ON THE OXIDATION OF MERCAPTANS AND THIO ACIDS TO THE CORRESPONDING SULFONIC ACIDS.*

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The object of the work on the oxidation of optically active thio compounds to the corresponding sulfo derivatives was discussed in the preceding series of articles. It will be referred to in this place very briefly. It is desired, first, to follow the effect on optical rotation of the change in polarity of a single group attached to the asymmetric carbon atom; second, to observe in substituted carboxylic acids the difference in the rotations of the free acids and of their salts.

With regard to the first point of interest, the following observations have been made up to the present.

In the series of secondary mercaptans, all showed a change in direction of their optical rotations on oxidation to the corresponding sulfonic acids. The mercaptans thus far analyzed in this respect are, 2-mercaptobutane, 2-mercaptoisohexane, 2-mercaptohexane, and benzylphenyl mercaptomethane. From these observations it is evident that derivatives of secondary alkyls analogous in configuration, but differing markedly in the polarity of the significant groups, rotate polarized light in opposite directions. On the basis of these considerations the conclusion was drawn that secondary alcohols and secondary halides rotating in opposite directions are configurationally related.

To these data and to the conclusions previously published we may now add the data on the oxidation of methylphenyl thiome-

* This is the eighth paper of the series on Walden inversion.

thane and also on the oxidation of some of its higher homologues and their isomers. Through the work of McKenzie, it is known that on halogenation of this alcohol two enantiomorphous halides can be obtained depending upon the nature of the halogenating reagent. By means of thionyl chloride a chloride was obtained which rotated in the same direction as the parent alcohol, whereas phosphorus pentachloride led to a chloride rotating in the opposite direction. Thus evidently a Walden inversion occurred in one of the two chlorides and it was not possible to ascertain in which of the two. From the preceding publication it is evident that several higher homologues of methylphenyl carbinol also behave abnormally on halogenation. Ethylphenyl carbinol behaves similarly to the lower homologue, whereas propylphenyl-, isopropylphenyl, and n-butylphenyl carbinols behave differently from the aliphatic secondary alcohols and from the above two alcohols, inasmuch as with either reagent they form halides rotating in the same direction as the parent alcohol. It was therefore very important to obtain data on the influence on rotation caused by the oxidation of the mercaptans of this series to the corresponding sulfonic acids. In this series an unexpected difficulty was encountered; namely, that the majority of mercaptans on oxidation were racemized. However, in the case of ethylphenyl thiomethane, the oxidation was not accompanied by complete racemization. In this case the sulfonic acid rotated in the opposite direction to that of the mercaptan.

Thus, using the same argument as that applied in connection with the series of aliphatic alcohols, it is permissible to conclude that alcohols and halides of the phenylmethyl carbinol series are configurationally related when they rotate in opposite directions.

The abnormal behavior of the alcohols of the methylphenyl carbinol series and of the methylphenyl thiomethane series is important particularly when compared with phenylbenzyl carbinol and the corresponding mercaptan. Phenylbenzyl carbinol behaves normally like an aliphatic secondary alcohol. In the methylphenyl series the mobilities of the groups attached to the asymmetric carbon atom seem much greater than in the corresponding derivatives of the aliphatic compounds, a phenomenon which may be attributed to a greater distortion of the tetrahedron of the asymmetric carbon atom.
Monocarboxylic Acids Substituted in Position (2).

Of this series only one acid has been observed thus far; namely, thiolactic acid. The sulfo acid prepared from it rotated in the same direction as the parent substance. However, the numerical value of the rotation of the thio acid was higher than that of the sulfo acid. Thus, in this instance, the change in polarity resulted only in a quantitative change in rotation and at first glance the observation on these two substances seemed of little value for correlating the configurations of lactic acid and of the halogen propionic acids substituted in position (2). However, on further analysis, these observations proved to possess a great significance.

It is characteristic of dextro-lactic acid, of dextro-alanine, and of other 2-hydroxy and 2-amino acids of the l series, that the difference between the rotations of the ionized and that of the free acid has a negative value, as seen from Table I. Thus the presence of sodium hydroxide in the solvent affects the rotations of all these substances in the same sense. Of the five substances, two (4 and 5) are definitely known to be configurationally related on the basis of direct evidence, and two (1 and 2) are regarded as configurationally related on the basis of indirect evidence. It now seems justifiable to classify dextro-bromopropionic acid in the same series with dextro-lactic acid, namely, in the l series.

Substituted Dicarboxylic Acids.

Of this class only the derivatives of succinic acid were analyzed. In Table II the rotations of the free acids and of the salts of the various derivatives are compared. In order to interpret these data it is necessary to bear in mind the progress of ionization of the individual groups in the substituted succinic acids (see Table III) with the decrease in hydron concentration (increase in pH values).

Comparing Table III with Table II it will be noticed that in malic and aspartic acids the ionization of the carboxyls in positions (2) and (3) leads to a change in rotation towards the left. In the thio acid, a peculiarity is noted; namely, that the ionization of the carboxyl in position (2) leads to a change in rotation towards the left as in the other two instances. The ionization of the carboxyl in position (3), on the other hand, leads to a change...
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in rotation to the right as compared with the rotation of the monion.

In the sulfo acid the optical change with the ionization of individual groups is the same as in the thio acid. If the ionization in the sulfo acid proceeded in the same order as in the thio acid, then the values of the fifth line of Table II would be in the following order: +57.53, +25.67, +37.80, +49.27.

Thus, the change in rotation with the ionization of the carboxyl in position (3) would be in the same sense as in the thio acid.

### Table I

<table>
<thead>
<tr>
<th></th>
<th>NaOH 2 equivalents [M]_p</th>
<th>NaOH 1 equivalent [M]_p</th>
<th>Free acid [M]_p</th>
<th>HCl [M]_p</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>per cent</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>Dextro-lactic acid*</td>
<td>5</td>
<td>-11.88°</td>
<td>+1.80°</td>
</tr>
<tr>
<td>2.</td>
<td>Dextro-alanine†</td>
<td></td>
<td>-9.34°</td>
<td>+37.96°</td>
</tr>
<tr>
<td>3.</td>
<td>Dextro-2-bromopropionic acid§</td>
<td></td>
<td>+7.32°</td>
<td>-5.58°</td>
</tr>
<tr>
<td>4.</td>
<td>Dextro-2-thiopropionic acid¶</td>
<td></td>
<td>-3.28°</td>
<td>+12.84°</td>
</tr>
<tr>
<td>5.</td>
<td>Dextro-2-sulfopropionic acid¶</td>
<td></td>
<td>-11.88°</td>
<td>+1.80°</td>
</tr>
</tbody>
</table>

† Clough, G. M., J. Chem. Soc., 1918, cxiii, 540, and observations in this laboratory.
§ Ionized condition.
¶ Partially racemized, unracemized [M]_p = +49.50°.

That the change in rotation with the ionization of the carboxyl in position (2) proceeds normally is seen from the behavior of thio- and sulfosuccinamide (NH₂ group on carboxyl in position (3)). Thus, on the basis of the above considerations, the conclusion is warranted that all the above mentioned substituted succinic acids belong to the l series.

In addition to these older data new data are now presented on the behavior of monocarboxylic acids substituted in position (3).
<table>
<thead>
<tr>
<th></th>
<th>HCl solution</th>
<th>Free acid</th>
<th>1 equivalent NaOH</th>
<th>2 equivalent NaOH</th>
<th>3 equivalent NaOH</th>
<th>Amide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Levo-malic acid*</td>
<td>10</td>
<td>-3.59°</td>
<td>-7.60°</td>
<td>-9.22°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Dextro-bromosuccinic acid†</td>
<td>+142.00°‡</td>
<td>+7.80°</td>
<td>-6.65°</td>
<td>+14.63°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Dextro-aminosuccinic acid§ (aspartic)</td>
<td>+42.60°</td>
<td>+73.06°</td>
<td>+38.04°</td>
<td>+48.57°</td>
<td>+41.09°</td>
<td></td>
</tr>
<tr>
<td>4. Dextro-thiosuccinic acid</td>
<td></td>
<td>+57.53°</td>
<td>+49.27°</td>
<td>+37.89°</td>
<td>+25.67°</td>
<td></td>
</tr>
<tr>
<td>5. Dextro-sulfosuccinic acid</td>
<td></td>
<td>+39.40°</td>
<td>+36.25°</td>
<td>+28.35°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Dextro-thiosuccinamide</td>
<td></td>
<td>+46.48°</td>
<td>+44.60°</td>
<td>+2.19°</td>
<td></td>
<td></td>
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<tr>
<td>7. Dextro-sulfosuccinamide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Schneider, G., Ann. Chem., 1881, ccvii, 266.
§ In ethyl acetate.
Oxidation of Mercaptans and Thio Acids

3-Halogen Acids.

There are fewer data on the basis of which to correlate the configuration of acids substituted in position (3). Dextro-3-hydroxybutyric acid was found configurationally related to dextro-lactic acid, and therefore was classified as an l acid. The rotation of this acid with the progress of ionization showed a shift to the left. Whether the same rule holds for acids substituted in position (3) by other groups cannot as yet be stated definitely. The existing data, however, indicate that in this

<table>
<thead>
<tr>
<th>Table III. Malic acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
</tr>
<tr>
<td>CHOH</td>
</tr>
<tr>
<td>CH₃</td>
</tr>
<tr>
<td>COOH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table III. Aspartic acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
</tr>
<tr>
<td>CH₃</td>
</tr>
<tr>
<td>CH₃</td>
</tr>
<tr>
<td>COOH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table III. Thiosuccinic acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
</tr>
<tr>
<td>CH₂H₃⁺</td>
</tr>
<tr>
<td>CH₂H₃⁺</td>
</tr>
<tr>
<td>CH₂H₃⁺</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table III. Sulfosuccinic acid.</th>
</tr>
</thead>
<tbody>
<tr>
<td>COOH</td>
</tr>
<tr>
<td>CH₂SO₃OH</td>
</tr>
<tr>
<td>CH₂SO₃O⁻</td>
</tr>
<tr>
<td>CH₂SO₄⁻</td>
</tr>
</tbody>
</table>

|                 |
|                 |
|                 |
|                 |
group of acids the direction of the change in rotation with the progress of ionization seems to depend on the polarity of the substituting group.

Thus, it was shown above that in the substituted succinic acids the change of rotation was to the left for dextro-malic and dextro-aspartic acids and to the right for dextro-thio- and dextro-sulfosuccinic acids. For the group of 3-hydroxy substituted acids, the data given in Table IV are available.

Taking it for granted that the oxidation of the 3-thio acid to the sulfonic acid proceeds without change of configuration, one may assume that on substitution of hydroxyl by halogen a similar change in optical behavior will take place. In that case, levo-

<table>
<thead>
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<th>TABLE IV.</th>
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<tbody>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Dextro-3-hydroxybutyric acid*</td>
</tr>
<tr>
<td>Levo-3-aminobutyric acid†</td>
</tr>
<tr>
<td>Levo-3-chlorobutyric acid †</td>
</tr>
<tr>
<td>Dextro-3-thiobutyric acid †</td>
</tr>
<tr>
<td>Dextro-3-sulfobutyric acid †</td>
</tr>
</tbody>
</table>


3-chlorobutyric acid will be configurationally related to dextro-3-hydroxybutyric acid. From the behavior of malic and aspartic acids, on ionization of the carboxyl in position (3), it may be concluded that configurationally related 3-hydroxybutyric acid and 3-aminobutyric acid should show similar optical change with the progress of ionization of the carboxyl and hence that the dextro-hydroxy and the levo-amino acids should be configurationally related. Hence, the substances enumerated in Table IV should all belong to the l series.
SUMMARY.

1. Methylphenyl, ethylphenyl, \( n \)-propylphenyl, isopropylphenyl, and \( n \)-butylphenyl thiomethanes were prepared and oxidized to the corresponding sulfonic acids.

2. The ethylphenyl methane sulfonic acid rotates in an opposite direction to the corresponding mercaptan.

3. 3-Thiobutyric acid was resolved and the dextro-form was prepared in pure state. Its rotation was \([\alpha]_D = +62.26^\circ\).

4. On oxidation, it gave dextro-3-sulfobutyric acid.

5. The latter acid was purified until its rotation reached a maximum which was found to be \([\alpha]_D = +6.68^\circ\).

6. With the progress of ionization of the carboxyl the change in the rotation of the thio acid was to the left, that of the sulfonic acid to the right.

7. Configurational relationships were discussed in the light of the optical behavior of the thio derivatives of the corresponding sulfonic acids in the following groups of substances: (a) in several secondary alcohols and the corresponding halides; (b) in 2-substituted propionic acids; (c) in substituted succinic acids; (d) in 3-substituted butyric acids.

8. The conclusions reached were in regard to (a) that configurationally related alcohols and halides rotate in opposite directions; in regard to (b) that dextro-lactic acid, dextro-alanine, and dextro-chloropropionic acid are configurationally related; in regard to (c) that levo-malic, dextro-chlorosuccinic, and dextro-aspartic acids are configurationally related; in regard to (d) that dextro-3-hydroxy-, levo-3-amino-, and levo-3-chlorobutyric acids are configurationally related.

9. All the acids enumerated in (8) belong to the \( \beta \) series. On the basis of other considerations, identical conclusions were reached by G. W. Clough.

10. It is realized that more experimental data are needed in order to give a firmer and more comprehensive character to the above conclusions.

\(^2\) Dextro or levo refers to the direction of rotation of the undissociated acids. \( d \) and \( l \) indicate configurational relationship to \( d \)- and \( l \)-lactic acids, \( d \)-lactic acid being the one for which the difference between the rotation of the ionic form and that of the free acid has a positive value.
EXPERIMENTAL.

\( \beta \)-Bromobutyric Acid.—The \( \beta \)-bromobutyric acid used in our work was prepared according to the directions of Brulé\(^3\) by passing hydrobromic acid gas through molten crotonic acid. The reaction mixture was maintained at 80–90°C. by means of a water bath, until slightly more than the calculated amount of hydrobromic acid had been absorbed. The bromo acid was then distilled under reduced pressure (about 16 mm.). At this pressure the acid distilled without decomposition at 115–116°C. as a clear colorless liquid which solidified readily on cooling to 0°C. 50 gm. of crotonic acid yielded 92 gm. of pure bromo acid.

\( \beta \)-Xanthobutyric Acid.—200 gm. of \( \beta \)-bromobutyric acid were dissolved in 600 cc. of water, cooled thoroughly, and neutralized with 80 gm. of potassium carbonate. While the solution was still cold, 206 gm. of potassium xanthate were added. The mixture was allowed to stand overnight at room temperature. The next day 400 cc. of concentrated hydrochloric acid were added and the mixture was heated for \( \frac{1}{2} \) hour on a steam bath to decompose the unchanged xanthic acid. On cooling, the xanthobutyric acid crystallized. It was extracted with ether, washed with water, and dried over sodium sulfate. On removal of the ether the residue solidified and was used for the preparation of \( \beta \)-thiobutyric acid without any further purification. Yield = 240 gm.

\( \beta \)-Thiobutyric Acid.—240 gm. of \( \beta \)-xanthobutyric acid were dissolved in 2.4 liters of absolute alcohol. 720 cc. of concentrated ammonia were then added and the mixture was allowed to stand at room temperature for 48 to 72 hours. The alcohol and excess of ammonia were then removed under reduced pressure, the residue was acidified with 240 cc. of concentrated hydrochloric acid, and was extracted several times with ether. The extract was washed with a little water, dried over sodium sulfate, the ether removed, and the residue distilled under reduced pressure (about 16 mm.). The thio acid distilled at 116–118°C. The substance analyzed as follows:

\[
0.1274 \text{ gm. substance: } 0.2538 \text{ gm. } \text{BaSO}_4. \\
\text{C}_4\text{H}_6\text{O}_2\text{S}. \text{ Calculated. } S \text{ 26.66.} \\
\text{Found. } S \text{ 27.37.}
\]

\(^3\) Brulé, M., Bull. Soc. chim., 1909, v. 1019.
Resolution of β-Thiobutyric Acid.—A warm solution of 100 gm. of β-thiobutyric acid in 500 cc. of acetone was treated with 278.3 gm. (1 mol) of pure quinine. On cooling and stirring, the salt separated in beautifully crystalline form. The salt was then repeatedly recrystallized from acetone until further recrystallizations no longer increased the optical activity of the thio acid. To decompose the quinine salt it was suspended in water and treated with a slight excess of ammonia. The quinine was filtered off, the filtrate concentrated, and extracted several times with chloroform. The aqueous layer was then acidified and extracted with ether. The ether extract was washed with water and dried over sodium sulfate. The ether was then removed and the residue fractionated under reduced pressure (about 16 mm.). The substance distilled at 116–118°C. Its optical activity was found to be

\[ [\alpha]_D = \frac{-3.26^\circ \times 100}{1 \times 7.876} = -41.05^\circ. \]

\[ [M]_D = -49.26^\circ \text{ in H}_2\text{O}. \]

To determine the activity of the monosodium salt, 0.9858 gm. of the thio acid was treated with 8.23 cc. of \( n \) NaOH. The solution was then made up to 10 cc. This corresponds to 1.1665 gm. of monosodium salt. Hence,

\[ [\alpha]_D = \frac{-3.24^\circ \times 100}{1 \times 1.1665} = -27.74^\circ. \]

\[ [M]_D = -39.33^\circ. \]

In a similar way, the activity of the disodium salt was determined by neutralizing 0.4006 gm. of thio acid with 6.67 cc. \( n \) NaOH (2 mols) and diluting the solution to 10 cc. This corresponds to 0.5475 gm. of disodium salt. Hence,

\[ [\alpha]_D = \frac{-0.77^\circ \times 100}{1 \times 5.475} = -14.06^\circ. \]

\[ [M]_D = -23.05^\circ. \]

In another experiment a thio acid was obtained which showed the optical rotation of

\[ [\alpha]_D = \frac{-3.94^\circ \times 100}{1 \times 7.592} = -51.89^\circ \text{ (in H}_2\text{O). } \]

\[ [M]_D = -62.26^\circ. \]

The substance analyzed as follows:

0.1306 gm. substance: 0.2650 gm. BaSO₄

\( \text{C}_4\text{H}_4\text{O}_2\text{S. Calculated. S 26.66.} \)

\( \text{Found. } "26.34. \)
Levo-β-Sulfobutyric Acid.—10 gm. of levo-β-thiobutyric acid ([α]_D^20 = -37.81°) were dissolved in 150 cc. of water. 9 equivalents of barium carbonate were then added. The mixture was thoroughly cooled and treated with 7 equivalents of bromine in small amounts. The last traces of unconsumed bromine were removed by adding a drop of the thio acid. The excess of barium carbonate was filtered off and the filtrate concentrated under reduced pressure. On addition of alcohol to the hot filtrate, the barium sulfonate separated in a beautifully crystalline form. The salt was redissolved in hot water and reprecipitated with alcohol. This operation was repeated until the salt obtained was free from bromides. About three recrystallizations usually sufficed to accomplish this purification. The salt showed an optical rotation of

\[ [\alpha]_D^20 = \frac{-1.21° \times 100}{1 \times 18.730} = -6.46°. \quad [M]_D = -19.59°. \]

To determine the rotation of the free acid and the acid salt, a given amount of the dibarium salt was treated with 2 and 1 equivalent, respectively, of hydrochloric acid. For the monosalt 2.1745 gm. of dry salt were treated with 7.17 cc. \( N \) HCl and the volume was made up to 10 cc. with water. The reading as determined in a 2 dm. tube was -1.01°. This corresponds to 1.6891 gm. of monobarium salt.

\[ [\alpha]_D^20 = \frac{-1.01° \times 100}{2 \times 16.891} = -2.99°. \quad [M]_D = -7.04°. \]

The salt analyzed as follows:

0.0937 gm. substance: 0.0683 gm. \( \text{BaSO}_4 \) (for \( \text{Ba} \)).
0.1547 “ “ : 0.1140 “ “ ( “ S).

\( \text{C}_7\text{H}_8\text{O}_2\text{BaS} \). Calculated. \( \text{Ba} \) 45.28, S 10.57.

For the free acid 1.4057 gm. of the dry salt was neutralized with 9.26 cc. \( N \) HCl. This corresponds to 0.7783 gm. of free acid. Hence,

\[ [\alpha]_D^20 = \frac{-0.64° \times 100}{2 \times 7.783} = -4.11°. \quad [M]_D = -6.90°. \]

Dextro-β-Sulfobutyric Acid.—Partly active dextro-β-thiobutyric acid was oxidized with bromine as described in the previous
The barium salt was purified and the barium removed quantitatively with sulfuric acid. On concentration under reduced pressure the acid was obtained as a thick colorless syrup. This was dissolved in water and treated with 2 mols of brucine. On cooling, the brucine salt crystallized. The salt was then recrystallized from water until the activity of the acid no longer increased. The brucine salt was then decomposed with an excess of barium hydroxide. The alkaloid was filtered off and the last traces were removed by extraction with chloroform. The solution was then saturated with carbon dioxide, the barium carbonate filtered off, and the filtrate concentrated under reduced pressure. The barium salt was then isolated and purified as in the previous experiment. The salt showed an optical rotation of

$$\left[\alpha\right]_D^\circ = \frac{+0.85^\circ \times 100}{1 \times 12.982} = +6.54^\circ. \quad [\text{M}]_D = +19.84^\circ.$$  

The salt analyzed as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>BaSO_4 (for Ba)</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0944 gm.</td>
<td>0.0990 gm.</td>
<td>0.1108</td>
</tr>
<tr>
<td>C_6H_7O_2S_Ba</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated</td>
<td>Ba 45.28, S 10.57</td>
<td></td>
</tr>
<tr>
<td>Found</td>
<td>&quot; 43.01, &quot; 10.73</td>
<td></td>
</tr>
</tbody>
</table>

Data on the Rotation of Thiosuccinamide and the Corresponding Sulfo Acid.

<table>
<thead>
<tr>
<th>Thiosuccinamide</th>
<th>Sulfo Succinamide</th>
</tr>
</thead>
<tbody>
<tr>
<td>+89.40°</td>
<td>+46.48°</td>
</tr>
<tr>
<td>[M]_D, Mono-salt.</td>
<td></td>
</tr>
<tr>
<td>+36.25°</td>
<td>+44.60°</td>
</tr>
<tr>
<td>[M]_D, Di-salt.</td>
<td></td>
</tr>
<tr>
<td>+28.35°</td>
<td>+2.19°</td>
</tr>
</tbody>
</table>

Optical Activity of Thiosuccinamide and Its Salts.—0.6596 gm. of thiosuccinamide was dissolved in water and made up to a volume of 10 cc. Reading was taken in a 2 dm. tube and was found to be +7.91°. Hence,

$$\left[\alpha\right]_D^\circ = \frac{+7.91^\circ \times 100}{2 \times 6.596} = +60.00^\circ. \quad [\text{M}]_D = +89.40^\circ.$$
To determine the rotation of the mono-salt, 0.9600 gm. of the thioamide was treated with 1 equivalent of sodium hydroxide and the volume was made up to 15 cc. This corresponds to 1.1017 gm. of the monosodium salt, or to 0.7344 gm. of salt per 10 cc. Rotation determined in a 2 dm. tube was

$[\alpha]_b^{20} = \frac{+4.64 \times 100}{2 \times 7.344} = +31.59^\circ$. $([\mathcal{M}]_b = +38.25^\circ$).

The activity of the disodium salt was determined as follows: 0.9212 gm. of the thioamide was treated with 2 equivalents of sodium hydroxide and the volume made up to 15 cc. This corresponds to 0.8402 gm. of the disodium salt per 10 cc. of solution. The rotation determined in a 2 dm. tube was

$[\alpha]_b^{20} = \frac{+3.68 \times 100}{2 \times 8.402} = +21.89^\circ$. $([\mathcal{M}]_b = +28.35^\circ$).

**Optical Activity of Sulfosuccinamide and Its Salts.**—2.377 gm. of the neutral barium salt were dissolved in water and the volume made up to 15 cc. The reading was found to be $+0.21^\circ$ in a 2 dm. tube. Hence,

$[\alpha]_b^{20} = \frac{+0.21 \times 100}{2 \times 15.85} = +0.66^\circ$. $([\mathcal{M}]_b = +2.19^\circ$).

To determine the rotation of the acid salt (monobarium salt), the above solution was treated with 1.90 cc. of 3.76 N HCl. The total volume was 16.9 cc., and the reading in a 2 dm. tube was $+3.76^\circ$. This corresponds to 1.1111 gm. of the acid salt per 10 cc. Hence, for the acid salt,

$[\alpha]_b^{20} = \frac{+3.76 \times 100}{2 \times 11.111} = +16.92^\circ$. $([\mathcal{M}]_b = +44.60^\circ$).

Another equivalent of normal hydrochloric acid was added. The total volume was then 18.8 cc., and the reading in a 2 dm. tube was found to be $+3.56^\circ$. Hence, for the free acid

$[\alpha]_b^{20} = \frac{+3.56 \times 100}{2 \times 7.482} = +23.78^\circ$. $([\mathcal{M}]_b = +46.48^\circ$).

**Levo-Methylphenyl Mercaptomethane.**—A mixture of 20 gm. of dextro-methylphenyl chloromethane, $[\alpha]_b^{20} = \frac{+0.62 \times 100}{1 \times 7.363} = +8.42^\circ$, and 3 mols of alcoholic potassium hydrogen sulfide was heated on the steam bath under a return condenser for 3 hours.
The solution was then diluted with water and extracted with ether. The extract was washed with water and dried over sodium sulfate. When dry, the ether was removed and the residue distilled under a pressure of about 15 mm. The mercaptan boiled constantly at 95°C. The optical rotation was determined in ether solution and was found to be

\[ [\alpha]_n = \frac{-0.51^\circ \times 100}{1 \times 6.272} = -8.23^\circ. \]

0.1476 gm. substance: 0.2500 gm. BaSO₄.

\[ C_{9}H_{16}S \text{ Calculated. } S 23.18. \]

\[ \text{Found. } 23.27. \]

**Methylphenyl Methane Sulfonic Acid.**—7 gm. of levo-methylphenyl mercaptomethane, \([\alpha]_n = -0.88^\circ \times 100 \quad \frac{1 \times 11.018}{1} = -7.98^\circ\), were dissolved in 70 cc. of acetone and 10 cc. of water. Then 16.10 gm. of potassium permanganate in acetone solution were added in small amounts with cooling until the permanganate was no longer decolorized. The mixture was then heated with an occasional addition of potassium permanganate until all the oxidizing agent had been consumed. The manganese dioxide was then filtered off and the filtrate decolorized with sulfur dioxide. The solution was then evaporated to dryness under reduced pressure. The residue was first washed several times with ether, then dissolved in absolute alcohol, and finally saturated with carbon dioxide. The precipitated salt was filtered off. On addition of ether to the filtrate the potassium sulfonate separated in an amorphous form. It was recrystallized twice from water. It was found to be inactive in both neutral and acid solutions.

0.0990 gm. substance: 0.0388 gm. K₂SO₄ (for K).

0.1107 " " : 0.1172 " BaSO₄ (" S).

\[ C_{9}H_{16}O_{3}S \text{ Calculated. } S 14.30, K 17.47. \]

\[ \text{Found. } 14.54, 17.58. \]

**Dextro-Ethylphenyl Mercaptomethane.**—17 gm. of levo-ethylphenyl chloromethane, \([\alpha]_n = -6.71^\circ \times 100 \quad \frac{1 \times 13.327}{1} = -50.34^\circ\), were heated with 4 mols of alcoholic potassium hydrogen sulfide for 3 hours under a return condenser. The solution was diluted with water and extracted with ether. The extract was dried over sodium sulfate, then distilled under a pressure of 15 mm. It
boiled at 103-104°. In ether solution the mercaptan was dextrorotatory.

$$\left[\alpha\right]_D^{20} = \frac{2.18° \times 100}{4.776 \times 1} = +45.22°.$$ 

0.1564 gm. substance: 0.2258 gm. BaSO₄.

C₈H₁₂S. Calculated. S 21.03.

Found. " 20.67.

Levo-Ethylphenyl Methane Sulfonic Acid.—4 gm. of dextro-ethylphenyl mercaptomethane, $\left[\alpha\right]_D^{20} = +2.21° \times 100\frac{1}{1 \times 5.182} = +42.63°$, were dissolved in 40 cc. of acetone and 5 cc. of H₂O. This was treated with 4.8 gm. of barium permanganate in acetone solution. The oxidizing agent was added in small amounts with cooling. The manganese dioxide was then filtered off and the slightly reddish solution was decolorized with an additional drop of the mercaptan. The solution was then evaporated to dryness under reduced pressure and the solid residue washed several times with ether. The residue was then recrystallized twice from water. To determine the rotation, 1.0152 gm. of substance was treated with 2 cc. of concentrated hydrochloric acid. This was then diluted to 10 cc. and the rotation was determined in a 1 dm. tube. The reading was -0.16°.

$$\left[\alpha\right]_D^{0} = \frac{-0.16° \times 100}{1 \times 10.152} = -1.50°. \quad [M]_D = -3.00°.$$ 

0.0985 gm. substance: 0.0856 gm. BaSO₄ (for S).

0.0971 “ “ : 0.0406 “ “ ( “ Ba).

C₁₄H₂₂O₆Ba. Calculated. S 11.34, Ba 24.36.


Dextro-n-Propylphenyl Mercaptomethane.—9 gm. of n-propylphenyl chloromethane, $\left[\alpha\right]_D^{20} = -40°$, were heated with 4 mols of potassium hydrogen sulfide for 3 hours under a return condenser. The mixture was diluted with water and extracted with ether. The extract was washed with water and then dried over sodium sulfate. After the ether had been removed, the residue was distilled under reduced pressure (about 15 mm.). It distilled at 132-133°C., and was dextrorotatory.

$$\left[\alpha\right]_D^{20} = \frac{+1.82° \times 100}{4.528 \times 1} = +40.19°.$$ 

0.1576 gm. substance: 0.2228 gm. BaSO₄.

C₁₄H₁₆S. Calculated. S 19.32.

Dextro-Isopropylphenyl Mercaptomethane.—A mixture of 10 gm. of levo-isopropylphenyl chloromethane, $[\alpha]_D^o = \frac{-1.38^\circ \times 100}{1 \times 8.398} = -16.56^\circ$, and 3 mols of alcoholic potassium hydrogen sulfide was heated for 4 hours under a return condenser. Water was then added and the mixture extracted with ether. The extract was washed with water and dried over sodium sulfate. When dry, the ether was removed and the residue distilled under a pressure of about 15 mm. All the substance distilled at 92–96°C. The mercaptan was dextrorotatory.

$[\alpha]_D^o = \frac{+ 1.02^\circ \times 100}{1 \times 6.728} = + 15.16^\circ$ (in ether).

0.1399 gm. substance: 0.1800 gm. BaSO$_4$.

C$_{10}$H$_{13}$S. Calculated. S 19.32.
Found. “ 17.76.

Dextro-n-Butylphenyl Mercaptomethane.—15 gm. of levo-n-propylphenyl chloromethane, $[\alpha]_D^\circ = \frac{-2.92^\circ \times 100}{1 \times 16.752} = -17.43^\circ$, were heated with 3 mols of alcoholic potassium hydrogen sulfide for 3 hours under a return condenser. The mercaptan was isolated as described in the experiment above. It distilled at 122–125°C. under a pressure of about 15 mm. It was dextrorotatory in ether solution.

$[\alpha]_D^\circ = \frac{+ 1.95^\circ \times 100}{1 \times 10.870} = + 17.94^\circ$.

0.1560 gm. substance: 0.1900 gm. BaSO$_4$.

C$_{11}$H$_{18}$S. Calculated. S 17.77.
Found. “ 16.70.

Oxidation of n-Propylphenyl Mercaptomethane and Some of Its Homologues.—The oxidation of optically active n-propyl-, isopropyl-, and n-butylphenyl mercaptomethanes was carried out with potassium and barium permanganates as described in the oxidation of ethylphenyl mercaptomethane. In every case, however, the sulfonic acid obtained was inactive. Oxidation was also carried out with potassium dichromate and with hydrogen peroxide. But with these, as with the permanganates, the oxidation products obtained were inactive.
ON THE OXIDATION OF MERCAPTANS
AND THIO ACIDS TO THE
CORRESPONDING SULFONIC ACIDS
P. A. Levene and L. A. Mikeska


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