

drochloric acid ( $b - 2a$ ); therefore the reaction does not take place between free amine and nitrous acid.

2. It must be concluded, especially from the results with small concentrations of hydrochloric acid, that the reaction proceeds between the salt of the amine (*pentavalent* nitrogen) and nitrous acid.

3. No agreement has been obtained with the

*calculated* velocity for this case. Mostly the influence is much more than can be accounted for by decreasing hydrolysis of the salt of the amine.

4. The excess of hydrochloric acid increases the velocity of diazotization for all the amines which were investigated, by (1) decreasing hydrolysis of the salt of the amine; and (2) a specific action.

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

## The Preparation of 1,4-Dithienes

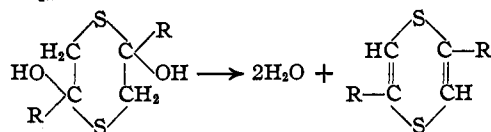
BY ROBERT H. BAKER AND CHARLES BARKENBUS

The preparation and chemistry of compounds containing the 1,4-dithiene ring structure have never been thoroughly investigated. Steude,<sup>1</sup> prepared this type of ring structure by hydrolyzing ethyl thioacetoacetate. The yields of 2,5-dicarbethoxymethyl-1,4-dithiene were very small, and though attempts to improve the yields were made, no successful method was discovered. Tcherniac<sup>2</sup> obtained 2,5-dimethyl-1,4-dithiene as a by-product in the hydrolysis of thiocyanacetone while Levi<sup>3</sup> synthesized 1,4-dithiene, the mother substance of this series, by heating thiodiglycolic acid with phosphorus trisulfide though again the yields were very small. Johnson<sup>4</sup> by hydrolyzing 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine obtained 2,5-diphenyl-1,4-dithiene instead of the expected phenacyl mercaptan. Groth<sup>5</sup> by the hydrolysis of phenacyl-dithiocarbaminoacetic acid prepared for the first time a  $\beta$ -ketomercaptan, namely, phenacyl mercaptan, and condensed this to 2,5-diphenyl-1,4-dithiene though no yields were given.

Our knowledge of the chemistry of this type of ring structure is practically non-existent. Levi was able to show that the Friedel and Crafts reaction is possible with 1,4-dithiene, while Johnson and co-workers nitrated 2,5-diphenyl-1,4-dithiene although the nature of the product obtained was not investigated. Groth has also shown that 2,5-diphenyl-1,4-dithiene will form addition products with phenacyl mercaptan. Apparently a

characteristic reaction for this type of ring structure is the intense red color produced when these compounds are dissolved in concentrated sulfuric acid, the color disappearing upon dilution.

The literature indicates that the most logical approach to this type of structure is through the condensation of  $\beta$ -keto mercaptans and the purpose of this work was to investigate the effect of different groups on this condensation. The condensation can be pictured as taking place according to the following equation although condensation through enolization would lead to the same product.



It has been observed that R must be an aryl group if ring formation as shown above is to take place to any extent. Preliminary work has indicated that if R is a methyl group other types of condensation take place in a manner similar to the condensation of acetone to mesityl oxide and phorone.

Phenacyl mercaptan, described by Groth, is the only  $\beta$ -keto mercaptan described in the literature and the method of synthesis is far from practical. It is an unstable oil which readily undergoes further changes when exposed to the air. The most direct method of preparation would be the action of sodium acid sulfide on  $\beta$ -keto halides but this procedure gives the sulfides as the main product.<sup>6</sup>

(1) Steude, *Ann.*, **261**, 45 (1891).

(2) Tcherniac, *J. Chem. Soc.*, **115**, 1071 (1919).

(3) Levi, *Chem. News*, **62**, 216 (1890).

(4) Johnson, Moran and Kohmann, *THIS JOURNAL*, **35**, 447 (1913).

(5) Groth, *Arkiv. Kemi. Mineral. Geol.*, **9**, No. 1, 63 (1924).

(6) Tafel and Mauritz, *Ber.*, **23**, 3474 (1890).

Of the many other methods investigated the most promising was the hydrolysis of the so-called Bunte salts.<sup>7</sup>

These salts can be readily prepared by the action of sodium thiosulfate on  $\beta$ -keto halides and, when subjected to acid hydrolysis, give the mercaptans. In our work the labile mercaptans were never isolated since the acid hydrolytic agent also acted as a condensation agent. Recently, phenacyl mercaptan has been prepared by this method though it was not used in the synthesis of dithienes.<sup>8</sup> The nature of the aryl group attached to the carbonyl group of the intermediate mercaptan seems to have very little effect. When R was a phenyl, *m*-nitrophenyl or  $\beta$ -naphthyl group the yields of the corresponding dithienes were approximately the same. Substitution on the  $\alpha$ -carbon, however, made the condensation much more difficult,  $\alpha$ -methyl phenacyl mercaptan giving a very small yield of the dithiene while desyl mercaptan did not condense in this manner at all.

A summary of the experimental results is given in Tables I and II.

TABLE I

PREPARATION OF  $\beta$ -KETO ALKYL SODIUM THIOSULFATES

Chloride	Source	Thiosulfate	% yield from		% sulfur	
			0.05 M	Anal.	Calcd.	Calcd.
Phenacyl	a	C <sub>8</sub> H <sub>7</sub> O <sub>4</sub> S <sub>2</sub> Na-H <sub>2</sub> O	91	23.70	23.60	
<i>m</i> -Nitrophenacyl	b	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub> NS <sub>2</sub> Na	89	21.26	21.43	
$\beta$ -Naphthacyl	c	C <sub>12</sub> H <sub>9</sub> O <sub>4</sub> S <sub>2</sub> Na	46	21.22	21.08	
$\alpha$ -Methylphenacyl		C <sub>9</sub> H <sub>9</sub> O <sub>4</sub> S <sub>2</sub> Na-H <sub>2</sub> O	87	22.20	22.39	
Desyl	d	C <sub>14</sub> H <sub>11</sub> O <sub>4</sub> S <sub>2</sub> Na	22	19.35	19.42	
Acetonyl	e	C <sub>8</sub> H <sub>7</sub> O <sub>4</sub> S <sub>2</sub> Na-3H <sub>2</sub> O	83	26.10	26.05	

<sup>a</sup> Adams and Marvel, "Organic Chemical Reagents," Vol. III, p. 54, University of Illinois Bulletin XIX, No. 6 (1921). <sup>b</sup> Barkenbus and Clements, THIS JOURNAL, 56, 1369 (1934). <sup>c</sup> Morgan and Stanley, *J. Soc. Chem. Ind.*, 44, 493-6T (1925). <sup>d</sup> "Organic Syntheses," John Wiley and Sons, Inc., 440 Fourth Ave., New York City, 1932, Vol. XII, 1932, p. 20. <sup>e</sup> Adams and Marvel, "Organic Chemical Reagents," Vol. III, p. 56, University of Illinois Bulletin XIX, No. 6 (1921).

TABLE II

## PREPARATION OF THE 1,4-DITHIENES

Dithiene	Yield, %	M. p., °C.	Mol. wt. (Rast)		% sulfur	
			Found	Calcd.	Found	Calcd.
2,5-Diphenyl	74	115-117	289	268		
2,5-Di- <i>m</i> -nitrophenyl	69	220-222	362	358	17.87	17.90
2,5-Di- $\beta$ -naphthyl	59	198-200	372	368	17.12	17.41
2,5-Diphenyl-3,6-dimethyl	11	135-138	255	296	21.61	21.65

(7) Bunte, *Ber.*, 7, 646 (1874); R. H. Baker, Thesis, University of Kentucky, 1931.

(8) Kretov, Panchenko and Konovalchik, *J. Gen. Chem.* (U. S. S. R.), 1, 396 (1931); *C. A.*, 26, 2442 (1932).

## Experimental

**Preparation of  $\alpha$ -Chloropropiophenone.**—One hundred and sixteen grams of anhydrous aluminum chloride and 780 cc. of benzene were placed in a three-necked flask equipped with a condenser, stirrer and dropping funnel. One hundred and eight grams of  $\alpha$ -chloropropionyl chloride, prepared from  $\alpha$ -chloropropionic acid and thionyl chloride, was slowly dropped in. The reaction mixture was heated for five hours, cooled, 125 cc. of concd. hydrochloric acid added, and the benzene layer separated. This was washed and dried and distilled. The oily layer left distilled between 135-150° at 30 mm. On redistillation practically all of the material distilled at 131-133° at 26 mm.; wt. 112 g. (66.4%).

**Preparation of Sodium Phenacyl Thiosulfate.**—Seven and seven-tenths grams of phenacyl chloride, 12.5 g. of sodium thiosulfate and 15 cc. of water were heated at 60° and stirred rapidly for thirty minutes. Upon cooling in ice water, the clear solution yielded crystals which were pressed between filter paper and recrystallized from alcohol. After drying in air for two days the yield of the monohydrated salt was 13.4 g. Desiccation over phosphorus pentoxide in vacuum for eight days produced the anhydrous salt, which is extremely hygroscopic.  $\beta$ -Naphthacyl and *m*-nitrophenacyl sodium thiosulfates were prepared in a similar manner except that a temperature of 100° was used, while the acetonyl derivative required room temperature. In the preparation of the desyl and  $\alpha$ -methylphenacyl derivatives it was found advantageous to use dilute alcohol as the solvent and to heat on a steam-bath for one hour. These salts were obtained by evaporation of the solvent under diminished pressure at 40° and purified by repeatedly throwing them out of alcohol solution with ether.

**Preparation of 2,5-Diphenyl-1,4-dithiene.**—A water solution of sodium phenacyl thiosulfate prepared from 7.7 g. of phenacyl chloride as described above was treated with 15 cc. of alcohol and 30 cc. of concd. hydrochloric acid. The mixture was refluxed and stirred for four hours and then allowed to cool until the red oil had solidified. The salt was removed by washing with water and the dithiene dissolved in 40 cc. of glacial acetic acid. The solution was bone-coated, filtered hot and allowed to cool. Two crops of crystals weighing 5 g. and melting at 115-117° were obtained, yield 74%.

While this method of condensation was applicable to the preparation of the other dithienes, better yields were obtained by treating boiling absolute alcohol suspensions of the thiosulfates with anhydrous hydrogen chloride for a period of five hours. For isolation, the salt was removed by filtering hot and the dithiene allowed to crystallize. An attempt to better the yield of the diphenyl-dimethyl derivative by suspending the salt in absolute alcohol, saturating this with hydrogen chloride in the cold, and then heating in a sealed tube at 170° for five hours was without avail. Condensation in sulfuric acid also failed to increase the yield. Acetonyl and desyl sodium thiosulfates failed to yield the expected dithienes, the former giving a foul-smelling oil which boiled at 77-78° at 5 mm. and contained 40.8% sulfur, while the latter gave vanishing quantities of a white crystalline compound which melted at 184.5-185° and contained 9.33% sulfur.

**Summary**

A convenient method for preparing aryl substituted 1,4-dithienes by the acid hydrolysis of  $\beta$ -keto alkyl sodium thiosulfates has been estab-

lished. The effect of substitution of different groups and their position on the yields obtained by this method has been investigated.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

**Hydroxy Furans. I. Beta Hydroxy Triphenylfuran**

BY E. P. KOHLER, F. H. WESTHEIMER AND M. TISHLER

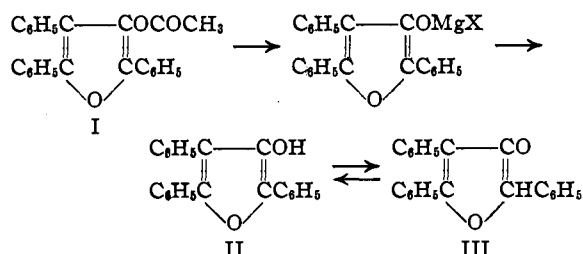
Hydroxy furans, though of considerable interest in connection with the recurrent idea that furan is aromatic in character, appear to be completely unknown. Dihydrofuran derivatives which might pass into  $\alpha$ -hydroxy furans by enolization and acyl derivatives from which  $\beta$ -hydroxy furans might be formed by hydrolysis have been in hand for many years but the former are not known to enolize and the latter have not been hydrolyzed successfully. Thiele<sup>1</sup> treated the acetate of  $\beta$ -hydroxy triphenylfuran with alcoholic potassium hydroxide but reported only that the product was a substance which was soluble in alkalis and which appeared to be a transformation product of the hydroxy furan.

On repeating Thiele's experiment we found that when the acetate is treated in the usual manner with acids or bases hydrolysis is accompanied by oxidation and the products bear no simple relation to the parent compound. By hydrolyzing with acids in an atmosphere of nitrogen, however, it was possible to secure a solution which manifestly contained the hydroxy furan because it decolorized bromine instantaneously and absorbed oxygen from the air. When this solution was saturated with oxygen it deposited a sparingly soluble, crystalline peroxide—a reaction which was employed to detect the presence of the hydroxy furan.

By appropriate manipulation of the solutions obtained by hydrolyzing the acetate with acids it is possible to isolate a crystalline solid which has the composition of the hydroxy furan. This solid is, doubtless, the furanone formed from the hydroxyl compound by ketonization, because the solutions from which it has been separated as completely as possible still form peroxide rapidly and in quantities far in excess of any that can be obtained from saturated solutions of the solid.

Moreover, solutions of the solid form peroxide much more slowly than those obtained from the acetate.

These relations indicate that the change from the acetate to the solid product occurs in two steps—hydrolysis and ketonization. These steps can be separated by treating the acetate with a Grignard reagent and cautiously acidifying the product with a mineral acid. The Grignard reagent converts the acetate quantitatively into a magnesium halide derivative of the hydroxy furan and the concentrated solution that is obtained by acidification in the presence of ether cannot contain more than minimal quantities of the keto form because it does not respond to inoculation until it has been left for several hours in the presence of acids. The successive steps in the process must, therefore, be represented as follows



The relations between the keto and hydroxyl forms is the same as that of open chained keto-enol tautomers but, for various reasons, it is difficult to determine the relative quantities of the two substances in equilibrium. Direct titration with bromine is not feasible because solutions of the resulting bromo compound are deep yellow in color and the results of indirect titrations are vitiated by the unavoidable formation of peroxide.

The peroxide appears to be constituted like the crystalline compounds which are formed by the autoxidation of the enolic modifications of mono ketones. Like these other peroxides it is easily

(1) Thiele, *Ber.*, **31**, 1249 (1898).