

Summary

It has been shown that ω -cyclohexylalkyl amines of the general formula $C_6H_{11}(CH_2)_xNR_2$ are bactericidal to *B. leprae* providing the molecules have the proper molecular weight. The compounds should contain fifteen to eighteen carbon atoms just as found necessary in the various acids already tested, distribution of the carbon atoms having very little effect.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NORTH CAROLINA AND SYRACUSE UNIVERSITY]

THE IDENTIFICATION OF MERCAPTANS WITH 2,4-DINITROCHLOROBENZENE

BY R. W. BOST, J. O. TURNER AND R. D. NORTON

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Due to the increasing interest shown in mercaptans and due to the paucity of good reagents whereby they may be identified, it seemed desirable to study methods for their identification. Numerous mercaptides^{1,2,3} have been prepared. Purification of these is not always easy and certain of the mercaptides are frequently unstable.⁴ Wertheim¹ has proposed 3,5-dinitrobenzoyl chloride and also 3-nitrophthalic anhydride as reagents for mercaptan identification. The use of these reagents is restricted, due to the close proximity of the melting points of certain of their derivatives. Reid⁵ and his co-workers have suggested the use of sodium anthraquinone α -sulfonate and also sodium anthraquinone 1,5- and 1,8- disulfonates, although the sulfonic group could not be replaced with phenyl mercaptan. The time required for these reactions to go to completion varies from a few minutes to several hours, while in certain cases several products are obtained.

In this paper the authors propose 2,4-dinitrochlorobenzene as a new reagent for the identification of mercaptans. It rapidly forms solids with all mercaptans thus far studied. The reagent is inexpensive, it is stable, and gives excellent yields of stable derivatives which are easily purified, having sharp melting points and definite crystalline structure. In no case was it necessary to heat the reactants for over ten minutes. The reagent is unique in that it forms solid sulfides that can be rapidly oxidized to the corresponding sulfones, thus ensuring complete identification in a remarkably short time.

¹ Wertheim, *THIS JOURNAL*, **51**, 3661 (1929).

² Bennett, *J. Chem. Soc.*, **121**, 2139 (1922).

³ Schacht, *Ann.*, **129**, 1 (1864).

⁴ Borgstrom, Ellis and Reid, *THIS JOURNAL*, **51**, 3649 (1929).

⁵ Reid, Mackall and Miller, *ibid.*, **43**, 2108 (1921).

Experimental

Preparation of Sulfide.—The general procedure used to make the condensation products with 2,4-dinitrochlorobenzene was carried out as follows. 0.01 Mole of the mercaptan was added to 30 ml. of absolute alcohol in the case of liquid mercaptans; in the case of solid mercaptans, the smallest amount of hot alcohol necessary to dissolve it was used. The sodium mercaptide was made by adding 0.01 Mole of sodium hydroxide dissolved in 3 ml. of water to the mercaptan solution. 0.01 Mole of 2,4-dinitrochlorobenzene was dissolved in 10 ml. of absolute alcohol in a 100-ml. balloon flask and the alcoholic solution of the sodium mercaptide added to the flask containing the reagent. At this point many mercaptans react almost instantly, as shown by the generation of heat and the precipitation of the sulfide. To ensure complete reaction the mixture was refluxed on the steam-bath for ten minutes. The hot solution was quickly filtered, whereupon the sulfide crystallized in beautiful golden-yellow needles from the filtrate on cooling. The product was recrystallized from absolute alcohol until a constant melting point was obtained. As a general rule the melting point was not raised after one recrystallization except in the case of iso-mercaptans. It has been found best to use a slight excess of mercaptan. This prevents the formation of a reddish-brown solution caused by an excess of sodium hydroxide which might affect the purity of the final product.

The melting points of the sulfides are given in Table I. In certain cases the melting points of the sulfides are not far enough separated to ensure complete identification. Thus further to ensure the identity of the mercaptan, the sulfide was converted into the sulfone by oxidation with potassium permanganate in acid solution at room temperature.

TABLE I
DERIVATIVES OF MERCAPTANS WITH 2,4-DINITROCHLOROBENZENE

Mercaptan	M. p., °C. (corrected)	Analysis for sulfur, %		Mercaptan	M. p., °C. (corrected)	Analysis for sulfur, %	
		Calcd.	Found			Calcd.	Found
Methyl	128	14.97	14.84	Octyl	78	10.27	10.12
Ethyl	115	14.05	14.11	Nonyl	86	9.83	9.38
<i>n</i> -Propyl	81	13.25	13.36	Cetyl	91	7.60	7.50
Isopropyl	94.5	13.25	13.47	Thiophenol	121	11.57	11.71
<i>n</i> -Butyl	66	12.51	12.54	<i>p</i> -Thiocresol	103	11.05	11.05
Isobutyl	76	12.51	12.76	Benzyl	130	11.05	11.08
<i>n</i> -Amyl	80	11.87	11.76	Phenylethyl	89.5	10.54	10.51
Isoamyl	59	11.87	11.88	Thienyl	119	22.61	22.72
Hexyl	74	11.28	11.02	Furfural	130	11.43	11.68
Heptyl	82	10.75	10.88	Biphenyl	146	9.09	9.21

Preparation of Sulfone.—0.01 mole of the sulfide was dissolved in just enough glacial acetic acid to put it into solution. In cases of difficultly soluble sulfides, solution may be facilitated by gentle warming. The solution was treated with 50% excess of the calculated amount of potassium permanganate dissolved in thirty times its weight of water to form the sulfone. The permanganate was added, with shaking, as fast as it was decolorized. Some of the less soluble sulfides have a tendency to precipitate on addition of the aqueous solution of the permanganate. In such cases, a slight excess of acid should be added to keep it in solution and ensure complete oxidation. When all the permanganate had been added, the excess was removed by treating with a solution of sulfurous acid at room temperature, avoiding an excess of the reagent. In most cases the sulfone occurs in the form of a colorless precipitate at this point. In cases where it is only incompletely precipitated at this point, two or three volumes of cracked ice is added.

The sulfone is filtered, dried and recrystallized from absolute alcohol. In a few cases purification was facilitated by the use of charcoal. Usually one recrystallization is sufficient. The sulfones are colorless needles having sharp melting points. Data on these compounds are found in Table II.

TABLE II
SULFONES OF 2,4-DINITROPHENYL THIOETHERS

Sulfone	M. p., °C. (corrected)	Analysis for sulfur, %		Sulfone	M. p., °C. (corrected)	Analysis for sulfur, %	
		Calcd.	Found			Calcd.	Found
Methyl	189.5	13.00	12.87	Heptyl	101	9.69	9.81
Ethyl	160	12.30	12.67	Octyl	98	9.30	9.31
<i>n</i> -Propyl	127.5	11.68	11.78	Nonyl	92	8.93	8.86
Isopropyl	140.5	11.68	11.55	Phenyl	161	10.38	10.40
<i>n</i> -Butyl	92	11.11	11.05	<i>p</i> -Cresyl	189.5	9.93	9.89
Isobutyl	105.5	11.11	11.04	Benzyl	182.5	9.93	9.90
<i>n</i> -Amyl	83	10.59	10.70	Phenylethyl	133.4	9.52	9.56
Isoamyl	95	10.59	10.69	Thienyl	143	20.38	20.14
Hexyl	97	10.12	10.22	Biphenyl	170	8.33	8.61

The above sulfides and sulfones may be prepared on a much smaller scale using 0.001 molar quantities of the reactants in the proportionate amounts of solvent and carrying out the reactions in test-tubes. Where only enough of the sulfide or sulfone is desired for a melting point, this procedure may be followed with gratifying results. Under ordinary conditions, the conversion of the mercaptan into the sulfide and thence into the sulfone may be accomplished in twenty to twenty-five minutes, although with a higher degree of technique it is possible to carry out the reactions in even shorter time.

Summary

1. 2,4-Dinitrochlorobenzene readily reacts with sodium mercaptides to form alkyl and aryl dinitrophenyl thioethers.
2. The dinitrophenyl thioethers are easily oxidized to the corresponding sulfones by potassium permanganate in acetic acid solution.
3. 2,4-Dinitrochlorobenzene is strongly recommended as a reagent for mercaptans.

CHAPEL HILL, NORTH CAROLINA
SYRACUSE, NEW YORK