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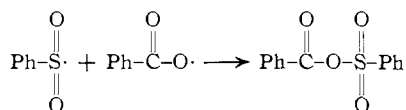
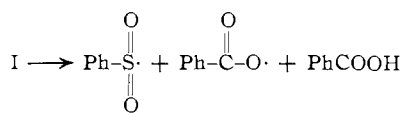
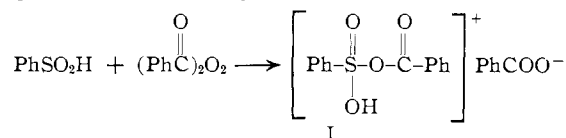
## Mixed Sulfonic-Carboxylic Anhydrides

BY C. G. OVERBERGER AND E. SARLO<sup>1</sup>

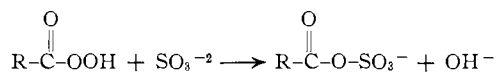
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Several mixed sulfonic-carboxylic anhydrides were prepared in order to study their chemical properties. They were: benzoyl benzenesulfonate (II), benzoyl *p*-toluenesulfonate (III), propionyl benzenesulfonate (IV), *p*-nitrobenzoyl *p*-toluenesulfonate (V), and terephthaloyl bis-(*p*-toluenesulfonate) (VI). These compounds were found to be active acylating agents, affording the acylated product in good yield and under mild conditions. No sulfonylation was observed.

Sulfonic acids, in the presence of peroxides, have found use as polymerization initiators.<sup>2</sup> Although the initiation mechanism is not known, it could conceivably be similar to that proposed for peroxides in the presence of tertiary amines.<sup>3</sup> The formation of



a mixed sulfonic-carboxylic anhydride may therefore be considered as a possible intermediate. It is also well known that several sulfur-containing oxidation-reduction systems can initiate vinyl polymerization.<sup>4</sup> Interestingly, Soloway and Friess<sup>5</sup> found that peracids and bisulfites can acylate amines, which suggests the involvement of a mixed anhydride.



The possibility of anhydride formation in the bisulfite-peracid system as well as the assumed similarity between the tertiary amine-peroxide and the sulfonic acid-peroxide systems suggested the preparation of several of these compounds in order to study their chemical properties and their possible utilization as initiators for polymerization.

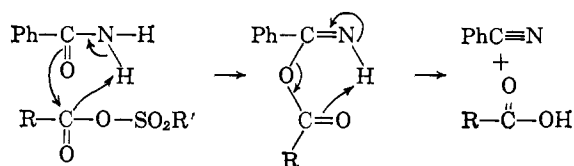
## Results

Benzoyl benzenesulfonate was prepared from silver benzoate and benzenesulfonyl chloride using the method of Baroni.<sup>6</sup> However, because of the rather drastic reaction conditions employed, an improved method of synthesis was sought. This was realized when an acetonitrile solution was treated with benzoyl chloride. Reaction, as evidenced by the precipitation of silver chloride, was immediate. In this manner the following compounds were prepared in yields of 45–65%: benzoyl benzenesulfonate (II), benzoyl *p*-

toluenesulfonate (III), propionyl benzenesulfonate (IV), *p*-nitrobenzoyl *p*-toluenesulfonate (V), and terephthaloyl bis-(*p*-toluenesulfonate) (VI). All of the anhydrides are crystalline solids. Compound IV is very hygroscopic, decomposing quickly on exposure to air. Compounds V and VI, however, are noticeably more stable, higher melting, and only partially soluble in many organic solvents. All show absorption in the infrared around 1780 cm.<sup>-1</sup>.

The reactivity of these anhydrides was demonstrated by their ability to acylate various substrates. In conformity to previous reports,<sup>7,8</sup> reaction with nucleophilic reagents took place solely at the carbonyl position. A description of these reactions is given in the Experimental. To contrast the benzoylating ability of these compounds with benzoyl chloride, the latter was allowed to react with phenol under conditions similar to those used during the reaction of the anhydrides with phenol. Under these circumstances essentially no reaction took place. This indicates that these anhydrides are substantially more reactive than benzoyl chloride.

It was found that benzoyl *p*-toluenesulfonate dehydrated rather than benzoylated benzamide, thereby supporting a proposed mechanism<sup>9</sup> for the dehydration of primary amides by *p*-toluenesulfonyl chloride. A logical sequence for dehydration might be formulated as



This same anhydride was found to react with both styrene and propylene oxides. From infrared and elemental analysis, the products were assumed to be 1-phenyl-2-benzoyloxyethyl *p*-toluenesulfonate and 1-methyl-2-benzoyloxyethyl *p*-toluenesulfonate. However, no rigorous investigation of structure was carried out.

An attempt was made to utilize mixed anhydrides for the preparation of polymers. Terephthaloyl bis-(*p*-toluenesulfonate) was prepared and treated with 1,5-pentanedithiol. A yellowish, somewhat rubbery and apparently polymeric material was obtained which possessed only a slight odor of mercaptan. It was found to be insoluble in common organic solvents.

## Discussion

Mixed anhydrides have been used for many years as acylating agents. Generally, derivatives of the stronger acids are formed.<sup>10</sup> However, in certain cases com-

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pounds derived from the weaker acids are obtained. Ethanol, for example, react with benzoic-mesitoic anhydride to give ethyl mesitoate exclusively.<sup>11</sup> Two mechanistic paths have been invoked to explain this difference in behavior. Reactions which proceed through an SN2 mechanism would favor the formation of derivatives of the stronger acids since attack on the more electron-deficient carbonyl is likely in these cases. An SN1 mechanism, on the other hand, involving the formation of an acylium ion, would favor the product derived from the weaker acid.

The reactivity of the mixed sulfonic-carboxylic anhydrides<sup>12</sup> as well as their singular path of reaction, *i.e.*, acylation rather than sulfonylation, resemble the trifluoroacetic anhydride method of acylation. There is adequate evidence that trifluoroacetic anhydride functions by first forming a mixed anhydride with the solute acid.<sup>13</sup> It has also been proposed<sup>14</sup> that certain equilibria are established when a weak oxyacid is dissolved in trifluoroacetic anhydride and a small amount of acylium ion is formed. Although present in small amounts, the extremely reactive acylium ion is believed to be responsible for the acylating properties of the system. With highly reactive nucleophiles, however, a bimolecular process may be accelerated while the ionization of the mixed anhydride to an acylium ion is unaffected. In these cases the SN2 process may compete to some extent with the SN1 mechanism.<sup>15</sup> The effectiveness of this reaction decreases as the strength of the solute acid increases,<sup>16</sup> for although the acylium ion which is formed is more reactive, the rate-determining ionization step is retarded.

Jeffery and Satchell<sup>17</sup> have investigated acid-catalyzed acylation by isopropenyl acetate and proposed a mixed anhydride as the active acylating agent. From kinetic studies on carboxylic anhydride-sulfuric acid systems, they suggested a mechanism which proceeded through an acyl hydrogen sulfate. These authors believe that these anhydrides exist partially in an ionized form which is in equilibrium with the un-ionized form. Russell and Cameron,<sup>18</sup> Franchimont,<sup>18</sup> van Peski,<sup>18</sup> and Murray and Kenyon<sup>18</sup> also proposed an intermediate of this type.

In this present work it has been found that the mixed sulfonic-carboxylic anhydrides behave as acylating agents and thus in their reactions they resemble alkylsulfonates. No sulfonylation was observed in any of the reactions which were carried out.

Cleavage of the C-O bond is enhanced by the electron-withdrawing properties of the sulfonyl group, the arylsulfonates being better leaving groups than the carboxylates.<sup>19</sup>

From the ease of handling, the relative stabilities of the mixed anhydrides appears to be of the descending order: V ~ VI > II ~ III > IV. This order of stability would be expected if a reaction mechanism similar to

that postulated for the trifluoroacetic anhydride system is assumed. An equilibrium between the ionized and the un-ionized forms of the anhydride would liberate the highly reactive acylium ion. The presence of sulfonic acid as a reaction product or from reaction with adventitious water would also catalyze acylium ion formation.<sup>20</sup>

Although sulfonylium ions have been proposed,<sup>21</sup> their formation should be less favored than the formation of acylium ions derived from the weaker carboxylic acids. From resonance considerations, the carbonium ions derived from V and VI should be less stable and therefore more difficult to form than those derived from either acetic or benzoic acids. Thus the ease of carbonium ion formation should be IV > II > V ~ VI. This is the reverse order for the apparent relative stabilities of these compounds. In support of this point of view, it was found that a benzene solution of III and phenol afforded, after 2 hr. of stirring at room temperature, a 68% yield of phenyl benzoate, whereas V gave only a minor yield of ester after refluxing a benzene solution for 0.5 hr. After 12 hr. at reflux, a 71% yield was isolated. It has also been observed<sup>16</sup> that 3,4-dinitrobenzoic acid cannot be satisfactorily esterified using the trifluoroacetic anhydride system.

Differences in reactivity also appear to depend on the nucleophilicity of the attacking reagent. Reactions with aniline, for example, took place on contact and gave nearly quantitative yields of product. Phenol, on the other hand, gave only 68 and 69% yields of phenyl ester with anhydrides II and III after 2 to 3 hr. Apparently a bimolecular mechanism is at least partially involved when highly reactive nucleophiles are used. Only acylated products were obtained, however, owing to the greater ease of attacking a carbonyl rather than a sulfonyl group. The lowest energy distributions of the sulfonyl moiety place a positive charge on the sulfur atom.<sup>22</sup> Nucleophilic attack on the positive sulfur will therefore be hindered by the negative charge on the oxygen atoms.<sup>23</sup> The positive charge on the sulfur should also hinder the formation of sulfonylium ions relative to the formation of acylium ions, for, in order to satisfy this charge, the sulfur atom would be required to expand its octet to allow d-orbital participation, a somewhat higher energy electron distribution.<sup>24</sup>

An investigation concerning the ability of these compounds in their conjugate acid form to initiate polymerization is being carried out.

### Experimental<sup>25</sup>

**Preparation of Benzoyl Benzenesulfonate (II).**—To a solution of 84.7 g. of silver benzenesulfonate in 250 ml. of acetonitrile there was added dropwise and with stirring 51.2 g. of benzoyl chloride while the temperature was maintained at 0°. Stirring at room temperature was continued for 4 hr. while the reaction mixture was protected from light. Solvent was removed under vacuum and the solid which remained was extracted several times with ether. The ether extracts were cooled below 0°, affording 46 g. (55%) of II, m.p. 75–78°. Some softening was observed before the melting points of II, III, and IV were reached. Infrared absorption was exhibited at 1780, 1390, 1190, and 1185 cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>13</sub>H<sub>10</sub>O<sub>4</sub>S: C, 59.53; H, 3.83; S, 12.23. Found: C, 58.99; H, 3.89; S, 12.46.

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**Preparation of Benzoyl *p*-Toluenesulfonate (III).**—This compound was prepared as described above. From 63.9 g. of silver *p*-toluenesulfonate and 28.1 g. of benzoyl chloride there was obtained 36.4 g. (63%) of III, m.p. 55–58°. The infrared spectrum was similar to that exhibited by compound I.

*Anal.* Calcd. for  $C_{14}H_{12}O_4S$ : C, 60.80; H, 4.38; S, 11.61. Found: C, 60.80; H, 4.74; S, 11.91, 12.29.

**Preparation of Propionyl Benzenesulfonate (IV).**—The same conditions as described above were used. From 75 g. of silver benzenesulfonate and 26 g. of propionyl chloride there was obtained 28.5 g. (48%) of a yellowish, very hygroscopic solid which was recrystallized from hexane; m.p. 44–46°. Infrared absorption was exhibited at 1800  $cm^{-1}$ .

*Anal.* Calcd. for  $C_9H_{10}O_4S$ : S, 14.97. Found: S, 14.46.

**Preparation of *p*-Nitrobenzoyl *p*-Toluenesulfonate (V).**—From 83.4 g. of silver *p*-toluenesulfonate and 55 g. of *p*-nitrobenzoyl chloride there was obtained a heavy precipitate of silver chloride and product. After stirring the mixture overnight, the solvent was removed and the residue extracted several times with hot benzene. Cooling afforded 42 g. (45%) of V, m.p. 167–169°. Infrared absorption was exhibited at 1780, 1540, 1390, 1350, 1190, and 1180  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{14}H_{11}NO_6S$ : C, 52.33; H, 3.45; N, 4.36. Found: C, 52.46; H, 3.44; N, 4.57.

**Preparation of Terephthaloyl Bis-(*p*-toluenesulfonate) (VI).**—Treatment of 33.1 g. of silver *p*-toluenesulfonate with 12 g. of terephthaloyl chloride as described above for V afforded 15.4 g. (55%) of VI, m.p. 174–176°. Infrared absorption was similar to that observed for the previously prepared compounds.

*Anal.* Calcd. for  $C_{22}H_{18}O_8S_2$ : C, 56.65; H, 3.89; S, 13.75. Found: C, 56.55; H, 3.89; S, 13.55.

**Reaction of II with Aniline.**<sup>26</sup>—To 19.4 g. of II dissolved in 200 ml. of anhydrous ether there was added 13.8 g. of aniline. Reaction began immediately as evinced by precipitation. The mixture was stirred for 0.5 hr. and then filtered. The solid which was obtained was extracted four times with 30-ml. portions of boiling ether. After drying in a vacuum oven, 17.9 g. (96.5%) of anilinium benzenesulfonate, m.p. 235–237° (m.p. 240°<sup>27</sup>), was obtained. Concentration of the ether solutions and cooling afforded 11.4 g. of benzanilide, m.p. 163–163.5° (m.p. 163°).<sup>28</sup> Evaporation of the remaining ether gave an additional 2.4 g. of benzanilide, m.p. 160–162°. The total yield of anilide was 94.5%. The infrared spectra of the anilinium salt and benzanilide were identical with those of known samples.

**Reaction of II with Phenol.**—A solution of 2.0 g. of II in 75 ml. of benzene was treated with 0.7 g. of phenol in 25 ml. of benzene. The solution was stirred for 2 hr. at room temperature after which time 50 ml. of water was added and stirring was continued for 0.5 hr. The benzene layer was separated and washed with a 10% sodium hydroxide solution. After drying over magnesium sulfate, the benzene was removed by freeze-drying, affording 1.0 g. (68%) of phenyl benzoate, m.p. 69–70° (m.p. 70°).<sup>29</sup> Infrared absorption was identical with that of a known sample.

**Reaction of III with Benzamide.**—To 150 ml. of ether there was added 6.3 g. of III and 2.66 g. of benzamide. After 12 hr. at reflux, insoluble materials were removed by filtration. The

ether was washed with a saturated solution of sodium carbonate and then dried over sodium carbonate. Distillation after removal of the ether afforded 1.2 g. (44%) of benzonitrile, b.p. 50° (1.5 mm.),  $n_D^{25}$  1.5272 (b.p. 190.7°,  $n_D^{20}$  1.5289).<sup>29</sup> The infrared spectrum was identical with that of a known sample. Acidification of the sodium carbonate extract afforded benzoic acid, m.p. 121–122° (m.p. 121°).<sup>30</sup>

**Reaction of III with Styrene Oxide.**—A benzene solution of 9.6 g. of III and 4.2 g. of styrene oxide was stirred for 24 hr. at room temperature and then washed with a 10% solution of sodium hydroxide. The benzene was dried over magnesium sulfate and then removed by freeze-drying. A viscous semisolid was obtained which was crystallized by trituration with methanol. Recrystallization from aqueous methanol afforded 2.0 g. (14%) of a white solid, m.p. 96–97°. Although a rigorous structure proof was not carried out, infrared and elemental analysis indicated that the product could be 1-phenyl-2-benzoyloxyethyl *p*-toluenesulfonate. Absorption was found at 1725, 1365, 1350, 1270, 1190, 1175, 950, and 920  $cm^{-1}$ .

*Anal.* Calcd. for  $C_{22}H_{20}O_5S$ : C, 66.64; H, 5.08; S, 8.09. Found: C, 66.46; H, 5.24; S, 8.22.

**Reaction of II with Propylene Oxide.**—The above reaction was repeated using ether as solvent. From 5.0 g. of II and 10 g. of propylene oxide there was obtained 1.5 g. (22%) of possibly 1-methyl-2-benzoyloxyethyl *p*-toluenesulfonate, m.p. 100–102° after recrystallization from aqueous methanol.

*Anal.* Calcd. for  $C_{17}H_{18}O_5S$ : C, 61.04; H, 5.42; S, 9.59. Found: C, 61.47; H, 5.36; S, 9.66.

**Reaction of V with Aniline.**—A solution of 1.77 g. of aniline in 25 ml. of ether was added to a partial solution of 3.0 g. of V in 200 ml. of methyl ethyl ketone. Reaction was immediate although the mixture was stirred for 2 hr. The insoluble materials were removed by filtration and washed with hot ether. The ether extracts were combined with the methyl ethyl ketone. Removal of solvents under vacuum afforded 2.48 g. of a tan solid. Recrystallization from methanol gave 1.23 g. (54%) of *p*-nitrobenzanilide, m.p. 210–212° (m.p. 210–211°).<sup>29</sup> Infrared absorption was noted at 1650, 1535, and 1350  $cm^{-1}$ .

**Reaction of V with Phenol.**—A benzene solution of 1.1 g. of phenol was added to 3.7 g. of V in 200 ml. of benzene. After refluxing for 12 hr., the solution was washed once with a 10% sodium hydroxide solution and then several times with water. After drying over magnesium sulfate, the benzene was removed by freeze-drying, affording 2.2 g. (76%) of phenyl *p*-nitrobenzoate, m.p. 124–128° (m.p. 129°).<sup>31</sup> Recrystallization from hexane gave 2.0 g. of product, m.p. 129–130°. Infrared absorption was found at 1735, 1535, and 1350  $cm^{-1}$ .

**Reaction of V with Ethanol.**—To 5.9 g. of V in 150 ml. of benzene there was added 2.5 g. of ethanol. After 2 hr. at reflux the benzene solution was washed with a saturated sodium carbonate solution and then dried over sodium carbonate. Removal of the benzene by freeze-drying afforded 3.3 g. (94%) of ethyl *p*-nitrobenzoate, m.p. 57–58° (m.p. 57°).<sup>28</sup> Infrared absorption was exhibited at 1725, 1535, and 1350  $cm^{-1}$ .

**Reaction of VI with 1,5-Pentanedithiol.**—Compound VI was treated with 1,5-pentanedithiol in refluxing benzene under a nitrogen atmosphere for 12 hr. Removal of solvent afforded a brown mass which was washed with a 10% solution of potassium hydroxide. Filtration afforded a yellowish, somewhat rubbery and apparently polymeric solid in 60% yield.

(26) Similar results were obtained for the reaction of anhydrides II, III, and IV with aniline and phenol.

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