[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-BROMOPHENYL-4-SEMICARBAZIDE[1]

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This paper is a continuation of studies[2] in this Laboratory on semicarbazides as ketone reagents. *p*-Bromophenylurea, from which the semicarbazide was prepared, has not been satisfactorily characterized. We prepared it by three different methods: (1) by the action of bromine on phenylurea in glacial acetic acid solution;[3] (2) by the action of bromine on an alcoholic solution of phenylurea; (3) by the action of potassium cyanate on *p*-bromo-aniline hydrochloride in hot water solution. Each method has its advantages. The impure product behaved so erratically on heating that much time was lost in arriving at a pure product. If heated rapidly, it melts; if slowly, it does not melt. In either case it decomposes at an elevated temperature. The statement of Pinnow that it decomposes at about 260° evidently is incorrect.

The semicarbazide was prepared according to the method of Curtius[4] and Burkhardt, who prepared phenylsemicarbazide. *p*-Bromophenylurea was heated for fifty hours with an excess of hydrazine hydrate. The pure product melts at 252 and at 254° decomposes to a claret-colored liquid.

Semicarbazones were obtained by treating alcoholic solutions of the semicarbazide with the following ketones: acetone, methyl ethyl ketone monochloro-acetone, α,γ-dichloro-acetone, acetophenone and benzophenone.

Experimental

p-Bromophenylurea, $C_6H_4BrNHCONH_2$.—This compound was first made by Pinnow.[3] He treated a glacial acetic acid solution of phenylurea with bromine. Two of the workers in this research (Pritchard and Andrews) preferred an alcoholic solution, while the others preferred a very different method, *i. e.*, the action of potassium cyanate on *p*-bromo-aniline hydrochloride in hot water. The product may be purified by hot water (soluble in 200 parts); hot alcohol (soluble in 7 parts); glacial acetic acid (soluble in 5 parts) or from benzene. If alcohol or acetic acid is used, the solution is poured into cold water. It crystallizes in long colorless needles which behave peculiarly on heating. If the rate of heating is 50° per minute or faster, the substance melts at 220°, resolidifies about 225° and decomposes at about 296° to a black rubber-like substance. When heated slowly no apparent change occurs until decomposition takes place at 296°. Pinnow states that decomposition without melting occurs at 260°.

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[1] This research was begun by Paul R. Bryan, continued by W. N. Pritchard, Jr., T. M. Andrews and J. A. Bender, and completed by J. G. Park.

[2] Wheeler and Bost, THIS JOURNAL, **46**, 2813 (1924); Wheeler and Walker, *ibid.*, **47**, 2792 (1925); Wheeler and Norton, *ibid.*, **50**, 2488 (1928); Wheeler and Park, *ibid.*, **51**, 3079 (1929).

[3] Pinnow, *Ber.*, **24**, 4172 (1891).

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

We have never observed any such behavior of the many preparations which we have made.

Anal. Calcd. for $C_7H_7ON_2Br$: Br, 37.20. Found: (Paul R. Bryan) 37.23; (W. N. Pritchard, Jr.) 37.37.

p-Bromophenyl-4-semicarbazide, $C_6H_4BrNHCONHNH_2$.—The semicarbazide was prepared by boiling an absolute alcoholic solution of bromophenylurea with hydrazine hydrate. Many variations of proportions of materials were tried. The time of boiling was also varied. The best yield was obtained by J. G. Park: 5.4 g. of bromophenylurea, 30 cc. of absolute alcohol and 7.5 g. of 42% hydrazine hydrate (2.5 equivalents) were boiled under a reflux condenser for fifty hours. After determining that an excess of hydrazine hydrate was necessary, it was found that prolonging the time of heating increased the yield. A gradually diminishing undissolved portion remained for eighteen hours, complete solution then occurring. The product was finally poured into a beaker, evaporated to one-half of its original volume and cooled. Dense crystallization took place. Water was added to effect complete separation and the yield of the crude product was 4.8 g. It was purified by adding it to 20 cc. of alcohol and 20 cc. of concd. hydrochloric acid and boiling. It was then cooled and the precipitate filtered off. Any unchanged phenylurea was isolated by boiling the product with 200 cc. of water to extract the semicarbazide hydrochloride. The insoluble bromophenylurea was filtered off and the semicarbazide in the filtrate precipitated by adding caustic potash solution. One gram of bromophenylurea was recovered. Bromophenylsemicarbazide crystallizes in small needles from hot alcohol. It is insoluble in cold water and cold alcohol. It decomposes with effervescence at 254° to a claret-colored liquid.

Anal. Calcd. for $C_7H_8ON_3Br$: Br, 34.78. Found: (Pritchard) 35.12.

Semicarbazones

p-Bromophenyl-4-semicarbazone of Acetone, $C_6H_4BrNHCONHN(CH_3)_3$.—0.25 g. of the semicarbazide was dissolved in 15 cc. of hot alcohol and an excess of acetone added. The mixture was boiled for twelve hours. Upon cooling the solution very beautiful prismatic crystals separated. The crystals had three wide faces and three narrow ones and the ends formed pyramids.

The product melts sharply at 174° (corr.) to a colorless liquid. It is insoluble in cold water or cold alcohol but dissolves in hot alcohol.

Anal. Calcd. for $C_{10}H_{12}ON_3Br$: Br, 29.62. Found: (Pritchard) 29.40.

TABLE I

SEMICARBAZONES

	Ketone	Crystal form	M. P.,[a] °C.	Time of heating
1	Methyl ethyl ketone	Rect. plates	175	1 Hour
2	Chloro-acetone	Needles	182 dec.	5 Min.
3	α,γ-Dichloro-acetone	Needles	196 dec.	5 Min.
4	Acetophenone	Bulky needles	218	5 Hours
5	Benzophenone	Bulky needles	205	10 Hours

[a] All temperatures are corrected except that for acetophenone.

	Formula	Bromine, % Calcd.	Bromine, % Found
1	$C_{11}H_{14}ON_3$	28.14	27.98
2	$C_{10}H_{11}ON_3ClBr$	26.24	25.90
3	$C_{10}H_{10}ON_3Cl_2Br$	23.58	23.68
4	$C_{15}H_{14}ON_3Br$	24.07	24.00
5	$C_{20}H_{16}ON_3Br$	20.28	20.15

This reaction was also carried out in the cold, using a vacuum to concentrate the solution.

Other semicarbazones are indicated in Table I. All were prepared by J. G. Park except No. 4, which was prepared by W. N. Pritchard, Jr. In all cases the reacting compounds were dissolved in alcohol and the products were recrystallized from alcohol.

Summary

The preparation of *p*-bromophenylurea by three methods is described and procedure is given for its conversion into *p*-bromophenyl-4-semicarbazide. The usefulness of the semicarbazide as a ketone reagent has been tested by the preparation of several semicarbazones.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

IV. THE CHEMICAL EFFECTS OF ELECTRICAL DISCHARGE IN BUTANE. FRACTIONATION OF THE LIQUID PRODUCT[1]

BY S. C. LIND[2] AND GEORGE GLOCKLER[3]

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Introduction

In a former paper[4] it was shown that butane, as well as other hydrocarbons, yields liquid condensates when subjected to the semi-corona electrical discharge. At the same time, however, it was found that solid condensation products are also formed on the inner walls of the discharge tubes. From previous experience it was known that this solid formation does not occur in an all-glass ozonizer, or at least that such action is very slow.

Since the *object of the present work was the production of a fairly large amount of liquid condensate from butane gas by electrical means and its fractional distillation*, it was decided to build an all-glass ozonizer apparatus consisting of twelve ozonizers connected in parallel as to gas flow and as to electrical wiring. This apparatus is shown in Fig. 1. It may be said at once that indeed the solid formation just mentioned was quite negligible and only near the upper ends of the ozonizers toward the close of the long experiment was there any solid product formed.

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[2] Director, Project No. 8.

[3] American Petroleum Institute Research Associate.

[4] Lind and Glockler, THIS JOURNAL, **51**, 2811–22 (1929).