for several days. Hydrogen sulfide was set free and some ammonia. The precipitate that formed was recrystallized from hot alcohol, separating as feathery needles; m. p., 83–84°. The crude oxime contained a small amount of yellow material which proved to be sulfur, presumably from the action of hydroxylamine on hydrogen sulfide.

$$NH_2OH + H_2S = NH_3 + H_2O + S$$

A similar procedure was followed in the preparation of the other thio-amides except that smaller amounts of isothiocyanates, usually 5–10 g., were used. The ether was removed by spontaneous evaporation, after addition of acid during stirring, in case the addition product could not be separated by filtration.

This work was aided by a grant from the Cyrus M. Warren Fund of the American Academy.

Summary

It has been shown that butylmagnesium bromide reacts readily and smoothly with aromatic isothiocyanates, forming substituted thio-amides of valeric acid.

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AN INVESTIGATION OF SOME PROPERTIES OF PHENYLHYDRAZINE AND FACTORS AFFECTING HYDRAZONE FORMATION

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This work was undertaken as a necessary preliminary to the evolution of a general iodimetric method for the estimation of carbonyl group content in organic compounds.

Iodine reacts with phenylhydrazine giving iodobenzene and hydriodic acid.[1] $C_6H_5NH.NH_2 + 2I_2 = C_6H_5I + 3HI + N_2$.

Consistent iodine values can readily be obtained for aqueous phenylhydrazine solutions, but only under certain conditions. The iodobenzene produced dissolves some iodine. The simplest method of titration is to add an excess of iodine, allow sufficient time for complete reaction, add an excess of thiosulfate, shake with a few cubic centimeters of ether, and finally titrate with iodine once more, using freshly prepared starch solution. Shaking with ether hastens the extraction of the iodine from the iodobenzene and hence expedites the determination. The ether does not affect the titration.

The presence of the sodium acetate[2] or other "buffer" salts usually recommended such as sodium bicarbonate, borate or phosphate, slows down the reaction and gives low results. Addition of hydrochloric or

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[1] von Meyer, *J. prakt. Chem.*, [2] **36**, 115 (1887).

[2] Fischer, *Ber.*, **17**, 572 (1884); **41**, 74 (1908).

sulfuric acid until the solution is just acid to methyl orange before beginning titration is all that is necessary to eliminate this source of error.

Aqueous solutions of phenylhydrazine or its salts change color fairly rapidly and deposit a brownish substance. This change appears to take place more rapidly in daylight than in the dark. The hydrochloride does not change in iodine value at a rapid rate at room temperature, but at 60° the rate of decrease is far from negligible. The acetate, or hydrochloride with sodium acetate added, does decrease appreciably in iodine value at room temperature.

Two series of experiments were carried out in diffused daylight with approximately 0.1 *M* phenylhydrazine hydrochloride: (a) using boiled distilled water saturated with nitrogen and a nitrogen atmosphere; (b) distilled water saturated with oxygen and an oxygen atmosphere.

Table I contains the results of these two series.

TABLE I

OXIDATION OF PHENYLHYDRAZINE HYDROCHLORIDE SOLUTION BY OXYGEN

Values in cc. of 0.1 *N* iodine solution per 5 cc.

	Room temperature, 21°		Water-bath, 60°	
Time, hours	Series *a* Nitrogen	Series *b* Oxygen	Series *a* Nitrogen	Series *b* Oxygen
0	18.35	18.35	18.35	18.35
0.25	..	..	18.35	17.75
0.5	18.35	18.1	..	..
1.0	..	..	18.4	17.6
1.5	..	..	18.4	17.25
2.0	18.4	17.7	..	..
18	18.4	14.9	..	..

With oxygen the solutions became lemon yellow in 15 minutes, even at room temperature, and in 18 hours they had become very turbid. The samples under nitrogen remained colorless.

This factor does not appear to have been taken into account in any of the determinations of the carbonyl group given in the literature. As far as we can ascertain, attention has never before been directed to this phenomenon. In all our subsequent work oxygen-free water was used, and an atmosphere of nitrogen maintained.

For the investigation of hydrazone formation acetone was used. It has two advantages, namely, (a) its strength can be accurately determined by Messinger's method[3,4] and (b) it is readily soluble in water.

Hydrazones are rapidly attacked by iodine, due to the fact that hydrazone formation is a reversible reaction. We suspended a few drops of acetone-phenylhydrazone in water, added an excess of 0.1 *N* iodine solution and found the decomposition to be 80.6% in 15 minutes. With benzaldehyde-phenylhydrazone suspended in a mixture of 50% by volume

[3] Ardagh, *Ind. Eng. Chem.*, **16**, 1133 (1924).

[4] Hermans, *Chem. Weekblad*, **18**, 348 (1921).

of methyl alcohol and water the decomposition was 47.3% in the same time. The iodimetric determination of the unchanged phenylhydrazine, therefore, requires the removal of the hydrazone formed. Von Meyer's method disregards this fact. Since acetone-phenylhydrazone has, at room temperature, a solubility in water amounting to about 0.015 *M* concentration, centrifugal separation of the oil is not sufficient. The hydrazone can be removed by shaking with such solvents as ether, chloroform or benzene. These also extract some of the phenylhydrazine. Since in hydrazone extraction ether is the most efficient of the three solvents we tried, this was used. A correction, however, must be applied to the aqueous volume increase due to ether solution. A partition coefficient for phenylhydrazine in water-ether must be determined and a correction for the phenylhydrazine in the ether extract made. The fact that consistent results were obtained using various quatities of ether shows that the hydrazone partition between water and ether is such as to give virtually complete extraction.

Our method for determining the unchanged phenylhydrazine in the following series of determinations was the following.

Twenty-five cc. of solution was pipetted into a nitrogen-filled separating funnel of about 75cc. capacity. To this was added enough ether to give a final ethereal layer of about 1 cc. (usually 3–4 cc. of ether was required) and the mixture was vigorously shaken for one minute. After two minutes had been allowed for separation, part of the aqueous layer was run out, 10 or 20 cc. just acidified with hydrochloric acid (methyl orange) and the titration carried out as already described. The volumes of aqueous and ethereal layers were accurately determined by running the remainder of the liquid into a small calibrated measuring cylinder with wide readings. The partition coefficient for the phenylhydrazine in the ethereal layer must be determined on a blank carried out under the same conditions as in the experiment, and then the iodine value of the unchanged phenylhydrazine in the original 25 cc. becomes a simple calculation. The partition coefficient for phenylhydrazine hydrochloride for ether-water is about 0.5, but the addition of sodium acetate increases this to 1.7 and under alkaline conditions it rises towards 3.0.

In the first series of experiments phenylhydrazine acetate was used because Michael[5] states that the hydrochloride reacts slowly or not at all with ketones. The phenylhydrazine acetate concentration in the reacting solution was approximately 0.04 *M* and the acetone 0.024 *M*. The rate of reaction is shown in Curve a, Fig. 1. To conserve space the calculations have been omitted.

It was qualitatively observed that the addition of sodium chloride increased the amount of hydrazone separated. The effects of various concentrations of sodium chloride were then tried quantitatively. The results are given in Curves c, d, e and f, Fig. 1.

The above results emphasize the fact that in the formation of hydrazone we are dealing with an equilibrium reaction. If it were possible to re-

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[5] Michael, *J. prakt. Chem.*, [2] **45**, 588 (1892).

move the hydrazone as formed, complete reaction could be secured. This cannot be done in the case of acetone with ether extraction because the ether also extracts unchanged acetone.

A greater concentration of sodium acetate than 20 g. per liter does not appreciably increase the yield of acetone-phenylhydrazone at equilibrium. The favorable influence of sodium chloride in increasing the amount of hydrazone formed is no doubt due to a salting out of the hydrazone.

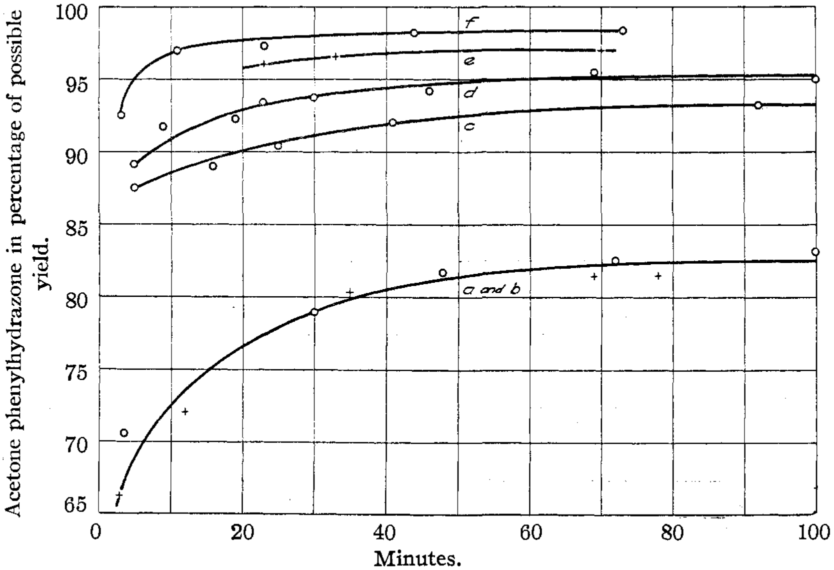

Fig. 1.

The effect of a 50 g. per liter concentration of sodium, potassium or ammonium chloride or sulfate on the equilibrium at the same concentration of 0.04 *M* for phenylhydrazine hydrochloride, and 0.024 *M* for acetone and 10 g. per liter for sodium acetate was found to be practically the same for each of these salts.

The addition of sodium acetate to phenylhydrazine hydrochloride greatly increases the amount of hydrazone formed. This appears to be due entirely, as will be shown later, to its "buffering" action.

In the straight reaction between the hydrochloride and acetone, hydrochloric acid is liberated as hydrazone formation proceeds, as shown by the following equation: $C_6H_5NH.NH_2.HCl + CH_3COCH_3 = (CH_3)_2C{:}N.NHC_6H_5 + H_2O + HCl$.

Hence the effect was tried of having acid and alkaline conditions initially present.

Twenty cc. of 0.2 *M* phenylhydrazine hydrochloride, 20 cc. of 0.12 *M* acetone and the recorded volume of 0.1 *N* hydrochloric acid or 0.1 *N* sodium hydroxide solution were added to a 100cc. flask and made up to the mark with air-free, distilled water. Between four and five hours was given for equilibrium to be reached.

The results are given in Table II and graphically in Fig. 2. The final concentration of acid and alkali has been calculated from the degree of reaction since, except where the reaction has gone almost to completion, it cannot be determined by direct titration owing to further reaction taking place. The Sörensen (*P*H) values recorded were determined after equilibrium had been reached by comparison with standard buffer solutions, using for the purpose a suitable series of indicators. Titrations over the maximum part of the curve gave final results agreeing with calculated values.

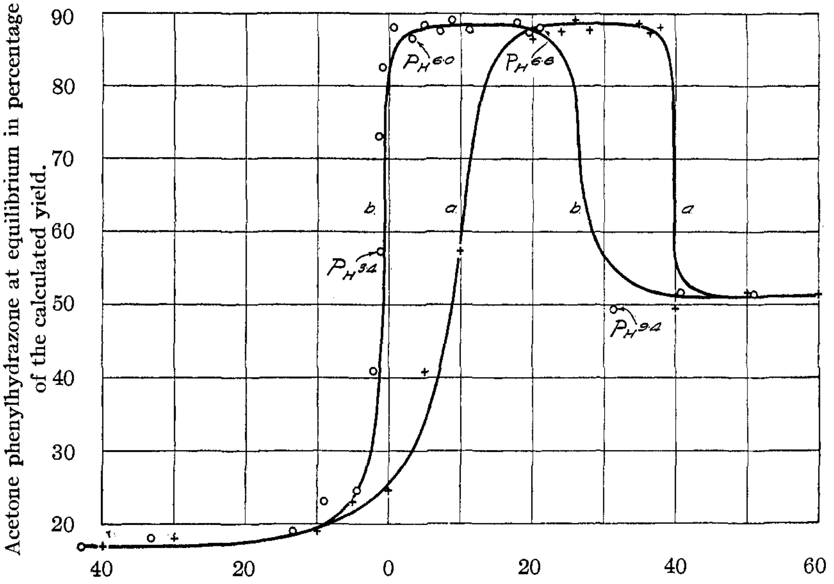

Fig. 2.

TABLE II

THE EFFECT OF ACIDITY AND ALKALINITY ON THE EQUILIBRIUM BETWEEN PHENYLHYDRAZINE HYDROCHLORIDE AND ACETONE AT 21°

1.	Initial concn.,[a] cc	40.0[b]	30.0[b]	10.0[b]	5.0[b]	neutral
2.	Amt. of hydrazone formed, %	17.1	18.1	18.95	23.0	24.55
3.	Final concn.,[a] cc	43.0[b]	33.15[b]	13.3[b]	9.0[b]	4.3[b]

1.	5.0	10.0	20.0	22.0	24.0	26.0	28.0
2.	40.9	57.3	86.5	88.4	87.5	89.1	87.7
3.	2.15[b]	1.0[b](*P*H 3.4)	3.4	5.0(*P*H 6.0)	7.2	8.9	11.2

1.	30.0	35.0	36.5	38.0	40.0	50.0	60.0
2.	92.0	88.8	87.4	88.0	49.5	51.8	51.5
3.	12.3	18.0	19.7	21.1(*P*H 6.6)	31.35(*P*H 9.4)	40.95	51.0

[a] Cc. of 0.1 *N* acid or alkali per 100 cc.

[b] These values are of cc. of acid; the others are of cc. of alkali.

In Table III, 0.05 *M* phenylhydrazine, 0.024 *M* acetone, some of the values enable us to locate additional points on the curve where they are most needed to determine its shape where the abrupt upward shoot occurs. These points have been indicated in Fig. 2 and show that at the instant the Sörensen value of the solution rises to 5, or thereabouts, the curve rises practically to a maximum and then continues horizontally until free caustic alkali is present at the final condition, when the curve falls again almost vertically.

From the table or graph it will be observed that there is an abrupt change in equilibrium when between 38 and 40 cc. of 0.1 *N* sodium hydroxide solution per 100 cc. is present; that is, with a sodium hydroxide concentration of about 0.04 *M*. The concentration of the phenylhydrazine hydrochloride itself was 0.04 *M*. This indicates that the abrupt fall in equilibrium value is due to the presence of free sodium hydroxide.

Table III

The Effect of Alkalinity on the Rate of Reaction between Phenylhydrazine Hydrochloride and Acetone at 21°

Initial concn., cc. per 100 cc.	8.1[a]	10.5[a]	13.2[a]	15.8[a]	18.5[a]	26.0[a]	34.0[a]
Hydrazone formed, %, 10 min.	56.0	62.0	69.4	81.0	86.1	88.5	91.0
70 min.	58.5	68.2	73.0	82.5	88.0	91.0	93.0
Final concn., cc. per 100 cc.	3.6[b]	3.1[b]	1.2[b]	0.7[b]	0.9[a]	7.8[a]	15.4[a]

[a] Cc. of 0.1 *N* NaOH. [b] Cc. of 0.1 *N* HCl.

It appears from these values that there is not any noticeable change in the rate of reaction, and the results accord with the rate curves in Fig. 1.

Shettle[6] states that the velocity of the reaction between acetone and phenylhydrazine decreases with the addition of small quantities of hydrochloric or acetic acid, and is reduced to zero on adding potassium hydroxide. This means that no hydrazone will be formed when free caustic alkali is present, which is certainly not the case under the conditions we used in carrying out our work. Our observations show that the presence of acid decreases the proportion of hydrazone formed, but not continuously with increase of acid. The presence of free sodium hydroxide also decreases the proportion of hydrazone formed, but to a less extent; it certainly does not reduce the velocity to zero.

A study of the reaction should be made to determine the shape of the "acetone phenylhydrazone-*P*H" curve. This, one of the authors hopes to do shortly. The shape of the curve may, of course, change to some extent for different ketones and aldehydes. This should also be investigated.

We had now gained the necessary insight into the chemistry of phenylhydrazine and the mechanism of hydrazone formation, as set forth in the opening paragraph of this paper.

[6] Shettle, *J. Russ. Phys. Chem. Soc.*, **43,** 1190 (1911).

Hydrazone formation is a reversible reaction peculiarly affected by hydrogen-ion concentration. The magnitude and range of this effect may differ with different carbonyl compounds, but it can be laid down definitely that the best condition for maximum formation of acetone phenylhydrazone is with a final Sörensen value between 5 and 7, in other words the solution should still be faintly alkaline to methyl orange when the reaction has reached equilibrium. Further work and other experiments in the evolution of a general analytical method are given in the following paper.

The assumption that under certain conditions hydrazone formation is quantitative[7] is obviously not absolutely correct. If we look at the problem from the viewpoint of chemical dynamics, however, we perceive that the more insoluble the hydrazone the more probably the reaction will approach completion.

The Fehling solution method of Benedikt and Strache,[8] which up to this date has been looked upon as a standard method for carbonyl group determination, assumes that the hydrazone reaction proceeds to completion under the conditions laid down for that method. The carbonyl compound, however, will not be completely converted into a hydrazone and, furthermore, the hydrazone formed will react with the Fehling's solution. These errors, it is true, will decrease in proportion as the insolubility of the hydrazone increases. Both errors tend to give low results. Atmospheric oxidation of the phenylhydrazine, on the other hand, tends to give high results and hence serves to counteract the other two errors.

Summary

1. The reaction between phenylhydrazine and iodine does not proceed normally in the presence of buffer solutions such as of sodium acetate, borate or phosphate. When a buffer is present, sufficient hydrochloric or sulfuric acid should be added to render the solution just acid to methyl orange.
2. Solutions of phenylhydrazine and its salts, especially the acetate, are fairly rapidly oxidized by exposure to air, even at room temperature.
3. Contrary to the general assumption, a very small change in the Sörensen value of the solution may very considerably affect the equilibrium in hydrazone formation.
4. Iodine solution rapidly attacks hydrazones, hence von Meyer's method[1,9] is of little value. Petrenko-Kritschenko[10] does not appear to appreciate the speed of this reaction.

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[7] Meyer (Tingle), "Determination of Radicles in Carbon Compounds," John Wiley and Sons, **1908**, p. 79.

[8] Benedikt and Strache, *Monatsh.*, **14**, 270 (1893).

[9] Sudborough and James, "Practical Organic Chemistry," Blackie and Sons, Ltd., London, **1920**, p. 225.

[10] Petrenko-Kritschenko, *Ann.*, **341**, 150 (1905).

5. Defects in the standard Fehling solution method for the determination of the carbonyl group are pointed out.

6. Acetone-phenylhydrazone formation can be forced almost to completion by adjusting the final Sörensen value of the solution to between 5 and 7, and at the same time salting out the hydrazone. If the hydrazone is now extracted by a selective solvent immiscible with water the reaction can be made practically quantitative.

TORONTO, CANADA

[CONTRIBUTION FROM THE SCHOOL OF ENGINEERING RESEARCH OF THE UNIVERSITY OF TORONTO]

AN ACCURATE GENERAL IODIMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF THE CARBONYL GROUP IN ORGANIC COMPOUNDS

BY E. G. R. ARDAGH AND J. G. WILLIAMS

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There are to be found in the literature[1] a number of methods for the quantitative determination of individual aldehydes[2,3,4,5] and ketones[2,4,6,7]. Owing to the greater reactivity of aldehydes as a class as compared with ketones more quantitative methods have naturally been proposed for the former. A few of these methods are applicable to the determination of a limited number of aldehydes and ketones. There are only two, however, that can in any sense be called general methods.

The one general method for the quantitative determination of the carbonyl group which has been considered by all chemists to be dependable is that of Benedikt and Strache.[8] This method, in which the excess of phenylhydrazine is oxidized by Fehling's solution and the liberated nitrogen measured, unfortunately gives only approximately correct results. The method, furthermore, is tedious and cumbersome. Its accuracy has been improved by Smith,[9] but even his results are merely close approximations. With *p*-nitrobenzaldehyde he obtained consistent results 4.3% low, and with hydroxybenzaldehyde his results were consistently 2.7% high.

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[1] Houben-Weyl, "Die Methoden der organischen Chemie," Georg Thieme, Leipsic, 2nd edition, **1921**, vol. 1, pp. 188 and 220.

[2] Lautenschläger, *Arch. Pharm.*, **256**, 84 (1918).

[3] Pauly, Schübel and Lockemann, *Ann.*, **383**, 288 (1911). Welmans, *Pharm. Ztg.*, **1898**, p. 634. Meyer, *Monatsh.*, **24**, 833 (1903). Burzeps, *Analyst*, **29**, 78 (1904).

[4] Ripper, *Monatsh.*, **21**, 1079 (1900).

[5] Lockemann and Croner, *Z. anal. Chem.*, **54**, 11, 22 (1915).

[6] Messinger, *Ber.*, **21**, 3366 (1888). Ardagh, *Ind. Eng. Chem.*, **16**, 1133 (1924).

[7] Sy, THIS JOURNAL, **29**, 786 (1907).

[8] Benedikt and Strache, *Monatsh.*, **14**, 270, 373 (1893).

[9] Smith, *Chem. News*, **93**, 83 (1906).