Tetrahedron Letters No.16, pp. 1137-1140, 1971. Pergamon Press. Printed in Great Britain.

SYNTHESES OF 1,3-OXATHIOL-2-YLIDENEPIPERIDINIUM SALTS, 1,4-DITHIAFULVENES, AND 1,4-OXATHIAFULVENES

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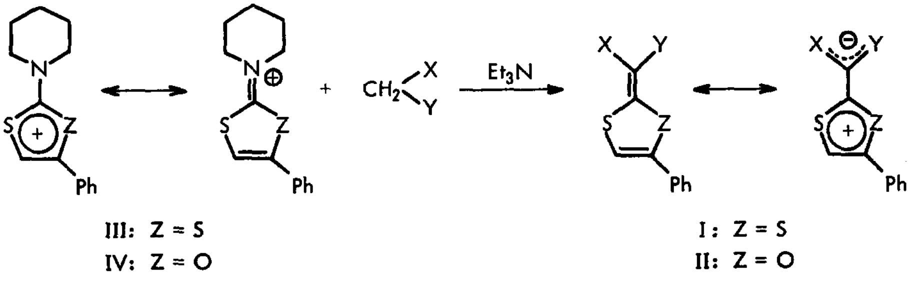
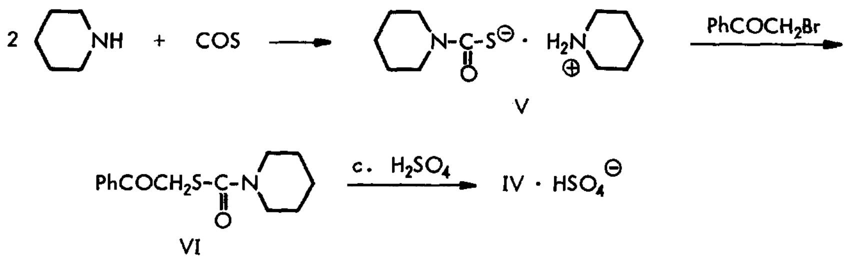
(Received in Japan 31 January 1971; received in UK for publication 19 March 1971)

1,3-Dithiol-2-ylidene derivatives (I), conveniently termed "1,4-dithiafulvenes" (1), have been prepared by a number of methods (2). However, 1,3-oxathiol-2-ylidene derivatives (II) have received little attention (3). Since, like I, II is isolectronic with heptafulvenes, II can be termed as "1,4-oxathiafulvenes." We now wish to report convenient syntheses of I and II, and some of their physical properties.

Jutz has reported (4) the preparation of dicyanoheptafulvenes from immonium heptafulvenes and malononitrile. It was found that 2-phenyl-1,4-dithiafulvenes (I) are produced in a good yield when 4-phenyl-1,3-dithiol-2-ylidenepiperidinium salt (III) (5) is reacted with a variety of active methylene compounds. This reaction proceeds at room temperature and the addition of Ac_2O has no effect on the yield. The results are listed in TABLE I (6).



For the synthesis of 1,4-oxathiafulvenes (II) by a reaction similar to the above, 5-phenyl-1,3-oxathiol-2-ylidenepiperidinium salts (IV) were prepared as follows:



Piperidine was allowed to react with COS giving piperidinium piperidinocarbothioate (V), then phenacyl bromide reacted with V to afford the phenacyl ester VI, which was easily cyclized with conc. H_2SO_4 to give IV as the hydrogensulfate, mp 193-194°, each step proceeding in good yield. The UV spectrum of IV in H_2O showed a maximum at 278 mμ (log ε 4.30), and the NMR spectrum in D_2O showed broad signals ascribable to the piperidine ring at τ 8.13 (6H), 6.27 (2H), and 5.98 (2H). A singlet (5H) due to phenyl protons appeared at τ 2.38 and a singlet (1H) ascribable to the C-4 proton in the 1,3-oxathiole ring appeared at τ 2.63. The chemical shift of the C-4 proton in the 1,3-oxathiole (IV) was at a higher field than that of the corresponding C-5 proton in III (τ 2.50 in D_2O). Treatment of IV hydrogensulfate with $HClO_4$ and HBF_4 gave the perchlorate, mp 154-157°, and the fluoroborate, mp 140-142°, respectively.

Reactions of IV with ethyl acetoacetate, indadione, and dimedone in the presence of Et_3N in CH_2Cl_2 readily gave the corresponding 1,4-oxathiafulvenes (IIa, b, c). These results are listed in TABLES I and II. Comparison of II with I reveales the following spectral differences: the UV spectra of II shows a blue shift and the NMR spectra of II exhibits a C-3 proton signal at a higher field than that of the corresponding C-3 proton in I. The IR spectra of II shows the carbonyl absorption bands shifting to a lower wave numbers, indicating the contribution of the enol structures, however, the degree of these shifts are smaller than those of I.

Similar reaction of IV with cyanoacetamide and ethyl cyanoacetate failed to give the corresponding 1,4-oxathiafulvenes, and the corresponding ketene S,N-acetals (VII) were obtained. These results are listed in TABLE III. The reaction mechanism may be rationalized as depicted below:

TABLE I

Yields of 1,4-Dithia- (I) and 1,4-Oxathiafulvenes (II)

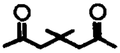
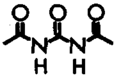
	Ia[2a,2c]	Ib	Ic[2a,2b]	Id[2a,2b]	Ie[2a]	If
$\overset{\frown}{X\;\;Y}$	CN CN		CN $COOC_2H_5$	CH_3CO CH_3CO		C_6H_5CO CH_3CO
Yield (%)	56	50	92	56	64	61
	Ig[2a]	Ih[2b]	Ii	Ij	Ik	Il
$\overset{\frown}{X\;\;Y}$	C_6H_5 C_6H_5CO	CH_3CO $COOC_2H_5$		H NO_2	CN $CONH_2$	CH_3 NO_2
Yield (%)	14	67	100	91	79	100
	IIa	IIb	IIc			
$\overset{\frown}{X\;\;Y}$	CH_3CO $COOC_2H_5$					
Yield (%)	22	46	56			

TABLE II

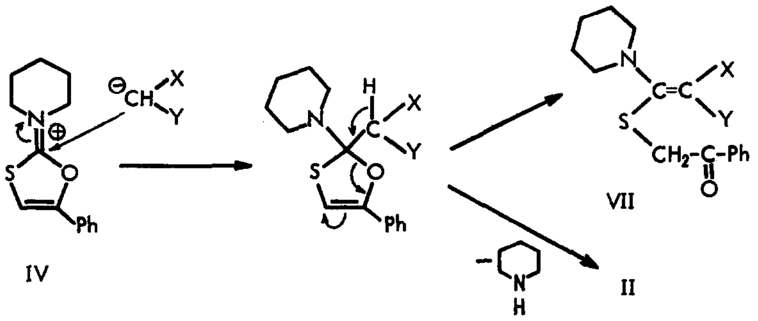
Comparison of Physical Properties of I and II

	mp (°C)	UV λ_{max}^{EtOH} mμ (log ε)	NMR ($\mathrm{H}{>}\!=$, τ) $CDCl_3$	d_6-DMSO	IR (cm^{-1})
Ih	101-102	232, 303, 385(4.37, 3.63, 4.45)	2.72, 2.77	2.05, 2.12	1600^s, 1665^s($CHCl_3$)
IIa	134-136	229.5, 290, 350(4.26, 3.90, 4.34)	3.22	2.35	1610^m, 1697^s($CHCl_3$)
Ie	249-250(decomp)	239, 423 (4.70, 4.72)		1.90	1658^s (KBr)
IIb	230-232(decomp)	231.5, 305, 384(4.59, 4.12, 4.56)		2.14	1669^s, 1708^w(KBr)
Ib	188-189	236, 274, 396(4.35, 3.95, 4.50)	2.57	1.83	1584^s, 1635^w($CHCl_3$)
IIc	164-165	227.5, 264, 361(4.17, 4.00, 4.40)	3.08	2.18	1604^s, 1663^m($CHCl_3$)

TABLE III

Yields and Physical Properties of Ketene S,N-Acetals (VII)

	X	Y	mp (°C)	Yield (%)	UV λ_{max}^{EtOH} mμ (log ε)	NMR (SCH_2-, τ, $CDCl_3$)
VIIa	CN	$CONH_2$	148-149	100	247, 276, 330 (4.18, 3.19, 4.14)	5.42
VIIb	CN	$COOC_2H_5$	118-120	63	247, 277, 331 (4.14, 3.91, 4.17)	5.36



The ease of ring opening of 1,3-oxathiole ring may be due to the ring strain with only a small stabilization by resonance contribution of the 6π-aromatic onium structure. In contrast, the 1,3-dithiole ring is quite stable due to the increased ability of a sulfur atom to conjugate in cyclic systems (7). Physical properties of I and II also support this consideration.

We are currently exploring the chemistry of the 1,3-oxathiole ring, including the reactions with a variety of nucleophiles, in our laboratory.

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