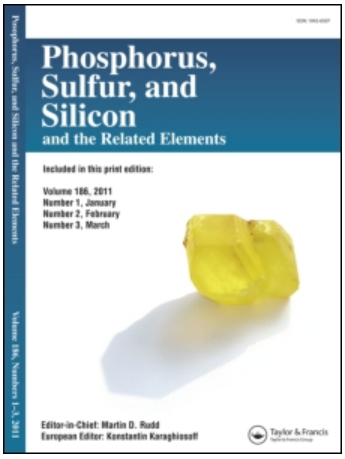

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THERMOLYSIS AND PHOTOLYSIS OF S-SUBSTITUTED 2,5-DIPHENYL-1,4-DITHIINS

Keiji Kobayashi[a]; Kiyoshi Mutai[a]
[a] Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo, Japan

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THERMOLYSIS AND PHOTOLYSIS OF S-SUBSTITUTED 2,5-DIPHENYL-1,4-DITHIINS

KEIJI KOBAYASHI and KIYOSHI MUTAI

Department of Chemistry, College of Arts and Sciences,
The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan

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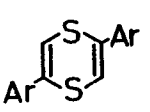
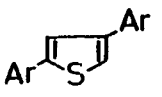
The thermolysis of 2,5-diphenyl-1,4-dithiin-1-oxide (**4**) in the liquid phase induced rearrangement to 2-formyl-2,4-diphenyl-1,3-dithiole (**7**) and extrusion of sulfur oxide to give 2,4-diphenylthiophene (**2a**) as well as deoxygenation to 2,5-diphenyl-1,4-dithiin (**1a**). Distribution among the three products was dependent on the initial concentration; low concentration suppressed the deoxygenation. For the formation of the thiophene occurrence of two mechanisms, one involving bimolecular disproportionation and another via unimolecular valence isomerization, was suggested by the kinetic study as well as the solvent effect. The photolysis of (**4**) afforded (**7**) and another 1,3-dithiole isomer, 2-benzoyl-4-phenyl-1,3-dithiole (**9**) which was not obtained in the thermolysis. The rearrangements are discussed in terms of a radical mechanism. In the thermolysis of 2,5-diphenyl-1,4-dithiin-1-(*N*-tosyl)imide (**6**), no rearrangements were observed and thiophene (**2a**) due to the extrusion of a thionitroso moiety was obtained together with the deoxygenated parent dithiin (**1a**). On the other hand, the photolysis of (**6**) resulted in ring transformation to a 1,3-dithiole compound.

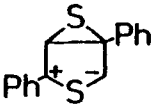
Thermal and photochemical extrusion reactions of sulfur heterocycles involving loss of sulfur, sulfur monoxide, and sulfur dioxide have been widely documented.[1] In particular, mechanistic details for the cheletropic decompositions of thiirane and its *S*-substituted derivatives have attracted considerable interest.[2] Our previous experimental work has provided a body of evidence that the thermolysis of 2,5-diphenyl-1,4-dithiin (**1a**) to yield 2,4-diphenylthiophene (**2a**) involves initial valence isomerization to a bicyclic thiirane compound such as (**3**).[3] In a continuing inquiry into the 1,4-dithiin ring system,[4] it seemed of interest to see whether a similar type



1a Ar = C_6H_5
1b Ar = C_6H_4-CH_3(p)



2a Ar = C_6H_5
2b Ar = C_6H_4-CH_3(p)



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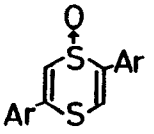
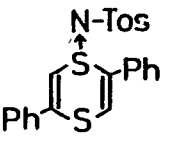


4 Ar = C_6H_5
5 Ar = C_6H_4-CH_3(p)



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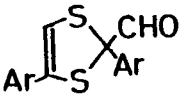


7 Ar = C_6H_5
8 Ar = C_6H_4-CH_3(p)

of valence isomerization could be effected on the thermolysis of this heterocycle having a substituent on a sulfur atom, namely the sulfoxide and the sulfilimine. Although the thermal decomposition of 1,4-dithiin-1-oxide has been known to give thiophene by the extrusion of a sulfur monoxide moiety,[5] there has been little study of the mechanistic aspect. With respect to sulfilimines, a variety of thermal reactions depending on the nature of the substituents on sulfur have been known,[6a] whereas the extrusion of a thionitroso fragment has rarely been observed.[6b] Thus, we have undertaken the investigation of the thermal behavior of 2,5-diphenyl-1,4-dithiin-1-oxide (**4**) and 2,5-diphenyl-1,4-dithiin-1-(*N*-tosyl)imide (**6**). In this paper we also report the results of the photolysis with the objective of comparison to the thermal reactions.

RESULTS AND DISCUSSION

Thermolysis of Sulfoxide (**4**)

Our present research began with a reinvestigation of the decomposition products. When a solution of (**4**) in acetonitrile (ca. 8×10^{-2} mol/l) was heated at 70°C for 50 min, quantitative decomposition of (**4**) was observed by high performance liquid chromatography (HPLC) of the reaction mixture. Chromatographic separation of the products on silica gel led to the isolation of thiophene (**2a**) and dithiin (**1a**) in 37 and 15% yields, respectively, as was anticipated from the earlier literature.[5] In addition, an isomeric product with molecular formula $C_{16}H_{12}OS_2$ was isolated in 19% yield. The structure of this unexpected product was elucidated on the basis of its spectral properties to be 2-formyl-2,4-diphenyl-1,3-dithiole (**7**).[7] The formation of (**7**) in the thermolysis of (**2a**) has previously been overlooked and represents a novel type of ring contraction.

Similarly, the thermal decomposition of 2,5-ditolyl-1,4-dithiin-1-oxide (**5**) afforded 2,4-ditolylthiophene (**2b**), 2,5-ditolyl-1,4-dithiin (**1b**), and 2-formyl-2,4-ditolyl-1,3-dithiole (**8**) in 45, 13, and 13% yields, respectively. Quantitative product analysis and kinetic measurements were carried out on thermolysis of (**5**), since the reaction mixture from (**5**) provided better separation of the HPLC peaks than the corresponding mixture from (**4**).

Distribution among the three products was affected by the initial concentration of sulfoxide (**5**), as shown in Table I.

TABLE I

Effect of the initial concentration of sulfoxide (**5**) on the product distribution of the thermolysis[a,b]

initial concentration (mol/l)	thiophene (**2b**) (%)	dithiin (**1b**) (%)	dithiole (**8**) (%)
5.13×10^{-3}	49	0	51
1.28×10^{-2}	46	6	48
3.43×10^{-2}	46	11	43
8.67×10^{-2}	57	20	23

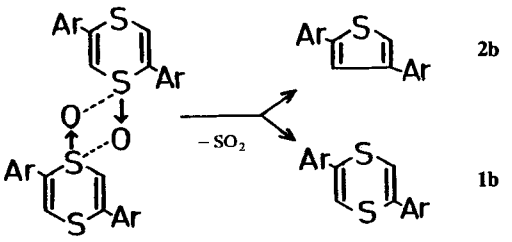
[a] The reactions were performed in acetonitrile at 70°C.
[b] Calculated from the peak intensities of HPLC corrected for the absorbances.

The deoxygenation to give (**1b**) increased with higher concentrations of (**5**), whereas an initial concentration lower than 5×10^{-3} mol/l gave no formation of (**1b**). These observations suggest that dithiin (**1b**) is not produced via a unimolecular process but is the result of the disproportionation by a bimolecular process with concurrent formation of thiophene (**2b**). As suggested earlier,[8] an association of two sulfoxide groups probably facilitates the loss of oxygen from one of the sulfoxide molecules, another molecule of (**5**) being converted into (**2b**) (Scheme 1). The sulfone of (**1b**) should not be involved as a precursor of the thiophene, as it is inert to thermolysis and gives no thiophene.[9]

The importance of association of the molecules for the deoxygenation was also supported by the solvent effect. In methanol (**5**) suffered the loss of sulfur monoxide and no dithiin was obtained. Coordination of the alcohol to the sulfoxide functionality might prevent the association of two molecules of (**5**), resulting in suppression of the disproportionation.

The observation that the yield of thiophene (**2b**) is always higher than that of dithiin (**1b**), regardless of the initial concentration, and that (**2b**) is still produced even though the solvation suppresses the formation of (**1b**), implies another mechanism leading to (**2b**) is operative, which requires no concomitant formation of (**1a**). Under the conditions of low initial concentration of (**5**), wherein (**1b**) is not formed, the thermolysis was followed by HPLC analysis. A typical profile is shown in Figure 1. The disappearance of the starting compound exhibits an induction period. It is obvious from the profile that the rearrangement to (**8**) is responsible for an induction period. This kinetic behavior is reminiscent of a radical mechanism for the isomerization to the 1,3-dithiole ring compound, which was suggested by the solvent effect as well; in carbon tetrachloride, the rearranged 1,3-dithiole (**8**) was the sole product, whereas in methanol, as was noted already, (**8**) was not obtained. Other than changing the solvent polarity, addition of excess triethylamine or pyridine to an acetonitrile solution of (**5**) resulted in the exclusive formation of (**2b**). These results can be rationalized by means of the solvation of the sulfoxide functionality, which might enhance the polarity of the S—O bond and adjacent C—S bonds, hence lower the homolytic reactivity of (**5**). Thus, solvation to the sulfoxide is unfavorable for both the deoxygenation and the rearrangement.

When the thermolysis was carried out in the presence of triethylamine and by using low concentration of (**5**), thiophene (**2b**) was the sole product, which should be formed by a different path from the disproportionation. Under those conditions, the rate of the thermolysis was measured by the HPLC analysis and was revealed to follow pseudo first-order kinetics. Kinetic measurements at three different tempera-



SCHEME 1

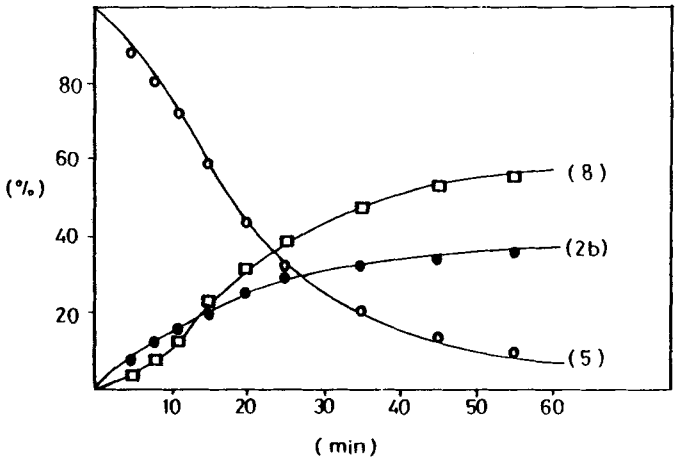


FIGURE 1 Product ratio vs. time plots for thermolysis of sulfoxide (5). Thermolysis was performed in acetonitrile at 70°C. Initial concentration of (5) is low enough to avoid the disproportionation. See text.

tures have allowed us to determine the activation parameters for the extrusion of sulfur monoxide from sulfoxide (**5**). The data are listed in Table II along with the activation data for the extrusion of sulfur from (**1b**).[3]

The negative entropy, in spite of the fragmentation reaction, is suggestive of a highly ordered transition state and precludes consideration of a simple ring opening as the rate-determining step. Thus we could assume the operation of valence isomerization to a bicyclic thiirane derivative, which would in turn collapse to the thiophene by cheletropic elimination of sulfur monoxide. The entropy value of the loss of sulfur monoxide from (**5**) is less negative than that of the loss of sulfur from (**1b**). This is probably owing to the coordination of triethylamine which was added to prevent the rearrangement; the amine would solvate the sulfoxide group extensively in the ground state.

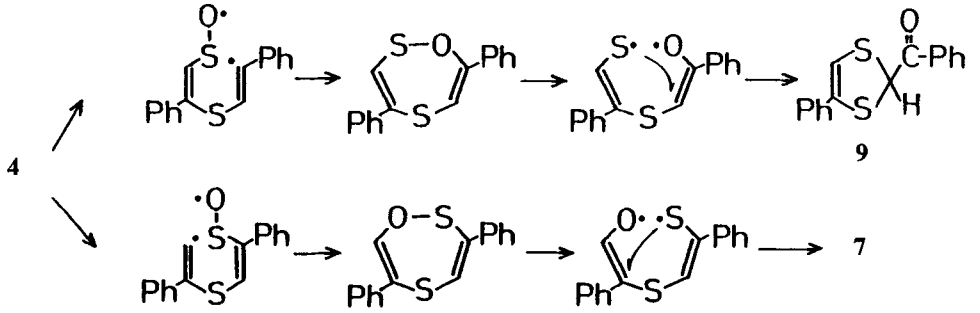
The ring transformation leading to 1,3-dithiole (**7**) or (**8**) seems most likely to occur by way of a cyclic sulfenate ester as an intermediate, which would generate the ring-opened diradical by O—S bond rupture followed by recyclization to give (**7**) (Scheme 2). The ring expansion of (**5**) to a cyclic sulfenate might involve a homolytic process as already noted. This type of an expansion of cyclic sulfoxide has been reported in a few cases[10] and has been more often encountered under the conditions of electron impact[11] and in photochemical processes.[12]

TABLE II

Activation parameters for the formation of thiophene (**2b**) by thermolysis of 1,4-dithiin (**1b**), sulfoxide (**5**) and sulfilimine (**6**)

	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (e.u)	solvent
1,4-dithiin (**1b**)[a]	21.6	−27.6	*o*-dichlorobenzene
sulfoxide (**5**)[b]	22.2	−9.8	acetonitrile
sulfilimine (**6**)	24.3	−10.6	*o*-dichlorobenzene

[a] See reference 3.
[b] In the presence of excess of triethylamine.



SCHEME 2

Photolysis of Sulfoxide (**4**)

A methanol solution of (**4**) was irradiated with a high pressure mercury lamp through a Pyrex filter under nitrogen gas. Photoproducts obtained by column chromatography were (**7**) and (**1b**) in 65 and 5% yields, respectively, as well as an alternative rearranged product, 2-benzoyl-4-phenyl-1,3-dithiole (**9**), in 9% yield. HPLC analysis of the product mixture indicated that (**7**) is a major photoproduct with a (**7**) : (**1a**) : (**9**) ratio of 79 : 8 : 13. A trace of (**2a**) was also detected. However, no photodimer was found in the products in contrast to the photolysis of the parent dithiin (**1a**).[13] The structural assignment of (**9**) was based upon microanalytical data and spectral properties.[14] As photochemical deoxygenation of sulfoxides has been known,[15] the most remarkable feature of the photolysis is the formation of two isomeric 1,3-dithioles. One of the isomers, (**7**), is essentially the same as the thermolysis product, indicating the mechanism is in line with the thermal rearrangement. Thus, in the photolysis either of two possible ring expansions might be considered to occur initially, probably by way of a radical path, to give rise isomeric cyclic sulfenates, each of which would afford different 1,3-dithioles (Scheme 2).

It is interesting to note that the mass spectrum of sulfoxide (**4**) exhibits abundant ions of m/e 255 (M^+—CHO), which must be formed in processes including a skeletal rearrangement to (**7**) preceding the loss of the CHO fragment. The possibility that the ring transformation took place prior to exposure to electron impact is ruled out because vapor-phase thermolysis in gas chromatography gave rise to thiophene (**2a**) exclusively. The ion of m/e 179 corresponding to the loss of C_6H_5CO from the parent ion was not observed, indicating the rearrangement to (**9**) does not occur under the conditions of electron impact. This behavior parallels the thermolysis rather than the photolysis.

Thermolysis of Sulfilimine (**6**)

The thermolysis of sulfilimine (**6**), which was obtained by treatment of (**1a**) with chloramine T, was carried out by heating in *o*-dichlorobenzene at 110°C. The reaction was complete within 1 h and then chromatographic separation of the pyrolysates afforded (**1a**), (**2a**), and tosylamine in 42, 45, and 13% yields, respectively. Attempts to trap the possible departing fragment of $C_7H_7SO_2$—N=S as an adduct to 2,3-dimethyl-1,3-butadiene or 1,3-cyclohexadiene were not effective, resulting in the detection of tosylamine and elemental sulfur as elimination fragments. The source of hydrogen in tosylamine is not considered as coming from the

TABLE III

Effect of the initial concentration of sulfilimine (**6**) on the product distribution of the thermolysis[a,b]

initial concentration (mol/l)	thiophene (**2a**) (%)	dithiin (**1a**) (%)
5.71×10^{-4}	51	49
1.37×10^{-3}	51	49
3.46×10^{-3}	49	51

[a] The reactions were performed in *o*-dichlorobenzene at 110°C.

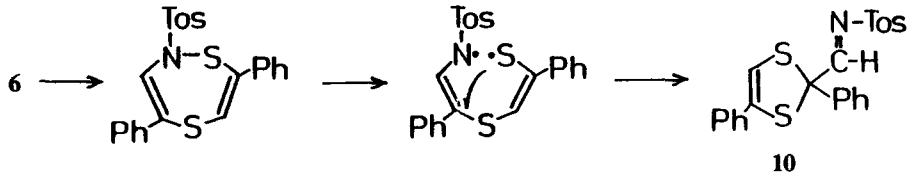
[b] Calculated from the peak intensities of HPLC corrected for the absorbances.

solvent,[16] since tosylamine was also obtained upon the thermolysis conducted in tetrachloroethylene. In spite of all attempts, the precursor of tosylamine could not be discovered and so the fate of thionitroso moiety remains ambiguous.

As clearly shown in Table III, the product composition was independent of the initial concentrations of (**6**), which is in contrast with the thermolysis of sulfoxide (**4**) and indicates that (**1a**) and (**2a**) are formed via independent unimolecular processes. It was found by the kinetic studies that the disappearance of the starting sulfilimine follows first-order kinetics. Throughout the reaction the product ratio of (**2a**) and (**1a**) was constant. This kinetic behavior is explained by simultaneous reactions each of which follows first-order kinetics. Thus, it was possible to estimate the activation parameters for the extrusion of thionitroso fragment to give rise thiophene (**2a**). The results are collected in Table II. The activation energies are similar in magnitude to those for the extrusion reaction in (**5**). This finding seems to indicate the involvement of the valence isomerization, as assumed in (**5**), in the rate-determining step preceding the fragmentation.

Photolysis of Sulfilimine (**6**)

A solution of (**6**) in acetonitrile was irradiated for ca. 1 h at 0°C. The photoproducts isolated by column chromatography on silica gel were the parent dithiin (**1a**) and the rearranged 1,3-dithiole (**7**) in 54 and 22% yields, respectively. The structure of (**7**) was consistent with its spectral characteristics and identical in all respects with the product obtained in the thermolysis of sulfoxide (**4**). The isolated (**7**), however, was revealed to be actually a secondary product derived via hydrolysis of the primary photoproduct; the nmr spectra of the photoreaction mixture which were taken immediately after evaporation of the solvent exhibited two distinct signals at 8.51 and 6.06 ppm but no signals due to (**7**) were observed. After chromatographic separation, these two signals disappeared and, instead, new signals ascribable to (**7**) appeared. A fow-field singlet at 8.51 ppm in the primary photoproducts is characteristic of a proton attached to an imino carbon. Thus, it can be suggested that the photolysis of (**6**) induced the rearrangement to the 1,3-dithiole ring compound (**10**), which would undergo facile hydrolysis during work-up procedures or chromatographic separation to afford (**7**). Attempts to isolate (**10**) were unsuccessful.



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SCHEME 3

The mechanism of the photochemical ring transformation of (**6**) would be rationalized by a scheme similar to that assumed in the sulfoxide photorearrangement; a cyclic sulfenamide may be involved as a transient species (Scheme 3). It is interesting to note that the sulfilimine undergoes only one of two possible rearrangements and affords no product corresponding to (**9**) in the photolysis of the sulfoxide.

EXPERIMENTAL

All melting points were uncorrected. ^{1}H NMR spectra were obtained on a Varian EM 390 spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded on a JASCO A-202 spectrophotometer. Mass spectra were measured on a Hitachi RMU-6MG spectrometer at an ionization potential of 70 eV. HPLC analyses were carried out with a JASCO FLC A10 high performance liquid chromatography with 4.6 mm × 250 mm columns packed with Finepack SIL C-18 and using UV detection at 254 nm or 305 nm. Acetonitrile containing 5% water was preferred as an eluent.

2,5-Diphenyl-1,4-dithiin-1-oxide (**4**) was prepared as described previously:[5c] mp 116°C (decomp) (lit,[5c] 109°C). IR (Nujol): 1025, 739, 690 cm^{-1}; NMR ($CDCl_3$): δ 7.26 (1 H, s), 7.35–7.55 (7 H, m), 7.72–7.76 (4 H, m); Mass (m/e): 284 (M^+, 3%), 268 (M^+—O, 27%), 255 (M^+—CHO, 29%), 236 (M^+—SO, 100%).

2,5-Ditolyl-1,4-dithiin-1-oxide (**5**). A solution of 2,5-ditolyl-1,4-dithiin (**1b**) (1.52 g, 5.13 mmol) in dichloromethane (40 ml) was added dropwise and stirring at 0°C to a solution of *m*-chloroperbenzoic acid (0.89 g, 5.13 mmol) in dichloromethane (10 ml). During 1 h of stirring at 0°C a yellow color of the solution disappeared, and then the solution was poured into ice water, and then extracted with dichloromethane. The extract was washed with an aqueous 0.1 N NaOH solution and then water. After the mixture was dried over anhydrous Na_2SO_4, the solvent was removed under reduced pressure and the crystalline residue was collected by filtration, washed with cold benzene to give (**5**) (1.25 g, 78%). A part of (**5**) was recrystallized from acetonitrile, by gently heating the solution below 40°C and cooling in a refrigerator to give colorless plates: mp 136°C (decomp). IR (Nujol): 1019, 808, 775 cm^{-1}; NMR ($CDCl_3$): δ 2.41(6 H, s), 7.24 (4 H, broad d, J = 7.5 Hz), 7.59 (4 H, broad d, J = 7.5 Hz), 7.45 (1 H, s), 7.30 (1 H, s); Mass (m/e): 312 (M^+, 2%), 296 (M^+—O, 42%), 283 (M^+—CHO, 34%), 264 (M^+—SO, 100%). Found: C, 69.50; H, 5.31; S, 20.75%. Calcd for $C_{18}H_{16}OS_2$: C, 69.23; H, 5.13; S, 20.51%.

2,5-Diphenyl-1,4-dithiin-1-(N-tosyl)imide (**6**). To a stirred suspension of 2,5-diphenyl-1,4-dithiin (**1a**) (2.18 g, 8.13 mmol) in methanol (300 ml) was added a solution of chloramine T (6.10 g, 21.6 mmol) in water (40 ml) and methanol (40 ml). The mixture was stirred at room temperature for 25 h. A white precipitate was extracted with four 200 ml portions of chloroform. Evaporation of the solvent under reduced pressure left a white solid, which was recrystallized from DMF under 60°C and dried to give (**6**) (2.38 g, 67%) as colorless needles: mp 185–186°C (decomp). IR (Nujol): 1281, 1138, 1088, 950, 962 cm^{-1}; NMR (DMSO-d_6): δ 3.27 (3 H, s), 7.12–7.57 (15 H, m with 6 distinguishable peaks), 8.42 (1 H, s); Mass (m/e): 268 (M^+-TosN), 236 (M^+-TosNS). Found: C, 63.12; H, 4.33; N, 3.26; S, 21.80%. Calcd for $C_{23}H_{19}NO_2S_3$: C, 63.15; H, 4.35; N, 3.20; S, 21.97%.

General Thermolysis Procedure. Thermolysis of (**4**) was carried out by heating a solution of (**4**) (1.03 g, 3.63 mmol) in acetonitrile (45 ml) for 50 min at 70°C using a thermostatically controlled oil bath. After the solvent was removed under reduced pressure, a small portion (ca. 0.5 ml) of the reaction mixture was withdrawn for quantitative HPLC analyses and the remainder was chromatographed on silica gel with benzene–hexane (gradient mixture) as eluent to give (**2a**) (0.32 g, 37%), (**1a**) (0.15 g, 15%), and 2-formyl-2,4-diphenyl-1,3-dithiole (**7**) (0.20 g, 19%). Physical properties of (**7**) are the following: yellow oil. IR (Neat): 2840, 2780, 1723 cm^{-1}; NMR ($CDCl_3$): δ 6.05 (1 H, s), 6.9–7.5 (10 H, m), 9.15 (1 H, s); Mass (m/e) 284 (M^+), 255 (M^+—CHO, base peak). Found: C, 67.32; H, 4.06; S, 22.51%. Calcd for $C_{16}H_{12}OS_2$: C, 67.70; H, 4.22; S, 22.53%.

In the same manner, (**5**) (0.89 g, 2.85 mmol) was converted into (**2b**)[17] (0.35 g, 45%), (**1b**) (0.11 g, 13%), and 2-formyl-2,4-ditolyl-1,3-dithiole (**8**) (0.12 g, 13%). The rearranged product (**8**) showed the following: mp 114–115°C. IR (Nujol): 1710, 813, 755 cm^{-1}; NMR ($CDCl_3$): δ 2.26 (3 H, s), 2.30 (3 H, s), 6.01 (1 H, s), 6.92 (2 H, broad d), 7.2–7.9 (6 H, m), 9.12 (1 H, s). Mass (m/e) 312 (M^+), 283 (M^+—CHO, base peak). Found: C, 69.24; H, 4.98; S, 20.33%. Calcd for $C_{18}H_{16}OS_2$: C, 69.19; H, 5.19; S, 20.52%.

Quantitative product analyses using a HPLC were made by comparison of the peak height of the products with those of standard solution (known concentrations) of authentic samples or purified products. The results are shown in Table I.

Thermolysis of (**6**) was carried out by heating a suspension of (**6**) (212 mg, 0.485 mmol) in *o*-dichlorobenzene (60 ml) at 110°C for 1 h. The resulting mixture was chromatographed on silica gel with hexane-benzene (gradient mixture) as eluent to afford (**2a**) (51.5 mg, 45%), (**1a**) (54 mg, 42%), and tosylamine (10 mg, 13%). The lower initial concentrations of (**6**) were employed for quantitative product analyses and kinetic measurements, which were examined by means of HPLC with UV detection at 305 nm.

Kinetic Measurements. The kinetics of the thermolyses of (**5**) and (**6**) were carried out by monitoring either the appearance of the thiophene or the disappearance of the starting *S*-substituted 1,4-dithiin. An aliquot of 0.5 ml of the mixture was withdrawn periodically and was transformed quickly to methanol (0.5 ml). The resulting solution was kept at −20°C and was subjected to HPLC analysis. Measurements were taken for more than 10 points of time up to 80–90% completion of the decomposition. For the thermolysis of (**5**) ca 10 molar equivalent of triethylamine was added and pseudo-first-order rate constants were obtained. The following temperature (accuracy of ±0.8°C) was utilized for obtaining activation parameters; 75, 90, and 110°C for (**5**); 90, 110, and 125°C for (**6**).

Photolysis Procedure. A 500 ml solution of (**4**) (150 mg, 0.53 mmol) in methanol (ca 1×10^{-3} mol/l) was irradiated, under nitrogen gas and at 0°C, with a 100 W high-pressure Hg lamp equipped with a Pyrex cooling jacket. After 30 min irradiation the photolysates solution was evaporated to about 5 ml and chromatographed on silica gel with benzene-hexane (gradient mixture) as eluent to give (**1a**) (7 mg, 5%), (**7**) (98 mg, 65%), and 2-benzoyl-4-phenyl-1,3-dithiole (**9**) (13 mg, 9%). The spectral data of (**9**) are the following: mp 144°C. IR (Nujol): 1688 cm^{-1}; NMR ($CDCl_3$): δ 6.15 (1 H, s), 6.22 (1 H, s), 7.2–7.7 (8 H, m), 7.95 (2 H, broad d); Mass (m/e): 284 (M^+), 179 (M^+—COC_6H_5, base peak). Found: C, 67.51; H, 4.16; S, 22.70%. Calcd for $C_{16}H_{12}OS_2$: C, 67.70; H, 4.22; S, 22.53%.

Irradiation of (**6**) (313 mg, 0.716 mmol) was carried out in acetonitrile (500 ml). After the evaporation of the solvent a portion of the residue was subjected to NMR measurement to reveal the involvement of a transient compound (**10**). The residue was chromatographed on silica gel using benzene–hexane (gradient mixture) as eluent to afford (**1a**) (103 mg, 54%) and (**7**) (88 mg, 22%).

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