

Summary

Through syntheses from opianic acid, 1,2,5-trihydroxy-anthraquinone and 1,2,5,6-tetrahydroxy-anthraquinone have been produced. These proved to be identical, respectively, with hydroxy-anthrurufin and rufopin, thus establishing with certainty the structures of these compounds.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF GENEVA]

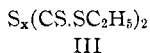
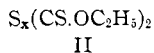
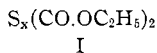
A STUDY OF ALIPHATIC POLYSULFIDES¹

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The compounds that form the subject of this investigation are the sulfides of ethyl formate (I), ethyl thioformate (II) and ethyl dithioformate (III).



The object of this work is to study in these series of sulfides the influence that the increase of the number of sulfur atoms might have on the reactivity of the terminal groups and, further, to examine to what extent the stability of the sulfur atoms between the terminal groups might be influenced when the oxygen in the latter is replaced by sulfur.

Of each of these series the mono-, di-, tri- and tetrasulfide was prepared and the same reactions were applied quantitatively to each compound. In Series I and II, the mono- and disulfides had already been made; the members of Series III have not yet been described in the literature.

The starting materials for the preparation of these sulfides were those derivatives of potassium ethyl carbonate ($\text{C}_2\text{H}_5\text{O}.\text{CO}.\text{OK}$) in which the oxygen atoms were successively substituted by sulfur, as follows: (1) potassium O-ethyl thiocarbonate ($\text{C}_2\text{H}_5\text{O}.\text{CO}.\text{SK}$), known as Bender's salt;² potassium O-ethyl dithiocarbonate ($\text{C}_2\text{H}_5\text{O}.\text{CS}.\text{SK}$), known as potassium xanthogenate;³ (3) potassium ethyl trithiocarbonate ($\text{C}_2\text{H}_5\text{S}.\text{CS}.\text{SK}$) prepared according to Chancel.⁴

Preparations

The monosulfide of ethyl dithioformate was prepared by the action of ethyl chlorodithiocarbonate on potassium ethyl trithiocarbonate in ether suspension: $\text{C}_2\text{H}_5\text{S}.\text{CS}.\text{SK} + \text{Cl}.\text{CS}.\text{SC}_2\text{H}_5 = \text{S}(\text{CS}.\text{SC}_2\text{H}_5)_2 + \text{KCl}$. The disulfide was obtained by the oxidation of potassium ethyl trithio-

¹ This publication is part of a thesis presented at the University of Geneva, Switzerland, in October, 1922.

² Bender, *Ann.*, **148**, 137 (1868).

³ Zeise, *Berzelius' Jahres-Ber.*, **3**, 81 (1824).

⁴ Chancel, *J. prakt. Chem.*, **53**, 176 (1851).

carbonate with iodine. Welde⁵ reports the preparation of this compound by Salomon, using this method, but the substance has not yet been described in the literature.

The tri- and tetrasulfides in the three series were prepared by the action of sulfur dichloride and sulfur monochloride on the calculated amounts of the above-mentioned potassium ethyl carbonates in ether suspension or in concentrated aqueous solution at room temperature. For example, $\text{SCl}_2 + 2\text{C}_2\text{H}_5\text{O} \cdot \text{CS} \cdot \text{SK} = \text{S}_3(\text{CS} \cdot \text{OC}_2\text{H}_5)_2 + 2\text{KCl}$; $\text{S}_2\text{Cl}_2 + 2\text{C}_2\text{H}_5\text{O} \cdot \text{CS} \cdot \text{SK} = \text{S}_4(\text{CS} \cdot \text{OC}_2\text{H}_5)_2 + 2\text{KCl}$. The reactions are spontaneous and the yields are very good. The last traces of ether are eliminated from the compounds thus obtained by heating on a water-bath in a vacuum. The compounds are all non-distillable oils, but when pure starting materials are used, they are sufficiently pure for analysis. The results are summarized in Table I.

TABLE I
ANALYTICAL DATA FOR THE NEW SULFIDES

	Mol. wt.		C, %		H, %		S, %		Decompn. temp., °C.	Color
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.		
Series I										
Trisulfide	248	242					40.11			
	250						40.15	39.67	120-125	Colorless
Tetrasulfide	280	274					47.09			
	279						46.99	46.72	120-125	Colorless
Series II										
Trisulfide	289	274	24.03		3.32					
	285		24.09	26.28	3.37	3.65	58.88	58.39	135	Yellow
Tetrasulfide	311	306	23.66		3.33		63.08			
	313		23.12	23.53	3.16	3.27	63.09	62.74	135	Yellow
Series III										
Monosulfide	231	242	30.22		3.64					
	234		30.30	29.75	3.69	4.13			100-110	Red
Disulfide	281	274	26.69		3.96		69.53			
	280		26.86	26.28	4.01	3.65	69.56	70.07	100-110	Red
Trisulfide	296	306	23.54		3.38		73.01			
	300		23.48	23.53	3.30	3.27	73.02	73.20	100-110	Red
Tetrasulfide	331	338	21.36		2.99		76.25			
	335		21.33	21.30	2.98	2.96	74.59	75.74	100-110	Red

Properties and Reactions

Sulfides of Ethyl Formate.—The four sulfides belonging to this series are soluble in the ordinary organic solvents, but the tri- and tetrasulfides only slightly in alcohol. The latter compounds are unstable and slowly change into the disulfide, depositing the excess of sulfur in the form of small crystals. The decomposition by heat takes place according to the equation $\text{S}_x(\text{CO} \cdot \text{OC}_2\text{H}_5)_2 = \text{CO}(\text{OC}_2\text{H}_5)_2 + \text{COS} + (x - 1)\text{S}$. The monosulfide undergoes the same decomposition after prolonged boiling. The action of alcoholic ammonia results in the formation of ammonium O-ethyl thiocarbonate and ethyl urethan: $\text{S}_x(\text{CO} \cdot \text{OC}_2\text{H}_5)_2 + 2\text{NH}_3 = \text{C}_2\text{H}_5\text{O} \cdot \text{CO} \cdot \text{NH}_2 + \text{C}_2\text{H}_5\text{O} \cdot \text{CO} \cdot \text{SNH}_4 + (x - 1)\text{S}$. The latter compound proved to

⁵ Welde, *J. prakt. Chem.*, **15**, 43 (1877).

be extremely unstable and could only be isolated in a very small quantity; with lead acetate it gave a white precipitate that soon turned black. The first compound, ethyl urethan, is transformed into urea by prolonged action of concd. ammonium hydroxide. The formation of allophanic ester ($C_2H_5O.CO.NH.CO.NH_2$), as stated by Debus⁶ in the case of the disulfide, could not be confirmed even with ammonia of different concentrations.

Sulfides of Ethyl Thioformate.—The tri- and tetrasulfides are only slightly soluble in alcohol. The four sulfides are stable, though the latter two derivatives undergo a slow oxidation in the air.

The decomposition of the four sulfides by heat follows the equation $S_x(CS.OC_2H_5)_2 = C_2H_5O.CS.SC_2H_5 + COS + (x - 1)S$. The decomposition of the disulfide by heat as stated by Debus⁷ could not be confirmed, but at that time carbon oxysulfide was not yet known. On shaking the ethereal solution of the tri- and tetrasulfide with a sodium sulfide solution, both compounds are transformed into the disulfide. The reaction with alcoholic ammonia leads to the formation of ammonium xanthogenate and xanthogene amide: $S_x(CS.OC_2H_5)_2 + 2NH_3 = C_2H_5O.CS.SNH_4 + C_2H_5.CS.NH_2 + (x - 1)S$. Ammonium xanthogenate is a stable compound, but by prolonged action of concentrated alcoholic ammonia it is decomposed with evolution of hydrogen sulfide, while the xanthogene amide is changed into ammonium rhodanate.

Sulfides of Ethyl Dithioformate.—These compounds have a disagreeable odor. Their solubility in ether, alcohol, benzene and acetone diminishes considerably with the increase in the number of sulfur atoms. The tri- and tetrasulfides oxidize slowly when exposed to the air. The decomposition by heat takes place mainly according to the equation $S_x(CS.SC_2H_5)_2 = S(C_2H_5)_2 + 2CS_2$. The tetrasulfide, however, does not give ethyl tetrasulfide, but ethyl trisulfide, which is due to the fact that ethyl tetrasulfide decomposes into trisulfide and free sulfur when distilled in a vacuum (ethyl trisulfide gives disulfide and free sulfur when distilled at atmospheric pressure). A side reaction in the decomposition by heat results in the formation of ethyl trithiocarbonate: $S_x(CS.SC_2H_5)_2 = CS.(SC_2H_5)_2 + CS_2 + (x - 1)S$. Only the monosulfide decomposes exclusively according to the first equation. Sodium sulfide in aqueous solution reacts only with the terminal groups, and the corresponding ethyl sulfides result; however, the tetrasulfide gives ethyl trisulfide. The action of alcoholic ammonia also leads to the formation of the ethylsulfides as the main reaction products: $S_x(CS.SC_2H_5)_2 + 4NH_3 = S_x(C_2H_5)_2 + 2NH_4.SCN$. The tetrasulfide is first broken down to the trisulfide of the same series and then transformed into the ethyl trisulfide: $S_4(CS.SC_2H_5)_2 \longrightarrow$

⁶ Debus, *Ann.*, **82**, 253 (1852).

⁷ Debus, *Ann.*, **75**, 122 (1850).

$S_3(CS.SC_2H_5)_2 \longrightarrow S_3(C_2H_5)_2$. The intermediate product could be isolated after a short action of a 5% solution of alcoholic ammonia.

A side reaction in the decomposition with alcoholic ammonia resulted in the formation of ethyl mercaptan: $S_x(CS.SC_2H_5)_2 + 4NH_3 = 2C_2H_5SH + H_2S + (x - 1)S + 2NH_4SCN$.

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Summary

The mono-, di-, tri- and tetrasulfides of ethyl formate, ethyl thioformate and ethyl dithioformate have been prepared and some of their reactions studied. The four sulfides show the same reactions in each group. Substitution of sulfur in the terminal groups intensifies the color of each series. Replacement of oxygen by sulfur in the terminal groups stabilizes the polysulfides. For example, the polysulfides of ethyl formate decompose spontaneously into the disulfide; in the ethyl thioformate series the group of sulfur atoms between the terminal groups is destroyed on heating; whereas, under the same conditions in the ethyl dithioformate series this group of sulfur atoms remains intact.

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

PARA-CYMENE STUDIES. VI. 2-AMINO-6-NITRO-PARA-CYMENE AND CERTAIN NEW AZO DYES

BY ALVIN S. WHEELER AND C. R. HARRIS¹

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2-Amino-6-nitro-*p*-cymene has not hitherto been described. We obtained it by the partial reduction of 2,6-dinitro-*p*-cymene with ammonium sulfide. This involved considerable study of the nitration of cymene. Kraut² first made dinitrocymene by dropping cymene into a mixture of concd. sulfuric and fuming nitric acids. Mazzara³ prepared it from 3-amino-2,6-dinitro-*p*-cymene by direct substitution of hydrogen for the amino group. In 1916, Aschan⁴ studied the nitration of cymene but his method was improved upon by Alfthan.⁵ This was similar to Kraut's method but a better yield (38%) was obtained. We tried many variations to better this yield, employing several concentrations of acids and different

¹ This paper is an abstract of a thesis submitted by C. R. Harris in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of North Carolina in June, 1926.

² Kraut, *Ann.*, **92**, 67 (1854).

³ Mazzara, *Gazz. chim. ital.*, **20**, 146 (1890).

⁴ Aschan, *Finska Kemistsamfundets Medd.*, **25**, 122 (1916).

⁵ Alfthan, *Ber.*, **53**, 78 (1920).