

THE REARRANGED PRODUCTS IN THERMAL DECOMPOSITION OF 2,5-DIARYL-1,4-DITHIIN.  
EVIDENCE FOR VALENCE ISOMERIZATION OF 1,4-DITHIIN SYSTEM.

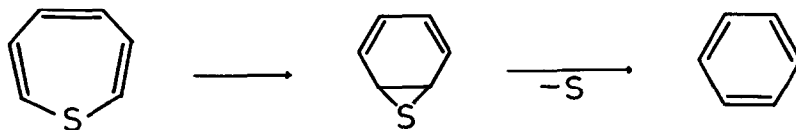
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Summary: Bis(2,4-diaryl-3-thienyl) disulfide was isolated in the thermal decomposition of 2,5-diaryl-1,4-dithiin. The formation of the rearranged product as well as the kinetic data suggest strongly the valence isomerization of 2,5-diaryl-1,4-dithiin in the course of the decomposition.

Thiepins undergo facile thermal elimination of sulfur to afford more stable ring system, i. e. benzene derivatives. There has been some indications for the existence of thianorcaradiene as an intermediate in sulfur extrusion,<sup>1,2)</sup> although it has not been isolated. In contrast to thiepin system, little is



known about thermal decomposition of 1,4-dithiin, which is also comprised of a cyclic 8  $\pi$ -electron system and eliminates sulfur readily upon heating. Valence isomerization has been assumed for the sulfur extrusion on the basis of stability of 2,5-disubstituted dithiins and of the position of sulfur eliminated.<sup>3)</sup> Crigg referred the extrusion reaction to thermal disrotatory electrocyclization and subsequent cheletropic elimination.<sup>4)</sup>

We report here the formation of rearranged products in the thermal decomposition of 2,5-diaryl-1,4-dithiin along with some kinetic data, which provide strong evidence for the participation of the valence isomer in the course of the extrusion reaction. Our report is the first example of the rearrangement in 1,4-dithiin ring system without loss of sulfur.<sup>5)</sup>

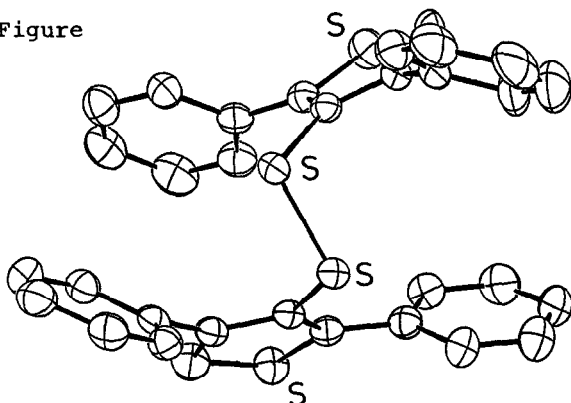
When 2,5-diphenyl-1,4-dithiin (1a) was heated in *o*-dichlorobenzene at 155°C for 15 hr, 2,4-diphenylthiophene (2a) was obtained in 47 % yield, as is anticipated. In addition, a yellow crystalline product was separated by column chromatography on alumina, m.p. 128-129 °C. MS: 267 ( $M^+$ /2). <sup>1</sup>H NMR(CDCl<sub>3</sub>):

$\delta$  7.04 (1H, s), 7.1-7.5 (10H, m). IR (nujol): 745, 695  $\text{cm}^{-1}$ . Its structure of bis(2,4-diphenyl-3-thienyl) disulfide (3a) was unambiguously established by the X-ray crystallographic study.

Crystal data:  $\text{C}_{32}\text{H}_{22}\text{S}_4$ , monoclinic, space group  $\text{P2}_1/\text{c}$ ,  $a=12.450$ ,  $b=20.486$ ,  $c=10.732$  Å,  $\beta=98.76^\circ$ ,  $U=2705.2$  Å<sup>3</sup>,  $Z=4$ ,  $D_{\text{obs}}=1.305$   $\text{gcm}^{-3}$ .

The structure was solved by the direct method and refinements proceeded by the block-diagonal least-squares calculations to  $R=0.058$  for 3471 observed reflections. A computer drawing of the molecular structure (excluding hydrogen) is shown in Figure. The S-S bond (2.06 Å) lies nearly perpendicular to the plane of each thiophene ring probably for the steric reason caused by the bulky phenyl substituents. The C-S-S-C dihedral angle<sup>6)</sup> and the average C-S-S angle is  $87.8^\circ$  and  $101.5^\circ$ , respectively. Thiophene rings adopt a trans conformation for each other with respect to the sulfur in the ring.<sup>8)</sup>

Figure



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Since no intermolecular reaction occurred between 2a and sulfur, the formation of 3a must obviously arise from the rearrangement of 1a; the rearrangement to thiophenethiol 4 followed by oxidation is most likely to lead to 3a, which has analogies in thiepin chemistry. Benzo[b]thiepin undergoes acid-catalyzed thermal isomerization to naphthalenethiol.<sup>2)</sup> Moreover, the formation of dinaphthyl disulfide has been reported.<sup>9)</sup>

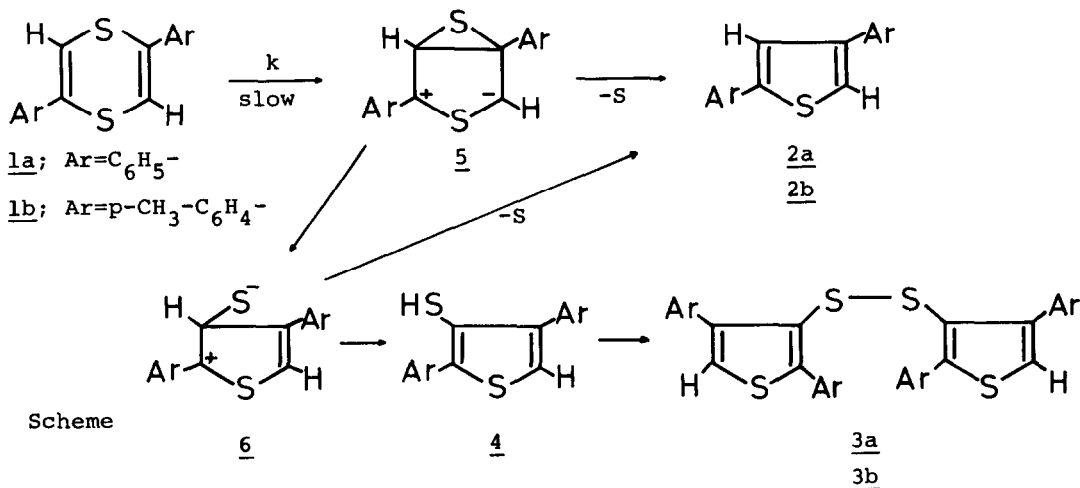


Table. Rate constants, activation parameters, and product ratios for the thermal decomposition of 2,5-di-p-tolyl-1,4-dithiin (1b).

| solvent           | T (°C) | $k \times 10^5$ (s <sup>-1</sup> ) | $\Delta H^\ddagger$ , $\Delta S^\ddagger$ a)                            | <u>2b</u> : <u>3b</u> <sup>b)</sup> |
|-------------------|--------|------------------------------------|---|-------------------------------------|
| o-dichlorobenzene | 145    | 4.06                               | $\Delta H^\ddagger = 21.6$ kcal/mol<br>$\Delta S^\ddagger = -27.6$ e.u. | 76 : 24                             |
|                   | 154    | 6.54                               |   | 82 : 18                             |
|                   | 165    | 13.87                              |   | 97 : 3                              |
| xylene            | 154    | 1.44                               |   | 100 : 0                             |

a) calculated for 25 °C. b) relative yield.

The rate of thermal decomposition of 2,5-di-p-tolyl-1,4-dithiin (1b) was followed by means of a high performance liquid chromatography (HPLC) with a UV spectrometer as the detector.<sup>10)</sup> The dithiin afforded the thiophene 2b and, depending on the reaction conditions, the corresponding disulfide 3b along with other minor by-products as detected by HPLC. 3b: m.p. 183-185 °C. MS: 295 (M<sup>+</sup>/2). <sup>1</sup>H NMR(CDCl<sub>3</sub>):  $\delta$  7.65(6H, s), 7.64(6H, s), 3.16(2H, s), 7.02(16H, m). IR(nujol): 805, 743 cm<sup>-1</sup>.

The kinetic data and product ratios are listed in Table. The satisfactory first-order kinetics were observed in each reaction condition, whatever the product distribution. For example, at 154 °C in o-dichlorobenzene first-order behavior was observed for 78 % conversion with a correlation coefficient of 0.9986. These results indicate that two types of the reactions, namely, decomposition with loss of sulfur and rearrangement without loss of sulfur, proceed via a common intermediate and its formation is the rate-determining step. The substantial negative activation entropy implies a highly ordered transition state. The value obtained here is comparable with those reported for the thermal decomposition of a benzo[b]thiepin ring and its rearrangement as well.<sup>2)</sup> Thus the rigid bicyclic thirane 5 due to valence isomerization of 1b seems to be the most reasonable common precursor of 2b and 3b.

A large rate enhancement in the polar solvent (relative rate at 154 °C = 1 : 4.5) further substantiates the formation of 5 as a common rate-determining intermediate because 5 contains a 1,3-dipole. Another dipole 6 may be involved in the process to the rearranged product as depicted in Scheme. The product ratios of 2b and 3b would be governed by the free energy difference between two competing processes leading to 2b and 6, respectively. The solvent effect on the product ratio shows that the formation of the disulfide 3b is preferred in the polar solvent. This can be accounted for by the reaction sequence given in Scheme, in which the transition state leading to 6, hence to 3b, is more polar as compared with that to 2b.

It is interesting to note that the product ratio depends also on the reaction temperature. This observation seems to be ascribable to the difference of entropy factors between the competing reactions to give 2b and 6, the latter leading to 3b finally.<sup>11)</sup> The extrusion of sulfur resulting in production of two molecules would demand more activation entropy than simple one-bond cleavage leading to 6. Thus employing higher temperature increases the formation of 2b. Another path to 2b, which bears a similar entropy requirement, is possible to serve to increase 2b; as predicted by Woodward-Hoffmann rules for the decomposition of thiirane, the stepwise desulfurization to give 2b via 6 must be also involved.

#### References and Notes

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- 6) The empirical rule<sup>7)</sup> between the S-S dihedral angle and the S-S bond length in aromatic disulfides applies successfully in this disulfide.
- 7) L. S. Higashi, M. Lundeen, and K. Seff, *J. Am. Chem. Soc.*, **100**, 8101 (1978).
- 8) List of atomic parameters and structure factors will be supplied on request by K. K.
- 9) H. Hofman and A. Molnar, *Tetrahedron Lett.*, **1977**, 1985.
- 10) Use of 1b for kinetic studies is for experimental reason. HPLC analysis of the reaction mixture from 1a was unsuccessful with poor separation.
- 11) As minor products other than 2b and 3b are not taken into account, argument based on the product ratio of 2b:3b may not be emphasized. However,  $\Delta\Delta G^\ddagger[\Delta G^\ddagger(2b) - \Delta G^\ddagger(6)]$  is estimated from  $\Delta\Delta G^\ddagger = -RT\ln[2b/(2 \times 3b)]$  and  $\Delta\Delta S^\ddagger[\Delta S^\ddagger(2b) - \Delta S^\ddagger(6)]$  is shown to be, at least, positive.

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