The amount of oxygen absorbed indicates the formation of a peroxide, similar to that formed in the case of triphenylmethyl:

$$2C_4H_3S(C_6H_5)_2\dot{C} + O_2 = C_4H_3S(C_6H_5)_2C.O.O.C(C_6H_5)_2C_4H_3S.$$

But the peroxide as such has not been isolated in a condition sufficiently pure for analysis.

Dithienylphenyl carbinol (m. p. 90°) has also been prepared by the Grignard synthesis from benzoic ester and thienyl iodide, but the conditions for its conversion into the chloride have not as yet been determined. In connection with the thiophene derivatives the corresponding furfurane derivatives will be studied.

ANN ARBOR, MICHIGAN.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

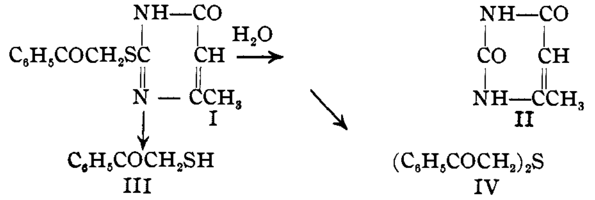
1,4-DITHIENES. I.

BY TREAT B. JOHNSON, ROBERT C. MORAN, AND EDWARD F. KOHMANN.

Received January 29, 1913.

This paper is a contribution to our knowledge of the chemistry of sulfur compounds containing the thioglycollide grouping —S—CH_2—CO—.

In a recent publication from this laboratory,[1] Johnson and Moran described the behavior of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine I, on hydrolysis. They made the interesting observation that this mercaptopyrimidine undergoes hydrolysis smoothly, by digestion with strong hydrochloric acid, forming 4-methyluracil II, as expected, and a crystallin sulfur compound, which did not possess the properties of a mercaptan III, and also was not identical with the phenacylsulfide (m. 77°) IV, described by Tafel and Mauritz.[2] The high percentage of sulfur obtained by analysis and the characteristic properties of the compound indicated that we were dealing with a representative of a new type of substances. The data, which we have obtained and now discuss in this paper, confirms our original assumption.



We now conclude that this hydrolytic product is a representative of a class of cyclic sulfur compounds to which we shall assign the name—*dithienes*. In other words, the compound is a diphenyl-derivative of the heterocycle VI, and its structure is to be represented by formula V. The

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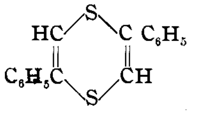
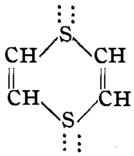
[1] *Am. Chem. J.*, 48, 307.

[2] *Ber.*, 23, 3474.

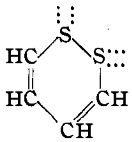
evidence, in favor of this constitution, is given in the experimental part of this paper. Compounds of this character correspond, in constitution, to the *p*-quinones VIII, and consequently in order to distinguish the type under consideration VI, from the theoretically possible *ortho* modification VII, corresponding to the *o*-quinones IX, we shall designate them as *para*- and *ortho*-dithienes or 1,4- and 1,2-dithienes respectively.



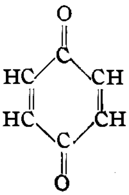
V



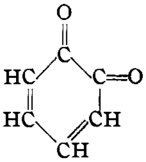
VI



VII



VIII



IX

The mechanism of the various changes involved in the formation of the *para*-dithiene V, from the mercaptopyrimidine I, is interpreted as follows: The hydrolysis of the pyrimidine I, is apparently normal, giving first 4-methyluracil II, and the mercaptoacetophenone III. The latter compound, however, is unstable in the presence of hydrochloric acid and instead of being oxidized it undergoes at once a dimolecular condensation forming a cyclic acetal X, which then loses two molecules of water forming the *para*-dithiene V. Every 2-benzoylmethylmercaptopyrimidine, which we have examined, has undergone hydrolysis giving this same dithiene, and the corresponding *para*-toluyl compound XIV behaves in a like manner also, giving the corresponding 2,5-ditolyl-1,4-dithiene XV. Apparently, it is a normal reaction for mercaptoketones to condense in this manner, in the presence of acids, with formation of *para*-dithienes. The characteristic sulfur compound $C_{12}H_{16}O_4S_2$, obtained by Steude[1] by heating ethyl acetylthioacetoacetate XI, with hydrochloric or sulfuric acid, was undoubtedly a *para*-dithiene derivative and its constitution is to be represented by formula XIII. These various condensations are represented by the following structural formulas:

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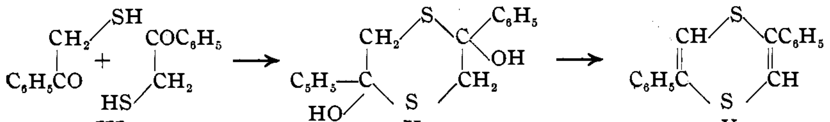
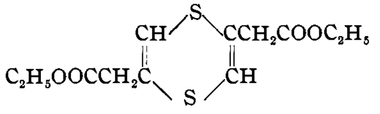
[1] *Ann.*, 261, 45.



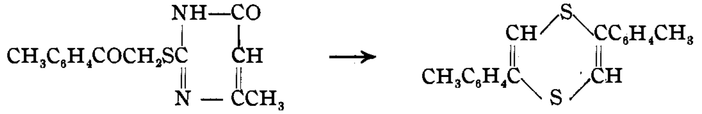
III X V

$CH_3CO{-}S\ CH_2.COCH_2.COOC_2H_5 \longrightarrow HSCH_2COCH_2COOC_2H_5 \longrightarrow$

XI XII

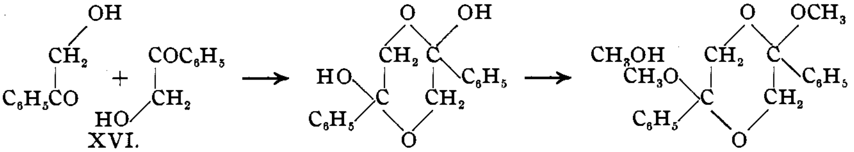


XIII



XIV XV

The acetal X, is the sulfur analogue of *bis*-benzoylcarbinol XVII, which Fischer[1] obtained in the form of its dimethyl ether XVIII, by heating benzoylcarbinol XVI, with methyl alcohol and hydrochloric acid. The corresponding diethyl ether has been prepared by Fritz.[2]



XVI. XVII. XVIII.

The most interesting and characteristic property of these dithienes, which we have so far observed, is that of halochromism. Both 2,5-diphenyl- and 2,5-ditolyl-1,4-dithienes are yellow but they dissolve at once in cold concentrated sulfuric acid giving most beautiful red-violet solutions. This is apparently due to the formation of colored salts. Colored combinations are also produced by the action of strong nitric acid and also by bromine in glacial acetic acid solution. In this respect the dithienes behave like the thianthrene compounds,[3] which have recently been carefully investigated by Fries and Volk.[4] They write as follows:[5] "unter den Eigenschaften der Thianthrene ist die hervorstechendste und merkwurdigste ihre Halochromie." The structural relationship between our dithienes XX, and *thianthrene* XIX, is apparent by inspection of the two structural formulas below:

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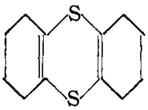
[1] *Ber.*, 28, 1161.

[2] *Ibid.*, 28, 3032.

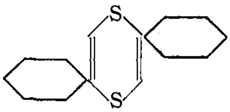
[3] Kraft and Lyons, *Ber.*, 29, 436; Genvresse, *Bull. soc. chim.* [3] 15, 409.

[4] *Ber.*, 42, 1170; *Ann.*, 381, 312.

[5] *Loc. cit.*



XIX.

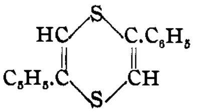


XX.

The investigation of dithienes will be continued in this laboratory.

Experimental Part.

2,5-Diphenyl-1, 4-Dithiene,



This cyclic sulfur compound is formed, together with 4-methyluracil, by hydrolysis of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine.[1]

The mercaptopyrimidine is suspended in about 20–25 parts by weight of concentrated hydrochloric acid and the mixture boiled on a sand bath for several hours. The pyrimidine slowly undergoes hydrolysis, the 4-methyluracil formed dissolves in the acid and the dithiene is obtained as a yellow oil. On cooling this immediately solidifies and generally melts at about 110° to a clear oil without decomposition. The yield of this substance is nearly quantitative. It was purified by crystallization from absolute alcohol and separated, on cooling, in characteristic, canary-yellow prisms, which melted at 118–119° to a transparent oil without decomposition. For analysis the dithiene was dried to constant weight in a desiccator over concentrated sulfuric acid.

I. 0.2691 gram substance gave 0.4645 gram $BaSO_4$ (Carius).

Calculated for $C_{16}H_{12}S_2$: S, 23.88. Found: 23.70.

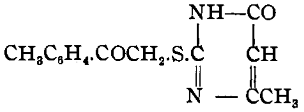
Molecular weight determination by the cryoscopic method:

I. 0.6743 gram substance in 10.71 grams C_6H_6 caused a depression in the freezing point of 1.194°.

Calculated for $C_{16}H_{12}S_2$: Molecular weight, 268. Found: 264.

2,5-Diphenyl-1,4-dithiene is very soluble in benzene, moderately soluble in alcohol and insoluble in water, hydrochloric acid and sodium hydroxide solution. It is especially characterized by its behavior towards concentrated sulfuric acid. It dissolves at once in this reagent (cold) giving a beautiful purple solution, which is immediately decolorized by dilution with water. The dithiene is extremely stable and is not desulfurized by digestion in alcoholic solution with silver nitrate, mercury oxide or lead acetate.

2-Paratoluylmethylmercapto-4-methyl-6-oxypyrimidine,



$$\begin{array}{rcl} & NH - & CO \\ & | & | \\ CH_3C_6H_4.COCH_2.S.C & & CH \\ \| & & \| \\ N & - & CCH_3 \end{array}$$

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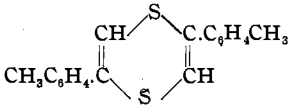
[1] Johnson and Moran, *loc. cit.*

This pyrimidine is easily prepared by suspending the sodium salt of 2-thio-4-methyl-6-oxypyrimidine[1] in absolute alcohol and then digesting with the required amount of *p*-chloracetyltoluene.[2] There was an immediate reaction with separation of sodium chloride and the solution was neutral to turmeric and blue litmus after heating only a short time. The sodium chloride was then separated and the filtrate concentrated and finally diluted with cold water. The pyrimidine then separated in a crystallin condition and was purified by crystallization from alcohol. It deposited, on cooling, in colorless, prismatic crystals, which melted at 194–195° to a brown oil without effervescence. The yield was 22 grams.

Analysis (Kjeldahl): Calculated for $C_{14}H_{14}O_2N_2S$: N, 10.21. Found: 10.4.

Hydrolysis of 2-Paratoluylmethylmercapto-4-methyl-6-oxypyrimidine with Hydrochloric Acid. 2,5-Ditolyl-1,4-Dithiene.



Ten grams of the mercapto pyrimidine were suspended in 150 cc. of 20% hydrochloric acid and the mixture then digested for 12 hours. The pyrimidine slowly underwent decomposition and the dithiene separated as a yellow oil. This immediately solidified on cooling and melted after one crystallization from 95% alcohol at 133–134° to a clear oil. It was purified for analysis by repeated crystallizations from alcohol and separated in yellow plates, which melted at 137–138° without decomposition. The yield was 4.9 grams or 88% of the theoretical. The dithiene is soluble in benzene and insoluble in water, but crystallizes from glacial acetic acid in yellow needles.

Subst., 0.1704, 0.1838; $BaSO_4$, 0.2644, 0.2845.

Calculated for $C_{18}H_{16}S_2$: S, 21.64. Found: S, 21.32 and 21.22.

Molecular weight determinations by the cryoscopic method:

I. 0.3280 gram substance in 11.67 grams C_6H_6 gave $\Delta = 0.500°$.
II. 0.5283 gram substance in 11.67 grams C_6H_6 gave $\Delta = 0.784°$.
III. 0.6520 gram substance in 11.67 grams C_6H_6 gave $\Delta = 0.961°$.

Calculated for $C_{18}H_{16}$: Molecular weight, 296. Found: Molecular weights, 281, 289, 291.

2,5-Ditolyl-1,4-dithiene is insoluble in hydrochloric acid and sodium hydroxide solution and is not desulfurized by digestion in alcohol with lead acetate, mercury chloride or silver nitrate. It gives Laubenheimer's reaction, and dissolves at once in cold concentrated sulfuric acid giving a very deep red solution. This color is immediately destroyed by dilution with a small amount of water. These color reactions with acids are very characteristic. When the dithiene is brought in contact with concentrated nitric acid there is an immediate reaction with forma-

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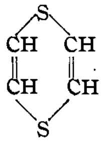
[1] List, *Ann*, 236, 12

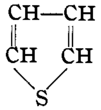
[2] Kunckell, *Ber.*, 30, 578; Ryan, *Ibid.*, 31, 2132; Collett, *Bull. soc. chim.*, [3] 17, 507.

tion of a deep red color, as in the case of sulfuric acid, but this gradually disappears and an orange colored substance finally deposits. This is probably a nitro-derivative and is practically insoluble in alcohol, water and glacial acetic acid, but crystallizes from benzene in yellow needles. The dithiene also reacts immediately with bromine. If some of the sulfur compound is dissolved in glacial acetic acid and a drop of bromine is then added, the solution assumes at once a beautiful, dark blue color. This slowly disappears, however, and a dark colored product finally deposits from the acid solution. These interesting reactions will be investigated later.

Addenda.

1,4-Dithiene VI, corresponding to thiophene XXI, and the mother


VI.


XXI.

substance of 2,5-diphenyl- and 2,5-ditolyl-1,4-dithienes, is not described in Beilstein's Handbuch nor in Richter's Lexikon der Kohlenstoff Verbindungen. A careful search of the literature, however, has revealed the fact that this interesting compound was synthesized in 1889 by Louis E. Levi.[1] He prepared it by heating phosphorus trisulfide with thiodiglycollic acid, $S(CH_2COOH)_2$ and described it as an oil, which boiled at 175–180°. The yield, however, was very small. Levi assigned the name *biophene* to this substance. He also applied Freidel and Craft's reaction successfully and obtained the corresponding acetyl- and benzoyl-derivatives. Both of these compounds were oils. The acetylbiophene was identified in the form of its phenylhydrazone, which melted at 128°. Benzoylbiophene boiled at 241° and underwent nitration giving a crystallin mononitro-derivative melting at 112°. Dr. Levi writes me that this work on *biophene* originated in the laboratory of Professor Dr. Victor Meyer, Göttingen, while he was employed as Professor Meyer's private assistant.

NEW HAVEN, CONN.

AN IMPROVED APPARATUS FOR THE DETERMINATION OF CARBOXYL GROUPS IN ORGANIC ACIDS.[2]

BY W. H. HUNTER AND J. D. EDWARDS.

Received January 31, 1913.

Fritz Fuchs[3] has described a very simple and neat method for the determination of carboxyl groups, which depends on the fact that even

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[1] *Technol. Quarterly*, 3, No. 2; *Chem. News*, 62, 216; *Centrabl.*, 2, 949 (1890).

[2] Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[3] *Monatsh.*, 9, 1132, 1143 (1888); 11, 363 (1890).