

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

THE BEHAVIOR OF 2-PHENYL SEMICARBAZONES UPON OXIDATION

BY G. T. WHYBURN AND J. R. BAILEY

RECEIVED DECEMBER 21, 1927

PUBLISHED MARCH 7, 1928

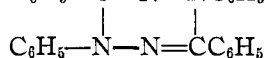
The class of compounds known as hydrazones, and in particular phenylhydrazones such as benzal phenylhydrazone, yield several different types of oxidation products. Certain aldehyde and ketone phenyl- and hexahydrophenylhydrazones yield, through the action of even atmospheric oxygen, peroxides of the general formula,¹



quite recently it has been observed that benzal phenylhydrazone, oxidized with benzoyl superoxide, is converted to benzal phenylhydrazone oxide, $\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{N}(\text{O})\text{NHC}_6\text{H}_5$.² Benzophenone phenylhydrazone shows a similar

behavior, but the reaction apparently cannot be extended to aliphatic phenylhydrazones.

In addition to the above reactions of benzal phenylhydrazone, the oxidation, depending on the conditions of the experiment, may proceed with the elimination of hydrogen between two molecules, and here four distinct products have been isolated: (I) dibenzal diphenyl dihydrotetrazone, $\text{C}_6\text{H}_5\text{CH}=\text{NN}(\text{C}_6\text{H}_5)\text{NC}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$;³ (II) benzil phenyl osazone, $\text{C}_6\text{H}_5\text{NHN}=\text{C}(\text{C}_6\text{H}_5)\text{C}(\text{C}_6\text{H}_5)=\text{NNHC}_6\text{H}_5$;⁴ (III) dehydrobenzal phenylhydrazone, $\text{C}_6\text{H}_5\text{NHN}=\text{C}(\text{C}_6\text{H}_5)\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{CHC}_6\text{H}_5$;⁵ and (IV) 1,3,4,6-tetraphenyl-1,4-dihydro-1,2,4,5-tetrazine,⁶



As von Pechmann points out, a combination of the reactions involved in the preparation of Products I and II might be expected to result in the formation of a 1,2,3,4-tetrazine, that is, a so-called osotetrazone. However, it has developed that only aliphatic aldehyde phenylhydrazones yield final oxidation products of this type;⁷ for instance, acetaldehyde phenylhydrazone goes to diacetyl phenyl osazone, and this on further oxidation with potassium dichromate in acetic acid solution is converted to 5,6-

¹ Busch and Dietz, *Ber.*, **47**, 3277 (1914); Harkins and Lochte, *THIS JOURNAL*, **46**, 450 (1924); Busch and Linsenmeier, *J. prakt. Chem.*, **115**, 216 (1927).

² Bergmann, Ulpts and Witte, *Ber.*, **56**, 679 (1923).

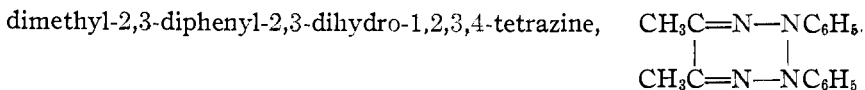
³ Von Pechmann, *Ber.*, **26**, 1045 (1893).

⁴ Ingle and Mann, *J. Chem. Soc.*, **67**, 606 (1895).

⁵ Minnuni and Rapp, *Gazz. chim. ital.*, **26**, I, 441 (1896).

⁶ Bamberger and Grob, *Ber.*, **34**, 526 (1901).

⁷ Von Pechmann, *Ber.*, **21**, 2751 (1888).



From the above discussion it is evident that in the oxidation of phenylhydrazones seven distinct types of compounds have been prepared, six of which are represented among the oxidation products of benzal phenylhydrazone. Two of the reactions involved here are simple additive reactions, while in the five others two molecules of the hydrazone are united by the removal of either two or four hydrogens from two molecules of the hydrazone as shown above.

It has been recently observed that acetone 2-phenyl semicarbazone, $\text{C}_6\text{H}_5\text{N}(\text{CONH}_2)\text{N}=\text{C}(\text{CH}_3)_2$, "reacts readily with potassium permanganate in acetone with the formation of a beautifully crystallizing yellow compound,"⁸ This rather unexpected reaction, which was not further studied at the time, gave rise to the present investigation.

The analytical data and a molecular weight determination show that the substance discovered by Goodwin and Bailey, and which will be referred to hereafter in this paper as "Product A," corresponds to the formula, $\text{C}_{17}\text{H}_{21}\text{ON}_5$. Its chemical behavior, taken in connection with the formula, leads to the conclusion that in the oxidation of acetone 2-phenyl semicarbazone there is formed methylene phenylhydrazone, $\text{CH}_2=\text{NNHC}_6\text{H}_5$, which combines immediately in molecular proportion with unchanged acetone 2-phenyl semicarbazone in accordance with the equation: $\text{C}_{10}\text{H}_{13}\text{ON}_3 + \text{C}_7\text{H}_8\text{N}_2 = \text{C}_{17}\text{H}_{21}\text{ON}_5$.

This view is supported mainly through the behavior of Product A towards acids. Although stable in alkaline media, it is readily decomposed by even weak acids, such as oxalic acid. In reaction with one mole of a dilute acid it yields among other substances 2-phenyl semicarbazide and acetone in molecular proportions. This indicates that in the preparation of Product A one-half of the acetone-2-phenyl semicarbazone employed enters the new compound unoxidized and in the disintegration of Product A is reformed with subsequent hydrolysis to acetone and 2-phenyl semicarbazide. Furthermore, when an excess of acid is used in the decomposition, phenylhydrazine, carbon dioxide and ammonia are formed instead of 2-phenyl semicarbazide. The formation of the above products is in accord with the behavior of 2-phenyl semicarbazide on acid hydrolysis.⁹ It seems certain, therefore, that in the formation of Product A there are involved one molecule of acetone 2-phenyl semicarbazone and one molecule of a product of the formula, $\text{C}_7\text{H}_8\text{N}_2$.

Further structural proof is afforded by the fact that in the acid decomposition not only is there formed the hydrolysis product of acetone

⁸ Goodwin and Bailey, *THIS JOURNAL*, **47**, 169 (1925).

⁹ Goodwin and Bailey, *ibid.*, **46**, 2831 (1924).

2-phenyl semicarbazone, referred to above, but an amount of nitrogen gas corresponding to two-fifths of that contained in a substance of the formula, $C_{17}H_{21}ON_3$, is liberated. There also results a large amount of benzene along with an appreciable amount of diphenyl. It is quite evident that the nitrogen, benzene and diphenyl have their origin in that part of Product A represented by the complex $C_7H_8N_2$.

Only two structures appear available for $C_7H_8N_2$, to wit, (1) $CH_2=NNHC_6H_5$ and (2) $CH_3N=NC_6H_5$, that is, methylene phenylhydrazone and phenylazomethane, respectively. However, were the assumption made that nitrogen, benzene and diphenyl result from either of these products on acid hydrolysis, it would not be in accord with the chemical behavior of compounds of either type. A substance of structure (1) would be expected to undergo simple hydrolysis to formaldehyde and phenylhydrazine, and a substance of structure (2) should be comparatively stable toward acid hydrolysis.

Either methylene phenylhydrazone or phenylazomethane might conceivably result from the oxidation of acetone 2-phenyl semicarbazone, but the former rather than the latter seems the more likely choice for the following reasons. Methylene phenylhydrazone has not as yet been isolated in the monomolecular form for a certainty.¹⁰ Its pronounced property of polymerization would indicate a probable strong tendency to react under favorable conditions at the moment of formation. Phenylazomethane is known, and its properties have been studied, but as yet no additive reactions of this substance have been observed. This is in accord with the non-reactivity in general of azo bodies. A limited number of azo compounds, in particular diethyl azocarbonate, $C_2H_5OOCN=NCOOC_2H_5$,¹¹ show additive reactions, but only in special cases, where strongly electro-negative radicals are attached to the azo group, has such a behavior been reported. All efforts in the course of this investigation to effect a reaction between phenylazomethane and acetone 2-phenyl semicarbazone in an alkaline medium in the hope of synthesizing Product A have met with only negative results. Furthermore, we have found diethyl azocarbonate non-reactive toward acetone 2-phenyl semicarbazone.

The possibility of synthesizing Product A by the action of formaldehyde upon an equimolecular mixture of phenylhydrazine and acetone 2-phenyl semicarbazone suggested itself, but here again all experiments were fruitless.

In a further attempt to clarify the mechanism of the reactions involved in the formation of Product A, a very simple method of preparation of tetrazones from ketone phenyl hydrazones was discovered. Although acetone phenyl hydrazone is not oxidized by amyl nitrite under the conditions employed by von Pechmann for aldehyde phenylhydrazones, it is con-

¹⁰ Ref. 9, p. 168.

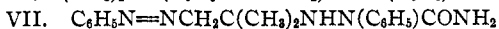
¹¹ Diels and Fritzsche, *Ber.*, **44**, 3018 (1911).

verted in almost quantitative yield to the hitherto unknown dipropylidene-diphenyldihydro-tetrazone, $(\text{CH}_3)_2\text{C}=\text{N}-\text{N}(\text{C}_6\text{H}_5)\text{N}(\text{C}_6\text{H}_5)\text{N}=\text{C}(\text{CH}_3)_2$, by the action of potassium permanganate in acetone solution. This reaction was extended to the phenylhydrazone of methylethyl ketone, although the tetrazone formed here has been obtained only as a yellow, viscous oil and was not analyzed.

In connection with the oxidation of acetone 2-phenyl semicarbazone, it may be pointed out that the behavior of acetone phenylhydrazone toward permanganate in acetone solution, as reported above, excludes the assumption of this latter hydrazone as an intermediary product in the formation of Product A. This leads to the conclusion that there is first formed methylene 2-phenyl semicarbazone, $\text{CH}_2=\text{NN}(\text{CONH}_2)\text{C}_6\text{H}_5$, from which the carbamyl group is hydrolyzed either before or after addition to unchanged acetone 2-phenyl semicarbazone. It was impossible, however, to submit this view to experimental proof due to the fact that conditions for the formation of methylene 2-phenyl semicarbazone have not been established.

Based on the assumption that Product A results from the union of one mole of methylene phenylhydrazone with one mole of acetone 2-phenyl semicarbazone, experiments were instituted to determine whether certain well-known phenylhydrazones, such as acetaldehyde phenylhydrazone and acetone phenylhydrazone would show a reactivity toward acetone 2-phenyl semicarbazone. It was found that beautiful, yellow products result here when potassium hydroxide is used as a catalyst, but unfortunately the analytical data on the substances isolated did not conform to the expected formulas, so this phase of the investigation has not been concluded. However, the results achieved apparently strengthen the views advanced on the mechanism of the permanganate oxidation of 2-phenyl semicarbazone.

As regards the structure of Product A, two formulas are suggested:



Both formulas indicate that Product A is not of hydrazone structure, an interpretation that conforms to its non-reactivity with benzaldehyde. Were the complex $(\text{CH}_3)_2\text{C}=\text{N}$ present in acetone 2-phenyl semicarbazone, still intact in its oxidation product, we might expect, as is so often the case, that the propylidene group could be substituted by the benzal group. For two reasons Formula VI is given preference over VII: (1) no evidence has been found of the presence of an imino group in Product A; (2) on acid decomposition of a product of structure VII the formation of acetone would not be expected. Formula VI is not open to these objections and, accordingly, Product A is most probably 1-isopropyl-1-phenylazomethyl-2-phenyl semicarbazide.

A confirmation of the interpretation advanced for the oxidation of

acetone 2-phenyl semicarbazone is furnished by the oxidation of methyl-ethyl ketone 2-phenyl semicarbazone, where there results a beautifully crystallizing, yellow compound with properties analogous in every way to those of Product A. It has the formula $C_{18}H_{23}ON_5$, which is the equivalent of one molecule of the original semicarbazone plus one molecule of methylene phenylhydrazone. This formula was confirmed by molecular weight determination, this substance being selected in preference to Product A because of its greater solubility in benzene.

As was to be expected, it was found that benzal 2-phenyl semicarbazone, where the formation of methylene phenylhydrazone is excluded, was not acted on by permanganate in acetone solution. The ethyl ester of pyruvic acid 2-phenyl semicarbazone was also not acted on by permanganate under similar conditions. However, pyruvic acid 2-phenyl semicarbazone in contrast to its ester is readily attacked by this oxidizing agent, but the reaction product was not isolated. Acetaldehyde 2-phenyl semicarbazone undergoes oxidation with permanganate in acetone solution very readily; here the problem is complicated by the possible formation of diacetyl-2-phenyl semicarbazone, $C_6H_5N(CONH_2)N=C(CH_3)C(CH_3)=NN(CO-NH_2)C_6H_5$, and no definite oxidation products were isolated.

With the view of studying its behavior toward permanganate, acetone 2,4-diphenyl semicarbazone, $C_6H_5N(CONHC_6H_5)N=C(CH_3)_2$, was prepared by the action of phenylisocyanate on acetone phenylhydrazone, but in the oxidation experiment no definite result was obtained.

Although benzal-2-phenyl semicarbazone is not attacked in the permanganate oxidation in acetone solution, it behaves analogously to benzal semicarbazone, in its conversion to 3-hydroxy-2,5-diphenyltriazole on oxidation with ferric chloride.¹²

Experimental Part

Oxidation of Acetone 2-Phenyl Semicarbazone.—To 100 g. of crude acetone 2-phenyl semicarbazone¹³ in 500 cc. of acetone is slowly added 125 g. of potassium permanganate, partially dissolved in acetone. The oxidation proceeds rapidly with considerable rise in temperature and after twelve hours the permanganate is completely reduced. The reaction product, designated as Product A, which is formed in a yield of about 64 g. and imparts a bright yellow color to the acetone, remains in solution for the most part but separates on concentration of the filtered solution or can be precipitated by the addition of an equal volume of water. Any of the substance remaining in the cake after filtration can be extracted with boiling acetone or alcohol. It is readily soluble in alcohol, benzene, acetone and acetic ether, less soluble in ether, and practically insoluble in water. Recrystallized from alcohol, it separates in fine, canary-yellow needles melting at 162° with violent gas evolution.

Anal. Calcd. for $C_{17}H_{21}ON_5$: C, 65.59; H, 6.75; N, 22.54. Found: C, 65.34; H, 6.76; N, 22.95.

¹² Young and Witham, *J. Chem. Soc.*, 77, 226 (1900).

¹³ Ref. 9, p. 2829.

Decomposition of Product A on Acid Treatment.—To 10 g. of Product A in a round-bottomed flask, connected to a condenser fed with ice water, is added 67 cc. of *N*/2 hydrochloric acid. As soon as the receiver is thoroughly chilled by immersion in a freezing mixture, the flask is heated with a low, smoky flame, whereupon a reaction with profuse evolution of nitrogen takes place. After half an hour the reaction may be considered at an end. The distillate, measuring about 4.5 cc., consists of a mixture of acetone and benzene, while in the flask there remain 2-phenyl semicarbazide in solution and in addition a small amount of insoluble tar from which can be isolated diphenyl. The methods of isolation and detection of the different decomposition products follow.

Identification of Acetone and Benzene.—The distillate obtained from the above reaction was fractionated at atmospheric pressure, four fractions boiling at 50–65°, 65–70°, 70–75° and 75–80°, respectively, being collected. In the lower boiling fractions acetone predominated, while the higher boiling fractions were rich in benzene. Only the last fraction solidified when chilled in ice water. The first fraction was treated with benzaldehyde in alcoholic sodium hydroxide solution,¹⁴ and the dibenzylidene acetone formed identified by analysis and comparison with a stock sample.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.18; H, 5.98. Found: C, 87.33; H, 5.88.

In order to confirm the formation of benzene, the last fraction was treated with a mixture of nitric and sulfuric acids as directed by Mulliken,¹⁵ and the *m*-dinitrobenzene formed identified by a nitrogen determination and comparison with a stock sample.

Anal. Calcd. for $C_6H_4O_4N_2$: N, 16.67. Found: N, 16.71.

Identification of 2-Phenyl Semicarbazide.—In the course of the investigation it was found that pyruvic acid 2-phenyl semicarbazone is admirably suited for the characterization of 2-phenyl semicarbazide. The acid solution remaining in the distillation flask after the decomposition of Product A with hydrochloric acid was concentrated to a small volume and, after the addition of an excess of sodium acetate, a little more than the calculated amount of pyruvic acid was added. This product was compared in the usual way with a sample of the semicarbazone prepared, as described later on, from 2-phenyl semicarbazide hydrochloride and pyruvic acid.

Anal. Calcd. for $C_{10}H_{11}O_3N_3$: N, 19.00. Found: N, 18.92.

Identification of Diphenyl.—The residual tar from the decomposition of Product A yielded on distillation in a vacuum a beautifully crystallizing, white solid. This was identified as diphenyl by its characteristic odor, by the usual comparison with a stock sample and finally by the intense blue coloration it developed in chloroform solution with sublimed aluminum chloride.¹⁶

Estimation of the Acetone Formed in the Decomposition of Product A.—The acetone from the decomposition of 0.216 g. of Product A with *N*/2 sulfuric acid was distilled off and converted to iodoform;¹⁷ 22.9 cc. of *N*/10 iodine solution was used, corresponding to 0.0442 g. of acetone. The calculated amount of acetone furnished in the decomposition of 0.2161 g. of Product A equals 0.0403 g.

Estimation of the Nitrogen Evolved in the Decomposition of Product A.—One gram of Product A was decomposed with 7 cc. of *N*/2 hydrochloric acid, as described above, in an atmosphere of carbon dioxide, and the gas evolved collected over 30% potassium hydroxide solution. The gas volume measured 77.1 cc. at 21° and 754 mm., corresponding to 40% of the total nitrogen in the original substance.

¹⁴ Mulliken, "Identification of Pure Organic Compounds," 1st ed., John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 148.

¹⁵ Ref. 14, p. 200.

¹⁶ Ref. 14, p. 196.

¹⁷ See Ullman, "Enzyklopädie der technischen Chemie," 1914, Vol. I, p. 112.

Pyruvic Acid 2-Phenyl Semicarbazone.—When to 6 g. of 2-phenyl semicarbazide hydrochloride in 20 cc. of water 8 g. of fused sodium acetate and 3.4 g. of pyruvic acid are added, there separates a fine, crystalline reaction product, difficultly soluble in all the common solvents. It can be purified by recrystallization from water and is thus obtained in the form of microscopic cubes melting with decomposition at 168°.

Anal. Calcd. for $C_{10}H_{11}O_3N_3$: N, 19.00. Found: N, 18.90.

The Ethyl Ester of Pyruvic Acid 2-Phenyl Semicarbazone.—Prepared similarly to the free acid by using pyruvic acid ester, this semicarbazone is obtained in a practically quantitative yield. It is readily soluble in alcohol, benzene and acetic ether and practically insoluble in water and can be purified by recrystallization from alcohol in the form of long rods melting at 149°. Unlike the free acid, the semicarbazone ester is quite stable toward permanganate in acetone solution.

Anal. Calcd. for $C_{12}H_{13}O_3N_3$: N, 16.87. Found: N, 17.02.

Oxidation of Methylethyl Ketone 2-Phenyl Semicarbazone.—This semicarbazone¹⁸ can be conveniently obtained by the method, previously referred to, that Goodwin and Bailey used in the case of acetone 2-phenyl semicarbazone. In its oxidation the following procedure will be found satisfactory: 8 g. of the semicarbazone is added to 100 cc. of acetone, in which is dissolved or suspended 25 g. of potassium permanganate, and the reaction mixture allowed to stand with occasional agitation for one week. Precipitation of the new substance is then effected by addition of water to the filtered solution. The crude product, in order to destroy any unchanged permanganate, is dissolved in boiling alcohol, from which on dilution to a permanent turbidity and chilling, it separates as a fine, granular, yellow solid melting at 144° with gas evolution. The new substance is extremely soluble in acetone, alcohol and benzene, less soluble in ether and practically insoluble in water. On treatment with acids this oxidation product decomposes in a way similar to Product A.

Anal. Calcd. for $C_{13}H_{23}ON_3$: C, 66.46; H, 7.08; N, 21.54. Found: C, 66.54; H, 7.33; N, 21.78. *Molecular weight determination.* 0.6634 of substance in 40.8 g. of benzene gave a boiling point elevation of 0.130°, and 0.4928 g. substance in 52.3 g. of benzene gave an elevation of 0.066°. Calcd. for $C_{13}H_{23}ON_3$: M. W., 325. Found: M. W., 313, 347.

Dipropylidene Diphenyl Tetrazone.—To 60 g. of acetone phenylhydrazine in 300 cc. of acetone, cooled in ice water, powdered potassium permanganate is slowly added until a permanent pink color persists, care being taken to avoid an elevation of temperature. A part of the tetrazone, which separates with the manganese dioxide, is extracted with hot acetone. From the combined acetone solutions, on dilution with two volumes of water and chilling, the tetrazone precipitates in a yield of 85% of that calculated. It is very soluble in alcohol, acetone and ether, insoluble in water, and can be purified by recrystallization from 95% alcohol, care being taken not to heat the solution longer than necessary. It crystallizes in thin, yellow plates melting at 89° undecomposed.

Anal. Calcd. for $C_{13}H_{22}N_4$: C, 73.47; H, 7.48; N, 19.04. Found: C, 73.81; H, 7.37; N, 18.98.

Action of Alcohol on the Tetrazone.—When the tetrazone is refluxed with a large excess of alcohol for an hour, and the alcohol then distilled off, there remains a slightly colored, rather mobile liquid. This was identified as acetone phenylhydrazine by its boiling point, by conversion to 2-phenyl semicarbazone and by a nitrogen determination.

Anal. Calcd. for $C_9H_{12}N_2$: N, 18.92. Found: N, 18.74.

Action of Acids on the Tetrazone.—If 2 g. of the tetrazone in 25.5 cc. of *N*/2 hydro-

¹⁸ Arnold, *Ber.*, 30, 1016 (1897).

chloric acid is heated for ten minutes, complete solution is effected and acetone distils off. On concentration of the solution to a small volume, phenylhydrazine hydrochloride crystallizes out in the form of white, lustrous flakes. This was identified by comparison with a stock sample as well as by conversion to benzal phenylhydrazone.

Behavior of the Tetrazone toward Pyruvic Acid.—Pyruvic acid reacts in the cold with the tetrazone suspended in water, effecting at first complete solution followed later by precipitation of pyruvic acid phenylhydrazone. The hydrazone was identified by comparison in the usual way with a sample prepared from phenylhydrazine and pyruvic acid.

3 - Hydroxy - 2,5 - diphenyltriazole.—Although benzal 2-phenyl semicarbazone is quite stable toward permanganate in acetone solution, it is oxidized to the corresponding triazole as follows: 1.5 g. of benzal 2-phenyl semicarbazone, 1.5 g. of ferric chloride and 10 cc. of alcohol are heated in a sealed tube at 125–135° for three hours. Only a slight pressure is developed and at the end of the reaction the contents of the tube solidify. For purification the triazole is dissolved in dilute sodium hydroxide and after filtration reprecipitated with hydrochloric acid. It is readily soluble in alcohol, acetic ether and glacial acetic acid, difficultly soluble in chloroform and ether, and can be recrystallized from absolute alcohol in a matted mass of very fine, hair-like needles melting at 233°.

Anal. Calcd. for $C_{14}H_{11}ON_3$: N, 17.73. Found: N, 17.22.

Acetone 2,4 - Diphenyl Semicarbazone.—When acetone phenylhydrazone and phenylisocyanate in molecular proportions are heated without a solvent at 100° in a sealed tube for two hours, a viscous reaction product results. This, purified by recrystallization from alcohol in the form of thin plates, melts at 191° and is readily soluble in alcohol, benzene and chloroform, difficultly soluble in ether and insoluble in water. The substance, prepared with a view of observing its behavior towards oxidizing agents, was found in contrast to acetone-2-phenyl semicarbazone to be quite stable toward permanganate in acetone solution.

Anal. Calcd. for $C_{16}H_{17}ON_3$: N, 15.73. Found: 15.68.

Summary

1. Acetone 2-phenyl semicarbazone, $(CH_3)_2C=NN(CONH_2)C_6H_5$, on oxidation in acetone solution with potassium permanganate gives a yellow product regarded as 1-isopropyl-1-phenylazomethyl-2-phenyl semicarbazide, $(CH_3)_2CH(C_6H_5N=NCH_2)N-N(C_6H_5)CONH_2$.

2. The behavior of this oxidation product indicates its formation from one mole of unchanged acetone-2-phenyl semicarbazone and one mole of methylene phenylhydrazone. A direct synthesis of the substance from these two products, however, has not been accomplished.

3. Methyl ethyl ketone 2-phenyl semicarbazone behaves similarly on oxidation, yielding a yellow product regarded as 1-sec-butyl-1-phenylazomethyl-2-phenyl semicarbazide. It is probable that all aliphatic ketone semicarbazones of the formula, $R'R''C=NN(C_6H_5)CONH_2$, will yield as primary oxidation product the complex, $C_7H_8N_2$, which in reaction with the original unchanged 2-phenyl semicarbazone will produce semicarbazides of the type, $R'R''CH(C_6H_5N=NCH_2)NN(C_6H_5)CONH_2$.

4. In the course of the investigation a convenient method of preparation of tetrazones by the oxidation of ketone phenylhydrazones with permanganate in acetone solution was discovered.