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A SYNTHETIC ROUTE TO FIVE-, SIX-, AND SEVEN-MEMBERED THIONOLACTONES[1]

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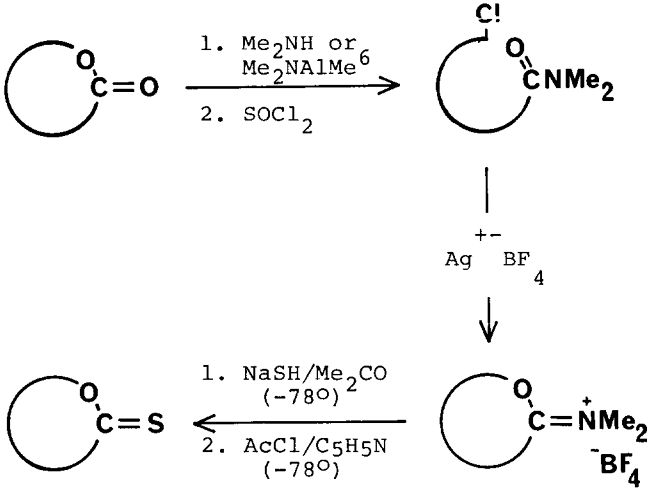
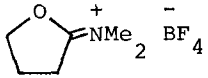
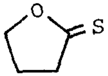
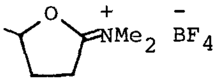
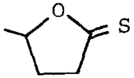
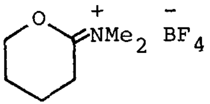
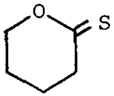
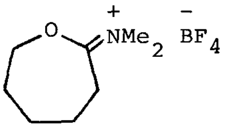
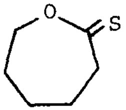
The chemistry of the thionester functional group (-C(=S)OR) has remained relatively dormant. While the recent literature describes a variety of thionating agents,[2] and various ways of synthesizing thionesters,[3] there appears to be no general method for making thionolactones.[4] We herein report on the first preparative route to five-, six-, and seven-membered thionolactones by a two-step, low temperature (-78°) sulfhydrolysis-acetylation of N,N-dimethyliminolactonium salts:[5]



The following Table summarizes our results:

Lactonium Salt[a,b]	Thionolactone[b,c]	Isolated Yield (%)[d]
 (1)	 (5)	**78**
 (2)	 (6)	**93**
 (3)	 (7)	**43**[e]
 (4)	 (8)	**84**

[a] Prepared by the method of Deslongchamps and coworkers;[7] the salts were crystallized from dichloromethane-diethyl ether.

[b] All new compounds gave satisfactory elemental analyses.

[c] Thionolactones were isolated as pale yellow oils.

[d] Yields have not been optimized.

[e] Chief by-product was $AcO(CH_2)_4C(=S)NMe_2$ (**30.6%** isolated yield).

In a typical procedure, anhydrous sodium hydrosulfide[8] (0.256 g, 4.37 mmol) was added, under nitrogen, to a rapidly stirring, cold (-78°) solution of N,N-dimethyliminocaprolactonium fluoroborate (0.500 g, 2.18 mmol) in dry acetone (30 ml).[9] The solution was stirred at -78° for 45 min and a cold (-78°) solution of dry pyridine-acetone (2.55 ml, 2:1 v/v) was then introduced from a jacketed Hershberg funnel, followed by distilled, cold (-78°) acetyl chloride (1.55 ml, 21.8 mmol). Stirring was continued for an additional hour at -78°, after which the temperature was gradually raised to room temperature. Anhydrous diethyl ether (45 ml) was then added, and the reaction mixture filtered and concentrated using a Vigreux column. The residue was chromatographed through Silica Gel (150 g, 100-200 mesh) in a 3.5 cm (i.d.) quartz column eluting with diethyl ether. Careful evaporation of the solvent led to caprothionolactone (0.238 g, 84.0%); NMR ($CDCl_3$): δ 1.82 (6H, m, ring methylenes), 3.16 (2H, m, $CH_2C(=S)O$), 4.46 (2H, m, CH_2O); IR(neat): 1295, 1235, 1170, 1070, 930 cm^{-1}; UV($CHCl_3$): λ_{max} 388(ε 17), 255 (ε 9760) nm. *Anal*. Calcd for $C_6H_{10}OS$: C, 55.35; H, 7.74. Found: C, 55.64; H, 7.98.

The availability of the thionolactones opens up a very fertile area of chemical and photochemical research. We are currently exploring the possible use of thionolactones as synthons for the construction of heterobicyclic systems.

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