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ORGANIC SULFUR COMPOUNDS I:
THERMOLYSIS OF 2,2-DIMETHYL-1-(P-TOLUENESULFONYLIMINO)THIOCHROMAN

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Thermolysis of acyclic sulfilimines has been well investigated. It is known that the thermolysis1) of phenyl alkyl N-p-toluenesulfonylsulfilimines having β-hydrogens give the corresponding olefins and phenyl-N-p-tolylsulfonyl sulfenamide in high yields. However, thermolysis of cyclic sulfilimines are little known2). This prompts us to do more detailed investigation on the thermolysis of cyclic sulfilimines. In this communication, we wish to report the thermolysis of one of cyclic sulfilimines, 2,2-dimethyl-1-(p-toluenesulfonylimino)thiochroman (I). Refluxing I in benzene for one hour afforded N-[2-(3-methyl-3-butenyl)phenylthio]-N-(2'-methylthiochroman-2'-ylmethyl)-p-toluenesulfonamide (V) quantitatively. The structural assignment is based on physical data (Table I). The initial step of this reaction is considered to be β-elimination involving the five membered transition state (II), then the compound (V) may be formed through the sulfenamide (III) and episulfonium ion (IV) as shown in Fig. I. The resulting product (V) further undergoes thermolysis in refluxing xylene to give 2-methyl-2-(p-toluenesulfonylaminomethyl)thiochroman (VI), N,N-bis(2-methylthiochroman-2-ylmethyl)-p-toluenesulfonamide (VIII), 3-methyl-2,5-dihydro-1-benzothiepin (IX) and 2,5-dihydro-1-benzothiepin-$\Delta^{3(4H)}$-methane (X). The physical data for the structural assignment of these compounds generated by the thermolysis of V are also summarized in Table I. The over-all scheme of these reactions is illustrated in Fig. I. A typical run of the reaction is the following;

Thermolysis of I in benzene

I (2.3 mmOl.) was refluxed in benzene for one hour. After the reaction, benzene was distilled off, then an oily product was obtained. The product was separated by column chromatography through a silica gel (Wakogel C-200) packed column, and V was obtained quantitatively with benzene as eluent.

The isomerization of V to VIII is also assumed to proceed via episulfonium ion (VII). Treatment of V with p-TsOH gave VI quantitatively. These reactions shown in Fig. I are the first example of 1,3-abnormal Pummerer-type reaction of sulfilimine. In addition, we found that the same reaction took place during the course of the preparation of the free sulfilimine of 2,2-dimethylthiochroman with

O-mesitylenesulfonylhydroxylamine[3].

The detailed and further studies of these reactions will be published elsewhere in near future.

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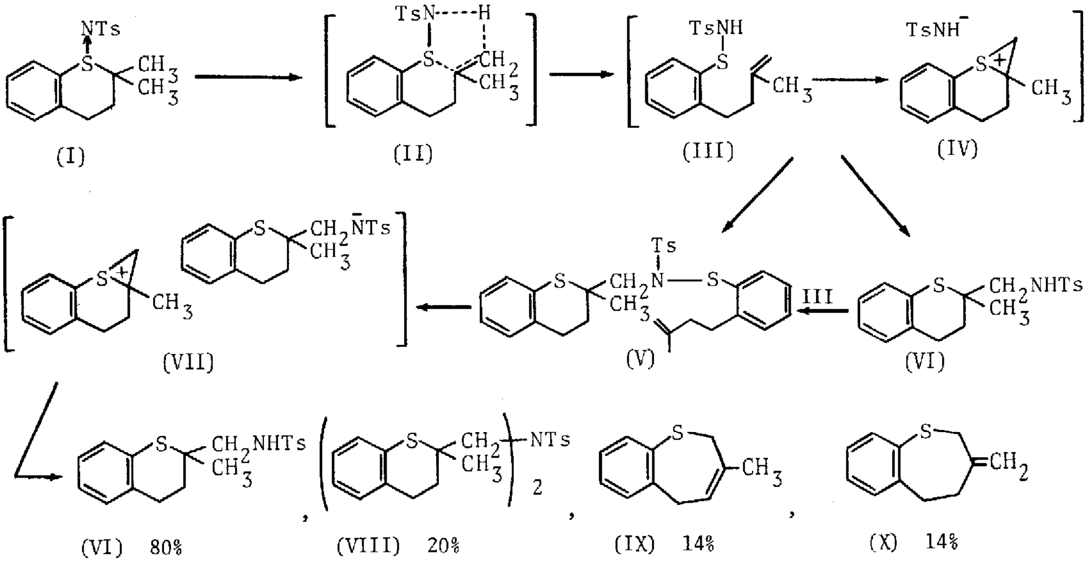
Table I. Physical Data for the Structural Assignment of the Compounds Generated by Thermolysis of I.

Compound	IR ν_{max} cm^{-1}	Mass m/e (M^+)	^{1}H-NMR ($CDCl_3$) δ
V	1650	523	1.50(3H,s),1.76(3H,br.s),1.85-2.30(4H,m),2.40(3H,s),2.55-3.10(4H,m),3.82(2H,s),4.73(2H,br.s),6.95-7.26(8H,m),7.26(2H,d,J=8.5Hz),7.80(2H,d,J=8.5Hz)
VI	3230 1330	347	1.35(3H,s),1.70-2.10(2H,m),2.37(3H,s),2.75-2.90(2H,m),3.0(2H,d,J=8Hz),5.12(1H,t,J=8Hz),6.90(4H,s),7.21(2H,d,J=8.5Hz),7.69(2H,d,J=8.5Hz)
VIII	1330 1155	523	1.37(6H,s),1.86(4H,t,J=7Hz),2.37(3H,s),2.80(4H,t,J=7Hz),3.90(4H,s),6.98(8H,s),7.21(2H,d,J=8.5Hz),7.69(2H,d,J=8.5Hz)
IX*	1650	176	1.68(3H,br.s),3.37(2H,br.s),3.58(2H,br.s),5.67(1H,m),7.20(4H,m)
X*	1650	176	2.4(2H,m),3.0(2H,m),3.28(2H,s),4.82(2H,br.s),7.2-7.5(4H,m)

* The structural assignment of IX and X was determined by the nmr of the authentic samples produced by the Morin's method[4].

Fig. I. Over-all Scheme of the Thermolysis of I.



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