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Sulfilimine and Sulfoximine VI

The reaction of N-sulfonylsulfilimine with sulfoxide

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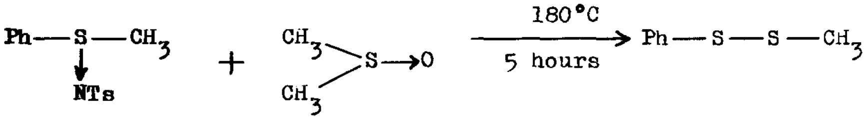
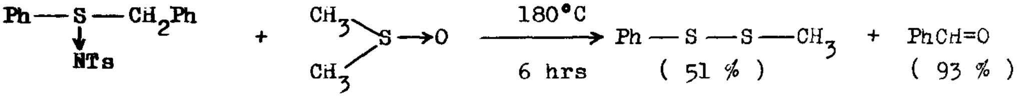
Recently, the substitution on S atom of sulfoxides has been studied extensively by means of ^{18}O tracer technique in our laboratories[1)] and evidence supporting the four-membered cyclic structure for the transition state or intermediate has been demonstrated.[2)] A similar four membered dipolar interaction was assumed to explain an unusually slow Ei reaction of N-sulfonylsulfilimine in DMSO.[3)] In an attempt to obtain further evidence to support the 1.2-dipolar interaction a mixture of a sulfilimine and DMSO was heated with a hope to find a new exchanged reaction between sulfoxide oxygen and sulfilimine.

However when methyl phenyl N-p-tolylsulfonylsulfilimine was heated with DMSO at 180°C for 5 hours, the exchange reaction was not found, but methyl phenyl disulfide was obtained unexpectedly in substantial yield.



The disulfide was identified by comparing it with the IR, NMR spectra and GLC behaviour of those of the authentic compound which was prepared from the reaction of phenylsulfenylchloride with methyl mercaptan.

Besides methyl phenyl disulfide (40 %), paraformaldehyde (33 %), p-tolylsulfoneamide (30 %) and diphenyldisulfide (30 %) were isolated. Since diphenyl disulfide was confirmed to be produced by disproportionation of methyl phenyl disulfide, the initial yield of methyl phenyl disulfide would be more than 70 %. Though a large number of reactions on DMSO have been known, this reaction is quite unique since it will be expected that DMSO can be used as a new reagent to synthesize unsymmetrical disulfides. Actually, when benzyl phenyl N-p-tolylsulfonylsulfilimine was heated with DMSO at 180°C for 6 hours, methyl phenyl disulfide and quantitatively benzaldehyde were obtained.

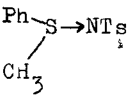
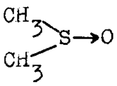
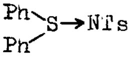
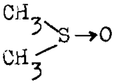
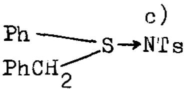
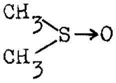
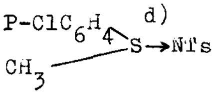
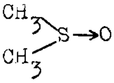
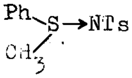
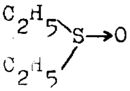
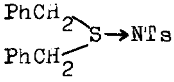
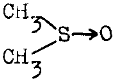


However diphenyl N-p-tolylsulfonylsulfilimine did not react under the same reaction condition and the sulfilimine was recovered.

This reaction, however is not confirmed to DMSO alone for ethyl phenyl disulfide (51 %) was obtained when methyl phenyl N-p-tolylsulfonylsulfilimine and diethyl sulfoxide was heated at 180°C for 2 hours.

Reaction products and yields were listed in Table I.

Table I Reaction of sulfilimine with sulfoxide

Sulfilimine	Sulfoxide	Condition	Products and yield (%)	
			disulfide	aldehyde
 a)		180° 6 hrs	Ph-S-S-CH_3 (40 %) Ph-S-S-Ph (30 %)	$(CH_2O)n$ (33 %)
 b)		180° 13 hrs	———	———
 c)		180° 6 hrs	Ph-S-S-CH_3 (51 %) Ph-S-S-Ph (36 %)	PhCH=O (93 %) $(CH_2O)n$
 d)		180°C 65 hrs	P-ClC_6H_4-SS-CH_3 (37 %) $(P\text{-}ClC_6H_4S)_2$ (54 %)	$(CH_2O)n$ (35 %)
		180°C 2 hrs	Ph-S-S-C_2H_5 (51 %) Ph-S-S-Ph (10%)	
		180°C 3 hrs	PhCH_2-SS-CH_3 (37 %)	PhCH=O (99 %)

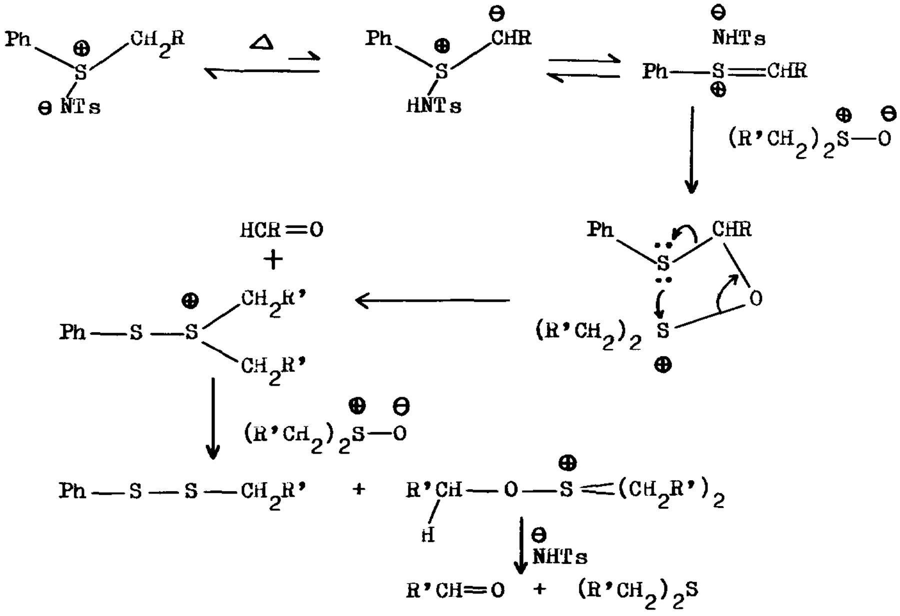
a) Ph-S-CH_3 (10 %) and $TsNH_2$ (30 %) were obtained and recovered sulfilimine (20 %).

b) sulfilimine was recovered quantitatively.

c) $TsNH_2$ (87 %) was obtained.

d) P-ClC_6H_4-S-CH_3 (8 %) was obtained.

From these results, the possible mechanism for this reaction is considered as shown below.



(Ts : P-$CH_3C_6H_4SO_2$- , R : H, Ph, R' : H, CH_3)

The detailed and further studies of this reaction will be reported soon from these laboratories.

Reference

1) S. Oae and M. Kise, Bull. Chem. Soc., Japan, 43, 1416~1429 (1970) The related references are cited therin.

2) S. Oae, M. Yokoyama, M. Kise and N. Furukawa, Tetrahedron Letters 1968, 4131

3) S. Oae, K. Tsujihara and N. Furukawa, Tetrahedron Letters 1970 to be published