

THE ISOLATION OF GEOMETRICAL ISOMERS OF THIONE S-IMIDES

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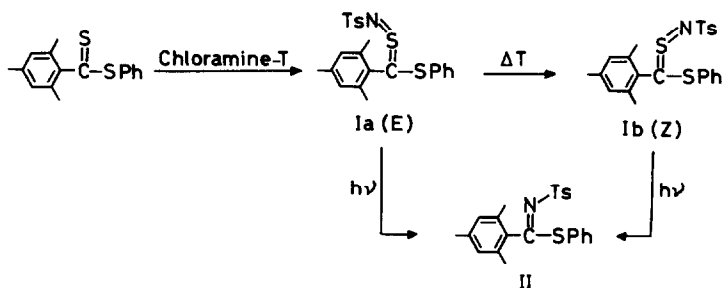
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Thione S-imides belong to the class of heterocumulenes containing a central tetravalent sulfur atom. Our interest in these compounds originates from their structural relationship with thione S-oxides (sulfines). It is now firmly established that sulfines have a bent structure<sup>1</sup>. As a consequence, geometrical isomers exist<sup>1</sup> for sulfines  $XYC=S=O$  with  $X \neq Y$ . For the thione S-imides which are the isoelectronic nitrogen analogs of sulfines, a bent structure and accordingly geometrical isomers may be expected. In this paper we wish to report the first isolation of stable geometrical isomers of thione S-imides.

The synthesis of thione S-imides was accomplished for the first time by Oae *et al.*<sup>2</sup> by reacting 1,2-dithiole-3-thiones (trithiones) with chloramine-T. The remarkable stability of these thione S-tosylimides was attributed to the presence of the  $6\pi$ -electrons system in trithiones. By an ultimate 1,3-dehydrochlorination Burgess *et al.*<sup>3</sup> prepared fluorenethione S-benzoylimide in solution at low temperature. Similarly, Senning *et al.*<sup>4</sup> obtained the thermally stable  $RSO_2C(SC_6H_5)=S=N-t-Bu$ . In none of these reports the possibility of geometrical isomerism was taken into account.

For the present study we chose as substrates phenyl 2,4,6-trimethyl-dithiobenzoate and mesityl phenyl thioketone anticipating a possible stabilization of the corresponding S-imides through steric hindrance. Reaction of phenyl 2,4,6-trimethyldithiobenzoate with 1 equiv. of chloramine-T in methanol at room temperature for 10 min. gave a nearly quantitative yield of the corresponding thione S-tosylimide Ia (see Scheme) as yellow-orange crystals, m.p. 131-133<sup>o</sup>. Anal. found: C, 62.38; H, 5.31; N, 3.11; S, 21.60. Calcd. for  $C_{23}H_{23}NO_2S_3$ : C, 62.55; H, 5.25; N, 3.17; S, 21.78. UV(EtOH):  $\lambda_{max}$  395 nm (log  $\epsilon$ : 3.97). IR(KBr): 955 (S=N), 1292, 1134 ( $SO_2$ )  $cm^{-1}$ . NMR( $CDCl_3$ ):  $\delta$  2.10 (s, 6H, o-Me's), 2.27 (s, 3H, p-Me), 2.32 (s, 3H, p-Me), 6.84 (s, 2H, m-H's), 7.05 and 7.40 (ABq,  $CH_3C_6H_4$ ), 7.53 (s, 5H,  $C_6H_5$ ) ppm. MS: m/e 300 (mes-C=NTs)<sup>+</sup>, 272 [mes-C(=S)-SPh]<sup>+</sup>, 264 (Ts-SPh)<sup>+</sup>, 163 (mes-C=S)<sup>+</sup>.

When Ia was heated in refluxing methanol for 1 h., a yellow compound Ib (see Scheme) was obtained in an almost quantitative yield, m.p. 162-163<sup>o</sup>.

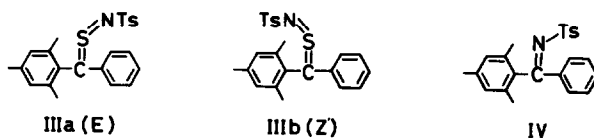


This product Ib gave the same elemental analysis as Ia and showed the following spectral features: UV(EtOH):  $\lambda_{\max}$  388 nm (log  $\epsilon$ : 4.08). IR(KBr): 973, 947 (S=N), 1273, 1129 (SO<sub>2</sub>) cm<sup>-1</sup>. NMR(CDCl<sub>3</sub>):  $\delta$  2.10 (s, 9H, *o*-Me's + *p*-Me), 2.37 (s, 3H, *p*-Me), 6.67 (s, 2H, *m*-H's), 7.12 (m, 5H, C<sub>6</sub>H<sub>5</sub>), 7.23 and 7.88 (ABq, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) ppm. The MS gave the same fragmentation pattern as Ia.

The analytical and spectral data strongly indicate that Ia and Ib are geometrical isomers. To further substantiate this conclusion both isomers were subjected to photolysis. Irradiation of Ia as well as Ib in benzene at 360 nm gave the tosylimine II (see Scheme) in 86% yield as white crystals, m.p. 146-148°. Anal. found: C, 67.61; H, 5.77; N, 3.31; S, 15.70. Calcd. for C<sub>23</sub>H<sub>23</sub>NO<sub>2</sub>S<sub>2</sub>: C, 67.45; H, 5.66; N, 3.42; S, 15.66. IR(KBr): 1577, 1562 (C=N), 1319, 1150 (SO<sub>2</sub>) cm<sup>-1</sup>. NMR(CDCl<sub>3</sub>):  $\delta$  2.23 (s, 3H, *p*-Me), 2.29 (s, 6H, *o*-Me's), 2.31 (s, 3H, *p*-Me), 6.79 (s, 2H, *m*-H's), 7.0-7.6 (m, 9H, aromatic) ppm. This extrusion of sulfur was also observed for the trithione *S*-tosylimides<sup>2</sup> and the isoelectronic sulfines<sup>5</sup>.

The geometrical configuration of isomers Ia and Ib was determined by means of ASIS experiments in analogy with the assignment of geometry in *Z*- and *E*-sulfines<sup>6</sup>. Benzene associates preferably with the positive end of a dipole in a molecule. Accordingly, in the *E*-thione *S*-tosylimide benzene should complex at the right hand side of the molecule and in the *Z*-isomer at the left hand side. Because of this solvent molecule orientation the *ortho*-methyl protons in the *Z*-isomer will experience a larger ASIS effect than the *ortho*-methyl protons in the *E*-isomer. The spectrum of the lower melting isomer Ia showed that the *o*-methyls were shifted upfield by 0.05 ppm; for the higher melting isomer IIb this upfield shift was 0.18 ppm<sup>7</sup>. Therefore, the *E* configuration is assigned to Ia and the *Z* to Ib.

Mesityl phenyl thioketone also reacted smoothly with chloramine-T in methanol at room temperature, yielding almost quantitatively the thione *S*-tosylimide IIIa as yellow crystals, m.p. 142-142.5°. IR(KBr): 959 (S=N), 1306, 1143 (SO<sub>2</sub>) cm<sup>-1</sup>. NMR(CDCl<sub>3</sub>):  $\delta$  2.08 (s, 6H, *o*-Me's), 2.32 (s, 3H, *p*-Me), 2.37 (s, 3H, *p*-Me), 6.96 (s, 2H, *m*-H's), 7.25 and 7.83 (ABq, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 7.42



(m, 3H, *m*- + *p*-H's of C<sub>6</sub>H<sub>5</sub>), 8.15 (m, 2H, *o*-H's of C<sub>6</sub>H<sub>5</sub>) ppm.

Refluxing of IIIa in methanol for 5 h. gave a mixture of the two geometrical isomers, which was separated by fractional crystallization from ether-pentane. The isomer of IIIa, *viz.* IIIb, was obtained in 50% yield as yellow-orange crystals, m.p. 121-122°. IR(KBr): 985 (S=N), 1308, 1142 (SO<sub>2</sub>) cm<sup>-1</sup>. NMR(CDCl<sub>3</sub>): δ 1.88 (s, 6H, *o*-Me's), 2.28 (s, 3H, *p*-Me), 2.35 (s, 3H, *p*-Me), 6.90 (s, 2H, *m*-H's), 7.17 and 7.68 (ABq, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 7.37 (s, 5H, C<sub>6</sub>H<sub>5</sub>) ppm.

Again irradiation of both isomers in benzene at 360 nm gave loss of sulfur yielding the tosylimine IV in 67% yield as white crystals, m.p. 118-119°. IR(KBr): 1557 (C=N), 1318, 1159, 1150 (SO<sub>2</sub>) cm<sup>-1</sup>. NMR(CDCl<sub>3</sub>): δ 2.04 (s, 6H, *o*-Me's), 2.30 (s, 3H, *p*-Me), 2.38 (s, 3H, *p*-Me), 6.87 (s, 2H, *m*-H's), 7.23 and 7.79 (ABq, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), 7.37 (m, 3H, *m*- + *p*-H's of C<sub>6</sub>H<sub>5</sub>), 7.67 (m, 2H, *o*-H's of C<sub>6</sub>H<sub>5</sub>).

On the basis of ASIS experiments (IIIa: Δ<sub>ASIS</sub> *o*-Me's = 0.22 ppm; IIIb: Δ<sub>ASIS</sub> *o*-Me's = 0.10 ppm) the *E* geometry was assigned to IIIa and the *Z* to IIIb (here, in the *E*-isomer benzene complexes at the left hand side).

In the NMR spectrum of the *E*-isomer IIIa the signal for the two *ortho*-hydrogens of the Ph group was observed at considerably lower field (8.15) than the remaining phenyl protons (7.42), whereas in the opposite isomer IIIb all the five phenyl protons absorb at the same field (7.37). The same phenomenon was encountered in aromatic sulfines for the *ortho*-protons *syn* to the sulfine oxygen<sup>8</sup>. Most likely, the *ortho*-hydrogens in the *E*-isomer IIIa turn around through the deshielding zone of the S=N bond.

The reaction of chloramine-T with the dithiobenzoate and the thioketone most likely is a kinetically controlled process, in both cases leading to only one isomer. On heating a thermodynamic isomerization takes place. For the thione *S*-imide Ia this results in the complete conversion into Ib. The thione *S*-imides IIIa and IIIb apparently are about equally stable, because of the 1:1 mixture of isomers obtained.

The reaction with chloramine-T was also attempted with the unhindered 4,4'-dimethoxythiobenzophenone<sup>9</sup>. At room temperature in MeOH the reaction resulted in an orange solution. However, this colour faded in a few seconds. From the colourless reaction mixture 4,4'-dimethoxybenzophenone and *p*-toluenesulphonamide were isolated in good yields. By performing the reaction at -30° the orange colour persisted. A quickly run TLC of this solution showed a yellow spot presumably belonging to the thione *S*-imide. Warming up to room temperature again gave the ketone and *p*-toluenesulphonamide. These products

most likely arise from hydrolysis (chloramine-T contains 3 moles of water of crystallization) of the thione *S*-imide. When the same reaction was performed in dry  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ$  together with a small amount of 18-Crown-6 (to dissolve chloramine-T) and  $\text{Na}_2\text{SO}_4$  (to trap the water of crystallization in chloramine-T), also an orange solution was obtained. Warming up to room temperature gave again a colourless solution from which the corresponding imine was isolated as the predominant product. This imine presumably arises from thermal desulfurization of the thione *S*-imide. Attempts to trap the thione *S*-imide by reaction with  $\text{MeLi}$ ,  $\text{CH}_2\text{N}_2$  or enamine at  $-30^\circ$  were hitherto unsuccessful.

From this study it may be concluded that for stable thione *S*-imides derived from dithiobenzoates or thiobenzophenones, sterical hindrance in the direct environment of the thiono carbon atom is a prerequisite.

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7. Because of the limited solubility in benzene ASIS is here defined as:  
 $\delta (\text{CDCl}_3) - \delta [\text{CDCl}_3 + \text{C}_6\text{D}_6 (1:1)]$ .
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9. Cf. M.M. Campbell and D.M. Evgenios, *J.C.S. Perkin I*, 2866 (1973).