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# THE IDENTIFICATION OF AROMATIC SULFONES

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The literature reveals little in the way of derivatives suitable for the identification of sulfones. The most recent method as applied to alkyl phenyl sulfones is that of Ipatieff and Friedman.[1]

In this investigation ten aromatic sulfones were studied. Since nearly all the sulfones contained alkyl groups, oxidation was resorted to first. In Table I the carboxylic acid thus obtained are listed. The value of these acids as derivatives is limited, for they are frequently not sufficiently characteristic, and their melting points are high. To overcome the latter difficulty conversion into the esters, as shown in Table II, was undertaken.

More satisfactory derivatives for the aromatic sulfones were obtained by nitration, a method already applied by Ipatieff and Friedman to some alkyl phenyl sulfones. The dinitro sulfones obtained are assembled in Table III. These compounds are easily prepared in a pure form in good yield, they melt sharply throughout a convenient range, and they permit a differentiation to be made among the sulfones investigated.

## EXPERIMENTAL

All sulfones were prepared by the Friedel-Crafts reaction, using anhydrous aluminum chloride, benzenesulfonyl, *p*-toluenesulfonyl or *p*-bromobenzenesulfonyl chloride, and the proper hydrocarbon or phenyl halide. The yields of the final products from 75 to 150 grams of the sulfonyl chloride varied from 47 to 79%. One of the sulfones, *p*-tolyl *p*-ethylphenyl, has not been described previously. It melted at 112.0–113.0° and gave S, 12.43% (theoretical, 12.35%). Since it gave a dicarboxylic acid (Table I) and a diethyl ester (Table II) agreeing in melting points with those obtained from *p*, *p'*-ditolylsulfone, its structure may be accepted as indicated.

The alkyl or dialkyl sulfones were oxidized by means of chromium trioxide in glacial acetic acid, a method similar to that employed by Newell[2]. The oxidation products with yields and melting points are given in Table I.

For esterification the mono- or dicarboxy sulfones were treated with absolute alcohol and concentrated sulfuric acid. The esters obtained with yields, melting points, and analyses are given in Table II.

In preparing the dinitro derivatives, 1.5 g. of sulfone was placed in a small beaker containing 6 cc. of concentrated sulfuric acid. After the beaker and its contents were immersed in cold water, 6 cc. of concentrated nitric acid was added, drop by

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[1] IPATIEFF AND FRIEDMAN, *J. Am. Chem. Soc.*, **61**, 684 (1939).

[2] NEWELL, *Am. Chem. J.*, **20**, 305 (1898).

drop, with constant stirring. Considerable heat was developed during this process, but at no time was the temperature allowed to rise above 60°. The mixture was then heated on a water bath maintained at 60° for fifteen minutes. At the end of this period, it was poured on 50 g. of cracked ice, and the solid that separated, was collected on filter paper. Purification was accomplished by one crystallization from

TABLE I

OXIDATION PRODUCTS OF AROMATIC SULFONES

| SULFONE | ACID FORMED | M.P., °C. | | % S | | % YIELD[a] |
|---|---|---|---|---|---|---|
| | | Found (uncorr.) | Lit. | Found | Calc'd | |
| Phenyl *p*-tolyl[b] | Phenyl *p*-carboxyphenyl sulfone | 266–68 | 273[c] | | | 38 |
| *p,p'*-Ditolyl[d] | Bis-*p*-carboxyphenyl sulfone | 358–63 | 370[e] | | | 64 |
| *p*-Chlorophenyl *p*-tolyl | *p*-Chlorophenyl *p*-carboxyphenyl sulfone | 274.1–275.3 | | 10.49 | 10.79 | 51 |
| *p*-Bromophenyl *p*-tolyl | *p*-Bromophenyl *p*-carboxyphenyl sulfone | 283.8–285.5 | | 9.26 | 9.39 | 68 |

[a] Based on 10 to 25 grams original sulfone.
[b] Result identical with phenyl *p*-ethylphenyl sulfone.
[c] NEWELL, *Am. Chem. J.*, **20**, 305 (1898).
[d] Result identical with *p*-tolyl *p*-ethylphenyl sulfone.
[e] MEYER, *Ann.*, **433**, 338 (1923).

TABLE II

ESTERS OF SULFONE ACIDS

| ACID | ESTER | M.P., °C. | | % S | | % YIELD[a] |
|---|---|---|---|---|---|---|
| | | Found (uncorr.) | Lit. | Found | Calc'd | |
| Phenyl *p*-carboxyphenyl sulfone | Phenyl *p*-carbethoxyphenyl sulfone[b] | 70.0–70.5 | | 10.99 | 11.08 | 24 |
| Bis-*p*-carboxyphenyl sulfone | Bis-*p*-carbethoxyphenyl sulfone | 156.0–156.5 | 158[c] | 8.77 | 8.85 | 27 |
| *p*-Chlorophenyl *p*-carboxyphenyl sulfone | *p*-Chlorophenyl *p*-carbethoxyphenyl sulfone | 132.0–133.0 | | 9.95 | 9.88 | 56 |
| *p*-Bromophenyl *p*-carboxyphenyl sulfone | *p*-Bromophenyl *p*-carbethoxyphenyl sulfone[d] | 133.0–134.0 | | 8.53 | 8.69 | 38 |

[a] Based on 3 to 8 grams acid.
[b] Has an odor similar to cooked cabbage.
[c] MEYER, *Ann.*, **433**, 338 (1923).
[d] Has an odor similar to onions.

## TABLE III

### Dinitro Derivatives of Aromatic Sulfones

| SULFONE | M.P., °C.[a] (UNCORR.) | DINITRO SULFONE | M.P., °C. | | | % S | | % YIELD[b] |
|---|---|---|---|---|---|---|---|---|
| | | | Found | | Lit. | Found | Calc'd | |
| | | | uncorr. | corr. | | | | |
| Diphenyl | 122.5–123.5 | Bis-*m*-nitrophenyl | 197.0–198.0 | 202.1–203.1 | 197[c] | 10.23 | 10.40 | 52 |
| Phenyl *p*-tolyl | 125.0–125.5 | Dinitro phenyl *p*-tolyl[d] | 149.0–150.0 | 151.7–152.7 | | 9.77 | 9.95 | 70 |
| Phenyl *p*-ethylphenyl | 93.0– 93.5 | Dinitro phenyl *p*-ethylphenyl[d] | 135.5–136.6 | 137.7–138.8 | | 9.63 | 9.54 | 72 |
| Phenyl *p*-chlorophenyl | 91.0– 91.5 | *m*-Nitrophenyl *m*-nitro-*p*-chlorophenyl | 144.0–145.0 | 146.6–147.6 | 146[e] | 9.24 | 9.36 | 65 |
| Phenyl *p*-bromophenyl | 104.0–105.0 | Dinitro phenyl *p*-bromophenyl[d] | 159.0–160.0 | 162.1–163.1 | | 8.17 | 8.28 | 62 |
| *p,p'*-Ditolyl | 156.0–158.0 | Bis-*m*-nitro-*p*-tolyl | 161.0–162.0 | 164.2–165.2 | 160[f] | 9.62 | 9.54 | 81 |
| *p*-Tolyl *p*-ethylphenyl | 112.0–113.0 | Dinitro *p*-tolyl *p*-ethylphenyl[d] | 115.0–116.0 | 116.4–117.4 | | 9.09 | 9.16 | 89 |
| *p*-Tolyl *p*-chlorophenyl | 123.0–123.5 | *m*-Nitro-*p*-tolyl *m*-nitro-*p*-chlorophenyl | 149.5–150.0 | 151.2–151.7 | 152[e] | 9.00 | 8.99 | 64 |
| *p*-Tolyl *p*-bromophenyl | 135.0–136.0 | Dinitro *p*-tolyl *p*-bromophenyl[d] | 158.0–159.0 | 160.1–161.1 | | 7.87 | 7.99 | 74 |
| Bis-*p*-bromophenyl | 170.0–171.0 | Dinitro bis-*p*-bromophenyl[d] | 234.4–236.4 | 235.3–237.3 | | 6.93 | 6.88 | 36 |

[a] Our own values.

[b] Based on 10 grams sulfone.

[c] Gnehm, *Ber.*, **9**, 79 (1876).

[d] Although the constitution of these compounds has not been determined, it is to be expected that the nitro groups are meta to the sulfone group.

[e] Louden, *J. Chem. Soc.*, **1936**, 221.

[f] Meyer, *Ann.*, **433**, 340 (1923).

ethyl acetate and two from glacial acetic acid. This procedure gave light-yellow, well-defined crystals. In Table III a list of the dinitro derivatives with yields, melting points, and analyses will be found.

## SUMMARY

In a study of the reactions of ten aromatic sulfones it was found that the dinitro derivatives are satisfactory for identification purposes.