# 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[1] and 10-alkyl salts,[2] there are few reports on the nitrogen analogues, thioxanthene *S*-imides. Recently we have noticed the unusual behaviour of a 10-aminothioxanthenium salt which, upon treatment with base, produced a dimeric compound presumably *via* the non-isolable *S*-imide (**2**).[3] In connection with our studies on cyclic *S*-imides,[4] 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)[5] 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

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† 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.

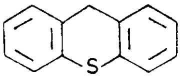
with excess of chloramine-T the secondary products (**4**)—(**6**) were obtained.

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

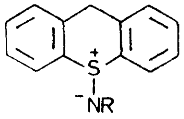
| Conditions | Isolated yield (%) (3) | (4) | (5) | (6) |
|---|---|---|---|---|
| Room temp., 20 h[a] | 39 | 46 | c | — |
| 60—70 °C, 5 h[a] | c | 35 | 24 | 5 |
| Room temp., 20 h[b] | c | c | 92 | c |
| 60—70 °C, 5 h[b] | — | c | 73 | 7 |

[a] 10 mmol of chloramine T. [b] 30 mmol of chloramine T. [c] Traces were detected on t.l.c. but not isolated.

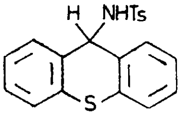
Compound (**3**),‡ m.p. 138—139 °C, shows $\lambda_{max}$ (MeOH) 227 and 264 nm; $\nu_{max}$ ($CHCl_3$) 1300, 1150, and 1095 ($SO_2$), and 970 (S–N) $cm^{-1}$; $\delta$ 4·10 (ABq, $J$ 17 Hz, benzylic-H); *m/e* 367 ($M^+$) and major peaks at 211 and 197. Refluxing (**3**) in methanolic KOH or in benzene 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 [$\nu_{max}$ ($CHCl_3$) 3367, 1152, 1092, 1015, 920 $cm^{-1}$; $\delta$ 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 by acid hydrolysis to thioxanthenone (**6**) and toluene-*p*-sulphonamide.



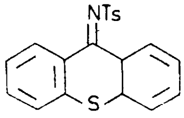
(1)



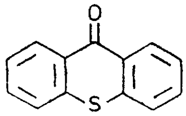
(2) R = H
(3) R = Ts



(4)



(5)



(6)

Ts = *p*-$MeC_6H_4SO_2$

The rearrangement of (**3**) to (**4**) is formally analogous to that observed with 10-alkylthioxanthenium salts which afford 9-alkylthioxanthenes upon treatment with base.[2]

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

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‡ All new compounds gave satisfactory elemental and spectral analyses.

[1] 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.

[2] 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.

[3] Y. Tamura, H. Matsushima, J. Minamikawa, M. Ikeda, and K. Sumoto, *Tetrahedron*, 1975, **31**, 3035.

[4] 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.

[5] K. Tsujihara, N. Furukawa, K. Oae, and S. Oae, *Bull. Chem. Soc. Japan*, 1969, **42**, 2631.