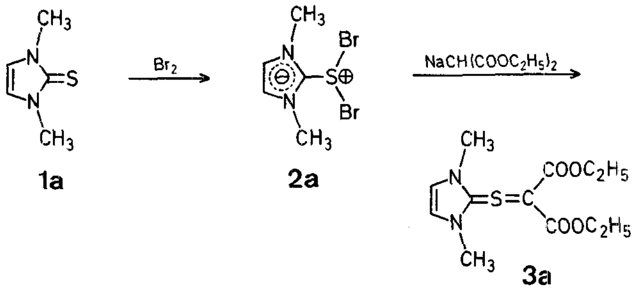
A New Synthesis of Thione *S*-Imides

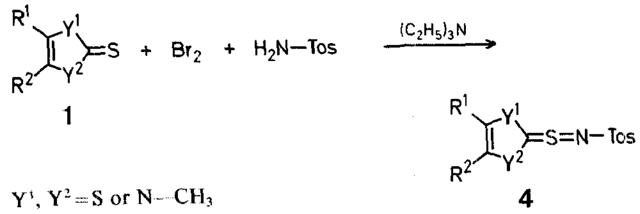
Atsuo Koide, Takao Saito, Masahiro Kawasaki, Shinich Motoki*

Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan

Recently, some thione *S*-imides have been isolated as stable compounds by two different methods: (a) by the reaction of thiocarbonyl compounds with chloramine-T[1,2] and (b) by base-promoted 1,3-dehydrohalogenation of substituted sulfenamides[3-6]. Previously, we had also reported the synthesis of thione *S*-imides by a Wittig-type reaction of a phosphonium ylid with *N*-sulfinyl-*p*-toluenesulfonamide[7]. On the other hand, Burgess et al.[8] reported that the reaction of 1,3-dimethyl-2-thioxo-1,2-dihydroimidazole (**1a**) with bromine and diethyl sodiomalonate afforded a thiocarbonyl ylid **3a** via a sulfurane intermediate **2a**.



This result suggested to us that the reaction of thiones with bromine and *p*-toluenesulfonamide might provide a new method of obtaining thione *S*-imides. Therefore, we have attempted the reaction of substituted 1,3-dimethyl-2-thioxo-1,2-dihydroimidazoles, 3-methyl-2-thioxo-1,3-thiazoles and 2-thioxo-1,3-dithioles **1** with bromine and *p*-toluenesulfonamide in the presence of triethylamine.



$Y^1, Y^2 = S$ or $N-CH_3$

The new thione *S*-imides (**4**) were obtained in 18–75% yields (Table). The stability of **4** can be recognized by effective charge delocalization in the "push-pull" substituted system[8].

0039-7881/81/0632-0486 $ 03.00

Table. Thione *S*-Imides **4** from Thiones **1**, Bromine, and *p*-Toluenesulfonamide

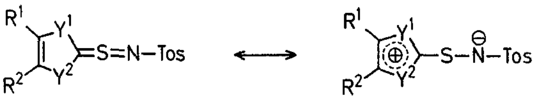
Product No.	R^1	R^2	Y^1	Y^2	Yield [%]	m.p. [°C]	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}] SO$_2$	I.R. (KBr) ν [cm^{-1}] C=S=N	M.S. (70 eV) *m/e* (relative intensity %)
4a	H	H	N—CH$_3$	N—CH$_3$	18	121.5–123.0° (dec.)[b]	$C_{12}H_{15}N_3O_2S_2$ (297.4)	1140, 1090	960	265 (M$^+$ – S, 5); 155 (42); 128 (76)
4b	—(CH=CH)$_2$—		N—CH$_3$	N—CH$_3$	24	116.0–118.0° (dec.)[b]	$C_{16}H_{17}N_3O_2S_3$ (347.5)	1140, 1090	900	315 (M$^+$ – S, 3); 178 (100); 155 (6)
4c	—(CH=CH)$_2$—		N—CH$_3$	S	40 (84)[c]	121.0–121.5° (dec.)[b]	$C_{15}H_{14}N_2O_2S_3$ (350.0)	1140, 1090	950	318 (M$^+$ – S, 3); 181 (100); 155 (16)
4d	H$_3$COOC	H$_3$COOC	N—CH$_3$	S	75 (74)[c]	125.0–129.5° (dec.)[b]	$C_{15}H_{16}N_2O_6S_2$ (416.5)	1140, 1090	920	386 (M$^+$ – S, 4); 247 (100); 155 (4)
4e	C$_6$H$_5$	H	S	S	30	112.0–113.0° (dec.)[d]	$C_{16}H_{13}NO_2S_4$ (379.5)	1140, 1090	920	347 (M$^+$ – S, 58); 210 (7)

[a] Satisfactory microanalyses obtained: C ±0.45, H ±0.20, N ±0.19, S ±0.32.

[b] Colorless needles.

[c] Yield of reaction with chloramine-T.

[d] Yellow needles.



On the other hand, treatment of the thiones **1c, d** with chloramine-T also afforded **4c** and **4d**. However, reaction of **1e** gave *N*-*p*-toluenesulfonyl-2-imino-4-phenyl-1,3-dithiole, presumably formed by the decomposition of **2e**, and the reaction of **1a** and **1b** resulted in the recovery of the thione and *p*-toluenesulfonamide. Thus, the present method is especially suitable for the preparation of these heterocyclic thione *S*-imides.

Reaction of Thiones 1 with Bromine and *p*-Toluenesulfonamide; General Procedure:

To a stirred solution of **1** (0.01 mol) and *p*-toluenesulfonamide (1.71 g, 0.01 mol) in dry dichloromethane (20 ml), bromine (1.60 g, 0.01 mol) in dry dichloromethane (5 ml) is added dropwise at –15 °C under nitrogen. The mixture is stirred at –15 °C for an additional 0.5 h and then cooled to –78 °C. Triethylamine (2.02 g, 0.02 mol) in dry dichloromethane (10 ml) is added drop-wise with stirring. After 1 h, the mixture is allowed to warm to room temperature, water (50 ml) is then added with stirring, the organic layer is separated, and evaporated in vacuo. The residue is washed with ether (20 ml) and ethanol (10 ml) to give the corresponding product **4**. Only **4c** can be recrystallized without decomposition from dichloromethane/hexane as colorless needles.

Reaction of Thione 1c or 1d with Chloramine-T:

To the thione **1c** or **1d** (0.01 mol) in ethanol (30 ml) is added a ethanol solution (30 ml) containing a slight excess of chloramine-T (3.1 g, 0.011 mol) with stirring at 0 °C. After 0.5 h, the precipitated product **4c** or **4d** is filtered, washed with water and ethanol, and dried in vacuo.

Received: January 5, 1981

---

[1] S. Tamagaki, S. Oae, *Tetrahedron Lett.* **1972**, 1159.

[2] A. Tangerman, B. Zwanenburg, *Tetrahedron Lett.* **1977**, 259.

[3] S. Holm, J. A. Boerma, N. H. Nilsson, A. Senning, *Chem. Ber.* **109**, 1069 (1976).

[4] G. J. Wentrup, F. Boberg, *Justus Liebigs Ann. Chem.* **1978**, 387.

[5] F. Boberg, U. Puttins, G. J. Wentrup, *Justus Liebigs Ann. Chem.* **1979**, 689.

[6] E. M. Burgess, H. R. Penton Jr., *J. Org. Chem.* **39**, 2885 (1974).

[7] T. Saito, S. Motoki, *J. Org. Chem.* **42**, 3922 (1977).

[8] A. J. Arduengo, E. M. Burgess, *J. Am. Chem. Soc.* **98**, 5020 (1976).

0039-7881/81/0632-0487 $ 03.00