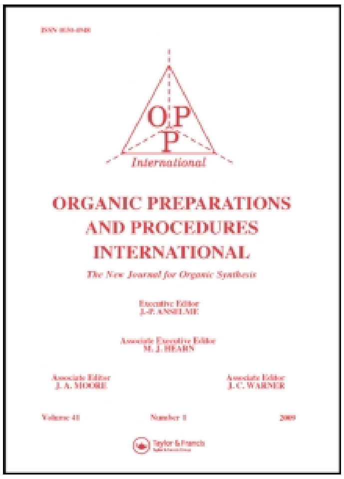

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S, S-DIARYL- AND S-(2-SUBSTITUTED ETHYL)-S-PHENYL-N-TOSYLSULFILIMINES FROM CHLORAMINE T UNDER PTC CONDITIONS

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OPPI BRIEFS

S,S-DIARYL- AND S-(2-SUBSTITUTED ETHYL)-S-PHENYL-N-TOSYLSULFILIMINES FROM CHLORAMINE T UNDER PTC CONDITIONS

Submitted by (12/19/86)
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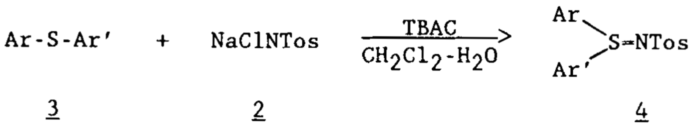
A previous paper[1] reported that tetrabutylammonium N-chlorotosylamide (1), prepared by the exchange reaction of chloramine T (2) trihydrate with tetrabutylammonium chloride, is very effective for the tosylimination of diaryl and 2-substituted ethyl sulfides. Tosylimination using 1 is superior to those using chloramine T trihydrate in acidic solution containing acetic acid[2] and anhydrous chloramine T in the case of 2-haloethyl phenyl sulfides.[3] Since the N-chlorotosylamide 1 is presumed to be an intermediate in the phase-transfer catalytic (PTC) reaction of chloramine T, the success of the above tosylimination suggests that the reaction of chloramine T with sulfides under PTC conditions may occur smoothly; there has been only one paper dealing with solid-liquid binary phase transfer reaction[4] and that report could not be found.[5] We now describe the preparation of sulfilimines by the PTC reaction in dichloromethane-water containing tetrabutylammonium chloride (TBAC).

The PTC reactions of diaryl sulfides (3) with chloramine T were carried out as shown below and in Table 1. Although the corresponding sulfilimines (4a-4e) were obtained in nearly quantitative yields, no traces of the corresponding sulfilimine 4f (from 3f) could be detected.



a) Ar = Ar' = Ph b) Ar = Ar' = 4-$CH_3C_6H_4$ c) Ar = Ar' = 4-$CH_3OC_6H_4$ d) Ar = Ar' = 4-ClC_6H_4 e) Ar = 4-$CH_3C_6H_4$ Ar' = 4-$NO_2C_6H_4$ f) Ar = Ar' = 4-$NO_2C_6H_4$

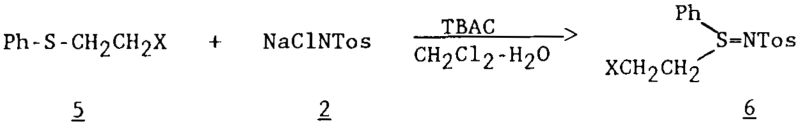
Monitoring of the reactions showed that diaryl sulfides having electron-withdrawing groups required longer reaction time for completion. This suggests that the effective intermediate in the PTC reaction is electron-deficient.

TABLE 1. PTC Reaction of Sulfides 3 with Chloramine T

	3 mmol	2 mmol	TBAC mmol	Temp (°C)	Time (hrs)	4 mp. (°C)	Y (%)
a	3.0	3.3	0.3	40	2	108-110 (108-110)[a]	≃100
b	3.0	3.3	0.3	40	2	150-151 (151-152)[b]	≃100
c	3.0	3.3	0.3	40	2	132-134 (132-133)[c]	≃100
d	3.0	3.3	0.3	40	9	123-124 (123-124)[b]	≃100
e	3.0	3.3	0.3	40	2	131-132 (131-132)[b]	87
f	3.0	3.3	0.3	40	15	-	≃0

a) D. S. Tarbell and C. Weaver, J. Am. Chem. Soc., 63, 2939 (1941). b) Ref. 1. c) A. Kucssman, I. Kapovits and M. Balla, Tetrahedron, 18, 75 (1962).

As shown in the previous paper,[3] the S-tosylimination of sulfides (5), which contain functional groups at the carbon β- to sulfur, such as 2-bromoethyl phenyl (5a), 2-chloroethyl phenyl (5b), 2-hydroxyethyl phenyl (5c) and 2-acetoxyethyl phenyl sulfides (5d) could not be carried out in high yield. We have found, however, that under PTC conditions, nearly



a) X = Br b) X = Cl c) X = HO d) X = AcO quantitative S-tosylimination of these sulfides occurred.

TABLE 2. PTC Reaction of Sulfides 5 with Chloramine T

	5 mmol	2 mmol	TBAC mmol	Temp (°C)	Time (hrs)	6 mp. (°C)	 Y (%)
a	3.0	3.3	0.3	40	2	98-99 (98-98.5)[a]	≈100
b	3.0	3.3	0.3	40	2	101-103	≈100
c	3.0	3.3	0.3	40	2	95-96 (95-96)[a]	≈100
d	3.0	3.3	0.3	40	2	106-107 (106-107)[a]	≈100

a) Ref. 3. 6b: IR(KBr): 1273(SO_2), 1132(SO_2), 980(S=N) cm^{-1}. ^{1}H-NMR($CDCl_3$): δ 2.33(s, 3H), 3.1-3.5(m, 2H), 3.5-3.9(m, 2H), 7.13(d, 2H, J = 8Hz), 7.3-7.9(m, 5H), 7.77(d, 2H, J = 8Hz). Calcd. for $C_{15}H_{16}ClNO_2S_2$: C, 52.69; H, 4.73; N, 4.10. Found: C, 52.41; H, 4.50; N, 3.94.

Consequently, the present method is very effective for the preparation of S,S-diaryl-N-tosylsulfilimines and S-(2-substituted ethyl)-S-phenyl-N-tosylsulfilimines. Moreover, it is more convenient than the previous method[1] since the preparation of 1 is avoided.

EXPERIMENTAL SECTION

All melting points are uncorrected. The IR spectra were recorded on a Shimazu IR-435 spectrophotometer and ^{1}H-NMR spectra on a JNM-PMX60 spectrometer using TMS as the internal standard. Chloramine T trihydrate and tetrabutylammonium chloride were obtained from Tokyo Chemical Industry Co. Ltd. Diaryl sulfides were prepared in according to known methods.[6] 2-Substituted ethyl phenyl sulfides were prepared by known methods.[3,7]

Preparation of Sulfilimines 4 and 6. Typical Procedure.- A solution of sulfide 3 (3 mmol) in dichloromethane (20 ml) and a solution of chloramine T (3.3 mmol) and TBAC (0.3 mmol) in water (20 ml) were separately prepared. The two solutions were mixed and vigorously stirred at 40° for 2-9 hrs. After the reaction was complete, the lower layer was separated, washed with water and dried over anhydrous sodium sulfate. The dried solution was evaporated to dryness and the resulting solid residue was recrystallized from methanol for 4, or reprecipitated from its dichloromethane solution with ether for 6. The structures of the sulfilimines were confirmed by the usual methods.

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