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FORMATION OF 2,5-DIARYL-1,3-DITHIOLYLIUM-4-OLATE IN THERMAL REACTION OF 4-ARYL-1,3,2-OXATHIAZOLYLIUM-5-OLATE

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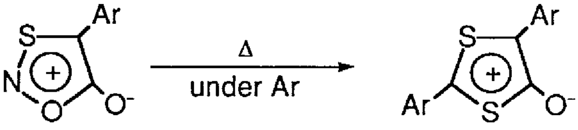
Abstract: The reflux of a meso-ionic compound, 4-aryl-1,3,2-oxathiazolylium-5-olate (**1**), in toluene, chlorobenzene, or xylene gives another meso-ionic compound, 2,5-diaryl-1,3-dithiolylium-4-olate (**2**), by a radical mechanism

Meso-ionic compounds have been studied extensively because of their unique electronic structures and reactivities.[1,2] The photochemical behavior of a series of meso-ionic compounds, 4-aryl-1,3,2-oxathiazolylium-5-olate (**1**), have attracted considerable interest. The photolysis of **1** proceeds by two pathways. One is the formation of a bicyclic system followed by the elimination of CO_2 to generate arenecarbonitrile sulfide *via* arylthiazirine and ultimately to give arenecarbonitrile and elemental sulfur (path A).[3,4] In the other process aryl(nitrosothio)ketene is produced by ring-opening of **1** (path B).[5] In contrast with the detailed studies on the photolysis, the thermolysis of **1** has been scarcely reported.

Here, we report the thermolysis of meso-ionic compound **1** to give another meso-ionic compound, 2,5-diaryl-1,3-dithiolylium-4-olate (**2**), as the main product.

When a solution of the meso-ionic 4-phenyl-1,3,2-oxathiazolylium-5-olate (**1a**)[6] was refluxed in xylene under Ar atmosphere, the yellow solution gradually turned violet, finally giving 2,5-diphenyl-1,3-dithiolylium-4-olate (**2a**)[7] in 26% yield.



1a-c **2a-c**

a: Ar= C_6H_5
b: Ar=2,3,4-$(CH_3O)_3C_6H_2$
c: Ar=4-BrC_6H_4

The reactions using meso-ionic 4-(2,3,4-trimethoxyphenyl)-1,3,2-oxathiazolylium-5-olate (**1b**)[6] and 4-(4-bromophenyl)-1,3,2-oxathiazolylium-5-olate (**1c**)[6] gave the products (**2b**)[8] and (**2c**),[9] respectively. These products are the same type as **2a** (Table 1). The substituent groups in **1** have a slight effect on the yield of **2**.

Table 1. Formation of **2** in Thermolysis of **1**.

1	Solvent	Temp. /°C	Time/h	Yield of **2**†/%
1a	Xylene	140	3	26
1a	Benzene	80	10	0††
1a	Toluene	110	5	10
1a	Chlorobenzene	132	4	22
1b	Xylene	140	3	18
1c	Xylene	140	3	20

† The yields of **2** were calculated on the assumption that two moles of **1** give one mole of **2**

†† Most of **1a** was recovered

The reaction of **1a** does not proceed at 80 °C under reflux in benzene. However, under reflux at temperatures higher than 110 °C, the reaction does occur. As the reaction temperature is raised, the rate of reaction and the yield of **2a** increase (Table 1).

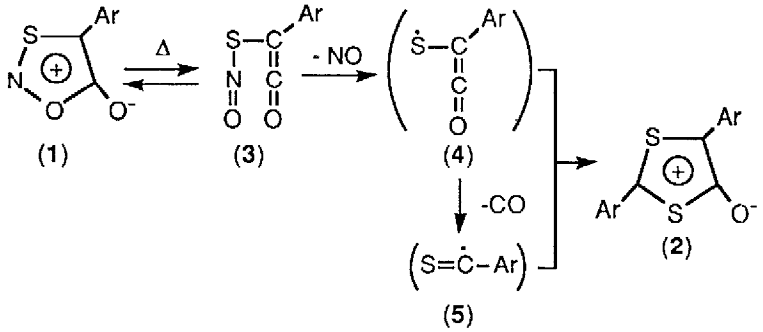
The formation of arenecarbonitrile is conceivable. However, benzonitrile was detected in only 1% yield in the reaction of **1a** in xylene. This suggests that benzonitrile sulfide is not generated in the thermolysis of **1** unlike in the photolysis (path A). Among byproducts,

The formation of **2** was inhibited by radical scavengers. Under O_2 bubbling, meso-ionic compound **2** was not formed, although the reactant **1** was not recovered. In the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), **2** was not formed. Therefore, the formation of **2** proceeds by a radical mechanism.

Although the thermolysis of **1** has not yet been clarified, it has been reported that analogous meso-ionic oxazolylium-5-olate gives ketene by ring-opening on thermolysis.[10,11] In the thermolysis of **1**, ring-opening may occur. In order to confirm the generation of (nitrosothio)ketene (**3**) in the thermolysis of **1**, 1-hexanol was added as a ketene trap in the thermolysis of **1a**. The yellow solution of **1a** turned colorless, and the ketoester was detected by MS. This result gives evidence for the generation of (nitrosothio)ketene.

A postulated mechanism for the formation of **2** is shown in Scheme 1.

Scheme 1



On thermolysis, the ring of **1** opens to give (nitrosothio)ketene (**3**). Then, with the elimination of NO, ArCSCO radical (**4**) is generated. Further, ArCS radical (**5**) is generated *via* the elimination of CO. In fact, the evolution of NO and CO was detected by gas analysis. The combination of radicals **4** and **5** would give the meso-ionic compound **2**.

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6. 4-Phenyl-1,3,2-oxathiazolylium-5-olate (**1a**) was synthesized according to the method of reference 3.

4-(2,3,4-Trimethoxyphenyl)-1,3,2-oxathiazolylium-5-olate (**1b**) was prepared by the method of Gotthardt *et al.* (Götthardt, H.; Reiter, F; Kromer, C., *Ann. Chem.* **1981**,1025-1034).

4-(4-Bromophenyl)-1,3,2-oxathiazolylium-5-olate (**1c**) was prepared by the method of reference 3.

7. 2,5-Diphenyl-1,3-dithiolylium-4-olate (**2a**) (mp 150-151 °C) was identified by the accordance of mp, NMR, MS, and UV-Vis. spectra of authentic sample prepared by the method of Gotthardt *et al.* (Götthardt, H.; Weisshuhn, M. C.; Christl, B., *Chem.Ber.* **1976**, 109, 740-752.). As an isomeric byproduct, only 4,5-diphenyl-1,2-dithiol-3-one was also obtained (yield < 4%).
8. 2,5-Bis(2,3,4-trimethoxyphenyl)-1,3-dithiolylium-4-olate (**2b**): mp 119-120 °C; Anal. Found: C, 55 60; H, 4.90%. Calcd for $C_{21}H_{22}O_7S_2$: C, 55.99; H,4.92%, MS (70 eV) *m/z* (rel intensity) 450(M+; 18), 358(5), 211(100), and 167(10); ^1H NMR (270 MHz, $CDCl_3$) δ=8.06(1H, d, *J*= 9 Hz, Ph), 7.39(1H, d, *J*= 9 Hz, Ph), 6 77(1H, d, *J*= 9 Hz,Ph), 6.74 (1H, d, *J*= 9 Hz, Ph), 4.06(3H, s, CH_3O), 3.93(3H, s, CH_3O), 3.92(3H, s, CH_3O), 3 91(6H, s, $2CH_3O$),and3.89(3H,s,CH_3O); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=182.1(C=O), 150.0(SCS),109.6 (CS), 155.7(Ph), 152.4(Ph), 150.7(Ph), 149.3(Ph), 142.5(Ph), 142.1 (Ph), 123.3(Ph), 122 3 (Ph), 119.7(Ph), 119.0(Ph), 108 1(Ph), 107.9(Ph), 61.0(CH_3O), 60.9(CH_3O), 60.6(CH_3O), 60 4(CH_3O), 56.3(CH_3O), and 56.1(CH_3O); UV-Vis. (CH_2Cl_2) λ_{max}(nm) 552(logε 3.92), 290(3.99), and 228(4.19); IR (KBr) 1582(C=O) and 798 cm^{-1}
9. 2,5-Bis(4-bromophenyl)-1,3-dithiolylium-4-olate (**2c**)· mp 213-215 °C; Anal. Found. C,42.52; H, 1.98%. Calcd for $C_{15}H_8Br_2OS_2$: C,42.08; H,1.88%; MS (70eV) *m/z* (rel. intensity) 430(M+;15), 428(M+,28), 426(M+13), 338(10), 336(20), 334(10), 201(100), 199(99), and 120(56); ^1H NMR (270MHz, $CDCl_3$) δ=7.73(2H, d, *J*=8.85 Hz, Ph), 7.60(2H, d, *J*=8.85 Hz, Ph), 7 50(2H, d, *J*=8.85 Hz, Ph), and 7.49(2H, d, *J*=8.85 Hz, Ph); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ=181.2(C=O), 151.8(CSC), 115.1(CS), 133 0(Ph), 132.1(Ph), 130.8(Ph), 130.7 (Ph), 129.7(Ph), 128.3(Ph), 127.2(Ph), and 126.4(Ph); UV-Vis. (CH_2Cl_2) λ_{max}(nm) 557 (logε 3.72), 287(3 83), 255(3.72), and 228(3.75) ; IR(KBr) 1584(C=O), 1568, and 804 cm^{-1}.
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