2. In an ionic base catalyzed mechanism which might be formulated similarly to the acid catalyzed mechanism, the reaction complex would be essentially the same. Weichselfelder[17] has prepared a nickel hydride allegedly of the formula NiH_2, which might indicate that hydrogen associated with nickel would have a negative character. Since the negative nature of hydrogen in this hydride has been questioned by Schmidt,[17] this type of mechanism would probably not apply in this case.

3. The third type of mechanism involving atoms could again be postulated with the same activated complex and the same steps using, however, uncharged radicals and assuming completely covalent bonds in the reaction complex. Atomic mechanisms have been usually postulated for heterogeneous chemical reactions. However, differences in electronegativities of the atoms involved would favor a mechanism involving charged radicals or ions.

The authors are greatly indebted to Professor Hugh S. Taylor for his helpful suggestions and criticisms.

Summary

1. Catalytic dehydrogenation of optically active (−)2-methylbutanol-1 and catalytic hydrogenation of optically active (+)2-methylbutanal-1 using nickel catalysts in the temperature range 128–250° have led to optically active products at low temperatures and increasingly racemized products at increasingly higher temperatures.

2. Racemization or "enolization" of the optically active aldehyde on a metal surface containing adsorbed hydrogen has been shown to occur at a fast rate.

3. A generalized mechanism involving carbon atom 2 has been formulated. An alternative low temperature mechanism not involving the second carbon has also been postulated. The mechanisms have been formulated either ionically in a manner similar to acid-base catalysis or involving atoms.

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[17] Weichselfelder, *Ann.*, **447**, 64 (1926); however, *cf.* O. Schmidt, *Z. physik. Chem.*, **165**, 216 (1933).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MISSOURI]

The Preparation of Some Alicyclic Amines

BY DOROTHY NIGHTINGALE AND VIRGIL TWEEDIE[1,2]

The purpose of this investigation was to prepare a series of substituted unsaturated alicyclic amines and the corresponding saturated amines preliminary to a study of the action of nitrous acid on these compounds.

The six alicyclic amines selected for study were prepared from the 4-nitrocyclohexenes obtained by the addition of nitrostyrene to butadiene, (I); 2,3-dimethylbutadiene, (II); and 1,4-diphenylbutadiene (III), respectively.[3,4] No pure addition compounds were obtained with aliphatic nitroolefins and these dienes. The nitrocyclohexenes (I), (II) and (III) were reduced selectively with hydrogen and Raney nickel to form either unsaturated amines or saturated amines.

The nitro group reduced at a lower temperature than the olefinic double bond. The reaction temperatures differed sufficiently that the nitro group could first be reduced quantitatively at 200 atmospheres followed by reduction of the double bond at a higher temperature except in the case of (I). The reduction curve for (I) indicated a two step reaction, at 50 and 75° at 200 atmospheres, but the product was a mixture at 50° or the saturated amine at 75°. The pure 6-phenyl-3-cyclohexenylamine was obtained by the reduction of the nitro group under low pressure at room temperature. The presence of the two methyl groups on the double bonded carbons slowed the hydrogenation considerably. The double bond in (II) did not hydrogenate below 165°. Reduction of (III) took place in two steps, but more slowly than (I).

Factors that affected the selective reduction of the nitro group were the age of the catalyst and the purity of the compound. Freshly prepared Raney nickel was much more selective and caused more rapid reduction than catalyst which was four to six months old.

(I) can be reduced with stannous chloride in dilute alcohol solution to form 6-phenyl-3-cyclohexenylamine in 50% yield, but (II) yielded a complex mixture under the same conditions. Other reducing agents such as zinc and acetic acid, ferrous sulfate and ammonia were unsatisfactory.

The products of the reaction of nitrous acid and the six amines apparently were alicyclic alcohols. They were viscous oils which distilled over a narrow range and the saturated alcohols did not absorb bromine in carbon tetrachloride. Molecular refractions agreed closely with the calculated values. The possibilities for both position isomerism and stereoisomerism are numerous in these reaction products and they may be mixtures of

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[1] Abstract of a portion of the dissertation of Virgil Tweedie for the degree of Master of Arts at the University of Missouri in August, 1942. This paper was presented at the 105th meeting of the American Chemical Society in Detroit, Mich., April, 1943.

[2] Present address: Commercial Solvents Corporation, Terre Haute, Indiana.

[3] Allen and Bell, THIS JOURNAL, **61**, 521 (1939).

[4] Allen, Bell and Gates, *J. Org. Chem.*, **8**, 373 (1943).

TABLE I

REDUCTION OF NITROCYCLOHEXENES

Nitrocyclohexene	Time, hr. NO₂	Time, hr. C=C	Reduction temp., °C. NO₂	Reduction temp., °C. C=C	Product
4-Nitro-5-phenylcyclohexene	3.5	1.2	50	75	2-Phenylcyclohexylamine
4-Nitro-5-phenylcyclohexene	12.0		26		6-Phenyl-3-cyclohexenylamine
4-Nitro-5-phenyl-1,2-dimethylcyclohexene	3.2	5.0	65	165	6-Phenyl-3,4-dimethylcyclohexylamine
4-Nitro-5-phenyl-1,2-dimethylcyclohexene	2.0		50		6-Phenyl-3,4-dimethyl-3-cyclohexenylamine
4-Nitro-3,5,6-triphenylcyclohexene	10.0	1.5	60	85	2,3,6-Triphenylcyclohexylamine
4-Nitro-3,5,6-triphenylcyclohexene	10.5		67		2,3,6-Triphenyl-3-cyclohexenylamine

TABLE II

ALICYCLIC AMINES

Amine	M. p., °C.	B. p., °C.	B. p., Mm.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Phenylcyclohexylamine[a]	58–59	110–112	3	82.29	9.71	81.65	10.05
6-Phenyl-3-cyclohexenylamine[b]		78–81	3	83.24	8.67	83.38	8.67
6-Phenyl-3,4-dimethylcyclohexylamine		110–111	3	82.72	10.39	82.47	10.57
6-Phenyl-3,4-dimethyl-3-cyclohexenylamine[b]		120–125	3	83.54	9.50	83.19	9.59
2,3,6-Triphenylcyclohexylamine	157–158	Sublimed *in vacuo*		88.02	7.70	88.21	7.93
2,3,6-Triphenyl-3-cyclohexenylamine	137–138	Sublimed *in vacuo*		88.62	7.07	88.45	7.27

[a] v. Braun, Gruber and Kirschbaum, *Ber.*, **55**, 3668 (1922). [b] Allen, Bell and Gates, *loc. cit.*

TABLE III

DERIVATIVES OF ALICYCLIC AMINES

Amine	Benzoyl derivative M. p., °C.	Benzoyl derivative Calcd., % C	Benzoyl derivative Calcd., % H	Benzoyl derivative Found, % C	Benzoyl derivative Found, % H	Hydrochloride M. p., °C.	Hydrochloride Calcd., % C	Hydrochloride Calcd., % H	Hydrochloride Found, % C	Hydrochloride Found, % H
2-Phenylcyclohexylamine	182	81.72	7.52	81.97	7.71	253[a]	...	..	...	..
6-Phenyl-3-cyclohexenylamine	163	82.31	6.86	82.22	6.95	220[b]	68.73	7.63	68.71	7.80
6-Phenyl-3,4-dimethylcyclohexylamine	205	82.35	7.84	82.23	8.04	259 d	70.14	9.18	69.97	9.48
6-Phenyl-3,4-dimethyl-3-cyclohexenylamine	146	82.90	7.23	82.62	7.38	173[b]	...	..	...	..
2,3,6-Triphenylcyclohexylamine	220	86.31	6.93	85.98	6.80	270 d	79.23	7.15	79.50	7.30
2,3,6-Triphenyl-3-cyclohexylamine	158	86.70	6.26	86.92	6.49	284	79.65	6.69	79.47	6.83

[a] v. Braun, Gruber and Kirschbaum, *Ber.*, **55**, 3668 (1922). [b] Allen, Bell and Gates, *loc. cit.*

isomers. Hückel and Wilip[5] report some *d*-neomenthol from *l*-menthylamine and nitrous acid. The detailed study of the structure of these compounds will be resumed after the war.

Experimental[6]

The nitrocyclohexenes were prepared by the procedure of Allen and Bell.[3,4]

Preparation of the Amines.—Most of the nitro compounds (0.07 to 0.10 mole) were reduced at high pressures with 3 g. of Raney nickel and 100 cc. of methanol as the solvent except in the case of the triphenyl compound which required 200 cc. of methanol. The initial pressure was 200 atm. at room temperature except for the reduction of the nitro group only in (I) for which the pressure was 3 atm. at room temperature throughout. The data are summarized in Table I. The physical constants of the amines are summarized in Table II and of their derivatives in Table III.

After removal of the catalyst, the solvent was distilled from a water-bath. The amines other than the triphenyl amines were transferred to a Claisen flask and distilled at 3 mm. The liquids were further purified by fractional distillation *in vacuo*. The triphenylamines were best purified by vacuum sublimation. Except for mechanical losses, yields were nearly quantitative.

The derivatives of the amines were prepared and purified by the usual procedures.

Reduction of 4-Nitro-5-phenylcyclohexene with Stannous Chloride.—The nitro compound (5 g.) dissolved in 45 cc. of alcohol was added to a solution of stannous chloride in 30 cc. of concd. hydrochloric acid at 50°. The solution was refluxed one and one-half hours or until the nitro compound had dissolved. The alcohol was removed by distillation. The tin double salt which separated on cooling was collected on a filter, covered with ether and decomposed with concentrated potassium carbonate solution. The ether solution of the amine was washed, dried over potassium carbonate and distilled; b. p. 110–112° (3 mm.); yield 2.25 g. The melting point of the benzoyl derivative of this amine was 163° and it did not depress the melting point of the benzoyl derivative of the amine prepared by reduction with Raney nickel.

Acknowledgments.—The authors wish to thank Dr. C. F. H. Allen of the Eastman Kodak Company for the directions for the preparation of the nitro compounds prior to their publication.

Summary

Six alicyclic amines have been prepared by the selective reduction of three alicyclic nitro compounds with hydrogen and Raney nickel.

The benzoyl derivatives and the hydrochlorides of these amines are described.

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(5) Hückel and Wilip, *J. prakt. Chem.*, **158**, 21 (1941).

(6) Semimicro analyses by Ernest Milberger and D. R. Smith.