A NOVEL METHOD FOR THE PREPARATION OF THIOLSULFONATES

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Thiolsulfonates were obtained in good yield by the reaction of N-(arylthio)-succinimides with alkali arenesulfinates and arene-sulfinic acid.

It has recently been shown that N-(alkylthio or arylthio)-imides (sulfenimides)<sup>1)</sup> react with thiols<sup>2)</sup>, hydrodisulfides<sup>2b)</sup>, alkoxides<sup>3)</sup>, phosphines<sup>4)</sup>, and amines<sup>5)</sup> to give disulfides, trisulfides, alkyl sulfenates, N-alkylimides, and sulfenamides, respectively. These reactions are believed to occur by the attack of the nucleo-philes on the sulfur atom of sulfenimides. Other references also report that N-(phenylthio)-phthalimide acts as an efficient sulfenylation reagent for active methylene compounds.<sup>6)</sup>

We wish to report a novel reaction of N-(arylthio or aralkylthio)-succinimides (1) with sulfinates. When 1 were treated with sulfinates (2) which behave as nucleophiles, a series of thiolsulfonates (3) were obtained in good yields conveniently. The results are summarized in Table 1.



For the preparation of thiolsulfonates, the reaction of sulfinates with arenesulfenyl chlorides has been the most popular and excellent method among others. The **present** method, however, has a particular advantage that precursor N-(arylthio)succinimides are easy to prepare and have enough stability as compared with arenesulfenyl chlorides.

The general procedure for the reaction of  $\underline{1}$  with alkali sulfinates ( $\underline{2}$ ) is as follows. The solution of  $\underline{1}$  (10 mmol) in benzene (50-100 ml) and an equivalent of alkali arenesulfinate in water (50 ml) were vigorously shaken (5-10 min) in a separatory funnel at room temperature. After 5 min, benzene layer was washed with water, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The resulting residue was then crystallized from ethanol or petroleum ether and purified by recrystallization. In case of using sulfinic acid as a starting material (Run 9 in Table 1), N-(p-tolylthio)-succinimide (10 mmol) and an equivalent of p-toluenesulfinic acid were stirred for 10 hrs in 50 ml benzene at room temperature. Succinimide was then filtered off and the filtrate was evaporated in vacuo. Succeeding procedure was the same as mentioned above.

Run	R	М	R'	%Yield	Mp°C <sup>a,b</sup>	Lit Mp°C
1	C6H5-	Na	C6H5-	92	38.4	45 <sup>7)</sup>
2	C <sub>6</sub> H <sub>5</sub> -	Na	p-CH3C6H4-	95	53.7	54 <sup>7)</sup>
3	C <sub>6</sub> H <sub>5</sub> -	Na	p-ClC <sub>6</sub> H <sub>4</sub> -	92	70.5	71-72 <sup>7)</sup>
4	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	К	C <sub>6</sub> H <sub>5</sub> -	98	78.5	74-75 <sup>7)</sup>
5	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	Na	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	87	79.0	76 <sup>7)</sup>
6	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	К	p-ClC <sub>6</sub> H <sub>4</sub> -	94	90.4	90 <sup>8)</sup>
7	p-CH 3C 6H 4-	K	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	54	58.7	60 <sup>9)</sup>
8	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	K	C <sub>6</sub> H <sub>5</sub> -	54	117.1	110-111 <sup>10)</sup>
9	р-СН <sub>3</sub> С <sub>6</sub> Н <sub>4</sub> -	н	p-CH 3C 6H 4 -	57	79.0	76 <sup>7)</sup>

Table 1. Preparation of Thiolsulfonates

a) Satisfactory elementaly analyses were obtained for all compounds.

b) Mp were measured by Mettler FPl melting and boiling point apparatus (2°C/min) and uncorrected.

## References

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