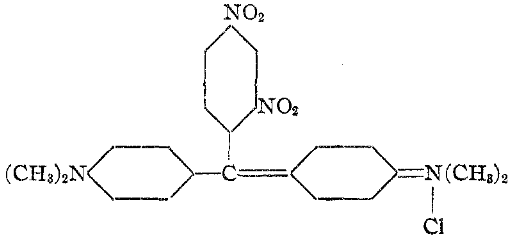
directions given for the preparation of malachite green by Gattermann[1] were followed. The product obtained was a green powder which dyed silk a bluish green shade very similar to that produced by malachite green. The following formula undoubtedly represents the structure of the dye:



The quantitative results, as stated above, will be published in a later paper.

## Summary.

1. The method described by Sachs and Kempf for the preparation of 2,4-dinitro-benzaldehyde was found to be unsatisfactory and a modified method for its preparation was worked out.
2. Eight derivatives of 2,4-dinitro-benzaldehyde were prepared and analyzed and certain physical properties and solubilities determined.
3. These compounds, like many other similar condensation products, are affected to a greater or less extent by the action of light.

PITTSBURGH, PENNA.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY. NO. 85.]

# A STUDY OF THE SULFUR DERIVATIVES OF BUTYL ALCOHOL.

BY H. LEB. GRAY AND GURNEY O. GUTEKUNST.

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In the course of our work in this laboratory, it was necessary to prepare large quantities of butyl sulfone. This involved not only a complete study of the methods of preparation of the sulfone but of butyl sulfide as well.

Grabowsky and Saytzeff[2] prepared butyl sulfide by heating an alcoholic solution of potassium sulfide with butyl iodide. A disadvantage of this method consists in the difficulty of preparing large quantities of alcoholic sodium or potassium sulfide so it was decided to prepare the butyl sulfide by distilling sodium sulfide with an aqueous solution of sodium butyl sulfate, the latter being prepared by the action of fuming sulfuric acid on butyl alcohol.

It was found that low yields were obtained by this method; this was

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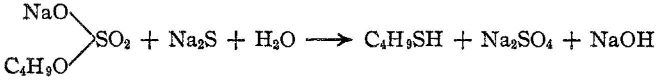
[1] "Practical Methods of Organic Chemistry."

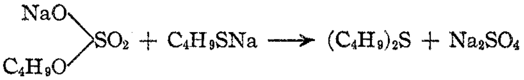
[2] *Ann.*, 171, 251 (1874).

not due to a poor yield of butyl sulfuric acid, but to the formation of butyl mercaptan as well as butyl sulfide. This could not be attributed to the presence of large amounts of sodium hydrosulfide in the sodium sulfide since the mercaptan is formed even in the presence of a slight excess of sodium hydroxide. It has been found that sodium butyl sulfate when distilled with sodium sulfide in presence of water tends to form butyl mercaptan in the following manner:



$$\begin{matrix} NaO \\ C_4H_9O \end{matrix}\rangle SO_2 + Na_2S + H_2O \longrightarrow C_4H_9SH + Na_2SO_4 + NaOH$$

We found that butyl sulfide is satisfactorily formed when the mixture of sodium butyl sulfate and sodium sulfide is refluxed, but that things go wrong when the mixture is distilled without first refluxing. This looks like a case of mass action, since butyl mercaptan is removed as fast as it is formed, but reacts further if it is kept in the reaction mixture. It was also found that the addition of a large excess of sodium hydroxide materially diminishes the formation of mercaptan when the mixture is distilled direct without refluxing. This is undoubtedly due to the formation of the sodium salt of butyl mercaptan, which reacts with sodium butyl sulfate in the following manner:



$$\begin{matrix} NaO \\ C_4H_9O \end{matrix}\rangle SO_2 + C_4H_9SNa \longrightarrow (C_4H_9)_2S + Na_2SO_4$$

Grabowsky[1] prepared butyl sulfone by the action of fuming nitric acid on dibutyl sulfide. This method was thoroughly investigated and was finally discarded owing to the fact that a large excess of nitric acid is necessary and that the method is not dependable. The yield varied from 30% to 70% under apparently the same conditions, and great difficulty is experienced in purifying the product.

An attempt was made to oxidize the sulfide with nitrogen dioxide but was unsuccessful.

Oxidation with sodium permanganate was then tried and proved to be very successful. Excellent yields were obtained, and the product was quite pure.

During the course of these experiments butyl mercaptan was oxidized by means of potassium dichromate. A yellow oil resulted which boiled at 228–230° (uncorr.) and which we assumed to be *n*-dibutyl disulfide.

## I. Butyl Sulfide.

**From Butyl Alcohol.**—350 g. of fuming sulfuric acid (20% sulfur trioxide) was gradually added to 1000 g. of butyl alcohol with constant stirring. The mixture was placed on the water bath and heated for 15 hours. It was then cooled and the excess acid was neutralized with a saturated solution

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[1] *Ann.*, **175**, 350 (1875).

of sodium carbonate, and the unchanged butyl alcohol distilled off. 690 g. of butyl alcohol was recovered. The use of sodium carbonate entirely in the place of lime eliminated 2 filtrations and does not affect the yield of butyl sulfide. The mixture was diluted to about 5 liters and slowly distilled with a solution of 217 g. ($^1/_3$ excess) of sodium sulfide, care being taken not to distil the sulfide too rapidly. The crude distillate was fractionated and yielded 107 g. (35%) of butyl sulfide and 61 g. of butyl mercaptan. It was thought that the small yield of sulfide might be due to a low yield of butyl sulfuric acid caused by the temperature of the reacting mixture being too low. The effect of refluxing at boiling temperature, the mixture of butyl alcohol and fuming sulfuric acid (20% sulfur trioxide) resulted in the formation of dibutyl ether.

**Dibutyl Ether.**—350 g. of fuming sulfuric acid was gradually added to 1000 g. of butyl alcohol as above. The mixture was boiled under a reflux condenser for 15 hours, cooled, neutralized with sodium carbonate solution, and the butyl alcohol distilled off. The residue was slowly distilled with 316 g. of sodium sulfide. Only 40 g. of butyl sulfide was obtained. The butyl alcohol distillate was fractionally distilled and yielded 400 g. of dibutyl ether, boiling sharply at 140°. This represents a yield of 45%. There is little doubt but that this method could be so developed that much larger yields of the ether could be obtained.

**Action of Sodium Butyl Sulfate on Butyl Mercaptan in Presence of Sodium Hydroxide.**—90 g. of butyl mercaptan and 176 g. of sodium butyl sulfate were mixed, made strongly alkaline with 40 g. of sodium hydroxide, and boiled under a reflux condenser for 3 hours. An oily layer separated. The reaction mixture was cooled, and the oil layer separated. This was dried over calcium chloride and fractionally distilled. 77 g. of pure butyl sulfide was obtained, representing a 53% yield.

**Effect of Refluxing with Sodium Hydroxide Solution.**—350 g. of fuming sulfuric acid was gradually added to 1000 g. of butyl alcohol with constant stirring and the mixture heated on the water bath for 15 hours. It was then neutralized with sodium carbonate, and the butyl alcohol distilled off. 636 g. of the alcohol was recovered. 261 g. of sodium sulfide and 200 g. of sodium hydroxide were dissolved in water and added to the reaction mixture. This was boiled under a reflux condenser for 3 hours and then slowly distilled. The crude sulfide was separated from the aqueous layer, dried and fractionally distilled. 266 g. (72 %) of butyl sulfide boiling between 180–185° was obtained.

## II. Butyl Sulfone.

**Oxidation with Nitric Acid.**—545 g. (40% excess) of fuming nitric acid (90%) was placed in a 3-liter round-bottom flask provided with a long reflux condenser, and heated to moderate boiling. 400 g. of butyl sulfide was added drop by drop through the condenser. A vigorous reaction took place in the condenser tube. After all the sulfide was added, the contents of the flask were boiled until nitrogen dioxide fumes ceased to be evolved (about one hour). The reaction mixture was poured into an evaporating dish and as much nitric acid as possible evaporated off on the water bath. The crude mixture was dissolved in ether, neutralized with sodium carbonate, the ethereal layer separated, and the water solution extracted once with ether. The ether extracts were washed with water and combined. On evaporating off the ether, a yellow oil was obtained which solidified on cooling in an ice and salt mixture. This yellow solid was broken up and centrifuged. The butyl sulfone was obtained as yellow crystals. A yellow oil also resulted. After several recrystallizations from alcohol, the sulfone crystallized as pure white flakes which melted at 43.5°. Yield, 308 g. or 63% of pure butyl sulfone. No further separation of crystals resulted on cooling the yellow oil. This oil on distillation decomposed yielding butyl sulfide.

The yields obtained by this method varied from 10 to 63%, although the experiments were apparently conducted under exactly the same conditions. The method is unreliable and not to be depended upon as a source of butyl sulfone.

**Oxidation with Nitrogen Dioxide.**—An attempt was made to oxidize butyl sulfide to butyl sulfone by means of nitrogen dioxide. For this purpose, 200 g. of butyl sulfide was placed in a 500-cc. round-bottom flask, and the gas bubbled through slowly until no more heat was generated. The reaction mixture was neutralized with sodium carbonate and extracted with ether. On distilling off the ether and cooling the residue, a few crystals of butyl sulfone were obtained.

**Oxidation with Sodium Permanganate.**—400 g. of dibutyl sulfide was placed in an open earthenware vessel and stirred by means of an efficient stirrer. Technically pure sodium permanganate solution was added in small portions. A very vigorous reaction took place with separation of a large quantity of manganese dioxide. A 25% solution of sulfuric acid (equivalent to 163 g. of conc. acid) was added from time to time in quantities just sufficient to keep the mixture thin enough to admit of efficient stirring. The permanganate was added until no more heat was generated, about 300 g. being necessary. The reaction mixture was allowed to stand until the manganese dioxide had settled and an almost colorless oil separated on top. This oil was poured off. The residual manganese dioxide was extracted with ether and the oil resulting from the ether extract added to the first. The oil solidified to a light yellow crystalline mass on cooling in an ice and salt mixture. This crystalline mass was broken up and centrifuged, yielding practically pure butyl sulfone and a few g. of a light yellow oil. One crystallization from alcohol was sufficient to obtain a pure product melting at 43.5°. A yield of 390 g., or 80%, resulted.

## Summary.

1. It has been found that butyl mercaptan in comparatively large yields is obtained on distilling a solution of sodium sulfide with sodium butyl sulfate.
2. It has been shown that no butyl mercaptan is obtained when a large excess of sodium hydroxide is used.
3. It has been found that butyl sulfide can be obtained by the interaction of butyl mercaptan and sodium butyl sulfate in the presence of sodium hydroxide.
4. A method for the preparation of dibutyl ether is given.
5. An improved method for preparing butyl sulfide has been described. Average yields of 72% can be obtained.
6. It has been found that the oxidation of butyl sulfide to butyl sulfone with fuming nitric acid, results in a product difficult to purify and that the method cannot be depended upon to give constant yields.
7. It was found impossible to oxidize butyl sulfide efficiently to butyl sulfone by means of nitrogen dioxide.
8. The conditions have been determined which permit the oxidation of butyl sulfide to butyl sulfone by means of sodium permanganate in yields which average 80%.

We are indebted to Miss Ethel Schram, Mr. Erle M. Billings, and Mr. Luther M. Curtice for their assistance in carrying out parts of the experimental work in this paper.

ROCHESTER, N. Y.

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