555. *Catalytic Hydrogenation. Part I. The Hydrogenation of Unsaturated Amines over Platinic Oxide.*

By J. M. Devereux, (in part) K. R. Payne, and E. R. A. Peeling.

The kinetics of hydrogenation of a number of unsaturated amines over platinic oxide in 95% aqueous ethanol containing varying amounts of hydrochloric acid have been determined. The results show that, while weakly basic aromatic amines are non-toxic to platinic oxide, the more strongly basic hydrogenated amines and aromatic amines are toxic; also that the faster hydrogenation of amines in acid solutions is due to the formation there of non-toxic ammonium ions in place of toxic free bases.

Catalytic hydrogenation of aromatic compounds containing basic nitrogen in solution over platinum is slow compared with, for instance, that of benzene. Hydrogenation of these bases is considerably faster in acid or if the hydrochloride is used instead of the free base.

Maxted and Walker [1] attributed slow hydrogenation of pyridine in aqueous solution to a self-poisoning effect of pyridine and piperidine. They suggest that the free electron pair on the nitrogen atom of pyridine and piperidine leads to a strong adsorption by the metallic catalyst and that in acid solution these toxic molecules will be rendered non-toxic by conversion into 'inium ions in which the free electron pair is shielded by a proton. In support of this they showed that the rate of hydrogenation of pyridine increased progressively with the addition of mineral acid and reached a maximum beyond the neutralisation point.

In this paper we report a kinetic study of the hydrogenation of a number of aromatic amines over Adams platinic oxide catalyst in 95% aqueous ethanol.

Results

The amines investigated were *NN*-dimethylaniline, *NN*-dimethyl-*m*- and -*p*-toluidine, pyridine, pyrrole, quinoline, and *NN*-dimethyl-phenethylamine and -benzylamine.

The kinetic results for pyridine and *NN*-dimethylaniline are shown in Figs. 1 and 2, in which the hydrogen absorbed is plotted against the time. With hydrochloric acid present the initial rate, after the reduction of the catalyst, is many times greater than that in the absence of acid and, for *NN*-dimethylaniline, is little affected by the amount of acid added. For pyridine the initial rate is virtually constant from 0·3 to 0·7 equivalent of acid but doubles between 0·7 and 2·0 equivalents of acid. The maximum rate of change of hydrogenation with change in acid amount occurs at 1·0 equivalent. In all cases the initial rate of hydrogenation is not very different from that of benzene under similar conditions.

Table 1.

HCl added (equiv.)	H_2 absd. rapidly (ml.)	H_2 absorbed for complete hydrogenation (calc.) (ml.)	Initial rate (ml./min.)	HCl added (equiv.)	H_2 absd. rapidly (ml.)	H_2 absorbed for complete hydrogenation (calc.) (ml.)	Initial rate (ml./min.)
	NN-Dimethyl-*p*-toluidine					Pyrrole	
0·22	100	430	11	0·00	—	220	~ 2
0·44	195	430	11	0·25	65	220	~12
0·66	300	430	11	0·50	120	220	~12
2·2	430	430	10	1·0	220	220	~12
	NN-Dimethyl-*m*-toluidine						
0·21	110	455	10				
0·42	210	455	11				
0·63	305	455	11				
0·84	410	455	11				
1·05	460	455	12				

In the absence of acid hydrogenation of pyridine and *NN*-dimethylaniline was very slow and stopped before completion.

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[1] Maxted and Walker, *J.*, 1948, 1093.

The most notable feature, however, of the hydrogenations in the presence of acid is the variation of the extent of the fast reaction with the amount of acid added initially. Figs. 1 and 2 show that the reaction becomes much slower when the amount of hydrogen absorbed corresponds to the formation of a quantity of hydrogenated amine equal to the amount of acid added initially. The slow rate is similar to the rate without the addition of acid.

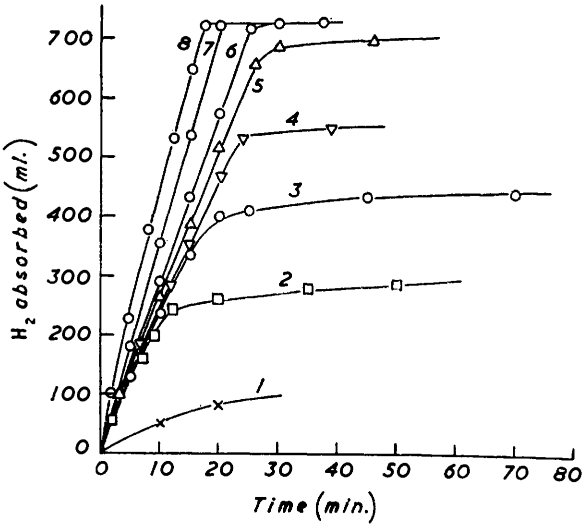


FIG. 1. *Hydrogenation of pyridine in presence of* HCl, *as follows* : (1) 0, (2) 0·3, (3) 0·5, (4) 0·7, (5) 0·9, (6) 1·0, (7) 2·0 *equiv. Curve* (8) *is for benzene with* HCl *as for* (7).

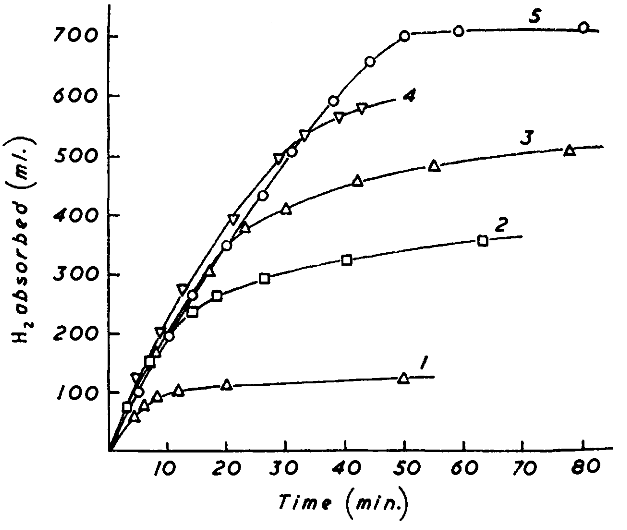


FIG. 2. *Hydrogenation of* NN-*dimethylaniline* (0·01 *mole*) *in* 100 *ml. of solution containing* HCl *as follows* : (1) 0, (2) 0·3, (3) 0·5, (4) 0·7, (5) 1·0 *equiv.*

Similar results were obtained with *NN*-dimethyl-*m*- and -*p*-toluidine and pyrrole (see Table 1).

NN-Dimethyl*cyclo*hexylamine reduces the extent of the fast stage in hydrogenation of *NN*-dimethylaniline in acid (Fig. 3), the effect increasing with the amount added.

Fig. 4 shows that hydrogenation of quinoline proceeds in two stages, consecutively complete conversion into 1 : 2 : 3 : 4-tetrahydroquinoline and reduction to decahydroquinoline. The rate of the first stage is independent of the amount of acid added. The reaction in absence of acid is slower than in its presence but the amount of acid needed to increase the rate is so small that the slow rate is undoubtedly due to the presence of the small amount of alkali often found in Adams catalyst. The effect of acid on the rate of the second stage is similar to that for *NN*-dimethylaniline.

In hydrogenation of *NN*-dimethylphenethylamine (Fig. 6) the initial rate increases with the amount of acid added and there is no abrupt change in the rate during the reaction.

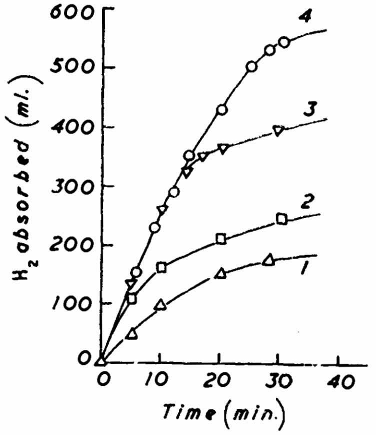
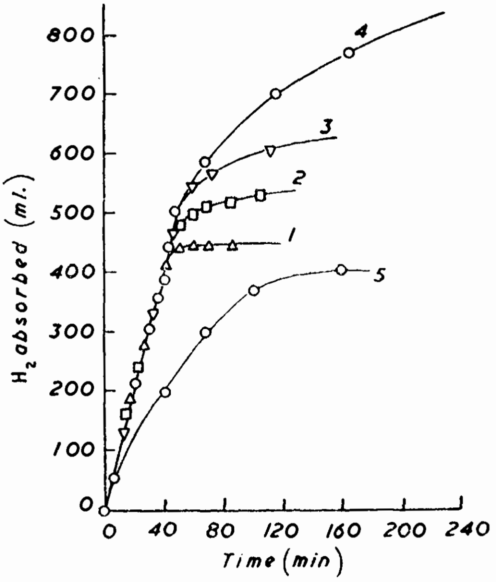


FIG. 3. *Hydrogenation of* NN-*dimethylaniline* (0·0071 *mole*) *in* 100 *ml. of solution in presence of* 1 *equiv. of* HCl *and* NN-*dimethyl*cyclo*hexylamine as follows*: (1) 1·0, (2) 0·8, (3) 0·4, (4) 0 *equiv.*

FIG. 4. *Hydrogenation of quinoline* (0·0073 *mole*) *in* 100 *ml. of solution containing* HCl *as follows*: (1) 0·1, (2) 0·3, (3) 0·5, (4) 1·0, (5) 0 *equiv.*



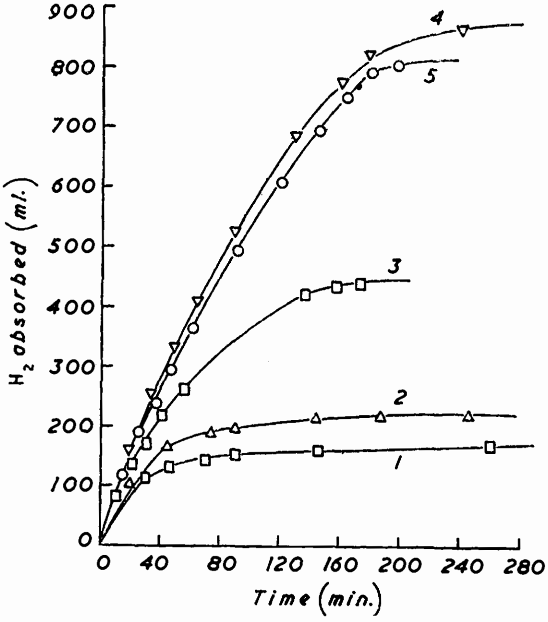


FIG. 5. *Hydrogenation of* NN-*dimethylbenzylamine* (0·01 *mole*) *in* 100 *ml. of solution containing* HCl *as follows*: (1) 0·25, (2) 0·50, (3) 1·0, (4) 1·1, (5) 1·5 *equiv.*

The fastest hydrogenation is obtained with >1 mol. of acid. The product was exclusively *NN*-dimethyl-2-*cyclo*hexylethylamine.

Hydrogenation of *NN*-dimethylbenzylamine differed in many respects from that of the other substances (see Fig. 5). The volumes of hydrogen absorbed in presence of >1 mol. of acid disclosed hydrogenolysis in addition to ring hydrogenation, and the products formed in the presence of < 1 mol. of acid were exclusively those of hydrogenolysis, namely toluene and dimethylamine. No detectable dimethylaminomethyl*cyclo*hexane was formed under these conditions.

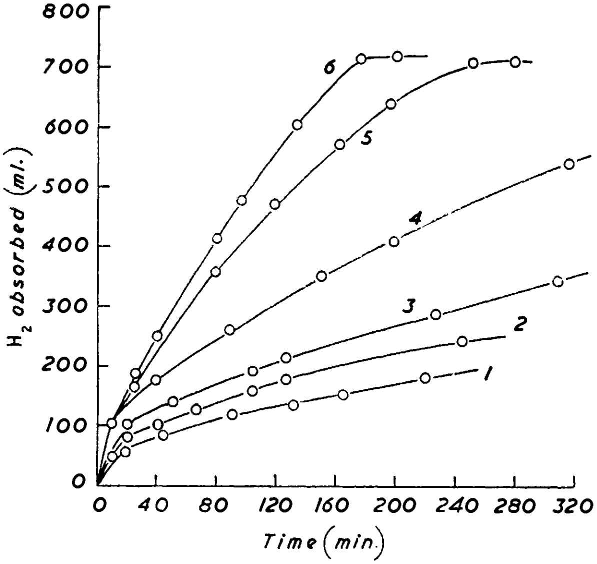


FIG. 6. *Hydrogenation of* NN-*dimethylphenethylamine* (0·01 *mole*) *in* 100 *ml. of solution containing* HCl *as follows*: (1) 0·1, (2) 0·5, (3) 0·9, (4) 1·0, (5) 1·1, (6) 1·5 equiv.

DISCUSSION

The general conclusion which we draw from our results is that an "unshielded" nitrogen atom is non-toxic if it is adjacent to an aromatic ring, as in *NN*-dimethylaniline and pyridine, and toxic if it is adjacent to a saturated system as in *NN*-dimethyl*cyclo*hexylamine, piperidine, and *NN*-dimethylbenzylamine. When a nitrogen atom is adjacent to an aromatic ring the availability of the nitrogen lone electron pair for co-ordinate-bond formation with the platinum catalyst surface is much less than when the nitrogen atom is adjacent to a saturated system, and we suggest that this reduced availability of the lone electron pair accounts for the non-toxicity of *NN*-dimethylaniline and pyridine. The availability of the nitrogen lone electron pair is also reflected in the basic strength of the amine and we find that it is the very weak aromatic bases which are non-toxic while the stronger alicyclic bases are toxic. We shall discuss our results in this general light.

Pyridine, *NN*-dimethyl-aniline, -*m*-toluidine, and -*p*-toluidine, and pyrrole are hydrogenated similarly in the presence of varying amounts of hydrochloric acid. In its absence the rate is slow compared with that for benzene. Hydrochloric acid leads to some 8—10 times faster rates, the extent of this fast reaction being greater the more acid is added initially.

NN-*Dimethylaniline.*—The initial rates of hydrogenation in the presence of up to 1 mol. of hydrochloric acid are virtually constant and similar to that of benzene: *NN*-dimethylaniline is present at the start and it cannot therefore be toxic to the catalyst. *NN*-Dimethyl*cyclo*hexylamine formed in the reaction, being a much stronger base than *NN*-dimethylaniline, progressively displaces it from its hydrochloride until the displacement is complete. After this, free *NN*-dimethyl*cyclo*hexylamine will be formed and at this point the rate of hydrogenation falls to a value similar to the rate in the absence of acid; that is, the system behaves as though the catalyst has been poisoned. The only change that has occurred is that free *NN*-dimethyl*cyclo*hexylamine has started to be formed and this substance must be a catalyst poison.

Substantially similar results should occur whenever a weak base is converted on hydrogenation into a strong base. This is so also with *NN*-dimethyl-*m*- and -*p*-toluidine, pyridine, and pyrrole (for pK_a values see Table 2).

TABLE 2.

Amine	pK_a (25°)	Solvent	Ref.
NN-Dimethylaniline	5·06	H_2O	3
NN-Dimethyl-*m*-toluidine	4·94	H_2O	3
NN-Dimethyl-*p*-toluidine	5·33	H_2O	3
Pyridine	5·19	H_2O	3
Pyrrole	0·4	H_2O	4
Quinoline	5·06	H_2O	5
NN-Dimethyl*cyclo*hexylamine	10·48	H_2O	6
NN-Dimethyl-3-methyl*cyclo*hexylamine	10·51 *	H_2O	6
NN-Dimethyl-4-methyl*cyclo*hexylamine	10·46 *	H_2O	6
Piperidine	11·12	H_2O	7
Pyrollidine	11·10	H_2O	8
1 : 2 : 3 : 4-Tetrahydroquinoline	3·1	MeOH	9
NN-Dimethylphenethylamine	8·6	45% $EtOH/H_2O$	6
NN-Dimethylbenzylamine	8·25	,,	6
NN-Dimethyl-2-*cyclo*hexylethylamine	8·92	,,	6
Dimethylaminomethyl*cyclo*hexane	9·05	,,	6

* For the *cis*-isomer.

Pyridine.—Hydrogenation of this differs from that of *NN*-dimethylaniline in two respects. Its rate in the absence of acid is slower, and its initial rate is almost doubled when the amount of hydrochloric acid is increased from 0·3 to 2·0 equivalents.

Hydrogenation of *NN*-dimethylaniline in the absence of acid leads to the formation of only a small quantity of *NN*-dimethyl*cyclo*hexylamine, the main products being dimethylamine and benzene. The rate measured, therefore, is not the rate of ring hydrogenation but the rate of hydrogenolysis. The rate of ring hydrogenation of *NN*-dimethylaniline is therefore not very different from the rate of ring hydrogenation of pyridine.

The difference in the change in initial rates with change in amounts of acid is probably due to the different toxicities of piperidine and *NN*-dimethyl*cyclo*hexylamine. Some unpublished experiments carried out in this laboratory show that piperidine is more toxic than *NN*-dimethyl*cyclo*hexylamine. Owing to hydrolysis by the solvent some free piperidine will always be present and the amount will decrease as the acid concentration increases; the rate of hydrogenation will increase as the amount of acid increases. The lower toxicity of *NN*-dimethyl*cyclo*hexylamine causes only a small rise in rate for the same change in amount of added acid.

Quinoline.—Hydrogenation of quinoline occurs in stages, first to 1 : 2 : 3 : 4-tetrahydroquinoline and then to decahydroquinoline. In the first stage the product is a weaker base than the reactant. So, on our suggestion, the absence of change in rate with addition of acid is to be expected.

The second stage of the hydrogenation leads to the more strongly basic decahydroquinoline and, as Fig. 4 shows, the extent of the non-poisoned reaction is determined by the amount of acid added initially.

NN-*Dimethylphenethylamine.*—Both *NN*-dimethylphenethylamine and *NN*-dimethyl-2-*cyclo*hexylethylamine are strong bases, compared with pyridine. Both amines should therefore be toxic and, as the results show, the initial rate of hydrogenation of *NN*-dimethylphenethylamine increases as the concentrations of the free bases are reduced by the addition of acid. The rate reaches a maximum beyond the equivalence point because hydrolysis

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[2] Baltzly and Phillips, *J. Amer. Chem. Soc.*, 1946, **68**, 261.
[3] Hall and Sprinkle, *ibid.*, 1932, **54**, 3469.
[4] Hall, *ibid.*, 1930, **52**, 5123.
[5] Arnall, *J.*, 1920, 835.
[6] Brewster, Ph.D. Thesis, London, 1956.
[7] Adams and Mahan, *J. Amer. Chem. Soc.*, 1942, **64**, 2588.
[8] Craig and Hixon, *ibid.*, 1931, **53**, 4370.
[9] Oldham, *ibid.*, 1939, **61**, 3289.

of the amine ions by the solvent produces sufficient free base partially to poison the catalyst. No hydrogenolysis of the dimethylamino-group occurred and the only product isolated was the corresponding hexahydro-compound.

NN-*Dimethylbenzylamine.*—The hydrogenation of benzyl compounds frequently leads to hydrogenolysis in addition to hydrogenation of the aromatic ring. The results show that for $Ph\cdot CH_2\cdot NMe_2$ hydrogenolysis exclusively occurs in solutions containing less than one equivalent of acid and to a substantial extent in solutions containing more than an equivalent of acid. Also the toluene formed in the hydrogenolysis is only later hydrogenated to methyl*cyclo*hexane in solutions containing more than an equivalent of acid. Since both the reactant and the product are strong bases, they will both be catalyst poisons to the ring hydrogenation, which should be slow in solutions containing less than an equivalent of acid and rapid only in solutions containing more than an equivalent of acid, as found experimentally. However, the hydrogenolysis is not susceptible to poisoning by the strong bases, although the subsequent hydrogenation of toluene only proceeds in the solutions containing more than an equivalent of acid. Probably therefore hydrogenolysis and hydrogenation proceed by different mechanisms rather than by the mechanism proposed by Baltzly and Phillips.[2]

EXPERIMENTAL

Materials.—Absolute ethanol was shaken with alumina (chromatographic grade; 5 g./l.) to remove potential catalyst poisons, filtered, and fractionally distilled. 95% Aqueous ethanol was prepared by diluting the purified ethanol with 5% v/v of conductivity water. Successive batches of solvent were checked for composition by measurement of density. The acid solutions were prepared by diluting 2N-ethanolic hydrochloric acid which had been prepared by passing dry hydrogen chloride into 95% aqueous ethanol. Adams platinic oxide catalyst was prepared [10] from chloroplatinic acid (3·5 g.) and sodium nitrate (35 g.). The catalysts from a number of such experiments were suspended in water, mixed, filtered off, dried at 80°, and passed through a 100-mesh sieve before use. The activities of various batches of catalyst were determined by measuring the rate of hydrogenation of pyridine under standardised conditions. Hydrogen was prepared by electrolysing 6N-potassium hydroxide with nickel electrodes.

"AnalaR" pyridine, "AnalaR" *NN*-dimethylaniline, *NN*-dimethyl-*m*-toluidine and -*p*-toluidine, pyrrole, and quinoline were purified and dried by standard methods. *NN*-Dimethylbenzylamine (75% yield), b. p. 75°/26 mm., and *NN*-dimethylphenethylamine (50% yield), b. p. 121·2°/57 mm., were prepared by methylating the corresponding primary amines with formic acid and formaldehyde.[11] *NN*-Dimethyl*cyclo*hexylamine, b. p. 94°/86 mm., was prepared by hydrogenating *NN*-dimethylaniline in 95% aqueous ethanol containing an excess of hydrochloric acid, over platinic oxide.

Kinetic Measurements.—Hydrogenations were carried out in a 250 ml. bottle or flask attached to a shaker, immersed in a water-bath at 30° ± 0·1°, and connected by means of polyvinyl chloride tubing to a gas burette containing hydrogen. The rates of hydrogenation could be reproduced to ±5%.

Isolation and Analysis of Products.—*Hydrogenation of* NN-*dimethylbenzylamine.* (a) *In solutions containing less than one equivalent of acid.* *NN*-Dimethylbenzylamine (2·7 g.) in 95% aqueous ethanol (100 ml.) with platinic oxide (0·4 g.) absorbed 490 ml. of hydrogen. The platinum was filtered off, and the filtrate made acid by hydrochloric acid and fractionated (60 cm. column packed with glass helices). To the fraction boiling up to 78° (5 ml.), saturated calcium chloride solution was added and the upper layer (0·5 ml.) separated, dried ($CaCl_2$ and Na), and distilled; it had b. p. 108°/760 mm., n_D^{25} 1·490 (toluene: 110°/760 mm., n_D^{25} 1·494). The residue from the fractionation was made alkaline with sodium hydroxide solution and refractionated. The first fraction was passed into dilute hydrochloric acid, which on evaporation gave a buff-coloured solid forming a picrate, m. p. 158° (dimethylamine picrate, m. p. 156°). (Dimethylamine was quantitatively estimated in other experiments by passing the first fraction from the fractionation from alkaline solution into an excess of standard hydrochloric acid and back-titration with sodium hydroxide to methyl-red.) Fractionation was

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[10] *Org. Synth.*, Coll. Vol. I, 1st Edn., p. 452.

[11] Clarke, Gillespie, and Weisshaus, *J. Amer. Chem. Soc.*, 1933, **55**, 4571.

continued until the whole of the solvent had been removed. Water was added to the residue and the upper layer (0·5 ml.) separated, dried (KOH), and distilled; it had b. p. 181°/750 mm., n_{D}^{25} 1·4985 (*NN*-dimethylbenzylamine, b. p. 182°/760 mm., n_{D}^{25} 1·4996).

(b) *In solutions containing more than one equivalent of acid.* A solution of *NN*-dimethylbenzylamine (0·96 g.) in 95% aqueous ethanol (100 ml.) with platinic oxide (0·2 g.) absorbed 540 ml. of hydrogen. Fractionation as described above gave three compounds : b. p. 101°/760 mm., n_{D}^{25} 1·4205 (methyl*cyclo*hexane, b. p. 101°/760 mm., n_{D}^{25} 1·4206); a gaseous amine giving a picrate, m. p. 158° (dimethylamine picrate, m. p. 156°); and an *amine*, b. p. 173°/751 mm. (Found : C, 76·3; H, 13·3; H, 10·1. $C_9H_{19}N$ requires C, 76·5; H, 13·6; N, 9·9%). The picrate had m. p. 133°.

Hydrogenation of NN-*Dimethylphenethylamine.*—A solution of the amine (1·5 g.) in 95% aqueous ethanol (100 ml.) containing the required amount of hydrochloric acid and platinic oxide (0·2 g.) absorbed 670 ml. of hydrogen. The platinum was filtered off, and the filtrate made acid, if not already so, by hydrochloric acid, and fractionated. To the first 5 ml. of distillate saturated calcium chloride solution was added. No separation into two layers occurred. To the residue from the fractionation, sodium hydroxide solution was added until the solution became alkaline and the residue was then fractionated. No low-boiling amine was obtained. After removal of the solvent the residue had b. p. 93—94°/28 mm. and gave a hydrochloride, m. p. 244°. Blicke and Monroe [12] record m. p. 238—239° for *NN*-dimethyl-2-*cyclo*hexylethylamine hydrochloride.

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THE UNIVERSITY, LEICESTER.

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[12] Blicke and Monroe, *ibid.*, 1939, **61**, 91.