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THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 1,4-DITHIIN SULFOXIDES

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Summary: Thermolysis of 2,5-diphenyl-1,4-dithiin-1-oxide afforded 2-formyl-2,4-diphenyl-1,3-dithiole, which was obtained also in photolysis along with another rearranged product, 2-benzoyl-4-phenyl-1,3-dithiole.

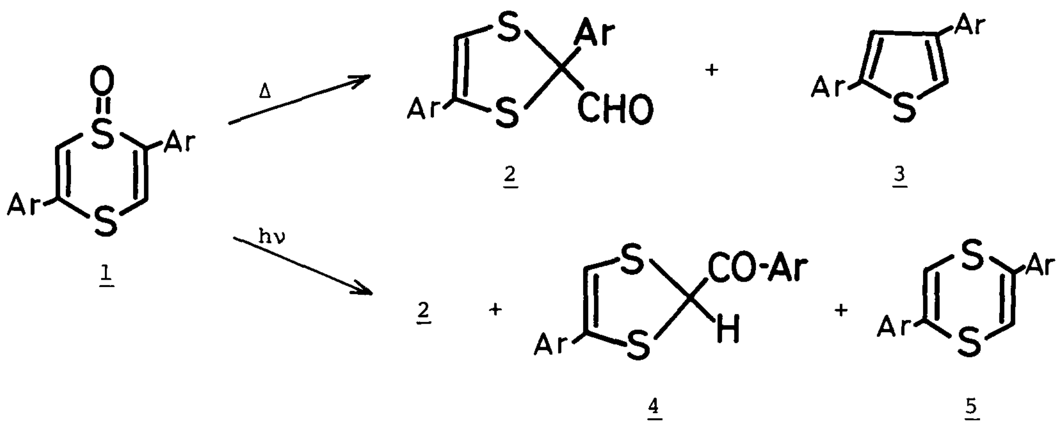
The thermal decomposition of 1,4-dithiin sulfoxides has been known for a long time to produce thiophenes by extrusion of sulfur oxide moiety.[1] In the course of studies on mechanistic detailes of this reaction, we have found that a new type of sulfoxide rearrangement is actually involved in the thermolysis. In the present paper we wish to report the thermal and photochemical transformations of 1,4-dithiin sulfoxides to 1,3-dithiole ring compounds.

Upon heating acetonitrile solution (*ca.* 5×10^{-3} M)[2] of 2,5-diphenyl-1,4-dithiin-1-oxide (1a) around 70°C for 40 min, 2-formyl-2,4-diphenyl-1,3-dithiole (2a) was isolated in 13 % yield by chromatography on silica gel, together with 70 % of 2,4-diphenylthiophene (3a) as is expected. The structure of a rearranged product, 2a, was deduced from elemental analysis and spectral informations. 2a; yellow oil, NMR($CDCl_3$) δ 6.17(1H, s), 7.15-7.64(10H, m), 9.30(1H, s); IR IR(neat) 2840, 2780, 1723 cm^{-1}; mass m/e 284(M^+), 255(M^+-CHO, base). The product composition was dependent on the solvent. The exclusive formation of 2a was effected using carbon tetrachloride. In methanol or dimethyl sulfoxide, on the contrary, sulfoxide 1a did not undergo the rearrangement but rather suffered the loss of sulfur oxide. Addition of approximately equimolar triethylamine or pyridine to acetonitrile solution of 1a caused no rearrangement and afforded only

Table 1. Thermal decomposition of 2,5-diaryl-1,4-dithiin-1-oxides at 75°C[a)]

Ar-		in acetonitrile		in carbon tetrachloride	
		2	3	2	3
p-Cl	1b	3 %	97 %	68 %	32 %
p-H	1a	17	83	100	0
p-CH_3	1c	51	49	100	0
p-CH_3O	1d	61	39	100	0

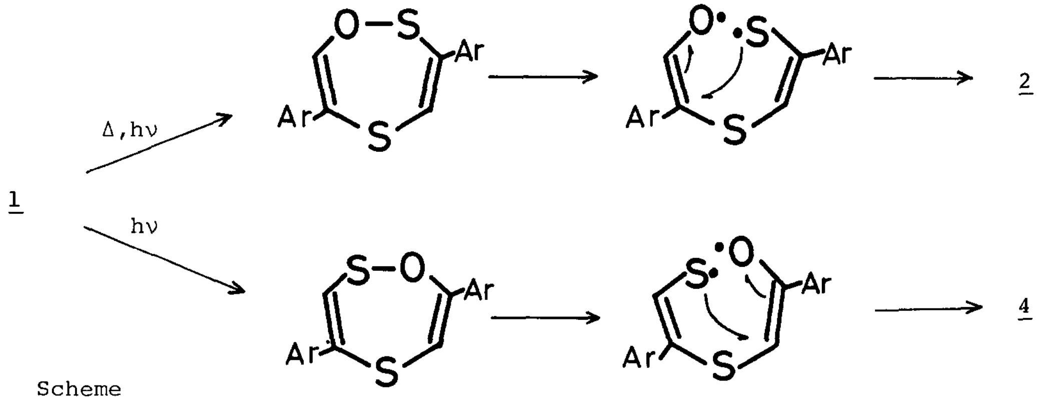
a) Calculated from the peak intensities of HPLC corrected for the absorbance



3a.2) Thus polar media which are capable of solvation with sulfoxide group suppress the formation of 2a. Similar thermal decompositions were applied to *para*-substituted derivatives of 1a and the results are shown in Table 1.3)

The skeletal rearrangement seems most likely to occur by way of cyclic sulfenate ester as an intermediate, which seems to be formed *via* a radical or concerted process. The sulfenate would in turn generate the ring-opened diradical by O-S bond rupture followed by cyclization to give 2a, as depicted in Scheme. Thermal expansion of cyclic sulfoxide to cyclic sulfenate has been proposed,4) although this conversion has been more often observed under conditions of electron impact5) and in photochemical processes.6)

The mass spectra of 1a operated at 70 eV consist of the following major peaks;7) m/e 284(M^+, 3%), 268(M^+-O, 27%), 255(M^+-CHO, 29%), 236(M^+-SO, 100%), and 121($C_6H_5CS^+$, 22%). A most interesting feature is the occurrence of mass 255 with considerable abundance. This ion must be formed in processes including a skeletal rearrangement to 2a preceding the loss of CHO. The ion corresponding



Scheme

to the loss of C_6H_5CO from the molecular ion was not observed, which should be formed if the rearrangement were initiated by cleavage of another C-S(O) bond in 1a. These observation would imply that the strength of the C(Ar)-S(O) bond is greater than that of the C(H)-S(O) bond in the isolated molecular ion. Mass spectral behaviour of 1a with respect to the rearrangement is paralell to the thermal transformation of 1a to 2a.

In contrast, either of the two possible rearrangements occured when methanol solution of 1a was irradiated with a high pressure mercury lamp through a Pyrex filter under nitrogen gas. Thus, 2-benzoyl-4-phenyl-1,3-dithiole (4a) was isolated in 21 % yield as well as 2a and 2,5-diphenyl-1,4-dithiin (5a). A small amount of 2a was detected by means of HPLC, probably arising from secondary photolytic decomposition of 5a.[8] Product distribution calculated from the relative intensities of their characteristic nmr signals are summarized in Table 2. The structure of compound 4a is consistent with its spectral characteristics and identical in all respects with the product derived from the additive Pummerer reaction of 1a.[9] Photolysis of *p*-substituted derivatives of 1a showed similar results except for 1d, which gave rise to a complex mixture of products.

Table 2. Photolysis of 2,5-diaryl-1,4-dithiin-1-oxides in methanol at 0°C[a]

Ar-		2	4	5
p-Cl	1b	38 %	56 %	6 %
p-H	1a	32	46	22
p-CH_3	1c	79	13	8

a) Relative % yields calculated from the intensities in nmr

Although the photolysis of 1a afforded partially the different rearranged product from the thermolysis, the photochemical formation of 2 may be suggested still to proceed *via* the sequence in Scheme and, furthermore, it would be reasonable to account for the photochemical formation of 4 on the basis of a similar sequence. The reason why the photolysis gave rise to the ring expansion leading to an isomeric sulfenate is not clear at this stage.

As to the photoproduct 5 its formation may be understood in terms of photochemical oxygen transfer to the solvent prior to the rearrangement. Photoinduced deoxygenation of sulfoxides has been known.[10]

Photochemical and thermal transformations of 1,4-dithiin sulfoxides described here could prove to be an interesting and efficient means of obtaining 1,3-dithiole compounds.

References and Notes

1) H. H. Szmant and L. M. Alfonso, *J. Amer. Chem. Soc.*, 70, 205 (1975).

2) Thermolysis was carried out under the conditions of rather low concentration of 1 in order to avoid bimolecular processes. If higher concentrations were applied, the disproportionation reaction is induced to afford the deoxygenated dithiin and the thiophene as described originally by H. H. Szmant,$^{1)}$ although the rearranged product is still obtained in low yield. We have found that the thermal decompositions of 1a in methanol and acetonitrile with added pyridine show first order kinetics, giving the thiophene as a sole product due to extrusion of sulfur oxide. These results with respect to extrusion mechanism are to be published elswhere.

3) The IR, NMR, and mass spectra fully support the structures assigned to all new compounds.

   2b: yellow oil; NMR(CDCl$_3$) δ 6.13(1H, s), 7.26(4H, s), 7.35(4H, s), 9.34(1H, s); IR(neat) 1725 cm^{-1}; m/e 352,354,356(*ca.* 10:7:1, M$^+$), 323,325,327(*ca.* 10:7:1, M$^+$-CHO, base).

   2c: mp 114-115°C; NMR(CDCl$_3$) δ 2.30(3H, s), 2.26(3H, s), 6.14(1H, s), 7.05-7.40(8H, m), 9.29(1H, s); IR(nujol) 1710 cm^{-1}; m/e 312(M$^+$), 283(M$^+$-CHO, base).

   2d: yellow oil; NMR(CDCl$_3$) δ 3.79(6H, s), 6.02(1H, s), 6.75(2H, bd), 6.86(2H, bd), 7.25-7.40(4H, m), 9.29(1H, s); IR(nujol) 1720 cm^{-1}; m/e 344(M$^+$), 315(M$^+$-CHO, base).

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7) The possibility that 1a has decomposed prior to exposure to electron impact is ruled out because vapour phase thermolysis in VPC gave rise to the thiophene exclusively.

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