sym-diphenyl benzidine prepared according to the method of Kadiera[18] showed no depression.

Styrylmagnesium Bromide and Cupric Chloride.—Styrylmagnesium bromide, prepared from β-bromostyrene, when treated with an equivalent amount of cupric chloride gave a 17.6% yield of *sym*-diphenylbutadiene. The apparently ready polymerization of the butadiene makes it difficult to separate this compound from the tarry substances generally present. A check experiment showed 10% of this compound to be formed in the preparation of the Grignard reagent.

In another experiment the ether was replaced by benzene. The vigor of reaction appeared to increase with this solvent; however, the product was a tar from which the butadiene was obtained with difficulty and in a scarcely appreciable quantity.

Summary

A study has been made of the reaction between RSMgX, ROMgX, R_2NMgX and RCH=CHMgX compounds and cupric chloride. Coupling, in varying yields, takes place with all types other than ROMgX. This gave no compound of the type ROOR.

AMES, IOWA

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

2-PHENYL SEMICARBAZIDE[1]

BY R. C. GOODWIN AND J. R. BAILEY

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Arnold[2] found that the hydrochloride of acetone phenylhydrazone reacts with potassium cyanate with the formation of acetone-2-phenyl semicarbazone.

$$C_6H_5NHN{=}C(CH_3)_2.HCl + KCNO \longrightarrow C_6H_5N(CONH_2)N{=}C(CH_3)_2 + KCl$$

Arnold states that "on boiling with water the compound passes to 'Phenylhydrazinsemicarbazid' with the elimination of acetone." From the text it is not clear whether "Phenylhydrazinsemicarbazid" means 2- or 1-phenyl semicarbazide, since the properties of the compound are not reported. On repetition of Arnold's work we find that neutral hydrolysis of acetone-2-phenyl semicarbazone gives 1-phenyl semicarbazide, $C_6H_5NHNHCONH_2$. That 2-phenyl semicarbazide is not an intermediary product in the hydrolysis and that the transformation of the carbamyl group from one nitrogen to the other is coupled in some way that remains to be explained with the elimination of acetone from the semicarbazone, is indicated by the fact that 2-phenyl semicarbazide itself on steam distillation is not changed to 1-phenyl semicarbazide.

[18] Kadiera, *Ber.*, **38**, 3575 (1905).

[1] This name is in accordance with the system of numbering given in Beilstein-Prager-Jacobsen, Handbuch "Handbuch der Organischen Chemie," 4th ed., J. Springer, **1921**, vol. 3, p. 98, for semicarbazide, $NH_2NHCONH_2$.
1 2 3 4

[2] Arnold, *Ber.*, **30**, 1016 (1897).

Busch and Walter[3] deserve priority in the discovery of 2-phenyl semicarbazide. Their process involves the following series of reactions:

$$C_6H_5NHN{=}CHC_6H_5 + COCl_2 \longrightarrow C_6H_5N(COCl)N{=}CHC_6H_5 + HCl$$
$$C_6H_5N(COCl)N{=}CHC_6H_5 + 2NH_3 \longrightarrow C_6H_5N(CONH_2)N{=}CHC_6H_5 + NH_4Cl$$
$$C_6H_5N(CONH_2)N{=}CHC_6H_5 + H_2O \longrightarrow C_6H_5N(CONH_2)NH_2 + C_6H_5CHO$$

The hydrolysis of benzal-2-phenyl semicarbazone is effected with sulfuric acid, with a yield of about 32% of that calculated. Unlike acetone-2-phenyl semicarbazone, benzal-2-phenyl semicarbazone as reported by Bailey and Read[4] cannot be prepared from benzal phenylhydrazone by the direct addition of cyanic acid, a result not unexpected in view of the fact that even phenyl isocyanate reacts with this hydrazone only at high temperatures.[5] However, a much more convenient way of making benzal-2-phenyl semicarbazone than the one given by Busch and Walter is described in the experimental part of this article.

Pellizzari,[6] apparently without knowledge of the work of Arnold or that of Busch and Walter, prepared 2-phenyl semicarbazide from 2-cyanophenylhydrazine, $C_6H_5N(C{\equiv}N)NH_2$, by the hydration of the $C{\equiv}N$ group to $CONH_2$.

Although the method proposed by Arnold by hydrolyzing acetone-2-phenyl semicarbazone leads to 1-phenyl semicarbazide, we find that a practically quantitative yield of 2-phenyl semicarbazide can be obtained by acid hydrolysis, and it is now possible to obtain this hydrazine in any quantity desired with very little labor. One essential feature of the process is the employment of the semicarbazone and hydrochloric acid in molecular proportions, a method of hydrolyzing acetone hydrazones originally employed by Bailey and Acree[7] in the preparation of semicarbazide hydrochloride from acetone semicarbazone.

From the work of Bailey and Read[8] on the use of cyanic acid in glacial acetic acid and the subsequent employment of this method in the synthesis of complex ureas or ureides,[9] it appeared probable that acetone-2-phenyl semicarbazone might be most conveniently prepared by using glacial acetic acid as a medium for the reaction between cyanic acid and acetone phenylhydrazone. This method is preferable to the one of Arnold referred to above, but we find it better to operate with aqueous acetic acid here, as well as in the addition of cyanic acid on phenyl-hydrazo-*iso*propyl, a reaction that will be described in a subsequent paper.

[3] Busch and Walter, *Ber.*, **36**, 1359 (1903).

[4] Bailey and Read, This Journal, **37**, 1888 (1915).

[5] Ref. 3, p. 1360.

[6] Pellizzari, *Gazz. chim. ital.*, [1] **37**, 621 (1907).

[7] Bailey and Acree, *Ber.*, **33**, 1523, footnote 2 (1900).

[8] Ref. 4, p. 1884.

[9] Bailey and Mikeska, This Journal, **38**, 1784 (1916). Bailey and Moore, *ibid.*, **39**, 279 (1917). Hale and Lauge, *ibid.*, **42**, 113 (1920). Kendall and Osterberg, *J. Biol. Chem.*, **40**, 327 (1919).

The employment of acetic acid as the medium of reaction in cyanic acid addition makes it possible to use to advantage the crude melt obtained in the preparation of alkali cyanates on fusion of sodium cyanide with red lead or on heating a mixture of potassium bichromate and potassium ferrocyanide. This modification of the ordinary procedure offers a convenient way of preparing with little labor a very active solution of cyanic acid, obviates the loss of cyanate entailed in isolation and purification, and allows the substitution of the cheaper sodium cyanide for potassium cyanide in making cyanate. Sodium cyanate[10] has hitherto not found application in synthetic work. Thus, as described in the experimental part of this article, a good yield of acetone-2-phenyl semicarbazone is obtained by mixing acetone and phenylhydrazine, dissolving the hydrazone together with excess of acetone in acetic acid, and adding to this solution crude alkali cyanate.

Because of the close structural relationship of 2-phenyl semicarbazide to both phenylhydrazine and semicarbazide, the hydrazines widely employed as aldehyde and ketone reagents, it appeared desirable to investigate the formation of 2-phenyl semicarbazones. Rolla[11] found that 2-phenyl semicarbazide reacts normally with a number of ketones and aldehydes and that semicarbazone formation is accelerated by means of a small amount of hydrochloric acid as catalyst. Our experiments with certain terpene ketones, where the formation of 2-phenyl semicarbazones was attempted under experimental conditions similar to those employed in making simple semicarbazones, gave only negative results. Furthermore, we find that with glucose-2-phenyl semicarbazide gives phenylglucosazone instead of a normal reaction product.

The ease of hydrolysis of 2-phenyl semicarbazide to phenylhydrazine probably accounts for the poor yield of 2-phenyl semicarbazide in the Busch-Walter method of preparation. As shown in the experimental part of this article, the use of an excess of hydrochloric acid in hydrolyzing acetone 2-phenyl semicarbazone leads to the formation of phenylhydrazine hydrochloride. Furthermore, even 2-phenyl semicarbazide hydrochloride in aqueous solution on refluxing gradually evolves carbon dioxide, thereby passing to phenylhydrazine. Although the carbamyl group of acetone 2-phenyl semicarbazone is readily hydrolyzed on steam distillation in alkaline solution, 2-phenyl semicarbazide is comparatively stable under the same conditions.

Experimental Part

Acetone-2-phenyl Semicarbazone, $C_6H_5N(CONH_2)N{=}C(CH_3)_2$.—To 50 g. of acetone-phenylhydrazone[12] in 150 cc. of glacial acetic acid and 50 cc. of water, is added

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[10] Mulder, *Rec. trav. chim.*, **6**, 181 (1887).

[11] Rolla, *Gazz. chim. ital.*, **38**, 327 (1908).

[12] Reisenegger, *Ber.*, **16**, 662 (1883).

over a period of 20 minutes, 30 g. of potassium cyanate (a 10% excess). A temperature of 60° is then maintained for 30 minutes to complete the reaction or, instead, the mixture is allowed to stand at room temperature for a period of 12 hours. The greater part of the acetone-2-phenyl semicarbazone crystallizes and an additional yield is obtained by diluting the solution to 400 cc. and precipitating with ammonium hydroxide. This method of preparation gives a yield of about 93% of that calculated. A slightly yellow color can be removed by recrystallization of the product from water with the addition of Filtchar. For further purification, the substance may be recrystallized from ethyl acetate in needles which melt at 140°, as given by Arnold. Employing the method of Arnold in making this semicarbazone, we obtained a yield of 77%.

Anal. Calc. for $C_{10}H_{13}ON_3$: C, 62.82; H, 6.81; N, 21.99. Found: C, 62.95; H, 6.63; N, 21.87.

Acetone-2-phenyl semicarbazone was prepared by the use of crude alkali cyanate as obtained on fusion of (1) sodium cyanide with red lead[13] and (2) potassium ferrocyanide with potassium dichromate.[14]

In Process 1, 7.5 g. of sodium cyanide is fused with 25 g. of red lead. The powdered melt, separated from the lead, is added in small portions to 8 g. of acetone-phenylhydrazone in 25 cc. of 75% acetic acid. The further procedure corresponds to that given above where pure cyanate is employed. This method gives a yield of 70–75%.

In Process 2, 74 g. of dehydrated potassium ferrocyanide, mixed with 55 g. of fused potassium dichromate, is converted to cyanate in the usual way. The acetone-phenylhydrazone, formed by mixing 15 g. of phenylhydrazine and 9 g. of acetone, is dissolved in 200 cc. of 75% acetic acid, and to this solution the cyanate is added over a period of 20 minutes with the temperature kept below 40°. The reaction mixture is allowed to stand overnight, 400 cc. of water added, and the precipitated acetone-2-phenyl semicarbazone filtered off. A small amount of the semicarbazone remaining in solution can be extracted with chloroform. The greater part of the product is in the cake and can be dissolved out with alcohol or chloroform. This method gives a yield of acetone-2-phenyl semicarbazone amounting to about 80% of that calculated on the basis of the phenylhydrazine used.

Hydrolysis of Acetone-2-phenyl Semicarbazone in Neutral Solution.—As stated by Arnold, acetone-2-phenyl semicarbazone hydrolyzes on boiling with water with the elimination of acetone. In one experiment the semicarbazone was refluxed in water solution for six hours, and in another it was distilled in steam for one hour. The formation of acetone was proved by its conversion to dibenzylidene acetone with benzaldehyde and sodium hydroxide in the usual way. The formation of 1-phenyl semicarbazide was confirmed by comparison with a sample of this substance made from phenylhydrazine and potassium cyanate. The ready solubility in chloroform of the 2-, in contrast to the difficult solubility of the 1- modification, affords a convenient method of separation of the two isomers; Busch and Walter[15] report that 2-phenyl semicarbazide at its fusion point transforms to the 1-form, but this rearrangement under the conditions of our experiment was rather unexpected.

Anal. Calc. for $C_7H_9ON_3$: N, 27.81. Found: 28.10.

Action of Potassium Hydroxide on Acetone-2-phenyl Semicarbazone.—When the semicarbazone is suspended in a dilute aqueous solution of one molecular equivalent of

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[13] Cohen, "Theoretical Organic Chemistry," MacMillan and Co., 2nd edition, 1920, p. 221.

[14] Bell, *Chem. News*, **32**, 99 (1875). Gattermann, *Ber.*, **23**, 1224 (1890). Erdmann, *Ber.*, **26**, 2442 (1893).

[15] Ref. 3, p. 1360.

potassium hydroxide and steam-distilled, ammonia and acetone-phenylhydrazone are volatilized. The hydrolysis in alkaline solution, which takes place very readily, proceeds as follows: $C_6H_5N(CONH_2)N{=}C(CH_3)_2 + KOH + H_2O \longrightarrow C_6H_5NHN{=}C(CH_3)_2 + NH_3 + KHCO_3$. The acetone-phenylhydrazone can be readily identified by reconversion to acetone-2-phenyl semicarbazone by the action of potassium cyanate in acetic acid solution.

Hydrolysis of Acetone-2-phenyl Semicarbazone in Acid Solution.—A solution of 50 g. of acetone-2-phenyl semicarbazone in 23.2 cc. of hydrochloric acid (d., 1.19) is diluted with 225 cc. of water and the mixture evaporated to dryness in a vacuum at water-bath temperature. The residue consists of 2-phenyl semicarbazide hydrochloride in a yield of about 97%. For purification the hydrochloride is dissolved in the least amount of alcohol, to which a little water has been added, and is then precipitated with ether. When so purified, it shows the correct melting point, 186°.

Preparation of 2-Phenyl Semicarbazide, $C_6H_5N(CONH_2)NH_2$.—The hydrochloride is dissolved in the least amount of water and the base precipitated with ammonium hydroxide. Any 2-phenyl semicarbazide remaining in solution can be extracted with chloroform. 2-Phenyl semicarbazide, in contrast to phenylhydrazine, can be extracted with chloroform from an aqueous solution of its hydrochloride, a proof that the former is a weak base. Furthermore, the position of the carbamyl group on phenylhydrazine has an influence on the basicity of the molecule as shown in the claim of Busch and Walter that "2-phenyl semicarbazide differs from the long known 1-phenyl semicarbazide in its more strongly basic character (the hydrochloride of the latter dissociates in water)."

When two molecular equivalents of hydrochloric acid were used in hydrolyzing acetone-2-phenyl semicarbazone, a considerable amount of phenylhydrazine hydrochloride was obtained. This remained in the mother liquor after extraction of the 2-phenyl semicarbazide with chloroform and, upon concentration of the solution, crystallized in characteristic, thin, lustrous plates. It was identified by comparison with a stock sample of phenylhydrazine hydrochloride, by conversion to benzal phenylhydrazone and by a nitrogen determination.

Anal. Calc. for $C_6H_9N_2Cl$: N, 19.37. Found: 19.37.

The ease with which 2-phenyl semicarbazide hydrolyzes to phenylhydrazine can be shown by refluxing an aqueous solution of the hydrochloride. There results a gradual evolution of carbon dioxide with the formation of phenylhydrazine and ammonium chloride.

Benzal-2-phenyl Semicarbazone.—This semicarbazone can be conveniently made by dissolving acetone-2-phenyl semicarbazone in one molecular equivalent of dil. hydrochloric acid and treating the solution thus obtained with benzaldehyde. It is difficultly soluble in water and, in contrast to benzal phenylhydrazone, is readily soluble in chloroform. Recrystallized from alcohol, it gave the correct melting point, 154°.

Action of 2-Phenyl Semicarbazide on Glucose.—Where either 2-phenyl semicarbazide or its hydrochloride is employed in acetic acid solution with sodium acetate under conditions usually followed in making phenyl-glucosazone,[16] there results the same osazone that is obtained with phenylhydrazine. A further proof that 2-phenyl semicarbazide is hydrolyzed was indicated by the evolution of carbon dioxide during the reaction. A comparison of the product obtained was made with a stock sample of phenylglucosazone and a nitrogen determination agreed closely with the osazone formula.

Anal. Calc. for $C_{18}H_{22}O_4N_4$: N, 15.64. Found: 15.47.

Cyclohexanone-2-phenyl Semicarbazone.—A mixture of 5 g. of 2-phenyl semicarbazide hydrochloride, 5 g. of fused sodium acetate and 3 g. of cyclohexanone is added

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[16] Fischer, *Ber.*, **23**, 374 (1890).

to 25 cc. of alcohol which is then diluted with 10 cc. of water and the whole shaken until complete solution is effected. After 72 hours an equal volume of water is added. Upon further standing, the reaction product separates and is recrystallized from dil. alcohol in the form of slender needles; m. p., 177°.

Anal. Calc. for $C_{13}H_{17}ON_3$: C, 67.53; H, 7.36; N, 18.18. Found: C, 67.71; H, 7.25; N, 18.07.

Summary

1. An improved method of preparation of acetone-2-phenyl semicarbazone is given.

2. It is shown that the crude cyanate melt obtained in the fusion of (*a*) sodium cyanide and red lead or (*b*) potassium ferrocyanide and potassium dichromate furnishes a very satisfactory source of cyanic acid in the preparation of acetone-2-phenyl semicarbazone.

3. Acetone-2-phenyl semicarbazone (*a*) on neutral hydrolysis passes to 1-phenyl semicarbazide; (*b*) on acid hydrolysis 2-phenyl semicarbazide hydrochloride is formed; (*c*) on alkaline hydrolysis, acetone-phenylhydrazone results.

4. Although closely related to both semicarbazide and phenylhydrazine, 2-phenyl semicarbazide is apparently of no value in connection with terpene ketones or sugars.

Austin, Texas

[Contribution from the Chemical Laboratory of Tufts College]

THE ACTION OF HYDROXYLAMINE AND OF HYDRAZINE ON THE ARYL MONOTHIO-AMIDES OF ETHYL ACETYLMALONATE. II

By David E. Worrall

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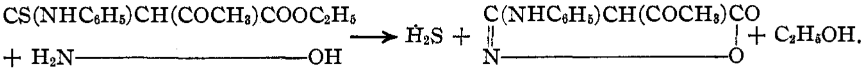
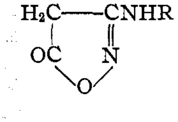
Hydroxylamine[1] reacts smoothly and easily with thio-amides obtained by the action of mustard oils on ethyl aceto-acetate, forming isoxazones.

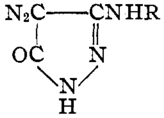


$$\begin{array}{l}\mathrm{CS(NHC_6H_5)CH(COCH_3)COOC_2H_5}\\ +\ \mathrm{H_2N}\text{——————}\mathrm{OH}\end{array}\longrightarrow \mathrm{H_2S}+\begin{array}{l}\mathrm{C(NHC_6H_5)CH(COCH_3)CO}\\ \|\qquad\qquad\qquad\qquad\quad |\\ \mathrm{N}\text{——————}\mathrm{O}\end{array}+\ \mathrm{C_2H_5OH}.$$

The acetyl group is eliminated as a result of hydrolysis; consequently isoxazolones of the general formula I are obtained. A similar series of changes



I



II

take place with hydrazine resulting in the formation of pyrazoles of the type II. These reactions have been extended to a number of new thio-amides described in the preceding article. Hydrazine has been used successfully

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[1] Worrall, This Journal, 44, 1551 (1922).