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SEMICYCLIC THIOACETALS AS SYNTHETIC BUILDING BLOCKS

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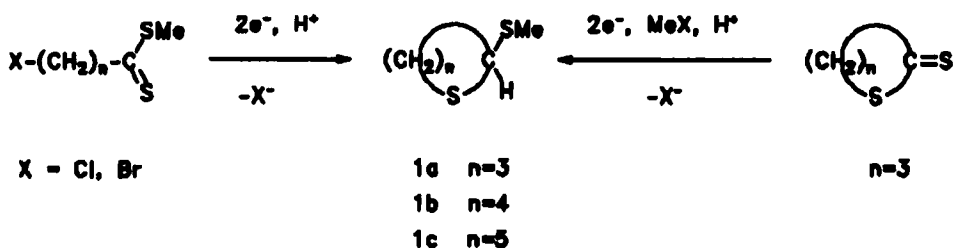
SEMICYCLIC THIOACETALS AS SYNTHETIC BUILDING BLOCKS

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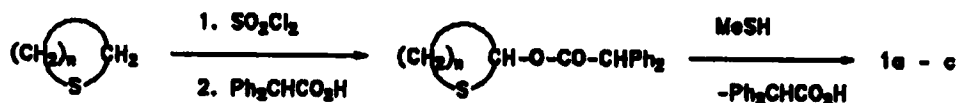
1,3-Dithianes are very well known as "Umpolung" reagents, whereas open-chained thioacetals are far less useful for carbon-carbon bond formation reactions¹.

It was, therefore, an interesting question, whether "semicyclic" thioacetals of type 1 were suitable substrates for electrophilic attack at the 2-position.

The hitherto unknown compounds 1 are formed on electroreduction of methyl halogenoalkanedithioates or γ -dithiolactones².

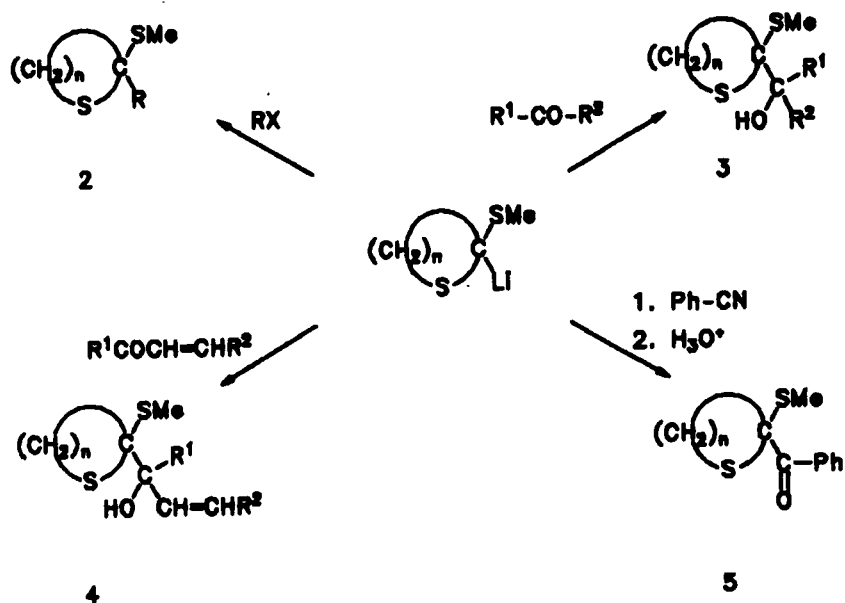


However, the thioacetals **1** are more conveniently obtained from the corresponding cyclic thioethers via diphenylacetates.

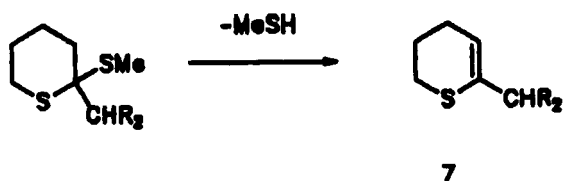
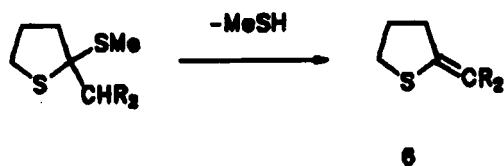


Butyllithium readily removes the α -proton of **1a-1c** and the resulting carbanions react in the desired way with various electrophiles.

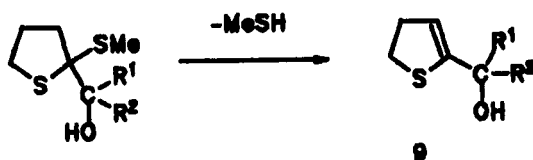
Alkyl derivatives **2** and carbinols **3** are formed on reaction with alkyl halides or carbonyl compounds, respectively. - 2-Bromobutane, aldehydes or unsymmetric ketones ($R^1 \neq R^2$) yield 1:1-mixtures of diastereomers. Exclusive 1,2-addition to form the allyl alcohols **4** rather than 1,4-(Michael-)addition occurs with α,β -unsaturated carbonyl compounds. Acylation of 2-methylthio-thiolane (**1a**) has been achieved using benzonitrile as reagent.



Elimination of the exocyclic methylthio substituent in some cases occurs spontaneously during work-up. It can, however, be better achieved by alkylation (*Hofmann-Elimination*) or, more effectively, with catalytic amounts of p-toluenesulfonic acid. 2-Alkylidenethiolanes **6** or 6-alkyl-3,4-dihydro-2*H*-thiopyranes **7** respectively are formed from the five- and six-membered alkyl derivatives **2**.



The secondary carbinols **3** ($\text{R}^1 = \text{H}$) yield ketones **8** whereas allylic alcohols **9** with an endocyclic double bond are obtained from the tertiary alcohols **3** ($\text{R} = \text{H}$).



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