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A NOVEL SMALL RING FORMATION USING METHYLSULFINYL GROUP AS A LEAVING GROUP

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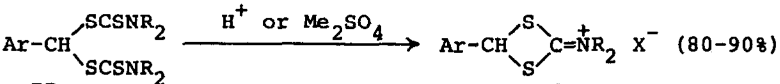
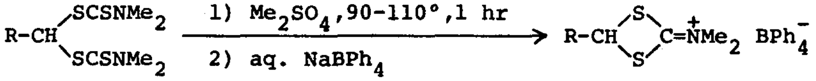
In our previous paper we reported the preparation of four-membered heteronium salts (I) from bis(dithiocarbamates) (II) on treatment with acid or dimethyl sulfate[1].



II I

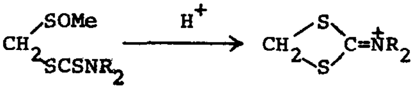
However, applications of this reaction to methylene-(IIa)[2] and ethylidene-bis(N,N-dimethyldithiocarbamate) (IIb)[2] using Me_2SO_4 resulted in the formation of corresponding heteronium salts only in poor yields as described bellow.



(1)

IIa R=H, mp: 150-2° 23% (R=H)
b R=Me, mp: 105-6° 39% (R=Me)

Strong acids such as c.H_2SO_4 or 70% $HClO_4$ were not effective for the cyclization of IIa and IIb. So we sought the more acid-sensitive eliminating group than thiocarbamoylthio group (R_2NCS-S-) and found facile cyclization of the compound (III) having methylsulfinyl group (MeSO-) as an eliminating group.



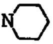
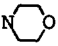
(2)

III I

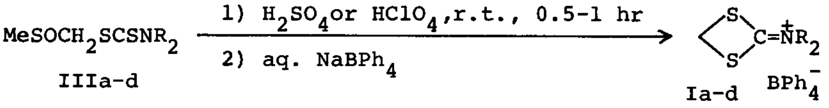
Methylsulfinylmethyl N,N-dialkyldithiocarbamates(IIIa-d) were prepared by the reaction of chloromethyl methylsulfoxide ($MeSOCH_2Cl$)[3] with appropriate sodium N,N-dialkyldithiocarbamates in EtOH at 50-60°C for 5 hrs. After the solvent was evaporated, the residues were poured into water and extracted with methylene chloride to give dithioesters in 78-82% yields. The results are summarized in TABLE I.

$$MeSOCH_2Cl + NaSCSNR_2 \longrightarrow \underset{\text{IIIa-d}}{MeSOCH_2SCSNR_2} \qquad (3)$$

TABLE I. Methylsulfinylmethyl N,N-dialkyldithiocarbamates (III)[4]

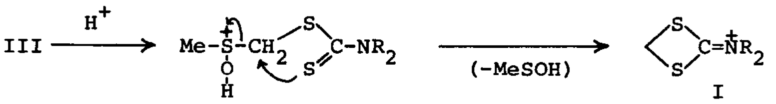
		Yield(%)	Mp(°C)	IR ν_{SO}(cm^{-1})	UV λ_{max}^{EtOH} (nm)
IIIa	$MeSOCH_2SCSNMe_2$	80	68-9	1035	245, 278
b	$MeSOCH_2SCSNEt_2$	79	57-8	1020	248.5, 280.5
c	$MeSOCH_2SCSN$ 	78	94-5	1030	250, 281.5
d	$MeSOCH_2SCSN$ 	82	120-1	1020	253, 283

Successful cyclization of III was found to take place only by dissolving the dithioesters III in 95% H_2SO_4 or 70% $HClO_4$ at room temperature in high yields. The products were isolated as tetraphenylborate by anion exchange on treatment with aq. $NaBPh_4$. The results are summarized in TABLE II.



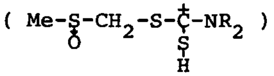
(4)

A plausible mechanism for the formation of (I) from (III) may be shown by the following reaction scheme. Thus the initial protonation at sulfoxide oxygen atom and successive elimination of methyl sulfenic acid seems to lead the cyclization products I.



(5)

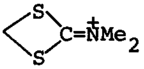
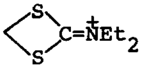
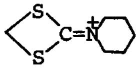
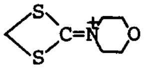
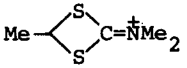
Products via the initial protonation at thiocarbonyl sulfur atom were not obtained at all.



$$(Me-\underset{O}{S}-CH_2-S-\underset{\underset{H}{S}}{\overset{+}{C}}-NR_2)$$

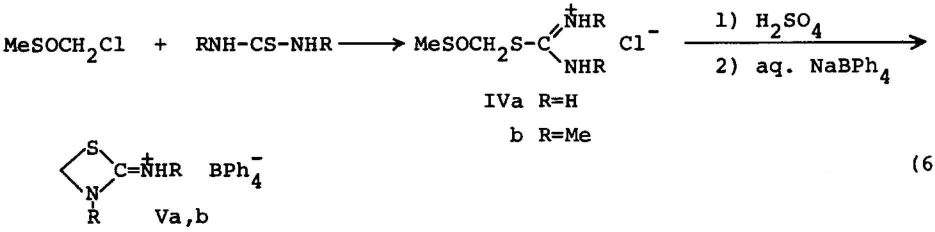
This indicates that the methylsulfinyl group is more acid-sensitive than thiocarbamoylthio group ($R_2NCS-S-$).

TABLE II. 2-Dialkylamino-1,3-dithietan-2-ylium tetraphenyl borates I[4] from Methylsulfinyl derivatives III

1,3-Dithietan-2-ylium salts (BPh_4^-)		Yield (%)	Mp(°C)	IR $\nu_{C=\overset{+}{N}}$ (cm^{-1})	UV λ_{max}^{EtOH} (nm)	NMR($DMSO-d_6$) δ($-SC\underline{H}_2S-$)
Ia		65	194-5	1630	238	4.05
b		78	107-8	1600	239	3.84
c		80	111-2	1615	239	4.10
d		53	125-6	1610	240	4.16
e	 a)	39	192-4	1640	231	4.56 (Me-C$\underline{H}$<)

a) Ie was prepared by the method described in eq. (1).

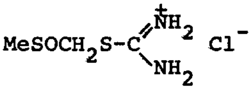
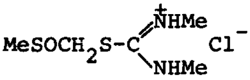
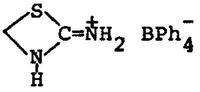
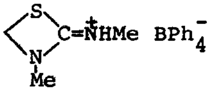
This new cyclization reaction seems to be quite general and to be successfully applicated to the other hetero atom systems such as N,N,S as formulated bellow.



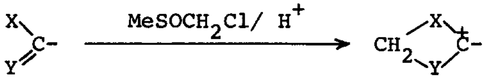
(6)

Isothiuronium chlorides IVa and IVb were prepared on the reaction of chloromethyl methylsulfoxide with thioureas in neat conditions at 85°C for 10 hrs. The salts IVa and IVb were recrystallized from ethanol. On treatment of IV with c.H_2SO_4 in a similar manner as described before, new cyclization products, 1,3-thiazetidin-2-ylium salts V were obtained in high yields. These results are summarized in TABLE III. The four-membered cation Va and Vb were recrystallized from acetone (or acetone-water).

TABLE III. Isothiuronium and 1,3-Thiazetidin-2-ylium Salts[4]

		Yield (%)	Mp(°C)	IR(cm^{-1})	NMR(DMSO-d_6,δ)
IVa	 $MeSOCH_2S\text{-}C(=\overset{+}{N}H_2)(NH_2)\ Cl^-$	60	134-5	1640 (C=$\overset{+}{N}$) 1020 (SO)	
IVb	 $MeSOCH_2S\text{-}C(=\overset{+}{N}HMe)(NHMe)\ Cl^-$	50	137-8	1630 (C=$\overset{+}{N}$) 1010 (SO)	
Va		84	127-8	1640 (C=$\overset{+}{N}$)	4.44 (CH_2,s,2H) 7.68 8.00 (NH,br.,3H)
Vb		91	167-8	1630 (C=$\overset{+}{N}$)	4.50 (CH_2,d,J=16Hz,1H) 4.86 (CH_2,d,J=16Hz,1H) 9.40 (NH,br.,1H)

In conclusion, methylene transfer from chloromethyl methylsulfoxide into adjacent hetero atoms X,Y in the compound of type A such as dithiocarbamate anion or thiourea gives the four-membered heteronium salts which are difficult to obtain in other methods.



(A)

References

1) Y. Ueno and M. Okawara, Chem. Lett., 863 (1973).

2) These compounds are easily prepared quantitatively by the reaction of CH_2Cl_2 or CH_3CHBr_2 with sodium N,N-dimethyldithiocarbamate.

3) G. Tsuchihashi and K. Ogura, Bull. Chem. Soc. Japan, 44, 1726 (1971).

4) All new compounds in this letter gave satisfactory elemental analyses and spectral data.