SYNTHESIS AND REACTIONS OF 2-ARYL-1,3-OXATHIOLIUM SALTS[1]

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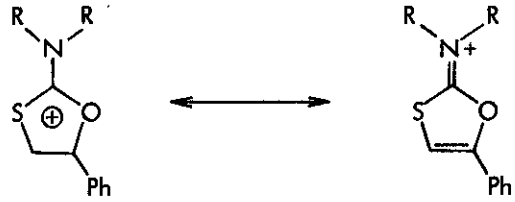
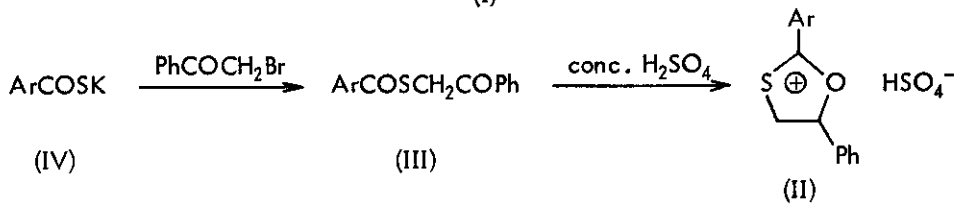
A convenient method for the preparation of 2-aryl-1,3-oxathiolium salts and their conversion into thiophene derivatives are described.

We recently reported the synthesis of 2-dialkylamino-1,3-oxathiolium salts (I) and their conversion into a number of heterocyclic compounds.[2-6] 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.[7-9] These results prompted us to report an alternative method for the preparation of (II) and the reaction of (II) with some active methylene compounds.

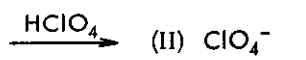
Thiolester (III) was prepared by the reaction of potassium thiolbenzoate (IV) and phenacyl bromide (IIIa: mp 82-83°, IIIb: mp 101-103°, IIIc: mp 106-109°).[10] Cyclization was carried out by dissolving (IIIa, b, c) in conc. H_2SO_4.[11] Addition of AcOEt to this solution separated 2-aryl-1,3-oxathiolium hydrosulfate which was converted into the perchlorate by addition of 70% $HClO_4$ in CH_3CN suspension. The perchlorates



(I)



(IV) (III) (II)



a: Ar = C_6H_5; b: Ar = C_6H_4-MeO-p; c: Ar = C_6H_4-Cl-p

Table. 2-Aryl-1,3-oxathiolium (II) perchlorate

	Ar	M.p. (°C) (decomp.)[a]	Yield (%)	$\lambda_{max.}$ (CH_2Cl_2) nm (log ϵ)	δ (CF_3COOD) Hetero ring proton
IIa	C_6H_5	217-218[b]	50	273, 285[sh], 387[e] (4.16, 4.12, 4.20)	8.12[h]
IIb	C_6H_4-MeO-p	176-178[c]	48	248, 283, 307[sh], 418[f] (4.22, 3.95, 3.83, 4.52)	7.86
IIc	C_6H_4-Cl-p	202-204[d]	53	241, 273, 304, 397[g] (4.13, 4.11, 4.07, 4.33)	8.10

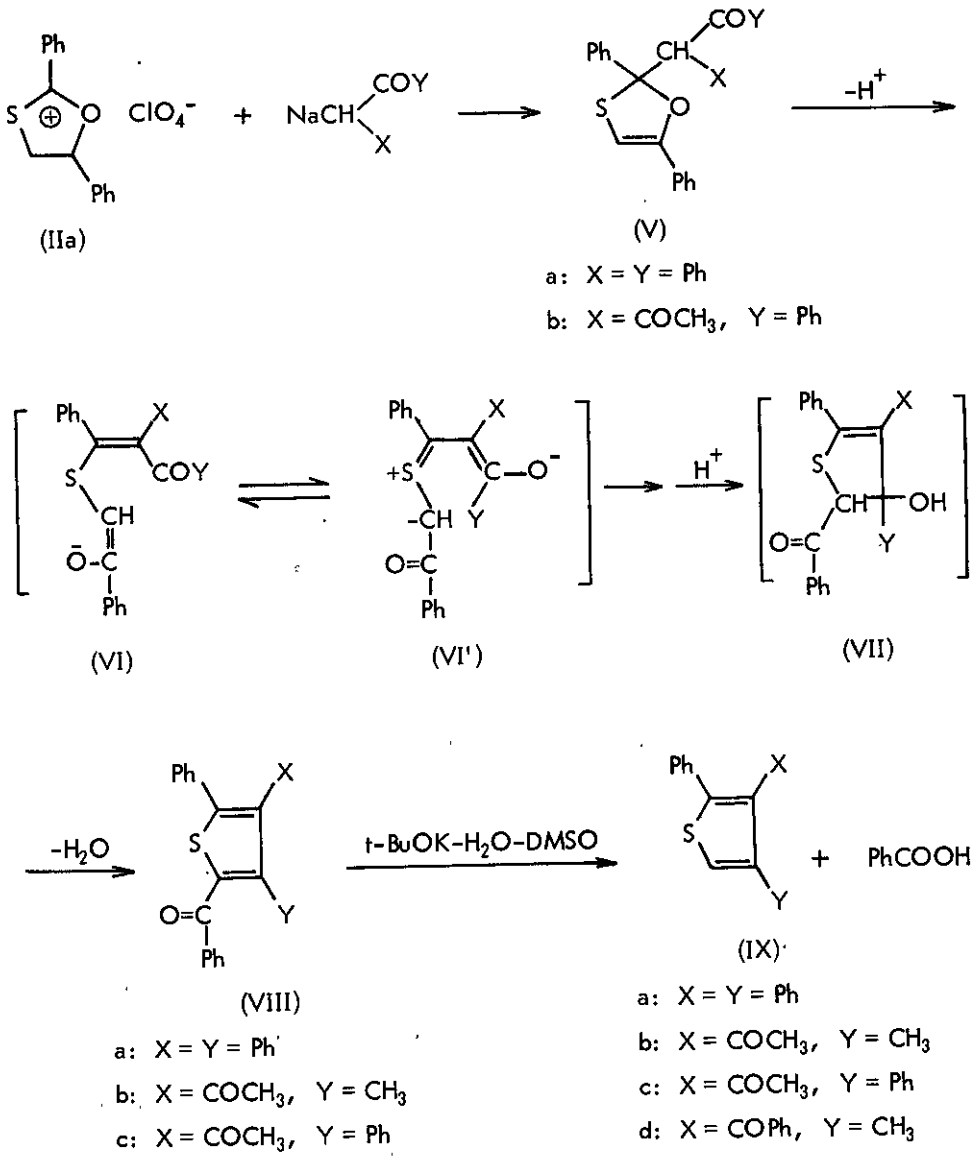
[a] Recryst. from CH_3NO_2-AcOH. [b] Ref. 7, 228-230. [c] Ref. 7, 178-180. [d] Ref. 7, 213-215. [e] Ref. 7, 386 (4.22). [f] Ref. 7, 415 (4.43). [g] Ref. 7, 396 (4.11). [h] Ref. 7, 8.00.

(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°: δ ($CDCl_3$), 5.67 and 5.70 (methine protons); ν_{max}: 1670 cm^{-1} (C=O). Treatment of (Va) with NaOEt in EtOH gave thiophene (VIIIa) (94%), colorless needles, mp 164-165°: λ_{max} (EtOH): 240, 261^{sh}, and 331 nm (log ε 4.47, 4.28, and 4.09); ν_{max}: 1649 cm^{-1} (C=O). Treatment of (VIIIa) with t-BuOK-H_2O-DMSO gave benzoic acid and 2,3,4-triphenylthiophene (IXa), colorless needles, mp 209-211°,[12] in 95% yield. Analogous reaction of perchlorate (IIa) with sodium salt of acetylacetone in tetrahydrofuran gave thiophene (VIIIb) (91%), colorless prisms, mp 72-73°: λ_{max} (EtOH): 260 and 313 nm (log ε 4.26 and 4.18); ν_{max}: 1687 (CH_3CO) and 1636 cm^{-1} (PhCO); δ ($CDCl_3$): 2.12 (4-CH_3) and 2.40 (3-CH_3CO). Treatment of (VIIIb) with t-BuOK-H_2O-DMSO also gave benzoic acid and thiophene (IXb) (78%), oil: λ_{max} (EtOH): 234, 262, and 294 nm (log ε 4.04, 3.98, and 3.75); δ ($CDCl_3$): 2.05 (3-$COCH_3$), 2.28^{d} (J = 1 Hz, 4-CH_3), and 6.85^{q} (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°: δ ($CDCl_3$): 1.72 (CH_3CO), 5.07 (CH<), and 5.30 (CH=), and thiophene (VIIIc) (20%), colorless plates, mp 138-139°: λ_{max} (EtOH): 237, 262^{sh}, and 319 nm (log ε 4.36, 4.29, and 4.11); ν_{max}: 1697 (CH_3CO) and 1644 cm^{-1} (PhCO); δ ($CDCl_3$): 1.92 (CH_3CO), 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_2O-DMSO to give


Ph
S
O
ClO4-
+
NaCH
COY
X
Ph
(IIa)
COY
Ph
CH
X
S
O
Ph
(V)
-H+
a: X = Y = Ph
b: X = COCH3, Y = Ph
Ph
X
S
COY
CH
O-C
Ph
(VI)
+S
C—O-
-CH
Y
O=C
Ph
(VI')
H+
OH
(VII)
-H2O
(VIII)
a: X = Y = Ph
b: X = COCH3, Y = CH3
c: X = COCH3, Y = Ph
t-BuOK-H2O-DMSO
+
PhCOOH
(IX)
a: X = Y = Ph
b: X = COCH3, Y = CH3
c: X = COCH3, Y = Ph
d: X = COPh, Y = CH3

Scheme

thiophene (IXc) (96%), pale yellow pillars, mp 114°; λ_{max} (EtOH): 243 and 295^{sh} nm (log ϵ 4.42 and 3.75). The ir spectrum of (IXc) showed C=O stretching of the CH_3CO group at 1693 cm^{-1} and the nmr signals due to 3-$COCH_3$ and ring C-5 protons appeared at δ 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.[3] 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.[3]

The reaction pathway may be rationalized as indicated in scheme, and 1,5-cyclization[13,14] of the sulfonium ylide intermediate (VI': X = $COCH_3$, Y = Ph) gives dihydrothiophene (VII: X = $COCH_3$, Y = Ph) from which loss of H_2O yields thiophene (VIIIc).

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10 All new compounds gave satisfactory elemental analyses.

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Received, 25th January, 1975