double salt of zinc chloride, but the amount of zinc chloride that is retained by the compound is variable. Analysis showed this new compound to be the furan analog of benzoflavin or dimethyl-diamino-furyl-acridine hydrochloride. In its properties it is like a typical acridine dye. It dyes silk, wool and unmordanted cotton and in fastness and stability is indistinguishable from its analog, benzoflavin.

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4-PARA-TOLYLSEMICARBAZIDE AND CERTAIN DERIVATIVES[1]

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In certain cases where an aldehyde or ketone is particularly sensitive to alkaline reagents, semicarbazide and phenylsemicarbazide have a great advantage over hydroxylamine as reagents for the carbonyl group. There may be cases where phenylsemicarbazide has an advantage over semicarbazide on account of its increased negativity. Of the three known phenylsemicarbazides the 1-phenylsemicarbazide has not been employed. The 2-phenylsemicarbazide seems to have been used in one case, its condensation with benzaldehyde.[2] The 4-phenylsemicarbazide was first used by Curtius and Hofmann[3] who condensed it with acetone. Its value was further shown by Wheeler and Edwards[4] who prepared a phenylsemicarbazone of tetrahydroxy-naphthalene, an oxime not being obtainable.

In this paper we propose another reagent, 4-*p*-tolylsemicarbazide, describing its preparation and its condensation products with acetone, acetophenone, benzophenone, *p*-quinone and camphor.

Two *p*-tolylsemicarbazides have been described in the literature. Bamberger[5] obtained what should be called 1-*p*-tolylsemicarbazide by the action of potassium cyanate on *p*-tolylhydrazine, analogous to Fischer's method of preparing 1-phenylsemicarbazide. Bamberger states that it crystallizes in silky white leaflets, melting at 190–191°. Pinner[6] treated *p*-tolylhydrazine with urea and obtained what should be called 4-*p*-tolylsemicarbazide as glistening leaves, melting at 157–158°. Young and Stockwell[7] prepared 1-*p*-tolylsemicarbazide by Bamberger's method but

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[1] This paper is a portion of a thesis submitted by R. W. Bost in partial fulfilment of the requirements for the degree of Master of Arts at the University of North Carolina.

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

[3] Curtius and Hofmann, *J. prakt. Chem.*, [2] **53**, 526 (1896).

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

[5] Bamberger, *Ber.*, **35**, 1424 (1902).

[6] Pinner, *Ber.*, **21**, 1219 (1888).

[7] Young and Stockwell, *J. Chem. Soc.*, **73**, 368 (1898).

gave 187–188° as the melting point. We adopted the method of Curtius and Burkhardt[8] who prepared 4-phenylsemicarbazide by the action of hydrazine on phenylurea. *p*-Tolylurea in alcoholic solution was heated with 100% hydrazine hydrate. The purified product consists of silvery, white leaflets, m. p. 157–158°, thus corresponding to Pinner's compound. However, as to its behavior when heated Pinner states merely that it melts at 157–158°, but we find that it contracts to a soft mush at 157–158°, remaining opaque and then decomposing at 274° with effervescence. This latter product must be *p*-tolylurazole, since Pinner observed that phenylsemicarbazide, held for some time in a melted state, was partly converted into phenylurazole.

Experimental Part

Preparation of 4-*p*-Tolylsemicarbazide.—To a solution of 40 g. of *p*-toluidine in 40 cc. of hot alcohol was added a 25% excess of concd. hydrochloric acid. The hydrochloride crystallized abundantly, weighing 46 g. when dried; m. p., 232–234°. This melting point was not raised by recrystallizing the salt from alcohol. The substance was converted into *p*-tolylurea according to the method of Davis and Blanchard[9] who described the preparation of phenylurea. A solution of 50.4 g. of urea and 121 g. of *p*-toluidine hydrochloride in 500 cc. of water was boiled under a reflux condenser. At the end of 20 minutes crystals of di-*p*-tolylurea suddenly appeared. The boiling was continued until the mixture bumped. The hot liquid was immediately filtered with suction and the di-*p*-tolylurea was washed with hot water. *p*-Tolylurea crystallized as the filtrate cooled. It was filtered off and the filtrate again boiled under the reflux condenser until it bumped, again filtered hot and the filtrate cooled for a second crop of tolylurea. After four such operations the final filtrate was concentrated to one-half of its volume for final small crops of the two products. The yield of di-*p*-tolylurea, m. p. 253°, amounted to 46.3 g. The *p*-tolylurea, melting over the wide range of 169–180°, weighed 58.6 g. Of several methods for purifying the product the following proved to be the best. A hot saturated solution was made in glacial acetic acid and filtered into cold water. A dense mass of crystals formed, was filtered off and washed several times with water. The yield was highly satisfactory and the product was pure. It consists of glistening, white plates, melting at 184°. Steiner[10] gave 180° as the melting point, whereas Cosack[11] at a later date gave 172°.

The tolylsemicarbazide was prepared by heating 9 g. of tolylurea with 9 g. of hydrazine hydrate (100%) in 30 cc. of absolute alcohol in a flask with the condenser tube sealed to it. The solution was boiled gently for 12 hours. It was then poured out into a beaker, the flask was rinsed with water and the rinsings were added to the main solution. The solution was filtered hot to remove some fine, black particles that are always present. It was then concentrated to its original volume or somewhat less and set aside to cool. A dense crystallization took place. The product was practically pure. It is best purified through its hydrochlor-

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[8] Curtius and Burkhardt, *J. prakt. Chem.*, **58,** 205 (1898).

[9] Davis and Blanchard, This Journal, **45,** 1816 (1923).

[10] Steiner, *Ber.*, **8,** 519 (1875).

[11] Cosack, *Ber.*, **12,** 1450 (1879).

ide. A hot saturated alcoholic solution is treated with ice-cold concd. hydrochloric acid. The precipitated salt is redissolved in water and the base set free with sodium hydroxide solution. Pure 4-*p*-tolylsemicarbazide crystallizes in colorless plates which contract to a soft mass at 157–159°, remaining opaque and then decomposing at 274° with effervescence. It reduces ammoniacal silver solution, also Fehling's solution, and gives a green color with copper sulfate and a green precipitate after standing for some time.

Condensation Products

Acetone-4-*p*-tolylsemicarbazone, $(CH_3)_2NNHCONHC_6H_4CH_3$.—One g. of tolylsemicarbazide was dissolved in about 20 cc. of alcohol, 5 drops of glacial acetic acid were added and then 1.05 g. of acetone. The mixture was heated on the steam-bath for 20 minutes, the product crystallizing during the heating. It was then poured into a beaker and crystallization was allowed to become complete. The product was purified by recrystallizing it from alcohol. It consists of fine, colorless prismatic needles that decompose at 205° with effervescence.

Anal. Subs., 0.1580: CO_2, 0.3611; H_2O, 0.1089. Subs., 0.1586: 32 cc. of N (27°, 748 mm.). Calc. for $C_{10}H_{15}ON_3$ (mol. wt., 193): C, 67.17; H, 7.77; N, 21.76. Found: C, 62.33; H, 7.71; N, 21.79.

Acetophenone-4-*p*-tolylsemicarbazone, $C_6H_5CH_3CNNHCONHC_6H_4CH_3$.—The condensation with acetophenone was carried out as with acetone. The product was recrystallized from alcohol, forming beautiful, colorless needles, arranged in clusters. It melts at 165° to a colorless liquid. The product is also soluble in ether, benzene and chloroform. The substance is very bulky, the crystals being long and very flexible. It was noted that the melted substance solidifies as it cools and then on being reheated softens only slightly at 165° and at 198° melts to a yellow liquid. Its melting point is also changed when the substance is exposed to the sunlight for several days. This change is undoubtedly analogous to that of acetophenone-semicarbazone, which is converted by heat into methylphenyl-ketazine and hydrazo-dicarbamide.

Anal. Subs., 0.1608: CO_2, 0.4236; H_2O, 0.0938. Subs., 0.1264: 17.4 cc. of N (23°, 750 mm.). Calc. for $C_{16}H_{17}ON_3$ (mol. wt., 267): C, 71.91; H, 6.36; N, 15.73. Found: C, 71.84; H, 6.52; N, 15.22.

Benzophenone-4-*p*-tolylsemicarbazone, $(C_6H_5)_2CNNHCONHC_6H_4CH_3$.—To a saturated alcoholic solution of 1 g. of tolylsemicarbazide were added 5 drops of glacial acetic acid and a saturated alcoholic solution of 1.1 g. of benzophenone. Four hours' boiling was necessary in order to complete the reaction. The solution was then poured into a beaker and a small amount of water added. The product consisted of colorless needles that melted at 162° to a light yellow liquid.

Anal. Subs., 0.1434: CO_2, 0.3998; H_2O, 0.0698. Subs., 0.1166: 13.2 cc. of N (25°, 753 mm.). Calc. for $C_{21}H_{19}ON_3$ (mol. wt., 329): C, 76.59; H, 5.77; N, 12.76. Found: C, 76.03; H, 5.44; N, 12.44.

***p*-Quinone-4-*p*-tolylsemicarbazone,** $CO(CHCH)_2CNNHCONHC_6H_4CH_3$.—For 1 g. of tolylsemicarbazide, 0.65 g. of *p*-quinone was used according to the method described above. Crystals began to form as soon as the materials were mixed. Nevertheless, the mixture was heated for 20 minutes to insure completion of the reaction. The product was recrystallized from alcohol and consisted of lustrous brown leaflets that melted to a dark brown liquid at 165°.

Anal. Subs., 0.1328: CO_2, 0.3205; H_2O, 0.0619. Subs., 0.1552: 24 cc. of N_2

(29°, 745 mm.). Calc. for $C_{14}H_{13}O_2N_3$ (mol. wt., 255): C, 65.88; H, 5.09; N, 16.47. Found: C, 65.82; H, 5.21; N, 16.44.

Camphor-4-*p*-tolylsemicarbazone, $C_{10}H_{16}NNHCONHC_6H_4CH_3$.—Difficulty was experienced in bringing about the condensation with camphor and the method used above could not be employed. It was modified as follows. To a saturated solution of 0.2 g. of tolylsemicarbazide hydrochloride and 0.18 g. of sodium acetate in water was added 0.18 g. of camphor dissolved in 20 cc. of glacial acetic acid. The mixture was boiled under a reflux condenser for 25 minutes to effect solution and then set aside for slow crystallization. A small amount of water aided the separation. The product consisted of colorless needles that melted at 225–229° to a brownish liquid.

Anal. Subs., 0.1058: CO_2, 0.2810; H_2O, 0.0773. Subs., 0.0724: 9.5 cc. of N_2 (23°, 746 mm.). Calc. for $C_{18}H_{25}ON_3$ (mol. wt., 299): C, 72.24; H, 8.36; N, 14.04. Found: C, 72.43; H, 7.73; N, 14.57.

Summary

1. 4-*p*-Tolylsemicarbazide was prepared by the action of hydrazine hydrate on tolylurea and obtained as lustrous plates, contracting at 157–159° and decomposing at 274°, doubtless forming tolylurazole by loss of ammonia.

2. This tolylsemicarbazide was condensed with acetone, acetophenone, benzophenone, *p*-quinone and camphor.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A STUDY OF THE OPTIMUM CONDITION FOR THE PREPARATION OF NORMAL VALERIC ACID FROM BUTYLMAGNESIUM BROMIDE AND CARBON DIOXIDE

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Introduction

In connection with studies on some relationship between physiological action and chemical constitution it was necessary to synthesize relatively large quantities of certain aliphatic carboxylic acids from the Grignard reagent and carbon dioxide. This reaction has found rather general application in the synthesis of a wide variety of carboxylic acids. Scattered through the very comprehensive literature on the subject are detached accounts of methods of manipulation which are helpful in the preparation of certain acids with improved yields. Unfortunately, the results of some of the few apparently complete studies have been questioned.

The experiments described here concern the effect of the variation of some factors on the yield of *n*-valeric acid from butylmagnesium bromide and carbon dioxide. The yields of two other acids, benzoic and cyclo-

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[1] This paper is an abstract of a part of a thesis presented by Harold H. Parker in fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.