**Bromination of Potassium Salt of I.**—One mole of Ib was dissolved in a solution of 180 g. of potassium bromide in 1500 cc. of water. The solution was cooled in an ice-bath and exposed to direct sunlight. A solution of 160 g. of bromine and 180 g. of potassium bromide in 600 cc. of water was added as it was utilized. The solution was acidified with 40% hydrobromic acid yielding a crude bromo acid mixture which was purified by heating with a 10% solution of sodium carbonate. The solution was cooled and acidified giving 170–190 g. of a bromo acid melting at 126–127°.

This material was dissolved in 10 volumes of 10% sodium carbonate solution and cooled overnight in an icebox. The precipitate yielded 15–18 g. of IIb and the filtrate 100–125 g. of impure IIa melting at 132–136°. This was recrystallized from 3 volumes of ethyl acetate giving pure IIa melting at 139–140°.

## Summary

1. Cinnamic acid in methyl alcohol solutions reacts with mercuric acetate giving a product whose composition and properties vary with the length of time of mercuration.

2. The bromination of the mercuration products under various conditions yields a mixture of the two diastereomeric α-bromo-β-methoxy-β-phenylpropionic acids.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

# Sulfur Studies. XIV. Some Derivatives of Certain Higher Mercaptans

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Very little work has been done on mercaptans and derived sulfur compounds of a molecular weight greater than that of the decyl series. Noller and Gordon[1] prepared the four *n*-aliphatic mercaptans from undecyl through myristyl. Collin, Hilditch, and others[2] synthesized dodecyl, hexadecyl, and octadecyl mercaptans and the corresponding *n*-disulfides. In the present work the *n*-disulfides from dodecyl through nonadecyl (excepting pentadecyl), the lead salts of the parent thio alcohols, the corresponding 2,4-dinitrophenyl thioethers, and a few of the dinitrophenylalkyl sulfones were prepared. The starting point for the synthesis in each particular series was the appropriate alcohol, of which lauryl, myristyl, palmityl, and stearyl were kindly furnished in quantity by the du Pont Company. Access to the odd numbered carbon atom alcohols was had through treatment of the next lower alkylmagnesium bromide with polymerized formaldehyde.

The procedure for the preparation of the bromides was essentially that outlined in "Organic Syntheses."[3] The yields ranged from 58 to 70%. Tri-, hepta- and nonadecyl alcohols were prepared by the method of Courtot[4] in yields of 62, 48 and 50%, respectively.

**The Mercaptans and Lead Mercaptides.**—The mercaptans were prepared from the bromides by the interaction with potassium hydrosulfide in absolute alcohol. It was found convenient to convert the crude mercaptans directly to the lead salts without preliminary purification. The crude product was precipitated from the hot reaction mixture by the addition of cold water and ice, and the mercaptan was removed by filtration or in a separatory funnel. After a thorough washing with water to remove any potassium hydrosulfide, the product was dissolved in boiling ethyl alcohol and enough alcoholic lead acetate added to ensure the complete precipitation of the yellow lead derivative. Following an hour's digestion, the precipitate was filtered hot, washed with cold water, and then with successive portions of hot acetone and boiling ether until no more soluble material could be extracted. Since the free mercaptans were oxidized with the greatest ease by air, it was found best to store the dried mercaptides as such in tightly stoppered bottles.

The melting points of the lead mercaptides are given below. They were analyzed for lead by fuming down with sulfuric acid and then digesting

TABLE I

LEAD MERCAPTIDES

| Lead salt | M. p., °C. Darkens | M. p., °C. Melts | % Lead Calcd. | % Lead Found |
|---|---|---|---|---|
| Tridecyl | 97 | 100 | 32.4 | 33.0 |
| Tetradecyl | 99 | 104–105 | 31.1 | 31.8 |
| Hexadecyl | 99 | 106–107 | 28.7 | 29.1 |
| Heptadecyl | 100 | 108–109 | 27.6 | 27.7 |
| Octadecyl | 106 | 110–111 | 26.6 | 27.1 |
| Nonadecyl | 108 | 112–114 | 25.7 | 26.2 |

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[1] Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

[2] Collin, Hilditch, Marsh and McLeod, *J. Soc. Chem. Ind.*, **52T**, 272 (1933).

[3] *Org. Syntheses*, **15**, 24, 35 (1935).

[4] Courtot, "Le Magnesium en Chimie organique," 1926, p. 158.

with sulfuric–nitric acid until the organic matter was destroyed. The lead sulfate formed was taken up in hot ammonium acetate, the solution filtered, and the lead precipitated and weighed as the chromate in the usual way.

**The 2,4-Dinitrophenyl Thioethers and Corresponding Sulfones.**—The 2,4-dinitrophenylalkyl ethers and sulfones were made by the method of Bost, Turner and Norton.[5] To obtain the necessary sodium salts, 0.005 mole of lead mercaptide was triturated thoroughly with a few cubic centimeters of warm, concentrated hydrochloric acid, and the liberated mercaptan extracted with ether. This extract, after being washed with water, was added to a hot alcoholic solution containing 0.01 mole of sodium hydroxide, and was followed by 0.01 mole of 2,4-dinitrochlorobenzene. The mixture was refluxed for one-half hour, filtered hot, cooled, and the precipitated thioether recrystallized from alcohol. The products were lustrous, light golden yellow plates. A portion of the ether was oxidized in acetic acid with permanganate to give white, amorphous sulfones. These were purified from alcohol.

TABLE II

2,4-DINITROPHENYL THIOETHERS AND SULFONES

| No. carbon atoms | Thioethers | | | Sulfones | | |
|---|---|---|---|---|---|---|
| | | S, % | | | S, % | |
| | M. p., °C. | Calcd. | Found | M. p., °C. | Calcd. | Found |
| 13 | 94.0–94.5 | 8.38 | 8.42 | 101.5 | 7.74 | 7.75 |
| 14 | 93.5–94.0 | 8.09 | 8.16 | Insufficient material to obtain sulfone | | |
| 16 | 95.5–96.0 | 7.56 | 7.40 | Reported previously[5] | | |
| 17 | 98.5–99.0 | 7.31 | 7.36 | 106.5 | 6.82 | 6.75 |
| 18 | 97.0–97.5 | 7.09 | 6.99 | 107.5 | 6.62 | 5.93 |
| 19 | 99.5–100 | 6.87 | 6.88 | Insufficient material to obtain sulfone | | |

**The Disulfides.**—Since the lead mercaptides were more easily available than the mercaptans, they were oxidized directly with iodine, to give the disulfides. One hundredth mole of lead salt was suspended in 200 cc. of hot glacial acetic acid and a slight excess of iodine in the same solvent was dropped in. The mixture was diluted with water and cooled, the precipitated disulfide and lead iodide filtered off and washed with water. The residue was then shaken thoroughly in a stoppered flask three times with 50-cc. portions of 20% potassium iodide in order to convert the lead iodide to the soluble complex, $KPbI_3$, filtering and washing with a little potassium iodide solution after each operation. The now nearly white disulfide was freed of excess potassium iodide by carefully washing with water, and was crystallized from glacial acetic acid until a constant melting point was obtained.

TABLE III

| Disulfide | M. p., °C. | S, % Calcd. | S, % Found |
|---|---|---|---|
| Di-*n*-duodecyl[a] | 33.5–34 | 15.94 | 15.80 |
| Di-*n*-tridecyl | 43.5–44 | 14.89 | 14.93 |
| Di-*n*-tetradecyl | 45.5–46 | 13.98 | 14.05 |
| Di-*n*-hexadecyl[a] | 53.5–54 | 12.46 | 12.35 |
| Di-*n*-heptadecyl | 59.5–60 | 11.81 | 11.80 |
| Di-*n*-octadecyl[a] | 62.0–62.5 | 11.24 | 11.13 |
| Di-*n*-nonadecyl | 68.5–69 | 10.71 | 10.62 |

[a] Collin[2] found, respectively: 32, 54, 62.5.

Grateful acknowledgment is made to the du Pont Company for the generous supply of alcohols which made this work possible.

## Summary

A number of new disulfides, lead mercaptides, and the corresponding 2,4-dinitrophenyl thioethers and dinitrophenylalkyl sulfones have been prepared and characterized.

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(5) Bost, Turner and Norton, THIS JOURNAL, **54**, 1985 (1932).