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Esters of Dithiodiglycolic Acid

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The esters of dithiodiglycolic acid reported here were prepared as a part of the general program of research in these laboratories on compounds reacted to thioglycolic acid and its derivatives.

Although the methyl[1] and ethyl[1,2] esters of dithiodiglycolic acid were described many years ago, to our knowledge only one other ester, namely, the dimethylaminoethyl ester,[3] has been reported during the intervening years.

Claesson prepared the ethyl ester by direct esterification of the dithio acid with alcohol, using dry hydrogen chloride as a catalyst. As noted by Price and Twiss the ester that Claesson obtained was impure. These authors[1] prepared the dimethyl and diethyl esters by electrolysis of the Bunte salts prepared from ethyl or methyl bromoacetate and sodium thiosulfate.

In a later report[4] these same authors describe the preparation of the dimethyl ester by the oxidation of the Bunte salt with iodine.

All the esters reported here were prepared by direct esterification of dithiodiglycolic acid with the corresponding alcohol. The usual acid catalyst, sulfuric acid, benzene- or toluenesulfonic acid, was used. Several of the esters were also prepared by oxidation of the corresponding ester of thioglycolic acid with the hydrogen peroxide. The average yield of crude ester was about 95%. The physical properties of the liquid esters were determined on the middle fraction of a doubly distilled product. All esters were distilled in presence of a slow stream of nitrogen.

Dithiodiglycolic acid was prepared by the oxidation of thioglycolic acid with hydrogen peroxide, or by the reaction of chloroacetic acid with sodium polysulfide. It was recrystallized from ethylene dichloride or from a mixture of benzene and ethyl acetate (9:1), m. p. 106–107° (uncor.).

In general 0.5 mole of dithiodiglycolic acid was refluxed with 1.0–1.1 moles of the alcohol in the presence of 150 cc. of toluene or benzene and 2 g. of benzene- or toluenesulfonic acid. The vapors were condensed and the lower layer of the benzene–water azeotrope was separated in a Dean–Stark trap. Esterification was generally completed in thirty minutes to two hours. The solution of the ester was washed with 5% bicarbonate solution and water, dried over anhydrous sodium sulfate, and then distilled in vacuum.

The tetra-, hexa- and octadecyl esters separated when the reaction mixture was cooled. The cyclohexyl ester crystallized after the toluene was removed.

All liquid esters are colorless when pure and are practically odorless. They are immiscible with water but soluble in most organic solvents.

TABLE I

ESTERS OF DITHIODIGLYCOLIC ACID $(SCH_2COOR)_2$

R	B. p. °C.	Mm.	$n^{25}D$	$d^{25}{}_{25}$	M_D Calcd.	Obs.	% Sulfur Calcd.	Found
n-Propyl	104–6	0.1	1.4903	1.1380	67.9	67.6	24.07	24.26
i-Propyl	91–3	.1	1.4838	1.1240	67.9	67.7	24.07	23.85
n-Butyl	121.5–122.5	.1	1.4870	1.1018	77.1	76.8	21.77	22.44
i-Butyl	112–114	.1	1.4839	1.0936	77.1	76.9	21.77	22.41
n-Octyl	202–207	.5	1.4780	1.0096	114.1	114.0	15.77	15.72
n-Dodecyl[b]			1.4769	0.9687	151.0	151.3	12.36	12.42
n-Tetradecyl	34.5–35[a]						11.15	11.22
n-Hexadecyl	44.0–44.5[a]						10.16	9.98
n-Octadecyl	52.0–52.5[a]						9.33	9.33
Methylcellosolve	150–154	0.3	1.4990	1.2337	71.2	71.0	21.49	21.76
Cyclohexyl	55–56[a]						18.50	18.15

[a] Melting points, uncor. [b] Precipitated as an oil from petroleum ether by methanol.

Summary

Eleven new esters, seven liquids and four solids, of dithiodiglycolic acid have been prepared and some of their physical properties determined.

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(1) T. S. Price and D. F. Twiss, *J. Chem. Soc.*, 1645–1653 (1908).

(2) Claesson, *Ber.*, **14**, 411 (1881).

(3) J. M. Gulland, M. W. Partridge and S. S. Randall, *J. Chem. Soc.*, 419–425 (1940).

(4) T. S. Price and D. F. Twiss, *ibid.*, 1489–1491 (1909).