at 40° (bath temperature), filtered through a Millipore filter, dialyzed, and reconcentrated to 20 ml. The solution was found to contain 240 units of activity/ml. when assayed in the manner described by Nelson, *et al.*[2]

Hydrolysis of the (1→3,1→6)-Linked D-Glucan.—A portion of the enzyme solution (5 ml.) was added to the polysaccharide (5 g.) dispersed in 0.05 *M* acetate buffer (1.0 l.), pH 4.8. The hydrolysis was allowed to proceed at 50°, samples being removed after 1, 2, 4, 6, 10, and 21 hr. The samples were heated in a steam bath for 2 min. to deactivate the enzyme and centrifuged; the reducing sugar content was determined by the method of Nelson–Somogyi[16] and a constant value was obtained after 4 hr.

The hydrolysis was terminated after 21 hr. by autoclaving for 2 min. at 110–120°. A small amount of inorganic material (160 mg.) was removed by centrifugation after which the solution was neutralized by the addition of 10% sodium hydroxide and concentrated *in vacuo* to approximately 50 ml.

Alternately, the hydrolysate was treated with washed baker's yeast (5 g.). The disappearance of glucose by this somewhat more time-consuming procedure was followed by thin layer chromatography on Kieselguhr G according to Stahl.[17] The cells were removed by centrifugation, and the solution was neutralized and concentrated to approximately 50 ml.

Isolation of Gentiobiose by Charcoal Column Chromatography.—The hydrolysate (50 ml.) before or after treatment with yeast was added to a column of charcoal[15] (2.5 × 18 cm.) and washed successively with water (7.0 l.), 5% ethanol (4.0 l.), and finally with 10% ethanol (2.0 l.), the eluate being collected in 500-ml. fractions. The fractions were concentrated *in vacuo* and the contents were analyzed by thin layer and paper chromatography. The 10% aqueous ethanol eluate contained the gentiobiose which was obtained as a chromatographically pure sirup (1.68 g.) by evaporation of the solvent *in vacuo*. The sirup was dissolved in refluxing absolute methanol and the product (1.41 g.) crystallized by cooling: m.p. 84° dec.,[9] $[\alpha]^{23.5}D$ +13.0° (*c* 33, water) (after 15 min.), changing in 24 hr. to +8.4° (equilibrium value); lit.[12,18,19] m.p. 85–86°, $[\alpha]^{20}D$ +21.4 → +8.7° in water.

Acetylation of a small portion of the product with acetic anhydride and anhydrous sodium acetate[4] yielded β-gentiobiose octaacetate, m.p. and m.m.p. 191° (after recrystallization from methanol), lit.[12,18] m.p. 193°.

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(17) E. Stahl and U. Kaltenbach, *J. Chromatog.*, **5**, 351 (1961).
(18) G. Zemplén, *Z. phys. Chem.*, **85**, 399 (1913).
(19) E. Bourquelot, H. Hérissey, and J. Coirre, *Compt. rend.*, **157**, 732 (1913).

Phenylcyclobutane Amino Acids

ALFRED BURGER AND WILLIAM E. COYNE

Department of Chemistry, University of Virginia, Charlottesville, Virginia

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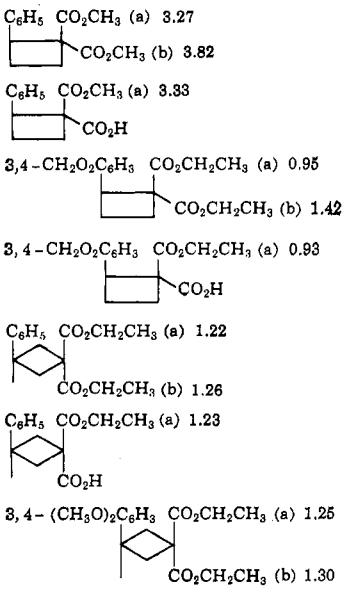
Conversions of 2- and 3-phenylcyclobutane-1,1-dicarboxylic acids[1a,b] and of alkoxy-substituted derivatives to the corresponding 1-amino-2- and -3-arylcyclobutane-1-carboxylic acids have been carried out by partial hydrolysis of the dicarboxylate esters of these acids, and Curtius degradation of the carboxyl group of the resulting monoalkyl esters, followed by hydrolysis of the remaining ester group.

In the 2-aryl series, sterically homogeneous monoalkyl esters were obtained in good yields. The assumption that the more readily hydrolyzed ester group of the dicarboxylate esters would be *trans* to the sterically hindering aromatic moiety was supported by the greater interference of the bulkier 2-(3,4-methylenedioxyphenyl) compared with the 2-phenyl group. Under conditions which hydrolyzed the 2-phenylcyclobutane-1,1-dicarboxylate ester completely, the 2-(3,4-methylenedioxyphenyl) ester was only hydrolyzed partially. In this methylenedioxy series, the Curtius degradation was also interrupted at intermediate stages; alkaline hydrolysis of 1-carbethoxy-2-(3,4-methylenedioxyphenyl)cyclobutane 1-isocyanate led only to an ester urea, and refluxing the corresponding ester carbamate with hydrochloric acid gave the amino ester instead of the amino acid.

(1) (a) C. Beard and A. Burger, *J. Org. Chem.*, **26**, 2335 (1961); (b) **27**, 1647 (1962).

TABLE I

N.M.R. CHEMICAL SHIFTS FOR METHYL PROTONS OF SOLUTIONS OF ALKYL ARYLCYCLOBUTANE-1,1-DICARBOXYLATES[a]



[a] Relative to tetramethylsilane; given in parts per million.

The amino group of the amino acids prepared by Curtius degradation must have the same configuration (*trans*) as the carboxyl group of these half esters.

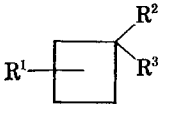
In the 3-aryl-substituted series, less steric hindrance may be expected and, therefore, less difference in the rate of the hydrolysis of the two ester groups. Indeed, oily mixtures of half esters were obtained upon hydrolysis of the dicarboxylate esters, and only in one case could a pure stereoisomer be elaborated in smaller yields.

Models of the ethyl hydrogen 2-phenylcyclobutanedicarboxylate esters show that in the favored conformation the ethyl group is perpendicular to the benzene ring. If the ester group is in the plane of the benzene ring, its carbonyl oxygen interferes with the orthohydrogens. In the n.m.r. spectrum, the *cis* ethyl protons should appear more shielded and thus upfield with respect to *trans* ethyl protons. This has actually been observed (Table I).

In the case of the ethyl hydrogen 3-phenylcyclobutane-1,1-dicarboxylates, the chemical shifts of the *cis* and *trans* protons of the methyl groups are very close as expected from the increased distance of the aromatic ring to either of these groups (Table I). The only pure isomer obtained was probably the *trans* carboxy compound.

TABLE II

DERIVATIVES OF CYCLOBUTANE



R¹	R²	R³	Yield, %	M.p., °C.	Solvent of crystallization	Composition	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-C_6H_5	*trans*-CO_2H	CO_2CH_3	97[a]	141–141.5	EtOH–H_2O	$C_{13}H_{14}O_4$	66.65	6.02	66.72	6.04
2-C_6H_5	*trans*-$NH_2\cdot HCl$	CO_2H	94	222–229 dec.	EtOH–Et_2O	$C_{11}H_{14}ClNO_2$	58.02	6.20	58.12	6.11
3-C_6H_5	*trans*(?)-CO_2H	$CO_2C_2H_5$	46[b]	107–108.5	Ligroin	$C_{14}H_{16}O_4$	67.72	6.50	67.71	6.29
3-C_6H_5	*trans*(?)-$NH_2\cdot HCl$	CO_2H	72[c]	275–281 dec.	EtOH–Et_2O	$C_{11}H_{14}ClNO_2$	58.02	6.20	58.11	6.02
3-C_6H_5	CONHNHCO		70	251–253	EtOH	$C_{12}H_{12}N_2O_2$	66.65	5.60	66.72	5.52
2-C_6H_5	*cis*-CO_2CH_3	$CON(C_6H_{11})$-$CONHC_6H_{11}$	85	93–94	Petr. ether	$C_{26}H_{35}N_2O_4$	71.04	8.03	71.19	8.11
2-C_6H_5	*cis*-CO_2CH_3			84–87	EtOH–H_2O	$C_{16}H_{16}N_2O_3$	67.59	5.67	67.40	5.70
2-(3,4-$CH_2O_2C_6H_3$)	*trans*-CO_2H	$CO_2C_2H_5$	10	138–139.5	$CHCl_3$–petr. ether	$C_{15}H_{16}O_6$	61.64	5.52	61.84	5.52
[2-(3,4-$CH_2O_2C_6H_3$)]$_2$	*trans*-NHCONH	$[CO_2C_2H_5]_2$		210–211	EtOH	$C_{29}H_{32}N_2O_9$	63.03	5.84	62.98	5.70
2-(3,4-$CH_2O_2C_6H_3$)	*trans*-$NHCOOCH_2C_6H_5$	$CO_2C_2H_5$	>54	81–83	C_6H_6–petr. ether	$C_{22}H_{23}NO_6$	66.49	5.83	66.35	5.82
2-(3,4-$CH_2O_2C_6H_3$)	*trans*-NH_2	CO_2H	>90	218–220 dec.	MeOH or Me_2NCHO	$C_{12}H_{13}NO_4$	61.27	5.57	61.39	5.49
3-[(3,4-OCH_3)$_2$]C_6H_3	$CO_2C_2H_5$	$CO_2C_2H_5$	54	*d*			*e*			
3-[(3,4-OCH_3)$_2$]C_6H_3	$NH_2\cdot HCl$	CO_2H[c]	25	225–228	MeOH–Et_2O		*e*			
3-[(3,4-OCH_3)$_2$]C_6H_3	NH_2	CO_2H[f]	23	240–245	MeOH	$C_{13}H_{17}NO_4$	62.13	6.82	61.94	6.84

[a] Based on the dimethyl ester. This was obtained from the dicarboxylic acid[1a] with excess ethereal diazomethane in 94% yield, b.p. 120–121° (0.5 mm.). [b] From the diester.[1b] [c] Prepared by method A. [d] B.p. 178–181° (0.2 mm.). [e] This product was not analyzed. [f] Prepared essentially by method B.

Experimental[2]

Alkyl Hydrogen Arylcyclobutane-1,1-dicarboxylates.—A solution of 75 mmoles of the dialkyl arylcyclobutane-1,1-dicarboxylate in 100 ml. of ethanol was stirred with 75 mmoles of KOH in a minimum of water at 26° overnight. The solution was then heated to 50° for 1.5 hr., and the excess solvent was evaporated. The residue was taken up in water, washed with ether, cooled, and acidified. The colorless precipitate was recrystallized (see Table II).

1-Amino-(2- or 3-aryl)cyclobutanecarboxylic Acids. A. *trans*-1-Amino-2-phenylcyclobutanecarboxylic Acid.—Working by a modification of the Curtius reaction[3] a solution of hydrogen methyl 2-phenylcyclobutane-1,1-dicarboxylate was prepared by adding sufficient acetone to a suspension of 13.68 g. (61 mmoles) of the ester in 11 ml. of water. The solution was cooled to 0° and 71 mmoles of triethylamine in 125 ml. of acetone was added with stirring. A solution of 78 mmoles of ethyl chloroformate in 32 ml. of acetone was added slowly at 0°, the mixture was stirred for 30 min. at 0°, and a solution of 92 mmoles of sodium azide in 21 ml. of water was added dropwise. After being stirred at 0° for 1 hr., the mixture was poured into excess ice–water, and the separated oil was extracted with ether and dried ($MgSO_4$). The oily residue from the ether was heated in a minimum of anhydrous toluene at 95° until nitrogen evolution ceased. The solvent was removed, and the yellow oily isocyanate ester (infrared band, 2250 $cm.^{-1}$) was stirred with 20% aqueous HCl at 25° overnight. The amino acid hydrochloride separated as colorless crystals (see Table II).

B. 1-Amino-2-(3,4-methylenedioxyphenyl)cyclobutanecarboxylic Acid.—Ethyl hydrogen 2-(3,4-methylenedioxyphenyl)-cyclobutane-1,1-dicarboxylate was converted to the oily isocyanate by method A [infrared spectrum, 2230 $cm.^{-1}$ (–NCO), 1720 $cm.^{-1}$ (ester)]. Hydrolysis with 20% HCl at 26° resulted in extensive decomposition. The yield of amino acid was only 1%. Hydrolysis with 15% aqueous KOH gave N,N-bis[1-ethoxycarbonyl-2-(3,4-methylenedioxyphenyl)cyclobutyl]urea as the major product (see Table II).

A mixture of 3 g. of the isocyanate and 3 g. of benzyl alcohol was heated to 100° for 2 hr. and excess benzyl alcohol removed at 65° (1 mm.). The crude benzylurethane solidified on trituration with petroleum ether (b.p. 30–60°) (see Table II). A solution of 2.35 g. of this urethane in 100 ml. of anhydrous ethyl acetate was hydrogenated at 25° with slight positive pressure using 350 mg. of 10% palladium–carbon catalyst. In 3 hr., 80% of the required hydrogen was absorbed; the remaining 20% was absorbed after 15 hr. The mixture was worked up as usual, the oily product being refluxed with 1 g. of KOH in 50 ml. of ethyl alcohol for 1 hr. The ethyl alcohol was removed, and the colorless amino acid (1.8 g.) was obtained from the solid potassium salt by neutralization to pH 6–6.5. For additional data, see Table II.

Cyclic Hydrazide of 3-Phenylcyclobutane-1,1-dicarboxylic Acid.—Ethyl potassium 3-phenylcyclobutane-1,1-dicarboxylate was prepared by hydrolysis of 10 g. of the diethyl ester with 1 equiv. of KOH at 25 and 50° as described above. A solution of the salt in 50 ml. of absolute ethanol was refluxed with 100 ml. of 100% hydrazine hydrate for 10 hr. and then evaporated. The solid hydrazide was identified by its infrared spectrum.

N-[1-Carbomethoxy-2-phenylcyclobutanecarbonyl]-N,N-dicyclohexylurea.—In an attempt to prepare *trans-t*-butyl-*cis*-methyl 2-phenylcyclobutane-1,1-dicarboxylate, 1 g. of the monomethyl ester was added to a solution of 0.319 g. of *t*-butyl alcohol and 1 g. of freshly distilled dicyclohexylcarbodiimide in 20 ml. of dimethylformamide at 50°. The solution was stirred at 20° for 4 hr., then allowed to stand at 0° for 12 hr., and filtered from dicyclohexylurea; the solvent was removed. The solid residue was purified (see Table II).

N-(1-Carbomethoxy-2-phenylcyclobutanecarbonyl)imidazole.—When 0.73 g. of N,N'-carbonyldiimidazole was added to a solution of 1 g. of hydrogen methyl 2-phenylcyclobutane-1,1-dicarboxylate, CO_2 was evolved vigorously. In an attempt to prepare the *t*-butyl ester, 0.319 g. of *t*-butyl alcohol was added and the mixture was refluxed for 3 hr. The solvent was removed; the residue was extracted with ether and washed with water; the ether was evaporated. The colorless crystals were purified as indicated in Table II.

3,4-Methylenedioxycinnamyl Chloride. A.—3,4-Methylenedioxycinnamyl alcohol[4] was prepared by reduction of ethyl 3,4-methylenedioxycinnamate[5] with lithium aluminum hydride in ether in 65.5% yield, with m.p. 75–76° (from ligroin).

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.58; H, 5.38.

The α-naphthyl isocyanate, colorless crystals from benzene–petroleum ether, melted at 141–142.5°.

Anal. Calcd. for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93. Found: C, 72.62; H, 4.81.

B.—Dry hydrogen chloride was passed vigorously through a solution of 4 g. of 3,4-methylenedioxycinnamyl alcohol in 40 ml. of chloroform at 0° for 10 min. The solution was poured immediately into ice–water; the aqueous layer was washed once with chloroform; and the combined chloroform solutions were washed quickly with ice–water, 2% sodium bicarbonate solution, and again with water. The dried ($MgSO_4$) chloroform extract gave, on evaporation, 3.96 g. of colorless crystals which turned dark on standing or further purification. The product was identified by its n.m.r. spectrum and by its S-alkylthiuronium picrate[6]: yellow needles, m.p. 178–180°.

Anal. Calcd. for $C_{17}H_{15}N_5O_9S$: C, 43.87; H, 3.25. Found: C, 43.63; H, 3.44.

Diethyl (3,4-Methylenedioxycinnamyl)malonate.—3,4-Methylenedioxycinnamyl chloride, prepared from 55 g. (0.31 mole) of 3,4-methylenedioxycinnamyl alcohol, was added to a solution of diethyl sodio malonate [from 56 g. (0.35 mole) of diethyl malonate and 14 g. (0.31 mole) of sodium hydride (53% in mineral oil)] in 100 ml. of dimethyl sulfoxide, and the solution was stirred at 26° for 13 hr. The resulting suspension was poured into 1.5 l. of water and extracted three times with ether; the ether extracts were washed with water and dried (Na_2SO_4). The crude ester was passed through a column of neutral alumina with dry ether and distilled, giving a product with b.p. 194–198° (0.5 mm.); the yield of product, 47.65 g., was contaminated with some mineral oil. The malonate ester was identified by its n.m.r. spectrum and by alkaline hydrolysis to **3,4-methylenedioxycinnamylmalonic acid.**

Anal. Calcd. for $C_{13}H_{12}O_6$: C, 59.09; H, 4.58. Found: C, 59.05; H, 4.59.

Diethyl (3,4-Dimethoxyphenyl)malonate. A.—A mixture of 11 g. (0.05 mole) of ethyl 3,4-dimethoxyphenylacetate [b.p. 121° (0.06 mm.), lit.[7] b.p. 191° (0.025 mm.)] and 7.3 g. (0.05 mole) of diethyl oxalate was stirred at 20°, and a solution of sodium ethoxide [from 1.725 g. (0.075 mole) of sodium and 40 ml. of absolute ethyl alcohol] was added dropwise. After being stirred at 20° for 15 hr., the solution was refluxed for 1 hr. and poured into 20 ml. of concentrated hydrochloric acid and ice; the ester was extracted into ether and dried (Na_2SO_4). The colorless oil from the ether solution was heated with ground soft glass at 165–170° for 4 hr. until no more carbon monoxide was evolved. The residual oil was washed in ether solution with 10% sodium bicarbonate solution, dried, and distilled. The yield of oil, b.p. 181–182° (1.1 mm.), was 5.1 g. (35%).

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80. Found: C, 61.08; H, 6.71.

B.—A mixture of 290 g. (1.29 moles) of the ethyl 3,4-dimethoxyphenylacetate and 466 g. (3.94 moles) of diethyl carbonate was added to a refluxing mixture of toluene and 1.29 moles of sodium ethoxide, prepared by adding 79.0 g. of absolute ethyl alcohol to a mixture of 29.70 g. (1.29 moles) of sodium in 1 l. of toluene at 105°. After addition was complete, the solvent was distilled until the distillate was pure toluene, and the solution was poured into ice–water containing 400 ml. of concentrated HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers after drying and evaporation of the solvent gave 305.5 g. (79.5%) of a colorless oil, b.p. 160–162° (0.25 mm.).

Anal. Found: C, 60.87; H, 7.00.

2-(3,4-Dimethoxyphenyl)propane-1,3-diol.—To a suspension of 47.5 g. (1.25 moles) of lithium aluminum hydride in 1 l. of

(2) All melting points are corrected and were measured in a stirred bath. Infrared spectra were determined on a Perkin-Elmer Infracord, the n.m.r. spectra on a Varian A-60 spectrometer. Microanalysis was by Mrs. W. E. Coyne.

(3) J. Weinstock, *J. Org. Chem.*, **26**, 3511 (1961).

(4) C. F. H. Allen and J. R. Byers, Jr., U. S. Patent 2,545,439 (1951).

(5) I. A. Pearl and D. L. Beyer, *J. Org. Chem.*, **16**, 216 (1951).

(6) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1957, p. 456.

(7) J. C. Cain, J. L. Simonsen, and C. Smith, *J. Chem. Soc.*, **103**, 1038 (1913).

anhydrous ether in a nitrogen atmosphere was added dropwise 305.5 g. (1.03 moles) of diethyl (3,4-methylenedioxyphenyl)-malonate over a period of 5 hr. The solution was refluxed for 20 hr., cooled in an ice–salt bath, and decomposed with 770 g. of ammonium sulfate in 1500 ml. of water. The ether layer was removed, and the aqueous layer was extracted twice with ether. The ether extracts after drying and evaporation yielded 25.40 g. of an unidentified fraction, b.p. 160–165° (1.5 mm.). This contained some of the expected diol as shown by the formation of a dinaphthylurethane derivative, m.p. 297–298°. However, no diol could be crystallized by seeding the oil with pure diol. The diol was isolated by continuous extraction of the aqueous suspension from the reduction, with chloroform for 48 hr., evaporation of the chloroform, and recrystallization from benzene. The yield was 62 g. (30%), m.p. 79–81°.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.11; H, 7.34.

2-(3,4-Dimethoxyphenyl)propane-1,3-diol Ditosylate.—A solution of 40 g. (0.188 mole) of 2-(3,4-dimethoxyphenyl)propane-1,3-diol in 200 ml. of dry pyridine was cooled to 0° and 80 g. (0.5 mole) of *p*-toluenesulfonyl chloride was added keeping the temperature below 10°. The solution was left overnight at 20° and then poured into an ice solution containing 300 ml. of concentrated hydrochloric acid. The solid which separated on scratching was recrystallized from absolute ethyl alcohol to give 72.5 g. (74%) of the ditosylate, m.p. 112.5–114.5°.

Anal. Calcd. for $C_{25}H_{28}O_6S_2$: C, 57.67; H, 5.42. Found: C, 57.69; H, 5.27.

Diethyl 3-(3,4-Dimethoxyphenyl)cyclobutanedicarboxylate.—To a solution of 88.3 g. (0.17 mole) of 2-(3,4-dimethoxyphenyl)-propane-1,3-diol ditosylate and 30.20 g. (0.19 mole) of diethyl malonate in 600 ml. of dioxane at 100° was added slowly (3 hr.) 7.65 g. (0.17 mole) of 53.3% sodium hydride in mineral oil. The mixture was refluxed for 3 hr., and then an additional 0.17 mole of sodium hydride was added. The mixture was refluxed an additional 15 hr., and the solvent was removed. The diester was extracted from the residue with ether, washed with water, and dried. It was purified partially before distillation by passing through an alumina column with ether. The diester (30.94 g., 54%) was a colorless oil, b.p. 178–181° (0.2 mm.), and was identified by its n.m.r. spectrum.

Acknowledgment.—We are grateful to Smith Kline and French Laboratories for support of this work.

Hydrogenation of Aniline to Cyclohexylamine with Platinum Metal Catalysts

HAROLD GREENFIELD

Naugatuck Chemical Division of U. S. Rubber Company, Naugatuck, Connecticut

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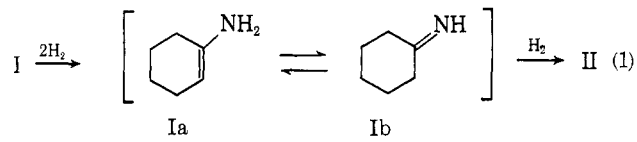
The platinum metals—rhodium, ruthenium, platinum, and palladium—have been investigated as catalysts for the liquid-phase hydrogenation of aniline (I) to cyclohexylamine (II). A major objective was to determine the extent and mechanism of formation of dicyclohexylamine (III). The effects of the addition of ammonia and of III were studied.

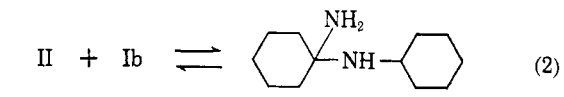
The literature indicates that ruthenium is the best of the platinum metal catalysts for the hydrogenation of aromatic amines to alicyclic amines.[1-4] Among the base metals, cobalt has been used with considerable success, although it requires rather high temperatures and pressures.[5-8]

The catalytic hydrogenation of I to II probably proceeds stepwise with the formation of enamine and imine intermediates (eq. 1).



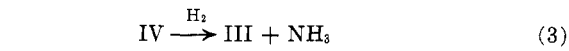
Ia Ib

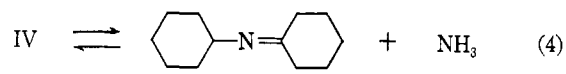
The mechanism of formation of the major by-product (III) probably is the same as proposed for the production of secondary amines in the hydrogenation of nitriles.[9] This involves the addition of II to the imine Ib (eq. 2). IV then may undergo hydrogenolysis



IV

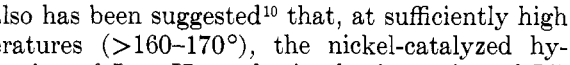
directly to III (eq. 3) or lose ammonia to form a ketimine (V) (eq. 4), which then is reduced to III.



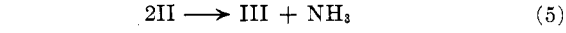


V

It also has been suggested[10] that, at sufficiently high temperatures (>160–170°), the nickel-catalyzed hydrogenation of I to II results in the formation of III by the following reaction.



In addition to the formation of secondary amine, an important side reaction at very high temperatures is the production of cyclohexane. This reaction is



noticeable below 300° but not important below 325° with nickel and cobalt catalysts.[5] Cyclohexane formation becomes excessive with the more active ruthenium catalyst at about 200° and is not diminished by the addition of III or ammonia.[11]

Experimental

Each experiment on the hydrogenation of I was run in a 1-l., stainless steel, rocking autoclave with 186 g. (2.0 moles) of I and, unless otherwise specified, 1.86 g. of a dry 5% metal-on-carbon catalyst (Engelhard Industries, Inc.) at 800–1000 p.s.i.g.

The effect of adding each of the following substances was studied: III (18.0 g., 0.10 mole, 5 mole % based on I), concentrated aqueous ammonia (14 ml., 0.2 mole, 10 mole % based on I), and ammonia (5 ml. as liquid ammonia, *ca.* 0.2 mole, 10 mole

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