Preparation of Tetraalkylammonium *N*-Chloro-*p*-toluenesulfonamides and Their Application to Imination of Phosphorus Compounds and Sulfides

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Synopsis. Tetraalkylammonium *N*-chloro-*p*-toluenesulfonamides were prepared from chloramine T and tetraalkylammonium chlorides as a substance corresponding to anhydrous chloramine T, and found to give rise to the effective tosylimination of phosphorus compounds and diaryl sulfides.

Chloramine T (sodium *N*-chloro-*p*-toluenesulfonamide **1**) is a useful reagent for tosylimination but commercially available as its trihydrate. In general the tosylimination is effectively accomplished using the trihydrate in water or alcohol containing water. With triphenyl phosphine, however, the trihydrate gives a phosphonium salt $[(Ph_3P^+\text{-}NHT_s)_2NT_s^{2-}]$ in stead of the phosphine imide, while the anhydrous **1** gives the latter product.[1)]

$$Ph_3P + \mathbf{1}(H_2O)_0 \longrightarrow Ph_3P{=}NTs$$

$$Ph_3P + \mathbf{1}(H_2O)_3 \longrightarrow (Ph_3P^+\text{-}NHTs)_2NTs^{2-}$$

$$Ts = p\text{-}CH_3C_6H_4SO_2$$

Furthermore, with the special sulfides, such as 2-haloethyl phenyl sulfides, the tosylimination using the anhydrous **1** has been known to give better result than that using the trihydrate.[2)]

On the other hand, recently Sharpless *et al.* have developed a new use of the anhydrous chloramine T, allylic amination of olefins.[3)]

As described above, the anhydrous chloramine T is very interesting. However, it is explosive and is not easily available. On the basis of the fact that most quaternary ammonium salts are anhydrous, we tried to prepare tetraalkylammonium *N*-chloro-*p*-toluenesulfonamides (**2**) and to apply to imination of phosphorus compounds and sulfides.

Results and Discussion

Preparation of Tetraalkylammonium N-*Chloro*-p-*toluenesulfonamides (2).* Initially tetrabutylammonium *N*-chloro-*p*-toluenesulfonamide (**2**a) was prepared by the ion-exchange reaction of chloramine T trihydrate with tetrabutylammonium halides (chloride and bromide) in water. For obtaining well crystallizable **2**a, the use of tetrabutylammonium chloride and an excess amount of **1** to the ammonium salt are required.

Similarly other tetraalkylammonium *N*-chloro-*p*-toluenesulfonamides (**2**b—**2**e) were prepared from the corresponding tetraalkylammonium chlorides and chloramine T trihydrate.

$$\mathbf{1}(H_2O)_3 + \underset{\mathbf{3}}{R^1{}_3R^2N^+X^-} \longrightarrow \underset{\mathbf{2}}{R^1{}_3R^2N^+N(Cl)\text{-}Ts^-}$$

$$X = Cl,\ Br$$

Although these ammonium salts **2** were obtained in solid state, the purification by recrystallization was unsuccessful. The structures of **2** were confirmed by IR and NMR spectra and determination of active chlorine. The results are given in Table 1.

To know the thermal stability of **2** their decomposition temperatures were measured by a thermal differential analyzer. As shown in Table 1, the compounds **2** have such high decomposition temperatures, but they gradually decompose even at room temperature and so the storing in a freezer is recommended.

Tosylimination of Phosphorus Compounds and Tosylimination of Phosphorus Compounds and Sulfides Using **2**a. The reaction of **2**a with triphenylphosphine (**4**a) in dichloromethane was carried out at room temperature for 5 h to give *N*-(*p*-tolylsulfonyl)-*P*,*P*,*P*-triphenylphosphine imide (**5**a) in a 96% yield. This shows that **2**a can be used as an alternate to the anhydrous chloramine T. Similarly the reactions of **2**a with tributyl (**4**b) and triphenyl phosphites (**4**c) gave the corresponding phosphorimidates, (**5**b)[4)] and (**5**c), in 91 and 96% yields, respectively.

$$\underset{\mathbf{4}}{R_3P} + \mathbf{2a} \xrightarrow{CH_2Cl_2} R_3P{=}NTs + n\text{-}Bu_4N^+Cl^-$$

$$\mathbf{5}\text{a: } R=Ph,\ \mathbf{b}\text{: } R=n\text{-}BuO,\ \mathbf{c}\text{: } R=PhO$$

TABLE 1. PREPARATION OF **2**[a)]

	3		**2**				
	R¹	R²	Mp θ_m/°C	Y/%[b)]	Cl/%[c)]	NMR(CDCl₃): δ	T_d/°C[d)]
a	n-C_4H_9	n-C_4H_9	74—76	99	7.85 (7.93)	1.00(bt 12H J=5 Hz), 1—2(m 16H) 2.36(s 3H), 3.20(bt 8H J=6 Hz), 7.24(d 2H J=8 Hz), 7.73 (d 2H J=8 Hz)	156
b	CH_3	n-$C_{12}H_{25}$	100—101	86	8.18 (8.18)	0.89(bt 3H J=5 Hz), 1—2(m 20H), 2.36(s 3H), 3.33(s 9H), 3.45(m 2H), 7.24(d 2H J=8 Hz), 7.73(d 2H J=8 Hz)	132
c	CH_3	n-$C_{16}H_{33}$	98—99	94	7.08 (7.25)	0.88(bt 3H J=5 Hz), 1—2(m 28H), 2.36(s 3H), 3.33(s 9H), 3.40(m 2H), 7.24(d 2H J=8 Hz), 7.73(d 2H J=8 Hz)	162
d	CH_3	n-$C_{18}H_{37}$	107—108	85	6.64 (6.85)	0.87(bt 3H J=5 Hz), 1—2(m 32H), 2.36(s 3H), 3.33(s 9H), 3.38(m 2H), 7.24(d 2H J=8 Hz), 7.73(d 2H J=8 Hz)	163
e	CH_3	$C_6H_5CH_2$	oil	83	9.92 (9.99)	2.36(s 3H), 3.15(s 9H), 4.71(s 2H), 7.24(d 2H J=8 Hz), 7.73(d 2H J=8 Hz), 7.3—7.7(bs 5H)	122

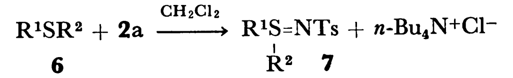
a) The molar ratios of reactants (**1**/**3**) were taken as follows: **1**/**3a**, **1**/**3b**, and **1**/**3e**=1.2, **1**/**3c**=1.6, and **1**/**3d**=1.8. b) The yields are based on **3**. c) Active chlorine content (parentheses show the calcd values). d) Decomposition temperature.

Table 2. *S*-Tosylimination of sulfides **6** using **2a** in dichloromethane

	6		Temp	Time	**7**		Method[a]
	R^1	R^2	°C	h	Mp θ_m/°C	Y/%	
a	$-(CH_2)_4-$		35—40	5	132—134	61	A
					(134—135)[b]	88	B
b	$C_6H_5CH_2$	$C_6H_5CH_2$	35—40	5	191—192	63	A
					(193)[c]	59	B
c	C_6H_5	C_6H_5	35—40	5	108—110	93	A
					(108—110)[b]	6	B
d	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	35—40	5	151—152	89	A
					(152—155)[d]	58	B
e	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	35—40	5	123—124	93	A
						22	B
						53	C
f	$4\text{-}CH_3C_6H_4$	$4\text{-}NO_2C_6H_4$	35—40	5	131—132	90	A
						0	B
						42	C
g	C_6H_5	$BrCH_2CH_2$	35—40	5	98—99	84	A
					(98—98.5)[e]	47[f]	B
						62[f]	D

a) A, B, C and D show the methods using **2a**, $\mathbf{1}(H_2O)_3$ (in MeOH, 40 °C, 5 h), $\mathbf{1}(H_2O)_3$ (presence of AcOH in MeOH, 40 °C, 5 h), and $\mathbf{1}(H_2O)_0$ (in absolute EtOH), respectively. b) D. S. Tarbell *et al.*, *J. Am. Chem. Soc.*, **63**, 2939 (1941). c) F. G. Mann *et al.*, *J. Chem. Soc.*, **121**, 1052 (1922). d) I. W. J. Still, *et al.*, *Synthesis*, **1978**, 540. e) T. Yamamoto *et al.*, *Chem. Lett.*, **1975**, 581. f) From Ref. 2.

For the reactions of **2a** with sulfides (**6**), seven kinds of sulfides listed in Table 2 were chosen. The reactions were carried out at 35—40 °C for 5 h, the resulting mixture worked up in common way. The results together with those obtained in the reactions using chloramine T trihydrate in methanol with or without acetic acid, are given in Table 2. The yields of sulfilimines (**7**) using **2a** are almost independent of their structures.



$$\underset{\mathbf{6}}{R^1SR^2} + \mathbf{2a} \xrightarrow{CH_2Cl_2} \underset{R^2}{\underset{|}{R^1S}}{=}NTs\ \mathbf{7} + n\text{-}Bu_4N^+Cl^-$$

This is contrasted with hydrated chloramine T, the reactions of which with diaryl sulfides give the corresponding sulfilimines only in low yields. In addition the *S*-imination of 2-bromoethyl phenyl sulfide (**6g**) with **2a**, is more effective than that with anhydrous **1**.[5] The *S*-imination of diaryl sulfides using **2a** may be more effective than that using trihydrated **1** in the presence of acetic acid.[6] Such an effective tosylimination by **2a** may be brought *via* radical mechnism in which more active species (radical) than *N*-choro-*p*-toluenesulfonamide[6] is included, since **2a** decolors the violet of *N*,*N*-diphenyl-*N*′-picryl hydrazyl and in the presence of H·donor (hydroquinone) does not give rise to the tosylimination of diaryl sulfides.

Experimental

All melting points are not corrected. The ^{1}H-NMR spectra were measured with a JEOL JNM-PMX60 spectrometer using TMS as the internal standard. The mass spectra were obtained on a JEOL JMS-D300 mass spectrometer with an ionizing potential of 70 ev. The decomposition temperatures were obtained with a Rigaku Denki E-1 thermal differential analyzer.

Preparation of Tetraalkylammonium N-*Chloro*-p-*toluenesulfonamides (2). General Procedure*: To a stirred solution of 12—18 mmol of **1** $(H_2O)_3$ in 20 ml of water was dropped 10 mmol of tetraalkylammonium chloride in 20 ml of water below 5 °C. After stirring below 5 °C for 5 h, the resulting mixture was extracted with CH_2Cl_2 and dried over anhydrous sodium sulfate. The dried solution was evaporated to dryness under vacuum to give **2**.

Tosylimination of Phosphorus Compounds Using **2a**. To a stirred solution of 3.3 mmol of **2a** in 15 ml of CH_2Cl_2 was added a solution of 3.0 mmol of phosphorus compound **4** in 15 ml of CH_2Cl_2. After the solution was stirred at 35—40 °C for 5 h, the resulting solution was washed with water and dried over anhydrous sodium sulfate. The dried solution was evaporated to dryness and the residue obtained was triturated or washed with ether. **5a**: Yield 96%; mp 186—188 °C (from EtOH)(187 °C);[1] IR (KBr): 1140 cm^{-1} (P=N). **5b**: Yield 91%; oil (after several washing with ether). IR (NaCl): 1310 and 1130 (SO_2), 1150 (P→N), and 1020 cm^{-1} (P-O-C), NMR ($CDCl_3$): δ=0.89 (t, 9H J=5 Hz), 1.0—1.9 (m 12H), 2.35 (s 3H), 4.05 (m 6H), 7.21 (d 2H J=8 Hz), and 7.79 (d 2H J=8 Hz). MS m/z (%): 419 (M^+ 11), 364 (28), 363 ($M^+-C_4H_8$ 90), and 251 (100). **5c**: Yield 96%; oil (after several washing with ether). IR (NaCl): 1270 and 1140 (SO_2), 1180 (P-O-C), and 1160 cm^{-1} (P=N). NMR ($CDCl_3$): δ=2.21 (s 3H), 7.06 (d 2H J=8 Hz), 7.64 (d 2H J=8 Hz), and 7.21 (broad s 15H). MS m/z (%): 479 (M^+ 19), 386 ($M^+-C_6H_5O$ 90), 385 ($M^+-C_6H_6O$ 95), and 325 (100).

Tosylimination of Sulfides. General Procedure: To a stirred solution of 3.3 mmol of **2a** in 15 ml of CH_2Cl_2 was added a solution of 3.0 mmol of sulfide **6** in 15 ml of CH_2Cl_2. After the solution was stirred at 35—40 °C for 5 h, the resulting solution was washed with water and dried over anhydrous sodium sulfate. The dried solution was evaporated to dryness and the residue obtained was triturated with ether. **7e**: Yield 93%; mp 123—124 °C (from MeOH). IR (KBr): 1290 and 1135 (SO_2), and 968 cm^{-1} (S=N). NMR ($CDCl_3$): δ=2.37 (s 3H), 7.24 (d 2H J=8 Hz), 7.2—7.7 (m 8H), and 7.73 (d 2H J=8 Hz). Found: C, 53.45; H, 3.56; N, 3.56%. Calcd for $C_{19}H_{15}Cl_2NO_2S_2$: C, 53.77; H, 3.57; N, 3.30%. **7f**: Yield 90%; mp 131—132 °C (from MeOH). IR (KBr): 1520 and 1342 (NO_2), 1298 and 1140 (SO_2), and 960 cm^{-1} (S=N), NMR ($CDCl_3$): δ=2.37 (s 6H), 7.13 (d 2H J=8 Hz), 7.24 (d 2H J=8 Hz), 7.52 (d 2H J=8 Hz), 7.69 (d 2H J=9 Hz), 7.78 (d 2H J=8 Hz), and 8.22 (d 2H J=9 Hz). Found: C, 57.78; H, 4.36; N, 6.66%. Calcd for $C_{20}H_{18}N_2O_4S_2$: C, 57.95; H, 4.39; N, 6.76%.

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