

flask with 25 grams of concentrated sulphuric acid and heated on an oil-bath to  $110^{\circ}$  for two hours. A slight evolution of gas was observed and the odor of sulphur dioxide was distinctly noticeable at the mouth of the flask. The dark red solution when poured into ice water gave a brown amorphous solid. This was sparingly soluble in cold sodium carbonate solution and readily soluble in hot sodium carbonate solution and in concentrated ammonia solution. It was reprecipitated from both by the addition of mineral acids. The ammonia solution when evaporated on the water-bath or allowed to evaporate at the temperature of the room deposited a red solid which was insoluble in water, but soluble in ammonia and alkalis. When heated with caustic alkalis it did not evolve ammonia. Its alkaline solutions stained the skin and dyed silk and wool orange-yellow. We did not succeed in isolating any compound in a pure condition from the crude transposition product, judging from the analytical data. As the product is insoluble in ordinary solvents and does not melt below  $300^{\circ}$  its purification is very difficult.

UNIVERSITY PLACE, NEB.

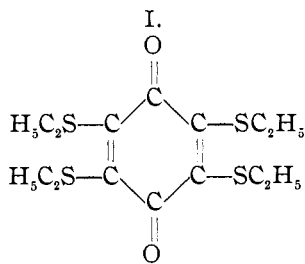
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

### THE ACTION OF MERCAPTIDES ON QUINONES.

BY JOHN LANGLEY SAMMIS.

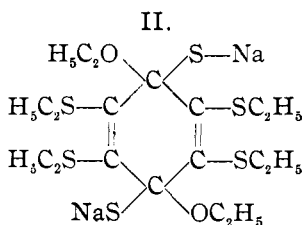
Received July 14, 1905.

IN A previous paper by Professor H. S. Grindley and the writer upon this subject<sup>1</sup>, it was concluded that the reaction of sodium mercaptide on dichlorodiphenoxyquinone in dry ether consisted of *substitutions* and of *addition* and, at that time, three substances resulting from this reaction were given the following formulas:

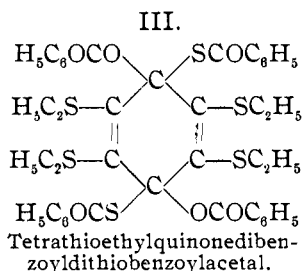


Tetrathioethylquinone.

<sup>1</sup> *Am. Chem. J.*, 19, 293 (1897).



Addition-product of sodium mercaptide and tetrathioethylquinone.



Tetrathioethylquinonedibenzoylethylthiobenzoylacetal.

Tetrathioethylquinone, I, was made from sodium mercaptide and dichlordiphenoxyquinone, by substitution; and also from chloranil in larger quantity, though this latter substance was not mentioned at that time. Substance II was not isolated or analyzed, but was supposed to be formed by addition when two molecules of sodium mercaptide were mixed with one molecule of tetrathioethylquinone in dry ether, or by substitution and addition when six molecules of sodium mercaptide were mixed with one molecule of chloranil or of dichlordiphenoxyquinone. Substance III was made by adding four molecules of benzoyl chloride to substance II, prepared in any of these ways. Substances II and III were considered to be somewhat analogous to the hemiacetal derivatives described by Jackson and Grindley.<sup>1</sup> The fact was observed by the authors of the paper referred to (but not mentioned at that time) that if substance III was prepared from chloranil, sodium mercaptide, and benzoyl chloride, then another substance was simultaneously formed, which, after recrystallizing from alcohol, proved to be the dibenzoate of tetrachlorhydroquinone described by Levy and Schulz.<sup>2</sup> It is clear that the formation of this latter substance involves no addition, but consists of reduction of the chloranil to tetrachlorhydroquinone, which in alkaline solution reacts with benzoyl chloride, forming the dibenzoate. In view of this, it appeared to the writer to be desirable to search for additional facts to aid in determining whether the action of mercaptides on quinones consists in general of *addition* or of *reduction* or of both.

In the course of this work, the method of making tetrathioethylquinone (Formula I above) was improved so that 95 per cent. of the theoretical yield can now be obtained, instead of 10 per cent. or less by the former methods. It was found that in the

<sup>1</sup> *Am. Chem. J.*, **17**, 577 (1895).

<sup>2</sup> *Ann. Chem. (Liebig)*, **210**, 156.

reaction of chloranil upon sodium mercaptide, the substitution of chlorine proceeds almost exclusively, if the substances be mixed in water; while if ether be used instead of water, the reaction consists largely of reduction of the quinone to the hydroquinone, with very little substitution. Another case was observed and is described below, in which the use of ether as a solvent caused the formation of one product, while if a different solvent was used, a totally different product was obtained. For the preparation of tetrathioethylquinone, in large quantities, four molecules of potassium hydroxide are dissolved in two parts of water and cooled. Four molecules of mercaptan are mixed with an equal volume of 95 per cent. alcohol, and after cooling, the solution is added to the potassium hydroxide, keeping the temperature below 20°. The chloranil in the proportion of one molecule is boiled with water in a flask, in order to thoroughly wet the substance, and is then cooled to 20°. The mercaptide is now poured into the chloranil and water, and stirred vigorously. The black solid mass is filtered and washed on paper, until the wash-water comes through neutral and colorless, and is then dried in air. Traces of an ill-smelling impurity are removed by mixing the substance with dilute nitric acid (sp. gr. 1.10) to a thin paste, which is to be warmed on the water-bath for half an hour or less, and then filtered, washed with water and recrystallized once from 95 per cent. alcohol. The yield is about 95 per cent. of the theoretical quantity. By acidulating the first aqueous filtrate a small amount of tetrachlorhydroquinone may be obtained. The molecular weight of the substance was determined by the boiling-point method in benzene, and was found to accord with the formula previously given.

Calculated for  
 $C_8(SC_2H_5)_4O_2$ .  
 Mol. wt. = 348.

Found, average of  
 ten determinations.  
 352.

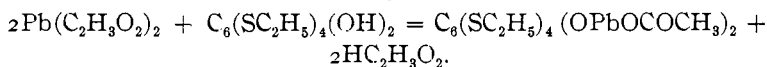
LEAD SALT OF TETRATHIOETHYLHYDROQUINONE AND ACETIC ACID,  
 $C_8(SC_2H_5)_4(OPbOCOCH_3)_2$ .

When pure crystallized tetrathioethylhydroquinone (one molecule) is dissolved in 95 per cent. alcohol and treated with a strong solution of two molecules of lead acetate in alcohol, a yellow crystalline precipitate forms at once in long fibrous needles at low temperatures, changing to less bulky canoe-shaped crystals when warmed, or if formed at a high temperature. The sub-

stance was purified by repeated boiling with small quantities of alcohol containing 2 per cent. acetic acid, followed by thorough washing on the filter with hot alcohol. Lead was determined by suspending the substance in 95 per cent. alcohol and adding dilute sulphuric acid, which dissolved the substance, but precipitated lead sulphate at once. This was washed thoroughly with alcohol, ignited separately, heated with nitric and sulphuric acids in the crucible, and weighed. Sulphur was determined by heating the substance in a sealed tube with fuming nitric acid and a little pure lead nitrate to 260° for six hours. On opening the tube, the contents were evaporated to dryness to remove nitric acid, water was added, and also some pure sodium bicarbonate. After 48 hours, the lead carbonate, thus formed, was filtered and washed, and from the filtrate the sulphur was precipitated as barium sulphate. The lead carbonate precipitate was found to be easily and completely soluble in acetic acid, which served to show that it contained no lead sulphate. The filtrate from the barium sulphate was found to contain no trace of lead, by test with sulphuretted hydrogen.

	Calculated for $C_6(SC_2H_5)_4(OPbOCOCH_3)_2$ ,	Found.	
		I.	II.
Lead.....	47.0	46.6	47.4
Sulphur.....	14.41	14.51	.....

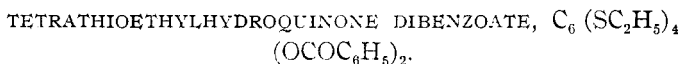
A portion of the substance used for analysis on being gently warmed with dilute sulphuric acid, evolved acetic acid vapors. The substance is formed according to the equation:



In one experiment, using 14.5 grams of lead acetate, the acidity of the filtrate was found to be 80 per cent. of the theory. The substance is insoluble in water and in all common solvents, but is slightly soluble in boiling alcohol. It is decomposed by glacial acetic acid, sulphuric, or hydrochloric acids. Suspended in alcohol or ether, and treated with benzoyl chloride, it forms lead chloride and tetrathioethylhydroquinone, but no dibenzoate of tetrathioethylhydroquinone.

On account of its insolubility the formation of this lead salt serves as a delicate test for the presence of tetrathioethylhydroquinone. When a solution of lead acetate in alcohol is mixed with a solution of tetrathioethylquinone in alcohol, no apparent

change occurs, but if one drop of sodium ethylate solution is added, a copious precipitate of this yellow lead salt appears, showing that the reduction is immediate. If lead mercaptide be mixed with lead acetate and chloranil in alcohol, a quantity of this same yellow lead salt is formed, showing that the action of lead mercaptide on chloranil proceeds partly by substitution forming lead chloride, and partly by reduction of the substituted quinone. This yellow lead salt had been obtained on various occasions previously, but only after the completion of the analyses reported above, could any significance be attached to its appearance.



This substance was made and analyzed in December, 1896, but was at that time supposed to be represented by the formula  $C_6(SC_2H_5)_4(OCOC_6H_5)_2(SCOC_6H_5)_2$ <sup>1</sup> (see Formula III above). For the purposes of this study it was prepared again precisely as in 1896, and used for a molecular weight determination by the boiling-point method in benzene.

Calculated for  $C_6(SC_2H_5)_4(OCOC_6H_5)_2SCOC_6H_5)_2$ , mol. wt., 832.

Calculated for  $C_6(SC_2H_5)_4(OCOC_6H_5)_2$ , mol. wt., 558.

Found: 546, 580, 597, 601, 611, 615, 624, 639.

The substance can be made in various ways. It was first made by mixing sodium mercaptide and  $C_6(SC_2H_5)_4O_2$ , and benzoyl chloride in ether as previously described. But it can be made with equal ease if sodium ethylate be substituted for the sodium mercaptide, and therefore it cannot contain more than four atoms of sulphur in the molecule. It was made in greater purity and better yield as follows: 11.5 grams of  $C_6(SC_2H_5)_4O_2$  were dissolved in glacial acetic acid and reduced by means of zinc dust to the colorless hydroquinone  $C_6(SC_2H_5)_4(OH)_2$  as described in the earlier paper. The mixture was poured into water, stirred, filtered, and the mixture of zinc dust and precipitated tetrathioethylhydroquinone was washed with water till neutral. The drained mixture was extracted with 60 cc. of hot alcohol, and to the alcoholic solution thus obtained was added a solution of 1.4 grams sodium in 40 cc. of absolute alcohol. Immediately, more than half a liter of ether was added, which precipitated a solid mass. Eight cc. of benzoyl chloride were stirred in, and the solid dissolved. After evaporating the last traces of ether and

<sup>1</sup> *Am. Chem. J.*, 19, 293.

alcohol on the water-bath, the residue was digested hot with 10 per cent. aqueous sodium carbonate solution to remove any excess of benzoyl chloride. The oily layer was filtered out, and washed with water, when it solidified rapidly. It was washed with ether to remove traces of coloring-matter, and recrystallized from 95 per cent. alcohol in rhombic plates, varying in form somewhat, when crystallized at different temperatures. The substance having a constant melting-point at  $131^{\circ}$  was analyzed.

	Calculated for $C_6(SC_2H_5)_4(OCOC_6H_5)_2$ .	Found.	
		I.	II.
Carbon.....	60.21	60.17	59.94
Hydrogen.....	5.38	5.36	5.90
Sulphur.....	22.95	23.16	23.07
Mol. wt., 558. 572.1, 531.4, 548.1, 566.8, 584.5; Average, 560.6.			

Prepared in this way, the substance was found to be identical in properties with the substance described in the paper referred to, as tetrathioethylquinonedibenzoyldithiobenzoylacetal (formula III above). The percentage compositions calculated from the two formulas are almost identical, but the molecular weights differ widely.

	Calculated for Formula III, $C_6(SC_2H_5)_4(OCOC_6H_5)_2(SCOC_6H_5)_2$ .	Calculated for $C_6(SC_2H_5)_4(OCOC_6H_5)_2$ .
Carbon.....	60.57	60.25
Hydrogen.....	4.81	5.38
Sulphur.....	23.07	22.95
Mol. wt.....	832	558

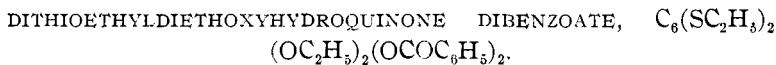
The method of preparation, analyses, molecular weight determinations and the chemical reactions of the substance show that the earlier formula, III, is incorrect, and that the substance is really tetrathioethylhydroquinone dibenzoate.

It is very easily soluble in ethyl acetate, soluble in benzene, ethyl alcohol, or methyl alcohol, nearly insoluble in water, ligroin or 80 per cent. alcohol. It can be recrystallized from benzene or 95 per cent. alcohol. The substance is decomposed by boiling with alcohol and sodium carbonate. Twenty-five per cent. aqueous potassium hydroxide attacks it very slowly at the boiling temperature, but if alcohol be added to the mixture, mercaptan odors are freely evolved and, in six hours, the substance is entirely dissolved. In this respect it differs from the dichloro-diethoxyquinonedibenzoyldiethylacetal described by Jackson and Grindley<sup>1</sup> which is stated to be unaffected by boiling alcoholic soda solution.

<sup>1</sup> *Am. Chem. J.*, **17**, 637.

The effect of various solvents in modifying the course of the reactions has already been referred to. Sodium mercaptide acting on dichlordiphenoxyquinone suspended in ether, gave 36 per cent. of the theoretical yield of the substitution-product,  $C_6(SC_2H_5)_4O_2$ . The same materials mixed in water gave 65 per cent. of the same product.

When a solution of sodium in alcohol is added to tetrathioethylquinone in a little alcohol, the further addition of ether precipitates a yellow solid which probably contains the sodium salt of tetrathioethylhydroquinone. The subsequent addition of benzoyl chloride dissolves the solid, forming the dibenzoate of tetrathioethylhydroquinone, described in this paper. But if the same process be carried out omitting the ether, then benzoyl chloride forms the dibenzoate of dithioethyldiethoxyhydroquinone.



On dissolving two atoms of sodium in a minimum quantity of absolute alcohol, and adding the alcoholate solution to one molecule of  $C_6(SC_2H_5)_4O_2$  moistened with a little alcohol, heat is evolved, the mass turns brown, and all dissolves. If the bulk of alcohol be small, a granular crystalline precipitate soon separates which is easily soluble in alcohol. On adding to this mixture two molecules of benzoyl chloride, much heat is evolved and the solid dissolves. After removing alcohol by evaporation, and the excess of benzoyl chloride by the use of hot aqueous sodium carbonate solution, the oily residue is washed with water and made to crystallize by adding a little warm alcohol. The substance is difficultly soluble in 95 per cent. alcohol, is insoluble in water, ligroin or 80 per cent. alcohol. It is soluble in benzene, chloroform or ether. It can be recrystallized from glacial acetic acid, or better from ethyl acetate. It forms equilateral six-sided plates and melts at  $184-184.5^\circ$ . Analysis gave the following results:

	Calculated for $C_6(SC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2$ .	Found.	
		I.	II.
Carbon.....	63.87	64.21	64.62
Hydrogen.....	5.70	5.70	5.95
Sulphur.....	12.16	12.45	11.92
Mol. wt.....	526	587	

The substance is not affected by boiling with sulphuric acid of specific gravity 1.40.

As a result of the work here reported, the following conclusions have been reached:

(1) The action of the mercaptides of lead and sodium on the quinones used consists of substitution and of reduction, and no addition-products have as yet been isolated.

(2) The substance described as an addition-product in the paper referred to, under the name tetrathioethylquinonedibenzoyldithiobenzoylactal, does not possess the formula there assigned to it, but is really the dibenzoate of tetrathioethylhydroquinone, a reduction-product of tetrathioethylquinone.

(3) It was shown that the solvent used determines or largely modifies the course of several reactions between the substances under examination.

(4) By the selection of a suitable solvent and in other ways, the method of making tetrathioethylquinone, was improved so that 95 per cent. of the theoretical yield can now be obtained instead of 10 per cent. or less by the older methods.

(5) The preparation, solubilities and analysis of the dibenzoate of tetrathioethylhydroquinone (m. p. 131°), of the lead double salt of acetic acid and tetrathioethylhydroquinone and of the dithioethyldiethoxyhydroquinone dibenzoate (m. p. 184-184.5°) are here described.

In conclusion, I wish to express my thanks to Professor H. S. Grindley, of the Department of General Chemistry, for permission to undertake this work, in a field of research previously entered by himself.

UNIVERSITY OF ILLINOIS,  
URBANA, ILLINOIS.

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 107.]

## THE CONDENSATION OF SUCCINYLOSUCCINIC ACID DIETHYL ESTER WITH GUANIDINE, A DERIVATIVE OF 1,3,5,7-NAPHTTETRAZINE, A NEW HETEROCYCLE.<sup>1</sup>

BY MARSTON TAYLOR BOGERT AND ARTHUR WAYLAND DOX.

Received July 21, 1905.

IN extending the work upon the quinazoline compounds, which has been going on in this laboratory for several years,<sup>2</sup>

<sup>1</sup> Read at the meeting of the New York Section of the American Chemical Society, April 7, 1905.

<sup>2</sup> This Journal, **22**, 129, 522 (1900); **23**, 611 (1901); **24**, 1031 (1902); **25**, 372, 935 (1903); **27**, 649 (1905).