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FACILE PHOTOREARRANGEMENT OF AROMATIC DISULFIDES

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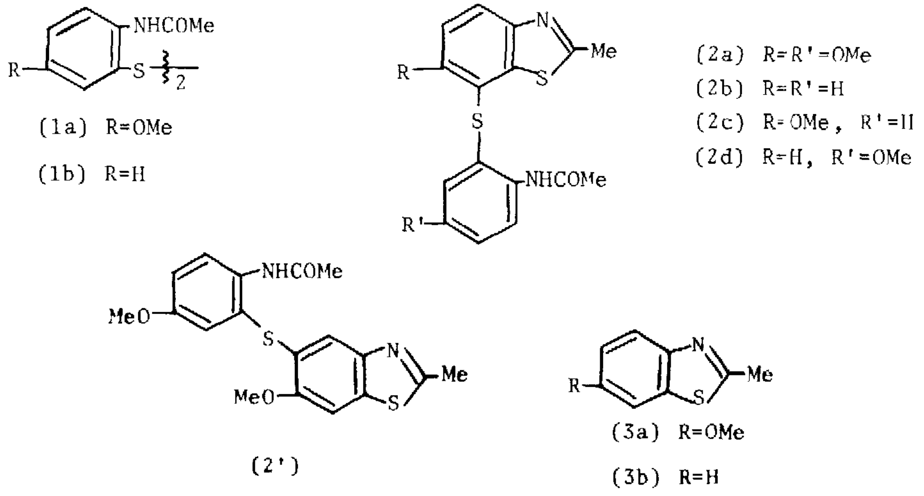
Homolytic cleavage of the S-S bond is a significant primary process in photolysis of disulfides[1,2] In the case of aromatic disulfides, subsequent reactions of the labile thiyl radicals result in the formation of thiols, disulfides and polymers[3,4] The source of the abstracted hydrogen in arylthiol formation has been pointed to be another arylthiyl radical rather than the solvent employed.[3,4] Details of the photochemistry of aromatic disulfides, however, still remain equivocal.

The present communication describes an intriguing example which sheds some light on comprehensive understanding of the solution photochemistry of aromatic disulfides. We found that irradiation of bis-(o-acetylaminophenyl)disulfides (1a,b) causes a facile photorearrangement leading mainly to 7-(2'-acetylaminophenylthio)-2-methylbenzothiazoles(2a,b). This observation implies the following facts(see Scheme 2) (a) Recombination of an initially generated arylthiyl radical with another arylthiyl radical to form intermolecularly the S-C bond (b) Aromatization of the intermediate thus formed via 1,3-hydrogen shift to give a thiol, which rationalizes that a hydrogen of the thiol does not originate from solvent. (c) Intramolecular trapping of the intermediary thiol with an ortho-situated acetylamino grouping to form the thiazole ring, preventing further complicated photoreactions of the thiol such as polymerization

Irradiation of (1a) in acetonitrile (1×10^{-2}M) was carried out by using a 400W high-pressure mercury arc lamp through a Pyrex filter under nitrogen until disappearence of (1a) was completed(monitored by TLC, about 1 hr). Chromatographic separation allowed to isolate(2a), mp 83-85°, and 2-methyl-6-methoxybenzo thiazole(3a), an oily substance, in 62% and 10% yields, respectively Other determinable products involving expected 5-(2'-acetylamino-5'-methoxyphenylthio)-2 methyl-6-methoxybenzothiazole(2') were not isolated



(1a) R=OMe
(1b) R=H

(2a) R=R'=OMe
(2b) R=R'=H
(2c) R=OMe, R'=H
(2d) R=H, R'=OMe

(2')

(3a) R=OMe
(3b) R=H

Scheme 1

The structure of (3a) was confirmed by ir and nmr spectral comparison with these of a sample prepared independently.

The spectral data and microanalytical results fully accommodate to the structure of (2a) [ir(KBr)cm^{-1} 3300(NH), 1680($\underline{CO}$NH), NMR($CDCl_3$)δ 2.17(3H, singlet, NHCOC$\underline{H}_3$), 2.78(3H, singlet, =C-C$\underline{H}_3$), 3.76(3H, singlet, OC$\underline{H}_3$), 3.97(3H, singlet, OC$\underline{H}_3$), 6.80-8.50(6H, N$\underline{H}$ and aromatic protons), mass spectrum m/e M^+= 374, M^+-210 = 164, uvλ_{max}^{MeOH}(ε) nm 308(sh. 5×10^3), 297(sh. 6×10^3), 246(sh. 2×10^4)] The nmr spectrum of (2a) showed an well-resolved AB-type signal(δ7.13 and 7.94, each J= 9 Hz), which was apparently distinguished from NH [δ8.46 (1H, broad)] and other aromatic protons[δ6.87(1H, quartet, J_1= 3 Hz, J_2= 9 Hz, 4'-H), 7.15(1H, doublet, J= 3 Hz, 6'-H), 8.18(1H, doublet, J= 9 Hz, 3'-H)], assignable to the vicinal phenyl ring protons of the benzothiazole moiety Thus, an alternative structure(2') can be eliminated

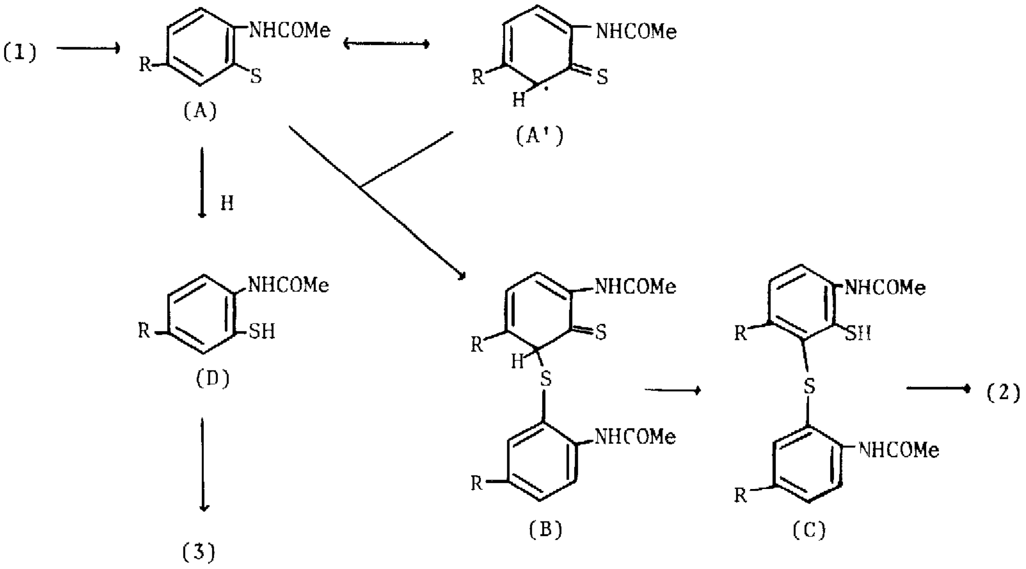
Upon employment of methanol as solvent, analogous irradiation of (1a) gave (2a) and (3a) in 66% and 22% yields, respectively

Irradiation of (1b) in methanol under similar conditions led to the formation of (2b), mp 153-5°, and (3b) in 40% and 30% yields, respectively The structures of these products were established by comparison of their spectral data with these of (2a) and an authentic sample of (3b).

When a mixture of (1a) and (1b)(1 1) in methanol was irradiated under the same conditions and the resulting reaction mixture was submitted carefully to chromatography, a crossover product(2c), mp 160-163°(10%), was isolated together with (2a)(15%), (2b)(13%), (3a)(10%) and (3b)(10%)

The structure of (2c) was confirmed on the basis of spectral data, in particular, fragmentation patterns of its mass spectrum and nmr spectral comparison with that of (2a)[ir(KBr)cm^{-1}3360(NH),1690(NH$\underline{\mathrm{CO}}$), NMR(CDCl$_3$)δ2 18(3H,singlet, NHCOC$\underline{\mathrm{H}}_3$),2 77(3H,singlet,=C-C$\underline{\mathrm{H}}_3$), 3 97(3H,singlet,OC$\underline{\mathrm{H}}_3$),7 00-9 00(7H,N$\underline{\mathrm{H}}$ and aromatic protons, the signals contain an AB-type quartet centered atδ 7.13 and 7 92 with each J=9Hz), mass spectrum m/e M$^+$=344, M$^+$-210=134, uvλ_{max}^{MeOH}(ε)nm 308(sh. 5×10^3), 297(sh 6×10^3), 242(sh. 2×10^4)] The nmr spectrum of the residue showed a pair of signals atδ 2 02(3H,singlet,NHCOC$\underline{\mathrm{H}}_3$), 2.86(3H,singlet,=C-C$\underline{\mathrm{H}}_3$)and 3.77 (3H,singlet,OC$\underline{\mathrm{H}}_3$), suggesting the formation of another crossover product(2d).

Thus, the rearrangement of (1) to (2) can be concluded to involve an intermolecular radical-combination process



Scheme 2

On the basis of above findings, we present a most conceivable reaction sequence as depicted in Scheme 2.

Homolytic cleavage of the S-S bond of (1) in an excited state gives arylthiyl radicals The resulting arylthiyl radical(A) could combine intermoleculaly with another arylthiyl radical(A') at its ortho-position. The coupling product(B) could be aromatized most likely via 1,3-hydrogen shift to give the thiol intermediate(C) which cyclizes spontaneously to (2).

Although it has been proposed that the first step in photolysis of the divinyl disulfide system might be a concerted suprafacial 1,3-sigmatropic rearrangement, allowed in an excited state[5] the concerted process is not a major pathway at least in the case of the aromatic disulfides

It is precedent that photolysis of S-phenylthioacetates gives photo Fries-type products even in low yields arising from combination of an acetyl radical with an arylthiyl radical at its ortho-and para-positions[4] In our case, a notable observation is the highly preferential formation of ortho-coupling product(2) in fairly good yields. At present, however, we have no information available for its precise explanation

The source of a hydrogen for the formation of (3), which is a minor process in every case, appears to arise from undetectable side reactions

Several examples of addition of thiyl radicals to the aromatic system are now known[6] In this view, an alternate process for the formation of (2) via addition of an arylthiyl radical(A) to the initially formed benzothiazole(3) can be considered. However, no formation of (2c) upon irradiation of a mixture of (1b) and (3a), clearly eliminates this alternate process

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