

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

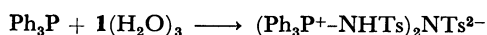
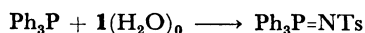
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Synopsis. Tetraalkylammonium *N*-chloro-*p*-toluenesulfonamides were prepared from chloramine T and tetraalkylammonium chlorides as a substance corresponding to anhydrous chloramine T, and found to give rise to the effective tosylation of phosphorus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

Chloramine T (sodium *N*-chloro-*p*-toluenesulfonamide **1**) is a useful reagent for tosylation but commercially available as its trihydrate. In general the tosylation is effectively accomplished using the trihydrate in water or alcohol containing water. With triphenyl phosphine, however, the trihydrate gives a phosphonium salt [(Ph₃P⁺-NHTs)₂NTs²⁻] in stead of the phosphine imide, while the anhydrous **1** gives the latter product.¹⁾



Furthermore, with the special sulfides, such as 2-haloethyl phenyl sulfides, the tosylation 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⁾

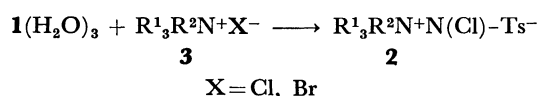
As described above, the anhydrous chloramine T is very interesting. However, it is explosive and is not easily available. On the basis of the fact that most quaternary ammonium salts are anhydrous, we tried to prepare tetraalkylammonium *N*-chloro-*p*-toluenesulfonamides (**2**) and to apply to imination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

Results and Discussion

Preparation of Tetraalkylammonium N-Chloro-p-toluenesulfonamides (2). Initially tetrabutylammonium *N*-chloro-*p*-toluenesulfonamide (**2a**) was

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

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



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.

Tosylation of Phosphorus Compounds and Sulfides Using 2a. The reaction of **2a** with triphenylphosphine (**4a**) in dichloromethane was carried out at room temperature for 5 h to give *N*-(*p*-tolylsulfonyl)-*P,P,P*-triphenylphosphine imide (**5a**) in a 96% yield.

This shows that **2a** can be used as an alternate to the anhydrous chloramine T. Similarly the reactions of **2a** with tributyl (**4b**) and triphenyl phosphites (**4c**) gave the corresponding phosphorimides, (**5b**)⁴⁾ and (**5c**), in 91 and 96% yields, respectively.

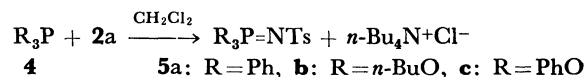


TABLE 1. PREPARATION OF **2**^{a)}

	3		Mp θ _m /°C	Y/% ^{b)}	Cl/% ^{c)}	NMR(CDCl ₃): δ	T _d /°C ^{d)}
	R ¹	R ²					
a	<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	74—76	99	7.85 (7.93)	1.00(bt 12H <i>J</i> =5 Hz), 1—2(m 16H) 2.36(s 3H), 3.20(bt 8H <i>J</i> =6 Hz), 7.24(d 2H <i>J</i> =8 Hz), 7.73 (d 2H <i>J</i> =8 Hz)	156
b	CH ₃	<i>n</i> -C ₁₂ H ₂₅	100—101	86	8.18 (8.18)	0.89(bt 3H <i>J</i> =5 Hz), 1—2(m 20H), 2.36(s 3H), 3.33(s 9H), 3.45(m 2H), 7.24(d 2H <i>J</i> =8 Hz), 7.73(d 2H <i>J</i> =8 Hz)	132
c	CH ₃	<i>n</i> -C ₁₆ H ₃₃	98—99	94	7.08 (7.25)	0.88(bt 3H <i>J</i> =5 Hz), 1—2(m 28H), 2.36(s 3H), 3.33(s 9H), 3.40(m 2H), 7.24(d 2H <i>J</i> =8 Hz), 7.73(d 2H <i>J</i> =8 Hz)	162
d	CH ₃	<i>n</i> -C ₁₈ H ₃₇	107—108	85	6.64 (6.85)	0.87(bt 3H <i>J</i> =5 Hz), 1—2(m 32H), 2.36(s 3H), 3.33(s 9H), 3.38(m 2H), 7.24(d 2H <i>J</i> =8 Hz), 7.73(d 2H <i>J</i> =8 Hz)	163
e	CH ₃	C ₆ H ₅ CH ₂	oil	83	9.92 (9.99)	2.36(s 3H), 3.15(s 9H), 4.71(s 2H), 7.24(d 2H <i>J</i> =8 Hz), 7.73(d 2H <i>J</i> =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 **1/3c**=1.2, **1/3e**=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.

