BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1268—1269 (1972)

Tracer Study of the Reaction of *p*-Toluenesulfinyl Chloride-^{36}Cl with Chloramine-T[1]

Shigeru OAE, Mamoru NAKAI,* Naomichi FURUKAWA, and Reiko KIRITANI**
Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka
***Department of Chemistry, Radiation Center of Osaka Prefecture, Sakai, Osaka*

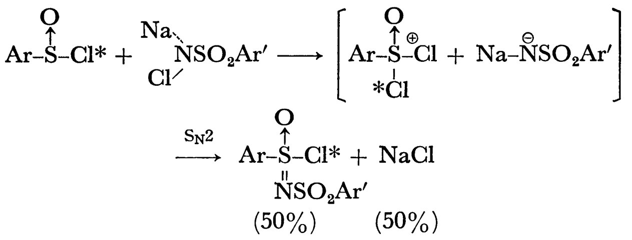
(Received May 26, 1971)

Recently, *N*-arenesulfonylareneiminosulfonyl chlorides were synthesized by the reaction of arenesulfinyl chlorides with dry *N*-arenesulfonyl chloramide,[2] while *N*-alkaneiminosulfonyl chlorides were also prepared by treating the corresponding sulfinyl chlorides with *N,N*-dichloramine.[3] However, the mechanism of the formation of these compounds has not been clarified. Therefore, in order to understand the nature of the reaction a tracer study on the reaction of *p*-toluenesulfinyl chloride-^{36}Cl with chloramine-T was carried out both in benzene and in THF solutions. This paper describes a detailed account and implications of the tracer experiments.

Results and Discussion

Following three mechanistic routes *i.e.* (1), (2), and (3) may be conceivable for this reaction.

(1) Initial Halogenation and Subsequent Nucleophilic Replacement.

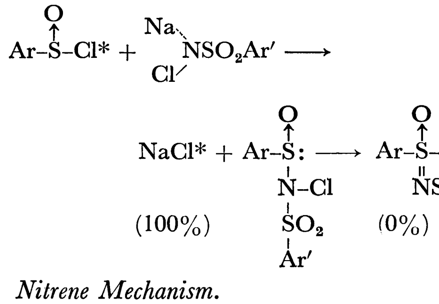


$$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\mathrm{{-}Cl^{*}} + \underset{\mathrm{Cl}\nearrow}{\overset{\mathrm{Na}\searrow}{\mathrm{NSO_2Ar'}}} \longrightarrow \left[\mathrm{Ar{-}}\underset{{}^{*}\mathrm{Cl}}{\overset{\overset{\mathrm{O}}{\uparrow}\oplus}{\mathrm{S}}}\mathrm{{-}Cl} + \mathrm{Na{-}}\overset{\ominus}{\mathrm{N}}\mathrm{SO_2Ar'}\right]$$

$$\xrightarrow{\mathrm{S_N2}} \mathrm{Ar{-}}\underset{\underset{\mathrm{NSO_2Ar'}}{\|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{{-}Cl^{*}} + \mathrm{NaCl}$$

$$(50\%) \qquad (50\%)$$

(2) Initial S_N2 Process Followed by Rearrangement of Chlorine Atom.

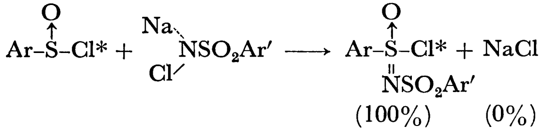


$$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\mathrm{{-}Cl^{*}} + \underset{\mathrm{Cl}\nearrow}{\overset{\mathrm{Na}\searrow}{\mathrm{NSO_2Ar'}}} \longrightarrow$$

$$\mathrm{NaCl^{*}} + \mathrm{Ar{-}}\underset{\underset{\mathrm{Ar'}}{\underset{|}{\underset{\mathrm{SO_2}}{\underset{|}{\mathrm{N{-}Cl}}}}}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{:} \longrightarrow \mathrm{Ar{-}}\underset{\underset{\mathrm{NSO_2Ar'}}{\|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{{-}Cl}$$

$$(100\%) \qquad\qquad (0\%)$$

(3) Nitrene Mechanism.



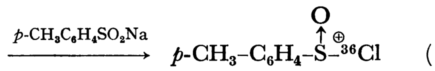
$$\mathrm{Ar{-}}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\mathrm{{-}Cl^{*}} + \underset{\mathrm{Cl}\nearrow}{\overset{\mathrm{Na}\searrow}{\mathrm{NSO_2Ar'}}} \longrightarrow \mathrm{Ar{-}}\underset{\underset{\mathrm{NSO_2Ar'}}{\|}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\mathrm{{-}Cl^{*}} + \mathrm{NaCl}$$

$$(100\%) \qquad (0\%)$$

According to the first mechanism the sulfinyl chloride is chlorinated first by chloramine-T to form the dichlorosulfoxonium cation intermediate which upon nucleophilic attack of sulfonyl amide anion gives the product. Since the two chlorine atoms in the cation intermediate are equivalent, the iminosulfonyl chloride thus formed will retain 50% of the original ^{36}Cl-activity. The second mechanism which involves the initial nucleophilic attack of *N*-chlorosulfonyl function on sulfinyl chloride to form *N*-chlorosulfonylsulfineamide intermediate and the subsequent intramolecular migration of chlorine is quite reasonable and requires the final product to contain no ^{36}Cl-activity. The last mechanism which assumes the initial nitrene formation from chloramine-T will give the final product holding all the ^{36}Cl activity.

p-Toluenesulfinyl chloride-^{36}Cl was synthesized by the scheme outlined in Eq. (1).

$$\mathrm{H^{36}Cl + SOCl_2 \xrightarrow{AlCl_3} SO^{36}Cl_2}$$

 (1)

$$\xrightarrow{p\text{-}\mathrm{CH_3C_6H_4SO_2Na}} p\text{-}\mathrm{CH_3{-}C_6H_4{-}}\overset{\overset{\mathrm{O}}{\uparrow}\oplus}{\mathrm{S}}\mathrm{{-}^{36}Cl} \qquad (1)$$

The reaction between *p*-toluenesulfinyl chloride-^{36}Cl thus obtained and dry chloramine-T was carried out in refluxing dry benzene or in dry THF at room temperature (Eq. 2). Since chloramine-T is insoluble in benzene, the reaction mixture is heterogeneous in benzene, while that in THF is homogeneous. In order to measure the ^{36}Cl activity, *p*-toluenesulfinyl chloride-^{36}Cl was oxidized to *p*-toluenesulfonyl chloride-^{36}Cl which was used as the standard sample. Meanwhile, the activity of the product, *N*-*p*-toluenesulfonyl-toluene-iminosulfonyl chloride-^{36}Cl, without further treatment, was measured with a liquid scintillation counter.

Furthermore, in order to check the possible chlorine atom exchange between the original sulfinyl chloride and iminosulfinyl chloride or sodium chloride obtained, an equimolar mixture of the ^{36}Cl-labeled sulfinyl chloride (4.85×10^4 dpm/mmol), the inactive iminosulfonyl chloride and sodium chloride was treated under the same condition as described above. Then it was found that the recovered iminosulfonyl chloride was incorporated with very little ^{36}Cl activity (1.21×10^2 dpm/mmol only, 0.25%), probably by the contamination during work up, indicating that actually ^{36}Cl-exchange between the starting material and the products did not take place. The above experimental results are summarized in Table 1.

The reaction proceeds faster in THF than in benzene and the value of the ^{36}Cl-activity of the product formed in THF is only 7.3%, while that formed in benzene is 23.7%. Perhaps, the sodium atom of chloramine-T

---

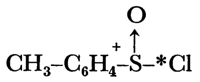
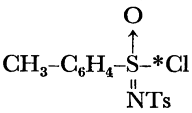
* Present address: Ube Industries Ltd., Ube, Yamaguchi-ken.

1) Sulfilimine and Sulfoximine Part VIII. Part VII. S. Oae, T. Aida, K. Tsujihara, and N. Furukawa, *Tetrahedron Lett.*, **1971**, 1145.

2) E. S. Levchenko, N. Ya. Derkash, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 1971 (1960).

3) C. R. Johnson and E. U. Joneson, *J. Amer. Chem. Soc.*, **92**, 3815 (1970).

Table 1. The ^{36}Cl-counting data

		^{36}Cl-activity (dpm/mmol)	
Solvent	Condition	 $CH_3\text{-}C_6H_4\text{-}\overset{\overset{O}{\uparrow}}{\overset{+}{S}}\text{-}{}^*Cl$	 $CH_3\text{-}C_6H_4\text{-}\underset{\underset{NTs}{\Vert}}{\overset{\overset{O}{\uparrow}}{S}}\text{-}{}^*Cl$
benzene	reflux 1 hr heterogeneous	4.85×10^4 (100%)	$1.15\ \times10^4$ (23.7%)
THF	room temp. 1 hr homogeneous	4.85×10^4 (100%)	0.352×10^4 (7.3%)

is better solvated by THF than in benzene and hence the initial nucleophilic substitution of chloramine-T anion on the *p*-toluenesulfinyl chloride is facilitated, while the subsequent cleavage and migration of chlorine from the N-atom to the S-atom of the *N*-chlorosulfonylsulfinyl amide would also be faster in THF than in benzene. On the other hand, the reaction in benzene ought to be slow and somewhat different since the reaction mixture is heterogeneous and hence the reaction of the sulfinyl chloride would have to react with unionized chloramine. Therefore, it is somewhat complicated, though the main pathway would be a simple S_N2 process.

Thus the second mechanism which involves the initial nucleophilic attack of chloramine-T anion on the sulfinyl chloride and the subsequent chlorine migration seems to be the most plausible.

Experimental

The Preparation of Toluenesulfinyl Chloride-^{36}Cl. A small amount of aluminum chloride and sodium sulfate was added to 10 m*l* of thionyl chloride, then to this solution added 0.1 m*l* of active 3.55N hydrochloric acid-^{36}Cl (about 0.3 mCi/m*l*). After two hours, the solution was diluted with inactive thionyl chloride and then distilled twice.

p-Toluenesufinyl chloride-^{36}Cl was prepared by the same way as in the previous case[3] from the reaction of 19 m*l* of freshly distilled thionyl chloride-^{36}Cl with 7.4 g of sodium salt of toluenesulfinic acid.[5]

Oxidation of p-*Toluenesulfinyl Chloride-^{36}Cl.* An aliquote (about 0.2 m*l*) of *p*-toluenesulfinyl chloride-^{36}Cl was added to a solution of 1 g of anhydrous chromic acid in 5 m*l* of acetic acid. After half an hour, the reaction mixture was quenched into water, and then extracted twice with ether. The crude *p*-tosyl chloride-^{36}Cl thus obtained was recrystallized from ethanol - water.

The Reaction of p-*Toluenesulfinyl Chloride-^{36}Cl with Chloramine-T.* The reaction in benzene was carried out according to the procedure used by Levchenko and his co-workers.[2] The reaction in tetrahydrofuran was carried out at room temperature for one hour. The subsequent treatment of the product was performed in the same way as in benzene. The crude *N*-*p*-toluenesulfonyl-*p*-tolueneiminosulfonyl chloride thus obtained was recrystallized twice, from methanol, yield 70%, mp 76—77°C.

Measurement of the Activities. All the compounds were counted by a liquid scintillation counter (TRI-CARB), in toluene solution using POPOP and POP as scintillators.

We wish to thank Dr. M. Hamada of the Radiation Center of Osaka Prefecture, for his advices and affording facilities for the measurement of the activities.

---

4) I. B. Douglass and R. V. Norton, *J. Org. Chem.*, **33**, 2104 (1968).

5) H. Gilman, "Organic Synthesis," Coll. Vol. I (1941), p. 492.