α-Furfuryl Ethyl Sulfide.—The furfuryl mercaptan was converted into the previously unknown sulfide by treatment of its sodium derivative with ethyl bromide in alcoholic solution. Sodium bromide precipitated immediately and the reaction mixture was heated on a steam-bath for one hour. On cooling the solution was decanted from the sodium bromide and after extraction of the sodium bromide with ether the solution and extract were distilled and the residue was fractionated in vacuum. The product, a colorless liquid of pungent odor, boiled at 90.5–91° at 28 mm.; yield, 80%; d_{20}^{20} 1.05144; d_4^{20} 1.04958; n_D^{20} 1.5140; M_D (calcd.) 41.005; M_D (obs.) 40.773.

Anal. Subs., 0.1983: $BaSO_4$, 0.3379. Calcd. for $C_7H_{10}OS$: S, 22.55. Found: S, 23.40.

Summary

1. By using α-furfuryl chloride as the starting material, the following new substances have been prepared: ethyl-α-furfurylmalonic ester, ethyl-α-furfurylbarbituric acid, α-furfurylacetoacetic ester, α-furfuryl nitrile, α-furylacetic acid, α-furfuryl thiocyanate and α-furfuryl ethyl sulfide.
2. The following substances, which had previously been prepared by indirect methods starting with furfural, have now been directly synthesized from α-furfuryl chloride: α-furfurylmalonic ester, α-furfurylbarbituric acid, 2-α-furfurylacetic acid, α-furfurylacetone and its semicarbazone and α-furfuryl mercaptan.
3. Ethyl-α-furfurylbarbituric acid has possibilities as an hypnotic. Its physiological activity is being studied and will be published later. It is expected that this study will yield some information concerning the effect of the α-furfuryl group upon physiological action.

HOUSTON, TEXAS

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

PARA-CYMENE STUDIES. XIII. PARA-CYMYLHYDRAZINE-2 AND DERIVATIVES[1]

BY ALVIN S. WHEELER AND CHARLES L. THOMAS

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Phenylhydrazine is widely used in the identification of aldehydes and ketones. A limited number of its homologs have been prepared but phenylhydrazine remains the most available from the cost standpoint. The tolylhydrazines should follow and then cymylhydrazine. The latter compound seems to have been made so far in only one investigation.[2] It was not analyzed and a wide fraction, boiling at 110–120° at 1.5 mm., was taken as cymylhydrazine. The authors prepared the hydrochloride, the acetate and the hydrazones of glucose, mannose and galactose. The cymylhydra-

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[1] This paper is an abstract of a thesis submitted by Charles L. Thomas in partial fulfilment of the requirements for the degree of Master of Science at the University of North Carolina in June, 1929.

[2] Kremers and Demonbreun, *J. Am. Pharm. Assocn.*, **12**, 589 (1923).

zine was made by diazotizing 2-aminocymene with ethyl nitrite and reducing the diazo compound with stannous chloride. They found that when sodium nitrite was used a reddish brown tar was obtained. We used sodium nitrite, however, with very satisfactory results, but used sodium sulfite[3] instead of stannous chloride as reducing agent. Sometimes a tar was obtained but by boiling this with concd. hydrochloric acid it was partly converted into cymylhydrazine hydrochloride.

Not all condensation products of cymylhydrazine are stable. Kremers and Demonbreun could not isolate any product of the action of benzaldehyde or furfural. If obtained, it decomposed as soon as separated from the reaction mixture. The authors attributed these results to the steric hindrance of the *iso*propyl group. In our own work we failed to get a product with methyl ethyl ketone, acetophenone or benzaldehyde sufficiently pure for a good analysis. A peculiar reaction, as yet unexplained, was noted with carbon disulfide. Analysis gave exact figures for a ratio of two atoms of nitrogen for each atom of sulfur.

We prepared the hydrochloride, hydrobromide, sulfate and picrate of cymylhydrazine and condensations with benzophenone, salicylaldehyde and cinnamic aldehyde. The semicarbazide and thiosemicarbazide were readily made, also the *p*-nitrobenzoyl derivative. The product obtained from benzoyl chloride was amorphous and contained chlorine. No products were obtained by the action of methyl nonyl ketone, thionyl chloride, Michler's ketone and benzoylacetone.

Experimental

p-Cymylhydrazine-2, $C_{10}H_{13}NHNH_2$.—Sixty cc. of 2-aminocymene (0.4 mole) was added with stirring to 88 cc. of concd. hydrochloric acid cooled by a freezing mixture; 100 g. of ice was then added and the stirring continued until a thick paste resulted. A solution of 33 g. of sodium nitrite in 75 cc. of water was added slowly, with ice also to keep the temperature around 0°. More sodium nitrite was added if complete solution did not take place. It is best to keep the temperature below 5° to prevent the formation of a green scum. The diazo solution was then poured rapidly with stirring into a freshly prepared solution of sodium sulfite, cooled to 5°. The sodium sulfite solution was prepared by dissolving 89 g. of sodium hydroxide in 600 cc. of water and passing in sulfur dioxide until the solution was slightly acid to phenolphthalein. After the diazo solution has been added to the sulfite solution it should be reddish-orange in color. The flask, which then contained 1 to 1.5 liters of solution, was heated on a hot-plate to 80–90° for one and one-half hours. The color darkened somewhat. Hydrochloric acid was then added until the odor of sulfur dioxide was distinctly noticeable. The heating was then continued for ten hours. The solution became a light yellow. After the period of ten hours a sample of about 10 cc. was removed and an equal volume of concd. hydrochloric acid added. If a reddish-brown tar separated, the heating was continued. If crystals were formed, the reaction was complete. The solution was cooled and 300 cc. of concd. hydrochloric acid added. The crystals obtained were dried

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[3] G. H. Coleman, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1922**, Vol. II, p. 71.

and weighed; 58 g. or 72.5% of the theoretical yield. The crude product usually melts about 189°. It may be purified by boiling the aqueous solution with charcoal and reprecipitating with hydrochloric acid. Slow crystallization yields long white needles melting at 198°. This salt was prepared by Kremers and Demonbreun but they gave 186–187° as the melting point. On analysis we found for HCl, 17.95; calcd., 18.18. The free base was obtained by neutralizing the salt with sodium hydroxide, extracting with ether, drying and distilling at 5 mm. The fraction boiling from 129 to 132° was used for the determination of the constants. The drops of liquid at the top of the condenser appeared colorless but those falling into the receiver already had a slight yellow color. The liquid on standing in the dark slowly deepens in color. One preparation became cherry-red in the dark and sunlight brought the yellow color back. Cymylhydrazine is odorless and dissolves as completely in 50% acetic acid as phenylhydrazine. It melts at 26.5° and boils at 129–132° at 5 mm. Its density is d_{28}^{28} 0.9863; index of refraction at 25°, 1.5551. In the solid state it takes the form of long yellow needles.

Anal. Calcd. for $C_{10}H_{16}N_2$: N, 17.07. Found: N, 16.70.

Salts

Hydrobromide, $C_{10}H_{16}N_2 \cdot HBr$.—Long white needles, melting at 174°.

Anal. Calcd. for HBr: 33.05. Found: HBr, 33.00.

Sulfate, $C_{10}H_{16}N_2 \cdot H_2SO_4$.—Sulfuric acid of 1:1 strength was used. The last traces of acid were difficult to get rid of and the color was always slightly brown; small scales, melting at 130°.

Anal. Calcd. for H_2SO_4: 37.40. Found: H_2SO_4, 37.10.

Picrate, $C_{10}H_{16}N_2 \cdot C_6H_2OH(NO_2)_3$.—To a solution of 2 g. of the hydrochloride in 25 cc. of alcohol was added 2.3 g. of picric acid dissolved in the least possible amount of water. After several days the picrate separated out in long yellow needles. These decompose suddenly at 124°.

Anal. Calcd. for $C_{16}H_{19}O_7N_5$: N, 17.80. Found: N, 17.63.

Hydrazones

Cinnamylaldehyde-*p*-cymylhydrazone-2, $C_{10}H_{13}NHN{=}CHCH{=}CHC_6H_5$.—Equimolecular amounts of cinnamylaldehyde and cymylhydrazine were mixed. A noticeable rise in temperature took place and a yellow solid separated. The yield may be increased by heating for a short time on the water-bath. The product was recrystallized from dilute alcohol as thick picric yellow needles melting at 90°. The product is quite stable, for it turns brown only after standing about two months.

Anal. Calcd. for $C_{19}H_{22}N_2$: N, 10.08. Found: N, 9.88.

Salicylaldehyde-*p*-cymylhydrazone-2, $C_{10}H_{13}NHN{=}CHC_6H_4OH$.—Equal volumes of the components were mixed and heated for an hour on the water-bath. On cooling a mass of crystals separated. They crystallized from dilute alcohol in yellow needles melting at 87°. No signs of decomposition were visible after three months.

Anal. Calcd. for $C_{17}H_{20}ON_2$: N, 10.41. Found: N, 10.28.

Benzophenone-*p*-cymylhydrazone-2, $C_{10}H_{13}NHN{=}C(C_6H_5)_2$.—This compound could not be prepared by heating the components together. It was made by dissolving 2 g. of cymylhydrazine hydrochloride and 2 g. of benzophenone in 50 cc. of alcohol, adding a little sodium acetate and heating under a reflux for six hours. Upon cooling and adding water an oil separated. On standing for several days it turned red and red needles separated. The crystals came out of dilute alcohol in needles which were slightly brown, melting at 88°. No change in color occurred in two months.

Anal. Calcd. for $C_{23}H_{24}N_2$: N, 8.54. Found: N, 8.47.

Other Hydrazones.—A reaction was obtained with methyl ethyl ketone, the product consisting of plates, slightly brown, melting at 57°. It is unstable and the percentage found for nitrogen was 1.2 low. Acetophenone gave a product, consisting of mustard-yellow needles, melting at 84°. This was also unstable and the percentage for nitrogen was 1.2 low. The reaction with benzaldehyde gave an oil sometimes and again crystals which were light yellow leaflets. This product begins to decompose before it is dry. The crystals are exceedingly thin and give a fine display of interference colors.

Semicarbazides

***p*-Cymyl-1-semicarbazide-2,** $C_{10}H_{13}NHNHCONH_2$.—Three g. of urea was added to 4 cc. of cymylhydrazine. Upon heating the urea melted and formed a layer underneath the hydrazine. Heating was continued until the two layers united. Upon cooling crystals separated. These were recrystallized from dilute alcohol, filtered and washed with water and ether, giving fine snow-white plates melting at 171°.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.30. Found: N, 20.20.

***p*-Cymyl-1-thiosemicarbazide-2,** $C_{10}H_{13}NHNHCSNH_2$.—An attempt to prepare this compound by heating the hydrazine with thiourea proved a failure. It was made by dissolving 3 cc. of cymylhydrazine in 10 cc. of glacial acetic acid and adding an excess of potassium thiocyanate. The mixture was warmed until complete solution took place. It was then cooled and poured into water. The solid product was recrystallized from dilute alcohol as flat white plates melting at 184°. It turns slightly brown on standing.

Anal. Calcd. for $C_{11}H_{17}SN_3$: N, 18.84; S, 14.35. Found: N, 18.25; S, 14.28

Other Reactions

***p*-Nitrobenzoyl-*p*-cymylhydrazine-2,** $C_{10}H_{13}NHNHCOC_6H_4NO_2$.—An attempt was made to prepare this compound by treating a mixture of cymylhydrazine hydrochloride and *p*-nitrobenzoyl chloride with sodium hydroxide, but no product could be isolated. It was then found that cymylhydrazine and nitrobenzoyl chloride unite in benzene solution without the evolution of hydrochloric acid gas to give a light yellow crystalline compound. It contained hydrochloric acid and melted at 160°. If sodium hydroxide and dilute alcohol are added to the product, the liquid becomes deep purplish-brown. If the mixture is heated until all of the solid goes into solution and then is neutralized with acid, a precipitate is thrown down. This was recrystallized from dilute alcohol, forming long yellow needles melting at 177°.

Anal. Calcd. for $C_{13}H_{19}O_3N_3$: N, 13.41. Found: N, 13.16.

Reaction with Carbon Disulfide.—Two volumes of the hydrazine were mixed with five volumes of carbon disulfide and heated on the water-bath for an hour. Hydrogen sulfide was evolved and a deep yellow to green precipitate formed. Upon cooling the substance turned to a transparent resin. This was covered with much petroleum ether and worked with a glass rod. The resin turned to a mass of small white crystals which melted at 177°.

Anal. Found: N, 18.75; S, 21.25. These results indicate two atoms of nitrogen for one of sulfur.

Summary

1. *p*-Cymylhydrazine-2 was prepared by diazotizing 2-aminocymene and reducing the product with sodium sulfite. The hydrochloride, hydrobromide, sulfate and picrate were made.

2. Cymylhydrazones of cinnamylaldehyde, salicylaldehyde and benzophenone were made. The hydrazones of methyl ethyl ketone, acetophenone and benzaldehyde were found to be unstable.
3. *p*-Cymyl-1-semicarbazide-2 and *p*-cymyl-1-thiosemicarbazide-2 were prepared.
4. A *p*-nitrobenzoyl derivative was prepared.
5. Cymylhydrazine reacts with carbon disulfide to give a product whose nature was not solved.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY, FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE, IN COÖPERATION WITH THE UNIVERSITY OF WISCONSIN]

SEQUOYITE, A CYCLOSE FROM REDWOOD (SEQUOIA SEMPERVIRENS)

BY E. C. SHERRARD[1] AND E. F. KURTH[2]

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In a recent paper[3] we reported the isolation of a new cyclose which occurs with pinite in the cold-water extract of the heartwood of redwood. First analyses indicated that the new compound might have the empirical formula $C_8H_{16}O_7$, but later analyses upon purer and larger amounts of the material proved that it is a monomethyl ether of *i*-inosite and is isomeric with pinite, bornesite and quebrachite. The present paper describes the details of isolation, the experimental results that convinced us of its structural formula and the preparation of some of its derivatives.

Sequoyite, as we have named it, was isolated from the aqueous extract of redwood in a manner similar to that employed for pinite. The two cycloses crystallized out together upon the addition of alcohol to the thick, concentrated extract. They were separated from each other by fractional crystallization; sequoyite, being less soluble in either alcohol or water, crystallized readily from a 50% alcoholic solution, while the pinite crystallized slowly from a 70% solution.

The impure sequoyite crystals were purified by warming with a small amount of barium hydroxide, then filtering off the precipitated gums and coloring matter and acidifying the filtrate with sulfuric acid to remove the excess barium. The solution that remained after filtering off the barium sulfate was nearly colorless. The new cyclose was obtained from this solution by concentrating it to a thin sirup and then diluting it with

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[1] Senior Chemist, U. S. Forest Products Laboratory, Forest Service, Madison, Wisconsin.

[2] Junior Chemist, U. S. Forest Products Laboratory, Forest Service, Madison, Wisconsin.

[3] Sherrard and Kurth, *Ind. Eng. Chem.*, **20**, 722 (1928).