

REACTION OF THIOKETAL DERIVATIVES WITH $\text{Pb}(\text{OAc})_4$

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In a recent year there have been published a few examples of the ring enlargement reactions of thioketal derivatives by migration of thio groups.

We wish to report herein an alternative transformation of 2-(1-hydroxyalkyl) or 2-alkylidene-1,3-dithiolanes or 1,3-dithianes into 1,4-dithianes or 1,4-dithiepanes respectively, by an oxidative ring expansion reaction with $\text{Pb}(\text{OAc})_4$.

Treatment of 2-(1-hydroxybutyl)-2-phenethyl-1,3-dithiane with $\text{Pb}(\text{OAc})_4$ (2.4 eq.) in benzene at room temperature or 55° induced a ring enlargement reaction with migration of a sulfur group to give 3-benzyl-1,4-dithiepan-2-one as colorless plates of mp $109-110^\circ$ in 67 % and 50 % yields respectively. Replacement of the solvent with CHCl_3 , CCl_4 , THF, and Et_2O in the same reaction afforded the corresponding 1,3-dithiepan-2-one or 2-acetoxy-3-benzyl-2,3-dehydro-1,4-dithiepane.

The ring expansion reaction of other 1,3-dithiane derivatives such as 2-(1-hydroxyethyl), 2-(1-hydroxybutyl), or 2-(1-hydroxybenzyl)-2-methyl-1,3-dithiane and 2-(1-hydroxybutyl)-2-ethyl-1,3-dithiane, with $\text{Pb}(\text{OAc})_4$ (2.4 eq.) produced the corresponding 1,4-dithiepan-2-one; 1,4-dithiepan-2-one (34-49 %) and 3-methyl-1,4-dithiepan-2-one (51 %). Oxidative cleavage of 2-benzyl-2-(1-hydroxybutyl)-1,3-dithiane with $\text{Pb}(\text{OAc})_4$ (2.4 eq.) was carried out in the same manner to give 2-acetoxy-2,3-dehydro-3-phenyl-1,4-dithiepane in 67 % yield.

The method described above is applicable to 1,3-dithiolane systems. Reaction of 2-(1-hydroxyethyl)-2-methyl-1,3-dithiolane with $\text{Pb}(\text{OAc})_4$ (2.4 eq.) in benzene at 55° resulted in the formation of 1,4-dithian-2-one in 80 % yield.

An oxidative ring enlargement reaction of 2-benzylidene-1,3-dithiolane and 2-ethylidene-1,3-dithiane was performed with $\text{Pb}(\text{OAc})_4$ (1.2 eq.) at room temperature or 55° to produce the corresponding ring expanded compounds; 2-acetoxy-3-phenyl-5,6-dihydro-1,4-dithiin (86 %) and 3-methyl-1,4-dithiepan-2-one (74 %).

We described here a general method for an oxidative ring expansion of cyclic 1,3-dithio compounds, which would permit a facile and direct entry for heterocycles containing sulfurs at 1 and 4 positions. A most possible pathway for this transformation involves a ring enlargement with migration of the thio group with $\text{Pb}(\text{OAc})_4$.