Summary of Discussion

1. Our results confirm the fact that acetone may be enolized in aqueous solutions, thus giving rise to the formation of iso-acetone which is in dynamic equilibrium with acetone, a relationship entirely analogous to the well-known behavior of ethyl aceto-acetate, malonic ester, acetaldehyde and many other compounds.

2. The effect of increasing the concentration of the alkali up to 3.69×10^{-2} M is one that gives rise to a corresponding increase in the concentration of iso-acetone molecules. The weight of the basic mercuric iso-acetone obtained at this concentration of alkali is equivalent to 26.5% of the original acetone used.

Beyond this concentration of alkali the acetone and iso-acetone are in equilibrium.

3. It is possible to determine quantitatively the relationship of iso-acetone concentration to the alkali concentration at the end of 24 hours at 25° through the formation of basic mercuric iso-acetone, $(CH_3.CO{=}CH_2)_2Hg.2HgO$, by adding freshly precipitated mercuric oxide to aqueous solutions of acetone containing various concentrations of potassium hydroxide.

4. The relationship between the amounts of basic mercuric iso-acetone obtained and the concentration of the alkali used between 0.2116×10^{-2} and 3.69×10^{-2} M potassium hydroxide solution was found to be logarithmic.

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[Contribution from the Chemical Laboratory of the University of North Carolina]

4-META-NITROPHENYLSEMICARBAZIDE AND CERTAIN DERIVATIVES

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The following paper is a continuation of our study of the reaction between phenylsemicarbazide and ketones. The smooth character of the reaction between phenylsemicarbazide and the keto isomer of β-hydrojuglone, observed by Willstätter and Wheeler,[2] led to further studies with phenylsemicarbazide and substituted phenylsemicarbazides. Wheeler and Edwards[3] used phenylsemicarbazide to detect the keto form of tetrahydroxynaphthalene. Wheeler and Bost[4] prepared *p*-tolylsemicarbazide.

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[1] An abstract of a thesis submitted in June, 1925, to the Faculty of the University of North Carolina by T. T. Walker in candidacy for the degree of Master of Science.

[2] Willstätter and Wheeler, *Ber.*, **47**, 2800 (1914).

[3] Wheeler and Edwards, This Journal, **38**, 390 (1916).

[4] Wheeler and Bost, *ibid.*, **46**, 2813 (1924).

The present investigation was started by an attempt to prepare 4-*p*-nitrophenylsemicarbazide, a compound not hitherto made. The required nitrophenylurea had been made by Pierron,[5] who treated *p*-nitro-aniline with cyanogen bromide and hydrolyzed the resulting cyanamide. In a number of attempts we were unable to duplicate Pierron's experiments although we were able to prepare the *meta* compound by his method. Although the latter compound could be thus prepared, we found it better to use the method of Walther and Wlodkowski[6] who treated *m*-nitro-aniline in glacial acetic acid with potassium cyanate. The urea was converted into the semicarbazide by the method of Curtius and Burkhardt[7] who boiled it with hydrazine hydrate. Curtius and Hofman[8] prepared the benzoyl derivative of 4-*m*-nitrophenylsemicarbazide but did not isolate the free base. They obtained this derivative by the action of *m*-nitrophenylazo-imide on benzohydrazide. The 1-*m*-nitrophenylsemicarbazide has been obtained by Young and Stockwell[9] by the action of potassium cyanate on *m*-nitrophenylhydrazine hydrochloride. They state that it consists of delicate, white needles; m. p., 195°, with decomposition. We find that the 4- isomer melts at 138–139°.

We have condensed the 4-*m*-nitrophenylsemicarbazide with acetone, chloro-acetone, methylethyl ketone, acetophenone, benzophenone, camphor and cyclohexanone. The *p*-quinone compound was insoluble in organic solvents and we did not succeed in purifying it.

The reaction with ketones takes place with the elimination of one molecule of water: $(CH_3)_2CO + H_2NNHCONHC_6H_4NO_2 = (CH_3)_2C.NNHCONHC_6H_4NO_2 + H_2O$.

Experimental Part

The Preparation of 4-*m*-Nitrophenylsemicarbazide, $NH_2NHCONHC_6H_4NO_2$.—*m*-Nitrophenylurea was best prepared by the method of Walther and Wlodkowski.[6] To a solution of 50 g. of *m*-nitro-aniline in 250 cc. of warm glacial acetic acid was slowly added 40 g. (an excess) of powdered potassium cyanate. Much gas was evolved. The hot solution was quickly filtered and poured into 1500 cc. of cold water. The product immediately crystallized; m. p., 174–184°. It was purified by recrystallization from 2500 cc. of boiling water. The pure *m*-nitrophenylurea consists of flexible, fine yellow needles; m. p., 187–194°; yield, 52 g., or 80%.

The *m*-nitrophenylurea was converted into the semicarbazide by the method of Curtius and Burkhardt[7] with some modifications. Ten g. of *m*-nitrophenylurea and 9 g. (3 molecular equivalents) of 100% hydrazine hydrate were dissolved in 10 cc. of alcohol and the solution was boiled for 30 hours in a flask sealed to a condenser tube. The reaction mixture was poured into 50 cc. of water and the flask washed out with more

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[5] Pierron, *Bull. soc. chim.*, [3] **33,** 69 (1905).

[6] Walther and Wlodkowski, *J. prakt. Chem.*, **59,** 266 (1899).

[7] Curtius and Burkhardt, *ibid.*, **58,** 205 (1898).

[8] Curtius and Hofman, *ibid.*, [2] **53,** 513 (1896).

[9] Young and Stockwell, *J. Chem. Soc.*, **73,** 372 (1898).

water. The crystalline mass (at first a red liquid) that separated on standing consisted of unchanged nitrophenylurea and the nitrosemicarbazide. The impure product weighed 4.5 g. and melted at 96–99° to a semi-solid and at 120° to a reddish-brown liquid. Purification was effected by dissolving the product in 45 cc. of hot alcohol and adding 22 cc. of concd. hydrochloric acid. The hydrochloride of the semicarbazide separated in abundance in flake-like crystals. It was filtered off, washed with a little alcohol, redissolved in 200 cc. of water and precipitated with a slight excess of potassium hydroxide. The free base was filtered off and washed with water. The crude product melted at 136–137°. It was purified by recrystallization from 50 cc. of hot alcohol. The pure substance consists of very bulky, flexible, fine, pale yellow needles; m. p., 138–139°; yield, 2.4 g., or about 22%.

A better yield was obtained by using 42% hydrazine hydrate prepared by the Eastman Kodak Company. The presence of a larger proportion of water may have been the cause. Fifty g. of nitrophenylurea and 65 g. (2 molecular equivalents) of 42% hydrazine hydrate were dissolved in 110 cc. of alcohol and the solution was boiled 50 hours; yield, 19.5 g., or nearly 36%.

Anal. Subs., 0.0899: 22.7 cc. of N (23°, 756 mm.). Calcd. for $C_7H_8O_3N_4$ (mol. wt., 196): N, 28.57. Found: 28.15.

The carbazide reduces Fehling's solution and ammoniacal silver nitrate in the cold. It dissolves in about 4 parts of boiling alcohol and is only slightly soluble at room temperature. It is soluble in hot water, chloroform and benzene and insoluble in ether. It dissolves readily in dilute acids and gives a red coloration with strong alkalies.

4-*m*-Nitrophenylsemicarbazide Hydrochloride, $C_7H_8O_3N_4.HCl$.—Two g. of the semicarbazide was dissolved in 20 cc. of hot alcohol, and 5 cc. of alcohol added. After the mixture had been cooled, the hydrochloride was filtered off and washed with alcohol. The salt consists of glistening, white, flake-like crystals, readily soluble in water, soluble in about ten parts of hot alcohol and readily hydrolyzed by aqueous solutions of strong alkalies.

Anal. Subs., 0.2985: AgCl, 0.1860. Calcd. for $C_7H_9O_3N_4Cl$ (mol. wt., 232.5): Cl, 15.27. Found: 15.45.

Condensation Products

Acetone-4-*m*-nitrophenylsemicarbazone, $(CH_3)_2C.NNHCONHC_6H_4NO_2$.—Two g. of the semicarbazide hydrochloride was dissolved in 40 cc. of hot alcohol and 2 g. of acetone was added. A dense crystallization took place rapidly. After the mixture had been cooled, 50 cc. of water was added, the product filtered off and washed with water. The yield was more than one gram. Recrystallization from 100 cc. of hot alcohol gave very bulky, flexible, yellow needles; m. p., 210–211°; yield, about 1 g.

Anal. Subs., 0.1158: 24.7 cc. of N (25°, 748 mm.). Calcd. for $C_{10}H_{12}O_3N_4$ (mol. wt., 236): N, 23.73. Found: 23.49.

The product is soluble in methyl alcohol, chloroform and nitrobenzene at room temperature, soluble in hot alcohol and benzene and insoluble in water and carbon tetrachloride.

Chloro-acetone-4-*m*-nitrophenylsemicarbazone, $CH_3CH_2ClC.NNHCONHC_6H_4$-$NO_2$.—One g. of chloro-acetone was mixed with 1 g. of the semicarbazide salt in 30 cc. of hot alcohol. The reaction was immediate; yield, 1.3 g. The product was recrystallized from 700 cc. of boiling alcohol as fine, pale yellow needles, melting to a semi-solid at 223° and to a dark brown liquid at 238°.

Anal. Subs., 0.2585: AgCl, 0.1460. Calcd. for $C_{10}H_{11}O_3N_4Cl$ (mol. wt., 270.5): Cl, 13.12. Found: 13.39.

This compound is difficultly soluble in hot alcohol and nearly insoluble in the usual organic solvents.

Methylethylketone-4-*m*-nitrophenylsemicarbazone, $CH_3C_2H_5C.NNHCONHC_6H_4NO_2$.—One g. of the hydrochloride, 30 cc. of hot alcohol, 2 g. of the ketone and 0.4 g. of sodium acetate were used in this preparation. Crystallization took place at once; yield, about 1 g. The product was recrystallized thrice from hot alcohol, using 120 cc. each time; yield, 0.7 g. of very bulky, pale yellow needles; m. p., 205°.

Anal. Subs., 0.1388: 27.9 cc. of N (21°, 755.4 mm.). Calcd. for $C_{11}H_{14}O_3N_4$ (mol. wt., 250): N, 22.40. Found: 22.63.

This compound is insoluble in water, but soluble in cold chloroform and in other organic solvents when hot.

Acetophenone-4-*m*-nitrophenylsemicarbazone, $CH_3(C_6H_5)C.NNHCONHC_6H_4NO_2$.—Two parts of acetophenone for one part of the hydrochloride were used; the reaction was immediate. The product was recrystallized from 150 cc. of hot benzene as very bulky, fine, white needles; m. p., 211–212°; yield, 0.8 g.

Anal. Subs., 0.1484: 26.5 cc. of N (28°, 751 mm.). Calcd. for $C_{15}H_{14}O_3N_4$ (mol. wt., 298): N, 18.79. Found: 19.25.

The product is soluble in cold chloroform, carbon tetrachloride or nitrobenzene, soluble in hot alcohol or benzene and insoluble in water.

Benzophenone-4-*m*-nitrophenylsemicarbazone, $(C_6H_5)_2C.NNHCONHC_6H_4NO_2$.—Sodium acetate was necessary in this condensation; 1 g. of the semicarbazide salt, 30 cc. of hot alcohol, 0.9 g. of benzophenone and 0.4 g. of sodium acetate were used. The mixture was boiled for 20 minutes and cooled; yield, 1.1 g.—Recrystallization from 40 cc. of hot alcohol gave light yellow needles that were long, brittle and very bulky; m. p., 133–136°.

Anal. Subs., 0.1792: 24 cc. of N (19.5°, 752.7 mm.). Calcd. for $C_{20}H_{16}O_3N_4$ (mol. wt., 360): N, 15.55. Found: 15.17.

This substance is soluble in cold chloroform or nitrobenzene, and in hot alcohol or benzene.

Camphor-4-*m*-nitrophenylsemicarbazone, $C_{10}H_{16}NNHCONHC_6H_4NO_2$.—The same mixture was used that is given above except that it contained a little less camphor than benzophenone. The boiling was continued for four hours, the product crystallizing during the heating; yield, 0.7 g. It was recrystallized from 100 cc. of hot alcohol and obtained as very short, thick, colorless prisms; m. p., 240–242°.

Anal. Subs., 0.1284: 19.7 cc. of N (20.5°, 751.5 mm.). Calcd. for $C_{17}H_{22}O_3N_4$ (mol. wt., 330): N, 16.96. Found: 17.22.

The solubilities are the same as for the benzophenone product.

Cyclohexanone-4-*m*-nitrophenylsemicarbazone, $(CH_2)_5C.NNHCONHC_6H_4NO_2$.—A mixture similar to that used with camphor gave a yield of 1.3 g. from 1 g. of the hydrochloride. Recrystallization from 200 cc. of hot alcohol gave a pure product, consisting of very bulky, colorless needles; m. p., 219–220°. The solubilities correspond to those of the camphor product.

Anal. Subs., 0.1185: 21.2 cc. of N (23°, 750 mm.). Calcd. for $C_{13}H_{16}O_3N_4$ (mol. wt., 276): N, 20.29. Found: 19.80.

Summary

1. 4-*m*-Nitrophenylsemicarbazide was prepared for the first time by the action of hydrazine hydrate on *m*-nitrophenylurea, being obtained as yel-

low needles; m. p., 138–139°. The hydrochloride was obtained as white flakes.

2. Semicarbazones were prepared by condensation with ketones in alcoholic solution, the addition of sodium acetate sometimes being necessary. The following ketones were used: acetone, chloro-acetone, methylethyl ketone, acetophenone, benzophenone, camphor and cyclohexanone.

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

THE STABILITY OF HEXA-SUBSTITUTED ETHANES

BY A. E. GRAY[1] WITH C. S. MARVEL

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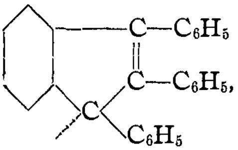
Since the discovery of triphenylmethyl by Gomberg,[2] a large number of variously substituted triaryl methyls have been prepared. However, not so much attention has been given to the study of the ethanes into which large saturated or unsaturated aliphatic groups have been introduced.

In most of the known compounds of this series the three groups attached to the trivalent carbon are aryl groups, but a few are known where this is not the case. Kohler[3] discovered 1,2,3-triphenylindyl,  in which only two of the groups attached to the trivalent carbon are aryl groups. However, the third valence carries a radical containing two phenyl groups. Schlenk and Mark[4] have prepared pentaphenylethyl. Ziegler and Ochs[5] have discovered a series of the general type $(Ar)_2—\underset{|}{C}—CH=C(C_6H_5)_2$ which exist entirely in the monomolecular state. More recently he has shown that *sym.*-tetraphenyl-dicyclohexylethane[6] dissociates to some extent since it forms a peroxide with oxygen. Conant and Sloan[7] have obtained benzylxanthyl, $O<(C_6H_4)_2>\underset{|}{C}—CH_2C_6H_5$

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[1] This communication is an abstract of a thesis submitted by A. E. Gray in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[2] Gomberg, THIS JOURNAL, **22**, 757 (1900); *Ber.*, **33**, 3150 (1900).

[3] Kohler, *Am. Chem. J.*, **40**, 228 (1908).

[4] Schlenk and Mark, *Ber.*, **55B**, 2285 (1922).

[5] Ziegler and Ochs, *Ber.*, **55B**, 2257 (1922). Ziegler, *Ann.*, **434**, 34 (1923).

[6] Ziegler and Schnell, *Ann.*, **437**, 252 (1924).

[7] Conant and Sloan, THIS JOURNAL, **45**, 2466 (1923); **47**, 572 (1925).