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Reaction of 2,3-Dihydro-1,4-benzodithiine and 2,3-Dihydro-1,4-benzoxathiine with Sodium Methoxide

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2,3-Dihydro-1,4-benzodithiines and 2,3-dihydro-1,4-benzoxathiines react with sodium methoxide in DMA to give 1,3-benzodithioles and 2-(vinylthio)phenols, respectively.

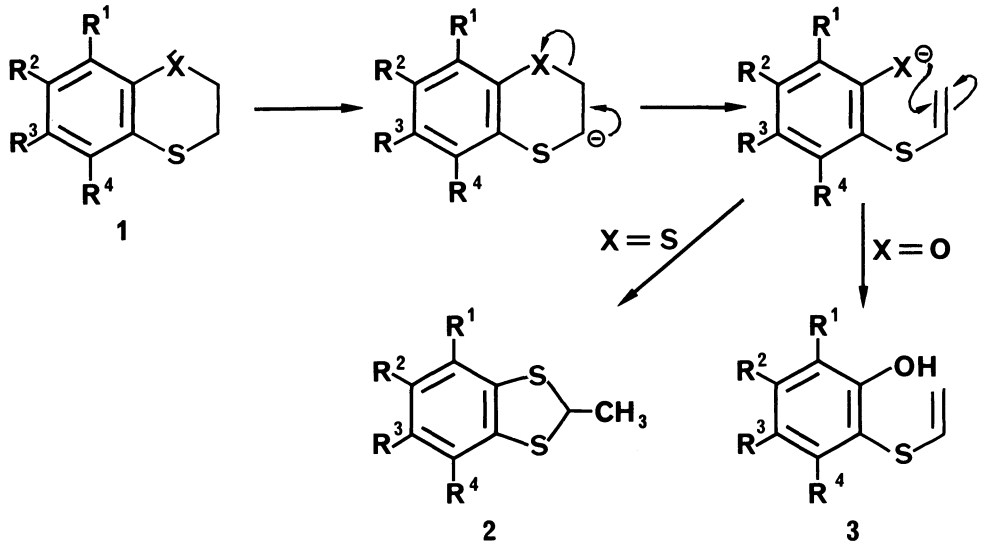
Recently, we reported on a new route to 2,3-dihydro-1,4-benzodithiines and 2,3-dihydro-1,4-benzoxathiines from the hemithio- and dithioacetals of cyclohexanones, respectively.[1] In order to synthesize benzene-1,2-dithiols and 2-mercaptophenols, therefore, we attempted to react these benzodithiines **1a** - **e** and benzoxathiines **1f** - **j** with sodium methoxide in DMA, according to Tiecco et al.[2] We now report that the heterocyclic ring contraction and ring cleavage occur in these reactions to give 1,3-benzodithioles **2a** - **e** and 2-(vinylthio)phenols **3f** - **j**, respectively. The results are summarized in Table 1.

Table 1. Reactions of 2,3-dihydro-1,4-benzodithiines **1a** - **e** and 2,3-dihydro-1,4-benzoxathiines **1f** - **j**

Starting material **1** and products **2** and **3**		Substituents					Products **2** and **3** Isolated yield/%	Bp (°C/mmHg) or [Mp /°C]
		X	R^1	R^2	R^3	R^4		
1a,	**2a**[3]	S	H	Me	H	H	54	oil
1b,	**2b**	S	H	Bu^t	H	H	62	[68-70]
1c,	**2c**	S	Me	H	H	Me	52	[230-232]
1d,	**2d**	S	Me	H	Me	H	70	oil
1e,	**2e**	S	Pr^i	H	H	Me	68	oil
1f,	**3f**[4]	O	H	H	Me	H	64	56-57(5)
1g,	**3g**	O	H	Bu^t	H	H	65	72-74(5)
1h,	**3h**	O	Me	H	H	Me	78	63-64(5)
1i,	**3i**	O	Me	H	Me	H	80	80-81(7)
1j,	**3j**	O	Pr^i	H	H	Me	89	63-64(4)

All compounds reported here gave satisfactory IR and NMR spectra, which will be reported elsewhere.

The reaction would proceed through the pathway shown below.



It is well known that 2 and/or 3-substituted 1,4-benzodioxines,[5] 1,4-dithiane,[6] 1,4-oxathiane,[7] and 1,4-dithiine monosulfoxide[8] undergo ring contraction to give five membered heterocyclic compounds. The present reaction is the first case of the heterocyclic ring contraction of 2,3-dihydro-1,4-benzodithiines, which have neither electron delocalizing groups nor leaving groups at $C_{(2)}$ and/or $C_{(3)}$, to form 1,3-benzodithioles. Moreover, this reaction, utilizing 1,4-oxathiine derivatives readily available by the route developed in our preliminary work,[1] thus affords an improved method for synthesizing the 2-(vinylthio)phenol derivatives with alkyl groups in desired positions.

References

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3) 2,5-Methyl-1,3-benzodithiole (**2a**); ^{1}H NMR ($CDCl_3$, δ): 1.71 (d, J=7 Hz, 3H, CH-C**H**$_3$), 2.30 (s, 3H, Ar-CH_3), 4.98 (q, J=7 Hz, 1H, C**H**-CH_3), 6.65-7.40 (m, 3H, Ar-H); m/z 182 (M^+).
4) 4-Methyl-2-(vinylthio)phenol (**3f**); ^{1}H NMR: ($CDCl_3$, δ) 2.30 (s, 3H, Ar-CH_3), 4.95 (d, J=17 Hz, 1H), 5.25 (d, J=9 Hz, 1H), 6.10 (s, 1H: disappeared by D_2O), 6.25 (dd, J=9, 17 Hz, 1H), 6.80-7.20 (m, 3H); m/z : 166 (M^+).
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