column of alumina. Some black cupric bromide was formed during the synthesis of the benzyl derivative in Table II indicating that a portion of the dihalide underwent a typical Ullmann biaryl coupling.

Cuprous Benzenethiolate.—Following the same method, but without added halide, a mixture of 15.2 g. (0.07 mole) of phenyl disulfide and 8.9 g. (0.14 g.-atom) of copper powder in 200 ml. of dimethylacetamide was heated to reflux for 3 hr. Water was added to precipitate all the cuprous salt as a light yellow solid, which was collected and washed with ethanol. There was obtained 21 g. (87.5% yield) of dry cuprous benzenethiolate, char point 255°, soluble in pyridine, insoluble in water.

Anal. Calcd. for C_6H_5CuS: S, 18.57. Found: S, 18.4. These results are identical to those produced by the same salt prepared by another method[1] from benzenethiol and cuprous oxide in ethanol.

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The Preparation of Cycloheptylamine

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The need in this laboratory for pure cycloheptylamine prompted an investigation of methods of synthesis in which readily available or easily prepared intermediates could be used. Since the Ritter reaction with cycloheptanol gives a mixture of products[1] and chemical reduction of cycloheptanone oxime results in poor yield,[2] they were not considered. A more logical approach appeared to be reductive amination of cycloheptanone (A) or catalytic hydrogenation of its oxime (B). While method A gave a good yield, the resultant product was found to be contaminated with cycloheptanol. High pressure reduction of the oxime in the presence of Raney nickel and ammonia gives a good yield.[3] However, except in small size runs, the exothermicity of the reaction even with a low catalyst ratio made us aware that the reduction could get out of hand. Rhodium-on-alumina on the other hand proved highly satisfactory even with undistilled oxime in low pressure hydrogenations in the absence of ammonia. Under these conditions, uptake of hydrogen was entirely too slow when Raney nickel was used.

Experimental

Method A.—A solution of 101.5 g. (0.905 mole) of cycloheptanone,[4] 100 cc. of ethyl alcohol and 100 cc. of liquid ammonia was placed in a 1-l. rocker bomb. Raney nickel (20.0 g.) was added and the mixture hydrogenated at 70° and 100 atm. Uptake of hydrogen was complete in less than 1 hr. The reaction mixture was filtered from the catalyst and the solution and washings concentrated. The residue was treated with 20% hydrochloric acid and the mixture extracted with ether to remove cycloheptanol (about 20 g. of crude alcohol was obtained). The acidic solution was kept at room temperature while adding solid potassium hydroxide until the mixture was strongly basic. The mixture was then extracted thoroughly with ether (some water may be added to dissolve potassium chloride). The extract was dried over potassium hydroxide. The solution was filtered and the ether distilled. The residue on fractionation yielded 61% of cycloheptylamine boiling at 172–175° (750 mm.).[5]

Low pressure reductions with a higher catalyst ratio (30%) required a longer time but gave about the same yield.

Method B. Cycloheptanone Oxime.[6]—A solution of 4000 g. (35.72 moles) of cycloheptanone in 3500 cc. of methyl alcohol was treated with 3000 g. (43.16 moles) of hydroxylamine hydrochloride. It was then stirred for 1 hr. while heating to 80°. While this temperature was maintained, a solution of 1560 g. of sodium hydroxide in 3500 cc. of water was added over a 4-hr. period. The reaction mixture was then refluxed for 1–2 hr. and allowed to cool to room temperature. An oily layer separated, which was removed and dried over anhydrous magnesium sulfate. The oil,[7] after filtration from the drying agent, was dissolved in 9000 cc. of methyl alcohol and placed in a 10-gal. glass-lined reactor, to which 450 g. of 5% rhodium-on-alumina[8] was added. The mixture was hydrogenated under 0.75 to 1.0 atm. The temperature rose gradually to 60° and was maintained there until reduction was complete. The solution was filtered from the catalyst and concentrated. The residue was fractionated. An over-all yield of 80% of cycloheptylamine based on cycloheptanone was obtained.

Hydrogenation of distilled oxime carried out in a Parr shaker under 3 atm. pressure gave about the same over-all yield.

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(1) R. Jacquier and H. Christol, *Bull. Soc. Chim.*, 560 (1954).

(2) W. Markownikoff, *J. Russ. Phys. Chem. Soc.*, **25**, 365 (1893), and V. Prelog, M. F. El-Neweihy, and O. Häflinger, *Helv. Chim. Acta*, **33**, 365 (1950).

(3) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(4) Aldrich Chemical Co., Milwaukee, Wis.

(5) R. Willstatter, *Ann.*, **317**, 204 (1901), reports 169°.

(6) The method is essentially as described for benzophenoneoxime by A. Lachman, *Org. Syntheses*, Coll. Vol. I, 10 (1930).

(7) Cycloheptanoneoxime from a 675-g. run was distilled successfully. An 86% yield of product boiling at 125–130° (22 mm.) was obtained. When distillation of a larger run was attempted, decomposition took place, resulting in the thermometer being blown from the stillhead.

(8) Baker and Co., Division of Engelhard Industries, 113 Astor Street, Newark, N. J.

A Correlation in the Infrared Spectra of Some C-Benzoylated Nitrogen Heterocycles

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In the course of studies related to heterocyclic chemistry[3] we have had occasion to examine the

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