Werf<sup>1</sup> reported the only previous reductive system used on (I), a modified Clemmensen method which was unsatisfactory because of the formation of resinous products.

In general, the Clemmensen<sup>1</sup> and the Wolff-Kishner,<sup>2</sup> or modifications of these, are used for the reduction of aromatic ketones. Benzophenone has been reduced in excellent yield by both of these methods.<sup>1,2</sup> Using the techniques of the modified Clemmensen method, however, Bradlow and Van der Werf<sup>1</sup> obtained only a 25% yield of (II). The Wolff-Kishner reduction has apparently not been applied to (I), but the reduction of p,p'-dichlorobenzophenone<sup>3</sup> by this method gave only 21% of p,p'-dichlorodiphenylmethane.

Although catalytic methods have not been widely used for the reduction of ketones, a number of studies have been made. Hartung and Crossley<sup>4</sup> reduced a number of propiophenones with palladized carbon, and the work was extended to a few aromatic systems by Baltzly and Buck.<sup>5</sup> Horning and Reisner<sup>6</sup> described the palladium catalyzed reduction of several  $\beta$ -aroylpropionic acids to the  $\alpha$ arylbutyric acids.

As a result of the limited number of hydrogenations previously reported using palladium, it was not possible to predict what effect hydroxyl substituents on benzophenone would have on the reduction. Thus, it was interesting that catalytic reduction of (I) with palladium-carbon catalyst absorbed 100% of the theoretical hydrogen uptake. On using platinum under similar conditions, the hydrogenation resulted in the reduction of the aromatic ring.

#### EXPERIMENTAL

To a solution of 10.7 g. (0.05 mole) of p,p'-dihydroxybenzophenone in 100 ml. isopropyl alcohol was added 3 g. of 5% palladium on carbon powder (Baker and Co., Inc.). The reduction, carried out in a low pressure Parr hydrogenator, was complete in about 5 hours at 25°C. with a 100% theoretical hydrogen uptake. The catalyst was removed by filtration, and after the filtrate was reduced to a small volume, a crystalline solid settled out upon addition of an equal volume of water. Recrystallization of this material from water gave a 95% yield of p,p'-dihydroxydiphenylmethane, m.p. 161–162°.<sup>7</sup> A diacetoxy derivative was prepared, m.p. 70–71°.<sup>7</sup>

HIGH POLYMER LABORATORY

INDUSTRIAL RAYON CORPORATION

Cleveland, Ohio

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# Some New Quaternary-Substituted Alkyl Morpholinium Chlorides and Pyrrolidinium Alkyl Sulfates<sup>1</sup>

WILLIAM F. HART AND MARTIN E. MCGREAL

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Studies in the fields of morpholinium halides and alkyl sulfates and thiamorpholinium alkyl sulfates<sup>2</sup> have been extended to include a group of N-alkyl-N-substituted alkyl morpholinium chlorides and two series of symmetrical, N,N-dialkyl pyrrolidinium alkyl sulfates prepared from a group of five N-alkyl pyrrolidines. These quaternary morpholinium and pyrrolidinium compounds were prepared for the purpose of determining their bactericidal properties in comparison with those of quaternary morpholinium and thiamorpholinium compounds previously described. The results of these bacteriological tests are as yet not complete.

No systematic study of the longer chain N-alkyl pyrrolidines and the corresponding N-alkyl pyrrolidinium alkyl sulfates has been made. A recent German patent<sup>3</sup> describes the preparation of N-ndodecyl-N-methyl pyrrolidinium methosulfate. Ames, Bowman, Buttle and Squires<sup>4</sup> have described the preparation of N-n-dodecyl pyrrolidine and the hydrochloride of this compound. Jerchel and Kimmig<sup>5</sup> have prepared N-n-dodecyl-N-phenyl pyrrolidinium bromide. Erickson and Keps<sup>6</sup> have recently described the preparation of N-n-dodecyl and N-n-octadecvl pyrrolidine and N.N-di-n-dodecyl and N,N-di-n-octadecyl pyrrolidinium chlorides by the reaction of the appropriate primary or secondary amine with 1,4-dichlorobutane in the presence of excess sodium carbonate in butyl alcohol solution. The N-alkyl pyrrolidines were analyzed as their picrates.

#### EXPERIMENTAL

 $N\text{-}Alkyl\ morpholines$  were prepared by the method previously described.²

N-Alkyl-N-substituted alkyl morpholinium chlorides were prepared by reacting equimolar quantities (approximately 0.02 mole) of the N-alkyl morpholine and the substituted alkyl chloride without solvent or in an equal volume of dry

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JANUARY 1957

NOTES

87

<sup>a</sup> Melting points are uncorrected. <sup>b</sup> Reference 3.

NOTES

toluene (Table I, compounds V through IX). The reaction mixture was refluxed until upon cooling a semi-solid waxy mass was formed. The time required varied from 4-82 hr. Compound I was formed by reaction at room temperature. Compound X required heating in an oil bath for five hours at  $200^{\circ}$  to complete the reaction.

At the end of the reaction period the solidified waxy mass was washed several times with ether, and recrystallized twice from ethyl acetate. The products are insoluble in ether and cold ethyl acetate, soluble in alcohol, and from slightly soluble to very soluble in water.

N-Alkyl pyrrolidines (Table II) were prepared by refluxing for 24 hr. 0.3 mole pyrrolidine, 0.2 mole of the alkyl bromide and 0.11 mole anhydrous potassium carbonate in a 100 ml. of methanol. The reaction mixture was filtered while hot on a sintered glass filter, and the insoluble salts were washed with two portions of boiling methanol.

The alcoholic filtrate was treated with 1 g. of decolorizing carbon and filtered while hot. The methanol and excess pyrrolidine were removed at reduced pressure and the residue was taken up in ethyl acetate and again filtered to remove a small amount of inorganic salts. The ethyl acetate was removed at reduced pressure and the N-alkyl pyrrolidine was isolated by fractional distillation in vacuo.

N-Alkyl pyrrolidines were also prepared by long refluxing of the appropriate primary amine with a 10% excess of 1,4-dichlorobutane in the presence of a large excess of potassium carbonate in ethyl alcohol solution. The yields obtained by this procedure were lower than those obtained by alkylation of pyrrolidine.

Symmetrical N,N-dialkyl pyrrolidinium alkyl sulfates (Table III) were prepared by reacting equimolar quantities (approximately 0.01 mole) of the N-alkyl pyrrolidine and redistilled dimethyl or diethyl sulfate in 5 g. of acetone.<sup>3</sup> The alkyl sulfate was added gradually with stirring to the boiling acetone solution of the N-alkyl pyrrolidine. The reaction mixture was allowed to cool slowly to room temperature and was then allowed to stand overnight. The n-decyl and ndodecyl pyrrolidinium alkyl sulfates which formed as yellow oils were triturated several times with small volumes of petroleum ether and crystallized upon drying in vacuo over phosphorous pentoxide. The n-tetradecyl, n-hexadecyl and n-octadecyl pyrrolidinium alkyl sulfates formed as waxy solids. These were triturated three times with small volumes of petroleum ether, recrystallized three times from acetone or ethyl acetate, and finally dried in vacuo over phosphorous pentoxide. These compounds are all white, water soluble solids. The lower members of the series are hygroscopic.

CHEMICAL LABORATORIES LAFAYETTE COLLEGE EASTON, PA., and

ST. JOHN'S UNIVERSITY BROOKLYN, N. Y.

# Hydrazinolysis of 1-(Alkyldithioate)piperidine

EUGENE LIEBER AND RONALD C. ORLOWSKI

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A study of the hydrazinolysis of 1-(alkyldithioate)-piperidine,<sup>1</sup> II, was undertaken for the purpose of preparing a thiosemicarbazide in which the fourth position embraced a reduced ring system in-

cluding the nitrogen. These have not been previously described in the literature. The required II, also not previously described in the literature, were prepared by the following sequence of reactions:



It was found that the I need not be isolated and that the alkylation step could be carried out in the suspension of I obtained in the initial reaction. Surprisingly, the hydrazinolysis of II ( $R = C_2 H_{5}$ -) proceeded chiefly with the elimination of both the thioalkyl- and piperdyl-radicals, thiocarbohydrazide, III, being the major product, while the desired product, 1-(aminothiocarbamyl)-piperidine,<sup>2</sup> IV, was obtained in only minor quantity.

$$II + 2N_{2}H_{4} \longrightarrow (H_{2}NN)_{2}C = S$$

$$III$$

$$II + N_{2}H_{4} \longrightarrow O(S)NHNH_{2}$$

$$IV$$

Both III and IV were identified by analysis and conversion to benzylidene derivatives which were also analyzed. III was first described by Stolle and Bowles.<sup>3</sup> Its preparation by hydrazinolysis of various thiocarbonic acid derivatives has recently been reported.<sup>4</sup>

### EXPERIMENTAL<sup>5,6</sup>

1-(Sodium carbodithioate)-piperidine. In a three-necked 1-l. round bottomed flask, surrounded by an ice-salt bath and fitted with mechanical stirrer, reflux condenser, thermometer, and dropping funnel were placed 82.2 g. (63 cc., 1.08 moles) carbon disulfide and a cold solution of 43.2 g. (1.08 moles) of sodium hydroxide in 96 cc. water. The mixture was cooled to 0 to 5°. While stirring, 91.8 g. (1.08 mleos) of piperidine as a cold 35% aqueous solution was added over a period of 30 minutes. Stirring was continued for two hours in order to insure complete precipitation. The product recovered by filtration weighed 178 g. (90%) and was used without further purification.

1-(Ethyl carbodithioate)-piperidine. A mixture comprising 183 g. (1 mole) of 1-(sodium carbodithioate)-piperidine, 161 g. (1 mole) ethyl iodide and 200 cc. ethanol (95%) was refluxed for two hours. At the end of this period, 200 cc. of

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<sup>(1)</sup> The name for this structure is derived from the C. A., 39, 5968 (1945) nomenclature for the radical-C(S)SH, carbodithioic and the 1-position of the piperidine ring.