

A Convenient Preparation of "Free" Sulfilimines by Hydrolysis of N-p-Tosyl-sulfilimines in Sulfuric Acid

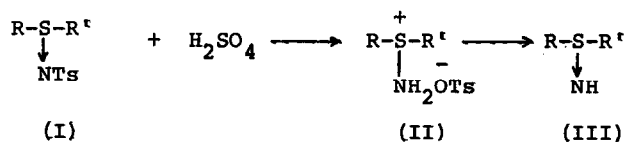
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The acid catalyzed hydrolysis of aryl methyl N-p-tosylsulfilimines has been known to give the corresponding sulfoxides.¹⁾ However, the mechanism of the reaction has been unexplored. In order to understand in detail the mechanism of the acid hydrolysis of N-p-tosylsulfilimines several types of N-p-tosylsulfilimines were prepared by the usual method²⁾ and were allowed to react with concentrated sulfuric acid. Unexpectedly however, diphenyl N-p-tosylsulfilimine was found to give iminosulfonium p-toluenesulfonic acid salt (II) which upon neutralization with aqueous sodium hydroxide solution give the "free" sulfilimine.³⁾ A typical reaction with concentrated sulfuric acid was carried out in the following way. Diphenyl N-p-tosylsulfilimine (1.0g) was dissolved in 1.0 ml of concentrated sulfuric acid (95% commercial special grade) at room temperature. The solution was kept for 10 min, and then poured onto ice. The oily material precipitated out immediately. The aqueous solution was extracted with chloroform. After chloroform was removed, the residue solidified to give quantitatively crystals, m.p. 127.5°C, which upon recrystallization from acetone-methanol give colorless crystals of m.p. 128.5°C. The product was identified as iminosulfonium p-toluenesulfonic acid salt (II) on the basis of elemental analysis, ir. and nmr. Anal, Found C; 60.83 H; 5.21 N; 3.48, Calcd. for

Table I. Products and Yields.



(I)		Reaction Time, Temp.		Method	Products and Yields		
R	R ^t	min.	°C		II	III	Others
C ₆ H ₅ , C ₆ H ₅		10	r.t.	B	quantitative (m.p. 128.5°C)	75 (m.p. 71°C)	
p-CH ₃ C ₆ H ₄ , C ₆ H ₅		10	r.t.	B	quantitative (oil)	quantitative (m.p. 54-54.5°C)	
p-ClC ₆ H ₄ , C ₆ H ₅		10	r.t.	B	quantitative (oil)	quantitative (oil)	
p-NO ₂ C ₆ H ₄ , C ₆ H ₅		10	r.t.	B		76 (m.p. 95.5-97.5°C)	
C ₂ H ₅ , C ₂ H ₅		15	40°	A		(oil) as Picrate m.p. 110-111° b)	TsOH
-(CH ₂) ₅ -		15	r.t.	A		quantitative (oil) as picrate m.p. 191°C a)	TsOH
C ₆ H ₅ , CH ₃		5	r.t.	A	quantitative	mixture (oil) as picrate m.p. 112-112.5°C a)	TsOH
C ₆ H ₅ , C ₂ H ₅		15	40	A	quantitative	(oil) as picrate m.p. 90-91°C	TsOH (quant.)
"		15	40	B			sulfoxide (quantitative) (NH ₄) ₂ SO ₄ TsOH

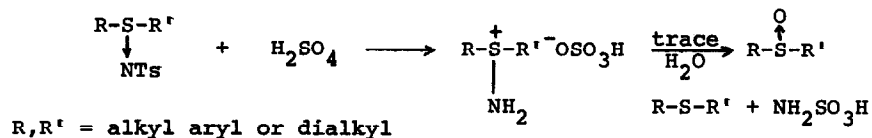
a. bisulfate

b. lit. m.p. 110°C³⁾

Method A : The acid solution was quenched in cold ether.

B : The acid solution was poured onto ice.

corresponding "free" sulfilimines, but afforded the sulfoxides, sulfides and sulfamic acid as shown below.



R, R' = alkyl aryl or dialkyl

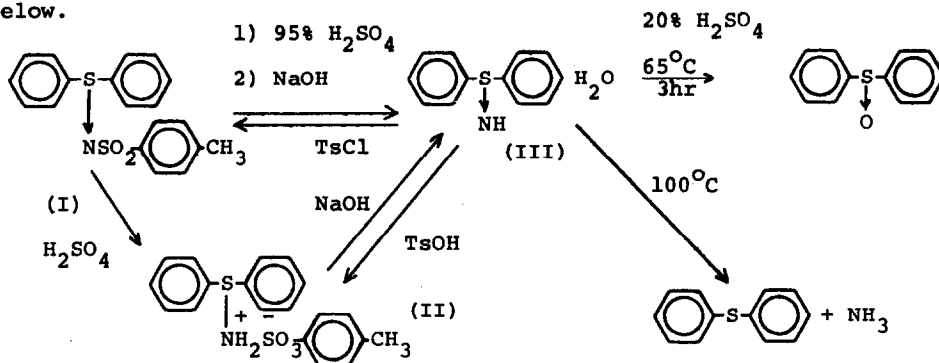
However, when the acid solution of alkyl aryl or dialkyl sulfilimines was quenched in cooled ethyl ether, the oily materials isolated were found to be sulfuric acid salts of "free" sulfilimines from which "free" sulfilimines were obtained upon treatment of acetone-methanol solution of the salts with liq. NH₃. Alkyl aryl or dialkyl "free" sulfilimines are usually unstable under the room temperature and decompose to the sulfides, NH₃ and N₂. Therefore the "free" sulfilimines were converted to the picrates as soon as they were isolated.

The products and their yields are summarized in Table I. These results indicate that this method is the first universal method to prepare all kinds of "free" sulfilimines. Prior to this, p,p'-dimethoxyaiphenyl sulfilimine^{3b)} was the only "free" diaryl sulfilimine which was known and synthesized by the treatment of the halogen-sulfide complex with liq. ammonia.³⁾ Further work on this and related reactions are now underway in these laboratories.

References

- 1) a) B.H.Nicolet, and J.Willard, *Science*, 53, 217 (1921).
 b) F.G.Mann, and W.T.Pope, *J. Chem. Soc.*, 121, 1052 (1922).
 c) J.Day, and D.J.Cram, *J. Amer. Chem. Soc.*, 87, 4398 (1965)
- 2) K.Tsujihara, N.Furukawa, K.Oae, and S.Oae, *Bull. Chem. Soc. Japan*, 42, 2631 (1969)
- 3) a) R.Appel, W.Buchner, and E.Guth, *Ann.* 618, 53 (1958).
 b) R.Appel, and W.Buchner, *Chem. Ber.* 95, 849, 855, 2220 (1962).
 c) J.B.Lambert, C.E.Mixan, and D.S.Bailey, *Chem. Commun.*, 316 (1971).
 J.B.Lambert, C.E.Mixan, and D.S.Bailey, *J. Amer. Chem. Soc.*, 94, 1208 (1972).

$C_{19}H_{19}NO_3S_2$ C; 60.45 H; 5.07 N; 3.71. The salt (II) was then dissolved into chloroform again and washed with 20% aqueous alkali solution. After washing the chloroform layer with water and drying, chloroform was evaporated, to give a crystalline product in 75% yield, m.p. $70-71^\circ C$ (recrystallized from benzene-hexane). This product was identified as "free" sulfilimine monohydrate (III) on the basis of spectroscopic and elemental analyses. Anal. Found C; 64.84 H; 5.78 N; 6.40. Calcd. for $C_{10}H_{13}NOS$ C; 65.80 H; 5.98 N; 6.39. The compound (III) has strong i.r. absorption bands at 940 cm^{-1} ($-S=N-$), 3130 cm^{-1} ($-N-H$) 3450 cm^{-1} (OH). The mass spectrum was completely identical to that of diphenyl sulfide. This suggests that S-N bond cleavage is very facile at the temperature of m.p. of (III) and actually (III) was also found to give the sulfide upon heating at around $100^\circ C$. The structure of (III) was elucidated further by the chemical methods. Namely, (III) gave the starting N-p-tosylsulfilimine quantitatively when it was treated with p-toluenesulfonyl chloride in ether solution in the presence of pyridine while (III) was hydrolyzed to the sulfoxide when it was treated with dil. aq. solution of sulfuric acid. Thus the whole scheme of all these reactions may be summarized as shown below.



Similarly other diaryl N-p-tosylsulfilimines having various substituents are found to give the corresponding "free" sulfilimines upon treatment with sulfuric acid under the same reaction condition. In the case of alkyl aryl or dialkyl sulfilimines the same treatment did not give the