

## Reactions of *p*-Toluenesulfonyl Chloride and *p*-Toluenesulfonyl Cyanide with Sodium Cyanide and with Sodium *p*-Toluenesulfinate

FRED P. CORSON AND R. GARTH PEWS\*<sup>1</sup>*Hydrocarbons and Monomers Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640*

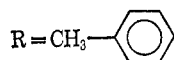
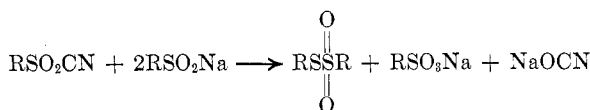
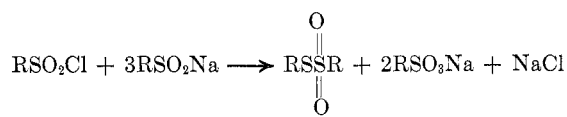
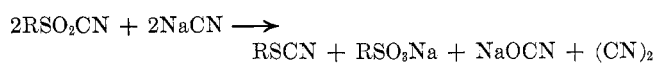
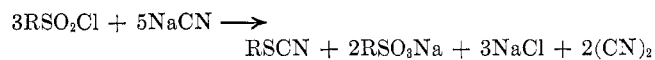
Received October 26, 1970

The reactions of *p*-toluenesulfonyl chloride and *p*-toluenesulfonyl cyanide with sodium cyanide and with sodium *p*-toluenesulfinate in acetonitrile at 70° were investigated. The stoichiometry and products of each reaction were shown in Scheme I.

The reactions of sulfonyl halides with inorganic cyanides have not been well documented. Van Leusen<sup>2</sup> recently stated that sulfonyl cyanides cannot be prepared by the reaction of sulfonyl chlorides with potassium, cuprous, silver, or lithium cyanides, but he did not report the actual course of the reaction. Loew<sup>3</sup> and McGowan<sup>4</sup> reported that reaction of trichloromethanesulfonyl chloride with potassium cyanide in water gave potassium trichloromethylsulfinate, cyanogen, and potassium chloride. Trichloromethanesulfonyl chloride, however, is not a representative sulfonyl halide.<sup>5</sup>

As part of a search for a facile synthesis of sulfonyl cyanides,<sup>6</sup> we investigated the reaction of *p*-toluenesulfonyl chloride (1) with sodium cyanide (2). As part of the effort to elucidate the mechanism of this reaction, we also investigated the reaction of 1 with sodium *p*-toluenesulfinate (4) and the reactions of *p*-toluenesulfonyl cyanide (3) with 2 and with 4. The reactions of sulfonyl cyanides with 2 or 4 have not been previously reported (see Scheme I).

SCHEME I

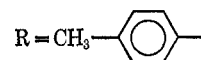
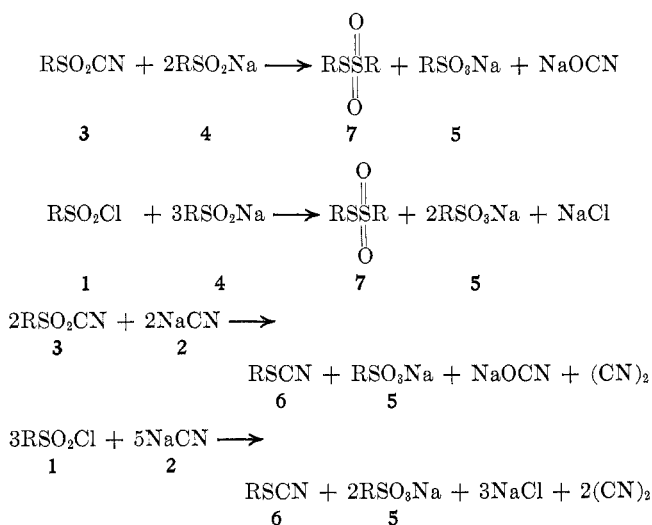


The reaction of sulfonyl chlorides with sulfinate salts has been reported to give  $\alpha$  disulfones. Kohler and MacDonald<sup>7</sup> report isolation of 4,4'-dimethyldiphenyl disulfone from the reaction of 1 with 4 in mixed water-diethyl ether solvent. They give no yield data. Uru-

shibara and Koga<sup>8</sup> report the isolation of a 4.3% yield of 4,4'-dimethoxydiphenyl disulfone from the reaction of *p*-methoxybenzenesulfonyl chloride with sodium *p*-methoxybenzenesulfinate in mixed water-acetone solvent. No other products are described.

### Results and Discussions

The reactions of 1 and 3 with 2 and 4 in acetonitrile at 70° were investigated. The products, product distributions, and stoichiometry of each reaction were determined. The results are described in Scheme II.

SCHEME II  
STOICHIOMETRY OF REACTIONS

The reactions were followed by disappearance of starting 1 or 3 as determined by vpc. The reactions were complete as soon as 1 or 3 had disappeared. Work-up and analysis of reaction mixtures before 1 or 3 had completely disappeared resulted in product distributions identical with those at complete reaction. No other intermediates or products were detected. Therefore, 1 or 3 is involved in the slow step in each reaction. The relative rates of these reactions were  $3 + 4 > 1 + 4 > 3 + 2 > 1 + 2$ .

Postulated mechanisms for each of these reactions will be discussed. The faster reactions will be discussed first since they are logical intermediate steps in the slower reactions.

(1) To whom inquiries should be addressed: The Halogens Research Laboratory, The Dow Chemical Co., Midland, Mich.

(2) A. Van Leusen, A. Iedema, and J. Strating, *Chem. Commun.*, **18**, 440 (1968).

(3) O. Loew, *Bull. Soc. Chim. Fr.*, **11**, 486 (1869).

(4) G. McGowan, *J. Prakt. Chem.*, **19**, 456 (1896).

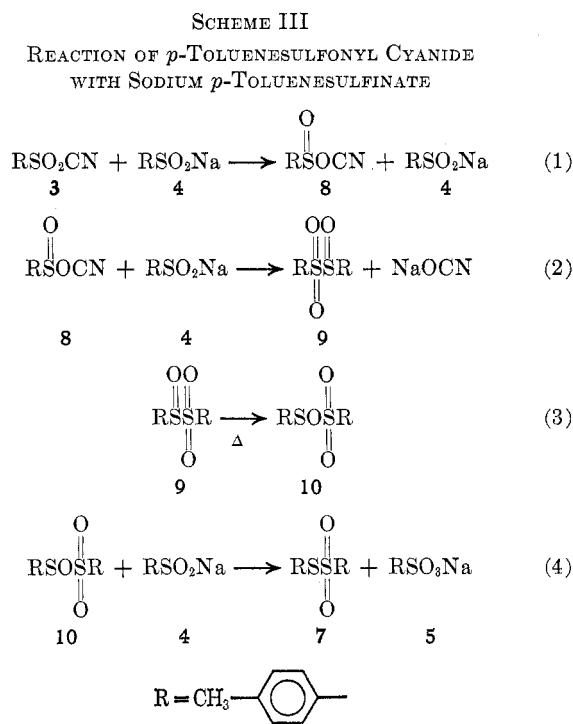
(5) N. Kharasch, *Org. Sulfur Compounds*, **1**, 371 (1961).

(6) Three independent syntheses of sulfonyl cyanides have now been published: (a) ref 2; (b) J. Cox and R. Ghosh, *Tetrahedron Lett.*, **39**, 3351 (1969); (c) R. G. Pews and F. P. Corson, *Chem. Commun.*, 1187 (1969).

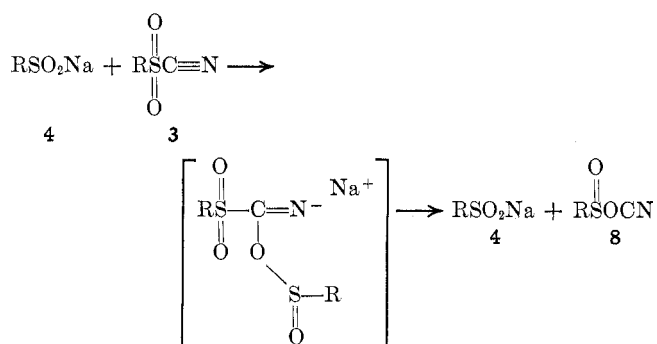
(7) E. Kohler and M. MacDonald, *Amer. Chem. J.*, **22**, 219 (1899).

(8) Y. Urushibara and G. Koga, *Nippon Kagaku Zasshi*, **81**, 1615 (1960).

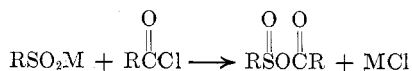
The postulated course of the reaction of **3** with 2 molar equiv of **4** to give 1 molar equiv each of sodium *p*-toluenesulfonate (**5**), *p*-tolyl *p*-toluenethiosulfonate (**7**), and sodium cyanate is described in Scheme III.



Each of the reactions 1 through 4 has precedent or analogy in the literature. Van Leusen<sup>9</sup> has reported the reaction of **3** with a wide variety of nucleophiles including phenoxide, hydroxide, and thiophenoxide, all of which attacked at the cyanocarbon to displace the sulfinate and transfer the cyano group to the nucleophile. Reaction 1 would be expected to occur by the same mechanism. Attack by sulfinate sulfur would simply regenerate **3** and **4**. Attack by the sulfinate oxygen would give the sulfinyl cyanate **8**.

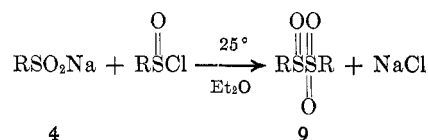


Precedent exists for nucleophile attack by the sulfinate oxygen at the unsaturated carbon, albeit the carbonyl rather than the cyano carbon. Reaction of metal sulfonates with acid chlorides has been shown to give mixed anhydrides by O-acylation.<sup>10,11</sup>



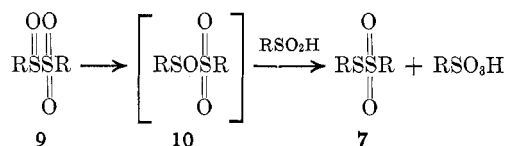
(9) A. Van Leusen and J. Jagt, *Tetrahedron Lett.*, **12**, 967 (1970).  
(10) H. Böhme and K. Meyer-Dulheuer, *Justus Liebigs Ann. Chem.*, **688**, 78 (1965).  
(11) M. Kobayashi, *Bull. Soc. Chem. Jap.*, **39**, 967 (1966).

Nucleophilic attack of **4** on the sulfinyl sulfur of **8** would be expected to occur with sulfur as one nucleophile to give the *p*-toluenesulfinyl *p*-toluenesulfone (**9**) and sodium cyanate (reaction 2, Scheme III). Kice and coworkers<sup>12</sup> have shown sulfinyl sulfur to be a soft electrophilic center in the HSAB<sup>13,14</sup> nomenclature and more readily attacked by soft nucleophiles such as iodide and thiocyanate than by hard nucleophiles such as acetate. In addition, the reaction of **4** with *p*-toluenesulfinyl chloride has been shown to give **9**.<sup>15</sup>



Attack by the sulfinate oxygen of **4** at the cyanate carbon of **8** would simply regenerate **4** and **8**. Attack by the sulfinate sulfur at the cyanate carbon would regenerate **4** and **3**.

The thermal decomposition of **9** has been well documented by Kice and coworkers.<sup>16</sup> It occurred in acetonitrile at 50° with a first-order rate constant of 5.4 × 10<sup>-4</sup> sec<sup>-1</sup>.<sup>16</sup> The initially formed intermediate **10** was shown to react with *p*-toluenesulfonic acid to give *p*-tolyl *p*-toluenethiosulfonate (**7**) and *p*-toluenesulfonic acid.<sup>16</sup> On this basis, the **9** formed in the reaction of **8**

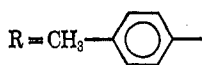
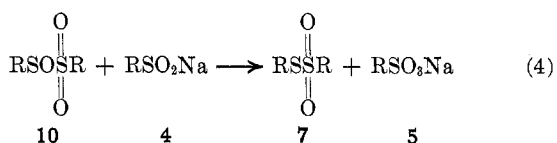
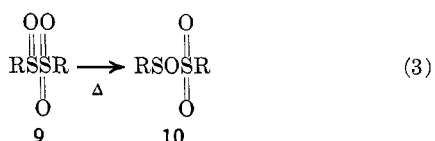
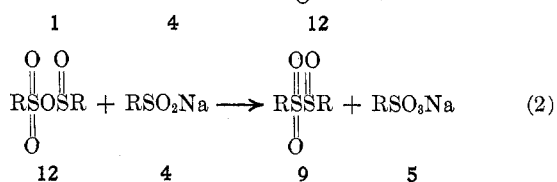
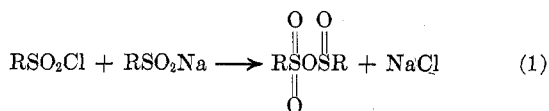


with **4** would be expected to undergo isomerization to **10** (reaction 3, Scheme III) at 70° in acetonitrile. Reaction of **10** with **4** would give the final sulfur-containing products **7** and **5** (reaction 4, Scheme III). The nucleophilic attack on the sulfenyl sulfur of **10** by the sulfur of **4** or of *p*-toluenesulfonic acid is expected. Kice and coworkers<sup>12,17</sup> have shown that sulfenyl sulfur is a softer electrophilic center than even sulfinyl sulfur. Nucleophilic attack of **4** on **9**, if it competes with isomerization to **10**, would be expected to occur at the sulfinyl sulfur by the sulfinate sulfur to simply regenerate **4** and **9**. It is well known that the electrophilicity of sulfur increases rapidly in the order sulfonyl < sulfinyl < sulfenyl.<sup>18</sup>

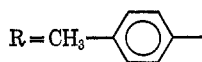
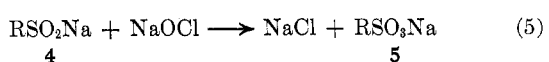
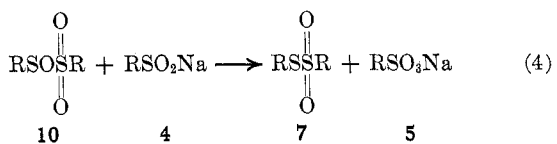
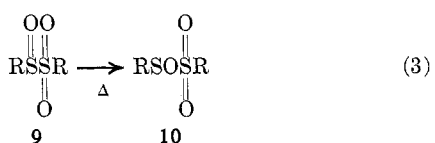
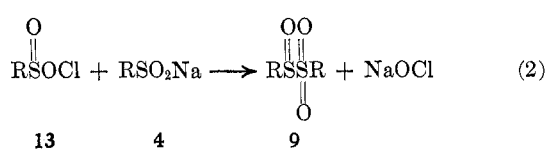
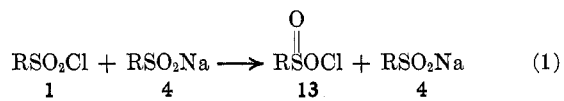
The reaction of **1** with 3 mol of **4** gave 2 mol of **5**, 1 mol of **7**, and 1 mol of sodium chloride. These products could arise *via* initial attack of the sulfinate oxygen of **4** at either sulfur (Scheme IV) or chlorine (Scheme V) of **1**. Attack by the sulfinate sulfur at chlorine would regenerate **1** and **4**. Attack by the sulfinate sulfur at sulfur would produce 4,4'-dimethyldiphenyl disulfone (**11**) which is observed in 4% yield. This is in agreement with the results of Urushibara and Koga described earlier.<sup>8</sup> A control experiment showed that **11** does not react further with **4** under the reaction conditions.

(12) J. Kice and G. Guaraldi, *J. Amer. Chem. Soc.*, **90**, 4076 (1968).  
(13) R. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).  
(14) R. Pearson, *ibid.*, **85**, 3533 (1963).  
(15) H. Brederbeck, A. Wagner, H. Beck, and R. Klein, *Ber.*, **93**, 2736 (1960).  
(16) J. Kice and N. Pawlowski, *J. Amer. Chem. Soc.*, **86**, 4898 (1964).  
(17) J. Kice and G. Large, *ibid.*, **90**, 4069 (1968).  
(18) See the data in ref 12 and 17.

SCHEME IV  
REACTION OF *p*-TOLUENESULFONYL CHLORIDE  
WITH SODIUM *p*-TOLUENESULFINATE.  
INITIAL ATTACK AT SULFUR



SCHEME V  
REACTION OF *p*-TOLUENESULFONYL CHLORIDE  
WITH SODIUM *p*-TOLUENESULFINATE.  
INITIAL ATTACK AT CHLORINE

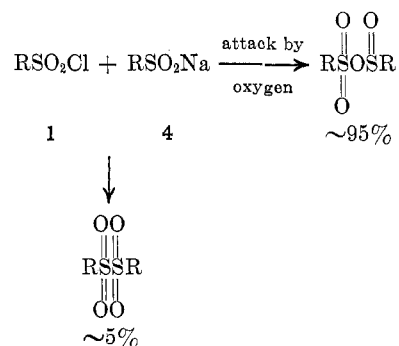


There is no precedent in the literature for attack of an oxygen nucleophile at the chlorine of **1** (reaction 1, Scheme V). Reaction of **1** with alkoxides or phenoxides<sup>19</sup> gives sulfonate esters and with hydroxide<sup>20</sup> gives *p*-toluenesulfonic acid. In addition, control experiments showed that sodium hypochlorite (reaction

**2**, Scheme V) was not present in the reaction mixture. Oxidation of a mixture of 0.1 mol each of **4** and  $\beta$ -methyl naphthyl ketone in acetonitrile at 70° by dropwise addition of Clorox (0.07 mol of sodium hypochlorite total) gave 11% conversion of the  $\beta$ -methyl naphthyl ketone to  $\beta$ -naphthoic acid. Reaction of **1** with **4** in the presence of  $\beta$ -methyl naphthyl ketone gave no conversion to  $\beta$ -naphthoic acid and did not alter the course of the reaction. On the basis of this evidence, Scheme V is eliminated and Scheme IV is postulated as the major reaction pathway.

Attack by the sulfinate oxygen of **4** at the sulfonyl sulfur of **1** (reaction 1, Scheme IV) would give the sulfinyl sulfonyl anhydride **12** and sodium chloride. Reaction of **12** with **4** to give **9** and **5** (reaction 2, Scheme IV) is analogous to the reaction of **4** with the sulfinyl cyanate **8** previously discussed (reaction 2, Scheme III), the only difference being the leaving group is sulfonate rather than cyanate. The rearrangement of **9** to **10** and the reaction of **10** with **4** to give the final products (reactions 3 and 4, Scheme IV) are identical to reactions 3 and 4, Scheme III.

Thus, reaction of **1** with **4** appears to occur completely by attack at the sulfonyl sulfur, about 95% of the attack occurring by the sulfinate oxygen. This prefer-



ential attack by oxygen is compatible with the data obtained by Kice and coworkers<sup>12</sup> which indicates that sulfonyl sulfur is a much harder electrophilic center than sulfinyl sulfur and more readily attacked by hard nucleophiles such as acetate and fluoride than by soft nucleophiles such as bromide and thiocyanate.

The postulated course of the reaction of **3** with 1 mol of sodium cyanide (**2**) to give 0.5 mol each of **5**, 4-thiocyanotoluene (**6**), cyanogen, and sodium cyanate is outlined in Scheme VI. Reactions 2, 3, 6, and 8 are identical with reactions already described.

As previously discussed, initial nucleophilic attack on **3** is expected at cyanocarbon. Reaction of **2** would give **4** and cyanogen (reaction 1, Scheme VI). Reaction of **4** with **3** to give **8** (reaction 2, Scheme VI) has already been discussed. The reaction of **4** with **3** must be significantly faster than the reaction of **2** with **3**, or the isolated products would be **4** and cyanogen. A control experiment showed that **4** will not react with cyanogen under the reaction conditions. The only information obtained on the relative rates of these reactions is that the reaction of **3** with **4** is complete in 3 hr at 70° while the reaction of **3** with **2** requires 10 hr at 70°.

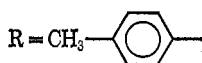
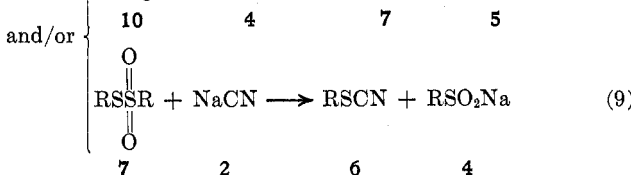
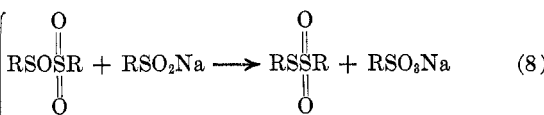
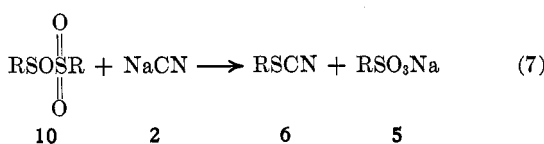
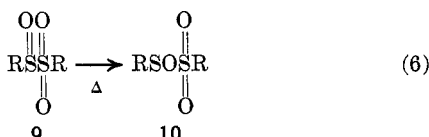
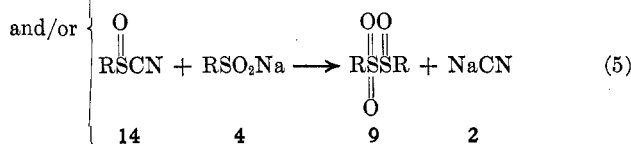
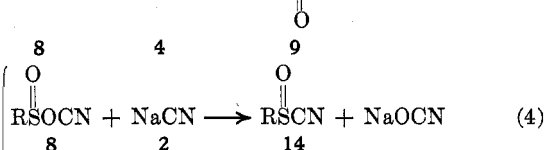
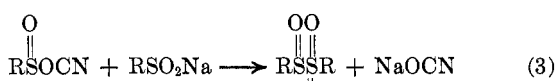
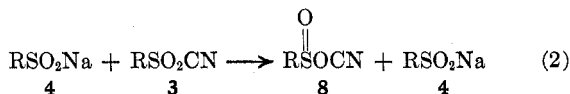
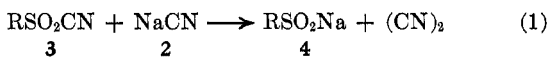
Nucleophilic attack on **8** by **4** to give **9** (reaction 3, Scheme VI) has been discussed. Attack by **2** would be expected to give the sulfinyl cyanide **14** and sodium cyanate (reaction 4, Scheme VI). Reaction of **14** with

(19) J. Bunnett, *Adv. Phys. Org. Chem.*, **2**, 271 (1963).

(20) C. Suter, "Organic Chemistry of Sulfur Compounds," Wiley, London, 1944, p 497.

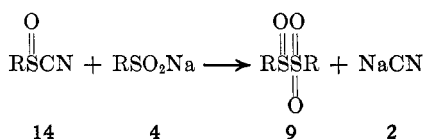
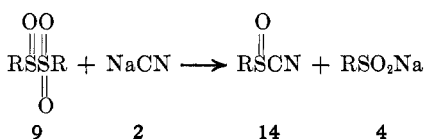
SCHEME VI

REACTION OF *p*-TOLUENESULFONYL CYANIDE WITH SODIUM CYANIDE



4 could lead to 9 and regenerate 2 (reaction 5, Scheme VI). The overall result of reactions 4 and 5 is identical with that of reaction 3.

Isomerization of 9 to 10 might be in competition with nucleophilic attack on 9. As discussed previously, attack by 4 would simply regenerate 4 and 9. Attack by cyanide would be expected to also lead to regeneration of 9 in two steps.

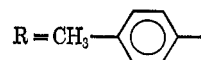
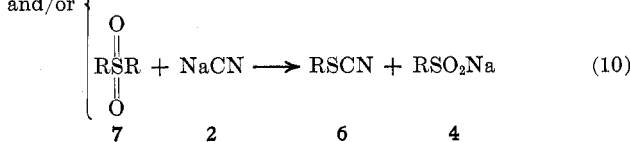
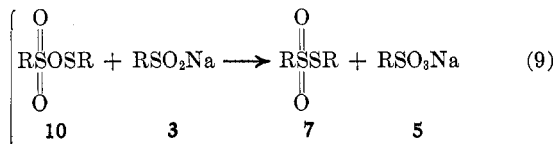
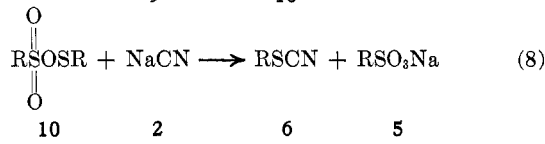
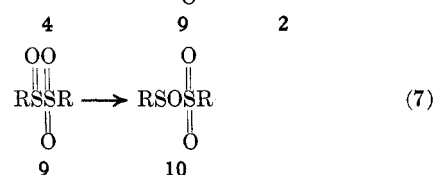
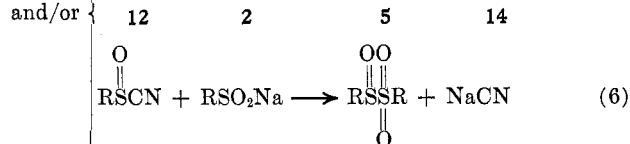
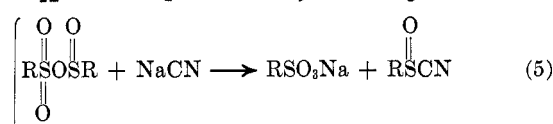
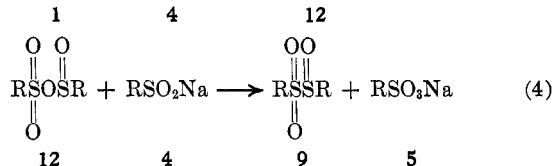
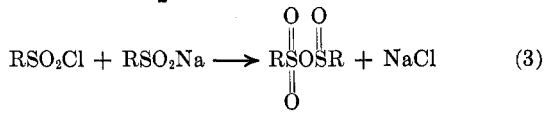
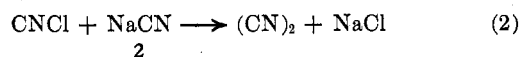
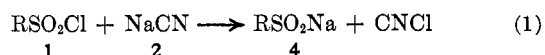


The intermediate 10 can undergo nucleophilic attack at the sulfenyl sulfur by either 2 or 4. Attack by 2 (reaction 7, Scheme VI) would give the stable products 6 and 5. Reaction with 4 (reaction 8, Scheme VI), as discussed previously (reaction 4, Scheme II and reaction 4, Scheme III), would give 7 and 5. 7 should react with 2 to give the stable product 6 and regenerate 4 (reaction 9, Scheme VI). The overall result of reactions 8 and 9 would be identical with that of reaction 7. The reaction of the S esters of thiolsulfonic acids with cyanide is known to give thiocyanates and sulfinates.<sup>21</sup>

The postulated course of the reaction of 3 mol of 1 with 5 mol of 2 to give 2 mol each of cyanogen and 5, 1 mol of 6, and 3 mol of sodium chloride is outlined in Scheme VII. Reactions 3, 4, 6–9, and 10 are identical

SCHEME VII

REACTION OF *p*-TOLUENESULFONYL CHLORIDE WITH SODIUM CYANIDE



(21) R. Otto and A. Rossing, *Chem. Ber.*, 20, 2079 (1887).

with reactions already discussed. The only reactions which do not follow directly from previous discussion are 1, 2, and 5.

As discussed for the reaction of 1 with 4, hard nucleophiles have been shown to react with 1 at sulfur. In contrast, soft nucleophiles such as amines, mercaptides, and carbanions have been shown to react with 1 to give products best explained as occurring *via* initial attack at chlorine.<sup>19</sup> On this basis, cyanide would be expected to attack 1 at chlorine to give 4 and cyanogen chloride (reaction 1, Scheme VII). Attack by the cyanide at the sulfur of 1 would give the sulfonyl cyanide 3 which has been shown to react with the cyanide ion to give sodium cyanate, which was not observed in this reaction.

The reaction of 1 with 4 to give 12 (reaction 3, Scheme VI) must be fast compared to initial reaction of 1 with 2, just as the reaction of 3 with 4 must be fast compared to reaction of 3 with 2 (reactions 1 and 2, Scheme VI). Likewise, reaction of cyanogen chloride with cyanide to give cyanogen must be fast compared with reaction with 4 to give 3. The latter reaction would eventually lead to sodium cyanate. Unfortunately, there appear to be no obvious reasons why these relative rates should prevail.

The remaining reactions leading to products have already been discussed except for reaction 5, Scheme VII. Attack of the cyanide on 12 would be expected to occur at the sulfinyl sulfur to give the already described sulfinyl cyanide 14.

In conclusion, the courses of the reactions of 1 and 3 with 2 and with 4 have been determined. Mechanisms have been proposed and supported which are internally consistent and consistent with the many pertinent facts in the literature: attack of hard nucleophiles at the sulfur of 1;<sup>19,20</sup> attack of soft nucleophiles at the chlorine of 1;<sup>19</sup> attack by a large variety of nucleophiles at the cyanocarbon of 3;<sup>9</sup> increasingly hard electrophilicity of the sulfur in the order sulfenyl < sulfinyl < sulfonyl;<sup>12,17</sup> the very low yield of the disulfones in the reaction of sulfinates with sulfonyl chlorides.<sup>7,8</sup> The original question of why reactions of sulfonyl halides with cyanide ion do not give sulfonyl cyanides has been answered. Further evidence has been provided that application of the HSAB concept is a useful tool in predicting, or at least explaining, the course of many ionic reactions at sulfur.

### Experimental Section

*p*-Toluenesulfonyl chloride (1) Aldrich Chemical Co., was recrystallized. Sodium cyanide (2) was Fisher Scientific Co. reagent grade. Sodium *p*-toluenesulfinate (4) was prepared exactly as described by Field and Clark.<sup>22</sup> Acetonitrile, Burdick and Jackson Laboratories, Inc., was distilled over calcium hydride. Cyanogen chloride was obtained from American Cyanamide.

**Reaction of *p*-Toluenesulfonyl Chloride (1) with Sodium Cyanide (2).**<sup>23</sup>—A mixture of 1 (45.3 g, 0.25 mol) and 2 (24.5 g, 0.50 mol) in acetonitrile (500 ml) in a 1-l., three-necked flask equipped with a reflux condenser leading to a CO<sub>2</sub>-acetone cooled trap, a mechanical stirrer, and a nitrogen inlet tube was stirred at 70° for 20 hr. Vpc analysis indicated complete reaction of 1. The reaction mixture was filtered to give a solid residue, 29.4 g. The acetonitrile was removed from the filtrate to give a residue,

29.8 g. The combined residues were extracted with two 200-ml portions of hot benzene. The benzene was removed by distillation and the residue distilled giving 10.1 g (27.1% based on 1) of 4-thiocyanotoluene (6): bp 77° (0.8 mm) [lit.<sup>24</sup> bp 155–158° (40–50 mm)]; ir (CCl<sub>4</sub>) 2170 (SC≡N).

Anal. Calcd for C<sub>8</sub>H<sub>7</sub>NS: C, 64.43; H, 4.70; N, 9.40. Found: C, 64.41; H, 4.81; N, 9.43.

The residue from the benzene extraction was extracted with two 200-ml portions of methanol. The methanol was removed to give 30.7 g (62% based on 1) of sodium *p*-toluenesulfonate (5); the ir, nmr, and mass spectral data were identical with those of an authentic sample obtained from Matheson Coleman and Bell. The residue from the methanol extraction weighed 15.1 g. Standard Volhard potentiometric titration showed it to contain 78% NaCl (11.9 g, 0.21 mol, 84% based on 1); ir (Fluorolube) 2085 cm<sup>-1</sup> (weak, presence of NaCN), no absorption at 2150–2200 cm<sup>-1</sup> (no NaOCN).

The liquid trapped in the CO<sub>2</sub>-acetone cooled trap weighed 11.1 g. Mass spectral analysis showed the presence of cyanogen (73%, 8.1 g, 0.155 mol, 0.62 mol/mol of 1), N<sub>2</sub>, acetonitrile, and CO<sub>2</sub>.

Exact repetition of the reaction using a 1:1 mol ratio of 1 to 2 gave the same products in the same proportion with unreacted 1. Reaction for 20 hr at 70° using a 3:5 mol ratio of 1 to 2 gave complete conversion of both starting materials. Reaction with a 3:5 mol ratio for 10 hr at 70° gave the same product distribution with unreacted 1.

**Preparation of *p*-Toluenesulfonyl Cyanide (3).**<sup>25</sup>—Cyanogen chloride (70.0 g, 1.14 mol) was bubbled into a slurry of sodium *p*-toluenesulfinate (167.0 g, 0.94 mol) in acetonitrile (1 l.) in a flask equipped with CO<sub>2</sub>-acetone cooled condenser with a calcium chloride drying tube, mechanical stirrer, and gas inlet tube. The mixture was stirred for 1 hr at 25° and filtered, and the solvent was removed on a rotary evaporator. The resulting solid was recrystallized from hexane to give 131.6 g (77%) of 3: mp 47–48° (lit.<sup>4</sup> mp 49–50°); bp 105–106°; ir (film) 2194 (C≡N) and 1375 and 1173 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CCl<sub>4</sub>) δ 7.93 (m, 2), 7.49 (m, 2), and 2.52 (m, 3); mass spectrum (decreasing intensity) *m/e* 91, 181, 155, and 65.

Anal. Calcd for C<sub>8</sub>H<sub>7</sub>NOS: C, 53.04; H, 3.87; N, 7.73. Found: C, 53.20; H, 4.09; N, 7.72.

**Reaction of *p*-Toluenesulfonyl Cyanide (3) with Sodium Cyanide (2).**—A mixture of 3 (45.3 g, 0.25 mol) and 2 (12.3 g, 0.25 mol) in acetonitrile (500 ml) in the equipment described above for the reaction of 1 with 2 was heated at 70° for 10 hr. Vpc indicated complete reaction of 3. The reaction mixture was worked up and analyzed exactly as described above to give the following products (per cent yields based on 3): 6 (16.4 g, 44%), 5 (23.3 g, 48%), cyanogen (5.7 g, 44%), sodium cyanate (7.8 g, 48%). Reaction for 5 hr at 70° gave the same product distribution with recovered 3.

**Reaction of *p*-Toluenesulfonyl Chloride (1) with Sodium *p*-Toluenesulfinate (4).**—A mixture of 1 (19.05 g, 0.1 mol) and 4 (53.4 g, 0.3 mol) in acetonitrile (600 ml) was stirred under nitrogen at 70° for 5 hr. The reaction mixture was cooled to 25° and filtered to give 46.0 g of white solid. Standard Volhard potentiometric titration showed the presence of 12.4% sodium chloride (5.7 g, 97% based on 1). The ir and nmr spectra of this solid were identical with those of the authentic sample of 5 (assuming only sodium chloride and 5 to be present, 40.3 g, 210% based on 1).

The acetonitrile filtrate was cooled to 0° overnight. The resulting white crystals were collected and dried to give 1.5 g (4.8% based on 1) of 4,4-dimethyldiphenyl disulfone (11): mp 208–210° (lit.<sup>26</sup> mp 211°); ir (CS<sub>2</sub>) 1335 and 1135 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CD<sub>3</sub>CN) δ 7.45 (m, 2), 7.65 (m, 2), and 2.47 (s, 3); mass spectrum *m/e* 310, 262, 246, 155, 139, and 91.

Anal. Calcd for C<sub>14</sub>H<sub>14</sub>O<sub>4</sub>S<sub>2</sub>: C, 54.19; H, 4.52; S, 20.65. Found: C, 54.23; H, 4.49; S, 20.61.

The acetonitrile was removed from the filtrate by distillation to give a white, crystalline solid, which was recrystallized from hexane to give 20.4 g (73% based on 1) of *p*-tolyl *p*-toluenethiosulfonate (7): mp 77–78° (lit.<sup>27</sup> mp 77–78°); ir (CS<sub>2</sub>) 1335 and

(24) C. Rabaut, *Bull. Soc. Chim. Fr.*, **27**, 690 (1902).

(25) This preparation, discovered independently, is very similar to that described in ref 6b.

(26) H. Gilman, L. Smith, and H. Parker, *J. Amer. Chem. Soc.*, **47**, 860 (1925).

(27) J. Carson and F. Wong, *J. Org. Chem.*, **26**, 3028 (1961).

(22) L. Field and R. Clark, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 674.

(23) Observation of 4-thiocyanotoluene in this reaction was initially made by E. B. Nyquist in this laboratory.

1148  $\text{cm}^{-1}$  ( $\text{SO}_2$ ); nmr ( $\text{CCl}_4$ )  $\delta$  7.2 (m, 8), 2.4 (s, 3), and 2.3 (s, 3); mass spectrum  $m/e$  278, 214, 155, 139, 123, and 91.

Anal. Calcd for  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{S}_2$ : C, 60.43; H, 5.04; S, 23.02. Found: C, 60.43; H, 4.98; S, 23.11.

Exact repetition of the reaction with a 1:2 mol ratio of 1 to 4 gave the same products in the same proportions with recovered 1. Reaction with a 1:3 mol ratio for 3 hr at 70° gave the same product distribution with unreacted 7.

**Reaction of *p*-Toluenesulfonyl Cyanide (3) with Sodium *p*-Toluenesulfinate (4).**—A mixture of 3 (18.1 g, 0.1 mol) and 4 (35.6 g, 0.2 mol) in acetonitrile (600 ml) was stirred under nitrogen at 70° for 3 hr. The reaction mixture was cooled to 25° and filtered. The resulting solid residue was extracted with two 100-ml portions of methanol and the methanol removed to give 19.7 g (94% based on 3) of sodium *p*-toluenesulfonate (5); properties exactly as described above. The residue from the methanol extraction had an ir spectrum identical with that of sodium cyanate (5.9 g, 91% based on 3).

The acetonitrile filtrate was cooled to 0° overnight. There were no crystals formed. The acetonitrile was removed by distillation. The resulting solid was recrystallized from hexane to give 24.7 g (89% based on 3) of *p*-tolyl *p*-toluenethiosulfonate (7); properties exactly as described above.

Reaction of a 1:3 mol ratio of 3 to 4 resulted in formation of the same products in the same yields with recovery of unreacted 4. Reaction of a 1:2 mol ratio for 2 hr at 70° gave the same product distribution with recovered 3.

**Reaction of Sodium Hypochlorite with Sodium *p*-Toluenesulfinate (4) and  $\beta$ -Methyl Naphthyl Ketone.**—To a mixture of 4 (17.8 g, 0.1 mol) and  $\beta$ -methyl naphthyl ketone (Eastman Organic Chemicals, 17.0 g, 0.1 mol) maintained at 70° in acetonitrile (500 ml) was added dropwise over 2 hr Clorox (100 g of solution, 5.25 g NaOCl, 0.07 mol). The white solid residue was collected by filtration and dried to give 18.1 g of solid. Ir and nmr showed this to be a mixture of sodium *p*-toluenesulfinate (4) and sodium *p*-toluenesulfonate (5). No attempt was made at quantitative analysis.

The acetonitrile was removed from the filtrate. The residue (17.3 g) was dissolved in 100 ml of hot 95% ethanol. Standing overnight at 25° resulted in formation of 1.3 g (11% based on NaOCl) of  $\beta$ -naphthoic acid, mp 182–184° (lit.<sup>28</sup> mp 183–184°). The ir and nmr spectra were identical with those of an authentic sample from Eastman.

**Reaction of *p*-Toluenesulfonyl Chloride (1) with Sodium *p*-Toluenesulfinate (4) in the Presence of  $\beta$ -Methyl Naphthyl Ketone.**—The reaction of 1 and 4 (1:3 mol ratio) was carried out exactly as described above except for the presence of  $\beta$ -methyl naphthyl ketone (17.0 g, 0.1 mol). The reaction mixture was worked up exactly as described above to give, from the residue, sodium chloride (5.6 g, 96%) and sodium *p*-toluenesulfonate (39.3 g, 195%), and, from the filtrate, *p*-tolyl *p*-toluenethiosulfonate (20.6 g, 74%) and  $\beta$ -methyl naphthyl ketone (16.7 g, 98% recovery). There was no evidence for the presence of  $\beta$ -naphthoic acid.

**Attempted Reaction of Sodium *p*-Toluenesulfinate (4) with 4,4'-Dimethyldiphenyl Disulfone (11).**—A mixture of 4 (1.78 g, 0.01 mol) and 11 (1.40 g, 0.0045 mol, isolated from reaction of 1 with 4) in acetonitrile (100 ml) was heated at 70° for 10 hr. The reaction mixture was cooled and filtered to give 1.68 g (95% recovery) of 4. The filtrate was concentrated to 50 ml and cooled to 0° overnight. The resulting crystals were collected and dried to give 1.29 g (92% recovery) of 11.

**Attempted Reaction of Sodium *p*-Toluenesulfinate (4) with Cyanogen.**—A sealed glass ampoule containing 4 (1.78 g, 0.01 mol) and cyanogen (0.52 g, 0.01 mol) in acetonitrile (10 g) was heated at 70° for 8 hr. The cyanogen and acetonitrile were removed to give 1.69 g (95% recovery) of 4.

Registry No.—1, 98-59-9; 2, 143-33-9; 3, 19158-51-1; 4, 824-79-3.

(28) M. Newman and H. Holmes, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 428.

## The Reactivity of Some Imide and Sulfonamide Anions with Methyl Iodide in Methanol<sup>1</sup>

J. F. BUNNETT\*<sup>2</sup> AND JOHN H. BEALE

*Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island 02912*

Received September 17, 1970

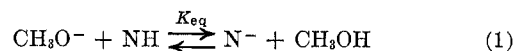
Rate coefficients for reactions of the anions of succinimide phthalimide, benzenesulfonamide, *N*-methylbenzenesulfonamide, and *N*-phenylbenzenesulfonamide and of methoxide ion with  $\text{CH}_3\text{I}$  in  $\text{CH}_3\text{OH}$  have been determined. Reactivity among the nitranion nucleophiles correlates with basicity, except that the benzenesulfonamide anion is about one-third as reactive as expected from its basicity.

Although the conjugate base anions of phthalimide, of succinimide, and of sulfonamides with at least one hydrogen on nitrogen are well known to be alkylated readily, the reactivity of such anions toward saturated carbon appears not previously to have been measured.

We have determined rates of reactions of the anions of succinimide, phthalimide, benzenesulfonamide, *N*-methylbenzenesulfonamide, and *N*-phenylbenzenesulfonamide with methyl iodide in methanol. Rates were determined by potentiometric titration of the iodide ion released. For reasons mentioned below, the rate of reaction of  $\text{NaOCH}_3$  with  $\text{CH}_3\text{I}$  was also determined. Results are summarized in Table I.

When the amide or imide is quite acidic and the reactivity of its anion toward  $\text{CH}_3\text{I}$  is quite high compared to that of methoxide ion, such a study is straightforward. However, when these conditions are not met

there is a complication stemming from incompleteness of conversion of the amide or imide to its conjugate base. The pertinent acid-base equilibrium is that of eq 1, in which "NH" represents the amide or imide and "N<sup>-</sup>" its conjugate base.



The total rate of displacement of the iodide ion is the sum of components due to  $\text{CH}_3\text{O}^-$  and to the nitranion nucleophile,  $\text{N}^-$ . When the amide or imide is furnished in excess over  $\text{NaOCH}_3$ , we may write eq 2 and 3, where  $[\text{CH}_3\text{O}^-]_{\text{st}} = [\text{CH}_3\text{O}^-] + [\text{N}^-]$ .

$$d[\text{I}^-]/dt = k_2[\text{CH}_3\text{I}][\text{CH}_3\text{O}^-]_{\text{st}} \quad (2)$$

$$= k_{\text{N}}[\text{CH}_3\text{I}][\text{N}^-] + k_0[\text{CH}_3\text{I}][\text{CH}_3\text{O}^-] \quad (3)$$

By equating the right sides of eq 2 and 3 and substituting for  $[\text{N}^-]$  the product  $K_{\text{eq}}[\text{NH}][\text{CH}_3\text{O}^-]$  (cf. eq 1), one obtains eq 4. Inasmuch as  $[\text{CH}_3\text{O}^-]_{\text{st}} = (1 +$

$$k_2[\text{CH}_3\text{O}^-]_{\text{st}} = (k_{\text{N}}K_{\text{eq}}[\text{NH}] + k_0)[\text{CH}_3\text{O}^-] \quad (4)$$

(1) Based on the Ph.D. Thesis of J. H. Beale, Brown University, 1966. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society.

(2) University of California, Santa Cruz, California 95060.