Catalytic Hydrogenation of 1.—A solution of 233 mg (1.0 mmol) of **1** in 15 ml of ethyl acetate was added to a prereduced mixture of 24 mg of catalyst (10% palladium on carbon) in 5 ml of ethyl acetate in a conventional (1 atm pressure) hydrogenation apparatus. After stirring for 45 min, *ca.* 24 ml of hydrogen had been absorbed and the reduction was interrupted. Catalyst was removed by filtration and solvent was evaporated under reduced pressure. The residue was submitted to column chromatography on 17 g of silicic acid with chloroform eluent. Product was eluted first, followed by 83 mg of recovered 1. Since the new substance could only be obtained as an oil contaminated with 1, it was directly isomerized. Chromatographic fractions containing reduced material were combined and dissolved in *ca.* 1 ml of trifluoroacetic acid and the solution was refluxed for 1.5 hr. After removal of solvent the residue was submitted to column chromatography as before. After combination of appropriate chromatographic fractions and recrystallization from hexane, there was obtained 66 mg of *cis*-2,*cis*-4-dimethyl-3-oxo-*cis*-perhydro-*trans*-1,8a-butanonaphthalene (**8**): mp 91.5–92.5°; ir ν_{max}^{KBr} 1700 cm^{-1}; mass spectrum *m/e* 234; nmr (see text).

Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.01; H, 11.23.

Registry No.—**1**, 32670-24-9; **4**, 32670-25-0; **5**, 32670-26-1; **6**, 32670-27-2; **7a**, 32653-54-6; **8**, 32653-55-7.

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Hydride Reduction of *N*-Cyclopropylimines

CARL L. BUMGARDNER,* ERNEST L. LAWTON,[1] AND JAMES G. CARVER

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607

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The fate of intermediates generated by hydride addition to the carbon atom of *N*-cycloalkylimines was studied to determine the stability of species which have a negatively charged nitrogen atom adjacent to a small ring. When sodium aluminum hydride or lithium aluminum hydride was used as the hydride source, cleavage of the three-membered ring accompanied reduction of the carbon–nitrogen double bond. However, only the imine group was reduced when sodium borohydride, lithium borohydride, or hydrogen and platinum were employed. Results are rationalized in terms of isomerizations analogous to the cyclopropylcarbinyl allylcarbinyl anion conversion.

The proclivity for cyclopropylcarbinyl anions to undergo ring opening to give the isomeric allylcarbinyl anions is well known.[2] For example, reactions[3,4] of cyclopropylcarbinyl Grignard and lithium reagents, Wolff–Kishner reduction[2] of certain cyclopropyl aldehydes, treatment of cyclopropylcarbinyl quaternary salts with sodium amide,[2] and addition of isopropyllithium[5] to substituted vinyl cyclopropanes all lead to products which involve ring opening of a cyclopropylcarbinyl species having some carbanoid character. In like manner, cyclopropoxides rearrange to carbonyl compounds.[6]

To determine the stability of intermediates which have a negatively charged nitrogen atom adjacent to the small ring, we examined the consequence of adding hydride to the carbon atom of a number of *N*-cycloalkylimines. The imines studied included *N*-(3-phenylpropylidene)cyclopropylamine (**1**), *N*-benzylidenecyclobutylamine (**2**), *N*-benzylidene(*trans*-2-phenylcyclopropyl)amine (**3**), *N*-(3-phenylpropylidene)benzylamine (**4**), and *N*-benzylidenecyclopropylamine (**5**). Lithium aluminum hydride, sodium aluminum hydride, lithium borohydride, and sodium borohydride were employed as hydride sources. The course of catalytic hydrogenation was also investigated.

In previous work, Kaiser, Burger, and coworkers[7] observed that reduction of *N*-(2-phenylcyclopropyl)-formamide with lithium aluminum hydride gave not the expected *N*-methylamine but *N*-methyl-3-phenylpropylamine. In addition, 2-phenylcyclopropylamine was found to be unstable to lithium aluminum hydride. Our results are in accord with theirs and also establish the requirements for ring opening in a variety of *N*-cycloalkylimine–hydride reductions.

Results

Condensation reactions between the appropriate amines and aldehydes provided the desired imines. These preparations are summarized in Table I.

Imine reductions were accomplished by refluxing an ether or tetrahydrofuran (THF) solution approximately 0.05–0.5 *M* in the imine with an excess of the complex hydride. Reactions were quenched by addition of a 1:1 mixture of 10% sodium hydroxide and ethanol or 10% hydrochloric acid and methanol and the products were isolated by distillation and characterized by nmr analysis and in some cases by independent synthesis. Results are collected in Tables II and III.

Discussion

The results in Table III may be divided into two groups: those reactions in which reduction of the carbon–nitrogen bond is accompanied by ring cleavage (runs 1, 2, 5, 7, 8, 10, 11) and those examples in which reduction leaves the small ring intact (runs 4, 13–19). The aluminum-containing reagents belong to the former group, the borohydrides and catalytic hydrogenation to the latter.

Runs 1 and 5 show that ring opening is not a function of the group attached to the imine carbon atom, and run 4 demonstrates that ring cleavage is unimportant in the case of *N*-cyclobutyl compounds.

Ring-opened products can be accounted for by a scheme involving isomerization of intermediate I to

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(4) P. T. Lansbury and V. A. Pattison, *ibid.*, **85**, 1886 (1963).

(5) J. A. Landgrebe and J. D. Shoemaker, *ibid.*, **89**, 4465 (1967).

(6) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

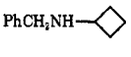
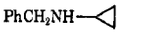
(7) C. Kaiser, A. Burger, L. Zirngibl, C. S. Davis, and C. L. Zirkle, *J. Org. Chem.*, **27**, 768 (1962).

TABLE I
IMINES

Compd	$R_1CH=NR_2$ R_1	R_2	Bp, °C (Torr)	$n^{25}D$	Yield, %	Nmr,[a] δ (ppm)
1[b]	$PhCH_2CH_2$ a		75.8 (0.5)	1.5502	62	7.72 (vinyl), 7.15 (phenyl), 2.72 (benzyl), 2.50 (a) 0.90 (cyclopropyl)
2[b]	Ph		128–130 (0.5)	1.5885	42	8.07 (vinyl), 7.70, 7.32 (phenyl), 3.13, 2.16, 1.90 (cyclobutyl)
3[b]	Ph		135–137 (0.5)	1.5950	45	8.38 (vinyl), 7.66, 7.30 (phenyl), 3.15, 2.50, 1.70 (cyclopropyl)
4[b]	$PhCH_2CH_2$ c b		75–76 (0.5)	1.5598	73	7.70 (vinyl), 7.17 (phenyl), 4.50 (a), 2.83 (c), 2.60 (b)
5[b]	Ph		56–58 (0.5)	1.5750	60	8.40 (vinyl), 7.69, 7.38 (phenyl), 3.00, 0.91 (cyclopropyl)

[a] Ratios of signals were in agreement with assigned structures. Spectra were run as approximately 5% by volume solutions in deuteriochloroform with the probe temperature at 25°. [b] Satisfactory analytical data (±0.4%) for C, H, and N were reported: Ed.

TABLE II
AMINES

Compd	Structure[a]	Bp, °C (Torr)	$n^{25}D$	Nmr,[b] δ (ppm)
6[c]	$PhCH_2CH_2CH_2NHCH_2CH_2CH_3$ f e d c b a	71–73 (0.5)	1.5094	7.16 (phenyl), 2.55 (f, d, c), 1.77 (e), 1.43 (b), 0.98 (amine), 0.90 (a)
7[d]	$PhCH_2NHCH_2CH_2CH_3$	57–59 (0.5)	1.5068	7.13 (phenyl), 3.72 (benzyl), 2.52, 1.48, 0.90 (propyl), 1.18 (amine)
8[d]	$PhCH_2NHCH_2CH_2CH_2Ph$ d c b a	145–147 (0.5)	1.5732	7.25, 7.17 (phenyl), 3.75 (d), 2.62 (c, a), 1.79 (b), 1.29 (amine)
9[d]		81–82 (0.3)	1.5248	7.19 (phenyl), 3.55 (benzyl), 3.17, 2.10, 1.56 (cyclobutyl), 1.31 (amine)
10[d]		53 (0.2)	1.5309	7.26 (phenyl), 3.77 (benzyl), 2.07, 0.45 (cyclopropyl), 1.85 (amine)

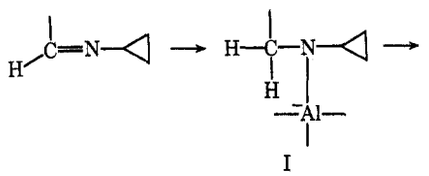
[a] The infrared and mass spectra were consistent with assigned structures. [b] Ratios of signals were in agreement with assigned structures. Spectra were run as approximately 5% by volume solutions in deuteriochloroform with the probe temperature at 25°. [c] *Anal.* Calcd for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.90. Found: C, 80.68; H, 10.16; N, 8.40. [d] Satisfactory analytical data (±0.4%) were reported: Ed.

TABLE III
IMINE REDUCTIONS

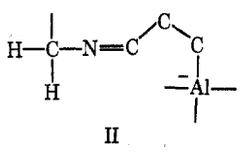
Run no.	Imine	Reducing agent	Solvent	Time, hr	Products	Product ratios[a]	Yield, %	Ring opening
1	1	$LiAlH_4$	Ether[a]	12	6		43	Yes
2	3	$LiAlH_4$	Ether[a]	12	8		85	Yes
3	4	$LiAlH_4$	Ether[a]	12	8		85	
4	2	$LiAlH_4$	Ether[a]	12	9		45	No
5	5	$LiAlH_4$	Ether[a]	12	7		80	Yes
6	5	$LiAlH_4$	Ether[b]	4	10		59	No
7	5	$LiAlH_4$	THF[b]	12	7		50	Yes
8	5	$LiAlH_4$	THF[b]	4	7 + 10	9:1	58	Yes
9	5	$NaAlH_4$	Ether[b]	12				
10	5	$NaAlH_4$	THF[b]	24	7 + 10	1:1	47	Yes
11	5	$NaAlH_4$	THF[b]	12	7 + 10	1.5:8.5	60	Yes
12	5	$NaAlH_4$	THF[b]	4	10		30	No
13	5	$LiBH_4$	Ether[b]	12	10		45	No
14	5	$LiBH_4$	THF[b]	12	10		47	No
15	5	$LiBH_4$	THF[b]	24	10		52	No
16	5	$NaBH_4$	Ether[b]	12	10		42	No
17	5	$NaBH_4$	THF[b]	12	10		57	No
18	5	$NaBH_4$	THF[b]	24	10		67	No
19	5	H_2/Pt	EtOH[c]	12	10		72	No
20	10[e]	$LiAlH_4$	Ether	12	7 + 10	2:8	49	Yes

[a] 200 ml ether, 0.10 mol imine, 0.12 mol $LiAlH_4$. [b] 100 ml solvent, 0.0050 mol imine, 0.0070 mol of the complex metal hydride. [c] 100 ml ethanol, 0.050 mol imine, 30 psig H_2. [d] Based on nmr analyses. [e] Amine.

intermediate II, in analogy with carbon (and oxygen) derivatives which tend to transfer by ring cleavage the negative center from the cyclopropylcarbinyl to an allylcarbinyl site.

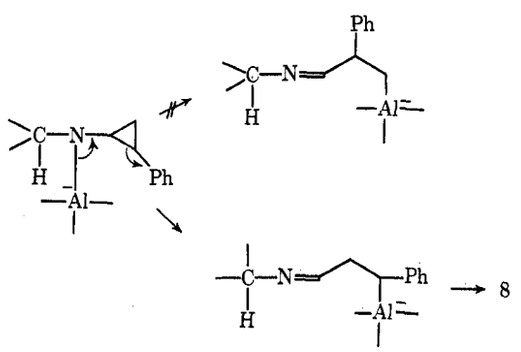


I



II

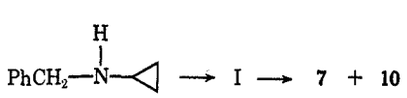
Consistent with this picture are runs 2 and 3, which show that phenyl substitution on the small ring results in unidirectional cleavage to give only the 3-phenylpropylamine and not the isomeric 2-phenylpropyl compound. The low-energy path should be the one lead-



ing to an intermediate having a partial negative charge adjacent to the phenyl ring.

Catalytic hydrogenation (run 19), which presumably does not involve highly polar intermediates such as I, does not yield ring-opened products. Similarly, runs 13–18, which probably proceed through intermediates having nitrogen bound to the small, nonmetallic boron atom, do not result in ring cleavage.

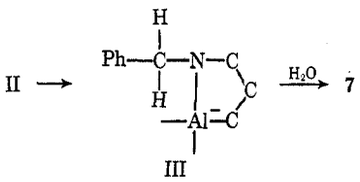
The fact that the ratio of amine **7** to amine **10** is time-dependent (runs 5–8, 10–12) indicates that intermediate I is present and capturable, *i.e.*, that conversion of starting material into II is not concerted. Additional support for the role of intermediate I is available from run 20. This reaction, starting with *N*-benzylcyclopropylamine and lithium aluminum hydride, provides another route to intermediate I and the products **7** and **10**.



Even under conditions where some starting imine was recovered, no *N*-propylidene derivatives (expected from hydrolysis of intermediate II) were isolated. Intermediate II may undergo, as previously suggested,[7] rapid conversion into the five-membered cyclic intermediate III,[8] hydrolysis of which yields the final saturated acyclic product.

In any event, we conclude from the results summarized in Table III that intermediates having a nega-

(8) For a possible oxygen analog of III, see W. T. Borden, *J. Amer. Chem. Soc.*, **92**, 4900 (1970).



III

tively charged nitrogen atom adjacent to a three-membered ring are not stable and isomerize readily *via* ring opening.

Experimental Section[9]

General.—The following materials were used: benzaldehyde (N.F.) (Baker), benzylamine (Matheson Coleman and Bell), cyclobutylamine (Ash-Stevens), cyclopropylamine (Columbia Organic Chemicals), hydrocinnamaldehyde (Practical) (Matheson Coleman and Bell), *trans*-2-phenylcyclopropylamine (Aldrich), lithium aluminum hydride (Metal Hydrides), sodium borohydride (Metal Hydrides), lithium borohydride (Alfa Inorganics), sodium aluminum hydride (Alfa Inorganics).

Preparation of Imines.—To approximately 0.1 mol of the amine in an ice bath, approximately 0.1 mol of the aldehyde was slowly added with stirring. After 90 min 3 g of ground KOH was added to remove water; 30 min later the solution was extracted with five 10-ml portions of ether. The decanted ether layers were combined and dried over magnesium sulfate. The ether was removed on a rotary vacuum apparatus and the remaining imine was distilled under reduced pressure using a Vigreux column. A viscous red residue remained after distillation.

Physical constants, yields, and analyses of the distillates are recorded in Table I.

Imine Reduction with $LiAlH_4$ and $NaAlH_4$.—The imine was added with stirring to the hydride in either tetrahydrofuran or ether and the mixture was refluxed for 4–24 hr (Table III). After removing the heat, 20 ml of a 1:1 mixture (by volume) of 10% NaOH and 95% ethanol was added. The ether was decanted and the residue was washed with ether. (When THF was used as the solvent, it was removed on a rotary vacuum apparatus and the residue was mixed with 50 ml of ether.) The combined ether layers were extracted with five 10-ml portions of 10% HCl. The acid solution was made basic with aqueous NaOH and extracted with five 10-ml portions of ether. The combined ether layers were dried over magnesium sulfate and the ether was removed on a rotary vacuum apparatus. Distillation through a Vigreux column under reduced pressure separated the amines from a small amount of a viscous red residue.

Physical constants and analyses of the distillates are listed in Table II. Yields and product ratios are collected in Table III.

Imine Reduction with $NaBH_4$ and $LiBH_4$.—The procedure for imine reduction with $NaBH_4$ and $LiBH_4$ was identical with that for imine reduction with $LiAlH_4$ and $NaAlH_4$ except that the hydride was destroyed with 25 ml of a 1:1 mixture (by volume) of 10% HCl and methanol instead of a 1:1 mixture of 10% NaOH and 95% ethanol.

For physical constants and analysis of the products see Table II. For yields and product ratios see Table III.

Imine Reduction by Catalytic Hydrogenation.—Approximately 0.05 mol of the imine in 100 ml of 95% ethanol was reduced at room temperature in a Parr pressure apparatus with 0.09 g of platinum oxide under hydrogen at 30 psig.

Results are recorded in Tables II and III.

Registry No.—**1**, 32861-45-3; **2**, 32861-46-4; **3**, 22783-18-2; **4**, 32861-47-5; **5**, 3187-77-7; **6**, 28031-50-7; **7**, 2032-33-9; **8**, 32861-51-1; **9**, 32861-52-2; **10**, 13324-66-8; $LiAlH_4$, 16853-85-3; $NaAlH_4$, 13770-96-2; $LiBH_4$, 16949-15-8; $NaBH_4$, 1333-73-9; H_2, 1333-74-0; Pt, 7440-06-4.

Acknowledgment.—We are grateful to the National Science Foundation for financial support.

(9) Boiling points are uncorrected. Nuclear magnetic resonance spectra were obtained using either a Varian T-60 or A-100 high-resolution spectrometer using tetramethylsilane as an internal standard. Infrared spectra were determined with a Perkin-Elmer infrared spectrophotometer Model 521 with a sodium chloride prism. Mass spectra were obtained using an Associated Electronics Model MS-12 mass spectrometer. Elemental analyses were performed on a F & M Scientific CHN Analyzer Model 185.