H), 4.04 (s, 1.14H), and 3.4-2.5 (m, 8H).
7. H. Günther, "NMR-Spektroskopie," Georg Thieme Verlag: Stuttgart, 1973.
8. (a) A.G. Schultz, W.Y. Fu, R.D. Licci, B.G. Kurr, K.M. Lo, M. Boxer, J. Am. Chem. Soc. 100, 2140 (1978); (b) A.G. Schultz, M.B. DeTar, J. Am. Chem. Soc., 98, 3564 (1976); (c) A.G. Schultz, M.B. DeTar, J. Am. Chem. Soc., 96, 296 (1974).
9. T. Wolff, J. Am. Chem. Soc., 100, 6157 (1978).
10. (a) A. Padwa, A. Au, G.A. Lee, W. Owens, J. Am. Chem. Soc., 98, 3555 (1976); (b) A. Padwa A. Au, J. Am. Chem. Soc., 98, 5581 (1976).
11. Since no enol tautomer could be detected by IR and ^1H NMR ($CDCl_3$, CD_3OD, and CD_3CN), the possibility of photochemical enolization cannot be ruled out.
12. The photochemically generated thiocarbonyl ylides were shown to be sufficiently basic to be protonated by alcohols like methanol.[8b]

(Received in Japan 27 June 1980)