

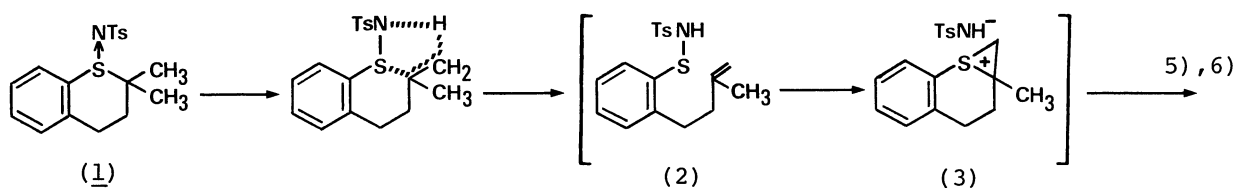
REACTIONS OF 2,2-DIMETHYL-1-(P-TOLUENESULFONYLIMINO)THIOCHROMAN<sup>1)</sup>  
WITH NUCLEOPHILES SUCH AS THIOLS, AMINES, AND GRIGNARD REAGENTS<sup>2)</sup>

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The reactions of 2,2-dimethyl-1-(p-toluenesulfonylimino)thiochroman (1) with nucleophiles such as thiols, amines, and Grignard reagents give the sulfenic acid derivatives. The mechanisms of these reactions are discussed.

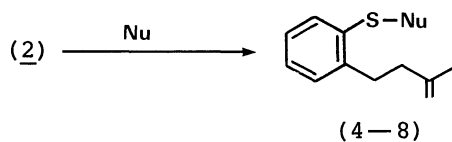
Trapping experiments of the sulfenic acid intermediates derived from penicillin S-oxides are clearly established and have been a topic of extensive researches.<sup>3)</sup> However, investigations on cyclic sulfilimines are scant.<sup>4)</sup> In this communication, we wish to report the trapping of the sulfenamide derived by thermolysis<sup>5)</sup> of (1).

We have recently demonstrated that the sulfenamide (2) and episulfonium ion (3) derived by thermolysis of (1) reacted with acetic anhydride to give the 1,3-abnormal Pummerer-type rearrangement products, inter- and intramolecularly.<sup>6)</sup> Dimerization<sup>5)</sup> of (1) and oxidation<sup>6)</sup> of (1) with sulfoxides have also been reported.



During the course of the extension of these reactions, we examined the reaction of (1) with other nucleophiles such as thiols, amines, and Grignard reagents. In these reactions, we found the different types of reaction from those mentioned above took place to give the sulfenic acid derivatives.<sup>7)</sup> Namely, the reaction of (1) with thiophenol or sodium thiophenolate in refluxing ethanol gave 2-(3-methyl-3-butenyl)phenyl phenyl disulfide (4). Similarly, the reaction of (1) with primary amines such as benzyl- and cyclohexyl-amines afforded sulfenamides; N-benzyl- and N-cyclohexyl-2-(3-methyl-3-butenyl)benzenesulfenamides (5-6). The reaction of (1) with large excess of Grignard reagents such as phenyl- and p-anisylmagnesium bromides gave the products, (7-8).

These reactions are considered to proceed along the sulfenamide (2) formed by the initial sigmatropic reaction, followed by nucleophilic displacement on the sulfur atom of (2) to give the final products, illustrated.



In addition, the product (9) was formed in the reaction of (1) with potassium hydroxide in refluxing methanol for 72 hrs. The products, yields, and conditions of these reactions are summarized in Table I.

The detailed and further studies of these reactions will be reported from these laboratories.

Table I. Reactions of (1) with Nucleophiles<sup>8)</sup>

Nucleophiles (Nu)	Mole Ratio (Nu)/(1)	Reaction Conditions			Products and Yields(%)	
		Solvent	Temp	Hr	Nu in	
C <sub>6</sub> H <sub>5</sub> SH	1.1	EtOH	Reflux	4	(4), Nu; C <sub>6</sub> H <sub>5</sub> S-	66
C <sub>6</sub> H <sub>5</sub> SNa	1.1	EtOH	Reflux	4	(4), Nu; C <sub>6</sub> H <sub>5</sub> S-	89
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH <sub>2</sub>	1.1	CH <sub>3</sub> CN	Reflux	4	(5), Nu; C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> NH-	36
<sup>9)</sup>	1.1	EtOH	Reflux	4	(6), Nu;	17
<sup>9)</sup>	1.1	CH <sub>3</sub> CN	Reflux	4	(6), Nu;	12
C <sub>6</sub> H <sub>5</sub> MgBr	10	THF	Reflux	5	(7), Nu; C <sub>6</sub> H <sub>5</sub> -	57
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> MgBr	6	THF	Reflux	5	(8), Nu; p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> -	70
KOH	13	MeOH	Reflux	72	(9), Nu;	31

#### References and Notes

- (1) 2,2-Dimethyl-1-(p-toluenesulfonylimino)benzo[b]thian
- (2) Organic Sulfur Compounds 3; Part 2 on this series, Y. Tamura, K. Sumoto, M. Ikeda, M. Murase, and M. Kise, *J. Chem. Soc. Chem. Commun.* (in press).
- (3) P. G. Sammes, *Chem. Rev.*, **76**, 113(1976); T. S. Chou, J. R. Burgdorf, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, *J. Am. Chem. Soc.*, **96**, 1609(1974).
- (4) M. M. Campbell, G. Johnson, A. F. Cameron, and I. R. Cameron, *J. Chem. Soc., Perkin I*, 1208(1975); M. M. Campbell and G. Johnson, *ibid.*, 1212(1975).
- (5) M. Kise, M. Murase, M. Kitano, T. Tomita, and H. Murai, *Tetrahedron Lett.*, 691(1976).
- (6) Idem, "Abstract of the 8th Congress of Heterocyclic Chemistry, Kyoto, Japan," p-113(1975).
- (7) E. Kuhle, "The Chemistry of the Sulfenic Acid," Georg Thieme Publishers, Stuttgart, 1973.
- (8) All new compounds had satisfactory elemental analysis and/or mass spectra; ir and NMR spectra were consistent with their structures.
- (9) In these reactions, 2-methyl-2-(p-toluenesulfonylaminomethyl)thiochroman is also formed in yields of 5 and 7%, respectively.

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