

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARKANSAS]
DERIVATIVES FOR THE IDENTIFICATION OF MERCAPTANS¹

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For the identification of mercaptans the preparation of lead or mercury salts has been recommended in the literature. These are reported to be easy of preparation and purification and to have definite melting points. Reid² has advocated the use of 1,5-butyl-anthraquinone-sulfone sodium sulfonate. From this compound he has prepared derivatives of mercaptans having high and sharp melting points. So far as the writer is aware this compound is not on the market and would need to be prepared for individual use.

On account of the growing importance and availability of the mercaptans, it seemed of interest to review the subject of their identification and to fill the gaps in the literature regarding mercaptans now available.

The literature reports of lead and mercury salts are very scanty; the inference is that all of them have not been prepared. In this work the salts were made by adding 6 drops of the mercaptan to about 2 cc. of ethanol, subsequently adding an excess of lead acetate solution (20%) or mercuric cyanide solution (10%). After shaking and cooling the mixture for a few minutes the resulting precipitates were separated by filtration and dried in the air for a short time on a porous plate. They were purified by one recrystallization from the appropriate solvent. The mercury salts were crystallized from ethanol. The solvents used for the lead salts are shown in the following table. The melting points of the lead and mercury salts are given in Table I. The values shown in parentheses were obtained from the literature.

TABLE I
 MELTING POINTS OF LEAD AND MERCURY SALTS OF MERCAPTANS

Alkyl	Lead salt, °C.	Mercury salt, °C.
Methyl	...	(175)
Ethyl	(150°)	(76)
Propyl	...	(68) 71-72
Isopropyl	91-92 ^a	62-63
Butyl	80-81 ^b	85-86
Isobutyl	...	94-95
Amyl	...	74-75
Iso-amyl	...	(100)
Heptyl	94-95 ^c	76-77

^a Solvent, ethanol. ^b Solvent, chloroform and ethanol. ^c Solvent, benzene.

¹ This problem was originally assigned to C. H. Adams for a Master's thesis. However, owing to a combination of circumstances, he was unable to continue the work. I wish to thank Mr. Adams for the preparation of several of the compounds described.

² Reid, *THIS JOURNAL*, **45**, 1837 (1923).

It will be noted that several of the lead salts are not reported. These precipitated as gummy masses which did not harden for some time and were deemed unsuitable for the purpose at hand. The melting points of the mercury compounds are seen to lie within a small range and several are practically identical.

In this work mercaptan derivatives were also prepared from 3,5-dinitrobenzoic acid and from 3-nitrophthalic anhydride, both of these compounds having proved of value for the identification of alcohols.

Preparation of Derivatives of 3,5-Dinitrobenzoic Acid.—3,5-Dinitrobenzoyl chloride was prepared as directed by Mulliken³ from 4 g. of 3,5-dinitrobenzoic acid and 5.5 g. of phosphorus pentachloride. Two grams (one mol) of the resulting acid chloride was placed in a test-tube with 1.5 mols of the mercaptan. The reaction was catalyzed by the addition of 4 drops of pyridine. The tube was then gently heated from time to time until the fumes of hydrogen chloride ceased to appear. In most instances the reaction was complete in about ten minutes; where this was not the case the tube was placed in hot water until the reaction had been completed.⁴ A few drops of water were added to the mixture, then pyridine was added dropwise until the odor showed an excess of this reagent. Upon vigorous stirring the mass within the tube quickly solidified. It was brought upon a filter, washed with water and then placed upon a porous plate. One or two recrystallizations of the dried product from dilute alcohol or dilute acetic acid usually gave compounds of constant melting point.

On the small scale (for identifications) 0.2 g. of acid chloride, 6 drops of the mercaptan and 1 or 2 drops of pyridine were treated essentially as described above. For the preparation of the amyl and *iso*-amyl derivatives it was necessary to use an excess of the acid chloride.

The pure compounds are colorless or very faintly yellow and are odorless. They were made in lots of several grams as indicated above and analyzed

TABLE II
DERIVATIVES OF MERCAPTANS WITH 3,5-DINITROBENZOIC ACID

Alkyl	M. p., °C.	Analysis for sulfur	
		Calcd.	Found
Ethyl	61-62	12.50	12.57
Propyl	51-52	11.85	11.60
<i>Isopropyl</i>	83-84	11.85	11.74
Butyl	48-49	11.27	11.14
<i>Isobutyl</i>	63-64	11.27	11.25 10.92
Amyl	39-40	10.74	10.31 10.76
<i>Iso</i> -amyl	42-43	10.74	10.65
Heptyl	52-53	9.82	9.85
Phenyl ^a	148-149	10.52	10.27
Benzyl ^b	119-120	10.06	10.08

^a M. p. of the benzoyl derivative is 56. ^b M. p. of the benzoyl derivative is 30.

³ Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1911, Vol. I, p. 168.

⁴ If the odor at this time proves the presence of a considerable excess of mercaptan, more of the acid chloride should be added and the heating continued. This may occur with the higher less volatile mercaptans.

in order to make sure that the reaction took the same course in each instance. The melting points and analytical data are given in Table II.

The melting points of the derivatives with 3,5-dinitrobenzoic acid are closer than would be desired and are, moreover, rather low.⁵ Mixed melting points were taken for all compounds whose melting points lie within a few degrees of each other; a depression of melting point was observed in every such instance.

The use of 3-nitrophthalic anhydride for the identification of alcohols has been recommended by Nicolet and Sacks.⁶ The compounds secured are especially convenient because they contain a free carboxyl group and may, accordingly, be titrated to secure the neutralization equivalent and thus the equivalent weight of the alkyl radical concerned.⁷

The derivatives of mercaptans and 3-nitrophthalic anhydride are exceptionally easy of preparation. The yields are good and these compounds may be recommended for the identification of mercaptans (excepting methyl mercaptan).

Preparation of Derivatives of Mercaptans with 3-Nitrophthalic Anhydride.—3-Nitrophthalic anhydride was prepared from the corresponding acid as directed by Nicolet and Bender.⁸ Two grams (one mol) of the anhydride was treated in a test-tube with 1.5 mols of the mercaptan. After heating with a free flame for about one-half minute the tube was set aside. When cool about 20 drops of 10% sodium hydroxide solution was added in several portions. The tube was vigorously shaken between additions of the base and subsequently. It was cooled from time to time in an ice-bath if necessary. The mixture quickly assumed a plastic or oily consistency. About 10 drops of 5% hydrochloric acid solution was added and the tube again vigorously shaken. The solid was separated by filtration and dried on a porous plate. One or two recrystallizations from aqueous acetone or dilute acetic acid sufficed to give products of constant melting point.

For identifications 0.2 g. of the anhydride was treated with 6 drops of the mercaptan and approximately proportional amounts of sodium hydroxide and hydrochloric acid solutions. The products secured are colorless or very faint yellow; they are odorless. Analytical data and melting points are reported in Table III. The neutralization equivalents for several of these compounds were obtained and are also reported in the table.

⁵ It was to be predicted that these melting points would be lower than those of the known oxygen compounds. Part of the reason for their preparation was to see how much this difference would be.

⁶ Nicolet and Sacks, *THIS JOURNAL*, 47, 2348 (1925).

⁷ McKenzie has shown (reference in Nicolet and Sacks' paper⁶) that of the two possible mono-esters formed by the reaction of certain alcohols with 3-nitrophthalic anhydride, one is present in very small amount. Nicolet and Sacks' work indicates that this trace must be removed during the purification process. If in the reaction with mercaptans two mono-esters are produced it must again be true that one of them is lost during the purification, for the evidence given by the melting points of the compounds secured is that they are chemical individuals and not mixtures of isomers.

⁸ "Organic Syntheses," John Wiley and Sons, Inc., New York, 1927, Vol. VII, p. 74.

TABLE III
DERIVATIVES OF MERCAPTANS WITH 3-NITROPHthalic ANHYDRIDE

Alkyl	M. p., °C.	Analysis for sulfur			Neutralization equiv.	
		Calcd.	Found		Calcd.	Found
Ethyl	148-149	12.55	12.69		255	256.7
Propyl	136-137	11.82	11.19	11.76	269	267.3
Isopropyl	144-145	11.82	11.89	
Butyl	143-144	11.31	11.17	11.12
Isobutyl	135-136	11.31	11.28	11.59	283	284
Amyl	131-132	10.77	10.64	10.50	297	297.4
Iso-amyl	144-145	10.77	10.62		297	298.5
Heptyl	131-132	9.84	9.91	9.88	325	326.2
Phenyl	130-131	10.56	10.56	10.36
Benzyl	136-137	10.09	10.22	10.04	317	318.8

The melting points given were secured when the bath was previously heated to about 100° and the temperature quickly raised to within about 10° of the true melting point. They are higher than those obtained when the compound is slowly heated from room temperature. The majority of the compounds show a slight decomposition at the melting point, liberating a gas. In identifications these compounds should be prepared from known samples of mercaptans, and the melting points of the known and unknown compounds should be taken together along with a mixed melting point.

Observation of the results given in the table will show that the melting points of these compounds again lie within a small range as Nicolet and Sacks noted for the oxygen compounds. Mixed melting points were taken for all pairs of compounds having melting points within a few degrees of each other. In every case a depression of the melting point was noted.

Summary

Derivatives of mercaptans have been prepared from lead and mercuric ions and from 3,5-dinitrobenzoic acid and 3-nitrophthalic anhydride. Their melting points and some other properties are reported. 3-Nitrophthalic anhydride is recommended for the identification of mercaptans (with the possible exception of methyl mercaptan, for whose identification the mercury salt appears to be preferable). Twenty-eight of the compounds reported are new.

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