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A Convenient Synthesis of 1,3-Oxathiole-2-thione Derivatives. Reaction between Sodium 1-Imidazolecarbodithioate and α-Haloketones

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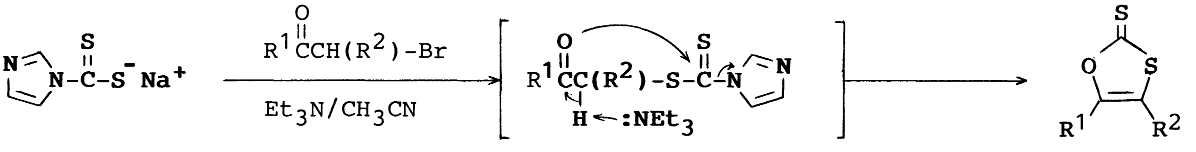
Reaction between sodium 1-imidazolecarbodithioate, prepared from sodium imidazole and carbondisulfide, and α-haloketone gave the corresponding 1,3-oxathiole derivatives1) in high yields.

Thiocarbonyl compounds have been the subjects of intensive studies, because of its usefulness for synthesis of heterocycles. Previously we reported some convenient synthesis of sulfur containing heterocycles, such as, 2-alkylidene-1,3-dithioles,2a) 1,3-thiazoles,2a,b) and 1,2-thiazoles2c,d) via cyclization of phenacyl and 2-(hydroxyimino)alkyl arenecarbodithioate and dithiocarbamates.

In this paper we wish to report a convenient *one-pot* synthesis of 1,3-oxathiole-3-thione derivatives **2**3) from sodium 1-imidazolecarbodithioate (**1**)4) and α-haloketones. The salt (**1**) was easily prepared from sodium imidazole and carbondisulfide in ether at 25 °C under nitrogen in nearly quantitative yield. After drying in vacuo, the salt **1** was used without further purifications.5) The reaction between **1** and phenacyl bromide was carried out in acetonitrile at 25 °C for 0.7 h. After addition of a catalytic amount of triethylamine, the reaction mixture was stirred for additional 2 h to give 5-phenyl-1,3-oxathiole-2-thione **2a** in 90% yield. The reaction may proceed as illustrated in Scheme 1. The salts **1** reacted with phenacyl bromide to give the corresponding ester, phenacyl 1-imidazolecarbodithioate **3**, whose isolation failed in spite of many efforts. Enolization of **3**, followed by intramolecular cyclization gave 1,3-oxathiole-2-thione **2a**. Reaction without using base gave poor results (Table 1).



1 **3**

2a: 90%
R^1= Ph, R^2= H

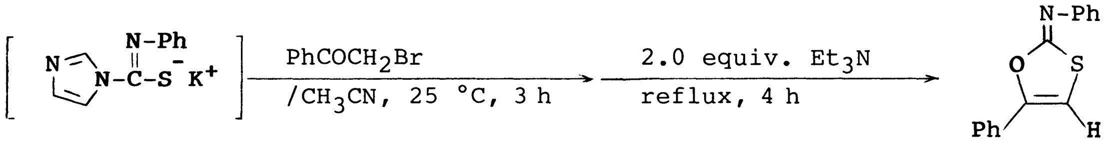
Scheme 1.

A modification of this *one-pot* method was shown in Scheme 2. The salt 5 was prepared *in situ* from potassium imidazole and phenyl isothiocyanate. The reaction of 5 with phenacyl bromide gave **4a** in 90% yield.

Table 1. Reaction Conditions and Yields of 1,3-Oxathiole-2-thiones 2

Run	Reaction conditions Temp/°C	Time/h$^{c)}$	Base	Product R^1	R^2	No.	Yield$^{a,b)}$ %	Mp θ_m/°C
1	25	5.0 (0)	none	C_6H_5	H	**2a**	66	91-93
2	25	0.7 (2)	Et_3N	C_6H_5	H	**2a**	90	91-93
3	25	0.7 (2)	Et_3N	$4\text{-}CH_3C_6H_4$	H	**2b**	63	118-120
4	25	0.5 (2)	Et_3N	$4\text{-}CH_3OC_6H_4$	H	**2c**	80	85-88
5	25	0.3 (2)	Et_3N	$4\text{-}BrC_6H_4$	H	**2d**	70	139-141
6	25	3.0 (0)$^{d)}$	none	C_6H_5	C_6H_5	**2e**	66	131-133$^{6)}$

a) Isolated yields. b) Micro analyses [C:±0.3;±H: 0.3] were obtained. c) Time after addition of triethylamine is in parentheses. d) 2.0 equiv. of **1** was used without addition of triethylamine.



5 (2.0 equiv.)

4a: 90%
mp 136-138 °C$^{7)}$

Scheme 2.

References

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4) Recently *in situ* preparation of **1** was reported: H. Sugimoto, I. Makino, and K. Hirai, J. Org. Chem., 53, 2263 (1988).

5) The salt **1** was very hygroscopic yellow powder: mp > 300 °C. UV and Vis. (CH_3OH), 302 nm (log ε=3.45), 375 nm (log ε=1.95); IR(KBr) 1615, 1450 cm^{-1}.

6) Lit. mp 132-133 °C; D. A. Lightner and C. Djerassi, Steroids, 2, 583 (1963).

7) Lit. mp 137-138 °C; G. Ottmann and H. Hooks, Jr., Angew. Chem., 79, 470 (1967).

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