

TABLE IV

PREPARATIONAL DATA, PHYSICAL CONSTANTS AND ANALYSES OF SELENIUM DIBROMIDES

| Ethers used | Product, selenium dibromide | M. p., °C. | Yield, % |
|---------------------------|---------------------------------|------------|----------|
| 1 Anisole | Bis-(<i>p</i> -methoxyphenyl)- | 125 | 76 |
| 2 Phenetole | Bis-(<i>p</i> -ethoxyphenyl)- | 117 | 80 |
| 3 Propylphenyl | Bis-(<i>p</i> -propoxyphenyl)- | 69 | 77 |
| 4 Butylphenyl | Bis-(<i>p</i> -butoxyphenyl)- | 65 | 60 |
| 5 Diphenyl | Bis-(<i>p</i> -phenoxyphenyl)- | 113 | 85 |
| 6 <i>o</i> -Bromoanisole | Bis-(3-bromo-4-methoxyphenyl)- | 87 | 80 |
| 7 <i>o</i> -Methyl cresyl | Bis-(3-methyl-4-methoxyphenyl)- | 136 | 63 |

| | Formulas | Bromine, % | |
|---|--|------------|-------|
| | | Calcd. | Found |
| 1 | (CH ₃ OC ₆ H ₄) ₂ SeBr ₂ | 35.3 | 35.8 |
| 2 | (C ₂ H ₅ OC ₆ H ₄) ₂ SeBr ₂ | 33.2 | 32.4 |
| 3 | (C ₃ H ₇ OC ₆ H ₄) ₂ SeBr ₂ | 31.4 | 31.8 |
| 4 | (C ₄ H ₉ OC ₆ H ₄) ₂ SeBr ₂ | 29.8 | 29.7 |
| 5 | (C ₆ H ₅ OC ₆ H ₄) ₂ SeBr ₂ | 27.7 | 27.3 |
| 6 | (CH ₃ OC ₆ H ₃ Br) ₂ SeBr ₂ | 52.2 | 51.9 |
| 7 | (CH ₃ OC ₆ H ₃ CH ₃) ₂ SeBr ₂ | 33.2 | 33.5 |

Summary

1. The reaction between selenium oxychloride and certain ethers has been studied in which two molecules of the ether condensed with one molecule of selenium oxychloride.

2. The action of alkali on the resulting selenium dichlorides produces selenium dihydroxides.

3. The reduction of the selenium dichlorides by zinc gives selenides.

4. The selenides readily add bromine, forming selenium dibromides.

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

REACTIONS OF CARBON DISULFIDE. II.¹

REACTION WITH ACETONE

By E. WERTHEIM

RECEIVED JULY 3, 1931

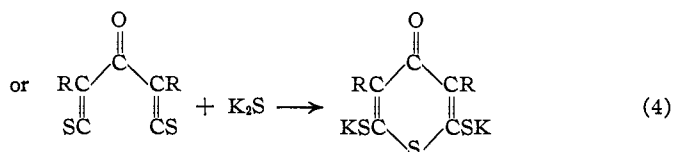
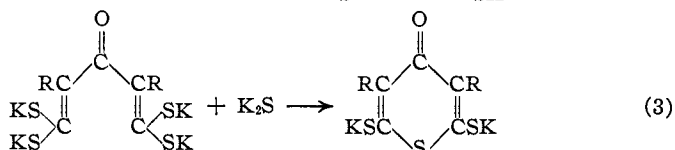
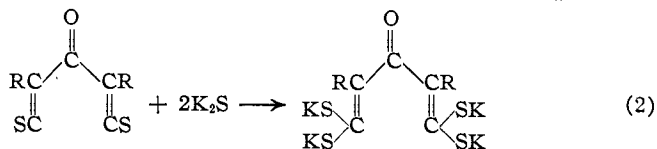
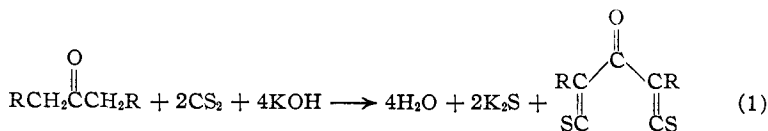
PUBLISHED NOVEMBER 5, 1931

The reaction of carbon disulfide with ketones has been a subject of investigation since the discovery of the desaurins by Victor Meyer.² During 1904 and later years Apitzsch³ studied the reaction between various aromatic and aliphatic ketones of the type RCH₂(C=O)CH₂R with carbon disulfide in the presence of solid potassium hydroxide. In this way he secured derivatives of 1,4-thiopyrone, which were supposed to be formed as indicated in the following series of equations

¹ Paper No. 245, Journal Series, University of Arkansas.

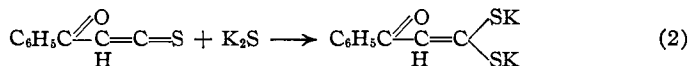
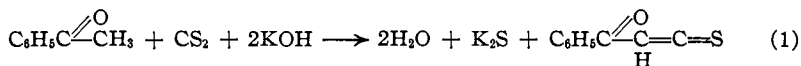
² Meyer, *Ber.*, **21**, 353 (1888); **23**, 1571 (1890); **24**, 3535 (1891); **25**, 1727, 2239 (1892).

³ Apitzsch, *ibid.*, **37**, 1599 (1904); **38**, 2888 (1905); **41**, 4028 (1908).



Apitzsch, however, was unable to isolate either a final or intermediate product from the reaction of acetone, carbon disulfide and potassium hydroxide, though he states that this reaction without doubt takes the same course as observed with the other ketones used in his work.

Kelber, working with acetophenone, carbon disulfide and solid potassium hydroxide, obtained the acid $\text{C}_6\text{H}_5\text{OS}_2$.⁴ This could, conceivably, have been formed in the same manner as shown above, *i. e.*



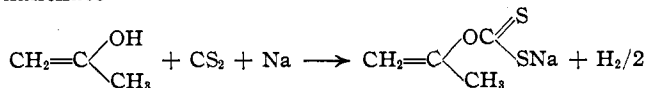
The production of this compound gives support to equation (2) proposed by Apitzsch; however, the intermediate "thioketene" compound was not isolated in this work, and neither of these researches demonstrated whether such a compound is capable of existence.

The writer repeated the work of Apitzsch, in which acetone was treated with solid potassium hydroxide and carbon disulfide. There was evidence of the production of an acidic sulfur compound, but it proved impossible of isolation. The results indicated that a small amount of mesityl oxide was also produced in the reaction.

The reaction of acetone with carbon disulfide in the presence of metallic sodium was then reinvestigated. It proved to be very complex, and

⁴ Kelber, *Ber.*, **43**, 1252 (1910).

productive of a number of compounds. It was expected⁵ that acetone would react in its enol form with the carbon disulfide to give sodium isopropenyl xanthate



However the amount of hydrogen released in the early experiments appeared to be only 50 to 60% of the quantity required by theory. This observation apparently accorded with the work of Freer,⁶ who, carrying out the reaction of sodium with acetone in xylene in varying dilutions, obtained a maximum yield of hydrogen amounting to 62.7% when the acetone was diluted with 100 volumes of xylene. Among other products Freer secured acetone-sodium, and sodium isopropylate. A careful search for isopropyl alcohol in the present instance failed to reveal any of it, and later experiments, in which a more nearly perfect apparatus was used to collect the hydrogen, showed that the full amount required by theory was evolved, none being used for reduction.⁷ Freer found that the amount of hydrogen evolved increased with increasing dilution of acetone with xylene; therefore, since the concentration of acetone in carbon disulfide (considering the latter merely as solvent) was higher in this work than that employed by Freer, these experiments show a decided difference in the action of sodium upon acetone with a change of solvent from xylene to carbon disulfide.⁸ The mixture of sodium, acetone and carbon disulfide assumed the red color characteristic of trithiocarbonate solutions⁹ in about five minutes, and soon deposited a red-brown solid. About 25% of the theoretical amount of hydrogen was liberated in the first ten to fifteen minutes; after about forty-five minutes the evolution of gas became very slow; the reaction was entirely completed in about fifty-three hours.

The precipitated solid was a mixture of sodium salts. It consisted largely of sodium trithiocarbonate. This salt was isolated and analyzed. Also, in experiments in which the mixture of salts was treated with methyl iodide, methyl trithiocarbonate was isolated. The addition of benzoyl chloride to the filtrate from the sodium salt mixture produced a red compound which proved to be the benzoyl derivative of acetone-1,3-bis-carbithio acid (thiono-thiol acid). The corresponding methyl derivative was prepared from the above benzoyl compound.

⁵ Wertheim, *Science*, **58**, 494 (1923).

⁶ Freer, *Am. Chem. J.*, **15**, 586 (1893).

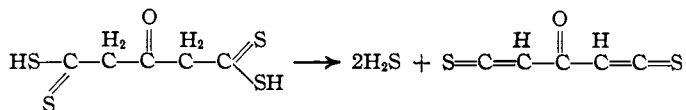
⁷ In experiments in which the reaction mixture was allowed to become hot in the early stages, there was an *extremely* small yield of isopropyl alcohol (secured as methyl isopropyl xanthate).

⁸ See work of Norris and Prentiss on adjuvance, *THIS JOURNAL*, **50**, 3042 (1928).

⁹ O'Donoghue and Kahan, *J. Chem. Soc.*, **89**, 1813 (1906); Yeoman, *ibid.*, **119**, 41, 51 (1921).

When the filtrate was acidified in order to prepare the free carbithio acid, a salmon-colored compound resulted which soon became black. This was probably the free carbithio acid. It had a strong and characteristic odor and produced black stains upon the skin; both of these properties are noted in carbithio acids.¹⁰

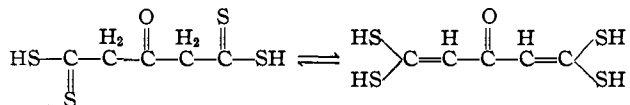
The compound easily lost hydrogen sulfide, either when suspended in water or when heated. That which was kept cool and quickly dried and analyzed showed a sulfur percentage of about 50 to 58% (the theoretical value for the carbithio acid is 60.95%). If the compound had stood for some time, or had been heated, the percentage of sulfur fell to lower values, finally to that required for bis-thiocarbonyl acetone



The bis-thiocarbonyl acetone, which corresponds to the intermediate compound posited by Apitzsch and Kelber, is a black, amorphous substance resembling carbon, devoid of odor. Due to its slight solubility the compound could not be completely purified, and the analytical results secured were not perfect. The silver salt was obtained by the action of silver nitrate upon a sample which had been heated until the transformation shown above was nearly but not quite complete. Under these conditions it was slightly soluble in ammonium hydroxide solution and gave a small yield of silver salt.

An attempt was made to secure the carbithio acid in purer form by the hydrolysis of the benzoyl derivative. Upon acidification of the alkaline solution resulting from the hydrolysis the salmon-colored precipitate was obtained having properties identical with those described above. Analysis for carbon, hydrogen and sulfur gave values intermediate between those required for the carbithio acid and for thiocarbonyl acetone. The decomposition of the carbithio acid with loss of hydrogen sulfide could not be prevented.

There is a possibility of a tautomerism between the carbithio acid and a tetramercapto compound analogous to those discussed by Apitzsch and Kelber



However, the evidence at hand indicates that if this tautomerization takes place, the equilibrium point lies far to the left under the experimental

¹⁰ The compound is an effective dye for silk and wool, dyeing a beautiful light tan color, which seems to be permanent and fast. See Meyer's work on dyeing possibilities of desaurin, *Ber.*, 21, 353 (1888).

conditions maintained. Thus the benzoyl derivative easily formed a di-silver salt. Also the physical properties of the free acid are not at all similar to those of the derivative made by Kelber, while resembling those of an aliphatic carbithio acid.¹¹

There was no evidence in this work of the formation of a thiopyrone compound as suggested in equation (3) of Apitzsch.

As Freer has shown¹² that sodium and acetone react to produce acetone-sodium and hydrogen, an attempt was made to form isopropenyl xanthates from the reaction of acetone-sodium and carbon disulfide. Apparently three or more sulfur-containing compounds were formed in this reaction (as well as high-boiling oxygen compounds and mesityl oxide, as noted by Freer). A very small yield of methyl isopropyl xanthate was secured (after reaction with methyl iodide), somewhat contaminated with mesityl oxide (b. p. 167-70°; n_D^{20} 1.5175; S, 32.04%). None of the other sulfur-containing compounds could be positively identified on account of the impossibility of obtaining a sharp separation of the mixture by fractional distillation. A detailed report of these experiments is accordingly omitted from this paper.

When acetone was treated with solid potassium hydroxide and the resulting salt allowed to react with carbon disulfide in an attempt to form potassium isopropenyl xanthate, potassium trithiocarbonate was formed. This action took place even when precautions were taken to exclude moisture. It was later found that mesityl oxide was formed in this reaction in small yield; the efforts made to exclude water were on this account futile. The trace of water introduced by the formation of mesityl oxide evidently sufficed to initiate the reaction



which, in its turn, added more water to the reacting materials, thus promoting the formation of trithiocarbonic acid in good yield.¹³

The writer's original assumption that isopropenyl xanthates would result from the reaction of carbon disulfide with acetone still lacks a positive confirmation. Substances were isolated in this work which appeared to be derivatives of isopropenyl xanthic acid, but the amounts at hand were too

¹¹ See Houben, *Ber.*, **35**, 3696 (1902); **39**, 3225 (1906); **40**, 1306, 1727 (1907). Other compounds of the free acid were prepared (di-sodium salt, dimethyl ester), which are not reported herein as they could not be completely rid of other unknown compounds produced in the reactions. Their analysis and physical properties render quite certain the conclusion that they are di-derivatives. Attempts to prepare tetra-substituted esters invariably produced the di-esters.

¹² Freer, *Am. Chem. J.*, **15**, 592 (1893).

¹³ This experiment confirms the work of Nasini and Scala [*Ber.*, **20**, R707 (1887)], who reported that a mixture of sodium amalgam and carefully dried carbon disulfide and ethyl iodide failed to react, while in the presence of moisture ethyl trithiocarbonate was produced.

small to afford a definite indication of structure. Research on the subject will be continued in this Laboratory.

Experimental Part

s-Methylisopropyl-xanthate.—This compound is not fully reported in the literature. It was therefore prepared in order to compare its constants with those of compounds produced in the reaction being studied. Twenty-three and one-half grams of potassium hydroxide was dissolved in 25 g. of isopropyl alcohol (b. p., 79.9–82°) with the gradual addition of 57 g. of carbon disulfide. The resulting crystals were washed on the filter with acetone, then with ether. The dry salt was pink-white, 43 g. This was gently heated under a reflux condenser with 40 cc. of methyl alcohol and 59 g. of methyl iodide. The resulting mixture was filtered, and the crystalline precipitate was washed on the filter with ether. The dried filtrate gave, after several distillations, 6.1 g. of yellow oil, b. p. 65–68° (5 mm.); 86–89° (25 mm.); 175–177° (729 mm.); n_D^{21} 1.5372; d_4^{20} 1.0777.

Anal. Calcd. for $C_6H_{10}OS_2$: S, 42.67. Found: 42.44, 42.37, 42.68. *Mol. wt.* (Menzies' method, ether as solvent). Calcd. for $C_6H_{10}OS_2$: 150. Found: 165.5.

Reaction of Carbon Disulfide, Acetone and Metallic Sodium

In a typical experiment 6 g. of sodium was melted under xylene and broken into fine granules. After removal of the xylene by decantation, these were washed with dry ether and covered with a mixture of 60 g. each of acetone and carbon disulfide. The flask was placed under a reflux condenser. The mass within the flask was broken up at daily intervals. At the end of a week dry ether was added to cause the precipitation of salts dissolved in the excess acetone. The mixture was then filtered. The filtrate (A) was reserved for further treatment. About 15 g. of yellow-orange salt was obtained. This "mixed sodium salt" was used in the experiments described below.

Measurement of Evolved Hydrogen.—Amounts of sodium ranging from one to three grams were brought into reaction with acetone and carbon disulfide in the proportions shown above. The escaping gas was passed through three wash bottles, two containing xylene, another concentrated sulfuric acid and was then collected over xylene. The average yield of gas in several such experiments was 98.2%. Appropriate tests showed that the gas was hydrogen, free of any trace of hydrogen sulfide.

Separation of Sodium Trithiocarbonate.—Forty grams of the "mixed sodium salts" was dissolved in absolute alcohol; the solution was then filtered. Ether and acetone were added until maximum precipitation had occurred, when the precipitated salt was removed by filtration and transferred to an apparatus in which it was again dissolved in absolute alcohol and precipitated with dry ether in the absence of air. The dried salt weighed 6 g.; estimated yield about 12 g. (losses occurred during the transfer of the salt, also some impure salt was rejected in the filtrates). It was a light yellow powder, which quickly became red when exposed to air and moisture.

Anal. Calcd. for CS_2Na_2 : Na, 29.87. Found: Na, 29.60.

Monobenzoyl Derivative of Acetone-bis-carbithio Acid.—The filtrate (A) of a typical experiment (see above) was treated with 35 g. of benzoyl chloride. After the first reaction had subsided, the mixture was warmed and allowed to stand for twenty-four hours. The scarlet-colored precipitate was removed by filtration and purified by crystallization from xylene as yellow-orange needles, m. p. 155–156°, with preliminary shrinking; wt., about 3.5 g.; soluble in the common organic solvents; only sparingly soluble in petroleum ether. It dissolves in concentrated sulfuric acid to give a pale yellow solution.

Anal. Calcd. for $C_{12}H_{10}O_2S_4$: C, 45.87; H, 3.19; S, 40.76; mol. wt., 314. Found: C, 46.32, 46.23; H, 3.20, 3.19; S, 40.46, 40.87; mol. wt., 312.5.

Silver Salt.—Two grams of the benzoyl derivative (see above) was dissolved in a large excess of acetic acid. To the hot, filtered solution was added 2.2 g. of silver nitrate in 5 cc. of water. The resulting amorphous precipitate was washed with acetic acid and with water, then dried. When dry the salt had an orange color.

Anal. Calcd. for $C_{12}H_8O_2S_4Ag_2$: Ag, 40.92. Found: Ag, 41.15.

Methyl Ether of Acetone-bis-carbithio Acid (Enol Form).—Two and seven-tenths grams of the benzoyl derivative (see above) was treated with 0.4 g. of sodium in methyl alcohol solution. The benzoyl compound dissolved at once, giving a dark-colored solution which soon took the odor of methyl benzoate. Five grams of methyl iodide was added, and the mixture set aside for six hours. The red precipitate which had collected was removed by filtration and purified by recrystallization from a mixture of acetone and ethanol; wt., 0.9 g.; dark red, amorphous powder; m. p. 150–151°.

Anal. Calcd. for $C_8H_8OS_4$: C, 32.14; H, 3.57; S, 57.15; mol. wt., 224. Found: C, 32.02, 32.48; H, 3.45, 3.90; S, 56.66; mol. wt., 215.9.

The filtrate (A) described above gave evidence of containing a small amount of mesityl oxide. This was identified by its odor, boiling point, its index of refraction and its reaction with phenylhydrazine.

Acetone-1,3-bis-carbithio Acid. Transformation to 1,3-Bis-thiocarbonyl Acetone.—The filtrate (A) from a typical experiment was treated with dry ether to precipitate dissolved salt, filtered, allowed to stand for eighteen hours and again filtered. The ether and other low-boiling liquids were removed by evaporation at reduced pressure. The odorless liquid residue was treated with sodium hydroxide solution and twice extracted with ether. Remaining ether was again removed by evaporation as above. To the chilled aqueous solution acetic acid was added until its odor was noticeable. Hydrogen sulfide was freely evolved, and a black scum appeared, which was removed. After a lapse of thirty minutes (time allowed for the decomposition of trithiocarbonic acid), concentrated hydrochloric acid was added. A salmon-colored precipitate appeared, which quickly became purple-black during filtration.¹⁴ The dried solid was sometimes dark brown, but usually the surface was nearly black; wt., about 3.5 g.; m. p. of various samples was 84–85°, 82–84°, 83–84°. This compound had a disagreeable, fecal odor. It was very soluble in alcohol, acetone, ether, benzene, pyridine, chloroform; insoluble in water or petroleum ether.

Anal. Calcd. for $C_8H_8OS_4$: S, 60.95. Found: S, 57.77, 57.22, 56.25, 54.06.

The higher percentages of sulfur represent compounds which were dried and analyzed as quickly as possible. In experiments in which the acetic acid solution was left for three hours before adding concentrated hydrochloric acid, the precipitate secured was almost black.

Anal. Found: S, 46.50, 46.30, 45.95.

When the acetic acid solution was left for some hours and treated from time to time with small amounts of hydrochloric acid, a black, nearly odorless gum was obtained. This was much less soluble in the solvents noted above than the compounds of higher sulfur percentage. The gum, after a number of washings with hot solvents, yielded a black, amorphous compound; wt., about 2 g.; no definite melting point, but decomposes at about 200°; very slightly soluble in hot pyridine or hot nitrobenzene; soluble in

¹⁴ The compound at times precipitated as a dark-colored oil, which quickly solidified.

cold, concentrated sulfuric acid. When the compound was heated in air, the odor of sulfur dioxide was noted at once. This substance was also produced from the "mixed sodium salt" by a treatment somewhat similar to that given here (temperature of decomposition, about 170°; 1.7 g. from 20 g. of sodium salt). The analyses were made on samples from both sources.

Anal. Calcd. for $C_6H_2OS_2$: C, 42.26; H, 1.41; S, 45.07. Found: C, 43.05, 41.50; H, 1.02, 1.37; S, 45.36, 45.35, 45.02, 44.85.

Thiocarbonyl acetone was also made as follows: the compound melting at 84–85° was dissolved in hot pyridine, and, after filtration of the solution, again precipitated by the addition of hydrochloric acid. After the resulting precipitate had been washed and dried, it was heated in nitrobenzene at 170–180° for several hours, until all hydrogen sulfide had been driven off. Last traces of nitrobenzene were removed by washing with hot alcohol. It was not feasible to recrystallize the compound and complete purity was not attained, as is indicated in the analysis for carbon, above.

Silver Salt.—A portion of the acetone-bis-carbithio acid which had been largely transformed to thiocarbonyl acetone (S content, 50.06%) was dissolved in warm ammonium hydroxide solution. In one hour the solution was filtered, and treated with silver nitrate solution. The dry salt was black.

Anal. Calcd. for C_6HOS_2Ag : Ag, 43.37. Found: Ag, 43.55.

Methyl Trithiocarbonate

From Reaction of "Mixed Sodium Salt" with Methyl Iodide.—Twenty-five grams of sodium salts obtained from the reaction of carbon disulfide, acetone and sodium, was mixed with 35 cc. of methyl alcohol and 50 g. of methyl iodide. The mixture was refluxed for a short time. Ether was then added and the mixture was well washed with several changes of water. The dried ether layer gave, upon distillation, 6.3 g. of maroon liquid, b. p. 95–98° (10 mm.). Upon redistillation the compound was secured with b. p. 88–91° (5 mm.) (Compound I in Table I below). Four grams of this compound was heated under a reflux condenser with 10 g. of aniline and a little alcohol. The resulting solid, after several recrystallizations from alcohol, had m. p. 146–147°. A mixed melting point determination with a known sample of triphenylguanidine (m. p. 142–144°) gave m. p. 143–144.5°.

From Reaction of Acetone, Carbon Disulfide and Solid Potassium Hydroxide.—A mixture of 10 g. of finely powdered potassium hydroxide, and 20 g. of acetone was refluxed for one hour. The solid was washed by decantation with ether, after which 30 g. of carbon disulfide, 5 drops of acetone and 2 drops of water were added. After several days the upper layer of liquid was decanted, and 15 cc. of methyl alcohol, and 20 g. of methyl iodide were added to the solid remaining in the flask. When the reaction was complete, the mixture was treated with water, extracted with ether, etc. From three such experiments about 15 g. of liquid was obtained, b. p. 90–97° (9 mm.) (Compound II in Table I). This liquid, by reaction with aniline gave thiocarbanilide, whose identity was confirmed by a mixed melting point determination with an authentic sample of thiocarbanilide.

In another run of experiments carefully dried materials were used; neither acetone nor water was employed to promote the reaction with carbon disulfide, and the apparatus was protected from ingress of moisture by calcium chloride tubes. Two experiments combined gave 8 g. of liquid, b. p. 94–96° (8 mm.) (Compound III in Table 1).

From Reaction of Ammonium Trithiocarbonate and Methyl Iodide.—The identity of the three samples described in the preceding paragraphs was further established by a comparison of their physical properties with those of methyl trithiocarbonate prepared

by a known method. The procedure outlined in a previous paper¹⁵ was followed in making this substance. The compound had b. p. 85-88° (5 mm.) (Compound IV in Table I).

TABLE I
METHYL TRITHIOCARBONATE¹⁶

| Compound | B. p., °C. | n_D | d_4^{20} | Mol. wt. | | Anal. for S | |
|----------|---------------|----------------------|------------|----------|-------|-------------|-------|
| | | | | Calcd. | Found | Calcd. | Found |
| I | 88-91 (5 mm.) | 1.6740 ²⁰ | 1.2538 | 138 | 134.3 | 69.57 | 69.63 |
| II | 90-97 (9 mm.) | 1.6745 ¹³ | | | | | 70.16 |
| III | 94-96 (8 mm.) | 1.6776 ¹⁸ | 1.2549 | | | | 68.91 |
| IV | 85-88 (5 mm.) | 1.6844 ¹⁵ | 1.2541 | | | | 69.04 |

Summary

Additional data are presented with relation to the reaction between acetone and carbon disulfide in the presence of metallic sodium. Acetone-bis-carbithio acid is shown to be a product of this reaction. Three new compounds derived from the latter are described in part. By loss of hydrogen sulfide the carbithio acid is converted to thiocarbonyl acetone, whose properties are described. Because of the aldoling of acetone in the presence of sodium, water is produced, hence a considerable yield of sodium trithiocarbonate results. Trithiocarbonic acid is also formed when carbon disulfide is brought into reaction with solid potassium hydroxide, after treatment of the latter with acetone.

This research was aided by a grant from the Arts and Science Research Fund of the University of Arkansas, for which the writer wishes to express his thanks.

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¹⁵ Wertheim, THIS JOURNAL, 48, 826 (1926).

¹⁶ See THIS JOURNAL, 48, 828 (1926), for effect of distillation upon this substance. There appears to be but a slight decomposition when the distillation is carried on at pressures below 10 mm.