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

The Identification of Mercaptans with 2,4-Dinitrochlorobenzene. II

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In a previous paper[1] it was shown that 2,4-dinitrochlorobenzene is a valuable reagent for the identification of mercaptans. In view of the favorable reception which this reagent has received, the authors submit herewith an additional list of mercaptan derivatives.

The method of preparation of both the sulfides and the sulfones was the same as given in the previous paper.[1] The sulfides of the mono-thiols are odorless, and consist of golden yellow needles while those of the dimercaptans are amorphous. All have definite melting points. The derivatives of the mono-thiols were purified from alcohol. It was necessary to recrystallize lauryl dinitrophenyl sulfide several times from alcohol to obtain a constant melting point. The derivatives of the dimercaptans were recrystallized from nitrobenzene. The sulfones are snow white, felty needles with sharp melting points. They were purified by recrystallization from alcohol.

TABLE I

DERIVATIVES OF MERCAPTANS WITH 2,4-DINITROCHLOROBENZENE

Mercaptan	M. p., °C. (corr.)	Sulfur analyses, % Calcd.	Sulfur analyses, % Found	Mercaptan	M. p., °C. (corr.)	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
Decyl	85	9.41	9.55	β-Thionaphthol	145	9.81	9.42
Undecyl	90	9.04	8.92	Cyclohexyl	148	11.34	11.05
Lauryl	89	8.69	8.52	Ethylene thiohydrin	100.5	13.11	13.25
Allyl	71.5	13.33	13.60	Dimethylene di-	248	15.04	14.86
o-Thiocresol	101	11.05	11.08	α-Methyl dimethylene di-	226	14.57	14.35
m-Thiocresol	90.5	11.05	10.87	Trimethylene di-	194	14.57	14.36
p-Chlorothiophenol	123	10.30	10.05	Tetramethylene di-	176	14.09	14.17
p-Bromothiophenol	142	9.01	9.29	Pentamethylene di-	170	13.69	13.80
α-Thionaphthol	176	9.81	9.45	Hexamethylene di-	218	13.29	13.26

TABLE II

SULFONES OF 2,4-DINITROPHENYL THIOETHERS

Sulfone	M. p., °C. (corr.)	Sulfur analyses, % Calcd.	Sulfur analyses, % Found
Decyl	93	8.60	8.46
Undecyl	97	8.29	8.18
Lauryl	101	7.99	7.96
Cetyl	105	7.07	6.91
o-Thiocresol	155	9.93	9.81
m-Thiocresol	144.5	9.93	10.00
p-Chlorothiophenol	170	9.34	9.43
p-Bromothiophenol	190	8.27	8.40
Cyclohexyl	172	10.19	10.05

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

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Summary

1. 2,4-Dinitrochlorobenzene, a reagent previously proposed by the authors, has now been studied more extensively and found to be valuable for both mono- and di-mercaptans.

2. Melting point and analyses are presented for eighteen 2,4-dinitrophenyl alkyl and aryl thio-ethers. In addition, data are presented for nine of the corresponding sulfones.

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The Mechanism of Carbohydrate Oxidation. XVI.[1] The Action of Aqueous Solutions of Potassium Hydroxide on *l*-Rhamnose

BY GALE FRANCIS NADEAU, MILDRED RATLIFF NEWLIN AND WM. LLOYD EVANS

Since *l*-rhamnose differs from *l*-mannose by having a methyl group in place of the primary alcohol group of the hexose sugar, it follows that the behavior of rhamnose toward aqueous solutions of potassium hydroxide must have certain restrictions placed upon it when this sugar is considered as a possible source of lactic acid through its reaction with the base. Among these limitations is the structural inability of the rhamnose molecule to form two molecules of glyceric aldehyde which in turn are partially converted into pyruvic aldehyde, the precursor of lactic acid. To determine the general extent to which the presence of the methyl group prevents *l*-rhamnose from acting like the hexose sugars in this respect was the first objective in this work.

It has been shown previously in this series of studies that the temperature employed and the concentration of the alkali used exercise marked effects in the yields of lactic acid obtained from certain sugars when they are subjected to the action of potassium hydroxide solutions, during forty-eight hours, a period of time which seemed sufficient to indicate the general tendency of the various sugars studied under these conditions.[2] To ascertain if this was equally true for *l*-rhamnose was the second objective in this work.

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(1) Contribution XV of this Series, THIS JOURNAL, **54**, 698 (1932).

(2) Evans and co-workers, (a) THIS JOURNAL, **48**, 2665 (1926); (b) **48**, 2703 (1926); (c) **50**, 486 (1928); (d) **50**, 1496 (1928); (e) **50**, 2543 (1928); (f) **52**, 294 (1930); (g) **52**, 3680 (1930); (h) **53**, 4384 (1931).