

## Thioxanthene *S*-(Tosylimide): Preparation and Rearrangement to 9-(*N*-Tosylamino)thioxanthene

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**Summary** The preparation of thioxanthene *S*-(tosylimide) and its rearrangement to 9-(*N*-tosylamino)thioxanthene are described.

DESPITE current interest in the chemistry of thioxanthene 10-oxides<sup>1</sup> and 10-alkyl salts,<sup>2</sup> there are few reports on the nitrogen analogues, thioxanthene *S*-imides. Recently we have noticed the unusual behaviour of a 10-aminothioxanthanium salt which, upon treatment with base, produced a

dimeric compound presumably *via* the non-isolable *S*-imide (2).<sup>3</sup> In connection with our studies on cyclic *S*-imides,<sup>4</sup> we report the preparation and some chemical properties of the *S*-(tosylimide) (3).†

Treatment of thioxanthene (1) with chloramine-T in methanol-acetic acid (20:1)<sup>5</sup> followed by conventional isolation procedures gave four products (3)—(6), whose relative yields depended upon the conditions (see Table). The desired *S*-(tosylimide) (3) was obtained only under mild reaction conditions; at higher temperature (60—70 °C) or

† Although Shah has recently claimed the synthesis of (3) (J. J. Shah, *Canad J. Chem.*, 1975, 53, 2381) its m.p., and u.v. and i.r. spectral data are incompatible with ours.

with excess of chloramine-T the secondary products (4)—(6) were obtained.

by acid hydrolysis to thioxanthenone (6) and toluene-*p*-sulphonamide.

TABLE. Reactions of (1) (10 mmol) with chloramine-T (10 or 30 mmol).

Conditions	Isolated yield (%)			
	(3)	(4)	(5)	(6)
Room temp., 20 h <sup>a</sup> .. ..	39	46	c	—
60—70 °C, 5 h <sup>a</sup> .. ..	c	35	24	5
Room temp., 20 h <sup>b</sup> .. ..	c	c	92	c
60—70 °C, 5 h <sup>b</sup> .. ..	—	c	73	7

<sup>a</sup> 10 mmol of chloramine T. <sup>b</sup> 30 mmol of chloramine T.  
<sup>c</sup> Traces were detected on t.l.c. but not isolated.

Compound (3),<sup>‡</sup> m.p. 138—139 °C, shows  $\lambda_{\max}$  (MeOH) 227 and 264 nm;  $\nu_{\max}$  (CHCl<sub>3</sub>) 1300, 1150, and 1095 (SO<sub>2</sub>), and 970 (S—N) cm<sup>-1</sup>;  $\delta$  4.10 (ABq, *J* 17 Hz, benzylic-H); *m/e* 367 (*M*<sup>+</sup>) and major peaks at 211 and 197. Refluxing (3) in methanolic KOH or in benzene containing a small amount of conc. HCl gave (4), m.p. 172—173 °C, as yellow prisms in high yield, whose structure was assigned on the basis of its physical [ $\nu_{\max}$  (CHCl<sub>3</sub>) 3367, 1152, 1092, 1015, 920 cm<sup>-1</sup>;  $\delta$  5.43 (ABq, *J* 8 Hz)] and chemical properties. Treatment of (4) with an equimolar amount of chloramine-T in methanol-acetic acid (20:1) at room temperature gave (5), m.p. 212 °C, in 72% yield. Structure (5) was confirmed

<sup>‡</sup> All new compounds gave satisfactory elemental and spectral analyses.

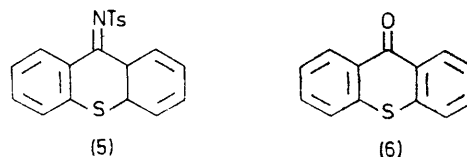
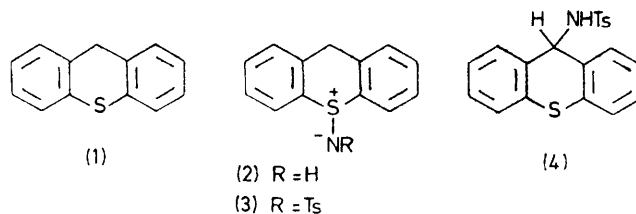
<sup>1</sup> For examples, H. J. Shine and L. Hughes, *J. Org. Chem.*, 1966, **31**, 3142; D. W. Chasar, A. L. Ternay, Jr., L. Hughes, H. J. Shine, and S. A. Evans, *J. Org. Chem.*, 1975, **40**, 1737, and references therein; M. Hori, T. Kataoka, and H. Shimizu, *Chem. Letters*, 1974, 1073.

<sup>2</sup> For examples, M. Hori, T. Kataoka, and H. Shimizu, *Chem. Letters*, 1974, 1117; B. E. Maryanoff, J. Stackhouse, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, 1975, **97**, 2718.

<sup>3</sup> Y. Tamura, H. Matsushima, J. Minamikawa, M. Ikeda, and K. Sumoto, *Tetrahedron*, 1975, **31**, 3035.

<sup>4</sup> Y. Tamura, H. Matsushima, M. Ikeda, and K. Sumoto, *Synthesis*, 1974, 277; M. Kise, M. Murase, M. Kitano, T. Tomita, and H. Murai, *Tetrahedron Letters*, 1976, 691.

<sup>5</sup> K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, 1969, **42**, 2631.



Ts = *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>

The rearrangement of (3) to (4) is formally analogous to that observed with 10-alkylthioxanthenium salts which afford 9-alkylthioxanthenes upon treatment with base.<sup>2</sup>

(Received, 3rd March 1976; Com. 220.)