

SYNTHESIS AND REACTIONS OF 2-ARYL-1,3-OXATHIOLIUM SALTS<sup>1</sup>

Kentaro Hirai\* and Teruyuki Ishiba

Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka, 553 Japan

A convenient method for the preparation of 2-aryl-1,3-oxathiolium salts and their conversion into thiophene derivatives are described.

We recently reported the synthesis of 2-dialkylamino-1,3-oxathiolium salts (I) and their conversion into a number of heterocyclic compounds.<sup>2-6</sup> An aryl group substituted at the C-2 position of 1,3-oxathiolium cation is expected to stabilize the cation by conjugation. Recently, Hartmann reported the synthesis of 2-aryl-1,3-oxathiolium salts (II) and the reactions of (II) with nucleophilic reagents.<sup>7-9</sup> These results prompted us to report an alternative method for the preparation of (II) and the reaction of (II) with some active methylene compounds.

Thiolester (III) was prepared by the reaction of potassium thiolbenzoate (IV) and phenacyl bromide (IIIa: mp 82-83°, IIIb: mp 101-103°, IIIc: mp 106-109°).<sup>10</sup> Cyclization was carried out by dissolving (IIIa, b, c) in conc. H<sub>2</sub>SO<sub>4</sub>.<sup>11</sup> Addition of AcOEt to this solution separated 2-aryl-1,3-oxathiolium hydrosulfate which was converted into the perchlorate by addition of 70% HClO<sub>4</sub> in CH<sub>3</sub>CN suspension. The perchlorates

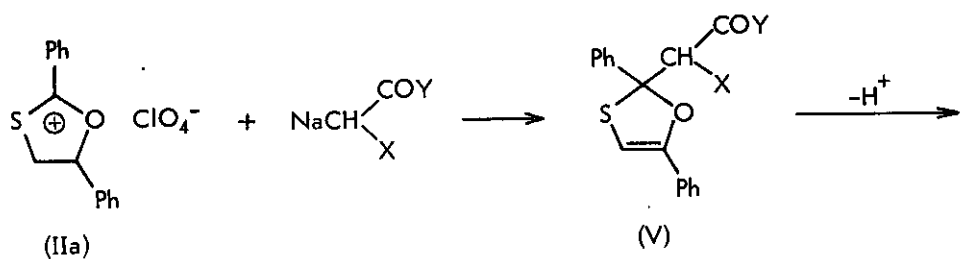


(IIa, b, c) were stable yellow crystals. Their physicochemical properties are listed in Table.

Reaction of perchlorate (IIa) with the sodium salt of deoxybenzoin in tetrahydrofuran gave the C-2 adduct (Va) (40%), colorless prisms, mp 176-177°:  $\delta$  (CDCl<sub>3</sub>): 5.67 and 5.70 (methine protons);  $\nu_{\max}$ : 1670 cm<sup>-1</sup> (C=O). Treatment of (Va) with NaOEt in EtOH gave thiophene (VIIIa) (94%), colorless needles, mp 164-165°:  $\lambda_{\max}$  (EtOH): 240, 261<sup>sh</sup>, and 331 nm (log  $\epsilon$  4.47, 4.28, and 4.09);  $\nu_{\max}$ : 1649 cm<sup>-1</sup> (C=O). Treatment of (VIIIa) with *t*-BuOK-H<sub>2</sub>O-DMSO gave benzoic acid and 2,3,4-triphenylthiophene (IXa), colorless needles, mp 209-211°,<sup>12</sup> in 95% yield. Analogous reaction of perchlorate (IIa) with sodium salt of acetylacetone in tetrahydrofuran gave thiophene (VIIIb) (91%), colorless prisms, mp 72-73°:  $\lambda_{\max}$  (EtOH): 260 and 313 nm (log  $\epsilon$  4.26 and 4.18);  $\nu_{\max}$ : 1687 (CH<sub>3</sub>CO) and 1636 cm<sup>-1</sup> (PhCO);  $\delta$  (CDCl<sub>3</sub>): 2.12 (4-CH<sub>3</sub>) and 2.40 (3-CH<sub>3</sub>CO). Treatment of (VIIIb) with *t*-BuOK-H<sub>2</sub>O-DMSO also gave benzoic acid and thiophene (IXb) (78%), oil:  $\lambda_{\max}$  (EtOH): 234, 262, and 294 nm (log  $\epsilon$  4.04, 3.98, and 3.75);  $\delta$  (CDCl<sub>3</sub>): 2.05 (3-COCH<sub>3</sub>), 2.28<sup>d</sup> (J = 1 Hz, 4-CH<sub>3</sub>), and 6.85<sup>q</sup> (J = 1 Hz, 5-H).

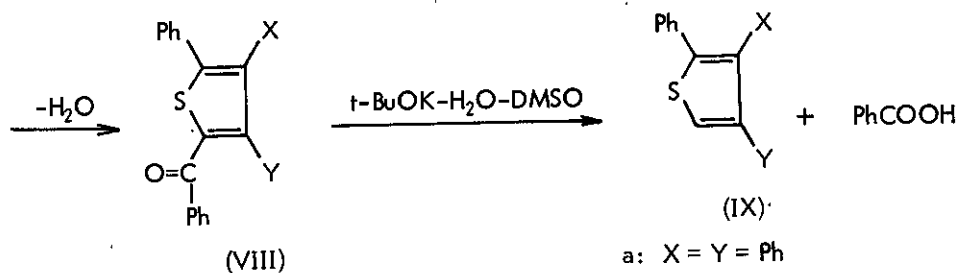
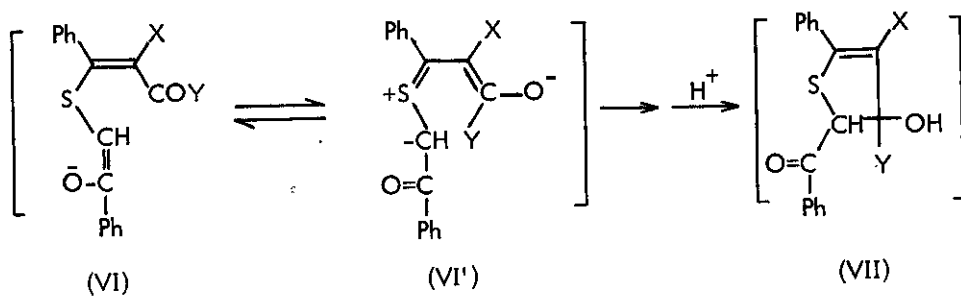
When perchlorate (IIa) was allowed to react with the sodium salt of benzoylacetone in tetrahydrofuran, a mixture of the C-2 adduct (Vb) (17%), colorless prisms, mp 138-139°:  $\delta$  (CDCl<sub>3</sub>): 1.72 (CH<sub>3</sub>CO), 5.07 (CH<), and 5.30 (CH=), and thiophene (VIIIc) (20%), colorless plates, mp 138-139°:  $\lambda_{\max}$  (EtOH): 237, 262<sup>sh</sup>, and 319 nm (log  $\epsilon$  4.36, 4.29, and 4.11);  $\nu_{\max}$ : 1697 (CH<sub>3</sub>CO) and 1644 cm<sup>-1</sup> (PhCO);  $\delta$  (CDCl<sub>3</sub>): 1.92 (CH<sub>3</sub>CO), was obtained. The C-2 adduct (Vb) was easily converted in 90% yield into thiophene (VIIIc) by treatment with NaOEt or pyridine.

Ketone cleavage of (VIIIc) was carried out using *t*-BuOK-H<sub>2</sub>O-DMSO to give



a: X = Y = Ph

b: X = COCH<sub>3</sub>, Y = Ph



a: X = Y = Ph

b: X = COCH<sub>3</sub>, Y = CH<sub>3</sub>

c: X = COCH<sub>3</sub>, Y = Ph

a: X = Y = Ph

b: X = COCH<sub>3</sub>, Y = CH<sub>3</sub>

c: X = COCH<sub>3</sub>, Y = Ph

d: X = COPh, Y = CH<sub>3</sub>

Scheme

thiophene (IXc) (96%), pale yellow pillars, mp 114°;  $\lambda_{\max}$  (EtOH): 243 and 295<sup>sh</sup> nm (log  $\epsilon$  4.42 and 3.75). The ir spectrum of (IXc) showed C=O stretching of the CH<sub>3</sub>CO group at 1693 cm<sup>-1</sup> and the nmr signals due to 3-COCH<sub>3</sub> and ring C-5 protons appeared at  $\delta$  2.07 and 7.19 as singlets, respectively. If a methyl group is attached at the C-4 position of the thiophene ring, the C-5 proton should appear as a quartet by an adjacent C-4 methyl group.<sup>3</sup> These results exclude the possibility of (IXd) arising from condensation in another direction. This is in sharp contrast with the direction of ring closure in the reaction of (I) with benzoylacetone, in which 2-dialkylamino-3,5-dibenzoyl-4-methylthiophene was obtained.<sup>3</sup>

The reaction pathway may be rationalized as indicated in scheme, and 1,5-cyclization<sup>13, 14</sup> of the sulfonium ylide intermediate (VI': X = COCH<sub>3</sub>, Y = Ph) gives dihydrothiophene (VII: X = COCH<sub>3</sub>, Y = Ph) from which loss of H<sub>2</sub>O yields thiophene (VIIIc).

## REFERENCES AND NOTES

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