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REGIOCHEMISTRY OF THERMAL EXTRUSION OF SULFUR FROM 2,6-DIARYL-1,4-DITHIINS YIELDING 2,5- AND 3,4-DIARYLTHIOPHENES

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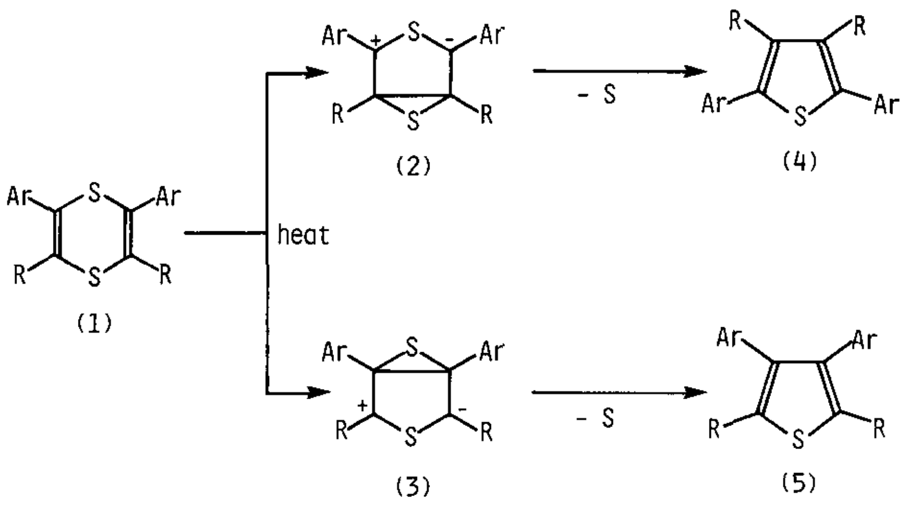
Abstract —— The predominant formation of 2,5-diarylthiophenes over the 3,4-diaryl isomers by thermolyses of a series of 2,6-diaryl-1,4-dithiins supports that this sulfur extrusion reaction proceeds by the mechanism involving the valence isomerization to thiocarbonyl ylide intermediate possessing a thiirane structure in the rate-determining step.

Substituted 1,4-dithiins undergo the thermal extrusion of sulfur to afford the corresponding thiophenes. The proposed mechanism for this reaction involves the valence isomerization to thiocarbonyl ylide intermediate possessing a thiirane structure in the rate-determining step.[1-3] Sulfur is cheletropically extruded from this intermediate to give thiophenes. Kinetic study on the thermolysis of 2,5-diaryl-1,4-dithiins provides some supporting evidences for this mechanism.[4] Recently we reported a convenient preparation of 2,6-diaryl-1,4-dithiins (**1**) from diketo sulfides.[5] If the above mechanism is truly operative in the thermolysis of the dithiins **1**, two isomeric thiocarbonyl ylides (**2**) and (**3**) are probable intermediates. The ylides **2** whose cationic and anionic centers stabilized by aryl groups are stabler than the ylides **3**, and therefore 2,5-diarylthiophenes (**4**) resulting from **2** should be predominantly formed over the 3,4-diaryl isomers (**5**). Keeping this in mind, we investigated the thermolysis of the dithiins **1**.

When 2,6-diphenyl-1,4-dithiin (**1a**) was heated in refluxing *o*-dichlorobenzene for 60 min, **1a** was completely consumed and afforded 2,5- and 3,4-diphenylthiophenes (**4a**) and (**5a**) in a 72% total yield in a ratio of 12:1. Shortening the refluxing time to 20 min afforded **4a** and **5a** in a ratio of 12:1 with 20% recovery of **1a**.[6,7]



This shows that the isomerization of the resulting thiophene to its positional isomers is negligible under the applied conditions. A series of **1** were similarly heated in refluxing *o*-dichlorobenzene until they were completely consumed. The isomeric mixtures of thiophenes **4** and **5** were obtained in good yields. The isomer ratio was determined by HPLC (see Table 1).[8] Thiophenes **4** were easily isolated in pure forms by recrystallizing the isomeric mixtures. All of the authentic samples of **5** were obtained by an independent synthesis.[9] Predominant formation of **4** over **5** is in harmony with the mechanism involving the formation of thiocarbonyl ylides **2** and **3** in the rate-determining step. The small change of the isomer ratio with the change of aryl group implies that the electron-donating aryl group stabilizes the cationic center of **2**, but destabilizes its anionic center, and does not contradict the above mechanism. The smallest isomer ratio observed in entry 5 mainly comes of the destabilization of the transition state leading to **2** by steric repulsion between two ethyl groups.

Table 2 shows the results of the thermolysis of **1a** at refluxing temperature in various solvents which have similar boiling points but have different polarities. The isomer ratio increases with the increase of the polarity of the solvents. Although this solvent effect cannot be fully explained at present, it is in harmony with a mechanism involving the formation of a polar intermediate such as thiocarbonyl ylide.

Trapping of the thiocarbonyl ylide with a dipolarophile such as dimethyl acetylenedicarboxylate (DMAD) failed. The dithiin **1a** directly reacted with DMAD as observed in the reaction of DMAD with 2,5-diphenyl-1,4-dithiin.[10] The thermolysis of 1a in refluxing styrene brought about the polymerization of styrene considerably to give the thiophenes 4a and 5a in decreased yields.

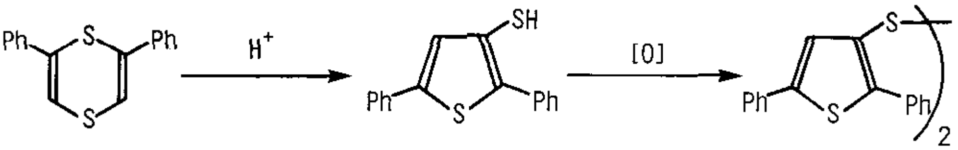
The thermolysis of 1a in *o*-dichlorobenzene affords a small amount of the disulfide (6)[11] in addition to the thiophenes 4a and 5a. The yield of 6 increased to 80% with the decreased yields (10%) of 4a and 5a, when a solution of 1a in decane was heated at 180 °C in a sealed glass tube. The disulfide 6 results from the oxidation of the thiol (7) which may be formed by an acid-catalyzed rearrangement of 1a. Hydrogen sulfide (easily detected by its characteristic smell) formed from decane and sulfur produced from 1a may act as an acid catalyst in this case. In fact, when a solution of 1a in *o*-dichlorobenzene was heated in the presence of a catalytic amount of *p*-toluenesulfonic acid, chromatographic workup gave the disulfide 6 in 85% yield, while the extraction of the reaction mixture with 2N-KOH followed by acidification allowed the isolation of the thiol 7[12] in 68% yield. Structure of 7 was determined by its conversion into 4a by treatment with Raney nickel (W-2) at room temperature in ethanol.

Table 1 Thermolysis of a Series of 2,6-Diaryl-1,4-dithiins (1) in Refluxing *o*-Dichlorobenzene

Entry	Ar	R	Yield of 4 + 5 (%)	Isomer Ratio 4/5
1	*p*-MeOC_6H_4	H	80	15
2	2-Thienyl	H	70.5	13
3	p-MeC_6H_4	H	73	13
4	C_6H_5	H	72	12
5	C_6H_5	C_2H_5	92	8.5

Table 2 Thermolysis of 2,6-Diphenyl-1,4-dithiin (1a) in Various Solvents at Their Refluxing Temperature

Solvents	Yield of 4a + 5a (%)	Isomer Ratio 4a/5a
Decane	87	7
1,2,3-Trimethylbenzene	78.5	8
Indane	58	9
o-Dichlorobenzene	72	12
Benzonitrile	85	15



(1a) (7) (6)

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6. The dithiin **1a** exists in two crystalline forms (polymorphism). One is long orange needles melting at 62-63 °C as previously reported[5] and the other is bright yellow needles melting at 79-80 °C.
7. The original solution of **1a** is yellow. The solution turns red on heating and then becomes pale yellow on the complete consumption of **1a**. The similar change of the color was observed in the thermolysis of other 2,6-diaryl-1,4-dithiins. The cause of this phenomenon is unknown at present.
8. Isomers **4** and **5** could be isolated in pure forms by column chromatography on alumina. The isomer ratio based on the isolated thiophenes is in good agreement with that obtained by HPLC.
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11. **6**: yellow prisms (from cyclohexane); mp 112-113 °C; Mass spectrum, m/e 534 (M^+); ^{1}HNMR ($CDCl_3$) δ 7.0-7.5 (complex multiplet). Found: C, 71.86; H, 4.16; S, 23.98%. Calcd for $C_{32}H_{22}S_4$: C, 71.87; H, 4.15; S, 23.87%.
12. **7**: mp 46.5-48.5 °C (from hexane); IR (KBr) 2550 cm^{-1} (SH); ^{1}HNMR ($CDCl_3$) δ 3.33 (1H, s, SH, disappears on addition of D_2O), 7.00 (1H, s), 7.0-7.6 (10H, m).

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