4. The α-naphthyl isocyanate derivative condenses with aldehydes only after hydrolysis. It, therefore, appears that the ordinary enol form of diketopiperazine has double bonds between carbon atoms.

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

PARA-CYMENE STUDIES. XII. 2-PARA-CYMYL-4-SEMICARBAZIDE AND CERTAIN DERIVATIVES

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This paper presents a continuation of studies of semicarbazides as ketone reagents.[2] In view of the fact that cymene is a fair priced product, its derivatives are more available than formerly. Ketone reagents such as hydroxylamine, phenylhydrazine and semicarbazide differ in their properties from strongly basic to neutral. This series is extended in the acid direction by using phenylsemicarbazide with its negative phenyl group and finally the substituted phenylsemicarbazides containing bromine or the nitro group. It is desirable to have such a variety for detecting and characterizing ketones since no one is applicable to all cases.

2-*p*-Cymyl-4-semicarbazide, not known hitherto, was prepared by known methods. 2-Amino-*p*-cymene was converted into *p*-cymylurea, a compound first mentioned by Kremers and Demonbreun,[3] who made only a very brief note about it and gave no analysis. We believe their product was impure since our product melts six degrees higher. Three methods of preparation were tested. The first was Davis and Blanchard's method[4] of preparing phenylurea. An aqueous solution of aminocymene hydrochloride and urea was heated. This was unsatisfactory on account of the simultaneous production of di-*p*-cymylurea, a compound not hitherto described. The second method was that of Kelbe and Warth,[5] who prepared *m*-cymylurea. The hydrochloride of aminocymene was heated with potassium cyanate. No dicymylurea was produced but the yield was poor. The method adopted was to heat an acetic acid solution of aminocymene with potassium cyanate. In a similar way Walther and Wlodkowski[6] made *o*-tolylurea. The yield was better and the product readily purified.

[1] This paper is an abstract of a thesis submitted by J. G. Park in partial fulfilment of the requirements for the degree of Master of Arts at the University of North Carolina in June, 1929.

[2] Wheeler and Bost, THIS JOURNAL, **46**, 2813 (1924); Wheeler and Walker, *ibid.*, **47**, 2792 (1925).

[3] Kremers and Demonbreun, *J. Am. Pharm. Assocn.*, **12**, 591 (1923).

[4] Davis and Blanchard, THIS JOURNAL, **45**, 1816 (1923).

[5] Kelbe and Warth, *Ann.*, **221**, 171 (1883).

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

The urea was converted into the cymylsemicarbazide on heating with hydrazine hydrate as Curtius and Burkhardt[7] made phenylsemicarbazide.

Cymylsemicarbazide readily condenses with ketones, forming semicarbazones which are very stable. It was noted that the purely aliphatic and mixed aliphatic-aromatic ketones condensed with great readiness, whereas the purely aromatic ketones as well as camphor and carvone required the presence of some acetic acid and one or more hours of heating.

Experimental

Di-*p*-cymylurea, $(C_{10}H_{13}NH)_2CO$.—(a) A solution of 6 g. of urea and 18.5 g. of aminocymene hydrochloride in 75 cc. of water was boiled until bumping due to separated crystals became violent. The crystals were filtered off and proved to be dicymylurea. They were quite bulky and the weight was extremely small. The filtrate was cooled and the crystals which separated consisted of a mixture of dicymylurea and probably cymylurea. The solution was boiled again until bumping occurred and the process completed as above. The products proved to be the same so the method was given up.

(b) Baeyer's method[8] of preparing phenylurea was found to be much better. Two moles of aminocymene were heated with one mole of urea at 150–170° until the evolution of ammonia greatly slackened. This required about three hours. On cooling the mixture solidified. The product was extracted with ligroin and hot dilute hydrochloric acid to remove any unchanged aminocymene and urea. Coloring matter was removed with charcoal. The product crystallized from alcohol in bulky microscopic needles, melting at 240° to a dark brown viscous liquid. It is soluble in chloroform and slightly soluble in ether, benzene and carbon tetrachloride; 1.2 g. of urea gave 1.4 g. of the pure diurea.

Anal. Calcd. for $C_{21}H_{28}ON_2$: N, 8.64. Found: N, 8.79.

***p*-Cymylurea,** $C_6H_3(CH_3)(C_3H_7)NHCONH_2$.—To 74.5 g. of aminocymene dissolved in 200 cc. of warm glacial acetic acid was slowly added with stirring 48 g. of powdered potassium cyanate. After heating nearly to boiling the mixture was poured into a liter of cold water; yield, 84.7 g. The product was recrystallized by dissolving in glacial acetic acid and reprecipitating with water. It was finally recrystallized from 40% alcohol; yield of pure product, 55 g. Cymylurea is soluble in chloroform, moderately soluble in ether and slightly soluble in carbon tetrachloride. It dissolves in warm benzene but on cooling separates as a gelatinous mass. *p*-Cymylurea may also be prepared by the action of potassium cyanate on aminocymene hydrochloride, but the yield is lower.

Anal. Calcd. for $C_{11}H_{16}ON_2$: N, 14.58. Found: N, 14.47.

2-*p*-Cymyl-4-semicarbazide, $C_6H_3(CH_3)(C_3H_7)NHCONHNH_2$.—38.5 g. of cymylurea and 60 g. (2.5 equivalents) of 42% hydrazine hydrate were dissolved in 200 cc. of 95% alcohol and the mixture boiled for thirty hours under a reflux condenser, though not continuously. The solution was filtered hot to remove some black particles and concentrated to one-half of its original volume. A small amount of a yellow oil separated. In order to bring about crystallization some water was added, the mixture was cooled with ice water and vigorously stirred. A mass of yellowish crystals formed weighing 33.5 g. and melting at 96–105°. A saturated ice-cold ether solution was made and treated with a stream of hydrogen chloride. The salt was filtered off, redissolved in warm water and sufficient potassium hydroxide added to precipitate the free base; yield, 25.7 g.

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

[8] Baeyer, *Ann. Chem. Pharm.*, **131**, 251 (1864).

The carbazide crystallizes from warm dilute alcohol in colorless microscopic prisms, melting at 112°. It is soluble in benzene, ether, chloroform and warm carbon tetrachloride.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.28. Found: N, 19.77.

The hydrochloride forms colorless microscopic needles from water, melting at 166–168° with decomposition. The melting point varies somewhat with the rate of heating.

Anal. Calcd. for $C_{11}H_{17}ON_3 \cdot HCl$: HCl, 14.97. Found: HCl, 14.86.

Semicarbazones.—The semicarbazones were prepared by dissolving one mole of cymylsemicarbazide in alcohol (1 g. per 10 cc. of alcohol) and adding two moles of the ketone. Unless otherwise stated crystallization of the carbazone began at once. The mixture was heated for ten minutes on the steam-bath and cooled for complete crystallization. The product was recrystallized from alcohol or benzene as found best. All thermometer readings were made with a set of Wheeler Standard Thermometers, each instrument having a small 50-degree scale for complete immersion.

TABLE I

SEMICARBAZONES

	Ketone	Crystal form	Solvent	M. p., °C., (corr.)	Liquid
1	Acetone	Fluffy needles	Alcohol	182	Colorless
2	Methylethyl	Rect. plates	Alcohol	182–183	Colorless
3	α,γ-Dichloro-acetone	Prisms	Benzene	173	Decomposes
4	Mesityl oxide	Fluffy needles	Alcohol	163	Colorless
5	Acetoacetic ester	Fluffy needles	50% alc.	133.5	Colorless
6	Cyclohexanone	Fluffy needles	Alc.–Bz	192.5	Yellow
7	Camphor	Micro needles	Alc.–Bz	217	Yellow
8	Carvone	Micro prisms	70% alc.	97	Yellow
9	Benzophenone	Fluffy needles	Alcohol	150	Colorless
10	Acetophenone	Fluffy needles	Benzene	212	Colorless
11	Benzoin	Fluffy needles	Alcohol	172	Yellow

1. Soluble in chloroform, benzene, slightly soluble in ether; yield, 90% of weight of semicarbazide. 3. Alcohol for reaction medium not satisfactory. Benzene used. 5. Soluble in chloroform, ether and benzene. 6. Slightly soluble in hot alcohol and in ether. 7. One cc. of glacial acetic acid added to the reaction mixture before heating; mixture heated for two hours. 8. One cc. of acetic acid required and one hour of heating. In order to isolate the product water was added dropwise as long as it dissolved. On cooling a viscous oily product separated. This crystallized on a porous plate after two days. 9. One cc. of glacial acetic acid was added and heating for two and one-half hours was necessary. The crude product was gummy but became crystalline on a porous plate. In recrystallizing from alcohol seeding was a great aid. 10. The product weighed 20% more than the weight of the semicarbazide used. 11. Acetic acid needed and an hour and a half of heating.

TALBE II

ANALYSES OF SEMICARBAZONES

	Formula	Subs., g.	Vol. of N in cc.	Nitrogen, % Calcd.	Nitrogen, % Found
1	$C_{14}H_{21}ON_3$	0.1437	22.9 (31°, 745.6 mm.)	17.00	16.76
2	$C_{15}H_{23}ON_3$	.1546	23.1 (31°, 748 mm.)	16.09	15.77

TABLE II (*Concluded*)

	Formula	Subs., g.	Vol. of N in cc.	Nitrogen, % Calcd.	Found
3	$C_{14}H_{19}ON_3Cl_2$	0.1728	22 (31°, 743.3 mm.)	13.29	13.35
4	$C_{17}H_{25}ON_3$	.1396	19.1 (32°, 749.8 mm.)	14.63	14.39
5	$C_{17}H_{27}O_3N_3$	.1737	21.6 (33.5°, 749.5 mm.)	13.16	12.95
6	$C_{17}H_{25}ON_3$	.1535	20.5 (30°, 750.1 mm.)	14.63	14.22
7	$C_{21}H_{31}ON_3$	.1785	21.1 (32.5°, 745.6 mm.)	12.31	12.32
8	$C_{21}H_{29}ON_3$	.1504	18.1 (36°, 748 mm.)	12.39	12.31
9	$C_{24}H_{25}ON_3$	.2103	21.9 (31°, 747.1 mm.)	11.32	10.98
10	$C_{19}H_{23}ON_3$	.1643	21.4 (31°, 746 mm.)	13.59	13.71
11	$C_{25}H_{27}O_2N_3$	.1915	19.0 (34°, 747.3 mm.)	10.47	10.27

Summary

1. Di-*p*-cymylurea is obtained in small amount by the action of urea upon aminocymene hydrochloride in aqueous solution. The best method is to heat aminocymene and urea together at 150–170°.

2. *p*-Cymylurea is best prepared by the action of potassium cyanate upon aminocymene in glacial acetic acid solution.

3. 2-*p*-Cymyl-4-semicarbazide is best made by the action of hydrazine hydrate on *p*-cymylurea.

4. *p*-Cymylsemicarbazide yields semicarbazones with the following ketones: acetone, methyl ethyl ketone, α,γ-dichloro-acetone, mesityl oxide, acetoacetic ester, cyclohexanone, camphor, carvone, benzophenone, acetophenone and benzoin. The products are very stable. The reactions are immediate except those with camphor, carvone and the purely aromatic ketones. These require some acetic acid and a period of heating.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE INDUCED CHLORINATION OF ETHYLENE DICHLORIDE. THE EFFECT OF OXYGEN UPON THE REACTION BETWEEN ETHYLENE AND CHLORINE

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Gaseous chlorine and gaseous ethylene react to form ethylene dichloride. The reaction takes place upon the surface of the containing vessel.[1,2]

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2 \qquad (1)$$

The reaction rate may be expressed by the equation

$$-\frac{d(C_2H_4)}{dt} = K_a'' (C_2H_4)(Cl_2)$$

in which the bracketed formulas represent partial pressures of the respective gases. The specific reaction rate varies with the nature of the

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[1] Stewart and Fowler, THIS JOURNAL, **45**, 1014 (1923).

[2] Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).