## PHOTOCHEMICAL REDUCTION OF N-TOSYLSULFILIMINES WITH THIOLATE ANION

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The reaction between N-tosyldiarylsulfilimines and p-toluenethiolate anion did not take place in the dark even upon heating up to 62° but proceeded smoothly upon irradiation with visible light in DMF at room temperature, affording S-N bond cleavage products.

We reported earlier that the following  $S_N^2$  reaction took place when an optically active alkyl N-tosylsulfilimine was treated with thiolate anion (Eq.1),<sup>1)</sup> whereas the reaction between N-tosylsulfilimines and *p*-toluenethiolate anion was deemed to result in the reductive S-N bond cleavage of the sulfilimine (Eq.2).<sup>1)</sup> In order to examine the possibility that the

$$Ph-S-C \xrightarrow{n-C_6H_{15}} Ph-S-\overline{N-TS} + Ph-S-\overline{N-TS} + H \xrightarrow{n-C_6H_{13}} C-S-Ph$$
(1)

$$Ar^{1}-S-Ar^{2} + 2p-To1-S^{-} \xrightarrow{(1) \text{ DMF}} Ar^{1}-S-Ar^{2} + (p-To1-S)_{2} + TS-NH_{2}$$
(2)  
N-TS (2)

latter reaction (Eq.2) proceeds via formation of a  $\sigma$ -sulfurane as the reaction of sulfoxides with Grignard reagents, the reaction between N-tosyldiarylsulfilimines and sodium *p*-toluenethiolate has been reexamined and found to be a photochemical reduction.

When a solution of N-tosyldiarylsulfilimine and sodium p-toluenethiolate in DMF was heated to 62° in the dark, practically no reaction took place, while the reaction did proceed only under irradiation with visible light. Thus, a mixture of an N-tosylsulfilimine and sodium ptoluenethiolate was irradiated with 150 W tungsten lamp (W-lamp) in DMF in degassed sealed tubes at 20°-26°. Then, the tubes were opened, diluted with dil. aq. HCl and extracted with

\*present address: Okayama University of Science, Ridai-cho 1-1, Okayama, 700 Japan. +present address: Institute of Organic Synthesis, Academy of Science, Latvia SSR, Riga, 226011, Latvia SSR. benzene. The reaction products separated from the starting sulfilimine by column chromatography was subjected to gas chromatographic analysis. The results are summarized in Table 1.

The photochemical reaction of N-tosyldiarylsulfilimines with sodium *p*-toluenethiolate gave diaryl sulfides, bis(*p*-tolyl) disulfide and tosylamide as major products, together with trace amounts of aryl *p*-tolyl sulfides formed by ipso substitution on aryl carbon of sulfilimines by *p*-toluenethiolate. In the reaction of N-tosyldialkylsulfilimines with sodium *p*-toluenethiolate (runs 16 and 17), however, one of the major products was unsymmetrical sulfide formed by the  $S_N^2$  reaction shown in Eq. 1. In some cases a substantial amount of *p*-tolylthio-N,N-dimethyl carbamate was isolated from the reaction mixture (run 14). The thiocarbamate is presumed to be formed by a radical process, i.e. a coupling of *p*-TolS· and (CH<sub>3</sub>)<sub>2</sub>NCO· generated by hydrogen abstraction of DMF. In all photochemical runs listed in Table 1, we found a noticeable amounts of toluene which is originated from p-toluenethiolate. The formation of toluene is undoubtedly related to the low yield of bis(*p*-tolyl) disulfide than the stoichiometry shown in Eq.2, and considered to be due to a radical process.

In order to examine if this photochemical reaction could be a radical chain reaction initiated by irradiation with visible light, the effect of radical scavengers was tested with galvinoxyl and hydroquinone which may suppress the chain reaction.<sup>3)</sup> However, hydroquinone did not affect the rate of reduction of the sulfilimine (run 8) and galvinoxyl could not stop the reaction (run 7). A substantial retardation caused by galvinoxyl would be due to the internal filter effect of galvinoxyl; i.e. galvinoxyl strongly absorbes the light of visible region  $(\lambda_{max}=420 \text{ nm}, \varepsilon=200,000)$ .<sup>3a)</sup> These observations suggest that the reaction is not a photoinduced radical chain reaction. This was further evidenced by the following observations; i.e. when a DMF solution of N-tosyldiphenylsulfilimine, sodium *p*-toluenethiolate and azobisisobutyronitrile (AIBN) was heated at 60°, the reduction of the sulfilimine did not take place, but only the partial oxidation of the thiolate to the disulfide was observed (run 9).

One interesting aspect of this reaction is the following. When a colorless solution of the sulfilimine and a very pale yellow solution of sodium *p*-toluenethiolate is mixed, the color of the solution immediately changes to deep yellow, while no reaction takes place yet, suggesting the formation of a CT-complex between the sulfilimine and the thiolate anion. This can be shown by the spectral data depicted in Fig.1, where the CT-band is observed in the region of 400-500 nm.

These characteristic observations on this new photochemical reduction of these sulfilimines with thiolate anion suggest that this photochemical reduction of N-tosyldiarylsulfilimines

Run	N-Tosylsul	filimiı	ne Reaction Conditon	Product(mol/mol%)					
	R <sup>1</sup> ──Ş ─ N-Ts	- R <sup>2</sup>		Recovd. sulfilimine	R <sup>1</sup> -S-R <sup>2</sup>	p-Tol-S-R <sup>1</sup>	(p-To1S) <sub>2</sub>	TsNH <sub>2</sub>	
1	Ph	Ph	dark/62°/28.5h	89	1	0	4	g)	
2	Ph	Ph	dark/20°/4days	87	1	0	6	g)	
3	Ph	Ph	room light/21°/5days	75	13	0	19	g)	
4	Ph	Ph	150W W-lamp/21°/2h	77	11	0	21	g)	
5	Ph	Ph	150w W-lamp/21°/16.5h	39	58	trace	38	g)	
6	Ph	Ph	150W W-lamp/21°/44h	0	85	0.6	41	96	
7	Ph	Ph	150W W-lamp/26°/44h <sup>b)</sup>	68	32	trace	23	g)	
8	Ph	Ph	150W W-lamp/25°/44h <sup>C)</sup>	0	83	0.5	93	g)	
9	Ph	Ph	room light/60°/12h <sup>d)</sup>	90	3	trace	10	g)	
10	p-To1	Ph	150W W-lamp/22°/44h	2	77	trace	29	g)	
11	p-MeO-Ph	Ph	150W W-lamp/26°/44h	27	59 p-Tol-S	trace -Ph:0.6	27	g)	
12	p-MeO-Ph	Ph	150W W-lamp/26°/77h	7	80 p-To1-S	trace -Ph:0.4	25	94	
13	p-MeO-Ph	p-Me0	-Ph 150W W-lamp/26°/44h <sup>e)</sup>	39	40	1.5	22	g)	
14	p-Cl-Ph	Ph	150W W-lamp/26°/46h <sup>f)</sup>	7	14	0	8	g)	
				c1-@-s-	Cl-O-S-Ph:68 ; p-Tol-S-Ph:trace (CH <sub>3</sub> ) <sub>2</sub> N-G-S-Tol-p:21				
15	p-Cl-Ph	Ph	dark/26°/113.5h	0	trace	trace	10	g)	
				p-To1-S-	O-Ş-Ph NTs	35;p-Tol-S- <b>(</b>	⊙-S-Ph:t	race	
16	n-Bu	n-Bu	150W W-lamp/26°/81h	49	19.2 p-Tol-SS	15 S-Bu-n:6 ; (	18 (n-BuS) <sub>2</sub> :2	g)	
17	n-Bu	n-Bu	150W W-lamp/26°/205h	24 p-Tol-SS-	26 Bu-n:8;	29 (n-BuS) <sub>2</sub> :5;	1.3 Toluene:10	g) <sub>D</sub> h)	
18	n-Bu	n-Bu	dark/26°/228h	42	4	32	4	g)	
19	↓ S Ň-Ts		150W W-lamp/26°/76.5h	55	12	g)	10	g)	

Table 1 The Reaction of N-Tosylsulfilimines with Sodium p-Toluenethiolate in DMF<sup>a</sup>)

a) In degassed sealed Pyrex tube. Initial concentration: [Sulfilimine]=0.3M;  $[p-TolS^Na^+]=0.9M$ . b) In the presence of 0.024M galvinoxyl. c) In the presence of 0.45M hydroquinone. d) In the presence of 0.17M AIBN. e) Initial concentration: [Sulfilimine]=0.223M;  $[p-TolS^Na^+]=0.69M$ . f) Initial concentration: [Sulfilimine]=0.17M;  $[p-TolS^Na^+]=0.9M$ . g) Not determined.

h) The formation of substantial amounts of toluene was observed in all other photochemical runs.

would proceed through the following mechanistic paths in Scheme 1. A similar mechanism was proposed by Nickol and Kampmeier for the photolysis of triphenylsulphonium iodide in CHCl<sub>3</sub> in which the initial single electron transfer from iodide to the sulfonium ion and subsequent homolysis of C-S bond give diphenyl sulfide, iodobenzene, benzene and hexachloroethane.<sup>4</sup>

The reaction of N-tosyl-S-(p-chlorophenyl)-S-phenylsulfilimine gave p-tolyl p-phenylthiophenyl sulfide as the major product (run 14). The control experiment showed that the ipso substitution on N-tosyl-S-(p-chlorophenyl)-S-phenylsulfilimine (Eq.3) proceeds at 26° in the dark in a moderate rate (run 15). However, since this dark reaction in Eq.3 is slower than the photochemical reaction (run 14), the dark reaction in Eq. 3 cannot explain the formation of whole p-tolyl p-phenylthiophenyl



explain the formation of whole p-tolyl p-phenylthiophenyl sulfide in run 14, suggesting that the ipso substitution of Cl by p-TolS<sup>-</sup> took place through the photochemical process.

Further investigations on this and related reactions are now underway in these laboratories.

$$C1 \longrightarrow S-Ph + p-To1-S^{-} \xrightarrow{dark} p-To1-S \longrightarrow S-Ph + C1^{-}$$
(3)  

$$R^{1}-S-R^{2} + ArS^{-} \xrightarrow{DMF} \begin{pmatrix} R^{1}-\overset{S}{S}-R^{2} \\ R^{1}-\overset{S}{S}-R^{2} \\ N-TS \end{pmatrix} CT \xrightarrow{h\nu} [R^{1}-\overset{S}{S}-R^{2} ArS \cdot] \xrightarrow{[R^{1}-S-R^{2}, TSN^{-}, ArS \cdot]} \\ \xrightarrow{(ArS)_{2} + TSNH_{2}} \xrightarrow{ArS^{-}} ArS^{-} ArS\overline{NTS} + R^{1}-S-R^{2} R^{1}-S-R^{2}, TSNH_{2}, (CH_{3})_{2}NCSAr, ArH$$

Scheme 1 Possible Mechanism for Photochemical Reaction of N-Tosylsulfilimine with Thiolate [References]

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  - (Received in Japan 25 October 1984)