***m*-Aminobenzalacetone,** $NH_2C_6H_4CH{=}CHCOCH_3$.—The procedure was the same as for the *m*-aminobenzalacetophenone and the free amine was isolated as an oil. It was refluxed with benzoyl chloride in order to obtain a solid derivative. This melted[6a] at 122–124° after crystallization from alcohol.

***m*-Aminobenzylacetone,** $NH_2C_6H_4CH_2CH_2COCH_3$.—The product was isolated as the amine hydrochloride, converted into the amine and benzoylated, thus yielding a product which, upon crystallization, melted[6b] at 93–95°.

Summary

1. The relative rates of reduction of nitrobenzene and substituted nitrobenzenes in various solvents are given.

2. The effect of acids, alkalies and various salts upon the rates of reduction of nitrobenzene and certain substituted nitrobenzenes is discussed.

3. It has been shown that *m*-nitrobenzalacetophenone and *m*-nitrobenzalacetone are reduced in alcohol to the corresponding amino compounds quantitatively and no further absorption of hydrogen takes place. If, on the other hand, a small amount of acetic acid is present, sufficient hydrogen is absorbed to give the reduction of the olefin as well as the nitro groups.

4. Competitive experiments on unsaturated compounds in the presence of certain poisons and promoters are given.

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THE CATALYTIC REDUCTION OF DI- AND TRIPHENYLAMINES WITH HYDROGEN AND PLATINUM-OXIDE PLATINUM BLACK. XV[1]

BY G. S. HIERS AND ROGER ADAMS

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The catalytic reduction of certain aromatic amines by means of platinum-oxide platinum black and hydrogen was recently described.[2] This work has been extended to the reduction of diphenylamine and triphenylamine with the formation of dicyclohexylamine and tricyclohexylamine, respectively.

The tricyclohexylamine is of particular interest because it represents that class of tertiary amines in which three secondary carbon atoms are attached to the nitrogen. Although it is reported in the literature that tri-*iso*propylamine[3] and tri-*sec.*-butylamine were obtained in very

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[6] Miller and Rohde [*Ber.*, **23,** 1886 (1890)] give (a) 125°, (b) 94–95°.

[1] Previous articles in this field are listed in a footnote in Article No. XIV, THIS JOURNAL, **49,** 1093 (1927).

[2] Hiers and Adams, *Ber.*, **59,** 162 (1926).

[3] Mailhe, *Compt. rend.*, **141,** 114 (1905).

small amounts as by-products from the catalytic reduction of acetone oxime and methylethyl ketoxime, these tertiary amines were not isolated and no constants were given.[4] The only definitely established tertiary amines of the type mentioned above which could be found in the literature were the tricyclopentylamine[5] and trimethylcyclopentylamine, which were formed in small amounts as by-products in the reduction of the oximes of cyclopentanone and methylcyclopentanone. The dicyclohexylamine, tricyclohexylamine and cyclohexylphenylamine (which was made by the condensation of cyclohexyl bromide and aniline) are to be used in the study of the nature of the valences of nitrogen.

Dicyclohexylamine has previously been prepared in a variety of ways, mostly involving catalytic reduction of aniline, diphenylamine or cyclohexanone derivatives.[2,6] As a laboratory procedure, however, the reduction of diphenylamine hydrochloride, as used in this investigation, is much more satisfactory than any of the others and gives a very pure product in excellent yields. As a standard procedure, 0.1 mole of diphenylamine hydrochloride was dissolved in 150 cc. of absolute alcohol at 50° and added to a suspension of platinum black made by reducing 0.25 g. of platinum oxide in 50 cc. of absolute alcohol. The reduction was complete in 100–110 minutes.

A brief statement as to the effect of changing the conditions from those just mentioned may be outlined. Diphenylamine in alcohol with hydrochloric acid added does not give as satisfactory results as when pure diphenylamine hydrochloride is used. With the former conditions the reduction is frequently slower and incomplete. As the diphenylamine hydrochloride is not completely soluble in the amounts of solvent used at 25°, the higher temperature must be used; moreover, the higher temperature increases the rate of reduction. During the reduction the highly insoluble dicyclohexylamine hydrochloride separates. The presence of water in the alcohol as, for instance, the use of 95 or 75% alcohol, somewhat increased the time for the reduction. Moreover, if the platinum oxide was reduced to the platinum black in the presence of the diphenylamine hydrochloride, the reduction proceeded more slowly. C. P. chloro-

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[4] In a physical-chemical article [Rimbach and Volk, *Z. physik. Chem.*, **77**, 385 (1911)] certain physical constants of tri-*iso*propylamine are given, but no boiling point nor any mention as to how it was prepared.

[5] Sabatier and Mailhe, *Compt. rend.*, **158**, 985 (1914).

[6] Cyclohexanone, ammonium formate and acetic acid [Wallach, *Ann.*, **343**, 61 (1905)]; reduction of diphenylamine with hydrogen under pressure and elevated temperature, and nickel oxide as a catalyst [Ipatiew, *Ber.*, **41**, 991 (1908)]; cyclohexanol and ammonia over thorium oxide at 300° [Sabatier and Mailhe, *Compt. rend.*, **153**, 160 (1911)]; aniline or diphenylamine over nickel at 190° [Sabatier and Senderens, *ibid.*, **138**, 458 (1904)]; aniline and hydrogen with platinum as a catalyst [Willstätter and Hatt, *Ber.*, **45**, 1476 (1912). Fouque, *Compt. rend.*, **165**, 1062 (1917); **166**, 394 (1918)].

platinic acid for preparing the platinum oxide was essential to the best results.

As triphenylamine will not form a hydrochloride, it was necessary to suspend the amine in alcohol and add hydrochloric acid. Good results were obtained by suspending 0.1 mole of triphenylamine in 150 cc. of absolute alcohol at 50° to which was added 15 cc. of concd. hydrochloric acid (0.15 mole of hydrogen chloride) and pouring this into a suspension of platinum black in 50 cc. of absolute alcohol made by reducing 1 g. of platinum oxide. Although triphenylamine is only partially soluble in the quantity of alcohol used, the reduction proceeds smoothly. The time required for complete reduction was approximately four hours, the reaction product being completely soluble in the alcohol.

The temperature of 50° was necessary for rapid reduction. At least 1 g. of catalyst was necessary, amounts of 0.5 g. or less always resulting in partial reduction only. Acetic acid or acetic anhydride were not satisfactory solvents, for even when 2.5 g. of catalyst was used the reduction would not go to completion. Ethyl acetate was not as satisfactory as alcohol. The time required, if only 0.1 mole of hydrochloric acid was used, was much greater than if 0.15 mole was used.

Even under the best conditions somewhat more than the calculated amount of hydrogen was absorbed and there was always isolated from the reaction mixture cyclohexane, dicyclohexylamine (8–10%) and 50 to 60% of the calculated amount of tricyclohexylamine. In a number of runs where a small amount of catalyst was employed, and where hydrogenation was incomplete, the chief products isolated from the reaction mixture were triphenylamine, dicyclohexylamine, tricyclohexylamine and traces of cyclohexane. Whether the dicyclohexylamine and the cyclohexane are formed from the tricyclohexylamine, directly from the triphenylamine, or the triphenylamine is partially hydrogenated and the cyclohexane then eliminated before the complete reduction takes place, has not been determined.

The tricyclohexylamine which has not been previously described is an almost colorless oil, boiling at 170–171° at 4 mm., with almost no odor. It forms a constant-boiling mixture with triphenylamine (b. p., 192–193°, at 10 mm.), which contains approximately 10 to 12% of triphenylamine. Its hydrobromide and picrate were prepared and purified.

Experimental Part

The platinum oxide and the apparatus were those used in the previous work in the field. A distinctly inferior catalyst was obtained if c. p. chloroplatinic acid was not used as the starting material for the platinum oxide.

The diphenylamine used was prepared by twice distilling commercial diphenylamine under diminished pressure. The pure, water-clear amine boiling over 1° was dissolved in dry ether, and the solution saturated with dry hydrogen chloride. The diphenylamine hydrochloride separated, was filtered and washed with dry ether. The triphenylamine was prepared by the action of bromobenzene upon diphenylamine, details for which will be described in "Organic Syntheses," vol. 8. It melted at 126.5–127°.

Procedure.—For the reduction of these compounds the platinum oxide and 50 cc. of the solvent to be used were placed in a reaction flask and reduced with hydrogen at 3 atm. for about two minutes. The diphenylamine hydrochloride or triphenylamine (together with the desired amount of hydrochloric acid) in 150 cc. of the same solvent was added to the reaction bottle. The reductions were carried out in the usual way.

Isolation of Reaction Products.—After filtration of the platinum from the reaction mixture, the alcohol was distilled. The residual diphenylamine hydrochloride was dissolved in 50 cc. of warm water, and an excess of 50% potassium hydroxide solution was added. The dicyclohexylamine was separated and extracted with ether. This was dried over potassium hydroxide and metallic sodium, then distilled under diminished pressure. The pure dicyclohexylamine[7] boiled at 136–138°, at 26 mm., and was isolated in 80–90% yields.

The reduction of the triphenylamine in the presence of hydrochloric acid was carried out in essentially the same way. However, if the first 100 cc. of the alcohol was distilled and saturated with sodium chloride, there separated a small amount of cyclohexane which was distilled, and melted and identified as this product; b. p., 78–78.4°, at 740 mm.; m. p., 6–6.5°; n_D^{27}, 1.4211. Upon distillation of this reaction mixture, dicyclohexylamine was obtained and then tricyclohexylamine; b. p., 170–171°, at 4 mm.; d_4^{20}, 0.9993; n_D^{18}, 1.5468.

Anal. Subs., 0.2364: 7.89 cc. of 0.1126 *N* HCl. Calcd. for $C_{18}H_{33}N$: N, 5.30. Found: 5.26.

The tricyclohexylamine, upon being mixed with an alcoholic solution of one mole of picric acid, gave a yellow, crystalline compound which was readily purified by crystallizing from alcohol; m. p., 179–180°.

The tricyclohexylamine was neutralized with hydrobromic acid and the salt crystallized several times from ethyl acetate; m. p., 225–226°.

Anal. Subs., 0.1127, 0.1163: 6.48, 6.78 cc. of 0.502 *N* $AgNO_3$. Calcd. for $C_{18}H_{34}NBr$: Br, 23.22. Found: 23.06, 23.38.

When the triphenylamine was not completely reduced owing to the character of solvent or because the amount of catalyst was too small, there was always obtained from the reaction mixture a fraction boiling at 192–193°, at 10 mm., which showed a nitrogen content of 5.4–5.8%. This is equivalent to 10–12% of unchanged triphenylamine. This mixture melts at 88–90°. The two amines were readily separated by treating with hydrobromic acid and then washing free from unchanged triphenylamine.

Cyclohexylaniline.—Although cyclohexylaniline has been obtained as the by-product in the reduction of aniline and diphenylamine, it was quite readily prepared by mixing 245 g. of cyclohexyl bromide with 175 g. of freshly distilled aniline in 300 cc. of absolute alcohol, and refluxing for 48 hours. The alcohol was distilled, benzene was

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[7] Diphenylamine hydrochloride was first reduced to dicyclohexylamine by Mr. E. M. McColm as part of his work for the degree of Master of Science in Chemistry at the University of Illinois (1923), but lack of time prevented a careful study to find the best conditions.

added and the salt which separated was filtered; yield, 173 g. The hydrobromide, upon recrystallization from alcohol, melts at 177–178°.

Anal. Subs., 0.1170: 9.18 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{12}H_{18}NBr$: Br, 31.21. Found: 31.47.

The free amine boils at 134–135°, at 6 mm. The picrate melts at 164–165°.

Condensation of Cyclohexyl Bromide with Cyclohexylaniline and Dicyclohexylamine.—It was hoped that by the condensation of cyclohexyl bromide with cyclohexylaniline in molecular quantities in the presence of absolute alcohol, it might be possible to prepare dicyclohexylphenylamine. The results were entirely negative, however, resulting products consisting of cyclohexylaniline hydrobromide and cyclohexene.

A similar reaction took place between dicyclohexylamine and cyclohexyl bromide. The salt which separated was dicyclohexylamine hydrobromide, which sublimes at 310–320°.

Anal. Subs., 0.1191: 9.08 cc. of 0.0502 *N* $AgNO_3$. Calcd. for $C_{12}H_{24}NBr$: Br, 30.60. Found: 30.57.

This reaction is apparently analogous to the first one, the cyclohexyl bromide being converted into hydrogen bromide and cyclohexene.

Summary

1. Upon catalytic reduction of diphenylamine hydrochloride with platinum-oxide platinum black, excellent yields of dicyclohexylamine were obtained.

2. Triphenylamine in the presence of a little hydrochloric acid was reduced to tricyclohexylamine with some by-products of cyclohexane and dicyclohexylamine.

3. Cyclohexylphenylamine was prepared from cyclohexyl bromide and aniline. Upon attempting the condensation of cyclohexylphenylamine with cyclohexyl bromide, there resulted merely the formation of cyclohexene and the hydrobromide of the original amine.

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A PHENYLSTEARIC ACID FROM OLEIC ACID

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Ethylene and benzene react in the presence of aluminum chloride[2] to form ethylbenzene and further substitution products. To maintain the efficiency of the reaction, hydrogen chloride must occasionally be supplied to take the place of that lost during the run.

That this reaction is somewhat general for olefins is indicated by the

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[1] The material presented here was submitted by Clara M. deMilt in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Chicago, **1925**.

[2] Balsohn, *Bull. soc. chim.*, [2] **31**, 539 (1879). Milligan and Reid, THIS JOURNAL, **44**, 206 (1922).