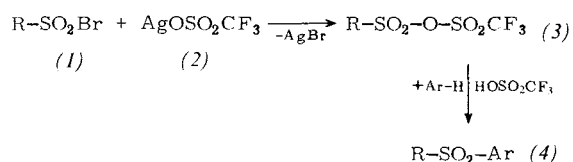


## Preparation and Reactions of Trifluoromethanesulfonic Arenesulfonic Anhydrides<sup>[1][\*\*]</sup>

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Dedicated to Professor Hellmut Bredereck on the occasion of his 70th birthday

In the course of our investigations on new electrophilic agents, we have reported on the preparation of trifluoromethanesulfonic carboxylic anhydrides and their high acylating potential<sup>[2]</sup>. We have now succeeded in obtaining the mixed sulfonic anhydrides (3) from sulfonyl bromides (1) and silver trifluoromethanesulfonate (2).



Since the anhydrides (3) are not stable in pure form, exact physical data cannot be given; their structure, however, is established unequivocally by <sup>1</sup>H-NMR and by their reaction with arenes, yielding aryl sulfones (4) (Table 1).

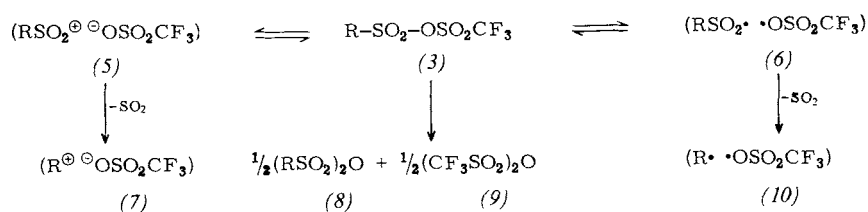
The extraordinary sulfonylating potential of the anhydrides (3) is apparent from the reaction with an arene as unreactive as chlorobenzene, which is sulfonylated in high yield even at 0°C (see Table 1). With sulfonyl halides, on the other hand, sulfones are formed from arenes only at elevated temperature and in the presence of Friedel-Crafts catalysts<sup>[3]</sup>.

The anhydrides (3) are thermolabile; in the absence of arenes which can be sulfonylated they decompose in various ways depending on the nature of R.

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For R = alkyl, heterolytic dissociation to (5) and subsequent loss of SO<sub>2</sub> yielding (7) are observed; the decomposition temperature falls as the stabilization of the carbenium ion



R<sup>⊕</sup> increases. Radicals (10) are formed preferentially from anhydrides with polyalkyl- and polyalkoxyarenesulfonic components, probably by homolysis to (6) and loss of SO<sub>2</sub>. The anhydrides listed in Table 1 suffer disproportionation into

Table 1. Preparation of trifluoromethanesulfonic arenesulfonic anhydrides (3) and their reaction with arenes to form sulfones (4) [a].

(1), R =	Starting materials Ar-H	sulfone	Products (4) yield [%]	m. p. [°C] [b]
4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -	benzene	4-nitrodiphenyl	34	142-143
4-Cl-C <sub>6</sub> H <sub>4</sub> -	benzene	4-chlorodiphenyl	80	94
C <sub>6</sub> H <sub>5</sub> -	benzene	diphenyl	90	126
4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	benzene	4-methyldiphenyl	98	126-127
4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	<i>p</i> -xylene	2,5,4'-trimethyldiphenyl	98	108
4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	toluene	di- <i>p</i> -tolyl [c]	100	
4-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	chlorobenzene	4-chloro-4'-methyldiphenyl [d]	80	123-124

[a] The anhydrides (3) were prepared from (1) and (2) at 0°C in nitromethane, and reacted with a threefold excess of arene (Ar-H) at the same temperature. The yields were determined by GLC. The yields obtained on a preparative scale are only slightly lower.

[b] The melting points of the sulfones (4) are in accordance with literature data. Mixed melting points with authentic material show no depression.

[c] Isomer distribution: 2,4':3,4':4,4' = 42:5:53.

[d] No other isomers could be detected.

(8) and (9) upon warming. Since this process already occurs at temperatures slightly above 50°C, the anhydrides (3) cannot be prepared from (2) and the less reactive sulfonyl chlorides.

#### 4-Methyldiphenyl sulfone, (4): R = *p*-tolyl, Ar = phenyl

Compound (2) (2.56 g, 0.01 mol) is dissolved in nitromethane (10 ml) at 0°C, and a solution of *p*-toluenesulfonyl bromide (2.35 g, 0.01 mol) in nitromethane (10 ml) is added. After 30 min stirring, benzene (2.34 g, 0.03 mol) is added. Stirring is continued for another 30 min, chloroform (20 ml) is added, the AgBr precipitate separated, and the organic phase is washed with sodium carbonate solution and with water. The solvent is stripped off and the residue recrystallized from ethanol: yield 2.15 g (93%), m. p. 126-127°C (127-128°C<sup>[4]</sup>); mixed m. p. 127°C.

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