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Arylsulfonoxylation of Aromatic Compounds. VI. Decomposition of *m*-Trifluoromethylbenzenesulfonyl Peroxide in the Absence of Solvent and in the Presence of Ethylbenzene and Cumene[1a,b]

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m-Trifluoromethylbenzenesulfonyl peroxide (1) has been synthesized and found to be slightly more stable than the nitrobenzenesulfonyl peroxides. The thermal decomposition of 1 in ethylbenzene and cumene gives exclusively nuclear substitution with no side-chain products characteristic of a homolytic reaction. The stability and heterolytic dissociation of sulfonyl peroxides substituted with electron-withdrawing groups (NO_2, CF_3) therefore are inherent and do not require the presence of a radical trap (e.g., a nitro group). Competitive *m*-trifluoromethylbenzenesulfonoxylations gave K_{Ar}/K_B: ethylbenzene, 14.8; cumene, 12.1. The ortho, meta, and para orientations (partial rate factors) are: ethylbenzene, 33.3, 5.8, 60.9% (14.8, 2.6, 54.2); cumene, 28.5, 7.8, 63.7% (10.3, 2.8, 46.1). The reactions of 1 with these two alkylbenzenes in ethyl acetate solution are first order with respect to the arenes and the enthalpies (entropies) of activation are: ethylbenzene, 16.7 (−17.4); cumene, 16.6 (−18.2). The reaction of 1 with benzene is first order with respect to the arene in methylene chloride, but in ethyl acetate an overall order of 0.66 is due to a competition to the reaction first order with respect to benzene ($\Delta H^{\ddagger}$, 18; $\Delta S^{\ddagger}$, −20) by a reaction zero order with respect to benzene ($\Delta H^{\ddagger}$, 30; $\Delta S^{\ddagger}$, 22). The $\Delta S^{\ddagger}$ for the zero-order reaction corresponds to a homolytic mechanism. The thermal decomposition of neat 1 (1.00 mol) and treatment of the reaction mixture with ethanol produced *m*-trifluoromethylbenzenesulfonic acid (0.538), 2-hydroxy-4-trifluoromethylbenzenesulfonic acid (0.617), ethyl *m*-trifluoromethylbenzenesulfonate (0.159), *m*-trifluoromethylphenyl *m*-trifluoromethylbenzenesulfonate (0.261), and *m*-trifluoromethylphenol (0.04). These products can be explained by a series of ionic intermediates.

Of all the arylsulfonyl peroxides reported up to this time (benzene-, *p*-toluene-, *p*-chlorobenzene-, *p*-bromobenzene-, 3,4-dichlorobenzene-, and *o*-, *m*-, and *p*-nitrobenzenesulfonyl peroxides),[2,3] only the nitro derivatives are sufficiently stable at room temperature for routine laboratory use. The nitrobenzenesulfonyl peroxides have been found to undergo a heterolytic scission in the presence of aromatic substrates leading to an electrophilic substitution.

$$(O_2NC_6H_4SO_3)_2 + C_6H_5X \longrightarrow O_2NC_6H_4SO_3C_6H_4X + O_2NC_6H_4SO_3H \quad (1)$$

There are two possible reasons for the stability of the nitrobenzenesulfonyl peroxides. First, the electron-withdrawing effect of the nitro group, by reducing the electron density on the peroxidic oxygens, may suppress any tendency for homolytic scission, similar to the stabilizing influence previously observed in the nitrobenzoyl peroxides.[4] Second, all sulfonyl peroxides may be inherently susceptible to an induced homolytic decomposition and the stabilizing effect of the nitro group could be due to its ability to interrupt such a chain reaction by acting as a radical trap.[5-8]

In the present work it was planned to synthesize *m*-trifluoromethylbenzenesulfonyl peroxide (1) and study its stability and some of its reactions. The *m*-trifluoromethyl group in its electron-withdrawing ability (σ 0.42) is similar to the *m*-nitro group (σ 0.71) but it is not a radical trap; therefore any unusual stability or reactions of 1 must be attributed specifically to the inductive effect of the trifluoromethyl group.

Results and Discussion

Synthesis of 1 was successfully accomplished by established methods[9] and it was found to be sufficiently stable at room temperature for routine laboratory use. Its high stability in contrast to that of most of the other arylsulfonyl peroxides can be due only to the inductive effect of the trifluoromethyl group, and the stability of the nitrobenzenesulfonyl peroxides now can similarly be attributed to the inductive effect of the nitro group.

Thermal decomposition of 1 in ethyl acetate solutions of alkylbenzenes was undertaken next. The nitrobenzenesulfonyl peroxides have been found to react in high yields with these hydrocarbons exclusively by an electrophilic substitution of the nucleus. The absence of any side-chain attack products characteristic of a homolytic dissociation of these peroxides conceivably could be attributed again to the nitro group acting as a radical trap. It has now been found that the reaction of 1 with ethylbenzene and cumene gives only nuclear substitution (Table I), although yields of as little as 1% of 2,3-diphenyl-2,3-dimethylbutane (the expected side-chain attack products) could have been detected. The result with cumene is particularly significant, for this hydrocarbon undergoes side-chain hydrogen abstraction readily with a variety of free-radical reagents.[10-12] Therefore, the tendency of the arylsulfonyl peroxides to undergo heterolytic scission in the presence of aromatic substrates is inherent and not dependent on the presence of a trapping agent for free radicals to prevent an induced decomposition from becoming predominant.

The relative reactivities with respect to benzene and the orientations of substitution of ethylbenzene and cumene using 1 (Table II) are characteristic of an electrophilic substitution and are similar to those obtained using *o*- and *m*-nitrobenzenesulfonyl peroxides. The greatest differences are the slightly greater ortho substitutions obtained with 1.

The kinetic orders of the reactions with respect to arene

Table I
Reaction of *m*-Trifluoromethylbenzenesulfonyl Peroxide with Mixtures of Alkylbenzenes and Benzene in Ethyl Acetate Solution

Compd or quantity	Ethylbenzene (0.10 *M*)		Cumene (0.10 *M*)		Cumene (0.20)	
	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Peroxide, mmol	0.545	0.453	0.476	0.471	1.01	1.03
Alkylbenzene, mol	0.005	0.005	0.005	0.005	0.01	0.01
Benzene, mol	0.025	0.025	0.025	0.025	0.05	0.05
Ethyl acetate	to 50 ml	to 50 ml	to 50 ml	to 50 ml	to 50 ml	to 50 ml
Sulfonate esters						
Total, % yield	84.3	84.2	77.4	78.1	84.6	82.6
Phenyl, mmol	0.141	0.095	0.109	0.107	0.209	0.208
o-Aryl, mmol	0.139	0.095	0.075	0.075	0.177	0.177
m-Aryl, mmol	0.022	0.018	0.020	0.021	0.053	0.060
p-Aryl, mmol	0.250	0.175	0.166	0.166	0.416	0.406
k_{ar}/k_B	14.5	15.2	11.9	12.2	15.4	15.4

Table II
Competitive Relative Reactivities with Respect to Benzene, Orientations, and Partial Rate Factors for the Arylsulfonoxylation ($XC_6H_4SO_3^-$) of Ethylbenzene and Cumene

Arene and quantity measured	X = *m*-CF_3	X = *o*-NO_2	X = *m*-NO_2
	Ethylbenzene		
k_{Ar}/k_B	14.8	11.5	17.6
% (k/k_H) ortho	33.3 (14.8)	30.6 (10.5)	29.9 (15.8)
% (k/k_H) meta	5.8 (2.6)	4.4 (1.5)	4.3 (2.3)
% (k/k_H) para	60.9 (54.2)	65.0 (44.8)	65.8 (69.4)
	Cumene		
k_{Ar}/k_B	12.1	9.0	13.5
% (k/k_H) ortho	28.5 (10.3)	22.3 (6.0)	23.5 (9.5)
% (k/k_H) meta	7.8 (2.8)	8.9 (2.4)	6.5 (2.6)
% (k/k_H) para	63.7 (46.1)	68.0 (36.8)	70.0 (56.7)

were obtained by direct measurements of the rate of *m*-trifluoromethylphenylsulfonoxylations via an iodometric titration of the disappearance of the peroxide to yield the data in Table III. Simple first-order (1.01) kinetics were obtained with respect to ethylbenzene in ethyl acetate just as first-order kinetics had been obtained for the *m*- and *p*-nitrophenylsulfonoxylation of all the alkylbenzenes studied.[13]

The *m*-trifluoromethylphenylsulfonoxylation of benzene in methylene chloride was found to be first order (0.97) with respect to the arene but in ethyl acetate solution the order was 0.66. Similarly the *m*-nitrophenylsulfonoxylation of benzene has been found to be first order in methylene chloride but 0.66 order in ethyl acetate.[13] These partial orders are due (eq 2) to the pseudo-first-order rate (k_1[P]) being the sum of a first-order (k_2[P]) dissociation to a reactive species plus a bimolecular nucleophilic displacement (k_3[P][B]) by the arene on an oxygen of the peroxide.[1b]

$$\frac{-d[P]}{dt} = k_1[P] = k_2[P] + k_3[P][B] \qquad (2)$$

From a plot (Figure 1) of k_1 (Table III) vs. the concentration of benzene, k_3 (the slope) and k_2 (the intercept) were obtained at three temperatures (Table IV). From these k_2 and k_3 values, as shown in Table V, the enthalpy (entropy) of activation for the k_2 process was found to be 30 kcal mol^{-1} (22 cal deg^{-1} mol^{-1}) and for the k_3 process, 18 kcal mol^{-1} (−20 cal deg^{-1} mol^{-1}). These values are of limited accuracy for minor deviations in k_1 are magnified in deriving k_2 and k_3. However, these parameters are very similar

Table III
Dependence of the Pseudo-First-Order Rate of Disappearance of *m*-Trifluoromethylbenzenesulfonyl Peroxide (0.01 *M*) in Ethyl Acetate Solution upon the Arene Concentration and the Temperature

Arene	Arene concn, *M*	Solvent	Temp, °C	$k \times 10^5$, sec^{-1}
Benzene	1	Ethyl acetate	0	0.170
Benzene	2	Ethyl acetate	0	0.312
Benzene	3	Ethyl acetate	0	0.453
Benzene	1	Ethyl acetate	10	0.730
Benzene	2	Ethyl acetate	10	1.07
Benzene	3	Ethyl acetate	10	1.48
Benzene	1	Ethyl acetate	20	2.82
Benzene	1.5	Ethyl acetate	20	3.44
Benzene	2.0	Ethyl acetate	20	4.16
Benzene	3.0	Ethyl acetate	20	5.87
Benzene	4.0	Ethyl acetate	20	7.06
Benzene	1.0	Methylene chloride	20	3.56
Benzene	2.0	Methylene chloride	20	7.14
Benzene	3.0	Methylene chloride	20	10.3
Ethylbenzene	1.0	Ethyl acetate	0	3.81
Ethylbenzene	1.0	Ethyl acetate	10	11.75
Ethylbenzene	0.1	Ethyl acetate	20	3.38
Ethylbenzene	0.5	Ethyl acetate	20	16.6
Ethylbenzene	1.0	Ethyl acetate	20	33.4
Ethylbenzene	1.5	Ethyl acetate	20	51.5
Cumene	1.0	Ethyl acetate	0	3.21
Cumene	1.0	Ethyl acetate	10	9.81
Cumene	1.0	Ethyl acetate	20	27.7

Table IV
k_2 and k_3 for the Trifluoromethylbenzenesulfonoxylation of Benzene in Ethyl Acetate

Temp, °C	$k_2 \times 10^6$, l. mol^{-1} sec^{-1}	$k_3 \times 10^6$, sec^{-1}
0	.29	1.42
10	3.43	3.75
20	13.2	14.56

to the corresponding values for the *m*- and *p*-nitrophenylsulfonoxylation of benzene (Table V).

The kinetics with **1** are much more reproducible than with any of the nitrobenzenesulfonyl peroxides. Traces of impurities in the solvent, etc., have smaller effects upon the rates with **1**, thus making it a better model reagent.

Reaction Parameters. The enthalpies of activation for

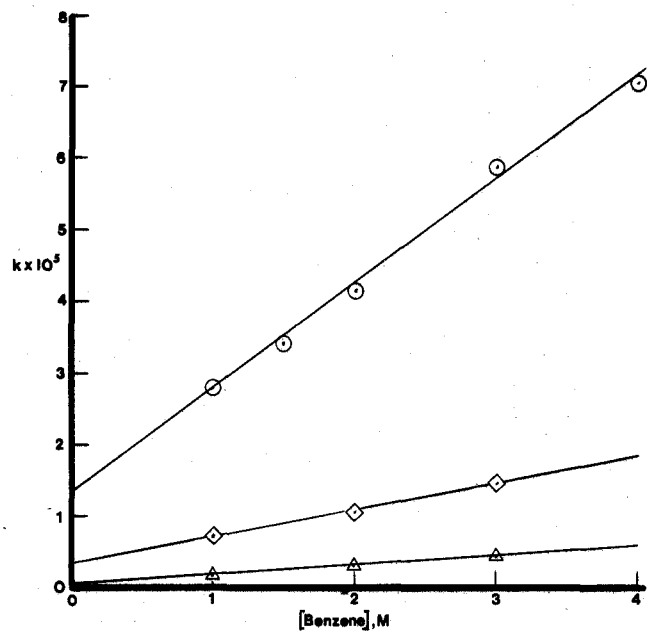


Figure 1. Plot of the pseudo-first-order rate constants for the disappearance of *m*-trifluoromethylbenzenesulfonyl peroxide in ethyl acetate solutions of benzene at the temperatures indicated: △, 0°; ◇, 10°; ○, 20°.

the *m*-trifluoromethylphenylsulfonoxylation in ethyl acetate of benzene (based on overall k_1), ethylbenzene, and cumene (Table V) are all about 1 kcal greater and the entropies of activation only a little less negative than the corresponding values for the *m*- and *p*-nitrophenylsulfonoxylation of the arenes.[13] This reflects the somewhat greater stability and longer half-lives of reaction of the trifluoromethyl peroxide observed in the laboratory as compared to the data for the nitro peroxides.

The entropies and enthalpies of activation for the bimolecular reaction of *m*-trifluoromethylphenylsulfonoxylation in ethyl acetate of benzene (based on k_3), ethylbenzene, and cumene are very similar. The differences observed based on the overall rate for benzene (k_1) result primarily from the competing (k_2) reaction. A similar relationship was observed for the nitrophenylsulfonoxylations of the arenes.[13]

The large negative entropies of activation for all the bimolecular arylsulfonoxylations are to be expected for electrophilic substitutions. The large positive entropy of activation for the k_2 *m*-trifluoromethylphenylsulfonoxylation of benzene in ethyl acetate is appropriate for a homolytic process. This is in agreement with the conclusions made with the nitrobenzenesulfonyl peroxides.[13] The similarity of competitiveness of the k_3 reactions with both the nitro and trifluoromethyl peroxides (as evidenced by the overall orders of reaction with respect to benzene) indicates that this homolytic decomposition of the peroxides is not induced, because then the nitro group, with its ability to act as a radical trap, would be expected to exert an influence different from that of the trifluoromethyl group.

Thermal decomposition of crystalline 1 in a sealed tube was undertaken as a model to determine what products might be expected from a cage reaction of 1 in solution and was found to give the products shown in eq 3. No excess pressure was observed upon opening the tube on a gas manifold. Gas chromatographic analysis of the products

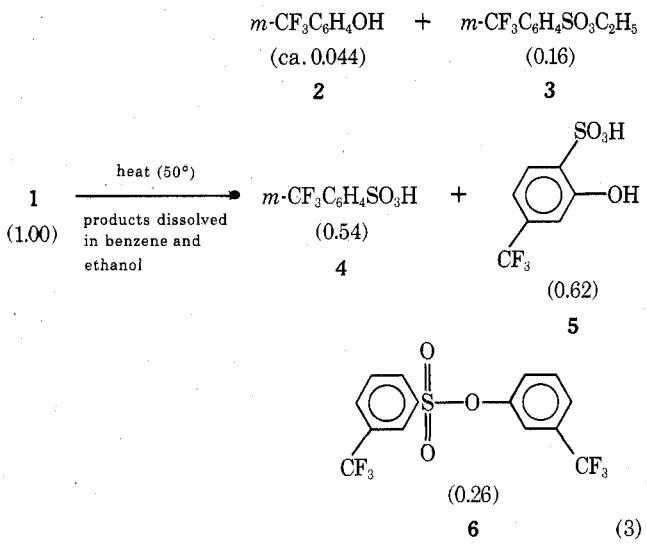
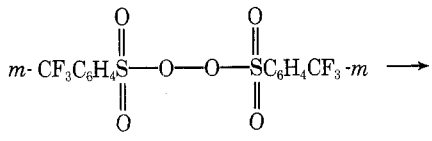


Table V
Reaction Parameters for the Arylsulfonoxylation of Benzene, Ethylbenzene, and Cumene

Arene and reaction	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Benzene		
m-Trifluoromethylbenzenesulfonoxylation[a]	21.8	−4.8
m-Trifluoromethylbenzenesulfonoxylation[b]	30	+22
m-Trifluoromethylbenzenesulfonoxylation[c]	18	−20
m-Nitrobenzenesulfonoxylation[a]	20.6	−7.8
m-Nitrobenzenesulfonoxylation[b]	32	+30
m-Nitrobenzenesulfonoxylation[c]	16	−22
p-Nitrobenzenesulfonoxylation[a]	21.2	−6.2
p-Nitrobenzenesulfonoxylation[b]	d	d
p-Nitrobenzenesulfonoxylation[c]	16 ± 2	−18
Ethylbenzene		
m-Trifluoromethylbenzenesulfonoxylation	16.7	−17.4
m-Nitrobenzenesulfonoxylation	15.5	−20.0
p-Nitrobenzenesulfonoxylation	15.6	−20.1
Cumene		
m-Trifluoromethylbenzenesulfonoxylation	16.6	−18.2
m-Nitrobenzenesulfonoxylation	15.3	−20.7
p-Nitrobenzenesulfonoxylation	15.3	−21.6

[a] From the pseudo-first-order rate constants (k_1). [b] From the reaction constants (k_2) calculated for the reaction whose rate is independent of the benzene concentration. [c] From the reaction constants (k_3) calculated for the reaction first order with respect to benzene concentration. [d] The k_2 values were not reproducible enough to justify additional calculations.

showed the presence of **2** and **6**. When ethanol was added to the reaction mixture, **3** was found and the yield of **2** approximately doubled. Inasmuch as **6** does not undergo alcoholysis under these mild conditions, **3** possibly may have some type of anhydride precursor. The following scheme (eq 4–6) includes a possible concerted mechanism for the decomposition similar to the carboxyl inversion observed with *p*-methoxy-*p'*-nitrobenzoyl peroxide.[14,15] Fichter and



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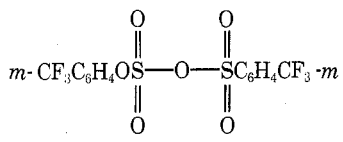

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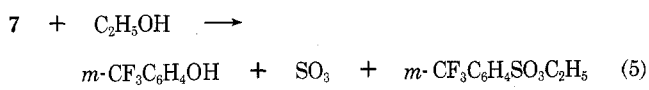
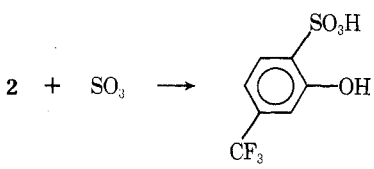


(5)

2 **3**



(6)

5

Stocker studied the decomposition of benzenesulfonyl peroxide in water[16] but because of the insolubility of this peroxide in water, its reaction might parallel a neat decomposition. It is therefore not surprising that they isolated benzenesulfonic acid and phenol (corresponding to **2** and **4**) as well as sulfuric acid (an alternative SO_3 product).

Experimental Section

Reagents. Anisole,[17] benzene,[17] cumene,[17] ethylbenzene,[17] nitrobenzene,[17] and ethyl acetate[18] were purified by standard procedures.

***m*-Trifluoromethylbenzenesulfonyl peroxide** was prepared by the literature method[9] for the nitro analog. A solution of *m*-trifluoromethylbenzenesulfonyl chloride[19] (12.2 g) dissolved in ethanol (10 ml) and a cold solution (−20°) of potassium carbonate (8.5 g) and 98% hydrogen peroxide (5 g) dissolved in a mixture of distilled water (100 ml) and ethanol (100 ml) were mixed at high speed in a prechilled Waring Blendor cup for about 90 sec. Ethanol (50 ml) was added and the mixture was stirred for 30 sec. The crude product (8.72 g, mp 74.5–76°) was collected by filtration, washed with water, and dried in vacuo. The peroxide was recrystallized from methylene chloride to give the pure product (4.77 g, 43%, mp 81–82°, purity 99.8% by peroxide titration[13]).

Anal. Calcd for $C_{14}H_8O_6S_2F_6$: C, 37.34; H, 1.79; S, 14.24. Found: C, 37.70; H, 2.09; S, 14.50.

Aryl Trifluoromethylbenzenesulfonates. The arenesulfonyl chloride (0.04 mol) and the phenol (0.04 mol) were heated together to 80° and a slight excess of aqueous 1 *M* potassium hydroxide was added dropwise over 30 min. The mixture was kept at 80° for an additional 1 hr and then extracted with methylene chloride. The methylene chloride solution was washed with 5% aqueous sodium hydroxide (20 ml), 5% hydrochloric acid (10 ml), and water (20 ml), and then dried with Drierite. The solvent was removed and the liquid esters were distilled at reduced pressure and the solids recrystallized from ethanol (Table VI).

2-Hydroxy-4-trifluoromethylbenzenesulfonic Acid (5). To *m*-trifluoromethylphenol (15 g) was added dropwise 20% fuming sulfuric acid (20 ml) and the mixture was kept at 100° for 1 hr. The mixture was stirred at room temperature with water (25 ml) for 2 days and then more water (100 ml) and sodium chloride were added. A tan solid (19.1 g) was collected by filtration. A portion of the product was dissolved in water and neutralized with aqueous potassium hydroxide, the mixture was cooled, and a cold solution of *S*-benzylthiouronium chloride was added. The *S*-benzylthiouronium arenesulfonate was collected by filtration and after recrystallization from hot 25% ethanol melted at 193–194°.

Anal. Calcd for $C_{15}H_{15}O_4N_2S_2F_3$: C, 44.11; H, 3.70; S, 15.70. Found: C, 44.00; H, 3.61; S, 15.67.

The structure of **5** was established from the NMR spectrum of its sodium salt, which consisted of four resonances: a singlet (H_3) at δ 7.10 overlapping a doublet (H_6) at 7.15; a doublet (H_5) at 7.70 ($J_{H_5H_6}$ = 8 Hz); and a singlet (OH) at 10.67 for an intramolecularly hydrogen-bonded phenol. These chemical shifts correspond to those of 2-amino-4-trifluoromethylbenzenesulfonic acid,[17] which similarly consist of a singlet (H_3) at δ 7.33 overlapping a doublet (H_6) at 7.25; a doublet (H_5) at 7.83; and a broad singlet at 5.67 for the amine salt hydrogens of the zwitterion, $J_{H_5H_6}$ = 7 Hz.

***S*-Benzylthiouronium *m*-trifluoromethylbenzenesulfonate** (mp 138–139°) was prepared by the method used above with hydroxysulfonic acid.

Anal. Calcd for $C_{15}H_{15}O_3N_2S_2F_3$: C, 45.91; H, 3.85; S, 16.34. Found: C, 45.82; H, 3.92; S, 16.33.

Competitive Reaction of 1 with Benzene and Cumene or Ethylbenzene in Ethyl Acetate. A solution 0.01 *M* in **1**, 0.1 *M* in arene, and 0.5 *M* in benzene was kept at 20° for 2 days. *m*-Tolyl *m*-trifluoromethylbenzenesulfonate was added as an internal standard and GLC analysis on a 20% SE-30 on Chromosorb W AW/DCMS column gave the results in Table I by comparison to chromatograms of the authentic esters.

Kinetics. The rates of disappearance of **1** in various solutions of arenes were measured by iodometric titration[13] and the data treated by a least-squares program.

Thermal Decomposition of Solid 1. A weighed amount of **1** placed in a Fischer-Porter aerosol compatibility tube half filled with glass helices was kept at 50° for 7 days. When the aerosol tube was cooled, attached to a gas manifold, and opened, no gas was evolved. The products were dissolved in methylene chloride and ethanol. This solution was washed with 5% aqueous potassium hydroxide to remove sulfonic acids and then chromatographed on silica gel, eluting with benzene. *m*-Trifluoromethylphenyl *m*-trifluoromethylbenzenesulfonate, identified by its melting point and comparison of its ir spectrum to that of an authentic sample, eluted first. Ethyl *m*-trifluoromethylbenzenesulfonate, identified by comparison of its ir spectrum to that of an authentic sample, eluted second.

Table VI
Physical Properties of *m*-Trifluoromethylbenzenesulfonic Acid Esters[a]

Ester	Registry no.	Mp or bp, °C (mm)	$n^{25}D$
Phenyl	55400-60-7	103–104 (0.2)	1.5103
o-Ethylphenyl	55400-61-8	97–98 (0.02)	1.5104
m-Ethylphenyl	55400-62-9	104–105 (0.03)	1.5065
p-Ethylphenyl	55400-63-0	107–108 (0.03)	1.5071
o-Cumyl	55400-64-1	125.5 (0.05)	1.5072
m-Cumyl	55400-65-2	122–123 (0.05)	1.5030
p-Cumyl	55400-66-3	44–45	
m-Trifluoromethylphenyl	55400-67-4	34.5–36.0	
Ethyl	55400-68-5	66 (0.08)	1.4576

[a] Analysis for the elements gave maximum deviations from the theoretical values as follows: all C values, ± 0.24; H, ± 0.14; S, ± 0.31.

A second decomposition mixture was dissolved in benzene, *m*-tolyl *m*-trifluoromethylbenzenesulfonate was added to an aliquot as an internal standard, and analysis by GLC on 5% SE-30 on Chromosorb W (Table I) showed successive peaks for *m*-trifluoromethylphenol and *m*-trifluoromethylphenyl *m*-trifluoromethylbenzenesulfonate. When absolute ethanol was added before GLC analysis, a new peak for ethyl *m*-trifluoromethylbenzenesulfonate appeared between the other two peaks and the peak for *m*-trifluoromethylphenol approximately doubled in area.

A second aliquot of the benzene solution of the reaction mixture was concentrated, methylene chloride was added, and the solution was extracted twice with water and once with 5% aqueous potassium hydroxide. The aqueous alkaline extract and the two water washes were combined and evaporated to dryness in a rotary evaporator. A portion of this residue was dissolved in 10 ml of water and adjusted to pH 6 with hydrochloric acid. This solution was cooled in an ice bath and added to a cold solution of *S*-benzylthiouronium chloride (5.0 g) in water (30 ml). The tan precipitate which formed was collected, dried, and recrystallized from hot 25% ethanol to give *S*-benzylthiouronium 2-hydroxy-4-trifluoromethylbenzenesulfonate (mp 193–194°). The mother liquor from the tan precipitate yielded *S*-benzylthiouronium *m*-trifluoromethylbenzenesulfonate (mp 133–134°). These salts were identified by melting point and ir spectra.

A new reaction mixture was prepared and concentrated, methylene chloride was added, and the methylene chloride solution was extracted twice with water and once with 5% aqueous potassium hydroxide. The combined aqueous layers were evaporated to dryness using a rotary evaporator. The solid residue was dissolved in a minimum amount of water (less than 10 ml), the solution was adjusted to pH 6 with hydrochloric acid, and a cold solution of *S*-benzylthiouronium chloride (3.0 g) in water (15 ml) was added. The precipitate which formed from this minimum amount of solution was collected by filtration, dried, and analyzed by ir using the base line technique to determine the relative amounts of the two component sulfuric acid salts.

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Registry No.—1, 35673-10-0; 5, 55400-69-6; *m*-trifluorobenzenesulfonyl chloride, 777-44-6; phenol, 108-95-2; *o*-ethylphenol, 90-00-6; *m*-ethylphenol, 620-17-7; *p*-ethylphenol, 123-07-9; *o*-cumenol, 88-69-6; *m*-cumenol, 618-45-1; *p*-cumenol, 99-89-8; *m*-trifluoromethyphenol, 98-17-9; ethanol, 64-17-5; *S*-benzylthiouronium chloride, 538-28-3; *S*-benzylthiouronium 2-hydroxy-4-trifluoromethylbenzenesulfonate, 55400-70-9; *S*-benzylthiouronium *m*-trifluoromethylbenzenesulfonate, 2342-60-1; benzene, 71-43-2; cumene, 98-82-8; ethylbenzene, 100-41-4.

References and Notes

(1) (a) Presented at the International Conference on the Mechanisms of Reactions in Solution at the University of Kent at Canterbury, July 1970. Taken in part from the Ph.D thesis of P. K. T., 1970. (b) For the previous paper of this series see R. L. Dannley, R. V. Hoffman, P. K. Tornstrom, R. L. Waller, and R. Srivastava, *J. Org. Chem.*, **39**, 2543 (1974). (c) NDEA Fellow, 1966–1969. This work supported in part by National Science Foundation Grant GP-19018.
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Preparation and Hydrolysis of Aminocyclopropyl and Aminocyclobutyl Sulfones[1]

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This report describes (1) the synthesis of aminocyclopropyl sulfides and their aqueous potassium permanganate oxidation to afford ring-opened sulfone acids and ketones; (2) the synthesis and facile hydrolysis of an aminocyclopropyl sulfone to afford a ring-opened aldehyde; and (3) the synthesis and hydrolysis of aminocyclobutyl sulfones to afford ring-opened aldehydes. It is proposed that these ring-opening reactions occur via zwitterionic intermediates.

There has been recent interest in the ring opening of cyclopropanes via zwitterionic intermediates.[1b-6] Ring-opening reactions of cyclopropylamines have also received recent attention.[1b,3,5-9] However, all of these systems require elevated temperatures and/or acidic or basic conditions. In contrast, we have found that aminocyclopropyl sulfones undergo a facile hydrolytic ring opening at room temperature. This report describes (1) the synthesis of aminocyclopropyl sulfides and their aqueous potassium permanganate oxidation to afford ring-opened products; (2) the synthesis and facile hydrolysis of an aminocyclopropyl sulfone; and (3) the synthesis and hydrolysis of aminocyclobutyl sulfones. We propose that these ring-opening reactions occur via zwitterionic intermediates, and discuss the factors influencing zwitterion formation.

Preparation and Aqueous Potassium Permanganate Oxidation of Aminocyclopropyl Sulfides. The reaction of thiocarbenes (or carbenoids[10]), generated from chloromethyl sulfides and potassium *tert*-butoxide in ether, with enamines afforded the aminocyclopropyl sulfides shown in Table I. The yields ranged from poor to good, the lowest being observed with chloromethyl methyl sulfide. Rationale for the configurational assignments and an explanation for the observed stereoselectivities have been presented.[1a] Oxidation of the aminocyclopropyl sulfides **3**, **9**, and **11** + **12** with potassium permanganate in aqueous acetic acid at 25–30° afforded ring-opened sulfone acids and/or ketones in good yields. The products and yields are summarized in Table II. Structural proof for the products has been previously described.[1b] These conversions can be best